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## GRANTSITE, A NEW HYDRATED SODIUM CALCIUM VANADATE FROM NEW MEXICO, COLORADO AND UTAH<sup>1</sup>

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### ABSTRACT

Grantsite, a new mineral with the formula  $\text{Na}_4\text{Ca}_x\text{V}^{4+}_{2x}\text{V}^{5+}_{(12-2x)}\text{O}_{32}\cdot 8\text{H}_2\text{O}$  (in analyzed samples  $x=0.6$  to  $0.9$ ) was found in the F-33 mine, near Grants, New Mexico; in the Golden Cycle and the La Salle mines in Montrose County, Colorado; and in the Parco No. 23 mine, Grand County, Utah. All localities are in partly oxidized "corvusite-type" vanadiferous uranium ores, one in limestone and three in sandstone.

Grantsite forms dark olive green to greenish black aggregates of microscopic fibrous or bladed crystals. At the F-33 mine it retains the habit of the haggite and paramontroseite from which it was derived by oxidation. It is soft and smears easily; luster is silky to subadamantine; and specific gravity (measured) is  $2.94 \pm 0.01$ . The mineral is biaxial negative; the fibers are length slow; indices of refraction are  $\alpha 1.82 \pm 0.01$ ;  $\beta > 2.0$  and  $\gamma > 2.0$ ; orientation and pleochroism are X, normal to the blade, green; Y, parallel to the intermediate dimension of the blade, greenish brown; and Z=b, parallel to the length of the blade, brown; absorption is  $Z > Y > X$ .

Grantsite is monoclinic, space group  $C2/m$  (or  $Cm$  or  $C2$ ). Unit-cell data on the sample from the Golden Cycle mine are:  $a=17.54_5 \pm 0.06 \text{ \AA}$ ,  $b=3.60 \pm 0.01 \text{ \AA}$ ,  $c=12.41 \pm 0.04 \text{ \AA}$ , and  $\beta=95^\circ 15' \pm 0^\circ 10'$ ;  $a:b:c=4.874:1:3.447$ ; cell contents  $\text{Na}_4(\text{Ca}, \text{Sr})_x\text{V}^{4+}_{2x}\text{V}^{5+}_{(12-2x)}\text{O}_{32}\cdot 8\text{H}_2\text{O}$ ; calculated density  $2.95 \text{ g cm}^3$ . The strongest lines of the x-ray diffraction powder pattern are  $8.76 \text{ \AA}$  (intensity 100),  $3.604(25)$ ,  $3.005(14)$ ,  $2.872(11)$ ,  $12.3(10)$ ,  $2.280(10)$ ,  $2.743(7)$ , and  $2.244(7)$ .

The name grantsite is for the town of Grants, New Mexico, near which it was discovered.

### INTRODUCTION AND ACKNOWLEDGMENTS

The new mineral grantsite,  $\text{Na}_4\text{Ca}_x\text{V}^{4+}_{2x}\text{V}^{5+}_{(12-2x)}\text{O}_{32}\cdot 8\text{H}_2\text{O}$ , was first collected in 1952 by T. W. Stern and L. B. Riley from Section 33, T. 12 N., R. 9 W., near the town of Grants, Valencia County, New Mexico. A. D. Weeks and M. E. Thompson considered this to be a new vanadium mineral on the basis of its physical properties and x-ray diffraction powder pattern. However, sufficient material to complete a satisfactory mineral description was not available.

<sup>1</sup> Publication authorized by the Director, U. S. Geological Survey.

In 1956, Weeks and Truesdell found grantsite in the Golden Cycle Mining Company's mine on Atkinson Mesa, Uravan district, Montrose County, Colorado and in a sample from the La Salle Mining Company's mine on Club Mesa. In 1957, Weeks and Truesdell revisited the Anaconda Company mine in the Grants area in New Mexico where grantsite had been collected in 1952. The mine had been greatly enlarged since 1952 and additional samples were found in several places.

Thanks are gratefully extended to Robert Lynn, Chief Geologist, and to Ray Coudray, mineralogist, of the Anaconda Company at Bluewater, New Mexico; also to the La Salle Mining Company and to the Golden Cycle Mining Company in the Uravan district, Colorado.

Thanks are due our Geological Survey colleagues, R. L. Boardman and his associates in the Uravan district of Colorado, and R. E. Thaden, O. B. Raup, and associates in the Grants district of New Mexico, and to Mary E. Thompson for data on a sample from near Thompson, Utah.

The preliminary investigation of grantsite was part of the program of geologic and mineralogic studies carried on by the U. S. Geological Survey in behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

The new mineral is named grantsite for the town of Grants, New Mexico, near which it was first found in 1952 and where the largest quantity of the mineral has been obtained. A preliminary description of grantsite was published by Weeks, Lindberg and Meyrowitz (1961).

#### OCCURRENCE OF GRANTSITE

Grantsite has been found in four mines, all in vanadiferous uranium deposits in the Colorado Plateau. One is in the Todilto Limestone (Upper Jurassic) and three are in the Salt Wash Sandstone Member of the Morrison Formation (Upper Jurassic).

