WILLEMITE MORPHOLOGY AND PARAGENESIS AT BALMAT, NEW YORK

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The occurrence of supergene willemite (Zn_2SiO_4) has been mentioned briefly in a paper on the St. Joseph Lead Company Mine at Balmat, St. Lawrence County, New York, by John S. Brown (1936). No other description of the willemite of this locality has appeared, though it is an unusual and interesting occurrence yielding splendid material for study. The writer of this paper wishes to express his appreciation to Dr. Brown for his cooperation at the time of a visit to the mine and since, through the gift of specimens, and a critical reading of the manuscript.

The willemite occurs in a lens extending to some depth below a strongly oxidized portion of the deposit. The upper levels contain considerable secondary sulphides, and oxide minerals. The willemite zone below this is marked by the dominance of a talc-chlorite replacement of the rock, and willemite, with some hematite. The willemite is present in some quantity and is potentially a considerable deposit, but no use of this ore is being made at the present time. The associated minerals include (in addition to the ubiquitous talc-chlorite) tremolite, hematite, galena, garnet, barite, and, though not in the same specimens, ilvaite.

There is general agreement among those who have studied the region (Smyth, 1894; Buddington, 1917; Brown, 1936) that most of the chlorite is supergene and that it is distinctive, and recognizable. The willemite and the ilvaite occur as euhedral crystals embedded in this chlorite, and appear to have been formed by rock replacement. A close study of the specimens shows several stages of mineral formation which are of great interest. Brown (1936) has described the appearance of the willemite-chlorite growth in thin-section, but gave no morphological data.

Two types of willemite crystals were observed in the specimens studied. The dominant and abundant crystals are embedded in the chlorite. They are small, about 1 mm. thick and 2 to $2\frac{1}{2}$ mm. in diameter. The habit is tabular, $c\{0001\}$ is small, $e\{01\bar{1}2\}$ large, and $a\{11\bar{2}0\}$ is the only prism form. They are often ideally developed, with perfect smooth, though dull, faces and sharp edges. The centers are colorless and transparent; toward the edge they tend to become increasingly cloudy with dendritic chlorite and hematite inclusions, which make them gray or red and opaque. Broken crystals have a good cleavage parallel to *a*. Corners of intergrown crystals were observed to project from *c*, but no regularity of orientation which would indicate a twin relationship was found. The crystals are easily removed from the talc-chlorite matrix in which they are embedded, and they leave sharp impressions of their outlines in the compact chlorite.

Not all of the willemite crystals have the small *c* face shown in Fig. 1; sometimes *c* is very large and *e* so small that the crystals look like flat hexagonal plates, as shown in Fig. 2. These also occur in the compact

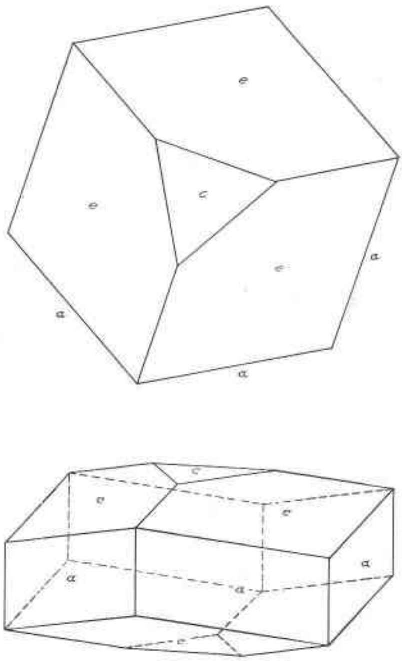

FIG. 1

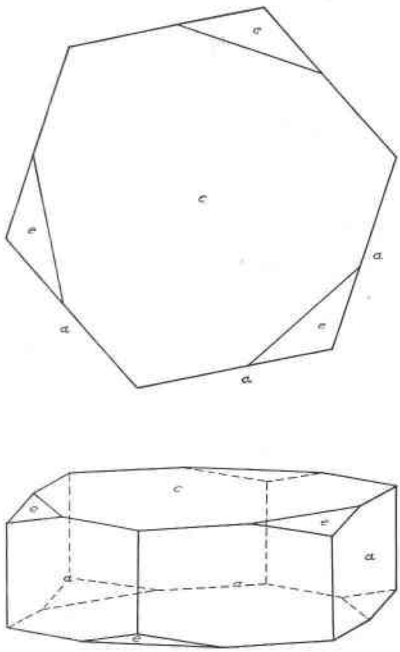

FIG. 2

chlorite and break cleanly from it. There is another type of willemite in this occurrence, however, which is different from the embedded crystals. Although the chlorite is, in general, very fine-grained and compact, a specimen was found containing numerous druses, lined with minute, irregular flaky crystals of chlorite, specular hematite and a limpid willemite. The cavities are very irregular in shape, full of angles and depressions, where the chlorite has coated the simple earlier willemite crystals. The later crystals have no, or very little, attached chlorite, are much smaller in size, rarely attaining even 1 mm. in diameter, and are outstanding for the complexity of the prism forms and their striated bases. Such a pocket is well shown in Fig. 4.

