Northwest Micro Mineral Study Group

MICRO PROBE

SPRING, 2000

VOLUME IX, Number 1

SPRING MEETING VANCOUVER, WASHINGTON

May 6, 2000

9:30 am to 6:30 pm

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

Rudy will be back meeting with us, so bring your new zeolites to share with him and the rest of us as well. Microscopes are a must as usual, and don't forget to bring your extra material for the give-away table so that others will have treasures to look over and take home.

Morning program:

10:30 Russ Boggs will talk and show slides of the recent collecting trips he has taken east of the mountains. If you have slides of minerals or of recent trips, please bring them along to share. We will have a projector and screen available.

Afternoon program:

2:00 Our usual informal business meeting, including reports on the status of local collecting spots.3:00 Don Howard will continue to talk informally, this time about how x-rays are used to do chemical analyses, and about some of the problems and limitations inherent in the procedure.

For the proposed field trip Sunday, see page 6.

The kitchen area is available as usual and we will provide lemonade, coffee, popcorn, etc. There will be a snack table, so bring snacks to share with others for lunch and during the day Restaurants are available in the local area. Some of us will plan to eat dinner together, so please plan to join us.





INTERGROWTH OF SCOLECITE AND MESOLITE AT THE BAIRD CREEK QUARRY, WOLF POINT, COWLITZ COUNTY, WASHINGTON

by Rudy W. Tschernich 526 Avenue A Snohomish, WA 98290

Zeolites are common in one flow exposed in a quarry at the headwaters of Baird Creek, southeast of Wolf Point in the Mount Saint Helens Region of southwestern Washington State. Zeolites were first found at this site in January 2000 by Warren Sorenson, area engineer for Weyerhaeuser. This section of road and quarry were probably made two years earlier but has been blocked by a big heavy yellow gate (Fig. 1) about 1/4 miles from the quarry. This area is closed to motorized vehicles although you are allowed walk to the site. Later this year the gate will be moved back another mile from the quarry.



Figure 1: Yellow gate 87 blocks the logging road 1/4 mile from the Baird Creek Quarry. Signs read "Closed to entry. No public access due to vandalism, theft, and garbage dumping. Violators will be prosecuted. Gate is subject to closure at any time." "Non-motorized entry allowed. Be cautious and watch for logging traffic". "Cars blocking gate will be towed".



Figure 2: View of the Baird Creek Quarry and the south wall that contains zeolites. The flat quarry floor near the wall is the top of the red breccia with the zeolite zone removed. The irregular area at the bottom of the picture is the source of the zeolite boulders when the red breccia with attached zeolite-bearing rock was removed and the boulders piled along the road.

This small quarry (Fig. 2) consists of three slightly dipping flows. The upper basalt flow is finegrained and a rusty-orange color due to surface weathering. The lower flow is a fine-grained, brittle, dark black basalt that breaks into small irregular chunks that are useful to build the logging roads. Neither of these flows contain zeolites. Only the middle flow contains zeolites. The middle flow is a massive basalt, about 10 feet thick, that is fine-grained and brittle in the lower portion and softer and porphyritic in the middle and upper portions. The lower portion is tightly welded to a reddish breccia. The base appears to be have formed when a thin red ash layer was covered and mixed with brecciated basalt at the bottom of the middle flow. The heat from the hot lava baked and oxidized the ash to a red color and cemented broken basalt fragments into a solid mass 3 to 4 feet thick. The red breccia layer, although soft, is very difficult to brake. A chisel just sinks into it without splitting it apart. Quarry men found this layer obnoxious, since it split into boulders the size of a car that would not break without redrilling and blasting each boulder; therefore, they stacked these boulders along the side of the road leading to the quarry (Figs. 3 & 4). The boulders consist of about the 3 feet of the breccia zone and 12 inches of vesicular rock that is rich in zeolites. Although a few pockets, up to 20 inches, are widely scattered throughout the middle flow, most of the workable pockets are in the boulders from the base of the flow. This is great for collecting because it is much easier to break a boulder than chisel crystals out of a rock face in the quarry. The iron-rich olivine and pyroxene in the soft porphyritic rock has been converted into masses of red hematite. Rain water and snow melt transfers the red hematite down cracks and joints in that rock and into any pockets intersected by the cracks, thus staining the naturally snow white scolecite needles an unattractive cream or a rust color. The stain appears to penetrate the crystal structure of the scolecite and lodges in the channels within the structure. The coloration has not been successfully removed with chemicals. If pure snow-white specimens are desired, the best cavities are those in the hardest rock not intersected by fractures. The fine-grained black basalt does not have the red iron stains; therefore, the crystals are usually fresh and colorless.

The coarse-grained porphyritic basalt contains the larger cavities, ranging from 3 to 20 inches in diameter. They are lined mostly with scolecite, a little laumontite and calcite while a few small cavities scattered in the same rock are lined with levync, analcime, or epistilbite. The fine-grained black basalt contains fewer cavities than the porphyritic rock and range from 1 to 4 inches in diameter. They are usually lined with mordenite, heulandite, yugawaralite, stilbite, laumontite, and calcite. Both of these types of rock appear to be attached to the red basal breccia.



Figure 3 Randy Tschernich collects scolecite from 3 to 12-inch pockets in the soft porphyritic basalt along the road.



