ZELLERITE AND METAZELLERITE, NEW URANYL CARBONATES[1]

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Abstract

The mineral zellerite, named after Howard D. Zeller, occurs at the Lucky Mc uranium mine, Fremont County, Wyoming, as pin-cushion clumps of needlelike orthorhombic crystals on oxidized uranium ore and is intimately associated with gypsum and secondary iron oxides. The recalculated analysis gives CaO 10.3, UO_3 53.9, CO_2 16.9, H_2O^+ (110°) 12.3, H_2O^- (110°) 6.6 after SiO_2+insoluble 0.5, R_2O_3 1.0, K_2O 0.2, Na_2O 0.4 were subtracted as impurities. This gives a ratio of CaO:UO_3:$CO_2$$H_2O$ of 1.00:1.03:2.09:5.81. This ratio and other considerations regarding the water content, yields the formula $CaUO_2(CO_3)_2 \cdot 5H_2O$ for the fully hydrated mineral. On partial dehydration, a probable metacalcium uranyl dicarbonate of formula $CaUO_2(CO_3)_2 \cdot 3H_2O$, metazellerite, is produced.

Single-crystal x-ray studies of both hydrated and dehydrated material yield: (1) zellerite, orthorhombic, probable space group $Pmn2_1$ or $Pmnm$, a 11.220, b 19.252, c 4.933 Å, cell contents $4[CaUO_2(CO_3)_2 \cdot 5H_2O]$, cell volume 1065.4 Å³; (2) metazellerite, orthorhombic, space group $Pbn2_1$ or $Pbnm$, a 9.718, b 18.226, c 4.965 Å, cell contents $4[CaUO_2(CO_3)_2 \cdot 3H_2O]$, cell volume 879.5 Å³.

The fully hydrated mineral is lemon yellow with a dull luster and no cleavage. Measured specific gravity is 3.25; calculated 3.24 gm/cm³. The optical properties are: α 1.536, β 1.559, γ 1.697, biaxial (+), 2V=30–40°, Z=c, dispersion weak v>r; pleochroism: Z=light yellow, Y=colorless, X=colorless. The mineral has a weak patchy green fluorescence under long and short ultraviolet light. It forms as an oxidation product of uraninite-coffinite in the weathering zone, where P_{CO_2} is greater than that in the atmosphere and pH is greater than 7.

Introduction

Studies on the uranium minerals making up the ores from the Gas Hills deposit in Wyoming have revealed a complex suite of secondary minerals in the oxidized zone. In July 1955, Howard D. Zeller, U. S. Geological Survey, discovered an unknown yellow, fibrous uranium mineral in the oxidized zone of the Lucky Mc mine. Preliminary x-ray studies by Daphne R. Ross indicated that the mineral has a structure distinct and different from previously described secondary uranium minerals. Chemical analysis confirmed that it is a uranyl carbonate of distinct composi-

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tion. The mineral, a calcium uranyl carbonate, $CaUO_2(CO_3)_2 \cdot 5H_2O$, is named zellerite after Zeller. Much of the preliminary geologic investigation on these uranium deposits carried out by him were instrumental in the later successful exploration and mining operations of this important uranium district (Zeller, 1957; Zeller *et al.*, 1956). The names zellerite and metazellerite have been approved by the New Mineral Names Committee, IMA.

OCCURRENCE

Zellerite is found as incrustations on arkosic country rock; it forms during surface oxidation of the uranium ore. The unoxidized ore in the Lucky Mc mine is a fine-grained mixture of uraninite, coffinite, and iron sulfides filling intergranular areas in arkose. The coarse and porous nature of the host rock allows rapid moist-air oxidation of these primary uranium minerals and sulfides. In the early stages of oxidation, black primary ore commonly contains fine seams of green liebigite $[Ca_2(UO_2)(CO_3)_3 \cdot 10H_2O]$ intergrown with gypsum. Rimming this dark ore is a rusty brown zone where the oxidation has effected the breakdown of all the primary uranium minerals and some of the iron sulfides. Zellerite is most commonly present in this zone where it is associated with gypsum, limonite and partially altered iron sulfides. It forms extremely fine fibers that aggregate into pincushion clumps (Fig. 1). Schoepite $[UO_2(OH)_2 \cdot H_2O]$, meta-autunite $[Ca(UO_2)_2(PO_4)_2 \cdot 2.5-6.5H_2O]$, uranophane $[Ca(UO_2)_2Si_2O_7 \cdot 6H_2O]$, and uraniferous opal are present in the more intensely oxidized zones contiguous to the zellerite.

