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Depositional environment for metatyuyamunite and related minerals from Caverns of Sonora, TX (USA)

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Abstract: A new mineral association composed of metatyuyamunite, celestite, opal and several minor crystalline phases has been identified in the Caverns of Sonora (Texas). The minerals were identified by means of X-ray diffractometry and optical and scanning electron microscopy. The main component of this association is metatyuyamunite, a uranyl vanadate mineral that appears as aggregates of sub-millimeter platy-like crystals that are often covered by botryoidal opal coatings. The orthorhombic unit cell of the Sonora metatyuyamunite had parameters a = 10.418, b = 8.508, and c = 17.173 Å. Opal and celestite formed either directly over the yellow crust or along the cracks that traverse the limy mud on which metatyuyamunite was precipitated. The secondary uranium-vanadium minerals described herein were precipitated in the final stages of cave development.

Key-words: metatyuyamunite, celestite, cave mineralogy, Sonora (Texas)

Introduction

Most speleothems (stalactites, stalagmites, and flowstone) have a simple mineralogy, as they are mainly composed of calcite, aragonite or gypsum. However, in a few caves over 250 other minerals have been recognized (Hill & Forti, 1997). Most of these minerals are formed because of unique sets of conditions within some given cave (*i.e.*, water chemistry, humidity, temperature, bat colonies and micro-organisms).

Out of 255 known cave minerals, only three contain the uranyl ion: tyuyamunite, metatyuyamunite and carnotite. Of these, tyuyamunite and carnotite were found at the beginning of the 20th century in the caves of Tyuya-Muyun and Fergana (Kirghizstan) (Nenadkevich, 1912; Kurbatov & Kargin, 1926). Later, these two minerals were described from caves in United States (a cave in Montana; Horse Thief Cave, WY; Corkscrew Cave, AZ; Lechuguilla Cave, NM) (Bell, 1963; Hill & Forti, 1997; Wenrich & Sutphin, 1994) and Bulgaria (Shopov's cave system) (Shopov, 1988).

Polyak & Mosch (1995) first reported metatyuyamunite as a cave mineral from Spider Cave (Guadalupe Mts., New Mexico). The present paper is the second reported cave occurrence of metatyuyamunite.

Geographic and geologic setting

The Caverns of Sonora, originally known as Mayfield Cave, is a show-cave located in Sutton County, Texas, in the central portion of Edwards Plateau. It consists of four major levels arranged as a maze of

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stacked parallel to near-parallel passages. The cave is not fully explored, but has a total surveyed length of 2.2 km while its depth is only 37 m (Fig. 1a). Most of the passages are highly decorated with a density and variety of calcite and gypsum speleothems seldom seen, which make Caverns of Sonora internationally renowned. A map and general description of the cave are provided by Tandy (1962) and Veni (1994).

The cave is formed in the Fort Lancaster Formation of the Cretaceous Edwards Limestone Group (Barker & Ardis, 1996). Barnes (1981) described the unit as an approximately 90-m thick massive, dolomitic, crystalline, fossiliferous, and cavernous rock. Chert is common in the formation but rarely seen in cave.

Following stratigraphic mapping 120 km to the east by Rose (1972), Kastning (1983a) placed the cave in the middle section of the Fort Lancaster Formation, with the uppermost part of the cave just below the Orr Ranch marker bed, and the lowest level on beds equivalent to the Allen Ranch Breccia. Breccia has not been observed locally and Rose (1972) found little breccia in Sutton County. Below the cave, the lowest section of the Fort Lancaster is a marly limestone.

The Fort Lancaster Formation is flat lying and essentially unfolded. Barnes (1981) mapped two 3.5 to 4-km long normal faults at 3 km and 9 km south of the cave, each with less than 10 m of drop to the east and bearing N15-25°E. No other significant faults or structural features were mapped within a 50-km radius.

Although the cave has been known for a long time, until recently research has been sporadic. The first reports describing the abundant calcite speleothems belong to Crisman (1956) and Tandy (1962). Later, analyses by Moore & Bukry (1968) identified moonmilk speleothems in the cave. Kastning (1983a and b) and Hill *et al.* (1989) provided preliminary assessments of the cave's geology and origin. This paper is the first arising from a more detailed ongoing geological investigation of Caverns of Sonora.

