BY-PRODUCT MATERIALS RELATED TO H_2S-H_2SO_4 INFLUENCED SPELEOGENESIS OF CARLSBAD, LECHUGUILLA, AND OTHER CAVES OF THE GUADALUPE MOUNTAINS, NEW MEXICO

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Carlsbad Cavern, Lechuguilla Cave, and other large caves of the Guadalupe Mountains, New Mexico, contain minerals and amorphous materials derived as by-products from H_2SO_4 speleogenesis (process of cave formation influenced by sulfuric acid). These materials, referred to as "speleogenetic by-products," are categorized as primary or secondary. Primary speleogenetic by-products are formed directly from H_2SO_4 speleogenesis by H_2S-H_2SO_4 reaction with carbonate bedrock and internal sediments. They are found in cave areas protected from flood or drip waters. Secondary speleogenetic by-products are minerals and amorphous materials that formed by the alteration of the primary speleogenetic by-products, or by the late-stage remobilization of elements concentrated during speleogenesis. Primary speleogenetic by-products in these caves are gypsum, elemental sulfur, hydrated halloysite, alunite, natroalunite, jarosite, hydrobasaluminite, quartz, todorokite, rancieite, and amorphous silica and aluminum sulfates. Gypsum is the most abundant by-product, whereas alunite is the most significant because it can reveal the timing of speleogenesis. Aluminite, tyuyamunite, quartz, opal, and gypsum are secondary speleogenetic by-products. Other possible speleogenetic by-products are celestite, hydrous iron sulfates, gibbsite, nordstrandite, goethite and dolomite. The carbonate bedrocks in which the caves have formed are predominantly dolostone and limestone; mineral assemblages of these host rocks include calcite, dolomite, quartz, illite, dickite, kaolinite, interstratified illite/smectite, montmorillonite, and mica. The process of H_2SO_4 speleogenesis for Carlsbad Cavern and Lechuguilla Cave, and its by-products provide a general model for similar cave and non-cave systems worldwide.

Caves formed solely by the most widely known process of cave formation, carbonic acid dissolution of limestone, are not known to contain obvious remnant by-product materials of speleogenesis. In contrast, speleogenesis influenced by H_2SO_4 (H_2SO_4 speleogenesis) produces by-product materials (speleogenetic by-products) by: (1) the alteration of insoluble sediments, (2) replacement or alteration of the carbonate rocks, or (3) precipitation of dissolved species. This is of importance to the subject of speleogenesis, because there is "left-over" material directly related to speleogenesis. Carlsbad Cavern, Lechuguilla Cave, and other caves of the Guadalupe Mountains, New Mexico, formed partly if not predominantly by H_2SO_4 speleogenesis. We do not imply that H_2SO_4 speleogenesis is influenced solely by H_2SO_4; carbonic acid generated from significant amounts of CO_2 must also play a role. These caves of the Guadalupe Mountains formed by H_2SO_4 speleogenesis, herein referred to as the "Carlsbad caves," contain an exceptional assemblage of materials generated by speleogenesis that will serve as a template for future studies. Figure 1 shows the study area with locations of caves most pertinent to this study.

The idea of H_2SO_4 speleogenesis was introduced by Morehouse (1968), Egemeier (1973, 1981), Jagnow (1977), Davis (1980), Hill (1981, 1987), and van Everdingen *et al*.
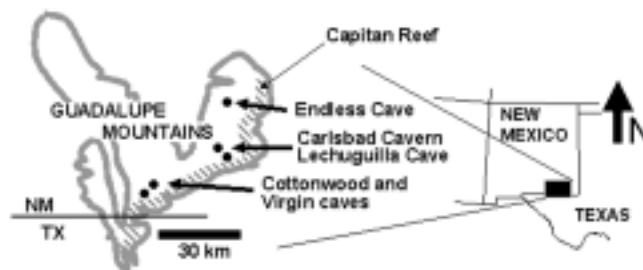
Figure 1. Map showing location of the study area. The approximate locations of the five most pertinent H_2SO_4 caves are also given. The stippled pattern shows the extent of the exposed section of the Capitan reef in the study area.

(1985). More recently, White (1988), Hill (1990, 1996), Palmer (1991), Ford and Williams (1992), Buck *et al*. (1994), Pisarowicz (1994), Polyak and Güven (1996), Polyak *et al*. (1998), Polyak and Provencio (1998), and Palmer and Palmer (2000) made contributions to strengthen the theories that caves form by the influence of H_2SO_4. Studies of H_2SO_4 caves thus far have been focussed on four cave systems: (1) the Kane caves in Wyoming, (2) the Carlsbad caves in New Mexico, (3) Cueva de Villa Luz in Tabasco, Mexico, and (4) caves of the

Umbria and Marche regions, Italy. Cueva de Villa Luz is an active H_2SO_4 cave, whereas the Carlsbad caves are relict H_2SO_4 caves. Lower Kane Cave is still actively forming, whereas Upper Kane Cave is relict. The Italian caves are also both relict and active (Galdenzi & Menichetti 1995). The lower passages of Movile Cave, Romania, are probably being formed in an active H_2SO_4 cave environment (Sarbu & Kane 1995). Mbobo Mkulu Cave in South Africa contains minerals that are characteristic of H_2SO_4 speleogenesis (Martini et al. 1997), and may be a relict H_2SO_4 cave. The Carlsbad caves are represented by at least 15 of the 300+ caves in the Guadalupe Mountains, five of which contain significant quantities of speleogenetic by-products.

