Active growth of non-hydrothermal subaqueous and subaerial barite (BaSO_4) speleothems in Lechuguilla Cave (New Mexico, USA)

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Abstract: Barite (BaSO_4) speleothems have been reported from caves around the globe and interpreted to have chiefly formed in phreatic, hypogene, hydrothermal settings. Here we report two contrasting types of barite speleothems (bluish tabular crystals in a shallow pool and actively dripping greenish stalactites), which today form at lower temperatures in the non-hydrothermal and vadose environment of Lechuguilla Cave, New Mexico, USA. Scanning electron microscopy analysis, along with energy- and wavelength-dispersive X-ray spectroscopy (EDS, WDS), as well as X-ray diffraction (XRD), characterize the habit and chemical composition as barite. Fractionation of the minor element calcium is related to growth along different crystal faces whereas variations in strontium concentration are mirrored in blue color zoning of the pool crystals. Two possible modes of non-hydrothermal barite precipitation are discussed: (1) intense evaporation driven by thermal atmospheric convection cells or (2) mixing of barium-rich, sulfate-poor water with water rich in sulfate. Both processes, in isolation or in combination, lead to supersaturation and could explain formation of the investigated barite speleothems. Observations of three types of microbes on the pool barite crystals showing evidence of incrustation raises the question whether there is a potential involvement of microbial activity in the temperate barite precipitation in Lechuguilla Cave.

Keywords: barite, speleothem, precipitation, microbes, incrustation

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INTRODUCTION

The mineral barite (BaSO_4) is best known for its high density (4.5 g/cm^3), which has led to its use in a number of economically important applications. Due to its low dissolution rate, barite is generally undersaturated in natural waters, although large quantities can be found in marine settings. There, barite can form in the water column, on the seafloor, or within the sediment, where (1) barium-rich organic matter decays, (2) precipitation is mediated by microbial activity, (3) waters rich in barium and sulfate mix, or (4) hydrothermal fluids rich in dissolved minerals cool down (Hanor, 2000; Griffith & Paytan, 2012).

In continental settings, the formation of barite is usually associated with hydrothermal activity supporting the formation of massive barite as a component of ore deposits (Hanor, 2000) including formation of colorful mineral aggregates

(Rustemeyer, 2015). The remobilization and phreatic reprecipitation of barite in a hypogene hydrothermal karst environment is believed to be responsible for the majority of the known occurrences of barite as a cave mineral (for review, see Hill & Forti, 1997). For some of those occurrences, a hydrothermal origin has been demonstrated by analysis of fluid inclusions and/or sulfur stable isotope analyses (for review, see Dublyansky, 1997). For at least one occurrence, the barite replacement boxwork recently reported from the Frasassi caves in Italy (Galdenzi, 2019), a non-hydrothermal origin is conceivable.

Barite speleothems that formed in the vadose zone under subaerial conditions in caves are rare. Occurrences include unique hollow barite helictites of a cave in the Silius barite-fluorite mine, southwest Sardinia (Hill & Forti, 1997), and helictites with a radial arrangement of surficial barite crystallites in Madoc Cave, Ontario, Canada (Walker, 1919). Reworking of hydrothermal mineral deposits by H_2S -

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rich condensation waters and redeposition as barite (and celestine) on the surface of calcite speleothems has been reported from the Cup-Coutunn Cave System, Turkmenia (Maltsev & Malishevsky, 1990; Maltsev & Self, 1992). More recently, barite crystals were detected in rims associated with floor vents that are considered hypogene in Cova des Pas de Vallgornera, Majorca, Spain (Fornós et al., 2010; Onac et al., 2014). Barite stalactites with typical vadose morphology (including a central canal and radial arrangement of crystallites) were reported from Tunisia (Rustemeyer, 2015). Active formation has not been demonstrated for any of these occurrences.

The fact that barite can form in non-hydrothermal settings in the ocean (Griffith & Paytan, 2012), such as cold vent sites (Greiner et al., 2002; Stevens et al., 2015), raises the question whether barite could also form in caves under non-hydrothermal conditions. In this paper we characterize two types of actively growing barite speleothems in a temperate environment (normal-temperature cave setting = 5–25°C sensu Dublyansky, 1997), both discovered in Lechuguilla Cave, New Mexico, USA.

Lechuguilla Cave is among the world's largest cave systems, with more than 240 km of mapped passages (Lyles & Davis, 2016; Lynch, pers. comm., 2019). The cave formed in carbonate rocks of the Permian Capitan Reef Complex in the Guadalupe Mountain uplift through hypogene sulfuric acid speleogenesis (DuChene, 2000; Hill, 2000a, b). During the Miocene and Pliocene, hydrogen sulfide (H₂S), derived in part from microbial activity in hydrocarbon reservoirs in the adjacent Delaware Basin, mixed with oxygenated waters of the karst aquifer to form sulfuric acid (H₂SO₄) that caused extensive carbonate dissolution and cave origin (Hill, 1987, 2000a, b; Jagnow et al., 2000; Palmer & Palmer, 2000; Barton, 2013; DuChene et al., 2017). Substantial deposits of gypsum (hydrated CaSO₄) were left behind as a byproduct and their secondary dissolution and reprecipitation led to the formation of a wide variety of speleothems (Davis, 2000; Palmer & Palmer, 2000; Polyak & Provencio, 2001; Palmer, 2006). Lechuguilla Cave contains a substantial suite of rare cave minerals, many of which are directly or indirectly related to sulfuric acid speleogenesis (Cunningham et al., 1993; DuChene, 1997; Davis, 2000; Polyak & Provencio, 2001). This inventory includes barite derived from the host rock and associated corrosion residues (Spilde, pers. comm., 2019). Near the entrance of Lechuguilla Cave, a deposit of pale blue tabular barite, intergrown with translucent blocky calcite, is thought to be related to local Mississippi Valley Type (MVT) ores that formed in the host rock long before the cave (Hill, 1993); a nearby occurrence, possibly of same origin, was recently noted at the top of the dome 'Purple Rain' (Hunter, pers. comm., 2019). Nonetheless, there is evidence of barite as a cave mineral that is currently forming speleothems within the cave. These include unusual greenish, subaerial stalactites that drip water, first identified in 1998 in an area called 'Frostworks' (Bosted, 1998; LaForge, 1998; Davis, 1999), and bluish, bladed barite crystals forming at the bottom of

