THE AMERICAN MINERALOGIST, VOL. 43, NOVEMBER-DECEMBER, 1958

HEINRICHITE AND METAHEINRICHITE, HYDRATED BARIUM URANYL ARSENATE MINERALS

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ABSTRACT

Heinrichite, $Ba(UO_2)_2(AsO_4)_2 \cdot 10\text{–}12H_2O$, and metaheinrichite, $Ba(UO_2)_2(AsO_4)_2 \cdot 8H_2O$, occur as tabular, yellow to green, fluorescent, transparent to translucent crystals belonging in the tetragonal system. Optically the minerals are uniaxial (−), sometimes anomalously biaxial with 2V up to 20°. The refractive indices of heinrichite are: $\omega = 1.605 \pm 0.002$ and $\epsilon = 1.573 \pm 0.002$. Those for metaheinrichite are: $\omega = 1.637 \pm 0.001$ (1.641 ± 0.002 for the mineral from the Black Forest, Germany) and $\epsilon = 1.609 \pm 0.002$. The calculated specific gravity of metaheinrichite is 4.09 and the measured specific gravity is 4.04. The space group of metaheinrichite is $P4_2$, $P4_2/m$, or $P4_222$; $a_0 = 7.07$ Å, $c_0 = 17.74$ Å, and $a_0 : c_0 = 1 : 2.509$, $Z = 2$.

The minerals have thus far been found near Lakeview, Oregon, and in the Black Forest of Germany. They are named for Professor E. William Heinrich, University of Michigan.

INTRODUCTION

In his description of the uranium deposits of the central Black Forest, Germany, Kirchheimer (1952, p. 56) mentioned a yellow secondary uranium mineral which he called meta-uranocircite or a similar barium uranyl arsenate. Bültemann (1954, p. 160) confirmed this, stating that he found small crystals of a secondary uranium mineral containing barium, uranium, arsenic, and water on specimens from the Anton mine. Walenta made a more thorough investigation of the Black Forest material which he described in an unpublished, preliminary report (Walenta, 1958).

In 1956 specimens of a mineral from the White King mine, Lakeview, Oregon, originally believed to be novacekite, were sent to the Mineralogy Laboratory, U. S. Atomic Energy Commission, Grand Junction, Colorado, by E. K. Thurlow, Salt Lake Exploration Branch, Atomic Energy Commission, and H. B. Wood, Geologic Branch, Atomic Energy Commission, Grand Junction. A spectrographic analysis of this mineral showed the presence of major amounts of barium, uranium, and arsenic. The material studied in the Atomic Energy Commission Mineralogy Laboratory was taken from ore shipped to Climax Uranium Company, Grand Junction.

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In his preliminary report Walenta called the minerals sandbergerite and metasandbergerite (Walenta 1958, pp. 4–7, Guillemin and Permingeat, 1958, pp. 68–69). Simultaneously Gross, Corey, and Mitchell named the minerals heinrichite and metaheinrichite, for Professor E. William Heinrich, Department of Mineralogy, University of Michigan. The names heinrichite for $Ba(UO_2)_2(AsO_4)_2 \cdot 10\text{-}12H_2O$ and metaheinrichite for the lower hydrate with $8H_2O$ have since been accepted by all the authors.

Both hydrates are common in the Black Forest material. Only traces of the higher hydrate were found during the study of the minerals from Oregon because heinrichite dehydrates readily to metaheinrichite and the laboratory investigations took place under conditions of low relative humidity. Only freshly broken crystals showed the lower refractive indices and these fragments very shortly dehydrated.

Occurrence

Heinrichite and metaheinrichite are found in the White King mine, sec. 30, T. 37 S., R. 19 E., approximately 14 miles northwest of Lakeview, Lake County, Oregon (Fig. 1). The minerals coat fractures and line vugs in light gray, altered, silicified rhyolite tuff. They are present at or near the surface, while at greater depth the uranium mineral is coffinite, which is associated with orpiment and realgar.

