

Characterization of a Yellow Substance on the Ceiling of the Snowball Dining Room, Mammoth Cave National Park using Energy Dispersive X-Ray Spectrometry and Electron Microscopy

FINAL REPORT

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ABSTRACT

An intensely yellow material appeared on the ceiling of the Snowball Dining Room, Mammoth Cave National Park, when black mildew was removed with bleach in 1993. This material forms a thin, soft coating on the gypsum, and covers less than 1 m² over the main tourist trail. It lies beneath pencil and burn mark graffiti dating from the early 1900's. Despite its conspicuous location, there is no record of its presence prior to the buildup of mildew. In order to characterize this material, small samples were observed with a range of light and electron microscopes, and their compositions inferred by energy dispersive X-ray spectrometry. Compared to the smooth, crystalline, blue-fluorescing gypsum, the yellow material has a spongy, wrinkled appearance, ranges from off-white to yellow-orange in color, and fluoresces green when excited with ultraviolet light. When viewed at high magnification in the transmission electron microscope, cross-sections of the material contained 50 nm diameter particles of 1.4 nm thick concentric layers. In order of decreasing abundance, the material is composed of O, Si, and Mg along with smaller amounts of S, Al, F, K, Ca and Fe. Some of the samples appeared to be associated with fluorite.

Although the characteristics of this material seem distinctive, I am not able to conclusively identify it. The material's composition most closely matches sepiolite, while the material's appearance in the TEM suggests that it is spherulitic halloysite. A conclusive identification will require someone either with more experience in identifying cave coatings, or access to analytical techniques not available in this project.

INTRODUCTION

The Snowball Dining Room is formed by the junction of Cleaveland and Marion Avenues roughly 75 m (250 feet) below the surface of Mammoth Cave Ridge at the contact between the Joppa and Karnak members of the Ste. Genevieve limestone (Palmer, 1981). The ceiling is coated with a flat crust of gypsum with frequent "flowers" that are reminiscent of snowballs stuck to a surface. According to Stan Sides, this room has seen significant tourist activity since the opening of the cave to visitors. Graffiti on the walls and ceilings date from the early 1900's, when the room was known as Washington Hall. Its use as an eating area did not begin until after 1936, when water was provided by the drilling of an "upside-down well". Actual food service was made possible by the installation of an elevator in 1952. A small cafeteria line,

including warming tables for hot foods, was installed to serve groups on tour. The peak of tourist activity was in the early 1970's, with "Half-Day Tours" of up to 140 people using the facility at one time. As one of the visitors in 1972, I know that the gypsum "snow" of the room was black with mildew by this time.

In 1997, I again took the half-day tour, now called the "Grand Avenue Tour". I was surprised to see that the speleothems in the Snowball Dining Room were sparkling white. According to Bob Ward of the NPS, volunteers of the National Speleological Society had cleaned the room in 1993. They hand-sprayed the features with a solution of 50% commercial bleach. The bleaching of the mildew was almost instantaneous; the bleach was then removed by gently hand spraying with water.

In addition to making graffiti visible again, the bleaching led to a surprise—the uncovering of a small area of the ceiling with an intense yellow color. This material was over the main walkway near the cafeteria line, and, according to Joe Meiman, became visible almost immediately after the bleach application. It was surprising because there was no record of yellow material in the Snowball Dining Room. Its identity and origin were unknown. The purpose of the project presented here was to characterize, and if possible, identify this yellow material.

MATERIALS AND METHODS

Samples of the yellow material were obtained on September 12th, 2002, by pressing double-sided carbon tape onto the ceiling of the Snowball Dining Room. The material proved to be resistant to attachment to the tape, so only a few small particles of yellow material with gypsum were obtained. The particles were carefully separated from the gypsum, and were affixed with double-sided carbon tape onto 2 mm thick carbon planchets on aluminum cylinders (stubs). The surface features of these samples were observed with a JEOL 5400LV scanning electron microscope (SEM). Uncoated samples were observed in low vacuum mode using a backscattered electron detector while samples sputter-coated with gold were observed in high vacuum mode with a secondary electron detector. The composition of the samples was inferred using a Kevex Quantum energy dispersive X-ray analysis unit. Analyses were carried out on very small, non-flat samples without standards, so considerable errors are present in quantification, especially with low atomic number elements.

After observation in the SEM, samples were also observed with an Olympus BH-2 epifluorescent microscope. For brightfield work, oblique illumination was provided by fiber optic lights. Epifluorescent illumination used a Chroma Technologies (Rockingham, VT) filter set exciting at 360 nm (320-390nm peak) and with dual emission at 450-480 nm and 580-670 nm. Images were obtained and processed using Automontage software (Syncroscopy USA, Fredrick, MD).

One of the particles was removed from the stub, immersed for several hours in epoxy resin (Spurr, 1969), and then hardened by incubation at 70°C for 20 hours. After trimming and thin-sectioning, 80 nm thick slices from the sample were observed with a JEOL JEM-100CX transmission electron microscope (TEM) at 100kV accelerating potential. The actual magnification of each micrograph was calculated using a micrograph of a replica of a diffraction grating. The cut surface of the remaining sample

was again observed and analyzed in the SEM to obtain a low magnification cross-sectional view and to confirm its composition by X-ray analysis.

A standard sample of sepiolite, from Eskihi-sheer, Turkey, was obtained from Ward's Natural Science Establishment (Rochester, New York). This material was analyzed as described above for the yellow material.

