

00)
72
694

Revised
Revised

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

By Mary E. Thompson, Carl H. Roach, and Robert Meyrowitz

Trace Elements Investigations Report 694

UNITED STATES DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

(200)
T67r
no. 694

Geology and Mineralogy

UNITED STATES DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

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

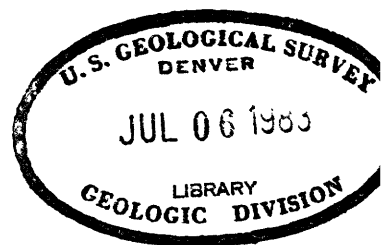
By

Mary E. Thompson, Carl H. Roach, and Robert Meyrowitz

August 1957

Trace Elements Investigations Report 694

This preliminary report is distributed without editorial and technical review for conformity with official standards and nomenclature. It is not for public inspection or quotation.



*This report concerns work done on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

PLEASE REPLACE IN BACK OF VOLUME
CANCELLED

USGS - TEI-694

GEOLOGY AND MINERALOGY

<u>Distribution</u>	<u>No. of copies</u>
Atomic Energy Commission, Washington	2
Division of Raw Materials, Albuquerque	1
Division of Raw Materials, Austin	1
Division of Raw Materials, Casper	1
Division of Raw Materials, Denver	1
Division of Raw Materials, Ishpeming	1
Division of Raw Materials, Rapid City	1
Division of Raw Materials, Salt Lake City	1
Division of Raw Materials, Spokane	1
Division of Raw Materials, Washington	3
Exploration Division, Grand Junction Operations Office	6
Grand Junction Operations Office	1
Technical Information Service Extension, Oak Ridge	6
U. S. Geological Survey:	
Foreign Geology Branch, Washington	1
Fuels Branch, Washington	1
Geochemistry and Petrology Branch, Washington	15
Geophysics Branch, Washington	1
Mineral Deposits Branch, Washington	2
P. C. Bateman, Menlo Park	1
A. L. Brokaw, Grand Junction	2
N. M. Denson, Denver	1
R. L. Griggs, Albuquerque	1
W. R. Keefer, Laramie	1
E. W. Lakin, Denver	1
E. M. MacKevett, Menlo Park	1
L. R. Page, Washington	1
P. K. Sims, Denver	1
Q. D. Singewald, Beltsville	1
A. E. Weissenborn, Spokane	1
TEPCO, Denver	2
TEPCO, RPS, Washington, (including master)	2

CONTENTS

	Page
Abstract	4
Introduction and acknowledgments	5
Occurrence	6
Physical and optical properties	7
X-ray data	9
Chemical analysis	11

ILLUSTRATION

Figure 1. Crystal drawing of sherwoodite showing the forms $\underline{m} \{110\}$ and $\underline{d} \{011\}$	8
---	---

TABLES

Table 1. Unit-cell constants and X-ray powder diffraction data for sherwoodite	10
2. Chemical analysis of sherwoodite	13
3. Calculations of the formula of sherwoodite using the molecular weight calculated from the unit-cell volume and the density	14

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

By Mary E. Thompson, Carl H. Roach, and Robert Meyrowitz

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 $I4/\text{amd}$, (D_{4h}^{19}), $a_0 = 27.8 \pm 0.08$ A, $c_0 = 13.8 \pm 0.08$ A, $a:c = 1:0.4964$, 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 ± 0.1 .

The chemical analysis, in percent, is as follows: CaO 13.2, MgO 0.5, V_2O_5 5.9, Al_2O_3 2.6, Fe_2O_3 0.8, V_2O_5 50.2, H_2O 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, Colo., 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, N. Mex., 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, Colo., 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, Colo.; the Fall Creek mine of Placerville, San Miguel County, Colo.; and on Wilson Mesa, Grand County, Utah.

We are happy to name this mineral for Alexander M. Sherwood, 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, Jr., for advice on the selection of the chemical formula. All are with the U. S. Geological Survey. This work is part of a program being conducted by the U. S. Geological Survey on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

OCCURRENCE

Sherwoodite is evidently widely distributed in the Uravan mineral belt. The Matchless mine, Mesa County, Colo.; the Shadyside mine, San Juan County, N. Mex.; the Peanut mine, Montrose County, Colo., 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, Colo., 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 ($4/\underline{m}2/\underline{m}2/\underline{m}$). 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, $\underline{m}\{110\}$ and $\underline{d}\{011\}$ (fig. 1). The crystals are equant and slightly flattened, and occur singly and as polycrystalline aggregates.

Unaltered sherwoodite is dark blue-black and has a light blue streak, 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 quinquivalent 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 ± 0.1 gram per cubic centimeter.

