

HENDERSONITE, A NEW CALCIUM VANADYL VANADATE FROM COLORADO AND NEW MEXICO¹

M. L. LINDBERG, A. D. WEEKS, M. E. THOMPSON,² D. P.
ELSTON, AND ROBERT MEYROWITZ, *U. S. Geological
Survey, Washington 25, D. C.*

ABSTRACT

In 1955, hendersonite, a new vanadium mineral with the theoretical formula $\text{Ca}_2\text{H}_x\text{V}^{4+}_{(1+x)}\text{V}^{5+}_{(8-x)}\text{O}_{24}\cdot 8\text{H}_2\text{O}$ (with $x \leq 0.1$ in the analyzed samples) was found in the J. J. mine on the south side of Paradox Valley, Montrose County, Colorado, and in one of the Eastside mines (on the east side of the Carrizo Mountains), in San Juan County, New Mexico. Both mines are in vanadium-uranium deposits in the Salt Wash Sandstone Member of the Morrison Formation (Upper Jurassic). The mineral occurs in partly oxidized ore.

Hendersonite is greenish black to black and forms aggregates of microscopic bladed to fibrous crystals in thin seams along bedding planes and in small arcuate veinlets bordering unoxidized ore. The mineral is biaxial, negative, with parallel extinction. Both β and γ indices are above 2.01 and the α index is lower than 2.0; the mean index calculated from the Gladstone-Dale formula is 2.10. The orientation is $X=a$ perpendicular to the platiness or blades, $Y=b$, and $Z=c$ parallel to the elongation. The optic angle $2V$ is medium; dispersion $r > v$ is weak; pleochroism moderate; absorption X yellow-green, Y green, and Z brown. H is about 2.5; G measured on J. J. mine samples is 2.77 ± 0.05 , and on the Eastside mine sample, 2.79 ± 0.01 .

Hendersonite is orthorhombic with probable space group $Pnam$ (No. 62) or $Pna2_1$ (No. 33). Unit cell data on the New Mexico sample are: $a = 12.40 \pm 0.04 \text{ \AA}$, $b = 18.92 \pm 0.08$, and $c = 10.77 \pm 0.03$; $a:b:c = 0.655:1:0.569$; cell volume 2527 \AA^3 ; cell contents $4[\text{Ca}_2\text{H}_x\text{V}^{4+}_{(1+x)}\text{V}^{5+}_{(8-x)}\text{O}_{24}\cdot 8\text{H}_2\text{O}]$ calculated density 2.80 g/cm^3 . The strongest lines of the x -ray diffraction powder pattern are 9.45 \AA (intensity 100), 3.113 (36), 4.70 (16), 3.237 (12), 2.788 (12), 3.788 (9), and 2.260 (9). The powder pattern is the most satisfactory means of distinguishing hendersonite from the other dark-colored vanadium minerals.

The new mineral is named for Edward P. Henderson of the U. S. National Museum in Washington, D. C.

INTRODUCTION AND ACKNOWLEDGMENTS

In April 1955 the first sample of this new vanadium mineral was collected by D. P. Elston during his mapping and geologic study of the J. J. mine, Paradox Valley, Montrose County, Colorado, and later he found additional material in the same mine. In June 1955, A. D. Weeks collected a suite of ore samples from the Eastside mines, San Juan County, New Mexico, and found more of the same new mineral. Mineralogic and preliminary x -ray study of the J. J. mine sample was made by M. E. Thompson. Elston studied the geologic setting of this occurrence (Elston and Botinelly, 1959). The mineralogy and geologic

¹ Publication authorized by the Director, U. S. Geological Survey.

² Present address, Department of Geology, Harvard University, Cambridge, Mass.

occurrence of the Eastside mine sample were studied by Weeks, and an extensive and definitive x-ray study of this sample was made by M. L. Lindberg. We are indebted to our colleagues H. T. Evans and C. L. Christ for suggestions in the preparation of the manuscript.

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

The new mineral is named hendersonite for Edward P. Henderson of the U. S. National Museum, Washington, D. C. Among his numerous mineralogic studies he contributed to the knowledge of the vanadium-uranium ores of the Colorado Plateau and described several new vanadium minerals: fermanite (Hess and Henderson, 1931), corvusite (Henderson and Hess, 1933) and steigerite (Henderson, 1935).

OCCURRENCE

Hendersonite, $\text{Ca}_2\text{H}_x\text{V}^{4+}_{(1+x)}\text{V}^{5+}_{(3-x)}\text{O}_{24}\cdot 8\text{H}_2\text{O}$, has been found in two mines that are 120 miles from one another. Both of the mines are in vanadium-uranium deposits in the Salt Wash Sandstone Member of the Morrison Formation (Upper Jurassic) and are on the Colorado Plateau.

The J. J. mine (Fig. 1) has been described by Elston and Botinelly (1959). It is adjacent to the Thunderbolt mine at the eastern end of the Jo Dandy mining area, and is on the south side of Paradox Valley, Montrose County, Colorado. The geology of a part of the Jo Dandy area and the location of the Thunderbolt mine are shown on the geologic map of the Naturita NW quadrangle, Colorado (Cater, 1955). Paradox Valley trends northwestward toward the La Sal Mountains in eastern Utah, and is incised along the axial part of an elongate salt structure. Although strata overlying and flanking the salt structure are cut by faults at many places, only a few minor faults are present in and near the J. J. mine. Near the portal of the mine the sandstone beds strike about N. 64° W. and dip 10°–14° SW. The mine workings, from the portal to about the middle of the mine, are nearly along the strike of the beds, but from the middle to the innermost part of the mine at the claim line the workings trend almost down the dip. In the rear one-third of the mine the workings intersect the local water table and the water saturation has protected the ore from oxidation.

Below the water table, the ore is largely unoxidized and consists of vanadium silicates, montroseite, uraninite, and coffinite. Disseminated pyrite and marcasite are commonly associated with unoxidized ore; where oxidation has occurred the rock is freckled and streaked light to dark brown by iron oxides.