Sample location

In early 1998, while giving a tour of the cave, Bill Sawyer noticed bright-yellow crusts within 2 m of the trail by shining his light into an unlit side passage that extends off of the Lower Room (the lowest known point in Caverns of Sonora).

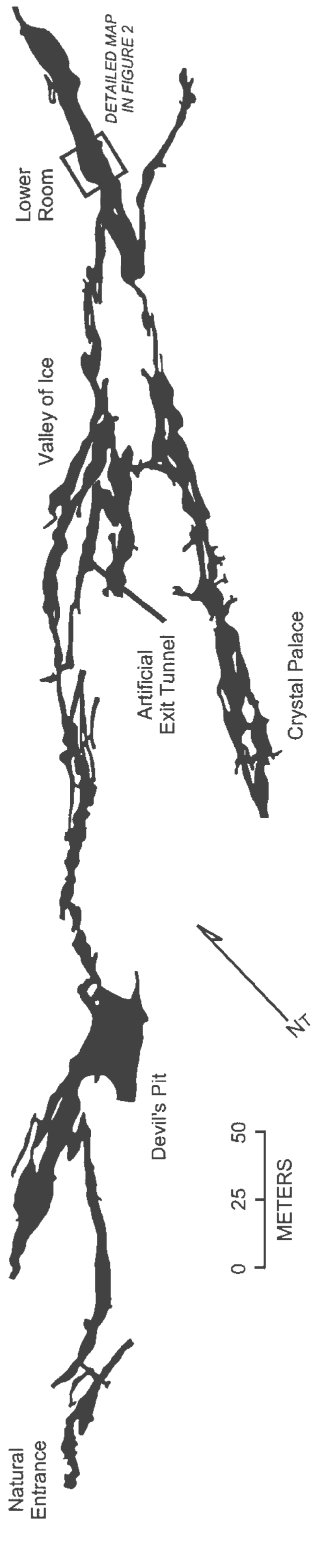

Fig. 1. (a) Outline map of Caverns of Sonora adapted from Veni (1994). (b) Detailed map of the Lower Room showing location of metatyuyamunite and related minerals.

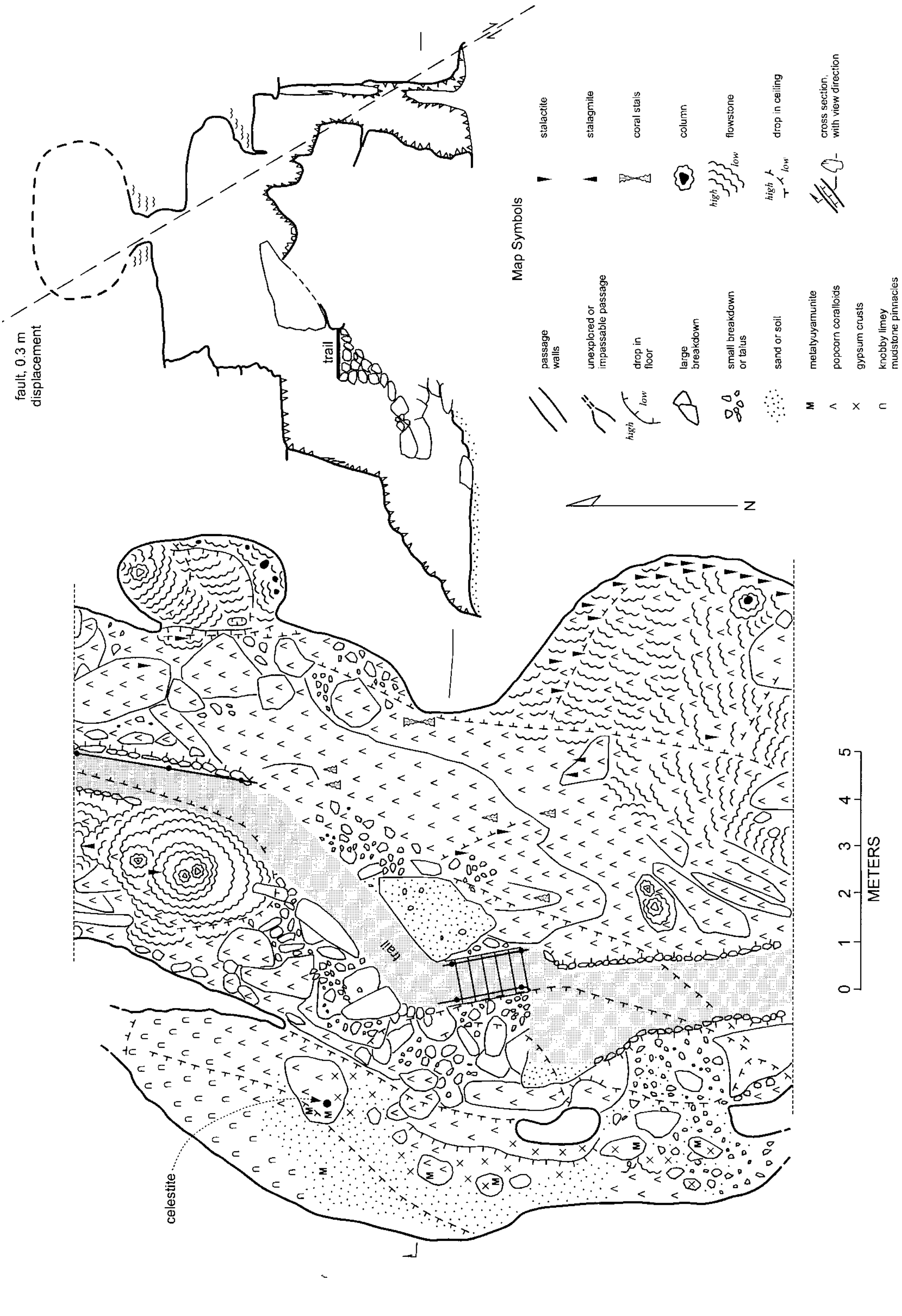
fault, 0.3 m displacement
trail
Map Symbols
passage walls
unexplored or impassable passage
drop in floor
high
low
large breakdown
small breakdown or talus
sand or soil
metatyuyamunite
popcorn coralloids
gypsum crusts
knobby limey mudstone pinnacles
stalactite
stalagmite
coral stals
column
flowstone
drop in ceiling
cross section, with view direction
N
0 1 2 3 4 5
METERS
trail
celestite
M

