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THE OCCURRENCE AND PROPERTIES OF BARNESITE, $Na_2V_6O_{16}\cdot 3H_2O$, A NEW HYDRATED SODIUM VANADATE MINERAL FROM UTAH[1]

ALICE D. WEEKS, DAPHNE R. ROSS AND RICHARD F. MARVIN,
U. S. Geological Survey, Washington 25, D. C.

ABSTRACT

Barnesite is a new hydrated sodium vanadate mineral found in the Cactus Rat group of mines, 15 miles east southeast of Thompson, Grand County, Utah. It is found in small cavities and fractures and as interstitial filling in sandstone in the oxidized zone of a vanadiferous uranium deposit. This deposit is in a conglomeratic bed in the basal part of the Brushy Basin Shale Member of the Morrison Formation (Late Jurassic).

Barnesite is dark red and consists of microscopic bladed to fibrous crystals either in loose aggregates or in radiating clusters. In continuous coatings, it is velvety with a botryoidal appearance. Barnesite has monoclinic symmetry with the b-axis parallel to the elongation. Optically the mineral is biaxial negative with parallel extinction on the fiber length (b-axis); $\alpha = 1.797 \pm .003$, β above 2.0, and γ above 2.0. The pleochroism is X yellow, Y orange-yellow, and Z red and the orientation is $Z = b$, parallel to the length of the blades or fibers, $Y = a$, and $X \wedge c$ about 5°. The chemical analysis shows 82.40 per cent V_2O_5, 9.10 per cent Na_2O, 7.73 per cent H_2O and 0.40 per cent SiO_2, total 99.63 per cent and indicates the formula $Na_2V_6O_{16}\cdot 3H_2O$. The strongest lines of the x-ray diffraction powder pattern are 7.90 Å (intensity 100), 3.12 (70), 3.45 (35), 12.28 (25), 2.27 (25), and 1.800 (25). Unit cell data derived from least squares refinement of the x-ray powder data, $a = 12.17$ Å, $b = 3.602$ Å, $c = 7.78$ Å and $\beta = 95°2'$, compare favorably with the data of Barnes and Qurashi (1952). The cell volume is 342.0 Å^3, cell contents $Na_2V_6O_{16}\cdot 3H_2O$; calculated density = 3.21 g/cm^3, measured density = 3.15 g/cm.^{3}

Barnesite is named in honor of Dr. William H. Barnes, National Research Council of Canada, who has made a major contribution to the knowledge of the crystal structure of many vanadium minerals.

INTRODUCTION AND ACKNOWLEDGMENTS

Barnesite ($Na_2V_6O_{16}\cdot 3H_2O$) was first studied in the spring of 1951 in a sample which had been collected by B. N. Webber and L. B. Riley (Union Mines Development Company) from the Cactus Rat group of mines near Thompson, Grand County, Utah, during World War II. This sample contained both barnesite and metahewettite, $CaV_6O_{16}\cdot 3H_2O$, of similar appearance and caused confusion until spectrographic analyses

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on very small samples aided in matching the *x*-ray diffraction powder patterns with the proper composition.

A reconnaissance of the Cactus Rat open pits in the summer of 1951 revealed only traces of carnotite but a more thorough search of the area in 1952 located a good occurrence of barnesite in a small underground mine (Weeks and Thompson, 1954). Study of the material confirmed it to be the sodium analogue of metahewettite and led to the recognition that unit cell data given by Barnes and Qurashi (1952, p. 410–413) for Harvard No. 98019 sample from the "Cactus mine" Grand County, Utah, are for sodium vanadate rather than calcium vanadate.

In 1954 A. D. Weeks and R. F. Marvin studied the area of the Cactus Rat mines with regard to the origin of barnesite and the unusual assemblage of minerals in the Thompson district and collected better material from the same mine where barnesite was found in 1952.

