Investigation of New Species for NH

Tom Mortimer

MMNE sponsored EDS analysis sessions in the fall of 2019 has provided confirmation of two new mineral species for New Hampshire. This article will also report further analytic data on frondelite from the Chickering Mine, Walpole, NH. Pinning down these uncommon species is an increasing challenge. Most of the "easy stuff" has been already done!

Species: **PITTICITE** (Fe, AsO_4, H_2O)

Locality: Oliver Trench, Moat Mnt., Hale's Location, NH

Photo: 0.5 mm field of view, orange-red globules

Field Collected: Bob Janules

Catalog No.: u2287

Discussion: Bob Janules suggested pitticite. The mindat.org formula is given as: (Fe, AsO_4, H_2O) (?). The (?) indicates a questionable species. These globules are on altering lollingite or arsenopyrite.

Mindat.org indicates pitticite is:

"An amorphous Fe3+ hydrous arsenate sulphate of questionable validity. Chemical composition appears to be variable."

"Microprobe analyses of 7 pitticites from various localities indicate that it is a gel-like mineral of widely varying composition with no apparent stoichiometry.

Previously reported minor amounts of Si, Ca, P and Al are constituents of pitticites but are non-essential. Pitticite is retained as a generic name for amorphous, gel-like, ferric iron arsenate minerals of varying chemical composition. (P. J. Dunn (1982) New data for pitticite and a second occurrence of yukonite at Sterling Hill, New Jersey. Mineral Mag., 46, 261-264.)"

An Oct. 2019 EDS analysis normalized for one Fe (BC338) gave a chemistry of $FeAs_{0.6},K_{0.1}O_{15}$

Checking the specimen with a B&L poloarizing microscope confirmed these globules are amorphous.

An initial search of the IMA data base for minerals with BC338 analysis chemistry (including H) yields 15 candidates. None of these were pitticite, because I assumed both the Fe and As were "essential" elements to the mineral's composition. An IMA data base search, with arsenic as non-essential, does include pitticite. I am convinced Bob's identification is correct. This is an excellent example of an experienced collector's intuition for a correct identification.

These lustrous jelly balls are impossible to photograph without bright reflections. This photo is the best of four attempts. There are a few millimeters of these globules on the specimen, but larger area photos are much worse. Sort of like trying to take a photo a group of silver garden balls in sunlight.

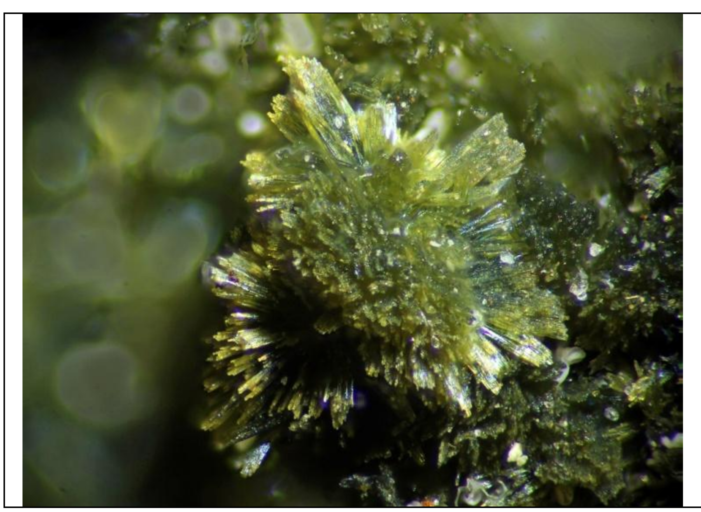
Species: **PUMPELLYITE** $Ca_2(Fe^{3+},Mg)Al_2(Si_2O_7)(SiO_4)(OH,O)_2 \cdot H_2O$

Locality: Basalt dyke, Industrial Interchange road cut, Merrimack, NH

Photos: 1 mm field of view left photo, 2.5 cm specimen right photo, pumpellyite is lower right of prehnite.

Field Collected: Tom Mortimer - 1990's

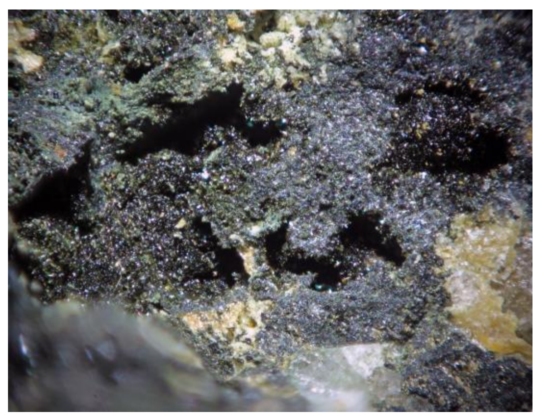
Catalog No.: 1150



Discussion: The pumpellyite species is indicated by EDS analysis, normalized for 3 Si.
APFU = Atoms per Formula Unit.
APFU from 1st probing: $Ca_{2.45}Fe_{0.35}Al_{2.61}Si_3O_{9.3}$ Fe + Al + Mg = 2.96
APFU from 2nd probing: $Ca_{2.41}Fe_{0.53}Mg_{0.21}Al_{2.30}Si_3O_{13.6}$ Fe + Al + Mg = 3.04