a calcite-lined pool in an area called 'Blanca Navidad', discovered in 2016 during a resurvey of this part of the cave.

The goal of this paper is to confirm the identity of these barite speleothems and to characterize them using a combination of crystallographic investigation, micro-structure analysis, and elemental mapping. The results confirm the presence of active barite speleothems forming in the cave under low-temperature conditions. Based on our results and circumstantial evidence from the geological and speleological setting, potential modes of barite precipitation are discussed.

MATERIALS AND METHODS

Sampling

A piece of a broken stalactite from the 'Frostworks' location was collected in 1998 near survey station EYWL38 as part of the Lechuguilla Cave Mineral Inventory Project (LCMIP). The sample was stored in a plastic film canister for transport before analysis. One barite crystal was removed in 2016 near station ECKR22B from a pool in 'Blanca Navidad', using sterile tweezers and stored in a sterile, 15 ml Falcon tube stabilized by Kimwipes.

Mineralogical and geochemical analyses

Samples were air-dried and photographed with a Nikon D700 DSLR camera and AF-S Micro NIKKOR 60 mm 1:2.8 G ED lens on a black as well as a white background for characterizing translucence and color zoning. Samples were then mounted on aluminum stubs, coated with gold using a Cressington 108auto sputter coater, and imaged via scanning electron microscopy (SEM) on a Tescan VEGA3 xmu at 20 keV, using secondary electron (SE) and backscatter electron (BSE) detectors.

For mineral identification, samples were ground to powder in a mortar. X-ray diffraction (XRD) analyses were carried out on a Philips PW1729 X-ray generator with a 2200 Watt 60 keV Cu X-ray source, monochromized with quartz. Powdered samples were analyzed at 40 keV and 30 mA in a 2 Theta range from 15 to 60°. Results were compared to barite reference spectra archived at www.mindat.org.

For a general element screening the SEMs OXFORD X-Max energy dispersive X-ray spectrometer (EDS) with INCA software (v. 5.05) was used. Spectral analyses were carried out at 10 and 30 keV acceleration voltage by scanning several areas of 100 x 100 µm for 300 seconds, with process time 5 at 10 keV and 3 at 30 keV, using 2000 channels and a beam intensity of 15, resulting in >1,000,000 counts per spectrum.

In preparation for high-resolution elemental mapping and quantification with wavelength dispersive X-ray spectroscopy (WDS), the samples were impregnated in R&G "water clear" epoxy resin in a Struers CitoVac vacuum chamber, trimmed on a Uniprec WOCO50 rock saw, ground on a Buehler Ecomet III grinder/polisher with P400 to P1200 grit SiC paper, polished on a 'G' cloth with 1 and 0.3 µm MicroPolish powder (all Buehler), cleaned in an

Elma Transsonic Ti-H-5 ultrasonic bath, rinsed with de-ionized water, air dried, and carbon coated with a Vacuum Coating Unit E306A of Edwards. For the WDS analyses a JEOL Superprobe JXA-8200 electron microprobe was utilized. Elemental maps (C, O, S, K, Ca, Fe, Co, Ni, Zn, Sr, and Ba) were produced on a 5 and 10 μm grid for overviews of the 'Blanca Navidad' and 'Frostworks' samples, respectively, with a 10 μm probe diameter at 100 ms dwell time, 15 keV acceleration voltage and a beam current of 100 nA. Detail maps of up to 200 x 200 μm in area were acquired on a 1 μm grid at the margin of the crystals, with a 1 μm probe diameter at 100 ms dwell time, 15 keV acceleration voltage and a beam current of 100 nA. For those five elements (O, S, Ca, Sr, and Ba) that returned a signal other than background noise (X-ray bremsstrahlung), quantitative transects were logged in 10 and 5 μm spacing across overview maps, and 1 μm spacing across detail maps, applying 5 or 1 μm probe diameters, respectively, at 15 keV acceleration

voltage, 50 nA beam current, and 20 s peak / 10 s background position time for each element. The detection limits were ~200 ppm (O), ~50 ppm (S), ~40 ppm (Ca), ~160 ppm (Sr), and ~240 ppm (Ba). Reference standards were barite (O, S, Ba), dolomite (Ca), and strontianite (Sr). Measurements with more than 3 % deviation from 100 (total) weight % were excluded from further analysis, as they reflect epoxy resin, embedded impurities, or cracks (22 out of 799 measurements in the 'Frostworks' sample and 15 out of 1764 measurements in the 'Blanca Navidad' sample).

RESULTS

Field description and mineralogical analysis of barite stalactites

All of the six sites in Lechuguilla Cave with confirmed or suspected barite stalactites are located within 500 m of each other in the western branch of the cave (Fig. 1).