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

<u>Indices</u>	<u>Dichroism</u>
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

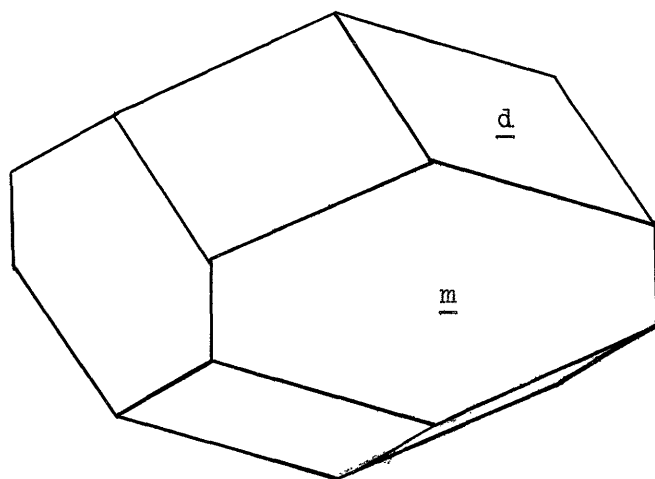


Figure 1.--Crystal drawing of sherwoodite showing the form $\underline{m}\{110\}$ and $\underline{d}\{011\}$.

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 $\underline{I}4/\underline{amd}$ (\underline{D}_{4h}^{19}), $\underline{a}_0 = 27.8 \pm 0.08$ A, $\underline{c}_0 = 13.8 \pm 0.08$ A, $\underline{a}:\underline{c} = 1:0.4964$.

X-ray powder-diffraction patterns of sherwoodite of various shades of blue and from several localities have been prepared. All these patterns 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 \underline{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 A radius, and $\text{CuK}\alpha$ radiation (Ni filter), $\lambda = 1.5418$ A.

Table 1.--Unit-cell constants and X-ray powder-diffraction data for sherwoodite.

Tetragonal, $4/m\bar{2}/m\bar{2}/m$, space group $I4/amd$ (D_{4h}^{19}), $a_0 = 27.8 \pm 0.08$ A,
 $c_0 = 13.8 \pm 0.08$ A, $a:c = 1:0.4964$, cell contents $16(Ca_3V_8O_{22} \cdot 15H_2O)$.

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 $Ca_3V_8O_{22} \cdot 15H_2O$ 2.86 g/cc	Molecular weight of $16(Ca_3V_8O_{22} \cdot 15H_2O)$ 18,400
	Density, calculated from analysis (table 3) 2.82 g/cc	Molecular weight from analysis (table 3) 18,111

<u>I</u>	<u>d</u> , measured	<u>d</u> , calculated	<u>hkl</u>
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

CHEMICAL ANALYSIS

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

(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_2O_3 , Fe_2O_3 , MgO , $\text{H}_2\text{O}(-)$, and total vanadium, a sample weighing 16 mg was dried to constant weight at $110 \pm 5^\circ \text{C}$. 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_2O_3 , which was done spectrophotometrically using the o-phenanthroline procedure.

Another aliquot was used for Al_2O_3 , 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_2O_4 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_2O_5 was calculated by difference.

The insoluble matter was determined by boiling a 9 mg sample with (1+3) sulfuric acid in a weighed Schwarz-Bergkampff micro-filter beaker. The residue was filtered and washed with water and dried to constant weight at $110 \pm 5^\circ \text{C}$. The weighings were made with a microbalance.

Total H₂O 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 percent	Recalculated	(Ca ₃ V ₈ O ₂₂ ·15H ₂ O)
CaO	13.2	13.7	14.6
MgO	0.5	0.5	
V ₂ O ₄	5.9	6.2	61.9 (V ₈ O ₁₉)
Fe ₂ O ₃	0.8	0.8	
Al ₂ O ₃	2.6	2.7	
V ₂ O ₅	50.2	52.1	
H ₂ O (total)	23.1	24.0	23.5
Insoluble	3.8	--	
Total	100.1	100.0	100.0
H ₂ O(-)	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.

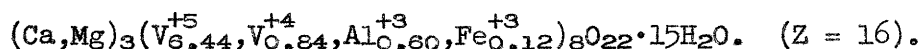
The simplest formula having the correct molecular weight, however, was obtained when all of the components shown by the analysis were considered in the calculation (except "insoluble"). Calcium oxide and MgO were summed, as were Al_2O_3 , Fe_2O_3 , V_2O_4 , and V_2O_5 . The details of the calculation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

Table 3.--Calculation of the formula of sherwoodite using the molecular weight calculated from the unit-cell volume and density.

Component	Analysis, less insoluble, recalculated to 100 percent	Analysis (X45) ^{1/}	Atomic proportions	Number of molecules per 1/4 cell
CaO	13.7	617	11.01	11.57
MgO	0.5	22.5	0.56	
V_2O_4	6.2	279	1.68	
Fe_2O_3	0.8	36	0.23	15.98
Al_2O_3	2.7	121.5	1.19	
V_2O_5	52.1	2345	12.88	
H_2O	24.0	1080	60	60
	<u>100.0</u>	<u>4501</u>		

^{1/} Molecular weight of content of quarter cell approximately 4500, calculated from unit-cell volume and measured density.

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 also offers an explanation for the observed variations in color and d-spacings. If V^{+4} and V^{+5} 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^{+4} and V^{+5} under the conditions of formation of sherwoodite. The observed variations then might be related to the oxidation of the V^{+4} , a process that would result in the gradual breakdown of the structure.