

SCHODERITE, A NEW PHOSPHOVANADATE MINERAL
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ABSTRACT

A new phosphovanadate mineral, schoderite, $2\text{Al}_2\text{O}_3 \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5 \cdot 16\text{H}_2\text{O}$, occurs as yellowish orange microcrystalline coatings associated with wavellite and vashegyite along fractures in phosphatic cherts of lower Paleozoic age near Eureka, Nevada. Schoderite is monoclinic, probably of the prismatic class, and forms microscopic bladed crystals that are tabular, parallel to (010), and elongate parallel to the c axis. Unit cell dimensions are: $a=11.4$, $b=15.8$, and $c=9.2$ Å, $\beta=79^\circ$. Biaxial positive, with $2V=61^\circ$ (calc.), $\alpha=1.542$, $\beta=1.548$, $\gamma=1.566$; $Y=b$. x -ray powder patterns show the following spacings and intensities for the stronger lines: 15.8 Å-4, 11.1 Å-2, 7.9 Å-10, 3.06 Å-2.

Schoderite loses up to $3\text{H}_2\text{O}$ at room temperature in a dry atmosphere and converts to a lower hydrate, $2\text{Al}_2\text{O}_3 \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5 \cdot 12\text{H}_2\text{O}$, which is termed metaschoderite. Metaschoderite may be rehydrated to schoderite by contact with water. Dehydration is accompanied by shrinkage of the unit cell along the b -axis to 14.9 Å. The β angle remains unchanged for both hydration states, since a and b are unaffected by state of hydration. Metaschoderite is biaxial positive, $2V=59^\circ$ (calc.), $\alpha=1.598$, $\beta=1.604$, $\gamma=1.626$; $Z=b$. Strongest x -ray lines are 14.9 Å-6, 11.1 Å-4, 7.5 Å-10, 3.02 Å-2.

The mineral is named in honor of William P. Schoder, research chemist employed for many years by Union Carbide Nuclear Company.

INTRODUCTION

Schoderite, an aluminum phosphovanadate, was first noted in late 1958 as a yellowish orange mineral resembling variscite in samples of phosphatic chert from Nevada. Microchemical tests indicated the mineral to be vanadiferous as well as phosphatic, and optical properties did not match those of any known mineral. Additional samples were collected during the summer of 1959, and examined spectrographically and by x -ray diffraction. Results of these examinations indicated the mineral to be unknown, and perhaps new. Later data from chemical analyses, differential thermal analyses and infrared spectra helped to characterize the mineral as a new and distinct species of phosphovanadate.

The mineral is named "schoderite," in honor of a devoted research chemist, William Paul Schoder, whose many outstanding contributions to the metallurgy of vanadium have received little outside recognition only because of the confidential nature of his work.

OCCURRENCE

Schoderite occurs sparsely in phosphatic cherts of lower Paleozoic age that outcrop in the Fish Creek Range about 30 miles south of Eureka, Nevada. The mineral is associated with wavellite and vashegyite as yellowish orange microcrystalline coatings along fractures in the chert.

The best crystalline material was obtained from a bulldozer cut about 15 feet below the surface on the Van-Nav-Sand Claim group, T 16 N, R 52 E, Section 34, where schoderite has crystallized partly from amber-colored phosphatic gels containing major amounts of aluminum, iron, vanadium and phosphorus.

Schoderite was apparently formed as the result of supergene alteration of phosphatic cherts containing small amounts of vanadium in the lattice of fluorapatite. Oxidation, hydration and solubilization of various components of the chert by meteoric waters was followed by reprecipitation along fractures of a variety of secondary minerals, *i.e.*, vashegyite, wavellite, schoderite, diadochite, and phosphatic gels of varying composition.

The Nevada locality represents a type of mineralization where vanadium and phosphorus are both present in significant and locally equivalent amounts and tend to form minerals that are suitable for the study of the replacement $(VO_4)^{3-}$ for $(PO_4)^{3-}$. The mineral assemblage at the Nevada locality is somewhat similar to that of the Kara Tau locality of the U.S.S.R. described by Ankinovich (1958, 1959, 1960), who regards deposits of the vanadium-phosphate type as "poorly or insufficiently completely studied" in the literature.

