Northwest Micro Mineral Study Group

MICRO PROBE

SPRING, 2023



VOLUME XIII, Number 7

SPRING MEETING

Saturday, May 13, 2023 9 AM to 4 PM

Sons of Norway Columbia Lodge 2400 Grant St, Vancouver, WA 98660

Our experience last Fall was very positive, so we will meet again at the same place. Remember that there is no designated parking spot. We will be unloading at the door and then parking on the street in the neighborhood. Please unload and then move on so others can have a turn to unload their things. There are a couple of steps up once inside. We will try to have people helping with the unloading process.

As usual, we will have sandwich makings and drinks provided. Bring salads, condiments, chips and deserts to round out our midday feast.

Directions:

FROM WASH. HWY 14: Continue west to Interstate 5, keep right and take I-5 North. Then keep right and continue to Exit #1D -Fourth Plain Blvd

FROM INTERSTATE 5: In Vancouver, take Exit #1D to Fourth Plain Blvd. Head west on Fourth Plain Blvd. to Grant St. and turn left. Go two blocks to 24th St.



IN MEMORY OF

Don Lown



Don has been a member of our Group since he moved to the Creswell area in the mid-1990's. He served as our treasurer for several years and was a regular attender at our meetings until recently. He passed away last November at an age of 89.

Don was curious about almost everything, and most especially about the things of the natural world. His property in Creswell was filled with a whole variety of birds and other creatures, and he had learned a great deal about their nature and habits through keen observation. He was curious about minerals and rocks, and had prowled around most of the quarries in the area just south of Eugene. He loved to work with his hands and made beautiful things out of a variety of kinds of wood.

Don had been a school teacher for many years before retiring and coming to Oregon. He loved working with children and introducing them to the wonders of nature. To that end, he volunteered at a variety places dedicated to Botany, Paleontology, Geology and the natural world. He loved to make things with his hands, especially for children. His quiet enthusiasm and love of learning and observing will be missed.

Don Howard

Filiform Pyrite and Zeolites at Tanner Creek, Multnomah County, Oregon

Clarence Keech

Tanner Creek is located within the Columbia River Gorge along interstate 84 at the Bonneville Dam exit no. 40. Tanner Creek trailhead is located to the right (south) at the base of the exit ramp. There is a typical parking fee required. The location is located approximately one mile along the trail. Although I call it Tanner Creek falls, the official name is Wahclella falls. The trail is generally well maintained. Information on the trail can be obtained from the forest service web site by the trail name. It is a popular hiking trail. The debris pile is on the west side of the creek just below the falls. The approximate coordinates of the rock block that I collected most of my specimens from is 45.6201; 121.931984. I recommend locating the site on google maps before going in. GPS may not work in the steep-walled canyon.

It has been over 40 years since I collected the specimens you have seen. The numbers on the labels refer to the year collected; I think most of the Tanner Creek specimens were collected in the summer of 1977 when I worked on the construction of the second Powerhouse at Bonneville just across the river. I was the assistant project geologist for the project. Fig. 1 shows the Tanner Creek landslide deposit. I think this slide occurred in 1974. It was mentioned in one of the scenic guide books on the Columbia River Gorge that came out some time between 74 and 77. The slide occurred on near vertical cliff which consists of Columbia River Basalts. Note, these basalts are underlaid by the altered contact with the Eagle Creek formation which is exposed just above stream level upstream of the slide. It has been significantly eroded, undermining the basalts above. The mineral zone appears to be a flow contact exposed in the canyon wall above.

I have found specimens along the length of Tanner Creek. However, the best material, especially filiform pyrite, is located in the landslide deposit. I have circled in red on Fig. 1 the basalt



Fig. 1 The slide on the west side of Tanner Creek as it appeared in 1977.

block that most of the specimens came from. This block appears to be the best source (arrow points to the part of the block I concentrated on the most; there should be a pile of small rock chips at its base), although occasional specimens were found throughout. A random fist size cavity was also encountered in a large block near the creek. It contained an amazing array of long pyrite filaments with impaled cube-octahedrons of pyrite. However the filaments were coated with a black material, possibly clinochlore. I still have some of these that I mounted in paleontological slide mounts.

