Northwest Micro Mineral Study Group



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FALL MEETINGVANCOUVER, WASHINGTON

November 6, 2010

9:00 am to 5:00 pm

Clark County P. U. D. Building 1200 Fort Vancouver Way Vancouver, Washington

Schedule for the day;

- 9:00 am Doors open at the PUD building for table set up. Helpers needed.
- 9:30 am Meeting starts: (trading, selling, free tables, viewing specimens, and visiting).

10:30 am Business meeting, including field trip reports and mineral news.

12:00 noon Lunch potluck: Club

provides sandwich makings (bread, meat, lettuce, cheese, dressings, and coffee, tea, cocoa). Please bring salads, chips, pop, nuts, chili, cookies, pie, or cake to add to the lunch.

1:30 pm Main program. Don Howard will narrate a short presentation on *the New Minerals Named from California in 2009*. Bob Meyer will also present some recent field trips he has been on. If you have mineral pictures or pictures of recent collecting trips, bring them to share with the group.

- 3:00 pm Study trays of minerals, clearing free tables, and visiting.
- 4:00 pm End of meeting and clean up. Please stay to put away tables and help clean up.
- 5:00 pm Dinner will be at the Country Buffet in Vancouver. Please join us if you can.



A Controversy at Washington Pass By Bob Meyer



Fergusonite-(Y), sharp, somewhat curved, tan-colored crystals, measuring 0.8 mm in length and possibly twinned, on Microcline, collected from near Washington Pass.

The Golden Horn batholith, located near Washington Pass in the North Cascades, is among Washington State's most fascinating mineral locales. A number of suites of uncommon to very rare species occur there, hosted by miarolitic cavities and pegmatites within the granite types (Boggs, 1984). The Golden Horn batholith is the type locale for three species, Zektzerite, Okanganite-(Y), and Calciohilairite, and has the potential to produce additional new mineral species. Additionally, Washington Pass has special significance to members of the Northwest Micro Mineral Study Group (NWMMSG). Past and present NWMMSG members were instrumental in first describing the mineralogy of this area, and current members continue to this day to aid in our understanding of the locality.

The basis for much of the current scientific understanding of the mineralogy of the area is Dr. Russell C. Boggs' *Mineralogy and Geochemistry of the Golden Horn Batholith, Northern Cascades, Washington*, published in 1984 as his doctoral dissertation. Boggs spent years studying the mineralogy of the area, analyzing the species, and describing the mineralogical associations and paragenesis. Since then, this work has stood essentially unchallenged. Recently, though, the identity of β -Fergusonite-(Y), one of the rarer species at Washington Pass, has been questioned by a number of individuals, most notably Pavel Kartashov of the Institute of Geology of Ore Deposits (IGEM RAN) in Moscow. These individuals assert that the β -Fergusonite-(Y) at Washington Pass is actually Fergusonite-(Y).

Fergusonite occurs in miarolitic cavities within various border granite phases in the Golden Horn batholith. The crystals are typically elongated to needle-like, often somewhat curved, with the elongation occurring along the b-axis. The crystals often show some roughness on the faces and their color ranges from golden to grayish-brown (Howard, 1990).



Crystal Drawings of Fergusonite from Vlasov. Crystals from the Golden Horn are typically more elongated.

The controversy began after three NWMMSG members, the author, Saul Krotki, and Doug Merson, posted a number of photographs of β -Fergusonite-(Y) on Mindat. All three members were contacted about the identity of this material, and based on the arguments presented, all three members have currently changed the identity listed on the photographs under the belief that the preponderance of the evidence now supports an ID of Fergusonite-(Y) over β -Fergusonite-(Y).

