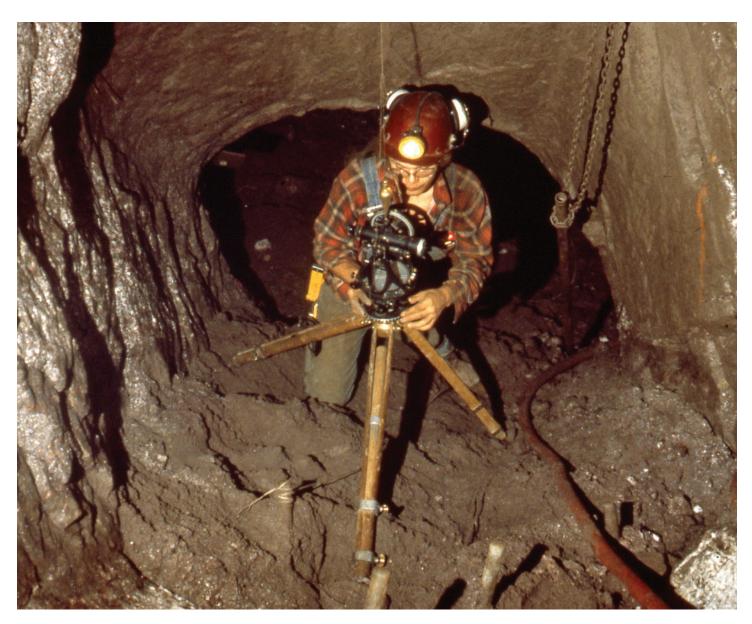
# **PICKING TABLE**

JOURNAL OF THE FRANKLIN-OGDENSBURG MINERALOGICAL SOCIETY

Vol. 58, No. 2 – Fall 2017

#### \$10.00 U.S.



## IN THIS ISSUE

- UNUSUAL CARBONATE CRYSTALS FROM FRANKLIN
- New Finds of Genthelvite at Sterling Hill
- WEATHERING OF CALCITIC ZINC ORES AT STERLING HILL
- REINERITE ADDED TO SPECIES LIST (TWO PAPERS)



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# PICKING TABLE



#### Vol. 58, No. 2 – Fall 2017

Fall and Winter 2017 Activity Schedule, Tema J. Hecht   2
Happenings at Sterling Hill, William Kroth    4
The 45th Annual New Jersey Earth Science AssociationGem & Mineral Show, April 29 & 30, 2017, Steven M. Kuitems, DMD5
Reinerite Added to the 2017 List of "Mineral SpeciesFound at Franklin and Sterling Hill, New Jersey,"Richard C. Bostwick and Earl R. Verbeek, PhD9
The Story of Sterling Hill Reinerite, James Horste    11
Unusual Carbonate Crystals From Franklin, New Jersey, John Ebner 13
New Finds of Genthelvite at Sterling Hill, Ogdensburg,New Jersey, Earl R. Verbeek, PhD15
The Super Diggg Esperite   18
Chemical Weathering of Calcitic Zinc Ore at Sterling Hill, New Jersey,

#### ABOUT THE FRONT COVER

#### Surveying a raise

This photograph, taken in the Sterling Mine by Resident Geologist Robert Svecz, shows a survey in progress within a raise being driven to the level above. The view is steeply downward toward 800 Stope; the axis of the raise is inclined about 55°. Such surveys were necessary to ensure that raises topped out at the desired location in the level above, and to calculate the volume of rock removed, which determined the amount of a miner's bonus pay.

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Members are encouraged to submit articles for publication. Articles should be submitted as Microsoft Word documents to Richard J. Keller, Jr. at: PTMemberFeedback@gmail.com.

The views and opinions expressed in *The Picking Table* do not necessarily reflect those of FOMS or the editors.

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#### THE PICKING TABLE, VOLUME 58, NO. 2 - FALL 2017

## FRANKLIN-OGDENSBURG MINERALOGICAL SOCIETY

## FALL AND WINTER 2017 ACTIVITY SCHEDULE

COMPILED BY TEMA J. HECHT 600 WEST 111TH STREET, APT. 11B NEW YORK, NY 10025 thecht@att.net

#### SATURDAY, SEPTEMBER 16, 2017

9:00 AM – NOON FOMS Field Trip

Sterling Hill Mining Museum. Collecting permitted on the Mine Run Dump and in the Fill Quarry, Passaic Pit, and "saddle" area. \$5.00 admission fee plus \$1.50 for each pound of material taken.

#### NOON – 1:15 рм

Future Rockhounds of America Franklin Mineral Museum. Parents are welcome to attend. For questions please contact Mark Dahlman at: fra@fomsnj.org or 301-428-0455.

1:30 рм – 3:30 рм FOMS Meeting Franklin Mineral Museum. Lecture: *Jasper, Chert and Flint*, by John Sanfaçon.

#### SATURDAY AND SUNDAY SEPTEMBER 23 AND 24, 2017 \*\*61ST ANNUAL FRANKLIN-STERLING GEM & MINERAL SHOW !!! NEW LOCATION !!!

Sponsored by the Franklin Mineral Museum. Littell Community Center (formerly the Franklin Armory), Franklin, New Jersey. 9:00 AM – 5:00 PM Saturday (indoors) 10:00 AM – 4:00 PM Sunday (indoors). The ticket price covers the show, *The Pond* outdoor swap, and admission to the Franklin Mineral Museum: \$7.00 per day for adults, \$4.00 per day for children (6-16).

#### The Pond Swap-and-Sell, sponsored by the FOMS,

takes place outdoors on the Littell Community Center grounds from 9:00 AM – 6:00 PM on Saturday, and from 10:00 AM – 5:00 PM on Sunday. Show admission required. The FOMS Annual Banquet starts at 6:30 PM on Saturday at the Lyceum Hall of the Immaculate Conception Church, located at the south end of Franklin's Main Street. Tickets may be obtained at the FOMS show table for \$20.00. The meal is an all-you-can-eat buffet; soda, tea, and coffee are included. ◆BYOB◆

After the banquet there will be an auction for the benefit of the FOMS. Please plan on donating a good specimen, artifact, book, etc.!

\*\*Saturday and Sunday: Events at the Sterling Hill Mining Museum.
For more information, please call: (973) 209-7212. Or you can visit the website at www.sterlinghillminingmuseum.org

#### SATURDAY, OCTOBER 21, 2017

9:00 ам – NOON FOMS Field Trip Collecting at the Braen Franklin Quarry Cork Hill Road, Franklin, N.J. If gate is open, drive through and park to the left of the gate. Please don't block the roadway. Safety equipment requirements such as hard hats, leather steel-tipped shoes, gloves and glasses will be rigidly enforced.

#### NOON – 1:15 pm

Future Rockhounds of America Franklin Mineral Museum. Parents are welcome to attend. For questions, please contact Mark Dahlman at: fra@fomsnj.org or 301-428-0455.

#### 1:30 рм – 3:30 рм FOMS Meeting

Franklin Mineral Museum. Lecture: *Raman Spectroscopy of Franklin-Sterling Hill Minerals*, by Dr. Earl Verbeek.

#### 3:30 рм – 4:15 рм MINERAL OF THE MONTH

(TBD at September meeting; see FOMS Facebook page for update.)

#### 6:00 рм — 10:00 рм

#### **\*\*Nighttime Mineral Collecting**

Sterling Hill Mining Museum. Collecting permitted on the Mine Run Dump and in the Passaic Pit and "saddle" areas. For museum members only. \$5.00 admission fee plus \$1.50 for each pound of material taken. For more information, call 973-209-7212.

#### SATURDAY AND SUNDAY OCTOBER 21 & 22, 2017 \*\*NORTH JERSEY MINERALOGICAL SOCIETY SWAP.

9:00 ам – 5:00 рм Sterling Hill Mining Museum.

#### SATURDAY, OCTOBER 28, 2017

\*\*28TH Annual ULTRAVIOLATION

9:00 ам – 4:00 рм A Show-Swap-Sell Session featuring fluorescent minerals *only*. First United Methodist Church, 840 Trenton Road, Fairless Hills, Pennsylvania. \$2 donation.

"If your rocks don't glow, you're at the wrong show." Table space available. For information, call 856-663-1383 or e-mail ultraviolation@yahoo.com.

#### SATURDAY, NOVEMBER 4, 2017

7:00 РМ – 10:00 РМ \*\*Night Dig on the Buckwheat Dump for the benefit of the Franklin Mineral Museum. Doors open at 6:30 РМ for check-in and mineral sales. Admission \$10.00 adult, \$8.00 children 3-12 years of age. Poundage fee charged. Call for details: 973-827-3481.

#### SATURDAY, NOVEMBER 18, 2017 9:00 AM - NOON

FOMS Field Trip Collecting at the Taylor Road site. Meet and park at the Franklin Mineral Museum, and walk from there. Do not park on Taylor Road! Fee charged.

#### NOON – 1:15 pm

Future Rockhounds of America Franklin Mineral Museum. Parents are welcome to attend. For questions, please contact Mark Dahlman at: fra@fomsnj.org or 301-428-0455. 1:30 рм – 3:30 рм FOMS Meeting

Franklin Mineral Museum. Lecture: *Reminiscences of the Mill Site, Part II*, by Jim Chenard.

6:00 рм

**\*\*Annual Museum Members-Only Mineral Sale and Auction** Franklin Mineral Museum.

#### SATURDAY, DECEMBER 2, 2017

9:00 ам — 4:00 рм

#### \*\*FLUORESCENT MINERAL SOCIETY MEETING

GeoTech Center, Sterling Hill Mining Museum. Lunch will be served (\$10.00 contribution).

**♦BYOB** 

!Reservations necessary!

Please contact Howie Green: royalp53@verizon.net.



Scheduled activities of the FOMS include meetings, field trips, and other events. Regular meetings are held on the third Saturdays of March, April, May, June, September, October, and November, and generally comprise a business session followed by a lecture. FOMS meetings are open to the public and are held at 1:30 PM, usually in Kraissl Hall at the Franklin Mineral Museum,
30 Evans St., Franklin, N.J. (check listings for exceptions).

Most FOMS field trips are open only to FOMS members aged 13 or older. Proper field trip gear required: hard hat, protective eyewear, gloves, sturdy shoes.

\*\*Activities so marked are not FOMS functions but may be of interest to its members. Fees, and membership in other organizations, may be required. Any information in this schedule, including fees, is subject to change without notice.

Thanks go to Gary Moldovany, Bernard Kozykowski, Richard Keller, Howie Green, Mark Dahlman, William Pazik, the Franklin Mineral Museum, and the Sterling Hill Mining Museum for this information.



On page 27 of the Spring 2016 *PT* is an unattributed photo of Richard and Elna Hauck at the grave of Lazard Cahn in Colorado Springs. That photo was taken by Robert Boymistruk of Castle Rock, Colorado.

#### THE PICKING TABLE, VOLUME 58, NO. 2 – FALL 2017

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# **Happenings at Sterling Hill**

WILLIAM KROTH PRESIDENT, STERLING HILL MINING MUSEUM 30 PLANT STREET, OGDENSBURG, NJ 07439 bill.kroth@shmmuseum.org

The Sterling Hill Mining Museum (SHMM) has awarded four \$2,500 scholarships to young Ogdensburg residents who will begin their college studies in the STEM (Science, Technology, Engineering, and Mathematics) disciplines this coming autumn (see photo). We hope to provide such scholarships every year to new freshman candidates and perhaps offer continuing support to past winners of our program.

This spring we took a major plunge into mineralogical research by obtaining a Raman spectrometer. This instrument will enable us to identify many of the unknowns in our local institutional collections and perhaps even identify minerals new to our area or new to science. Dr. Earl Verbeek has been using the Raman system for several months now to develop a library of spectra of known Franklin and Ogdensburg minerals. This library will form a database against which to compare the Raman spectra of unknown minerals. In addition, a second instrument will soon be added to the Sterling Hill lab: a Fourier Transform Infrared (FTIR) spectrometer. This instrument will provide another identification technique to augment the results of the Raman system. Also on our wish list is a LIBS (Laser Induced Breakdown) spectrometer, which provides quantitative information on the chemical makeup of minerals. Early candidates for species identification will be the hundreds of specimens from the John Kolic collection that defy easy sight-identification, plus many others from museum and private collections. Dr. Alan Rein, a member of the Sterling Hill Board and expert in this type of instrumentation, is coordinating efforts to get these amazing instruments for our facility.