Fig. 1b

The Lower Room is a passage formed along a small normal fault bearing N20°E, dipping 65°E, and with a 0.3 m throw down to the east. The side passage is actually a continuation of the main passage at the original floor level along the west wall. The main floor of the Lower Room rises to the north over breakdown that covers the original floor, and which partitions off the lower section into a separate side passage (Fig. 1b).

The side passage measures 14 m in length, 2–3 m in width, and ranges from 0.3 to 1.7 m in height. It is distinct from most of the cave, primarily due to the presence of gypsum crusts.

Speleothems

Besides a great variety of calcite and aragonite speleothems, gypsum is a third relatively minor secondary mineral forming speleothems in the Caverns of Sonora. It occurs as crusts over either limestone or calcite speleothems. The crusts are up to 5 cm thick and cover areas up to at least 5 m^2.

In the Lower Room's side passage, gypsum occurs below sections of walls and ceiling covered with aragonite needles (less than 1 mm long) and it is absent below the area where the aragonite has inverted to calcite corraloids that episodically drip. Underlying the needles and corraloids is a calcite crust of undetermined thickness that completely covers the limestone.

Much of the gypsum crust, especially near the floor, occurs as a sheet of gentle mounds that average 10–15 cm in diameter and about 2 cm high. Where gypsum crust has been removed by dripwater, an underlying crust of calcite mounds is usually present. The calcite mounds typically range from 5 to 8 cm in diameter and 1 to 2 cm in height. Slightly curved, pointed, cylindrical speleothems, about 1 mm in diameter and up to 5 mm long, extend from many of the calcite mounds. They appear to be aragonite needles that have been inverted to calcite, and they form where the gypsum has been most recently removed.

Where gypsum is retreating from sections of the floor, calcite or hardened lime mud is left behind in the form of knobby pinnacles that generally measure 5–10 cm in height and 4–6 cm in diameter. The pinnacles appear to be formed of desiccated lime mud, broken internally by convex outward fractures with their surfaces often covered by shallow desiccation cracks.

