

CLAYS IN CAVES OF THE GUADALUPE MOUNTAINS, NEW MEXICO

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The origins of clay minerals in the caves of the Guadalupe Mountains, New Mexico are categorized as (1) detrital, (2) inherited from the weathering of dolostone and siltstone, and (3) authigenic. Clay minerals found in these caves include hydrated halloysite, kaolinite, dickite, illite, montmorillonite, illite-smectite mixed-layers, palygorskite, and trioctahedral smectite. The detrital clay minerals are montmorillonite, illite, dickite and kaolinite. The clay minerals inherited from the bedrock by condensation-induced weathering (in wall residues) are illite and dickite. Cave-authigenic clay minerals include hydrated halloysite (endellite), trioctahedral smectite, montmorillonite, and probably palygorskite. Hydrated halloysite formed by the alteration of illite, montmorillonite, illite-smectite mixed-layers, kaolinite, or dickite during sulfuric acid-related speleogenesis. Trioctahedral smectite precipitated with Mg-carbonate minerals in dolomite crusts and huntite moonmilk. Montmorillonite formed in saturated ledge deposits of redistributed wall residues. Less clear is the origin of palygorskite in laminated silt and clay deposits in Carlsbad Cavern.

Clays in caves are most often related to surface stream-transported sediments and soils. Clays can also be inherited from the weathering of bedrock cave walls. Clay minerals may also form in caves, although there have been relatively few reports of clay authigenesis as indicated by Hill & Forti (1997). The study of cave clays and their associated minerals has the potential to yield information about clay genesis, the geologic history of the caves, and perhaps even the regional geologic history. The Guadalupe Mountains of southeastern New Mexico contain two world-renowned caves, Carlsbad and Lechuguilla, as well as other caves of geologic interest. The clay mineralogy and clay origin in these caves are summarized below.

THE CAVES AND CLAY-BEARING SEDIMENTS

The study area includes the caves of the Guadalupe Mountains in New Mexico (Fig. 1). Clay samples were collected in Carlsbad Cavern from the Big Room, Left Hand Tunnel, Guadalupe Room, Boneyard (near Lunchroom), New Mexico Room, Lower Devils Den, Nooges Realm, Green Clay Room, and Lower Cave. Samples were collected in Lechuguilla Cave from Apricot Pit, Boulder Falls, Glacier Bay, Lake Lebarge, The Great Beyond, and Tinseltown. Other samples were collected from Barranca, Cottonwood, Dry, Endless, Hell Below, Madonna, Spider, Three Fingers, Virgin, and Wind caves.

The cave deposits studied include (1) recent cave muds, (2) solution cavity fillings, (3) joint and fracture fillings, (4) pockets of altered bedrock, (5) floor deposits, (6) wall residues, (7) laminated silt deposits, (8) Permian clay beds in dolostone bedrock, and (9) clay-bearing carbonate speleothems.

Cave muds. Mud introduced into the caves from surface runoff accounts for relatively small-sized cave deposits in the Guadalupe Mountains. The largest, most recent mud deposits occur in Barranca, Cottonwood, Hidden, Madonna, Three Fingers, and Virgin caves. Old mud deposits occur in Endless Cave and in the Guadalupe Room of Carlsbad Cavern. All of these appear to result from short-lived flooding events when surface canyons dissected the cave systems. For example, the entrance to Cueva de la Barranca is located directly in the bot-



Figure 1. Location map showing general locations of caves in the Guadalupe Mountains pertinent to this study.

tom of a canyon. Accumulation of mud will continue in Cueva de la Barranca until down-cutting of the canyon progresses and positions the cave entrance on the slope above the flood level of the canyon. With the exception of Hidden Cave, the mud deposits in these caves are generally thin (<0.5 m thick). Samples of mud were collected from Barranca, Carlsbad, Cottonwood, Endless, Madonna, Spider, and Virgin caves.

Solution cavity fillings. Solution cavity (spongework) fillings are mostly exhibited in Carlsbad Cavern. Spongework, a network of irregular, interconnected solution cavities, is filled or partially filled with clay-rich sediments in Lower Cave, the Boneyard, and the Green Clay Room of Carlsbad Cavern. Less obvious solution cavity fillings have been observed in Cottonwood and Lechuguilla caves. These green, red, and brown clays filling the cavities are commonly laminated.

Joint and fracture fillings. Joint and fracture fillings sometimes consist of clay-rich material that is similar in appearance and texture to solution cavity fillings described above. Carlsbad Cavern and Lechuguilla Cave contain numerous joint and fracture fillings. Some of these deposits may be altered small siltstone/sandstone "dikes" similar to those described by Jagnow (1977) and Hill (1996).

