

STUDIES OF URANIUM MINERALS (XV): SCHROECKINGERITE FROM ARGENTINA AND UTAH*

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ABSTRACT

Schroekingerite crystals have been found at Moab, Utah, and San Isidro, Argentina. They are orthorhombic pseudo-hexagonal, flattened on {001} with additional forms {010}, {110}, {014}, {012}, {011}, {021}, {041}, {118}, {114}, {112}, {111}. Unit cell dimensions are; $a_0=9.69$ Å, $b_0=16.83$, $c_0=14.26$ ($a_0:b_0:c_0=0.5758:1:0.8473$). Space group *Cmmm*. $Z=4$. Optically biaxial (-), $X=c$, $Y=b$. Argentina: $nX=1.492$, $nY=1.543$, $nZ=1.544$. $2V=10^\circ$. $G=2.550$. Utah: $nX=1.490$, $nY=1.537$, $nZ=1.538$. $2V=18^\circ$. $G=2.544$. Calculated $G=2.547$. Dehydrated over H_2SO_4 , schroekingerite goes to $NaCa_3UO_2(CO_3)_3SO_4F \cdot 4H_2O$ and becomes hexagonal with unit cell dimensions: $a_0=9.72$ Å, $c_0=11.03$ ($a:b=1:1.1348$). $Z=2$. Optically uniaxial (-). $nO=1.581$, $nE=1.532$. Measured $G=2.86$, calculated $G=2.874$.

INTRODUCTION

Schroekingerite [$NaCa_3UO_2(CO_3)_3SO_4F \cdot 10H_2O$] from two widely separated localities arrived almost simultaneously at the Harvard Mineralogical Museum early in 1953. One specimen from the Shinarump No. 3 Mine, Seven Mile Canyon near Moab, Utah, was sent by Professor J. W. Gruner. The other material, from Mina "La Soberania" San Isidro, Mendoza Province, Argentina, had been acquired by the late Mr. Samuel Gordon and was generously given to Harvard by Mrs. Gordon. Schroekingerite has previously been described from three other localities: 1. Joachimsthal, Bohemia, by Schrauf (1873); 2. Wamsutter, Wyoming, by Larsen and Gonyer (1937), and called by them *dakeite*; 3. Yavapai County, Arizona, by Axelrod *et al.* (1951). Schroekingerite from all these localities is reported to be in minute scales aggregated into globular groups (Joachimsthal), pisolites (Wyoming) and rosettes (Arizona). The only mention of individual crystals was by Schrauf who described six-sided scales.

MORPHOLOGY

The Argentine schroekingerite collected by Mr. Gordon had been carefully separated by him so that the mineral association is unknown. It is in minute scales, some aggregated into rosettes, but others are isolated transparent crystals many of which show a hexagonal outline. The maximum dimension of individual crystals is one millimeter and the thickness rarely exceeds 0.02 millimeter. Five crystals, thicker than the

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others, had been mounted on pins by Mr. Gordon for goniometric measurement. The largest of these was about 1 millimeter in diameter and 0.2 millimeter thick and showed many crystal faces. Examination of the thin hexagonal plates showed that many of them also had truncating faces.

The schroeckingerite from Utah occurs associated with gypsum in seams in a shale. Much of it is in crusts but there are many isolated crystals with hexagonal outline showing truncating faces. All but the thinnest crystals are aggregates of superimposed crystals in nearly parallel position. When viewed through the microscope, the nonparallelism of the aggregated individuals appears as though the smaller crystals, when compared to the major crystal, had been rotated slightly about the c axis and that the (001) planes were parallel (Fig. 1). With the optical goniometer one can see that there is also a nonparallelism of the plates amounting to as much as three degrees. Aggregates similar to these are found also on some of the Argentine crystals.

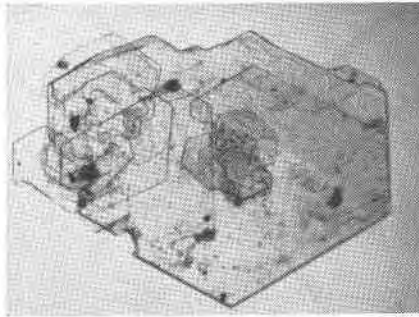


FIG. 1. Schroeckingerite, Moab, Utah. $\times 50$.