Bright-yellow crusts of metatyuyamunite spread sporadically through 9 m of the side passage, usually in patches less than 4 cm in diameter that are probably limited in size by the fracturing of the underlying rock or mineral. Some of these yellow patches were subsequently covered by micrometer-sized opal crusts. In one location the metatyuyamunite crust occurs more continuously over a 0.5-m long by 0.3-m wide area. This area includes the only known occurrence of blue-grayish delicate crystals which were identified as celestite. These were found to grow over an area of 20 cm by 10 cm, with the largest patch being 2 cm long by 0.5 cm wide, either over calcite or metatyuyamunite crusts.

Mineral characterization

The analytic work was conducted on the following instruments: Nikon binocular, Scintag V Pad diffractometer, Hitachi (model 4010) spectrofluoorophotometer, Philips XL20 scanning electron microscope, and ElectroScan environmental electron microscope. The observations are presented below.

Optical description

Platy, micrometer-sized, euhedral to anhedral metatyuyamunite $Ca[UO]_2[VO_4]_2 \cdot 3H_2O$ crystals with bright-yellow color and adamantine luster were found. Stand-out plate-like crystals of metatyuyamunite (not larger than 0.6 mm in length) can also be observed emerging from the crust (Fig. 2). These crystals were either deposited directly on limy mud, limestone bedrock, at the surface of thin silica (opal) crust, or over columnar crystals of celestite. In some places a botryoidal, transparent opal coating covers metatyuyamunite crystals.

Brown aggregates composed of sub-micrometer-sized bladed crystals were noted on some of the cracks that occur in the limy mud. Also, blue crystals with a lamellar habit were observed grown over metatyuyamunite or directly on calcite crusts. They never exceed 50 μm in length, are almost transparent, and show vitreous luster. Some of these crystals are contorted. Beside these blue crystals and among metatyuyamunite crystals, a few filamentary crystals have also been observed (Fig. 3).

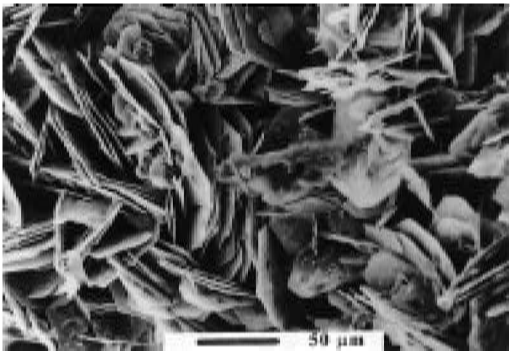

Fig. 2. Platelets of metatyuyamunite.

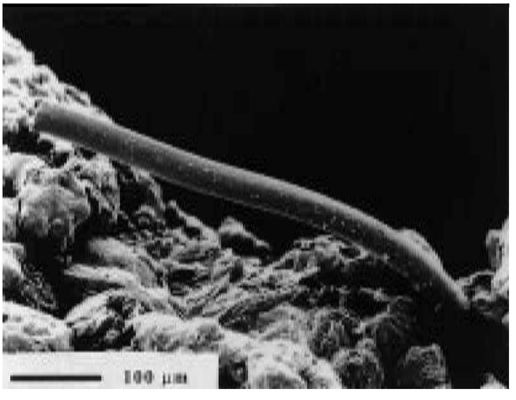

Fig. 3. Filamentary crystal growing on matrix of celestite and metatyuyamunite. EDX shows only Ca and Cl.

X-ray diffraction analysis

Diffraction patterns were measured on nine samples using 45 kV and 40 mA with Ni-filtered Cu-*K*a radiation. The diffraction patterns were found to fit exactly the reference patterns of metatyuyamunite.

The orthorhombic unit-cell parameters of metatyuyamunite from the Caverns of Sonora were calculated using the Scintag Lattice Refinement Program 3.0-WINNT. The calculated parameters (Table 1) are in good general agreement with the parameters of metatyuyamunite from Spider Cave (Polyak & Mosch, 1995) and those recorded in the ICDD file 8-287, but with some small but significant differences.

The X-ray powder diffraction pattern of the blue-gray crystals matched the reference pattern of celestite.

Luminescence

The yellow crystals luminesce a bright green under short-wave UV. Measurements of the emission and excitation spectra (Fig. 4) show the characteristic emission of the uranyl ion (Denning, 1992). The green emission arises from internal transitions of the UO_2^{2+} ion and is relatively insensitive to the crystalline host.

