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THE URANIUM MINERALS FROM THE HILLSIDE MINE, YAVAPAI COUNTY, ARIZONA*

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ABSTRACT

Coating gypsum on the 300-foot level of the Hillside Mine, Yavapai County, Arizona, was a small deposit in which were found several hitherto unknown uranium minerals, together with schroeckingerite, which had been previously known only from Wyoming and Czechoslovakia. The new species are named andersonite, swartzite, and bayleyite; they are, respectively, hydrous uranyl carbonates of sodium and calcium, of calcium and magnesium, and of magnesium, all of general formula $X_4UO_2(CO_3)_3 \cdot nH_2O$, where X_4 represents respectively, Na_2Ca, CaMg, and Mg_2, and n, respectively, 6, 12, and 18. With these minerals occur two other new substances, naturally occurring dehydration products of swartzite and bayleyite, respectively, whose definitive properties are not well enough known to propose them as valid species. Andersonite, swartzite, and bayleyite, previously unknown either as minerals or synthetic compounds, have been synthesized. Analyses, optical data, x-ray patterns, and crystallographic data of these new species are given, with x-ray patterns of the dehydration products above mentioned. Schroeckingerite also has been analyzed and its formula found to differ from that given in the older accounts in the literature; our analysis agrees closely with that of the Wyoming schroeckingerite recently reported by Jaffe, Sherwood, and Peterson.[1] The various uranium carbonate minerals recorded in the literature are briefly considered. Of them, liebigite (=uranothallite) and schroeckingerite are well established. Voglite is almost certainly valid; randite certainly, and rutherfordine probably, are to be discredited; sharpite may be valid; the status of studtite and diderichite is very doubtful.

LOCATION AND GEOLOGICAL SETTING

Dr. Charles A. Anderson, geologist of the U. S. Geological Survey, who first observed and collected the material in which the uranium minerals here described occur, has given us the following information concerning the Hillside Mine. It is located in Yavapai County, west-central Arizona, $3\frac{1}{2}$ miles north of Bagdad, and 43 miles by airline from Prescott. The mine produces gold, silver, lead, and zinc from a vein several feet

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[1] References are listed by numbers at end of this paper.

thick. Faulting, post- and pre-mineralization, has occurred. Sulfides present in the vein include pyrite, arsenopyrite, galena, sphalerite, chalcopyrite, tetrahedrite, and argentite; minerals of the oxidation zone include silver, cerargyrite, cerussite, anglesite, smithsonite, and hemimorphite. The country rock is pre-Cambrian mica-schist, intruded by pre-Cambrian granite. The age of the mineralization is thought to be Cretaceous or early Tertiary because, in the lower levels of the mine, the vein is reported to cut porphyry dikes, as at Bagdad.

Uranium minerals were found in only one place, as a coating about $\frac{1}{8}$ inch thick on gypsum, in the oxidized zone, and about forty feet above the water level. The source of the uranium is not known; it may be related to small aplite-pegmatite dikes in the pre-Cambrian schist that are associated with the granite, or it may have been deposited with the ore vein. In any case, the uranium carbonate minerals are clearly of secondary origin, and were deposited on the walls of the drift. Subsequent mining operations have completely obliterated the occurrence of the secondary uranium minerals.

No published data appear to exist on the Hillside Mine, and a recent publication listing the known minerals of Arizona does not mention any uranium minerals as occurring in Arizona.[2]

Very recently a specimen of uranium-bearing ore from the 400′ level has been received by us, and is now under investigation. An altogether different uranium mineralogy is present, the minerals johannite (hydrous copper uranium sulfate), pitchblende, and a probably new zinc uranium sulfate having been recognized thus far. A further account of these minerals will appear in a subsequent issue of the *American Mineralogist.*

APPEARANCE OF SPECIMENS

Adhering to the micaceous schist are scattered green rosettes of schroeckingerite, with sulfur-yellow bayleyite. Overlying this schist is a layer of snow-white granular gypsum containing small clusters of vivid green swartzite. Coating gypsum is a mass of yellow bayleyite, most of it now altered to a pale-yellow powder. The rare andersonite is easily overlooked; superficially, it resembles swartzite, but when the two minerals are seen together, the distinctive characters are apparent. In general, the several uranium minerals are intergrown with one another and with the gypsum and schist minerals; only schroeckingerite can be easily obtained in relatively large masses (about a pin-head in size) of a fair degree of purity.

In the mine, bayleyite crystals are sharp and well faceted. In the drier atmosphere of Washington, they soon become dull, losing their luster and finally disintegrate to a yellow powder. Swartzite behaves similarly to a lesser extent; andersonite is stable. The stability is inverse to the degree of hydration.

Typical crystals of swartzite and andersonite are illustrated in Figs. 1 and 2. No natural bayleyite was available for the reason above stated. However, synthetic bayleyite (Figs. *3a* and *3b*) is illustrated.

Method of Study

The study of the minerals from the Hillside Mine involved special difficulties, and at first sight it seemed almost impossible to separate the components of the specimens. However, the separation was made; and in order that other workers, who may encounter material of like nature in the future, may not be unduly discouraged in undertaking similar investigations, our methods of separation, identification, and analysis are presented in more detail than they would otherwise be.

The individual mineral crystals are very small, usually almost microscopic; the largest seldom exceed a millimeter in length, except schroeckingerite, which occurs in fairly pure rosette-like aggregates of flat plates a few tenths of a millimeter in diameter. Moreover, the various minerals occur more or less mixed, surrounded by and intergrown with the minerals of the mica schist and with gypsum. To obtian reasonably pure material for study it was therefore necessary to crush—not grind—the aggregate, to sift out the dust and coarse particles, and to pick out with a needle under a binocular microscope, particle by particle, the several samples to be analyzed—a tedious process, but the only course feasible. At first, before becoming familiar with the varied habit of the individual minerals, and their rather subtle variations in shades of yellow and green, it was also necessary to check the hand-picking frequently by examination under ultra-violet light making use of the characteristic fluorescence (see below) of the several species. After a suitable quantity of material had been thus obtained, a further selection from the picked material was made of the clearest possible crystals, which were spectrographically analyzed. The data thus obtained were invaluable in planning the quantitative analysis, for, because of the small sample available for many determinations, modifications of customary methods had to be devised. Furthermore, this pilot spectrographic analysis on the purest possible material indicated which of the minor constituents in the quantitatively analyzed sample were present as contaminants and not as essential constituents of the mineral. Later, synthesis of the minerals from C.P. chemicals checked the conclusions drawn from the spectrographic and quantitative analyses. At the same time that the spectrographic study was in progress, the individuality of the analyzed materials was established by their *x*-ray diffraction patterns.

