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NAVAJOITE, A NEW VANADIUM OXIDE FROM ARIZONA*

By

Alice D. Weeks, Mary E. Thompson, and Alexander M. Sherwood

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By

Alice D. Weeks, Mary E. Thompson, and Alexander M. Sherwood

ABSTRACT

Navajoite, hydrated vanadium pentoxide, is a new mineral found in the Monument No. 2 mine, on the Navajo Indian Reservation, Apache County, Ariz. It occurs as a coating around pebbles and sand grains and in thin seams in sandstone and clay lenses in a vanadium-uranium deposit in the Shinarump conglomerate (Triassic). It is dark brown, soft, and fibrous, with silky luster and brown streak. The specific gravity measured on the Berman balance is 2.56. The mineral is optically biaxial, probably negative, has parallel extinction, and $\alpha = 1.905 \pm 0.003$, β about 2.02, and γ slightly above 2.02. X = yellowish brown, Y = yellowish brown, Z = dark brown parallel to fiber length. A chemical analysis shows V_2O_5 71.68 percent, V_2O_4 3.08, Fe_2O_3 3.58, H_2O 20.30, SiO_2 1.20, CaO 0.22, total 100.06 percent, and indicates the formula $V_2O_5 \cdot 3H_2O$. The d-spacings and intensities of lines in the X-ray powder pattern are listed. The unit cell length along the fiber is 3.65 ± 0.03 Å. Tentative indexing of the powder pattern suggests that the mineral is monoclinic with $a_o = 17.43 \pm 0.10$ Å, $b_o = 3.65 \pm 0.03$ Å, $c_o = 12.25 \pm 0.10$ Å, $\beta = 97^\circ \pm 30'$, and $Z = 6$.

INTRODUCTION AND ACKNOWLEDGMENTS

Several impure samples of navajoite were collected from the Monument No. 2 mine, in the Garnet Ridge quadrangle, Apache County, Arizona, in 1951. The first seen by the writers was collected by

A. Rosenzweig, at that time mineralogist for the Atomic Energy Commission in Grand Junction, Colo. In July 1951 A. D. Weeks, D. H. Johnson, and other U. S. Geological Survey mineralogists collected several samples. Clifford Frondel of Harvard University sent the writers a sample that had been submitted to him. All of these samples were sandstone or shaly sandstone impregnated with the brown vanadium mineral, but they contained too small a concentration of pure mineral for chemical analysis.

In July 1952 A. D. Weeks and M. E. Thompson visited the mine again with several Survey geologists and found enough relatively pure material to establish the new mineral.

When the chemical composition was found to be hydrated vanadium pentoxide, an effort was made to compare this mineral with alaite reported from Russia as a hydrated vanadium oxide (Nenadkovich, 1909). No alaite specimen has been located and the original description gives no chemical analysis or adequate description of physical properties. It has been suggested that alaite may be hewettite or metahewettite (Hillebrand, Merwin, and Wright, 1914, p. 49, and Fersman, 1930, p. 33), probably because of its red color. Therefore it seemed unwise to use the uncertain name alaite for the new Arizona material and the name navajoite has been chosen in honor of the Navajo Indians on whose reservation this new mineral occurs.

Thanks are gratefully extended to A. Rosenzweig and Clifford Frondel for an opportunity to examine their samples, to H. T. Evans for X-ray data, and to W. T. Schaller and D. H. Johnson for helpful suggestions.

This investigation is part of the project of mineralogic studies on the Colorado Plateaus being carried out by the U. S. Geological Survey

on behalf of the Division of Raw Materials of the Atomic Energy Commission.

OCCURRENCE

All of the samples collected by the writers came from the South Rim workings of the Monument No. 2 mine, operated by the Vanadium Corporation of America in Apache County, Ariz. (It is not known whether Frondel's and Rosenzweig's samples came from the same part of the mine.) The mine is in a vanadium-uranium deposit located just north of Comb Ridge in Monument Valley. The ore occurs in a wide, complex channel that is filled with Shinarump conglomerate (Triassic) and that extends down through the Moenkopi formation (Triassic) into the DeChelly sandstone member of the Cutler formation (Permian) (Witkind and others, 1953).