Scanning electron microscopy (SEM)

Observations were conducted on both standard and environmental scanning electron microscopes (ESEM). Under ESEM metatyuyamunite crystals appear either as lath-shaped or well-developed rhombic prisms, partly covered by coalescing opaline silica spheres that form botryoidal coatings (Fig. 5). The silica coatings were identified by EDX analysis. Although the largest metatyuyamunite crystal seen was about 0.6 mm in width, their average size is around 25 to 30 µm.

EDX analysis of the filamentary crystal (Fig. 3) reveals only Ca and Cl. These crystals were too sparse to be separated for X-ray diffraction analysis. EDX analysis of the sub-micrometer brown aggregates gives a very complex composition of Si, Ca, V, Fe, K, and Al with minor Mg.

The size of individual spheres of opal does not exceed 10 µm in diameter. Their surface can be either smooth or covered by a complex network of what appear to be bacterial filaments that have been silicified (Fig. 6). In close-up these spheres have their surface covered by hundreds of small beads (Fig. 7). The gaps between neighboring silica spheres are bridged and sometimes completely filled

Table 1. Comparative crystallographic data for metatyuyamunite.

Cell parameters		Metatyuyamunit	
	This paper	Polyak & Mosch (1995)	ICDD file 8-287
a (Å)	10.418 (6)	10.397 (4)	10.54
b (Å)	8.508 (3)	8.403 (2)	8.49
c (Å)	17.173 (9)	16.692 (12)	17.34

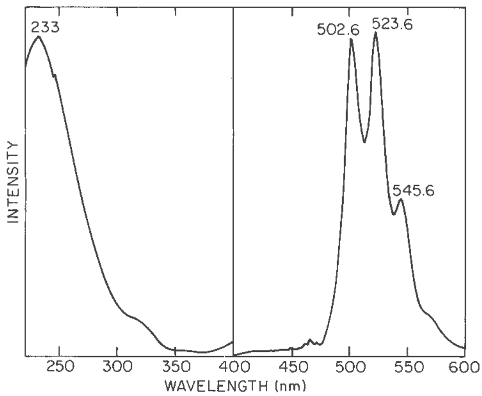

Fig. 4. Emission (400 – 600 nm) and excitation (200 – 400 nm) spectra from metatyuyamunite.

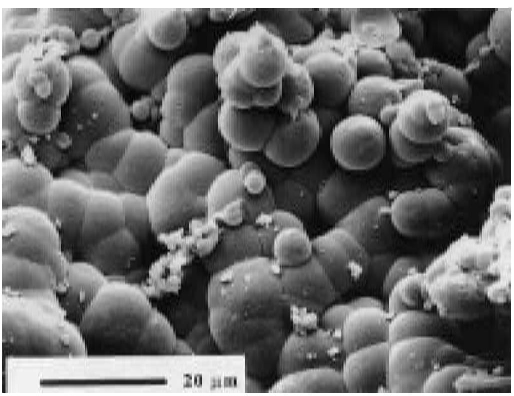

Fig. 5. Opaline silica nodules formed on metatyuyamunite

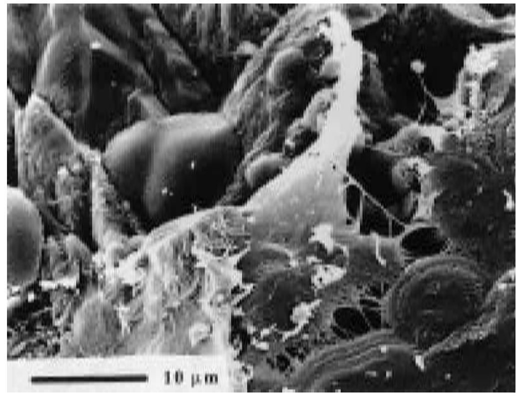

Fig. 6. Bacterial filaments covering opaline silica nodules.