The Tanner Creek specimens contain zeolites with clay minerals as well as lesser amounts of filiform pyrite. I recall that the loss for the filiform pyrite was about 50%. Many would pop off the matrix before trimming the rock to size. Note, I would breakout the specimens at site. Retaining natural moisture content appears vital to the recovery of these specimens. Once the specimen dries out, the clay minerals degrade and become brittle and disintegrate. This appears to be the case for many mineral specimens, particularly the zeolites and their associates.

Filiform pyrite is only one of a number of species found in this rock block; all are micro in size and include erionite-offretite, phillipsite, heulandite, chabazite, stilbite, thomsonite calcite, chlorite, garronite(?) and opal. The pyrite, erionite-offretite and phillipsite make up the significant species in this area. They can be quite attractive and intriguing. I collected approximately 100 of the pyrite and non pyrite specimens from the area. Last spring when I was downsizing I gave the flat of pyrite specimens to Steve Falconbury who passed them on to Pam Harris and others.

As I look back over the years, I realize that my greatest pleasure is in the discovery and recovery of these specimens. The specimens I collected were mainly through my own prospecting and I have discovered a number of unique localities as well as unique specimens from known localities. I have concentrated mostly on micos but have picked up some larger specimens as I came across them. Although I have worked on and off on the processing of the specimens, I have come up sadly short of achieving my entire goal. I am happy that others can pick up the "torch" on these specimens.

The filliform pyrites are quite varied. About two- thirds of the samples consisted of simple filaments. The others were complex with bends and complex growths. Some are mind-blowing. The specimens also show the variability of the associate minerals; not all are associated with heulandite. I have included a micro photo of a filament that extended across a good portion of the cavity before making two right angle bends and returning back to its starting point (Fig. 2).



Fig. 2 *A filiform pyrite with double right angle bends.* **Fig.** 3 *Filiform pyrite filaments growing around the side of a cavity longer than cavity.*

The filiform pyrite specimens from Tanner Creek appear to be nearly identical to those from the Starvation Creek site. I too have found filiform pyrite with a similar appearing translucent coating but I called it opal rather than thomsonite for lack of proper id tools. I have also found filiform pyrite across the river in the Bonneville landslide but not of specimen quality. Although the specimens appear identical, the overall mineral assemblages are not. I collected over 200 mineral specimens from the rock block I pointed out to you. All specimens came from a volume of no more than a cubic foot from the end of that boulder. The variability from vesicle to vesicle even within an inch of one another was extreme. Some vesicles were bare, some contained filiform pyrite with heulandite, some only contained erionite-offretite, while in rare instances some contained phillipsite. It appears from the start of mineralization of the vesicles they were closed isolated systems.



Fig. 4 Coated filiform pyrite from Tanner Creek

Fig. 5 A coated filiform pyrite with 90° bends from Tanner Creek

Editor's note

Several very interesting, well made micromounts were placed on the free table at the Fall meeting by Pam Harris. Several were labelled 'filiform pyrite' and had the designation 'TC' and '77'. Further inquiry disclosed that they were the work of Clarence Keech. The preceding article is the result of several email exchanges between the editor and Mr. Keech. The text has been collected and rearranged by the editor. The map and pictures are by Mr. Keech. The TC was an abbreviation for Tanner Creek and the 77 indicated that the specimens were collected in 1977.

Although the minerals were collected over 40 years ago, this still seems like a timely issue. First of all, it adds yet another location where filiform pyrite has been found. But more importantly, it underscores the value of carefully checking out landslides involving Columbia River Basalts. In light of the recent large forest fires in the Eagle Creek area just to the east, and in the Clackamas River canyon above Estacada, there should be a number of such landslides. We look forward to more locations for zeolites, pyrite and siderite in the near future.