RESULTS

Observations in the Cave

Significant clues can be obtained simply by looking closely at the distribution of the yellow material in the cave. After bleaching, the material appeared in a relatively small area, a curving strip perhaps 1 m x 0.2 m (Figure 1A). Within this strip the distribution is uneven, mainly on the flatter areas, with a few traces on the surface of gypsum "snowballs" (Figure 1B).

Graffiti in the form of pencil and burn marks are visible in all the photographs in Figure 1. Adjacent dates suggest that the pencil graffiti was made in the early 1900's. The pencil marks are around the burn marks, suggesting that the burn marks are even older. Both burn and pencil marks can traverse both yellow and gray areas, as shown in Figures 1B and 1C, respectively.

Physical Characteristics

The yellow material is a very thin layer (perhaps < 0.1 mm thick) tightly adhering to the gypsum beneath it. It was granular in appearance, ranging in color from off-white to orange (Figure 2A). When illuminated with ultraviolet light, the particles strongly fluoresced green (appearing red in Figure 2B due to the filter set employed). In the SEM, the yellow material had a spongy appearance that was easily distinguished from the smooth gypsum crystals (Figure 2C). In cross-section in the SEM, the yellow material contained small voids, similar in size to the indentations on the surface (not shown). Exposure of the yellow material to the electron beam appeared to damage it, darkening its color and reducing its fluorescence (arrows, Figures 2A and 2B).

Preliminary analysis of the composition of the yellow material suggested that it might be sepiolite (meerschaum clay). To test this, samples from Eskihi-sheer, Turkey were analyzed in tandem with the yellow material (Figure 3). At low magnifications, the yellow material shared some characteristics with the sepiolite; both were light colored and granular, fluoresced, and were damaged by the electron beam. However, the fluorescence of the sepiolite was much less than the yellow material, appearing more blue than green in the absence of the red microscope emission filters.

At higher magnifications, the yellow material was clearly different from sepiolite. When observed at high magnifications in the SEM, the yellow material was not fibrous (Figure 4A), while the sepiolite was clearly composed of relatively long fibers (Figure 4B). In the TEM, instead of being composed of fibers, the yellow material contained spherules of concentrically layered material (Figure 5). When measured carefully at the location indicated by the arrow, the layers were about 1.4 nm apart.

The composition of both the yellow material and sepiolite were inferred using energy dispersive X-ray spectrometry in the SEM. The overall composition of the two

materials was very similar with the three most abundant elements being oxygen, silica and magnesium (Figure 6). "Ideal" sepiolite has an approximate formula of $\text{Mg}_8\text{Si}_{12}\text{O}_{30}(\text{OH})_4(\text{OH}_2)_4 \cdot n(\text{R}^{2+}(\text{H}_2\text{O})_8)$ giving a ratio of Mg to Si of 0.67 (Moore and Reynolds, 1997). The observed ratio in the yellow material ranged from 0.5 to 0.7 when several different particles were analyzed. In one instance, no magnesium was detected at all (not shown).

Fe, K, Ca, S, and F were present in the yellow material in trace amounts (Figure 6A). C may also have been present, although that signal may have been due to the carbon substrate. On some particles of the yellow material, a brighter substance was observed in the SEM in the backscattered electron image (Figure 7A). On close analysis with the energy dispersive X-ray spectrometer, the bright substance was found to be enriched in Ca and F, with little S (Figure 7B). The calculated atomic percentage of F was greater than Ca, suggesting that the material was fluorite.

DISCUSSION

Any hypothesis on the identity of the yellow material must explain all of the observations made concerning its color, distribution, composition and ultrastructure. Specifically, it must account for its limited distribution on gypsum under old graffiti, its high ratio of Si to Mg, and the presence of concentrically layered spherules. Various hypotheses fall into two categories—that the material is man-made, or that it was produced by natural processes.

Man-made coating?

The "deus ex machina" hypothesis is that the yellow material is a human applied coating. This would very easily explain its limited location and its composition seemingly incongruous with its surroundings. This hypothesis requires that the coating be applied before the graffiti, and that its composition be consistent with some sort of coating material in use in the early 1900's or before.

Unfortunately, there are several reasons why this is unlikely to be yellow paint. First, there is no record of paint being used in this heavily trafficked area. According to Joe Meiman, the only recollections of yellow marking materials used in this part of the cave were the yellow chalk used by the 1930's "Walker" benchmark survey. Second, the yellow material is too homogeneous to be a paint. Although talc, $4[\text{Mg}_3\{\text{Si}_4\text{O}_{10}\}(\text{OH})_2]$ is used as a filler in paint, it is usually used with other components (Soderberg, 1959) that give paint a very inhomogeneous appearance in the SEM. A final problem with the paint hypothesis is that it fails to explain why the yellow material is not uniform in its coverage. If paint, it would have been applied evenly. Given that the graffiti did not flake off significantly over nearly a century, any paint should have remained attached as well. Yet as shown in Figures 1B and 1C, the yellow material was patchy when the graffiti was applied.

Given the problems with the yellow paint hypothesis, an alternative is that the material was originally applied as a whitewash or white paint that somehow turned unevenly bright yellow over time or as a result of the bleaching treatment. It seems plausible that a small part of the Snowball Room could have been whitewashed,

perhaps to enhance the appearance for tourists. The color change is somewhat more far-fetched, but an uneven color change would explain the patchiness of the yellow coating. A bigger problem with this hypothesis is that whitewashes usually contain calcium hydroxides, not magnesium silicates (Soderberg, 1959).

