Gothic-Arch Calcite from Speleothems of the Bohemian Karst (Czech Republic): Its Occurrence, Microscopic Ultrastructure and Possible Mechanism of Growth

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Abstract: Gothic arch calcite, a specific crystallographic variety of calcite known from some hot springs and tufa streams, has been newly recognized in the Koněprusy Caves. The gothic-arch calcite occurs on the exteriors of exotic coralloid speleothems where it coexists with scalenohedral (dogtooth) spar crystals. The crystals exhibit microscopic ultrastructural features including deeply eroded topography, etch pits, and spiky and ribbon calcite crystallites, pointing to its extensive natural etching. Many gothic-arch calcites originated as late-stage, secondary overgrowths on older, etched dogtooth calcite crystals. Its characteristic outward curvature resulted from the recrystallization of etching-liberated fine carbonate grains and newly formed needle-fiber calcite laths, which were accumulated and bound on the faces and at the bases of corroded crystals. These intimately coexisting destructive and constructive processes of carbonate crystal corrosion and growth were probably mediated by bacteria, fungi, or other microorganisms. Fluid inclusions embedded in calcite crystals point to a vadose setting and temperatures below ~50 °C. This, combined with the wider geological context, indicates that the gothic arch calcite crystals originated only during the late Pleistocene to Holocene epochs, when the cave, initially eroded by hypogene fluids in the deeper subsurface, was uplifted to the subaerial setting and exposed to the meteoric waters seeping from the topographic surface. The radiocarbon analysis shows that gothic-arch calcite crystals are generally older than ~55,000 years, but the surface layers of some crystals still reveal a weak 14C activity, suggesting that microbiologically mediated alterations of the speleothems may have been occurring locally until now.

Keywords: coralloids; fluid inclusions; radiocarbon; biocrystals; microbes; ribbon calcite; trigonal calcite; spiky calcite

1. Introduction

During the last four decades, a number of studies were undertaken that have demonstrated a remarkable variability in calcite, in terms of both its crystal size and morphology, which occurs within calcareous cave deposits [1–4]; (see also [5–9] for the reviews). It has been shown that the size of speleal calcite crystals may range widely from micron-sized crystallites to entire stalactites composed of a single crystal [1,2], while the habit of individual crystals may vary from acicular [10] through columnar crystals with rhombohedral terminations [11] to variable forms of rhombohedrons and scalenohedrons [9], and even to the trigonal prisms [11]. Some recent studies have suggested that variable crystal habits of speleal calcite depend on the level of supersaturation, or other factors such as the specific kinetics of growth or the presence of foreign ions [3,12,13]; however, the concrete processes leading to many particular calcite crystal habits found in the speleothems are, for the most part, still unknown and await further detailed research.
In this study, we report on the occurrence of yet another unusual crystal form of so-called gothic-arch calcite that has been recently recognized in Pleistocene speleothems of the Koněprusy caves, Czech Republic. Although calcite crystals forming bizarre steep rhombs with convex edges evoking gothic arches have been known for a long time from some hot-spring travertines, and even freshwater stream tufas [14–18], only very few examples of this specific calcite crystal habit have been described so far from speleal deposits [19].

By combining optical and scanning electron microscopy with the techniques of microthermometric analysis of fluid inclusions and radiocarbon analysis, we attempt to elucidate the conditions and timing under which these calcite crystals precipitated. We also describe several intriguing ultrafine fabrics that were observed in the interiors of the gothic-arch calcite crystals and have now been exposed through natural etching. We propose a model explaining how microbial-induced corrosion and precipitation may have jointly contributed to its specific crystal habit.

2. Geological Setting

The Koněprusy Caves are the biggest cave system of the Bohemian Karst, a karstic area developed in a 35-km long syncline of lower Palaeozoic carbonate rocks extending between Prague and Beroun in the central part of the Czech Republic. The caves represent more than 2000 m long sub-horizontal passages and domes stratified into three levels and interconnected through vertical chimneys that are situated beneath the Zlatý kůň Hill near the Koněprusy village. The caves were discovered in 1950, subsequently opened to the public and in 1972, the caves were declared a protected natural monument of national importance [20].

The cave morphology was largely influenced by slightly inclined bedding planes of bioclastic Devonian limestones intersected with sub-vertical tectonic veins and fractures ([21], Figure 1 [22]). The exact mechanism by which the caves originated remains a matter of ongoing debate [23–26]. Due to the spatial link between the caves and the hydrothermal calcite veins, the missing relationship of the caves to modern surficial hydrology, the presence of characteristic cupola-form cavities in cave ceilings, and the presence of exotic carbonate-siliceous speleothems, which are strongly similar to those of some presently active hydrothermal caves [27], several studies have suggested that the initial stages of cave development were associated with fracture-bound migration of heated, aggressive hypogene waters that ascended from underlying siliciclastic sedimentary strata [23,24,27,28], (see also [29,30] for geochemical characteristics of Lower Palaeozoic formations that occur at depth, below the caves). At present, however, the caves are cold, with an average annual air temperature of 10.5 °C, and completely devoid of any active water stream. The relative humidity of the cave air is close to 100%. The waters of meteoric origin that locally seep down into the cave from the topographic surface only precipitate typical dripstone speleothems [31].
Some domes and passages of the caves were decorated with a specific type of carbonate-siliceous speleothem known as “Koněprusy rosettes” that probably represent a testament to an early hypogene stage of cave development [32,33]. These represent cauliflower or bush-like branching, 10–20 cm long coralloids composed of fully crystalline calcite aggregates or grape-like pisolithic calcite units that grow at various angles to the limestone wallrock. The same type of specific coralloids also occurs in several small, isolated caves and karst cavities nearby the Koněprusy Caves ([28], Figure 2). The age of the “Koněprusy rosettes” was originally estimated based on indirect paleontological evidence, to be older than ~1.2 Ma [34], but more recent U-Th dating yielded somewhat younger Pleistocene ages ranging between ~200 and 600 ka [28,35,36].

