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ALUNITE, NATROALUNITE AND HYDRATED HALLOYSITE IN CARLSBAD CAVERN AND LECHUGUILLA CAVE, NEW MEXICO

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Abstract—Members of an alunite-natroalunite solid solution series occur in intimate association with hydrated halloysite in deposits within caves of the Guadalupe Mountains, namely Carlsbad Cavern and Lechuguilla Cave. The alunite and natroalunite crystals consist of cube-like rhombs; crystal diameters range from 0.5 to 8 μm. This mineral association is found in sediments within bedrock pockets, solution cavity fills, floor deposits and wall residues. Sulfur stable isotope values ($\delta^{34}S$, CTD) for cave alunite and natroalunite are negative [+0.1 to −28.9 per mill (‰); $n = 12$ and mean = −16.8‰] and are comparable to the cave gypsum and native sulfur values reported by other investigators. The association of alunite/natroalunite with hydrated halloysite in these cave deposits suggests that the cave-forming waters contained significant concentrations of sulfuric acid. Formation of these minerals is related to the excavation of the carbonate rocks that formed Carlsbad Cavern, Lechuguilla Cave and other caves of the Guadalupe Mountains. The sulfuric acid-bearing waters, when exposed to clay-rich sediments, converted clay minerals and quartz to alunite/natroalunite and hydrated halloysite.

Key Words—Alunite, Carlsbad Cavern, Caves, Hydrated Halloysite, Lechuguilla Cave, Natroalunite, Sulfuric Acid, Sulfur Stable Isotopes.

INTRODUCTION

Alunite group minerals within cave sediments have been reported from only a few localities (Hill and Forti 1986). Alunite associated with halloysite has been reported in Lechuguilla Cave in the Guadalupe Mountains and has been assumed to be an alteration product due to the action of sulfuric acid (Palmer and Palmer 1992). Alunite or natroalunite mineralization in noncave sedimentary environments has been reported by Keller et al. (1967); Ross et al. (1968); Goldbery (1980); Chitale and Güven (1987); Rouchy and Pierre (1987); Khalaf (1990); and Long et al. (1992). These studies indicate that alunite, in the sedimentary environment, forms at low temperature from sulfuric acid-bearing waters or acidic waters containing aqueous sulfate.

Hydrated halloysite (also referred to as 10-Å halloysite) was first reported in caves of the Guadalupe Mountains from the New Mexico Room in Carlsbad Cavern by Davies and Moore (1957). Hill (1987) later reported hydrated halloysite from 2 other Guadalupe Mountains caves. The hydrated halloysite in these caves formed when montmorillonite was exposed to sulfuric acid-bearing solutions (Hill 1987, 1990).

This paper reports the presence of alunite [$KAl_3(SO_4)_2(OH)_6$] and natroalunite [$NaAl_3(SO_4)_2(OH)_6$] in the caves of the Guadalupe Mountains where the rocks of the Capitan Reef Complex are exposed at the northern margin of the Delaware Basin (Figure 1). Stable isotope geochemistry of alunite-group minerals ($\delta^{34}S$) is included.

Background: Speleogenesis of Guadalupe Mountain Caves

Several theories of cave development in the Guadalupe Mountains have been offered since the classic work of Bretz (1949). The idea that the caves of the Guadalupe Mountains formed primarily from dissolution by H_2SO_4 was first offered by Jagnow (1977) and Davis (1980). Both investigators recognized the unusual abundance of gypsum and/or rare occurrences of native sulfur in these caves, and the spacious horizontal passages connected by deep pits. Hill (1981) was the first to acquire sulfur isotope values on cave gypsum and sulfur, and suggested a sulfuric acid speleogenesis of the caves based on those values. Kirkland (1982) showed (from sulfur isotope data) that the gypsum in the Big Room of Carlsbad Cavern was derived from a sulfide formed by microbial reduction of a sulfate. Kirkland concluded that gypsum in these caves formed from sulfuric acid that was derived from oxidation of elemental sulfur. The elemental sulfur was, in turn, derived from oxidation of H_2S that migrated from the Delaware Basin. Hill (1987, 1990, 1995) demonstrated from sulfur isotope data that the acidic solutions that formed the caves were derived from oxidation of H_2S that originated from hydrocarbons in the basin and then migrated into the Capitan Reef Complex. According to Hill, the pits found in these caves were pathways for migration of the H_2S to the water table. Phreatic dissolution occurred along these pathways, forming deep blind pits, and major dissolution occurred at the water table above these vertical pathways, forming large horizontal chambers. Exten-