Naturally formed coating?

Several hypotheses have been proposed to explain the yellow material as a result of natural processes. At this point, no one hypothesis can explain all of its characteristics.

The bright yellow color almost immediately suggested that the material was elemental sulfur, somehow reduced from the sulfate in the gypsum by the fungi/bacteria growing on the ceiling. This would be a plausible hypothesis except that the material proved not to be sulfur.

Alternatively, the yellow color could have resulted from the action of bleach on organic acids. This is not totally unreasonable, as bleach reacts with fungal acids produced by lichens to form yellow, orange or red colored compounds (Hale, 1979). There are two possible sources for the acids: either from the fungus that made up the mildew, or from humic acids that leached into the cave from the surface (as reported by Quinlan and Traverse, 1967 in Salts Cave). These would be worthy of further investigation except that they again do not explain the high Mg and Si found in the yellow material.

The ultrastructure of the material, with its concentric layers, is as distinctive as its color (Figure 4A). In searching the literature, I have found only one clay, halloysite, that has this structure. Sudo et al. (1981) described the spherules of halloysite as "onion-like" and said they were "considered to be a product in the crystallization of allophane into halloysite." Moore and Reynolds (1997) state that the spacing between layers in hydrated halloysite is 1 nm as determined by X-ray diffraction. However, the spacing might be different when embedded in resin. To judge that spacing, I calculated the distance between layers of halloysite from a micrograph in Sudo et al.'s text. Assuming that the magnification they give is correct, the halloysite layers in resin are 1.5 nm apart, very close to the 1.4 nm observed in the yellow material. Halloysite has actually been found near Mammoth Cave in Hart County (McGrain, 2001), suggesting that it could have washed into the cave and formed a thin coating (as described by Finlayson and Webb, 1988 in western caves). But this hypothesis also fails when composition is considered; halloysite contains significant amounts of aluminum while the yellow material does not.

Considering only elemental composition, the best match seems to be sepiolite. As shown in Figure 6, the yellow material has an EDS spectrum very similar to sepiolite. Sepiolite has been found as a thin layer in caves (e.g. Finlayson and Webb, 1988), and can be formed in association with gypsum and calcite under alkaline conditions (Velde, 1977). Although normally sepiolite is distinctly fibrous, one form found in a cave was described as "poorly crystalline" (Finlayson and Webb, 1988). At this point, however, I have no evidence that sepiolites can form concentrically layered spherules as observed in the yellow material.

Why is it yellow?

Any explanation of the material's color must explain three observations—that its color is variable, ranging from off-white to orange, that it lies beneath old graffiti, and that it remained unnoticed until after the bleach treatment. Taken together, these observations suggest that the material itself predates the graffiti but was not yellow when it formed. Presumably either the mildew or bleach treatment caused the color change, perhaps by oxidizing some contaminant in the clay such as iron or organic acids.

If the "yellow material" is not intrinsically yellow, its off-white form might be coating substantial areas of gypsum in the cave. Its presence could be determined easily using a handheld UV light—the gypsum would fluoresce blue while the material would fluoresce green.

CONCLUSIONS

The exact identity and origin of the yellow material remain unknown. Given its structure and elemental composition, it seems likely to be a clay. Although similar to halloysite in ultrastructure and sepiolite in composition, it seems unlikely to be either. More detailed analyses (such as X-ray diffraction) could be difficult, given the small amount of yellow material in the cave. However, if this material were more abundant in its off-white form, enough might be obtained for further analysis. Perhaps in the future someone will use the clues presented here along with other analyses to help identify this material and determine how it formed.

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Dave Finklestein, Indiana University, confirmed that the material could be sepiolite, but could not provide any evidence that sepiolites could ever form concentrically layered spherules.

Mark Krekeler, a graduate student at the University of Illinois-Chicago, commented on the TEM pictures, suggesting that they did NOT look like any sepiolite that he had worked with.

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FIGURE LEGENDS

- Figure 1. Photographs of the yellow material on the ceiling of the Snowball Dining Room, September 12, 2002. A) Overview of the total amount of yellow material. Although most of the coating is bright yellow, some is an orange yellow (arrow). The ruler is approximately 16 cm long. B) Enlarged view, showing that the material, although mainly on the flat areas, can also be found in a few patches on raised gypsum "snowballs" (arrow). Note that material is underneath both pencil and burn mark graffiti. C) Further enlarged view, showing the patchiness of the yellow material, and how a single pencil mark can traverse both yellow and gray surfaces on the gypsum (arrow).
- Figure 2. Low magnification surface features of the yellow material. Particles of material from the ceiling of the Snowball Dining Room were affixed to black carbon tape and observed by A) reflected light microscopy, B) epifluorescence microscopy using a blue/red emission filter, and C) scanning electron microscopy. On EDS analysis in the SEM, the smooth, barely blue fluorescent particles proved to be gypsum while spongy, green (shown as red) fluorescent particles all had compositions consistent with the "yellow material". The arrows indicate a rectangular region where EDS analysis was performed. The electrons hitting this region during the analysis appear to have caused discoloration (shown in A) and reduced fluorescence (shown in B). The scale marker in each picture represents 50 μm .
- Figure 3. Low magnification surface features of standard sepiolite from Eskihi-she, Turkey. One freshly fractured fragment was affixed to black carbon tape and observed by A) reflected light microscopy, B) epifluorescence microscopy using a blue/red emission filter, and C) scanning electron microscopy. The arrows indicate a rectangular region where EDS analysis was performed. The electrons hitting this region during the analysis appear to have caused a slight discoloration (shown in A) and reduced fluorescence (shown in B). The scale marker in each picture represents 50 μm .
- Figure 4. SEM micrographs of the yellow material and standard sepiolite at high magnification. Samples were sputter coated with gold and observed with a secondary electron detector. A) View of the top middle yellow particle shown in Figure 2 showing the spongy character of the material. B) View of the sepiolite particle shown in Figure 3 showing the fibrous structure of sepiolite. The scale marker in each picture represents 1 μm .
- Figure 5. TEM micrographs of the yellow material and standard sepiolite at high magnification. Samples were embedded in resin, thin sectioned and observed as described in the Materials and Methods. A) Under-focused image of a cross-section through a particle of yellow material. The arrow points to an area where several layers are clearly visible allowing the distance between layers to be measured. B) Under-focused image of a