*Grants, New Mexico.* The first sample and the largest quantity of subsequent samples of grantsite were collected from the F-33 mine of the Anaconda Company in Section 33, T. 12 N., R. 9 W., Valencia County, about six miles northeast of Grants, New Mexico (Fig. 1). In the vicinity of the mine, the Todilto Limestone dips gently to the east-northeast. A series of outcrops of the limestone form a discontinuous cuesta-like escarpment that extends northwest from the mine. The strike changes from NNW at the mine to NW and WNW in a distance of about 15 miles. The Jurassic formations, in general in this area, dip gently north-eastward from the Zuni uplift toward the San Juan basin. Several resistant sandstone strata in the sedimentary series as well as the Todilto Limestone form irregular southward-facing escarpments.

Vanadium is spottily distributed in the uranium deposits in the Todilto Limestone, both in the area as a whole and in the F-33 mine which has more vanadium than many of the deposits in the Todilto.

In the F-33 mine (as studied in 1957), vanadium minerals were found in an elongate pod along the main ore body. The pod was observed in five crosscuts about 50 to 80 feet north of the main haulage way which trends easterly; it is roughly 2 to 8 feet wide by one half foot to 3 feet high. Although the overall length is more than 500 feet, it is not known whether the pod is continuous through the unmined (1957) areas between the crosscuts. Grantsite was found in four of the crosscuts, but not in an intermediate crosscut where the ore is more highly oxidized along a post-

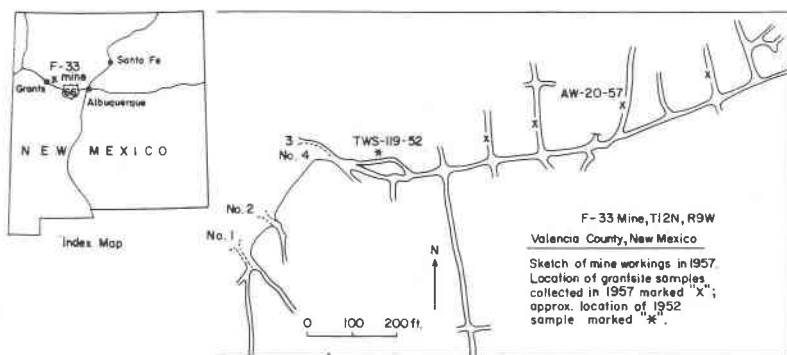


FIG. 1. Location of grantsite samples in F-33 mine, 6 miles northeast of Grants, Valencia County, New Mexico.

ore fracture. According to Ray Coudray, mineralogist of the Anaconda Company, the 1952 sample of grantsite was collected 150 feet within Tunnel no. 3, an early prospect which became merged with Tunnel no. 4 and enlarged to the present mine. The location of the first sample was roughly 250 feet west of the series collected in 1957 and probably it was in a small pod of ore parallel to and slightly separated from the large pod.

Much of the vanadiferous ore in the F-33 mine is unoxidized and consists of haggite, paramontroseite, and vanadium clay with uranium minerals—uraninite and coffinite—and minor amounts of galena, pyrite, marcasite, and hematite (Truesdell and Weeks, 1960). As the ore in the Todilto Limestone is only slightly permeable, little oxidation of the ore has taken place except along joints and fractures. In partly oxidized ore, bundles of fibrous grantsite have replaced the stubby haggite and paramontroseite prisms with little or no movement of material. Grantsite in thin seams showing no relict structure of low-valent minerals may have

formed from vanadium that migrated a short distance during oxidation—probably fractions of an inch or perhaps as much as a few feet. The sodium in the grantsite is probably derived from alteration of alkali feldspar grains. Detrital quartz and feldspar grains in very thin beds in the limestone are commonly corroded. Spectrographic analyses of the acid insoluble fraction of the limestone show Na in the semiquantitative ranges 0.07 to 0.15 and 0.15 to 0.7 per cent. The sodium also could have

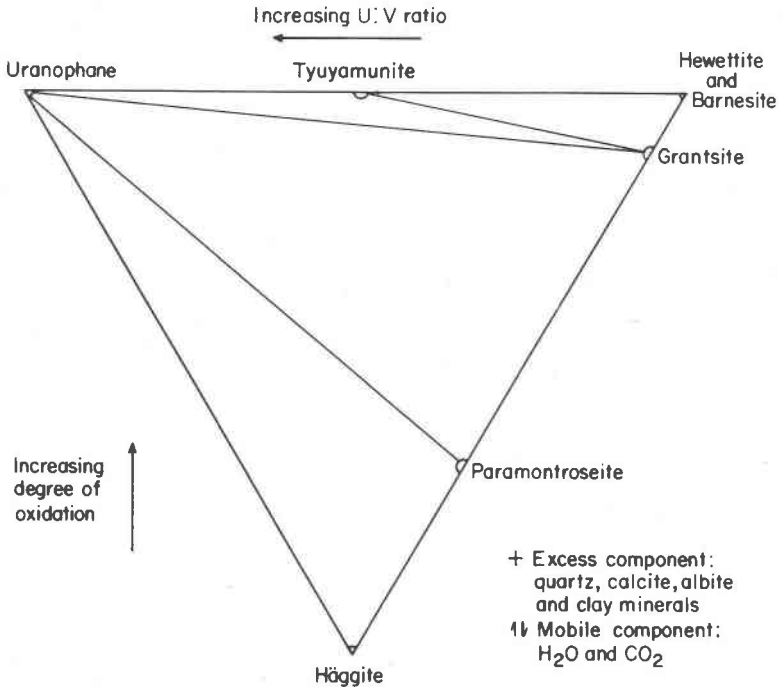


FIG. 2. Schematic mineral assemblage diagram for the F-33 mine in the Todilto Limestone.

been derived from salt included in the connate water of the limestone or from possible salt layers higher in the formation, which is at least partly evaporitic in character.