To elaborate further, both Fergusonite-(Y) and β -Fergusonite-(Y) are Yttrium Niobates of identical ideal composition, and differ in that Fergusonite-(Y) is tetragonal, while β -Fergusonite-(Y) is monoclinic. In practice, the two species are very difficult to distinguish, due to a number of issues relating to these species. For one, the angle of inclination for β -Fergusonite-(Y) is close to 90°, [(85°,30') (Vlasov, 1966), (92°, 30') (Howard, 1990)] and it was commonly assumed among students of Washington Pass mineralogy that the β -Fergusonite-(Y) from there essentially mimicked a tetragonal habit. Secondly, Fergusonite, in common with other "rare earth" minerals of the alkaloid granitoids, is not found in examples with ideal composition. Instead, Fergusonite typically possesses a whole host of rare earth and other chemical elements in small percentages (Vlasov, 1966; Boggs 1984). This is significant in that the radiation from small percentages of elements such as thorium, which is typically present in Fergusonites, will destroy over time the orderly arrangement of atoms within the mineral, a process known as metamictization (Wikipedia, 2010). Such minerals are referred to as metamict, and because they no longer have a crystal structure, they cannot be identified as-is using X-Ray diffraction (XRD) methods. Therefore, it is routine practice for analysts to heat-anneal metamict crystals in order to recrystallize them. Unfortunately, Fergusonite behaves strangely when heated. If either Fergusonite or β -Fergusonite-(Y) is heated to 800-1200° C and allowed to slowly cool, it will change to the monoclinic [β-Fergusonite-(Y)] form (Vlasov, 1966). This makes the possibility of an erroneous identification of β -Fergusonite-(Y) quite likely. To get a tetragonal XRD pattern on actual Fergusonite-(Y), the analyst must either heat the material to a lower temperature of 450-750° C (Vlasov, 1966), or the material must be cooled quickly from the higher temperature, which does not allow for the gradual change to the monoclinic form (Kartashov, 2009).

Dr. Russell Boggs, in his 1984 dissertation, states that "Golden Horn beta-fergusonite is nonmetamict or only partially so and gives an X-ray powder diffraction pattern that compares favorably with synthetic monoclinic YNbO₄." This seems straightforward, but missing from Dr. Boggs' dissertation are any records of his techniques in analyzing the Fergusonite. The primary objections to the identification of this material as β -Fergusonite-(Y) raised by Kartashov include the following: 1) nothing in Dr. Boggs' dissertation indicates that he did not heat the material prior to performing the powder XRD analysis; 2) if you heat-anneal metamict Fergusonite-(Y) to 1000° C or more, it recrystallizes to the tetragonal alpha phase, but if it is allowed to cool slowly it will transform into a monoclinic phase identical with β -Fergusonite-(Y); 3) such heat-annealing is common lab practice, and this subtle recrystallization issue was not well widely known until recently; 4) the presence of substantial ThO₂ (3.5-4.5%) (Boggs, 1984) in the Golden Horn Fergusonite makes it hard to accept that material of this age 46-48 m.y. (Boggs, 1984) could be non-metamict; and 5) the form and appearance of the Golden Horn material is consistent with Fergusonite-(Y) from other, similar, deposits.

One major weakness in Kartashov's reasoning surfaced during the preparation of this report. Vlasov, in the 1966 *Mineralogy of Rare Elements*, clearly describes this recrystallization problem, and Boggs extensively used this work in preparing his dissertation. Thus, Kartashov's assertion that this property was not really understood until recently does not hold water.

Without the possibility of contacting Dr. Boggs, or subjecting the material to additional analysis, there is still a substantial possibility that this material is Fergusonite-(Y) and not β -Fergusonite-(Y). It will be interesting to address this controversy in the future and settle the matter. NWMMSG can be instrumental in that effort. What is needed for a start are several samples of Fergusonite from Washington Pass that can be spared. This is a difficult proposition, because Fergusonite is quite rare from Washington Pass, and the crystals are quite small. Nevertheless, NWMMSG members are encouraged to contact the author in this effort.

References:

Boggs, R. C. (1984). *Mineralogy and Geochemistry of the Golden Horn Batholith, Northern Cascades, Washington,* Santa Barbara: University of California.

Howard, D. G. (1990). The Golden Horn Batholith, Part I. The Microprobe. VII (1), 4.

- Kartashov, P. (2009). Personal communication. E-mail received 11 Oct 2009.
- Vlasov, K.A. (Ed.). (1966). Geochemistry and Mineralogy of Rare Elements and Genetic Types of Their Deposits, Volume II, Mineralogy of Rare Elements. Jerusalem: Israel program for Scientific Translations.
- Wikipedia. (2010). *Metamictization*. Retrieved March 20, 2010, from <u>http://en.wikipedia.org/wiki/Metamictization</u>.

The 32 Crystal Classes

Don Howard

Last issue, George Williams put together a fascinating account of the past history of our group, including some rationale for why it was established and some suggestions for how it might move forward. Many of those suggestions have been realized over the years. One statement, however, stood out for me: *Ford Wilson had previously suggested members develop a collection of micro specimens from each of the 32 crystal classes.* I certainly recognized that I was not aware of anyone trying to do this. After a little thought, I began to wonder if such a project was even possible.