cross-section through a particle of standard sepiolite. The scale marker in each picture represents 50 nm.

Figure 6. Representative Energy dispersive X-ray spectra from the A) yellow material and B) standard sepiolite. Note that a trace amount of Fe was found in the yellow material but was truncated from the spectrum (Fe $K_{\alpha 1}$ peak is 6.4 KeV).

Figure 7. Evidence for fluorite on the yellow material. A) Higher magnification SEM micrograph of a particle shown in Figure 2. The scale marker represents 10 μm . The box shows the area analyzed to obtain the energy dispersive X-ray spectrum shown in B).

Figure 1

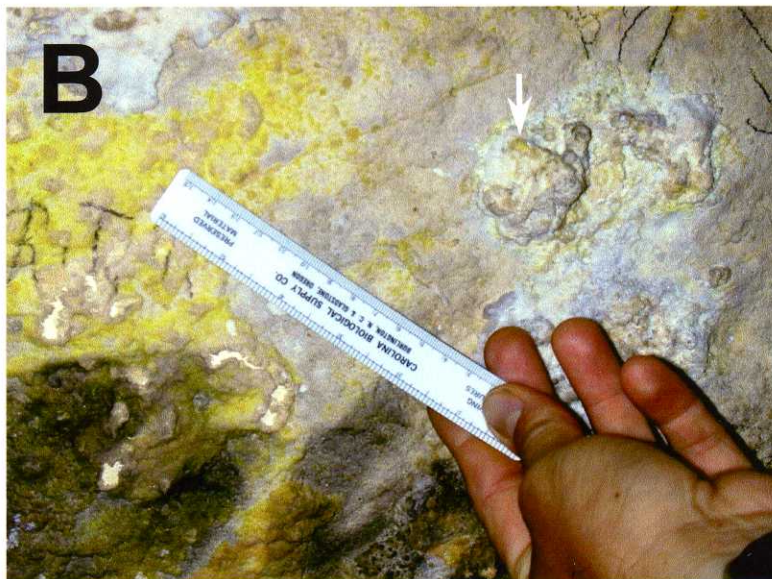


Figure 2

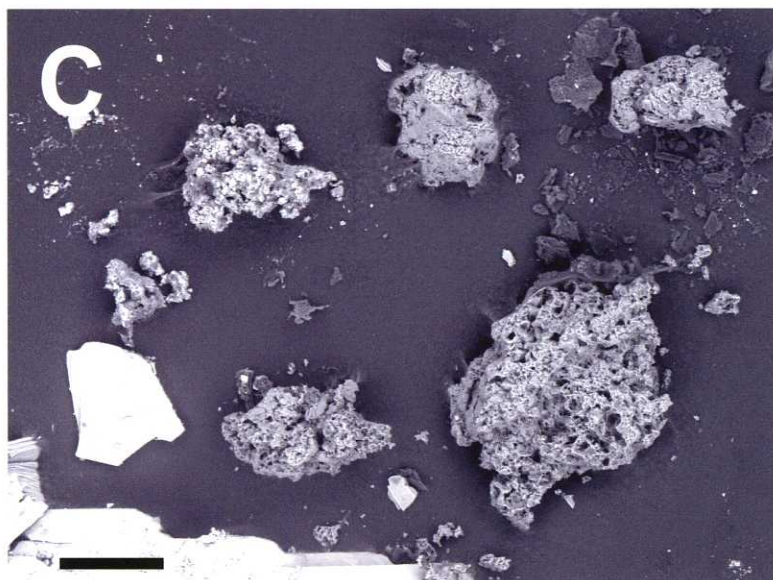
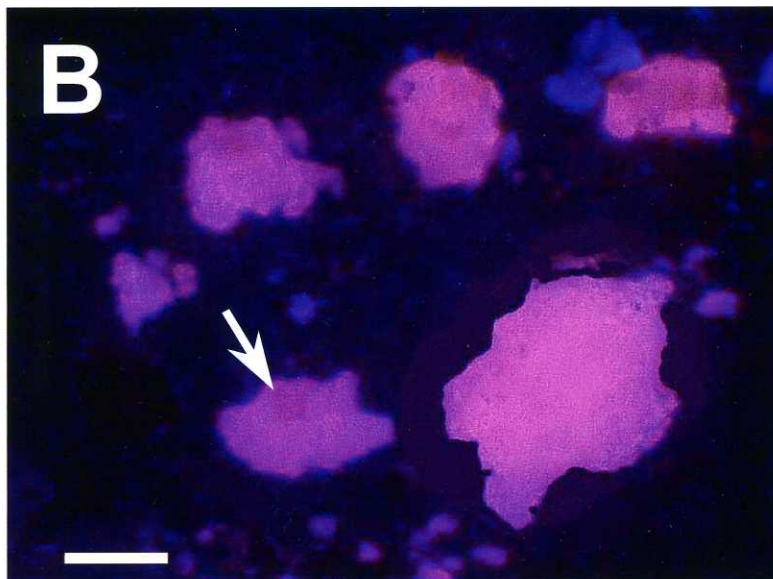
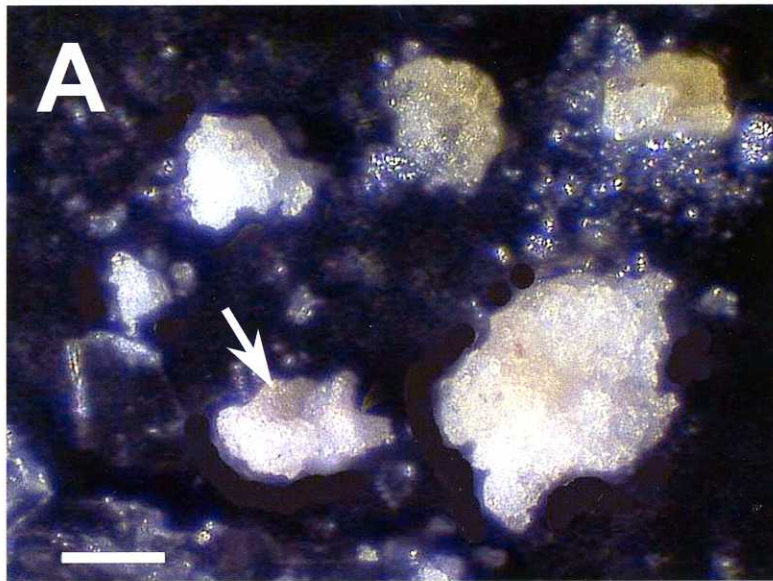


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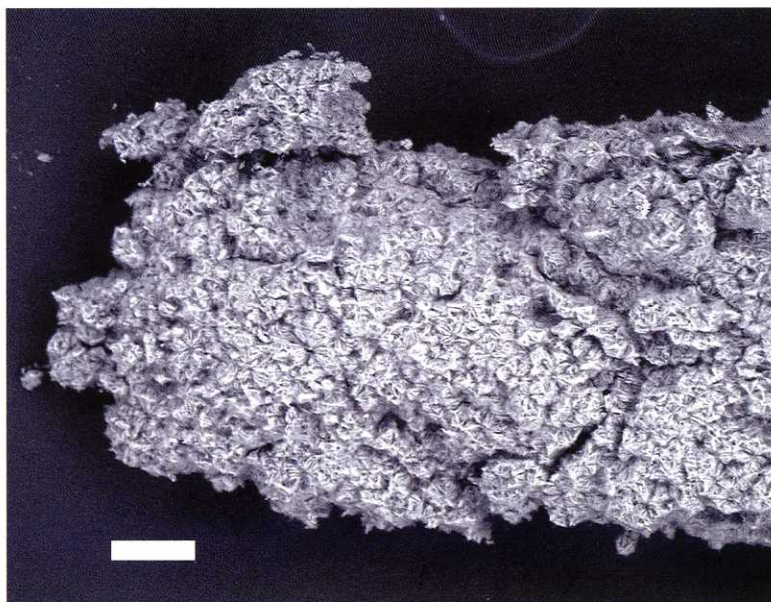
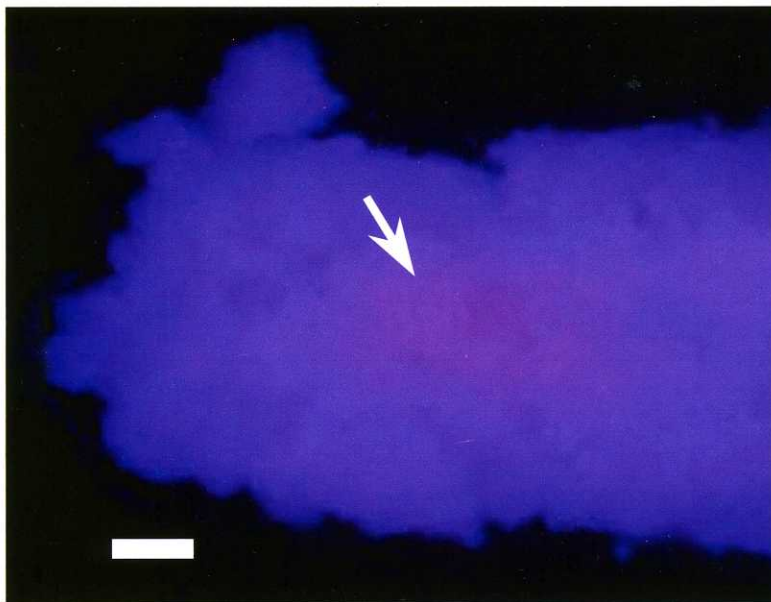
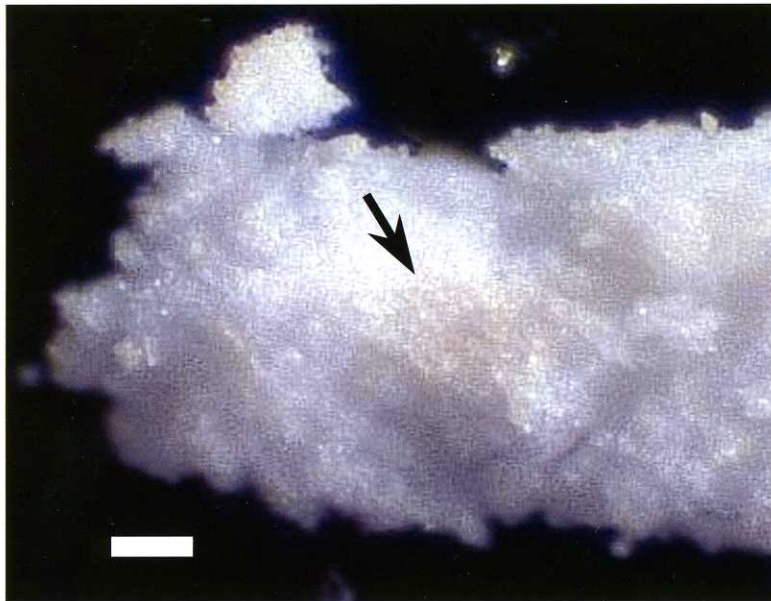