Figure 1. Simplified geologic cross-section of the Koněprusy Caves, adjusted according to [22]. Some cave parts were filled with limestone breccias due to collapsed ceiling.

Figure 2. Petrographic aspects of coralloids from the Koněprusy Caves (A–D) and the Kobyla Quarry (E). (A)—A natural view of a coralloid from the Prošek’s Dome. Notice the branching shape and coarsely crystalline exterior of the speleothem that includes gothic-arch calcite crystals. The sandy yellow colour of the speleothems is due to the staining by fine cave clays. (B,C)—Scanning electron
microphotographs showing details of the speleothem’s exterior. (B)—Fine internal structure of a naturally broken pisolitic branch of the speleothem. Corroded calcite crystals (1) overgrowing feather-like calcite aggregates (3) are clearly visible. Note also a thin gap separating the two calcite growth zones (2). (C)—The coulisse-like arrangement of successive calcite crystals grown on the speleothem’s exterior. Some slightly convex, flat gothic-arch calcite crystals are visible. (D)—A longitudinal section through a coralloid from the Petrbok’s Hall showing a snowy white speleothem interior and its crude internal lamination. (E)—Drawing based on microscopic observations of a thin section showing a finely zoned internal structure of a coralloid and well-developed dogtooth and gothic-arch calcite crystals growing on its exterior. Rectangular fine-grained intraclasts of vein calcite and radiaxial aggregates of clay minerals at the base of the coralloid provided crystallization cores on which the speleothem grew. See the text for more details.

3. Samples and Methods

Most samples examined in this study were carbonate-siliceous coralloids (the “Koněprusy rosettes”) from various domes of the Koněprusy Caves, particularly from the Petrbok’s Hall, Prošek’s Dome, and the nearby Nová propast Chasm where these specific speleothems were typically developed. Some coralloids were also collected from karst cavities located immediately below the Koněprusy Caves, which had been temporarily exposed due to industrial mining in the Čertovy schody Quarry, and from the relict Chlupáčova služ Cave in the abandoned Kobyla Quarry located about 1 km to the SE of the Koněprusy Caves [28].

A stereomicroscope (Bresser Advance ICD, Bresser, Rhede, Germany) and a polarizing optical microscope (Orthoplan, Leitz, Wetzlar, Germany) (Magnification 10× to 1000×) were used to examine small 3D samples and standard unpolished petrographic thin sections of the coralloids, respectively. For scanning electron microscopic (SEM) analysis of the carbonate crystals, six representative samples, each about 1 cm in diameter, were mechanically separated from the surface of the speleothems. No chemical treatments of the samples were undertaken before the SEM examination. The speleothem chips were gently washed with distilled water only, then thinly coated with gold, and examined on a Quanta 450 scanning electron microscope at the Institute of Rock Structure and Mechanics of the CAS, Prague. An accelerating voltage of 30 kV was used for the observations.

The fluid inclusions analyses were performed on 250 µm thick, doubly polished wafers of well-crystallized, about 1 cm high crystals of gothic-arch calcite. The calcite crystals were mechanically separated from the outermost layers of two coralloid speleothems from the Petrbok’s Hall (S30) and the Prošek’s Dome (S31). A polarizing microscope (DMPL, Leica, Wetzlar, Germany) (magnification up to 1000×) was used to study the fluid inclusion petrography. Microthermometric analyses were performed using the LINKAM THMSG-600 heating-freezing stage coupled with an Olympus BX-50 microscope (20× and 50× ULWD objectives) at the facilities of the Charles University, Prague. A 360 nm UV-source (Hg lamp) was used to excite the samples in order to reveal the presence of potential organic inclusions. The 0 °C temperature of the stage was calibrated against double-distilled water. The precision of the ice-melting temperature was better than 0.1 °C. The fluid inclusion salinities were calculated according to the method of Bodnar [37].

Radiocarbon analysis was applied to seven speleothem samples, with the aim of determining the age of the calcite crystals on their exterior. Only a surface layer, about 0.3 mm thick, forming the exterior of the carbonate crystals, was analyzed to evaluate the youngest age of the coralloids. Following sample decomposition by concentrated H3PO4, the released carbon dioxide was purified and transferred to graphitization reactor. Graphitization with pure Zn as a sole reducing agent was used [38,39]. The AMS measurements were carried using the MICADAS system working at the HEKAL ATOMKI HAS Laboratory in DEBRECEN, Hungary [40]. The results of the AMS measurement reported in years of Conventional Radiocarbon Age (CRA) were calibrated using the OxCal 4.4 software and the IntCal20 calibration curve [41,42].
4. Results
4.1. Optical Microscopy

Under the optical stereomicroscope, the coralloid speleothems (“Koněprusy rosettes”) appeared as bush-like branching, fully crystalline columnar or cauliflower-like bodies covered with numerous idiomorphic to hypidiomorphic dogtooth spar and gothic-arch calcite crystals (Figure 2).