Eighteen crystals from Argentina and twenty crystals from Utah were mounted for measurement on the two-circle goniometer with the largest face (001) polar. Of these, eleven gave no reflections except from the polar face, but the others all showed two or more measurable faces. Similar form development was shown at the top and bottom of the crystals. There were no observed systematic differences in the angular measurements of the crystals from the two localities. On many crystals curved faces made it impossible to read some rho values closer than two degrees.

All the faces are arranged in vertical zones at 60° or nearly 60° to one another (Fig 2). There is no regularity in the divergence from 60° , for on some crystals all zones fall within a few minutes of 60° , whereas on others the zones may be $58\frac{1}{2}^\circ$ to $61\frac{1}{2}^\circ$ apart but without systematic ar-

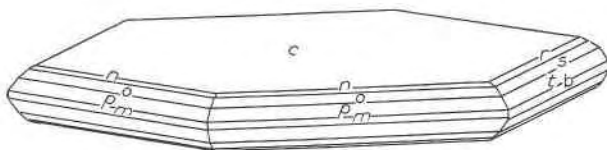


FIG. 2. Schroeckingerite, Argentina.

rangement. This may be due in part to the slight disorientation of the superimposed plates.

From the morphology alone one might conclude that schroeckingerite is hexagonal, but from other evidence it appears to be orthorhombic with a striking pseudohexagonal symmetry. All the faces fall in the hkl and $0kl$ zones, and with the poor angular readings, it is impossible to tell in which zone a face lies. Consequently, in the measured values of Table 1, the forms of the two zones having similar rho readings are grouped together and the phi readings are given as though all forms belonged in the $0kl$ zone. The principal forms are shown in Fig. 2. This drawing is a fair representation of the largest Argentine crystal but appears many times thicker than the average plate.

TABLE 1. SCHROECKINGERITE—TWO-CIRCLE MEASUREMENT

| Forms | Mean | | Range | | No. of Faces |
|----------------------------|--------|--------|-------------|---------------|--------------|
| | ϕ | ρ | ϕ | ρ | |
| <i>c</i> 001 | — | 0°00' | — — | — — | 27 |
| <i>b</i> 010, <i>m</i> 110 | 0°06' | 90 05 | 1°20'—1°10' | 89°45'—90°25' | 22 |
| <i>n</i> 114, <i>h</i> 118 | 0 06 | 11 51 | 1 20—1 10 | 11 38—12 18 | 3 |
| <i>r</i> 012, <i>n</i> 114 | 0 06 | 23 09 | 1 20—1 10 | 22 15—23 58 | 7 |
| <i>s</i> 011, <i>o</i> 112 | 0 06 | 41 02 | 1 20—1 10 | 39 50—42 55 | 43 |
| <i>t</i> 021, <i>p</i> 111 | 0 06 | 59 34 | 1 20—1 10 | 58 05—61 35 | 18 |
| <i>u</i> 041, or 221 | 0 06 | 73 30 | 1 20—1 10 | 73°30' | 1 |

Because of the wide range in the angles measured for any given form as well as the inability to distinguish forms in one zone from those in another, it is felt that axial ratios calculated from the mean values would be much less accurate than those derived from the x -ray measurements of the unit cell. The axial ratios and calculated angles in Table 2 are, therefore, based on unit cell measurements.

UNIT CELL AND SPACE GROUP

Rotation and Weissenberg x -ray photographs using copper radiation and nickel filter were taken of schroeckingerite rotating about the c

TABLE 2. ANGLE TABLE FOR SCHROECKINGERITE*

Orthorhombic; dipyramidal— $2/m\ 2/m\ 2/m$
 $a:b:c=0.5758:1:0.8473$ $p_0:q_0:r_0=1.4715:0.8473:1$
 $q_1:r_1:p_1=0.5758:0.6769:1$ $r_2:p_2:q_2=1.1802:1.7367:1$

