

Straczekite, a new calcium barium potassium vanadate mineral from Wilson Springs, Arkansas

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ABSTRACT. Straczekite, a new calcium barium potassium vanadate from Wilson Springs (formerly Potash Sulfur Springs), Arkansas, occurs as a rare secondary mineral in fibrous seams in gangue. The dark greenish-black crystals are very soft, thin laths up to 0.5 mm in length, forming thick masses. No single-crystal X-ray patterns could be obtained, but good electron diffraction patterns yielded a monoclinic unit cell in space group $C2/m$, $C2$, or Cm . The cell parameters were refined by least squares analysis of Guinier-Hägg X-ray powder data: a 11.679(2), b 3.6608(4), c 10.636(2) Å, $\beta = 100.53(4)^\circ$ (strongest lines are: 003, 3.486, 100; 001, 10.449, 50; 020 1.8306, 50; $\bar{6}01/510$, 1.9437, 15; 111/ $\bar{2}03$, 3.255, 10; 311/ $\bar{3}12$, 2.492, 10; 021, 1.8030, 10). Chemical analysis yields the formula: $(Ca_{0.39}Ba_{0.31}K_{0.33}Na_{0.11})(V_{1.59}^{4+}V_{6.31}^{5+}Fe_{0.10}^{3+})O_{20.02}(H_2O)_{2.9}$. The calculated density is 3.21 g/cm³. The mineral conforms to a series of synthetic vanadium bronzes, typified by $Ag_{1-x}V_2O_5$ of known structure. It represents a new series of layer vanadate minerals of general formula $M_xV_8O_{20} \cdot yH_2O$, similar in properties but distinct from the hewettite series ($M_xV_6O_{16} \cdot yH_2O$).

STRACZEKITE was first observed as a significant mineral component in the ore from the Union Carbide vanadium mine in Wilson Springs (formerly Potash Sulfur Springs), Garland County, Arkansas. It was found in a specimen submitted by Don R. Owen, Union Carbide geologist, in the course of an investigation of the complex mineralogy of this major vanadium deposit.

The geologic setting for the vanadium deposit has been described by Hollingsworth (1967) as being near a contact zone between folded Palaeozoic country rock and the Potash Sulfur Springs intrusive complex, in a setting that is similar to that characteristic of the Magnet Cove intrusive about six miles to the east. The vanadium constitutes about 1% of the ore, erratically disseminated in altered alkalic igneous and metamorphosed sedimentary rocks. Straczekite occurs as a secondary

mineral along with other vanadium minerals such as hewettite [$CaV_6P_{16} \cdot nH_2O$], duttonite [$VO(OH)_2$] and fervanite [$Fe_4(VO_4)_4 \cdot 5H_2O$]. Schoderite and metaschoderite [$Al_2(PO_4)(VO_4) \cdot nH_2O$] have also been described from this locality (Pabst, 1979).

Straczekite (strā'chek-ite) is named for John A. Straczek, Chief Geologist at Union Carbide Corp., who has made this study possible. The name has been approved by the International Commission on New Minerals and Mineral Names.

Physical properties. Straczekite occurs as fibrous, greenish-black, foliated masses in seams as much as 1 cm across, in argillaceous gangue. Individual fibres, up to 0.5 mm long, are opaque, but very thin flakes are yellowish green in transmitted light. The fibres have a greasy black luster, give a greenish-black streak, and have a perfect cleavage $\parallel (100)$ that separates the fibres into thin laths. The laths have very high indices of refraction (the Gladstone-Dale law predicts $n = 1.99$) and consistently show parallel extinction. A centred acute bisectrix figure appears normal to the plane of the lath, showing a moderate to large $2V$ angle, with the optic plane lying normal to the elongation direction (b axis). The colour is too dark to permit a test of the optic sign, but because of the layered structure of the mineral, the sign is presumably negative. A slight pleochroism is apparent in the plane of the laths: the colour is apple green in the plane normal to, and olive green parallel to, the elongation direction. Fig. 1 shows scanning electron micrographs that illustrate the typical habit of straczekite.

