Schoderite, a new locality and a redescription

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Abstract

Schoderite has hitherto been known from only one locality, near Eureka, Nevada. Recognition of schoderite of better quality in the ores of the Wilson Springs vanadium deposit, Garland County, Arkansas, makes possible a redescription with improved values of most of the physical constants. The formula of schoderite is confirmed to be $Al_2(PO_4)(VO_4) \cdot 8H_2O$. Schoderite is monoclinic, diffraction symbol $P2_1/*$, $a = 16.26$, $b = 30.60$, $c = 12.55A$, $\beta = 91.77(8)°$; density (obs.) 1.92, (calc.) 1.931; $Z = 18$. Schoderite is biaxial negative, $\alpha = 1.560(1)$, $\beta = 1.563(1)$, $\gamma = 1.565(1)$, $2V = 42(3)°$, Y deep yellow, Z yellow, X paler yellow; X parallel b, $Y \wedge c = 26(5)°$ in obtuse angle β. Upon moderate heating (27–39°C) schoderite loses $2H_2O$ per formula unit, and the spacing of (020) is reduced from 15.30A to 12.62A. Upon immersion in water the loss is quickly regained, and d(020) returns to its initial value. Upon heating to somewhat higher temperatures, schoderite becomes X-ray amorphous but eventually (at least at *ca.* 700°C) recrystallizes to an unidentified phase or phases.

Introduction

Schoderite, $Al_2(PO_4)(VO_4) \cdot 8H_2O$[1], was named and described by D. M. Hausen (1962) from lower paleozoic phosphatic cherts near Eureka, Nevada, where it occurs as yellowish-orange microcrystalline coatings. In 1976 Charles Milton recognized as schoderite material received from Don Owens, Union Carbide geologist at the Wilson Springs (formerly known as Potash Sulfur Springs, Arkansas) vanadium mine, about six miles west of the Magnet Cove intrusive complex. These specimens, with type material from the original Nevada locality supplied by D. M. Hausen, were referred by Milton to the writer for further examination.

Hollingsworth (1967) describes the vanadium ore as associated with the Potash Sulfur Springs complex, which intruded folded and faulted Paleozoic rocks, and as occurring near the contact of the alkalic rocks and the intruded sedimentary rocks. It contains about one percent V_2O_5; montroseite (V,Fe)O(OH), fervanite $Fe_4(VO_4)_4 \cdot 5H_2O$, and hewettite $CaV_6O_{16} \cdot 9H_2O$ have been noted.

Milton (personal communication, 1978) notes that the schoderite occurs in a clayey matrix, which is more or less similar to the matrix or host rock of other vanadium minerals in the ore, usually includes crystals of apatite, K-feldspar (sanidine), and in lesser amount sphene with or without rutile–anatase, and sometimes quartz. The schoderite-bearing ore came from open cuts, which are now under water.

Material

Material from the Arkansas locality available for examination consisted of (1) three lots of broken tiny clusters and loose flakes of schoderite, received at different times, with a total weight of a few milligrams, and (2) three small pieces of matrix with a total weight of 9 grams. These pieces of matrix consist mostly of ragged quartz and unidentified grayish fine-grained material. Sparsely implanted in reentrants or open spaces on each of the matrix pieces are clusters or rosettes of yellow or orange-yellow schoderite. A few of these clusters are almost spherical, the largest being *ca.* one mm in diameter. In one spot three such clusters were in juxtaposition, and it was possible to detach half of the triplet by splitting along the schoderite cleavage through the middle of