Gothic-arch crystals were abundant in the youngest growth zones and on the exterior of the speleothems, where they coexisted face-to-face with more common dogtooth scalenohedral calcite crystals (Figure 2C,E). The gothic-arch calcite, forming both solitary, 2–8 mm high crystals and more complex, coulisse-like arranged crystal aggregates, exhibited an idiomorphic, steep rhombic habit with outwardly convex faces, which gives the crystals their characteristic appearance resembling gothic cathedral arches (Figure 3). Some of these crystals revealed the development of several successive flat iron-like slabs of similar convex sub-crystals that were stacked on top of one another (Figure 3A). In the thin sections, they appeared as triangles, with associated slabs attached in a coulisse-like manner around the central “mother” crystal (Figure 4D). The interior of the gothic-arch calcite crystals was crudely zoned, with distinct gaps between some growth zones (Figure 4A). Some crystals of this specific habit exhibited undulatory extinction under cross-polarized light. Many, if not most, gothic-arch crystals appeared to overgrow older, often corroded scalenohedral calcite crystals (Figure 4B,C and Figure 11A). Natural etch pitting, which often affects the central parts of the crystals, suggests that biofilms may have influenced their growth ([16,43,44], Figure 3D).

Figure 3. Sketches showing the morphology of gothic-arch calcite crystals from the Koněprusy Caves (A–C) and the Chlupáčova služ Cave (D), as seen under the stereomicroscope. (A)—A well-formed
gothic-arch calcite crystal exhibiting a series of triangular flat iron-like slabs added to the rhomb faces; the Petrbok’s Hall. (B,C)—The aggregates of steep-rhombic crystals with small “daughter” trigonal crystals attached to their faces; the Prošek’s Dome. (D)—A complex aggregate of gothic-arch calcite crystals forming a secondary cement in cave calcareous tufa, the Chlupáčova sluť Cave. Note distinct circular pit holes in the centers of some calcite crystals that are believed to be of microbial origin (arrowed).

Figure 4. Thin-section microphotographs showing petrographic aspects of the gothic-arch calcite from various localities of the Koněprusy area. Transmitted white light, slightly crossed polars. (A)—A large crystal of gothic-arch calcite. Coralloid speleothem from a sub-vertical karst cavity, the eastern
sector of the Čertovy schody Quarry. The cavity has been excavated since this photograph was taken in the dark gaps between the individual growth zones are filled with a clayey substance. (B)—A gothic-arch calcite crystal showing distinct growth zones lined with abundant dark inclusions. Notice that only younger growth zones of the crystal reveal a characteristic convexity, while the crystal core exhibits a dogtooth spar-shaped habit. Prošek’s Dome, the Koněprusy Caves. (C,D): Details of calcite crystals forming the outer growth zones of the coralloids from the Chlupáčova sluj Cave, the Kobyla Quarry. Notice the slightly convex “gothic” shape of younger overgrowths, which precipitated on eroded dogtooth-shaped calcite crystals (C, arrowed), and calcite crystals showing the development of multiple successive flat slabs (D).

The internal structure of the individual speleothems was more complex and essentially devoid of gothic-arch or scalenohedral calcite crystals. It consisted of multiple growth zones of semi-spheroidal fibrous fans and feathery aggregates of fine, elongated calcite crystals ([45]; Figure 2B,E and Figure 5A–C). The present-day composition of these acicular and feather-like aggregates is low-magnesium calcite, but its characteristic crystallographic features may point to a replaced aragonite precursor [46]. Several other exotic crystallographic forms of calcite were also recognized inside the speleothems, including calcite spar prisms with triangular cross sections (Figure 5D,E), and chevron-like aggregates of elongated lath-shaped calcite crystals similar to herringbone calcite ([47]; Figure 5F). The interiors of some coralloids underwent a secondary silicification by opal to quartz (Figure 5C,D).

**Figure 5.** Optical photomicrographs of thin sections showing petrographic aspects of the inner growth zones of coralloid speleothems from the Koněprusy caves (C–F) and the nearby Nová propast Chasm (A,B). Aspects of secondary silification of the speleothems by moganite and quartz spherulites (C) and opal silica filling large, rounded pores in the speleothem matrix (D, arrowed) can be seen. See text for the details. Transmitted white light, partly (A–C,F) to completely crossed polars (D,E).
4.2. Scanning Electron Microscopy of Speleothem Exterior

4.2.1. Etched Calcite Crystals

The SEM revealed that most of the calcite crystals forming the exterior of the speleothems, including many gothic-arch calcite crystals, exhibited a bizarre, rugged micro-topography that apparently resulted from a type of natural etching (Figure 6). The tips of calcite rhombohedra were found to be especially prone to these corrosive processes, which, in some cases, resulted in an almost complete dissolution of the individual crystals (Figure 6A–D). Many calcite crystals also displayed irregular to rounded cavities etched in their faces (Figure 6B), while some other crystals revealed morphological evidence that their growth involved several successive stages of calcite dissolution and re-precipitation (Figure 6E,F).

Figure 6. Scanning electron micrographs showing aspects of etched calcite crystals from the surface of coralloids, Petrbok’s Hall, the Koněprusy Caves. (A)—Dramatic topography of deeply corroded and etched scalenohedral and gothic-arch calcite crystals. (B)—Variously corroded gothic-arch calcite crystals. Notice almost completely destroyed tip and an irregular hole in the center of a crystal in the foreground (arrow). (C)—A detailed view of an etched tip of another calcite crystal. (D)—A detail of a deeply etched face of a gothic-arch calcite crystal. The corrosion exposed numerous spear head-shaped calcite subcrystals protruding from the corroded face (arrowed). Observe that minute calcite debris, which probably resulted from the microbial breakdown of the calcite substrate, was trapped in between these sub-crystals. (E)—A detail of a face of a calcite crystal showing lower layer, exposed through an irregular hole in the upper layer that was etched prior to precipitation of the upper layer. The etching of the lower layer has exposed a number of spear-head-shaped calcite sub-crystals. (F)—A detailed view of a well-developed spear-head calcite sub-crystals showing that these represent, in fact, tiny hexagonal prisms.
4.2.2. Spiky Calcite

Upon increasing SEM magnification, many partially etched faces of the rhombohedral calcite crystals were found to be covered with a forest of tiny, spike-like calcite sub-crystals reminiscent of a fakir’s bed (Figure 7). The spike-like terminations of these sub-crystals formed in a direction parallel to the c axis of the calcite crystals and commonly protruded from its etched faces for about 40–50 μm. Some etched crystal faces exhibited only a few isolated spikes, but some others were covered entirely with a forest of spikes that were mutually interconnected at the base like saw teeth (Figure 7A). Similar sharply pointed calcite sub-crystals have been described from Italian travertines and termed spiky calcite [14].