PHYSICAL AND CHEMICAL DATA

The physical data are given in Table 1 and the chemical data in Table 2.

Fluorescence, optics and other physical properties

The fluorescence of the minerals was examined under two kinds of mercury vapor lamps, one providing "short ultraviolet" radiation (Mineralight, model V-41) and the other, "long ultraviolet" radiation (Hanovia Inspectolight). Spectrograms of the radiation emitted by these lamps have already been published.[3] The relative brightness and color of the fluorescence of each mineral were the same under both lamps.

TABLE 1. OPTICAL AND PHYSICAL DATA ON ANDERSONITE, SWARTZITE, BAYLEYITE, AND DEHYDRATION PRODUCTS

	Andersonite	Swartzite	Bayleyite
α	1.520 (ω) colorless	1.465 colorless	1.455 pinkish?
β	1.540 (ϵ) pale yellow	1.51 yellow	1.490 pale yellow
γ		1.540 yellow	1.500 pale yellow
color (daylight)	bright yellow-green	green	yellow
habit	pseudo-cubic	prismatic	prismatic
symmetry	rhombohedral	monoclinic	monoclinic
extinction			$c:\alpha=15°$
sign	(+)	(−)	(−)
2V (calc.)	0°	40°	30°
density (measured)	2.8	2.3	2.05
(calc.)	2.86	2.32	2.06
solubility in water	easy	easy	easy
fluorescence	bright whitish-green	bright yellowish-green	weak, color uncertain
formula	$Na_2CaUO_2(CO_3)_3 \cdot 6H_2O$	$CaMgUO_2(CO_3)_3 \cdot 12H_2O$	$Mg_2UO_2(CO_3)_3 \cdot 18H_2O$
		Dehydration product	Dehydration product
α			1.502
γ			1.551
color		whitish dull-yellow	whitish
habit		pseudomorphous after swartzite	pseudomorphous after bayleyite
fluorescence		weak, color uncertain	moderate whitish-green

The fluorescent colors observed were greens and yellows, typical of secondary uranium minerals. As is well known, this fluorescence is due to the uranyl ion, and consists of five or more discrete bands of wave lengths distributed throughout the visible spectrum. The wave length ranges and relative intensities of these bands vary slightly from mineral to mineral, resulting in a range of color of fluorescence between green and yellow. A thorough study of the fluorescence of secondary uranium minerals, therefore, requires precise spectrographic measurements. This study was not possible with the minerals described in this paper because of the small amounts of pure samples available.

In lieu of a spectrographic study, the fluorescence of the different

TABLE 2. ANALYTICAL DATA

ANALYSES OF URANIUM MINERALS FROM ARIZONA (AND SYNTHETIC ANDERSONITE)

	Andersonite (*a*)	Synthetic Andersonite	Swartzite	Bayleyite (*d*)	
MgO	0.5±0.1(*b*)	—	5.24	9.03	8.97
CaO	8.9±0.5	8.80	8.40	3.42	2.75
Na_2O	9.3±0.5	9.61	.25	—	.19
K_2O	—	—	.47	—	.09
UO_3	43.4±1.5	44.27	37.19	30.80	32.42
Total H_2O	16.7(*c*)	16.50	29.31	35.19	36.60
CO_2	19.6±0.5	20.61	17.16	14.60	15.36
SO_3	1.6±0.3		1.98	4.43	3.95
F	—	—	—	—	—
Acid insol., Ignited	—	—	.30	2.27	.45
Total	100.0	99.79	100.30	99.74	100.78
Formula	$Na_2CaUO_2(CO_3)_3 \cdot 6H_2O$		$CaMgUO_2(CO_3)_3 \cdot 12H_2O$	$Mg_2UO_2(CO_3)_3 \cdot 18H_2O$	
Sp. Gr. (determined)	2.8		2.3	2.06	2.05
(calculated)	2.86		2.32		2.06
Analyst	F. S. Grimaldi	Marie Eiland	F. S. Grimaldi	F. S. Grimaldi	

(*a*) Only 3.8 mg. of andersonite was available for the complete analysis.
(*b*) Spectrographically by K. J. Murata.
(*c*) By difference.
(*d*) The two analyses were made on separate samples.

TABLE 2 (continued)

ANALYSES OF SCHROECKINGERITE ("DAKEITE")

	Arizona	*Wyoming*	*Wyoming*	*Joachimsthal*
		$Si0_2$.95 R_20_3.08		
MgO	0.63	—	—	—
CaO	18.44	18.14	18.31	19.1
Na_2O	3.19	3.63	7.31	n.d.
K_2O	.23	—	—	—
UO_3	31.28	31.44	30.27	32.4
H_2O	20.20	20.15	19.95	20.2
CO_2	14.67	14.20	13.71	n.d.
SO_3	9.24	9.17	9.61	9.1
F	2.09	2.15	—	—
Insol.	1.53		1.05	.4
	101.50	99.91	100.22 (Sic)	
O=F	.88	.90		
	100.62	99.01		
Sp. Gr.	2.5			
Analyst	F. S. Grimaldi	A. M. Sherwood[1]	F. Gonyer[4]	R. Novácek[5]

[1,4,5] See references at end of paper.

minerals was characterized visually according to the following scheme. Two readily available minerals, schroeckingerite and autunite, were selected as standards for comparison of fluorescent colors. The fluorescent color of schroeckingerite under the Mineralight lamp was designated *bright whitish-green;* that of autunite, *bright greenish-yellow.* The fluorescent colors of the minerals studied were close to one or the other, but one (that of swartzite) was definitely intermediate. This was called *yellowish green.* This three-step classification, though rather crude, was found adequate for the purpose, and it has the important advantage that the colors are defined in terms of standards that can be reproduced easily by other investigators. The results of our observations are included in Table 1.

