MINERALOGY OF KARTCHNER CAVERNS, ARIZONA

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The mineralogy of Kartchner Caverns is both diverse and significant. Six different chemical classes are represented in this one cave: carbonates, nitrates, oxides, phosphates, silicates, and sulfates. It is significant primarily because: (1) the silicate minerals, nontronite and rectorite, have never before been reported from a cave occurrence; (2) the nitrate mineral, nitrocalcite, has never been described using modern techniques; (3) 'birdsnest' needle quartz has been reported only from one other, non-cave, locality; and (4) extensive brushite moonmilk flowstone has not been reported from anywhere else in the world. Kartchner is a beautiful cave because its carbonate speleothems are colorful (shades of red, orange, yellow and tan) and 'alive' (still wet and growing).

Kartchner Caverns is in the Whetstone Mountains, ~13 km south of Benson, Arizona, USA, just west of Arizona State Highway 90. The cave developed in a downdropped block of Mississippian Escabrosa Limestone. It is a wet, 'live' cave, >3 km long, which features a wide variety of multicolored speleothems.

Kartchner Caverns has a diverse mineralogy that ranks it among the most mineralogically interesting caves in the world (Hill & Forti 1997). Unlike most limestone caves, Karchner is adjacent to an igneous and metamorphic terrain. Alaskite granite borders the Escabrosa Limestone along fault zones to the west and the Pinal Schist underlies the cave. These fault zones, within an active tectonic region with a high geothermal gradient, have previously acted as avenues for ascending hydrothermal solutions and for the formation of the minerals quartz, illite and rectorite. The dry Arizona desert also contributes to cave mineral formation; e.g., the low relative humidity causes the efflorescence of nitrocalcite in the entrance zone of the cave. Periodic flooding of the cave allows for pH-Eh conditions favorable for forming the mineral nontronite. Bats add the last ingredient, bringing phosphates and nitrates into the cave via their guano and urine.

Cave minerals and speleothem types and subtypes in Kartchner Caverns are listed in Table 1. Figure 1 is a map of Karchner Caverns that shows the location of the most important minerals and speleothems in the cave. Of these, only the more unusual or new minerals/speleothems will be discussed.

CARBONATE MINERALS AND SPELEOTHEMS

Carbonate minerals include both calcite and rare aragonite speleothems, such as poorly developed frostwork. Magnesium carbonate minerals do not exist in the cave because the Escabrosa Formation is a relatively pure limestone containing very little dolomite.

Calcite speleothems are abundant, but only a few types are unusual. The world's longest known soda straw, 6.45 m, resides in the Throne Room (Figs. 1 & 2). Shields are a common speleothem in the cave, and form especially where the bedrock has been highly fractured by Basin and Range tectonism. Welts, a variety of shields, formed along horizontal bedding or on fractured speleothems. 'Turnip' shields formed along vertical fractures in the ceiling of the Big Room. The origin of these turnip-like speleothems has not yet been completely determined, but they may be the vertical equivalent of welts. Coral pipes are unusual as they formed in bat guano rather than mud. Red, orange, yellow, and tan flowstone is exceptionally beautiful (cover photo). The dripstone column in the Throne Room, 'Kubla Khan', is 17.7 m (58 ft) high (Fig. 3), and is the tallest column in Arizona. The Big Room displays well-developed 'fried-egg' stalagmites (Fig. 4).

NITRATE MINERALS AND SPELEOTHEMS

Nitrocalcite has been found in Kartchner Caverns as cave cotton growing from sediment in scattered areas along the entrance passages (Hill & Buecher 1992). Mineralization occurs as efflorescent mats consisting of colorless to milky-white, silky to transparent, slender needle crystals up to 0.5 mm long and <0.1 mm wide (Fig. 5).