Pockets of altered bedrock. Bedrock pockets are usually black due to manganese mineralization, and commonly contain blue hydrated halloysite (endellite) nodules. These pockets are products of the sulfuric acid-related speleogenesis (Polyak & Güven, 1996). The pockets of altered bedrock range in diameter from 5 cm to 1 m. They have been observed in Carlsbad, Cottonwood, Endless, Lechuguilla, and Virgin caves. Pockets of altered bedrock are widely distributed within these caves. In Carlsbad and Lechuguilla caves, pockets are observed where bedrock in the caves has been protected from water; these areas are coincident with the occurrence of gypsum blocks.

Floor and ledge deposits from autochthonous sediments. Floor and ledge deposits are numerous and diverse in the Guadalupe caves. These sediments have been derived from within the caves and have not been transported by water. The clay mineralogy in these deposits can vary considerably. Good examples of this type of sediment are deposits in Spider Cave, which consist of autochthonous wall residues that have gently fallen and accumulated on the floor and ledges. In Carlsbad Cavern, some floor deposits consist of fallen bedrock pocket materials and solution cavity fillings. Floor deposits of bluish-white hydrated halloysite (endellite) occur in the New Mexico Room of Carlsbad Cavern and in Endless Cave.

Wall residues. Wall residues appear to have formed by the alteration of bedrock. The residue left behind from weathered dolostone bedrock has been referred to as "condensation-corrosion" residue (Hill, 1987; Cunningham *et al.* 1995). In Lechuguilla Cave, many of these residues are black from manganese enrichment. In other Guadalupe caves, wall residues are commonly brown and clay-rich. Hill (1987) suggested that these residues are inorganic in origin and due to condensation and corrosion. However, Cunningham *et al.* (1995) suspected

that biochemical and biomechanical alteration of the bedrock plays a major role in the origin of the wall residues. Wall residues occur in Cottonwood, Endless, Hell Below, Lechuguilla, Spider, and Wind caves.

Laminated silt deposits. Carlsbad Cavern is perhaps the only cave that contains significant volumes of laminated quartz-rich silt. Large quantities of silt are located in Lower Devils Den, Left Hand Tunnel, the Big Room, and Lower Cave. The laminated silts to which we refer are equivalent to the orange-silt banks of Left Hand Tunnel reported by Hill (1987). The silt deposits are up to 3 m thick in some areas. They differ from the cave muds by having a coarser texture, detrital calcite and dolomite, and lesser clay content. The laminated silts from Lower Cave and Left Hand Tunnel contain 10-40% clay, 30-50% silt, 25-35% fine sand, and <4% medium sand.

Permian clay beds. Beds of clay within and parallel to the bedding of dolostone have been observed in four caves (Cottonwood, Dry, Endless, and Spider). All of these clay beds are less than 0.3 m thick and occur in the caves only in backreef units in the upper Seven Rivers Formation near the contact with the Yates Formation. These clay beds are probably an exposed Permian shale unit.

Clays associated with carbonate speleothems. Clay minerals and magnesium silicates have been found in some carbonate speleothems such as dolomite and huntite moonmilk and crusts (Polyak & Güven 1997).

METHODS

Samples were dispersed in deionized water to collect the clay-fraction for X-ray diffraction (XRD) and electron microscopy analyses. Both powder and particle-oriented diffraction patterns were obtained from the clay-fractions. Samples were examined with a JEOL JEM 100CX analyzing electron microscope, which allows scanning electron microscopy (SEM), transmission electron microscopy (TEM), scanning transmission electron microscopy, and energy dispersive X-ray (EDX) microanalysis. Semiquantitative and quantitative chemical analyses were determined by EDX microanalysis.

CLAY MINERALS IN GUADALUPE CAVES

The clay minerals in caves of the Guadalupe Mountains are kaolinite, dickite, hydrated halloysite (endellite), illite, montmorillonite, trioctahedral smectite, and palygorskite. Mixed-layers of illite and smectite also occur in these caves.