In the mineral assemblage of the F-33 mine, schematically shown in Fig. 2, grantsite takes the paragenetic place of corvusite which occurs in most partly oxidized vanadiferous deposits. The  $V^{4+}:V^{5+}$  ratio of grantsite is in the same range as that of corvusite, between 1:5 and 1:7. Grantsite is less common than corvusite, either because of too little sodium or because highly soluble sodium decavanadate may be washed

out of a deposit. Slightly reducing and slightly more acid conditions are necessary to precipitate grantsite from a decavanadate solution. In the mineral assemblage, excess components are quartz, calcite, albite, and clay minerals, and mobile components are  $H_2O$  and  $CO_2$ . Grantsite is more abundant in the mine than are the completely oxidized vanadium minerals; in fact, hewettite was found only in a highly oxidized zone along a fracture and no barnesite was identified. The relative scarcity of hewettite (and barnesite) may be due to spotty and incomplete oxidation as well as an overall U:V ratio greater than 1:1.

*Uravan, Colorado.* In 1956 grantsite was found in the Golden Cycle Mining Company's mine on Atkinson Mesa, north of Uravan, Montrose County, Colorado. The top of the mine shaft is at 6100 feet above sea level and 0.85 mile due north of the Ophir mine, which is shown on the Red Canyon  $7\frac{1}{2}$  minute quadrangle, Colorado (McKay, 1955). At the mine the rocks strike N.  $55^\circ$  W. and dip about  $2\frac{1}{2}^\circ$  NE. and are on the southwest flank of the San Miguel syncline and the northeast flank of the Paradox Valley anticline. Access to the mine was through a 630-foot vertical shaft, the deepest in the Uravan district in 1956. The ore is in the Salt Wash Sandstone Member of the Morrison Formation and is overlain by the Brushy Basin Shale Member (also Morrison), the Burro Canyon Formation, and part of the Dakota Sandstone.

The mine is moist but not water-saturated. The ore is partly oxidized with a few remnants of black unoxidized ore in high-grade pockets and some yellow and brown oxidized ore. The ore minerals are chiefly vanadium silicates containing  $V^{4+}$  and vanadium oxides and vanadates containing  $V^{4+}$  and  $V^{5+}$ . The nonsilicate minerals include paramontroseite, corvusite, grantsite, and an unnamed K-Fe-vanadyl vanadate (Weeks, Lindberg and Meyrowitz, unpublished data). The ore minerals are accompanied by small amounts of pyrite, marcasite, sphalerite, dolomite, and barite. Small amounts of carnotite and tyuyamunite are disseminated in the sandstone and in a few places high-grade oxidized ore has conspicuous yellow uranyl vanadates and iron oxide. A small amount of coffinite but no uraninite was found in the least oxidized ore. The partly oxidized ore contains amorphous black uranium oxides and some rauvite.

The analyzed sample of grantsite (AW-43-56) came from a stope above the main haulageway, about 300 feet southeast of the shaft and near drill hole AM-227 (Atkinson Mesa). The wall of the stope at the sample locality was about six feet high. The top two feet had several layers of rich blue-black to brownish-black ore that was nearly parallel to the bedding. The grantsite was in thin discontinuous seams close to the top of this zone. Beneath this zone was sandstone with scattered clay pellets and at

the base were several thin gray clay beds. The sandstone was low-grade ore that was spotted in yellow, brown, and gray, and was mostly oxidized. Some of the clay pellets were mineralized dark gray to black. Fine-grained pyrite was common along the top border of the clay bed and in some of the clay pellets.

Grantsite was also found in the La Salle Mining Company's shaft mine near Uravan. A group of samples was collected in 1954 but grantsite was not recognized in one of them (AW-47-54) until after the study of the Golden Cycle material. The La Salle mine is on the east side of Club Mesa and is about 1.7 miles west southwest of Uravan. Although the mine is not marked on the Davis Mesa quadrangle (Cater, 1955), it may be located as 1.3 miles due east of the Tramp No. 2 mine and close to a 6007-foot elevation, both of which are shown on the quadrangle map. In the vicinity of the mine, the rocks strike N. 45° W. and dip about 3° NE. and are on the northeast flank of the Paradox Valley anticline. The mine has a vertical shaft about 265 feet deep to reach the ore zone. The mine workings are relatively dry with no seepage of water and very little efflorescence on the mine walls.

The ore is chiefly oxidized and disseminated in sandstone; some is banded parallel to the bedding and some ore bands cut across the bedding in typical "ore rolls." A few richly mineralized logs that were partly oxidized were found in the mine and the grantsite sample was associated with one of these. Grantsite constituted a small proportion of the complex ore sample in which it was found. It was in a small pocket of high-grade ore that included coalified wood and sandstone and clay balls around the wood. One small piece of grantsite was botryoidal and pseudomorphous after low-valent vanadium oxides (like the Grants, New Mexico sample), but most of it had grown between sand grains or around the borders of irregular clay pellets. With the grantsite was corvusite, rauvite, vanadium clay, and a little hewettite and carnotite or tyuyamunite. Also present was yellow-orange barite that was highly radioactive from the precipitation of radium during the recent oxidation of the uranium. This assemblage of minerals is typical of many partly oxidized high-grade "logs" in the Uravan mineral belt.

