

MINERALOGICAL NOTES

THE SIGNIFICANCE OF HABIT AND MORPHOLOGY OF WULFENITE

SIDNEY A. WILLIAMS, *Phelps Dodge Corp.*

INTRODUCTION

This study attempts to relate the habit and morphology of wulfenite crystals to their conditions of formation and minor element content. For this purpose 64 samples were obtained from as many localities as possible. Crystals from each specimen were measured on a Stoe two-circle goniometer and then pulverized for quantitative  $x$ -ray fluorescence analysis. Each sample was also studied microscopically to determine the associated species and paragenesis. From the paragenetic study it was possible to estimate the Eh and pH at the time of crystallization. Other factors, such as the rate of crystallization, must also influence the habit of wulfenite but these factors could not be assessed and so were neglected. However, the habit and morphology of wulfenite can be related to the factors considered in this paper, suggesting that the latter are important and possibly dominant ones.

CONDITIONS OF FORMATION

It is assumed that the temperature and pressure of formation of all wulfenites studied were similar to normal atmospheric conditions so that Eh and pH are left as the only factors with which to assess the conditions of formation. The chemistry of dilute aqueous solutions carrying lead and molybdenum has been discussed by several workers (Takahashi, 1960; Titley and Anthony, 1961; Williams, 1963). Generally, wulfenite can crystallize over a wide pH range but rather extreme conditions are required for it to be stable at a pH less than 3 or greater than 9. It can crystallize in a slightly reducing environment but normally forms in a moderately to extremely oxidizing environment.

As a guide to Eh and pH of crystallization, the samples were pigeonholed according to close temporal association with one of five species commonly found with wulfenite. These are cerussite, mimetite, willemite, hemimorphite, and plattnerite. Wulfenite earlier than or contemporaneous with cerussite was assumed to have formed in mildly acid waters at a fairly low Eh. Then, in order, association with mimetite, hemimorphite-willemite, and plattnerite indicates increasing pH and Eh. The conditions of all of these species are fairly well known with the exception of willemite. Some willemite, particularly that of acicular habit, has almost certainly formed under surface conditions of oxidation. Other willemite occurrences

TABLE 1. RANKS OF FORMS IN DIFFERENT ASSOCIATIONS

Form	Average	Cerussite	Mimetite	Hemimorphite	Willemite	Plattnerite
c 001	1.000	1.157	1.000	1.500	1.000	1.440
n 011	1.166	1.000	1.229	3.938	2.231	1.000
e 112	1.503	1.571	1.456	2.250	1.400	1.727
s 013	2.272	1.458	1.653	1.000	3.786	22.91
u 114	2.315	4.762	1.695	x	1.690	3.682
a 010	7.895	6.845	9.333	4.500	27.04	6.545
$\beta$ 014	19.30	x	12.00	x	13.52	x
t 116	25.83	33.33	72.00	x	10.14	x
y 113	26.32	7.143	x	x	40.56	x
z 115	30.32	9.524	30.00	x	15.21	x
A 015	30.32	9.524	15.00	x	x	x
k 130	31.58	14.29	27.00	x	33.80	13.09
g 120	33.34	33.33	30.00	x	x	7.364
$\epsilon$ 111	37.43	28.57	72.00	x	33.80	3.273
$\rho$ 017	43.67	x	33.00	6.750	x	x
$\gamma$ 016	49.13	x	60.00	x	13.52	x
$\alpha$ 250	49.91	57.13	30.00	x	x	x
2.2.11	53.03	38.09	x	x	15.21	x

x = not observed.

seem to be best explained by elevated temperatures as suggested by the work of Roy and Mumpton (1956). This seems to be especially true of crystals with short prismatic habit. Since wulfenite has also been grown under elevated temperatures and in hydrothermal conditions (Dem'yanets *et al.*, 1963) it may be that some of the peculiarities of wulfenite found with willemite reflect elevated temperatures.