Now some of you are probably thinking: '32 crystal classes? I thought there were only 7.' It is true that there are only 7 Crystal Systems. But within those systems, there are a number of further possible symmetry conditions that affect the outward shape of the crystals that can form. So in order to discuss this, I thought I would spend some time talking about symmetry and the usual notation used to represent symmetry. At the end of that discussion, I will present how far I have come toward developing such a collection. I hope by then that you will be able to understand why I am skeptical that such a project could ever in fact be realized.

Rotation

One of the primary symmetries in a crystal involves an axis of rotation. Rotation about such an axis will return the crystal to an identical position for all the atoms that make up the crystal. The presence of such a rotation axis is represented by a number, representing how many times that identical position occurs during 360° of rotation. The possible rotation symmetries are: 6, 4, 3 & 2. A 6-fold rotation symmetry axis is present only in crystals that belong to the **hexagonal** crystal system. 4-fold axes can be found in **isometric** and **tetragonal** system crystals. 3-fold axes are found in **isometric** and **trigonal** system crystals. And 2-fold axes are present in all systems except **triclinic**.

Reflection

Another important symmetry element is the mirror plane. Does a plane exist that, were it a mirror, the reflected image would look identical to the original crystal? Such a plane is represented by a lower-case letter m. Generally, the presence of such mirror planes are spatially related to the rotation axes present. To indicate this (say with relation to a 2-fold axis), the symbol 2/m is used if the axis is perpendicular to the mirror plane and 2m if it is parallel to it. This means that reading the symbol gives you a clue as to how things are related.

Inversion

The third symmetry element is what is called a center of inversion. This is a more mathematical concept and a little harder to visualize. What it boils down to is, if there is an atom at the point (x,y,z), does there need to be one at (-x.-y,-z)? Perhaps this can be made clearer by considering crystal faces. A crystal with a face (hkl) also will always have a face (-h-k-l). Most of the crystal systems of higher symmetry have such a center, but for the lower symmetry systems, such as **monoclinic** and **triclinic**, no such center may exist. Crystals of materials without inversion symmetry can be pretty strange and hard to analyze.

Inversion symmetry is normally indicated by a minus sign, usually written in front of or over the symbol for one of the rotation axis. If no rotation axis exists, it is written -1.

Isometric crystals

To see how this applies, let us look at the symmetry elements of a simple cubic crystal, where the atoms are equally spaced along each of three orthogonal directions. Each of those directions will be a 4-fold axis, since a rotation of 90° reproduces the original structure.

There is also a 3-fold axis along each body diagonal [111], where a rotation of 120° takes x into y, y into z, and z into x. But we do not need to list all of those axes, because all four body diagonals are "equivalent" due to just one 4-fold axis, and all three 4-fold axes are equivalent by the action of one of the 3-fold rotations.

There are also 2-fold rotation axes perpendicular to one of the three orthogonal directions but equidistant between the other two [110]. There are actually six such axes, but again through the action of the 4-fold and 3-fold axes, all six are equivalent, so we need mention only one.

There are a whole bunch of mirror planes. One set, perpendicular to the 4-fold axes, represent the faces of a cube. These we can represent as 4/m. Another set, not equivalent to the first, is perpendicular to the 2-fold axes, which we similarly represent as 2/m. Notice that this is NOT a mirror plane perpendicular to the 3-fold axes. There is, however, a center of inversion.

So the full representation of the highest symmetry isometric crystal is: 4/m-32/m. Crystals of many simple substances, such as halite (NaCl), belong to this crystal class.

But not all chemical compounds are so simple. There may be more atoms scattered around the unit cell, and not necessarily in very symmetric positions. Pyrite (FeS₂) is an example of such a compound. In pyrite, the iron atoms make up a simple face-centered cubic array, but the sulfur atoms are squeezed in much less symmetrically. The result is that the 4-fold axis no longer exists, nor does the mirror plane that was perpendicular to it. The 3-fold axes are still there, and the lengths along each crystal axis are therefore identical and the crystal is still isometric, but it belongs to the crystal class: 2/m-3.