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[1] Hausen (1962) had given the composition or formula in the oxide form, "$2Al_2O_3 \cdot V_2O_5 \cdot P_2O_5 \cdot 16H_2O$."
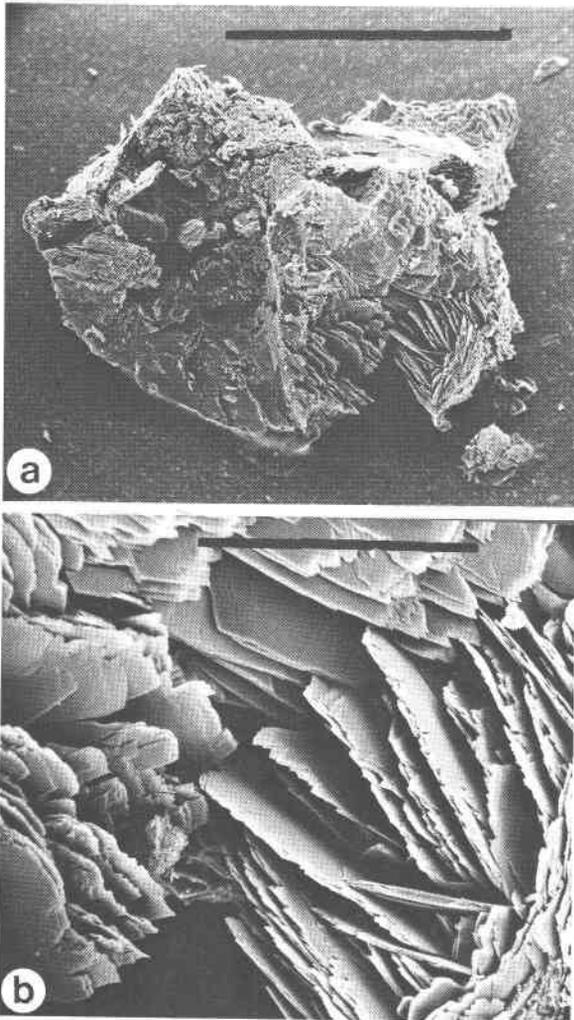
Fig. 1. Scanning electron microscope pictures of cluster of schoderite from Arkansas. (a) Overall dimensions 0.9 mm, bar length 0.5 mm. (b) Detail of lower part of cluster, bar length 0.1 mm.

the central cluster. The whole of the detached half is shown in Figure 2a. These clusters consist almost entirely of schoderite, but one SEM photograph revealed a minute, perfectly formed, quartz crystal with a maximum dimension of 0.03 mm among the schoderite platelets, apparently crystallized together with the schoderite. Traces of quartz were also detected in X-ray "powder" patterns made from aggregates of bits of schoderite clusters. No other constituents were found in the clusters.

The Nevada material consisted of *ca.* 6 mg of impure schoderite powder plus about 80 mg of fine-grained, gray rock in several bits on some of which remnants of schoderite coatings were visible. Though

a few bits of detached coating are up to one mm long, individual crystals making up the coating mostly do not exceed 0.1 mm in dimension.

Confirmation of identification

The identity of the yellow vanadium mineral occurring as aggregates of thin platelets at the vanadium mine of the Union Carbide Corporation in Arkansas, which had been recognized as schoderite by Dr. Milton, was confirmed by direct comparison of "powder" diffraction photographs with those obtained from schoderite from type locality in Nevada (Hausen, 1962). Due to the scanty supply of material from each locality, the "powder" patterns were prepared from bits of clusters or rosettes of crystallites mounted together at the tip of a glass or horse hair fiber, allowing all of the precious material to be preserved. As a result of this procedure some orientation effects were readily visible in the diffraction patterns.
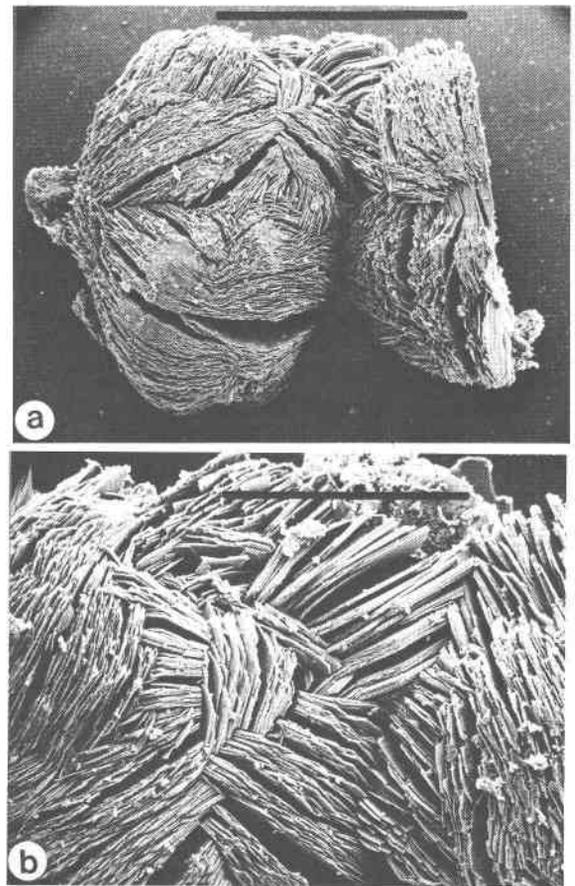

Fig. 2. (a) Adjoining spherulites of schoderite from Arkansas; total width 1.0 mm, bar length 0.5 mm. (b) Junction of the spherulites, bar length 0.2 mm.

