# AUTHIGENESIS OF TRIOCTAHEDRAL SMECTITE IN MAGNESIUM-RICH CARBONATE SPELEOTHEMS IN CARLSBAD CAVERN AND OTHER CAVES OF THE GUADALUPE MOUNTAINS, NEW MEXICO

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**Abstract**—Trioctahedral smectite is a constituent of Mg-rich carbonate crusts and moonmilks (pasty deposits) in caves of the Guadalupe Mountains of southeastern New Mexico. Energy dispersive X-ray microanalysis of individual crystallites and their aggregates along with the X-ray diffraction analysis indicates that the smectite is probably stevensite. Saponite is likely present in some samples also. The smectite is intimately associated with dolomite crusts and huntite moonmilks in Carlsbad Cavern, Lechuguilla Cave, and other dolostone caves. Clay particles appear as fibers and films, with aggregates comprising decimicron-sized filamentous masses that envelop crystals of dolomite, huntite, and magnesite. The occurrence of smectite is related to the genesis of the Mg-rich carbonate minerals. In water films, progressive evaporation and carbon dioxide loss results in the sequential precipitation of Mg-rich calcite, aragonite, dolomite, huntite, and magnesite. This sequence of carbonate precipitation removes Ca and greatly increases the Mg/Ca ratio in the solutions. Silica is commonly available probably because of high pH conditions, and consequently, smectite forms in the Mg-rich alkaline environment. Along with the Mg-rich carbonate minerals, opal, quartz, and uranyl vanadates may precipitate with the smectite.

**Key Words**—Authigenesis, Carlsbad Cavern, Caves, Dolomite, Huntite, Moonmilk, Stevensite, Trioctahedral Smectite.

## INTRODUCTION

Caves such as Carlsbad Cavern and Lechuguilla Cave in the Guadalupe Mountains of southeastern New Mexico are well known for their natural beauty and their mineralogy. These caves have formed in a thick, dolomite-rich carbonate rock sequence and contain abundant chemical sediments known as speleothems, which contain a variety of Mg-bearing minerals. See Jagnow (1977), Hill (1987), and Polyak *et al.* (1998) for a detailed geologic history of Carlsbad Cavern and for the general location of the caves, and Hill and Forti (1997) for descriptions of speleothems. We report the authigenesis of trioctahedral smectite in Mg-rich carbonate speleothems, such as crusts and moonmilks from Carlsbad Cavern and other caves of the Guadalupe Mountains. To our knowledge, authigenesis of trioctahedral smectite (saponite and sauconite) in caves has been reported only in Bulgaria, Romania, and Turkmenistan (Hill and Forti, 1997).

## MATERIALS AND METHODS

### Sample descriptions and cave setting

Samples from six caves (Table 1) were selected for this study. Carbonate crusts and moonmilks are common in caves of the Guadalupe Mountains. They occur most often on the cave walls and floor. Carbonate crusts are thin incrustations of carbonate minerals that have a rough "stucco" or "plaster" appearance. Moonmilks are thin, pasty to powdery deposits that

may resemble "cottage cheese" when moist. In these caves, some crusts consist primarily of dolomite, whereas moonmilks commonly consist primarily of hydromagnesite or huntite. Dolomite crusts exhibit desiccation and curling. Mg-rich crust and moonmilk speleothems occur throughout these caves, but more abundantly deep within the zone of total darkness. Areas where samples 90031, 94012, 94027, and 94044 (crusts and moonmilk) were collected had relative humidities (RH) at 90–95%. Measured RH in areas where samples 88014, 89037, and 90018 (rimstone and stalagmites) were collected varied more widely (70–95%) because they were located in the zone of indirect light near the cave entrances. Temperatures measured in these areas were 10–17°C.