![Figure 7](image)

Figure 7. Scanning electron micrographs of the spiky calcite, the Petrbok’s Hall, the Koněprusy Caves. (A)—A forest of sharp, spiky sub-crystals exposed on a face of a calcite crystal. (B)—A detailed view of a framed area shown in (A) showing the enlarged structure of calcite “spikes”, which, in turn, appear also to be etched. Note also solitary needle-like calcite crystallites that still rest on the sample (arrows).

4.2.3. Needle-Like Calcite and Micrite Grains

Tiny randomly oriented, needle-like or rod-shaped calcite crystallites, often less than 1 μm in diameter, formed porous accumulations on the rugged, etched faces of many rhombohedral calcite crystals (Figure 8). Individual needles were the most frequent morphology, but some crystals composed of two parallel aligned needles cemented together also occurred (Figure 8A). Similar needle-like calcite crystals have already been mentioned in the literature, where they were described under various names (e.g., calcite whiskers, needle-fiber calcite, lublinite, moonmilk) from calcareous soils [48], travertine deposits [49], and caves [50,51].

Numerous irregular or partly rounded micrite grains, ranging between 2–5 μm in diameter, were commonly found, along with needle-like calcite rods and larger-diameter calcite debris, on the faces of some calcite crystals (Figure 8A,B). The SEM images also revealed details of the internal structure of outer layers of many calcite crystals, consisting of dense accumulations of countless needle-like sub-crystals and micrite grains that were tightly cemented together (Figure 8C,D).
4.2.4. Ribbon Calcite

Some rhombic calcite crystals exhibited bizarre streak-like microstructures that were exposed in the interior of intensely corroded crystals. These intriguing microstructures were made of numerous parallel, elongated streaks of several tens of microns-long calcite stranded in the direction of the c-axis of the respective calcite crystals (Figure 9). In detail, each streak consisted of an alternation of spear head-shaped, probably flat hexagonal platelets that often protrude from etched calcite crystals and thin interconnecting calcite threads that jointly formed a 3D pattern evoking a porous lattice network (Figure 9B–D,F). Many of these calcite threads were straight and only about 1 µm thick (Figure 9C), but some appeared to be helically twisted (Figure 9D). A similar type of peculiar streak-like calcite sub-crystals have been described from Italian hot-spring travertines and termed ribbon calcite [14].

4.2.5. Trigonal Calcite Crystals

Specific, small, only 0.5–1.0 mm high, “daughter” calcite crystals, which appeared as pyramid-like equilateral trigonal prisms, were found attached to the faces of some gothic-arch calcite crystals. These tiny prisms did form aggregates, but were present only as solitary, euhedral sub-crystals, with their c axis perpendicular to the substrate (Figure 10).
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4.3. Fluid and Solid Inclusions

Gothic-arch calcite crystals contained numerous intimately coexisting solid and fluid inclusions. The interiors of individual calcite crystals revealed the development of multiple light growth zones and distinct, dark cloudy inclusion-rich cores and rims (Figure 11). Essentially all the inclusions recognized in calcite defined individual growth zone boundaries or formed 3D clusters in the inclusion-rich crystal cores, which indicates their primary origin (Figure 11A,B). The inclusion morphology was highly variable and ranged from regular elongated forms to completely irregular planar or sub-isometric shapes. The size of the individual inclusions was also variable, with a diameter ranging between several microns and ~500 µm. Some of these inclusions contained a fluid phase (Figure 11C,D),

Figure 9. SEM pictures showing aspects of the ribbon calcite. The exteriors of the coralloids, Petrbok’s Hall, the Koněprusy Caves. (A)—A general view of deeply etched calcite crystals. Elongated ribbon calcite sub-crystals can be seen inside a framed area. (B)—A detail of (A) showing a system of parallel, thin calcite ribbons that interconnect partly amalgamated parallel rows of lozenge-shaped platelets (arrowed). (C)—An enlarged view of calcite ribbons shown in (B). (D)—A deeply etched surface of calcite crystals exposing a system of sharp, spear head-shaped (center) and ribbon calcite sub-crystals (upper right). Some calcite ribbons visible in the right background appear to be helically twisted. (E)—A system of spear head-shaped calcite sub-crystals etched-out from a corroded calcite crystal. Notice also a number of small ball-like bodies, probably microbial calcareous spheroids covering the sub-crystals (arrows). (F)—Spear head-shaped sub-crystals that were partly overgrown with a newly precipitated calcite. Some sub-crystals acquired a new, slightly asymmetrical nose-like shape (1). Relicts of calcite ribbons hidden under a thin layer of newly formed carbonate can still be recognized (2). Observe also the delicate, thin hair-like blanket, possibly fungal hyphae or microbial mucus, covering some sub-crystals (arrowed).
while many others were solid, composed of quartz or opaline silica (EDX and microscopic identification; Figure 11E).