*Thompson, Utah.* Grantsite was identified from the Parco No. 23 mine, Grand County, Utah (M. E. Thompson, written communication). The mine is south of U. S. Highway 50, about 13 miles southeast of Thompson, and it is in the southeastern part of Section 1, T. 23 S., R. 21 E., Salt Lake Meridan. The small ore body was broken by a nearly vertical normal fault striking N. 60° W. The ore on the northeast or upthrown side of the fault was only a few feet below the surface of the ground and

was mined in an open pit. A very unusual variety of minerals was found within an area of a few hundred square feet, some associated with coalified logs and some in coatings along bedding planes. It is unusual because the minerals include the low-valent (unoxidized) uraninite and montroseite, the partly oxidized minerals corvusite and grantsite, and the high-valent minerals Na-zippeite, schroeckingerite, tyuyamunitite, and metarossite. Native selenium was also present. The assemblage represents both a wide range of pH and of oxidation conditions (Evans, 1959). In contrast to the Grants, New Mexico area, here the presence of sodium in the grantsite, schroeckingerite, and Na-zippeite is due to sodium sulfate (thenardite) that washes into the ore zone in the upper part of the Salt Wash Sandstone Member of the Morrison Formation from the overlying Brushy Basin Shale Member of the Morrison. The chief locality for barnesite, hydrated sodium vanadate, is in the base of the Brushy Basin about 2.5 miles northeast of this mine.

#### PHYSICAL AND OPTICAL PROPERTIES

Grantsite is dark olive-green to greenish black. It occurs as aggregates of microscopic fibers in thin seams and as interstitial filling in sandstone, and in fracture fillings in coalified wood. It is also in botryoidal coatings pseudomorphous after the low-valent vanadium oxides paramontroseite and häggite from which it was derived by oxidation. Very rarely it forms microscopic bladed single crystals—too fragile for single crystal x-ray study. Grantsite is monoclinic with the fibers or blades elongated parallel to the *b*-axis, as in the hewettite group (Qurashi, 1961). The mineral is too fine grained for a satisfactory hardness determination, but it is soft and smears easily, a characteristic of most of the corvusite and hewettite groups of minerals. The streak is olive green to brownish green. The luster is silky or pearly to subadamantine. The measured specific gravity is  $2.94 \pm 0.01$ . Finely divided fibers of grantsite change from dark olive green to orange red in HCl, and dissolve to form a yellow to orange solution. When heated in an open tube in a Bunsen burner flame, grantsite fuses easily—probably about 2 on the fusibility scale—and forms a dark-red globule with metallic steely luster.

The optical properties of grantsite cannot be determined completely because of the very fine grain size and the high refraction and absorption. The mineral is biaxial negative and the blades or fibers are length slow. The indices of refraction are  $\alpha 1.82 \pm 0.01$ ;  $\beta > 2.0$  and  $\gamma > 2.0$ . The orientation and pleochroism are X, normal to the blade, green; Y, parallel to the intermediate dimension of the blade, greenish brown; and  $Z = b$  parallel to the length of the blade, brown. The absorption is  $Z > Y > X$ .

## X-RAY CRYSTALLOGRAPHY

Grantsite occurs in bundles of fibers oriented parallel to the  $b$ -axis of the monoclinic crystal system. Individual fibers are bladelike; the  $b$ - and  $c$ -axes are the long and short dimensions of the blade; the  $a$ -axis is inclined to the blade at the angle  $\beta = 95^\circ 15'$ . Fiber patterns with random orientation around  $b$  are easily obtainable. One very small blade of grantsite from the Golden Cycle mine yielded very weak single-crystal patterns from which the data of Table 1 were obtained by precession camera techniques. On the  $h0l$  photograph, 42 reflections of the type  $h = 2n$  were obtained. Only a limited number of upper level  $hkl$  reflections

TABLE 1. CRYSTALLOGRAPHIC DATA FOR GRANTSITE GOLDEN CYCLE MINE, MONTROSE COUNTY, COLORADO

Symmetry	Monoclinic	
$a$	17.54 <sub>5</sub> ± 0.06 Å	
$b$	3.60 ± 0.01	
$c$	12.41 ± 0.04	
$\beta$	95°15' ± 0°10'	
$a:b:c$	4.874:1:3.447	
Volume	781 Å <sup>3</sup>	
Unit cell contents	Na <sub>4</sub> (Ca, Sr) <sub><math>x</math></sub> V <sup>4+</sup> <sub>2<math>x</math></sub> V <sup>5+</sup> <sub>(12-2<math>x</math>)</sub> O <sub>32</sub> ·8H <sub>2</sub> O	
Space group	C2/ $m$ (or $Cm$ or $C2$ )	
Density		
Calc. from Na <sub>4</sub> Ca <sub>0.7</sub> V <sup>4+</sup> <sub>1.4</sub> V <sup>5+</sup> <sub>10.6</sub> O <sub>32</sub> ·8H <sub>2</sub> O		2.95 g cm <sup>-3</sup>
observed		2.94 g cm <sup>-3</sup>

were observed. The observed  $hkl$  reflections,  $h+k=2n$  indicate a probable choice of space group,  $C2/m$  (No. 12),  $Cm$  (No. 8), or  $C2$  (No. 5). The  $d$ -spacings measured from  $h0l$  photograph obtained from a fiber mounted in a powder camera are compared with the powder data for grantsite in Table 2.