Several other micromounts were labelled 'crystal garden' and had the designation 'HM'. At the request of the editor, Mr. Keech has prepared the following article as an explanation of the area from which they came. Again, the pictures are by the author. And again, as the author points out, this next Summer would be an excellent time to check the area out.

Don Howard

Harter Mountain Crystal Garden and Neighboring Zeolite Site

Clarence Keech

The Harter Mountain "crystal garden" specimens consist of a suite of primary cavity minerals that line vesicles within an inclosing intrusive rock. Generally the crystals are the same as those of the enclosing rock but larger and perfectly formed. This site contains the following mineral assemblage: feldspar, hornblende, tridymite, hematite, apatite, a minute pink columnar mineral though to be zircon, and probably others. Please note, my mineral identifications are based on visual only and can be tentative.

Hornblende is the most significant mineral at this site, forming well developed, elongated medium brown individuals up to dense clusters of randomly oriented crystals. The length of the crystals is generally 2mm or less. The crystal forms are somewhat varied; some being thinner and longer than others suggesting perhaps two species (see photos). The larger cavities displayed larger crystals with more color variation from yellow to dark brown and can form dense tangles of crystals.

Secondary minerals are lacking from much of the specimens. However, opal can cover the crystals either with a transparent layer of hyalite or an opaque white layer of common opal. From what I remember, vesicle size is generally an inch or less; the shape somewhat irregular. I recall finding some larger vesicles perhaps up to fist size in large rock blocks closer to Harter Mountain on the east side of Holman Creek

The Harter Mountain crystal garden site is a rock-block strewn area on the north side of Harter Mountain along the Holman Creek drainage. The source of the blocks has not been located but believed to be somewhere higher up on Harter Mountain. The rock blocks scattered over much of the area range up to about 4 feet. I do remember finding larger rock blocks as much as 6-feet in size closer to the mountain east of Holman Creek.

Only a few of my original specimens survive. These specimens do not reflect the full variation that I saw there. Some vesicles were empty, some contained only minute crystals, others contained the nice hornblende crystals shown in the accompanying photos. A few large fist-size or larger cavities contained dense clusters of hornblende of larger size. Although I attempted to preserve these specimens, they were lost over time (too many moves, not enough storage space).

It has been over 40 years since I collected the specimens. At that time the area had been clear cut exposing the rock field. I have been back to the site a number of times since but have not collected additional specimens because the area became too wild and overgrown with forest. The current Google photo map of the area (2023) shows that again part of the area has been clear cut and the rock blocks can be seen at highest magnification. The time is therefore right to explore this area again.

The site is located in a remote part of the Willamette National Forest, just upstream of the Middle Santiam Wilderness Area. A Forest Service map of the area displaying road numbers is considered essential for navigating the complex network of roads that cut through this area. It is also highly recommended to plot the travel course on a map before the trip. Note, the Forest Service no longer maintains the forest roads for multi-purpose use as they once did. The roads are unpaved. Roads not being used for logging operations can be blocked by fallen trees or landslides. The main line roads (4-digit numbers) in this area are gravel. The roads are generally narrow and in places not wide enough for two cars to pass let alone a log truck. There are frequent turnouts to allow for passing. Road conditions can vary greatly. Parts of the forest in this area are private timber lands where active logging operations and hauling are occurring. Best time for access would be on weekends in the early summer



months before fire danger becomes too great. It is recommended to check with the local forest service office (Sweet Home) before making the trip to understand the conditions in the area. Basic fire-fighting equipment may be required. High clearance vehicles are highly recommended.

Significant Waypoints:

- 1---Junction US Hwy 20 with Sheep Cr. Road FS2047
- 2---Sheep Creek Rd FS2047 with FS 2045
- 3---FS 2045 with Harter Mtn Zeolite site
- 4---FS 2045 with Holman Creek

44.405,473; 122.210,519 44.425,504; 122.170,405 44.454,833; 122.165,708 44.457,320; 122.189,931

(Note, coordinates were taken from google map and give only an approximate location of the waypoint and can have an error of several hundred feet or more. Moreover, this area is located on the north side of the divide between the south and middle Santiam Rivers. GPS may not function for all the points.)