We gratefully acknowledge the cooperation of W. H. Barnes and his associates M. M. Qurashi and H. G. Bachmann for discussion and data on the hewettite group minerals. Thanks also are gratefully extended to our colleagues on the U. S. Geological Survey, H. T. Evans, Jr., E. A. Cisney, and Malcolm Ross for discussion of *x*-ray and electron diffraction data on vanadium minerals and to C. L. Waring, A. M. Sherwood and G. B. Magin, Jr., for spectrographic and chemical analyses. The mineral barnesite has been previously mentioned in papers by Ross (1959) and Weeks (1961)

OCCURRENCE AND ORIGIN

All samples of barnesite for which the locality is known have come from the Cactus Rat group of mines, 15 miles east southeast of Thompson, Grand County, Utah. These mines are chiefly in the NE. $\frac{1}{4}$ of Section 33 and near the border of Section 34, T. 22 S., R. 22 E. Salt Lake meridan. They are accessible by two improved dirt roads leading south from U. S. Highway 50,—one 5 miles east of Thompson and the other 7 miles west of Cisco. This group of mines consists chiefly of shallow open pits which were bulldozed and reworked in an everchanging pattern in the early 1950's. Several small samples of barnesite came from these open pits but the best material (used for chemical analysis) came from the only mine in the group that had underground workings and a track along the haulageway. This mine is about 200 yards north of the improved road through the mining district, and near the Section 33–34 line.

The Cactus Rat mines are in the basal conglomeratic sandy beds of the Brushy Basin Shale Member of the Morrison Formation (Late Jurassic), in contrast to the other mines in the Thompson district which are in the Salt Wash Sandstone Member of the Morrison and are stratigraphically next below the Brushy Basin. Although carnotite was known in this district as early as 1904, no significant production began until the expansion of vanadium mining in the Colorado Plateau in the late 1930's.

In the vicinity of Cactus Rat, the Brushy Basin Member is about 450 feet thick (D. C. Alvord, written comm., 1952). It is predominantly red, purple, and gray, variegated, bentonitic mudstone grading from pure clay to sandy mudstone. The conglomeratic sandy beds at the base of the member are discontinuous. At the Cactus Rat mines they contain fragments of vertebrate bones and coalified twigs and pieces of tree trunks. The climate of the area is very hot and dry in the summer. This causes the accumulation of a thick salt crust wherever moisture seeps from the bentonitic rocks. The salt crust consists chiefly of sodium sulfate (thenardite) and is found along the outcrop of certain layers of rock, along the bed of dry gullies, and on mine walls. The abundance of sodium sulfate locally in the Cactus Rat mine area led to the idea that its presence may have caused hewettite to change to barnesite by cation exchange. Credence is given this possible origin by the ease with which hewettite is converted to barnesite in the laboratory (see Chemical Analysis and Synthesis section and *x*-ray diffraction data in Table 3). Barnesite also may have formed directly as an oxidation product of primary low-valent vanadium minerals (which are still preserved in some of the deep, water-saturated ores two miles west of Cactus Rat and one and one half miles east of it) if sodium was available at the time of oxidation.

Evans and Garrels (1958) and Evans (1959) have used all available thermodynamic data to determine the stability fields of the various vanadium minerals in the oxidation sequence on the Colorado Plateau. The theoretical fields agree with the assemblages of minerals noted in the partially oxidized and oxidized deposits. The laboratory synthesis of barnesite and the hewettite minerals indicates also that they formed in slightly acid environments.

PHYSICAL AND OPTICAL PROPERTIES

Barnesite is brilliant, dark red with an adamantine luster when it is fresh, and it forms microscopic bladed to fibrous crystals. On exposure, the color becomes slightly brownish red, and the luster decreases somewhat. This is due in part to handling because the grains are fragile, soft and easily smeared. Barnesite forms small clusters of subparallel to radiating fibers as well as continuous coatings of bedding plane fractures or small cavities where fragments of wood have weathered out. In these coatings the grains stand vertically in a velvety mass that is nearly black on the ends of the grains but the usual dark red on a broken surface. Some nearly spherical aggregates of barnesite form on the irregular surface of the sandstone and give a botryoidal growth of the coating. The thickness of these coatings is $\frac{1}{4}$ to $\frac{1}{2}$ mm; this represents the maximum length of the bladed crystals. Barnesite is easily fusible in the Bunsen burner flame and probably is about 2 on the fusibility scale. It is slowly soluble in dilute HCl.

