A Palermo Mineral Identification Search

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***Forward**: Mineral collectors take great satisfaction in placing accurate labels on their specimens. This article follows my 22 year quest to identify a self-collected Palermo specimen. I have recently narrowed my initial choices to the most plausible species. However my investigation illustrates that even those collectors with access to modern tools of mineral ID such as EDS, they may still be left with ambiguities. This is the forth re-write of this article. My thanks to Jim Nizamoff and Bob Wilken for their most helpful reviews.*

Background:

Locality: Palermo #1 Mine, N. Groton, NH
Specimen Size: 2.8 cm specimen
Field Collected: Tom Mortimer - 1997
Catalog No.: # 217
Notes: This specimen was in my NH Species Display as fairfieldite for several years. It was visually identified by Bob Whitmore as fairfieldite. I understood that this was the spherical form of fairfieldite referred to in Bob Whitmore's book, *The Pegmatite Mines Known as Palermo.*

The Story:

A goal of my New Hampshire mineral species web site and display is to confirm species with analytic testing. This is particularly true for uncommon species and specimens where a visual identification is problematic. A 2017 investigation of NH fairfieldite and messelite revealed that my specimen #217 was not fairfieldite. A first polished grain Energy Dispersive Analysis (EDS) (BC77a – set 6) indicated a Ca, Mg, Fe, phosphate with a Ca:Fe:Mg:P ratio of about 2:1:1.4:5. No Mn was detected, essential for fairfieldite. Fairfieldite chemistry is: $Ca_2(Mn^{2+},Fe^{2+})(PO_4)_2 \cdot 2H_2O$.
My initial,(post EDS), species considerations were segelerite: $Ca_2Mg_2Fe_2(PO_4)_4(OH)_2 \cdot 8H_2O$.
and collinsite: $Ca_2(Mg,Fe^{2++})(PO_4)_2 \cdot 2H_2O$.

Because these balls showed radial zoning, multiple probing is recommended to explore chemistry variations. A total of five polished grain EDS data collections were obtained from samples of # 217, (two probings from one grain and three probings from a second grain). The APFU's (Atoms Per Formula Unit) for these analyses are tabulated below. These APFU's were normalized for two calcium atoms, for reference to my consideration of the segelerite and collinsite identifications.

APFU's calculated from atomic element percents of EDS analyses with comparison to ID candidates

Reference	Ca	Mg	Fe	P	O
Segelerite Ideal	2.0	2.0	2.0	4.0	26.0
Collinsite Ideal	2.0	Σ(Mg + Fe) =1.0		2.0	10.0
Zanazziite *	2.0	3.0	1.6	6.0	34.0
BC77a (EDS)	2.0	0.94	1.33	4.64	6.74
BC77b (EDS)	2.0	1.37	1.04	4.81	16.71
BC323 (EDS)	2.0	1.87	1.11	5.64	24.05
BC323b (EDS)	2.0	1.90	1.11	5.66	22.21
BC323c (EDS)	2.0	2.30	1.06	6.24	21.58
BC avg. (EDS)	2.0	1.68	1.13	5.40	18.23

*Empirical[i] formula with optional Al and Mn eliminated, but unknown how to distribute this removed 0.5 APFU between Mg and Fe. Fe^{2+} and Fe^{3+} oxidations combined.

For the above analyses, Ca, Mg, Fe, P, and O were the only elements detected. The BC detector cannot detect Be. From a RRUFF database search (http://rruff.info/ima/) of IMA approved species, I found four minerals with only Ca, Mg, Fe, P, O and Be. Alphabetically these are: atencioite, jahnsite-(CaFeMg), calcioferrite, and segelerite. I note that calcioferrite has 4 x Fe per Mg. Jahnsite-(CaFeMg) and atenciote have 1.5 x Fe per Mg. Since all my analyses except BC77a show Mg > Fe, I initially settled on segelerite, $Ca_2Mg_2Fe_2^{3+}(PO_4)_2(OH)\cdot 4H_2O$ as the "best fit."