A recent Russian publication by Ankinovich (1960) describes the new hydrated ferric vanadate, rusakovite $(Fe, Al)_5 (V, P)O_4 \cdot 2(OH)_9$, whose formula suggests some resemblance to schoderite.

CHEMICAL COMPOSITION

According to spectrographic analyses (Table I), the mineral contains major amounts of aluminum, phosphorus, and vanadium, and trace amounts of barium, calcium, copper, iron, magnesium, molybdenum, and

TABLE I. SPECTROGRAPHIC ANALYSIS OF SCHODERITE¹

Element	Per Cent
Vanadium	10.0
Phosphorus	>1.0, <10.0
Aluminum	6.0
Silicon	0.6
Iron	0.5
Calcium	0.5
Molybdenum	0.3
Barium	0.2
Magnesium	0.08
Copper	0.01

¹ Spectrographic analysis by B. D. McCarty, UCNC, Grand Junction Laboratory.

TABLE II. CHEMICAL ANALYSES AND MOLAR RATIOS OF SCHODERITE¹

Constituents	Per Cent		Ratios	
Al ₂ O ₃	23.8	0.233	0.118 × 2	0.959 × 2
Fe ₂ O ₃	0.27	0.002		
V ₂ O ₅	24.6	0.135	0.135 × 1	1.098 × 1
P ₂ O ₅	17.4	0.123	0.123 × 1	1.000 × 1
H ₂ O ⁻	26.6	1.48	0.122 × 16	0.992 × 16
H ₂ O ⁺	7.5	0.47		
Total	100.27			

Empirical Formula: 2Al₂O₃ · V₂O₅ · P₂O₅ · 16H₂O

¹ Chemical analysis by J. P. Moore, UCNC, Grand Junction Laboratory.

silicon. Chemical analyses (Table II) and calculated molar ratios indicate that the mineral is an aluminum phosphovanadate whose empirical formula may be expressed, 2Al₂O₃ · V₂O₅ · P₂O₅ · 16H₂O. Substitution of small amounts of iron for the alumina is suggested from the analysis.

The mineral occurs in two hydration states. The higher loses water at

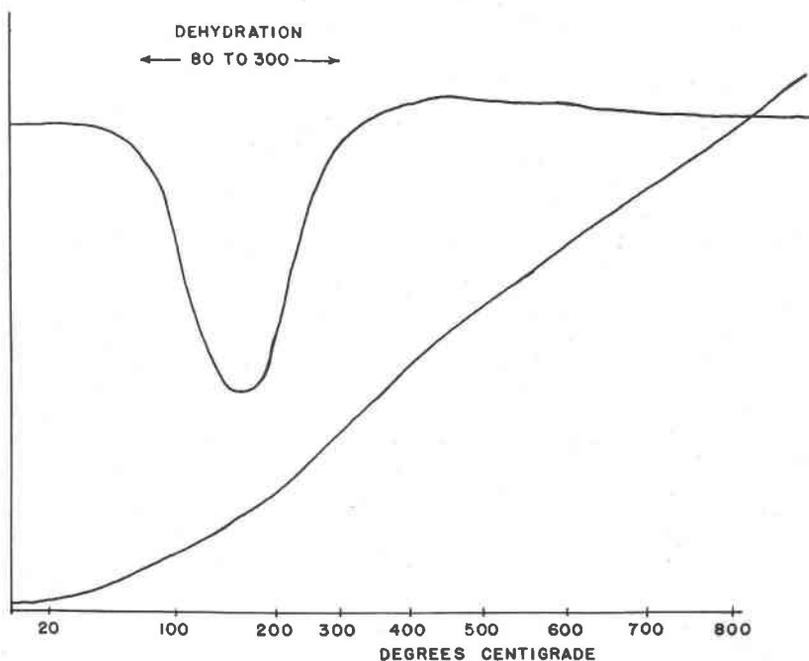


FIG. 1. Differential thermal analysis of schoderite.

room temperature and converts to a lower state of hydration, retaining approximately 12 moles of water. The lower hydrate is termed "metaschoderite," and usually occurs in samples exposed to the air for several days. "Metaschoderite" may rehydrate back to the fully hydrated schoderite on contact with water, or dehydrate further on heating above 100° C. to a virtually amorphous residue. Differential thermal analyses (Fig. 1) show only one broad endothermic reaction associated with dehydration, beginning near 100° C. and extending to nearly 300° C. Phase changes between hydration states could not be distinguished from DTA records.