Figure 4: Randy Tschernich works on the zeolite-rich portion of a boulder along the road. Red breccia makes up half the boulder.

In the soft porphyritic basalt, nearly all the cavities over 1 inch are lined with attractive thin needles of scolecite, 5 to 15 mm long (Fig. 5). The needles are flattened with striations parallel to the length of each needle and are terminated by four flattened pyramidal faces. The scolecite closely resembles scolecite found on Elk Mountain, some 6 miles away. Upon very close observation at 70 magnification, a small phantom is seen less than one mm from the termination. Observation of these crystals with a polarized light microscope clearly shows that 99% of each needle is scolecite that is usually twinned into two or more parts and is terminated by a cap of mesolite (Fig. 6).

The scolecite/mesolite needles are usually found alone in the pockets. Scolecite/mesolite has been rarely found on elongated amber calcite and heulandite and is very rarely found on yugawaralite and levyne. Needles of scolecite/mesolite have been observed passing through stilbite which indicates stilbite grew over the needles.

Two generations of calcite have been recognized in the Baird Creek Quarry. Small amber-colored dog-tooth calcite is the first mineral to crystallize in the cavities. It is always covered by white scolecite needles, heulandite, or a later-formed colorless calcite. The late-formed calcite is the last mineral to crystallize in the cavities. It forms tiny colorless rhombohedra on the scolecite that resemble chabazite



Figure 5: A 3-inch cavity lined with 8-mm long scolecite/mesolite needles along with one 0.5 inch colorless calcite rhombohedron.



Figure 6: A single needle composed of twinned scolecite (S1 and S2) capped by mesolite (M).

and enlarged the existing calcite to form scepter heads on the terminations of the dog-tooth calcite. Rarely rhombohedra calcite, up to 15 mm across, are present on the scolecite. The presence of an amber colored calcite that predates the zeolite crystallization and a colorless rhombohedral calcite that forms after the zeolites is common in the volcanic rock on Elk Mountain and many localities in the Pacific Northwest.

Small cavities, generally under one inch, are not abundant in the porphyritic basalt in the quarry and are widely scattered. The small cavities often contain levyne or analcime. The levyne usually forms complexly twinned, colorless to white crystals that do not display the characteristic large flat c-face or any overgrowth of offretite/erionite. This type of levyne displays many triangular faces and striations that are similar to the levyne present in the 200/237 Quarry. Some pockets are lined with rhombohedral levyne or simple twins that are also found on Elk Mountain (See Figs. 360, 375 & 376 in Zeolites of the World). A few pockets show evidence that the levyne lining had broken free from the walls of the cavity and then regrew cementing the loosened plates of levyne to the newly formed levyne. Levyne is rarely covered by scolecite. Analcime forms colorless trapezohedra, commonly 2 to 3 mm across, with a very few reaching 10 mm in diameter. Analcime is usually alone in the small pockets; although, it has been found on calcite in one cavity.

A different assemblage of minerals is found in the dark black brittle rock. They are all rather scarce in the quarry. This group includes mordenite, heulandite, stilbite, laumontite, yugawaralite, calcite, chabazite, and epistilbite. Mordenite is the first zeolite to crystallize in many of the cavities in the finegrained, dense, black basalt. It was identified by optical properties. It does not occur in the scolecite-rich cavities in the porphyritic basalt. The mordenite formed radiating tufts of colorless to white needles, up to 4 mm long, scattered on dark green to black clay and is always covered by heulandite. Less commonly, mordenite forms compact, zoned, radiating hemispheres, up to 8 mm in diameter, also covered by heulandite. The mordenite needles are easily seen as white inclusions within the colorless heulandite crystals but they never extend beyond the heulandite. Some radiating hemispheres display a gap in the mordenite where there is no protective heulandite. It is apparent that the mordenite needles at one time did extend beyond the heulandite but that any mordenite not protected by heulandite was dissolved away. This relationship of mordenite and heulandite has also been observed at Big Tree Creek at Yacolt and the Dutch Army site on the Lewis River. Heulandite is the second zcolite to form in the cavities and is far more obvious than the mordenite that precedes it. It forms lustrous to frosty, colorless, blocky crystals, up to 8 mm across, that appear dark green or black from the dark color of the clay being transmitted through it. Parallel growths of heulandite similar to that found at the 237/200 Road Quarry are rare. White mordenite needles are commonly included within the colorless transparent heulandite. Dark green spheres of a clay mineral are also seen included within the heulandite and on the mordenite inclusions. These green spheres of clay oxidize to a brown color where they are not completely covered by the heulandite. Several generations or growth periods of heulandite are recognized. The first forms tiny white crystals on the cavity wall that are covered with colorless transparent heulandite containing clay inclusions. The final growth of heulandite is clear without clay inclusions. This last phase engulfs the edges of stilbite, yugawaralite, and epistilbite which appear to have grown on the second (clay included) phase. Besides enlarging existing heulandite crystals, the last phase of heulandite crystals. One specimen shows levyne covering amber colored large heulandite crystals while the levyne is covered by minute colorless heulandite.

