Tilasite from Sterling Mine, Ogdensburg, New Jersey: a Newly Recognized Assemblage

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Available at: https://works.bepress.com/james_vanfleet/34/
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About the Front Cover
The far southeastern wall of the Lime Crest Quarry, as seen during a summer 2000 FOMS field trip. Dark-colored gneisses in the upper part of the quarry overlie the lighter-colored Franklin Marble. This is the part of the quarry that yielded the corundum and spinel assemblages described by Warren Cummings in this issue of The Picking Table. Photo courtesy of Bernard Kozykowski.

Publisher
THE FRANKLIN-OGDENSBURG MINERALOGICAL SOCIETY, INC.

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Printing
ACORN GRAPHICS, INC.

Subscription to The Picking Table is included with membership in FOMS. For membership, back issues, and information, write to:

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The Picking Table is the official publication of the Franklin-Ogdensburg Mineralological Society, Inc. (FOMS), a nonprofit organization, and is sent to all members. The Picking Table is published twice each year and features articles of interest to the mineralogical community that pertain to the Franklin-Ogdensburg, New Jersey, area.

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.

FOMS is a member of the Eastern Federation of Mineralogical and Lapidary Societies, Inc. (EFMLS).

The Picking Table is printed on acid-free, chlorine-free paper.
In 2015 Jim Van Fleet purchased from Claude Poli a specimen identified as “smithsonite,” indicating the locality as Sterling Hill. The specimen, labeled P561, featured a white, fine-grained coating of secondary minerals—the purported smithsonite—on a dark matrix of massive franklinite with subordinate willemite. Under shortwave ultraviolet (UV) light, parts of the specimen fluoresced bright green, followed by a prolonged green phosphorescence, and parts of the coating fluoresced red, with a bright but brief red phosphorescence. Under longwave UV, however, the coating fluoresced bright orange-yellow, and additional seams and thin veins of the same material were visible throughout the matrix. The green and red fluorescences were ascribed to the usual willemite and calcite, respectively, but the origin of the orange-yellow longwave fluorescence was unknown.

Dr. Earl Verbeek studied this specimen under a stereo microscope, using both white and UV light. He observed that there are two sets of veinlets, not just one, transecting the specimen. The veinlets of the first set, containing the orange-fluorescent mineral, are long and sinuous, parallel to one another, and generally 1 mm or less in thickness. Also present are willemite veinlets, but these are far shorter, quite irregular, and present only locally in the specimen; many are mere films. In a few places the secondary willemite veinlets cut across the ones containing the orange-fluorescent mineral, so at least some of the secondary willemite is younger.

Jim Van Fleet also inspected the specimen under a microscope, with the aid of a longwave UV lamp, and observed that the orange-yellow fluorescence of the coating was due to small, submillimeter grains of a yellowish-tan mineral embedded in the white coating (Fig. 1), and that only these grains were fluorescing. A sample of this coating was removed and crushed in an attempt to separate the minerals of which it is composed. However, it proved difficult to separate the tan grains from the white mineral(s) since both were quite fragile. To try to confirm that the fluorescent response was limited to the tan grains, part of the crushed sample was washed in weak (10%) HCl acid, and rinsed. This removed the tan mineral from the sample and completely quenched the orange-yellow fluorescence. Soaking a larger piece of the matrix with associated vein/coating minerals in strong 1 molar HCl acid completely removed both the tan mineral and the white coating, leaving only willemite and franklinite. We had now confirmed that the orange fluorescence was limited to the tan mineral, and that this mineral was readily soluble in dilute HCl, but we had almost no clues to its identity.

Analysis moved to the geology laboratory at Bucknell University, and a sample of the tan grains in white powder was run through a 3-hour X-ray diffraction (XRD) test. The instrument used was a Philips (now PANalytical) X’Pert Pro MPD powder diffractometer with a Cu-Kα radiation source.
X-ray settings were 45 kV and 40 mA. The analysis software used was X’Pert Highscore, which matches the resulting diffraction peaks to mineral IDs in an internal library.

This initial XRD test yielded a maximum peak of over 1,690 counts, and indicated the presence of tilasite [CaMg(AsO₄)₂F], magnesian kutnohorite, and calcite. This “hasty” analysis required follow-up. A fresh sample was prepared, and a 14-hour XRD test was conducted. This second test yielded a maximum peak of over 4,900 counts, and identified tilasite, kutnohorite, and willemite in the sample. A note here on the process: XRD testing requires the destruction of a small sample of the rock under investigation. The material is crushed, and carefully sorted under a microscope, sometimes with the help of UV light. Sometimes breaking or scraping a sufficient sample from the matrix is a challenge, and it is always possible for two samples from the same rock to vary in content.

Our suspected minerals at this point were willemite (from the secondary veins), kutnohorite and/or magnesian calcite present as a white coating, and yellow grains of tilasite. The test results for tilasite (Fig. 2) were reasonably good, with observed peaks matching the known strong reflections (d-spacings) for this mineral at 3.73 Å, 3.48 Å (39% relative intensity), 3.07 Å, and 2.63 Å (33.5% relative intensity). Matching peaks for weaker reflections were present at 5.06, 4.81, 4.46, 3.24, 2.85, 2.68, 2.34, 2.26, 1.74, and 1.68 Å. Four of these peaks, two strong ones and two weak ones, are also close to the XRD pattern for willemite. Only one of these matching peaks is also found in the XRD reference pattern for kutnohorite, and only one also matches the pattern for magnesian calcite. So, without much overlap, the XRD analysis showed peaks conforming to the diagnostic patterns for tilasite, willemite, kutnohorite, and calcite. It can be noted that the XRD results conclusively eliminated smithsonite as a possible match, as none of the diagnostic peaks for that mineral were present.