However, close scrutiny of a total of seventeen such patterns gave assurance of the identification. The sequence of four or five strong lines in the very low angle region (2θ 11.5° or less for Cu$K\alpha$) is highly characteristic and invariably seen in all of the patterns. Later much better Guinier-Hägg powder patterns were obtained by Dr. H. T. Evans, Jr. (see below).

Scanning electron microscopy

Clusters or sheaves of schoderite from Arkansas are partly irregular or open aggregates (Fig. 1). The individual platelets within such aggregates are but a few hundredths of a millimeter or less in thickness. Spherulites or rosettes of schoderite range up to about 1 mm in diameter, and several such spherulites may be in contact. Figure 2 shows the junction of two spherulites, part of a group of three, broken apart on the cleavage of the platelets at the middle of

Fig. 4. SEM photograph of schoderite from near Eureka, Nevada. Semiquantitative analysis of this specimen in the scanning electron microscope shows that the poorly crystallized or apparently "amorphous" material does not differ from the well-formed crystals in composition. Length of bar 0.2 mm.
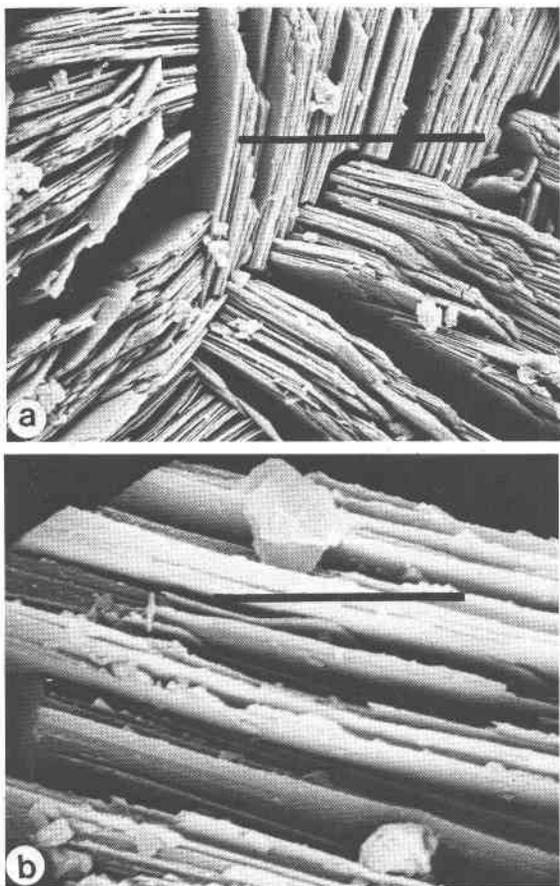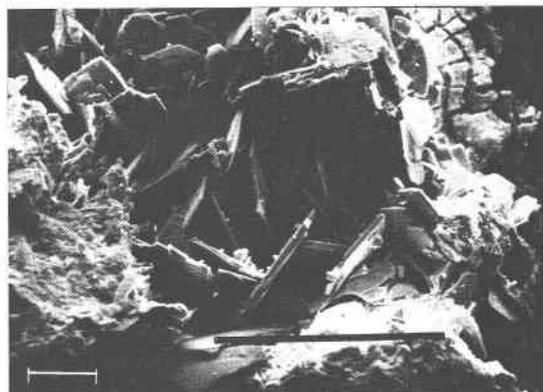

Fig. 3. (a) Finer detail of junction seen in Fig. 2b; length of bar 0.05 mm. (b) Thin, diverging platelets from right central part of Fig. 3a; length of bar 0.005 mm.

the central spherulite. At low magnification such spherulites appear closely packed, but they are composed of many tiny packets of diverging platelets. Truly single crystals are rarely separable. Divergence from parallelism of opposite cleavage surfaces cannot be measured by SEM observations (Fig. 3) but was found to be of the order of 3° on the best mounted "crystals," as measured in immersion at 100×.

Figure 4 shows a bit of schoderite from the Nevada type locality, only a part of which has recognizable crystals, somewhat similar to those from Arkansas but not in such tight packets.