Epistilbite is very rare in the quarry. It forms colorless to white wedge-shaped crystals with frosted terminations. Some of the crystals are partly cyclic twinned. In one cavity epistilbite forms, 0.5-mm, etched or frosted white crystals that are partly embedded within last phase of heulandite and partly covered by yugawaralite. The crystals show evidence of being partly dissolved, frosted, and etched becoming skeletal. Other cavities contain epistilbite covered by colorless chabazite. The rarity of epistilbite and yugawaralite (which have the same chemical composition) existing in the same pocket and when together, the epistilbite is partly dissolved, might mean that they are not stable together because they use the same ions from the fluid.

Yugawaralite is a rare zeolite. This is the second locality for it in Washington State. The other site is in the 237/200 Road Quarry only a mile east of the Baird Creek Quarry. It forms water-clear, glass-like blades that have a large lustrous b-face and beveled faces on the edges. To distinguish it from stilbite and heulandite, the yugawaralite crystals show no cleavage, no pearly luster, or intersecting striations on the broad b-face, while it does have a glassy fracture. The yugawaralite crystals display a typical asymmetric blade-like crystal form. The yugawaralite occurs on the early phases of heulandite and calcite. It very rarely occurs on epistilbite and is covered by scolecite, laumontite, stilbite, and chabazite. Yugawaralite appears to have crystallized at about the same time as epistilbite and is partly engulfed by the last phase of heulandite. Yugawaralite is rarely found in the same cavity as scolecite/mesolite needles. Most of the yugawaralite-bearing cavities are 1 to 3 inches in diameter although a few 6 to 10 inch cavities were found that contained an abundance of yugawaralite blades on heulandite while being covered by stilbite and laumontite. Yugawaralite is not rare in the Baird Creek Quarry. It is found in nearly all the heulandite-lined cavities in the fine-grained black basalt. Yugawaralite crystals are uniformly 4 mm long. They usually extend perpendicular from the heulandite on the walls of the cavity into the center of the pocket. Yugawaralite, like stilbite, forms more densely packed crystals on the floor of a cavity than on the roof, which aids in determining the direction of pockets in the basalt flows.

Stilbite is not abundant in the quarry. In a few cavities, it forms colorless to light cream colored pointed blades, up to 15 mm long. In other cavities the stilbite is colorless the stepped flat terminations. It covers heulandite, epistilbite, and yugawaralite. Some cavities contain needles of scolecite/mesolite passing through the stilbite, which indicates the stilbite formed after the scolecite/mesolite needles. One exceptional 10-inch cavity was encountered that contained beautiful groups of 1-inch long transparent stilbite crystals on colorless heulandite and yugawaralite. Unfortunately, the pocket did not come out intact.

Laumontite fortunately is not abundant in the quarry but it does occur sparingly in many of the pockets. It forms small, white, doubly terminated, four-sided prisms, 2 to 6 mm long, with a single sloping face at each termination. It is found on the scolecite needles in a few of the cavities in the porphyritic basalt and is scattered on heulandite, stilbite, yugawaralite, epistilbite, and calcite in the fine-grained rock. Only chabazite is clearly found on top of laumontite; although, a few crystals appear to be covered by the terminations of stilbite.

Chabazite appears to be the last zeolite to crystallize in the cavities, although, it is rather scarce in the cavities. It forms colorless, transparent rhombohedra, up to 8 mm across, with a high luster and numerous striations on its faces. Chabazite is found on heulandite, epistilbite, yugawaralite, scolecite, and laumontite. Thin veins and joints commonly cut the red basal breccia and some of the dark vesicul-basalt welded to it. These veins are covered with minute colorless rhombohedra of chabazite that sparkle in the sun like diamonds. Minute pyrite crystals also cover some of the veins. Where a vein intersects a vesicle, drusy chabazite covers the zeolites already in the cavity.

The mineralogy in the Baird Creek Quarry is far more complex than it first appears. The presence of several rare zeolites, multiple crystallization phases of the same mineral, and evidence of disturbances in the cavities from faulting, volcanism, or changes in the hydrothermal water makes this site complex. Much more collecting and study is required.

The minerals appear to have crystallized in the cavities in the following order: clay > amber calcite > mordenite > heulandite 1 > (levyne ?>epistilbite > yugawaralite > scolecite > mesolite > stilbite) > heulandite 2 > laumontite > fractures and chabazite or pyrite > colorless calcite. Placement of analcime is not known.

Nearly all the species found in the quarry are very calcium-rich. With more collecting additional calcium-rich species will be found in this quarry. The following minerals are expected in the quarry but have not yet been found: quartz, apophyllite, cowlesite, phillipsite, thomsonite, wairakite, gyrolite, and okenite.

FIELD TRIP IS PLANNED SUNDAY MAY 7, 2000 TO THE BAIRD CREEK QUARRY

Weather permitting, Rudy Tschernich will lead a field trip to the Baird Creek Quarry on Sunday May 7th, the day after the Micro Meeting in Vancouver, WA. Those wishing to participate will meet in the parking lot of the Rose Tree Restaurant at the Castle Rock exit number 49, just east of Interstate 5 at 9:00 am. We will leave by 9:15 so be on time. It takes about 45 minutes to reach the quarry. We will have to park near the gate and walk about ¼ mile down the road to the quarry and later walk back up the road, what seems like a mile, loaded with tools and specimens. No motorized vehicles are allowed beyond the gate. Weyerhaeuser has plans to move the gate another mile further from the quarry later this summer; therefore, collecting now is recommended. The rock is hard and difficult to work. Four and eight-pound hammers and chisels are required. A backpack, eye protection, boxes, wrapping material, hand lens, camera, and drinks are useful. Directions to the quarry will not be given out in advance of the field trip. Come with your friends and enjoy the day high in the mountains among the trees looking for minerals.