The Sterling Hill Mining Museum will soon be featured on the popular TV reality show Cake Boss. On July 12, the entire film crew, the Cake Boss himself, and his family visited the museum and produced a complete segment that will air around the world in about five months. I recently learned that the show is even more popular abroad than in the USA. Each episode is based upon a surprise revealing of a custom-made cake that is produced by the Cake Boss (Buddy Valastro) in his famous Hoboken Bakery and then presented to the client. In this case, Sterling Hill was honored for its contribution to earth science education, and a special "mine cake" was made. Highlighting Sterling Hill's world-famous fluorescing minerals, the 25-pound cake included various colors of rock candy crystals glowing with LED lights (with batteries hidden in the frosting). It also included many layers of "Mississippi Mud" (a type of chocolate filling) with interspersed tunnels,



edible ladders, and even tasty little miners.

And speaking of television programs, the Sterling Hill Mining Museum was visited twice for two separate installments of *Mysteries at the Museum*. This popular television series features historical accounts of interesting events from the past and shows how specific items now reposing in museums have played important roles in those events. Expect to see us featured within the next few months!

Finally, our freshly restored 1942 N4B metal caboose is now complete. Prior to closing in the 1980s, the Sterling Hill lower property was visually more of a railroad yard than a mine, with track, switches, locomotives, and rolling stock covering most of the surface. The caboose pays tribute to the importance of ore transportation via railroad to Palmerton, Pennsylvania. It is now both structurally and cosmetically restored in accordance with its period of manufacture, complete with original woodburning stove, "direct deposit" toilet, original lamps, air whistle, and gauges. New windows have been installed, along with period-correct tongue-and-groove woodwork on the interior. I would like to thank the team of Mike Pierce, Matthew Vincent, Doug Francisco, Tom and Jason Hauck, and many others for doing such an excellent job. As many have commented, "This caboose has been restored to a level seen only on classic cars!" Be sure to stop by and see this piece of history...walk back in time and climb up to the caboose's majestic cupola.

So, as you can see by the types of activities and projects, the Sterling Hill Mining Museum is expanding beyond anything we ever thought it would be when it was first conceived. And with such good exposure and the completion of worthy projects, our reputation and visitation will grow proportionally! Thank you all.  $\bigstar$ 

#### THE PICKING TABLE, VOLUME 58, NO. 2 - FALL 2017

# The 45th Annual New Jersey Earth Science Association Gem & Mineral Show

APRIL 29 AND 30, 2017

STEVEN M. KUITEMS, DMD 14 FOX HOLLOW TRAIL BERNARDSVILLE, NJ 07924

This spring show was, as usual, an unrestricted assemblage of geological and mineralogical wonders. The eclectic nature of the displays, in both the white light exhibits and fluorescent exhibits, reminded me of the wide variety of springtime flowers and trees blooming outside the Franklin School.

There were fourteen cases of white light displays. The Franklin Mineral Museum presented "Friedelite," a singlemineral display of veins, masses, and crystals, with two superb cut-and-polished examples of the richest "beefsteak" friedelite one could hope to find. Dick and Elna Hauck put together a case called "Concretions," including a variety of sand spikes from Signal Hill, Imperial Co., California, and fossilized fern concretions from Mazon Creek, Illinois. The Morris Museum's case, titled "Ice Age Mammals," showcased a huge mammoth tooth, a smaller mastodon molar complete with roots, and two Pleistocene walrus tusks. The Delbarton School complemented that theme with "Pleistocene Extinctions:" a Siberian mammoth molar, a cave bear mandible from Romania, and a cast of the skull of a saber-toothed cat, Smilodon californicus, from the La Brea Tar Pits in present-day Los Angeles. The Morris Museum Mineralogical Society filled two cases of "Mineral Treasures" that included some New Jersey specimens, notably a fine calcite crystal from the Millington Quarry and a plate of green prehnite from the Eagle Rock Quarry in West Orange. This display also included a large "cave calcite" from Chihuahua, Mexico, and a fine sphere of eye agate from Brazil. Bernard Kozykowski also filled two cases, titled "Mineral Classics," highlighted by a choice example of wulfenite crystals on calcite from Los Lamentos, Chihuahua, Mexico, and a large cabinet-sized green smithsonite from the 79 Mine, Hayden, Arizona. Daniel and Steven Kuitems' case, "Franklin Classics," highlighted many species that can be found in the Franklin Marble, notably spinels, a dark brown uvite, several corundum crystals, and a large chondrodite crystal from the Lime Crest Quarry, Sparta, New Jersey. "Minerals of Bound Brook, N.J." was the title of Brad Plotkin's exhibit, which included two notable copper specimens, one in a quartz pocket and the other (with amethyst) that was a fissure-grown group of crude copper crystals. There were also two examples of



Stan Parker's display of colorful traprock minerals from New Jersey amply shows that not all of New Jersey's finest minerals are from Franklin and Sterling Hill. *Tema Hecht photo.* 

chalcopyrite "blister ore," one cleaned and the other with its original oxidized coating.

Brendan and Connie Dunn's case, "Mexican Calcites," included a scalenohedron-dominated specimen from Concepción del Oro, Zacatecas, Mexico, and a counterpart from Chihuahua, Mexico, that had tabular crystals with a fine overgrowth of scalenohedral crystals. For something totally different, Juan Gonzalez's case of "Man-Made Crystals" showed more than thirty examples, including synthetic rubies with the boule showing how they were grown, and a green synthetic zincite. Stan Parker's case of "Classic NJ Trap Rock Minerals" was certainly one of the more colorful displays, with orange stilbite crystals, mint-green prehnites collected from the I-80 road cuts in Paterson, and red heulandite crystals from Prospect Park. Arlene Castleman presented a case of her favorites, titled "New Jersey Fossils," with a large, sharp belemnite on matrix from Colts Neck, and several coelacanth fossils (Osteopleurus newarki) from the famous Granton Quarry on Route 9 in North Bergen. Stephen Sanford completed the daylight displays with an instructional case called "Reaction Rims: Classics & Others." This included a colorful pair of rhodonite slabs from Franklin, New Jersey, one

of light pink rhodonite in contact with calcsilicate minerals, the other of deep red rhodonite with a thick symplectite rim. Another specimen showed dark reddish-brown sonolite replacing masses of tan tephroite, from the hanging wall of the east limb, Sterling Mine, Ogdensburg, New Jersey.

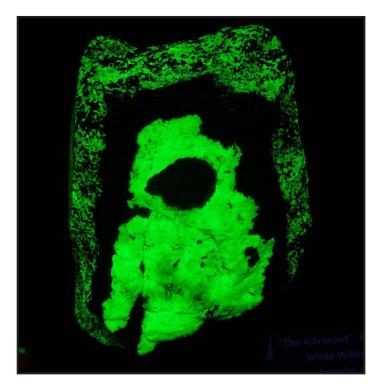
There were ten fluorescent exhibits, with enough variety to please anyone. The Franklin Mineral Museum's case, "Photonic Madness," included a wide variety of local specimens, including my favorite blue-and-red fluorescent combination from Franklin, margarosanite with axinite-(Mn), and from Sterling Hill, a cross-section of a willemite crystal in calcite that looked like a green rocket flying through red sky. The Sterling Hill Mining Museum's display, "Willemite & Calcite from Sterling Hill," was a full case of green-fluorescing willemite in red-fluorescing calcite under shortwave UV, each specimen with different visual patterns: some with veins, some with crystals, and one with two large grains together that resembled the horsehead logo of the New Jersey Zinc Company. A sign in the case read, "If you were a miner who carried a UV lamp in his lunchpail, this is what the ore looked like after it was blasted, then washed down to get rid of dynamite fumes."

Steven and Daniel Kuitems, whose display title was "Franklin Delights," had put together their first exhibit of minerals under longwave UV, heavily weighted with sphalerite from Franklin and Sterling Hill, plus greenish-yellow-fluorescing zincite from Sterling Hill, green-fluorescing genthelvite from the Passaic Pit at Sterling Hill, and orange-fluorescing sodalite from nearby Beemerville. Richard Keller's case, "Cache as Cabs Can," consisted entirely of cabochons made from local minerals, including blue-fluorescing diopside, yellowfluorescing esperite, violet-fluorescing hardystonite, and orange-fluorescing wollastonite. Chris Luzier's display, "Why Franklin and Sterling Hill Are Famous," showed classic, rare fluorescent specimens from the area, notably prehnite (fluorescent bluish-pink) with pectolite (fluorescent orange), a fine "second-find" wollastonite, several margarosanites, and a radiating willemite in the shape of an astronaut on the moon, all from Franklin. Among other remarkable specimens, Chris included a spectacular Sterling Hill example of a breccia with red-fluorescent calcite fragments appearing to float in green-fluorescent willemite. Alex Kerstanski put together a case of willemite and calcite "Vein Rocks" from Franklin and Sterling Hill. Of note was a "dead zone" specimen with parallel bands of nonfluorescent ore next to a willemite vein, and several brecciated ore specimens where veins of willemite ran parallel to the blocks of breccia. Andrew Mackey's case was "Boulders"! Yes, large, rich boulders of franklinite and willemite with minimal calcite, emblematic of the rich zinc ore mined at Sterling Hill. Pat Hintz's case, "Worldwide Fluorescent Minerals," included bright-red-fluorescing calcite specimens from Itinga, Brazil, and a large hyalite opal,

fluorescing brilliant green, from Little Switzerland, North Carolina. Brendan Dunn's case was "Minerals Aroused by Midwave," with many carefully selected specimens, including a large example of agrellite from the Kipawa alkaline complex, Les Lacs-du-Témiscamingue, Québec, Canada, and a multihued calcite from Terlingua, Texas, fluorescing pink, yellow, and light green.

Howie Green chose a two-mineral theme, "Calcite/ Fluorite from Around the Globe." All the specimens were either fluorite on calcite or calcite on fluorite, with the calcite fluorescing pink to pinkish-red and the fluorite fluorescing its characteristic blue-violet. Particularly fine were the specimens from Dal'negorsk, Primorskiy Kray, Russia, and (closer to home) the Kingston Traprock Quarry, Rocky Hill, New Jersey. Another handsome specimen, from the Pure Potential Mine, La Paz County, Arizona, featured alternating bands of fluorescent calcite and fluorite. Warren Miller's display, "Worldwide Fluorescent Minerals," had many classics with two centerpieces in particular, a superb yellow-fluorescing radiating quartz from La Sassa, Tuscany, Italy, and a beautiful radiating willemite from Lusaka, Zaire.

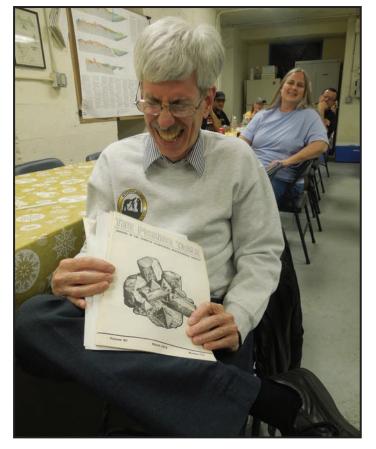
In many ways the exhibits' eclectic variety and scope typified the nature of the Earth Sciences that this show is named for. Thanks to all who worked hard to make this show, and these exhibits that were enjoyed by so many.  $\bigotimes$ 



This specimen from Chris Luzier's display is not only a nice example of radiating willemite but also a first-class mimetolith, affectionately known as "The Astronaut." *Tema Hecht photo*.



Max Mpoyi, proprietor of Malachite & Gems of Africa, Inc., has been attending the show for years and always offers a fine selection of colorful copper minerals. *Tema Hecht photo*.



Gary Weinstein bursts into tears upon winning old copies of our local rag. *Tema Hecht photo.* 



Bruce Moor, MD, an anesthesiologist who deals in minerals as Xanadu Fine Minerals, LLC, packs up during the final stages of the show. *Tema Hecht photo.* 



Ralph Bonard, Ogdensburg's genial postmaster and up-and-coming mineral hustler, usually has enough good rocks behind the P.O. counter to start a conversation. *Tema Hecht photo.* 

#### The Sterling Hill Mining Museum, Inc.

Featuring acres of things to see indoors, outdoors, and underground, including:

Antique mining equipment displays Mining memorabilia displays Historic buildings Underground guided tours Museum store stocked with minerals,

books, T-shirts, caps, etc. Food concession and picnic area And much more!

Every day a collecting site will be open for an additional \$5.00 fee.

Contact the mine office for details.

 $\otimes \otimes \otimes$ 

30 Plant Street, Ogdensburg, NJ 07439 Museum phone: 973-209-7212 Fax: 973-209-8505 Web: sterlinghillminingmuseum.org DON'T MISS THE RAINBOW ROOM!



