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X-RAY STUDY OF ALTERATION IN THE URANIUM MINERAL WYARTITE*

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ABSTRACT

X-ray examinations of the mineral wyartite, assigned the chemical formula $UO_3 \cdot 6UO_3 \cdot 2CO_2 \cdot 3CaO \cdot 12\text{-}14H_2O$ by Guillemin and Protas (1959), show that with passage of time the mineral is altering. Up to the present time two phases, both orthorhombic, have been found from repeated precession *x*-ray examination of a single crystal: wyartite I (comparable to "ianthinite" described by Bignand, 1955), $a=11.25\pm0.03$, $b=7.09_8\pm0.03$, $c=20.80\pm0.06$ Å, space group $P2_12_12_1$-D^4_2 (no. 19), pseudo space-groups $P2_1cn$-C^9_{2v} (no. 33) or $Pmcn$-D^{16}_{2h} (no. 62); wyartite II (not previously described), $a=11.25\pm0.03$, $b=7.09_8\pm0.03$, $c=16.83\pm0.05$ Å, space groups $P2_1cn$-C^9_{2v} (no. 33) or $Pmcn$-D^{16}_{2h} (no. 62), pseudo space-group $Pbcn$-D^{14}_{2h} (no. 60). Indexed *x*-ray powder diffraction data for both phases are given. The alteration occurs without visible external change in the crystals, so that interpretation of chemical analyses on macroscopic samples may be open to question. The precise nature of the alteration is still unknown, although oxidation of U^{+4} to U^{+6}, with formation of uranyl ions, possibly also accompanied by some dehydration, seems to be a plausible explanation.

INTRODUCTION

In the course of studies in this laboratory on uranyl oxide hydrates and related compounds (Christ and Clark, in press), interest in ianthinite led to *x*-ray examination of the uranium mineral described as "ianthinite" (Bignand, 1955). The material of Bignand was later said to be distinct from ianthinite (Destas, Vaes, and Guillemin, 1958) and has recently been named wyartite (Guillemin and Protas, 1959).

The wyartite crystals used in the present study are from the sample originally described as "ianthinite" by Bignand (1955). The crystals occur on Shinkolobwe specimen no. 2222, Museum of the Belgian Congo, Tervuren, Belgium (M.C.B. no. 2222) and were made available to the author through the courtesy of Dr. Claude Guillemin, Bureau de Recherches Géologiques, Géophysiques, et Minières, Paris, France.

SINGLE-CRYSTAL STUDIES

X-ray examinations of single crystals were made on a quartz-calibrated precession camera with both Mo/Zr and Cu/Ni radiations ($\lambda MoK\alpha = 0.7107$ Å; $\lambda CuK\alpha = 1.5418$ Å). Film measurements were corrected for both horizontal and vertical film shrinkage.

Crystallographic data found in this study for one crystal at different times are given in Table 1. The phase associated with crystal data found in August, 1956, is referred to in this paper as wyartite I, and the later phase, associated with data of January, 1959, is referred to as wyartite

* Publication authorized by the Director, U. S. Geological Survey.

TABLE 1. CRYSTALLOGRAPHIC DATA FOR WYARTITE I AND WYARTITE II†

	Wyartite I	Wyartite II
a	11.25±0.03 Å	11.25±0.03 Å
b	7.09$_8$±0.03	7.09$_8$±0.03
c	20.80±0.06	16.83±0.05
$a:b:c$	1.585:1:2.930	1.585:1:2.371
Cell Volume	1661 Å^3	1344 Å^3
True Space-Groups	$P2_12_12_1-D^4_2$ (no. 19)	$P2_1cn-C^9_{2v}$ (no. 33) or $Pmcn-D^{16}_{2h}$ (no. 62)
Pseudo Space-Groups	$P2_1cn-C^9_{2v}$ (no. 33) or $Pmcn-D^{16}_{2h}$ (no. 62)	$Pbcn-L^{14}_{2h}$ (no. 60)

† All measurements are from patterns obtained of one crystal; patterns for wyartite I were taken in August, 1956; patterns for wyartite II were taken in January, 1959. See also Figs. 1 and 2.