The colors of the natural and synthetic andersonites are distinctly different, the former being bright yellow-green and the latter greenish yellow; and likewise the fluorescence differs, that of natural andersonite being whitish green and that of the synthetic compound yellow-green and weaker. Whether or not this variation is to be ascribed to the 0.5% MgO found in the natural andersonite is not known. The relation of green and yellow color in the uranium compounds to cation or other variables is an interesting question.

Methods of analysis

The weight of each mineral available for chemical analysis was: andersonite 3.8 mg., swartzite 0.25 g., bayleyite 0.5 g., and schroeckingerite, several grams. With the exception of schroeckingerite it would have been desirable if more material had been available for analysis.

In general, U, Ca, Mg, the alkalies, and acid insoluble, were determined on one portion; CO_2 and SO_3 on another; and F and H_2O on separate portions. The sample weights in grams taken for analysis are given in Table 2A. For andersonite all the determinations reported were made on the total sample of 3.8 mg.

TABLE 2A. SAMPLE WEIGHTS IN GRAMS, TAKEN FOR ANALYSIS

	Swartzite	Bayleyite	Schroeckingerite
Insol., U, Ca, Mg, Na, K	0.1	0.2	0.3
CO_2, SO_3	.05	.1	.15
H_2O	.06	.1	.15
F			.02

Accepted standard procedures were used in the analyses and for this reason only a very brief description of the procedures is given below. The analysis of andersonite involved a few unusual procedures and these are described separately.

PROCEDURES:

1. *Determination of insoluble material, U, Ca, Mg, Na, K*

Dilute HCl was added to the sample in a platinum dish and the mixture was digested on the steam bath for 30 minutes. The solution was then evaporated to dryness. It was taken up in hydrochloric acid and evaporated to dryness again. Dilute HCl was next added and the solution digested a few minutes. The insoluble material was filtered off, washed with dilute HCl, ignited, and weighed. The filtrate was boiled gently to insure the removal of carbon dioxide and a double precipitation with a slight excess of redistilled ammonia was then made. The R_2O_3 group obtained was filtered off, ignited, and weighed. The R_2O_3 group was then fused with $K_2S_2O_7$ and the melt dissolved in 50 ml. of dilute H_2SO_4 (7+93). After cooling to room temperature, the solution was passed through a small Jones reductor. It was then aerated and titrated with standard $KMnO_4$. The U_3O_8 figure obtained by titration agreed very closely with the weight of the ignited R_2O_3 precipitate obtained previously. The titrated solution was then concentrated to 50 ml. by evaporation and the reduction and titration repeated as a check.

The filtrate from the ammonia precipitate was treated with oxalic acid and the calcium oxalate obtained after double precipitation was ignited to CaO and weighed.

Magnesium was determined in the filtrate from the calcium oxalate by first destroying ammonium salts and oxalate, precipitating magnesium with 8-hydroxy-quinoline, igniting the precipitate under cover of oxalic acid to MgO, and weighing. The filtrate from the magnesium was taken to dryness and the ammonium salts and organic matter were destroyed by gentle ignition. Sulfuric acid was added to the residue, the solution evaporated on the steam bath and then on hot plate to remove the excess sulfuric acid. The sulfates obtained were ignited (temp. about 750°) and then weighed as $Na_2SO_4+K_2SO_4$. Potassium was then determined as potassium chloroplatinate and the sodium determined by difference.

2. *Determination of CO_2 and SO_3*

Carbon dioxide was determined, using a standard absorption train. The SO_3 content was obtained gravimetrically as $BaSO_4$ on the solution from the CO_2 determination.

3. *Determination of fluorine*

The fluorine was distilled with perchloric acid and then titrated with standard thorium nitrate after the solution was adjusted to a pH of 3.0 with monochloracetic acid-sodium monochloracetate buffer. Sodium alizarin sulfonate was used as indicator.

4. *Determination of total water*

Water was determined by the Penfield method after first mixing the sample with dry Na_2WO_4 to hold back oxides of sulfur. Before weighing and after the water was collected in the tube, the tube was inclined at an angle of about 45° for 30 minutes, open end down to allow the carbon dioxide released by the sample to be replaced by air.

Analysis of andersonite

The sample was weighed and transferred to a platinum dish. About 5 ml. of water was added and carbon dioxide was determined by titrating the sample with standard $0.01N$ HCl to the methyl orange end-point. This method for the determination of carbon dioxide was used after testing the more abundant bayleyite by titration and absorption train. The two methods gave good agreement in the results for carbon dioxide. After the titration a drop of concentrated HCl was added and the solution boiled gently. It was then cooled and 5 drops of dilute barium chloride solution were added. The cloud of $BaSO_4$ was then matched against standards and the value for SO_3 was thus obtained. The $BaSO_4$ was then digested for some time and allowed to settle overnight. This was filtered off and rejected. In the filtrate uranium was precipitated as before, and after fusion of the ignited ammonia precipitate in $K_2S_2O_7$ it was determined colorimetrically with $NaOH$-H_2O_2.

The filtrate from the ammonia precipitate was taken to dryness and the ammonium salts destroyed. Calcium was precipitated again as the oxalate but from very small volume. It was filtered off and ignited to CaO. The CaO was then titrated with standard $0.01N$ HCl. A check on the calcium figure was obtained as follows: Oxalic acid was added to the titrated solution and the mixture was evaporated on the steam bath to remove chloride. The dish was then heated gently over a flame to remove the oxalate and finally the sample was ignited to CaO. The residue was then titrated with standard HCl. Bromthymol blue is recommended for acid-base titrations with $0.01N$ solutions.

The filtrate from the calcium oxalate was taken to dryness and the ammonium salts destroyed. The alkalies were weighed as sulfates and then sodium was determined by precipitating with zinc uranyl acetate.

DISCUSSION OF THE ANALYSES. *Contamination with gypsum*

Andersonite, swartzite, and bayleyite contained $CaSO_4 \cdot 2H_2O$ (gypsum) as impurity.