ORIGIN OF THE CARLSBAD CAVES

Five Carlsbad caves important to this study are Carlsbad, Lechuguilla, Cottonwood, Endless, and Virgin (Fig. 1), which are located in the Permian Capitan Limestone, Goat Seep Dolomite, and associated backreef carbonate rocks in the Guadalupe Mountains of southeastern New Mexico and West Texas (Hill 1987, 1996). These caves formed when H_2S was oxidized to H_2SO_4 as it migrated upward and mixed with fresh waters in the thick Capitan reef and forereef limestones and dolostones (Hill 1987). The ascending H_2S-rich water exchanged its sulfur with many of the by-product minerals of speleogenesis. Light isotopic values of sulfur from speleogenetic by-products [$\delta^{34}S$ = -30 to 0 per mil (‰); relative to the Cañon Diablo troilite] reported by Hill (1987), Pisarowicz (1994), and Polyak & Güven (1996) indicated that the H_2S-H_2SO_4 associated with speleogenesis was derived from biogenic alteration of hydrocarbons. The dissolved H_2S gas was most likely produced at the base of the highly impermeable Permian Castile (anhydrite) Formation in the Delaware Basin immediately south of the Guadalupe Mountains (Hill 1987).

The gross morphology of the Carlsbad caves suggests large horizontal passages were formed at the water table, and vertical pits and fissures were formed below the water table along the paths of rising H_2S (Hill 1987; Palmer 1991). Formation of these caves followed an apparent decline of the water table, which created the multi-levels of Carlsbad Cavern and Lechuguilla Cave (Jagnow & Jagnow 1992; Polyak et al. 1998). Large quantities of carbonate rocks were dissolved or replaced with gypsum by H_2SO_4-bearing waters during this process. Recently published ages of formation for the Carlsbad caves, using the $^{40}Ar/^{39}Ar$ dating of alunite, indicated that H_2SO_4 speleogenesis took place in the late Miocene and Pliocene (Polyak et al. 1998). A simple schematic of this type of speleogenesis is presented in figure 2.

ENVIRONMENT OF H2SO4 SPELEOGENESIS

The environment of H_2SO_4 speleogenesis in the Carlsbad area during the late Miocene was probably similar to the low temperature cave environment reported for the active H_2SO_4 caves today. Studies of Lower Kane Cave and Cueva de Villa Luz are providing significant insight into the environment of
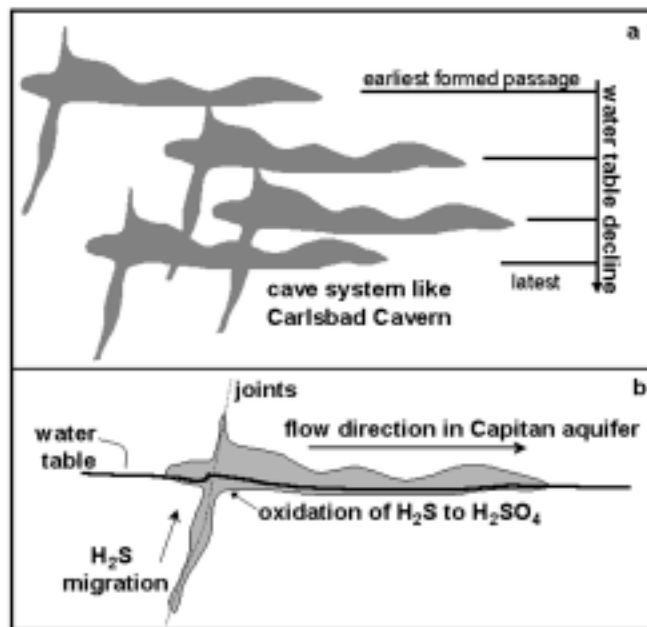
Figure 2. (a) Proposed progression of speleogenesis that formed the large complex multi-level caves such as Carlsbad Cavern and Lechuguilla Cave. Major speleogenesis occurred mainly along the water table as the water table declined relative to the strata during the Miocene. Deeper phreatic development occurred along paths of H_2S input. The younger caves or cave sections comprise the passages at the lowest elevation intervals. (b) Simple model of H_2SO_4-influenced speleogenesis for a single level in the Carlsbad caves. This simplified model comes from ideas of Hill (1987), Jagnow & Jagnow (1992), Polyak et al. (1998), and Palmer & Palmer (2000).

H_2SO_4 speleogenesis, especially at and above the water table. This is an environment conducive to the production of speleogenetic by-products. For example, Lower Kane Cave and Cueva de Villa Luz have microbe-bearing, bubbling, sulfurous springs, and gypsum-encrusted cave walls. Some bacteria and other organisms seemingly thrive in the H_2SO_4-bearing cave environment (Kane et al. 1994, Sarbu & Kane 1995, Lavoie et al. 1998, Taylor 1999, Engel et al. 2000, Hose et al. 2000). In Cueva de Villa Luz, Pisarowicz (1994) reported acid burns to clothing worn by investigators. Skin burns were experienced by investigators, and values of pH <1 were measured on some drip water and microbial substances in this cave (Hose 1998; Lavoie et al. 1998; Palmer & Palmer 1998; Hose & Pisarowicz 1999; Taylor 1999). Maslyn and Pisarowicz (1994) described seepage of H_2S and small globules of hydrocarbons from springs in Lower Kane Cave. Palmer and Palmer (2000) provide important constraints on the hydrologic and chemical conditions for the H_2SO_4 speleogenesis of the Carlsbad caves based on cave patterns and speleogenetic by-products.