X-ray crystallography

The symmetry and cell dimensions initially reported for schoderite (Hausen, 1962, p. 640–646) were based on interpretation of powder diffraction data by the Hesse-Lipson method because "crystals of schoderite were too small for single-crystal manipulation." A dozen "crystals" of schoderite from Arkansas were mounted for X-ray diffraction and determination of optical properties, as well as such goniometry as was possible on a few of them. Useful Weissenberg and precession patterns were obtained from several of these "crystals," permitting determination of the diffraction symbol and the lattice dimensions. In agreement with Hausen (1962) it was found that schoderite is monoclinic with b normal to the cleavage and the plane of the platelets. Also, Hausen recognized that two of the stronger lines of the powder pattern at 15.8 and 7.9 (now corrected to 15.30 and 7.65A) correspond to reflections from structural planes parallel to the cleavage. Beyond this
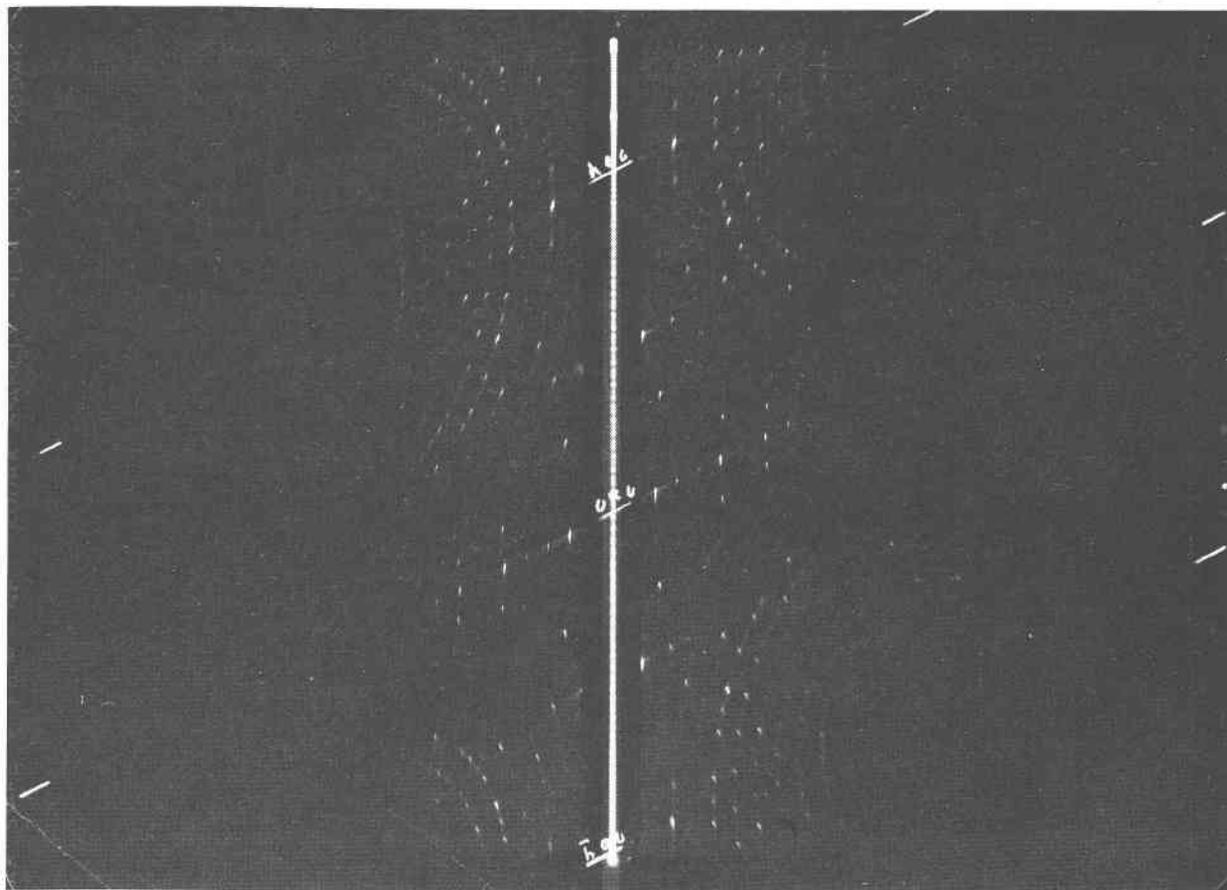
Fig. 5. $hk0$ Weissenberg pattern of schoderite from Arkansas. Notice diffuseness of spots with k even and slight streaking in b^* direction. There are no diffraction spots at 2θ angles greater than 60°.

there is no agreement between the cell determined from single-crystal data and that derived by Hausen.