The growth of nitrocalcite in the entrance passage correlates with episodes of low relative humidity in the winter months. A humidity of about 50% appears to be needed for the crystallization of nitrocalcite (Hill & Forti 1997), and this humidity needs to remain low before significant cotton can effloresce. These conditions correspond to a time in Kartchner when the cave is "breathing in"; that is, when cold, dry, winter air moves in along the entrance passage (Buecher 1999). The nitrocalcite in this passage is highly transient. Once the cave "breathes out" again, warm, moist, cave air quickly (in a matter of hours to days) causes the nitrocalcite to deliquesce and disappear back into the cave sediment.

OXIDE MINERALS AND SPELEOTHEMS

Red hematite powder was collected and identified (by X-ray diffraction) from two locations in Kartchner Caverns: (1) the Red River Passage, where it alternates with greenish-gray,

Table 1. Cave minerals and speleothems, Kartchner Caverns. Classification of types and subtypes after Hill & Forti (1997).

CARBONATES
- Aragonite, $CaCO_3$
  - Coatings and crusts
  - Frostwork
  - Helictites
    - beaded
  - Stalactites
    - spathites
- Calcite, $CaCO_3$
  - Boxwork
  - Coatings
  - Conulites
    - bird baths
  - Coralloids
    - popcorn
    - grape
    - subaqueous
  - Coral pipes
  - Crusts
  - Draperies
    - bacon
    - sawtooth
  - Flowstone
    - waterfall
    - canopies
    - bell canopies
  - Helictites
    - anemolites
  - Moonmilk
  - Pearls, cave
  - Rafts, cave
  - Rims
  - Rimstone dams
    - Chinese walls
  - Shelfstone
    - crescent
  - Shields
    - welt
    - turnip
  - Spar
    - phreatic
    - pool
  - Stalactites
    - soda straw
  - Stalagmites
    - columns
    - broomstick
    - fried eggs

NITRATES
- Nitrocalcite, $Ca(NO_3)_2 \cdot H_2O$
  - Cotton

OXIDES
- Hematite, Fe_2O_3
  - Powder

PHOSPHATES
- Brushite, $Ca_4PO_4 \cdot 2H_2O$
  - Moonmilk
- Hydroxylapatite, $Ca_5(PO_4)_3(OH)$
  - Crusts

SILICATES
- Nontronite, $Na_{0.3}Fe_2^{3+}(Si,Al)_4O_{10}(OH)_2 \cdot nH_2O$
- Rectorite, 1:1 interstratification of mica & smectite
- Quartz, SiO_2
  - Boxwork
  - Needles

SULFATES
- Gypsum, $CaSO_4 \cdot 2H_2O$
  - Cotton
  - Starburst

RELATED FORMS
- Rootsicles
- Vermiculations

illite-clay layers (Fig. 6); and (2) in the Thunder Room area, where it occurs as colloidal hematite staining illite and rectorite clay. The hematite is most likely derived from primary pyrite, which occurs along the fault zones, and it may be of hydrothermal origin due to hot waters having moved up the fault zones.

PHOSPHATE MINERALS AND SPELEOTHEMS

The phosphate minerals brushite and hydroxylapatite have both been identified by X-ray diffraction analysis. The hydroxylapatite in the Big Room forms a thin, orangish-brown crust, but is not particularly extensive or noteworthy in its occurrence. The brushite in the Big Room, however, is noteworthy. It is one of the most extensive brushite deposits ever reported from a cave. This brushite consists of masses of creamy-colored material (moonmilk) over 2 m long, 0.3 m wide, and 6 cm thick. The moonmilk issues forth from beneath a fresh bat guano pile on a large piece of breakdown in the Big Room, it has 'crept' down the side of the breakdown, and then it continues out of sight beneath the breakdown. Brushite derives from decaying bat guano in an acid-rich (pH<6), damp environment (Hill & Forti 1997). Both of these conditions exist beneath bat roosts in the Big Room (Buecher & Sidner 1999).