The repeat period along the fiber axis is 3.60 Å and is close to that found for chains of vanadium linked in five-fold (Christ *et al.*, 1954) or in mixed five-fold and six-fold coordination with oxygen (Evans, 1959, p. 99); or as one repeat period of V<sub>3</sub>O<sub>8</sub> formed by VO<sub>6</sub> octahedra and VO<sub>5</sub> distorted trigonal bipyramids sharing edges and corners (Wadsley, 1957).

## CHEMICAL ANALYSES

Samples from three of the four localities yielded sufficient grantsite for microchemical analyses and semiquantitative spectrographic analyses.



TABLE 2. X-RAY POWDER DATA FOR GRANTSITE

Present Study <sup>1</sup>								Ross <sup>2</sup>	
Monoclinic $C 2/m: a = 17.54_5 \pm 0.06$ , $b = 3.60 \pm 0.01$ , $c = 12.41 \pm 0.04 \text{ \AA}$ , $\beta = 95^\circ 15' \pm 0^\circ 10'$									
Calculated		Measured						Measured	
		Single Crystal	Fiber	Powder				Powder	
				$d(\text{ \AA})$ Cu/Ni $\lambda = 1.5418$	$d(\text{ \AA})$ Cu/Ni $\lambda = 1.5418$	$d(\text{ \AA})$ Cr/V $\lambda = 2.29092$	$d(\text{ \AA})$ Cr/V $\lambda = 2.29092$		
$hkl$	$d_{hkl}$	$I_{h0l}$	$d_{h0l}$	I	$d_{hkl}$	I	$d_{hkl}$	I	$d_{hkl}$
001	12.36	3	12.4	10		18	12.4	18	12.4
200	8.74	3	8.76	100	8.76	100	8.74	100	8.69
20 $\bar{1}$	7.46	3							
201	6.85	3				1	6.83		
				1 <sup>5</sup>	6.45	2 <sup>5</sup>	6.46		
002	6.18	M	6.18	4	6.22	6	6.19	9	6.21
202	5.28	W	5.27	1	5.29	2	5.28	2	5.27
202	4.84	W	4.85	1	4.85	2	4.84	2	4.85
400	4.368	M	4.37	6	4.36	10	4.37	6	4.34
40 $\bar{1}$	4.241	4				2 <sup>6</sup>	4.25		
003	4.120	W	4.12			1	4.12		
401	4.005	W	4.01			1	4.00	2	3.96
20 $\bar{3}$	3.864	W	3.864						
40 $\bar{2}$	3.730	M	3.730	4	3.723	7	3.737	5	3.71
203	3.601	S	3.604	25	3.604	28	3.606	35	3.60
110	3.526								
402	3.421	4		3	3.413	6	3.408	9	3.41
11 $\bar{1}$	3.407								
111	3.374			2 <sup>6</sup>	3.339	5 <sup>6</sup>	3.340		

<sup>1</sup> Grantsite sample AW-43-56, Golden Cycle Mine, Atkinson Mesa, Uravan, Colorado. Camera diameter 114.59 mm; lower limit of  $2\theta$  measurable, approximately  $6.5^\circ$ ; films corrected for film shrinkage.

<sup>2</sup> Grantsite sample AW-20-57E (RM-35), F-33 mine, Anaconda Company, Grants District, New Mexico. Camera diameter 114.59 mm.; lower limit of  $2\theta$  measurable, approximately  $6.5^\circ$ ; Film no. 13202, not corrected for film shrinkage; measurements by Daphne R. Ross (written communication).

<sup>3</sup> Single crystal precession patterns, radiation Mo/Zr,  $\lambda_{\text{MoK}\alpha} = 0.71069 \text{ \AA}$ ; reflections cut-off at center of film.

<sup>4</sup> Reflection observed to be not detectable from background.

<sup>5</sup> Extra reflection in powder pattern from impurity. This reflection is not present in  $h0l$  zone of fiber pattern and, since the repeat period of  $b$ -axis = 3.60 A, the reflection cannot be  $hkl$  reflection.

<sup>6</sup> Extra reflection in powder pattern from quartz impurity; quartz reflections are spotty in pattern.

TABLE 2—(continued)