#### **Schedule of operation:**

April 1 through November 30, Museum store is open 7 days a week, 10:00 AM to 3:00 PM. General public tours at 1:00 PM. Group tours may be scheduled by appointment at other times during the day.

December 1 through March 31, **WEEKENDS** - Museum store is open 10:00 AM to 3:30 PM and general public tours are at 1:00 PM (weather permitting). Group tours may be scheduled during weekdays by appointment (weather permitting). Please call if you have any questions.

In April, May, June, September, October, and November, tours at 1:00 PM or by appointment.

The temperature in the mine is 56°F.



32 Evans Street/P.O. Box 54, Franklin, NJ 07416 (Between Main Street and Buckwheat Road) Phone: 973-827-3481 www.franklinmineralmuseum.com



Exhibited by means of guided tours: Franklin-Sterling Hill mineral specimens, educational exhibits in mining methods and history, including a life-size replica of underground workings, artifacts, gemstones, zinc uses, and a 32-foot-long fluorescent mineral display.

Included in the tours is the Jensen-Welsh Memorial Hall, built especially to contain the Wilfred Welsh collections of fossils, Native American relics, and worldwide minerals and rock specimens assembled for teaching purposes.

Mineral collecting on the Buckwheat Dump. Ample parking. Picnic grounds. Gift shop offering for sale: local and worldwide minerals, fluorescent specimens, agate slabs, onyx carvings, UV lamps, hammers, mineral books, T-shirts, postcards, and much more. Separate admission fees to the Museum and the Buckwheat Dump. Admission to the Museum includes guided tour.

#### **OPERATING SCHEDULE:**

Open to the public March – Weekends Only April 1 – December 1 Monday through Friday: 10 ам – 4:00 рм Saturday: 10 ам – 5:00 рм Sunday: 11 ам – 5:00 рм Closed Easter, July 4th, and Thanksgiving Groups by reservation, please

Franklin, New Jersey "The Fluorescent Mineral Capital of the World"

#### THE PICKING TABLE, VOLUME 58, NO. 2 – FALL 2017

# Reinerite Added to the 2017 List of "Mineral Species Found at Franklin and Sterling Hill, New Jersey"

RICHARD C. BOSTWICK 600 W. 111TH ST., APT. 11B NEW YORK, NY 10025 rbostwick@att.net

Reinerite, Zn<sub>3</sub>(AsO<sub>3</sub>)<sub>2</sub>, is a rare zinc arsenite first described from the Tsumeb mine in Namibia. It was named in 1959 for Willy Reiner (1895-1965), Senior Chemist for the Tsumeb Corporation, who analyzed the type material. Reinerite is listed on Mindat.org as having been found at the Lalongla Pb-Zn deposit in Tibet (though its presence there is marked as questionable) and at an ancient slag locality in Germany. Now, however, reinerite has been verified from the Sterling Mine, New Jersey, by X-ray diffraction (XRD) analysis and Raman spectrometry, as a colorless mineral found in veins of yellow zincite from the west limb of the Sterling Hill orebody. Sterling Hill reinerite was discovered by James (Jim) Horste, who noticed its unusual fluorescence and had the mineral analyzed. His account, "The Story of Sterling Hill Reinerite," follows this introduction.

In the few specimens so far known, including those photographed by Jim Horste in his "Story," Sterling Hill reinerite is colorless, transparent, with vitreous luster, and on first glance can be mistaken for quartz, but is softer (hardness 5-5<sup>1</sup>/<sub>2</sub>). Cleavage is present but indistinct. Jim's attention was first drawn to the mineral by its fluorescence, which in his specimens is of moderate intensity, best under shortwave (SW) ultraviolet (UV) light, and is described by him as "olivegreen". This color is accurately portrayed in his photos and has been described by others as "mustard yellow." The color of fluorescence in the Horste specimen is imparted, in part, by co-existing sphalerite, zincite, and fluorite, all of which have been confirmed by the second author via Raman spectroscopy. A specimen of reinerite in the collection of the Franklin Mineral Museum, also confirmed as reinerite by the second author, fluoresces weak brownish orange SW, a color probably more indicative of the reinerite itself.

Descriptions on the website Mindat.org and in *Dana's New Mineralogy* (1997) indicate that reinerite from Tsumeb can be colorless, or blue to yellow-green, and has good to fair cleavage; there is no mention of fluorescence. Sterling Hill reinerite has been found in veins of fine-grained yellow zincite, in calcitic ore rich in deep red zincite, reddish-brown willemite, and franklinite. The quantity of yellow zincite specimens of this general type is in the hundreds, most of them found in EARL R. VERBEEK, PhD FRANKLIN MINERAL MUSEUM 32 EVANS STREET FRANKLIN, NJ 07416

the 1970s and 1980s during the last decade the Sterling mine operated. Such specimens were generally described as coming from workplaces in the upper levels of the west limb of the orebody. One such workplace is 980 stope on 500 level, and another is 800 stope on 430 level, but the exact locality for the few verified reinerite specimens is not known. Nor is there any way at present to know how many Sterling Hill reinerite specimens may emerge once the mineral is better-known, and informed collectors look for it.

The fluorescence of Sterling Hill reinerite is best seen under shortwave UV, is of moderate to weak brightness, and may be variable in hue in that its fluorescence has been described as olive-green, mustard yellow, and brownish orange in the few specimens seen to date. The most abundant fluorescent minerals in the yellow zincite assemblage are yellow zincite (fluorescent pale greenish-vellow, best midwave (MW) and LW), brownish-red willemite (fluorescent and phosphorescent bright yellow-green, best SW); and calcite (fluorescent and phosphorescent orange-red SW). Less common fluorescent minerals in the assemblage are sphalerite grains and veinlets (fluorescent and phosphorescent orange and blue, best LW), fluorite (fluorescent blue, best LW), and white coatings of hydrozincite (fluorescent blue, best SW). Jim's "Story" includes descriptions and analyses of two additional fluorescences in his specimens, the brick-red fluorescence of magnesian calcite and the blue fluorescence of a mixture of reinerite and hemimorphite. Both merit further study.

As mentioned in the first paragraph of this introduction, the discovery of reinerite from Sterling Hill is entirely due to the persistence of James (Jim) Horste, a West Coast collector and Fluorescent Mineral Society member who broke up one of his two specimens of yellow zincite to expose the vein further, and noticed an unfamiliar mineral with unusual fluorescence. He showed it to local collectors, got little satisfaction there, and finally sent an example of the unknown mineral back east to the authors, who agreed they had never seen anything like it, but had no way at the time to analyze it. Jim, bless him, had the opportunity to send his Sterling Hill unknown to Attard's Minerals. John Attard is a professional chemist known for his skills in XRD analysis, and the results were conclusive: the

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#### REINERITE ADDED TO THE 2017 LIST OF "MINERAL SPECIES FOUND AT FRANKLIN AND STERLING HILL, N.J." RICHARD C. BOSTWICK AND EARL R. VERBEEK, PhD

unknown mineral is reinerite. Since then, with the acquisition of a Raman spectrometer by the Sterling Hill Mining Museum, Earl Verbeek confirmed the earlier XRD results: the Raman spectrum of the Horste specimen (Fig. 1) closely matches that of a reference spectrum of reinerite in the RRUFF database (see http://rruff.info/about/about\_general.php) of the University of Arizona (Fig. 2). Jim was then kind enough to send Earl Verbeek superb photos of his remaining larger specimens, Attard's data, and a personal account of this discovery. We thank Jim for having "made it happen," and rejoice in adding a new species to both the Franklin and Sterling Hill mineral list and the related list of fluorescent minerals from the district.

Jim's personal account, "The Story of Sterling Hill Reinerite," now follows. Enjoy it!

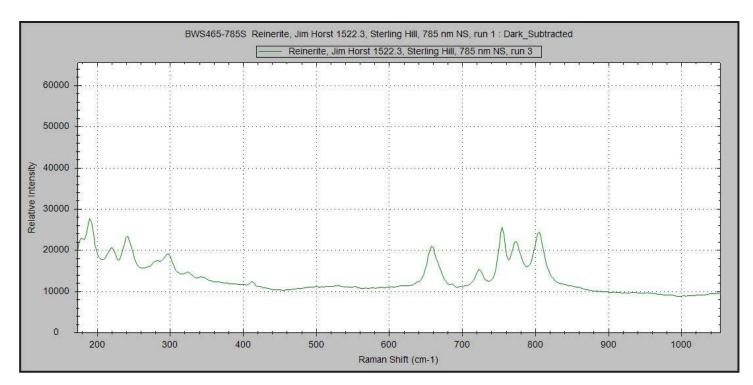


Figure 1. Raman spectrum of the Horste specimen of reinerite.

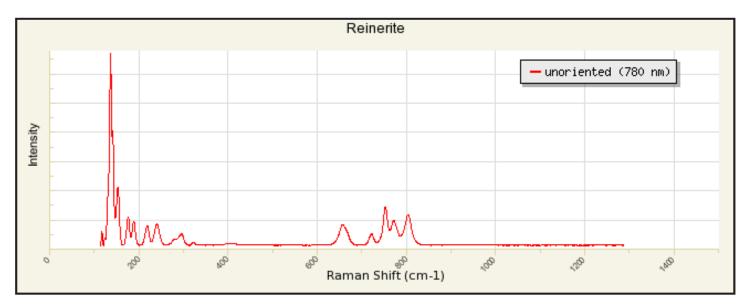


Figure 2. Reference Raman spectrum of reinerite from the RRUFF database, showing near identity of spectrum to that of Figure 1.

#### THE PICKING TABLE, VOLUME 58, NO. 2 – FALL 2017

# **The Story of Sterling Hill Reinerite**

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The specimen that turned out to include reinerite (Fig. 1) was purchased in 2006 from a local California collector. It appeared to be an average piece of fluorescent zincite from Sterling Hill, with sphalerite, willemite, and calcite. The minerals of interest were in a vein that ran through the center of the specimen. There I could see an unusual mineral that fluoresced an olive color under shortwave ultraviolet (SW UV) light. I asked local members of the Fluorescent Mineral Society about this, and the consensus was that it was an unusual form of fluorescent zincite. At the time I was fairly new to the fluorescent mineral hobby and didn't realize how significant an "unusual" specimen from the Franklin-Sterling Hill area could be!

I had only two fluorescing zincites in my collection at the time, and the other one was much prettier, so I decided to sell

this specimen. I had it up on my website for a while and it didn't sell. I thought if I could split it in two, it might expose more of the interesting minerals. The specimen split perfectly! I could now see that this was a beautiful and significant specimen, so I decided to keep the two major pieces (Fig. 2).

By 2012 I had seen quite a few Sterling Hill zincite/sphalerite/ willemite/calcite specimens, and none of the others had this olive-colored fluorescence, so I decided to investigate further. I sent photographs to Earl Verbeek and Richard (Dick) Bostwick. They too were puzzled and asked to see the specimen in person to investigate further. After both had examined the specimen I sent, Richard Bostwick declared, "Your zincite-plus specimen from Sterling Hill is just plain weird, and neither Earl nor I have seen anything like it."

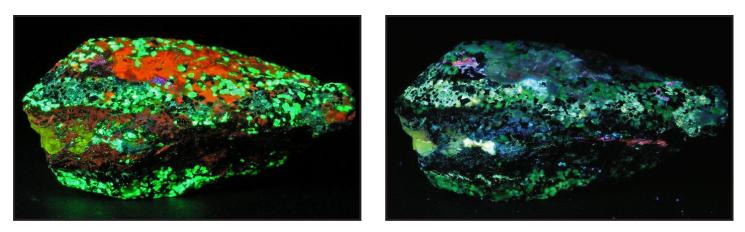


Figure 1. The original specimen of Sterling Hill reinerite before being broken up, photographed under shortwave UV (left) and longwave UV (right). Note the olive-colored fluorescence on the left side of the specimen, just below center. Horste specimen 1522, 4.6 × 3.6 × 2.0 inches (11.7 × 9.1 × 5.1 cm). James Horste photos.

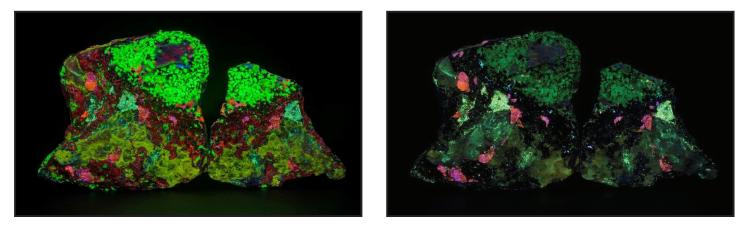


Figure 2. The two major pieces of the reinerite specimen after being split, under shortwave UV (left) and longwave UV (right). Horste specimen 1522.1, 4.6 × 3.6 × 1.5 inches (11.7 × 9.1 × 3.8 cm) on left; specimen 1522.2, 3.3 × 2.8 × 0.8 inches (8.4 × 7.1 × 2.0 cm) on right. James Horste photos.