![Figure 10](image1.png)

**Figure 10.** Scanning electron micrographs showing trigonal calcite crystals attached to an aggregate of gothic-arch calcite crystals, the Petrbok’s Hall, the Koněprusy caves (A, detail in B). Note the almost equilateral triangular shape of crystal faces. Notice also a circular hole in a crystal face (B, arrowed), which probably resulted from microbial-mediated corrosion.

Fluid inclusions recognized in gothic-arch calcite were mainly mono-phase fluid inclusions containing only homogenous liquid or vapor. The mono-phase liquid inclusions, which were optically similar to solid SiO₂ inclusions, appeared transparent under the transmitted light microscope, whereas vapor or vapor-rich inclusions were commonly dark and poorly transparent. Minor two-phase inclusions consisting of a liquid and a gas phase also occurred (Figure 11C) and these were subjected to microthermometric analysis to determine the temperature, diagenetic environment, and salinity of formation. The degree of filling of these inclusions was highly variable. Upon heating and freezing, all two-phase inclusions, irrespective of their morphology and positions within the crystals, revealed identical phase transitions. They froze down to about −40 °C, and their last ice melted at 0 °C, indicating a freshwater content with very low salinity close to 0 wt.% NaCl equivalent. No liquid hydrocarbon inclusions were recognized in the samples. The variable liquid-to-vapor ratio of two-phase inclusions that coexisted with prevailing monophase gas or water-containing inclusions suggests entrapment in the vadose zone. A variable degree of fill of two-phase inclusions may have resulted from the maturation of fluid inclusions at a relatively low temperature [52]. These inclusions, therefore, would not be used for the determination of homogenization temperatures [53]. The presence of abundant all-liquid inclusions in the samples, however, indicates that the formation of gothic-arch calcite crystals probably occurred at temperatures below ~50 °C [54].

### 4.4. Radiocarbon Analysis of the Speleothems

The physical appearance of most calcite crystals from the speleothem exterior examined during this study indicates that the crystals were old and not actively growing today. This observation is supported by the results of the radiocarbon analysis, which revealed that all but one of the seven analyzed carbonate crystals did not show any presence of ¹⁴C. This means that their age was beyond the upper dating limit of about 55,000 years for ¹⁴C. Only one sample exhibited a significant presence of ¹⁴C, the activity of which was determined to be 44,203 ± 396 years BP of Conventional Radiocarbon Age [55]. Assuming that the analyzed material did not contain an admixture of any fossil (dead) carbon, this activity would correspond to the calibrated age interval of 47,656–45,724 years BP. However, a repeat analysis of this sample yielded a statistically different value of ¹⁴C activity, 53,174 ± 1801 years BP of Conventional Radiocarbon Age, which was close to the detection limit of the analysis and approached the upper age range of the actual IntCal20 radiocarbon calibration curve [42].
Figure 11. Transmitted light microphotographs of primary inclusions in gothic-arch calcite of crystalline coralloids from the Petrbok’s Hall (S30) and the Prošek’s Dome (S31), the Koněprusy Caves. (A)—A composite scan of two polished wafers showing internal growth zone banding and inclusion-rich rims and cores of the crystals. A characteristic convex outward curvature of calcite crystal faces that developed by successive overgrowing of dogtooth-shaped calcite cores can also be seen. (B)—Detail of a crystal rim of the S30 sample formed by two generations of calcite (older CC$_1$ and younger CC$_2$) separated by a thin layer of SiO$_2$ and solid inclusions. Growth zone boundaries are lined by numerous tiny fluid (black arrows) and solid silica inclusions. (C)—A group of primary mono-phase liquid (white arrows) and two-phase inclusions (black arrow) in the S30 sample. (D)—A group of primary inclusions with a variable degree of fill embedded in the S31 sample. Notice that two-phase liquid-rich inclusions (black arrows) coexist with dark, vapor-only or vapor-rich inclusions (white arrows). (E)—Primary solid silica inclusion in calcite of the S31 sample coexisting with primary two-phase liquid-rich inclusions (arrowed).

5. Interpretation and Discussion

5.1. The Occurrence of Gothic-Arch Calcite

Calcite crystals forming steep rhombs with outwardly convex edges evoking gothic arches were originally discovered in minidam pools of Italian hot spring travertines [14] and subsequently recognized in many other travertines worldwide [16,56–58]. Calcite crystals of this specific habit were also reported from some present-day cold-water tufa deposits [17,18] and fossil spring carbonates deposited from waters of uncertain original temperature [15,49,59,60]. More recently, calcite microcrystals forming steep rhombohedra with characteristically curved faces and edges have been found as components of fine-grained precipitates deposited from some natural mineral waters stored in PET bottles [61].

In the speleal depositional settings, however, gothic-arch calcite has seldom been reported. Gary and Sharp [62] recognized gothic-arch calcite among dogtooth spar crystals...
that covered subaqueous sinkholes of the volcanogenic Zacatón hydrothermal karst system in Mexico. Gradziński et al. [19] reported these characteristically convex calcite crystals from phreatic flowstones filling fissures in calcareous sandstones in the Polish Carpathians. Most recently, gothic-arch calcite, associated with sulfur-containing minerals including gypsum, stibnite (Sb$_2$S$_3$), opal silica and Mn-oxides, were described as a secondary mineral cement from the calcareous tufa deposited in some caves of the Bohemian Karst during the late hypogene stage of cave development [28].