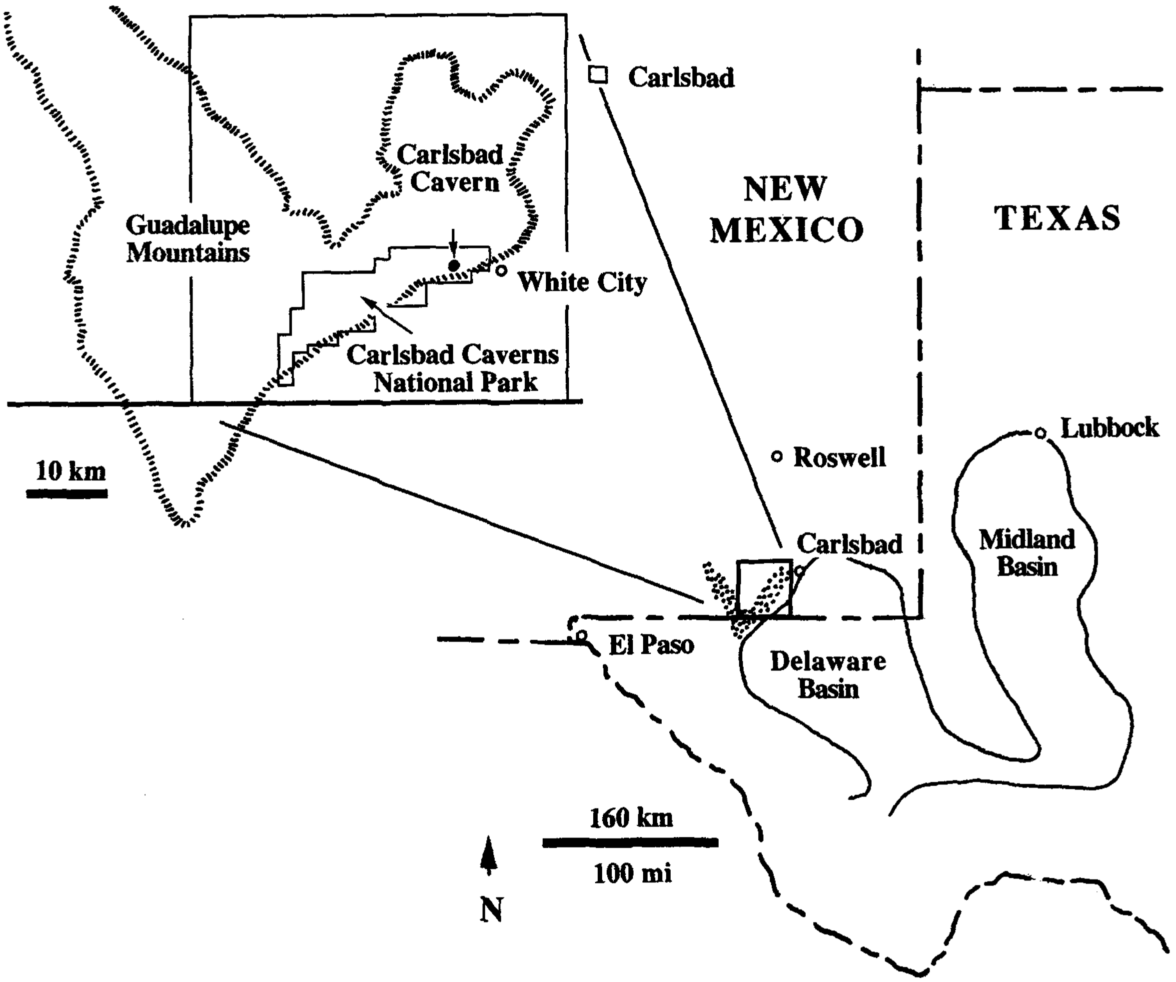

Figure 1. Map showing location of study area in relation to the Permian Delaware Basin.

sive gypsum deposits within these caves were byproducts of the reaction of H_2SO_4 with carbonate bedrocks. Hill (1990) suggested that the isotopically-light sulfur isotope signatures ($\delta^{34}S$) of the gypsum and native sulfur in these caves are evidence that the large passages were formed primarily by H_2SO_4 derived from biochemical fractionations of sulfur in the basin.

