

## SHERWOODITE, A MIXED VANADIUM(IV)-VANADIUM(V) MINERAL FROM THE COLORADO PLATEAU\*

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### ABSTRACT

Sherwoodite, a new vanadium mineral that has the probable formula  $\text{Ca}_3\text{V}_8\text{O}_{22} \cdot 15\text{H}_2\text{O}$ , has been found in small amounts in many vanadium-uranium mines on the Colorado Plateau. The new mineral occurs as dark blue-black holohedral tetragonal crystals bounded by {110} and {011}. The space group is  $I4/am\bar{d}$ , ( $D_{4h}^{19}$ ),  $a_0 = 27.8 \pm 0.08 \text{ \AA}$ ,  $c_0 = 13.8 \pm 0.08 \text{ \AA}$ ,  $a:c = 1:0.4964$ , cell contents 16 ( $\text{Ca}_3\text{V}_8\text{O}_{22} \cdot 15\text{H}_2\text{O}$ ). Sherwoodite is uniaxial negative,  $\omega = 1.765 \pm 0.003$ ,  $\epsilon = 1.735 \pm 0.003$ , dichroism strong, O green, E blue. The hardness is about 2. The measured specific gravity is  $2.8 \pm 0.1$ .

The chemical analysis, in per cent, is as follows: CaO 13.2, MgO 0.5,  $\text{V}_2\text{O}_4$  5.9,  $\text{Al}_2\text{O}_3$  2.6,  $\text{Fe}_2\text{O}_3$  0.8,  $\text{V}_2\text{O}_5$  50.2,  $\text{H}_2\text{O}$  23.1, insoluble 3.8, total 100.1.

Sherwoodite is named for Alexander M. Sherwood of the U. S. Geological Survey.

### INTRODUCTION AND ACKNOWLEDGMENTS

Sherwoodite was first found in the Matchless mine, Mesa County, Colorado, by Alice D. Weeks and other members of a U. S. Geological Survey field party, in the summer of 1952. Another sample was collected later that summer from the Shadyside mine, on the east side of the Carrizo Mountains, San Juan County, New Mexico, by the same field party, but the two samples contained only enough of the mineral for  $x$ -ray powder patterns, preliminary determination of the optical properties, and a qualitative spectrographic analysis.

Early in 1954, as a result of a detailed study of the Peanut mine, Montrose County, Colorado, Carl H. Roach was able to collect enough sherwoodite for a chemical analysis and  $x$ -ray study. Because the material used for the mineral description was collected from the Peanut mine, that should be considered the type locality.

More recently, sherwoodite has been found in the vanadium-uranium ores of the J. J. and Mineral Jo mines of the Jo Dandy group in Montrose County, Colorado; the Fall Creek mine of Placerville, San Miguel County, Colorado; and on Wilson Mesa, Grand County, Utah.

We are happy to name this mineral for Alexander M. Sherwood (1888- ), an analytical chemist of the U. S. Geological Survey, who has made many excellent and difficult mineral analyses for both the U. S. Bureau of Mines and the U. S. Geological Survey.

Thanks are due to Gabrielle Donnay for the unit-cell data, to C. S. Annell and K. V. Hazel for spectrographic analyses, and to H. T. Evans,

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#### OCCURRENCE

Sherwoodite is evidently widely distributed in the Uravan mineral belt. The Matchless mine, Mesa County, Colorado; the Shadyside mine, San Juan County, New Mexico; the Peanut mine, Montrose County, Colorado, and several other mines in which sherwoodite occurs are in the Salt Wash member of the Morrison formation of Late Jurassic age. Another locality, the Fall Creek mine, San Miguel County, Colorado, is in the Entrada sandstone of Late Jurassic age.