SILICATE MINERALS AND SPELEOTHEMS

Silicate minerals found in Kartchner Caverns are illite, nontronite, rectorite and quartz. Illite fills fault zones and also occurs as clay floor deposits derived from the dissolution of the cave and fault zones (Hill 1999). Rectorite is a mixed-layer clay composed of a 1:1 regular interstratification of a dioctahedral mica and dioctahedral smectite (Newsom 1978). It has been identified at two localities in the cave: (1) along the main fault zone in the Main Corridor where it appears to have replaced illite; and (2) in the Subway Tunnel as pure rectorite showing contorted foliation. Rectorite is a rare mineral, only known from a few surface localities, the most noted being the Jeffrey Quarry just north of Little Rock, Arkansas, USA (Miser & Milton 1964). The Arkansas rectorite occurrence is interpreted to have formed directly from hydrothermal solutions, and a similar origin may also apply to the Kartchner Caverns occurrence. The Karchner rectorite is associated with 'birds nest' quartz along fault zones in the cave, where the quartz appears to have grown into a matrix of rectorite clay.

A brown, unctuous, nontronite floor clay in the Echo Passage contains layers, pods, and seams of a black, amorphous, manganese-rich material (Fig. 7). Nontronite forms under alkaline (pH = 7 to 10) and reducing (Eh = 0.2 to -0.8) conditions in areas of restricted drainage (Harder 1976). It has a marked cation exchange capacity, which means that cations like calcium, potassium, manganese, and metal ions can readily exchange within the structure of the mineral. In addition, nontronite forms from solutions containing high amounts of