METHODS

X-ray diffraction (XRD) of random powders and suspended mounts were performed using a Philips Norelco diffractometer operated at 40 kV and 20 mA with nickel-filtered Cu*K*α radiation. Characteristic X-ray spectra were obtained on single crystals of alunite and clays using energy dispersive X-ray spectroscopy (EDS) interfaced to a JEOL JEM-100CX electron microscope. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were used to study mineral morphology.

Unit-cell parameters were determined using the indexing and least-squares powder diffraction program by Appleman and Evans (1973) revised for the PC by Benoit (1987). Stable isotope analyses were provided by Geochron Laboratories, 711 Concord Avenue, Cambridge, Massachusetts 02138.

Samples were collected from the Big Room, Guadalupe Room, Boneyard (near lunchroom), New Mexico Room, Lower Devil's Den and Lower Cave in Carlsbad Cavern. Samples were collected from Apricot Pit, Boulder Falls, Glacier Bay, Lake LeBarge, The Great Beyond and Tinsel Town in Lechuguilla Cave. Other alunite/natroalunite and hydrated halloysite samples were collected from Endless, Hell Below, Virgin and Cottonwood caves.

DEPOSITIONAL ENVIRONMENT

In all of the caves studied, alunite group minerals and hydrated halloysite are found together in 4 depositional settings: 1) bedrock pockets, 2) solution cavity fills, 3) floor deposits and 4) bedrock wall residues (Figure 2). Bedrock pockets are usually less than 50 cm in diameter and are characterized by the occur-

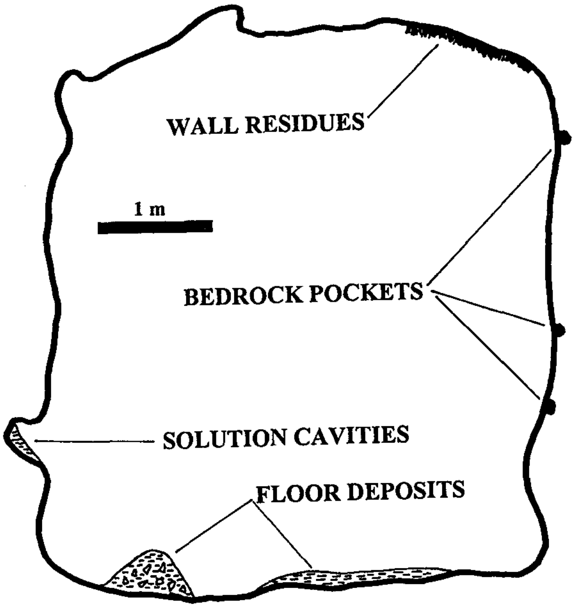

Figure 2. Idealized section of cave passage showing the 4 depositional settings in which alunite and natroalunite are found.

rence of iron- and manganese-rich minerals that generally have a distinct black appearance. Bluish white nodules of hydrated halloysite are occasionally observed in this setting, as well. The bedrock pocket setting is the most characteristic for sediments containing hydrated halloysite and alunite group minerals. Solution cavities, particularly in Carlsbad Cavern, are sometimes filled or partially filled with laminated silty clay-rich sediment. Numerous cm-sized solution cavities give bedrock in the Green Clay Room a "Swiss cheese" appearance. This network of cavities, called "spongework" (Hill 1987; Ford and Williams 1992), can form complex 3-dimensional mazes of cave passages. These solution cavity fills sometimes contain hydrated halloysite and alunite group minerals. Floor deposits that contain hydrated halloysite and alunite group minerals range in size from <10 to >100 m^2. Floor deposits of this type in Lower Cave and the Big Room of Carlsbad Cavern are piled silt and clay layers (not to be confused with the extensive brown silt deposits of the cavern). These deposits contain fragments of red silt, brown and gray clay and nodules of hydrated halloysite, and appear to have fallen from the ceiling bedrock pockets and solution cavities located 10 to 100 m above. In the New Mexico Room and in Endless Cave, floor deposits are dominated by hydrated halloysite. Wall residues, black in color due to associated manganese minerals, contain alunite, natroalunite and hydrated halloysite and are most apparent in Lechuguilla Cave. Although areas throughout much of the larger caves still exhibit outcrops of these materials, in many places they are mostly covered by later depositions of gypsum blocks and crusts, or carbonate crusts, flowstones and dripstones.