Kaolinite [$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$] is the major constituent of a thin clay bed in backreef dolostone near the contact of the Seven Rivers and Yates formations, exposed in the walls of Cottonwood, Dry, and Endless caves. Kaolinite is also a minor constituent in cave muds and detrital cave sediments in all of the study area caves. Crystals are anhedral to euhedral, micron- to submicron-sized platelets (<4 μm in diameter). Kaolinite

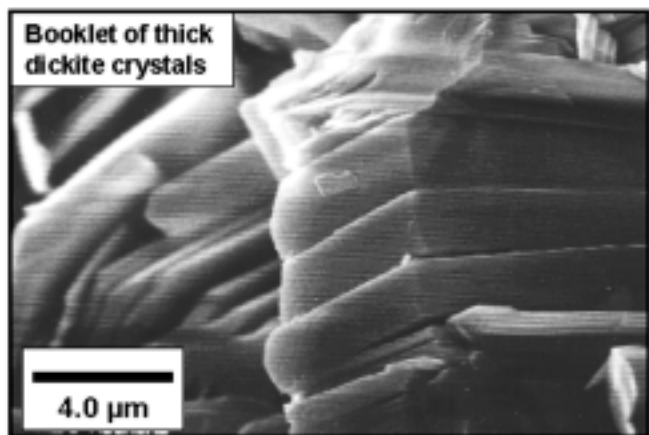


Figure 2. Thick platelets of dickite crystals from a Spider Cave ledge deposit. Booklets of dickite are well preserved after low-energy transport from the bedrock to wall residue to the ledges.

from the Cottonwood Cave clay bed is well crystallized.

Dickite $[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4]$, a polymorph of kaolinite, occurs as authigenic pods in the Permian backreef dolostones throughout the Guadalupe Mountains adjacent to the Capitan reef (Polyak & Güven 1995; Polyak 1998). In the caves, it is found disseminated in ledge and floor deposits, and is abundant in weathering-induced wall residues. Dickite crystals are thick, relatively large euhedral platelets (Fig. 2), with diameters up to 100 μm . Millimeter-sized pods are moderately abun-

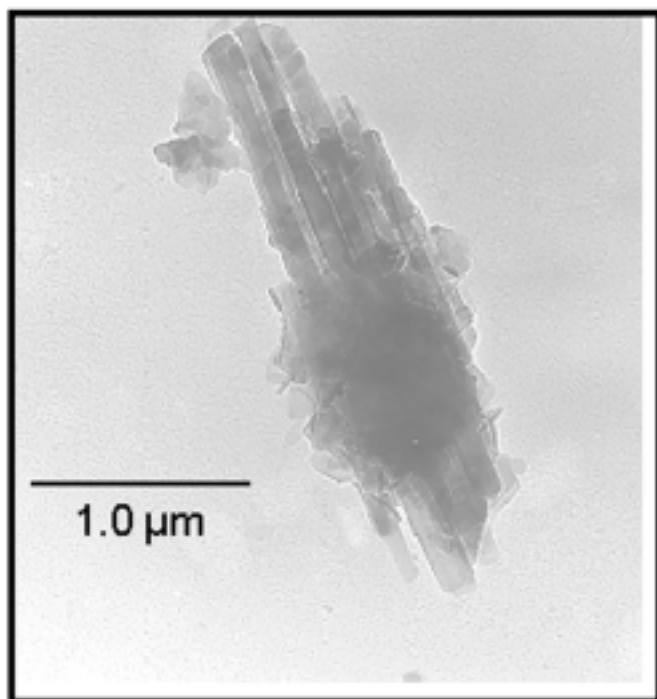


Figure 3. TEM image of illite particle from wall residue (illite laths extend from illite lamella, Wind Cave sample).

dant in the dolostone (in the caves and on the surface) and are sometimes found in ledge and floor deposits, and in wall residues in the caves. Dickite occurs in Cottonwood, Endless, Hell Below, Three Fingers, Spider, Virgin, and Wind caves. It has also been reported in Lechuguilla Cave (Palmer & Palmer 1992).

Illite is disseminated within the backreef dolostone adjacent to the Capitan reef. In the caves, it is a major constituent of brown wall residues and ledge and floor deposits of these wall residues. Illite is also a minor component in cave muds, and laminated silt and clay deposits. Illite particles occur as lamellar aggregates and euhedral to subhedral laths (Fig. 3). The laths represent authigenic crystals in the dolostone, whereas the aggregates are probably Permian detrital particles (Polyak 1998). The composition of the illite has been estimated from EDX microanalysis of several platelets and aggregates as $\text{K}_{0.90}(\text{Al}_{1.60}\text{Mg}_{0.25}\text{Fe}_{0.15})(\text{Si}_{3.25}\text{Al}_{0.75})\text{O}_{10}(\text{OH})_2$. The random powder XRD patterns of two relatively pure illite samples (<1- μm fractions of wall residues from Spider and Three Fingers caves) are comparable to Marblehead illite (Clay Mineral Society source clay). The particle-oriented patterns show a moderate degree of crystallinity (crystallinity index $>0.5^\circ 2\theta$, consistent with a diagenetic grade of illite; Weaver 1989).