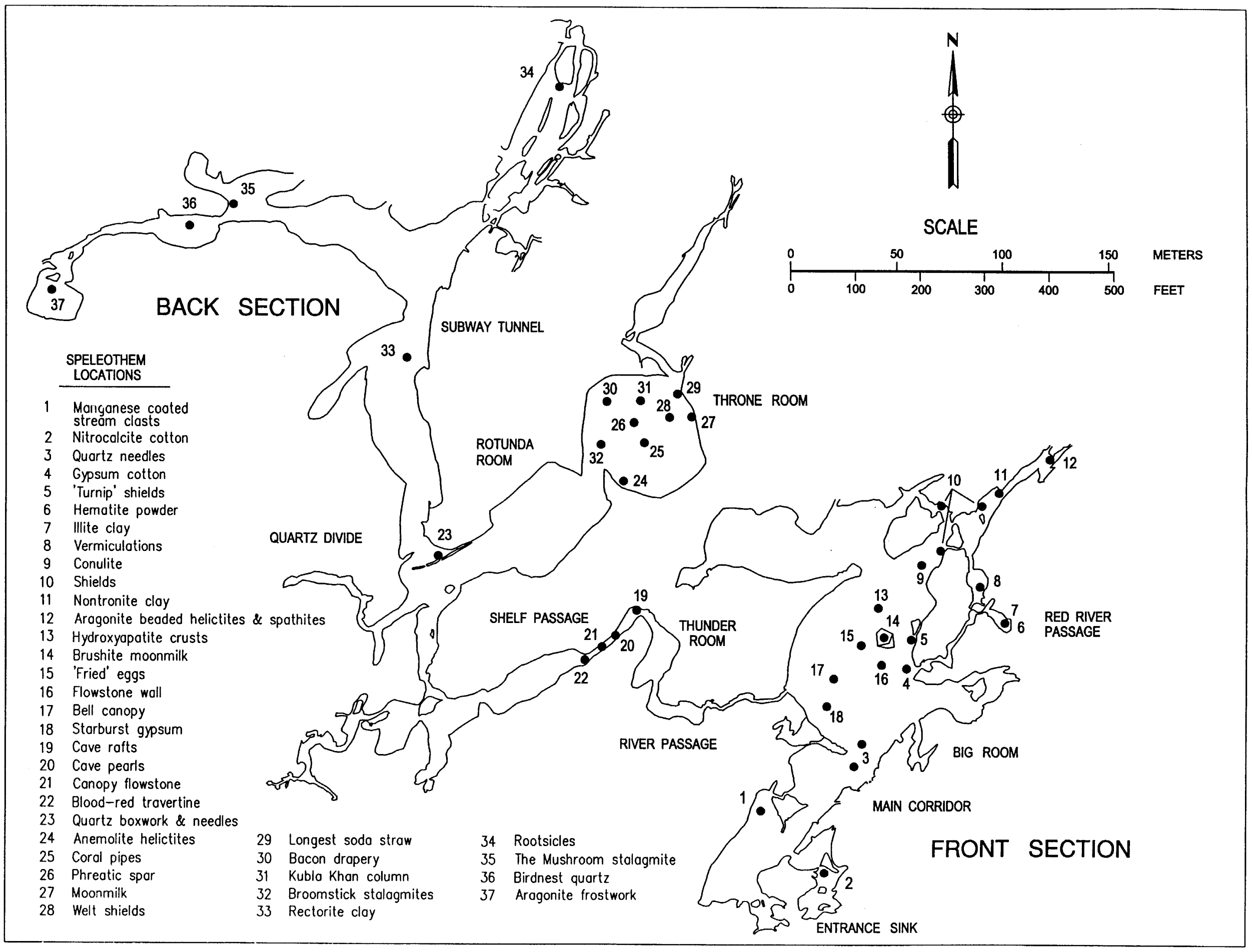

Figure 1. Map of Kartchner Caverns showing the location of the most important mineral and speleothem occurrences and other places mentioned in the text.

iron and silica. All of these conditions fit the environment of the Kartchner Caverns nontronite sites. Silica and iron (as red-orange hematitic material) are present along fault zones that have been exposed by cavern dissolution. Drainage in Echo Passage is retarded, and the pH of the water is between 7-9 (R. Buecher, pers. com.). Such high pH's favor rapid nontronite formation at normal temperatures.

Quartz occurs in four different modes in the cave as: (1) vein-boxwork (Fig. 8); (2) stubby prismatic crystals on top of the boxwork, (3) 'birdsnest' needle crystals on cave walls and ceilings along fault zones (Fig. 8); and (4) prismatic crystals replacing limestone bedrock along fault zones. The Quartz Divide displays the best example of quartz boxwork. A 30 cm wide quartz vein extends from the floor to the ceiling and was left standing while the cave dissolved out around it. This quartz boxwork (and other examples in the cave) is petromorphic rather than speleothemic (i.e. it is a fault zone vein deposited long before the cave existed). Fluid inclusion measurements indicate a crystallization temperature of 125-170°C for the vein quartz.

The most unusual occurrence of quartz is as needles. These needles form as tiny (up to 2 cm long and 0.25 cm wide), slender, euhedral, prismatic crystals that cluster together in mats in a 'birdsnest'-like fashion. The elongate structure of the needles is caused by crystals growing outward into a saturated silica 'soup'—either into a silica-rich solution or into a porous rectorite clay medium. The quartz needles appear to be speleothemic. The 'birdsnest' needle clusters either grew into open space (during an earlier, paleokarst episode) or into voids filled with clay along the faults.

The 'birdsnest' quartz in Kartchner is similar to 'haystack' quartz at the Jeffrey Quarry, Arkansas (Miser & Milton 1964), only the crystals are much smaller. The Arkansas quartz occurs along 30-cm wide, quartz vein-filled fractures and faults, suspended in a semi-liquid filling of gelatinous rectorite clay. Single quartz crystals grew suspended in a rectorite matrix while the 'haystack' quartz crystals grew out from vein quartz into the rectorite clay. Both the rectorite and 'haystack' quartz in the Arkansas occurence formed from hydrothermal solutions, at temperatures of 146-159°C, according to fluid inclusion studies on this quartz. The similarity of the Arkansas 'haystack' quartz and the Kartchner Caverns 'birdsnest' quartz—in its position along faults, its occurrence with rectorite, and its fluid inclusion temperatures—suggests a similar, fault-related, hydrothermal origin for the Kartchner Caverns needle quartz.