RESULTS

Mineralogy

Other minerals accompanying hydrated halloysite and K- or Na-alunite vary in the 4 settings described previously. Smectite, todorokite, goethite, detrital quartz and occasionally gibbsite occur with hydrated halloysite and the alunites in bedrock pockets. Hydrated halloysite and alunite group minerals are associated with silt-sized quartz grains, smectite and kaolinite in floor deposits and solution cavity fills. Wall residues contain nordstrandite, goyazite, goethite, illite, dickite and manganese minerals such as rancieite. Todorokite, rancieite, lithophorite, quartz, poorly crystalline or amorphous iron oxide and an aluminum hydroxide mineral in wall residues of Lechuguilla Cave were reported by Modreski (1989) and Cunningham et al. (1995). Hydrated halloysite and alunite-group minerals are usually associated in all of these settings.

Hydrated halloysite is present in caves of the Guadalupe Mountains mostly as vitreous to waxy nodules or as moist powder. The color of the hydrated halloysite is white, bluish white, bluish green, red, yellow, brown and pink. The mineral sometimes occurs as a pure floor deposit, as in the middle maze of Endless Cave and the New Mexico Room of Carlsbad Cavern. Halloysites from caves of the Guadalupe Mountains were identified as the hydrated (10-Å) phase, with the possible exception of a partially dehydrated sample (metahalloysite) from Cottonwood Cave. Transmission electron micrographs of hydrated halloysite crystals exhibit typical tubular morphology. Crystal size and morphology are similar in all samples; tube dimensions are variable in their length and consistent in their width. Bailey (1993) noted that changes in the morphology and dimensions of the hydrated halloysite can be related to the chemical composition of the tubes; for instance, long tubes favor an Al_2O_3 content of 46 to 50% (Al-rich) and an Fe_2O_3 content of < 1 wt%. Hydrated halloysites from Guadalupe caves exhibit tubular crystal morphology of variable length. Average tube length and width are 0.28 and 0.06 μm, respectively, with some tubes exceeding 1 μm in length. Iron was not detected in the halloysite found in these cave deposits.

Alunite or natroalunite is generally found disseminated within waxy nodules of hydrated halloysite, or concentrated in white, light brown and pink pasty or powdery nodules. At the Under-The-Cross in the Big Room in Carlsbad Cavern, alunite occurs in reddish brown clay-rich floor sediment as mm-sized white pods. In other deposits, some pods of alunite are up to several cm in size and are almost pure except for minor amounts of hydrated halloysite. Natroalunite

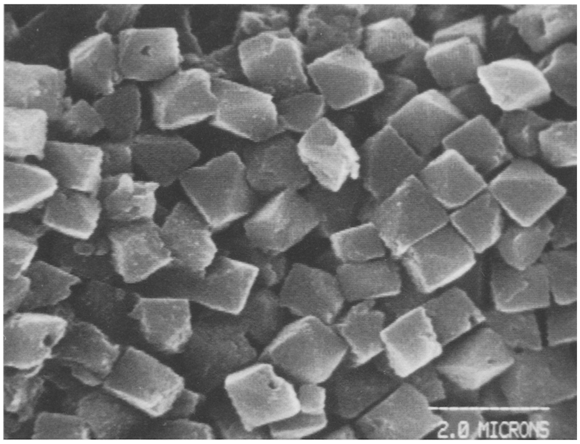

Figure 3. SEM image of cube-like alunite crystals.

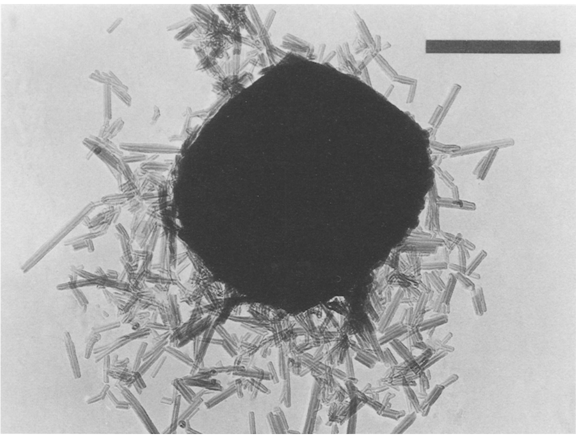

Figure 4. TEM photograph of an alunite crystal and intimately associated halloysite tubes. Bar length = 1.0 μm.

and alunite crystals are cube-like rhombs that range in diameter from 0.5 to 8 μm (Figure 3) and are intimately associated with hydrated halloysite (Figure 4).

Mole percent of natroalunite in the samples was estimated by:

$$X_{Na} = (17.331 - c)/0.635 \qquad [1]$$

where c is the c-axis dimension (Å) of the alunite as determined by XRD data (Stoffregen and Alpers 1992). Samples analyzed represent an almost complete solid solution between alunite and natroalunite end-members from approximately 5 to 86 mol% natroalunite.