PHYSICAL AND OPTICAL PROPERTIES

Schoderite is yellowish orange in color and relatively soft with a hardness of about 2 (Mohs scale). A specific gravity of 1.88 was determined on microcrystalline aggregates of schoderite.¹

Schoderite may form by nucleation within amorphous phosphatic gels or by crystallization directly from solution along fracture surfaces in chert. Nucleation from gels results in spherulitic to prismatic crystals elongated parallel to the *c*-axis. Larger crystals, 20 to 50 microns in length, may crystallize directly from solution, and are bladed to scaly in habit (Fig. 2), and tabular parallel to (010).

The two hydration states are both monoclinic, probably of the prismatic class, and readily distinguished from one another by optical properties and *x*-ray diffraction patterns. Optical properties are given in Table III. Indices of refraction and optical angles vary on dehydration, increasing from schoderite to metaschoderite. Both forms are biaxial positive, but differ in orientation of the indicatrix (Fig. 3) with the optic plane parallel to 010 in schoderite, and normal to 010 in metaschoderite.

X-RAY DIFFRACTION DATA

Crystals of schoderite were too small for single crystal manipulation, and unit cell data were necessarily computed from *x*-ray powder data by means of the Hesse-Lipson method of $\sin^2 \theta$ differences. Differences between $\sin^2 \theta$ values of measured *d* spacings were tabulated (Table IV) to compare their frequencies and to correlate them with pinacoidal reflections. The frequency distribution of $\sin^2 \theta$ differences are compared with low order pinacoidal reflections in Fig. 4.

Indexing of low order reflections by the Hesse-Lipson procedure was

¹ Specific gravity was determined by E. E. Anderson of the A.E.C., Grand Junction office. The determination was made on a Berman Balance by the toluene immersion method.



FIG. 2. Microcrystals of schoderite, tabular parallel to the 010 pinacoid. $\times 250$.

facilitated by the use of microscopic data and x -ray powder patterns of oriented aggregates. Microcrystals of schoderite show preferred orientation in slide mounts lying on their 010 pinacoid. X -ray powder patterns of

TABLE III. OPTICAL PROPERTIES OF SCHODERITE AND METASCHODERITE

Schoderite— $(2Al_2O_3 \cdot V_2O_5 \cdot P_2O_5 \cdot 16H_2O)$	
α	1.542
β	1.548
γ	1.566
$(+)$ $2V$	$= 61^\circ$
$Z \wedge C$	$= +29^\circ$
Optic plane parallel to 010.	
Metaschoderite— $(2Al_2O_3 \cdot V_2O_5 \cdot P_2O_5 \cdot 12H_2O)$	
α	1.598
β	1.604
γ	1.626
$(+)$ $2V$	$= 56^\circ$
$Y \wedge C$	$= -20^\circ$
Optic plane and Z normal to 010.	