In the central Black Forest, heinrichite and metaheinrichite have thus far been discovered at three different localities: Wittichen (Sophia mine), Anton mine near Schiltach, and Reinerzau. They occur as small crystals and coatings of scaly aggregates on granite and on the gangue minerals, barite and quartz. They are formed from the alteration of pitchblende, a primary constituent of the Co-Ni-Bi-Ag-U veins of the region, and are

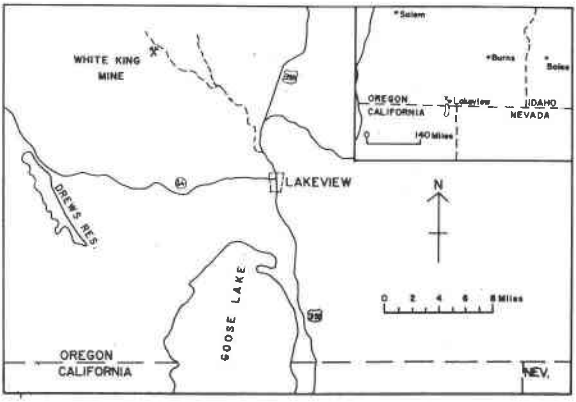

FIG. 1. Map of Lakeview, Oregon, and vicinity, showing location of the White King mine.

associated with other secondary uranium minerals, mainly zeunerite and novacekite, and with erythrite, arseniosiderite, and pitticite.

PHYSICAL AND OPTICAL PROPERTIES

The physical appearance of heinrichite and metaheinrichite crystals (Fig. 2) is identical. The crystals are transparent to translucent and yellow to green in color and have a vitreous to pearly luster. The minerals fluoresce bright green to greenish yellow under short and long wave ultraviolet light.

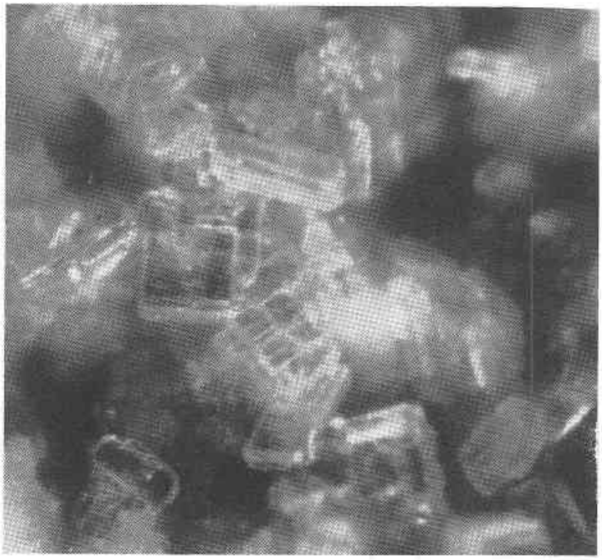

FIG. 2. Tabular crystals of metaheinrichite in vug from Oregon. ×50.

The crystals from Oregon are tabular {001} and are up to one mm. on a side, and not more than 0.1 mm. thick. Cleavage is perfect on {001} and distinct on {100} (Fig. 3). The forms observed are {001}, {100}, and {110}. Crystals from the Black Forest show the same cleavage and the same forms, but in part are elongated along a horizontal axis so that in their aspect they resemble the monoclinic bassetite crystals described by Frondel (1954, p. 348).

The hardness is 2.5. The calculated specific gravity of metaheinrichite is 4.09. A specific gravity of 4.04 was measured on material from Oregon dried at 110° C. using kerosene and a 10 ml. Leach pycnometer. Repeated grindings and separations using acetylene tetrabromide failed to eliminate a small percentage of host rock so that the measured value is slightly lower than the calculated one. Attempts to measure the specific gravity of

TABLE I. OPTICAL PROPERTIES OF HEINRICHITE AND METAHEINRICHITE

Black Forest	Oregon
Heinrichite	
Refractive indices Pleochroism	Refractive indices Pleochroism
$\omega=1.605\pm0.002$, pale yellow $\epsilon=1.573\pm0.002$, colorless Uniaxial (−), sometimes anomalously biaxial with 2V up to 20°.	$\omega=$- - - - - - - - - - - $\epsilon=1.574\pm0.001$, colorless Uniaxial (−), sometimes anomalously biaxial.
Metaheinrichite	
$\omega=1.641\pm0.002$, pale yellow $\epsilon=1.609\pm0.002$, colorless Uniaxial (−), sometimes anomalously biaxial with 2V up to 18°.	$\omega=1.637\pm0.001$, pale yellow $\epsilon=1.609\pm0.001$, colorless Uniaxial (−), sometimes anomalously biaxial with 2V up to 10°.

the Black Forest minerals failed because of the small amount of material available.

The optical properties of heinrichite and metaheinrichite are given in Table I.