Sample	*Impurity (% of Sample)*	*To be subtracted from the analysis*
Andersonite	3.4% $CaSO_4 \cdot 2H_2O$	1.6% SO_3, 1.1% CaO, 0.7% H_2O
Swartzite	4.26% $CaSO_4 \cdot 2H_2O$	1.98% SO_3, 1.39% CaO, 0.89% H_2O
Bayleyite	8.45% $CaSO_4 \cdot 2H_2O$	3.93% SO_3, 2.75% CaO, 1.77% H_2O

The contamination of these minerals was to be expected in view of their intimate association with gypsum. Only the schroeckingerite, which occurs in relatively large homogeneous aggregates, appears to be essentially free from gypsum. That the contaminant was gypsum was shown by optical examination. Further, it appeared that, by synthesizing the several substances in the absence of sulfate ion, the SO_3 of the analyses was not part of these minerals. X-ray diffraction patterns did not reveal the gypsum, as it was in too small a quantity.

In Table 3 are the analyses with the constituents of the admixed gypsum deducted. The molecular ratios are then computed to obtain the formulas of the new minerals. The SO_3 of the analyses was the basis for allotment of CaO and H_2O to $CaO \cdot SO_3 \cdot 2H_2O$, gypsum; a reasonable and proper assumption, inasmuch as andersonite, swartzite, and bayleyite contain no SO_3; and the analyzed schroeckingerite, which does contain SO_3, was known to be free from admixed gypsum.

Notes on analytical data

Although the analysis indicates 17.43 molecules of water in the bayleyite formula, there is a strong presumption that 18 is the correct figure, and that the lower value indicates that spontaneous dehydration of bayleyite had already commenced before the water determination was made. The 12 and 6 molecules of water present in swartzite and andersonite, respectively, suggest that a similar multiple of 6, that is 18, is more likely than an odd number such as 17. Furthermore, the density calculated for 18 H_2O agrees better with the measured density. For these reasons, the higher water content is assumed to be the correct one.

Except for bayleyite, specific gravities were obtained by suspending one or two grains of the mineral in a liquid of the same gravity.

Table 3. Computation of Formulas from Analyses

	Andersonite	Gypsum	Remainder	Ratio	
MgO	0.5		0.5	0.12	1.50× 1.0
CaO	8.9	1.1	7.8	1.39	
Na_2O	9.3		9.3	1.50	1.50× 1.0
UO_3	43.4		43.4	1.52	1.50× 1.0
H_2O	16.7	0.7	16.0	8.88	1.50× 5.9
CO_2	19.6		19.6	4.45	1.50× 3.0
SO_3	1.6	1.6			
	100.0	3.4	96.6		

Deduced formula $CaO \cdot Na_2O \cdot UO_3 \cdot 3CO_2 \cdot 6H_2O$
or $Na_2Ca(UO_2)(CO_3)_3 \cdot 6H_2O$. As indicated, a slight replacement of calcium by magnesium may exist.

The formula of andersonite also can be computed from the analysis of the synthetic material:

	Andersonite (synthetic)	Ratio	
CaO	8.80	1.57	1.55× 1.01
Na_2O	9.61	1.55	1.55× 1.00
UO_3	44.27	1.55	1.55× 1.00
H_2O	16.50	9.17	1.55× 5.91
CO_2	20.61	4.69	1.55× 3.03
	99.79		

Deduced formula $CaO \cdot Na_2O \cdot UO_3 \cdot 3CO_2 \cdot 6H_2O$
or $Na_2Ca(UO_2)(CO_3) \cdot 6H_2O$

	Swartzite	Gypsum	Remainder	Ratio	
MgO	5.24		5.24	1.30	1.30× 1.00
CaO	8.40	1.39	7.01	1.25	1.30× .96
Na_2O	.25		.25	.04	1.30× .03
K_2O	.47		.47	.05	1.30× .04
UO_3	37.19		37.19	1.30	1.30× 1.00
H_2O	29.31	.89	28.42	15.80	1.30×12.15
CO_2	17.16		17.16	3.90	1.30× 3.00
SO_3	1.98	1.98			
Insol.	.30				
	100.30	4.26	95.74		

TABLE 3 (continued)

Deduced formula $MgO \cdot CaO \cdot UO_3 \cdot 3CO_2 \cdot 12H_2O$
or $MgCa(UO_2)(CO_3)_3 \cdot 12H_2O$

	Bayleyite	Gypsum	Remainder	Ratio	
MgO	8.97		8.97	2.220	1.11× 2.00
CaO	2.75	2.75			
Na_2O	.19		.19	.03	
K_2O	.09		.09	.01	
UO_3	32.42		32.42	1.133	1.11× 1.02
H_2O	36.60	1.77	34.83	19.350	1.11×17.43
CO_2	15.36		15.36	3.491	1.11× 3.15
SO_3	3.95	3.93	.02		
Insol.	.45				
	100.78	8.45	91.88		

Deduced formula $2MgO \cdot UO_3 \cdot 3CO_2 \cdot 18H_2O$
or $Mg_2(UO_2)(CO_3)_3 \cdot 18H_2O$

	Schroeckingerite	Ratio	
MgO	.63	.16	
CaO	18.44	3.29	1.09× 3.02
$Na_2O(Na)$	3.19 (2.36)	(1.03)	1.09× .95
K_2O	.23	.02	
UO_3	31.28	1.09	1.09× 1.00
H_2O	20.20	11.22	1.09×10.29
CO_2	14.67	3.33	1.09× 3.05
SO_3	9.24	1.16	1.09× 1.06
F	2.09	1.10	1.09× 1.01
Insol.	1.53		
	101.50		
Less O=F	.88		
	100.62		

The deduced formula is $Ca_3Na[UO_2(CO_3)_3SO_4F] \cdot 10H_2O$, which is the same as that derived by Jaffe, Sherwood, and Peterson.

In view of the small quantity (3.8 milligrams) of andersonite available for analysis, it was thought proper to verify the calculated formula by means of a second analysis made on synthetic material. Mrs. Marie Eiland, chemist of the U. S. Geological Survey, kindly made this analysis. Both analyses are given in Table 2 above, and it is evident that the agreement is satisfactory.