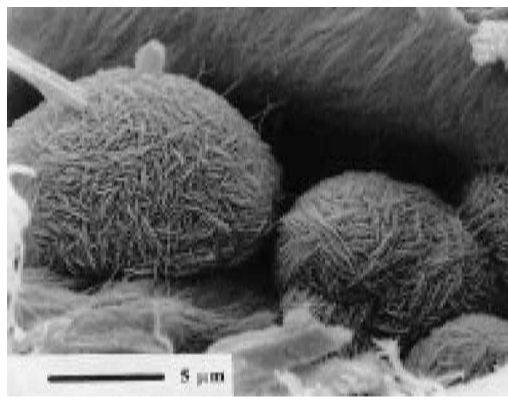

Fig. 7. Nodules coated with beaded rods of silica.

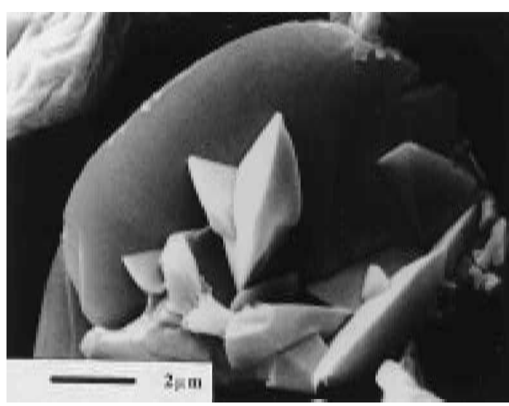

Fig. 8. Dolomite crystals formed on opaline silica.

by mucus strands. Multiple X-ray microanalysis (EDX) of these filaments was carried out using a Kevex analyzer attached to the SEM. The tests show Si and Mg as main components with significant amounts of K, Ca, Sr and Cl.

Minute crystals of dolomite, as interpreted from crystal morphology and EDX analysis, were found precipitated on some of the opal spheres (Fig. 8).

SEM images of the celestite crystals revealed their columnar habit, consisting of vertical prisms terminated by a combination of more or less steep pyramids or/and prisms (Fig. 9).

Radiation survey

An Industrial Test System RDX Nuclear DX-1 radiation monitor was used to survey the cave for gamma, X-ray and beta radiation. The survey revealed that most of the cave has a background level of about 0.9 mSv/year. However, when the monitor was placed within 10-20 cm of most sedi-

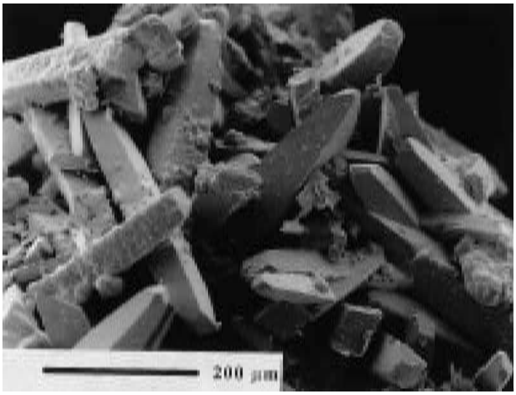

Fig. 9. Crystals of celestite, some with coatings of opaline silica.

ments or sediments covered by calcite speleothems, radiation increased to 2–3 mSv/year, suggesting they contain traces of uranium.

Background radiation in the Lower Room and northward 80-m to Halo Lake was slightly elevated to 2–3 mSv/year. Radiation from the metatyuyamunite was 9–26 mSv/year, and decreased to background levels within a distance of 1 m.

Although the radiation levels are considerably higher than the rates reported by Polyak & Mosch (1995) for both background (0.4 mSv/year) and metatyuyamunite deposit in Spider Cave (1.2 mSv/year), all radiation levels measured in Cavern of Sonora are well within the occupational body safety limits of 50 mSv/year established by the US Environmental Protection Agency (1987).

During a survey by the Texas Department of Health in the early 1990s, only low levels of radon were found in the cave, including the Lower Room (Cheryl Chevalier, personal communication).

Discussion and conclusions

The mineral deposits of Caverns of Sonora including those described in this paper and those described previously may be summarized:

Calcite – profuse active speleothems of many types.
Aragonite – occurs throughout the cave in relatively minor amounts.
Gypsum – thin crystals and fibrous crystals.
Metatyuyamunite – minor phase deposited on what appears to be hardened calcite mud.
Celestite – minor crystals on hardened calcite mud near metatyuyamunite deposits.
Opal – thin coatings associated with metatyuyamunite.
Dolomite – very minor micrometer-size euhedral crystals.
Unidentified blue-green Ca–Cl phase.
Unidentified brown phase, possibly a K, Ca, V, Fe, Al silicate.