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I didn't do much more with this specimen until late 2016 when John Attard, of Attard's Minerals, took an interest in some Chinese eucryptite I was selling. He offered to trade some X-ray diffraction (XRD) services for a specimen. I immediately thought of the mystery zincite from Sterling Hill and sent him a chip. The analysis came back: reinerite! This was significant because reinerite was not then known from Sterling Hill and was not known to fluoresce. The chemical formula for reinerite is  $Zn_3(AsO_3)_2$ , so chemically it isn't out of place at a zinc mine. The type locality for reinerite is the Tsumeb mine in Namibia. Mindat.org lists only two other localities for this mineral: the Ochsenhütte slag locality in Germany and the Lalongla Pb-Zn deposit in China, though Mindat.org questions the latter listing.

There were two other unusual fluorescent responses in this specimen, as shown in Figures 3 and 4 of the smaller of the split halves. One was a brick-red-fluorescing mineral that was a significantly different shade of red than the typical calcite found elsewhere on the specimen, and the other was a blue fluorescence on the upper left part of the specimen that I had not seen in other specimens. Please note that the camera recorded this blue fluorescence brighter than it appears to the eye. XRD showed the brick-red-fluorescing mineral to be magnesian calcite and the blue-fluorescing mineral to be hemimorphite and reinerite. The blue-fluorescing area was directly adjacent to solid reinerite, so the presence of reinerite admixed with hemimorphite, the probable source of the blue fluorescence, is not surprising. Because willemite fluoresces much brighter than the other minerals in the specimen, High Dynamic Range photography techniques had to be used to keep the willemite from being overexposed in the image. 🛠

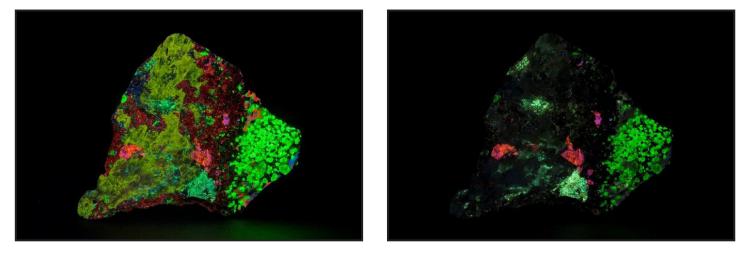
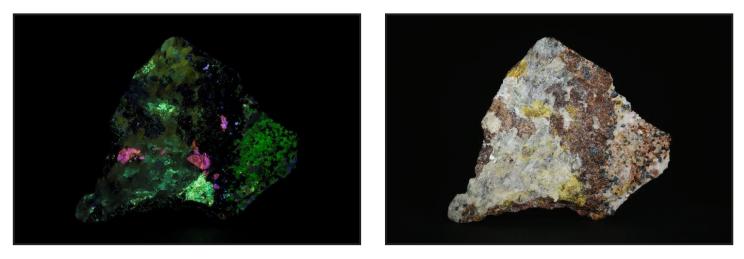


Figure 3. Two views of Horste specimen 1522.2. On left, under shortwave UV: reinerite ("olive"), magnesian calcite (brick-red), sphalerite (orange), zincite (pale yellow), and willemite (green) with minor calcite (red). On right, under midwave UV: sphalerite (orange to pink), willemite (green) and zincite (pale greenish yellow). Specimen measures 3.3 × 2.8 × 0.8 inches (8.4 × 7.1 × 2.0 cm). *James Horste photos*.



**Figure 4.** Two more views of Horste specimen 1522.2. On left, under longwave UV: reinerite (pale "olive"), sphalerite (orange to pink with minor blue), zincite (pale greenish yellow), and reinerite + hemimorphite (pale blue, at top of specimen). In white light: reinerite (colorless), zincite (yellow in vein at left, red in ore matrix at right), willemite (brownish red), magnesian calcite (brownish red mixture with willemite and zincite), and sphalerite (colorless). Specimen measures 3.3 × 2.8 × 0.8 inches (8.4 × 7.1 × 2.0 cm). *James Horste photos.* 

#### THE PICKING TABLE, VOLUME 58, NO. 2 - FALL 2017

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# **Unusual Carbonate Crystals From Franklin, New Jersey**

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Figure 1. The Dr. William B. "Doc" Thomas micromount of purported xonotlite (originally labeled calciothomsonite). *Vandall King photograph*.



**Figure 2.** Broomlike sprays of white crystals, the supposed xonotlite, on bladed crystals of axinite-(Mn). Width of field-of-view is 5 mm. *Vandall King photograph.* 

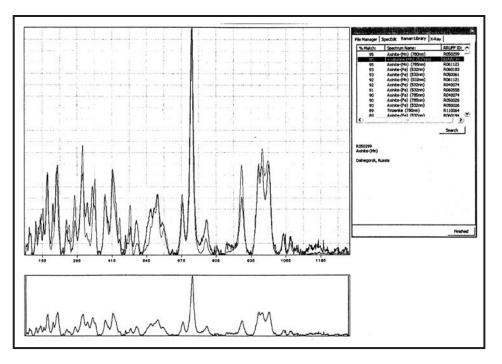
Franklin minerals have enjoyed or suffered scientific examination through the years, and this has been doubly true for micromounts, which often have little material to test. In 1992 I bought, from Ralph Thomas, 256 micromounts that Ralph had purchased directly from Dr. William B. "Doc" Thomas (no relation). These micromounts were logged in to my collection but not carefully studied at the time. Recently, while examining my Franklin-Ogdensburg micromounts for inclusion in the upcoming "Franklin book," I noticed that mount T-393 (Fig. 1) was labeled "calciothompsonite xl on axinite xs, rhodonite, Franklin NJ" with a secondary label, "xnoto-lite?" (sic). Examination of the specimen revealed tiny white crystal clusters resembling brooms (Fig. 2) on crystals of axinite-(Mn), plus tiny crystals of rhodonite. These bundles of needle-like crystals roughly matched descriptions of calciothomsonite/thomsonite and xonotlite in Charles Palache's 1935 monograph, The Minerals of Franklin and Sterling Hill, Sussex County, New Jersey. Both xonotlite and thomsonite are now known to fluoresce, so the white crystal "brooms" were examined under a UV lamp but proved nonfluorescent. A further diligent search of various Franklin/ Sterling Hill reference works did not find a similar-appearing mineral or paragenesis. To sum up, I was not satisfied with either labeled ID for those tiny white "brooms."

The specimen was taken to the University of Arizona's RRUFF<sup>TM</sup> laboratory for analysis by Raman spectroscopy. As expected, axinite-(Mn) was confirmed (Fig. 3), but the Raman peaks for the white "brooms" strongly suggested siderite. Another scan about two weeks later yielded a 92% match for siderite (Fig. 4). Other carbonates, including calcite and rhodochrosite from non-Franklin localities, were scanned for comparison, but their peaks were not as good a match to those of the supposed calciothomsonite or xonotlite needles on "Doc" Thomas's micromount.

White siderite is rare, but this color is not unknown in carbonates of intermediate composition within the sideriterhodochrosite series. Nevertheless, further examination was desirable to either confirm or dispute the suggestion via Raman spectroscopy that the white broomlike crystals are siderite. The specimen was sent to Professor Ronald Gibbs at the University of Arizona for chemical analysis by EDS (energy-dispersive spectroscopy), which showed the mineral is calciumdominant and contains little iron. Given these findings, the mineral was subjected to a more detailed Raman analysis by Dr. Hexiong Yang, using additional scanning parameters and a carefully focused laser beam. The results proved an exact match for calcite.

Two conclusions are warranted from study of this small specimen. First, white microcrystal clusters of similar appearance to those shown here have often been found in vintage Franklin micromounts, generally sight-identified as either xonotlite or calciothomsonite. In view of recent results, such IDs seem unwarranted. Second, as has long been known, for some mineral species it is often necessary to employ multiple laboratory techniques to conclusively identify them. In this particular case, although chemically pure specimens of siderite, calcite, and rhodochrosite can be distinguished by Raman spectroscopy, difficulties can arise due to peak shifts in chemically intermediate members of these carbonate species. For this reason mineralogists are often skeptical of a mineral ID based on a single laboratory technique and commonly seek additional data.

The author gratefully acknowledges Dr. Hexiong Yang for acquiring the Raman scans, Professor Ronald Gibbs for the EDS work, and Vandall King for photographing the tiny white "brooms" on axinite-(Mn) crystals in mount T-393.



**Figure 3.** Raman spectrum of axinite-(Mn) in the micromount specimen (lower graph, and heavy line in upper graph) compared to RRUFF database reference spectrum for axinite-(Mn) (light line in upper graph).

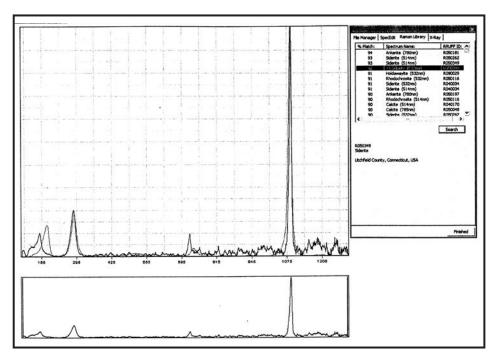


Figure 4. Raman spectrum of the unknown white mineral in the micromount specimen (lower graph, and heavy line in upper graph) compared to a Raman spectrum for siderite (light line in upper graph).

THE PICKING TABLE, VOLUME 58, NO. 2 – FALL 2017

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# New Finds of Genthelvite at Sterling Hill, Ogdensburg, New Jersey

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#### INTRODUCTION

Two newly recognized finds of genthelvite, both from Sterling Hill, are described below. The first is from a specimen recently collected from the Mine Run Dump at Sterling Hill, and the second is from a decades-old collection.

#### FIND NO. 1

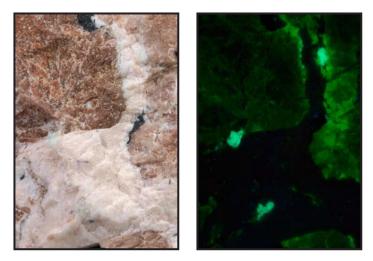
During the April 2016 Super Dig at Sterling Hill, Michael Isaacson, a mineral collector from Ardmore, Pennsylvania, collected a bucket of typical, coarse-grained Sterling Hill zinc ore consisting of tan-brown willemite, white calcite, and black franklinite (Fig. 1). Finding that the willemite did not fluoresce as brightly as he had hoped, he kept three pieces and placed the rest back onto the rock pile. Nearly a year later, while randomly lamping minerals with a longwave (LW) ultraviolet LED flashlight, he noticed that one of the three specimens contained several small grains (and two tiny veins) of a mineral that fluoresced bright green (Fig. 2), a hue distinct from the yellowish-green fluorescence of the associated willemite. These grains under the LW lamp also fluoresced much brighter than the willemite, but the opposite was true under shortwave (SW) and medium-wave (MW) ultraviolet light. This, combined with the pale green color of the mineral in daylight, led Mr. Isaacson to suspect the green-fluorescing mineral was genthelvite, but the matrix was wholly different from that of any other Sterling Hill genthelvite then known.

There the matter rested until April 2017, when Mr. Isaacson again attended the Super Dig and brought the suspected genthelvite specimen to the author, with whom he left it for examination. The specimen was examined via Raman spectroscopy the following day and provided a spectrum that perfectly matched that of known genthelvite (Fig. 3), thereby proving the identity. In all particulars but one—the matrix this new find of genthelvite matches that of other Sterling Hill specimens: The grains are pale green in daylight, of equant form (one appears to be a fragment of a tetrahedral crystal), lack discernable cleavage, and fluoresce bright green LW, but dim green SW and MW.