The analysis of the Arizona schroeckingerite was made before the publication of the study of the Wyoming schroeckingerite by Jaffe, Sherwood, and Peterson.[1] In these circumstances, it is gratifying to note that the two analyses agree closely. Better agreement could hardly be expected, considering that the respective samples are from different localities, were analyzed by different chemists, and are substances of complex composition. The agreement is of special significance in that the deduced formula $Ca_3Na[UO_2(CO_3)_3(SO_4)F]\cdot 10H_2O$ (which may be rewritten $3CaCO_3\cdot NaF\cdot (UO_2)SO_4\cdot 10H_2O$) independently obtained by Jaffe, Sherwood, Peterson, and by ourselves differs from the formula hitherto ascribed to dakeite (=schroeckingerite) by Larsen and Gonyer[4] namely $3CaCO_3\cdot Na_2SO_4\cdot UO_3\cdot 10H_2O$, in having only half as much Na_2O, and in containing essential fluorine.

Dr. Clifford Frondel[6] of Harvard University has observed (personal communication) that there is a difference in size of the unit cells of the Bohemian and the two American schroeckingerites. Both of the latter agree closely in *x*-ray pattern as well as chemical composition. If a similarly good analysis of the Bohemian mineral were available, a significant difference in composition might be shown.

Spectrographic Data

TABLE 4. SPECTROGRAPHIC STUDY

	Major elements $>1\%$	Minor elements $<1\%$	Not found
Schroeckingerite	U, Ca, Na	Mg, Al, Fe, K, Mn	Sr and*
Bayleyite	U, Mg, Ca(3%)	Al	Fe, Mn, Na, K, Sr, and*
Bayleyite (purer sample)	U, Mg, Ca(1%)	Al	Fe, Mn, Na, K, Sr, and*
Andersonite	U, Ca(14%), Na(11%)	Al, Mg(0.5%)	Fe, Mn, K, Sr, and*
Swartzite	U, Ca(14%), Mg(5%)	Al, Sr	Fe, Mn, Na, K, and*
Dehydration product of bayleyite and of swartzite (mixture)	U, Mg, Ca(1%)	Al, Fe	Mn, Na, K, Sr, and*

* Not found in any: Be, B, Pb, Cu, Mo, W, As, Sb, Sn, Tl, Zn, Cd, Co, Ni, Ge, In, Cr, V, Y, La, Bi, Ag, Li, Rb, Cs, Ti, Zr, Ba, Th.

The numbers in parentheses indicate the spectrographically estimated percentages; they indicate order of magnitude rather than exact percentages, and are thus in reasonable agreement with Grimaldi's analytical figures.

The minor elements detected spectrographically are referred to impurities—in part, the "insoluble" of the analyses. A possible exception is the 0.5% Mg found in the andersonite.

The notably less Ca in the purer sample of bayleyite indicates that the Ca present is not a constituent of the mineral.

SYNTHESIS OF THE NEW MINERALS

The synthesis of these compounds was undertaken in order to verify beyond question that the *x*-ray diffraction patterns were those of compounds of the deduced chemical compositions, and, also, in the case of the andersonite to have an analysis free from the uncertainty arising from the minute quantity of natural substance available. The literature did not show that they had been previously prepared, but the homologous substances listed below had been.[7]

$(NH_4)UO_2(CO_3)_3 \cdot 2H_2O$ (The indicated H_2O content, or its absence, is of doubtful validity.)
$Na_4UO_2(CO_3)_3$
$K_4UO_2(CO_3)_3$
$Ag_4UO_2(CO_3)_3$
$Tl_4UO_2(CO_3)_3$
$Ca_2UO_2(CO_3)_3$
$Ba_2UO_2(CO_3)_3$

The methods given for preparing these compounds were successfully employed by us to prepare synthetic andersonite, swartzite, and bayleyite.

Details of the synthesis follow:

For bayleyite, $Mg_2UO_2(CO_3)_3 \cdot 18H_2O$.
Proportions used of starting materials:

	Mol. Ratio	*Weights*
$Mg(NO_3)_2 \cdot 6H_2O$	2	5.13 gm.
$UO_2(NO_3)_2 \cdot 6H_2O$	1	5.02 gm.
K_2CO_3	3	4.14 gm.

Add slowly the uranium nitrate solution to the K_2CO_3 solution in the presence of phenolphthalein as indicator. If the indicator decolorizes, add K_2CO_3 solution until the indicator is just barely pink. Now add magnesium nitrate solution. If the phenolphthalein decolorizes, add K_2CO_3 solution until the indicator is just barely pink. Allow to crystallize at room temperature.

Bayleyite also was synthesized by first preparing the insoluble silver uranyl carbonate, reacting an excess of the silver uranyl carbonate with magnesium chloride, filtering off the precipitate of AgCl and excess silver uranyl carbonate, and allowing the filtrate to crystallize. Sometimes a gelatinous mass formed on drying, but by "seeding" this mass crystallized nicely (Figs. 3*a* and 3*b*). The reaction is $Ag_4UO_2(CO_3)_3 + 2MgCl_2 + 18H_2O \rightarrow \text{bayleyite} + 4AgCl$.

Andersonite was synthesized similarly to bayleyite.

	Molecular Ratio	*Weights*
$Ca(NO_3)_2 \cdot 4H_2O$	1	2.36 gm.
$NaNO_3$	2	1.62 gm.
K_2CO_3	3	4.14 gm.
$UO_2(NO_3)_2 \cdot 6H_2O$	1	5.02 gm.

Again the uranium solution was added to K_2CO_3 solution and the acidity was adjusted with K_2CO_3 until the phenolphthalein was just pink. Then a solution of $NaNO_3$ and $Ca(NO_3)_2$ was added, the acidity was adjusted as before and the mixture was allowed to crystallize at room temperature.

At first there was some difficulty in synthesizing swartzite by similar procedures; on evaporating a solution of the constituents a greenish-yellow glass, or better, gel, of refractive index near 1.53 forms, but on "seeding" with a fragment of the natural mineral, excellent crystals develop.