The site is best accessed from US highway 20, east through the town of Sweet Home. The Sheep Creek Road, junction, waypoint 1, is approximately 40 miles above the town of Sweet Home. Sheep Creek Road, FS 2047, runs in a northeasterly direction. Parts of it can be quite rocky. The junction with FS 2045, waypoint 2, will be encountered 4 to 5 miles along the road. Several roads diverge here This road will trend northerly after a short westerly jog. Check your map and the road markers to verify the proper road. Note, numerous spur roads will be encountered along the routes; these are generally marked with 3-digit numbers; they are dead end roads and not well maintained. It is best to avoid them. At 4.5 miles from the junction, a small zeolite exposure is present on the left (upslope) side of the road, waypoint 3. This is a small but very productive site for well-developed micro stellate rosettes of bladed thomsonite. If collecting here, it is recommended to collect only the fallen material and not the from the road cut which could lead to slope instability. Additional material can be found at the base of the cliff below the right side of the road. Other minerals present include analcime, natrolite, heulandite, stilbite, calcite and others. Continue along 2045 for another 2.5 miles or so to Holman Creek, waypoint 4. This spot marks the center of the rock block field and is within the recent clear-cut area. Rock blocks should be visible from the road throughout the clear-cut area. Large sledge hammers will be needed to break off pieces of this material. Look for vesicular rock. There will probably be a weathering rind around the blocks that will need to be broken through before getting to fresh rock. Good Hunting!

Further notes:

Peck, 1964, shows a small intrusion downstream of the site (see attached map, Tg). It is not considered to be the source, but could be another potential mineral site. (Note, personal communications with corps of engineers geologist report finding elongated brown crystals in cavities along the upper reaches of the Middle Santiam River during recon mapping for Green Peter dam.) These vesicular phases of intrusives are believed to be cupolas or the upper pinnacle of a buried intrusive body. This is where the volatiles from the magma collect and the most likely zone to find crystals. Expect to find them near the top of the igneous mass.





Fluorine – Lucky Thirteen

Steven Ullrich

The element fluorine is thirteenth (544ppm) in order of abundance in the Earth's crust -- lucky thirteen!¹ This means that fluorine is far more abundant than a number of elements with which we are far better acquainted. And yet, this is not so strange: how many of you have seen a piece of gold, and how many of you have seen a piece of thulium? With a relative abundance of 0.5ppm, thulium is over a hundred times as common as gold (0.004ppm).

What causes this difference in familiarity? Part of the reason lies in the fact that gold occurs in concentrated, easy to identify deposits, while thulium is scattered in small concentrations in many kinds of rock. Like thulium, fluorine is an element in hiding; it will be the purpose of this paper to look at some of the minerals the element fluorine is hiding in, and examine some of the lessons these minerals have taught us about our world.

When people talk about the abundance of fluorine in nature, they are not usually talking about the abundance of the free element. Free fluorine gas is one of the most dangerously reactive substances known; it vigorously attacks the glass in which we trust to keep most of our chemicals safe, and burns the rubber sometimes used in laboratories to convey gases. Therefore most of the fluorine found in the earth is available as fluoride compounds.

Most of the fluorine but not all. ² A dark purple fluorite found in Wo"Isendorf, Bavaria was called "stinking fluorite" by the miners who came across it. Whenever fresh surfaces of a sample were broken open, the distinctive, pungent odor of ozone could be noticed. Investigation of this peculiar case showed that the fluorite had bubbles of fluorine gas entrapped inside; when the surface of the specimen had been broken, the fluorine was released and immediately reacted with the damp air to form ozone: $F_2 + O_2 + H_2O = 2 HF + O_3$

Apparently the fluorine had been produced as a side effect of radioactive decay. When the mineral sample was formed from volcanic melt, volatile uranium fluorides were present, dissolved in the fluorite. As the uranium in the solid that formed decayed, thorium and other elements that cannot combine with as much fluorine as uranium can were produced. The free fluorine had no place to go, so it stayed entrapped in bubbles enclosed in protective fluorite until the miners broke samples of the purple mineral open.