A second occurrence of zellerite in Wyoming from the Pat No. 8 mine, Powder River Basin, Wyo., was brought to the attention of the senior author by William Sharp (*in* Sharp and Gibbons, 1964), U. S. Geological Survey, and a third occurrence in New Mexico has been confirmed by Granger (1963). These occurrences are similar to that at the Lucky Mc mine in that the zellerite forms as small veins and clumps in oxidized zones surrounding the unoxidized ore.

PROPERTIES

Physical. Zellerite crystals are so fine that indivudual crystal faces could not be discerned. The habit of these crystals was always found to be fibrous and hairlike, aggregating into pincushion clumps (Fig. 1). The mineral is quite soft, with a hardness similar to gypsum. Cleavage was not observed; however, the aggregated clumps always fracture in the direction of elongation.

The measured specific gravity of the mineral is 3.25 ± 0.01 as determined by suspension in a mixture of bromoform and methylene iodide.

The variation in density noted among the individual specimens was attributed to differences in state of hydration.

Zellerite is a light lemon yellow and on dehydration assumes a chalky yellow color. In long and short wave ultra-violet light, zellerite shows a weak patchy green fluorescence; however, as compared with other uranium carbonates, particularly liebigite, it is practically nonfluorescent.

Optical. In ordinary white transmitted light, zellerite is transparent and light yellow. Individual crystals seldom exceed 2 mm in length and 5μ in
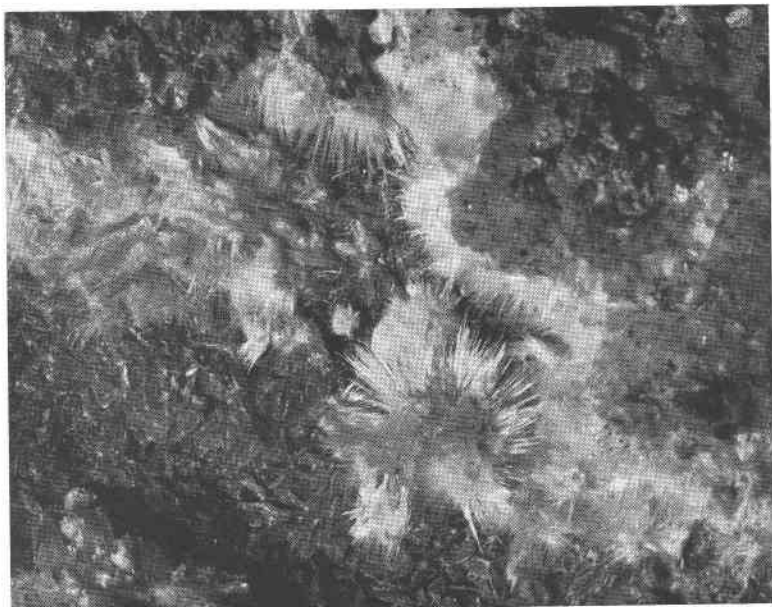

FIG. 1. Zellerite showing crystalline habit. The pin-cushion clumps are implanted on gypsum. ×4.5.

width. Variations in indices were noted and could be related to the changes in the hydration state of the mineral. Indices of the lower hydrate were not measured because suitable crystals could not be obtained. The optical constants of zellerite given in Table 1 are considered to characterize the fully hydrated zellerite. Using the Gladstone-Dale law (Jaffe, 1956), the average index calculated for zellerite compares favorably with the average measured index.

Chemistry. The one-gram sample used for analysis was carefully purified by centrifuging in organic heavy liquids. The final concentrate was con-

sidered to be at least 98 per cent pure; the remaining 2 per cent includes minor amounts of clay, quartz and limonite. The metastability of zellerite means that even though the final separate was pure, some metazellerite was present and no precautions were taken to control the humidity. Spectrographic analysis and x-ray studies of the concentrate confirm the optical estimate of sample purity.