II. Wyartite I data correspond to those given by Bignand (1955) for "ianthinite"; the two sets of data are compared in Table 2. The crystal under present examination is tabular on {001} and nearly square, being only slightly elongated [010]; at one end the crystal has the {110} forms as shown on a sketch of an "ianthinite" crystal by Bignand (1955). The color of the crystal is dark violet in reflected white light, pale violet in transmitted white light.

During the observation interval of slightly more than two years a

TABLE 2. COMPARISON OF CRYSTAL DATA FOR WYARTITE I AND IANTHINITE

	Wyartite I		Ianthinite
	Present Study	Bignand (1955)	Guillemin and Protas (1959)
a (Å)	11.25 ±0.03	11.25±0.03	11.52±0.05
b (Å)	7.09$_8$±0.03	7.08±0.02	7.15±0.02
c (Å)	20.80 ±0.06	20.98±0.05	30.3±0.1
Cell Volume (Å^3)	1661	1671.06	2496*
Space Group	$P2_12_12_1-D^4_2$	—	—
Chemical Formula	—	$UO_2{\cdot}6UO_3{\cdot}2CO_2{\cdot}3CaO{\cdot}10H_2O$	$UO_2{\cdot}5UO_3{\cdot}10{\cdot}56H_2O$
Z	†	2	4
Density, g.cm.$^{-3}$			
(calc.)	—	4.81*	5.03*
(obs.)	—	4.94±0.03‡	5.16±0.05

* Calculated by present author from data of original investigator.

† Space group $P2_12_12_1$ contains positions of fourfold multiplicity only.

‡ Guillemin and Protas (1959) point out that for this determination wyartite crystals were dried at 50° C.; they find 4.69±0.05 g.cm.$^{-3}$ for crystals not subjected to heat.

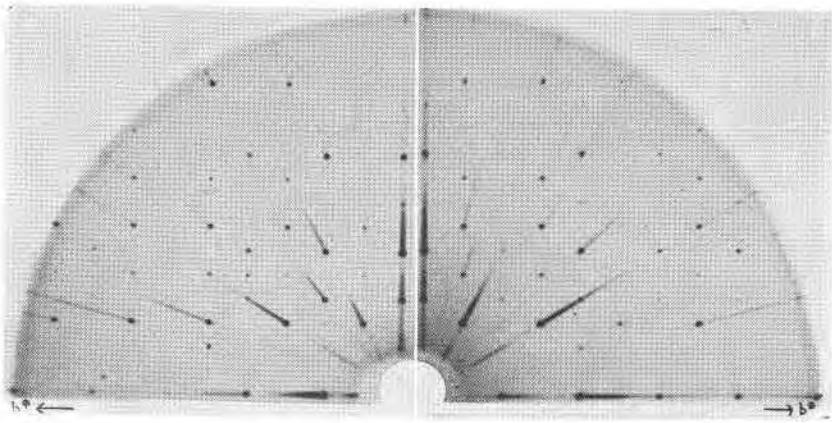

FIG. 1. (Left) Precession *hk*0 pattern of wyartite I crystal, taken August, 1956, with Mo/Zr radiation. (Right) Precession *hk*0 pattern of same crystal, now altered to wyartite II, as shown by the changed intensity distribution. Film taken January, 1959, with Mo/Zr radiation.

shrinkage of about four Ångstroms has occurred in the *c*-length; the shrinkage is accompanied by a change in space group (Table 1). In addition, extensive changes in the overall intensity distribution have taken place (Fig. 1) indicating that shifts in atomic positions have occurred. Taken together, the evidence shows that alteration on an atomic scale is in progress within the crystal; yet its external appearance is unchanged except for a slight splitting-apart of the (001) plates. The color of the crystal is unchanged from the violet originally described for "ianthinite" by Bignand (1955) and illustrated in Destas, Vaes, and Guillemin (1958).

No *x*-ray patterns of this crystal were ever obtained without appearance of some wyartite II reflections (Fig. 2). Patterns taken in 1956 of another wyartite crystal were later interpreted as showing both phases approximately equally represented. Comparison with results from previous study of schoepite alteration products (Christ and Clark, in press) shows that the stage of alteration present in any one crystal can be determined only by *x*-ray examination, preferably by precession camera techniques. It follows that chemical analyses and density determinations carried out to date on macroscopic samples cannot be directly correlated with the crystal data for either one of the phases.