Fluorine is usually present in the seas as fluoride ion as well. The concentration is not particularly high – about 1.4 milligrams/liter. ³ The reason that this concentration is so much smaller than the concentration for the crust taken as a whole is that sea water contains a number of ions of elements which form insoluble fluorides. ⁴ Of these,

calcium (400 milligrams/liter ³) is the most common, so the calcium concentration helps to limit the solubility of fluoride ion in sea water. Since the equilibrium constant is: $[Ca^{+2}]x[F^{-}]^{2} = 3.4x10^{-11}$ (18 C)

if we have $[Ca^{+2}] = 400 \text{ mg/L}$, then we get $[F^{-}] = 1.1 \text{ mg/L}$; this compares favorably with the experimental value of 1.4 mg/L. For this reason, there is a great deal of fluoride ion available in the oceans of the world – but at rather low concentration.

The first fluorine mineral to be discovered was fluorite, which we now know to be the same insoluble calcium fluoride just mentioned $- \text{CaF}_2$. Fluorite ⁶ is a transparent mineral that is colorless when pure, but can take on any number of colors – yellow, green, blue, purple,



Fig. 1. Fluorite in octahedral crystals Vick's Peak, New Mexico

pink, or even black. Fluorite belongs to the isometric crystal system, which means that the mineral crystallizes primarily in cubes and octahedrons.

Fluorite was first used in the smelting of metals as a flux ⁷; the fluorite is placed in the heated mixture and melts, allowing impurities interfering with the metal-making process to float away in the melt. This use gave fluorite its name, from the Latin word, *fluere*, to flow.

Special properties of fluorite made it an object of wonder in early researchers. Some specimens of fluorite had the curious habit of glowing in the dark after being heated; the famous mathematician G. W. Liebnitz reported that the powder from one sample gave off a cool blue light while sitting on a metal plate not even red hot. ^{8,9} Pieces of fluorite were discovered to give off light when rubbed. ¹⁰ George Green was later to find that some specimens of the mineral when exposed to visible light gave off visible light of a longer wavelength; he observed that other materials behave in a similar fashion, and decided to call the phenomenon *fluorescence* after fluorite. ¹¹ It would take us far from our subject to explain the underlying physics that governs these interesting luminescent properties of fluorite. ¹²

These physical properties did not exhaust fluorite's fascination, however.¹³ The German glassmaker Heinrich Schwanhard of Nurenberg discovered that if you treat fluorite with strong acids, the resulting vapors would etch glass. Today, we recognize that hydrofluoric acid was being produced, and that this was responsible for the destruction of the silicate in the glass: ¹⁴

$$CaF_2 + H_2SO_4 = CaSO_4 + 2 HF$$

SiO₃⁻² + 6 HF = 3 H₂O + SiF₆⁻²

Hydrofluoric acid is a treacherous substance that delivers painful, slow-healing wounds; the early accounts do not mention this kind of problem, however.

Schwanhard knew an opportunity when he saw one; he was able to use this chemical etching procedure for artistic purposes. Figures of people, animals, and plants could be portrayed on glass vessels against an etched background through the aid of varnishing the parts of the glass where etching was unwanted. Schwanhard had a single customer for these pieces, the emperor Charles II, but probably did not suffer much from a lack of other business.

Karl Wilhelm Scheele also produced the corrosive vapors from fluorite, and after some investigating came to the conclusion that a new acid was responsible for the etching. ¹⁵ In due time, the acid would be recognized as a relative of hydrochloric acid, and would be chosen as the compound from which Henri Moissan finally prepared elemental fluorine. ¹⁶ Hydrofluoric acid would prove to be the chemical key to the preparation of many of the other fluorine-containing compounds known to the modern chemist.