SULFATE MINERALS AND SPELEOTHEMS

Sulfate minerals in the cave are sparse. Small patches of gypsum cotton and starburst gypsum occur in sections of the Big Room where bat guano exists. Leaching of bat guano almost always forms gypsum as a by-product (Hill & Forti 1997) and therefore it is not surprising that this mineral exists in the bat guano-rich Big Room setting.

RELATED FORMS

"Related forms" are those deposits that resemble speleothems but are not speleothems in the strictest sense because they are not composed of true minerals but of mud or organic material (Hill & Forti 1997). Related forms in Kartchner Caverns are rootsicles and vermiculations. Parts of the cave are near the surface and in these places roots seeking cave water have become calcified. They are called 'rootsicles' by cavers.

Leopard-spot vermiculations have been found at the Quartz Divide and tiger-skin vermiculations in the Red River Passage, but neither occurrence is outstanding in terms of size or level of development. Vermiculations are thin, irregular, discontinuous deposits composed of incoherent materials (usually clay or mud) found on cave walls, floors or ceilings (Hill & Forti 1997). Their origin is still somewhat controversial, but is believed to be related to the flocculation of drying, liquid films containing fine-grained material.

COLOR OF SPELEOTHEMS

The calcite speleothems in Kartchner Caverns vary from a dark blood-red (Fig. 9) to red-orange to orangish-brown to delicate-peach to pure white. Color in speleothems can be caused by various factors: humic and fulvic acids, metal ions, and inorganic pigments (White 1997). Most of the coloration in Kartchner is probably derived from inorganic pigments, specifically, iron-rich hematitic fault-clay residue incorporated into the speleothem while it is growing. Some of the most vividly colored speleothems in Kartchner occur along or near fault zones where red-orange clay is exposed in the ceilings or walls of the cave. Black coatings on stream clasts and clay sediments are due to manganese metal ions.

CONCLUSIONS

Kartchner Caverns is only a small cave but it possesses minerals from six different chemical classes. A number of factors have been responsible for the diverse mineralogy of the cave:

1. A tectonic setting where faults allowed the ascension of hydrothermal solutions and the deposition of the minerals illite, rectorite and quartz.
2. A nearby igneous/metamorphic terrain where 'unusual' ions (such as Na) are supplied to the cave, in addition to the 'usual' calcium and carbonate ions derived from limestone.
3. Bat guano/urine which supplies phosphate, nitrate and sulfate ions to the cave.
4. An arid climate so that the highly soluble mineral nitrocalcite can effloresce in the entrance zone.
5. Flooding of the cave which allowed nontronite to form in a high pH-low Eh environment.

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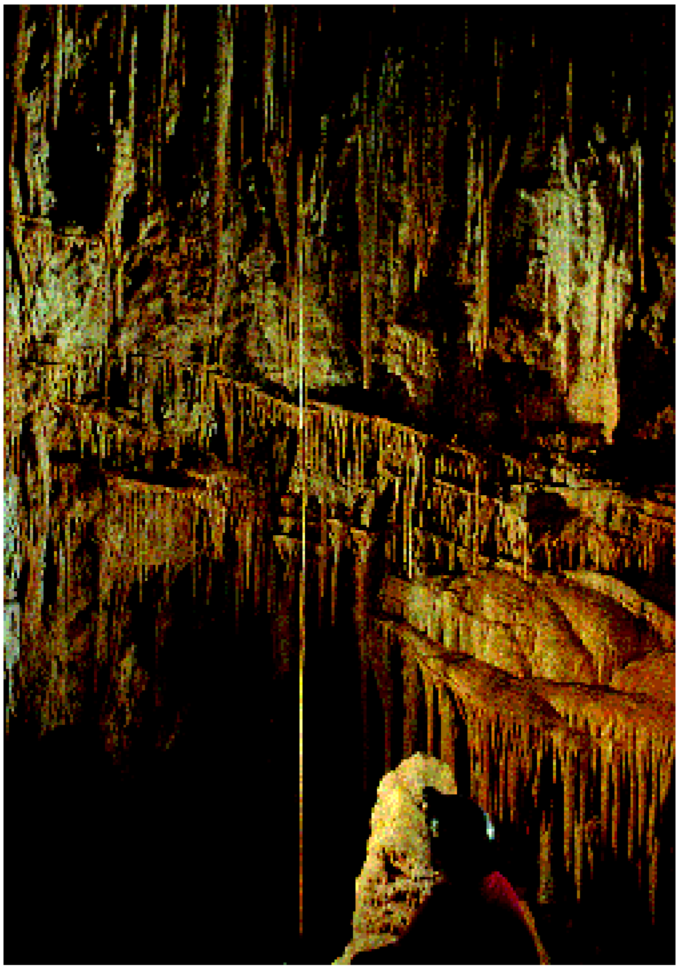