Montmorillonite was reported by Davies (1964), Friesen (1967, 1970), and Hill (1987) as the major component of green, red, and brown clays in Lower Cave and other areas of Carlsbad Cavern. As Friesen noted, most of these clays are located below the 200-m depth level of Carlsbad Cavern. Montmorillonite is also a major constituent of the <2- μm fraction of laminated silts and clays in Carlsbad Cavern. It is abundant in cave muds, and it is found in saturated ledge and floor deposits of Spider Cave. Montmorillonite particles in the green and brown clays of Carlsbad Cavern are predominantly rounded oval-shaped lamellar aggregates, and poorly developed thin films (Fig. 4). The composition of montmorillonite in these cave deposits is probably somewhat aluminous as indicated by EDX microanalysis of several aggregates and whole rock analysis of green clay from Carlsbad Cavern. A formula has not yet been established for these samples due to inclusions of illite, kaolinite, iron oxides, and aluminum hydroxides within the aggregates. The chemical composition for montmorillonite is: $(\text{E})_{x+y}(\text{Al}_{2-y}\text{Mg}_y)(\text{Si}_{4-x}\text{Al}_x)\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$; where E is the interlayer cation (i.e., Na, K, Ca), y and x are octahedral and tetrahedral substitutions, and $y > x$ (Güven 1988). Montmorillonite in the clays of Lower Cave, laminated silts of Left Hand Tunnel and Lower Cave, and in the cave muds is associated with lesser amounts of illite and trace amounts of kaolinite. XRD patterns indicate that the proportions of montmorillonite to illite to kaolinite are similar in most of these deposits.

Palygorskite $(\text{Mg}, \text{Al})_2\text{Si}_4\text{O}_{10}(\text{OH}) \cdot 4\text{H}_2\text{O}$ was reported by Davies (1964) from Lower Cave, Carlsbad Cavern as a pink, calcite-hardened clay. Palygorskite also occurs as disseminated fibers in brown and green clay from Lower Cave, and in laminated silt from Left Hand Tunnel and Lower Cave.