The late willemite crystals are similar in habit to the common crystals, definitely tabular, with c large and strongly striated parallel to its intersections with $e\{01\bar{1}2\}$. The striations mark an intergrowth with that form. Toward the edge, e is frequently cut off by the development of smaller forms, commonly $u\{2\bar{1}\bar{1}3\}$ or $S\{11\bar{2}3\}$, and $r\{10\bar{1}1\}$.

A crystal of this type is shown in Fig. 3. The small size and frequent etching of the crystals made some of the new terminal forms measured

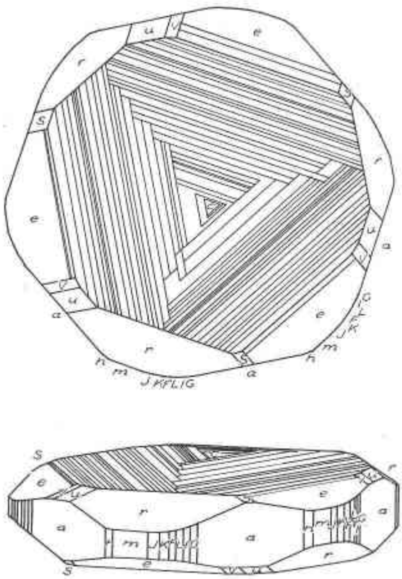

FIG. 3

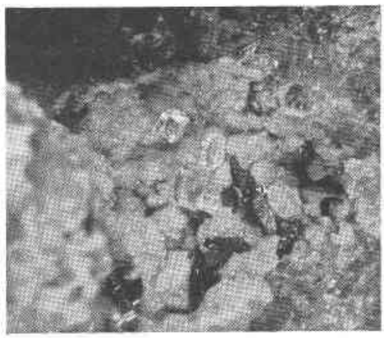

FIG. 4

very doubtful and none are acceptable as new forms. Palache (1928) mentions several new prisms which require confirmation, two of which were frequently found on the 15 crystals measured. The prism zone in the Balmat willemites showed a strongly striated character, and the reflections from the many faces appeared on the goniometer as a continuous train. It would be possible to add many more forms to the list of prisms, as planes could be found in almost any position on the proper half of the sextant, but it was not felt that they would be of any significance. Occasional stronger reflections were found repeatedly in the train, and these have been accepted as prism forms, with simple indices. The table shows the measured and calculated ϕ angles of the new accepted prisms, and lists a and m for comparison regarding the number of times observed.

Observer	*Bravais*	*Meas. Av.* ϕ	*Obs.*	*Calc.* ϕ	*Letter*
Common	$10\bar{1}0$	—° ′	63	0°00′	*a*
New	$8.5.\overline{13}.0$	+ 7 58	5	+ 7 35	*G*
Palache? 1928	$21\bar{3}0$	+10 41	4	+10 53	*I*
New	$52\bar{7}0$	+13 05	3	+13 54	*L*
New	$41\bar{5}0$	+20 10	7	+19 06	*K*
Palache? 1928	$71\bar{8}0$	+23 50	6	+23 25	*J*
Common	$11\bar{2}0$	—	19	+30 00	*m*
Common	$12\bar{3}0$	—	2	−10 53	*h*

In addition to the cases in which the new forms, and old ones needing confirmation, were specifically measured, they were observed frequently in approximate positions in the train, but so indefinitely located that accurate measurements could not be made. Many other forms were observed and measured but were either irrational in their indices or not duplicated on other crystals, and so were not considered. It was felt that the truest picture of the striated zone of the Balmat willemites could be derived from these few good forms and a recognition of the multiplicity of planes in this zone.

The important conclusion to be derived from these observations is that the tetartohedry is pronounced and shows in the prism zone as well as elsewhere. The crystal in Fig. 3 was selected to show the tetartohedry of the mineral, the nature of the prism forms and their distribution, and the striated character of the base. As may be seen, the prism forms occupy principally one-half of each sextant, and the train-of-reflections in that half is practically continuous. The complimentary half is either all dark, or lightened only by a streak near $h\{12\bar{3}0\}$.