### Methods

Samples were collected by permission from the Carlsbad Caverns National Park Service, Lincoln National Forest Service, and the Bureau of Land Management. The carbonate minerals in crust and moonmilk samples were removed by the sodium acetate method of Jackson (1974). We used 5% hydrochloric acid to extract insoluble materials from a stalagmite (sample 89037). Insoluble residues were dried in an oven at 40°C for 24 h, lightly ground, and the powders were analyzed using X-ray diffraction (XRD) and transmission electron microscopy (TEM). XRD of random powders and oriented clay aggregate mounts were performed using a Philips Norelco diffractometer

317

Table 1. General information on cave samples.

| Sample | Cave | Speleothem | Mineralogy | Remarks |
|--------|------|------------|------------|---------|
| 88014 | Cottonwood | rimstone | cc, as | 1% ir |
| 89037 | Hidden | calcitic stalagmite | cc, ar, as | 1% ir |
| 90018 | Gunsight | aragonitic stalagmite | ar, cc, as | 1% ir |
| 90031 | Hell Below | crust | ar, as, ps | 1% ir |
| 94012 | Spider | floor crust | do, ts, as | nd |
| 94027 | Hell Below | moonmilk | hu, do, ma, ts | 6% ir |
| 94044 | Carlsbad | wall crust | do, ts, qz | 2% ir |

ar = aragonite, as = amorphous silica, cc = calcite, do = dolomite, hu = huntite, ir = non-carbonate insoluble residue, ma = magnesite, nd = not determined, ps = poorly crystallized silicate (kerolite-like), qz = quartz, ts = trioctahedral smectite.

operated at 40 kV and 20 mA with CuKα radiation. Oriented clay mounts were dried at 25°C and 50% RH. Samples were treated with ethylene glycol vapor for 24–48 h. Characteristic X-ray spectra were obtained on films and aggregates of clays using energy dispersive X-ray (EDX) microanalysis interfaced to a JEOL JEM-100CX analytical electron microscope. Micrographs of clay particles were obtained in TEM mode. Small fragments of freshly fractured samples were mounted, coated with gold, and examined with scanning electron microscopy (SEM) on the same microscope.

## RESULTS

### Trioctahedral smectite

Filamentous materials compose a small fraction (1–10%) of Mg-rich carbonate speleothems in these caves. These materials are intrinsically associated with dolomite, huntite, magnesite, opal, quartz, and uranyl vanadates in crusts and moonmilks. The filamentous materials consisted of fiber-like particles and films of trioctahedral smectite.

The crusts (samples 94012, 94044) consist of micron-sized rhombohedral-shaped dolomite, and the moonmilk (sample 94027) is composed of micron-sized huntite platelets. The dolomite and huntite crystals are intertwined with filamentous smectite. Figure 1 shows SEM and TEM images of smectite from crusts (Figure 1a and 1b) and a moonmilk (Figure 1c and 1d). In places, the filaments are relatively large and complex. In moonmilk, they are composed of smaller fiber-like particles as shown in Figure 1c with platelets of huntite (sample 94027). In these samples, the smectite particles are predominantly fibrous in appearance, although some particles are films. EDX microanalysis of crystals in sample 94027 indicates that the smectite lacks Al. Microanalysis of sample 94044 shows a mixture of Al-bearing and Al-free Mg-rich smectite. In all cases Al is absent or minor and the $d(060)$ value ranges from 1.516 to 1.528 Å, which indicates that the smectite is trioctahedral (probably stevensite). Minor to trace amounts of fibrous Mg-rich silicates such as sepiolite may be present, but we could not identify them because of the small sample sizes.

Figure 2 shows the XRD patterns for the insoluble residues of samples 94027 and 94044.

### Silicates in other speleothem types

Other carbonate speleothems were examined for the presence of smectite. A sample of aragonite crust (sample 90031) was digested and found to contain 1% insoluble residue consisting of a mixture of amorphous silica and a poorly crystallized Mg-rich kerolite-like silicate (Brindley *et al.*, 1977). A fragment of stalagmite (sample 89037) was also digested and found to contain 1% insoluble residue consisting of amorphous silica, preserved mites and arthropod parts, and trace amounts of detrital silt-sized quartz, mica, and dickite grains. The stalagmite is composed of Mg-rich calcite and aragonite. Amorphous silica, which was especially abundant along thin layers of aragonite, formed molds of the aragonite crystals. X-ray microanalysis of the arthropod parts revealed amorphous silica incorporated in the chitinous remains. No authigenic clays were found in the insoluble residue of the stalagmite sample. Samples of an aragonite stalagmite (sample 90018) and a calcite rimstone (sample 88014) were digested and found to contain ~1% insoluble residue that also consisted mostly of amorphous silica. The rimstone fragments consisted of low magnesian calcite with minor aragonite.