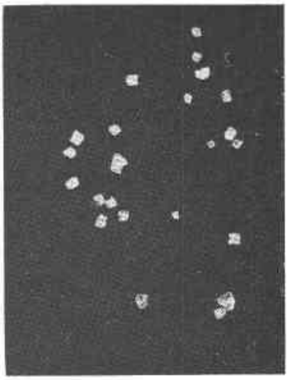

FIG. 1 ×15
Swartzite $CaMgUO_2(CO_3)_3 \cdot 12H_2O$
Yavapai County, Arizona

FIG. 2 ×15
Andersonite $Na_2CaUO_2(CO_3)_3 \cdot 6H_2O$
Yavapai County, Arizona

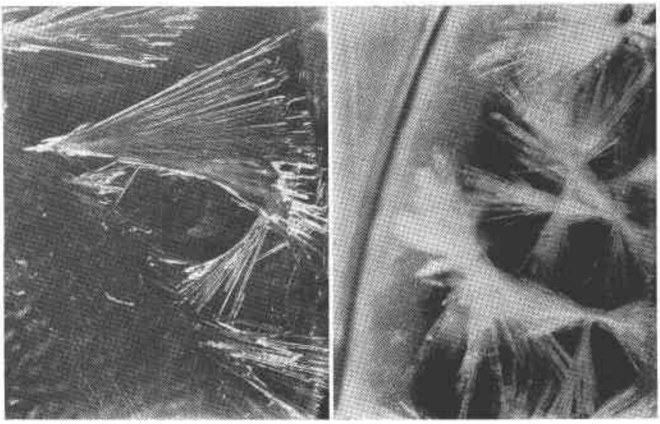

FIG. 3*a* ×38 FIG. 3*b*

Bayleyite $Mg_2UO_2(CO_3)_3 \cdot 18H_2O$ (Synthetic)
The synthetic preparations yield acicular crystals; the natural bayleyite was stubby prismatic, with good terminal faces.

REMARKS ON THE HOMOLOGOUS $X_4UO_2(CO_3)_3\cdot nH_2O$ SERIES

As already mentioned, numerous synthetic compounds of the above general formula are known, in which X_4 may represent four univalent ions, two similar divalent, or, as in the naturally occurring minerals,

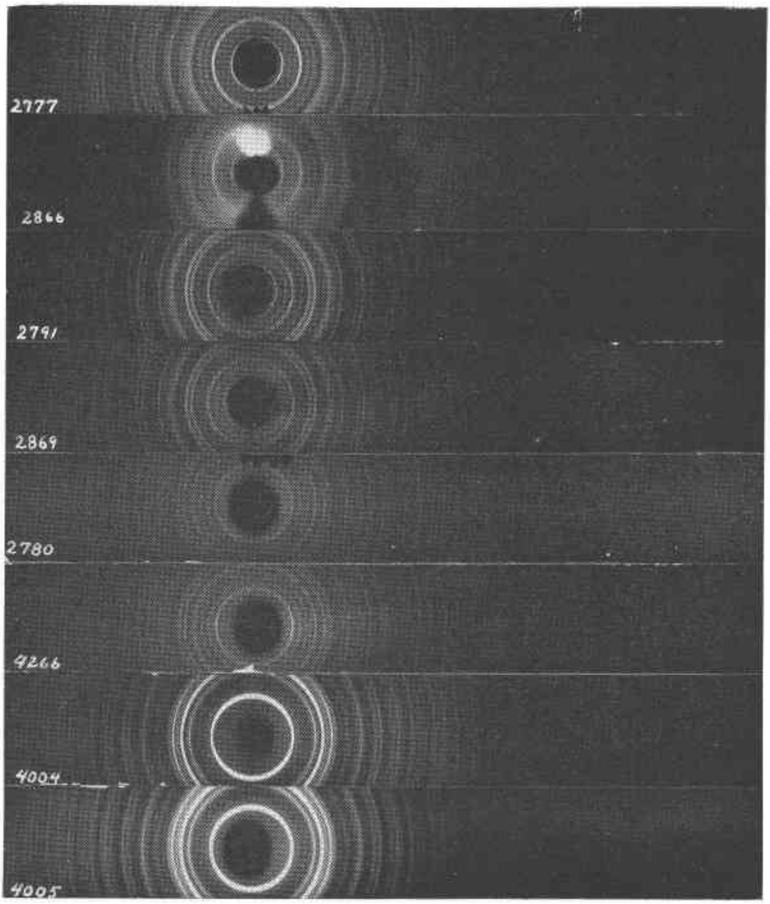

FIG. 4. Powder patterns of uranium minerals and synthetic preparations (filtered copper radiation)

2777	Bayleyite, Arizona
2866	Bayleyite, Synthetic
2791	Andersonite, Arizona
2869	Andersonite, Synthetic
2780	Swartzite, Arizona
4266	Swartzite, Synthetic
4004	Dehydration product of bayleyite, Arizona
4005	Dehydration product of bayleyite, Synthetic

two different divalent, or two univalent and one divalent, ions. It would be of interest to determine how extensively the series extends, whether a univalent and a trivalent ion, or a single quadrivalent ion could function as X_4. The varying value of n, determined for a large number of the compounds, should be of interest from a theoretical structural viewpoint. Also, the variation in fluorescence of the naturally occurring compounds with varying states of hydration, now an unexplained feature of this class of substances, could perhaps be clarified by a study of a large number of these homologues, in which the variations in cation and water content are known factors.

X-RAY INVESTIGATION

X-ray powder and Weissenberg diffraction patterns were made of andersonite, swartzite, and bayleyite. Powder patterns were made of the dehydration products of swartzite and bayleyite, and also of schroeckingerite. "Randite" (=β-uranotile), uranothallite (=liebigite), "voglite" (often actually liebigite), "rutherfordine" (=an undescribed calcium uranium silicate) also were studied by their powder patterns.

Data from powder patterns

Table 5 gives the powder pattern data on the new minerals.