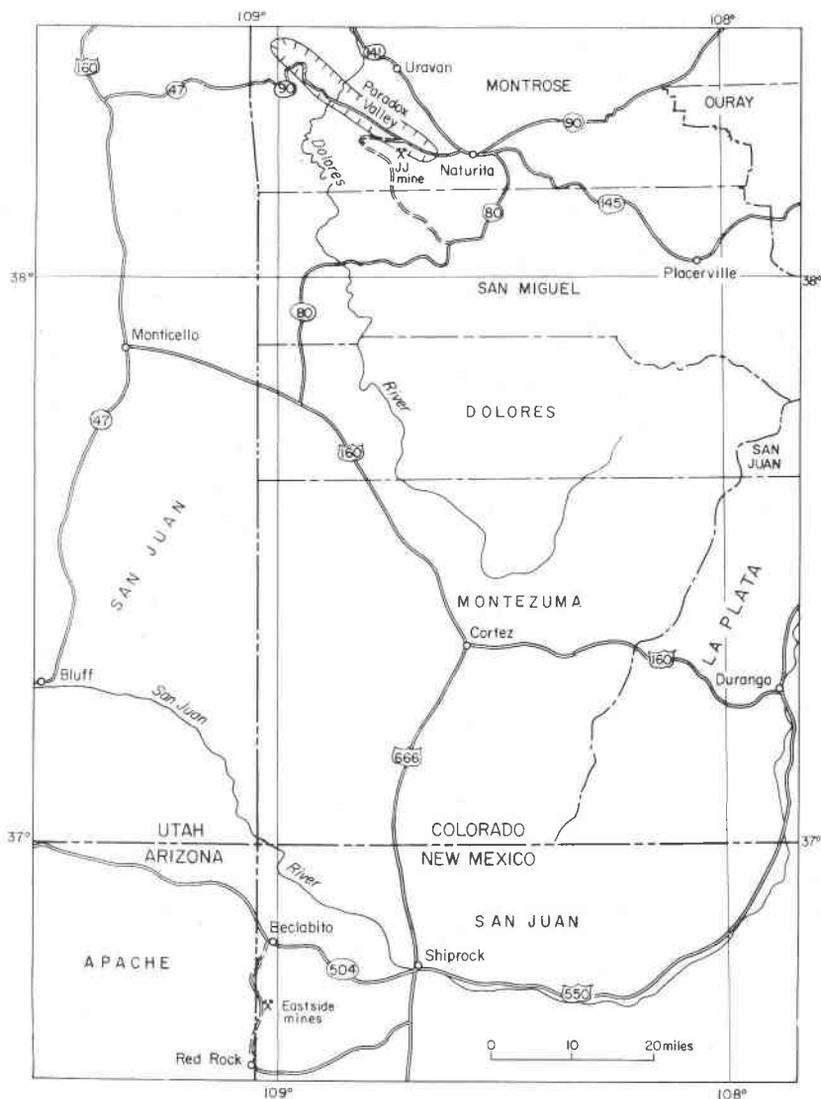


FIG. 1. Index map of part of Colorado Plateau, showing location of J. J. mine, Montrose County, Colorado, and Eastside mines, San Juan County, New Mexico.

Above the water table, in the middle part of the mine, remnants of relatively unoxidized rich ore associated with abundant coalified plant material are surrounded by oxidized lower-grade ore that is disseminated in sandstone (Fig. 66, Elston and Botinelly, 1959). Hendersonite is in partly oxidized ore that borders unoxidized ore, and it is associated with

paramontroseite (VO_2), simplotite ($\text{CaV}_4\text{O}_9 \cdot 5\text{H}_2\text{O}$), melanovanadite ($2\text{CaO} \cdot 2\text{V}_2\text{O}_4 \cdot 3\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$?), sherwoodite ($\text{Ca}_3\text{V}_8\text{O}_{22} \cdot 15\text{H}_2\text{O}$) and corvusite ($\text{V}_2\text{O}_4 \cdot 6\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$?). Close to the portal of the mine the ore is mostly oxidized and consists chiefly of carnotite and vanadium silicates. Evans and Garrels (1958, p. 142-147) considered the fields of thermodynamic stability for the vanadium minerals, and the sequence of minerals formed by progressive oxidation; the J. J. mine displays this oxidation sequence very well.

Hendersonite forms in thin seams and veinlets, filling fractures that are roughly parallel to the bedding of the sandstone within pods and thin layers of rich, partly oxidized ore. The seams of hendersonite are a few tenths of an inch or less in thickness, and are commonly less than 12 inches long. Exposed surfaces of the veinlets are tarnished blue-black. The high luster of the hendersonite veinlets is distinctive against the generally dull background of the surrounding sandstone.

The formation of hendersonite is spatially related to sulfide-rich "eyes," many of which are enclosed in pods or thin layers of rich ore. The sandstone in the "eyes" is light gray, friable, and weakly cemented by abundant microscopic crystals of pyrite and marcasite. It is poor in vanadium and uranium minerals. Small amounts of goethite, metatyuyamunite, and unidentified, sooty black (carbonaceous ?) material are present in the outer part of the sulfide eye. At one place a thin arcuate veinlet of hendersonite is faintly distinguishable on the periphery of the partly oxidized border of a sulfide eye. The veinlet is bounded on the outside by a thin zone of pale-red, yellow and green minerals admixed with fine-grained black to blue-black minerals, which in turn grades into the enclosing rich black ore. At another place a thicker and distinct veinlet of hendersonite fills part of a fracture that is parallel to the bedding. The fracture transects, in succession, weakly mineralized and barren rock, rich ore, and a sulfide eye that is enclosed in the rich ore. The fracture filling consists of hendersonite where it is bordered by rich ore but consists of gypsum where it is bordered by weakly mineralized rock and by sulfide-bearing rock.

The field relations at the J. J. mine indicate that hendersonite is formed in places where rich ore that is in proximity to sulfide-rich rock is subjected to fairly rapid but restricted oxidation.

Hendersonite also was found in one of the Eastside mines in San Juan County, New Mexico (Figs. 1 and 2). The mines are on a small, irregular-shaped mesa (indicated as King Tut Mesa by Stokes, 1953) the surface of which is a dip slope of sandstone gently inclined to the east, on the flank of the Carrizo Mountains (Strobell, 1956). Because the Salt Wash Sandstone Member (Morrison Formation) is exposed on the entire mesa,