Figure 4

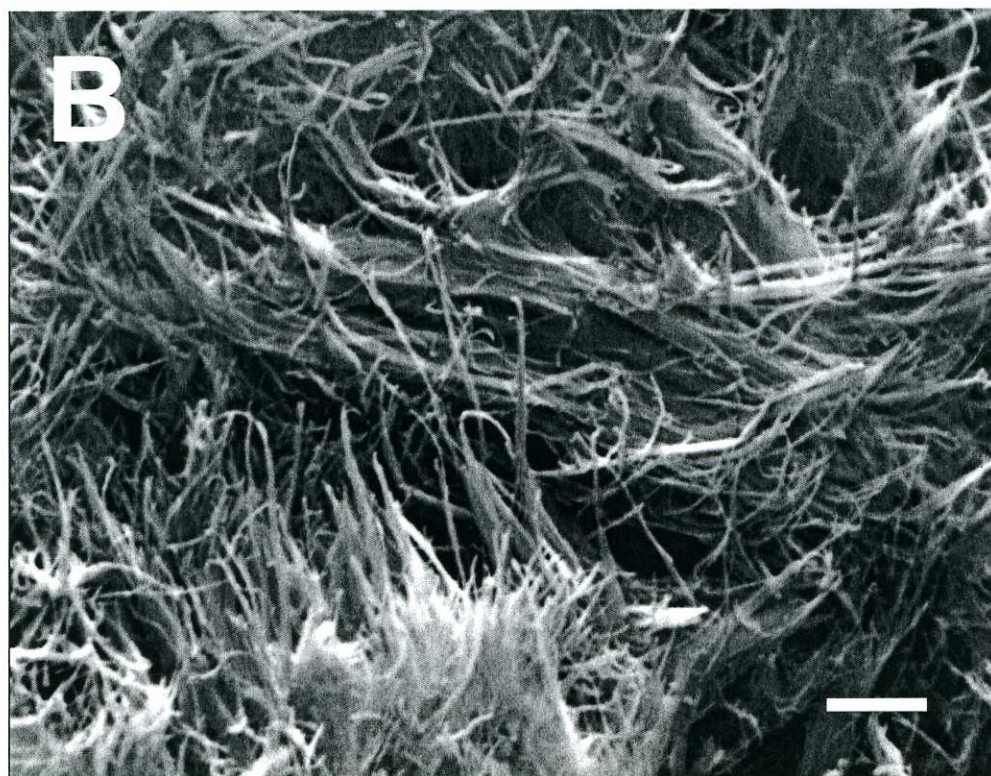
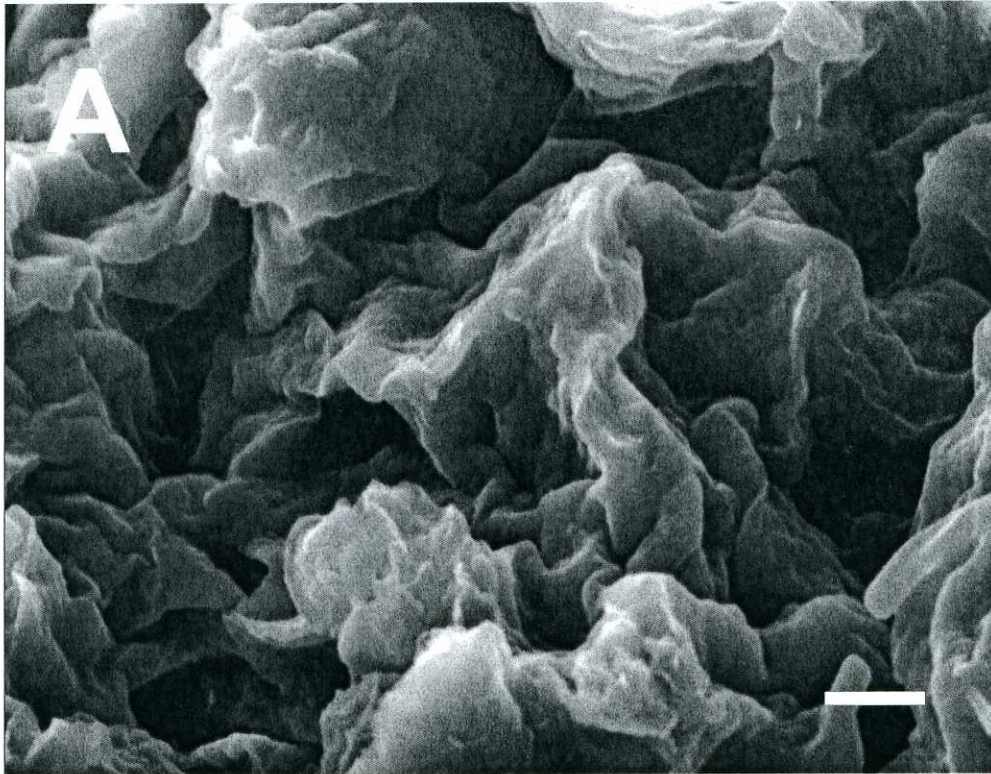