Unit cell parameters and calculated mol% natroalunite are listed in Table 1. A sample of alunite from the New Mexico Room in Carlsbad Cavern was calculated to be 52 mol% natroalunite by the XRD method and 46 mol% natroalunite by inductively coupled plasma (ICP) analysis. Strontium and phosphorus detected in many samples represent a minor intergrowth of goyazite. For example, ICP and EDS results of the New Mexico Room sample provide the chemical composition $(K_{0.49}Na_{0.46}Sr_{0.05})\ Al_3(SO_4)_{1.91}\ (PO_4)_{0.09}(OH)_6$ and indicate the presence of K, Na and Sr as the alkali

Table 1. List of alunite samples, occurrence, unit cell parameters, mol% natroalunite and $\delta^{34}S$ (CTD) values in per mill.

Sample	Cave	a-axis (Å)	c-axis (Å)	Volume (Å^3)	Mol% natro-alunite	$\delta^{34}S$ (CTD)
92015	Carlsbad (NM Room)	6.985(2)	17.00(2)	718.3(1)	52	nd§
93009	Carlsbad (Big Room)	6.992(2)	17.14(2)	725.4(6)	30	−22.7
93011	Carlsbad (Big Room)	6.993(8)	17.18(8)	727(2)	24	−18.1
93012	Carlsbad (Big Room)	6.991(4)	17.14(2)	725(1)	30	nd
93013	Carlsbad (Big Room)	6.985(2)	17.26(1)	729.3(6)	11	nd
93014	Carlsbad (Boneyard)	6.989(4)	17.01(7)	720(2)	51	−6.7
93018	Lechuguilla (Gr. Beyond)	7.004(3)	17.18(1)	729.7(5)	25	−28.7
93020	Lechuguilla (L. LeBarge)	7.007(5)	17.03(5)	724(1)	47	nd
93041	Carlsbad (Gr. Clay Room)	6.996(2)	17.20(2)	728.8(8)	21	−14.0
94006	Carlsbad (Guad. Room)	6.994(2)	16.785(2)	711.0(3)	86	−27.1
94017	Cottonwood (Balcony)	7.007(7)	17.21(2)	732(2)	19	0.01
94034	Lechuguilla (L. LeBarge)	6.983(5)	17.04(9)	720(3)	46	−21.4
94042b	Carlsbad (NM Room)	7.004(3)	17.12(8)	727(3)	33	−9.8
94042w	Carlsbad (NM Room)	6.993(5)	17.30(3)	733(2)	5	−22.2
94043	Carlsbad (NM Room)	7.003(3)	16.99(2)	721.6(9)	54	−19.4
94054	Virgin	6.983(3)	17.27(1)	729.6(7)	9	nd
Natroalunite†		6.9786(7)	16.696(3)	704.2(2)	100	
Alunite†		6.981(1)	17.331(4)	731.5(2)	0	
Hydrodium Alunite†		7.005(2)	17.114(7)	727.2(4)		
Goyazite‡		7.015(3)	16.558(6)			

† Unit cell dimensions for natroalunite, alunite and hydronium alunite used here as end members were taken from Stoffregen and Alpers (1992).

‡ The goyazite unit cell used here as an end member was taken from Kato (1987).

§ nd = not determined.

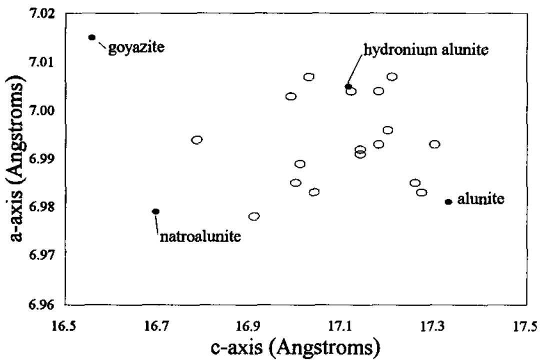

Figure 5. Unit-cell parameters of alunite and natroalunite found in caves of the Guadalupe Mountains in relation to goyazite and alunite-group end members. Alunite-group end-member data taken from Stoffregen and Alpers (1992), and goyazite end-member data taken from Kato (1987).