The error figures are estimates. The diffraction data for andersonite and swartzite were inconclusive as to the presence of a center of symmetry, so piezoelectric tests were made through the kindness of Paul L. Smith at the Naval Research Laboratory in Washington. The crystals showed no piezoelectricity, so that this test also was inconclusive. None of the crystals had enough faces to determine the crystal class from morphology or good enough faces to make etch tests practicable.

THE NEW MINERAL NAMES

Andersonite is named after Charles A. Anderson, geologist of the United States Geological Survey, who first observed and collected the material from which these minerals were isolated and identified.

Swartzite is named for Charles K. Swartz (1861–1949), professor of geology and mineralogy at The Johns Hopkins University, an inspiring teacher of many generations of students.

Bayleyite is named in honor of William S. Bayley (1861–1943), for many years professor of mineralogy and geology at the University of Illinois, and geologist with the United States Geological Survey.

The naturally formed dehydration products of bayleyite and swartzite are not proposed as species. Although the dehydration product of the bayleyite, at least, yields a characteristic and definite *x*-ray diffraction-

TABLE 5. POWDER PATTERN DATA (FILTERED COPPER RADIATION)
$\lambda = 1.5418$ Å

Andersonite, Arizona			Swartzite, Arizona		
d	*I*	*hkl*	*d*	*I*	*hkl*
13.0	10	100	8.76	10	110
9.51	3	101	7.31	9	020
7.97	10	111	6.37	5	001
6.56	2	200	5.83	1	011
5.68	10	$10\bar{2}$, 112	5.50	10	$11\bar{1}$, 200
5.22	10	$\bar{1}12$, $11\bar{2}$	5.13	1	210
4.35	6	$\bar{1}22$	4.82	8	111, 021
4.19	6	103	4.62	2	$12\bar{1}$
4.04	4	113, $10\bar{3}$, 222	4.46	2	$20\bar{1}$, 130
3.82	3	$11\bar{3}$	4.37	2	220
3.71	8	203, $\bar{2}22$	3.85	2	201
3.49	2	$\bar{1}23$	3.66	7	040, 230
3.34	2	223	3.53	5	310
3.15	5*b*	303, $\bar{2}23$, $22\bar{3}$	3.39	1	221
3.00	7	$\bar{1}33$, $11\bar{4}$, $30\bar{3}$	3.31	1	$23\bar{1}$, $31\bar{1}$
2.79	6		3.25	1	320
2.45	5		3.19	7	$10\bar{2}$, 002
2.39	5		3.11	2	$32\bar{1}$
2.36	4		3.04	1	240, 231
2.21	7		2.91	8	022, $21\bar{2}$, 311
2.04	4		2.82	2	
2.01	4		2.61	5	
1.977	4		2.28	4	
1.957	4		2.23	3	
1.933	4		2.19	2	
1.895	4		2.10	2	
1.852	6		2.06	8	
1.749	5		1.817	5	
1.684	3		1.707	8	
1.573	4		1.375	2	
1.393	3		1.268	2	
1.344	3		1.217	3	
1.262	3		.9615	2	
1.232	3				
1.038	2				
.9803	2				
.9505	2				
.8192	2				
.8011	2				

(The dehydration product of swartzite is amorphous to *x*-rays)

b: Broad

TABLE 5 (continued)

Bayleyite, Arizona			Dehydration product of bayleyite, Arizona	
d	*I*	*hkl*	*d*	*I*
13.1	9	200, 110	8.27	10
7.66	10	310, 020	7.25	2
6.53	4	400, 220, 001	6.24	1
5.85	4*b*	201, 111, $11\bar{1}$	5.54	1
5.08	4	311	5.34	5
4.89	4	021, $31\bar{1}$, 401	5.13	3
4.71	1	221, $22\bar{1}$	4.77	9
4.54	2	$40\bar{1}$	4.62	2
4.41	2	330, 600	4.51	3
3.83	6	620, 040	4.42	3
3.70	2	331, 710, 530, 240	4.23	7
3.26	4	002	4.00	3
3.15	2	$11\bar{2}$, 212 (*n.r.*)	3.75	2
3.05	2	312 (*n.r.*), 730, 911	3.56	2
2.96	2		3.49	3
2.88	4		3.20	3
2.69	5		3.11	4
2.42	2		3.07	3
2.37	2		3.02	3
2.30	2		2.89	2
2.21	5		2.86	2
2.12	4		2.76	3
1.908	3*b*		2.71	3
1.796	2*b*		2.64	4
1.754	2*b*		2.47	2
1.682	1		2.44	3
1.378	1		2.32	4
1.247	1		2.26	3
			2.14	3
			2.12	3
			2.08	2
			2.05	3
			1.973	2
			1.881	4
			1.848	3
			1.811	2
			1.787	3
			1.752	2
			1.695	3
			1.578	3
			1.551	2
			1.352	2*b*

n.r.: Not recorded on any Weissenberg film
b: Broad

TABLE 6. CRYSTALLOGRAPHIC DATA FROM SINGLE CRYSTAL WEISSENBERG *X*-RAY STUDY

Andersonite: $Na_2CaUO_2(CO_3)_3 \cdot 6H_2O$

$a = 13.11 \pm .02$ Å Space group: $R\bar{3}(C_{3i}^2)$ or $R3$ (C_3^4), rhombohedral
$\alpha = 86°56' \pm 30'$ Z=6.
For the hexagonal description:
$a = 18.04 \pm .05$ Å Z=18
$c = 23.90 \pm .05$ Å
$c/a = 1.325$. Calculated density=2.86 (2.8 measured).

Swartzite: $CaMgUO_2(CO_3)_3 \cdot 12H_2O$

$a = 11.12 \pm .05$ Å Space group: $P2_1/m(C_{2h}^2)$ or $P2_1(C_2^2)$, monoclinic
$b = 14.72 \pm .05$ Å Z=2
$c = 6.47 \pm .02$ Å. Calculated density=2.32 (2.3 measured).
$\beta = 99°26' \pm 30'$

Bayleyite: $Mg_2UO_2(CO_3)_3 \cdot 18H_2O$

$a = 26.65 \pm .05$ Å Space group: $P2_1/a(C_{2h}^5)$, monoclinic
$b = 15.31 \pm .05$ Å Z=4
$c = 6.53 \pm .02$ Å. Calculated density=2.06 (2.05 measured).
$\beta = 93°4' \pm 20'$.

pattern, this is not considered sufficient grounds for establishing a new mineral species, for the pattern may be that of a mixture.