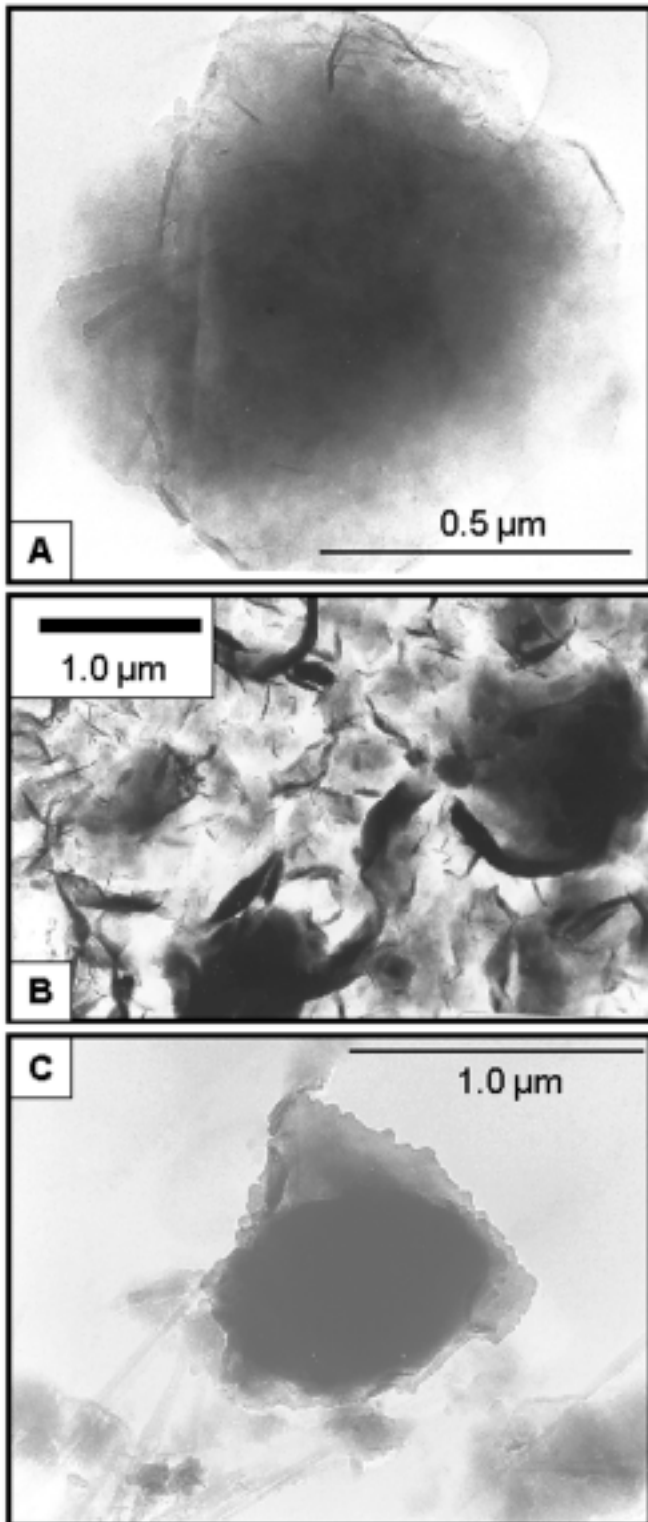


Figure 4. TEM images of montmorillonite films and aggregates. (A) Aggregate of films from green clay in Green Clay Room. (B) Films and rounded lamellar aggregates from brown clay in Lower Cave. (C) Oval-shaped lamellar aggregate from laminated silt in Lower Cave.

Palygorskite is associated with montmorillonite, illite, and kaolinite in the <math><2\text{-}\mu\text{m}</math> fraction of these deposits. TEM micrographs show fibers of palygorskite radiating from oval-shaped montmorillonite aggregates (Fig. 5). SEM images show palygorskite fibers disseminated in the clay-rich matrix of the laminated silt, and sometimes concentrated along quartz grain surfaces.

Illite-smectite mixed-layers and kaolinite are the main constituents of a clay bed in Endless and Dry caves. This clay bed is probably a thin Permian shale unit, exposed in the cave walls, which was truncated by sulfuric acid-related speleogenesis. The clay is a mixture of random and regular interstratified illite-smectite, and the illite/smectite is approximately 70-80% (Polyak 1998).

Trioctahedral smectites (probably a stevensite and minor amounts of saponite) are found associated with Mg-carbonate speleothems (Polyak & Güven 1997). Crystals occur as fibers, ribbons, and films. Aggregates of these form filaments that intertwine with dolomite, huntite, and magnesite crystals in crusts and moonmilk (Fig. 6). The smectite is intimately associated with quartz or opal, and in some settings, uranyl vana-

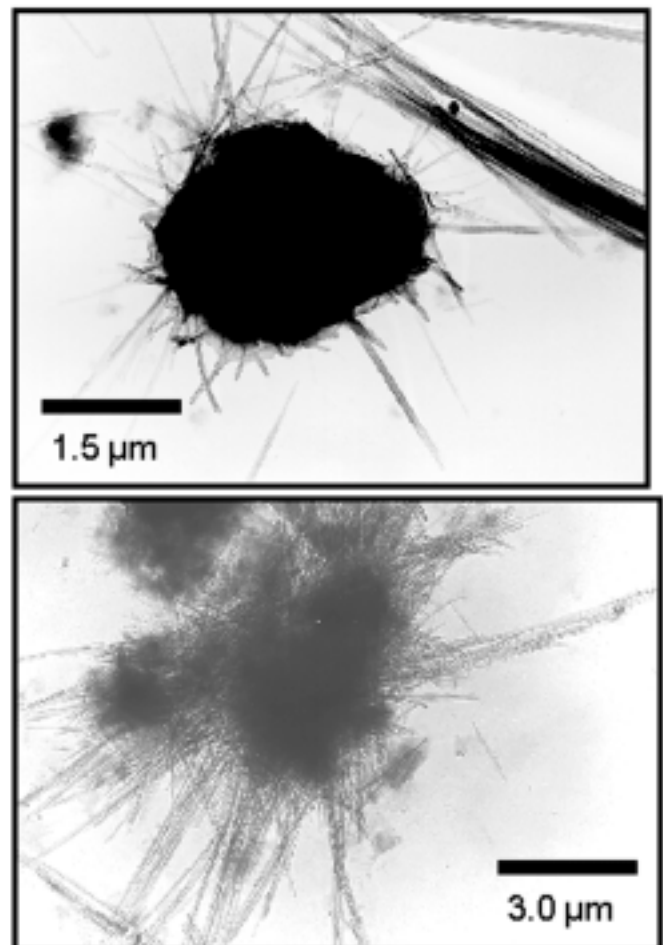


Figure 5. TEM images of palygorskite fibers radiating from montmorillonite aggregates.