Sherwoodite is an oxidation product of lower valent vanadium minerals. It occurs as coatings on fracture surfaces and along partings in vanadium-bearing sandstones, and along fracture surfaces in mineralized coalified wood. It is commonly associated with hexagonal native selenium, metatyuyamunite, melanovanadite, and an undescribed vanadium mineral resembling hewettite. It alters to an ill-defined, fine-grained green material, probably a poorly crystallized compound of quinquivalent vanadium.

#### PHYSICAL AND OPTICAL PROPERTIES

Sherwoodite is tetragonal, ditetragonal-dipyramidal ( $4/m2/m2/m$ ). Morphological measurements give a ratio of  $a:c=1:0.497$ , in agreement with the  $x$ -ray determination of  $1:0.4964$  (measurements by Gabrielle Donnay). Crystals display only two forms,  $m\{110\}$  and  $d\{011\}$  (Fig. 1). The crystals are equant or slightly flattened, and occur singly and as polycrystalline aggregates.

Unaltered sherwoodite is dark blue-black and has a light blue streak,

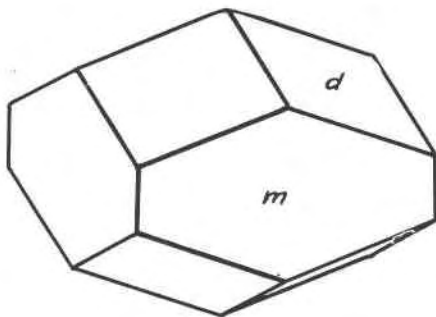


FIG. 1. Crystal drawing of sherwoodite showing the forms  $m\{110\}$  and  $d\{011\}$ .

but slightly altered specimens exhibit an apparently progressive color change to blue-green and yellow-green. This color change is accompanied by only very slight changes in the refractive indices and in the  $x$ -ray powder diffraction spacing, and is probably related to the oxidation of quadrivalent vanadium to the quinivalent state. The luster is vitreous to earthy and the fracture is subconchoidal to uneven. The hardness is about 2. The specific gravity measured by flotation in a mixture of bromoform and acetone is  $2.8 \pm 0.1$ .

Sherwoodite is uniaxial negative. The indices of refraction and dichroism of blue-black sherwoodite and yellow-green material are presented below.

<i>Indices</i>	<i>Dichroism</i>
Blue-black crystals	
$\omega = 1.765 \pm 0.003$	O green
$\epsilon = 1.735 \pm 0.003$	E blue
Yellow-green material, finer grained	
$\omega = 1.765 \pm 0.003$	O yellow-brown
$\epsilon = 1.738 \pm 0.003$	E deep blue-green

#### X-RAY DATA

X-ray precession photographs by Gabrielle Donnay of the U. S. Geological Survey of crystals of sherwoodite from the Peanut mine yielded the following data: tetragonal, space group  $I4/amd$  ( $D_{4h}^{19}$ ),  $a_0 = 27.8 \pm 0.08 \text{ \AA}$ ,  $c_0 = 13.8 \pm 0.08 \text{ \AA}$ ,  $a:c = 1:0.4964$ .

X-ray powder diffraction patterns of sherwoodite of various shades of blue and from several localities have been prepared. These patterns all have the three strongest lines in common and these lines on a powder pattern are sufficient for the identification of the mineral, but many of the other lines of the patterns show slight differences in spacing and variations in intensity. It has not been possible to index the powder patterns of sherwoodite with any degree of certainty because the large unit cell results in a very large number of weak and faint diffraction lines.

The unit cell constants and the  $d$ -spacings of a powder pattern of sherwoodite, showing the indices of some of the stronger lines, are listed in Table 1. The powder pattern was made by Mary E. Mrose of the U. S. Geological Survey with a Debye-Scherrer camera of 114.59 mm. diameter and  $\text{CuK}\alpha$  radiation (Ni filter),  $\lambda = 1.5418 \text{ \AA}$ .