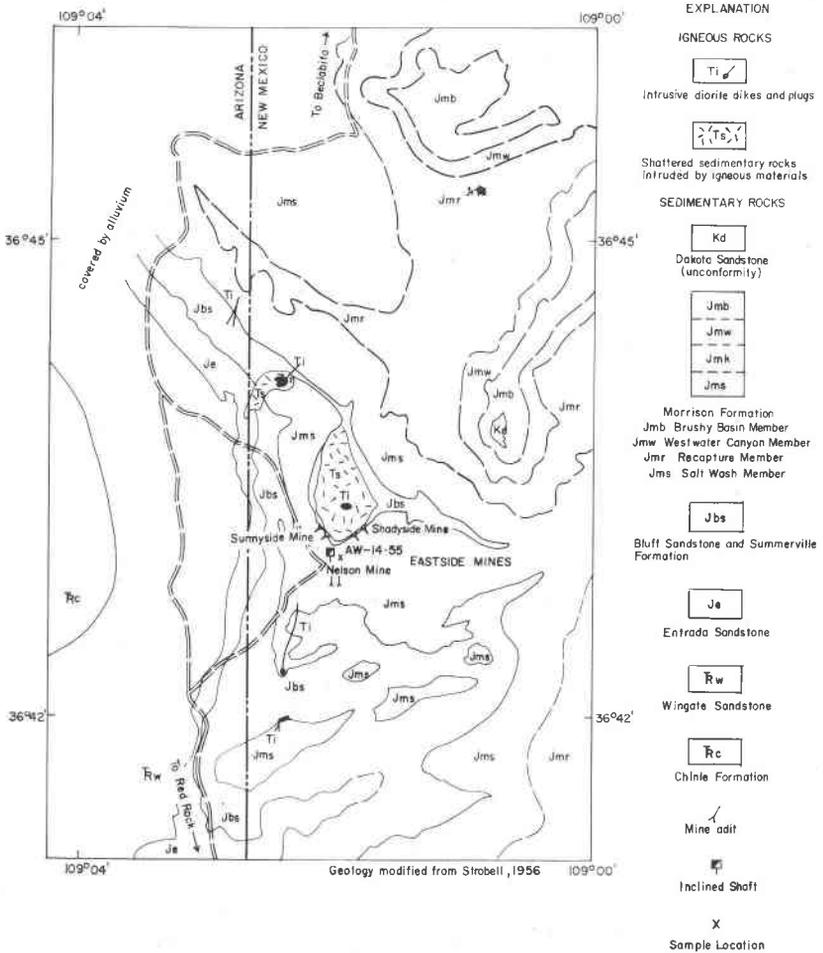


FIG. 2. Geologic map of vicinity of Eastside mines, San Juan County, New Mexico.

the ore is at shallow depth and is mostly oxidized (Weeks, *et al.*, 1959, p. 77). The chief ore minerals are vanadium silicates, carnotite, and tyuyamunite.

Within the Eastside group of mines, hendersonite was found in the mine which has the thickest cover. This mine is located about midway between the mesa rims at the "neck" of the mesa; it was called the Nelson mine at one time (J. D. Strobell Jr., writt. comm., 1961). In June 1955, when the hendersonite was collected, access to the workings was obtained through two nearly horizontal adits from the south side of the mesa. The workings connected from the westernmost of the two

adits to the base of the only inclined-shaft on the mesa. The new mineral was found in the working face of a drift that extended about 60 feet eastward from the foot of the incline. The roof of the mine at the face consisted of hard, tightly cemented sandstone, underlain by two feet of thinly bedded mineralized sandstone. Many bedding planes in the ore zone contained films and seams, as much as one-fourth inch thick, of vanadium minerals, chiefly hewettite and hendersonite. Gypsum was present along many bedding planes in the vanadium-rich zone, as well as in irregular fracture fillings in $1\frac{1}{2}$ feet of mudstone beneath the sandstone.

Although most of the ore in the Eastside group of mines is oxidized because of its shallow depth, partly oxidized ore minerals in addition to the hendersonite were found in several places. In a drift from the east adit of the Nelson mine, greenish-black corvusite occurs as a mineralized border between a sandstone bed and a pelletal clay bed. In the Shadyside no. 1 mine which is just northeast of the incline and which has a horizontal adit below the rim of the mesa, one long drift extends toward the Nelson mine. The Shadyside no. 1 mine is the locality from which one of the first samples of sherwoodite, another calcium vanadyl vanadate, was found in 1952 (Thompson *et al.*, 1958). A revisit to the Shadyside mine in 1955 showed that the deepest part of the mine, which was close to but was not interconnected with the Nelson mine, contains several patches of partly oxidized blue-black corvusite ore. Bright orange coatings of pascoite formed by evaporation of moisture from the corvusite ore are present in small quantity. The mines on this mesa, in general, are moderately dry and very little modification of the ore is still in progress.

In contrast to the J. J. mine, the Eastside mines now contain little or no unoxidized ore and only a few patches of partly oxidized ore in protected places. Iron oxide stains and streaks indicate the former presence of disseminated pyrite and are typical of oxidized ore sandstone on the Colorado Plateau. There is no reason to suspect that the oxidized and partly oxidized ore at the Eastside mines was not derived from unoxidized ore, as at the J. J. mine.

PHYSICAL AND OPTICAL PROPERTIES

The crystal system of hendersonite is orthorhombic, as suggested by optical properties and indicated by *x*-ray study. Fresh surfaces of the mineral are dark greenish black to black, with luster ranging from pearly to subadamantine. Exposed surfaces gradually turn brownish. The mineral occurs chiefly as aggregates of subparallel to parallel microscopic fibers or blades. Some of the material from the J. J. mine is in

elongated, six-sided platy crystals and displays a perfect cleavage parallel to the platiness. One of these relatively rare platy crystals is shown in an electron micrograph taken by Ross (1959, Fig. 3) and the more common bladed to fibrous habit of the mineral from the Eastside mine is shown in Ross's Fig. 5 (1959). The fiber aggregates from the Eastside mine break into smaller bundles when pressed gently with a needle but the fibers begin to smear when pressed further. They are only slightly less smearing than typical corvusite, and much less brittle than the nonsmearing microscopic needles of nontroseite. In general, the corvusite-type minerals and carnotite and tyuyamunite all smear very easily because of their layer structures. The streak of hendersonite is dark brownish green.

Hendersonite is about 2.5 on the Mohs scale of hardness. Under the binocular microscope, a fiber bundle can be seen to scratch gypsum easily, but it rubs off on calcite. Coherent aggregates of hendersonite from the J. J. mine, weighed on a Berman balance, yield a specific gravity of 2.77. A different method of determining the specific gravity of the sample from Eastside mines—diluting bromoform until loose

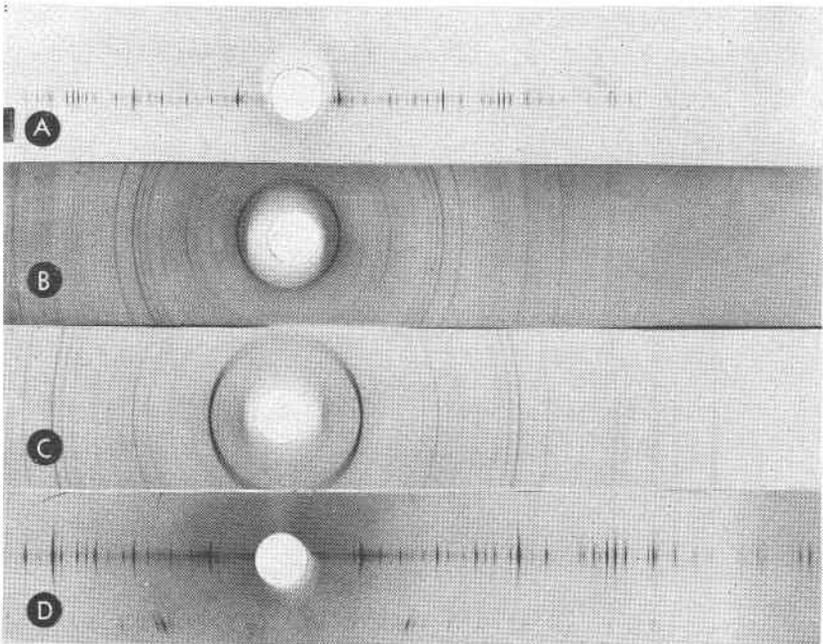


FIG. 3. Powder and fiber x -ray patterns of hendersonite from the Eastside Carrizo mine: (A) fiber pattern, Ni-filtered Cu radiation; (B) powder pattern, Ni-filtered Cu radiation; (C) powder pattern, V-filtered Cr radiation; (D) fiber pattern, V-filtered Cr radiation.

fibers of hendersonite were suspended in the liquid and weighing the liquid, gave 2.79. The measured values agree satisfactorily with the calculated density of 2.80_5 g/cm^3 .