MINERALS OF THE LAST CHANCE MINE, SKAMANIA COUNTY, WASHINGTON

Don Howard and Bill Tompkins

Men exploring the hills of western Washington just north of the Columbia River discovered evidence of copper mineralization over 100 years ago. This resulted in a cluster of mines along the Washougal River straddling the line between Clark and Skamania counties that have come to be known as the Washougal mining district.¹

The area is composed geologically of the Skamania Volcanics, andesite flows, tuffs, and volcanic breccias into which the Silver Star granodiorite has intruded in places. About a dozen specific copper-bearing seams and veins have been identified in this area, and a number of mines and placers have been established to explore these deposits.

During this last fall, together with Martin Jones, we have been examining one of these mines, the Last Chance. This appears to be the southernmost of the mines in the district. It is located along the west fork of the Washougal River about a mile and a half from the Clark Co. line. The Last Chance mine is on deeded land in the center of S1/2 SE1/4 sec. 29, T. 3 N., R. 5 E., and at an elevation of 1,600 feet. From Washougal, State Highway 8B, County Road 11, and logging roads may be followed for 16 miles to the property. The last 2 miles of the road are not maintained, and are generally inaccessible to vehicle travel. The Last Chance mine was discovered and developed at the same time as the Skamania mine, which is 1.5 miles north of the Last Chance. The properties are often confused with each other because the mine workings are almost identical at both properties. Although Washougal Consolidated Copper Mining Co. undertook considerable development work at the Last Chance in the early 1900's, no shipments of ore were made. The mine has been idle for at least 20 years and all mining equipment has been removed.

The Last Chance operation consists of a shaft and two horizontal tunnels. One tunnel, located on the west side of the river, is difficult to reach from the road, which is on the east side. That tunnel, which is reported to be 267 feet long,¹ was not explored. The other tunnel and the shaft are on the east side of the river just below the level of the road. A small dump, consisting mostly of fine-grain material, lies directly below the adit. Some green color is evident, but since the material has been undisturbed for many years, it does not appear very productive for collecting.

The tunnel is cut back into very solid rock and has not needed timbering except at the very mouth. There, the tunnel appears to be located under a small stream only a few yards above, and the first few tens of yards provide a shower bath, even when it is not raining outside. Water collects a foot or so deep in this area and must be waded, so appropriate raingear and boots are a must. The shaft, which is just to the north of the adit to this tunnel, has completely filled with water. It is reported to be 540 feet deep, and to have side shafts cut at five different levels.¹

The east tunnel runs some 936 feet into the hillside; it slopes up very gradually, just enough for the water dripping inside to drain out the mouth. Except for the first twenty to thirty yards, the floor is only shallowly covered in pooled water and it is possible to walk in most areas on solid footing on one side or the other of the old, iron

covered boards that served as rails for ore cars. The ceiling is everywhere high enough to be able to walk upright without danger of hitting your head.

The tunnel follows a pair of quartz veins, each several inches to a foot wide, that form an inverted V that met about ceiling level. The seams are clearly seen running along the center of the ceiling throughout the length of the tunnel, and the V structure can clearly be seen at the back end of the tunnel. Numerous short crosscuts show that a second similar quartz seam runs parallel a few yards to the south. Traces of these seams have been followed for nearly two miles.²

The central region of the quartz seam in several places opens into gaps that are lined with quartz crystals, the terminations generally being half a centimeter or less. The seam originally consisted of both quartz and calcite, as witnessed by numerous regions of angular, rhombohedral cavities where the calcite has been completely dissolved away. These cavities indicate that the original calcite rhombs were up to a centimeter or two in diameter. Some of these cavities are still sharp, while others have been nearly filled with the growth of drusy quartz crystals. Many of the cavities show thin wall-like partitions where the quartz filled into cleavage cracks in the calcite. Currently, calcite is quite rare in the mine.

Copper mineralization is mainly in the form of chrysocolla. Some radial, fibrous growths indicate that at least at one time, this was at least partly in the form of malachite, but currently all the green to blue material is the silicate chrysocolla. Bornite, pyrite, chalcocite, and chalcopyrite have been reported as forming blebs disseminated within the quartz vein.¹ Much of the chrysocolla is present in greater or lesser amounts on the contact on either side of the quartz vein; this is several inches thick in places and in the wet environment appears intensely green. Much of the color fades, however, upon drying. The chrysocolla is mostly botryoidal, and except for the fibrous places indicating malachite alteration, there is not much evidence of pseudomorphs of previous minerals. Surfaces examined at higher magnification look like masses of wet, matted fibers.

The most interesting mineral in the mine forms as yellow to ocher coatings and stains on the quartz crystals in the gaps in the seam. This material was described as "descloizite (lead vanadate)" in the summary article.¹ In fact, it contains practically no zinc at all; zinc is quite rare in the minerals of the mine. The material is essentially endmember mottramite – Cu Pb (VO₄) (OH). While being a very interesting occurrence, the material makes particularly ugly specimens. The color is not at all attractive, and the crystalline structure of the crusts is only evident at a magnification above x200 (see micrograph #339). The material is quite plentiful, however, and can be easily collected.