The mineralogy in these carbonate speleothems indicates that silica is precipitating from cave waters. Amorphous silica is the main precipitate phase in the insoluble residues of calcite and aragonite stalagmites. Both amorphous silica and a poorly formed Mg-rich silicate are major components of insoluble residues in an aragonite crust, whereas trioctahedral smectite is the main constituent of insoluble residues in the Mg-rich carbonate crusts and moonmilks. Opal or quartz, and tyuyamunite are found associated with the carbonate minerals and trioctahedral smectite.

## DISCUSSION

### Authigenesis of smectite and origin of Mg-rich carbonates

The formation of trioctahedral smectites in caves is obviously related to carbonate precipitation, particu-
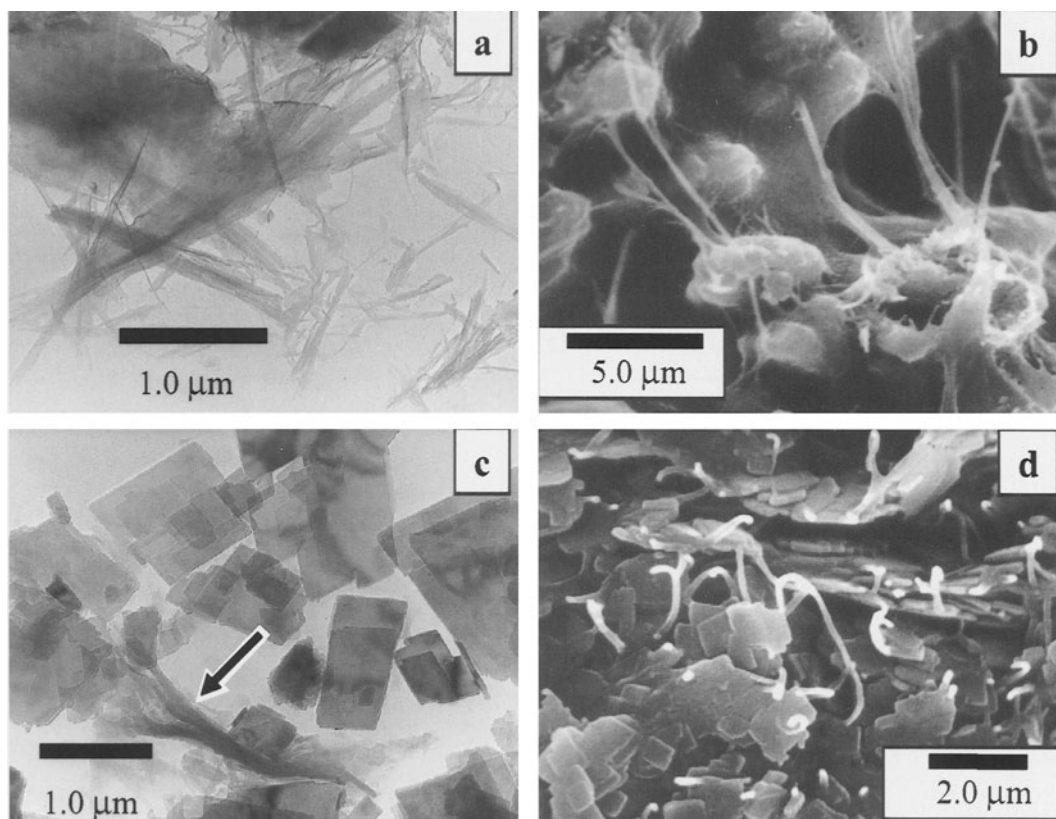
Figure 1.    Scanning and transmission electron micrographs of trioctahedral smectite from caves. (a) Fibrous-like smectite particles (sample 94044). (b) Filamentous smectite intertwined with dolomite crystals (sample 94044). (c) Filament associated with platelets of huntite. Note that the filament fragment is comprised of fiber-like smectite (sample 94027). (d) Filamentous smectite intertwined with huntite platelets (sample 94027).