5.2. The Physico-Chemical Conditions of the Gothic-Arch Calcite Precipitation

The conditions under which the gothic-arch calcite precipitated can be partly inferred from the wider geological context of the Koněprusy Caves. The morphology of the caves, notably its missing relationship to the surficial hydrology, the presence of characteristic blind-ended cupola-form cavities, and the exotic petrography of the speleothems collectively indicate a hydrothermal (hypogene) origin [63–66]. The research on calcite veins located nearby the caves has shown that 40 to 115 °C warm, hypogene waters, probably basinal fluids of variable salinity (0.4 to 22 wt.% NaCl equiv.), ascending from underlying lower Palaeozoic sedimentary strata, were instrumental in the dissolution of the caves [27,33,67]. Moreover, the petrographic characteristics of the Koněprusy coralloids, particularly the feather-like and acicular calcite aggregates suggestive of replacement of an aragonite precursor, the dogtooth spar and the gothic-arch calcite crystals, and the silica interlayers suggest that the speleothems originated during the final, vanishing stage of the hypogene karstification when the fluids penetrating the cave had probably been still lukewarm and slightly saline [32,67]. The early petrographic and microthermometric fluid inclusion research on the “Koněprusy rosettes” has already indicated the presence of low-salinity (<3 wt.% NaCl equiv.) NaCl and CaCl$_2$ solutions, possibly with a minor admixture of hydrocarbons and siliceous pseudomorphs after evaporite minerals that were preserved in the inner growth zones of the coralloids [32,33]. In contrast, our present microthermometric study, concentrating specifically on gothic-arch calcite crystals from the speleothems’ exterior, revealed only the presence of freshwater inclusions of very low salinity (close to 0 wt.% NaCl equiv.) entrapped at temperatures below ~50 °C. These data collectively indicate a gradual decrease in temperature and salinity of fluids from early hydrothermal vein calcite to the late-stage spelean carbonates, which can best be interpreted in terms of the wider geological evolution of the Coenurus Caves. In particular, this includes their gradual ascent from a deeper hypogene setting dominated by warm, saline waters, to the shallow subaerial setting in which the caves were influenced by an influx of meteoric waters from the topographic surface. Similar hydrological evolution, driven by tectonic uplift of the Bohemian Massif during the Pleistocene, has been recently documented for some other caves in the Bohemian Karst, close to the Koněprusy Caves [28].

5.3. The Microscopic Ultrastructure of Gothic-Arch Calcite Crystals

The origin of spiky calcite has already been interpreted. It was originally suggested that the spiky calcite was probably a product of growth and dissolution [14]; however, later studies have experimentally verified that it resulted from dissolution mediated by fungi and possibly associated bacteria that had infested the calcite crystals [68]. Fungal enzymes, along with microbial mucus, have been shown to be especially efficient in the geologically rapid dissolution of calcite, leading to the formation of spiky calcite [69–73]. The analysis of SEM images of the Koněprusy coralloids confirmed that the spiky calcite represents a dissolution feature that generally developed in a direction parallel to the c axis of gothic-arch calcite crystals, a fact noted in previous studies [14,68]. The SEM images also revealed that many, if not most, of these calcite “spikes” represent, in fact, the exposed tips of spear head-shaped, flat hexagonal crystallites of ribbon calcite (see below), a sub-microscopic structure that was exhumed inside the calcite crystals by intense etching (Figure 6D, Figure 7A,E and Figure 12). The presence of small calcite ball-like bodies, about 10 µm in diameter (Figure 9E), possibly microbial carbonate spheroids [74], sparmicite
monticule [69], or calcified fruiting bodies of fungi [75], which are commonly associated with spiky calcite, suggest that processes induced by microorganisms had possibly been involved in its formation [33]. The exact affinity of these spherical bodies is, however, unknown due to their heavy calcification.

Precipitation of needle-fiber calcite, which was found in abundance covering the faces and etch pits of the corroded calcite crystals, has been previously attributed to various organic and inorganic processes. Many studies have linked precipitation to the activity of fungi, filamentous microbes, and/or bacteria [50,60,76], but examples of its abiotic precipitation from soil-derived seepage waters or hot springs have also been provided [77]. In caves, needle-like calcites have often been interpreted as bio-sedimentary crystals that were actively precipitated within specific fungal or bacterial hyphae, which, upon decomposition, released the needles into the medium [48,51,78,79].

Micritic grains, such as those recognized on the exterior of the Koněprusy coralloids, are commonly found on the outward surface of speleothems that had long term contact with water, especially on the tips of elongated speleothems [80]. The dissolution of calcite crystals and the formation of micrite grains may also be mediated and/or escalated by microbial or bacterial activities and biofilms. In many cases, these fine organic tissues have disappeared due to natural decay so that only needle-like crystals and micrite grains remained within the deposit [51,69,81].

Trigonal calcite crystals, such as those found on the exterior of some gothic-arch calcite crystals, have been recognized from some paleosols [82] and lacustrine deposits [83,84]. More recently, calcite crystals with trigonal prism morphologies, often forming composite trigonal prismatic aggregates made by numerous smaller-scale trigonal prismatic sub-crystals, were described from some spring deposits, both cold-water tufas [18,85–87] and hot-spring travertines [16,88–90]. Trigonal calcite crystals have also occasionally been reported also from some speleothems [6,10,19,91], however, the factors that control their precipitation are poorly understood. It seems that variables other than temperature and saturation levels, particularly poisoning of the crystal growth surface by other elements or organic matter, may be responsible for the specific habit of the crystals [88].