The speleogenetic by-products from H_2SO_4 speleogenesis are important indicators of the cave-forming environment, and

probably equally important for some non-cave environments. We present the mineral assemblage associated with relict H₂SO₄ caves of the Guadalupe Mountains, New Mexico and briefly discuss the significance of this assemblage to geology and speleology.

## SAMPLE COLLECTION AND IDENTIFICATION

Samples were collected with the permission of the National Park Service, Lincoln National Forest, and Bureau of Land Management. Mineral assemblages were established using X-ray diffraction (XRD), energy dispersive X-ray (EDX) microanalysis, transmission electron microscopy (TEM), and optical microscopy. Table 1 lists all the speleogenetic by-products identified, states chemical composition, and establishes the by-products as primary, secondary, and not-yet-classified. All of the materials listed in table 1, with the exception of sulfur and celestite, were examined by this study.

SPELEOGENETIC BY-PRODUCTS AND THEIR GENETIC CLASSIFICATION

We refer to speleogenetic by-products that formed as a direct result of H₂SO₄ speleogenesis as "primary speleogenetic by-products." Speleogenetic by-products that have formed from the alteration of primary speleogenetic by-products or by late-stage remobilization of elements associated with speleogenesis are referred to as "secondary speleogenetic by-products." Primary speleogenetic by-products of H₂SO₄ speleogenesis are gypsum, elemental sulfur, hydrated halloysite, alunite, natroalunite, jarosite, hydrobasaluminite, quartz, todorokite, and rancieite. Amorphous materials produced by this process are opal and aluminum sulfates. Secondary speleogenetic by-products are aluminite, tyuyamunite, gypsum, opal, and quartz. Less-understood, and therefore not-yet-classified, speleogenetic by-products are celestite, hydrated Fe-sulfates, gibbsite, nordstrandite, goethite, dolomite, and perhaps crandallite-beudantite group minerals such as goyazite and svanbergite. Speleogenetic by-products are preserved in the Carlsbad caves only in areas that have been protected from post-speleogenesis drip and flood water. For this reason, many other H₂SO₄ caves in the Guadalupe Mountains that were subjected to extensive drip and floodwaters are devoid of these materials.

PRIMARY SPELEOGENETIC BY-PRODUCTS

Gypsum. Gypsum is the most abundant primary speleogenetic by-product in the Carlsbad caves. Gypsum may also occur as a secondary precipitate (speleothem) unrelated to speleogenesis (Hill 1987). In the Carlsbad caves, speleogenetic gypsum is observed as thick floor blocks and wall/ceiling rinds. Floor blocks in Lechuguilla Cave exceed 6 m in thickness, and 3 m in Carlsbad Cavern. Egemeier (1973, 1981) and Jagnow (1977) first recognized the exceptional quantities of gypsum floor blocks and wall rinds as evidence of speleogen-
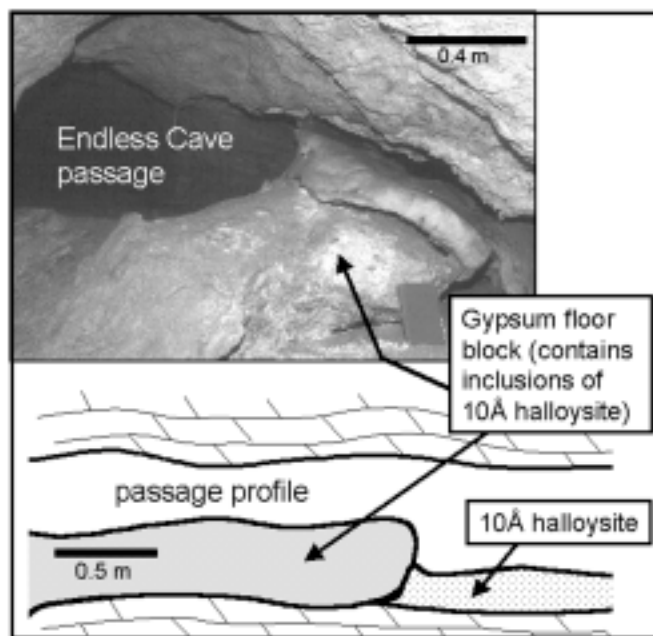
Figure 3. Photograph and sketch of speleogenetic gypsum in a passage in Endless Cave. The gypsum floor block is a replacement of the dolomitic bedrock. The bedrock contains a moderate amount of quartz, illite, and dickite, and these minerals have apparently been altered to hydrated halloysite, which is found as small pods in the gypsum. The hydrated halloysite fell out onto the passage floor as the gypsum is removed by condensation-induced weathering.

esis related to H₂SO₄. Later, Hill (1981, 1987) showed that negative sulfur isotope values measured for the gypsum blocks and rinds linked the source of sulfur to hydrocarbons in the adjacent Permian Delaware Basin. Queen *et al.* (1977) and Egemeier (1981) described some of these wall rinds as replacement of dolostone by gypsum. Hill (1987) showed that gypsum could either replace bedrock during speleogenesis, or be precipitated during and soon after speleogenesis as thick floor blocks. Buck *et al.* (1994) provided a genetic classification for H₂S-H₂SO₄–derived gypsum, which includes: (1) subaqueous replacement crust; (2) subaqueous sediment; (3) subaerial replacement crust; (4) subaerial replacement-crust breccia; and (5) evaporitic crust. This genetic classification is particularly significant as it shows a spatial relationship to the water table, thus adding information about the cave-forming environment. Figure 3 shows primary speleogenetic gypsum in a passage in Endless Cave.