The specimen was examined closely under a low-power binocular microscope to study the relation of the genthelvite



**Figure 1.** Coarse-grained willemite-franklinite-calcite ore from Sterling Hill, containing three grains of pale green genthelvite, the largest about 3 mm across. The genthelvite grains (circled), one just above the center of the specimen and two in the lower left quadrant, are inconspicuous in daylight but stand out brilliantly under LW ultraviolet light. Michael Isaacson specimen,  $3.0 \times 2.4 \times 1.6$  inches ( $7.5 \times 6 \times 4$  cm). *Earl R. Verbeek photo.* 



**Figure 2.** Detail view of the three genthelvite grains in daylight (left) and under LW ultraviolet light (right). Field of view is 1.7 inches (4.4 cm) high. The genthelvite fluoresces a rich green color, much like that of a traffic light, but this is not a color that most printing inks can satisfactorily duplicate. The actual fluorescence is considerably more saturated than shown here. *Earl R. Verbeek photo.* 

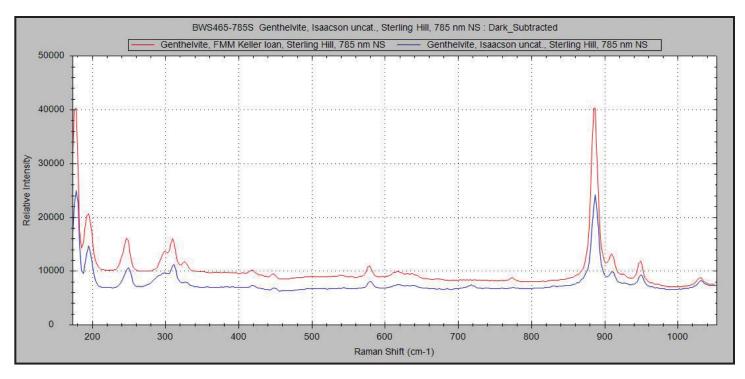


Figure 3. Raman spectra of the Isaacson genthelvite (blue line) compared to that of a reference specimen (red line).

to the other minerals present. The tiny genthelvite veinlets mentioned above, both of them about 10 mm long and less than 1 mm thick, lie within a calcite-filled fracture that contains, within the calcite, several small, broken slivers of franklinite. This fracture is a tiny fault, movement along which opened voids within which hydrothermal fluids later deposited both the calcite and the genthelvite. The genthelvite in this specimen is thus a secondary mineral that formed much later than the primary metamorphic minerals of the host rock, as it has in all other local occurrences of this mineral, both at Sterling Hill and Franklin.

Further study revealed the specimen to be pervaded by dozens of fractures, most of them much smaller than the one containing the genthelvite veinlets, but readily visible at magnifications of 50-100×. These fractures are present in all three primary minerals-willemite, franklinite, and calciteand are of diverse orientation. Some of them appear to have opened along cleavage planes in the willemite, and others are grain-boundary cracks along the contacts between willemite and calcite, willemite and franklinite, or franklinite and calcite. Most are filled with thin seams of white calcite. They are thus easiest to see in franklinite, where they appear as white lines against a black background, and some are readily visible in willemite as well, for the same reason (e.g., lower left part of Fig. 1). Within the calcite matrix, however, they are difficult to follow. Nevertheless, grain-size differences between the primary and fracture-filling calcite, plus thin, patchy films of brightly fluorescent secondary willemite on the fracture

surfaces, allow them to be traced under magnification. All three genthelvite grains lie along such fractures, and two of them, as shown in Figure 2, lie along grain-boundary cracks. Figure 4 shows the largest genthelvite grain astride a grainboundary crack between willemite and calcite.

The significance of these fractures is that, collectively, they allowed hydrothermal fluids to migrate through and react with the host rock. Visible evidence of this process includes discoloration of the willemite along some of the fractures and, as noted above, the deposition of at least three new minerals secondary willemite, calcite, and genthelvite—within and along them. The mottled fluorescence of the primary willemite grains is possibly to be ascribed to hydrothermal alteration as well; the two large grains shown in Figure 1, for example, fluoresce brightest toward their edges and less brightly in the interior.

#### FIND NO. 2

The polished cabochon shown in Figure 5 contains, toward the right side as photographed, two grains of genthelvite, the most prominent measuring  $11 \times 6$  mm in area. Under LW ultraviolet light, the fluorescence perfectly matches that of known genthelvite specimens and is quite different in hue from that of nearby willemite grains, the genthelvite utterly lacking a yellow component to its fluorescence. The fluorescence under SW ultraviolet light is of similar hue but weaker, much weaker than that of finely divided willemite in the breccia

THE PICKING TABLE, VOLUME 58, NO. 2 - FALL 2017



**Figure 4.** The largest genthelvite grain (3 mm across) in the Isaacson specimen. A grain-boundary crack between willemite (top) and calcite (bottom) is visible to either side of the genthelvite. Note, just to the right of the genthelvite grain, the color difference between the thin lens of white, fine-grained, secondary calcite within the grain-boundary crack and the faintly pink primary calcite of the ore. *Earl R. Verbeek photo.* 



**Figure 5.** A prominent grain of pale green genthelvite in breccia matrix from Sterling Hill. The polished cabochon, from the Richard and Elna Hauck collection, measures  $2.4 \times 1.4 \times 0.2$  inches ( $6.2 \times 3.5 \times 0.5$  cm). The red tinge in lower left is not original but is jeweler's rouge from polishing. *Earl R. Verbeek photo.* 

matrix. The rock from which this cabochon was cut is a breccia containing angular fragments of willemite, franklinite, and red-fluorescent calcite in a pale buff, sandy matrix. The matrix is suffused with microscopic grains of secondary hydrothermal willemite that impart to it a bright yellowish-green fluorescence. Although it is difficult to determine the cause of brecciation from such a small specimen, the lack of preferred orientation of the fragments, combined with a lack of any visual evidence of shearing, suggest this is not a fault breccia. Instead it is probably a solution-collapse breccia (see Verbeek, 2015 for a brief explanation), one in which the fragments have been roughly size-sorted by flowing water in a cavern system. This specimen, from the collection of Richard and Elna Hauck, is one of the many cabochons originally in the collection of Floyd Steinmetz of Ogdensburg, N.J.

#### DISCUSSION

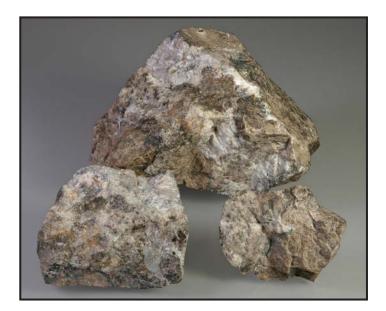
Genthelvite in all specimens known so far, from both Sterling Hill and Franklin, is a secondary mineral that postdates the original peak-metamorphic rocks of the orebodies. The original find at Sterling Hill (Cianciulli and Verbeek, 2003; Leavens et al., 2009) was in a retrograde metamorphic assemblage; to this we can now add hydrothermally altered ore (this paper, plus Verbeek, 2009) and altered solution-collapse breccia. At Franklin, too, genthelvite occurs in secondary assemblages with such hydroxyl-bearing minerals as cummingtonite, nelenite, and serpentine (Cianciulli and Verbeek, 2006). In all of these occurrences, hydrothermally altered willemite may have been the source of the beryllium necessary to form the genthelvite, the ideal composition of which is  $Be_3Zn_4(SiO_4)_3S$ . Beryllium in minor amounts is known to be hosted by local willemite, as noted by Dunn (1995, p. 280), citing analyses performed by Dr. Jun Ito at Harvard University. Zinc and silica were available from the same source, and possible sources of sulfur include disseminated sulfide minerals in the marble, plus primary sphalerite locally present in the ores. As noted by many observers over the years, hydrothermal redistribution of elements already present in the Sterling Hill and Franklin orebodies gave rise, over time, to the many dozens of secondary minerals that have made these deposits famous among mineralogists for more than two centuries.

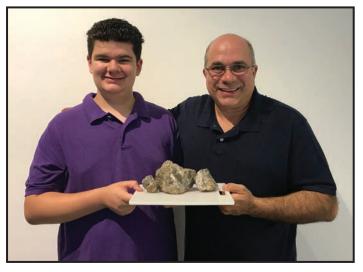
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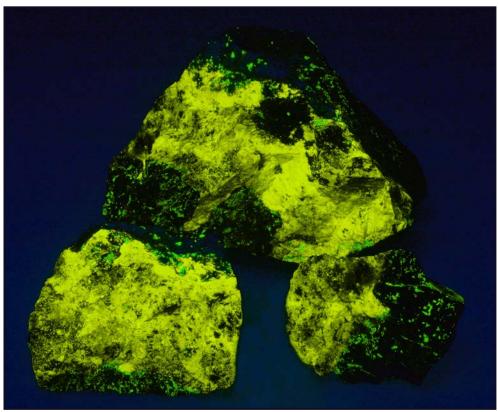
# **The Super Diggg Esperite**

This spring, during the Super Diggg sponsored by the Delaware Valley Earth Science Society at the Franklin Mineral Museum, the huge pile of rocks that nine years ago had been trucked to the Buckwheat Dump from the site of Mill No. 2 (a.k.a. the Palmer Mill) was opened to collectors for the first time. Nearly 220 collectors swarmed over that pile on Saturday, April 29. As expected, some of them found hardystonite, clinohedrite, etc. in addition to the usual willemite and calcite, but one lucky father-and-son team found the esperite specimen shown here. Jim and Charlie Breidenbach, of Walnutport, Pennsylvania, said they were new to the hobby but figured they had something special when they broke a rock into three pieces and saw bright lemon-yellow fluorescence staring back at them. Their find is one of the largest and richest esperite specimens to ever come from the Mill Site. Talk about "beginner's luck"! The largest specimen measures  $4.8 \times 3.8 \times 3.1$  inches  $(12 \times 9.5 \times 8 \text{ cm})$ .





Charlie and Jim Briedenbach



#### THE PICKING TABLE, VOLUME 58, NO. 2 - FALL 2017

# **Chemical Weathering of Calcitic Zinc Ore at Sterling Hill, New Jersey**

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#### INTRODUCTION

The Sterling Hill zinc-iron-manganese orebody, a sedimentary exhalative deposit hosted by the structurally complex, Late Proterozoic Franklin Marble, has long been famous for its mining history, mineralogical complexity, and spectacular fluorescent minerals. The normal ore consists of variable proportions of franklinite, willemite, zincite, and calcite. Of these, calcite and willemite generally fluoresce brightly (red and green, respectively), but franklinite is nonfluorescent, and so is nearly all zincite. The fluorescence of the calcite, the environmental degradation of which is the main subject of this paper, is due to minor amounts of divalent manganese (Mn<sup>2+</sup>) substituting for calcium (Ca<sup>2+</sup>). Redfluorescent, manganoan calcite is common within and near the Sterling Hill orebody, but beyond about 6 ft (2 m) from the ore the manganese content of the host rock falls to zero and the calcite does not fluoresce.

It has long been known that the local manganoan calcite, which on fresh surfaces is pale gray to white, develops a pronounced brown coating when left outdoors (Fig. 1), and that development of this coating is accompanied by a marked decrease in brightness of the red fluorescence. Calcite lacking manganese develops no such coating. It has also long been realized that this coating can, in some cases, develop quickly. Specimens of calcitic ore freshly excavated from the Fill Quarry at Sterling Hill, for example, showed noticeable yellowing after only three days. Such observations have suggested to many that exposure to sunlight, through photochemical oxidation of manganese, is a major factor in development of the brown coating and dimming of the calcite fluorescence. However, blocks of ore lying outdoors have not routinely been noted to show different levels of browning on northfacing versus south-facing surfaces, casting some doubt on the importance of light to the browning process. Moreover, brown coatings on calcite have also been observed to form, albeit slowly, on specimens that have lain for some years in storage sheds outdoors, shielded from light. Conversely, specimens that for many years have routinely been exposed to visible and ultraviolet light in people's homes, in a stable, temperaturecontrolled environment, commonly show no hint of a brown



**Figure 1.** A large specimen of weathered, coarse-grained, manganoan calcite from Sterling Hill, showing the bronzy brown coating that develops upon weathering outdoors.

coating or degradation of fluorescence. These observations suggest a complex interplay of multiple factors is involved in the browning of the calcite—but which factors? And what is their relative importance?