Present Study <sup>1</sup>		Measured						Ross <sup>2</sup>	
Monoclinic $C 2/m: a = 17.54_3 \pm 0.06, b = 3.60 \pm 0.01,$ $c = 12.41 \pm 0.04 \text{ \AA}, \beta = 95^\circ 15' \pm 0^\circ 10'$									
Calculated		Single Crystal	Fiber	Powder		Powder		Measured	
			$d(\text{Å})$ Cu/Ni $\lambda = 1.5418$	$d(\text{Å})$ Cu/Ni $\lambda = 1.5418$		$d(\text{Å})$ Cr/V $\lambda = 2.29092$		$d(\text{Å})$ Cr/V $\lambda = 2.29092$	
$hkl$	$d_{hkl}$	$I_{hkl}$	$d_{hkl}$	I	$d_{hkl}$	I	$d_{hkl}$	I	$d_{hkl}$
40 $\bar{3}$	3.144	M	3.148	5	3.145	6	3.144		
004	3.090	4							
11 $\bar{2}$	3.086								
310	3.063								
112	3.039								
31 $\bar{1}$	3.006								
20 $\bar{4}$	3.000	M	3.008	14	3.005	14	3.008	5	3.01
600	2.912	W						18	3.00
60 $\bar{1}$	2.894	W	2.880						
403	2.869	S	2.867	11	2.872	12	2.869	13	2.87
204	2.832	M	2.831			2	2.837	2	2.84
31 $\bar{2}$	2.797								
601	2.778	4							
60 $\bar{2}$	2.731	M	2.734	7	2.734	9	2.733	6	2.72
11 $\bar{3}$	2.703								
312	2.693					1	2.695		
113	2.655			1	2.654				
40 $\bar{4}$	2.639	W	2.642			1	2.646	<1	2.66
602	2.546	4							
31 $\bar{3}$	2.516								
510	2.508								
51 $\bar{1}$	2.489					1	2.489		
603	2.488	4				1	2.477	2	2.48
20 $\bar{5}$	2.437	M	2.443	3	2.437	3	2.439	5	2.44
511	2.427								
404	2.421	4	2.423	2	2.424	3	2.422	5	2.42
313	2.403								
51 $\bar{2}$	2.378								
11 $\bar{4}$	2.346								
205	2.323								
114	2.303								
603	2.282	S	2.281	10	2.280	11	2.280	6	2.28
512	2.272								
40 $\bar{5}$	2.241	S	2.246	7	2.244	7	2.243	6	2.24
31 $\bar{4}$	2.229								
60 $\bar{4}$	2.223	W							
51 $\bar{3}$	2.208								
80 $\bar{1}$	2.185	4							

TABLE 2—(continued)

		Present Study <sup>1</sup>						Ross <sup>2</sup>	
		Monoclinic $C 2/m: a = 17.54_3 \pm 0.06, b = 3.60 \pm 0.01,$ $c = 12.41 \pm 0.04 \text{ \AA}, \beta = 95^\circ 15' \pm 0^\circ 10'$							
Calculated		Measured						Measured	
		Single Crystal	Fiber	Powder				Powder	
			$d(\text{Å})$ Cu/Ni $\lambda = 1.5418$	$d(\text{Å})$ Cu/Ni $\lambda = 1.5418$	$d(\text{Å})$ Cr/V $\lambda = 2.29092$	$d(\text{Å})$ Cr/V $\lambda = 2.29092$	$d(\text{Å})$ Cr/V $\lambda = 2.29092$		
$hkl$	$d_{hkl}$	$I_{h0l}$	$d_{h0l}$	I	$d_{hkl}$	I	$d_{hkl}$	I	$d_{hkl}$
800	2.183	W		1	2.179	1	2.184	<1	2.17
314	2.124								
80 $\bar{2}$	2.121	W	2.123	1	2.124	1	2.126		
801	2.118	4							
513	2.082								
405	2.071	4							
006	2.060	4		1	2.058	2	2.049	5	2.05
710	2.051								
71 $\bar{1}$	2.048								
20 $\bar{6}$	2.047								
115	2.042								
604	2.028	4	2.020	1	2.027	1	2.031	<1	2.03
514	2.012								
803	2.007	4							
115	2.006								
802	2.002	4							
			1.975	4	1.978	4	1.979	6	1.971
						1	1.891	2	1.887
			1.845	2	1.861	3	1.860	2	1.855
			1.802	3	1.802	4	1.802	6	1.803
						1	1.784	2	1.783
								2	1.766
			1.722	2	1.725	3	1.723	2	1.713
								2	1.695
				1	1.648	1	1.647	2	1.645
			1.613	2	1.613	2	1.614	2	1.613
			1.547	3	1.545	2	1.548	5	1.550
						1	1.535	1	1.528
			1.498	3	1.498	2	1.500	3	1.500
						1	1.493	2	1.490
				1	1.458			2	1.450
			1.433	2	1.433			2	1.433
								2	1.421
				1	1.403			2	1.404

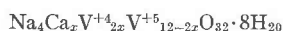
Two samples from Colorado were in moderately friable, fine-grained sandstone with considerable quartz embedded or enclosed in the seams and interstitial aggregates of grantsite. A concentrate of aggregates 1 mm or less in size was hand picked and these were gently crushed to release the detrital quartz without breaking it or overly disaggregating the finely fibrous grantsite. Bromoform separation and final handpicking yielded samples 97 to 98 per cent pure. Likewise minute aggregates of grantsite were handpicked from an irregular seam between limestone and coarse calcite in the sample from New Mexico. Not all the calcite could be separated; traces of tyuyamunite coating or penetrating the fibrous grantsite aggregates was also inseparable. These impurities were calculated from chemical determinations of  $\text{CO}_2$  and  $\text{UO}_3$ . The analyses were made on approximately 100 mg of each sample.

The selection of the micro and semimicrochemical methods used for the chemical analysis of the mineral was guided by the semiquantitative spectrographic analyses of the mineral (Table 3) by K. V. Hazel, U. S. Geological Survey. AW-47-54, AW-141-56, and AW-20-57E were analyzed by procedures essentially the same as those reported for the analyses of hendersonite (Lindberg *et al.*, 1962).