#### CHEMICAL ANALYSIS

Material for the chemical analysis was taken from samples collected from the Peanut mine, and consisted chiefly of fragments of dark blue

TABLE 1. UNIT-CELL CONSTANTS AND X-RAY POWDER DIFFRACTION  
DATA FOR SHERWOODITE

Tetragonal,  $4/m2/m2/m$ , space group  $I4/amd$  ( $D_{4h}^{19}$ ),  $a_0=27.8\pm 0.08 \text{ \AA}$ ,  $c_0=13.8\pm 0.08 \text{ \AA}$ ,  
 $a:c=1:0.4964$ , cell contents  $16(\text{Ca}_3\text{V}_8\text{O}_{22} \cdot 15\text{H}_2\text{O})$ ?

Cell volume	Density, measured	Molecular weight of cell contents	
10,666 $\text{A}^3$	$2.8\pm 0.1 \text{ g/cc}$	17,985	
$\frac{10,666}{16 \times 37} = 18 \text{ A}^3$ per oxygen	Density, calculated for $\text{Ca}_3\text{V}_8\text{O}_{22} \cdot 15\text{H}_2\text{O}$ $2.86 \text{ g/cc.}$	Molecular weight of $16(\text{Ca}_3\text{V}_8\text{O}_{22} \cdot 15\text{H}_2\text{O})$ 18,400	
	Density, calculated from analysis (table 3) $2.82 \text{ g/cc.}$	Molecular weight from analysis (table 3) 18,111	
I	$d$ , measured	$d$ , calculated	$hkl$
S	12.3	12.37	011
S	10.0	9.82	220
MS	9.3	9.24	121
W	7.8	7.63	141
W	7.1	6.95	040
W	5.2		
F	5.0		
MW	4.65		
F	4.46		
F	4.19		
F	3.39		
W	3.25		
F	3.21		
W	3.10		
F	3.06		
F	2.96		
W	2.85		
F	2.77		
W	2.71		
M	2.61		
F	2.56		
W	2.28		
M, b	2.10		
W	2.07		
W	1.989		
W, b	1.743		

S strong, M medium, W weak, F faint, b broad.

crystals. The sample was handpicked under the binocular microscope. After a spectrographic analysis indicated that the sample might not be pure, it was rinsed with water, crushed to a slightly smaller grain size, re-handpicked, floated in bromoform of density 2.89 and sunk in bromoform of density 2.7. A second (microqualitative) spectrographic analysis showed no significant change in the proportions of elements present, and it may be that the "impurities" are really contained in the crystals in diadochic substitution for Ca or V. The semiquantitative spectrographic analysis of the handpicked sample gave the following results in per cent:

(C. S. Annell, analyst)

Over 10		V		
5-10		—		
1	-5	Ca	Al	Si
0.5	-1	Mg		
0.1	-0.5	Fe		
0.05	-0.1	Na	Sr	
0.01	-0.05	Pb	Ti	Ba
0.005	-0.01	—		
0.001	-0.005	Mn	Cr	Sc
0.0005-0.001		—		
0.0001-0.0005		Ag		

For the determinations of CaO, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, MgO, H<sub>2</sub>O(-), and total vanadium, a sample weighing 16 mg. was dried to constant weight at 110 ± 5° C. The mineral was then dissolved in nitric acid and filtered to separate the insoluble residue.

Calcium oxide was determined as the sulfate after separation from the filtrate as the oxalate. Total vanadium was determined on an aliquot of the filtrate from the CaO determination after the oxalate had been destroyed by boiling with nitric acid. Total vanadium was determined spectrophotometrically using the hydrogen peroxide procedure. Another aliquot of the filtrate from the CaO determination was used to determine Fe<sub>2</sub>O<sub>3</sub>, which was done spectrophotometrically using the o-phenanthroline procedure.

Another aliquot was used for Al<sub>2</sub>O<sub>3</sub>, which was determined spectrophotometrically using the ferron procedure after the separation of aluminum, iron, and magnesium from vanadium by the use of 8-hydroxyquinoline. An aliquot of this solution was used for the spectrophotometric determination of MgO, using Clayton Yellow.