### Figure 12

A schematic sketch showing fine ultrastructural features of the gothic-arch calcite crystals described in the text (A). Enlarged details of spiky (B) and ribbon calcite sub-crystals (C) are also shown. The spear head-shaped platelets of the ribbon calcite are, in fact, very flat hexagonal prisms, with two greatly developed faces, while the other two are suppressed. Note that the spiky calcite, calcite ribbons and spear head-shaped platelets all point in the direction of the c-axis of calcite crystals, suggesting that they probably represent various elements of the same ultrastructure, which is intrinsic to calcite crystals. See the text for the details.
Ribbon calcite, another microscopic ultrastructure recognized in the interior of deeply etched gothic-arch calcite crystals, was originally described from some Italian hot-spring travertines [14]. Its occurrence has been also noted in laminated flowstones from a cave in the Slovakian Karst and, although not described as such, the photographs hint at its presence [92]. A microfabric superficially similar to ribbon calcite was also identified in the cave fills of some Italian caves, which had probably been affected by hot hydrothermal waters [93]. The origin of ribbon calcite has been variously explained. The rhythmical alternation of dense laminae of diamond-shaped platelets and more porous laminae of calcite strands were interpreted as micro-laminae resulting from daily, annual or longer-term climatically contrasting periods that fluctuated during speleothem growth [14,92,93]. In contrast, some authors concluded that this fabric formed due to crystallographic reasons, notably by alternating episodes of calcite crystal splitting and coalescence [93].

Although the origin of ribbon calcite remains ambiguous, the analysis of SEM images of the Koněprusy speleothems allows for two conclusions to be made: (1) The regular arrangement of the individual calcite ribbons, the long axes of which ran parallel to the direction of the c-axis of the calcite crystals, suggest that calcite ribbons represent, in fact, sub-microscopic building units that have been exposed by deep etching and are fully intrinsic to the calcite crystals (Figure 12). (2) The presence of fine hair-like blankets, possibly mucus of fungal or microbial origin, which cover the tips of some actively growing ribbon-like calcite sub-crystals and ball-like carbonate bodies, about 5–10 µm in diameter, possibly bacterial calcite spheroids [74,94,95], or calcified sporangia of microscopic fungi [75] that commonly occur in between calcite ribbons, indicate a possible influence of microbiological processes on the precipitation of ribbon calcite (Figure 9E,F).

5.4. Curved Crystal Faces of Gothic-Arch Calcite and a Possible Mechanism of Their Growth

The characteristic curvature of gothic-arch calcite crystals was originally explained by the substitution of minor amounts of sulfate ions into the calcite lattice structure, which takes place in S-rich environments [14]. The tetrahedral SO\(_4^{2–}\) group with four oxygens is larger than the planar CO\(_3^{2–}\) group, so that an intermittent SO\(_4^{2–}\) group uptake into the calcite lattice inevitably causes the following carbonate sheet to bend upward. In accordance with this hypothesis, the curvature of gothic-arch calcite crystals should be indicative of sulfur-rich, often hydrothermal, aqueous environments inhabited by sulfur-oxidizing bacteria. Indeed, many occurrences of the gothic-arch calcite, both from fossil deposits and present-day springs, have been reported to be associated with waters that once may have been, or still are, sulfate-rich, lukewarm or warm, and with rich bacterial activity [14,15,18,19,28,57,58,61,62].

According to other hypotheses, however, the convex crystal morphology of gothic-arch calcite may be due to the presence of other specific impurities and foreign ions, such as SiO\(_2\), Na, Sr, Al and Ba, which, at higher concentrations, are known to inhibit the calcite crystal growth [19,61].

Different explanations for the curvature of the gothic-arch calcite crystals are based on various crystallographic deformations in the crystal lattice, particularly the bending of individual crystallites in the vicinity of crystallites that were growing at a slower rate [96], the displacement along a curved path of individual crystallites composing the macroscopic crystals [12], or the radial growth of calcite crystallites within each crystal [59].

Although the potential influence of sulfate ions or other crystallographic factors on the crystal shape of gothic calcite still remains a viable hypothesis [14], we currently believe that the characteristic convex habit of these crystals may have been due to a specific combination of microbiologically mediated processes of calcite dissolution and precipitation.

An analysis of the SEM images clearly shows that the surface of many Koněprusy coralloids has been affected by extensive natural etching and corrosion. These destructive processes led to the formation of various dissolution features ranging from irregular, etched crystal surfaces and etch pits in crystal faces, to the almost complete erosion of individual calcite crystals and the formation of spiky calcite sub-crystals, loose clay- and silt-sized
grains of calcite, and residual micrite produced during sparmicritization [80,97]. The SEM images show that these particles, which resulted from the breakdown of the individual calcite crystals, were transported downward over the corroded crystal faces by gravity or water flowing over the speleothems and intermixed with newly formed needle-like laths of lublinite. These were trapped and bound in between the spines of spiky calcite or on other irregular surfaces protruding from the etched crystal faces, or eventually deposited at the base of the crystals (Figure 13). The SEM images have also revealed further details of this process in which the bounding, cementation, and recrystallization of carbonate particles on the surface of corroded calcite crystals eventually resulted in the formation of new, compact, slightly convex crystal faces. In this way, by a combination of inter-related processes of carbonate destruction and construction that coevally acted on the speleothem crystalline surface, many gothic-arch calcite crystals may have originated by neomorphism of etched scalenohedral (dogtooth) calcite crystals (Figure 13).

Figure 13. A conceptual model for the formation of gothic-arch calcite crystals through a combination of microbial erosion and recrystallization of erosion-derived calcite debris. See the text for the details.
The similar close coexistence of destructive and constructive processes has been documented from many cave substrates worldwide and attributed to the mediation activity of various microorganisms including bacteria and their biofilms, and fungi [69,70,98,99]. In many cases, such as in the Koněprusy Caves, these microscopic organisms colonizing the speleothem surface were rarely preserved by calcification and their presence can only be inferred from certain by-products of their activity (i.e., etched calcite crystals, spiky calcite, spar micrite, microbial carbonate spheroids, etc.). The exact identity of these putative microorganisms can only be hypothesized, and specific additional methods, such as biochemical tests or DNA sequencing, would be needed to reach more concrete conclusions. Nevertheless, our previous research has already shown that abundant fossil microbes, including undetermined filamentous and coccolid microbes, were entombed in siliceous laminae that occurred in deeper growth zones of the Koněprusy coralloids [33].