A similar train-of-reflections, usually without significant lighter patches, runs from *c* to each face of *e*. A strongly etched crystal with well-formed triangular pits showed two planes in this train, at $\{01\bar{1}3\}$ and $\{01\bar{1}6\}$, but as they were observed only on etched crystals, they cannot be termed acceptable forms. The tetartohedry of the mineral was not pronounced in these etch pits nor in the striations on *c*, although a few of the etched crystals did give an indication of a break and change in direction of the outer striations.

The form development, however, does show a tetartohedral character, and it is possible to determine the top and bottom of the crystal in this way. Since $V\{\bar{1}3\bar{2}5\}$ was originally described as a right form, it was taken as the criterion for top and bottom whenever it was observed. It occurred with a reasonable frequency on the Balmat crystals and permitted the distinction to be made with confidence. $u\{2\bar{1}\bar{1}3\}$ was more common than $S\{11\bar{2}3\}$ and often larger, the series *e*-*V*-*u* was observed many times, the signals following each other closely, with what amounted almost to a train-of-reflections, with a gap before the other forms of the zone, *r* and *a*.

With all tetartohedral minerals there is great danger of confusion of right and left forms. It seems probable that there has been some in the case of willemite, and a re-study of Franklin willemites might be advisable to clear up this question and to establish criteria upon which distinctions between the forms might be based. The Balmat willemite, interesting as it is, is too poor in forms for certainty, and later work may prove that the striated prism zone should be oriented in the left of the sextant. Until that time it is unwise to change the letter usage as given to make it conform to a tetartohedral treatment, but some confusion has arisen through the use by Palache (1928) of *H* and *h*, once as $h\{13\bar{4}4\}$ and later as $H\{13\bar{4}4\}$, with $h\{12\bar{3}0\}$ (Palache, 1935). It would probably be better in the future to assign a new letter to this form.

The Balmat willemite is not fluorescent and appears to be very pure. The only color ever observed in the crystals is from actual inclusions of chlorite, and hematite, and the crystals are opaque and greenish gray or reddish, as would be expected.

A considerable suite of other minerals was observed, more or less intimately associated with the willemite. Of these, the most interesting and unusual is the ilvaite mentioned by Brown (1936). It was not observed by the writer in any of the willemite specimens, but occurs in a darker and more compact chlorite as distinct crystals several mm. long.[1] The matrix in which these lie is darker and, according to Brown, most strongly altered. Sphalerite and pyroxene, the latter in process of alteration, were observed in the same specimens, and galena was seen to coat one of the ilvaite crystals and to form small thread-like veins in the chlorite.

A crystal of ilvaite was measured and the smooth brilliant faces found to be those of the unit prism. The terminations of all the crystals are irregular and dull, the growing ilvaite probably replaced the chlorite very successfully in developing its prism faces, but was less powerful normal to the *c*-axis and developed only irregular planes. On the goniometer these gave fair signals, none the less, for $r\{101\}$ and $k\{106\}$. No base was found, and only a very narrow *a*.

Hematite is abundant and occurs as an earthy red material, as compact pseudomorphs after pyrite and wall rock, and as specular crystals. These latter are very small, about the size of the willemite crystals of the vugs, and (in many specimens) occur with them. They are well shown in their typical occurrence in Fig. 4. Some of the specular hematite is

[1] Brown writes "I have it in one willemite-bearing thin section, I think."

found embedded in the chlorite or in the red hematite, but most of the crystals are found in the little druses in the chlorite in which the willemite occurs. They are, in fact, good guides to the willemite, for with their brilliant luster and dark color they are much more easily seen than the clear willemite crystals. The crystals are thin tablets, with a small base and $\mu\cdot\{01\bar{1}5\}$ dominant and strongly striated, $\phi\cdot\{02\bar{2}1\}$, $\delta\cdot\{01\bar{1}2\}$, $\lambda\{22\bar{4}3\}$ and $p\{10\bar{1}1\}$ are also present on most crystals. (Letters of Maurice (1932) used.)

Tremolite and barite are present in the specimens but as residual grains, of irregular outline and largely replaced by the chlorite and willemite. Brown speaks of them both as being seen in thin sections in the process of being altered, and all that were observed in the hand specimens were similarly changed. However, one mineral in apparently fresh crystals, but which may be a residual silicate, was observed. Andradite garnet is described by Brown as being abundant in some of the secondary sphalerite ore, and small clusters of it were found in the vuggy willemite specimen.