Although the morphology of these gypsum deposits has been moderately well described, the purity of the gypsum remains relatively unknown. For example, gypsum in Endless Cave contains pods of hydrated halloysite in replacement floor blocks. Removal of the gypsum by later condensation-induced weathering has left remnant floor deposits of the halloysite (Fig. 3). Minerals and amorphous materials incorporated within primary speleogenetic gypsum have potential to reveal fur-

Table 1: List of known speleogenetic byproducts in the Carlsbad caves.

Mineral	Formula	Cave
Primary speleogenetic byproducts		
alunite	$KAl_3(SO_4)_2(OH)_6$	Ca,C,E,H,Le,V
amorphous silica	$SiO_2 \cdot nH_2O$	C
gypsum	$CaSO_4 \cdot 2H_2O$	B,Ca,C,D,E,H,K,Le,S,V
hydrated halloysite	$Al_2Si_2O_5(OH)_4 \cdot 2H_2O$	Ca,C,E,H,Le,V
hydrobasaluminite	$Al_4(SO_4)(OH)_{10} \cdot 12\text{-}36H_2O$	C
jarosite	$KFe_3(SO_4)_2(OH)_6$	C,Le
natroalunite	$NaAl_3(SO_4)_2(OH)_6$	Ca,Le
quartz	SiO_2	Ca,C,E,
rancieite	$(Ca,Mn)Mn_4O_9 \cdot 3H_2O$	Le,Sp
sulfur (elemental)	S	C,Ca,Le
todorokite	$(Mn,Ca)Mn_5O_{11} \cdot 4H_2O$	Ca,Le
Secondary speleogenetic byproducts		
aluminite	$Al_2(SO_4)(OH)_4 \cdot 7H_2O$	C
amorphous silica	$SiO_2 \cdot nH_2O$	Ca,C,E,H,Le,V
gypsum	$CaSO_4 \cdot 2H_2O$	Sp
metatyuyamunite	$Ca(UO_2)_2(VO_4)_2 \cdot 3H_2O$	Ca,Le,Sp
quartz	SiO_2	Ca,Le
tyuyamunite	$Ca(UO_2)_2V_2O_8 \cdot 5\text{-}8H_2O$	Ca,Le
Other possible or less-understood speleogenetic byproducts		
celestite	$SrSO_4$	Ca,Le
copiapite	$(Fe,Mg)Fe_4(SO_4)_6(OH)_2 \cdot 20H_2O$	Ca
coquimbite	$Fe_2(SO_4)_3 \cdot 9H_2O$	Ca
dolomite	$CaMg(CO_3)_2$	Le
gibbsite	$Al(OH)_3$	C,V
nordstrandite	$Al(OH)_3$	Le
römerite	$Fe_3(SO_4)_4 \cdot 14H_2O$	Ca
Bedrock minerals		
calcite	$CaCO_3$	
crandallite-beudanite group	$AB_3(XO_4)_2(OH)_6$, where A=Ca, Ce, Sr, Th; B=Al, Fe; X=P, S, As	
dickite	$Al_2Si_2O_5(OH)_4$	
dolomite	$CaMg(CO_3)_2$	
illite	$K(Al,Mg,Fe)_2(Si,Al)_4O_{10}(OH)_2$	
illite-smectite mixed-layers	$KAl_4(Si,Al)_8O_{10}(OH)_4 \cdot 4H_2O$	
kaolinite	$Al_2Si_2O_5(OH)_4$	
montmorillonite	$(Na,Ca,K)_{0.3}(Al,Mg)_2Si_4O_{10}(OH)_2 \cdot nH_2O$	

B=Black Cave, Ca=Carlsbad Cavern, C=Cottonwood Cave, D=Dry Cave, E=Endless Cave, H=Hell Below Cave, K=KFFC Cave, Le=Lechuguilla Cave, S=Slaughter Canyon Cave, Sp=Spider Cave, V=Virgin Cave
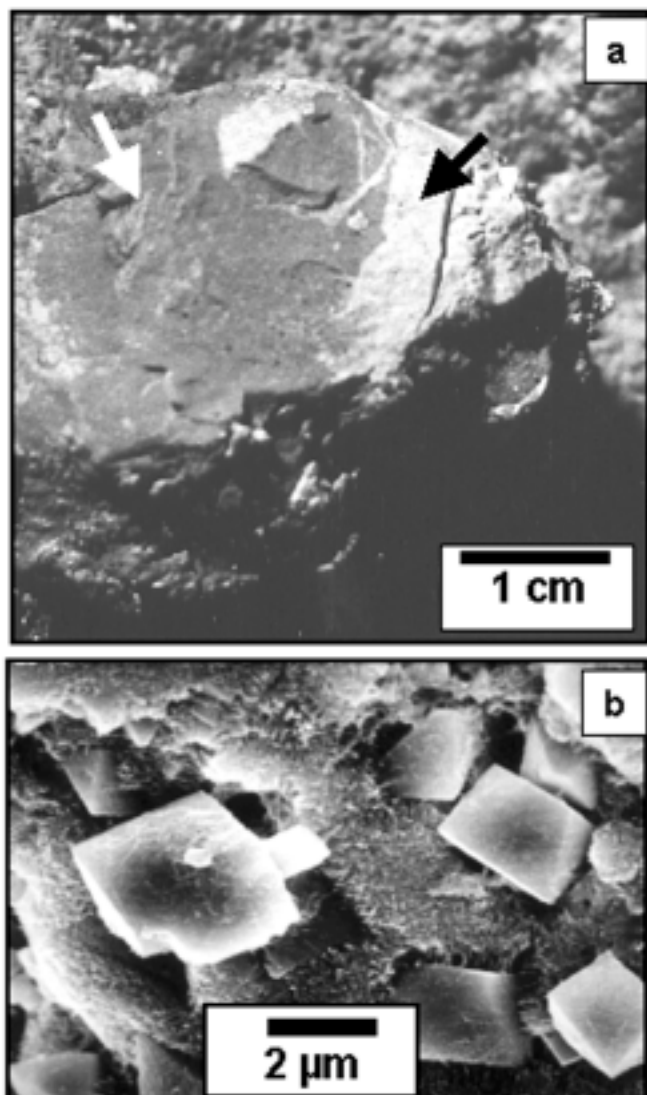
Figure 4. (a) Photograph of green montmorillonite-rich clay pod with white alteration rims of hydrated halloysite and alunite. (b) Scanning electron micrograph of alunite rhombs in a matrix of hydrated halloysite tubes. These two minerals are usually found together as white pasty to chalky material in the alteration zones.