Since the gothic-arch calcite crystals occur principally on the outward, geologically youngest, and intensely corroded exteriors of the speleothems, it follows that their formation must have occurred relatively late during the geological history of the caves. The radiocarbon analysis of these calcite crystals generally showed that they were older than ~55 ka; a result consistent with the previous U-Th dating of these speleothems, which indicated the age of its internal growth zones to be ~200–600 ka [35,36]. However, statistically significant differences in $^{14}$C activities, which were recorded upon repeated analyses of one single crystal point to the non-homogeneous distribution of $^{14}$C in its surface layers. This effect could be caused by patchy occurrences of newly formed, microbial-induced carbonate particles, which were involved in the remodeling of the outer surface of the crystals over a relatively recent period. In other words, it seems likely that the sample that yielded an age younger than the upper $^{14}$C dating limit, contained a mixture of both outermost, microbial-affected layers and older (fossil) carbonate layers forming deeper crystal interiors, on a scale smaller than the sampling technique could resolve. Similar complexities associated with microbial alterations of thin outermost surfaces of cave samples can influence on the $^{14}$C analysis of these materials [100].

Published results of experimental studies on microbial-mediated calcite corrosion have already illustrated that beneath the fungal mucus, a substantial dissolution of calcite crystals may have developed in as few as 253 days [68]. Thus, it is relatively easy to envisage that the characteristic convex shape of gothic-arch calcite crystals that originated through the outlined mechanisms of microbiologically enhanced calcite corrosion and recrystallization, may have occurred rapidly, and probably only during the latest stage of cave development. What exactly triggered the process of biologically mediated corrosion of the speleothems and the coeval precipitation of the gothic-arch calcite on the speleothem exterior remains uncertain. Perhaps, these specific conditions established during the tectonic ascent of the caves by a regional uplift that followed the gradual extinction of the hypogene processes in the Pleistocene. At that time, the speleothems were exposed to meteoric waters seeping into the cave from the topographic surface, which, by virtue of microbiological activity, may have contributed to the corrosion of the speleothems and precipitation of specific gothic-arch calcite crystals.

Further research, including culturing of microbiological samples collected from speleothem surfaces and its genomic DNA extraction, is now in progress in order to identify specific microorganism(s) involved in these processes.

6. Conclusions

Our research on gothic arch calcite from the Koněprusy Caves provides the following insights into the petrography and origins of this specific calcite crystal habit.

1. Steep rhombic, slightly convex, up to 8 mm high crystals of gothic-arch calcite are abundant on the exteriors and in the youngest growth zones of coralloid speleothems in the Koněprusy Caves, in which gothic-arch calcite commonly coexists with scalenohedral (dogtooth) calcite crystals.
(2) Both gothic-arch and dogtooth calcite crystals grown on speleothem exteriors exhibit ultrastructural features characteristic of microbial etching and corrosion, including the development of intensely corroded calcite crystals, etch pits, spiky and ribbon calcite sub-crystals, and residual micrite and needle-fiber calcite accumulated on the faces of corroded calcite crystals.

(3) Primary fluid inclusions entrapped in gothic-arch calcite are two-phase aqueous-air and mono-phase aqueous-only inclusions containing low salinity fluids (~0 wt.% eq. NaCl), which point to a freshwater vadose setting and temperatures lower than ~50 °C.

(4) A hypothesis explaining the characteristic convex habit of gothic-arch calcite is presented pointing to a combination of microbiologically mediated corrosion of scalenohedral (dogtooth) calcite spar crystals and its subsequent overgrowth by new convex crystal faces. The latter resulted from the recrystallization of corrosion-derived carbonate grains that accumulated preferentially on the faces of etched calcite crystals.

(5) Specific conditions that favored the formation of gothic-arch calcite crystals established during the final, subaerial stage of cave development starting in the Pleistocene when, following the gradual vanishing of the hypogene processes, the cave was flooded with meteoric waters from the topographic surface. Under these conditions, the microbiologically mediated corrosion of a spelean substrate and formation of gothic-arch calcite crystals may have been a rapid process, lasting from years to centuries.

Author Contributions: Conceptualization, field sampling, optical petrography and writing of the draft, V.S.; radiocarbon analysis, visualization of the results, and editorial handling, K.P.B.; fluid inclusion analysis and editing of the text, J.Z.; funding acquisition, general supervision on laboratory analyses, and editing of the text, I.S.; SEM analyses, L.B. All authors have read and agreed to the published version of the manuscript.

Funding: A part of this research benefited from support provided by OP RDE, MEYS, under the project “Ultra-trace isotope research in social and environmental studies using accelerator mass spectrometry” (Reg. No. CZ.02.1.01/0.0/0.0/16_019/0000728).

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Acknowledgments: We wish to acknowledge the assistance of Alexandr Komaško, the Head of the Koněprusy Caves, who kindly released part of the samples analyzed in this study, and Petra Přidalová (Museum of the Bohemian Karst, Beroun), who enabled us to study the speleothem samples from the museum collections. Margit Žaloudková, (Institute of Rock Structure and Mechanics of the CAS) performed several SEM images. Antonín Zeman, (formerly the Institute of Theoretical and Applied Mechanics of the CAS) and Petr Dobeš, (Czech Geological Survey, Prague) kindly made photomicrographs shown in Figures 4B and 5, respectively. Three anonymous reviewers are thanked for their constructive comments, which substantially improved this paper.

Conflicts of Interest: The authors declare no conflict of interest.

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