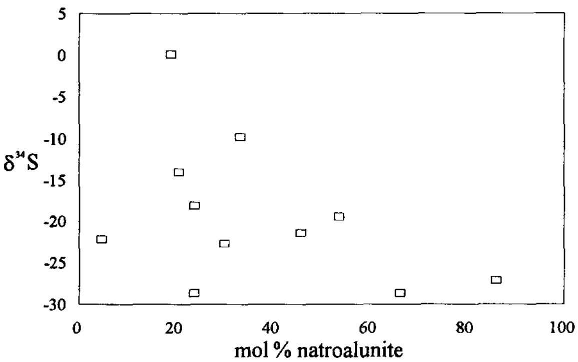

Figure 6. Mole percent natroalunite for alunite-group minerals in samples from caves in the Guadalupe Mountains compared to δ^{34}S (CTD) values per mill (‰) for those samples.

exchangeable cations. Iron is lacking as a substitute for Al. The absence of iron explains the scarcity of jarosite, although jarosite has been identified as trace constituents of 2 cave deposits from the study area. Unit-cell dimensions of the cave alunite and natroalunite are plotted in Figure 5 against end-member unit-cell dimensions reported for alunite, natroalunite, hydronium alunite and goyazite. These data seem to indicate the presence of hydronium alunite, as well.

Stable Isotope Data

Sulfur isotope values of alunite/natroalunite from Carlsbad Cavern, Lechuguilla Cave and Cottonwood Cave were determined for 12 samples. Values of δ^{34}S for the alunite-group minerals ranged from +0.1‰ to −28.7‰ (CDT) with a mean of −16.8‰. The highest δ^{34}S value for alunite was +0.1‰ from Cottonwood Cave. The mean δ^{34}S values for alunite-group minerals from Carlsbad Cavern and Lechuguilla Cave were −17.5‰ and −26.2‰, respectively. These values compare well with Kirkland (1982), Hill (1987) and Spirakis and Cunningham (1992) for gypsum and native sulfur. Kirkland (1982) and Hill (1987, 1990) reported δ^{34}S values from Carlsbad Cavern with a mean of −18.8‰, whereas Spirakis and Cunningham (1992) reported δ^{34}S values from Lechuguilla Cave native sulfur and gypsum with a mean of −23.74‰. Also, Hill (1987) reported the heaviest sulfur isotope values from Cottonwood Cave in gypsum, as was the case for alunite from that cave. Mole percents of natroalunite in the samples are also plotted against sulfur isotope values (Figure 6). The sulfur isotope data are listed in Table 1 and Table 2.

DISCUSSION

Berthier (1826) was the first to describe halloysite and reported it as blue material from solution cavities in limestone (associated with alunite); the type locality was a zinc and iron mining district in Liege, Belgium. Other early reports of halloysite were also from solution cavities in limestone associated with alunite (Ross and Kerr 1935). The depositional settings observed for this mineral assemblage within caves of the Guadalupe Mountains are apparently characteristic.

Alunite-group minerals associated with kaolinite group minerals such as hydrated halloysite are known to form in various acid-sulfate environments (Rye et al. 1992). Ambers and Murray (1995) summarized that the prerequisite for the origin of halloysite-rich indianaite was the interaction of clay minerals with H_2SO_4-bearing vadose solutions. Hill (1987, 1990) suggested that hydrated halloysite formed in Guadalupe Mountain caves by the transformation of montmorillonite during excavation of the large caves by sulfuric acid. Thus, the occurrence of alunite/natroalunite with hydrated halloysite in Carlsbad Cavern, Lechuguilla and other Guadalupe caves is significant because it further supports this theory of cave development by H_2SO_4-bearing solutions.

Höller (1967) postulated that alunite can be produced from illite. Goldbery (1980), Chitale and Güven (1987) and Rouchy and Pierre (1987) summarized that alunite in the sedimentary environment forms from the reaction between H_2SO_4 and clay minerals. According to Chitale and Güven (1987), natroalunite formed from the reaction of kaolinite with H_2SO_4 in laterite. In caves of the Guadalupe Mountains, alunite and hydrated halloysite formed in a similar way, from the reaction of H_2SO_4 with clay minerals.

Throughout the Guadalupe Mountains, the most abundant clay minerals available prior to cave development were probably illite, mica and dickite/kaolinite, as indicated by bedrock weathering residues (Polyak and Güven 1995) and insoluble residues of various samples of dolostones. However, deposits of green and brown, smectite-rich sediments are also found in solution cavities and early cave passages prior to de-

Table 2. Comparison of $\delta^{34}S$ (CTD) values for alunite, gypsum and native sulfur from caves of the Guadalupe Mountains.