Table 1 shows the common forms of wulfenite in order of decreasing rank for each mineralogical association. After each crystal was measured, the forms were listed in order of decreasing quality of their faces (in terms of signal quality, size, and number of face of the form). Each form on this list was assigned an integer in order of decreasing quality. If the integer is  $q$ , and  $x$  is the number of crystals showing the form, the following relation gives the "rank" ( $R$ ) of the form:

$$R = \frac{\sum q}{x^2 R_0}$$

where  $R_0$  is the rank of the best form on a given crystal or group of crystals. This treatment differs from that employed by Bach (1926) but has the advantage of combining all of the factors which he considered in three separate lists.

The first column in Table 1, which summarizes the ranks of forms for all samples studied, shows that five forms are overwhelmingly the most important: {001}, {011}, {112}, {013}, and {114}. A comparable listing by Bach (1926) based on 137 crystals is: {001}, {011}, {013}, {114}, {110}, and {112}. The position of {110} in the list is rather surprising; it was found only twice in this study. Padurova (1929) lists {001}, {112}, {011}, {114}, and {013} in terms of frequency of occurrence.

A total of 57 forms was found during the study and no attempt was made to distinguish upper and lower forms. Four crystals showed {014} and two showed {016}; each of these forms gave good signals on one crystal.

Crystals found with willemite are perhaps the most aberrant, although crystals in each assemblage have certain peculiarities. Forms such as {229}, {029}, {2.2.11}, and {0.2.11} are particularly characteristic of wulfenite with willemite.

The habit of wulfenite in each of the five groups varies in the following way:

- 1) with cerussite tabular with edges dominated by either {hhl} or {0kl} (Fig. 1-A);
- 2) with mimetite tabular with edges dominated by {hhl}, {0kl}, and minor {hk0} (Fig. 1-B);

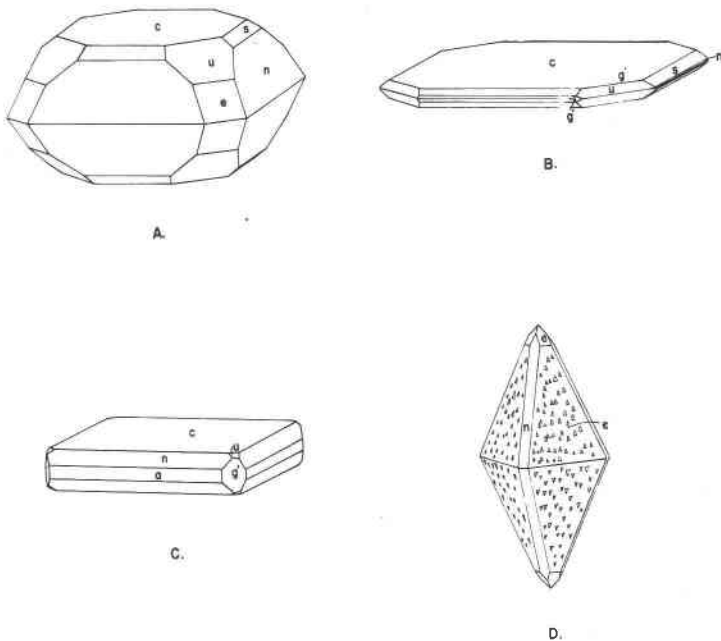


FIG. 1. Characteristic habits of wulfenite crystals.

- 3) with hemimorphite like above but with {hk0} somewhat more important;
- 4) with willemite tabular to equant-dipyramidal with edges dominated by {hhl};
- 5) with plattnerite steep dipyramidal or prismatic with {hk0} dominant (Fig. 1-C and 1-D).

Of all the pure crystals examined 21 have long edges parallel to [110] and 20 have them parallel to [010]. With the exception of willemite noted above, wulfenites in other associations were generally equally divided into groups with edges parallel to [010] and [110].

Study of the paragenesis indicates that at low pH and Eh {001}, {013}, {011}, {112}, and {015} are stable; at low Eh and high pH {013}, {011}, {114}, and {116} are stable; and at high pH and Eh {111}, {113}, and {114} are stable. Generally the stability of {hhl} increases while the stability of {0kl} decreases during normal oxidation.