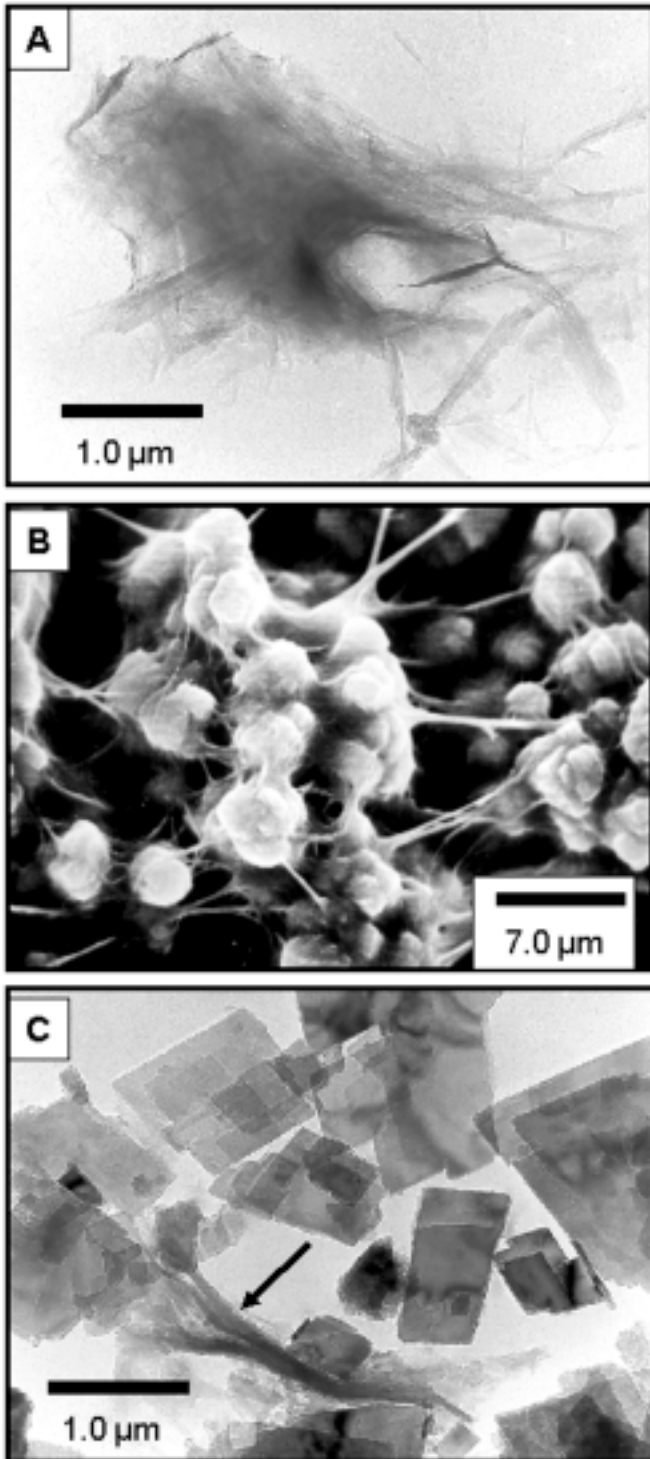


Figure 6. TEM images of trioctahedral smectite lamellae and fiber-like particles. (A) Insoluble residue after Na-acetate digestion of dolomite crust (Christmas Tree Room, Carlsbad Cavern). (B) SEM photograph of smectite filaments intertwined with dolomite rhombs (from same room as A). (C) Filaments consist of fiber-like smectite in huntite moonmilk (plates are huntite, Hell Below Cave, after Polyak & Güven 2000).

dates. From EDX microanalysis of several films and fiber aggregates, the approximate formula for one phase of trioctahedral, poorly crystallized smectite in these caves is $(Ca,Na,K)_{0.55}(Mg_{2.90}Al_{0.10})(Si_{3.95}Al_{0.05})O_{10}(OH)_2 \cdot nH_2O$.