X-RAY POWDER DIFFRACTION DATA

In August, 1956, a powder spindle (no. 8596) of wyartite was prepared from the crystals of M.C.B. no. 2222. An *x*-ray powder pattern was taken with a 114.59 mm. diameter powder camera using Cu/Ni radiation

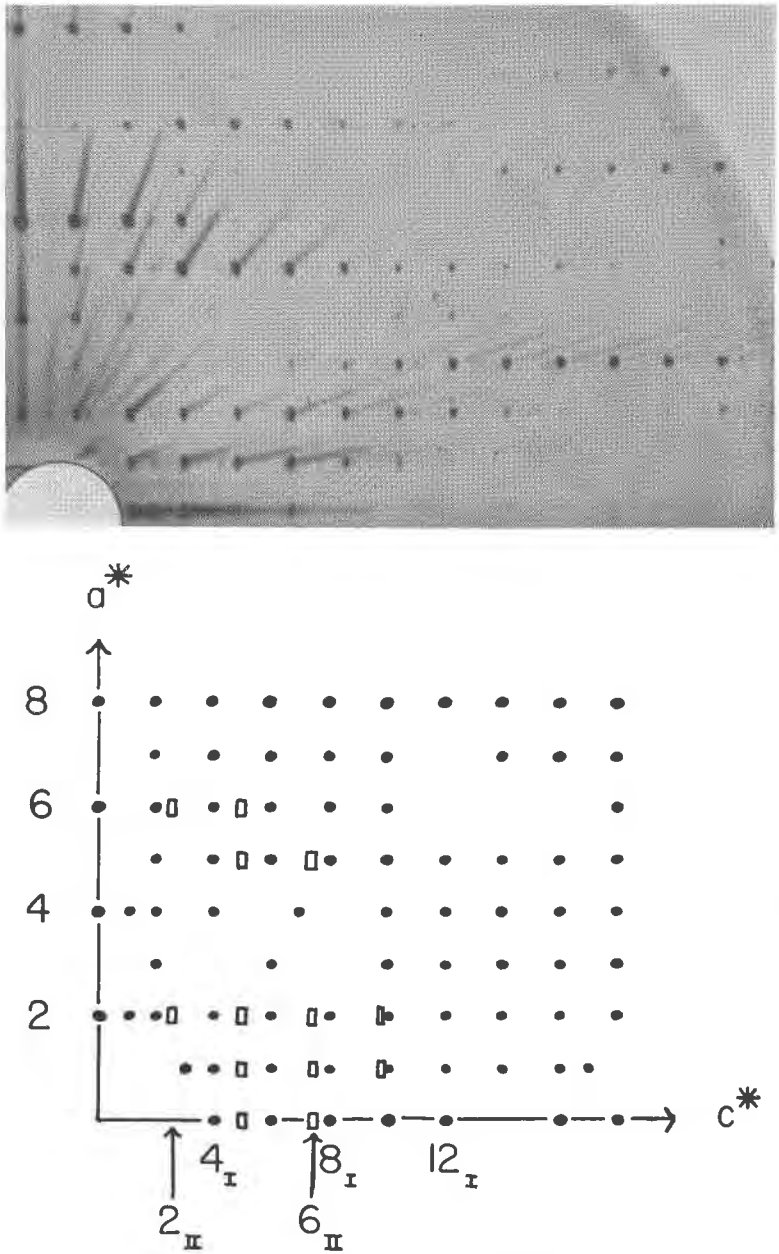

FIG. 2. (Above) Precession *h0l* net of wyartite, showing dominant wyartite I pattern appearing together with diffuse reflections of wyartite II. Mo/Zr radiation. (Below) Indexed *h0l* net for wyartite. Dots correspond to reflections of wyartite I, rectangles to wyartite II.

TABLE 3. *X*-RAY POWDER DATA FOR WYARTITE I

($UO_2 \cdot 6UO_3 \cdot 2CO_2 \cdot 3CaO \cdot 12$–$14\ H_2O$, according to Guillemin and Protas, 1959)

Present Study: Film no. 11454, taken August 3, 1956; powder spindle no. 8596.
Orthorhombic: $P2_12_12_1 - D^4_2$ (no. 19), with pseudo space-groups $P2_1cn - C^9_{2v}$ (no. 33) or $Pmcn - D^{16}_{2h}$ (no. 62); $a = 11.25 \pm 0.03$, $b = 7.09_8 \pm 0.03$, $c = 20.80 \pm 0.06$ Å.