#### DERIVATION OF A FORMULA FOR GRANTSITE

In Table 4, chemical analyses of grantsite from the Golden Cycle and La Salle mines of the Uravan District, Montrose County, Colorado, and from the F-33 mine of the Anaconda Company, Grants County, New Mexico, are presented. The total number of metal and oxygen atoms per unit cell are calculated from the chemical analyses, and from the gram-molecular weight derived from the unit-cell volume and density, without consideration of possible combinations of the atoms.

The unit cell contents proposed for grantsite are:



For  $x=0$ , the simplest formula becomes



In the three analyzed samples,  $x=0.6-0.9$  calcium plus strontium per unit cell. This is less than the minimum number necessary to occupy fully one set of equivalent positions ( $=2$ ). The electrical charges consequent to a variable calcium content are compensated by an adjusted vanadium (IV): vanadium (V) ratio. The way in which the 12 vanadium and 40 oxygen atoms occupy their equivalent positions is not altered by the introduction of small quantities of calcium, statistically, into available space.

TABLE 3. SPECTROGRAPHIC ANALYSIS (IN PER CENT) OF GRANTSITE

Sample Number	Elements													
	V	Na	Ca	Si	Al	K	Sr	U	Fe	Zn	Mg			
AW-47-54 <sup>1</sup>	M	3.0	1.0	3.0	0.1	0.3	0.3	0	0.3	0.1	0.03			
AW-141-56 <sup>1</sup>	M	3.0	1.0	0.3	0.3	0.1	0.03	0	0.1	0.1	0.03			
AW-20-57E <sup>1</sup>	M	3.0	3.0	0.03	0.03	0	0.1	0.3	0.03	0	0.01			
	Ti	Ba	Pb	Sc	Mn	Cr	Cu	Mo	Co	Zr	Li			Be
AW-47-54	0.003	0.001	0.003	0	0.003	0.001	0.001	0.003	0.001	0.001	0			0.00003
AW-141-56	0.03	0.01	0.003	0.003	0	0.001	0.0001	0	0	0	0.001			0
AW-20-57E	0	0.01	0.01	0.003	0.003	0.003	0.003	0	0	0	0			0

<sup>1</sup> Semiquantitative spectrographic analyses by Katherine V. Hazel, U. S. Geological Survey.

0 = Looked for but not found.

M = Major constituent—greater than 10%

Figures reported to the nearest number in the series 10, 3, 1.0, 0.3, 0.1, 0.03, 0.01, 0.003, 0.001, etc., in per cent. Comparisons of this type of semiquantitative results with data obtained by quantitative methods, either chemical or spectrographic, show that the assigned group includes the quantitative value about 60% of the time (Waring and Annell, 1953).

TABLE 4. ANALYSES OF GRANTSITE

Analysis Sample AW-141-56 <sup>1</sup> (RM-29) Golden Cycle Mine, Uravan District, Montrose County, Colorado					Analysis Sample AW-47-54 (RM-31) LaSalle Mine, Uravan District, Montrose County, Colorado					
	Analysis	Anal. recalc. to 100% without insol.	Ratios	Metal Equiva- lent	Oxygen Equiva- lent	Analysis	Anal. recalc. to 100% without insol.	Ratios	Metal Equiva- lent	Oxygen Equiva- lent
Na <sub>2</sub> O	8.2	8.4	.135	.270	.135	8.7	9.1	.146	.292	.146
CaO	2.9	3.0	.053	.053	.053	2.1	2.2	.039	.039	.039
SrO	<0.1					0.5	0.5	.005	.005	.005
V <sub>2</sub> O <sub>4</sub>	9.3	9.5	.057	.114	.228	7.8	8.1	.049	.098	.196
V <sub>2</sub> O <sub>5</sub>	65.6	67.2	.370	.740	1.850	66.6	69.6	.382	.764	1.910
Insoluble	1.9					2.7				
Fe <sub>2</sub> O <sub>3</sub>	0.2	0.2	.001	.002	.003	<0.1	0.1	.0006	.001	.002
K <sub>2</sub> O	<0.1					<0.1				
Total H <sub>2</sub> O	11.4	11.7	.648	1.296	.648	10.0	10.4	.579	1.158	.579
UO <sub>3</sub>										
CO <sub>2</sub>										
Total	99.5	100.0	Total oxygen equivalent = 2.917			98.4	100.0	Total oxygen equivalent = 2.877		
H <sub>2</sub> O <sup>-</sup>	3.6					4.4				

Robert Meyrowitz, analyst.

<sup>1</sup> AW-141-56 is part of AW-43-56 sample used for x-ray study.

TABLE 4—(Continued)

Analysis Sample AW-20-57 (RM-35) F-33 Mine, Anaconda Company, Valencia County, New Mexico					Atoms per unit cell in analyzed samples <sup>4</sup>			
Analysis	Anal. recalc. to 100% without insol. and impurities <sup>2</sup>	Ratios	Metal Equiva- lent	Oxygen Equiva- lent		AW-141-56 (RM-29)	AW-47-54 (RM-31)	AW-20-57 (RM-35)
8.3	8.5	.137	.274	.137	Na	3.7	4.0	3.8
4.4	3.7	.065	.065	.065	Ca	0.7	.5	.9
0.1	0.1	.001	.001	.001	Sr		.1	
10.8	11.0	.067	.134	.268	V <sup>+4</sup>	1.6	1.4	1.9
65.2	66.5	.366	.732	1.830	V <sup>+5</sup>	10.2	10.6	10.1
0.3								
10.1	10.2	.569	1.138	.569	H	17.9	16.0	15.7
0.3 <sup>3</sup>								
0.6								
100.1	100.0	Total oxygen equivalent = 2.870			Oxygen	40.3	39.8	39.7
6.5								

Robert Meyrowitz, analyst.