Barnesite has monoclinic symmetry with the *b*-axis parallel to the long dimension of the blades or fibers. Optically it is biaxial negative and has parallel extinction on the *b*-axis; $\alpha = 1.797 \pm 0.003$, β and γ are both above 2.0. The pleochroism is X yellow, Y orange-yellow, and Z red, and the orientation is $Z = b$, parallel to the length of the blades, $Y = a$, and $X \wedge c$ about 5°.

CHEMICAL ANALYSIS AND SYNTHESIS

About 300 mg of barnesite were purified from sample AW-202-54 collected by Weeks and Marvin from the underground mine in the Cactus Rat group. This sample has irregular coatings about one-half millimeter thick which were gently pried off in small pieces and separated from the attached sand grains by handpicking. A semiquantitative spectrographic analysis by K. E. Valentine showed over 10 per cent V, between 5 and 10 per cent Na, and less than 0.5 per cent Si, Al, and Ca. A microchemical analysis (Table 1) by A. M. Sherwood shows 9.10 per cent Na_2O, 82.40 per cent V_2O_5, 7.73 per cent H_2O and 0.40 per cent SiO_2, total 99.63 and indicates the formula $Na_2V_6O_{16} \cdot 3H_2O$. Analyses of synthetic barnesite by G. B. Magin, Jr. (Table 1) are very similar to those of the natural material except for a slight difference in the water determination. This may be due to excess water held in the fine-grained, fibrous, crystalline mat of the synthetic material. The apparent 5 per cent deficiency in water in the

TABLE 1. CHEMICAL ANALYSES OF NATURAL AND SYNTHETIC BARNESITE

	1	2	3	4
Na_2O	9.10	9.20	9.13	9.36
V_2O_5	82.40	82.26	82.50	82.48
H_2O	7.73	8.84	8.77	8.16
SiO_2	0.40			
Total	99.63	100.30	100.40	100.00

1. Barnesite from Cactus Rat mine sample AW-202-54; analysis by A. M. Sherwood.
2. Synthetic barnesite, sample Na 1-1; analyst: G. B. Magin, Jr.
3. Synthetic barnesite, sample Na 4-1; analyst: G. B. Magin, Jr.
4. Theoretical composition for $Na_2O \cdot 3V_2O_5 \cdot 3H_2O$.

analysis of the natural sample may be due to analytical problems with a small sample.

Barnesite has been synthesized both by direct crystal growth and by cation exchange (Marvin and Magin, 1959, pp. 109–110). At 55° C., $Na_2V_6O_{16} \cdot 3H_2O$ formed directly from a slowly evaporating solution of NaOH (0.22 M) and V_2O_5 (0.11 M) adjusted with glacial acetic acid to a pH range between 3.0 and 6.0. The precipitate was identified as barnesite by *x*-ray diffraction powder pattern and chemical analyses. It would probably form at lower temperatures if the solution were evaporated very slowly; rapid evaporation produces a metastable polyvanadate phase analogous to $Ca_3V_{10}O_{24} \cdot 16H_2O$ (pascoite) that is common on mine walls in the Uravan district of Colorado. Barnesite was also formed by cation exchange of hewettite in a sodium-bearing solution with a pH between 3.0 and 6.0. Several grams of synthetic hewettite were placed in a solution of Na_2SO_4 (concentration varied from 0.1 N to 0.7 N) for three weeks and converted to barnesite. The *x*-ray pattern (Table 2) of this base-exchanged sample (I-Ca-18–23) is like that of natural and synthetic barnesite.

CRYSTALLOGRAPHY AND RELATION TO OTHER VANADATES

In 1951, preliminary *x*-ray and electron diffraction study of barnesite by E. A. Cisney and A. D. Weeks indicated that it is monoclinic with the blades elongated on the *b*-axis, like the hewettite minerals. When it was learned that W. H. Barnes and his associate M. M. Qurashi were engaged in an *x*-ray investigation of vanadium minerals and had determined the unit cell of an unknown hewettite-like vanadate (now barnesite), no further *x*-ray work on this mineral was undertaken by us except to gather *x*-ray powder data on our analyzed samples. The powder patterns of the synthetic (Na-4-1) and cation-exchanged (1-Ca-18-23) barnesite are listed in Table 2 with that of the analyzed, natural material from Cactus Rat mine. All three patterns have very similar d-spacings and intensities.