Based on speleothem morphology, most of the calcite and aragonite clearly have been deposited since the cave was drained. The metatyuyamunite and associated minerals are more problematic. Their occurrence on dried calcite mud in the lowest passages in the cave suggests that they may be indicators of the final solutions that filled the cave before it was drained. The presence of these minerals, therefore, relates to the processes that formed the cave itself.

In recent years (see, *e.g.*, Klimchouk *et al.* (2000) it has been realized that solution caves can result from at least four processes. These are (a) meteoric water caves – caves formed by circulation of cold ground water at relatively shallow depths. (b) Mixing zone caves – usually in coastal environments where dissolution results from salt water/fresh water mixing. (c) Hypogenic geothermal caves dissolved by warm to hot water from deep-seated sources. (d) Sulfuric acid caves which are dissolved by sulfuric acid derived from the oxidation of up-welling H_2S-bearing fluids. There is a great deal of evidence (Hill, 1987, 1990) that Carlsbad Caverns and other caves of the Guadalupe Mountains have formed by mechanism (d).

The Caverns of Sonora lie to the east of the Delaware Basin which is thought to be the source of the H_2S-bearing solutions responsible for the Guadalupe Mountain caves. Arguments based on the irregular, corroded passage shapes claim that the Caverns of Sonora also formed by the oxidation of H_2S in the mixing zone between deep-seated highly reducing fluids and oxidizing fresh ground water. However, the massive gypsum and native sulfur that characterize many of the Guadalupe caves have not been found in Caverns of Sonora.

Metatyuyamunite and related uranium and vanadium minerals are thought to be diagnostic for the sulfuric acid mechanism. However, unlike the only other known occurrence of metatyuyamunite in Spider Cave (New Mexico), where it occurrs on gypsum crusts, bedrock-breakdown blocks and clay-rich floor sediments (Polyak & Mosch, 1995), metatyuyamunite in Caverns of Sonora has only been found on carbonate-type bedrock or on celestite.

Precipitation of authigenic silicate minerals by micro-organisms (bacteria or microbes) is rather well studied in subaerial thermal springs (*e.g.*, Ferris *et al.*, 1986, 1987; Schultze-Lam *et al.*, 1995; Jones & Renaut, 1996; Konhauser & Ferris, 1996). The role of micro-organisms in the mineral precipitation (including silica) in the cave environment was summarized by Northup *et al*. (1997) (for more details see the references cited therein).

The described mineral assemblage in the Caverns of Sonora appears to be precipitated from waters enriched in calcium and strontium sulfates as well as in carbonate and uranyl silica-hydroxyl complexes. The first minerals to be precipitated were gypsum and celestite, followed by the tyuyamunite or metatyuyamunite when the pH-Eh conditions of the cave environment enabled this process (Langmuir, 1978). During deposition and in connection with evaporation and change in pH, micro-organisms could have deposited the opaline silica. The mucus produced by these bacteria has been found to provide favorable crystal nucleation sites for different crystals (Ferris *et al.*, 1986; Jones & Renaut, 1996). We believe a similar process has resulted in the deposition and binding of small dolomite crystals to the surface of opal spheres.

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References

Barker, R.A. & Ardis, A.F. (1996): Hydrogeologic framework of the Edwards-Trinity Aquifer System, west-central Texas. *U.S. Geol. Survey Prof. Paper*, **1421-B**, 61 p.

Barnes, V.E. (1981): Geologic atlas of Texas: Sonora sheet. *Texas Bur. Econ. Geol.*, **1** sheet.

Bell, K.G. (1963): Uranium in carbonate rocks. *U.S. Geol. Survey Prof. Paper,* **474-A**, 29 p.

Crisman, R. (1956): A cave with a long hidden secret. *Natl. Speleol. Soc. News*, **14**, 38-40.

Denning, R.G. (1992): Electronic structure and bonding in actinyl ions. *Structure and Bond*ing, **79**, 215-276.

Ferris, F.G., Beveridge, T.J., Fyfe, W.S. (1986): Iron-silica crystallite nucleation by bacteria in a geothermal sediment. *Nature*, **320**, 609-611.