<sup>2</sup> The calcite equivalent (CaO and CO<sub>2</sub>) corresponding to 0.6% CO<sub>2</sub> and the tuyamunite equivalent (CaO·2UO<sub>3</sub>·V<sub>2</sub>O<sub>5</sub>·6H<sub>2</sub>O) corresponding to 0.3% UO<sub>3</sub> was subtracted from the analysis before recomputing to 100%.<sup>3</sup> UO<sub>3</sub> determined fluorimetrically by J. W. Budinsky, U. S. Geol. Survey.<sup>4</sup> The atoms per unit cell are derived from the metal and oxygen equivalents by multiplying the equivalent by 0.01 to convert from a percentage to a fractional scale and by 1383, the gram formula weight derived from the unit cell volume and observed density for grantsite from the Golden Cycle Mine, Colorado.

## RELATION OF GRANTSITE TO OTHER VANADATES

The vanadium (V):vanadium (IV) ratio of these analyzed grantsite samples ranges from 5.5 to 7.8. This range is typical of a large group of dark green, red, brown, and blue-black, mixed-valence vanadium minerals in partly oxidized ores in the Colorado Plateau. These ores have been referred to in the field as corvusite-type ores or the corvusite-stage of oxidation (Weeks and others, 1959, and Evans, 1959). Corvusite was the only known vanadium (mixed IV and V) mineral in the Colorado Plateau ores prior to the 1950's.

Detailed studies of "corvusite ore" have revealed several distinct new mineral species: hendersonite (Lindberg *et al.*, 1962), grantsite, and

TABLE 5. COMPARISON OF DATA ON SODIUM VANADATE

Mineral	Formula	V <sub>5</sub> O <sub>8</sub> :H <sub>2</sub> O	Space group	a(Å)	b(Å)	c(Å)	β
Grantsite <sup>1</sup>	Na <sub>4</sub> Ca <sub>x</sub> V <sup>4+</sup> <sub>2x</sub> V <sup>5+</sup> <sub>3-2x</sub> O <sub>22</sub> ·8H <sub>2</sub> O	1:2	C2/m(Cm or C2)	17.54	3.60	12.41	95°15'
Barnesite <sup>2</sup>	Na <sub>2</sub> V <sub>6</sub> O <sub>18</sub> ·3H <sub>2</sub> O	1:1½	P2/m(?)	12.18	3.61	7.80	95°
Unnamed mineral <sup>3</sup>	(Ca, Na <sub>2</sub> )V <sub>6</sub> O <sub>18</sub> ·2H <sub>2</sub> O	1:1	P2 <sub>1</sub>	12.26	3.58	8.11	92°31'

<sup>1</sup> Orientation follows the convention for the monoclinic crystal system,  $c < a$ . The  $c$ -axis of grantsite is comparable to the  $a$ -axis of barnesite and the unnamed mineral.

<sup>2</sup> Mineral description of barnesite by Weeks *et al.* (1963); unit cell data, Qurashi, 1961.

<sup>3</sup> Data from Bachmann, 1962.

a potassium, magnesium, iron vanadyl vanadate. Partial unit cell data from electron diffraction study (Ross, 1959) and  $x$ -ray unit cell data of Lindberg show that hendersonite is more closely related structurally to the hewettite minerals than to the mineral corvusite ( $x$ -ray study by Lindberg). Likewise grantsite is closely related structurally to sodium vanadate, as shown in Table 5. Evans (1959, p. 100) reviewed the crystal chemistry of the mixed-valence vanadium minerals and showed that at least small differences in vanadium (IV) and vanadium (V) content concomitant to an adjusted alkali, alkaline earth, or water content, may be accommodated in the mixed valence minerals with little change in crystal structure. Wadsley (1957) described an artificial compound  $\text{Li}_{1+x}\text{V}_3\text{O}_8$  with a non-stoichiometric, variable lithium content and showed that lithium occupies octahedral interlayer sites and possibly additional tetrahedral positions. Bachmann and Barnes (1962) have shown that the crystal structure of a sodium-calcium variety of meta-hewettite is similar to that of  $\text{Li}_{1+x}\text{V}_3\text{O}_8$ , but there is trigonal bipyramidal coordination of oxygen around each of the three non-equivalent vanadium atoms. The trigonal bipyramids share edges to form zigzag chains along  $y$ , and the chains are joined through corners into spiral tubes. Cations and water are located between the chains.

Grantsite differs from sodium vanadates of the hewettite group in that it contains mixed-valence vanadium concomitant to an increased calcium content. The hewettite minerals as originally described ideally contain only pentavalent vanadium and have various ratios of  $V_3O_8:H_2O$ . The use of the terms hewettite group and corvusite group is going through a transition period as more minerals from "corvusite-type ores" are shown to be related crystallographically to hewettite.

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