Procedures of the chemical analysis are described briefly. The original

TABLE 1. X-RAY AND OPTICAL DATA FOR ZELLERITE

	Zellerite		Metazellerite	
Crystal system	Orthorhombic		Orthorhombic	
Space Group	$Pmn2_1$ or $Pmnm$ (probable)		$Pbn2_1$ or $Pbnm$	
	Powder data[1]	Single crystal	Powder data[1]	Single crystal
a	11.220 ± 0.015 Å	11.1_4 Å	9.718 ± 0.005 Å	9.7_5 Å
b	19.252 ± 0.016 Å	19.1_5 Å	18.226 ± 0.009 Å	18.2 Å
c	4.933 ± 0.016 Å	4.9_4 Å	4.965 ± 0.004 Å	4.9_4 Å
Cell volume	1065.4 ± 2.3 Å		879.5 ± 0.7 Å	
Cell contents (Ideal formula)	$4[CaUO_2(CO_3)_2 \cdot 5H_2O]$		$4[CaUO_2(CO_3)_2 \cdot 3H_2O]$	
Density (calc. for ideal formula)	3.24_2		3.41_4	
Specific gravity measured	3.25 ± 0.01		—	
Biaxial negative	$2V = 30 - 40°$		$2V$?	
α colorless	$1.536 \pm .005$			
β colorless	$1.559 \pm .005$			
γ light yellow	$1.697 \pm .005$			
Orientation	$Z = C$		$Z = C$	
Dispersion	$v > r$		?	
n average (measured)	1.597		—	
n calculated[2]	1.595		1.626	

[1] Data derived from least-squares refinement of x-ray powder data listed in Table 3 using the method of Evans *et al.* (1963).

[2] Calculated using the Gladstone-Dale law (Jaffe, 1956).

sample was air dried to a constant weight at $110° \pm 5°C$. The resulting loss in weight is reported as minus water. However, part of this minus water is thought to be essential to the mineral in order that there be 20 molecules of H_2O per unit cell. A modified microcombustion train of the type made for the determination of carbon and hydrogen in organic compounds was used to determine H_2O^+ and CO_2. For this, a 20-mg sample was decomposed by ignition at $900°C$ in a stream of oxygen.

The R_2O_3 was determined by difference after the total $R_2O_3 + U_3O_8$ had been determined gravimetrically using carbon dioxide-free NH_4OH and

methyl red as the indicator. UO_3 was determined spectrophotometrically by the ammonium thiocyanate procedure in acetone-water medium after solution of the R_2O_3 residue in $(1+1)$ HNO_3.

CaO was determined as the sulfate after it was separated from an $85 \pm$ per cent ethyl alcohol solution. Qualitative spectrographic analysis of the $CaSO_4$ precipitate showed that the only major constituent was calcium; there were no minor constituents.

K_2O and Na_2O were determined by flame photometry. The filtrate from the CaO determination was transferred to a platinum evaporating dish, and taken to dryness, then ignited. The remaining salts were dis-

TABLE 2. CHEMICAL ANALYSIS OF ZELLERITE
Analyst, Robert Meyrowitz

	1	2	3	4
CaO	10.8	10.3	.1836	1.00
UO_3	56.6	53.9	.1884	1.03
CO_2	17.7	16.9	.3840	2.09
H_2O^+	13.0	12.3	.6833	3.72
SiO_2+insol.	0.5			
R_2O_3	1.0			
K_2O	0.2			
Na_2O	0.4			
Total	100.2			
$H_2O(-)$	6.9	6.6	.3833	2.09
		100.0		

1. Weight percent of the oxides determined on sample air dried to 110°C.
2. Recalculation of analyses to 100% without SiO_2, R_2O_3, K_2O, Na_2O and insolubles.
3. Molecular proportions.
4. Molecular ratios.

solved in $(1+1)$ HCl and transferred to a volumetric flask and diluted to volume. Aliquots of this solution were used for the K_2O and Na_2O determinations, comparing them to standard potassium and sodium solutions. Twenty-five milligrams were used for the $H_2O(-)$, SiO_2+insoluble R_2O_3, CaO, UO_3, K_2O, and Na_2O determinations.