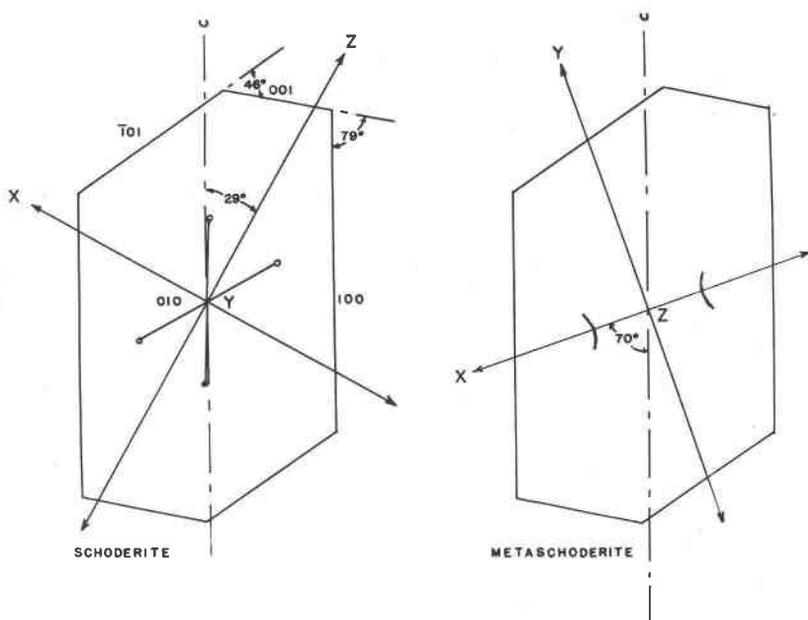


FIG. 3. Optical orientation diagrams of schoderite and metaschoderite.

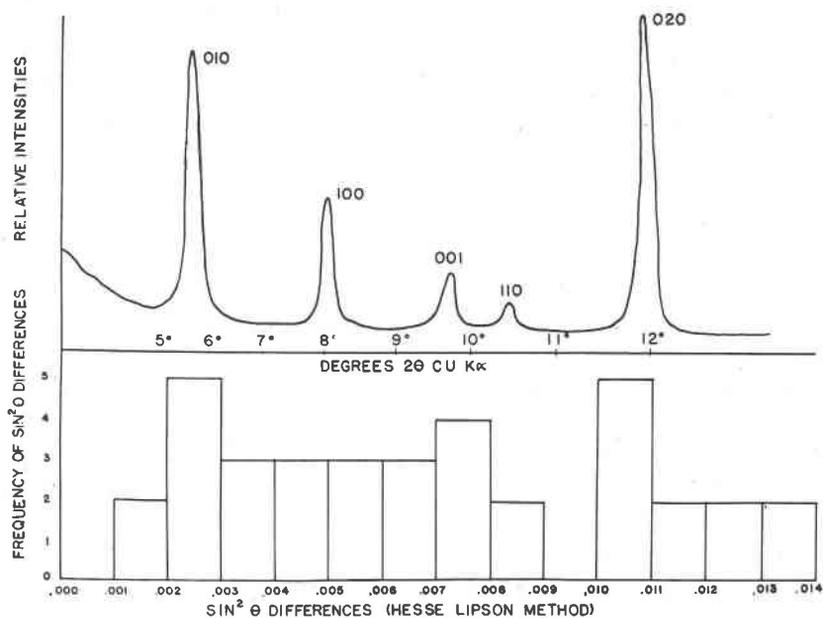


FIG. 4. Correlations of frequencies of $\sin^2\theta$ differences with x-ray reflections of metaschoderite.

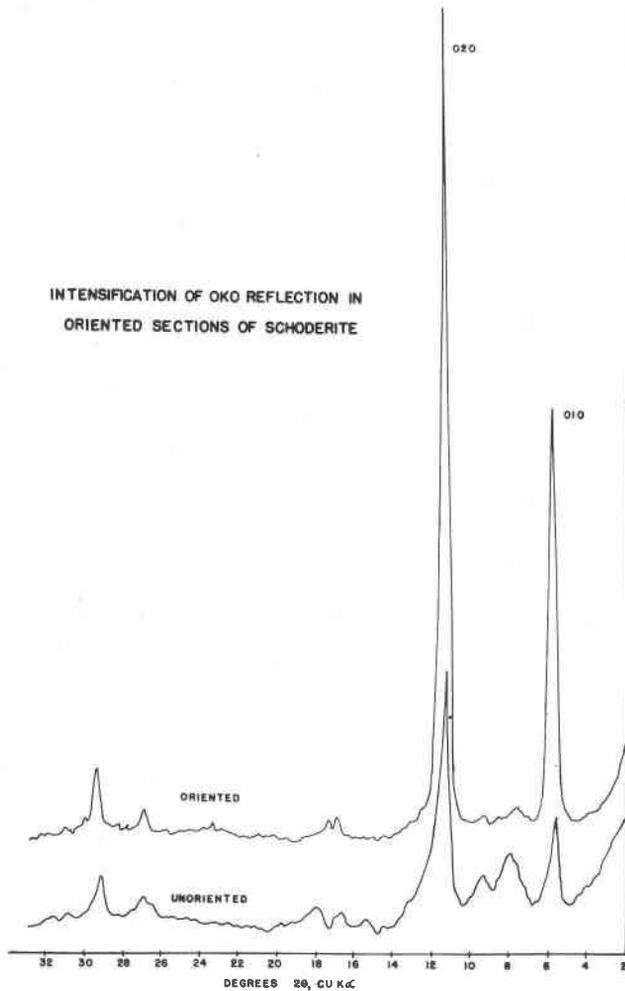
TABLE IV. DIFFERENCES BETWEEN $\sin^2 \theta$ VALUES (HESSE-LIPSON METHOD)¹