The mineral cryolite, ¹⁷ Na₃[AlF₆], was found in a tremendously large deposit at Ivigtut, Greenland, discovered, oddly enough, by C. L. Giesecke, the man who composed the words to Mozart's opera, The Magic Flute. ¹⁸ The name cryolite means "frost-stone" (from Greek *-kruos* and *-lithos*), and masses of the mineral look very much like pieces of ice – so much so that the Innuit natives used it for making anchors. ¹⁹ The refractive index of cryolite (1.34) is so close to that of water (1.33) that the anchor just seems to disappear when tossed into the cold Greenland deep.

Anchor-making is not the only use known for cryolite, however. Charles Martin Hall and Paul-Louis-Toussaint Heroult independently discovered a process for the production of aluminum by the electrolysis of aluminum oxide dissolved in molten cryolite. ²⁰ The



Fig. 2. Cryolite on Quartz Francon Quarry, Montreal Is., Quebec, Canada

effect of the method was to bring the price of aluminum to a fraction of what it had been. The Emperor Napoleon III had been in the habit of using aluminum dinnerware for state occasions. ²¹ After the Hall-Heroult process came into being in 1886, aluminum lost its conspicuous consumption glamor. The demand for cryolite then began, and grew to such an extent that the 30,000 metric tons a year that the

Ivigtut site now produces is not nearly enough for the world's needs; artificial cryolite is now made by the following reaction:

 $6 \text{ HF} + \text{Al}(\text{OH})_3 + 3 \text{ Na}(\text{OH}) = \text{Na}_3[\text{AlF}_6] + 6 \text{ H}_2\text{O}$

Further light on the set of electrochemical steps by which aluminum is obtained would be welcome; at present, this process is not fully understood.

The Ivigtut deposit is of a kind of which we will have need to speak further; it is called a pegmatite. ²³ In pegmatites, the fraction of molten material from deep within the Earth that is rich in volatile components can well up and form a deposit among rock already in place. The sizes of the resulting pegmatites can vary greatly; some are a few inches across, while others are thousands of feet long. Great variety is the rule for the shapes of pegmatites as well; lenses, turnips, dikes, hoods, veins, ellipsoids, funnels and splashes can turn up as possible formation shapes. This volatile fraction of igneous material then cools slowly, forming relatively large, coarse crystals. For some pegmatites, these crystals can be Texas-sized; one spodumene crystal found in a pegmatite was 42 ft. long, 5 ft. wide, and weighed at least 90 tons! ²⁴ The volatiles in question can contain water, fluorine, chlorine, sulfur and nitrogen. Here at Ivigtut, fluorine compounds must have been present, converting any aluminum available in cryolite.

Amblygonite, (Li,Na) Al (PO₄) (F,OH), is another fluorine mineral found in pegmatites; ²⁵ one such deposit in South Dakota yielded crystals of amblygonite weighing several metric tons. ²⁶ S. L. Penfield;s analysis of eight samples of amblygonite taken from many localities showed that fluoride and hydroxide present in the mineral vary from specimen to specimen. ²⁷ This is an important result: minerals do not need to have fixed chemical compositions; they may vary within a certain definite range of compositions. The crystal radius for F⁻ has been found to be 1.36 A, and that for OH⁻ to be 1.53 A ²⁸ – a rather close agreement. As a consequence, fluorides and hydroxyls can be interchangeable in crystal lattices; in many cases, the one can fit in as surely as the other without causing undue strain to the arrangement of atoms that form the crystal. If there should be more fluoride available, the amblygonite forming will be richer in fluoride; if there should be more hydroxyl, the amblygonite will be richer in hydroxyl. As we can see from the formula, sodium and lithium are likewise interchangeable in amblygonite.