larly the precipitation of Mg-rich carbonates. The sequence of carbonate deposition in caves is predicted from the phase diagram of the $CaCO_3$-$MgCO_3$-$H_2O$ system at 25°C (Lippmann, 1973). Ford and Williams (1992) and Hill and Forti (1997) modified this diagram to show the expected sequence of carbonate precipitation/neoformation in caves as water evaporates and loses carbon dioxide (Figure 3). From petrographic and field observations, we suggest that the sequence of anhydrous carbonate precipitation in these caves is Mg-rich calcite → aragonite → dolomite → huntite → magnesite. Precipitation of calcite depletes the thin cave water film on the speleothems of $Ca^{2+}$ and increases the $Mg^{2+}/Ca^{2+}$ ratio. Aragonite then precipitates, which further depletes the water film of $Ca^{2+}$ and further increases the $Mg^{2+}/Ca^{2+}$ ratio. There is a corresponding increase in alkalinity and pH of the cave water. The carbonate-mineral phase diagram suggests the precipitation of magnesite and brucite under conditions of extreme evaporation and carbon dioxide loss. Magnesite is a minor constituent of the huntite moonmilk (sample 94027); however, brucite has not been reported in caves (Hill and Forti, 1997). The smectite has formed with the Mg-bearing carbonate

minerals, indicating that the fluids have undergone significant evaporation and carbon dioxide loss. The rate of evaporation and loss of carbon dioxide is probably very slow during formation of the Mg-rich carbonate and smectite.

The silicates associated with the carbonates in these speleothems indicate that a sequence of silicate precipitation coexists with a sequence of carbonate precipitation with progressive evaporation and carbon dioxide loss. This path of sequential precipitation is illustrated in the carbonate phase diagram in Figure 3. The succession from amorphous silica in stalagmites to smectite in crusts and moonmilks is indicated by the XRD patterns of insoluble materials from these speleothems (Figure 4).

*Two depositional settings*

Two locations of Mg-rich smectite are areas: (1) where condensate forms and (2) near dripping water. In the first setting, condensate forms by mixing of incoming cool and dry air with outgoing humid, warm, and carbon dioxide-charged air. The condensate forms a water film that moves downward along the walls dissolving the dolostone bedrock. On the lower cave
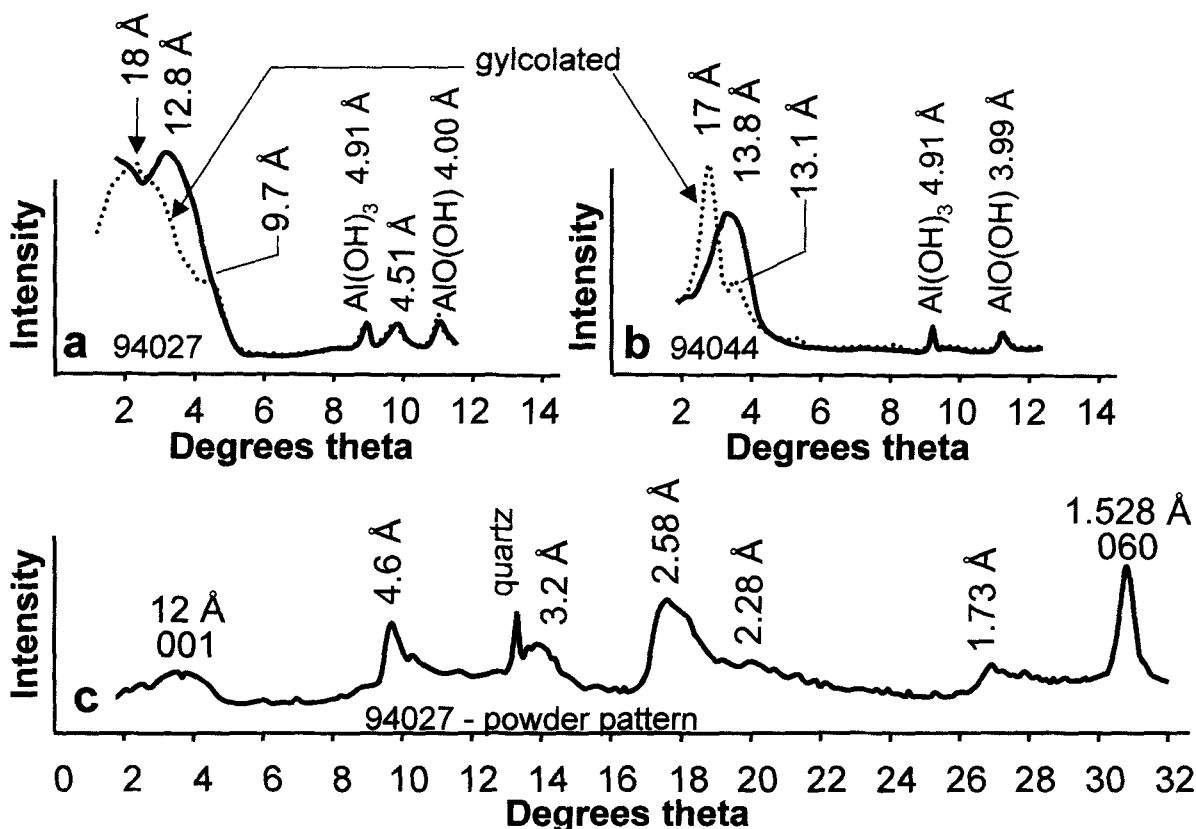
Figure 2. XRD patterns of oriented (a and b) and random (c) preparations of smectite fractions dissolved from Mg-rich carbonate speleothems (samples 94027 and 94044).