The V<sub>2</sub>O<sub>4</sub> was determined by dissolving a 15-mg. sample of the mineral in (1+3) sulfuric acid and titrating with approximately 0.03 N standard potassium permanganate. The V<sub>2</sub>O<sub>5</sub> was calculated by difference.

The insoluble matter was determined by boiling a 9 mg. sample with

(1+3) sulfuric acid in a weighed Schwarz-Bergkampf micro-filter beaker. The residue was filtered and washed with water and dried to constant weight at  $110 \pm 5^\circ$  C. The weighings were made with a microbalance.

Total  $H_2O$  was determined by use of a modified micro-combustion train of the type used for the determination of carbon and hydrogen in organic compounds. A 14-mg. sample was decomposed by ignition in a stream of oxygen.

The results of the chemical analysis are shown in Table 2.

TABLE 2. CHEMICAL ANALYSIS OF SHERWOODITE  
(Robert Meyrowitz, analyst)

Constituent	Weight Per Cent	Recalculated	( $Ca_3V_8O_{22} \cdot 15H_2O$ )
CaO	13.2	13.7	14.6
MgO	0.5	0.5	
$V_2O_4$	5.9	6.2	61.9 ( $V_8O_{14}$ )
$Fe_2O_3$	0.8	0.8	
$Al_2O_3$	2.6	2.7	
$V_2O_5$	50.2	52.1	
$H_2O$ (total)	23.1	24.0	23.5
Insoluble	3.8	—	—
Total	100.1	100.0	100.0
$H_2O(-)$	14.5		

The unit cell contents of sherwoodite have such a large molecular weight that the formula cannot be calculated with absolute certainty from just one analysis. Another source of uncertainty is the problem of whether all the components shown by this analysis belong in the mineral or whether some represent admixed impurities.

The simplest formula having the correct molecular weight, however, was obtained when all of the components shown by the analysis were considered in the calculation (except "insoluble"). The CaO and MgO were summed, as were  $Al_2O_3$ ,  $Fe_2O_3$ ,  $V_2O_4$ , and  $V_2O_5$ . The details of the calculation are shown in Table 3.

The calculation yields the formula



This formula is in good agreement with the chemical analysis and the unit cell data, including the molecular weight, and the cell volume per number of oxygen atoms (Table 1).

This formula not only brings into agreement the analytical data, but

TABLE 3. CALCULATION OF THE FORMULA OF SHERWOODITE USING THE MOLECULAR WEIGHT CALCULATED FROM THE UNIT-CELL VOLUME AND THE DENSITY

Component	Analysis, less insoluble, recalculated to 100 per cent	Analysis ( $\times 45$ ) <sup>1</sup>	Atomic proportions	Number of molecules per $\frac{1}{4}$ cell
CaO	13.7	617	11.01	11.57
MgO	0.5	22.5	0.56	
V <sub>2</sub> O <sub>4</sub>	6.2	279	1.68	15.98
Fe <sub>2</sub> O <sub>3</sub>	0.8	36	0.23	
Al <sub>2</sub> O <sub>3</sub>	2.7	121.5	1.19	
V <sub>2</sub> O <sub>5</sub>	52.1	2345	1288	
H <sub>2</sub> O	24.0	1080	60	
	<u>100.0</u>	<u>4501</u>		

<sup>1</sup> Molecular weight of content of quarter cell approximately 4500, calculated from unit cell volume and measured density.

also offers an explanation for the observed variations in color and *d*-spacings. If V<sup>+4</sup> and V<sup>+5</sup> are not distinguished in the sherwoodite structure, the relative amounts shown by this analysis of blue-black material may represent the equilibrium proportions of V<sup>+4</sup> and V<sup>+5</sup> under the conditions of formation of sherwoodite. The observed variations then might be related to the oxidation of the V<sup>+4</sup>, a process that would result in the gradual breakdown of the structure.

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