Barnes and Qurashi in 1952 gave unit-cell data for what they thought was a calcium hewettite (Harvard specimen No. 98019 from the Cactus Rat mine). Later Barnes (1955) showed that this specimen was in fact a sodium hewettite identical with specimen AW-202-54 described here. Qurashi (1961) has discussed the relation between hewettite, $CaV_6O_{16} \cdot nH_2O$/ and its sodium analogue, barnesite. He examined in detail the sensitivity of hewettite to humidity changes and showed that barnesite is insensitive to humidity.

Ross (1959) examined single crystals of specimen AW-202-54 by the technique of electron diffraction and obtained partial unit-cell data. His

TABLE 2. *X*-RAY DIFFRACTION POWDER DATA FOR BARNESITE

Calculated d-spacings, measured single crystal intensities			Natural barnesite, Cactus Rat Mine, Utah AW-202-54 CrKα, $\lambda=2.2909$ Å, V filter		Synthetic barnesite Na-4-1 Cr/V		Synthetic barnesite (cation exchanged) 1-Ca-18-23 CuKα, $\lambda=1.5418$ Å Ni filter	
hkl	I[1]	d(calc.)[2]	I	d(meas.)	I	d(meas.)	I	d(meas.)
100	W	12.12	25	12.2*	26	12.2	W	12.3
001	S	7.75	100	7.90*	100	8.08	VS	7.9
$\bar{1}01$		6.81						
101		6.28						
200	W	6.06	3	6.08*	4 vvd	6.09	VVF	6.1
$\bar{2}01$	W	4.99	2 d	5.14*	4 vvd	5.24	VVF	5.1
201		4.58						
300	W	4.04	2d	3.94				
002	W	3.875						
$\bar{1}02$		3.789						
$\bar{3}01$	S	3.719	9	3.70*	13	3.68	W	3.72
010		3.602						
102		3.601						
301	W	3.461	35	3.45	35	3.44	M	3.45
110		3.453						
$\bar{2}02$		3.403						
011		3.266						
$\bar{1}11$	W	3.184						
202	S	3.142	70	3.12	48	3.12	S	3.13
111	S	3.125						
210	W	3.097						
400	W	3.031						
$\bar{3}02$	S	2.928	18	2.92*	17	2.91	M	2.93
$\bar{2}11$	W	2.921						
$\bar{4}01$	W	2.911						
211		2.832					VF	2.82
401	W	2.742						
310	W	2.689	2	2.69*				
302		2.682						
311	W	2.588	2 vd	2.65-2.58[3]				
$\bar{2}12$	S	2.474	2 vd	2.49-2.42[3]				

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[1] Intensities were estimated by Qurashi (1961, Fig. 3) from single crystal photographs.

[2] d-spacings are calculated from the following unit-cell data: $a=12.17$ Å, $b=3.602$, $c=7.78$, and $\beta=95°2'$. This cell was obtained by least squares refinement of the *x*-ray powder data of natural barnesite indicated by an asterisk listed above. Calculated spacings less than 2.681 Å are listed only if indexed to an observed reflection.

[3] Extremely diffuse bands.

TABLE 2—(*continued*)

Calculated d-spacings, measured single crystal intensities			Natural barnesite, Cactus Rat Mine, Utah AW-202-54 CrKα, $\lambda = 2.2909$ Å, V filter		Synthetic barnesite Na-4-1 Cr/V		Synthetic barnesite (cation exchanged) 1-Ca-18-23 CuKα, $\lambda = 1.5418$ Å Ni filter	
hkl	I[1]	d(calc.)[2]	I	d(meas.)	I	d(meas.)	I	d(meas.)
500	W	2.425	2	2.38				
410	S	2.319	7	2.32*	4	2.31	VF	2.31
$\bar{3}03$	S	2.269	25	2.27*[4]	26	2.26	Md	2.26
501	S	2.258						
$\bar{4}12$	S	2.052	3 vd	2.06*				
502	S	1.979	3 vd	1.991*			VVFd	1.993
$\bar{3}04$	W	1.810	2	1.816				
020	S	1.801	25	1.800*	35	1.798	Wd	1.800
021	S	1.754	3	1.755*				
$\bar{2}14$	S	1.677	2 vd	1.670*	4	1.675	VVF	1.675
222	S	1.563	3 vd	1.558	4	1.562	F	1.558
800	S	1.515	2 vd	1.519	4	1.521	VVFd	1.519
$\bar{8}01$	S	1.512						
$\bar{8}02$	S	1.455	3 vd	1.458*	4	1.456	VVFd	1.459
$\bar{3}23$	S	1.411	3 vd	1.411*	4	1.410	VVFd	1.408