Hydrated halloysite $[Al_2Si_2O_5(OH)_4 \cdot 2H_2O]$ (endellite) is the most colorful clay mineral in the Guadalupe Mountains. It can be white to blue, or it can also have tints of brown and red. The blue hydrated halloysite is distinct in appearance; however, amorphous opal from Cottonwood Cave was found to display a similar blue color. Hydrated halloysite was first reported in caves of the Guadalupe Mountains by Davies & Moore (1957). Hill (1987) reported the hydrated halloysite (endellite) in Carlsbad, Cottonwood, and Endless caves as the by-product of sulfuric acid-related speleogenesis. Hydrated halloysite crystals from these caves are tubular and generally less than 1.0 μm in length and 0.05 μm in diameter (Fig. 7). Hydrated halloysite occurs in pockets of altered bedrock, in white alteration rims around solution cavity fillings, in some floor deposits, and in black wall residues (Polyak & Güven 1996). It can be intimately associated with alunite, natroalunite, gibbsite, hydrobasaluminite, and hydrous iron and manganese

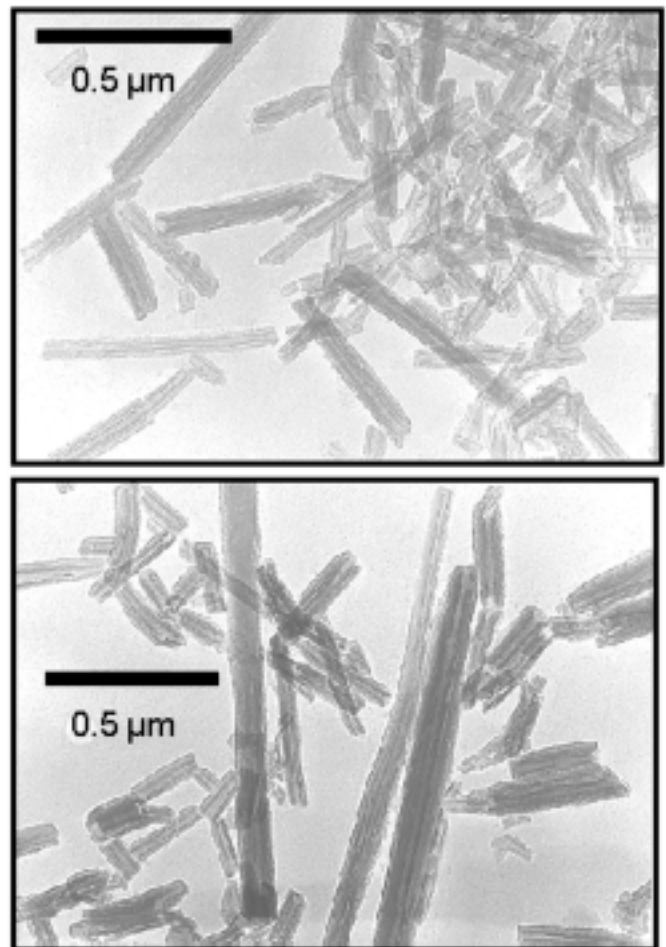


Figure 7. TEM image of hydrated halloysite (endellite) tubes (Virgin Cave).

oxides (Provencio *et al.* 1998).

DISCUSSION

The origin of clays in caves is placed in three categories: (1) detrital; (2) inherited from bedrock by weathering; and (3) cave-authigenic.

DETRITAL ORIGIN FOR CLAYS

Detrital clays are introduced into caves by streams or seeping waters, and consequently, they are constituents of muds, silts, sands, or gravels. In caves of the Guadalupe Mountains, detrital sediments are not abundant or widespread. In all of these detrital deposits, the clay minerals are montmorillonite with minor amounts of illite and kaolinite. The clay mineralogy of the laminated clay and silt deposits in Left Hand Tunnel and Lower Cave of Carlsbad Cavern is consistent with that of soils of the southwestern and midwestern U.S.A. (Allen & Hajek 1989; Borchardt 1989). This and other reasons suggest that the laminated silt and clay deposits of Carlsbad Cavern are detrital in origin, rather than autochthonous prior to, or from, speleogenesis as Hill (1987) reported. In all of these mud, silt, and clay deposits, montmorillonite is the major clay component.

CLAYS INHERITED FROM WEATHERING OF THE BEDROCK

Condensation-induced weathering of the dolomitic bedrock along cave walls and ceilings can dissolve the carbonate components of the bedrock, and form a layer containing predominantly acid-insoluble materials (condensation-corrosion residue). These residues are normally brown (color derived from goethite) on dolostone, and contain abundant illite and dickite. The same mineralogy occurs from dissolving samples of dolostone bedrock with Na-acetate or HCl, showing that the illite and dickite in the wall residues are inherited from the bedrock by condensation-induced weathering. In Spider Cave, dickite crystals in white pods in the wall residues are arranged in booklets. This arrangement of euhedral crystals gives a false indication that the dickite is cave-authigenic. Translocation and preservation of the dickite booklets from the cave walls to the ledges demonstrate that these deposits formed in a low-energy weathering environment.