Hendersonite is biaxial negative with extinction parallel to the fiber length and the long dimension of the platy grains. The indices cannot be accurately determined; two indices β and γ are above 2.01 (the highest available index liquid), and the α index, although lower than 2.01, is uncertain because the microscopically thin blades will not stand on edge. The mean index of refraction calculated by the Gladstone-Dale formula is 2.10. This is the same as the mean index of hewettite, which has indices $\alpha=1.77$, $\beta=2.18$, and $\gamma=2.35$ (Hillebrand *et al.*, 1914). The X axis is perpendicular to the platiness or broad surface of the blades, Y is across the blades, and Z is parallel to the elongation of blades and fibers; $X=a$, $Y=b$, and $Z=c$. The crystals are moderately pleochroic, the absorption is X yellow green, Y green, and Z yellow brown to brown.

X-RAY CRYSTALLOGRAPHY

Hendersonite consists of bundles of fibers oriented parallel to the fiber axis, c . Most bundles of fibers show random orientation around c . The sample from the Eastside mine in New Mexico was used for the detailed x-ray study. A multiple fiber yielding one stronger and several weaker diffraction nets has been studied by rotation, Weissenberg, and precession camera techniques, without remounting the fiber; the single crystal data derived from the strongest of the nets are listed in Tables 1, 2 and 3. The pattern obtained by rotation parallel to the c -axis shows very strong layer lines for $l=0$ and for $l=3n$ and very weak intermediate layer lines; the $hk0$ and $hk3$ lattice levels are the only Weissenberg patterns attempted. The precession patterns $h0l$, $h1l$, $0kl$ and $1kl$ are weaker patterns than are usually used to observe space group criteria.

Hendersonite has orthorhombic symmetry. Possible space groups consistent with the observed single crystal reflections are $Pnam$ (No. 62) or $Pna2_1$ (No. 33). All possible d -spacings, including those for reflections not permitted by the space group $Pnam$, (or $Pnc2_1$) have been calculated to determine whether the reflections observed on the powder or fiber patterns, Table 2 and Fig. 3, can be properly indexed on the basis of the space groups chosen. It was found that this was indeed the case.

The directions for the crystal axes in hendersonite have been chosen following the convention $c < a < b$ for the orthorhombic system. Ross (1959) in electron diffraction studies of hendersonite (then unnamed) interchanged the b - and c -axes; the direction labelled \mathbf{b}^* in the SAD spot pattern, his Fig. 4, p. 329, becomes \mathbf{c}^* in the present study. His electron

TABLE 1. CRYSTAL DATA FOR HENDERSONITE

	Present study Eastside Carrizo mine	Ross (1959) ¹	
		Eastside Carrizo Mine	J. J. mine
<i>a</i>	12.40 ± 0.04 Å	<i>a</i> 12.15 ± 0.01 Å	12.18 ± 0.01 Å
<i>b</i>	18.92 ± 0.08	<i>b</i> —	—
<i>c</i>	10.77 ± 0.03	3 <i>c</i> 10.836 ± 0.012	10.881 ± 0.009
$\frac{1}{3}c$	3.59 ± 0.01	<i>c</i> 3.612 ± 0.004	3.627 ± 0.003
<i>a</i> : <i>b</i> : <i>c</i>	0.655:1:0.569		
Vol. unit cell	2527 Å ³		
Gram-molecular weight (obs.)	4246		
Specific gravity (obs.)	2.79 ± 0.01 ²		
Specific gravity (calc.)	2.80 ₆		
Formula proposed	Ca ₂ H _x V ⁴⁺ _(1+x) V ⁵⁺ _(8-x) O ₂₄ ·8H ₂ O		
Z			
Space Group	<i>Pnam</i> (No. 62) or <i>Pna</i> 2 ₁ (No. 33)		

¹ Ross (1959) interchanged *b* and *c*; he noted the very weak spots which appeared to triple his *b*-axis, but recorded the axial length for the smaller cell; the transformation matrix from his cell to the present one is 100/001/030; data from electron diffraction studies of samples prepared by suspension in water.

² Determined by dilution of bromoform until mineral grains were suspended and measuring specific gravity of liquid.

diffraction pattern, if indexed as an *h*0*l* pattern, shows no systematic extinctions; on the *x*-ray diffraction patterns patterns only those *h*0*l* reflections for which *h* = 2*n* and only those 0*k**l* reflections for which *k* + *l* = 2*n* are observed. The intensity distribution includes differences not related to stronger electron diffraction and weaker *x*-ray diffraction patterns. The conditions obtained for hendersonite are probably similar to those described by Ross and Christ (1958) for colemanite; in both hendersonite and colemanite, the crystal is extremely thin in the **b*** direction, and electron-diffraction spot patterns are to be indexed with the *k* parameter as a variable (Table 3). Ross and Christ show that if a crystal is thin in the **b*** direction the reciprocal lattice points become rods elongated parallel to that direction. Upper level rods extend into the sphere of reflection and are coincident in projection with zero level rods; hence the appearance of "forbidden" *h*0*l* reflections.

Rotation patterns of hendersonite show that the repeat period of the fiber-axis is 3.59 Å in the small pseudo-cell and 10.77 Å in the large true cell. By analogy with other vanadium-oxygen coordinated minerals, the smaller repeat period is related to the stacking of units of V₃O₈; the repeat period 3.59 Å is of the same order of magnitude as 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 the length of sheets of V₃O₈ formed by VO₆ octahedra and VO₅ distorted trigonal bipyramids sharing edges and corners (Wadsley, 1957). The larger repeat period probably results from the way in which V₃O₈ units link with calcium and with water of crystallization.

