

NOTES AND NEWS

STUDIES OF URANIUM MINERALS (XVII): SYNTHETIC SCHROECKINGERITE*

VIRGINIA ROSS,** *Harvard University, Cambridge, Massachusetts.*

Schroeckingerite, $\text{Ca}_3\text{Na}(\text{UO}_2)(\text{CO}_3)_3\text{SO}_4\text{F} \cdot 10\text{H}_2\text{O}$, 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 $\text{UO}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ were unsuccessful. The synthesis was enacted by dissolving.

1. 0.05 m. NaF and 0.15 m. $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ in 600 ml. H_2O ,
2. 0.05 m. $\text{UO}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ in 200 ml. H_2O ,
3. 0.15 m. CaCl_2 in 100 ml. H_2O ,

and combining all three solutions. The resultant precipitate was greenish-yellow, 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_4OH 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, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ was substituted for CaCl_2 . 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^+ 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

* Contribution No. 351 of the Department of Mineralogy and Petrography, Harvard University, Cambridge, Massachusetts.

** Present address: Department of Chemistry, Brown University, Providence, Rhode Island.

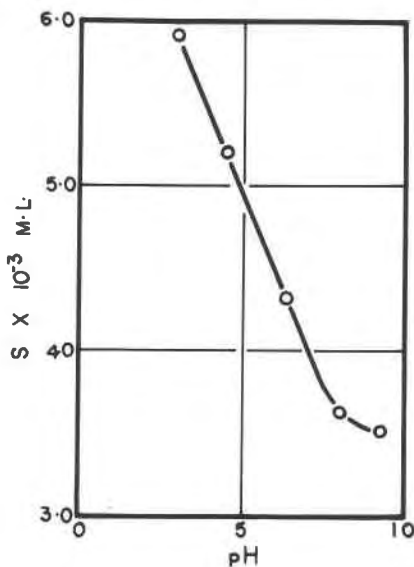


FIG. 1. The solubility of synthetic schroekingite as a function of pH at 22° C.

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

Solubility

The solubility of schroekingite 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 Schroekingite Analogues

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

TABLE 1. SOLUBILITY OF SCHROECKINGERITE

Temperature, °C.	pH	Solubility
22° C.	3.0	5.91×10^{-3} mols/liter
22° C.	4.5	5.20×10^{-3} mols/liter
22° C.	6.4	4.32×10^{-3} mols/liter
22° C.	8.0	3.64×10^{-3} mols/liter
22° C.	9.3	3.51×10^{-3} mols/liter
50° C.	4.5	10.17×10^{-3} mols/liter

(a) Chloride Analogue. Solutions containing 0.05 m. NaCl, 0.15 m. $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ and 0.05 m. $\text{UO}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$, and 0.15 m. CaCl_2 were combined with slight evolution of CO_2 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, $\text{Na}_2\text{CaUO}_2(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$, and traces of CaCO_3 were obtained. (Andersonite has been synthesized previously by Axelrod *et al.* (1951) from solutions of K_2CO_3 and uranyl, sodium and calcium nitrates.)

(b) Hydroxyl Analogue. The precipitation of a hydroxyl analogue of schroekingite 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_2CO_3 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, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 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 schroekingite 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 Schroekingite

The optical constants obtained for pure, synthetic schroekingite are compared with those recorded by several other analysts on naturally-occurring material.

TABLE 2. SCHROECKINGERITE, OPTICAL DATA

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

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

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

I/I_0	$d_{meas.}$	hkl	$d_{calc.}$
3	14.28	001	14.26
10	7.26	021 111	7.25 7.24
2	5.421	022 112	5.439 5.434
8	4.796	200 003	4.845 4.752
2	4.167	220 113 023	4.199 4.139 4.138
1	4.044	041 221 132	4.036 4.028 4.013
1	3.591	042 222 004	3.624 3.618 3.564
2	3.362	203	3.393
1B	3.303	024 114	3.282 3.281
<1 VB	3.13	310 043 223 151 241 311	3.172 3.150 3.147 3.101 3.101 3.096
7	2.876	134 204	2.873 2.871
1	2.767	061 331	2.753 2.747
1	2.706	025 115	2.701 2.700
2	2.393	261 401	2.393 2.388
<1	2.304	171 351 262 421	2.302 2.300 2.298 2.297

B—Broad, VB—Very Broad.

hydration to: $\text{Ca}_3\text{NaUO}_2(\text{CO}_3)_3\text{SO}_4\text{F}\cdot 4\text{H}_2\text{O}$, which is hexagonal, $n_O = 1.581$, $n_E = 1.532$. The loss of water was found to exert a marked decrease in the n_Y 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.

ACKNOWLEDGMENT

This investigation was carried out on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission, *Contract No. AT (30-1) 1403*. The method of synthesis was suggested by Dr. C. Frondel.

REFERENCES

1. 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).
2. 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).