CAVE-AUTHIGENIC CLAYS

Clay mineral authigenesis in caves is normally difficult to demonstrate. Cave sediments of detrital origin usually contain more than one clay mineral. Understanding the origin of the cave clays therefore requires extensive studies of the clays in the cave sediments, in the bedrock, and in soil, fluvial, and alluvial sediments above the caves. The following are examples of clay mineral authigenesis in caves of the Guadalupe Mountains.

Trioctahedral smectite. Trioctahedral smectite (stevensite and probably minor saponite) occurs with dolomite and huntite in carbonate speleothems such as crusts and moonmilks.

Amorphous and poorly developed Mg-bearing silicates occur in other carbonate speleothems such as aragonite crust and aragonite/calcite stalagmites. These silicates formed in a Mg-rich carbonate setting with Mg-calcite, aragonite, dolomite, and huntite. Authigenesis of trioctahedral smectite in carbonate speleothems took place because the precipitation of calcite and aragonite extracted Ca and increased the Mg/Ca ratio in water films. As a consequence, this process increased the pH and alkalinity (increase in Na, K, and probably $[\text{CO}_3^{2-}]/[\text{HCO}_3^-]$). Poorly crystallized trioctahedral smectite then formed under these Mg-rich and alkaline conditions (Polyak & Güven 2000).

Montmorillonite. In Spider Cave, montmorillonite is forming in ledge and floor deposits from eroded wall residues. The wall residues above a preexisting water line and above the ledge and floor deposits contain illite and dickite, while those below the water line contain abundant montmorillonite. Montmorillonite authigenesis took place when the ledge and floor deposits were submerged by floodwater, or when the sediments were later saturated with condensate water after the floodwater level descended (Polyak 1998).

Palygorskite. Suarez *et al.* (1994) showed palygorskite fibers radiating from lamellar micromicas, and they argued that the palygorskite fibers could not be detrital. Palygorskite fibers radiate from smectite aggregates in the laminated silt and clay samples collected from Left Hand Tunnel and Lower Cave in Carlsbad Cavern (Fig. 5). It is unlikely that these fibers could have survived transport from the surface, and palygorskite is not a clay constituent of the carbonate bedrock. So it is probable that it formed in a carbonate-alkaline environment produced by drip waters that saturated the silt and clay deposits, or by detrital grains of calcite and dolomite occurring in the laminated silt. The carbonate-alkaline environment containing aluminum and silicon (from abundant montmorillonite and illite) is conducive to palygorskite authigenesis (Jones & Galan 1988).

Hydrated halloysite. Hydrated halloysite is the product of the H_2SO_4 -speleogenesis-related alteration of montmorillonite (Hill 1987), illite, illite-smectite mixed-layers, dickite, and kaolinite (Polyak & Güven 1996; Polyak *et al.* 1998). It may be considered a cave-authigenic mineral, but more specifically it is a speleogenetic by-product mineral. Good examples of this type of alteration are exhibited in the Green Clay Room of Carlsbad Cavern, and in Endless Cave. Alunite or natroalunite usually occurs with hydrated halloysite. In Cottonwood Cave, hydrated halloysite is associated with hydrobasaluminite (Polyak & Provencio 1998).

CONCLUSION

Clays are not abundant in caves of the Guadalupe Mountains. Most are detrital in origin (muds and silts), and contain montmorillonite, illite, and kaolinite. Condensation-related wall residues are made up of insoluble residues of the bedrock, which usually contain abundant dickite and illite. Authigenesis of clay minerals in these caves occurs in only a

few settings. Authigenic montmorillonite occurs in saturated ledge deposits in Spider Cave. Authigenic palygorskite is found in laminated silt deposits and in the clay deposits of Carlsbad Cavern. The two more common and most obvious cave-authigenic clay minerals are trioctahedral smectite (stevensite) and hydrated halloysite (endellite). Trioctahedral smectite is authigenic in Mg-carbonate speleothems such as huntite moonmilk and dolomite crust. Hydrated halloysite is a primary speleogenetic by-product; it formed from the alteration of montmorillonite, illite, kaolinite, dickite, or illite-smectite mixed-layers during the sulfuric acid-related origin of these caves.

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