There is little significance to the presence or absence of rare forms in terms of the parameters considered in this paper. Of note, however, is the fact that {114} is invariably present on crystals which show rare forms; {114} is also characteristic of rounded or distorted crystals.

#### MINOR ELEMENTS

Oxides of Cr, As, V, Sb, and W were weighed and mixed with commercially available  $\text{PbMoO}_4$  as standards for *x*-ray fluorescence analysis. Standard curves covering the range of 0% to 2% metal were prepared for each of the five elements. Three samples later proved to contain more than 2% (all were tungstenian) and only one contained Sb, so this element was dropped from further consideration. Samples were examined with a Norelco *X*-ray fluorescence unit equipped with a tungsten target tube and LiF analyzer. The Pb count and the Pb/Mo count ratio were used as internal standards.

Twenty-seven of the samples contain at least one of the four elements and several contain more than one. The highest percentages detected, expressed as oxides, are as follows:  $\text{WO}_3 > 10\%$ ,  $\text{V}_2\text{O}_5$  1.10%,  $\text{Cr}_2\text{O}_3$  0.85%,  $\text{As}_2\text{O}_3$  0.75%, and  $\text{Sb}_2\text{O}_3$  1.32%. Tungsten is the element most commonly found, followed in order by chromium, arsenic, vanadium, and antimony.

All crystals containing vanadium have long edges parallel to [110]; all crystals containing tungsten, arsenic, or chromium have long edges parallel to [010]. No relation between the minor element content and morphology could be demonstrated.

The relation between the axial ratio and minor element content is shown in Fig. 2. The axial ratio was determined from {011} if possible, otherwise {112} or {013} was employed. Some crystals were unsuited for morphological determination so all samples were studied by *x*-ray meth-

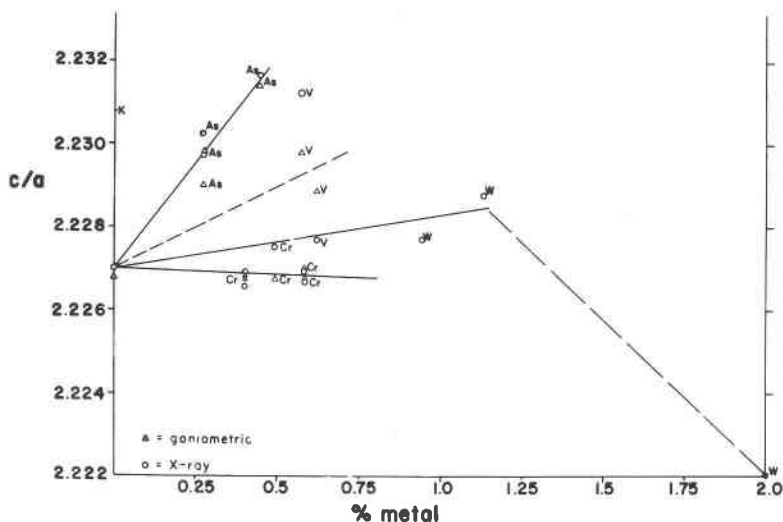


FIG. 2. Variation of  $a:c$  with content of Cr, As, V, and W in wulfenite.

ods using cameras of 114.59 mm diameter and  $\text{CuK}\alpha$  radiation. Several lines in the back reflection region were used to compute the axial ratio.

#### CRYSTALLOGRAPHIC DATA

The value of  $a:c = 1:2.2308$  used in Dana's System of Mineralogy, 7th. edition, has been selected from Kokscharov (1878). Others value have been reported by Padurova (1929), Koning (1948), Ingersoll (1894), Comucci (1926), Hlawatsch (1925), and Bach (1926). Values reported range from  $1:2.2217$  to  $1:2.2311$ . Since previous workers have not used crystals known to be free of other elements, the values give in Table 2 for pure wulfenite are considered superior. The value  $1:2.2268$  was accepted as the best value on the basis of this study.