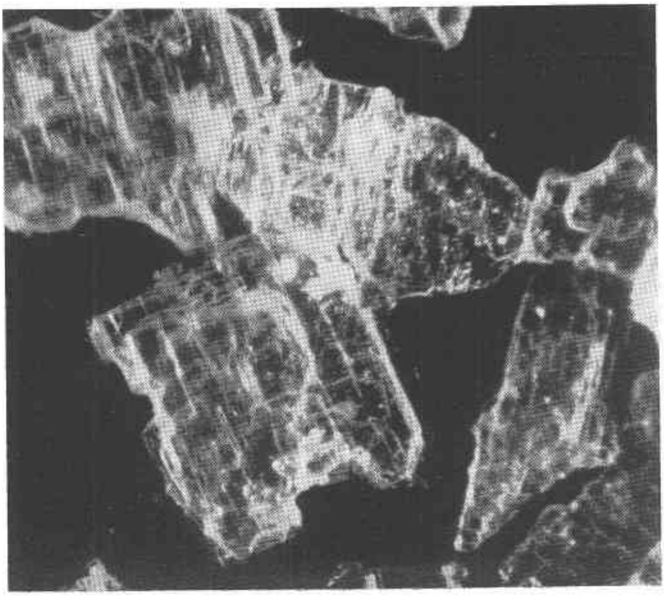

FIG. 3. Cleavage fragments of metaheinrichite from Oregon lying on (001), showing traces of (100) and (010) cleavages. ×100.

COMPOSITION

Two semi-quantitative spectrographic analyses of metaheinrichite from Oregon are given in Table II. The results agree closely with those of the chemical analysis (Table III). No phosphorus was detected in the heinrichite and metaheinrichite from the Black Forest, but a small quantity of copper was detected in some crystals.

The ideal formula for metaheinrichite, $Ba(UO_2)_2(AsO_4)_2 \cdot 8H_2O$, was derived from the recalculated chemical analysis given in Table IV. It

TABLE II. SEMI-QUANTITATIVE SPECTROGRAPHIC ANALYSES OF METAHEINRICHITE FROM OREGON

Element	(1) %	(2) %
Si	.3	.3
Al	.3	.3
Fe	.15	.1
Mg	.03	.003
Ca	.07	.1
P	1.5	1.0
Na	—	<.01
K	—	.003
Ti	—	.001
Mn	—	.003
As	M	M
Ba	M	M
Bi	<.1	—
Cu	.07	.003
Pb	.7	1.0
Sb	<.1	—
Sr	—	.003
U	M	M

M: Major constituent, greater than 10%.

—: Not looked for.

Looked for, but not detected: Ag, Au, B, Be, Cd, Ce, Co, Cr, Cs, Dy, Er, Eu, Ga, Gd, Ge, Hf, Hg, Ho, In, Ir, La, Li, Lu, Mo, Nb, Nd, Ni, Os, Pd, Pr, Pt, Rb, Re, Ru, Sc, Sn, Sm, Ta, Tb, Te, Th, Tl, Tm, V, W, Y, Yb, Zn, Zr.

(1) Analyst, Nancy Conklin: U. S. Geological Survey, Denver, Colorado. Figures are reported to the nearest number in the series 7, 3, 1.5, 0.7, 0.3, 0.15, etc. in per cent. Sixty per cent of the reported results may be expected to agree with the results of quantitative methods.

(2) Analyst: Katherine V. Hazel, U. S. Geological Survey, Washington, D. C. Figures are reported to the nearest number in the series 10, 3, 1, .3, etc. in per cent. Eighty per cent of the reported results may be expected to agree with the results of quantitative methods.

was assumed that some phosphorus has substituted for arsenic, and calcium for barium. The phosphorus and calcium were therefore recalculated as arsenic and barium respectively.

The portion insoluble in (1+3)HCl is rhyolite tuff carried down by metaheinrichite in the heavy separation. The role of lead and carbon dioxide is not known and they were also eliminated in the calculation of the ideal formula. It is assumed that most, if not all, of the $H_2O(-)$ (Table III) is zeolitic or adsorbed water since the material dried at 110° C. gives an *x*-ray powder pattern identical to that of the undried material.

Table III. Chemical Analysis of Metaheinrichite from Oregon
Analyst: Robert Meyrowitz, U. S. Geological Survey

Constituent	%	Note
BaO	13.3	*e, h*
UO_3	52.5	*d, h*
As_2O_5	15.8	*i*
P_2O_5	2.4	*f, h*
PbO	0.9	*c, h*
CaO	0.1	*g, h*
CO_2	0.6	*j*
H_2O	12.2	*j*
Insoluble, (1+3) HCl	2.4	*b, h*
Total	100.2	
$H_2O(-)$	10.6	*a, h*

Notes:

a. Dried to constant weight at 110±5 degrees C.

b. Insoluble determined by dissolving sample with cold (1+3) HCl. Residue filtered, washed with dilute HCl and water, and weighed to constant weight at 110±5 degrees C.

c. Lead determined as sulfate following separation as PbS after removal of arsenic.