TABLE 2. X-RAY POWDER DATA FOR HENDERSONITE

Hendersonite from New Mexico										Hendersonite from Colorado ⁴			
Calculated ¹		Measured								Calculated	Measured		
<i>hkl</i>	<i>d_{hkl}</i>	Single ² Crystal	Fiber ³		Powder ³				Powder				
		I	Cu/Ni $\lambda = 1.5418$ Å	Cr/V $\lambda = 2.2902$ Å	Cu/Ni $\lambda = 1.5418$ Å		Cr/V $\lambda = 2.2902$		Cu/Ni $\lambda = 1.5418$ Å				
			<i>d_{hkl0}</i>	<i>d_{hkl0}</i>	I	<i>d_{hkl}</i>	I	<i>d_{hkl}</i>	<i>d_{hkl}</i>	I	<i>d_{hkl}</i>		
010	18.92	C									18.80		
100	12.40	C									12.22		
001	10.77	C									10.95		
110	10.38	C	10.40	10.36	5	10.37	9	10.36	10.25	W	10.25		
020	9.46	S	9.46	9.44	100	9.45	100	9.43	9.40	VS	9.40		
011	9.36		P	P					9.46				
101	8.13								8.15				
120	7.52	W	7.50	7.50	6	7.50	8	7.51	7.47	W	7.47		
111	7.47		P	P					7.48				
021	7.11								7.15				
030	6.31	N							6.27				
200	6.20	M	6.21	6.21	8	6.20	11	6.20	6.11	W	6.17		
121	6.17		P	P					6.16				
210	5.89	N		6.88			<1	5.88	5.81				
130	5.62	N	5.59	5.61			<1	5.59	5.59				
031	5.44		P	P					5.46				
002	5.39	W			1	5.38	1	5.37	5.47	W	5.37		
201	5.37		P	P					5.33				
012	5.18								5.26				
220	5.18	W	5.17	5.17	8	5.17	11	5.18	5.12	W	5.18		
211	5.17		P	P					5.13				
102	4.94						1	4.98	4.99				
131	4.89		P	P					4.98	F	4.97		
112	4.78								4.83				
040	4.73	M	4.72	4.72	16	4.70	17	4.70	4.70	M	4.69		
022	4.68								4.73				
221	4.67								4.64				
140	4.42	N							4.40				
230	4.42	W	4.42	4.42	3	4.39	3	4.42	4.38	W	4.40		
122	4.38								4.41				

¹ *d_{hkl}* calculated from the following data: *a* = 12.40 ± 0.04, *b* = 18.92 ± 0.08, *c* = 10.77 ± 0.03 Å. All calculated d-spacings listed for *d* ≥ 2.07 Å.

² Single crystal intensities estimated visually from the *hk0* and *hk3* Weissenberg films from a multiple fiber yielding one strong and several weaker nets; exposure time approximately one week; S=strong, MS=medium strong, M=medium, W=weak, VW=very weak, C=cut-off, upper limit of measurable *d* approximately 10 Å, N=not distinguishable from background (absent or identification of reflection doubtful due to superposition of a reflection belonging to another net).

³ 114.59 mm diameter camera. Film measurements corrected for shrinkage. Lower limit of 2θ measurable: approximately 7°; Q=reflection corresponding to quartz, known to be present as impurity in the sample, intensity of reflection uneven and difficult to measure.

The approximate *d*-spacing of the *hk1* reflections visible in the fiber pattern is denoted by P; the actual *d*-spacings have not been measured because the arcs made by the reflections do not intersect the 0-level.

⁴ Data of Mary E. Thompson. *d_{hkl}* calculated from *a* = 12.22, *b* = 18.80, *c* = 10.95 Å. 114.59 mm diameter camera. VS=very strong, MW=medium weak, F=faint, VF=very faint, b=broad, other symbols in footnote 2.

TABLE 2.—(continued)

Calculated ¹		Hendersonite from New Mexico						Hendersonite from Colorado ⁴		
<i>hkl</i>	<i>d_{hkl}</i>	Single ² Crystal		Fiber ³		Powder ³		Powder		
		I	Cu/Ni $\lambda=1,5418$ Å	Cr/V $\lambda=2,2902$ Å	Cu/Ni $\lambda=1,5418$ Å	Cr/V $\lambda=2,29092$ Å	I	<i>d_{hkl}</i>	I	<i>d_{hkl}</i>
061	3.026									
133	3.026	M				3	3.026	1	3.021	3.05 F 3.02
152	3.004									
341	2.990		P	P						2.965
401	2.979		P	P						2.94 VF 2.95
223	2.952	W								2.97
420	2.945	N	2.940	2.940						2.90
411	2.943									2.90
161	2.940									
332	2.909									2.90
043	2.860	N								2.89
421	2.841									2.81
260	2.811	M	2.802	2.804						
350	2.790	M	2.799	2.790	12	2.788	8	2.803 2.786		MW 2.78
143	2.786	S								2.81
233	2.786	W								2.80
430	2.781	N								2.475
252	2.769									
062	2.721									
261	2.720		P	P						
303	2.711	N								2.71
070	2.703	N								
351	2.702		P	P						
342	2.695									2.68
004	2.693	W								2.74
431	2.693									2.665
402	2.687					2	2.686	1	2.689	2.67 F 2.68
313	2.683	W								2.69
014	2.666									2.71
412	2.660									2.637
162	2.657									
104	2.632									2.67
170	2.641	N								
071	2.621		P	P						
323	2.606	N								2.61
114	2.606									2.64
053	2.605	N								
243	2.597	W				2	2.597	1	2.586	2.61 F 2.59
440	2.592	N		2.586						2.56
024	2.590									2.63
422	2.583									2.565
171	2.565		P	P						
153	2.549	VW						1	2.540	
124	2.535									2.57
441	2.521									2.49
333	2.490	N				4	2.505	2	2.500	2.49 W,b 2.50

TABLE 2.—(continued)

Calculate		Hendersonite from New Mexico						Hendersonite Colorado ⁴			
<i>hkl</i>	<i>d_{hkl}</i>	Single ² Crystal	Fiber ³		Powder ³				Calculated	Measured	
			Cu/Ni $\lambda=1.5418$ Å	Cr/V $\lambda=2.2902$ Å	Cu/Ni $\lambda=1.5418$ Å	Cr/V $\lambda=2.2902$ Å			Cu/Ni $\lambda=1.5418$ Å		
		I	<i>d_{hk0}</i>	<i>d_{h0k}</i>	I	<i>d_{hkl}</i>	I	<i>d_{hkl}</i>	<i>d_{hkl}</i>	I	<i>d_{hkl}</i>
500	2.480	N									
270	2.478	M	2.471	2.472							
352	2.478										
034	2.476								2.51		
432	2.471								2.455		
204	2.470				4	2.468	3	2.472	2.495	W	2.46
510	2.459	N									
214	2.449								2.47		
134	2.428								2.46		
361	2.417								2.46		
072	2.415										
271	2.414										
253	2.401										
511	2.398										
520	2.398	M			5	2.399	7	2.399		W	2.40
450	2.398	W									
224	2.390								2.41		
172	2.371										
063	2.370	N									
080	2.365	M									
360	2.364	M	2.357	2.359	4	2.354	3	2.349		W	2.34
343	2.352	VW							2.35		
403	2.346	MS							2.34	MW	2.31
521	2.341		P	P							
451	2.340		P	P							
044	2.340								2.365		
442	2.336								2.32		
413	2.328	N							2.32		
163	2.327										
180	2.323	M			6	2.311	11	2.309			
081	2.310										
144	2.300								2.32		
234	2.300								2.32		
423	2.277	N					1	2.279	2.27		
181	2.271										
370	2.261	MS	2.260	2.260	9	2.260	16	2.257		MW	2.25
531	2.256		P	P							
304	2.256								2.27		
272	2.251										
314	2.241								2.25		
512	2.237										
263	2.213	W									
371	2.213										
460	2.210	N									
355	2.203										
433	2.198								2.19		