| Forms | ϕ | $\rho=C$ | ϕ_1 | $\rho_1=A$ | ϕ_2 | $\rho_2=B$ |
|--------------|--------|----------|----------|------------|----------|------------|
| <i>c</i> 001 | | 0°00' | 0°00' | 90°00' | 90°00' | 90°00' |
| <i>b</i> 010 | 0°00' | 90°00' | 90°00' | 90°00' | | 0°00' |
| <i>m</i> 110 | 60°04' | 90°00' | 90°00' | 29°56' | 0°00' | 60°04' |
| <i>f</i> 014 | 0°00' | 11°57½' | 11°57½' | 90°00' | 90°00' | 78°02½' |
| <i>r</i> 012 | 0°00' | 22°57½' | 22°57½' | 90°00' | 90°00' | 67°02½' |
| <i>s</i> 011 | 0°00' | 40°16½' | 40°16½' | 90°00' | 90°00' | 49°43½' |
| <i>i</i> 021 | 0°00' | 59°27½' | 59°27½' | 90°00' | 90°00' | 30°32½' |
| <i>u</i> 041 | 0°00' | 74°33½' | 73°33½' | 90°00' | 90°00' | 16°26½' |
| <i>h</i> 118 | 60°04' | 11°59' | 6°03' | 79°36½' | 79°34½' | 84°03' |
| <i>n</i> 114 | 60°04' | 23°00' | 11°57½' | 68°25' | 69°48' | 77°46' |
| <i>o</i> 112 | 60°04' | 40°20' | 22°57½' | 55°53' | 53°39½' | 71°09½' |
| <i>p</i> 111 | 60°04' | 59°30½' | 40°16½' | 41°41½' | 34°12' | 64°32' |

* Angles in Table 2 calculated by Miss Mary E. Mrose.

and the *a* axes. The corresponding photographs of crystals from Utah and Argentina proved to be identical. Even by selecting the smallest and apparently most perfect crystals, it was necessary to take photographs of several crystals before satisfactory results were obtained. The slightly disoriented superimposed crystals give rise to spurious spots and complicate the interpretation of the photographs.

A rotation photograph and zero, first, second, and third layer-line Weissenberg photographs were taken rotating around *c*, and a rotation, zero, first and second layer-line Weissenberg photographs were taken rotating around *a*. From measurements of these photographs $a_0=9.69$ Å, $b_0=16.83$, $c_0=14.26$, giving the ratios $a_0:b_0:c_0=0.5758:1:0.8473$.

The extinctions on the Weissenberg photographs show that schroeckingerite has a *C* centered lattice with space group either $C_{2v}^{11}-Cmmm$ or $D_{2h}^{19}-Cmmm$. The crystals are too small to determine whether or not they are piezoelectric and thus give a unique solution. However, if the crystal class is orthorhombic-dipyramidal as indicated by the morphology, the space group is $Cmmm$.

The chemical formula for schroeckingerite determined by Jaffe, Sherwood and Peterson (1948) from an analysis of material from Wyoming was found to be $\text{NaCa}_3\text{UO}_2(\text{CO}_3)_3\text{SO}_4\text{F}\cdot 10\text{H}_2\text{O}$. The same formula

was arrived at independently by Axelrod *et al.* (1951) from an analysis of schroeckingerite from Arizona. Assuming this formula to be correct, the molecular weight is $M = 888.56$. From the unit cell volume, $2322A^3$, and the average measured specific gravity, 2.547, the molecular weight of the cell contents is calculated as $M_0 = 3568$. These figures show that there are 4 formula weights of schroeckingerite per unit cell.

PHYSICAL AND OPTICAL PROPERTIES

Schroeckingerite from both Argentina and Utah have physical properties similar to those of the mineral as described from other localities. The chief difference lies in the specific gravity. The specific gravity of schroeckingerite from Argentina ($G = 2.550$) and Utah ($G = 2.544$), as determined by suspension in a mixture of bromoform and acetone, is slightly higher than that from Wyoming ($G = 2.51$) and Arizona ($G = 2.5$). These higher values are undoubtedly the result of using single crystals rather than aggregates as found in Wyoming and Arizona.

The optical properties of schroeckingerite from the two new localities, with those of the Wyoming material given for comparison, are summarized in Table 3.