No.	<i>d</i>	2θ	Sin ² θ	1	2	3	4	5	6	7	8	9	10	11	12
1	14.9	5.9°	0.0027	—	—	—	—	—	—	—	—	—	—	—	—
2	11.1	8.0°	0.0049	0.0022	—	—	—	—	—	—	—	—	—	—	—
3	9.6	9.2°	0.0067	0.0040	0.0018	—	—	—	—	—	—	—	—	—	—
4	8.6	10.3°	0.0080	0.0053	0.0031	0.0013	—	—	—	—	—	—	—	—	—
5	7.5	11.8°	0.0106	0.0079	0.0057	0.0039	0.0026	—	—	—	—	—	—	—	—
6	6.8	13.0°	0.0128	0.0101	0.0079	0.0061	0.0048	0.0022	—	—	—	—	—	—	—
7	5.68	15.6°	0.0184	0.0157	0.0135	0.0117	0.0104	0.0078	0.0056	—	—	—	—	—	—
8	5.30	16.7°	0.0210	0.0183	0.0161	0.0143	0.0130	0.0104	0.0082	0.0026	—	—	—	—	—
9	4.92	18.0°	0.0245	0.0218	0.0196	0.0178	0.0165	0.0139	0.0117	0.0061	0.0035	—	—	—	—
10	3.28	27.2°	0.0553	0.0526	0.0504	0.0486	0.0473	0.0447	0.0425	0.0369	0.0343	0.0308	—	—	—
11	3.02	29.6°	0.0653	0.0626	0.0604	0.0586	0.0573	0.0547	0.0525	0.0469	0.0443	0.0408	0.0100	—	—
12	2.86	31.2°	0.0723	0.0696	0.0674	0.0656	0.0643	0.0617	0.0595	0.0539	0.0513	0.0478	0.0170	0.0070	—
13	1.90	47.8°	0.1614	0.1614	0.1592	0.1574	0.1561	0.1535	0.1513	0.1457	0.1431	0.1396	0.1088	0.0988	0.0918

¹ A method of indexing powder patterns of orthorhombic crystals described by Hesse (1958) and Lipson (1959). The method may also be applied to the indexing of low order reflections of some monoclinic crystals.

TABLE V. UNIT CELL DIMENSIONS OF SCHODERITE AND METASCHODERITE

Mineral	Cell Dimensions				Cell Volume	Space Group
	<i>a</i>	<i>b</i>	<i>c</i>	β		
Schoderite, $2\text{Al}_2\text{O}_3 \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5 \cdot 16\text{H}_2\text{O}$	11.4	15.8	9.2	79°	1624 \AA^3	Probably $P 2/m?$
Metaschoderite, $2\text{Al}_2\text{O}_3 \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5 \cdot 12\text{H}_2\text{O}$	11.4	14.9	9.2	79°	1530 \AA^3	Probably $P 2/m?$

FIG. 5. Intensification of $0k0$ reflections in powder patterns of oriented schoderite.