The recalculated analysis of zellerite (Table 2) produces a formula that is distinct from the uranyl carbonates previously described. Assuming that part of the H_2O^- combined with H_2O^+ characterizes fully hydrated zellerite, the calculated formula is $CaUO_2(CO_3)_2 \cdot 5H_2O$. Variation in the measured physical constants indicates different hydration states of zellerite. If we assume that H_2O^- as determined is easily lost, then a lower hydrate metazellerite $CaUO_2(CO_3)_2 \cdot 3H_2O$ would become stable at higher

temperatures or lower humidities. Metazellerite was not available in amounts sufficient to obtain precise physical measurements related to the changes accompanying hydration-dehydration, but as is demonstrated by the x-ray results, the structural change on dehydration is distinct and can be characterized.

X-ray crystallography. The x-ray powder pattern made of the fresh "zellerite sample" showed only the fully hydrated phase, zellerite, to be present (Table 3). Powder patterns made subsequently, after the sample had been exposed to the laboratory atmosphere for several weeks, invariably showed the dehydrated phase, metazellerite, to be present with zellerite. One x-ray powder pattern (Table 3) showed almost total conversion of zellerite to metazellerite.

Several needlelike crystals from the "zellerite sample" were examined with the Buerger x-ray precession camera. Invariably a strong single-crystal pattern of the dehydrated metazellerite phase would appear in parallel orientation with the weaker single-crystal pattern of the fully hydrated zellerite phase. Zellerite is apparently unstable with respect to metazellerite under the conditions of the x-ray experiment, although it may persist metastably with metazellerite for long periods of time. Buerger precession photographs, exposed for 100 hours with molybdenum zirconium-filtered x-radiation, were made of the $0kl$, $1kl$, $h0l$, $h1l$, and $h2l$ reciprocal lattice nets. These photographs show both phases to be orthorhombic with the following unit-cell data: zellerite, a 11.1_4, b 19.1_5, c 4.9_4 Å, probable diffraction symbol Pmn^*; metazellerite, a 9.7_5, b 18.2, c 4.9_4 Å, diffraction symbol Pbn^*. Owing to the weakness of the x-ray pattern, the diffraction symbol of zellerite cannot be positively assigned.

In order to verify the unit-cell parameters obtained from the rather poor single-crystal patterns and also to obtain more accurate values for these parameters, the x-ray powder data of both phases was subjected to least-squares refinement (Evans *et al.*, 1963) using the single-crystal data as the starting parameters. The final parameters as obtained from the least-squares analysis are given in Table 1 along with the other pertinent crystallographic and optical data.

The dehydration of zellerite to metazellerite involves a decrease in cell volume of 186 Å^3. This volume change strongly suggests a loss of 8 or 10 H_2O molecules. The space group requires that there be an even number of atoms of each type in the unit cell. Therefore zellerite $CaUO_2(CO_3)_2$ $\cdot 5H_2O$, with $Z=4$ probably has two more H_2O molecules per unit formula than metazellerite, $CaUO_2(CO_3)_2 \cdot 3H_2O$, with $Z=4$ if it is assumed there is a loss of $8H_2O$ molecules. Should we presume a $10H_2O$ loss on dehydration, the formula would have to be written $Ca_4(UO_2)_4(CO_3)_8 \cdot 20H_2O$, with