Attempts to measure the density with the Berman balance gave erratically low results. The best determinations, made with a micropycnometer, are given in Table II.

Electron diffraction study. In the transmission

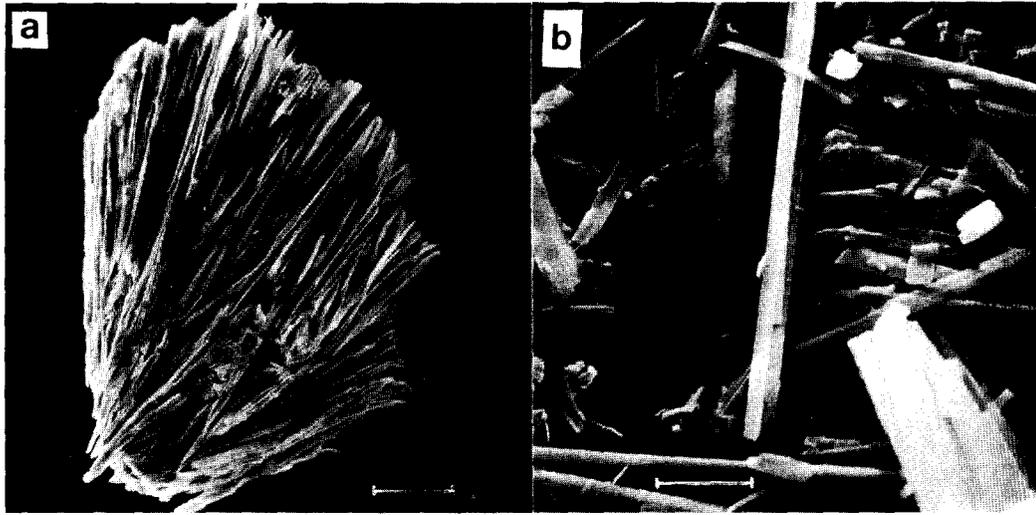


FIG. 1. Scanning electron micrographs of straczekite (by E. J. Dwornik and R. R. Larson, US Geological Survey), showing (a) fibrous aggregate and (b) individual lath-like fibres. The bars represent 0.1 mm in (a) and 0.01 mm in (b).

electron microscope the laths give sharp electron diffraction patterns in the plane of the laths. These patterns are rectangular and centred, corresponding to a lattice of dimensions $\sim 11.8 \times 3.6 \text{ \AA}$. The short spacing is along the length of the lath and corresponds to a strong line at 1.831 \AA on the X-ray powder patterns. A few crystals give very weak spots normal to the fibre spacing, which would double the layer axes ($23 \times 7.2 \text{ \AA}$). Fig. 2 shows the

electron diffraction patterns of a typical lath, such as that shown in fig. 1.

Fig. 2a shows the typical centred rectangular net obtained in the plane of the lath. To obtain the spacing normal to the laths, crystals were embedded in epoxy resin and ion thinned, a process that involves some heating of the specimen. After considerable trial and error, a crystal was found that showed the 11.8 \AA spacing (d_{100}) in the plane of