TABLE 2.—(continued)

Calculated ¹		Hendersonite from New Mexico								Hendersonite from Colorado ⁴	
<i>hkl</i>	<i>d_{hkl}</i>	Measured								Calculated	Measured
		Single ² Crystal	Fiber ³		Powder ⁵				Powder		
		I	Cu/Ni $\lambda=1.5418$ Å	Cr/V $\lambda=2.290$ Å	2	Cu/Ni $\lambda=1.5418$ Å	Cr/V $\lambda=2.29092$			Cu/Ni $\lambda=1.5418$ Å	
			<i>d_{hko}</i>	<i>d_{hko}</i>	I	<i>d_{hkl}</i>	I	<i>d_{hkl}</i>	<i>d_{hkl}</i>	I	<i>d_{hkl}</i>
540	2.196	M	2.196	2.197	6	2.199	6	2.194		W	2.20
324	2.194								2.21		
054	2.193										
522	2.191										
452	2.190										
244	2.189										
461	2.165		P	P					2.205		
082	2.165										
281	2.165		P	P							
154	2.160										
073	2.195	N									
005	2.154	N									
541	2.152										
015	2.140										
182	2.133										
173	2.127	N									
334	2.124						2	2.126	2.135		
105	2.122										
532	2.121										
115	2.109										
443	2.102	N							2.10		
090	2.102	N									
025	2.100										
372	2.086										
190	2.073	W									
125	2.071										
550	2.070	MS	2.075	2.076	2	2.069	2	2.069			
254	2.068										
600	2.067	W									
			2.050	2.051	4	2.049	6	2.046		MW,b	2.040
				2.036	2	2.034	3	2.033			
				2.021			3	2.021			
					3	1.996				F	1.989
					3	1.951	4	1.947			
					8	1.797	6	1.796			
					4	1.765					
					2	1.742					
					1	1.658	2	1.661			
					4	1.557					
					2	1.532	2	1.542			
					2	1.506					
					3	1.473					

TABLE 3. COMPARISON OF OBSERVED INTENSITIES: ELECTRON AND X-RAY DIFFRACTION STUDIES

<i>hkl</i>	Electron Diffraction ¹	X-Ray Diffraction ²			
		k=0	k=1	k=2	k=3
	I	I	I	I	I
1k0	C	C	—	W	—
2k0	MW	M	—	W	W
3k0	M	—	W	M	M
4k0	M	M	—	—	—
5k0	M	—	—	M	MS
6k0	M	W	—	—	—
7k0	MW	—	—	—	—
8k0	VS	MS	—	MS	W
0k1	C	—	—	—	—
1k1	C	—	—	—	—
2k1	VW	VW	—	—	—
3k1	VW	—	—	—	—
4k1	W	—	—	—	—
5k1	VW	—	—	—	—
6k1	W	—	—	—	—
7k1	VW	—	—	—	—
8k1	W	—	—	—	—
0k2	W	W	—	—	—
1k2	VW	—	—	—	—
2k2	VW	VW	—	—	—
3k2	W	—	—	—	—
4k2	W	—	—	—	—
5k2	VW	—	—	—	—
6k2	W	—	—	—	—
7k2	VW	—	—	—	—
8k2	W	—	—	—	—
0k3	MW	—	—	—	M
1k3	S	—	S	S	M
2k3	M	M	—	W	VW
3k3	M	—	W	—	—
4k3	S	MS	—	—	—
5k3	M	—	W	—	—

¹ Electron diffraction intensities estimated visually by Lindberg from electron-diffraction pattern taken by Ross; indexing based on orientation of the unit cell used by Lindberg, in the present study; for transformation matrix see Footnote 1, Table 1.

² Single crystal intensities estimated visually from various Weissenberg and precession films taken with different exposure times; for intensities of reflections with $k > 3$, see Table 2; for symbols used to describe intensities, see Footnote 2, Table 2.

TABLE 3.—(continued)

<i>hkl</i>	Electron Diffraction ¹	X-Ray Diffraction ²			
		k=0	k=1	k=2	k=3
	I	I	I	I	
6k3	M	W	—	—	—
7k3	M	—	—	—	—
8k3	M	VW	—	—	—
0k4	W	W	—	W	—
1k4	VW	—	—	—	—
2k4	VW	—	—	—	—
3k4	VW	—	—	—	—
4k4	VW	—	—	—	—
5k4	VW	—	—	—	—
6k4	VW	—	—	—	—
7k4	VW	—	—	—	—
8k4	VW	—	—	—	—
0k5	VW	—	—	—	—
1k5	VW	—	—	—	—
2k5	VW	—	—	—	—
3k5	VW	—	—	—	—
4k5	VW	—	—	—	—
5k5	VW	—	—	—	—
6k5	VW	—	—	—	—
7k5	VW	—	—	—	—
8k5	VW	—	—	—	—
0k6	VS	VS	—	S	—
1k6	MW	—	—	—	—
2k6	M	VW	—	—	—
3k6	M	—	—	—	—
4k6	M	VW	—	—	—
5k6	M	—	—	—	—
6k6	M	—	—	—	—
7k6	MW	—	—	—	—
8k6	S	W	—	—	—

CHEMICAL ANALYSES

Several hundred milligrams of hendersonite were handpicked out of relatively pure samples from the J. J. mine and the Eastside mine. Each sample was crushed and further checked for impurity, the principal contaminant being quartz sand grains enclosed in the hendersonite seam. The spectrographic analyses (Table 4) showed less than 0.5 per

TABLE 4. SEMIQUANTITATIVE SPECTROGRAPHIC ANALYSES OF HENDERSONITE
(Analyst: K. V. Hazel)

	GJM-70 J. J. Mine	AW-14-55 Eastside Mine
Over 10 per cent	V	V
5-10	—	—
1-5	Ca	Ca
0.5-1.0	—	—
0.1-0.5	Si, Sr	Si, Al, Fe
0.05-0.1	Mg	Sr, Mg
0.01-0.05	Al, Ti, Fe	Na, Ni
0.005-0.01	B	—
0.001-0.005	Mo	Ba, Mn, Sc, Ti
0.0005-0.001	Ba, Cr	Cr
0.0001-0.0005	Cu	—

cent Si, indicating probably less than one per cent impurity. The first two samples were then analyzed. Later, another sample (GJM-70-1, RM-30) from the J. J. mine was analyzed in more detailed to see if a separate determination of SrO and CaO would affect the molecular ratios and gram-molecular weight.