ther information about the environment of speleogenesis.

Elemental sulfur. Davis (1973) reported elemental sulfur in Cottonwood Cave. Later, Davis (1980) and Hill (1981) suggested that such elemental sulfur might be a by-product of H_2SO_4 speleogenesis. Hill (1981, 1987) and Pisarowicz (1994) measured negative stable isotope values for the elemental sulfur, which linked the source of sulfur to microbial activity and hydrocarbons (Hill 1987). Some deposits of elemental sulfur are so large in Lechuguilla Cave (>1000 kg, Cunningham *et al.* 1994) that open flame lights are no longer allowed in this cave.

Hydrated halloysite. Davies and Moore (1957) first reported hydrated halloysite (endellite) from Carlsbad Cavern. Hill

(1981, 1987, 1990) and Polyak and Güven (1996) later reported it as a primary by-product of H_2SO_4 speleogenesis by the alteration of smectite (montmorillonite) and other clays. In the Carlsbad caves, hydrated halloysite is most discernable as waxy, white or blue nodules in pockets of altered bedrock, disseminated in speleogenetic wall residues, and less commonly as floor deposits. Hydrated halloysite is generally associated with alunite, and the blue variety is relatively pure. The Green Clay Room of Carlsbad Cavern exhibits the most convincing evidence of green smectitic clay-filled solution cavities that were truncated and altered by the H_2SO_4 speleogenesis. The hydrated halloysite with alunite makes up a white reaction rind around the green montmorillonite clay (Polyak *et al.* 1998) (Fig. 4). In Endless Cave, hydrated halloysite in pockets of altered bedrock and floor deposits is probably the by-product of alteration of illite, interstratified illite-smectite, and dickite, which are the most common clay minerals in the surrounding Permian carbonate rocks (Polyak 1998).

Alunite group minerals. Alunite, natroalunite, and jarosite are primary speleogenetic by-products found in pockets of altered bedrock, some floor deposits, and in wall residues in the Carlsbad caves. Alunite and natroalunite are associated with hydrated halloysite in nearly all occurrences (Polyak & Güven 1996). The alunite occurs as white to pale-white chalky nodules of <1 to 30 μm diameter cube-like rhombs. Hydrated halloysite and alunite are the result of clay alteration by H_2SO_4 speleogenesis. Clay minerals such as illite and montmorillonite, in internal sediments and in the bedrock, provide the source of the potassium for alunite. Natroalunite instead of alunite may form if sufficient sodium is available (Polyak & Güven 2000). The alunite group minerals are probably the most significant speleogenetic by-products because they can be dated using the K-Ar or $^{40}Ar/^{39}Ar$ method. Their stable isotope geochemistry can also reveal important information about the environment of speleogenesis. Jarosite has been noted only in trace amounts. This iron-bearing, yellow mineral was found in association with opal near an occurrence of hydrobasaluminite in Cottonwood Cave (Polyak & Provencio 1998).

Hydrobasaluminite. Hydrobasaluminite occurs as white pods in pockets of altered bedrock. It results from the interaction of the H_2SO_4-bearing waters with kaolinite rather than with potassium-bearing clays such as illite and smectite. Crystals are micrometer-sized platelets, which dehydrate to basaluminite in <2 hours exposure to a relative humidity <70% at 25°C. In Cottonwood Cave, a kaolinite-rich seam in dolostone has been altered to hydrobasaluminite, amorphous silica, amorphous aluminum sulfate, and minor amounts of alunite and hydrated halloysite (Polyak & Provencio 1998) (Fig. 5).