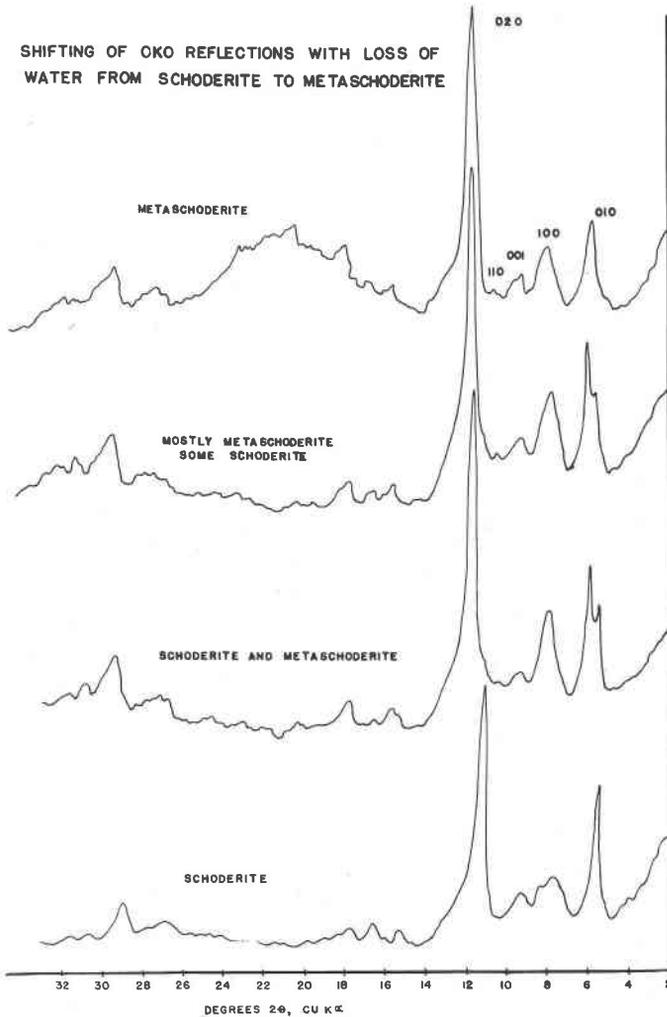


Fig. 6. X-ray diffraction patterns of different hydration states.

oriented aggregates accordingly display intensification of 010 and 020 reflections relative to other reflections (Fig. 5).

A β angle of 79° was estimated from crystal measurements of the interfacial angle $001 \wedge 100$, and checked by trial and error manipulation of unindexed $h0l$ and hkl reflections. The estimated angle was used to calculate a and c values from the Hesse-Lipson equation. Unit cell data for schoderite and metaschoderite are compared in Table V, and differ only by the smaller b in the lower hydrate. Shrinkage of the b -

TABLE VI. COMPARISON OF CALCULATED AND MEASURED *d* SPACINGS

Metaschoderite				Schoderite			
Indices	Measured <i>d</i>	I	Calculated <i>d</i>	Indices	Measured <i>d</i>	I	Calculated <i>d</i>
010	14.9	60	14.9	010	15.8	40	15.8
100	11.1	40	11.2	100	11.1	20	11.2
001	9.6	15	9.6	001	9.6	10	9.6
110	8.6	6	8.8		—	—	—
020	7.5	100	7.5	020	7.9	100	7.8
101	6.8	4	6.6	101	6.8	8	6.6
200	5.68	8	5.57	200	5.68	8	5.57
021	5.30	5	5.21	021	5.31	5	5.36
030	4.92	10	4.98	030	5.12	7	5.24
202(?)	3.28	4	3.23	202(?)	3.34	6	3.23
003	3.02	20	3.02	003	3.06	15	3.02
?	2.86	5	—	?	2.86	5	—
?	1.90	4	—	?	1.90	4	—

axis with dehydration is illustrated in *x*-ray patterns (Fig. 6), where 010 and 020 spacings shift to smaller values with loss of water in the transition of schoderite to metaschoderite. Removable water appears to be contained between 010 sheets that remain intact and undergo shrinkage along the *b*-*axis* on dehydration. Values of *a* and *c* in the 010 sheets are unaffected by changes in hydration state, and the β angle remains unchanged.

X-ray patterns are partially indexed, and interplanar spacings computed from unit cell data. Computed values agree closely with measured interplanar spacings (Table VI).