Figure 2. World's longest known soda straw, 6.45 m (21.16 ft) long in length, Throne Room. Photo by K.L. Day, A.C.P.I./Arizona State Parks Dept.

Figure 3. 'Kubla Khan' in the Throne Room: at 17.5 m (58 ft) high, it is the tallest column known in an Arizona cave. Photo by K.L. Day, A.C.P.I./Arizona State Parks Dept.

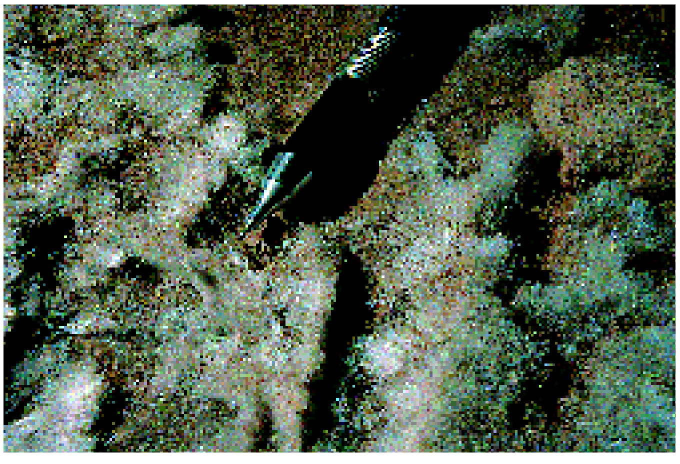

Figure 5. Efflorescent mats of nitrocalcite cotton in the entrance passage. Photo taken on 14 December 1989, when the relative humdity in the passage was ~50%. Photo by Bob Buecher.

Figure 7. Manganese-rich black layers exposed in non-tronite clay, Echo Passage. Photo by Bob Buecher.

Figure 4. A ‘fried-egg’ stalagmite in the Big Room. Width of the ‘yellow’ part of the ‘egg’ is about 5 cm (2 in). Photo by Bob Buecher.