SYNOPSIS OF URANIUM CARBONATE MINERALS

A tabulation of the known uranium carbonate minerals is given below in Table 7, followed by more detailed discussion of the status of the several species.

TABLE 7. URANIUM-CARBONATE MINERALS

Species	Year Discovered	Composition (reported)	Color	Remarks
liebigite	1848	$CaUO_2(CO_3)_2 \cdot 20H_2O$ (erroneous) see uranothallite below	apple-green	established species
voglite	1853	contains Ca, Cu, H_2O	emerald-green to bright grass-green	=liebigite? (in part)
schroeckingerite[8]	1873	$NaCa_3UO_2(CO_3)_3SO_4F \cdot 10H_2O$	green	well-established species
randite	1878	"hydrous Ca-U carbonate"	yellow	is impure β-uranotil
uranothallite	1853–1882	$Ca_2U(CO_3)_4 \cdot 10H_2O$	siskin-green	liebigite has priority
rutherfordine	1906	UO_2CO_3	yellow	dubious (not a carbonate)
sharpite	1938	$6UO_3 \cdot 5CO_2 \cdot 8H_2O$	yellow-green	needs further study
studtite	1947	U–Pb?–H_2O–CO_3	yellow	needs further study
diderichite	1947	U–H_2O–CO_3	yellow-green	needs further study
andersonite	1948	$Na_2CaUO_2(CO_3)_3 \cdot 6H_2O$	green	
swartzite	1948	$CaMgUO_2(CO_3)_3 \cdot 12H_2O$	green	
bayleyite	1948	$Mg_2UO_3(CO_3)_3 \cdot 18H_2O$	yellow	

Liebigite

Considerable confusion has existed in the past as to the status of liebigite. In 1848 J. Lawrence Smith[9] described a mineral under this name from Adrianople, Turkey, as a hydrous carbonate of calcium and uranium. He computed a formula $CaCO_3 \cdot (UO_2)CO_3 \cdot 20H_2O$. Later, in 1851,[10] he mentioned another occurrence of the same mineral from Johanngeorgenstadt. In 1853 the same mineral (as established by Evans and Frondel[11] in 1949) was described by Vogl[12] from Joachimsthaal under the name Uran-Kalk-Carbonate. Finally, in 1882, Schrauf[13] determined that Vogl's Joachimsthaal mineral differed in composition from that given by Smith, being $Ca_2U(CO_3)_4 \cdot 10H_2O$, and proposed the name uranothallite. Smith's original analysis of liebigite is therefore erroneous, but as Evans and Frondel have shown that his mineral is the same as the correctly determined uranothallite, Smith's name, liebigite, has priority. Weisbach[14] in 1875 proposed the name flutherite, which under the circumstances has no standing.

Voglite

Voglite was first described by Vogl[12] in 1853, from Joachimsthaal, as a copper calcium uranium hydrous carbonate. The name voglite was proposed by Haidinger in a footnote to the original description by Vogl. There is no reason to question its validity as a species, although, as noted by Frondel,[11] "Most specimens so labelled are uranothallite," i.e., liebigite. Such was the case with U. S. National Museum specimen R2763 from Joachimsthaal (Roebling collection).

Schroeckingerite

Schroeckingerite is discussed above.

Randite

Randite was first described by August Koenig[15] in 1878 as a canary-yellow incrustation of acicular tufts on granite, at Frankford, near Philadelphia, Pa. An analysis of 47 milligrams of impure material is cited by *Dana*, System, 6th Ed. p. 309, as indicating a hydrous calcium uranium carbonate. It differed from liebigite and voglite in color, being yellow, whereas these two are green. An imperfect analysis gave a formula $Ca_5U_2C_6O_{20} \cdot 3H_2O$. The author proposed the name randite, with a reservation that the mineral needed further study before acceptance as a new species.

A specimen from the United States National Museum R2765 (Roebling Collection) of so-called randite shows a thin waxy crust of greenish yellow color. Microscopically, extremely small needles with ill-defined optics can be seen, but it was impossible to obtain enough for quantitative analysis.

However, from Dr. Frondel it was learned that the original randite "is a gross mixture of β-uranotil, tyuyamunite, kaolin, and calcite, with the β-uranotil dominant and representing the acicular crystals. . . . "[16] Further, Frondel observes, "An authentic specimen of randite from Sam Gordon proved to be tyuyamunite. Other specimens labelled randite were β-uranotil."[17] The National Museum randite above mentioned (R2765) gave an x-ray powder pattern similar to that of β-uranotil from Joachimsthaal (H7644 from the Harvard collection).

The suggestion of Ramdohr[18] that randite may be uranothallite, is therefore untenable.

A definitive study of randite by Frondel[19] published recently shows it to be a mixture of known minerals, it is therefore to be discredited as a species.

Uranothallite

Uranothallite is discussed above.

Rutherfordine

Rutherfordine was described in 1906 by W. Marckwald[20] from German East Africa with the formula $UO_2 \cdot CO_3$. We have studied the U. S. National Museum specimen 93291 so labelled, and found its x-ray diffraction pattern to be the same as that of a presumably new calcium uranium silicate from Mitchell Co., N. C., in the Harvard collection (personal communication from Clifford Frondel). The species is therefore not to be included among the uranium carbonates.

Sharpite

Sharpite was described in 1938 by J. Melon[21] from Shinkolobwe, Belgian Congo, as $6UO_3 \cdot 5CO_2 \cdot 8H_2O$. No x-ray data are available, but its identity as a species rests on an analysis and optical data.

Studtite and diderichite

Studtite and diderichite were described in 1947 by J. Vaes[22] from Shinkolobwe, Belgian Congo, as possibly uranium carbonates. The comment of Michael Fleischer[23] on these proposed names is justified: "It is to be regretted that new names were given to these very poorly characterized minerals. . . . It would be better to hold up publication of descriptions like these until enough data at least were obtained so that future workers could recognize the minerals from the descriptions."

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