Cave and location	Alunite $\delta^{34}S$ values (this study)†	Gypsum and sulfur $\delta^{34}S$ values (other studies)†
Carlsbad Cavern		
Big Room	−18.1, −22.7	−13.9, −17.6, −19.0, −19.9, −21.1 (Hill 1987) −20.0 (Hill 1987) ns‡ −15.0, −15.2, −18.3, −18.9, −19.3, −22.0 (Kirkland 1982)
Boneyard	−6.7	
Green Clay Room	−14.0	
Guadalupe Room	−27.1	
New Mexico Room	−9.8, −19.4, −22.2	
Lechuguilla Cave		
Apricot Pit	−28.6	
Chandelier Ballroom		−25.55 (Spirakis and Cunningham 1992)
Ghost Town		−21.19, −22.96 (Spirakis and Cunningham 1992) ns‡
Great Beyond	−21.4	
Lake LeBarge	−28.7	
Void		−23.51, −25.80 (Spirakis and Cunningham 1992) ns‡
Cottonwood Cave		
Upper Gypsum Passage	+0.1	+5.0 (Hill 1987)
Lower Gypsum Passage		−0.8 (Hill 1987) −14.6 (Hill 1987) ns‡

† All values are reported as per mill (‰) relative to Canyon Diablo Triolite.

‡ ns = sulfur isotope values derived from native sulfur.

velopment of the major cave passages in Carlsbad Cavern (Hill 1987). The green clay (montmorillonite) deposits were partially converted to hydrated halloysite by interaction with H_2SO_4 (Hill 1987). Evidence of this conversion is very convincing in the Green Clay Room of Lower Cave, where white deposits of hydrated halloysite and alunite were noted as constituents of reaction rims around smectite clay sediment filling small solution cavities (Figure 7). The green clay sediment consists of silt-sized quartz grains, dioctahedral smectite, illite, palygorskite and kaolinite. The product of the conversion (the white "rim") consists of hydrated halloysite, alunite and, usually, lesser amounts of quartz and smectite. The absence of illite and palygorskite and a decrease in the amount of quartz and smectite indicate that smectite, illite and

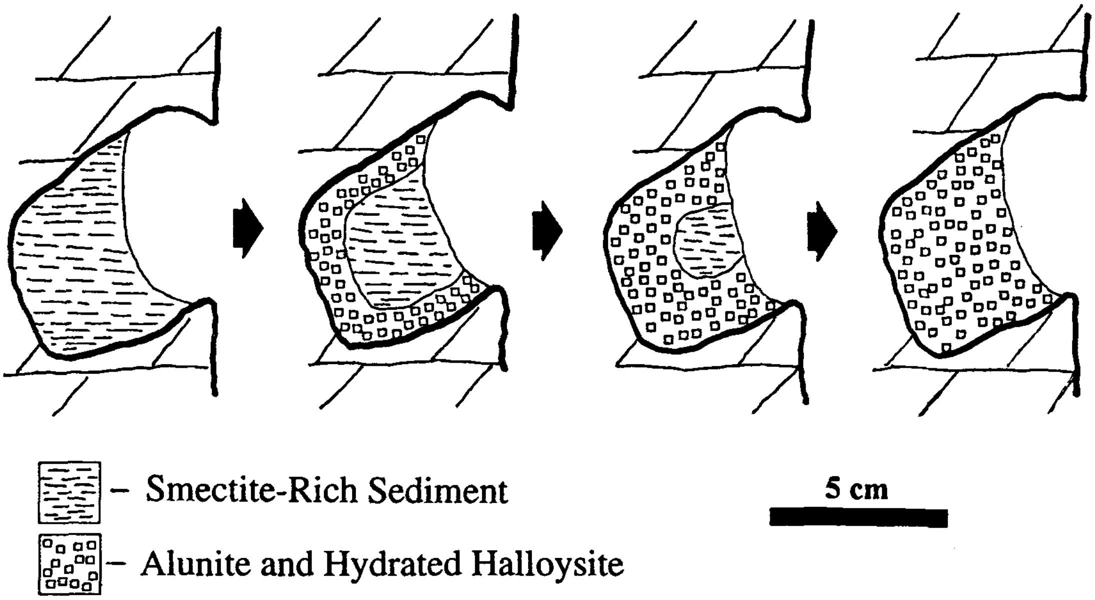

Figure 7. Idealized sketch showing the degrees of alteration of smectite-rich sediment to alunite and hydrated halloysite in solution cavity fills. The various degrees of alteration were observed in the Green Clay Room of Carlsbad Cavern.

palygorskite were converted to hydrated halloysite and alunite with quartz usually surviving the reaction. Abundant green clay deposits, however, have thus far only been reported in Carlsbad Cavern, yet alunite and hydrated halloysite have been found in several Guadalupe caves. This setting, where smectite-rich deposits have filled solution cavities, is present only in Carlsbad Cavern. In the other settings, hydrated halloysite and alunite group minerals most likely formed from the reaction of acidic solutions with mica, illite and dickite/kaolinite, the clay minerals that are probably more available than smectite in the rocks of the Capitan Reef Complex in the study area.