Fig. 1. Map of Lechuguilla Cave, colored by depth (red = shallow, blue = deep), showing occurrences of suspected and confirmed barite and barite speleothems in the cave (survey data and records of other suspected or confirmed barite occurrences, as listed in the Lechuguilla Cave mineral inventory, provided by Cave Resources Office at Carlsbad Caverns National Park, complemented by records from the literature and personal communications).

These sites include a tall room called 'Frostworks', with aragonite frostwork and calcite crystals on the bottom and corrosion residues that coat the walls and ceiling, reflecting evaporation and condensation, respectively, in a local convection loop. Near the ceiling (survey stations EYWL37 to 38), there are stalactites up to 20 cm in length, partly wavy to angled, composed of pale translucent greenish barite (Fig. 2A-B). The stalactites have a platy structure with parallel to sub-parallel sheets running lengthwise and showing flat cleavages or crystal faces. These speleothems are partly covered with a white calcite crust and rhomboid calcite crystals. All stalactites are located at low points of hanging breakdown blocks and have moist surfaces. Shortly after this discovery, a sample was taken and a preliminary examination of a powdered subsample via XRD analysis confirmed that the sample is barite (DuChene, 1998). The remainder of that sample is used for analysis here.

Additional greenish stalactites are found in 'Cephalopodunk' at station IJ17 (Allison, 2002). The site is located below a breakdown maze with orange/rusty corrosion residue, in an alcove decorated with aragonite frostwork. Two light green stalactites are active and dripping and similarly colored tabular crystals are found at the splash point below (Fig. 2C) (Lyles, pers. comm., 2018). More stalactites are found in 'Chandelier Graveyard'. One of these, near station EYE26A, is slightly more bluish in color, 20 cm in length, inclined about 10° from vertical, and also dripping water (Fig. 2D-E). A greenish-bluish splash point is forming on the floor below (Fig. 2F). A nearby stalactite at station EGAB8 is pale greenish in color, approximately 15 cm long, oriented about 5° from vertical, and partly covered by white aragonite or calcite crystals (Fig. 2G).

Fig. 2. Greenish to bluish stalactites in Lechuguilla Cave. A) Suspected barite stalactite, about 15 cm long, in 'Frostworks'; B) Another stalactite, found broken on the floor of 'Frostworks'; C) Actively dripping suspected barite stalactite and greenish splash zone below, found in 'Cephalopodunk'; D-E) Suspected barite stalactite in the 'Chandelier Graveyard' and more bluish in color; F) Close-up of bluish splash zone forming on the floor below the stalactite shown in D-E; G) Another suspected barite stalactite in the 'Chandelier Graveyard' with partial calcite/aragonite overgrowth; H-K) The analyzed barite sample taken from a broken 'Frostworks' stalactite.

Our sample of a 'Frostworks' stalactite (Figs. 2H-K, 3A) is composed of an aggregate showing parallel crystallites resulting from parting, tabular to the pinacoid base $c\{001\}$ in the orthorhombic system (see Fig. 4 for a diagram of the crystallographic properties). This is the face with most perfect cleavage (Fig. 2I, K) and was probably oriented parallel to the axis of stalactite growth. The outer surface of the stalactite primarily shows faces of the prism $m\{210\}$ and pinacoid

$a\{100\}$ (Figs. 2H, 3A), and subordinate combinations with prism faces $d\{101\}$ and $o\{011\}$ (Figs. 3A-C). In SEM images, crystal faces appear smooth and homogeneous in SE and BSE images (Figs. 3B-D, F-I), but there are signs of intergrowth with siliciclastics (Fig. 3B-E), such as quartz and clay minerals ('q' and 'c' in Fig. 3E). Some round patches of clay are found on the surface (Fig. 3F-H), and impurities are found also deeper inside (Fig. 3I). Voids are present where

impurities have disintegrated (Fig. 3F). Although some of the embedded mineral aggregates appear elongate and cylindrical (e.g., Fig. 3D), no obvious biosignatures were identified to suggest the former or contemporary presence of microbes.

Mineral identification via XRD analysis in the 15° to 60° (2 θ) range matches the peak signature of barite (Fig. 5A). No other mineral was detected in the sample.

A series of EDS spectra of the cross section and surface of the sample show the elemental composition to be chiefly oxygen (O), sulfur (S), and barium (Ba)

(Fig. 5B). In addition to these main elements, the La1 peak of the minor element strontium (Sr) was picked up by the peak detection algorithm of the INCA software in some of the spectra. Other trace elements that can substitute for Ba in barite (Ca, K, Ra, or Pb, and more rarely Fe, Cu, Zn, Ag, Ni, Hg, or V; Hanor, 2000; Griffith & Paytan, 2012), were not detected. Spot spectra of mineral aggregates intergrown with the barite correspond to SiO₂ (quartz; see 'q' in Fig. 3E), and unidentified clay minerals (see 'c' in Fig. 3E and the round aggregate in Fig. 3G-H).

Fig. 3. Micro-morphology of a 'Frostworks' barite stalactite revealed via SEM. A) Overview of the sample from two perspectives; arrows point out the location of B to I; B-C) Small crystallite resulting from parting (SE and BSE image); D) Elongate mineral aggregate embedded in the barite; E) Partially embedded grains of quartz (q) and a clay mineral (c); F) Irregular voids in the crystal; G-H) A round spot of clay minerals on the surface (SE and BSE image); I) Section of the sample showing several embedded impurities.

