# NOTES AND NEWS

# STUDIES OF URANIUM MINERALS (XVII): SYNTHETIC SCHROECKINGERITE\*

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Schroeckingerite,  $Ca_3Na(UO_2)(CO_3)_3SO_4F \cdot 10H_2O$ , has been described from several different localities, associated generally with gypsum. The unit cell and morphological constants were obtained by Hurlbut (1953) from pseudohexagonal platelets of the mineral.

# Synthesis

The synthesis of schroeckingerite was initially undertaken by C. Ruggles in the autumn of 1953. Attempts to prepare the mineral from calcite immersed in solutions of NaF and  $UO_2SO_4 \cdot 3H_2O$  were unsuccessful. The synthesis was enacted by dissolving.

- 1. 0.05 m. NaF and 0.15 m. Na<sub>2</sub>CO<sub>3</sub> · 10H<sub>2</sub>O in 600 ml. H<sub>2</sub>O,
- 2. 0.05 m. UO<sub>2</sub>SO<sub>4</sub>  $\cdot$  3H<sub>2</sub>O in 200 ml. H<sub>2</sub>O,
- 3. 0.15 m. CaCl<sub>2</sub> in 100 ml. H<sub>2</sub>O,

and combining all three solutions. The resultant precipitate was greenishyellow, highly fluorescent and the mother liquor, neutral (pH-7). Since the precipitate was exceedingly fine-grained, accurate optical data were unobtainable.

This work was recently continued by the writer. The original synthesis was repeated successfully by reducing the acidity of the resultant solutions with NH<sub>4</sub>OH and by avoiding the slow reaction between the salts of the latter two solutions, by rapid combination. Since chlorine invariably may have substituted for fluorine in the crystals of schroeckingerite synthesized in this manner,  $Ca(NO_3)_2 \cdot 4H_2O$  was substituted for CaCl<sub>2</sub>. The precipitation of schroeckingerite was evident on approaching the neutral pH range, and the yield was increased by further reducing the acidity and depressing the solubility of the Na<sup>+</sup> ions by adding 0.1 N NaOH. The precipitate consisted of very fine-grained schroeckingerite and gypsum. The final reaction between uranyl sulfate and calcium nitrate was avoided by substituting for the former, uranyl nitrate and sodium sulfate in the stoichiometric proportions.

Repeated crystallizations of the schroeckingerite by evaporation at 40° C. from distilled water solutions reduced the gypsum contamination

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FIG. 1. The solubility of synthetic schroeckingerite as a function of pH at 22° C.

of the samples and yielded tiny, pseudohexagonal plates of schroeckingerite, measuring about 0.5 mm. in size and suitable for optical study.

### Solubility

The solubility of schroeckingerite as functions of pH and temperature is indicated in Fig. 1 and Table 1. The solubility is slight, increasing with decreasing pH and it is roughly doubled between 22° and 50° C. This information was of value in obtaining sufficient concentrations of the mineral for recrystallization.

# Trial Syntheses of Schroeckingerite Analogues

Attempts, all of which were unsuccessful, based upon the original synthesis, were made to prepare chloride, hydroxyl, potassium, magnesium, and lithium analogues of schroeckingerite.

Temperature, °C.	$_{\mathrm{pH}}$	Solubility		
22° C.	3.0	$5.91 \times 10^{-3}$ mols/liter		
22° C.	4.5	$5.20 \times 10^{-3}$ mols/liter		
22° C.	6.4	$4.32 \times 10^{-3}$ mols/liter		
22° C.	8.0	$3.64 \times 10^{-3}$ mols/liter		
22° C.	9.3	$F3.51 \times 10^{-3}$ mols/liter		
50° C.	4.5	$10.17 \times 10^{-3}$ mols/liter		

TABLE 1. SOLUBILITY OF SCHROECKINGERITE

(a) Chloride Analogue. Solutions containing 0.05 m. NaCl, 0.15 m. Na<sub>2</sub>CO<sub>3</sub>·10H<sub>2</sub>O and 0.05 m. UO<sub>2</sub>SO<sub>4</sub>·3H<sub>2</sub>O, and 0.15 m. CaCl<sub>2</sub> were combined with slight evolution of CO<sub>2</sub> gas. On adding 0.1 N NaOH a precipitate of gypsum was obtained. The mother liquor (pH-6.5) was evaporated at 40° C. for three days and a fluorescent, yellowish-green precipitate of andersonite, Na<sub>2</sub>CaUO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, and traces of CaCO<sub>3</sub> were obtained. (Andersonite has been synthesized previously by Axelrod *et al.* (1951) from solutions of K<sub>2</sub>CO<sub>3</sub> and uranyl, sodium and calcium nitrates.)

(b) Hydroxyl Analogue. The precipitation of a hydroxyl analogue of schroeckingerite failed from neutral solutions of sodium carbonate, uranyl sulfate, and calcium nitrate.

(c) Potassium Analogue. The replacement of sodium by potassium in the original formula, using 0.05 m. KF and 0.15 m. K<sub>2</sub>CO<sub>3</sub> combined with uranyl sulfate and calcium nitrate in solution yielded only gypsum through slow evaporation in the neutral range.