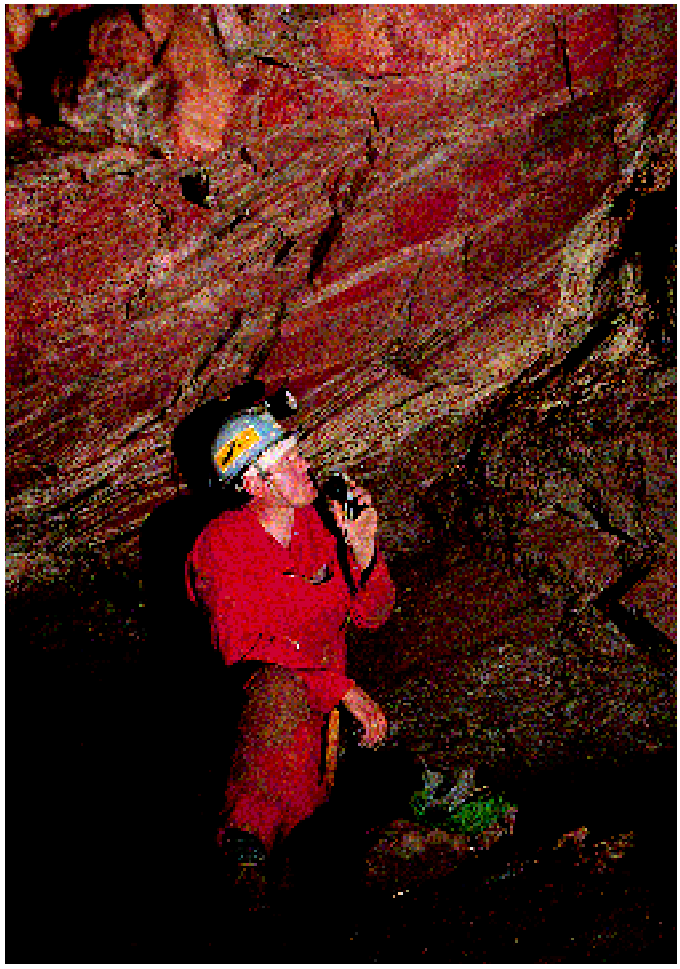

Figure 6. Red hematite alternating with greenish-gray illite layers, Red River Passage. Photo by Bob Buecher.

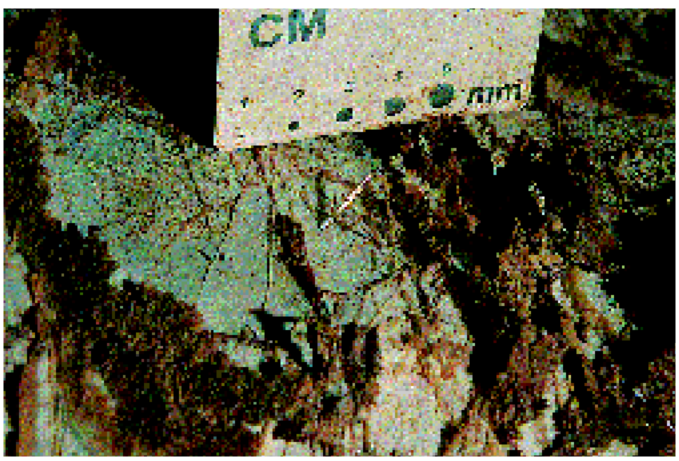

Figure 8. Quartz needles and boxwork, Subway Tunnel. Photo by Cyndi Mosch.

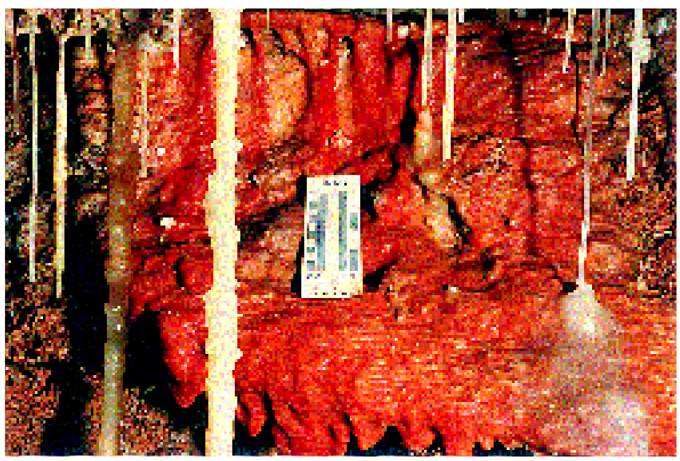

Figure 9. Blood-red flowstone in the Shelf Passage, located directly along a fault filled with iron-rich hematitic clay. Photo by Bob Buecher.