High-resolution element mapping via WDS shows a homogeneous distribution of the major elements Ba, S, and O, in a stoichiometric relationship corresponding to that of barium sulfate (BaSO₄), thus confirming that the crystal is barite (Fig. 6A; Table 1). This applies also to the outer margin of the crystal, which was mapped and profiled with 1 μ m resolution (Fig. 6D), thereby excluding the presence of a detectable layer of witherite (BaCO₃). The only trace elements that

were detected are calcium (Ca) and strontium (Sr) (Fig. 6B, E; Table 1). Their occurrences are confined to growth zones near the center of the stalactite where concentrations reach up to 736 ppm Ca and 473 ppm Sr. These zones are oriented parallel to the presumed stalactite growth increments formed primarily by radial growth along the faces of the prism m {210} and pinacoid a {100} (Fig. 6B). The outer portion of the stalactite has very low concentrations of Ca and no

Fig. 4. Diagram with the mineralogical properties of the barite speleothems sampled in Lechuguilla Cave. The crystallographic axes and principal faces are shown for an idiomorphic tabular crystal prismatic to the pinacoid base *c* {001}. Parting occurs parallel to *c* {001} and color zoning (Blanca Navidad pool crystals only) parallel to the prism faces *m* {210}. High growth rates along the *m* {210} and *a* {100} faces (the tabular crystal growing in size) are mirrored in low Ca concentrations, whereas very slow growth along *m* {210} (the tabular crystal growing in thickness) leads to relatively high Ca concentrations.

detectable Sr (Fig. 6E-F). Calcium shows the highest concentrations (up to 1,888 ppm) in areas of lateral growth, i.e., where radial growth along the prism base *c* {001} and the combined prism faces *d* {101} or *o* {011} has filled open space between radiating tabular crystallites (Fig. 6B & Fig. 4). In consequence, Ca/Sr ratios cluster according to the respective crystal faces (Fig. 6C).

Field description and mineralogical analysis of barite pool crystals

The ‘Blanca Navidad’ area (Fig. 1) consists of an ascending main corridor that leads to a series of steeply inclined passages with walls heavily coated with dark corrosion residues. The main passage is occupied by a large ‘glacier’ of massive gypsum and terminates about 170 m below the elevation of the entrance. The area contains a rich inventory of speleothems and cave minerals, including gypsum (rims, chandeliers, negative splash rings, drip holes), calcite (flowstone, pearls, stalactites, soda straws, draperies, popcorn, subaqueous helictites), aragonite (frostwork, trees, trays, anthodites), and several occurrences of massive elemental sulfur (Davis, 2000 and own observations). The bluish barite pool crystals are found at station ECKR22B in a N-S trending side passage (Fig. 7), a few meters from the ‘Gripping Hand’, a stalactite/drapery group with a pool containing subaqueous helictites, both believed to have formed via the common-ion-effect (Davis, 2000). The pool is less than a square meter in diameter and a few centimeters deep (Fig. 7A). It is lined with whitish to pale gray calcite pool spar, in parts forming indistinct shelfstone. Above the water line, pool spar grades into blocky to triangular popcorn and microcrystalline crusts coating the walls. Water feeding the pool seeps in along the calcite-coated wall and drips from active stalactites (e.g., Fig. 7A on the right). The outlet of the pool leads into a canyon with a stream of wet flowstone on its bottom (Fig. 7A to the left). There is no visible water flow.

Fig. 5. A) XRD spectrum of the sample of the ‘Frostworks’ stalactite, confirming barite as sole component; B) Two EDS spectra of the same sample, acquired at 10 and 30 keV, respectively, identifying barium, sulfur, and oxygen as main constituents, along with traces of strontium.

Table 1. Quantitative WDS analysis of the sampled ‘Frostworks’ barite stalactite. The mean ± SD is given for all spot measurements (n = 777) of the profiles, calculated as weight and atomic percent, complemented by the average stoichiometric elemental ratios relative to Ba.

Element	Weight %	Min – max	Atomic %	Min – max	Element / Ba
O	27.6058 ± 0.4713	24.5800 – 29.0700	66.7731 ± 0.4306	63.3420 – 68.9280	3.9933 ± 0.0794
S	13.6537 ± 0.1231	12.6000 – 14.7400	16.4847 ± 0.2265	15.0540 – 18.8220	0.9856 ± 0.0095
Ca	0.0162 ± 0.0317	0.000 – 0.1888	0.0157 ± 0.0305	0.0000 – 0.1811	0.0009 ± 0.0018
Sr	0.0008 ± 0.0047	0.000 – 0.0473	0.0004 ± 0.0021	0.0000 – 0.0207	0.0000 ± 0.0001
Ba	59.3274 ± 0.3770	55.7700 – 60.4000	16.7261 ± 0.2369	15.8990 – 18.2980	–

Fig. 6. WDS maps (same color scaling as Fig. 10) and profiles of the 'Frostworks' stalactite sample, showing the crystallographic properties, the position of the profiles, and the distribution of the major elements Ba, O, and S (A, D) as well as the precipitation patterns reflected in the trace elements Ca and Sr (B-C, E-F).

In the pool, there are several hundred bluish tabular crystals, up to 2 cm in size, commonly showing some parting. The most conspicuous cluster (Fig. 7B-C) is partly isolated from the rest of the pool by sills of calcite pool spar. The color of the transparent crystals ranges from pale brown to pale gray to a bluish tinge (Fig. 7B), the latter more concentrated in the outer part of the zoned crystals (Fig. 7C-E). Our sample (Figs. 7D-E, 8A) is a nearly idiomorphic platy crystal about 14 mm long and 3 mm high with a maximum thickness of 1 mm. The crystal is tabular to the pinacoid base $c\{001\}$ in the orthorhombic system, and lateral faces are formed by the prism $m\{210\}$ (see Fig. 4 for a diagram of the crystallographic properties). Along the latter, the crystal shows a blue color zonation (Fig. 7D-E).