(d) Magnesium Analogue. From the evaporation of solutions of NaF, Na<sub>2</sub>CO<sub>3</sub>·10H<sub>2</sub>O, UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and MgSO<sub>4</sub>·7H<sub>2</sub>O, rendered more alkaline with the addition of 0.1 N NaOH, only a colloidal precipitate of uranyl sulfate was ultimately obtained.

(e) Lithium Analogue. The corollary synthesis of a lithium analogue of schroeckingerite was hampered by the very great insolubility of lithium fluoride. However, no trace of lithium was apparent in any of the natural material as reported by Axelrod and co-workers.

# Optical and X-ray Data of Pure, Synthetic Schroeckingerite

The optical constants obtained for pure, synthetic schroeckingerite are compared with those recorded by several other analysts on naturallyoccurring material.

Source	Wamsutter, Wyoming	Moab, Utah	San Isidro, Argentina	Pure Synthetic
Analyst	Larsen	Hurlbut	Hurlbut	Ross
Character	Biaxial $(-)$	Biaxial $(-)$	Biaxial $(-)$	Biaxial (-)
nX = c (Pale yellow)	$1.489 \pm .002$	$1.490 \pm .001$	$1.492 \pm .001$	$1.495 \pm .001$
nY = b (yellow-green)	$1.542 \pm .001$	$1.537 \pm .001$	$1.543 \pm .001$	$1.543 \pm .001$
nZ = a (vellow-green)	$1.542 \pm .001$	$1.538 \pm .001$	$1.544 \pm .001$	$1.544 \pm .001$
2V	5°	18°	10°	16°.
Dispersion not per-				

TABLE 2. SCHROECKINGERITE, OPTICAL DATA

The crystals from Argentina were reported by Hurlbut to alter on de-

$I/I_{9}$	$d_{meas}$ .	hkl	$d_{calc.}$
3	14.28	001	14.26
10	7.26	021	7.25
		111	7.24
2	5.421	022	5.439
		112	5.434
8	4.796	200 003	4.845
2	4 167	220	1.102
4	4.107	113	4.139
		023	4.138
1	4.044	041	4.036
		132	4.028
1	3 501	042	2 604
	0.371	222	3.618
		004	3.564
2	3.362	203	3.393
1B	3.303	024	3.282
		114	3.281
<1 VB	3.13	310	3.172
		043	3.150
		220	3.147 3.101
		241	3 101
		311	3.096
7	2.876	134	2.873
		204	2.871
1	2.767	061	2.753
		331	2.747
1	2.706	025	2.701
2		115	2.700
Z	2.393	261 401	2.393
<1	2 204	171	2.000
< <u>1</u>	2.304	351	2,302
		262	2.298
		421	2.297

TABLE 3. SYNTHETIC SCHROECKINGERITE. X-RAY POWDER DIFFRACTION DATA Space Group-Cmmm,  $a_0$  -9.69 Å,  $b_0$ -16.83 Å,  $c_0$  -14.26 Å.  $I/I_0$ - Relative Intensity,  $d_{hkl}$ -interplanar spacing

B-Broad, VB-Very Broad.

hydration to:  $Ca_3NaUO_2(CO_3)_3SO_4F \cdot 4H_2O$ , which is hexagonal, nO = 1.581, nE = 1.532. The loss of water was found to exert a marked decrease in the nY index of refraction. The synthetic material, which was apparently fully hydrated, exhibited maximum refraction.

The complete x-ray analysis of synthetic schroeckingerite required the combined use of film and recording diffractometer techniques to compensate for the absence of high-angle reflections, which is characteristic of the mineral. From the unit cell dimensions and space-group provided by Hurlbut from single crystal analysis, the various powder reflections were accordingly indexed and are listed in Table 3.

It appears that the synthetic material is more fully hydrated as evidenced from the slightly larger d-spacings than those calculated on the basis of the natural single-crystal data, and from the comparatively higher refractive indices. The natural material was undoubtedly slightly dehydrated on constant exposure to the air. The d-spacings of the synthetic material are in fair agreement with those reported by Jaffe (1948) with the exception of a few lines which have been omitted. The latter lines, which were very weak, could not be indexed on the basis of the single crystal data and were attributed ultimately to traces of gypsum. It was observed during the synthesis of schroeckingerite that the water content, and consequently, the d-spacings of the co-precipitated gypsum were highly variable.

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#### References

- HURLBUT, C. S., JR., Studies of uranium minerals (XV): Schroeckingerite from Argentina and Utah: Am. Mineral., 39, 901-907.
- 3. JAFFE, H. W., SHERWOOD, A. M., AND PETERSON, M. J., New data on schroeckingerite: Am. Mineral., 33, 152-157, (1948).
- 4. LARSEN, E. S., JR., AND GONYER, F. A., Dakeite, a new uranium mineral from Wyoming: Am. Mineral., 22, 561-563, (1937).

<sup>1.</sup> AXELROD, J. M., GRIMALDI, F. S., MILTON, C., AND MURATA, K. J., The uranium minerals from the Hillside Mine, Yavapai County, Arizona: Am. Mineral., 36, 1-21, (1951).