wall and floor, the environment is conducive for precipitation of carbonates and eventually Mg-rich silicates. In the second setting, drip water charged with carbon dioxide and the appropriate chemistry for car-
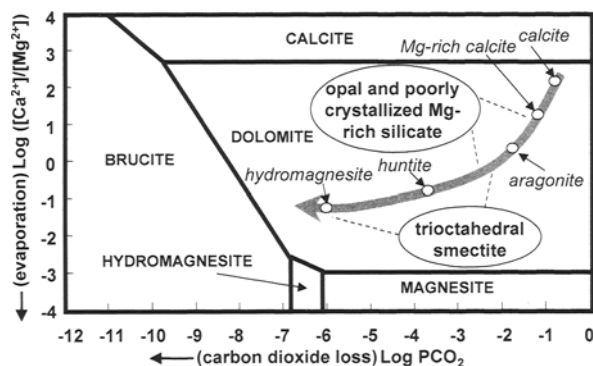


Figure 3. Carbonate phase diagram modified after Lippmann (1973), Ford and Williams (1992), and Hill and Forti (1997). The diagram shows the evolutionary path of carbonate precipitation from a hypothetical cave water. The evolution of silicates follows this path because of the presence of silica, extraction of $Ca^{2+}$, and progressive increase of $Mg^{2+}/Ca^{2+}$ as the cave water evaporates and degasses $CO_2$.

bonate precipitation, produces splashes, aerosols, and thin films, which are sensitive to evaporation and carbon dioxide loss. Mg-rich carbonates and smectite precipitate along the margin of the dripstones. In both settings (by slow evaporation, carbon dioxide loss), the $Ca^{2+}$ in solution is removed by the precipitation of calcite (Mg-calcite) and, with a subsequent increase in $Mg^{2+}$ content, by the precipitation of aragonite. Then dolomite, huntite, magnesite, and/or hydromagnesite precipitate utilizing the remaining $Ca^{2+}$ and much of the $Mg^{2+}$. The pH of these solutions is high (*i.e.*, pH > 8). The resultant solution is concentrated in $Mg^{2+}$ and silica. Smectite forms in crusts and moonmilks with occasional opal or quartz.

*Possible origin of trioctahedral smectite*

Detrital clays probably have not been altered to smectites in these settings. The fibrous-like morphology of the smectite, and the way in which they anastomose around the dolomite crystals is consistent with this conclusion. It is also not likely that sepiolite formed first and later converted to stevensite if temperatures needed for such a conversion approach 150°C (Güven and Carney, 1979). Presence of sepio-
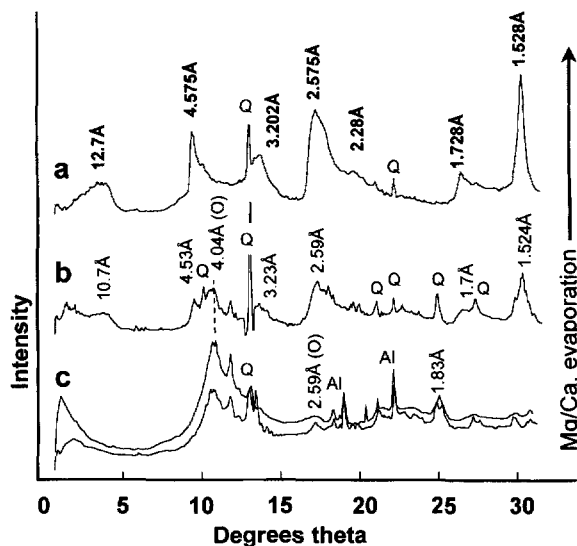
Figure 4. Powder XRD patterns for insoluble fractions of huntite moonmilk, aragonite crust, and stalagmites show an apparent progression of silicates with increasing $Mg^{2+}/Ca^{2+}$ of the carbonate speleothems. (a) Insoluble residue from huntite moonmilk consists of trioctahedral smectite and minor quartz. (b) Insoluble residue from aragonite crust consists of amorphous silica and poorly crystalline Mg-rich silicate. (c) Insoluble residue from calcite and aragonite stalagmites consists of amorphous silica and minor to trace amounts of quartz and other detrital components. Q = quartz, O = amorphous silica.