The mineral navajoite impregnates conglomeratic sandstone and silty sandstone, forms seams in the sandstone and crescent-shaped coatings above and below pebbles, and fills small fractures in clay lenses. The best specimens are the thickest crescent-shaped coatings and seam fillings with fibers perpendicular to the wall rock. The rock is porous and friable and most of the ore in this portion of the mine is highly oxidized. Associated minerals include only one with V^{+4} and V^{+5}, corvusite, and the rest are fully oxidized: tyuyamunite, rauvite, hewettite, steigerite, and limonite.

PHYSICAL PROPERTIES

Navajoite is dark-brown, silky to fibrous, with brown streak, and adamantine luster on freshly broken surfaces. The fibrous appearance is due to the growth habit as minute columns build up perpendicular to a fracture surface. The fibers are very soft and when finely ground on a glass slide they smear out to form a waxy yellow-brown film. Some corvusite has a similar growth habit, but it may be distinguished by its blue-black color and especially by its greenish color when smeared thin on a glass slide. The hardness of navajoite is less than 2 and the specific gravity, measured on a Berman balance, is 2.56. The mineral is so dark and fine grained that the optical properties have not been completely determined. It is biaxial, probably negative, has parallel extinction, and $\alpha = 1.905 \pm 0.003$, β approximately 2.02, and γ is slightly higher than 2.02. X = yellowish brown, Y = yellowish brown, Z = dark brown parallel to the fiber length. Although optically the mineral appears to be orthorhombic, X-ray study indicates it may be monoclinic and elongated parallel to the b axis, as hewettite was proved to be by Barnes and Qurashi (1952).

CHEMICAL ANALYSIS

The samples collected in 1951 contained quartz, clay, or other contaminants and were not suitable for a chemical analysis to determine the composition of a new mineral. In one of the 1952 samples a crescent-shaped mass of navajoite around a quartzite pebble about an inch and a half in diameter seemed very pure. About 1 g of this was prepared for chemical analysis and a portion of the original specimen was saved to

show the occurrence. The outer and inner surfaces of the crescent were scraped to remove any hewettite or rauvite that coated them, then the navajoite was ground and examined under the binocular microscope for impurities. A semiquantitative spectrographic analysis made by H. W. Worthing on 10 mg of the purified sample is as follows:

Over 10 percent	V
1 - 10	Fe
0.1 - 1.0	Si, Ca, Al
0.01 - 0.1	Ba, Na, Mg
0.001 - 0.01	Cr, Ti, Sr, Y, Mn, Cu

Because the analysis shows the constituent elements of the contaminating quartz and clay to be each less than one percent, this sample was the most suitable one available for chemical analysis.

Table 1.--Chemical analysis of navajoite. A. M. Sherwood, analyst.

	Percent
V_2O_5	71.68
V_2O_4	3.08
Fe_2O_3	3.58
SiO_2	1.20
CaO	0.22
H_2O	20.30
Total	100.06

The interpretation of the chemical analysis is chiefly concerned with the water content and with the question of impurities in the sample or the solid solution substitution of some minor constituents. The 1.20 percent of silica is probably due to quartz impurity. The