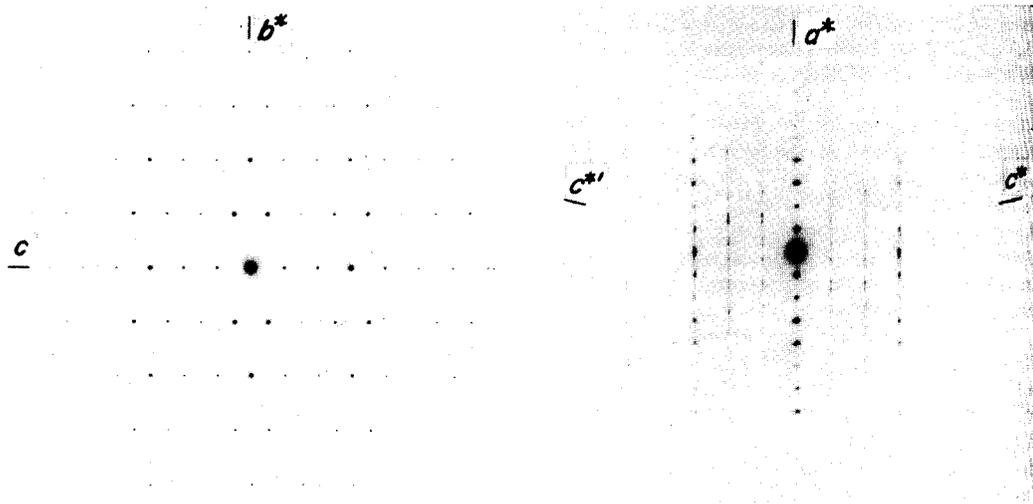


FIG. 2. Electron diffraction patterns of single lath-like crystals of straczekite: (a, left) centred hk net in the plane of a lath, with k vertical (fibre axis); (b, right) hl net showing twinning and streaking $\parallel (001)$ (vertical).

the lath referred to above, and normal to it a strong row of sharp spots clearly belonging to the interlayer spacing of $\sim 10.4 \text{ \AA}$ normal to the lath (d_{100}), as shown in Fig. 2b. This figure shows that the 11.8 \AA spacing is not normal to the interlayer row (designated 00*l*), but inclined at an angle of about 110° . The pairing of spots on the 20*l* and 40*l* rows and the similarity of the 60*l* row to the 00*l* row are characteristic of an inclined base-centred lattice twinned on (001), having such dimensions that the 60*l* rows of the twins nearly coincide.

From these diffraction patterns we deduced a unit cell for straczekite that is monoclinic in space group $C2/m$ (or $C2$ or Cm). The approximate dimensions can be used to interpret the X-ray powder patterns as described below. We note in addition that the 20*l* and 40*l* rows are somewhat diffuse and streaked along the *l* direction, indicating some degree of disorder in layer stacking in addition to the twinning.

X-ray study. We have not been able to obtain single crystal X-ray patterns for straczekite. A group of compressed parallel laths in the precession camera gave only a concentric series of arc-like reflections corresponding to the 3rd, 4th, and 5th order of the interlayer spacing of 10.44 \AA . The best X-ray diffraction data were obtained with the Guinier-Hägg focusing powder camera, using $\text{Cr-K}\alpha_1$ radiation ($\lambda = 2.28962 \text{ \AA}$) and CaF_2 ($a = 5.4638 \text{ \AA}$) as internal standard. On such a pattern taken in air twenty-one lines could be measured. When vacuum was applied to the sample, a somewhat poorer pattern was obtained showing thirteen lines. Notably, the first line corresponding to the interlayer 001 plane was reduced from 10.45 to 10.07 \AA , probably as a result of the loss of some interlayer water. With the aid of the approximate unit cell found in the electron diffraction study, we could index all but one or two very faint lines at low angles, and derive refined unit cell parameters by least-squares analysis. The indexing is confirmed by the interpretation of a fibre pattern made in a Debye-Scherrer camera using $\text{Cu-K}\alpha$ radiation. In this pattern only the *h0l* reflections are registered, and these are found to be completely consistent with the general analysis.

The X-ray powder data and the derived unit cell data are shown in Table I. It should be noted that one of the three strongest lines is the fibre axis spacing of 1.831 \AA , as shown in the Guinier-Hägg patterns. The intensity of this reflection (020) in Debye-Scherrer or diffractometer patterns is often severely suppressed by preferred orientation for this and similar minerals such as hewettite.