Other cavities in the quartz seam have been filled with chrysocolla (bright bluegreen) or other silicate crusts fading to almost white. Many of these are coated in turn with small dark spots and patches of a manganese oxide that also contains a wide variety of impurities, such as iron, copper, lead, and even a trace of zinc... Some regions have been stained orange by iron oxide – a distinctly different color from the mottramite stains.

A few small cavities have been found to contain tiny rhombohedrons of calcite. These are generally colored blue-green by copper or yellow by mottramite. Carbonates are not at all common in the mine.

Close examination has turned up a few specimens that show needle-like or ribbon-like scattering of crystals in the voids where the calcite has dissolved, or mounted

on the quartz crystals in the central openings. In few instances is there enough material to properly analyze. XRF done on the SEM shows a variety of compositions. At least four such unknowns have been identified:

- 1) Sprays of flattened needles, some terminated, which appear to be orthorhombic. Chemically they appear to be a calcium aluminum silicate with considerable iron content (perhaps 1/3 iron to calcium)
- 2) A rod-like crystal, squarish cross-section, that is dark green to black. Chemically, it appears to be a silicate with nearly equal iron and copper concentrations. There is also manganese (about 1/5 manganese to iron). This is mostly embedded in the quartz, with tiny quartz prisms growing on the surface, which is fuzzy like some of the chrysocolla surfaces.
- 3) Flat yellow blades, very thin with irregular ends, that occur in clusters. The chemistry is about equal parts of copper, iron and lead. There is some silicate present, but no other anion seems to be present (ie., no vanadium).
- 4) dark yellow lath-like crystals scattered individually around the inside of one of the rhombohedral holes. The blades look feathery, as if they have fractures at an angle, and the ends are sloping or forked where broken. The chemistry has not yet been determined.

Because so many of the cavities show thin coatings over the crystals, it is difficult to be sure of any of the chemistry - is the material intrinsic to the crystal or merely a stain on the surface? Further examination will be needed to isolate enough of any one form to properly analyze and identify it.

References

^{1.} Wayne Moen, *St. Helens and Washougal Mining Districts of the Southern Cascades of Washington*, State of Washington, Department of Natural Resources, Division of Geology and Earth Sciences, Information Circular 60 (1977).

^{2.} R.M. Brerton, *Plat of the Last Chance Mine*, Washington Division of Geology and Earth Sciences, unpublished map (1930).

ON SYMMETRY, TILING, AND CLUSTER FORMATION

Don Howard

Somewhere in the study of mineralogy, in a textbook or a College course or even in an informational article like this one, one comes across the old rule that the only rotational symmetries allowed for lattices are two-, three-, four- and six-fold rotations. That is, five- and eight-fold rotational symmetries are not allowed. The argument goes something like this: Pick as a basic representation of the unit cell either a pentagon or an octagon. When you try to tile a plane with such figures, they do not cover all the space. That is, parts of the plane fall outside the unit figures. Squares, triangles, and hexagons will tile the plane, so they can be used to represent all the space of the lattice, but pentagons and octagons don't work.

Now for a molecule, there is nothing wrong with having five-fold or eightfold symmetry. Indeed, the metal-organic molecule ferricene ($C_5 H_5 Fe C_5 H_5$) consists of an iron atom sandwiched between two five-membered carbon rings, and therefore has a five-fold axis of rotation. However, when ferricene crystallizes into a solid, that five-fold axis works only for a single molecule; groups of molecules condensed together have a lower overall symmetry in order to cover all of space.

That notion has been around for a long time. What, then, when transmission electron diffraction patterns taken in 1984 showed up with five-fold symmetry patterns for an aluminum-nickel-cobalt alloy¹? (See the inset in figure 1.) How can this come about? Alloys such as this, with what we would consider strange or exotic structures, are coming to be called *Quasicrystals*.

The answer to how such a structure can exist seems to lie in the complexity of the organization of atoms. The unit cells of such materials contain a large number of atoms. Often these atoms cluster into groups that are repeated several time within the unit cell in differing orientations. This allows the possibility of tiling a plane, not of purely contiguous cells, but of some cells that overlap! The units are so arranged that the overlapping parts have the same structure in each cell. Figure 1 shows a possible explanation of the structure of the alloy in question. The figure is composed of decagons (regular ten-sided polygons) with five similar quadrilaterals (shaded) in various positions inside them. Figure 2 shows that such a figure can overlap in two different ways, and this allows sufficient variety to manage to tile the plane completely, maintaining approximate five-fold symmetry on a long-range scale.

Such materials have been synthesized in alloy systems. Do similar structures exist in natural materials? I do not know of any that have yet been found. Perhaps there is something in the thermodynamics that makes such systems only metastable, not truly stable on a long-term basis. On the other hand, some natural systems that exist in several crystal structures are metastable (at least at ordinary temperatures) and they occur in nature just fine. Many of our silicates, such as the zeolites, certainly have large, complicated unit cells with many atoms. And the zeolite structures are composed of a few basic building block structures that are repeated over and over in various orientations. So it is certainly something that might happen in nature and something to be on the lookout for.