Measured[1]						Calculated[2]		
Bignand (1955)[3]		Guillemin and Protas (1959)[4]		Present Study[5]				Single Crystal Intensity[6]
I[7]	d_{hkl}	I[7]	d_{hkl}	I	d_{hkl}	d_{hkl}	*hkl*	
FF	10.29	FF	10.39	100	10.3	10.40	002	*
		fff	8.57	30	8.5_4	(8.42	002 W-II)[8]	*
ff	7.60	ff	7.63	3	7.6_4	7.64	102	m
				<1	6.7_7	(6.74	102 W-II)[8]	vw
						6.72	011	a
						6.00	110	*
						5.86	012	a
				<1	5.77	5.77	111	m
						5.62	200	m
mF	5.19	F	5.18	30	5.19	5.20	004	s
						5.20	112	a
						4.96	013	a
						4.95	202	m
		ff	4.68	3	4.72	4.72	104	m
						4.54	113	a
		ff	4.33			4.31	211	*
				4d[9]	4.26	(4.21	004 W-II)[8]	m
						4.20	014	a
m	4.07					4.06	212	*
				<1	3.98	(3.941	104 W-II)[8]	vw
						3.930	114	a
				<1	3.83	3.818	204	m
		ff	3.745	<1	3.72	3.720	213	*
						3.589	015	a
		m	3.53	4	3.55	3.549	020	s
						3.528	302	vw
						3.498	021	m

[1] Wyartite from M.C.B. specimen no. 2222 (Shinkolobwe, Katanga) was used to obtain each of the patterns. Radiation in each case, Cu/Ni: $\lambda CuK\alpha = 1.5418$ Å.

[2] Interplanar spacings are given for all *hkl* permitted by the pseudo space-groups and having $d_{hkl} \geq 2.750$ Å. The few additional *hkl* of the true space-group have intensities too weak for their appearance on the powder films.

[3] Camera diameter, 240 mm. Interplanar spacings converted from kX to Ångstrom units by present author.

[4] Camera diameter not given.

[5] Camera diameter, 114.59 mm. Film shrinkage negligible; lower limit of 2θ measurable, approximately 7° (13 Å). Film no. 11454 taken August 3, 1956, with powder spindle no. 8596. Compare to data in Table 4 for film no. 14253 taken January 9, 1959, of the same powder spindle.

[6] Intensities estimated visually from precession films of varying exposure times; radiation, Mo/Zr, $\lambda MoK\alpha = 0.7107$ Å. * means no observation could be made for a given reflection, either because an appropriate film was not available or because of the large low-angle cut-off for $MoK\alpha$ radiation. Other abbreviations are: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; a, absent.

[7] FF = very strong, F = strong, mF = medium strong, m = medium, mf or fm = medium weak, f = weak, ff = very weak, fff = very very weak.

[8] Line identified as wyartite II; see Table 4.

[9] d = diffuse.

TABLE 3 (*continued*)

Measured[1]						Calculated[2]		
Bignand (1955)[3]		Guillemin and Protas (1959)[4]		Present Study[5]				Single Crystal Intensity[6]
I[7]	d_{hkl}	I[7]	d_{hkl}	I	d_{hkl}	d_{hkl}	hkl	
		m	3.46	10	3.47	3.467	006	vs
						3.419	115	vw
						3.363	214	a
						3.359	022	s
f	3.35	m	3.35	7	3.36	3.341	121	w
						3.316	310	s
						3.313	106	m
mF	3.28	F	3.27	10	3.28	3.274	311	*
						3.218	122	m
		f	3.16	3	3.16	3.159	312	*
						3.159	023	m
						3.115	016	a
				<1	3.08_1	(3.085	312 W-II)[8]	*
						3.042	304	a
					3.03_5	3.042	123	vw
						3.026	215	s
						3.002	220	vw
m	3.01			5d[9]	to	3.002	116	vw
						2.991	313	*
					2.976	2.971	221	vw
		m	2.93	4	2.945	2.951	206	m
		f	2.91			2.931	024	s
						2.884	222	m
						2.837	124	m
						2.812	400	s
						2.796	313	*
						2.754	223	w
m	2.59	fm	2.59	5	2.592			
f	2.52	ff	2.52	4	2.532			
f	2.46	f	2.46	4	2.470			
				<1	2.420			
				<1	2.363			
f	2.20	f	2.21	<1	2.206			
				<1	2.095			
mf	2.03	f	2.05	5	2.047			
ff	2.00	ff	1.995	4	1.999			
ff	1.96	ff	1.963	1	1.969			
				<1	1.955			
		ff	1.922	1	1.928			
plus additional weak lines								