The selection of the methods used by R. Meyrowitz for the microchemical analyses of sample GJM-70-1, RM-30 (Table 5) was guided by a qualitative spectrographic analysis of the mineral by Katherine V. Hazel, U. S. Geological Survey, which showed aluminum in the range 0.1-0.5 percent and magnesium in the range 0.05-0.1 per cent; these elements were not determined chemically. Four portions of the mineral were used for the analysis. One portion was used for the total H₂O determination; a second portion for the "insoluble," CaO, and SrO determinations; a third portion for the V₂O₄, total vanadium, and Fe₂O₃ determinations; and a fourth portion for the H₂O (-) determination. The weight of the various portions ranged from 13 to 37 mg.

The H₂O was determined by use of a modified microcombustion train of the type used for the determination of carbon and hydrogen in organic compounds. The sample was decomposed by ignition at 900° C. in a stream of oxygen.

The "insoluble" was determined by boiling the sample with (1+3) HNO₃ in a weighed Emich microbeaker and sintered glass filter stick. The residue was filtered, washed with water, and dried to constant weight at 110 ± 5° C. The filtrate from the "insoluble" determination was used for the CaO and SrO determinations. CaO was determined by flame photometry (wave length = 554μ). The sample solution was compared to stand-

TABLE 5. ANALYSES OF HENDERSONITE

	Analysis	Analysis recalculated to 100% without insoluble	Ratios	Metal Equivalent	Oxygen Equivalent	Atoms per unit cell ¹
Analysis sample No. AW-14-55 ²						
CaO+SrO	8.84	9.33	.166	.166	.166	Ca+Sr 7.05
V ₂ O ₄	8.01	8.45	.051	.102	.204	V ⁴⁺ 4.33
V ₂ O ₅	63.44	66.97	.368	.736	1.840	V ⁵⁺ 31.25
Total H ₂ O	14.45	15.25	.846	1.692	.846	H 71.84
Insoluble	4.28					
Total	99.02	100.00		Total oxygen equivalent	3.056	O 129.8
H ₂ O(-)	7.52					
Analysis sample GJM-70 ³						
CaO+SrO	9.93	10.45	.186	.186	.186	Ca+Sr 7.90
V ₂ O ₄	7.98	8.40	.051	.102	.204	V ⁴⁺ 4.33
V ₂ O ₅	63.21	66.54	.366	.732	1.830	V ⁵⁺ 31.08
Total H ₂ O	13.88	14.61	.811	1.622	.811	H 68.90
Insoluble	4.67					
Total	99.67	100.00		Total oxygen equivalent	3.031	O 128.7
H ₂ O(-)	7.53					
Analysis sample GJM-70-1(RM-30) ⁴						
CaO	9.5	9.7	.173	.173	.173	Ca 7.34
SrO	1.3	1.3	.012	.012	.012	Sr 0.51
V ₂ O ₄	8.1	8.3	.050	.100	.200	V ⁴⁺ 4.25
V ₂ O ₅	64.6	65.8	.362	.724	1.810	V ⁵⁺ 30.74
Total H ₂ O	14.6	14.9	.827	1.654	.827	H 70.22
Fe ₂ O ₄	<0.1					
Insoluble	0.6			Total oxygen equivalent	3.022	O 128.31
Total	98.7	100.0				
H ₂ O(-)	7.7					

¹ In the three analyses, the atoms per unit cell are derived from the analyses recalculated to 100 per cent without insoluble by multiplying the metal and oxygen equivalents by 0.01 to convert from a percentage to a fractional scale, and by 4246, the gram-molecular weight of the unit cell contents, as derived from the unit cell volume and density of hendersonite from New Mexico; the gram-molecular weight from hendersonite from Colorado is assumed to be of the same order of magnitude.

² Hendersonite from the Eastside Carrizo mine, San Juan County, New Mexico; Alexander Sherwood, analyst; ratios of mixed CaO and SrO calculated as all CaO.

³ Hendersonite from the J. J. mine, Montrose County, Colorado; Alexander Sherwood, analyst; ratios of mixed CaO and SrO calculated as all CaO.

⁴ Hendersonite from the J. J. mine, Montrose County, Colorado; Robert Meyrowitz, analyst.

TABLE 5.—(continued)

Analysis	Analysis recalculated to 100% without insoluble	Ratios	Metal Equivalent	Oxygen Equivalent	Atoms per unit cell
$\text{Ca}_2\text{V}^5+\text{V}^{4+}_8\text{O}_{21}\cdot 8\text{H}_2\text{O}^5$					
CaO	10.51	.1874	.1874	.1874	Ca 8.0
V ₂ O ₄	7.78	.0468	.0936	.1872	V ⁴⁺ 4.0
V ₂ O ₅	68.20	.3749	.7498	1.8745	V ⁵⁺ 32.0
H ₂ O	13.51	.7498	1.4996	.7498	H 64.0
Total	100.00		Total oxygen equivalent	2.9989	O 128.0
$\text{Ca}_2\text{H}_{0.1}\text{V}^5+_{151}\text{V}^{4+}_{7.9}\text{O}_{21}\cdot 8\text{H}_2\text{O}^6$					
CaO	10.51	.1874	.1874	.1874	Ca 8.0
V ₂ O ₄	8.56	.0515	.1031	.2060	V ⁴⁺ 4.4
V ₂ O ₅	67.34	.3702	.7404	1.8510	V ⁵⁺ 31.6
H ₂ O	13.59	.7543	1.5086	.7543	H 64.4
Total	100.00		Total oxygen equivalent	2.9987	O 128.0

⁵ Theoretical composition and ratios $\text{Ca}_2\text{V}^5+\text{V}^5_8\text{O}_{21}\cdot 8\text{H}_2\text{O}$; the Σ of the gram atomic weights of four formula units is 4267.

⁶ Theoretical composition and ratios $\text{Ca}_2\text{H}_{0.1}\text{V}^{4+}_{1.1}\text{V}^{5+}_{7.9}\text{O}_{21}\cdot 8\text{H}_2\text{O}$; the Σ of the gram atomic weights of four formula units is 4267.

ard calcium solutions containing approximately the same concentration of vanadium present in the solution of the sample. The Sr-O was determined by flame photometry (wave length = 461 μ). The sample solution was compared to standard strontium solutions containing approximately the same concentrations of vanadium and calcium present in the solution of the sample.