The IMA (2019) lists five "flavors" of pumpellyite: pumpellyite-(Al), pumpellyite-(Fe2+), pumpellyite-(Fe3+), pumpellyite-(Mn2+), pumpellyite-(Mg).
The chemistry of pumpellyite has evolved over the years. Deer, Howie & Zussman *An introduction to Rock Forming Minerals*, 1966, gave a formula that required Mg as an essential element:
$Ca_4(Mg,Fe^{2+})(Al,Fe^{3+})_5O(OH)_3[Si_2O_7]_2[SiO_4]_2 \cdot 2H_2O$.
The IMA (2019 web site) makes reference to an earlier formula for pumpellyite-(Fe3+) of:
$Ca_2(Fe^{3+},Mg)Al_2(Si_2O_7)(SiO_4)(OH,O)_2 \cdot H_2O$, allowing some Mg substitution for Fe.
The *Encyclopedia of Minerals*, 1989, lists the pumpellyite group with general formula:
$Ca_2X(Y_2)(SiO_4)(Si_2O_7)(OH)_2 \cdot H_2O$
Where X = Al, Fe^{2+}, Fe^{3+}, Mg: Y = Al, Fe^{3+}, Al, Cr^{3+} , indicating the Al can be allocated to both the X and Y sites.
X + Y = 3
This mineral encyclopedia lists pumpellyite as:
$Ca_2MgAl_2(Si_2O_7)(SiO_4)(OH)_2 \cdot H_2O$, with no Fe and requiring Mg, but also lists a "pumpellyite-(Fe) (Ferropumpellyite)" as: $Ca_2Fe^{2+}Al_2(Si_2O_7)(SiO_4)(OH)_2 \cdot H_2O$.
Fleicher's 2008 Glossery gives a pumpellyite-(Fe3+) formula as: $Ca_2Fe^{3+}Al_2(SiO_4)(Si_2O_7)(OH)_2 \cdot H_2O$.

Peter Cristofono pointed out that pumpellyite has a chemistry essentially identical to epidote: $Ca_2Al_2(Fe^{3+}Al)Si_3O_{12}(OH)$. From a chemistry (EDS) viewpoint, both have the same Ca:Al:Fe:Si ratios. Both can occur in similar environments and be associated with prehnite. As a New Hampshire example, epidote and prehnite occur together at the Rt. 101 – 101A road cut locality in Amherst. In pumpellyite’s favor, this bladed, feathery, habit is very rare in epidote. Optically, pumpellyite is biaxial + while epidote is biaxial -. A polarizing microscope is thus the best way for the amateur mineral collector to distinguish between these two species.



Species: **FRONDELITE**
Locality: Chickering Mine, Walpole, NH
Photo: 5 mm field of view. Micro-crystalline frondelite
Field Collected: Tom Mortimer
Discussion: The rockbridgeite-frondelite series presents substantial difficulties for the amateur mineral collector. Ignoring oxidation states, end member frondelite is $MnFe_4(PO_4)_3(OH)_5$ and end member rockbridgeite is $Fe_5(PO_4)_3(OH)_5$. Dana's *System of Mineralogy*, seventh edition, provides analyses that indicate ferroan frondelite and manganoan rockbridgeite exist, blurring species definitions. A frondelite formula including oxidation states is given as $(Mn^{2+},Fe^{2+})Fe^{3+}_4(PO_4)_3(OH)_5$. Dana continues, "Divalent manganese and iron [tm, the Mn^{2+} & Fe^{2+} in the formula] substitute mutually and probably a complete series extends between the manganese and iron end-members. The names frondelite and rockbridgeite are applied to the halves of the series with $Mn^{2+} > Fe^{2+}$ and $Fe^{2+} > Mn^{2+}$ respectively."
A Dec. 2019 EDS analysis (BC368A) suggested this Chickering sample is frondelite, although the computed chemistry is not an optimal fit. The calculated APFU for the Chickering specimen, normalized for 3 P, yields $Mn_{0.49}Fe_{3.13}P_3O_{13}$.
An APFU normalized for Mn + Fe = 5 yields $Mn_{0.68}Fe_{4.3}P_{4.1}O_{17.9}$. (The P is high). With some "leap of faith", if we assume four of the 4.3 Fe are Fe^{3+} and the remaining 0.3 Fe is $^{2+}$, Then we have $(Mn^{2+}{}_{0.68},Fe^{2+}{}_{0.3})Fe^{3+}{}_4P_{4.1}O_{17.9}$. This would fit the Dana frondelite definition with $Mn^{2+} > Fe^{2+}$.

A discussion with Jim Nizamoff informed me that Fe and Mn oxidation states may be determined by Mossbauer spectroscopy (a gamma radiation instrument that very few laboratories possess) or wet chemistry titration (see https://www.khanacademy.org/science/chemistry/oxidation-reduction/redox-oxidation-reduction/v/redox-titration). Jim stated the titration method is occasionally used by the Maine Mineral Museum lab.