Chemical analysis. Spectroscopic examination showed Ba and V to be major constituents of straczekite. An energy-dispersive semiquantitative

analysis (EDAX) in the electron microscope revealed major V, minor Ca, Ba, and K, and traces of Fe. The dark colour shows that vanadium is

Table I. X-ray and crystallographic data for straczekite

hkl	In air					In vacuum		
	d(calc)	Pattern 1		Pattern 2		d(calc)	Pattern 3	
		d(obs)	I(obs)	d(obs)	I(obs)		d(obs)	I(obs)
001	10.457	10.449	50	10.49	100	10.066	10.067	35
200	5.741	5.740	7	5.77	5	5.718	5.710	3
201	4.684	4.711	1	4.69	1			
110	3.488					3.490	3.490	100
003	3.486	3.486	100	3.48	50	3.355	3.545	3
111	3.255					3.238	3.237	5
203	3.255	3.255	10			3.179		
111	2.979	2.978	5					
401	2.907	2.908	5	2.901	15	2.904	2.903	5
402	2.736	2.731	3	2.730	3			
310	2.646	2.644	5			2.645	2.644	10
311	2.645					2.642		
004	2.614	2.614	7	2.620	7			
311	2.491					2.474	2.475	1
312	2.490	2.492	10			2.482		
312	2.249							
313	2.249	2.249	3					
205	2.092							
005	2.091	2.092	5	2.092	10			
511	1.9682	1.9678	5			1.9672	1.9680	5
601	1.9465			1.943	10	1.9438		
510	1.9454	1.9437	15			1.9405	1.9436	20
600	1.9137							
602	1.9136	1.9129	5	1.912	3			
020	1.8304	1.8306	50			1.8327	1.8324	75
021	1.8030	1.8030	10			1.8030	1.8030	5
006	1.7428			1.739	2			
602	1.6997			1.698	3			
604	1.6993							
405	1.5601			1.562	1			
007	1.4938			1.4935	2			
606	1.4247			1.4253	1			
008	1.3071			1.3078	1			

Unit cells (monoclinic, space group $C2/m$, $C2$ or Cm) by least squares analysis of Guinier-Hägg data:

a, \AA	11.679(2)	11.663(3)
b, \AA	3.6608(4)	3.6653(7)
c, \AA	10.636(2)	10.266(19)
β , deg.	100.53(4)	101.31(9)
V, \AA^3	447.1(1)	430.3(7)

Pattern 1: Data from Guinier-Hägg pattern made in air with $\text{CrK}\alpha_1$ radiation ($\lambda = 2.28962 \text{ \AA}$) and CaF_2 internal standard ($a = 5.4638 \text{ \AA}$); plus very weak lines at 6.959, 5.822 \AA .

Pattern 2: Data from Debye-Scherrer fiber pattern made with $\text{CuK}\alpha$ radiation (by Mary E. Mrose, U. S. Geological Survey); only *h0l* reflections are registered.

Pattern 3: Data from Guinier-Hägg pattern made in vacuum with $\text{CrK}\alpha_1$ radiation; plus very weak line at 5.833 \AA .

Table II. Analytical chemistry of straczekite

	Anal. 1 ^a	Anal. 2 ^b	Avg. anal. ^c
V ₂ O ₅	79.7	66.8	66.4
V ₂ O ₄		15.6	15.3
Fe ₂ O ₃	1.0	0.7	0.9
Na ₂ O	0.4	0.5	0.4
K ₂ O	2.1	1.5	1.8
CaO	2.5	2.5	2.5
BaO	5.4	5.3	5.5
H ₂ O	7.6	6.8	7.2
SiO ₂		1.9	
Acid insol.	1.9		
Total	100.6	101.6	100.0
D _m , g/cm ³	3.29	3.09	
Formula ^d :	(Ca _{0.38} Ba _{0.31} K _{0.33} Na _{0.11})(V _{1.59} V _{0.31} Fe _{0.10})O _{20.02} (H ₂ O) _{2.9}		
Formula weight, 864.1; calculated density, D _x = 3.21 g/cm ³			

Notes:

- Procedure for analysis 1 (197 mg sample): Total V was determined by reduction to V^{4+} with SO_2 and titration with permanganate (correction made for Fe); total Fe after reduction to Fe^{2+} was determined photometrically with o-phenanthroline; Na, K, Ca and Ba were determined by atomic absorption; total H_2O was determined by the semimicro Penfield method.
- Procedure for analysis 2 (47 mg sample): Total V was determined by atomic absorption; V^{4+} was determined on a 1.3 mg sample by adding V^{5+} and Fe^{3+} , reducing acidity, and measuring Fe^{2+} (produced by V^{4+}) spectrophotometrically with o-phenanthroline (sample Fe was assumed to be Fe^{3+}); Na, Ca and Ba were determined by atomic absorption; Si was determined photometrically; total H_2O was determined on the C-H-O analyzer (by Zoe Ann Hamlin). K in this sample was estimated by X-ray fluorescence.
- Analyses 1 and 2 normalized to 100 percent for essential components and averaged.
- Formula constrained to make $(\text{V}+\text{Fe})=8$.

present as a mixture of valence states V^{4+} and V^{5+} . The Fe present is presumed to replace V in the Fe^{3+} state. Small amounts of Si detected are considered to come from gangue contamination.

Sufficient material was purified to allow two complete wet chemical analyses to be made on the same batch, which was carefully prepared by hand picking under the microscope. In one of these analyses, the valence state of vanadium was also determined.

The results of the two analyses (Table II) are not significantly different. The composition, based on $8(V + Fe)$ in the layer component, can be formulated as given in Table II. As the data in the table show, this formulation accounts very well for the chemical analysis and also is consistent with the measured density.

An idealized formula representing the contents of one unit cell may be written $(Ca, Ba, K, Na)_x (V_{1.6}^{4+} V_{6.3}^{5+} Fe_{0.1}^{3+}) O_{20} (H_2O)_{4-x}$. To be consistent with the C-centred crystallographic symmetry, which requires all atomic sites to be even in number, considerable non-stoichiometry must be invoked in the interlayer material. Thus, although the cation sum is close to unity, this sum may be variable, and in the crystal the cation sites may be either vacant or occupied by H_2O . The vacuum experiment referred to in the X-ray study shows the water content to be variable; the change in cell volume on evacuation corresponds to a loss of about one molecule of H_2O per unit cell. The inter-

layer material is undoubtedly zeolitic in character, as is common for this type of layer structure.

Crystal chemistry of straczekite. Because of the close similarity of the physical properties of straczekite to those of the hewettite group of minerals, considerable effort was made initially to relate them chemically. No formula based on a V_6O_{16} layer unit could be found that would fit the analytical, physical, and crystallographic data. Eventually it was found that a V_8O_{20} formula basis, characteristic of another series of anhydrous synthetic layer vanadates (known as vanadium bronzes), provides a wholly satisfactory account of these data. Thus, straczekite constitutes a member of a new mineral vanadate group, structurally and chemically distinct from the hewettite group.

Bachmann (1962) has shown the relationship of the crystallography of hewettite to that of the synthetic vanadium bronze compound LiV_3O_8 , whose structure was determined by Wadsley (1957). The layer consists of a condensed arrangement of distorted VO_6 octahedra, which has a planar repeat unit of approximately $12.1 \times 3.6 \text{ \AA}$ (see fig. 3a). This relationship was firmly established by a crystal structure analysis by Bachmann and Barnes (1962) of a sodium-calcium analogue of metahewettite $(Na, Ca)V_6O_{16} \cdot 3H_2O$ (Qurashi, 1961) and barnesite $Na_2V_6O_{16} \cdot 2H_2O$ (Weeks *et al.*, 1963). Although the space group of this monoclinic structure type has been stated to be $P2/m$ (Qurashi, 1961), the structure analyses (Wadsley, 1957; Bachmann and