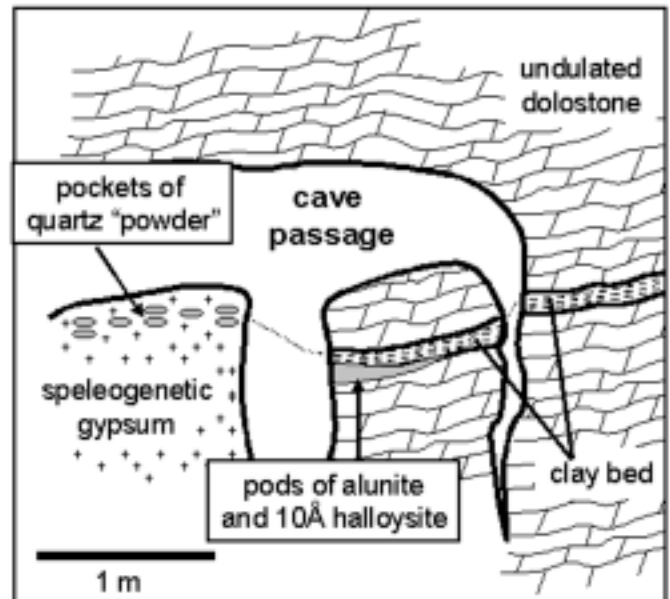*Quartz.* Chert was reported by Hill (1987) as a speleogenetic by-product of the alteration of montmorillonite (Big Room, Carlsbad Cavern). In other occurrences, quartz is found in the Carlsbad caves as chert and chalky unconsolidated powder in association with primary speleogenetic gypsum. A well-exposed gypsum block in Endless Cave, which replaced dolostone, contains a line of white chalky pods of micrometer- to
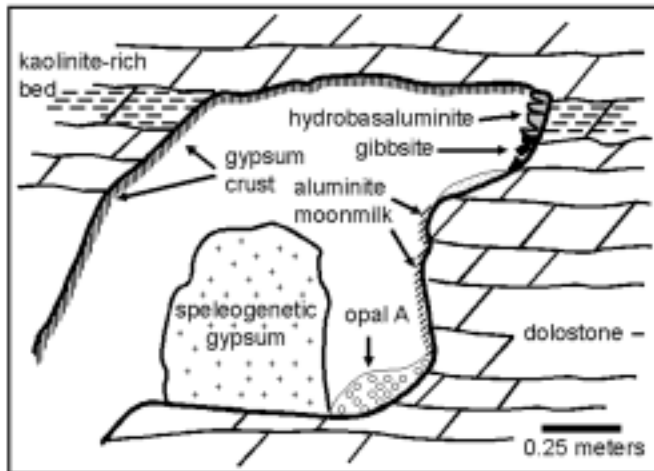
Figure 5. Sketch of a small room in Cottonwood Cave containing by-product materials such as hydrobasaluminite. In this case, kaolinite-bearing dolostone was altered to hydrobasaluminite during speleogenesis. Hydrobasaluminite was the primary speleogenetic by-product mineral because potassium and sodium were lacking in the bedrock. Figure modified after Polyak and Provencio (1988). Note that aluminite moonmilk (secondary by-product) formed along the cave walls below, and from the alteration of, the hydrobasaluminite.

Figure 6. Setting in Endless Cave showing the relationship between speleogenetic gypsum, quartz, alunite, hydrated halloysite, and a thin Permian clay bed. The clay bed containing kaolinite and interstratified illite-smectite was altered to alunite and hydrated halloysite at the gypsum-bedrock interface, and to quartz in the replacement gypsum. Note that the quartz pods are stratigraphically equivalent to the clay bed.

deci-micrometer-sized, double-terminated euhedral quartz crystals. These pods form a stratum that is in line with a Permian clay bed in the nearby unaltered cave wall (Fig. 6). It appears that during H_2SO_4 speleogenesis, the surrounding dolostone was replaced by gypsum and the clay was altered to quartz within the gypsum. The unaltered clay bed consists of kaolinite and interstratified illite/smectite. Between the gypsum block and the unaltered bedrock, the clay bed was partly altered to hydrated halloysite and alunite during H_2SO_4 speleogenesis (Fig. 6). A chert bed with the same thickness as the Permian clay bed (10 cm) is remnant along the same stratum in other areas of this cave. A similarly thick chert bed occurs in gypsum blocks in Cottonwood Cave. Near the Bottomless Pit in Carlsbad Cavern, a chalky layer of quartz has formed directly under a thick (3 m) gypsum block. Crystals in this deposit are clay-sized (0.2 – 0.5 μm) euhedral quartz. Clay and silt were altered to quartz, probably at low temperature during final stages of H_2SO_4 speleogenesis. Study of the stable isotope geochemistry of this quartz may yield important information about the environment of speleogenesis. Chafetz and Zhang (1998) reported a similar low-temperature occurrence of quartz in Quaternary evaporite-associated carbonate rocks.

Hydrous manganese oxides. Todorokite and other hydrous manganese oxides occur around the perimeter of many pockets of altered bedrock closely associated with alunite and hydrated halloysite (Polyak & Güven 1996, 2000). Todorokite and rancieite are also constituents of the black wall residues in Lechuguilla Cave. In silvery black wall residues, rancieite is most abundant on the surface of truncated schalenohedral calcite spar (Modreski 1989). The todorokite associated with alunite, natroalunite, hydrated halloysite, and hydrobasaluminite probably formed along sharp high-low pH or Eh boundaries produced by H_2SO_4 speleogenesis (Polyak 1998). TEM of todorokite, rancieite, and other hydrous manganese oxides show three-dimensional, box-like or dendritic crystal-fiber structures, platelets that consist of packed fibers, or individual fibers. Some occurrences of hydrous manganese oxides are probably secondary speleogenetic by-products, or unrelated to speleogenesis.

SECONDARY SPELEOGENETIC BY-PRODUCTS

Aluminite. In Cottonwood Cave, aluminite moonmilk drapes the walls below hydrobasaluminite (a primary speleogenetic by-product). It formed as a secondary speleogenetic by-product by the alteration of the overlying hydrobasaluminite (Polyak & Provencio 1998). Gypsum moonmilk, another secondary speleogenetic by-product, is associated with the aluminite moonmilk. Pods of dark gray gibbsite also occur in the hydrobasaluminite/aluminite setting.