TABLE 3. OPTICAL PROPERTIES OF SCHROECKINGERITE

| | Argentina n_{Na} | Utah n_{Na} | Wyoming n |
|-----------------------------|--|--|-------------------|
| $X = c$ very pale yellow | 1.492 | 1.490 | 1.489 ± 0.002 |
| $Y = b$ yellowish green | $1.543 \left. \vphantom{1.543} \right\} \pm 0.001$ | $1.537 \left. \vphantom{1.537} \right\} \pm 0.001$ | 1.542 ± 0.001 |
| $Z = a$ yellowish green | 1.544 | 1.538 | 1.542 ± 0.001 |
| | $2V = 10^\circ$ | $2V = 18^\circ$ | $2V = 5^\circ$ |
| Opt. | (-) | (-) | (-) |
| Measured specific gravity | 2.550 | 2.544 | 2.5 |
| Calculated specific gravity | 2.547 | | |

A real difference of about 0.001 exists in the refractive index between n_Y and n_Z in crystals from Argentina and Utah. A check of the Wyoming schroeckingerite during the present study showed that $n_Z - n_Y$ is less, not greater than 0.0005. The water content of the crystals has a marked effect on refractive index. Crystals from Argentina placed over water at room temperature for 24 hours show a change of n_Y from 1.543 to 1.541. No change was shown in the crystals from Utah treated in the same manner.

DEHYDRATION

Schroeckingerite from the two new localities was placed in a desiccator over concentrated sulfuric acid at room temperature. After 48 hours the

appearance had completely changed. The clear, transparent crystals had become cloudy and the formerly brilliant basal planes gave poor reflections. With this relatively mild treatment schroeckingerite had lost $6\text{H}_2\text{O}$ and changed to: $\text{NaCa}_3\text{UO}_2(\text{CO}_3)_3\text{SO}_4\text{F}\cdot 4\text{H}_2\text{O}$.

That such a lower hydrate exists might have been predicted from the dehydration curves published by Nováček (1939). His curves showed that schroeckingerite from Wyoming and Joachimsthal lost approximately 12 per cent of its weight on heating between 76°C . and 79°C . Since the mineral contains 20.28 per cent water, this represents 6 of the $10\text{H}_2\text{O}$ originally present. Insufficient material from either Utah or Argentina is available to run similar dehydration experiments. However, abundant schroeckingerite from Wyoming was at hand and 400 milligrams of this material was placed in a desiccator over concentrated sulfuric acid. After 6 days it lost 11.7 per cent of its original weight; thereafter no further weight loss took place. Since no great effort was made to purify this sample, it is assumed that the 0.5 per cent short of the theoretical 12.2 per cent loss is the result of impurities.

Rotation and Weissenberg x -ray photographs of dehydrated schroeckingerite were taken rotating about both the a and c axes. Although these were poor, good measurements could be made along the axial directions of the 0-layer Weissenberg photographs which gave the following unit cell dimensions: $a_0 = 9.72\text{ \AA}$ (an increase of 0.03), $b_0 = 16.83$ (unchanged), $c_0 = 11.03$ (a decrease of 3.23). The ratio of $a_0:b_0 = 9.72:9.72\sqrt{3}$ is the exact ratio of a hexagonal lattice. The dehydrated schroeckingerite is, therefore, hexagonal with $a_0 = 9.72\text{ \AA}$ and $c_0 = 11.03$; $a_0:c_0 = 1:1.1348$.

Using the above dimensions, the volume for the hexagonal unit cell is calculated as 902 \AA^3 . The specific gravity, measured by suspending crystals in a mixture of bromoform and acetone, is 2.86. Using these figures the molecular weight of schroeckingerite with $4\text{H}_2\text{O}$ instead of $10\text{H}_2\text{O}$ is $M = 781$. There are thus two formula weights in the hexagonal unit cell.

Accompanying dehydration there is a marked increase in the indices of refraction. Equally striking is the uniaxial character of the mineral with the complete disappearance of the optic angle. The optical properties are summarized in Table 4.

TABLE 4. OPTICAL PROPERTIES OF DEHYDRATED SCHROECKINGERITE

| | n_{Na} | |
|----------------------|-------------------|------------------------|
| <i>O</i> pale yellow | 1.581 ± 0.001 | Uniaxial (—) |
| <i>E</i> colorless | 1.532 ± 0.002 | |
| Measured $G = 2.86$ | | Calculated $G = 2.874$ |

Dehydrated schroëckingerite standing in air for two days at room temperature showed only a slight decrease in refractive index. The same crystals placed over water at room temperature for one day showed a complete return to the initial optical properties. These crystals did not, however, become clear and transparent but retained the cloudy appearance they assumed on dehydration.

The fluorescence of dehydrated schroëckingerite, although striking, is less brilliant than before dehydration.

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Manuscript received Aug. 11, 1953