#### **IMPETUS FOR STUDY**

The initial impetus for this study, beyond scientific curiosity, was primarily economic, as development of the brown coating has adversely affected several projects of the Sterling Hill Mining Museum. Chief among these is the Pillar of Light project, so-named after a large, remnant pillar of ore exposed at the surface along the west wall of the Fill Quarry at Sterling Hill. This ore pillar, about 50 ft tall, 20 ft thick, and 40 ft long, still fluoresces spectacularly under shortwave ultraviolet light (Fig. 2), but the fluorescence grows dimmer year by year. The fluorescence is brightest along the south wall and within a cavelike opening along the north wall, where, in both places, recent production of ore specimens exposed fresh surfaces. The weathered ore along the rest of the north wall,

THE PICKING TABLE, VOLUME 58, NO. 2 - FALL 2017

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Figure 2. The north face of the Pillar of Light in the Fill Quarry at Sterling Hill, as seen at night under shortwave ultraviolet light. *Bryan Duggan photo, December 2009.* 

and along the broad east wall of the pillar, fluoresces much less brightly. For some years it was hoped that a shell could be constructed around this pillar to shelter it from light and precipitation, or that some means could be found to slow or perhaps stop the browning of the calcite. Similarly, viewing of fluorescent ore underground, in the Rainbow Room of the mine, has been adversely affected by the inexorable dimming of fluorescence as the calcite gradually darkens. The exposed face of ore was chemically cleaned less than a decade ago, but is once again brown, and its fluorescence much diminished. And finally, nearly all of the ore on the Mine Run Dump at Sterling Hill has, since its placement there about 1990, turned dark brown, which reduces the value of that rock to specimen collectors and necessitates breaking the rock into ever smaller pieces. A need thus existed to determine the physical and chemical nature of the brown coating and the mechanism of its formation, in hopes of establishing a procedure to either stop or slow the onset of alteration, or at least determine the most effective method for restoring the fluorescence.

#### SCOPE OF STUDY

Our study of the weathering of calcite at Sterling Hill is best considered in two parts. The first involved collecting fresh samples of calcitic ore, subjecting those samples to a variety of controlled environmental factors, and measuring the degradation, if any, of their fluorescence. This simple, direct approach had been suggested numerous times in the past, but not conducted in an organized fashion until now. The second approach, as yet barely begun, involves a detailed microchemical study of the dark brown coating on a naturally weathered specimen to identify its constituents, in hopes that this information will lead to some understanding of the processes involved in its formation. Here we report some of the initial findings.

#### **EXPERIMENTAL METHODS**

An ideal opportunity for collecting fresh ore samples for study occurred during the spring and summer of 2013, when John Kolic (former miner at Sterling Hill) began excavation of the base of the east wall of the Fill Quarry ore pillar. Ore from this pillar shows a wide range in calcite content, locally as much as 70%, with the remaining constituents being disseminated franklinite, willemite, tephroite, sonolite, and zincite. Numerous large slabs of this ore, showing consistent mineralogical concentrations, were collected and later broken into smaller pieces to be used for experimentation. One additional sample was taken from a large, loose block of calcite with 10% disseminated franklinite from an area near the undercut stope along the west side of the Passaic Pit. The samples were then labeled according to their constituent minerals in descending order of content; for example, C<sub>50</sub>F<sub>25</sub>W<sub>15</sub>T<sub>5</sub>S<sub>5</sub> indicates a specimen containing 50% calcite, 25% franklinite, 15% willemite, 5% tephroite, and 5% sonolite.

Upon return to the testing facility, the initial (fresh surface) brightness of fluorescence of each sample was measured to establish baseline values for later comparison to the brightness values after the samples had been subjected to a variety of environmental conditions. For this purpose we used, as an ultraviolet (UV) light source, a 9-watt Way Too Cool handheld shortwave UV light, held at a standard distance of 15 cm from each sample. The samples were placed one at a time inside a shadow box lined with black construction paper and then placed in a completely dark room, where the brightness of fluorescence was measured using a Konica/Minolta light meter held at 10 cm, and at a slight angle from the incident UV source so as not to block any UV absorption. The fluorescent response measurements were taken for 5 seconds each over a surface area of about 25 cm<sup>2</sup>. Three separate readings were taken for the same area of each specimen and then averaged. The light meter measurements, which are accurate to 0.1 EV (exposure value), were then converted to foot-candles, a measurement more commonly understood. In this way we developed a quantitative record of changes in our samples, which we reasoned was more accurate than simply describing changes in the daylight coloration (browning) of the samples in subjective color terms, or by attempting to describe decreases in the brightness of fluorescence in equally subjective terms.

After the initial fluorescent brightness had been recorded for each sample, the samples were treated as follows:

- A. Four samples were vacuum-sealed and placed outdoors for three years.
- B. Four additional samples were also placed outdoors for three years, but left unwrapped for full exposure to atmospheric conditions.
- C. Four samples were vacuum-sealed and placed indoors, in a dark, closed compartment at 15° C, 50% humidity for three years.
- D. Four samples were treated as in (C), but left unwrapped.
- E. One sample was 60% submerged outdoors in tap water, with the remaining 40% left exposed to the air just above the water surface.
- F. One sample was sandblasted and placed outdoors.
- G. One sample was placed in a convection oven indoors at 55° C and sprayed with acidic water daily.
- H. One sample was placed in a convection oven as above, but kept dry.

At intervals ranging from five months to one year, the samples were again measured to document any changes in their brightness of fluorescence. Before each series of readings, a standard mineral sample was measured to ensure that there was no change in the sensitivity of the light meter. This standard sample, with composition  $C_{50}F_{35}W_{10}T_5$ , was taken from the excavation site at the same time as the other samples, and was vacuum-sealed and kept in a dark place at a temperature of 15° C and 50% relative humidity. The seal was broken for each set of readings, and then the standard was again vacuum-sealed and stored as before. For all series of measurements, three brightness readings were taken of each sample and then averaged to document their fluorescence. The results from this experiment are documented in Tables 1 and 2 and discussed below.

#### **DISCUSSION OF RESULTS**

Review of the data over a three-year period as listed in Tables 1 and 2 clearly indicates that samples which were vacuumsealed and placed in a temperature- and humidity-controlled environment indoors, in the dark (samples 1-4), showed no degradation in UV response. Similarly, samples that were not vacuum-sealed (nos. 5-8) showed no measurable change over the same time period. These results are in general accord with common experience, that storage of Franklin-Sterling Hill fluorescent minerals in the stable, controlled environments of people's homes does not, at least in the short term, result in any measurable decline in their brightness of fluorescence.

Samples left in the open (unwrapped) outdoors, and thus fully and continuously exposed to atmospheric and solar conditions (nos. 13-16), showed large and steady declines in fluorescence at all stages of the experiment. The fluorescence of these four samples decreased 5.8% to 9.5% (avg. 7.3%) after only 35 days, 29% to 34% at the end of two years, and 35% to 43% by the end of the third year. Samples that were vacuum-sealed (nos. 9-12) showed no detectable degradation in UV response during the first three measurement cycles of the first year, but then experienced declines totaling 18% to 23% by the end of the second year-significantly less than that of the unsealed samples, but still substantial. We attribute the lack of first-year degradation and its onset sometime during the second year to eventual loss of the vacuum seals under harsh weather conditions outdoors, which allowed air and moisture to seep into the failed bags. Following breach of the vacuum seals, this part of the experiment was terminated, and no data were gathered for the third year.

The results for sample 17, a large plate of ore partly submerged in water and placed outdoors, were interesting. The submerged portion showed no change in UV response for the first seven months, but by the end of the first year the fluorescence had declined by almost 15%. This sudden and steep decline was due mostly to development of an algal slime on the sample surface. After removal of the slime with bleach, the actual decline was shown to be only 2%. During the following two years, the measured declines were 10% and 20%, respectively. It thus appears that exposure to *atmospheric* oxygen is not necessary for degradation of calcite fluorescence to occur, but that dissolved oxygen in water can have a similar effect.

The above-water portion of this same sample showed no measurable decline during the first two months, but a steady decline over longer time periods thereafter. After three years, the UV response had dropped a full 35% from its original value, an amount comparable to that of samples 13-16 that had been left unwrapped outdoors. Although these results seemingly suggest that exposure to atmospheric oxygen causes higher rates of calcite degradation than exposure to dissolved oxygen in water, such may not be the case. The pH of the water ranged from 6.2 (initial value of the well water used to submerge the sample) to 5.8, declining with time due to rainwater that fell into the bucket. The mildly acidic water might thus have continually "freshened" the submerged portion of the sample surface by progressively dissolving some of the calcite.

The sandblasted sample (no. 18) held no surprises. Though sandblasting of weathered calcite surfaces restores the fluorescence by physical removal of the weathered coating, such practice also greatly accelerates any subsequent chemical

THE PICKING TABLE, VOLUME 58, NO. 2 - FALL 2017

No.	<b>Composition</b> <sup>a</sup>	FC initial 5/16/13	FC 7/2013	FC 12/2013	FC 5/10/14	FC 5/16/15	FC 5/01/16				
Vacuum sealed, stored inside. <sup>b</sup>											
1	$C_{40}F_{20}S_{20}T_{20}$	5.69	NC	NC	NC	NC	NC				
2	$C_{50}F_{35}W_{10}TS_5$	7.00	NC	NC	NC	NC	NC				
3	$C_{30}S_{20}T_{20}F_{20}W_{10}$	6.13	NC	NC	NC	NC	NC				
4	$C_{60}F_{40}$	8.05	NC	NC	NC	NC	NC				
Not sealed, stored inside.											
5	$C_{40}F_{20}S_{20}T_{20}$	5.69	NC	NC	NC	NC	4.96				
6	$C_{50}F_{25}W_{15}TS_{10}$	7.00	NC	NC	NC	NC	6.12				
7	$C_{_{30}}S_{_{20}}T_{_{20}}F_{_{20}}W_{_{10}}$	6.13	NC	NC	NC	NC	5.69				
8	$C_{70}F_{30}$	12.25	NC	NC	NC	NC	10.51				
Vacuum sealed, placed outside. <sup>b</sup>											
9	$C_{40}F_{20}S_{20}T_{20}$	5.69	NC	NC	NC	4.96	ND				
10	$C_{50}F_{25}W_{15}TS_{10}$	7.43	NC	NC	NC	6.56	ND				
11	$C_{35}S_{20}W_{20}T_{15}F_{10}$	6.13	NC	NC	NC	5.59	ND				
12	$C_{60}F_{40}$	10.51	NC	NC	NC	8.05	ND				
Not sealed, placed outside.											
13	$C_{50}F_{20}S_{20}T_{10}$	6.12	5.69	4.98	4.34	4.03	3.72				
14	$C_{55}F_{25}W_{15}TS_5$	7.43	7.00	6.56	5.69	4.96	4.65				
15	$C_{30}S_{20}T_{20}F_{20}W_{10}$	6.56	6.12	5.69	5.26	4.65	4.34				
16	$C_{65}F_{35}$	11.38	10.51	9.28	8.05	7.43	6.56				

#### **Table 1.** Change in SW fluorescent response over time. FC = foot-candles, NC = no change; ND = no data.

<sup>a</sup> C=calcite, F=franklinite, S=sonolite, T=tephroite, W=willemite.

<sup>b</sup> Seal had to be broken and then resealed after each reading.

Table 2. Change in SW fluorescent response over time for samples exposed to unique conditions.

No.	Composition	FC initial 5/16/13	FC 7/2013	FC 12/2013	FC 5/10/14	FC 5/16/15	FC 5/01/16			
17	$C_{50}T_{30}F_{20}$ (submerged)	8.22	NC	NC	8.05ª	7.43	6.56			
17	$C_{50}T_{30}F_{20}$ (above water line)	8.22	NC	8.05	7.43	6.12	5.26			
18	$C_{50}W_{25}F_{25}$ (sandblasted)	14.86	14.86 Declined to 7.00 in three weeks							
19	$C_{60}F_{30}W_{10}$ (acid spray daily)	5.69 Declined to 4.65 in 10 days, and to 3.72 by 7/2013 <sup>a</sup>								
20	$C_{60}F_{30}W_{10}$ (kept dry)	5.69	5.69 Declined to 4.65 in 20 days, and to 4.26 by 7/2013 <sup>a</sup>							

<sup>a</sup> Convection oven phase of experiment was stopped July 2013 due to cost.

weathering. This is due to micropitting of the calcite due to high-velocity impacts by the abrasive particles used in sandblasting. Collectively these micropits greatly increase the surface area of the sample exposed to weathering, and thus the rate of any chemical reactions that occur at that surface. Sandblasting is the equivalent of physical weathering, but instead of weathering over thousands of years, physical erosion effects are rendered in a matter of minutes.