d. Uranium determined spectrophotometrically by ammonium thiocyanate procedure in acetone-water medium.

e. Barium separated and determined as sulfate.

f. Phosphorus determined spectrophotometrically by molybdenum-blue procedure using stannous chloride as reducing agent.

g. Calcium determined by flame photometry (wave length = 554 mμ).

h. Sample size for $H_2O(-)$, (1+3) HCl Insoluble, PbO, UO_3, BaO, P_2O_5, and CaO determinations was approximately 52 mg.

i. Arsenic separated by distillation as $AsCl_3$, following reduction by hydrazine sulfate and potassium bromide, and determined by titration with potassium bromate using p-ethoxychrysoidine as indicator. Sample size was approximately 29 mg.

j. CO_2 and H_2O determined by use of a microcombustion train, after decomposition of sample by ignition at 900 degrees C. in a stream of oxygen. Sample size was approximately 30 mg.

The procedures used were selected on the basis of the semiquantitative spectrographic analysis by Katherine V. Hazel, given in Table II.

TABLE IV. CORRECTED ANALYSIS OF METAHEINRICHITE FROM OREGON

Constituent	I Corrected Analysis[1] %	II Analysis I corrected to 100% %	III $Ba(UO_2)_2(AsO_4)_2 \cdot 8H_2O$ %
BaO	13.6	13.9	13.94
UO_3	52.5	53.5	52.05
As_2O_5	19.7	20.1	20.90
H_2O	12.2	12.5	13.11
Total	98.0	100.0	100.00

[1] Analysis of Meyrowitz (Table III), after elimination of PbO, CO_2, and Insoluble, with P_2O_5 calculated as As_2O_5 and CaO calculated as BaO.

Metaheinrichite is a member of the torbernite group. Table V gives a comparison of metaheinrichite and its analog meta-uranocircite, another member of the group.

No chemical analysis was carried out on heinrichite. The formula, $Ba(UO_2)_2(AsO_4)_2 \cdot 10\text{–}12H_2O$, is assumed on the basis of the similarity of its x-ray powder pattern to that of zeunerite, $Cu(UO_2)_2(AsO_4)_2 \cdot 10\text{–}12H_2O$.

TABLE V. COMPARISON OF DATA FOR METAHEINRICHITE AND META-URANOCIRCITE

	Metaheinrichite	Meta-uranocircite
Composition	$Ba(UO_2)_2(AsO_4)_2 \cdot 8H_2O$	$Ba(UO_2)_2(PO_4)_2 \cdot 8H_2O$[1]
Specific gravity	4.09 (calc.) 4.04 (meas.)	4.10 (calc.)[2] 4.08 (meas.)[3]
Optical	Uniaxial (−)	Uniaxial (−)
Space group	$P4_2$, $P4_2/m$, or $P4_222$	$P4_222$
Cell values	$a_0 = 7.07$ Å $c_0 = 17.74$ Å	$a_0 = 6.98$ Å[4] $c_0 = 16.85$ Å
$a_0:c_0$	1:2.509	1:2.416[4]
Z	2	2[4]

[1] Called "meta-uranocircite" by Strunz (1957).
[2] Data from Donnay and Donnay (1955).
[3] Data from Nuffield and Milne (1953).
[4] Data from Strunz (1957).

X-Ray Data

Fragments of Oregon metaheinrichite exhibiting {001} and {100} cleavages were easily oriented for *x*-ray study. Good *a* axis rotation photographs as well as 0-*l*, 1-*l*, 2-*l*, and 3-*l* Weissenberg photographs were made using a camera of 5.73 cm. diameter and unfiltered Cu radiation. In addition to these, *c* axis 0-*l*, 1-*l*, and 2-*l* precession photographs were made using the same radiation. A study of these films showed that the system is tetragonal. The space group appears to be either $P4_2$, $P4_2m$, or $P4_222$, since the only characteristic missing reflections are 00*l* when $l \neq 2n$. At