The V₂O₄ was determined by dissolving the mineral in (1+3) H₂SO₄ and titrating with approximately 0.03 N standard KMnO₄. V₂O₅ was calculated by difference after the total vanadium was determined spectrophotometrically using the hydrogen peroxide procedure. Fe₂O₃ was determined spectrophotometrically by the o-phenanthroline procedure. Aliquots of the solution used for the V₂O₄ determination were used for the total vanadium and Fe₂O₃ determinations. The H₂O (-) was determined by drying the sample to constant weight at 110 ± 5°C.

DERIVATION OF A FORMULA FOR HENDERSONITE

Chemical analyses of hendersonite from the J. J. mine, Montrose County, Colorado, and from the Eastside Carrizo mine, New Mexico,

are given in Table 5. The numbers of atoms per unit cell, also listed in Table 5, have been calculated from the chemical analyses and from the unit cell data given in Table 1, without interpretation of possible combination of the atoms into a structural formula. The nearest numbers of atoms, divisible by four, which must be accommodated in the unit cell if all equivalent positions are fully occupied, are 36 vanadium of mixed valence, 128 (or possibly 132) oxygen, and 8 calcium plus strontium. These, plus hydrogen, may be combined as follows:

- 1) $4[\text{Ca}_2(\text{V}_3\text{O}_8)_3 \cdot 8\text{H}_2\text{O}]$ for 128 oxygen atoms
- 2) $4[\text{Ca}_2(\text{V}_3\text{O}_8)_3 \cdot 9\text{H}_2\text{O}]$ for 132 oxygen atoms

The chemical analyses show slightly more than four vanadium (IV) and slightly less than thirty-two vanadium (V). If the difference in electrical charges on the vanadium atoms is balanced by an adjusted hydrogen content formula 1 and 2 may be expanded so as to indicate the valence of the vanadium atoms:

- 3) $4[\text{Ca}_2\text{H}_x\text{V}^{5+}_{(1+x)}\text{V}^{5+}_{(8-x)}\text{O}_{24} \cdot 8\text{H}_2\text{O}]$ for 128 oxygen atoms
- 4) $4[\text{Ca}_2\text{H}_x\text{V}^{5+}_{(1+x)}\text{V}^{5+}_{(8-x)}\text{O}_{24} \cdot 9\text{H}_2\text{O}]$ for 132 oxygen atoms

where x approximates 0.1 in the three analyzed samples. The total oxygen content of the three analyses is in closer agreement with formula 3; the hydrogen content is in closer agreement with formula 4; formula 3 is preferred to formula 4 on the basis that the oxygen content is less variable than the hydrogen content. The variable water content may be explained either as essential water, varying concomitantly with a decreased calcium content, or as non-essential, adsorbed water.

The mixed vanadium (IV) vanadium (V) content represented by the formula $4[\text{Ca}_2\text{H}_x\text{V}^{4+}_{(1+x)}\text{V}^{5+}_{(8-x)}\text{O}_{24} \cdot 8\text{H}_2\text{O}]$ for hendersonite is characteristic of the corvusite group of minerals, to which group of minerals hendersonite belongs. The crystal chemistry of the corvusite group has been reviewed by Evans (1959, p. 100). He shows 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 corvusite minerals with little change in crystal structure. For hendersonite, the deficiency in vanadium (V) and the excess of vanadium (IV) concomitant to an increased hydrogen content ($x \sim 0.1$ in the proposed formula) is considered to be distributed statistically, and does not alter the way that the 36 vanadium and 128 oxygen atoms occupy their equivalent positions. The calcium-linked, oxygen-coordinated vanadium units remain intact in the structure.

REFERENCES

- CATER, FRED, JR. (1955) Geology of the Naturita NW quadrangle, Colorado. U. S. Geol. Survey Map GQ-65.

- CHRIST, C. L., JOAN R. CLARK AND H. T. EVANS JR. (1954) The crystal structure of potassium metavanadate monohydrate, $KVO_3 \cdot 8H_2O$. *Acta Cryst.* **7**, 801-807.
- ELSTON, D. P. AND THEODORE BOTINELLY (1959) Geology and mineralogy of the J. J. mine, Montrose County, Colorado; in *U. S. Geol. Survey Prof. Paper* **320**, Pt. 18, 203-211.
- EVANS, H. T., JR. (1959) The crystal chemistry and mineralogy of vanadium; in *U. S. Geol. Survey Prof. Paper* **320**, Pt. 7, 91-102.
- AND R. M. GARRELS (1958) Thermodynamic equilibria of vanadium in aqueous systems as applied to the interpretation of the Colorado Plateau ore deposits. *Geochim. Cosmochim. Acta.* **15**, 131-149.
- HENDERSON, E. P. (1935) Steigerite, a new vanadium mineral. *Am. Mineral.* **20**, 769-772.
- AND F. L. HESS (1933) Corvusite and rilandite, new minerals from the Utah-Colorado carnotite region. *Am. Mineral.* **18**, 195-205.
- HESS, F. L. AND E. P. HENDERSON (1931) Fervanite, a hydrous ferric vanadate. *Am. Mineral.* **16**, 273-277.
- HILLEBRAND, W. F., H. E. MERWIN AND F. E. WRIGHT (1914) Hewettite, metaheiwettite, and pascoite, hydrous calcium vanadates. *Am. Philos. Soc. Proc.* **53**, 31-54.
- ROSS, MALCOLM (1959) Mineralogical applications of electron diffraction. II. Studies of some vanadium minerals of the Colorado Plateau. *Am. Mineral.* **44**, 322-341.
- AND C. L. CHRIST (1958) Mineralogical applications of electron diffraction. I. Theory and techniques. *Am. Mineral.* **43**, 1157-1178.
- STROBELL, J. D., JR. (1956) Geology of the Carrizo Mountains area in northeastern Arizona and northwestern New Mexico. *U. S. Geol. Survey Oil Gas Invest.*, Map **OM 160**.
- STOKES, W. L. (1953) Primary sedimentary trend indicators as applied to ore finding in the Carrizo Mountains, Arizona and New Mexico. *U. S. Atomic Energy Comm. RME-3043*, pt. 1.
- THOMPSON, M. E., C. H. ROACH AND ROBERT MEYROWITZ (1958) Sherwoodite, a mixed vanadium (IV)—vanadium (V) mineral from the Colorado Plateau. *Am. Mineral.* **43**, 749-755.
- WADSLEY, A. D. (1957) Crystal chemistry of non-stoichiometric pentavalent vanadium oxides: crystal structure of $Li_{1+z}V_5O_8$. *Acta Cryst.* **10**, 261-266.
- WEEKS, A. D., R. G. COLEMAN AND M. E. THOMPSON (1959) Summary of the ore mineralogy, in *U. S. Geol. Survey Prof. Paper* **320**, Part 5, 65-79.

Manuscript received, May 12, 1962.