The age relationships of this garnet are very difficult to determine, from the small amount of material available. A few .2 mm. dodecahedral crystals were found in a pocket attached to the chlorite, in relationships which would ordinarily suggest a later crystallization, exactly as the hematite and the clear willemite crystals grew. Neither of these minerals was present in the cavity. Elsewhere garnet has replaced early minerals but has been replaced itself by sphalerite and willemite. Regarding this specimen Brown writes,[2] "As to the garnet, this gave me a great deal of trouble early in my paragenetic study, and I had to cut numerous thin sections to reach a decision, but I think the result was conclusive. Garnet is earlier than, and in some cases, definitely replaced by willemite, by secondary sphalerite, and by primary sphalerite. Therefore, barring the almost impossible assumption of two ages of garnet, it must be prior to all of them. I wonder if the crystals perched on chlorite or willemite cannot be interpreted as residuals left in relief by the (supergene) solution and removal of a matrix of carbonate or barite in which they formerly were embedded? Garnet is strongly stained and to some degree replaced by hematite, which frequently turns the yellow into a brilliant red aggregate."

Mention has already been made of the sphalerite and galena in the chlorite associated with the ilvaite. It is stated by Brown (1936) that "Willemite has nowhere been found microscopically in contact with sulphides, either primary or secondary." A careful study of the drusy willemite specimen revealed a few traces of sulphide, however, in what is

[2] Letter, dated April 3, 1940.

obviously a secondary relationship. Galena was found in a single case in distinct, though minute crystals, showing the cube with its corners truncated by the octahedron, actually grown upon a willemite crystal. It is shown in Fig. 5, the broad white face being the reflecting surface of the willemite base with small triangular etch pits, and several small groups of galena grown upon it. The crystals are about .6 mm. across, while the willemite crystal, 2.5 mm. across is the largest of the late willemite that was found. A few more galena crystals are attached to the prism planes and another group is visible at the margin between the large willemite and a smaller one.

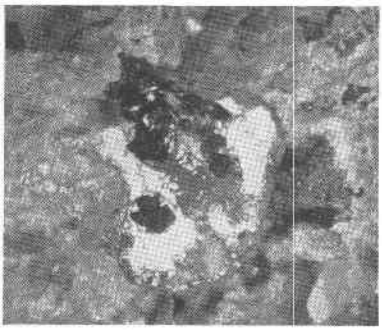

FIG. 5

The last mineral to form is a fibrous, serpentinous material which loosely fills many of the willemite-specularite druses. It is present in very small quantities and is so loosely grown in the pockets that it resembles wisps of smoke making a bluish haze through which one looks at the crystals. It is easily removed, but is often attached firmly enough to the crystals of the other two minerals so that they are drawn out with it. They are then easily freed from the serpentine, however, just as silk fibers or cobwebs might be pulled from a clean surface.

PARAGENESIS

The talcose-chloritic-willemite and chloritic-ilvaite rock is considered to be a replacement of an earlier silicate rock. Brown (1936) says, "The chlorite is an alteration product of diopside and talc, and to some extent of the tremolite, and is believed to have been formed by solutions high in ferrous iron derived from the oxidizing ore bodies. Much of it appears to be a conversion of talc, the principal change being the addition of ferrous iron with a corresponding development of green color." The now largely replaced barite and a few flecks of muscovite doubtless represent residual minerals of the earlier stage as well.

The formation of the willemite is clearly contemporaneous with some of the chlorite formation. Possibly, since there are clear crystal centers and the dendritic chlorite inclusions, it may have even preceded the chlorite. It certainly continued after the chlorite had ceased to form. On the other hand, colloform surfaces of chlorite, as shown in Figs. 4 and 5, coat early crystals of willemite in all of the druses. There must then have been two stages of willemite formation, the second after the chlorite had ceased forming. The indication is that there was a gap in willemite formation, only one late crystal was found attached as an integral part of an early simple crystal forming a druse wall. Preceding this late willemite stage, however, there was some change in the conditions of iron oxide deposition which resulted in the formation of crystals of specular hematite on the chloritic druse walls. Many of these were later included in the growing willemites.

At the close of the willemite formation there was a distinct change in conditions, which resulted in an etching of willemite and the deposition of late, secondary, sulphides. The prism zones were attacked more weakly than the terminations, many of the latter forms were so rounded that no sharp faces are visible. Less intense etching made the small triangular etch pits seen on *c* in Fig. 5. Succeeding this attack, or possibly simultaneous with it, the sulphides were deposited. The dullness of the galena faces indicates that some later oxidation has altered it and these last solutions may well have formed the threads of serpentinous felt which occupy the centers of some of the pockets.

Summary

The willemite of St. Joseph Lead Company mine at Balmat, St. Lawrence County, New York, is tabular in habit and reasonably constant in appearance, which indicates that it formed under relatively uniform conditions, unlike that of Franklin, New Jersey, which varies greatly in habit and appearance. While comparatively simple in development, good crystals are abundant and some new prism forms were noted. The manner of occurrence, entirely secondary, is, on first thought, unusual, but it is actually very typical of willemite, as the writer expects to emphasize still more strongly in a later paper, summarizing the occurrences of willemite.

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