Most recently, a new passage located directly above the barite pool was explored and found to contain more (suspected) barite speleothems of interest. This passage – now called 'Barite Boulevard' (survey stations EXHA1 to 7) – is occupied by an active (wet) cascade of calcite flowstone with several small pools, draining into the 'Lake of Liquid Sky'. One of these pools contains pool fingers (microbial filaments incrusting in pool spar) and pale gray to blue suspected barite crystals of the same type as in the sampled pool (Fig. 7F-G), while another pool contains similar crystals with

a yellow tinge (Fig. 7H). More of the gray to bluish crystals were found growing directly on the wet calcite flowstone that runs into the pools (Fig. 7I). In several places above the flowstone, there are massive deposits of gypsum featuring dissolution drip holes. Water that makes contact with this gypsum enters the pools in a discrete flow, where subaqueous helictites have formed. A few meters above the suspected barite speleothems, a deposit of bright yellow elemental sulfur (S_8) was discovered (Fig. 7J), some of which covered in a gray (microbial?) paste (e.g., Fig. 7J front right). Parts of the sulfur are exposed to dripping water and dislocated into the gypsum drip holes or surrounding splash rings. These chunks of sulfur are darker in color and rounded.

SEM analysis of the larger fragment reveals the micro-morphology of the crystal (Fig. 8). The pinacoid face $c\{001\}$ shows parting and intergrowth of smaller crystallites with faces of prism $m\{210\}$ and pinacoid $a\{100\}$, but only subordinate combinations with prism faces $d\{101\}$ or $o\{011\}$ (Figs. 8B-D, Fig. 4). The prism face $m\{210\}$ that originally had pointed towards the water surface shows distinct parting into crystallites with pinacoid $c\{001\}$, prism $m\{210\}$ and pinacoid $a\{100\}$ faces (Fig. 8E). All faces appear smooth and homogeneous in SE and BSE images (Fig. 8C-D, F-G).

Fig. 7. Barite pool crystals in Lechuguilla Cave. A) Calcite-lined shallow pool containing barite crystals, located in a side passage of 'Blanca Navidad'; the white arrow points to the barite crystal that was collected; the red arrow indicates the cluster of crystals shown in B-C; B) Cluster of barite crystals, some bluish in color, some pale gray; C) Close-up of B, showing the barite crystals with the most intense bluish color zoning; D-E) The sampled barite crystal in incident light on a black and a white background (larger fragment to the left of dashed line later investigated with SEM, EDS, and WDS; smaller fragment used for XRD); F-G) Overview and close-up of a calcite-lined pool in 'Barite Boulevard', with pool fingers and with bluish crystals in the corners; H) Yellowish crystals formed where discrete inflow from the flowstone cascade enters another pool; I) Bluish crystals found growing directly on the active calcite flowstone; J) Deposit of elemental sulfur on a block of gypsum located only few meters above the flowstone cascade and pools shown in F-I.

Fig. 8. Micro-morphology of the 'Blanca Navidad' barite pool crystals revealed via SEM. A) Overview from three perspectives; arrows point out the location of B to G; B) Lateral face of the tabular crystal, showing the effect of parting; C-D) Close-up of B (SE and BSE image); E) The narrow face that was oriented towards the surface of the pool, showing parting into smaller crystallites; F-G) Close-up of E (SE and BSE image).

The XRD spectrum of the bluish crystal, in the scan between 15° to 60° (2θ), is compatible with that of barite (Fig. 9A). A small amount of calcite was detected, stemming from the intergrowth with pool spar at the base. Two peaks are artifacts from the aluminum carrier, due to the small amount of sample.

EDS spectra of the cross section and outer surface of the sample determine the elemental composition as chiefly O, S, and Ba (Fig. 9B) in a stoichiometric relation close to that of BaSO_4 . In addition, only the La1 peak of strontium was detected.

High-resolution WDS element mapping shows a homogeneous distribution of the major elements Ba, S, and O, in a stoichiometric relationship corresponding to that of barium sulfate, confirming the identification as barite (Fig. 10A, G; Table 2). As in the stalactite sample, mapping and profiles on a $1\ \mu\text{m}$ grid showed that the elemental ratios remain consistent towards the margin of the crystal (Fig. 10D, J), thus excluding the presence of a detectable layer of witherite. Calcium (Ca) and strontium (Sr) were the only detected trace elements, showing a distinct zoning aligned with the direction of growth along the prism $m\{210\}$ faces, reaching concentrations of up to 4,820 ppm and 26,200 ppm, respectively (Fig. 10B-C, E-F, H-I, K-L; Table 2). Compared to the

'Frostworks' stalactite, these concentrations are one to two magnitudes higher for Ca and Sr, respectively. The section mapped perpendicular to the $c\{001\}$ face identifies dominant growth along the prism $m\{210\}$ faces and subordinate growth on (but parting along) the $c\{001\}$ faces (Fig. 10G-L). Calcium concentrations are higher in parts that grew along the pinacoid face $c\{001\}$ (Fig. 4), whereas Sr was found relatively depleted in these zones, thus showing an inverse pattern (compare Fig. 10B-C and K-L). The respective Sr/Ca ratios cluster accordingly (Fig. 10C, L). Average Sr/Ca ratios are 16.6 ± 12.4 ($n = 1,097$) for crystal growth on the $m\{210\}$ faces, and 1.6 ± 1.6 ($n = 652$) for growth along the $c\{001\}$ faces. There is no difference in concentrations between the neighboring $m\{210\}$ faces (Fig. 10B) or between the opposite $c\{001\}$ faces (Fig. 10H). Concentrations of Sr mirror the blue color zoning in that the outermost (youngest) zone shows the highest Sr concentrations and most intense coloration (compare Figs. 10C and 7E).