Even the best single-crystal patterns show a rapid drop of intensity with increase in 2θ (Fig. 5), attribut-

able to strong thermal motion correlated with weak bonding and softness. Only a few spots are discernible in the region with 2θ above 50° and none at all in the region 2θ over 100° for Cu radiation. Accordingly, high precision cannot be attained. The cell dimensions determined from Weissenberg and precession patterns for Arkansas schoderite, as well as the cell dimensions subsequently obtained by Dr. H. T. Evans from the Guinier-Hägg powder pattern mentioned above, are shown in Table 1 together with those reported by Hausen (1962, Table V) for the type material. The estimated errors for the values obtained by Dr. Evans are substantially less than those pertaining to the values from single-crystal data. However, the somewhat larger cell dimensions, especially the larger b of the single crystal data, may be due to a real difference in cell dimensions connected with difference in the state of hydration. The cell found is one that might be expected for a mineral with a sheet structure parallel to (010). Streaking of diffraction spots on Weissenberg and precession pat-

Table 1. Unit-cell dimensions of schoderite

	Nevada #	Arkansas ##	Arkansas ###
a	11.4	16.34(8) Å	16.26(1) Å
b	15.8	30.74(12)	30.60(4)
c	9.2	12.58(8)	12.55(1)
β	79°	92°00'(±30')	91.77(8)°
cell volume	1624 Å³	6315 Å³	6241 Å³
Space Group	"Probably $P2/m$?"	Diffraction symbol $P2_1/*$	

\# From Hausen (1962, Table V)

\#\# From Weissenberg and precession patterns, Cu-radiation; see text.

\#\#\# From Guinier-Hägg powder data, Cr-Kα_1, compare table 2.

Table 2. X-ray powder patterns of schoderite

Arkansas #				Nevada ##			
d(obs)	I	hkl	d(calc)	d(obs)	I	hkl	d(calc)
16.33	100	100*	16.25				
15.34	70	020*	15.31	15.8	40	010	15.8
11.63	9	011*	11.60				
11.15	18	120*	11.14	11.1	20	100	11.2
				9.6	10	001	9.6
7.64	35	040*	7.65	7.9	100	020	7.8
6.15	9	012,221		6.8	8	101	6.6
5.686	25	122*	5.688	5.68	8	200	5.57
5.410	25	300*	5.417				
5.346	1	032,310		5.31	5	021	5.36
5.038	18	$\overline{2}$02*	5.041	5.12	7	030	5.24
4.985	12	$\overline{2}$12*	4.974				
4.511	1						
4.165	6	$\overline{3}$02	4.164				
3.927	3	420*	3.927				
3.660	5						
3.643	5						
3.381	5						
3.345	18			3.34	6	202?	3.23
3.305	9						
3.285	9						
3.230	9						
3.135	3						
3.097	2						
3.058	5			3.06	15	003	3.02
3.029	3						
3.003	3						
2.958	3						
2.902	3						
2.893	35			2.86	5	?	
2.843	25						
18 more lines to 1.67							

Data provided by Dr. H.T. Evans, Jr., Guinier-Hägg method, CrKα₁ radiation.
* Indicates 10 lines used for least squares determination of cell constants. See text.

Data from Hausen (1962, Table VI).

be 1.92±0.02, only roughly checked by Berman balance due to the dearth and nature of the material. Hausen (1962) had reported 1.88 as the density of schoderite from Nevada, determined by Berman balance on "microcrystalline aggregates." Assuming the ideal composition, $Al_2(PO_4)(VO_4) \cdot 8H_2O$, and 18 formula units per cell, the calculated density is 1.931.

Qualitative analysis of both the Arkansas and Nevada schoderite in connection with SEM examination showed that the two are essentially identical in composition, and also that the poorly crystalline material visible in Figure 4 does not differ in composition from the well-formed crystals of schoderite. Subsequently two electron microprobe analyses of selected clean crystals from Arkansas yielded the results shown in Table 3, confirming the formula proposed by Hausen (1962), which is also supported by the fair agreement between calculated and measured density.

The cell contains 360 atoms, excluding hydrogen. Most, if not all, of these atoms are in "general" positions so that the number of positional parameters required to describe the structure would be of the order of 540, not counting thermal parameters and hydrogen parameters, if the space group is $P2_1$ or 270 if $P2_1/m$. As can be seen from Figure 5, probably no more than a very few hundred reasonably intense and well-defined spots can be observed on single-crystal diffraction patterns. It follows that the crystal structure cannot be fully determined with X-ray diffraction data obtained from crystals of the quality so far available.

Morphology and cleavage

Crystals mounted on goniometer heads transferable between X-ray cameras, a Stoe 2-circle go-

terns in the b* direction indicates stacking disorder of the sheets. Additionally all hk0's with k even are diffuse, and those with $k = 2$ and h less than 8 are absent.

The record of the Guinier-Hägg powder pattern is shown in Table 2, with calculated spacings based on the cell dimensions derived from this pattern together with the powder data of Hausen (1962, Table VI). Only those calculated spacings are given which correspond to observed lines, and indexing is carried only to $d = 3.927$. Even to this point there are 140 calculated spacings, and superposition precludes meaningful indexing beyond.