Gypsum. Speleothemic gypsum derived from speleogenetic gypsum is common in the Carlsbad caves, but may have little significance as a speleogenetic indicator mineral because speleothemic gypsum is common in all types of caves.

Uranyl vanadates. Tyuyamunite and metatyuyamunite have been found in association with quartz and opal coatings on dolomite and gypsum crusts and floor clay in three Carlsbad caves (Polyak & Mosch 1995; Polyak 1998). The uranyl vanadates precipitated long after speleogenesis as a result of excess silica from clay alteration and concentration of uranium and vanadium along oxidation/reduction zones created by H_2SO_4 speleogenesis. The quartz and opal coatings associated with the uranyl vanadates are also secondary speleogenetic by-products.

OTHER POSSIBLE SPELEOGENETIC BY-PRODUCTS

Celestite. Celestite occurs in Carlsbad Cavern (Hill 1987) and Lechuguilla Cave (DuChene 1997) as crusts and crystals on cave walls. The moderately light sulfur isotope compositions of -14.5 to +7.4‰ 9Hill 1996, DuChene 1997) suggest that celestite may also be a speleogenetic by-product. However, Hill (1987) reported celestite as probably speleothemic and unrelated to speleogenesis.

Hydrous iron-sulfate minerals. Hydrous iron-sulfate minerals (copiapite, coquimbite, römerite) are associated with some occurrences of celestite in Carlsbad Cavern, and were suggested to be speleogenetic by-products by Mosch and Polyak (1996).

Gibbsite. Gibbsite occurs in two Carlsbad caves in pockets of altered bedrock that were partly covered with calcite coatings. The pockets contain speleogenetic by-products that were subjected to alteration by the carbonate-bearing seepage water that deposited the calcite during post-speleogenesis weathering. The gibbsite may be a secondary speleogenetic by-product from the alteration of alunite. Gibbsite can be obtained from alunite by the Bayer Process (Ruvalcaba *et al*. 1995), by which alunite is dissolved slowly in alkaline solutions (i.e., containing CO_3^{2-}), and gibbsite is consequently precipitated.

Nordstrandite. Nordstrandite occurs in Lechuguilla Cave as a floor deposit below what appears to be leached speleogenetic wall residues, and may be the result of the alteration of hydrated halloysite and alunite in the black wall residues at this location.

Crandallite-beudantite group minerals. Goyazite-svanbergite and other crandallite-beudantite group minerals occur with the nordstrandite in this floor deposit. EDX microanalysis of some of the goyazite-svanbergite rhombs indicates the presence of rare earth elements. The crandallite-beudantite group minerals were noted in trace amounts in residues of dolomite bedrock dissolved in the laboratory (Polyak 1998). It is therefore possible that these minerals may be inherited from dissolved bedrock as insoluble residues.

Goethite. Goethite is the most abundant crystalline iron oxide phase in the Carlsbad caves. It is common in brown wall residues, which are probably products of condensation-induced weathering rather than speleogenesis. It is also commonly associated with pockets of altered bedrock. Provencio & Polyak (2001) suggested that goethite in the "Rusticles" is associated with speleogenesis. It is likely a speleogenetic by-

product, but may be difficult to show in many cases because of its widespread occurrences in these caves.

Dolomite. Dolomite occurs in Lechuguilla Cave as white clasts of a breccia with primary speleogenetic gypsum as the matrix between the clasts. The altered (dolomite) clasts contain *in situ* Permian fossils, which indicate they were fragments of altered bedrock. The stable isotope values of these dolomite clasts (two samples) are $\delta^{13}C$ = -5.49 to -4.95 and $\delta^{18}O$ = -6.02 to -4.40‰ V-PDB, which are in contrast with values for Permian dolostone samples ($\delta^{13}C$ = 6.4 to 7.1‰ and $\delta^{18}O$ = 0.6 to 2.8‰, Polyak *et al*., 2001). This at least suggests that the dolomite clasts inherited their lighter isotopes from meteoric waters. Palmer and Palmer (1992) reported similar replacement dolomite as crusts in Lechuguilla Cave, and Hill (1996) speculated the possible origin of speleogenetic dolomite. The dolomite clasts in the gypsum matrix are fragments of bedrock (originally limestone) that appear to have been altered by H_2SO_4 speleogenesis.

H_2SO_4 SPELEOGENETIC FEATURES

Pockets of altered bedrock. Polyak and Güven (1996) described centimeter-sized pockets of altered bedrock, which contain nodules of hydrated halloysite and alunite bounded by hydrous manganese- and iron-oxides. Pockets of altered bedrock are important features because they contain abundant amounts of primary speleogenetic by-products.

Cusp features. Buck *et al*. (1994) described gypsum-carbonate rock replacement boundaries as rounded and oblong bulges extending into the bedrock. They suggested that these oblong bulges were due to differential solubility of individual beds or varying rates of diffusion of ions through the developing gypsum-replacement crusts. Given this scenario, removal of the replacement gypsum bulges by post-speleogenesis weathering would expose cusp features in the cave walls. Such meter-sized scallop-like features appear to be exhibited throughout much of Carlsbad Cavern. In the New Mexico Room of Carlsbad Cavern, pockets of altered bedrock that contain alunite, hydrated halloysite, and hydrous manganese oxides are associated with these features possibly indicating that the pockets formed at the gypsum/bedrock interface (Fig. 7).