The samples placed in a convection oven (nos. 19-20) were derived from a single mass that was broken to produce two pieces of equal size. Both were heated to a constant temperature of 55° C (130° F) continuously for more than two months, at which time this portion of the experiment was terminated due to expense. A temperature of 55° C was chosen as indicative of rock-surface temperatures along the west wall of the Fill Quarry, adjacent to the ore pillar, during sunny days from noon to about 2:00 PM, from late June to early August.\* The chamber of the convection oven was kept unexposed to sunlight and incandescent light for the duration of the experiment. As shown in Table 2, one sample was sprayed daily with mildly acidic water of pH 5.6-5.8 to simulate wetting by rain in the natural environment, and the second sample was kept dry. After only ten days, the sprayed sample showed a degradation in UV response of 18%, and after two months the decline had increased to 35%, the equivalent of leaving similar samples outdoors for three years. The dry sample, too, showed significant degradation, but only about one-third as much; after two months its UV response had declined by 13%. As a general (but rough) rule, the rate of chemical reactions doubles for every 10° C increase in temperature, so the greatly accelerated rate of degradation of the sample surfaces upon heating was expected.

The greater rate of degradation for the sprayed vs. dry sample is likely due to two effects. First, the presence of a thin film of water, in contact with the specimen on one side and a limitless supply of atmospheric oxygen on the other, would have accelerated chemical reactions between them, due to the ease with which ions can freely move large distances (on a molecular scale) through a fluid. We thus expect reaction rates on periodically wetted samples to be significantly greater than on constantly dry ones. Second, during the time the acidic water was in contact with the sample surface, it was likely etching the calcite along cleavage planes, thereby increasing the surface area of the sample. Unlike sample 17, however-the one immersed in the bucket-any calcite that dissolved from the sample when wet was redeposited when it dried. Degradation of the calcite surface was thus cumulative because the degradation products were not removed.

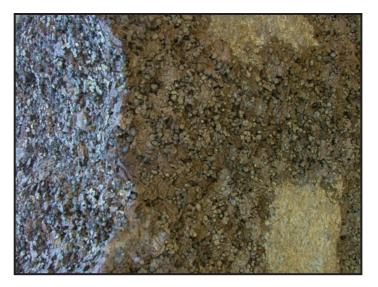
#### SUMMARY, PHASE 1 RESULTS

The results of this three-year simple set of experiments, combined with decades of informal observation, show clearly that combined exposure to atmospheric oxygen, precipitation, and solar radiation is detrimental to calcite fluorescence and results in high rates of degradation. Samples left unprotected outdoors, as on the Mine Run Dump at Sterling Hill, plus samples 13-16 of our sample set, show visible signs of surface browning within days to weeks, and steady declines in fluorescence as documented in Table 1. Comparable samples left exposed to the air, but not to precipitation and to lesser amounts of light, as in those parts of the Sterling Mine where ore is exposed, weather less quickly, though cooler temperatures within the mine during much of the year are also a factor.

High temperatures greatly accelerate the chemical weathering of exposed calcite surfaces, and surfaces that are periodically wetted rather than permanently dry seem also to weather at higher rates. This latter effect probably explains why specimens kept in the dark, but in an outdoor shed or garage, gradually develop a brown coating, whereas similar specimens stored indoors in the dark generally do not. Specimens stored in outdoor sheds experience significant temperature variations daily, and whenever the air temperature sinks below the dew point, as commonly happens at night (especially in spring and fall), a film of condensed moisture will form on their surfaces. This film, as explained previously, acts to increase weathering rates. Moreover, summer temperatures in outdoor storage facilities can exceed 32° C (90° F) for extended periods, sometimes with humidity in excess of 80% - conditions unlikely to be reached indoors, where temperatures remain fairly constant throughout the year, with relative humidity levels generally in the 40% to 60% range. Thus, the high temperature spikes in outdoor environments, coupled with high humidity and periodic wetting of specimen surfaces by condensation, are conducive to more chemical weathering than would occur indoors, even though the average temperature outdoors, on an annual basis (13° C, or 56° F) is about 7° C less than the average indoor temperature in most households (about 20° C, or 68° F).

The possible effect of light is difficult to assess, especially since sunlight, indoor light bulbs, and the fluorescent lamps used by collectors produce quite different wavelength distributions of light. Exposure to sunlight alone, however, seems not to cause degradation of the calcite, as shown by the lack of change, for more than a full year, in all four calcite samples that had been vacuum-sealed and placed outside, until harsh

<sup>\*</sup> Temperature data were obtained by three bimetal thermometers placed at key locations along the west wall of the Fill Quarry during the summers of 2013, 2014, and 2015.



**Figure 3.** Rough surface of a block of franklinite-calcite zinc ore, showing franklinite grains standing in strong relief due to dissolution of the enclosing calcite. Franklinite grains freed by weathering have, in places, accumulated in deposits several inches thick at the base of long-exposed blocks of ore.



**Figure 4.** A fragment taken from a weathered block of lean franklinitecalcite ore, showing the dark, rough, weathered surface and relatively fresh calcite beneath.

weather ultimately resulted in failure of the seals. Similarly, local specimens that for decades have been on display in the Franklin Mineral Museum, in one room under incandescent light and in another under shortwave UV light, display no obvious visible change in their appearance or fluorescence. Many collectors can cite similar experiences. Exposure of unprotected outdoor specimens to sunlight, however, may accelerate their degradation indirectly, through heating of the sample surfaces.

We conclude that elevated temperature in the presence of oxygen is the primary driver of the chemical reactions that result in browning of the calcite and decline in its fluorescence. Exposure to oxygenated, mildly acidic water (acid rain) and/ or high atmospheric humidity is a secondary but important driver as well. A third variable, of course, is time, for time is necessary for reaction kinetics to progress toward end products. The longer that manganoan calcite ore samples are exposed to warm temperatures, acidic moisture, and oxygen, the more degraded the UV response becomes. In addition, chemical erosion can become so severe as to erode the surfaces of many calcite grains into deep pits, or in some cases to completely dissolve the calcite (Fig. 3).

#### MICROCHEMICAL STUDY: INITIAL RESULTS

The results from the first phase of this study, discussed above, identified some of the factors that promote chemical weathering of calcite at Sterling Hill, but do not reveal the specific mechanisms of the weathering process at the molecular level. Knowledge of such mechanisms should prove useful to efforts to restore weathered, poorly fluorescent surfaces to their former brightness, and to either prevent or mitigate the effects of any future weathering. To that end we attempted to determine the chemical and mineralogical nature of the brown coatings on weathered calcite as a first step in understanding how they form.

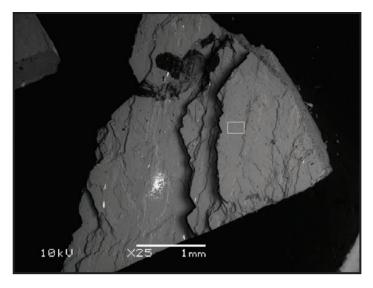
A sample of nearly pure calcite with only 5% franklinite, taken from a large float block, was selected for microchemical analysis because it broke in such a way that a fresh, newly exposed surface of manganoan calcite lay in immediate contact with a heavily altered weathering rind (Fig. 4), thereby affording an ideal opportunity to compare the bulk chemistry, texture, and mineralogy of both surfaces. In late December 2014, this sample was sent to RJ Lee Group in Monroeville, Pennsylvania, where microchemical data were obtained via energy dispersive X-ray spectrometry (EDS) and electron backscatter diffraction (EBSD) techniques.

Baseline results from a small chip of unaltered calcite are shown in Figures 5 and 6. The cleavage surfaces of the freshly broken chip are smooth, planar, and of uniform appearance in the EBSD image of Figure 5 (note the 1-mm scale bar). The small rectangle indicates the area where an EDS spectrum was obtained. Although standardless analyses of unprepared (rough) samples are semiquantitative only, the results (Fig. 6) conform well to that of manganoan calcite, with the atomic percent oxygen (53.91%) close to the required three times the total amount of ions in the calcium site (19.81%, = Ca + Mn + Mg). The manganese content of 3.80 wt. percent is well within the common range for fluorescent calcite from Sterling Hill. The data for two other chips of freshly broken calcite

THE PICKING TABLE, VOLUME 58, NO. 2 - FALL 2017

are similar, with the contents of (Ca + Mn + Mg), C, and O in approximate 1:1:3 ratios in atomic percent. Two of those chips show small amounts of lead, a known trace element in Sterling Mine calcite (Dunn, 1995, p. 282), and one contains a small amount of tungsten.

The results from a weathered surface on a portion of a second chip of calcite from the same specimen are shown in Figures 7 through 9. In Figure 7, at low magnification, the weathered portion is the mottled area just above the 500 µm (0.5 mm) scale bar. A detailed view of part of this area (Fig. 8) reveals the rough, chemically weathered nature of this surface, with the varied shades of gray indicating chemical inhomogeneity. In this image, the dark, rough-surfaced aggregates are areas where low-density material has accumulated (probably due to dissolution and redeposition of carbonate material), and the pale gray to white areas indicate areas of denser, more metalrich material. The small white rectangle near the right edge of this image shows where a chemical analysis (Fig. 9) was obtained of one of these areas of metal enrichment. Compared to the analysis of Figure 6, this area shows (a) greater chemical complexity, with elevated Zn, Pb, and W all evident in this material; (b) a much-elevated content of Mn, and



**Figure 5.** Scanning electron microscope (SEM) image of a small chip of calcite from the specimen shown in Figure 4. The rhombohedral cleavage directions of the calcite are clearly visible. The white rectangle at right, on a smooth, fresh cleavage face, indicates the area selected for chemical analysis (see Fig. 6). The bright white patch on a different cleavage face (lower left of chip) shows where weathering has occurred; this area too was analyzed.

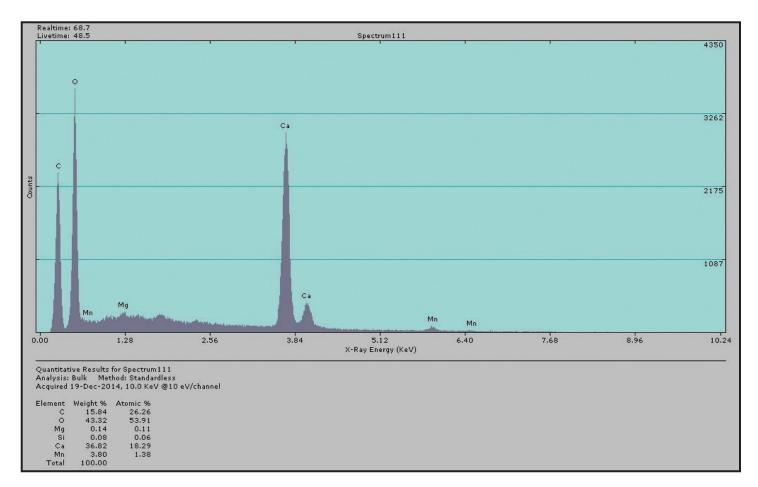
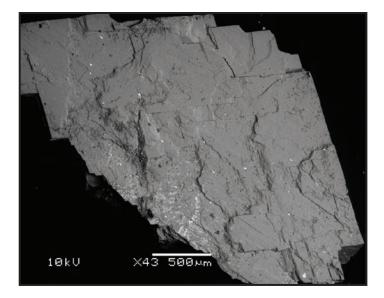
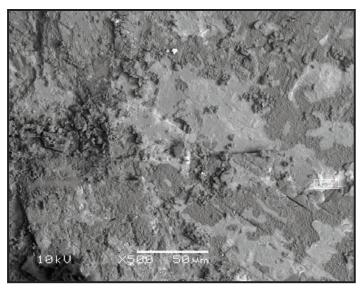


Figure 6. EDS results for the area of unweathered calcite shown in Figure 5. The chemical analysis is that of a manganoan calcite.

#### THE PICKING TABLE, VOLUME 58, NO. 2 – FALL 2017



**Figure 7.** A chip of calcite showing weathered cleavage surfaces (brighter areas above scale bar). Note that 500  $\mu$ m is equivalent to 0.5 mm. A magnified view of a portion of this same surface is shown in Figure 8.



**Figure 8.** Detail view of a portion of the weathered cleavage surfaces shown in Figure 7. Note the rough surface where new mineral coatings have formed, and the narrow clefts (lower right) due to dissolution of the underlying calcite along cleavage planes. White rectangle at far right indicates area of chemical analysis shown in Figure 9. Scale bar of 50  $\mu$ m is equivalent to 0.05 mm.