The result of this lower symmetry can be seen in some crystals, which have striations on the faces of the cube. Striations give a preferred direction, clearly showing the lack of 4-fold symmetry. But the direction of the striations on the three faces surrounding a corner preserve the 3-fold symmetry axis. The striations are due to the influence of {210} faces, which if completely formed create a pentagonal dodecahedron, also called a pyritohedron.

Pyrite Crystals



The cube at right shows striations caused by pyritohedral faces. Notice that the striations on each face are perpendicular to those on the adjacent face. 3-fold symmetry about the front corner is still maintained.

Below is a complete pyritohedron.



Diagrams of isometric crystals based on the class of faces {210} for the crystal class 2/m-3 that includes pyrite, and for full isometric symmetry



2/m-3

4/m-32/m

The 22 Constal Classes

Actually, there would be 24 faces of the [210] class in a fullsymmetry isometric crystal, as shown above. The fact that only half of them are present is a result of the lower symmetry of 2/m-3, and show how we can assemble specimens that will demonstrate the differences between the various members of the 32 crystal classes.

Another feature that can show the influence of symmetry is the types of twinning permitted. By definition, a mirror plane cannot be a twin plane, since the crystal is perfectly reproduced by the mirror operation. Twin planes must therefore be other planes in the crystal. For full symmetry isometric crystals, the only low-order plane that can serve as a twin plane is the {111}, since there is no mirror plane perpendicular to the 3-fold rotation axis. Minerals such as spinel and faujasite, which belong to 4/m-32/m, do form twins of this type.

The Crystal Classes

Now that we have a common understanding of symmetry symbols and what they represent, we can look at a list of the 32 crystal classes. I have grouped them by crystal system, and listed them in order of decreasing symmetry, with the full symmetry of each system at the top:

The 52 Crystal Classes				
Class symbol	Representative minerals			
Isometric				
4/m-32/m 432	Galena, Garnet, Analcime			
-43m	Sphalerite, Helvite			
2/m-3	Pyrite, Bixbyite			
23	• • •			
Tetragonal				
4/m2/m2/m	Zircon, Anatase, Apophyllite			
-42m	Chalcopyrite, Eddingtonite			
422				
4mm				
4/m	Wulfenite, Xenotime			
-4				
4				
Hexagonal				
6/m2/m2/m	Beryl, Gmelinite			
622				
6mm	D			
-6m2	Benitoite			
6/m	Apatite, Vanadinite			
-6				
6				
1 rigonal	Calaita Hamatita Comundum			
-52/111 2m	Millerite, Elbeite			
30	Quortz			
32	Qualiz Ilmenite Willemite			
-5	Innemite, winemite			
Orthorhombic				
$2/m^2/m^2/m$	Adamite, Topaz, Pseudobrookite			
222	Austinite			
mm2	Hemimorphite. Natrolite			
Monoclinic	F,			
2/m	Titanite, Orthoclase			
2	*see below*			
m				
Triclinic				
-1	Axinite, Turquoise			
1				

In the above list, I have included representative minerals that illustrate each class. Finding representatives for the full-symmetry class of each system is fairly easy, so I have listed only two or three fairly common minerals. For the lowest symmetry classes, the only one that I could find representative mineral for was the orthorhombic class mm2. In fact, there are 14 of the 32 classes that I have not yet found minerals for. Some comments about this are in order.

In the first place, there are many minerals for which the crystal class has not been determined. In general, in order to be certain where a crystal structure belongs, all the atoms in a unit cell must be located. This requires good single-crystal x-ray diffraction studies, and these have not been performed on many minerals. Nor are they likely to be performed unless there is a good reason for doing so. So part of the problem is a lack of complete information.

Another problem that arises is that many minerals actually can be in a number of crystal systems rather than just one. This comes about largely through the degree of order/disorder in individual crystals. Also, unlike laboratory chemicals, minerals in nature are generally not pure chemical compounds; they are fraught with impurities. All this complicates assigning a mineral to a particular crystal class.

But a more fundamental question would be: are there any natural minerals that fall in some of these classes? Crystals are, by their nature, ordered systems. Many of the classes without representatives in fact have very little symmetry – for instance, the triclinic system designated "1" has no symmetry at all! There may be little incentive for a material to readily form long-range crystal order if it has little or no symmetry to its structure.