Fig. 1 Inset: Experimental electron diffraction pattern for a particular AI-Co-Ni alloy Background: A possible tiling using overlapping decagonal cells with common regions



Fig. 2 A diagram of a possible decagonal unit with several similar regions. Overlap of two such units can be done in such a way that one of these regions or two of these regions are held in common. By allowing such overlaps, the entire plane above can be covered.

Whether quasicrystals occur in nature, however, is not the only issue related to these kind of complicated symmetries I wish to explore. Let me take a different tack, make a number of preliminary remarks about how crystals grow, and then return to this question of symmetries that do not simply "tile" space.

Crystals grow by adding units (atoms or molecules) onto their surfaces. Whether new units "stick" or not is a matter of the forces holding them together, or alternatively the energy necessary to make them come apart. For the sake of illustration, let us imagine atoms as spheres coming together to form a native solid. Forces are greatest where the spheres touch. It is therefore easier to add an atom to a step on a face, where it will be touching several neighbors, than it is to add it onto a completed face, where it will be in contact with at most two or three other spheres. Thus, steps grow out rather rapidly to form flat faces, and new faces are started only slowly. In fact, a single atom probably will not stay stuck to a completed face unless it is soon joined by several others to form a cluster, after which the new step around the edge of the cluster can grow out fairly rapidly. This process, called nucleation (of the cluster) is generally the limiting rate in forming the crystal.

There is a "short circuit" to this process, however. There could be a defect (like a bit of foreign matter) that the face grows around in such a way that the two sides do not come together exactly right. The resulting "face" resembles a spiral staircase, and a growth step is always present, circling around and around as more and more new atoms are added. Of course, there is a defect present at the center of the spiral, a line defect that is called a *screw dislocation*. (For further discussion, see ref. 2.) A face containing a screw dislocation at an angle to it will grow much more rapidly than one without. The growth of whiskers (such as filiform pyrite) is believed to be caused by these sorts of defects. If only one face has such a defect, it will grow much more rapidly than others. If all faces have defects, the growth will result in a more equant crystal.

The ultimate problem of nucleation involves starting the crystal in the first place. The regular crystal structure of an existing surface of a different substance may aid the first cluster to form. When this happens, the orientation of the new crystal may be aligned to that of the existing surface, and epitaxial overgrowths result. This is the case, for instance, of oriented offretite overgrowths on levyne. Alternatively, it may be an irregularity in the existing surface that helps nucleation. For many of our minerals, overgrowths of these types are responsible for the variety of crystal species we see occurring together in a single cavity on a specimen.

On the other hand, the material may have to organize the first cluster on its own. How does it go about doing this? Again, for simplicity, let us consider spheres that are held together on contact. The first two atoms have only one such contact -0.5 contacts per atom. Three atoms can come together to form a triangle, with three contacts – one contact per atom, energetically a stronger bond. We can add a fourth atom to form a tetrahedron; now there are six contacts with 1.5 contacts per atom. We see a steady trend of growing stability as the cluster gets larger.

Something interesting happens, however, as we keep adding atoms. Four atoms form a tetrahedron – a cubic structure. A fifth atom added to one of the triangles results in two triangular pyramids (9 contacts, 1.8 contacts per atom), but this structure has trigonal symmetry rather than cubic symmetry. A sixth atom would add three more contacts (2.0 contacts per atom), but would leave the cluster with low symmetry.

However, with a slight shift, we could form an octahedron (a square with additional atoms above and below) that also has twelve contacts total, the same binding energy and cubic symmetry to boot!

Let us add one more to either of the above clusters. That would give 15 contacts in either configuration. However, we could again rearrange things as a ring of 5 atoms with one above and one below – again 15 contacts, but the spheres above and below are almost in contact, perhaps close enough to count as 16 contacts and a more stable structure that has a five-fold axis of symmetry.

I think the point should be clear: the symmetry of the most stable configuration changes around and around as we add each additional atom. Some configurations will be cubic, some tetragonal, some trigonal or hexagonal, some pentagonal, and so forth. At some point the cluster is going to be so large that rearrangement is going to be awkward and it will instead just continue to grow in the form that the original cluster has developed. That is fine for clusters that have 2-, 3- 4-, or 6-fold symmetries. But what happens to a cluster that is stuck in a 5-fold symmetry, for instance? It cannot continue to add atoms that will maintain that overall symmetry. I suggest that a very interesting thing happens: parts of the crystal fall into its natural long-range order in one way, while other parts do so in another way, and we end up having boundaries between these regions that are mirror planes. We end up with a twinned crystal. Perhaps we end up with a multiply twinned crystal.