DISCUSSION OF PHOSPHOVANADATE COMPOUNDS

It is suggested that schoderite may represent not only a new mineral species, but possibly a new class of naturally occurring phosphovanadates. The mineral sincosite, $\text{CaV}_2\text{O}_2(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$, appears to be a close analogue of schoderite, but contains vanadium as the reduced V_2O_4 instead of pentavalent V_2O_5 (Schaller, 1924). Small amounts of vanadium (up to 0.32% V_2O_5) are also reported in the phosphate mineral, variscite, by Schaller (1912). A new vanadium mineral, rusakovite, a hydrated iron vanadate, described by Ankinovich (1960), contains iron and vanadium which are partly replaced by aluminum and phosphate, respectively. The

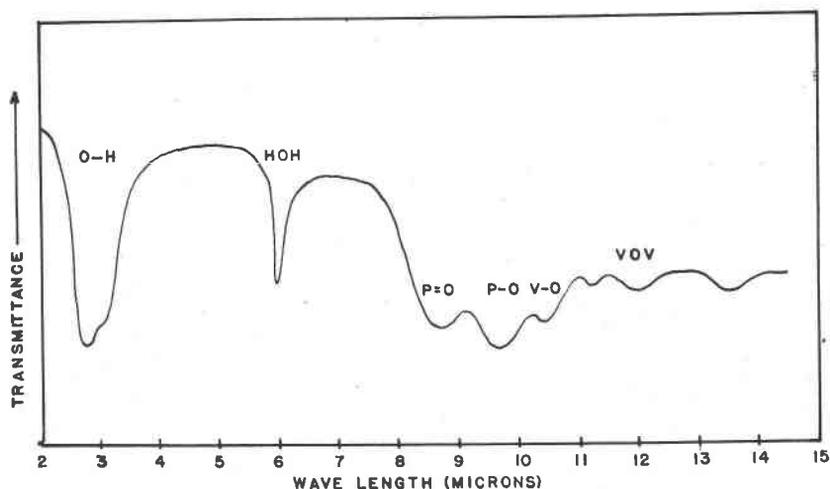
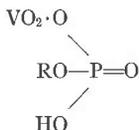


FIG. 7. Infrared spectra of schoderite.

formula of the mineral may be given as $(\text{Fe, Al})_6[(\text{V, P})\text{O}_4]_2(\text{OH})_9$, which resembles somewhat the formula for schoderite.

A number of synthetic yellow phosphovanadates has been prepared and reported by different inorganic chemists in past years, and are summarized in Mellor's *Treatise on Inorganic and Theoretical Chemistry*, Vol. IX. This group of artificial compounds termed "luteovanatophosphates" (from *Luteus*, yellow), have a 1 to 1 molar ratio of V_2O_5 to P_2O_5 , similar to schoderite, and bear a striking resemblance to the mineral. According to one investigator, Friedheim (1894), the luteo-compounds are salts in which the vanadium acts as a base towards the stronger phosphoric acid. The structural formula suggested by Friedheim is



where R represents univalent ions. In the case of schoderite, the RO may be substituted by R_2O_3 for aluminum and iron.

The structural relationship of vanadium and phosphorus derived before the turn of the century by Friedheim was found to be in apparent agreement with types of bonding inferred from infrared absorption spectra. Infrared absorption spectra were obtained with a Model 21 Perkin-

Elmer spectrophotometer, using KBr pellets. The broad absorption bands corresponding to the P=O and P-O stretching bands occur near 8.5 and 9.8 μ , respectively, and the V-O stretching band appears at about 10.4 μ (Fig. 7). Broader bands near 12 and 14.4 microns may correspond to the V-O-V and P-O-P bending modes. Hydroxyl and water bands appear in the spectra near 2.9 and 6.1 microns, respectively. The intensity of the OH relative to the H-O-H absorption, and the skewed shape of the O-H band toward longer wave lengths suggest some attachment of hydroxyl groups to the heavier elements, probably phosphorus as indicated by Friedheim's formula.

A limited number of samples of schoderite are available to other investigators for comparative study.

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