Density and cell content

The density of schoderite from Arkansas was determined by the method of Bloss (1961, p. 63–64) to

Table 3. Chemical analyses of schoderite

	Nevada #	Arkansas ##		$Al_2(PO_4)(VO_4) \cdot 8H_2O$
Al_2O_3	23.8	25.67	24.65	24.98
Fe_2O_3	0.27	0.47	0.16	
V_2O_5	24.6	22.37	21.96	22.29
P_2O_5	17.4	21.08	n.d.	17.40
H_2O-	26.6	)		
		) 30.41 (diff.)		35.33
H_2O+	7.5	)		
Total	100.27			100.00

\# J.P. Moore, analyst; from Hausen (1962, Table II)

\## R. Reeder, analyst; by ARL microprobe (n.d. = not determined)

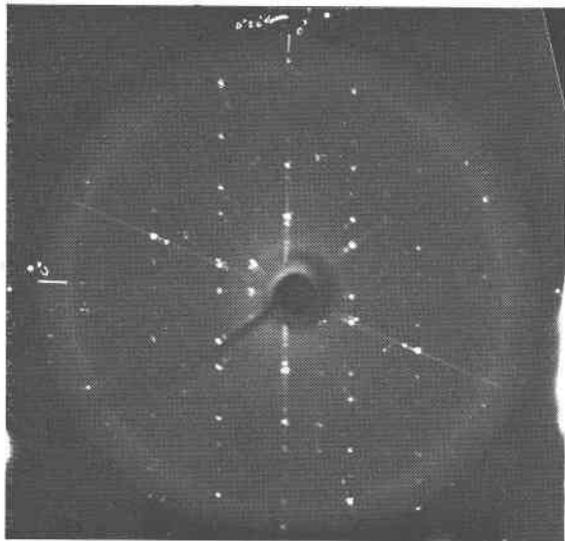See last paragraph of text for partial estimation of H_2O by physical methods.

Fig. 6. *h0l* precession pattern of schoderite from Arkansas. Precession angle 25°, Cu radiation, no filter, beam normal to cleavage. *β*, 92°, can be read directly from pattern.

niometer, and a device (Jones, 1960) for examining mounted single crystals in immersion in polarized light by orthoscopy or conoscopy, were used for X-ray, goniometric, and optical observations, assuring proper correlation. All crystals were aligned as far as possible by 2-circle goniometer. On a few of these crystals some narrow faces at the edges, in addition to the prominent {010} cleavage surfaces, were roughly measurable. By comparison with diffraction patterns, especially *h0l* precession patterns such as that shown in Figure 6, it was possible to identify the forms {100}, {001}, {101}, {$\bar{1}$01}, and {$\bar{2}$03}. Faint suggestions of *hkl* or $\bar{h}kl$ faces could not be assigned indices with any assurance. In addition to the prominent {010} cleavage, there may also be one or more transverse cleavages or partings, possibly one corresponding to {$\bar{2}$03}. No sure correspondence can be established between the minor forms just mentioned and the {*h0l*} forms shown on Hausen's Figure 3, as no basis for his reference system was found in the present work.

Optical properties

The optical properties of schoderite as reported by Hausen (1962, Table II) and as newly determined on mounted single crystals from Arkansas are shown in Table 4. Except for the correspondence of the *γ* values, there is no agreement. This may be attributable to the difficulty of observations on the Nevada material and the lack of control by correlated X-ray diffraction. In the present study all optical properties

were determined on single crystals for which the reference directions were established by X-rays, and *β* and *γ* were checked by observations on immersed loose plates in the usual manner. 2*V* was directly measured by conoscopy on crystals adjusted to rotate on *Y*. This involved preliminary X-ray and optical observations on the same crystal in each case. The very low partial birefringence ($\gamma - \beta = 0.002$) of crystals viewed normal to (010) combined with the yellow absorption colors gives rise to peculiar interference colors, gray + yellow, which may give the impression of being comparable to anomalous dispersion colors. No marked dispersion of the optic axes or the indicatrix was noted, and the general absence of color fringes at the edges when crystals are immersed in matching liquids indicates that their dispersion is of the same order as that of the immersion liquids, $nF - nC = 0.0182$. Figure 7 shows a sketch of the optical orientation of schoderite and two crystals used for the determination. As the crystals in this orientation furnish an acute bisectrix interference figure, there can be no question of the orientation, even though it cannot be determined with great precision because of the low birefringence of schoderite. The sketch is somewhat similar to that for schoderite in Figure 3 of Hausen (1962), but there is no correspondence in the designation of the three principal optic directions.