Three principal types of microbial morphology were identified on, and partly embedded within, the sampled barite crystal:

Type 1 microbes form filaments 300-400 nanometers in diameter and were found collapsed on the surface of the crystal (Fig. 11B-C). The tubular filaments exceed

Fig. 9. A) XRD spectrum of the crystal sampled in a pool at 'Blanca Navidad', confirming barite as main component, along with subsidiary calcite from the base of the sampled crystal; B) Two EDS spectra of the same sample, acquired at 10 and 30 keV, respectively, identifying barium, sulfur, and oxygen as main constituents, along with traces of strontium.

Table 2. Quantitative WDS analysis of the sampled 'Blanca Navidad' barite crystal. The mean $\pm$ SD is given for all spot measurements ($n = 1749$) of the profiles, calculated as weight and atomic percent, complemented by the average stoichiometric elemental ratios relative to Ba.

Element	Weight %	Min – max	Atomic %	Min – max	Element / Ba
O	27.8617 $\pm$ 0.6670	24.1800 – 30.4500	66.8464 $\pm$ 0.6144	63.6880 – 69.0210	4.1009 $\pm$ 0.1371
S	13.7755 $\pm$ 0.1841	13.0200 – 14.2800	16.4993 $\pm$ 0.2815	15.3020 – 17.9960	1.0118 $\pm$ 0.0210
Ca	0.1050 $\pm$ 0.0873	0.0116 – 0.4820	0.1000 $\pm$ 0.0820	0.0111 – 0.4485	0.0062 $\pm$ 0.0052
Sr	0.5479 $\pm$ 0.4160	0.0000 – 2.6200	0.2402 $\pm$ 0.1814	0.0000 – 1.1310	0.0148 $\pm$ 0.0115
Ba	58.3223 $\pm$ 0.7547	55.7600 – 60.1700	16.3142 $\pm$ 0.4174	14.8820 – 18.1680	–

100 μm in length, have a constant width and are partly flattened by desiccation. Although they are commonly touching or overlapping (Fig. 11B-C), it is unclear whether they represent branching cells. Coccoidal cells or spores $\sim 1 \mu\text{m}$ in diameter, were seen associated with the filaments (marked as 'c' in Fig. 11B). Some filaments enter or exit deep trenches in the crystal, or they disappear into (or emerge from) angular holes (Fig. 11B-E; marked 'b' in B) formed by crystal overgrowth.

The Type 2 microbes do not appear to have remained on the surface of the barite crystals after collection/processing. As such, their presence and morphology are only evident where the barite has grown around the original organic filaments, leaving incrustations that mimic their structure. The incrustations suggest filaments that were 200-400 nm in diameter and meander on the surface of the crystal (Fig. 11F). They commonly touch or overlap but unequivocal branching points were not observed. The filaments appear to have originated from a circular central area about 3-10 μm in diameter (Fig. 11F-I; marked by arrows in F) that has an irregular margin with minute protrusions (Fig. 11G). The presence of individual furrows (arrows in Fig. 11H) or the entire structure (Fig. 11I) being partially overgrown by younger barite crystallites, along with barite precipitating between filaments to form micro-terraces that are different in elevation on either side of the filaments (Fig. 11F-I), supports the incrustation of these microbes.

Evidence of Type 3 microbes are empty incrustation structures observed in broken sections of the crystal (Fig. 11J-K). These casts are rod-shaped, circular in

cross section, and appear narrower in the center. Individual cavities are three to five microns in length and about one micron in diameter, which is a common size for dividing bacteria.

DISCUSSION AND CONCLUSIONS

Mineralogy and origin of color

The EDS/WDS and XRD analyses identify the elemental composition and mineralogy of the sampled greenish stalactite and bluish pool crystal as barite. This is in agreement with the observed tabular shape and orthorhombic set of faces with a dominance of the pinacoid base $c\{001\}$ and prism faces $m\{210\}$. In both settings, the barite primarily grows along the $m\{210\}$ faces, whereas precipitation on the $c\{001\}$ face is limited (Fig. 4). As the crystals grow outward from their base at the bottom of the pool, or from the central canal of the stalactite, parting along the $c\{001\}$ faces increases the width of the tabular crystal aggregates.

The only minor elements detected, mapped and quantified via WDS analyses in the present samples are calcium (Ca) and strontium (Sr), which both substitute for barium in barite (Griffith & Paytan, 2012). The color of minerals and the speleothems they form is commonly a result of such minor or trace elements incorporated in the crystal lattice (White, 1997). Strontium is the most common impurity (apart from radium) in natural barite (e.g., Monnin & Cividini, 2006; Griffith & Paytan, 2012) and Sr concentrations have been related to zonal blue coloration by Gaškov

Fig. 10. A selection of WDS maps (same color scaling as Fig. 6) and profiles of the 'Blanca Navidad' pool crystal, showing the crystallographic properties, the position of the profiles, and the distribution of the major elements Ba, O, and S (A, D, G, J) as well as the precipitation patterns reflected in the trace elements Ca and Sr (B-C, E-F, H-I, K-L).

et al. (2017), who reported higher concentrations in darker blue growth zones compared to light colored zones in speleothems from Estonia. This pattern is in good accordance with the 'Blanca Navidad' pool crystal where the outermost (youngest) growth zone has the highest Sr concentrations and most conspicuous blue coloration (Fig. 4). The calcium distribution in the same sample, in contrast, is independent of the color zoning. Because no other trace elements were detected in our screening, we consider Sr the most

plausible cause of the bluish coloration of the 'Blanca Navidad' pool crystals.