TABLE 3. X-RAY DIFFRACTION POWDER DATA FOR ZELLERITE AND METAZELLERITE

	Zellerite				Metazellerite		
	Calculated[1]	Observed[2]			Calculated[1]	Observed[2]	
hkl	d_{hkl}	d_{hkl}	I	hkl	d_{hkl}	d_{hkl}	I
010	19.25			020	9.113	9.10*	100
110	9.69	9.66	100				
020	9.63			110	8.575		
120	7.31	7.33*	18	120	6.648		
030	6.42			130	5.152	5.140*	2
200	5.610	5.591	35	200	4.859	4.868*	13
130	5.570			210	4.695	4.695*	36
210	5.386	5.405*	3	040	4.557	4.552*	18
220	4.847	4.848*	50	101	4.422	4.412*	18
040	4.813			021	4.360		
011	4.778			111	4.297	4.296	36
101	4.515			220	4.288		
140	4.423			140	4.126		
111	4.396	4.407	25	121	3.978	3.978*	18
021	4.390			230	3.795	3.794*	50
230	4.224	4.240*	4	131	3.575	3.579*	6
121	4.088			150	3.413		
031	3.911			211	3.411	3.411	2
050	3.850			041	3.357		
131	3.693			240	3.323	3.330*	13
310	3.671			221	3.245		
240	3.653	3.651	35	310	3.189		
150	3.642			141	3.173	3.173*	18
211	3.638			320	3.052		
320	3.486			060	3.038	3.033*	9
221	3.457	3.463*	6	231	3.015		
041	3.445			250	2.916	2.915*	2
141	3.293			160	2.899		
330	3.231	3.232*	3	330	2.858	2.858*	4
060	3.209			151	2.813	2.812*	2
231	3.208			241	2.762	2.763*	2
250	3.175			301	2.713		
160	3.085			311	2.683	2.687*	6
051	3.035			340	2.640	2.639*	1
301	2.980			321	2.600		
340	2.953			061	2.591		
311	2.945	2.947	13	260	2.576	2.580*	2
241	2.935			170	2.515		
151	2.930			251	2.514		
321	2.847	2.851*	2	161	2.504	2.508*	6
400	2.805			002	2.483		
260	2.785			331	2.477	2.478*	18
410	2.776	2.778	2	400	2.430		
070	2.750			350	2.421	2.415	9
331	2.703			410	2.408		
420	2.693			022	2.395		
061	2.690	2.687	9	112	2.384		
350	2.683			420	2.348	2.344*	2
170	2.671			341	2.331		
251	2.670			122	2.326		
161	2.616			270	2.295	2.294*	13
430	2.570			261	2.286		
341	2.534	2.532*	3	080	2.278		
270	2.469 ⎫			430	2.256	2.257*	6
002	2.466 ⎭	2.468	3	171	2.244		
012	2.446			132	2.237		
360	2.435	2.433*	6	180	2.218	2.219	4
261	2.425			360	2.216		
440	2.423			202	2.211		

TABLE 3—(*Continued*)

Zellerite				Metazellerite			
Calculated[1]		Observed[2]		Calculated[1]		Observed[2]	
hkl	d_{hkl}	d_{hkl}	I	hkl	d_{hkl}	d_{hkl}	I
411	2.419			212	2.195		
080	2.406			042	2.180	2.178	13
071	2.402			351	2.176		
112	2.390			411	2.167		
022	2.389			222	2.149	2.147*	2
421	2.364			440	2.144		
351	2.357	2.359	3	142	2.127		
180	2.353			421	2.122		
171	2.349			271	2.083	2.080	13
122	2.337			232	2.078		
032	2.302			081	2.071		
431	2.279			280	2.063		
450	2.267	2.263	3	431	2.054		
202	2.258			370	2.029		
132	2.255			181	2.025	2.025	18
212	2.242			361	2.024		
510	2.229			450	2.022		
370	2.216	2.214	6	152	2.008		
280	2.212					1.98	1
271	2.208					1.93	3
222	2.198					1.90	1
042	2.195					1.87	9
520	2.185					1.84	2
361	2.184					1.82	2
441	2.175	2.173*	2			1.78	6
081	2.163					1.73	4
142	2.154					1.71	4
090	2.139	2.138*	2			1.68	6
232	2.130					1.67	1
181	2.124					1.62	6
530	2.118					1.60	2
460	2.112					1.57	2
190	2.101	2.103*	3			1.56	2
052	2.077						
451	2.060	2.057*	3				
312	2.047						
242	2.044						
501	2.043						
152	2.042						
540	2.034						
511	2.031						
380	2.024	2.023	6				
371	2.021						
281	2.018						
322	2.013						
		1.94	1				
		1.86	4				
		1.84	2				
		1.82	2				
		1.79	2				
		1.73	2				
		1.71	3				
		1.64	2				

[1] d-spacings were calculated from the unit-cell parameters listed in Table 1. These parameters were obtained from a least-squares refinement of the observed d-spacings marked with an asterisk in the table above.