The tetartohedrism of wulfenite is now well established (Hurlbut, 1955; also see Bach (1926); Russell (1946); Ingersoll (1894). Wulfenite has been studied many by workers and a review of the literature is most

TABLE 2. AXIAL RATIO OF WULFENITE

method	$\rho \{011\}$	$a:c$
x-ray powder method		$1:2.2270 \pm .002$
perfect crystals	$65^\circ 49.0' \pm 0.5'$	$1:2.2268 \pm .0009$
avg. from 41 crystals	$65^\circ 49' \pm 3.5'$	$1:2.2268 \pm .0061$

instructive regarding the ability of morphological study to prove merohedrism when other methods fail or give inconclusive results.

Of all the samples examined in this project, only one showed obvious tetartohedrism. These crystals, supplied by R. A. Bideaux from Silver Bell, Arizona, are smoky blue, calcian, and contain minor Cr and V. All of these crystals show  $\{13\bar{4}\}$  but not  $\{134\}$ . Many other specimens show crystals of tetartohedral appearance but no forms of polar character. Many other crystals also show preferential etching of  $\{001\}$ ,  $\{011\}$ , or  $\{112\}$  on one end or vicinal forms on  $\{00\bar{1}\}$  only.

#### ACKNOWLEDGMENTS

The writer is indebted to Mrs. Brooks Davis, E. McDole, R. E. Merrill, and especially R. W. Thomssen and R. A. Bideaux for supplying specimens. John W. Anthony kindly criticized the manuscript.

#### REFERENCES

- BACH, L. (1926) Ueber wulfenit. *Jahrb. Mineral., B.-B.*; **54**, 380-419.
- BARTHOUX, M. J. (1924) Description de quelques minéraux marocains. *Bull. Soc. Franc. Mineral.* **47**, 36-45.
- COMUCCI, P. (1926) Osservazioni sulla wulfenite e vanadinite di Oudida (Marocco). *Acc. Linc. Att.* **3**, 335-341.
- DEM'YANETS, L. N., L. S. GARASHINA AND B. W. LITVIN (1963) Crystallization of wulfenite ( $\text{PbMoO}_4$ ) under hydrothermal conditions. *Kristallografiya*, **8**(5), 800-803.
- HLAWATSCH, K. (1925) Wulfenit von Miess, Kärnten. *Ann. Mus. Wien*, **38** (15), 15-17.
- HURLBUT, C. S. JR. (1955) Wulfenite symmetry as shown on crystals from Jugoslavia. *Am. Mineral.* **40**, 857-860.
- INGERSOLL, C. A. (1894) On hemimorphic wulfenite crystals from New Mexico. *Am. Jour. Sci.* **48**, 193-195.
- KOKSCHAROV, N. V. (1878) *Materialien zur Mineralogie Russlands.* **8**, 394.
- KONING, L. P. G. (1948) On wulfenite from Dona Ana, New Mexico. *Proc. Kon. Nederl. Ak. Wet.* **51**, 390-395.
- PADUROVA, N. (1929) Krystalle des Wulfenites aus Almalik. *Mem. Soc. Russ. Mineral.* **58**, 109-115.
- ROY, D. M. AND F. A. MUMPTON (1956) Stability of minerals in the system  $\text{ZnO-SiO}_2\text{-H}_2\text{O}$ . *Econ. Geol.* **55**, 432-444.
- ROYER, L. (1936) De l'influence de la symétrie du milieu sur la symétrie des figures de corrosion dans les cristaux; nouveaux exemples. *Comptes Rendus* **202**, 1346-1348.
- RUSSELL, A. R. (1946) An account of the Struy lead mines, Inverness-shire, and of wulfenite, harmotome, and other minerals which occur there. *Mineral Mag.* **27**, 147-154.
- TAKAHASHI, T. (1960) Supergene alteration of lead and zinc deposits in limestone. *Econ. Geol.* **55**, 1083.
- TITLEY, S. R. AND J. W. ANTHONY, (1961) Some preliminary observations on the theoretical geochemistry of molybdenum under supergene conditions. *Ariz. Geol. Soc. Digest* **4**, 103-116.
- WILLIAMS, S. A. (1963) Oxidation of sulfide ores in the Mildren and Steppe mining districts, Pima County, Arizona. *Econ. Geol.* **58**, 1119-1125.