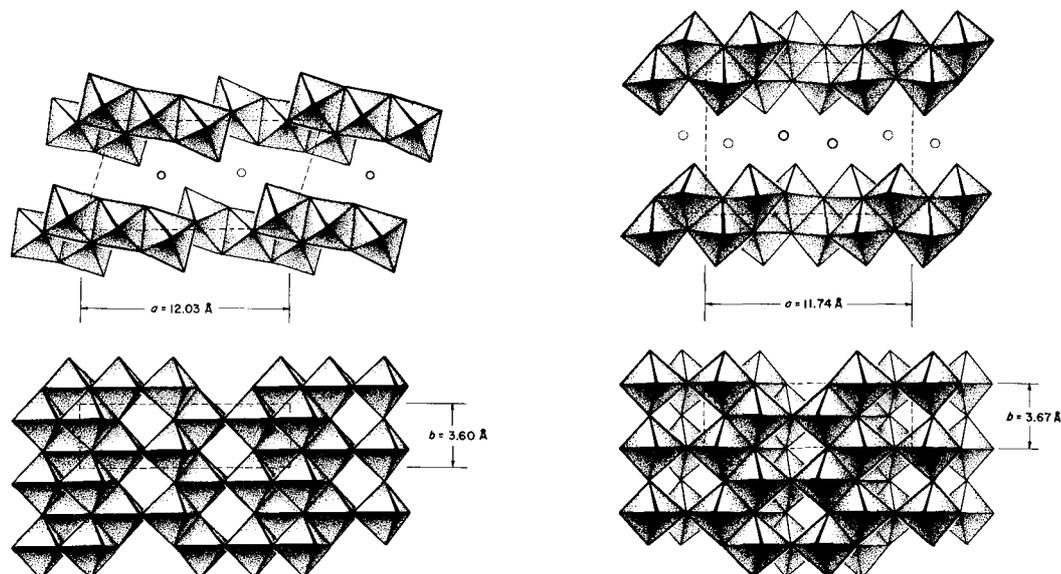


FIG. 3. Vanadium bronze structure types: (a, left) structure of $Li_{1+x}V_3O_8$ (Wadsley, 1957), prototype of the hewettite group of minerals; (b, right) $Ag_{1-x}V_2O_5$ (Andersson, 1965), prototype of straczekite.

Barnes, 1962) shows that the correct symmetry is $P2_1/m$. The c dimension and β angle vary from phase to phase depending on interlayer contents, while the symmetry and a and b dimensions remain little affected. When allowance is made for interlayer H_2O and cations in hewettite and barnesite, the molecular volume of the V_6O_{16} unit is about 275 \AA^3 .

The crystallography of straczekite has similar a and b dimensions in the plane of the layer ($11.7 \times 3.6 \text{ \AA}$), but a key distinguishing feature is the base-centred symmetry of the space group $C2/m$. Also, the molecular volume of the layer unit, after allowance is made for H_2O , Ba, and K, is about 360 \AA^3 . These critical data are incompatible with a V_6O_{16} layer unit of the LiV_3O_8 type, but can accommodate a V_8O_{20} unit (atomic volume of O $\sim 18 \text{ \AA}^3$). No vanadium minerals have been reported as yet that have these geometric properties, but a series of synthetic vanadium bronze compounds is known that does fit them. The compound $Ag_{2.72}V_8O_{20}$ has similar a and b dimensions (11.7 and 3.7 \AA), space group $C2/m$, and a layer unit volume of 376 \AA^3 . Its structure was determined by Andersson (1965), who found a layer arrangement of VO_6 octahedra (fig. 3b) that is completely different from that found in LiV_3O_8 (and hewettite). Subsequently, Pouchard and Hagenmuller (1967) found that the synthetic compound $v\text{-}K_2V_8O_{20}$ has a layer structure based on that of the Ag compound; also, the compound $(NH_4)_2V_8O_{20}$ described by Vidonne *et al.* (1971) evidently belongs to this group. We believe that

straczekite is the first described natural occurrence of a member of this series of layer compounds.

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