Table VI. *X*-ray Powder Data on Metaheinrichite from Oregon

hkl	*d*(calc.) Å	*d*(obs.) Å	I
002	8.87	8.90	vs
100	7.07	7.08	w
101	6.57	6.56	mw
102	5.53	5.54	ms
110	5.00	4.99	m
111	4.81	4.81	w
004	4.44	4.42	ms
104	3.76	3.75	s
200	3.54	3.55	ms
201	3.47	3.47	mw
202	3.28	3.28	ms
105	3.17	3.17	vw
203	3.03	3.05	w
122	2.98	2.98	m
115	2.89	2.89	vvw
123	2.79	2.79	mw
106	2.73	2.72	mw
124	2.57	2.57	w
205, 220	2.50	2.49	mw
222	2.41	2.41	mw
125, 300	2.36	2.35	vvw
301	2.34		
302	2.28	2.28	vvw
131, 008	2.22	2.22	m
224	2.18		
132	2.17	2.17	mw
126	2.16		
108	2.12	2.12	vw
133	2.09		
304	2.08	2.08	vw
118	2.03	2.02	mw
127	1.98	1.97	vw
305, 230	1.96		
231	1.95	1.95	vw
232, 226	1.91	1.92	vw
233	1.86	1.86	w
234	1.79	1.79	vw
00·10, 400	1.77		
401	1.76	1.76	w
		1.72	w
		1.67	mw
		1.64	vw
		1.60	vvw
		1.58	mw
		1.55	vw
		1.53	vvw
		1.48	w
		1.45	w
		1.42	w
		1.39	vw
		1.38	vw
		1.36	vvw
		1.34	vvw
		1.31	w
		1.28	vvw
		1.27	vw
		1.25	w
		1.23	w
		1.22	vw

vs very strong, s strong, ms medium strong, m medium, mw medium weak, w weak, vw very weak, vvw very very weak.

first the *hk*0 reflections also appeared to be missing when $h+k\neq 2n$, but closer inspection revealed that some of these reflections are present, though weak. Approximate unit cell values, which were of great value in the initial indexing of powder films, were also obtained from these single crystal films.

TABLE VII. *X*-RAY POWDER DATA ON HEINRICHITE AND METAHEINRICHITE FROM THE BLACK FOREST

Heinrichite

d(obs.) Å	I	*d*(obs.) Å	I	*d*(obs). Å	I
8.89	8	2.25	5	1.593	2
5.03	8	2.11	5	1.534	2
4.50	1	1.94	1	1.204	2
3.57	10	1.868	1	1.164	2
3.38	7	1.802	1	1.150	2
2.77	1	1.733	1	1.126	2
2.53	2	1.679	1		

Except for the strongest lines in the first part of the photographs, the lines are rather diffuse.

Metaheinrichite

9.26	4	2.70	4	1.481	3
8.55	10	2.57	2	1.449	2
5.41	9	2.48	1	1.422	3
4.96	2	2.41	4	1.385	2
4.36	9	2.22	5	1.316	1
3.71	10	2.15	4	1.276	1
3.52	5	2.10	1	1.253	2
3.45	1	2.02	5	1.237	2
3.27	6	1.966	1	1.218	1
3.15	1	1.763	3	1.179	2
3.01	1	1.709	2	1.121	2
2.96	3	1.676	5	1.110	2
2.75	1	1.579	5	1.098	2

The measured *x*-ray powder data on Oregon metaheinrichite, listed in Table VI, represent the average of values obtained from three films made with CuKα radiation in three different cameras, each with a diameter of 11.46 cm. After the films were partly indexed, using approximate unit cell values determined from single crystal data, the c_0 and a_0 constants were further refined using the powder data. The final values obtained are $a_0=7.07$ Å and $c_0=17.74$ Å, with $a_0:c_0=1:2.509$. Using these values an excellent correlation was obtained between the observed and calculated *d* spacings. In the study all possible *d* values down to 1.21 Å were calculated. This resulted in a list of 192 *hkl* reflections. In Table VI only calculated values down to 1.76 Å are included. Beyond this point the number of calculated values which corresponds to any one observed value is so large that the inclusion of these data seems pointless. All values observed for the films have their corresponding calculated values except for an extremely weak reflection at 4.09 Å which was not on all the films and which is probably due to an impurity. Using a molecular weight of 1099.32 for $Ba(UO_2)_2(AsO_4)_2 \cdot 8H_2O$ and a measured specific gravity of 4.04, with the unit cell dimensions determined by *x*-ray study, it was determined that $Z=2$ (calculated value, 1.96).

X-ray powder data for heinrichite and metaheinrichite from the Black Forest are given in Table VII. These films were obtained using FeKα radiation and a camera of 5.73 cm. diameter. Most of the differences between the data for metaheinrichite from the Black Forest and that from Oregon are smaller than possible error in line measurement.

The similarity between the *x*-ray data for metaheinrichite and its analog meta-uranocircite is illustrated in Table V.

ACKNOWLEDGMENTS

The writers wish to express their appreciation for the assistance in this study of Howard Dutro, Lakeview Mining Company (Thornburg Brothers), Lakeview, Oregon; Robert Meyrowitz, U. S. Geological Survey, Washington, D.C.; and William F. Giannini, University of Virginia, Charlottesville, Virginia.

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Manuscript received March 24, 1958.