At this point a review of the literature found little supporting information. Fred Parker had first reported tilasite from Sterling Hill in The Mineralogical Record in 1978, but from an assemblage quite different from that of the current specimens under study. The Mindat website shows photographs of several specimens with an assemblage physically similar to that of the current specimen, but from a different locality, the Djebel Guettara manganese deposit in Skikda Province, Algeria. The information on Mindat highlights some ambiguity concerning the fluorescent response of tilasite. The presence or absence of fluorescence, or color of fluorescence, are of little value in identifying the mineral. It is noted that the mineral is soluble in acid, consistent with the findings mentioned above, but this, too, is of little help, for many minerals are soluble in dilute acid. The literature review thus provided some interesting facts but added little to what we already knew about the identities of the minerals in the Sterling Hill specimens. Additional supporting data were desired to substantiate the X-ray identification of tilasite.

Dr. Chris Daniel, Mineralogist at Bucknell University, then offered to provide SEM/EDS chemical analyses of the specimen to supplement the XRD data. Under SEM magnification, the coating is obviously multiminerical and is quite fine-grained, with individual grains on the order of 10-50 µm across. Focusing on a field of about 1.5 mm, seven spots (Fig. 3) were deliberately chosen for analysis of the
different minerals present. The settings were 15 kV high voltage and 36,000 counts per second, with spot size adjusting to count rate (it varied a little, from about 2-8 nm). The test was run at a low vacuum pressure of 0.35 torr.

EDS spot 6 is centered on one of many ~10 μm spherules that the EDS analysis indicated is zinc sulphide (ZnS), and may possibly be sphalerite. Tiny spherules of sphalerite have often been found before at Sterling Hill in encrustation assemblages. Spot 2 is centered over a patch of white crust, and the analysis suggests a mixture, perhaps of sphalerite and hydrozincite, with a little carbonate, possibly calcite or kintonorite. Many of the “white crusts” from Franklin and Sterling Hill are mixtures of low-temperature minerals like this, and they are frequently so fine-grained and intergrown that they are not readily separated by sight, or even under low magnification with a stereo microscope. Spot 1 may be the franklinite matrix, and shows as black in the SEM image. Spots 3, 4, 5, and 7 are the mineral that is suspected to be tilasite; these show as gray areas in the SEM photo and correspond to one of the yellowish-tan grains seen under the microscope. Of those four spots, the EDS analyses for all of them showed only the presence of the elements in tilasite (Mg, Ca, As, F), and for three of them the quantitative data are in fair agreement with Parker’s published analyses of that mineral. EDS analyses are “semiquantitative,” giving relative percentages of the elements present. Calculating a chemical formula for the mineral under study is often not possible, or at least not advised, from EDS data alone. It is thus certainly gratifying, and significant, to find three analyses that pretty well match that of known tilasite:

<table>
<thead>
<tr>
<th>Elements</th>
<th>Parker</th>
<th>Spot #3</th>
<th>Spot #4</th>
<th>Spot #5</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>26.11</td>
<td>20.99</td>
<td>21.76</td>
<td>24.74</td>
<td>25.22</td>
</tr>
<tr>
<td>MgO</td>
<td>18.84</td>
<td>13.23</td>
<td>13.15</td>
<td>12.25</td>
<td>18.13</td>
</tr>
<tr>
<td>As₂O₄</td>
<td>51.51</td>
<td>50.09</td>
<td>51.83</td>
<td>51.77</td>
<td>51.70</td>
</tr>
<tr>
<td>F</td>
<td>6.85</td>
<td>10.72</td>
<td>9.18</td>
<td>7.82</td>
<td>8.85</td>
</tr>
</tbody>
</table>
Note that the SEM/EDS performed “quant analysis with oxides,” with a possible error of +/- 9%. In addition, it should be noted that this test was conducted on a rock specimen placed in the SEM equipment without any sample preparation. In ideal circumstances, the specimen should be cut or ground flat, polished, carbon-coated, and mounted on a stage to collect the most accurate readings.

Given that the XRD analysis produced a pattern with 14 peaks matching that of tilasite, and the EDS analyses produced chemical data in close agreement with the composition of that mineral, we regard the identity as well established. The evidence thus suggests that the specimen, though labeled smithsonite, is in fact a mass of willemite and franklinite traversed by thin veins of altered kutnohorite and calcite containing abundant, tiny, anhedral grains of tilasite and sphalerite. This represents a newly reported assemblage for tilasite, and one that may be more widely represented than had been previously recognized.

ACKNOWLEDGEMENTS

Thanks to Dr. Christopher Daniel, Professor of Geology, Bucknell University, and to Brad Jordan, Lab Director, Bucknell University, for their technical help and expertise in analyzing the minerals discussed in this paper.

REFERENCES


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.

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.