Apatite ²⁹ Ca₅(PO₄)₃ (F,Cl,OH), is a mineral with fluoride-chloride-hydroxyl interchangeability. Apatite is named from the Greek, *apate*, deceit; looking at the transparent-to-opaque crystals-or masses-or crusts in yellow-or-green-or-brown-or-redor-blue, it can be taken for any one of a number of other minerals - how deceitful! More of the Earth's fluorine is stored as apatite than as any other mineral. ³⁰ An interesting difference between the fluoride-rich form of the mineral, fluorapatite, and the hydroxylrich form, hydroxyapatite, is that pieces of fluorapatite have been found to have greater resistance to wear than pieces of hydroxyapatite. ³¹ This has an equally interesting practical application. It just so happens that bones and teeth are made from a calcium phosphate possessing the same crystal



Fig. 3. A clear needle of Fluorapatite Summit Rock, Klamath Co., Oregon

structure. ³² It has been found that giving people water with fluoride in it encourages the production of the more wear-resistant fluorapatite in the teeth. ³³ This is the reason that fluoridation of water supplies is recommended by dentists.

"Superphosphate" fertilizer is produced by reacting apatite with concentrated sulfuric acid. This process renders the phosphate soluble; plants treated with this fertilizer can then take up the phosphate it contains more easily. ³⁴ Plants need phosphate so that they can manufacture the RNA and DNA they need for reproduction and the ATP they require for the energy they need to live. ³⁵

A number of other minerals have interchangeable hydroxyl-fluoride groups in them. ³⁶ Among them are the micas (phlogopite, lepidolite, biotite) and amphiboles. ³⁷ These are important rock-forming groups.

Let us now consider volatile materials from deep in the Earth. Most people are familiar with the sulfur compounds that give their stink to volcanoes, but there are others as well: water, carbon dioxide, chlorine, hydrogen chloride, ammonia, and quite a few fluorine compounds. ³⁸ Of course, the composition of these volatile mixtures will vary from place to place. Fluorine-containing mixtures may have fluorine, hydrogen fluoride, boron trifluoride (BF₃), silicon tetrafluoride (SiF₄), stannic fluoride (SnF₄), or tungsten hexafluoride (WF₆) in them; all of these are good, strong Lewis acids more than willing to react with whatever they find available nearby.

Perhaps someone may wonder why it is that so many fluorine compounds are volatile; even heavy tungsten gives a volatile (boiling point of 17.5 C 39) fluoride. The atoms of boron, silicon, tin, and tungsten are in their maximum oxidation states in these fluorides, so their central atoms are not prone to interact with groups on neighboring atoms. The fluorines themselves are very stable, since they tend not to polarize, or to be polarized by other atoms. So these fluoride molecules have little tendency to attract each other; they are therefore easy to vaporize. ⁴⁰

In some cases, the volcanic gases deposit out minerals around vents. Species like the ones in the table at right form around the active volcanoes in southern Italy. As we can see, the Italians named the first of these

$KF + BF_3 = KBF_4$	(avogadrite ⁴¹)
$NaF + BF_3 = NaBF_4$	(ferruccite ⁴²)
$2 \ KF + SiF_4 = K_2SiF_6$	(hieratite ⁴³)
$2 \operatorname{NH}_4F + \operatorname{SiF}_4 = (\operatorname{NH}_4)_2 \operatorname{SiF}_6$	(bararite ⁴⁴ , cryptohalite ⁴⁵)
$2 NaF + SiF_4 = Na_2SiF_6$	(mallardite ⁴⁶)

mineralogical rarities after Amadeo Avogadro. Perhaps the villiaumite ⁴⁷, NaF, found in small cavities in nepheline syenite rock, was similarly deposited from hot volcanic vapor. Near the famous volcano, Mount Vesuvius, fluorite, sellaite (MgF₂) ⁴⁸, and phlogopite (a fluorine-containing mica) are found encrusted around vents. ⁴⁹