Figure 5

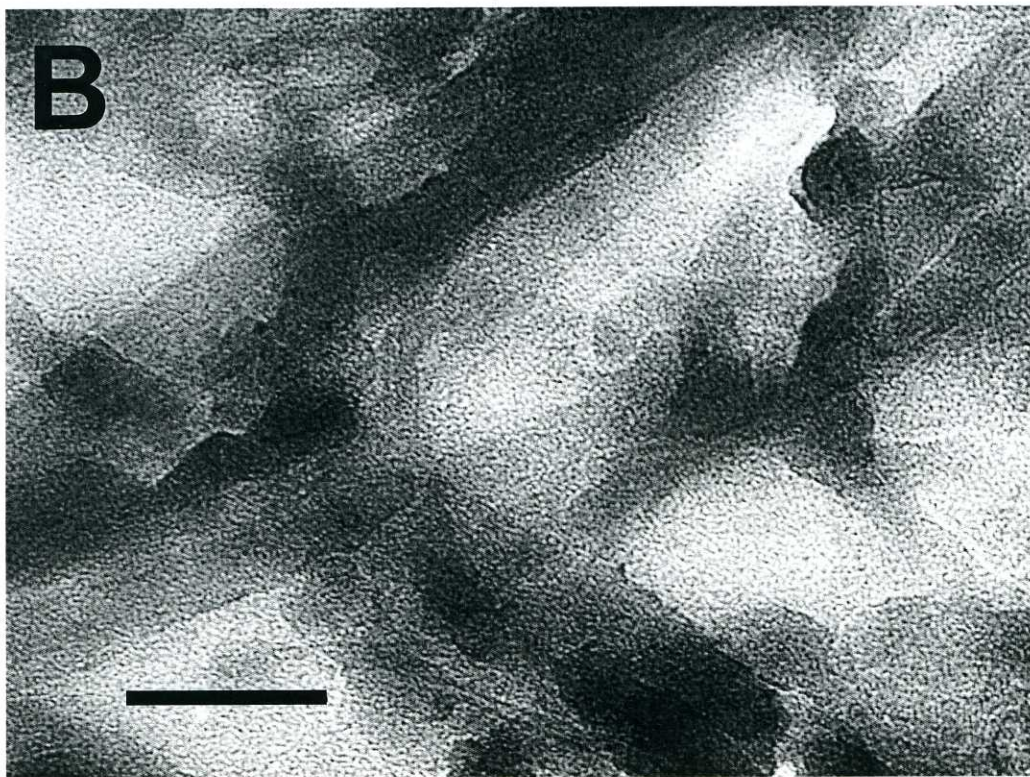
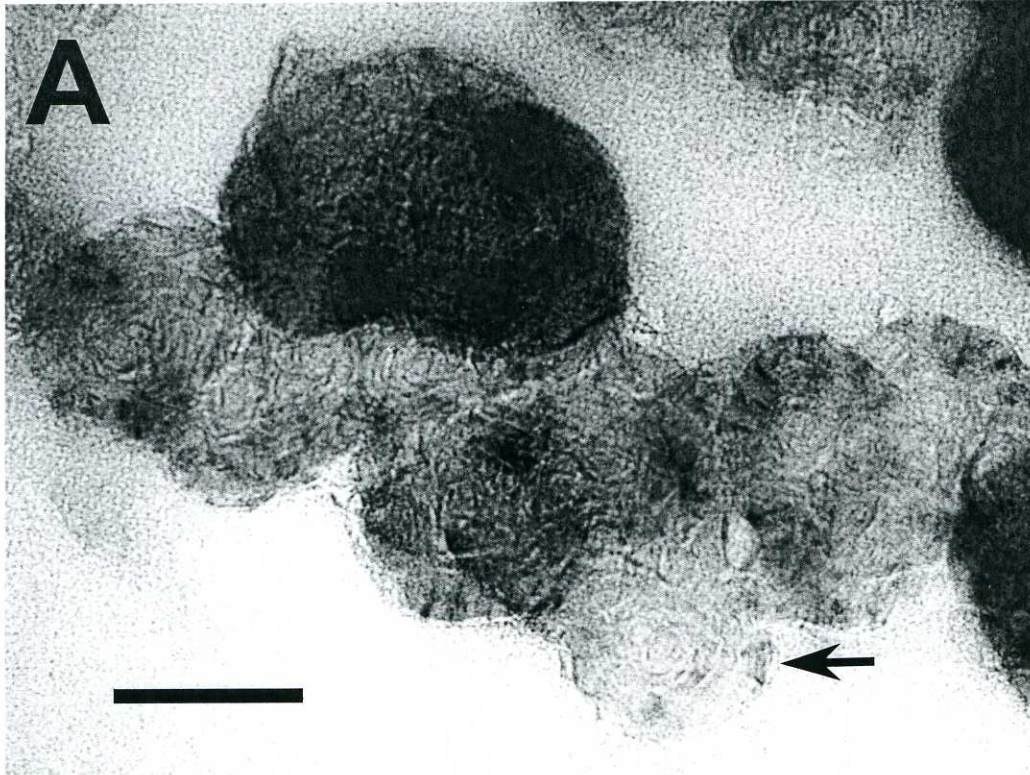