You might then ask: does it make any sense to have 32 crystal classes if there are no takers for some of them? Remember that the study of crystal structures goes far beyond naturally occurring minerals. There are a wide range of manufactured compounds and organic molecules that also crystallize, and these designations are intended to cover them as well.

Now I fully suspect that as we look through mineral studies, we will be able to find some candidates for the classes currently without representatives. But I am rather skeptical that we will be able to complete the list. And that is why I indicated at the top of this article that putting together a collection of specimens illustrating *all* 32 classes may not be feasible.

So is studying the 32 crystal classes a useful enterprise? I believe it is. As indicated in the case of pyrite, it can give us some insight into the forms of certain minerals. And in some cases, it can help us with identification, in that it gives us clues into telling one mineral from another. A case in point involves two colorless minerals that often occur together, adamite and austenite, that are both orthorhombic but belong to different crystal classes. Below we compare the form that a typical single austenite crystal would take in each of those classes, based on the classes of faces {110} and {101}. The actual form of austenite clearly shows the lower symmetry. The form of adamite, shown on the far right, also includes {110} but with {111} instead. The shape of the crystal is therefore a good way to differentiate the two minerals.



Crystal Models

Orthorhombic:

Another possible application involves trying to infer crystal class from observing the external shapes of a mineral. If you were to look up heulandite, say in the data section of the MINDAT.COM site, you would find it listed as monoclinic 2/m. For a monoclinic mineral, the 2-fold axis is the b-axis. The mirror plane is therefore (010). The combination of a 180° rotation plus a reflection in (010) is equivalent to an inversion, so the minus sign is not expressed even though 2/m class crystals possess a center of inversion.

Most heulandites follows the expected forms of class 2/m. However, some very unusual heulandites crystals were found a few years back by Rudy Tschernich near Clarkston, Washington. (Microprobe, Vol. VIII, #1, pg 4-10) The crystals had a very unusual tapered form composed of (010), (001), and (4-10). The crystal class 2/m would also have required (410) to be present because of the mirror plane, and it was conspicuously absent. Moreover, as the picture at right shows, some of the crystals appear to be twinned on the (010) plane, and *Twinned Heulandite from Clarkston, WA*.

twinning cannot occur on a mirror plane. It is therefore possible that heulandite is actually a member of the monoclinic class 2.



SEM micrograph at about 50x.

If true, then perhaps we have representatives for 19 of the crystal classes, and only have 13 more to find!

The following is an update on the current status of type minerals from Oregon and Washington. More research work is needed on those that do not have a Microprobe reference. If any have been omitted from the list, please notify the editor for their inclusion.

MINERALS FIRST REPORTED FROM THE NORTHWEST

	Mineral	Type Locality	Microprobe Ref.
Orego	n		
1.	Boggsite	Neer Road, Goble, Columbia Co.	Vol VI
2.	Cowlesite	Neer Road, Goble, Columbia Co.	Vol VI
3.	Cavansite	Goble, Columbia Co.	Vol VIII #1 pg14
		Owyhee Dam, Malheur Co.	Vol VII #10 pg13
4.	Erionite-K	Durkee Opal Mine, Durkee, Baker Co.	Vol VII #4 pg 11
5.	Heinrichite	White King Mine, Lake Co.	Vol VIII #2 pg11
6.	Metaheinrichite	White King Mine, Lake Co.	Vol VIII #2 pg11
7.	Oregonite	Josephine Creek, Josephine Co.	
8.	Paulingite-Ca	Three-Mile School, Grant Co.	Vol VII #4 pg3
9.	Pentagonite	Owyhee Dam, Malheur Co.	Vol VII #10 pg13
10	. Priceite	Lone Ranch, Brookings, Curry Co.	Vol X #10 pg23
11	. Slawsonite	Martin Bridge Formation, Wallowa Co.	
12	. Tschernichite	Neer Road, Goble, Columbia Co.	Vol VI
Wash	ington		
1.	Calciohilairite	Washington Pass, Okanogan Co.	Vol VII #3 pg20
2.	Ferrierite-Na	Altoona, Wahkiakum Co.	Vol VI
3.	Ferritungstite	Germania Mine, Fruitland, Stevens Co.	
4.	Okanoganite	Washington Pass, Okanogan Co.	Vol VII #3 pg21
5.	Paulingite-K	Rock Island Dam, Douglas Co.	Vol VII #4 pg3
6.	Zektzerite	Washington Pass, Okanogan Co.	

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