These fluorine-containing vapors can also change the rocks through which they pass. Boron trifluoride containing fumes can alter silicate minerals into tourmalines ⁵⁰; in some cases, conversion proceeds so far that some rocks are reduced to a mixture of tourmalines and quartz. Tourmalines ⁵¹ are a rather complex family of relater minerals, (Na,Ca)(Mg,Fe⁺²,Fe⁺³,Al,Mn,Li)₃Al₆(BO₃)₃(Si₆O₁₈)(OH,F)₄ that occur in prismatic crystals of ever so many different colors; crystals having two or three different colors are found, and those with one pink end and one green end are common enough that the nickname "watermelon tourmaline" has been applied to them. In 1703, Dutch travelers noticed that tourmaline crystals from Sri Lanka attracted ash when placed on burning peat; heating the tourmaline caused an



Fig. 4. Villiaumite in Nepheline Syenite Point of Rocks, Colfax Co., New Mexico

Fig. 5. Elbaite (a tourmaline) in Spodumene Cattlin Creek, Ravensthorpe, Western Australia



Fig. 6. Topaz crystal Thomas Range, Juab Co., Utah

electric charge to develop which in turn cause the peat ash to cling to the crystal – this is pyroelectricity. ⁵³ Tourmalines have a high hardness (7 on the Mohs scale) and consequently can be used as gems.

When fluorine-containing vapors act upon granitic rocks, topaz, $Al_2SiO_4(OH,F)_2$ ⁵⁴ may be the result. The deposits produced in this way are called greisens. ⁵⁵ In a manner similar to the production of tourmalines, the granitic rock can be transformed into a mixture of topaz and quartz. The hardness (8 on the Mohs scale) and the many colors of topaz make it a prized gemstone, but some topaz buyers have been deeply disappointed – the color has been known to fade in daylight, or through heating. Some of the color in topaz crystals arises because of the formation of color centers, imperfections in the

crystal structure that have excesses or deficits of electrons. When the electromagnetic field due to daylight or the increased vibration due to heat interact with these color centers, the arrangement of electrons is destroyed; the topaz color can change dramatically or disappear. ⁵⁶

Metals from deep within the Earth are sometimes brought to the surface as fluorides, which then hydrolyze when they reach the surface. ⁵⁷ This is what is thought to happen with stannous fluoride: $SnF_4 + 2 H_2O = SnO_2 + 4 HF$

This stannic oxide product is cassiterite, the major ore of tin. That this mechanism for conveying tin to the Earth's surface is possible is shown by the fact that cassiterite is frequently found with fluorine minerals in pegmatites and greisens. ⁵⁸

Likewise, tungsten hexafluoride is thought to hydrolyze: $WF_6 + 3 H_2O = WO_3 + 6 HF$ The tungsten trioxide thus formed can further react; if it finds some iron/manganese oxide mixture, it can
form wolframite: $(Fe,Mn)O + WO_3 = (Fe,Mn)WO_4$

But if it finds some calcium oxide, it can form scheelite: $CaO + WO_3 = CaWO_4$ Wolframite can be found in permatites and greisens with fluorine minerals; ⁵⁹ scheelite can be found with cassiterite and wolframite ⁶⁰ It is fitting that a mineral that may be formed through the agency of fluorine was named after the investigator who took notice of the uniqueness of a fluorine-containing acid, Karl Wilhelm Scheele.



Fig. 7. Durangite (NaAlAsO₄F) on Cassiterite Durangite Claim, Juab Co., Utah

Fig. 8. Thomsenolite (NaCaAlF₆·H₂O) Spider Mine, Juab Co., Utah

We have now seen some of the minerals in which fluorine hides. A few of these, like fluorite and topaz, can harbor fairly large quantities of the element; most of them, like the micas or amphiboles, have little. The seas have precipitated much of the fluoride they might have held because of the insolubility of many fluorides. Fluorine-rich vapors can deposit new minerals, or change the rocks through which they pass.

And yet, in spite of this tendency to rarity, fluorine minerals have shown us new phenomena in physics; they have made possible new processes like glass-etching and aluminum making. Fluorine helps put the bite in your teeth, and brings the tin and tungsten up so that miners can reach them. Fluorine minerals have benefited us in many ways; with fluorine, we are lucky indeed.

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