Black wall residues. Wall residues in the Carlsbad caves are complex. These have been referred to as condensation-corrosion residues (Hill 1987; Cunningham *et al*. 1995). Northup *et al*. (2000) favored a condensation-corrosion method of origin related to microbial-assisted dissolution of the bedrock. Our mention of condensation-induced weathering or speleogenesis-related weathering does not discriminate between inorganic or microbial-related origin for the wall residues. We suggest that at least two types of wall residues exist: (1) brown goethite- and clay-rich wall residues, and (2) black manganiferous wall residues. The brown wall residues appear to be related to weathering of dolostone bedrock by condensation water (condensation-corrosion). These contain abundant amounts of illite and dickite inherited from the bedrock
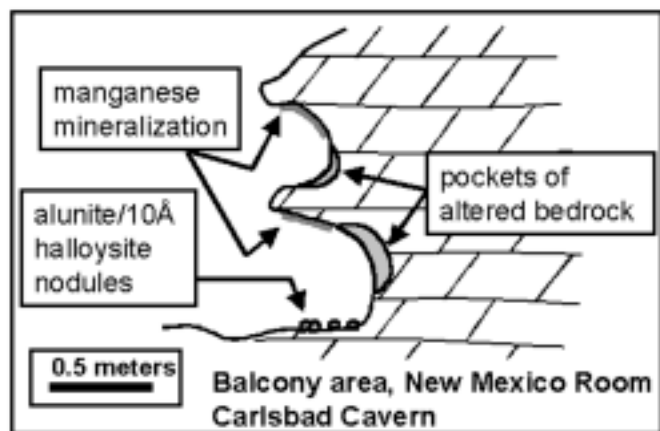
Figure 7. Sketch of cusp features in the New Mexico Room of Carlsbad Cavern. The cusp features are found throughout Carlsbad caves, and they probably result from differential replacement of the bedrock gypsum during speleogenesis as described by Buck *et al*. (1994).

(Polyak & Güven 2000), and formed during post-speleogenesis weathering. Samples of black residues from Lechuguilla Cave contain todorokite, alunite, and hydrated halloysite, and are probably indicative of differing pH and Eh boundaries related to H_2SO_4 speleogenesis (Polyak 1998). We therefore suggest that the black wall residues formed primarily during H_2SO_4 speleogenesis. These may have initially developed behind the speleogenetic gypsum blocks/rinds at the gypsum-bedrock contact. Condensation-induced weathering (after speleogenesis) probably removed the gypsum and later modified the wall residues. The black wall residues contain significant microbial communities (Northup *et al*. 2000), and may contain minor goethite, dickite, illite, and nordstrandite (Polyak 1998).

IMPLICATIONS

The material assemblages presented in this study have a potentially far-reaching impact, even beyond the study of caves. Hill (1981, 1987, 1990), Polyak and Güven (1996), Polyak and Provencio (1998), and Palmer and Palmer (2000) reported that the H2S- H2SO4–bearing waters that formed these caves also altered the carbonate rocks as well as the insoluble residues from their dissolution to produce various speleogenetic by-products. Carbonic acid generated from significant amounts of CO_2 that migrated with H_2S must have also played a role in the dissolution of the carbonate rocks to form these caves (Hill 1987). However, it was the H2S-oxidation-process that produced H_2SO_4 and other sulfur species that resulted in the formation of speleogenetic by-products. We suspect, because of the abundant microbial communities associated with active H_2SO_4 caves today (Engel *et al*. 2000, Hose *et al*. 2000), that microorganisms and their excretions also played a role in the alteration of clays and other insoluble minerals dur-
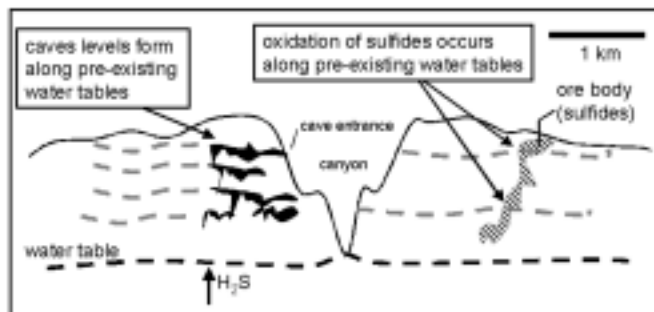

Figure 8. Idealized model of sulfide oxidation along a declining water table. The model of speleogenesis presented for the Carlsbad caves may apply in non-cave areas as well. For instance, water table decline through sulfide ore zones could also result in the same acid-sulfate by-product materials as found in the Carlsbad caves.

ing speleogenesis. Studies of the material assemblages associated with speleogenesis are important because they enable advanced interpretations of cave-forming environment, in this case, during and subsequent to the late Miocene.

The ages of formation of the Carlsbad caves, and the timing of an apparent regional water table decline during the late Miocene and Pliocene were derived from the study of speleogenetic by-products (Polyak *et al*. 1998). This has offered insight into the development of the Guadalupe Mountains, which took place concurrently with H_2SO_4 speleogenesis. This illustrates how understanding the origin of the by-products of H_2SO_4 speleogenesis offers a potentially powerful tool for the study of Cenozoic geologic history.

Furthermore, the substance of this study is not restricted to the cave environment. For instance, we predict that sulfide ore deposits, or clays above hydrocarbon reservoirs, can undergo alteration to similar mineral associations (where regional water table movement has been active, Fig. 8). A potential example of this is the Grand Canyon, Arizona, where similar minerals are found in association with a possible water table decline that may be related to the canyon's origin (Hill *et al*. 1999). Study of speleogenetic by-products has advanced our understanding of the Carlsbad caves and the Guadalupe Mountains, and will provide information that can be applied elsewhere.

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