I can think of an example of a material doing this about a point: okanoganite. Four crystals in the form of three-sided pyramids come together at a point to form a fourling that appears to be tetrahedral. (For more detail, see Microprobe, Vol. 7, #3, page 21.) I think this happens much more commonly about a line defect, and leads to what we know as a cyclic twin. Examples of such systems include:

- Phillipsite. This mineral is always found in at least fourlings about an axis, and often in eightlings. The mineral is monoclinic, but appears tetragonal after twinning. (See Minerals of the World, page 404.)
- Pentagonite. Apparent five-fold symmetry is accomplished by fivelings around a common axis. The crystal lattice is actually orthorhombic. (See Microprobe, Vol. 7, #10, page 15.)
- Dachiardite-Ca. The crystals from Elba, Italy are essentially eightlings, arranged around a common axis. (See Minerals of the World, page 131.)
- Epistilbite. The unusual twins from Wolf Point Quarry, Washington are eightlings. The lattice has monoclinic symmetry. (See Microprobe, Vol. 7, #10, page 6.)
- Tschernichite. A few unusual crystals showed a cyclic habit. The lattice is tetragonal. (See Minerals of the World, page 512.)
- Chabazite. Some phacolite crystals may be of this type. The mineral is nearly rhombohedral. (See Minerals of the World, page 93.)
- Sodalite. This cubic mineral forms elongated crystals that appear to be sixlings. Because only two orientations are spatially unique, they are usually described as penetration twins. (See Mineralogical Record, Vol. 31, #2, page 144.) Other cubic minerals that form similar cyclic twins include sphalerite and sal ammoniac.

The description above assumed all spheres were the same. This is an overly simplified discussion. In most minerals, several ions of different size are involved, and there is no reason to believe that ions behave like spheres. Bonding orbitals often favor specific angles between bonds, so the units do not fit together in just any arbitrary direction to each other. Thus, one would have to know many more parameters to be able to predict what sorts of clusters were favored for a particular mineral. My intent here was to indicate what I believe to be the root cause of the phenomenon of cyclic twinning.

And who knows? One of these days we may come across a material that really does manage five-fold or eight-fold symmetry in the manner of the quasicrystal alloys.

References

- 1. Ivars Peterson, A Quasicrystal Construction Kit, Science News, Vol. 155, #4, page 60, (Jan. 23, 1999).
- 2. W.A. Henderson, R.P. Richards, & D.G. Howard, *Elongated Twins of Sodalite and Other Isometric Minerals*, Mineralogical Record, 31, 141, (March/April, 2000).
- 3. R.W. Tschernich, Zeolites of the World, (Geoscience Press, Phoenix AZ, 1992.).



Fig. 3 The nature of cyclic twinning in sodalite. Six rhombo-Hedrons are oriented every 60° about the [111] axis. The twin planes are of the form [112]. The valley at the top has filled in to form a star-shaped (111) face. See micrograph #009.

OCCURRENCES OF NATIVE SELENIUM IN NEVADA

Don Howard and Dick Thomssen

In the last issue, native selenium was mentioned as a mineral coming from the Red House Mine^I. A picture was included, but not much detail was given. In this issue, we show another picture of native selenium (see Micrograph #205), this time from the Willard Mine. Again, the setting is in association with phosphate minerals. With more localities come more information.

Classic occurrences of native selenium include Kladno, Bohemia (burning heaps of carboniferous sediments rich in pyrite) and Jerome, Arizona (fire zone of the United Verde Mine encrusting quartzite and fritted sandstone)²; Glen Lyon, Pennsylvania (old burning coal-waste heaps), in many U-V mines in the Colorado Plateau, and the Pacajaka Mine, Colquechaca, Chile with selenide minerals³.

The current micrograph shows open sprays of selenium needles growing on wavellite crystals. Wavellite is a hydrated aluminum phosphate: Al₃ (OH)₃ (PO₄)₂ 5 H₂O. The water of crystallization is almost entirely lost between 100° and 200° C⁴. As can be seen in the micrograph, the surfaces of the wavellite crystals are sharp and unaltered. In the light microscope, they are clear and transparent. Clearly alteration has not occurred. The formation of the selenium must therefore be well below 200° C. Montgomeryite (the mineral the selenium is forming upon at the Red House Mine) is also a hydrated phosphate that would lose water at relatively low temperatures.

The first few occurrences for native selenium listed above are from vapor deposition, though admittedly from artificial fumerole conditions. Selenium boils at a temperature of about 220°C. It is therefore unlikely that the crystals can be forming from the vapor phase, since then the wavellite would be dehydrated and not be clear. This would indicate that formation must involve solution chemistry.

The next problem is to explore where the source of the selenium might be. Selenium is a relatively rare element and only very rarely forms minerals of its own. It does have a chemistry very similar to sulfur, the element directly above it in the periodic table. Since selenium ions tend to be only about 10% larger than sulfur, the usual source of selenium is as low-concentration impurities replacing sulfur in sulfates and sulfides. The Red House Mine has extensive bedding of massive barite, barium sulfate, but there are no common sulfates in large amounts at the Willard Mine. On the other hand, both localities have black, carboniferous, pyritic shales associated with the phosphates.

To understand what is probably going on, let us consider the chemistry of selenium and sulfur. Elemental selenium comes in three modifications: two monoclinic structures that are colored red and a hexagonal form that appears metallic. The red forms are obtained in the laboratory by reducing selenites, and can easily be converted by modest heating to the hexagonal form, which is the stable form at room temperature.

One way to depict the various ionic states that an element can take on is with an Eh-pH diagram, such as the ones shown at the top of the next page. pH is a measure of the acidity of the solution; small numbers (to the left) are very acid and larger numbers (to the right) are very basic. Neutral solutions have a pH of 7. and are located in the center of the scale. Eh (measured in volts) gives the oxidizing/reducing ability of the solution. The more positive the value, the greater the ability of the solution to oxidize.