In his second review of this article, Jim Nizamoff gave me a "wake-up call." A RRUFF data search is (mostly) limited to listing end-member chemistries. When I searched, I required the presence of Fe. So zanazziite (a beryllium mineral first reported 1990) and collinsite failed to show in my search. End member zanazziite is $Ca_2Mg_5Be_4(PO_4)_6(OH)_4 \cdot 6H_2O$, but Fleischer's Glossary (my 2008 copy) lists a zanazziite chemistry as $Ca_2(Mg,Fe^{3+})(Mg,Fe^{2+}, Al)Be_4(PO_4)_6(OH)_4.6H_2O$. Additionally, webmineral.com lists an empirical chemistry for zanazziite as:
$Ca_2(Mg_{0.6,}Fe^{2+}_{0.4})_{\Sigma 1.0}(Mg_{2.4}Fe^{2+}_{1.1}Al_{0.3}Mn^{2+}_{0.2}Fe^{3+}_{0.1})_{\Sigma 4.0}Be_4(PO_4)_6(OH)_{3.4}\cdot 6.6(H_2O)$,
indicating a Mg to Fe APFU ratio of 3:1.6. However, if no Al or Mn substitution is present, the Mg:Fe ratio might be as low as 3:2.1.

For collinsite, the end member chemistry is given as: $Ca_2Mg(PO_4)_2 \cdot 2H_2O$, but webmineral.com gives an empirical formula as: $Ca_2(Mg_{0.75}Fe^{2+}_{0.25})_{\Sigma 1.0}(PO_4)_2\bullet 2(H_2O)$.

In summary, the empirical chemistries for both zanazziite and collinsite indicate Mg >> Fe. In all my EDS analysis of this specimen, except BC77a, Mg is greater than Fe. My EDS BC average Mg:Fe ratio of 1.68:1.13 is very close to the Al, Mn deficient empirical zanazziite ratio of 3:2.1 noted above..

In his review of this article Jim Nizamoff expressed caution: A *"way to solve* [many species ambiguities] *is to analyze with the electron microprobe.* [For example] *The analytical total of all the cations expressed as oxides (water and OH excluded) for collinsite is around 90% whereas for segelerite it would be about 80%. Another tidbit is that segelerite contains iron 3+ so that indicates an oxidizing environment, so you should see other species with iron 3+. I see no reason why we couldn't encounter segelerite at Palermo but, I expect it would be pretty restricted."*

Following Jim's suggestion, I took a close look at my #217 specimen for associated minerals. These vitreous radial balls appear to be an overgrowth on clear apatite. There is some rusty oxidized siderite? on the top of some spheres. Yes, a microprobe analysis is a nice dream for all Palermo species collectors ! However, a microprobe analysis will not quantify beryllium content. Getting a microprobe analysis done on a submitted sample can take a lot of patience.

My next step was the acquisition of a Raman spectrum of this specimen. MMNE member George Adleman has a Raman spectrometer and volunteered to test my #217. The usefulness of this test depends in part on how many of my identification possibilities are in the Raman database library. Within a week, George provided the Raman spectra.

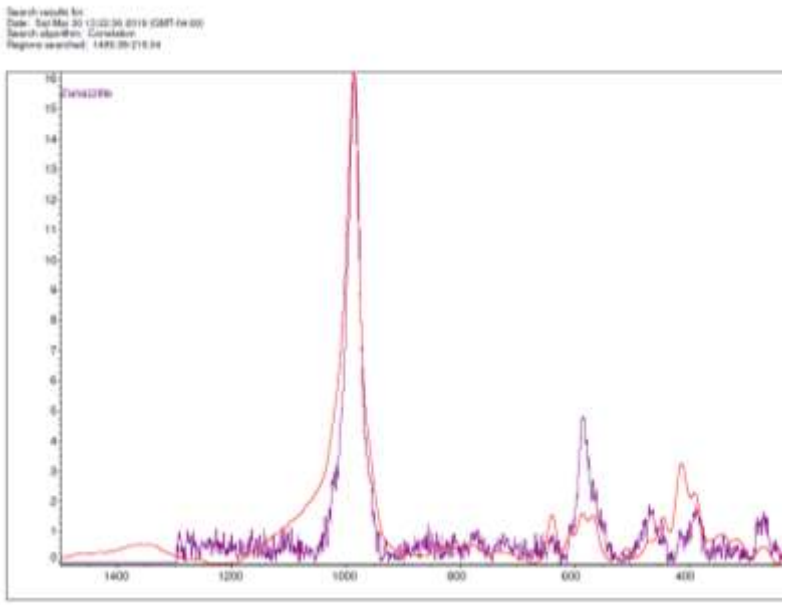
The top thirty species matches from the Raman analysis are listed in order below. Zanazziite came in at number 49 with a match coefficient of 54.9.[ii]

Search results for:
Date: Fri Mar 29 16:58:31 2019 (GMT-04:00)
Search algorithm: Correlation
Regions searched: 1499.38-219.04