[2] Zellerite from Lucky Mc mine, Wyo. CuK$_\alpha$ radiation, Ni filter ($\lambda = 1.5418$ Å) Camera diameter:114.59 mm. Lower limit 2θ measurable: approximately 8° (11.0 Å). Intensities measured with a calibrated intensity strip.

$Z=1$, for zellerite and $Ca_4(UO_2)_4(CO_3)_8 \cdot 10H_2O$, with $Z=1$, for metazellerite. The chemical analysis would suggest that an average of 20 H_2O molecules per cell is correct for zellerite and observed change in volume would indicate that $12H_2O$ molecules per unit cell for metazellerite is correct.

To test the validity of the formula for zellerite, $CaUO_2(CO_3)_2 \cdot 5H_2O$, we have a calculated density of 3.242 g/cm³, which compares favorably with the measured specific gravity of 3.25 ± 0.01. The calculated average refractive index (Jaffe, 1956) of zellerite, using the ideal formula and calculated density from the x-ray data, is 1.595, and the average of the measured values on the analyzed material is 1.597 ± 0.005. The close agreement between the measured and calculated values for density and refractive index substantiates the proposed formula for zellerite. Dehydration of zellerite probably involves loss of 8 or $10H_2O$ molecules, but verification of the metazellerite formula awaits further optical and specific gravity measurements on this lower hydrate.

Relationship to other uranyl carbonates. Zellerite is the only known natural representative of the uranyl dicarbonates having the general formula $M^{2+}(UO_2)(CO_3)_2 \cdot nH_2O$. Bayleyite, swartzite, liebigite, the more com-

TABLE 4. COMPARISON OF CALCIUM AND MAGNESIUM URANYL CARBONATES

	Zellerite $Ca(UO_2)(CO_3)_2$ $\cdot 5H_2O$	Liebigite[1] $Ca_2(UO_2)(CO_3)_3$ $\cdot 10H_2O$	Bayleyite[1] $Mg_2(UO)_2(CO_3)_2$ $\cdot 18H_2O$	Rabbittite[1] $Ca_3Mg_3(UO_2)_2$-$(CO_3)_6(OH)_4$ $\cdot 18H_2O$	Swartzite[1] $CaMg(UO_2)$-$(CO_3)_3 \cdot 12H_2O$
α	1.536 light yellow	1.497 colorless	1.455 pinkish?	1.502 colorless	1.465 colorless
β	1.559 colorless	1.502 pale greenish yellow	1.490 pale yellow	1.508 colorless	1.51 yellow
γ	1.597 colorless	1.539 pale greenish yellow	1.500 pale yellow	1.525 colorless	1.54 yellow
Color	Lemon yellow	Siskin green	Yellow	Pale green	Green
Optic sign	$(+)$	$(+)$	$(-)$	$(+)$	$(-)$
2V	30–40°	40°	30°	?	40°
Density	3.25 ± 0.01	2.41	2.05	2.57	2.3
Flourescence	Weak, patchy green	Bright green	Weak, color uncertain	Cream yellow	Bright yellowish green
	Long and short wave	Long and short wave	Long and short wave	Short wave	Short wave
Habit	Fibrous	Prismatic	Prismatic acicular	Prismatic acicular	Prismatic
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	$Pmn2_1$ or $Pmnm$	Bba_2	$P2_1/a$	—	$P2_1/m$ or $P2_1$
a	11.220 Å	16.71 Å	26.65 Å	32.6 Å	11.12 Å
b	19.252	17.55	15.31	23.8	14.72
c	4.933	13.79	6.53	9.45	6.74
β	—	—	93°04'	90°	99°26'

[1] Data from Frondell (1958).

monly reported uranyl tricarbonates, have the ratio of 1:3 for (UO_3): (CO_3) (Table 4). Rutherfordine, the anhydrous uranyl carbonate, UO_2CO_3, could be considered the end member of the uranyl carbonates if we consider a series as shown in Fig. 2.