HS1

10

12

14

H₂S

2

4

*1 bar

6

8

рH

-0.2

-0.4

-0.6

~0.8 L

One notices immediately that there are more ionic species in solution for selenium than there are for sulfur. However, most of these species require very strong oxidizing agents to form them. Most chemical environments are going to be in the vicinity of 0.0 Eh and 7, pH. For sulfur, this corresponds to sulfate ion, which is the normal form of sulfur in solution. For selenium the corresponding form is elemental selenium.

-0.2

-0.4

-0.6

-0.8L

2

Se-O-H

SeO4

b_{ar}

6

8

DН

25°C, 1 bar

SeO²⁻₃

HSe^{*}

10

12

14

Elemental sulfur has a very small stability region in solution, all located in very acidic solutions. Normally surface solutions in contact with metallic sulfides become very acid as the oxidizing ability of the dissolved oxygen converts the sulfides to sulfate and sulfuric acid results. Sulfide and sulfate can be at equilibrium with each other. Free sulfur is seldom formed from solutions; rather it comes from thermal breakdown of sulfides and is a vapor-phase mineral.

Over a wide range of pH values, selenide is at equilibrium with elemental selenium. It takes a very strong oxidizing agent to produce selenite and selenate ions, so these are formed only under unusual conditions. The oxidizing process that takes sulfide to sulfate will carry the selenide only to elemental selenium.

We therefore propose that the selenium is probably coming from impurities in the iron sulfides (pyrite and marcasite). As the system cools down and oxygenated nearsurface water is incorporated, the solutions will drop to a temperature and/or increasing concentration of phosphate, aluminum, calcium and selenium where, first, the aluminum will precipitate out as wavellite (or montgomeryite), the calcium next as apatite, and then later selenium will follow.

At the Willard Mine, the immediate wallrocks of the particular veinlet carrying the selenium do not show the effects of oxidation, so the plumbing system must be relatively extensive. Rocks some 15 or 20 feet away show the evidence of oxidized iron and this puts a minimum dimension on the system. A reasonably large mobility of the

solution is also indicated by the relatively large amount of phosphate and selenium which have been concentrated in the veinlet.

Native selenium has also been found at the Green prospect in the Mopung Hills, where metallic needles and bright red amorphous material were found with red sulfur within the alteration haloes of masses of oxidizing stibnite. The selenium reported from the Gold Quarry Mine⁵ would appear to be one of the monoclinic polymorphs. In neither case are there extensive phosphate beds present.

The moral of all this would seem to be that native selenium can be derived from solution chemistry, and could very well be present in a number of places, since oxidation of pyrite is a widespread phenomenon, and pyrite commonly contains selenium as an impurity.. This is certainly a simpler and more wide-spread type of oxidation/reduction system than the U-V system recognized for the occurrences in the Colorado Plateau. Selenium could very well be present in many places in small quantities that could easily be overlooked unless it becomes concentrated locally. It could often be mistaken for other minerals, particularly if only a few scattered small crystals were present. We have another mineral that we will need to keep looking out for.

References:

- 1. D. Howard, Montgomeryite, Microprobe, Vol. 8, #10, page 11, (Fall, 1999).
- 2. C. Palache, H. Berman & C. Frondel, *Dana's System of Mileralogy*, (John Wiley & Sons, New York, 1944) Vol. 1, page 136.
- 3. R. Gaines, H. Skinner, E. Foord, B Mason & A. Rosenzweig, *Dana's New Mineralogy*, (John Wiley & Sons, New York, 1997) page 30.
- 4. C. Palache, H. Berman & C. Frondel, *Dana's System of Mileralogy*, (John Wiley & Sons, New York, 1944) Vol.21, page 963.
- 5. M. Jensen, J. Rota & E. Foord, *The Gold Quarry Mine*, Mineralogical Record **26**, page 463, (1995).

FIGURE CAPTIONS

Micrograph Number is in the lower right corner of the front.

#393 Quartz on Mordenite

Squilax Mountain, Chase, British Columbia

Another example of tiny, tapered rice-grain crystals growing impaled on mordenite needles of various diameters. Only the quartz terminations show sharp faces.

#339 Mottramite on Quartz

Last Chance Mine, Washougal River, Skamania Co., Washington Bundles of parallel platelets gathered in groups standing up on the matrix underneath. The crystalline nature of the coating is evident only at high magnification.

#009 Sodalite

Wannenkopfe, Eifel, Germany

A cyclic twin of a cubic mineral. (See the diagram on page 14.) Only 4 of the six rhombohedrons are fully developed, so only 4 of the six star points are present. The other two rhombohedrons can be seen in the photo partially developed.

#205 Native Selenium on Wavellite

Willard Mine, Pershing Co., Nevada

Sprays of a few metallic needles resting on sharp, unaltered crystal blades of wavellite. The open nature of the sprays seems to be characteristic of selenium formed in this way.

Picture Credits

Micrographs Specimens: Quartz-Mordenite Mottramite Sodalite Selenium-Wavellite Don Howard

Stan Johnson Don Howard Bill Henderson Dick Thomssen

THE MICROPROBE

Published twice a year by the NORTHWEST MICROMINERAL STUDY GROUP

> Donald G. Howard, Editor 356 S. E. 44th Avenue Portland, Oregon 97215

DUES: \$15 per year per mailing address.

(x200)

(x750)

.

(x 150)

(x 200)