Figure 6

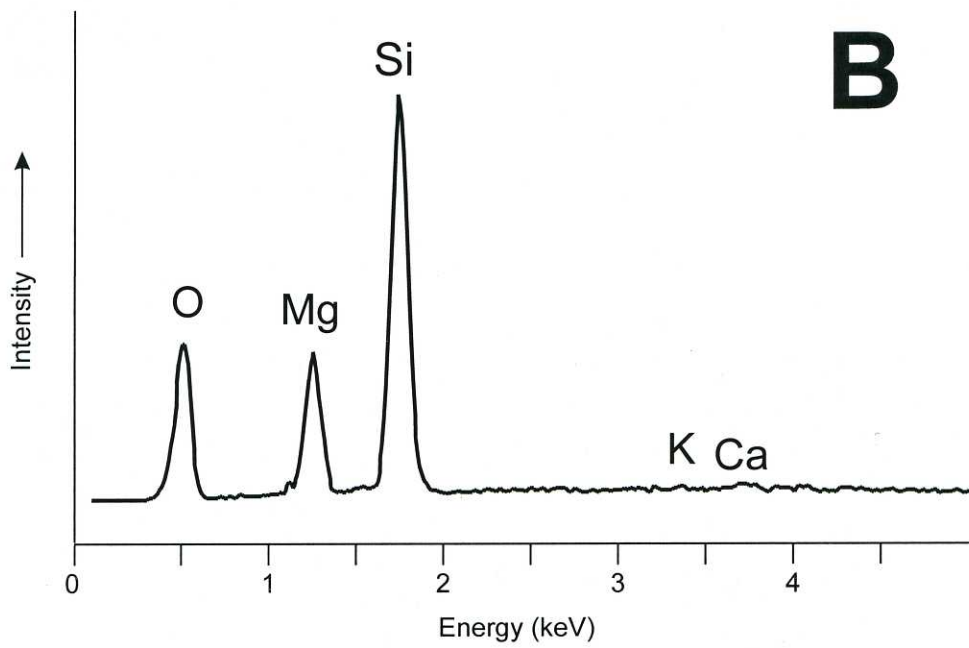
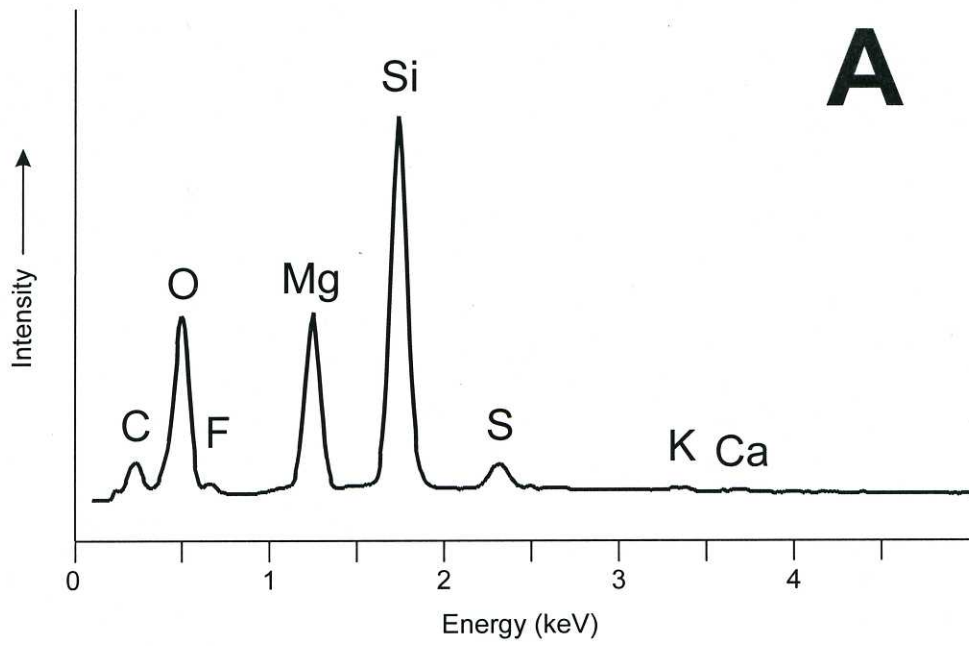


Figure 7