The low-temperature chemical relationships in the $U-O_2-H_2O-CO_2$ system have been explored adequately (Hostetler and Garrels, 1962; Garrels and Christ, 1959) so that the natural occurrence of uranyl carbonates can be explained. All of these authors have pointed out that both uranyl tri-
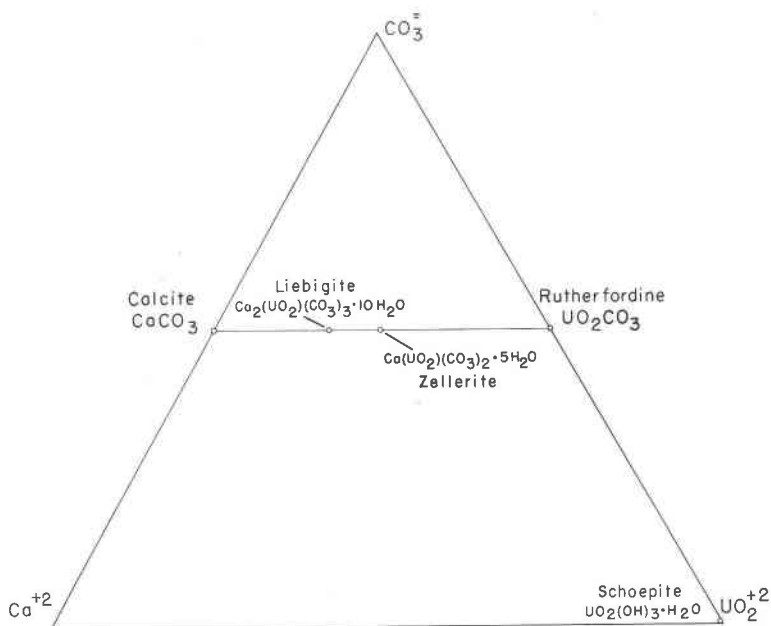
FIG. 2. Ternary diagram showing some mineral phases in the system $Ca^{2+} - CO_3^{2-} - UO_2^{2+}$ given in molecular per cent.

carbonate $[UO_2(CO_3)_3]^{4-}$ and uranyl dicarbonate $[UO_2(CO_3)_2 \cdot 2H_2O]^{2-}$ complexes may form in waters with $p_{CO_2} > 10^{-3}$ atmospheres and total ionic activity in excess of 10^{-6}. As one would suspect, the activities of the uranyl carbonate complexes are very sensitive to variations in p_{CO_2} and pH of the containing solutions. The Eh-p_{CO_2} diagrams constructed by Hostetler and Garrels (1962, p. 144–148) illustrate the stability fields of the uranyl carbonate complexes in response to changing conditions. Although these diagrams are representative of conditions at 25°C and 1 atmosphere, the environment of oxidation of the Lucky Mc uranium ore is so close to the depicted conditions that the natural occurrence of the uranyl carbonates can be related to the diagrams. Rutherfordine oc-

cupies a narrow field of stability with solutions whose pH is about 6, under oxidizing conditions, and with a total dissolved uranium activity in excess of 10^{-4}. When the partial pressure of CO_2 is near that of the atmosphere ($10^{-3.5}$ atmospheres), both schoepite ($UO_2(OH)_2 \cdot H_2O$) and rutherfordine (UO_2CO_3), are stable together (Garrels, 1957). Schoepite becomes unstable with an increase of p_{CO_2} in accordance with the reaction

$$UO_2(OH)_2 \cdot H_2O + CO_2 \rightarrow UO_2CO_3 + 2H_2O;$$
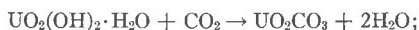
should the increase of p_{CO_2} be accompanied by increase in pH, the uranyl dicarbonate complex becomes stable and those solutions containing enough Ca^{2+} will precipitate zellerite on evaporation. By further increasing the pH at the same activities, the uranyl tricarbonate complex becomes stable instead of the dicarbonate, and solutions of this composition on evaporation would precipitate liebigite.

As stated earlier, liebigite forms as veins and incrustations in the primary dark ore during the early stages of oxidation at the Lucky Mc mine and before the breakdown of pyrite. Once the pH of the oxidizing surface is lowered by the pyrite alteration, zellerite is precipitated from these solutions rather than liebigite. In those areas removed from primary ore where CO_2 has been depleted, schoepite forms in association with uranyl silicates. Zellerite therefore must occupy a field of stability intermediate between rutherfordine and liebigite in the zone of weathering.

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