lite is not confirmed in these caves, and the cave temperatures probably never exceeded 30°C. Smectite may have formed by the conversion of hydromagnesite similar to that synthesized by Takahashi et al. (1997). Such an origin of the smectite is reasonable, but hydromagnesite is platy and most of the trioctahedral smectite particles are fibrous-like. The smectite may form by neoformation of brucite as discussed by Baird et al. (1971, 1973) and Harder (1972) for synthetic smectite. Although a brucite precursor is engaging, brucite is not known from caves. Stevensite probably forms in cave environments by the maturation of Mg-bearing amorphous silicate materials (Farmer et al., 1991), or by direct precipitation from cave waters. For the samples studied here, the progression of the complexity of silicate mineralization from amorphous silica to trioctahedral smectite observed in calcite, aragonite, dolomite, and huntite speleothems supports either mode of formation.

## REFERENCES

Baird, T., Cairns-Smith, A.G., MacKenzie, D.W., and Snell, D. (1971) Electron microscope studies of synthetic hectorite. *Clay Minerals,* **9,** 250–252.

Baird, T., Cairns-Smith, A.G., and MacKenzie, D.W. (1973) An electron microscopic study of magnesium smectite synthesis. *Clay Minerals,* **18,** 17–26.

Brindley, G.W., Bish, D.L., and Wan, H. (1977) The nature of kerolite, its relation to talc and stevensite. *Mineralogical Magazine,* **41,** 443–452.

Farmer, V.C., McHardy, W.J., Palmieri, F., Violante, A., and Violante, P. (1991) Synthetic allophanes formed in calcareous environments: Nature, conditions of formation, and transformation. *Soil Science Society of America Journal,* **55,** 1162–1166.

Ford, D.C. and Williams, P.W. (1992) *Karst Geomorphology and Hydrology.* Chapman and Hall, New York, 601 pp.

Güven, N. and Carney, L.L. (1979) The hydrothermal transformation of sepiolite to stevensite and the effect of added chlorides and hydroxides. *Clays and Clay Minerals,* **27,** 253–260.

Harder, H. (1972) The role of magnesium in the formation of smectite minerals. *Chemical Geology,* **10,** 31–39.

Hill, C.A. (1987) *Geology of Carlsbad Cavern and Other Caves in the Guadalupe Mountains, New Mexico and Texas.* New Mexico Bureau of Mines and Mineral Resources, Bulletin 117, 150 pp.

Hill, C.A. and Forti, P. (1997) *Cave Minerals of the World.* National Speleological Society, Huntsville, Alabama, 238 pp.

Jackson, M.L. (1974) *Soil Chemical Analysis—Advanced Course, 2nd edition.* Published by author, University of Wisconsin, Madison, Wisconsin, 895 pp.

Jagnow, D.H. (1977) Geologic factors influencing speleogenesis in the Capitan reef complex, New Mexico and Texas. M.S. thesis, University of New Mexico, Albuquerque, New Mexico, 197 pp.

Lippmann, F. (1973) *Sedimentary Carbonate Minerals.* Springer-Verlag, Berlin, 228 pp.

Polyak V.J., McIntosh, W.C., Güven, N., and Provencio, P. (1998) Age and origin of Carlsbad Cavern and related caves from $^{40}Ar/^{39}Ar$ of alunite. *Science,* **279,** 1919–1922.

Takahashi, N., Tanaka, M., Satoh, T., Endo, T., and Shimada, M. (1997) The study of synthetic clay-minerals. 4. Synthesis of microcrystalline stevensite from hydromagnesite and sodium-silicate. *Microporous Materials,* **9,** 35–42.

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