0.22 percent of CaO may represent contamination by about 3 percent of hewettite although no lines of hewettite show in the X-ray powder pattern of navajoite. The presence of a small amount of hewettite would not affect the calculation of the formula for navajoite because the proportion of V_2O_5 to H_2O is thought to be the same in both minerals. The X-ray pattern of navajoite does not have any lines which would indicate that the 3.58 percent of Fe_2O_3 is present as an impurity of goethite or of fervanite ($Fe_4V_4O_{16} \cdot 5H_2O$). Probably the iron substitutes for vanadium in this mineral as it does in montroseite (Weeks, Cisney, and Sherwood, 1953, and Evans and Block, 1953). If the 3.08 percent of V_2O_4 is present in admixed corvusite and if its formula is $V_2O_4 \cdot 6V_2O_5 \cdot 13H_2O$, corvusite would make up nearly 28 percent of the analyzed sample. Such a high contamination is unlikely for the following reasons: (1) the color is brown and the streak yellowish brown instead of black and greenish black as in corvusite; (2) the X-ray powder pattern of navajoite has been indexed (table 3) with reasonably satisfactory results and does not seem to be a mixed pattern; (3) the presence of corvusite is probably not indicated in the pattern of navajoite although the two minerals may have some structural features in common. The pattern of corvusite is not very well established and seems to be somewhat variable. It is believed that navajoite formed by oxidation of corvusite at the Monument No. 2 mine and that the conversion to navajoite structure took place in this sample before the oxidation was completed.

A redetermination of the water as H_2O (-) and H_2O (+) made nearly a year after the original chemical analysis shows 10.21 percent of H_2O (-) and 8.10 percent of H_2O (+). This represents a loss of 1.99 percent water while the sample was stored in the laboratory and indicates that

part of the water is easily released, perhaps as interlayer water. The 8.10 percent of H_2O (+) indicates that one molecule of water is held in the structure. Although the molecular proportion of water to V_2O_5 in the chemical analysis is slightly less than 3, the formula is probably $V_2O_5 \cdot 3H_2O$ with two molecules of interlayer water and one structural. If more pure material can be obtained, dehydration studies will be made.

X-RAY DIFFRACTION DATA

The X-ray powder pattern (table 2) of navajoite distinguishes it readily from hewettite and corvusite which it resembles in physical appearance. The best fibrous sample (same as chemically analyzed) gives an oriented X-ray pattern. The fibers are too small for single crystal X-ray photographs. However, a rotation photograph (taken by H. T. Evans, U. S. Geological Survey) of a small bundle of fibers indicates the unit cell length along the fiber is about 3.65 Å. A large-scale photograph of the zero layer was then obtained by placing the fiber bundle in a powder camera and using chrome radiation. An attempt to index the zero layer by use of the logarithmic form of Bjurstrom's chart (Bunn, 1946, p. 380) failed, indicating that the two axes other than the fiber length are not at right angles to each other and navajoite is probably monoclinic.

The reciprocal lattice spacings (1/d) of the (h0l) lines with spacing larger than $1/d_{010}$ were plotted. The best graphical solution found by trial and error suggests that $a_o = 17.43 \pm 0.10$ Å, $b_o = 3.65 \pm 0.03$ Å, $c_o = 12.25 \pm 0.10$ Å, and $\beta = 97^\circ \pm 30'$. This unit cell would hold approximately 6 formula weights of $V_2O_5 \cdot 3H_2O$. The tentative indexing

Table 2.--X-ray diffraction powder pattern of navajoite (average of 5 patterns). CuKα radiation

d (meas) (Å)	I
12.11	VS
10.61	M
9.41	F
8.67	F
7.44	F
5.79	Wb
4.35	W
3.95	F
3.53	W
3.47	W
3.10	Wb
2.90	M
2.79	F
2.68	F
2.49	W
2.39	VF
2.18	F
2.12	M
1.99	W
1.80	F

of the larger d-spacings is given in table 3. It is hoped that larger crystals will be found so that the crystallography may be checked.

Table 3.--Tentative indexing of h0l lines of navajoite powder pattern. Cr/V radiation

I	d (meas) Å	d (calc) Å	hkl	Assume:
W	17.4	17.33	(100)	a_o = 17.43 Å
VS	12.1	12.15	(001)	b_o = 3.65 Å
M	10.6	10.58	(101)	c_o = 12.25 Å
VF	9.4	9.42	$(10\bar{1})$	β = 97°
F	8.66	8.65	(200)	$V_2O_5 \cdot 3H_2O$
Fb	7.41	7.496	(201)	Z = 6
Wb	5.79	5.767	(300)	
F	4.32	4.325	(400)	
F	3.95	3.951	$(30\bar{2})$	

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