The origin of the less distinct and more homogeneous greenish coloration in the 'Frostworks' stalactite remains unknown. Sr was found occurring in much lower concentrations and only near the center of the stalactite, and the heterogeneous distribution of Ca likewise does not match the observed coloration. Other trace elements that may substitute for Ba and could cause the coloration were not detected.

Fig. 11. SEM images of microbes and barite incrustations found on and in the sampled 'Blanca Navidad' barite pool crystal. A) Overview from three perspectives; arrows point out the location of images in B to K; B-C) Filaments of Type 1, collapsed on the surface, associated with coccoidal aggregates (marked 'c') and emerging from angular holes (marked 'b'), visualized using SE and BSE; D-E) Examples of partially collapsed tubular filaments emerging from holes on the crystal's surface; F) BSE image of barite incrustations formed around meandering Type 2 filaments running along the surface of the crystal and radiating from a central area (arrows); G) Close up of F, showing circular central area; H) Evidence of partial to complete (arrows) incrustation; I) Angular view of terraced incrustations and large barite crystallites overgrowing the radiating incrustations; J-K) Overview and close-up of rod-shaped Type 3 microbes as recorded by empty incrustations in a broken face.

In both barite speleothem types we see a fractionation in the substitution of Ca and Sr that is related to growth along different crystallographic faces (Fig. 4). Ca was preferentially incorporated during growth along the c {001} prism faces, whereas Sr concentrations are higher in zones grown along the m {210} pinacoid faces. The reason for this fractionation could be grounded in the differing growth rates. Growth along the m {210} faces is much faster compared to the c {001} faces – and results in the tabular habit of the crystals. Or, physical properties of the crystal lattice might facilitate substitution by elements of different ionic radius. In any case, the present findings indicate that the observed fractionation needs to be taken into account when analyzing and interpreting variations in trace element composition of barite speleothems.

Formation of barite stalactites

The classical interpretation of barite speleothems as a result of phreatic hydrothermal activity can be excluded for the confirmed and suspected barite stalactites in Lechuguilla Cave. Instead, these stalactites and the greenish/bluish splash zone found beneath some of them, must have formed under subaerial conditions.

The stalactites have moist surfaces and actively drip water, showing that ongoing growth is possible. While we cannot provide proof for such active growth, the fact that the supporting bedrock is still intact (compromised in case of condensation corrosion) and the splash zones have not been overgrown by carbonate precipitates (as in the case of carbonate-saturated alkaline waters) suggest that the speleothems are a relatively recent phenomenon and are likely to still be growing.

These observations support non-hydrothermal growth in the present cave environment. Atmospheric temperatures in Lechuguilla Cave are relatively constant all year around, ranging from 17.3°C near the entrance to 20.4°C at the deep point in the cave (Northup et al., 1994), thus constituting a normal-temperature cave setting (5–25°C sensu Dublyansky, 1997).

Two different modes of non-hydrothermal mineral precipitation need consideration in explaining the formation of the barite stalactites: 1) evaporation, or 2) mixing of water rich in barium with water rich in sulfate. Both processes, in isolation or in combination, could ultimately lead to supersaturation and precipitation.

1) Prominent thermal atmospheric Rayleigh-Benard convection cells in Lechuguilla Cave have long been identified as drivers for condensation and evaporation, controlling the formation of corrosion residues / ferromanganese deposits and leading to directional growth of speleothems, respectively (e.g., Jones, 1990; Queen, 1994; Davis, 1999, 2000; Spilde et al., 2005). In some pools, intense concentration by evaporation results in brine with SO_4^{2-} levels as high as 25,175 mg/l (Turin & Plummer, 2000; Levy, 2008). In 'Frostworks', corrosion residues at the ceiling and aragonite frostwork on calcite popcorn at the bottom, together with the observation of significant airflow in the area, suggest that condensation and evaporation take place

(LaForge, 1998). This relationship led LaForge (1998) to hypothesize that condensation of upward-moving humid air has resulted in condensation-corrosion and uptake of minerals from the bedrock or corrosion residues, which were then carried by capillary flow to regions where evaporation caused the barite stalactites to crystallize. In support of this idea, all suspected or confirmed barite stalactites are located at low points in the ceiling. In 'Cephalopodunk' and the 'Chandelier Graveyard' the splash zones on the floor below are additional sites of greenish-bluish mineral formation, where evaporation of the dripping water is supported by less humid, descending air moving along the floor (Queen, 1994). Considering the poor solubility of barite in water (2.2 mg/l at 18°C; Seidell, 1940), this scenario requires immense amounts of water to evaporate (without other evaporates to precipitate) to form barite speleothems the size of the documented stalactites.

2) The alternative model is mixing of waters from two different sources, one rich in Ba^{2+} and devoid of SO_4^{2-} , the other rich in SO_4^{2-} . Mixing of such waters would result in supersaturation with respect to barite and instant precipitation until saturation is reached (Hanor, 2000; Griffith & Paytan, 2012). In Lechuguilla Cave, this scenario is conceivable where condensation water meets percolating meteoric water, or at mixing points of meteoric waters with different pathways. An obvious source of sulfate is contact with the abundant secondary gypsum deposits, whereas barium ions might derive from the host rock, corrosion residues, ore deposits, or other sources to be identified.