Isotopically light sulfur as H_2S was probably generated by sulfur-reducing bacteria from sulfate solutions produced by dissolution of anhydrite and gypsum of the Castile Formation in the basin (Hill 1987, 1990, 1995). The isotopically light sulfur was the ultimate source of sulfur for gypsum blocks and rinds and for native sulfur within the caves of the Guadalupe Mountains (Hill 1987, 1990, 1995). We suggest that the K- and Na-alunite associated with hydrated halloysite and having the same $\delta^{34}S$ values as the cave gypsum were also byproducts of the reaction of sulfuric acid with the rocks of the Capitan Reef Complex.

An H_2SO_4 cave genesis somewhat similar to that proposed for caves of the Guadalupe Mountains was described by Van Everdingen et al. (1985) for small caves located within a travertine deposit in Canada. They concluded that the caves were partly developed by H_2SO_4 formed by oxidation/hydrolysis of H_2S escaping from spring water. Gypsum crusts forming subaerially on the cave walls by reaction of H_2SO_4-bearing condensate with calcite resulted in $\delta^{34}S$ values of -5.2 to -12‰; these values reflect the microbiological reduction of dissolved sulfate in the spring waters. This was indicated by the $\delta^{34}S$ values of -1.4 to -12.0‰ of the HS^- in the spring water and H_2S in the cave air. Van Everdingen et al. (1985) reported $\delta^{34}S$ values of $+25.4$ to $+26.7$‰ for sulfate ions in spring water and $\delta^{34}S$ values of $+26.5$‰ for sulfate in inorganic gypsum within the travertine. Study of the Canadian travertine caves provide a "mini" model for showing the process of microbial reduction of dissolved sulfates and the resultant negative $\delta^{34}S$ values. Pisarowicz (1994) described a process in a cave in Mexico where biochemical fractionation of sulfur is taking place and yielding cave gypsum with $\delta^{34}S$ values similar to the gypsum and alunite found in the caves of the Guadalupe Mountains. Alunite and natroalunite, like gypsum, are sulfates and should inherit the same $\delta^{34}S$ values if they mineralized together from the same solutions.

Buck et al. (1994) described and categorized different types of gypsum deposits that form subaqueously and subaerially as byproducts during H_2S-H_2SO_4 speleogenesis. From the studies of Van Everdingen et al. (1985) and Buck et al. (1994), it is obvious that $\delta^{34}S$ values (coupled with $\delta^{18}O$ values) determined for carefully selected gypsum deposits could provide more detailed information about the origin of the cave gypsum as well as the solutions responsible for H_2S-H_2SO_4 speleogenesis. The same will apply for the study of alunite group minerals found in these caves. Alunite, however, can provide much more information because stable isotope data can be extracted from hydrogen and oxygen of the hydroxide, oxygen of the sulfate and sulfur of the sulfate (Wasserman et al. 1990; Rye et al. 1992). In addition to the stable isotope information, radiometric ages can be determined from the potassium and argon in the alunite (Bird et al. 1990; Wasserman et al. 1990; Rye et al. 1992). Stoffregen et al. (1994), however, caution that fine-grained alunite can undergo limited alkali exchange at surficial temperatures which would therefore alter their radiometric ages.

CONCLUSION

An assemblage of alunite group minerals and hydrated halloysite has been found in cave sediments within bedrock pockets, floor deposits, solution cavity fills and wall residues. These minerals are generally indicators of an acidic environment in which sulfuric acid is present. The $\delta^{34}S$ (CTD) values for the natroalunite and alunite are similar to $\delta^{34}S$ values for gypsum and native sulfur in these caves that have been previously reported by other investigators. Natroalunite/alunite and hydrated halloysite mineralized in caves of the Guadalupe Mountains through reaction of clay minerals with H_2SO_4 during the excavation of carbonate rocks that formed the large cave passages.

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