Lower hydration states—"metaschoderite"

Hausen (1962, p. 639–640) reported that schoderite "loses water at room temperature and converts to a lower state of hydration, retaining approximately 12

Table 4. Optical properties of schoderite

Refractive indices	Arkansas (this study)	Nevada (after Hausen, 1962, table III)
α	1.560(1)	1.542
β	1.563(1)	1.548
γ	1.565(1)	1.566
2V	(−) 42(3)°	(+) 61°
Optic plane	normal to (010)	parallel to (010)
	X parallel *b*	
	YΛ*c* = 26±5° in obtuse angle β	
Pleochroism	Y deep yellow Z yellow X paler yellow	

moles of water." He referred to the lower hydrate as "metaschoderite" and reported different optical properties, powder pattern, and cell dimensions for it. Under the temperature (*ca.* 21°C) and humidity conditions prevailing in the laboratory at Berkeley, no evidence of dehydration was observed during several months of work with schoderite crystals and aggregates from Arkansas.

Dr. H. T. Evans, Jr. kindly provided the following report of observations on Arkansas schoderite: "When schoderite is heated in the Guinier-Lenne ap-

Fig. 8. Schoderite from Arkansas; 0k0 loci on three Weissenberg films, Cu-radiation, no filter. Left, ×1,#12, untreated; center, ×1, #10, heated to 31°C, partly dehydrated; right, ×1, #10, rehydrated.

paratus, the lines generally shift to higher angles up to 55°C, where decomposition to an amorphous state occurs. At about 27°C there is an abrupt change of phase, no doubt to a lower hydrate (the initial specimen was moistened with water at the start of the heating run). There appears to be some relationship between the low and high phases, but detailed interpretation must be deferred until a structure analysis can be carried out. The observations nevertheless confirm Hausen's postulation of the existence of 'metaschoderite.'

"The role of water is obviously at least partly zeolitic. The Guinier-Lenne pattern indicates that decomposition at 55° is accompanied by considerable loss of water, but some may be retained up to as high as 350°C, where evidence of a new, poorly crystallized, probably anhydrous phase appears."

Subsequently heating experiments were carried out on several selected single crystals of Arkansas schoderite, X-ray observations being made on the crystals before and after heating and after rehydration. Upon heating to 31°C for a few hours, there is little change in color, $2V$ increases slightly, and the indices increase to about the values reported by Hausen for "metaschoderite," with β near 1.60, but birefringence remains low as in the unheated material. From single-crystal (Weissenberg and oscillation) X-ray patterns it was determined that b in the heated crystals is about 25.24A, whereas there is little if any change in a or c. Further heating of the crystals to about 40°C causes no change. Upon immersion in water at room temperature, the crystals regain their initial state of hydration; b returns to 30.74A, and the refractive indices return to their initial values. That the change is discontinuous is indicated by the discrete series of (0k0) reflection shown in Figure 8 for
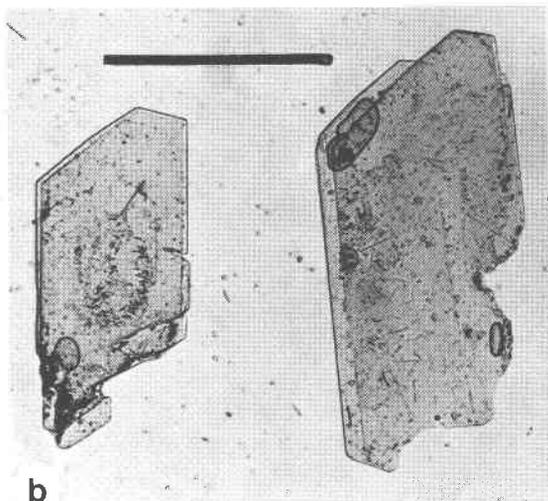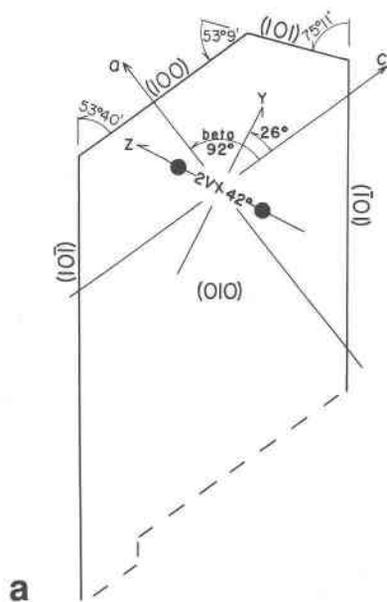