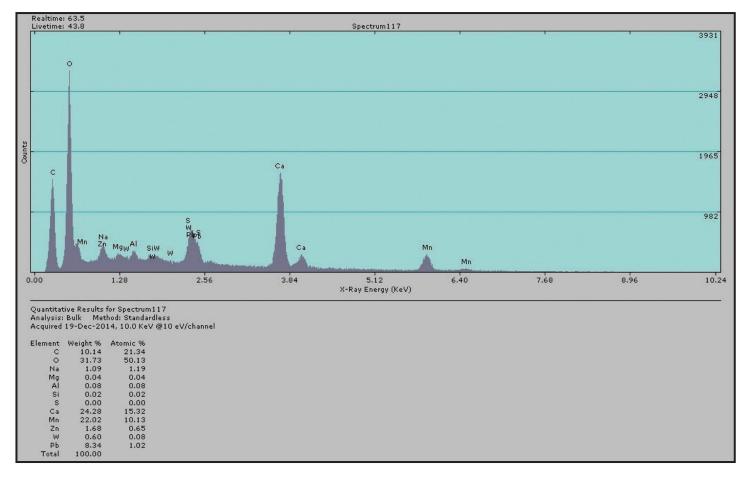
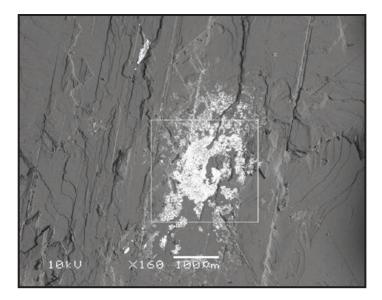


Figure 9. Chemical composition of the coating on the weathered calcite surface shown in Figure 8 (white rectangle). Elevated contents of Mn, Zn, Pb, and W are evident with respect to the composition of fresh, unweathered calcite (cf. Fig. 6).

#### THE PICKING TABLE, VOLUME 58, NO. 2 – FALL 2017



**Figure 10.** Detail view of part of the same calcite fragment shown in Figure 5, showing a patchy coating on a weathered portion of that fragment. The 100- $\mu$ m scale bar is equivalent in length to 0.1 mm.

(c) a corresponding marked decline in Ca content. The overall chemistry is still dominantly that of a carbonate mineral, but with a much different composition from its precursor calcite, and with an elevated metal content suggestive of the presence of additional mineral phases. Similar results were obtained for other such areas of weathered calcite surfaces (Figs. 10 and 11).

Whether the additional manganese, plus the lead, zinc, and tungsten, were precipitated as simple or mixed oxides, or as cryptocrystalline material, or are contained partly in secondary carbonates, could not be determined from the RJ Lee Group data because the observed material is in micron-sized particles, and none of the weathered surfaces produced usable EBSD patterns. Determination of any additional phases present is a daunting challenge and an opportunity for future study. Nevertheless, it is well known that calcite dissolves readily in mildly acidic rainwater, that the Mn<sup>2+</sup> ions so freed from the calcite lattice oxidize to Mn<sup>3+</sup> in the presence of atmospheric oxygen, and that, in many regions of the world, the manganese is reprecipitated locally as secondary manganese minerals (Liu and Broecker, 2000; Corathers and Machamer, 2006).

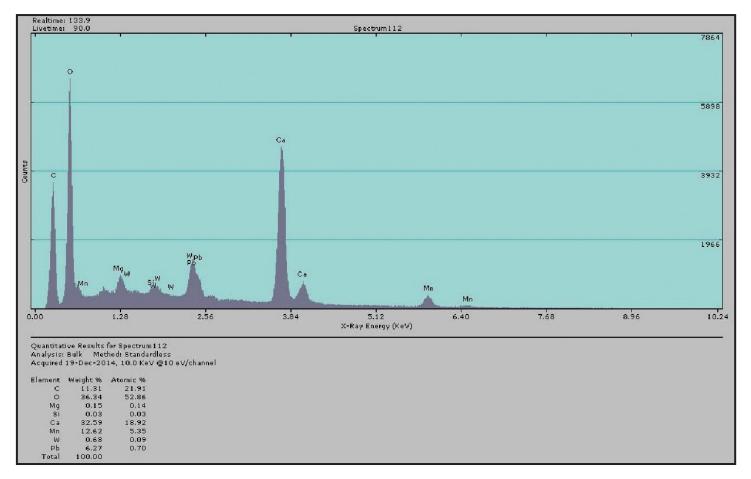


Figure 11. Chemical composition of the coating shown in Figure 10. Elevated contents of Mn, Pb, and W are evident with respect to the composition of fresh, unweathered calcite (cf. Fig. 6).

#### THE PICKING TABLE, VOLUME 58, NO. 2 – FALL 2017

Most such Mn3+-bearing minerals are brown or black; "desert varnish" and the dark coatings that develop on country rock near base-metal ore deposits are common examples. We thus presume that a similar process of manganese dissolution, oxidation, and reprecipitation has taken place at Sterling Hill to produce the brown surfaces on exposed rock in and near the orebody, and that the brown material is not simply discolored calcite, but coatings of secondary manganese minerals whose identities have yet to be determined. Some of the elevated contents of zinc, lead, and tungsten in these films could have been derived from local calcite, but chemical leaching of nearby willemite, tephroite, zincite, ± franklinite are also possible sources. The presence of tungsten is particularly interesting, given that tungsten in amounts ranging from 528 to 983 ppm was reported in four of five samples of bulk Sterling Mine ore analyzed in 2009 (data and specimens on file in Franklin Mineral Museum).

#### MITIGATION AND RESTORATION OF FLUORESCENCE

The gradual development of a nonfluorescent film of secondary manganese minerals on exposed surfaces of fluorescent calcite at Franklin and Sterling Hill represents a challenge to all who wish to protect that fluorescence, whether it be of large surfaces such as that of the Pillar of Light or the Rainbow Room at Sterling Hill, or of individual specimens in a personal collection. Similarly, considerable interest exists in methods of reversing the deleterious effects of weathering and restoring the original fluorescence.

Fortunately for specimen collectors, methods to "deweather" mineral specimens and restore their fluorescence are widely available. The first to appear on the local scene was a solution developed by Dr. Warren Miller, longtime collector of the local fluorescent minerals. Warren is a chemist who, years ago, formulated a solution, its composition still proprietary, for removing the brown coating from weathered specimens. It works quite well for specimens that are mildly to moderately discolored, but there is no way to restore deeply weathered, solution-etched mineral specimens to their original condition. In recent years another, almost equally effective, and inexpensive solution was developed, consisting of equal parts of vinegar and hydrogen peroxide (the 3% topical solution widely available in drug stores). Caution is advised in using these solutions to ensure they will not attack a mineral of interest; both, for example, quickly dissolve clinohedrite, and the acidic vinegar solution will dissolve calcite as well if the specimen is immersed in it for more than a brief period. Moreover, hydrogen peroxide is a powerful oxidant and potential fire hazard, for it releases oxygen when mixed with water. The mild solutions sold in drug stores, however, present little hazard.

Three other topical treatments were recently investigated by the primary author of this paper. One is a slurry/paste (hereafter referred to as Chem-OV) composed of sodium bicarbonate (baking soda), hydrogen peroxide, and potassium bitartrate (cream of tartar) in the ratio of 5:2:1. This slurry, when used on samples showing only the beginning signs of weathering, resulted in 100% removal of the weathered coating and caused no noticeable etching of the cleaned surfaces. The slurry was simply brushed on the surfaces of test samples, left in place for five minutes, and then washed off with pH-neutral water. More rigorous treatment was necessary for samples showing moderate weathering, as evidenced by their iridescent, light brown color and faint pitting of their surfaces. Submergence of such samples in the Chem-OV solution for 10 to 15 minutes, followed by washing and drying, and then repeating this treatment three or four more times reduced the weathered coating by 75% to 80%, but the cleaned surfaces displayed a slightly "frosted" appearance due to additional chemical etching of the calcite. Treatment of samples that showed advanced stages of oxidation, evidenced by a chocolate to dark brown coating and severely pitted surfaces, required reaction times on the order of days, but results were unsatisfactory.

In summary, Chem-OV shows promise in removing surface coatings from weathered calcite, but only for lightly weathered examples. A delivery system for treatment of large surfaces might consist simply of a pressure washer on a low power setting. Caution is advised, however, because the slurry liberates carbon dioxide and oxygen, and because it also produces caustic sodium hydroxide. The treated area must be liberally flushed with fresh water after treatment.

The second topical treatment, Diedrich 940, an industrial product manufactured by Diedrich Technologies Inc., rendered a separate, deeply weathered calcite surface 70% to 80% stain free. However, the product had to be applied numerous times, followed by prolonged flushing with fresh water. Disadvantages of Diedrich 940 are its cost, caustic components, and the fact that it cannot be shipped via UPS.

Waller Solution, the third mixture tested, is composed of sodium hydrosulfite, sodium bicarbonate, and sodium citrate in a ratio of approximately 1:1:2. This mixture is similar to Super Iron Out, widely available in stores such as Home Depot. Super Iron Out is effective in removing iron stains from a wide range of minerals, including calcite, though most commonly it is used on iron-stained quartz. Test results on the manganiferous surface coatings on weathered calcite from Sterling Hill, however, proved disappointing; the Waller Solution reduced the surface stains by only a small amount.

In general, the use of any chemical solvent to remove weathered coatings from calcite requires caution in mixing and application, as volatile products are often produced, and

THE PICKING TABLE, VOLUME 58, NO. 2 - FALL 2017

some of the components and reactants are harmful to humans. Users of such chemicals should consider consulting the MSDS (Materials Safety Data Sheet), widely available on the Internet, to become familiar with the potential hazards involved and the safety precautions to be observed.

Most of the treatments here discussed are viable and cost-effective for individual mineral specimens and small exposures, such as that in the Rainbow Room at Sterling Hill, but their practicality and cost-effectiveness decrease rapidly as the size of the affected area increases, particularly in areas of continuing exposure to the atmosphere, as in the ore pillar in the Fill Quarry at Sterling Hill. In outdoor areas, any method that removes the surface coating of manganese minerals while simultaneously attacking the underlying calcite will, as previously mentioned, result in accelerated weathering thereafter, due to etching and concomitant increase in exposed surface area of the calcite. Such methods are doomed to almost immediate failure.

#### **PREVENTIVE MAINTENANCE**

It is axiomatic that prevention of fluorescence degradation is preferable to its mitigation through any of the means discussed above. Suppression of chemical weathering is probably not cost-effective for large, outdoor exposures such as the Pillar of Light, but exposures underground, such as those in the "Rainbow Room" and in the lower stope at Sterling Hill, can be protected by compartmentalizing those areas to control air flow and lower the humidity to the degree practical. For indoor areas the situation is far simpler, and such measures as keeping temperatures fairly constant (58° to 68° F), minimizing the flow of moist air, and keeping mineral specimens out of direct sunlight (to avoid heating of mineral surfaces) should prove effective. Measurements of the brightness of fluorescence of selected specimens might, in some cases, be desired as baseline data to compare to future values to monitor changes over time.

#### CONCLUSIONS

The results from the SEM and EBSD studies bear out that dissolution of impure, manganoan calcite by mildly acidic rainwater frees metals such as Mn, Pb, Zn, and W into solution, which are then incorporated into coatings precipitated on exposed, solution-etched calcite surfaces. Chemical breakdown of other nearby minerals, including willemite, tephroite, zincite, and perhaps franklinite, might also play a role in liberating ions from the original rock. The bright red fluorescence of the original calcite, caused by Mn<sup>2+</sup> substituting for Ca<sup>2+</sup> in the calcite lattice, is progressively dimmed as the Mn<sup>2+</sup> oxidizes

to Mn<sup>3+</sup> in the presence of oxygen and is then reprecipitated as nonluminescent phases. The brown coating on weathered calcite surfaces is the visual manifestation of these processes. The mineralogical makeup of these coatings is not yet known.

Attempts to restore weathered calcite surfaces to their former fluorescent brilliance must be conducted before significant weathering has taken place. Even if the brown coating is successfully removed, the highly etched calcite beneath will quickly weather again because of its high surface area. Preventive maintenance through some of the steps mentioned in this paper, combined with conservative chemical cleaning, are to date the only known and sustainable measures to combat the dimming of fluorescence due to weathering.

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Large crystals of sphalerite and small, rhombohedral crystals of pale pink calcite lining a solution cavity in Franklin Marble from the Braen Franklin Quarry along Cork Hill Road, Franklin. The iridescent, blue-to-green color of the sphalerite crystals is due to a surface tarnish, similar to the tarnish that forms on many other sulfide minerals, notably bornite. The crystals are actually dark brown in color and transparent, as seen in the upper part of the left crystal in the photo. The inset photo shows the entire specimen, which is approximately 5 inches (12.5 cm) across. This specimen was found by Steven Kuitems during the May 20, 2017, FOMS field trip to the Franklin Quarry. *Earl R. Verbeek photos*.

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