The role of these two models in the formation of the barite stalactites requires more investigation with a focus on different local water sources and their chemistry.

We do not know when the stalactites started to form, but according to Hill (1987, 2000a) subaerial speleothem formation in Guadalupe caves is thought to have commenced in two main episodes in the late Pleistocene about 600 ka and 170–70 ka. Back then, the geothermal gradient (and temperature in Lechuguilla Cave) might have been higher than today, considering the late phase of cooling from its maximum of estimated 40–50°C/km in the early Miocene 25–12 Ma ago (Barker & Pawlewicz, 1987) to present day ~20°C/km.

Formation of barite pool crystals

We have characterized different types of unidentified microbes on the sample from the 'Blanca Navidad' pool. These organic filaments were partly embedded via crystal growth, resulting in incrustations, which suggests that the barite crystals are actively growing today. The micro-topography of the incrustations, including partial overgrowth and stepped terraces with walls at only one side of the microbial filaments, cannot be explained by microbial biocorrosion. Moreover, microbiocorrosion of the highly insoluble barite would require the microbes to produce organic chelators similar to EDTA or DTPA (Wang et al., 2000) or concentrated sulfuric acid (O'Neil, 2013) in large enough quantity to compensate for the buffering capacity of the pool water. Microbially mediated barite

dissolution has been reported in sulfate-limiting conditions (e.g., Phillips et al., 2001) and anoxic brines only (Ouyang et al., 2017), forming simple etch pits different from the complex incrustations observed in our material.

Therefore it appears reasonable that the barite crystals in the 'Blanca Navidad' pool are still growing today. The pools with similar crystals in the nearby 'Barite Boulevard' are part of an active flowstone cascade with a discrete flow of water and bluish crystals growing on top, thus providing further indication that these speleothems are actively growing today in the present non-hydrothermal, normal-temperature cave environment (5–25°C sensu Dublyansky, 1997). Maximum pool water temperatures in Lechuguilla Cave were determined as 20.0 (Northup et al., 1994) and 20.3°C (Turin & Plummer, 2000, Supplementary Data). Hence, the same two modes of non-hydrothermal mineral precipitation as outlined for the barite stalactites could apply.

1) Recharge and discharge of water into the sampled pool is via discrete seepage from flowstone, complemented by occasional drips from overlying stalactites, so that the retention time in the pool is considerable. This part of 'Blanca Navidad' is rich in aragonite frostwork and other speleothems that are indicative of surface diffusion and evaporation. This includes calcite pool spar grading into blocky to triangular calcite popcorn and into microcrystalline crusts coating the walls above the barite pool. On the basis of these signs of evaporation, it is conceivable that evaporation supports the precipitation of the barite crystals. This agrees with the highest density of crystals found in a shallow sub-basin, opposite the point of incoming seepage, filled with overflow water from the main pool. The observed Sr concentrations and color zoning might provide circumstantial evidence for episodes of increased evaporation and a temporarily closed system, as Ba is removed preferentially over Sr from aqueous solutions (Hanor, 2000), causing Sr/Ba ratios to increase in stagnant water and during episodes of low recharge. The overall increase in Sr from the center outward could indicate that crystals increasing in size and number remove proportionally more barite from the small body of pool water, thereby increasing the partitioning of Ba and Sr. As for the suspected barite crystals precipitating from the thin layer of water on the active flowstone cascade in 'Barite Boulevard', evaporation could likewise have a significant effect.

2) Mixing of waters of different Ba^{2+} and SO_4^{2-} ion load is conceivable for the sampled pool, given an influx of water via seepage and by droplets from stalactites. Passages higher up in the same fault contain deposits of massive gypsum as a possible source for SO_4^{2-} ions. Nearby subaqueous helictites and the 'Gripping Hand' formation, both believed to have formed via common-ion-effect (Davis et al., 1991), support this. Mixing of waters and the common-ion-effect are even more evident in 'Barite Boulevard', where gypsum deposits with dissolution drip holes are located above the active flowstone cascade and subaqueous helictites are forming in the water bodies directly below. Potential sources of Ba^{2+} ions in percolating meteoric waters are

again diverse. Targeted water samples are needed to further evaluate the ion load of the involved sources of water.

The discovery of microbes associated with the barite pool crystals (we cannot exclude their presence in the case of the stalactites) raises the question whether there could be microbial involvement in the precipitation of these barite speleothems, or whether the documented association is coincidence. There is a growing body of evidence that microbial activity is an integral component of barite formation, particularly in the marine realm (Stevens et al., 2015 and references therein), but also in terrestrial settings (Senko et al., 2004). Some bacteria are able to form barite within their cells (e.g., Gooday & Nott, 1982), whereas other bacteria indirectly mediate barite precipitation by serving as nucleation sites for barite precipitation or by means of sulfur/sulfide-oxidation (e.g., Gonzalez-Muñoz et al., 2003, 2012; Stevens et al., 2015; Martinez-Ruiz et al., 2018). In the latter context, the recent discovery of massive gypsum and a substantial deposit of elemental sulfur only few meters above the barite speleothems in 'Barite Boulevard' is a puzzling finding that may hold a key for the understanding of the barite precipitation below in terms of microbial sulfur-oxidizing activity. More research is needed to verify whether there are systematic barite-microbe associations, including molecular genetics to identify these microbes and laboratory cultivation experiments to explore their potential involvement in the formation of barite speleothems in Lechuguilla Cave.

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