Fig. 7. (a) Sketch showing optical orientation of schoderite. (b) Two schoderite crystals from Arkansas on which sketch is based; length of bar 0.3 mm. Crystallographic directions checked by oscillation patterns on [101], [$\bar{1}$01], [001] and associated zero-layer Weissenberg patterns on crystal at right.
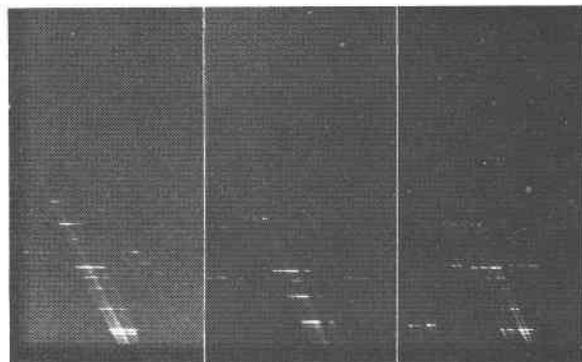
unheated, partly dehydrated and rehydrated crystals. The characteristic lines for the two states are:

	unheated or rehydrated			heated or partly dehydrated	
I	0k0	d	I	0k0	d
VS	040	7.685A	VS	040	6.310
M	060	5.123	MS	060	4.207
MW	080	3.842	S	080	3.155
S	0·10·0	3.074	VW	0·10·0	2.524
−	0·12·0	2.562	M	0·12·0	2.103
M	0·14·0	2.195	VW	0·14·0	1.803

No intermediate states were observed, but one incompletely rehydrated crystal yielded a combination of the two sets of reflections just listed.

Further heating to at least 40°C caused no more changes, but upon heating to 63°C the crystals are slightly darkened, less coherent, "X-ray amorphous" and n is increased to $ca.$ 1.65. Upon still further heating to 126°C schoderite is greatly darkened, almost black, and remains "X-ray amorphous." Upon heating 22 hours at 725°C schoderite is fully changed to a polycrystalline aggregate yielding a fine powder pattern of 30 or more lines, the most prominent of which are MS 4.36 and VS 4.11, presumably corresponding to the product of which Evans found evidence at 350°C. The newly formed phase (or phases) has not been identified.

The volume change attendant upon the shrinkage of b from 30.74 for unheated schoderite to 25.24A for moderately heated schoderite permits an estimate of the water loss attending this change. The volume change is $-1,130A^3$. In the dehydration of vermiculite with a shrinkage of $d(001)$ from 14.36 to 9.02A the loss in volume amounts to $32.5A^3$ per H_2O. This is also the volume per water molecule in ice. Assuming the same space requirements for water in schoderite, the indicated loss per cell for moderately heated schoderite is $1,130/32.5 = 34.8$ molecules of water. This is close to the expected 36 molecules, which would correspond to a change from 8 to 6 H_2O per formula unit with 18 such units per cell both in the fully hydrated and the partly dehydrated state. This result confirms the formulas proposed by Hausen for the two states.

The calculated density for crystals in the partly dehydrated state is 2.12. The value obtained by the method of Bloss for one of the heated crystals, 1.98, may be low due to partial rehydration, as suggested by the slightly low value of n, and (or) the production

of voids between thin sheets attendant upon dehydration.

All material used in this study will be placed in the National Museum of Natural History, Smithsonian Institution, Washington, D. C., under catalog number NMNH 144479.

Appendix (April 24, 1979)

A report (Zientek, M. L., A. S. Radtke and R. L. Oscarson (1979) Mineralogy of oxidized vanadiferous carbonaceous siltstone, Cockalorum Wash, Nevada. *Geol. Soc. Am. Abstracts with Programs, 11,* 137) on a new study of the locality from which Hausen (1962) obtained the first-recognized schoderite was presented several months after this paper had been accepted for publication. The report gives additional information on the occurrence and association of schoderite at the type locality as indicated by the following quotations: "The mineralogy of the multicolored fracture coatings and veins was studied... Metahewettite, $CaV_6O_{16} \cdot 3H_2O$, forms brick-red coatings which consist of aggregates of minute lath-like crystals. Fine-grained desiccated orange coatings are a combination of schoderite and metaschoderite, ... Bokite, $KAl_3Fe_6V_{26}O_{76} \cdot 30H_2O$, was tentatively identified in maroon fracture coatings. Yellow coatings are fine-grained mixtures of gypsum, clays, and minor amounts of unidentified iron vanadates and iron-phosphorous vanadates...."

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