Hill, C.A. (1987): Geology of Carlsbad Cavern and other caves in the Guadalupe Mountains, New Mexico and Texas. *New Mexico Bur. Mining Tech. Bull.,* **117**, 150 p.

– – (1990): Sulfuric acid speleogenesis of Carlsbad Cavern and its relationship to hydrocarbons, Delaware Basin, New Mexico and Texas. *Am. Assoc. Petrol. Geol. Bull.,* **74**, 1685-1694.

Hill, C. & Forti, P. (1997): Cave Minerals of the World, (2nd edition). National Speleological Society, Huntsville, AL, 463 p.

Hill, C.A., Jagnow, D.H., DuChene, H., McLean, J. (1989): Preliminary report on the geology and mineralogy of Caverns of Sonora, Texas. *Cave Res. Foundation Ann. Rpt.*, 22-26.

Jones, B. & Renaut, R.W. (1996): Influence of thermophilic bacteria on calcite and silica precipitation in hot springs with water temperatures above 90 °C: Evidence from Kenya and New Zealand. *Can. J. Earth Sci.*, **33**, 72-83.

Kastning, E.H, Jr. (1983a): Geomorphology and hydrogeology of the Edwards Plateau karst, central Texas. Ph.D. dissertation, University of Texas at Austin, 656 p.

– (1983b): Relict caves as evidence of landscape and aquifer evolution in a deeply dissected carbonate terrain: southwest Edwards Plateau, Texas, U.S.A. *J. Hydrol*., **61**, 89-112.

Klimchouk, A.B., Ford, D.C., Palmer, A.N., Dreybrodt, W. (2000): Speleogenesis. Evolution of karst aquifers. National Speleological Society, Huntsville, AL, 527 p.

Konhauser, K.O. & Ferris, F.G. (1996): Diversity of iron and silica precipitation by microbial mats in hydrothermal waters, Iceland: Implications for Precambrian iron formations. *Geology,* **24**, 323-326.

Kurbatov, I.D. & Kargin, V.A. (1926): About the occurrence of alkaline elements in uranovanadates of Tyuya-Muyun. *Dokl. Akad. Nauk SSSR,* **Ser. A1926**, 235-238.

Langmuir, D. (1978): Uranium solution - mineral equilibria at low temperatures with applications to sedimentary ore deposits. *Geochim. Cosmochim. Acta*, **42**, 547-569.

Moore, G.W. & Bukry, D. (1968): Electronmicrograph of moonmilk in Caverns of Sonora. *Natl. Speleol. Soc. News,* **26**, 121-122.

Nenadkevich, K.A. (1912): Tyuyamunite – a new mineral. *Izv. Akad. Nauk SSSR*, **Ser. 6**, **6**, 945-946.

Northrup, D.E., Reysenbach, A.L., Pace, N.R. (1997): Microorganisms and speleothems. *in* "Cave minerals of the world, 2nd Ed.", C.A. Hill & P. Forti, eds. *Natl. Speleol. Soc.*, Huntsville, AL, 261-266.

Polyak, V.J. & Mosch, C.J. (1995): Metatyuyamunite from Spider Cave, Carlsbad Caverns National Park, New Mexico. *Natl. Speleol. Soc. Bull.*, **57**, 85-90.

Rose, P.R. (1972): Edwards Group, surface and subsurface, central Texas. T*exas Bur. Econ. Geol. Rpt. Investigations*, **74**, 198 p.

Schultze-Lam, S., Ferris, F.G., Konhauser, K.O., Wiese, R.G. (1995): *In-situ* silicification of an Icelandic hot spring microbial mat: Implications for microfossil formation. *Can. J. Earth Sci*., **32**, 2021-2026.

Shopov, Y.Y. (1988): Bulgarian cave minerals. *Natl. Speleol. Soc. Bull.*, **50**, 21-24.

Tandy, M. (1962): Mayfield Cave, Texas. *Natl. Speleol. Soc. Bull.*, **24**, 31-39.

Veni, G. (1994): Caverns of Sonora. *in* "The caves and karst of Texas, Natl. Speleol. Soc. Convention Guidebook", W.R. Elliott & G. Veni, eds. 138-139, 147, 309 + 1 plate.

Wenrich, K.J. & Sutphin, H.B. (1994): Grand Canyon caves, breccia pipes and mineral deposits. *Geol. Today*, **10**, 97-104.

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