Search results list of matches

	Index	Match	Compound Name
1	1774	83.70	Greifensteinite
2	4336	82.21	Wagnerite
3	1775	82.06	Greifensteinite
4	302	77.72	Arrojadite-(KFe)
5	4337	76.03	Wagnerite
6	303	73.60	Arrojadite-(KFe)
7	1881	72.25	Hauyne
8	3008	71.96	Orthoserpierite
9	3006	71.33	Orthoserpierite
10	4335	70.84	Wagnerite
11	1177	70.29	Davyne
12	1772	69.89	Greifensteinite
13	3457	69.22	Ruifrancoite
14	4086	68.65	Triplite
15	3068	68.61	Paravauxite
16	687	64.66	Brushite
17	2918	64.32	Newberyite
18	3603	64.03	Serpierite
19	1459	63.74	Evansite
20	3604	63.26	Serpierite
21	2950	62.94	Nosean
22	4468	62.91	Zektzerite
23	2342	62.69	Ktenasite
24	1879	62.16	Hauyne
25	2951	61.87	Nosean
26	3009	61.73	Orthoserpierite
27	307	61.52	Arrojadite-(NaFe)
28	3456	61.20	Ruifrancoite
29	3066	60.35	Paravauxite
30	230	60.31	Antlerite

Raman spectrum for # 217 (red) with reference plot for zanazziite purple.



Several of these top matches are phosphates reported from Palermo, including:

Species	**Formula**	**Reason for #217 ID rejection**
Greifensteinite,	$Ca_{1.96}Be_{4.07}Fe^{2+}_{3.44}Mn^{2+}_{0.86}Al_{0.23}Mg_{0.09}(PO_4)_{5.96}(OH)_{3.65}\cdot 6.5(H_2O)$	Mg not essential
Arrojadite group	Varied, a 15 species group	requires Al or Ba
Brushite	$Ca(HPO_4)\cdot 2(H_2O)$	Neither Mg nor Fe in formula
Paravauxite	$Fe^{2+}Al_2(PO_4)_2(OH)_2\bullet 8(H_2O)$	Al required, no Mg in formula

Several other phosphate species not reported from Palermo are also in the top 30, including:

Species	**Formula**	**Reason for #217 ID rejection**
Wagnerite	$(Mg,Fe^{2+})_2(PO_4)F$	No Ca in formula
Ruifrancoite	$Ca_2(\square,Mn)_2(Fe^{3+},Mn,Mg)_4Be_4(PO_4)_6(OH)_6\cdot 4H_2O$	Requires Mn, Fe > Mg
Triplite	$(Mn^{2+},Fe^{2+})_2(PO_4)F$	No Mg in formula
Newberyite	$Mg(PO_3OH)\cdot 3H_2O$	Formed from bat guano
Evansite	$Al_3(PO_4)(OH)_6\cdot 8H_2O$	No Mg in formula

Neither segelerite nor collinsite were in the top 200 Raman matches. I visually compared the RRUFF Raman plots for segelerite and collinsite with George's #217 plot. Gross differences were obvious.

In summary, then, when the EDS chemistry results are combined with the Raman analysis, zanazziite becomes the species of choice. MMNE member Bob Wilken pointed out that the habit of my #217 zanazziite is very different from the one illustrated in Bob Whitmore's book[iii], *The Pegmatite Mines Known as Palermo.* However, many zanazziite photos on mindat.org, particularly those from Brazil, have a similar radial ball appearance.

[i] [wikipedia] "In chemistry, the **empirical formula** of a chemical compound is the simplest positive integer ratio of atoms present in a compound.[1] A simple example of this concept is that the empirical formula of sulphur monoxide, or SO, would simply be SO, as is the empirical formula of disulfur dioxide, S_2O_2. This means that sulfur monoxide and disulfur dioxide, both compounds of sulfur and oxygen, will have the same empirical formula. However, their molecular formulas, which express the number of atoms in each molecule of a chemical compound, may not be the same.

An empirical formula makes no mention of the arrangement or number of atoms. It is standard for many ionic compounds, like calcium chloride($CaCl_2$), and for macromolecules, such as silicon dioxide (SiO_2)."

[ii] [Jim Nizamoff comment] "I would like to point out that a number of roscherite group species appear in the top 30 matches. This is significant as it tells us that the structure type seems to be a good match. I think that Raman isn't good at differentiating small chemical differences by itself – this is why I always advocate confirming via one additional analytical technique if possible."

[iii] [Jim Nizamoff – personal communication] Jim did the analysis of the Palermo zanazziite illustrated in Whitmore & Lawrence's book