[4] This ambiguous line was erroneously included in the least squares calculation, but the result is not significantly affected by it.

VS = very strong; S = strong; M = medium; W = weak; F = faint; VF = very faint; VVF = very, very, faint; d = diffuse; vd = very diffuse; vvd = very, very, diffuse. Powder patterns made with 114.6 mm diameter camera; error due to film expansion is less than 0.2% of d; cut-off for Cr radiation is 20 Å and for Cu radiation, 15 Å.

Table 1 (Ross, 1959, p. 328) shows the close similarity between barnesite and the hewettite minerals in the *a–b* plane.

In Table 3 are tabulated the crystallographic data of Barnes and Qurashi (1952), Qurashi (1961), and Ross (1959) along with the unit-cell data obtained for the natural barnesite from the Cactus Rat mine, and the synthetic barnesite (Na-4-1). These unit-cell data were obtained from least squares refinement of the *x*-ray powder data given in Table 2. The refinement was carried out on the Burroughs 220 computer by Howard T. Evans, Jr. with a program written by H. T. Evans, Jr., D. E. Appleman and D. S. Handwerker. The measured lines of the *x*-ray powder patterns were indexed by comparing them to the calculated d-spacings based on the unit cell of Barnes and Qurashi (1952) and to the intensities ob-

TABLE 3. CRYSTALLOGRAPHIC DATA FOR BARNESITE

	Single crystal data		X-ray powder data (Table 2)[3]	
	(Barnes and Qurashi)[1]	(Ross)[2]	(Cactus Rat)	(Synthetic Na-4-1)
a (Å)	12.18	12.17±0.02	12.17±0.04	12.18±0.09
b (Å)	3.614	3.604±0.005	3.602±0.010	3.596±0.016
c (Å)	7.80	—	7.78 ±0.04	7.79 ±0.08
β	95°	—	95°2′ ±24′	94°50′ ±1°43′
$a:b:c$	3.370:1:2.158	—	3.379:1:2.160	3.387:1:2.166
Volume (Å^3)	342.0	—	339.7	340.0
Cell contents	$Na_2V_6O_{16} \cdot 3H_2O$	—	$Na_2V_6O_{16} \cdot 3H_2O$	$Na_2V_6O_{16} \cdot 3H_2O$
Space Group[4]	$P2/m$	—	—	—
Density (measured)	—	—	3.15 g/cm^3	—
Density (calculated)	3.21 g/cm^3	—	3.23 g/cm^3	3.23 g/cm^3

[1] Single crystal x-ray data from Barnes and Qurashi (1952, p. 411), on material referred to as hewettite, but later shown to be sodium vanadate (Barnes, 1955)

[2] Single crystal electron diffraction data from Ross (1959, p. 328), on material from Cactus Rat mine.

[3] Unit cell data obtained from least squares refinement of the x-ray powder data given in Table 2.

[4] Space group from Qurashi (1961, p. 660).

tained by Qurashi (1961, Fig. 3) from single crystal Weisenberg photographs. In this figure Qurashi shows the intensities of the h0l and h1l reflections as either missing, weak, or strong. Because of the nature of the crystal structure (Bachmann and Barnes, 1962), the h2l pattern must be similar to the h0l pattern. This information made it possible to index all of the powder lines for barnesite without serious discrepancy. The unit cell given by Barnes and Qurashi (1952) was used as a starting point in the refinement. All of Qurashi's "strong" reflections are observed on the powder patterns, and most of his "weak" ones. The fact that all the unit cell constants given in Table 3 are indistinguishable within the experimental error strongly supports the conclusion that all the material represented is essentially the same and characteristic of the mineral barnesite.

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