(λCuKα=1.5418 Å). The interplanar spacings and intensities of the lines observed on this pattern are given in Table 3, together with data for material from M.C.B. no. 2222 reported by Bignand (1955) and by Guillemin and Protas (1959). All the experimental observations are in good agreement and most of the observed lines can be indexed from the single-crystal data for wyartite I. All calculated interplanar spacings for $d \geq 2.750$ Å are given in Table 3.

TABLE 4. *X*-RAY POWDER DATA FOR WYARTITE II

Film no. 14253, taken January 9, 1959; powder spindle no. 8596.

Orthorhombic: $P2_1cn-C^9_{2v}$ (no. 33) or $Pmcn-D^{16}_{2h}$ (no. 62), with pseudo space-group $Pbcn-D^{14}_{2h}$ (no. 60); $a=11.25\pm0.03$, $b=7.09_8\pm0.03$, $c=16.83\pm0.05$ Å.

Measured[1]			Calculated[2]	
I[3] (Single Crystal)	I (Powder)	d_{hkl}	d_{hkl}	hkl
*	13	10.7	(10.40	002 W-I[4])
*	100	8.4_6	8.42	002
m	3	6.7_5	6.74	102
*	1d[5]	6.08 to 5.66	6.00	110
vw			5.65	111
vw			5.62	200
w	3	5.18	(5.20	004 W-I[4])
*			4.89	112
s	2	4.68	4.68	202
w			4.26	211
vs	18	4.22	4.21	004
*			4.10	113
s	6	3.94	3.941	104
s			3.905	212
s	9	3.56	3.549	020
vs	21	3.47	3.473	021
s			3.466	213
a			3.445	114
vw			3.425	302
m		3.37 ↑	3.369	204
w			3.318	121
vs	6b[6]	3.31 ↓	3.316	310
m			3.270	022
vs		3.24	3.253	311

[1] Wyartite from M.C.B. specimen no. 2222, originating in Shinkolobwe, Katanga. Camera diameter, 114.59 mm; radiation, Cu/Ni:λCuK$\alpha=1.5418$ Å. Film shrinkage negligible; lower limit of 2θ measurable, approximately 7°(13 Å).

[2] Interplanar spacings are given for all hkl permitted by the pseudo space-group and having $d_{hkl}\geq2.700$ Å. The few additional hkl of the true space-group have intensities too weak for their appearance on the powder film.

[3] Intensities estimated visually from precession films of varying exposure times; radiation, Mo/Zr, λMoK$\alpha=0.7107$ Å. *means no observation could be made for a given reflection, either because an appropriate film was not available or because of the large low-angle cut-off for MoKα radiation. Other abbreviations are: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; a, absent.

[4] Line identified as wyartite I; see Table 3.

[5] d=diffuse.

[6] These three lines are unresolved on the pattern; measurements were taken at end points of the broad intensity band and at the central strong region; b=broad.

TABLE 4 (*continued*)

Measured[1]			Calculated[2]	
I[3] (Single Crystal)	I (Powder)	d_{hkl}	d_{hkl}	*hkl*
vw	1	3.16	3.140	122
s	2	3.09_2	3.085	312
w			3.044	214
a			3.002	200
vs	9	3.00_2	2.999	023
w			2.955	221
w	1	2.934	2.936	115
m			2.898	123
s	2	2.858	2.854	313
vw			2.827	222
s			2.812	400
s	2	2.802	2.805	006
vw			2.799	304
m	2	2.723	2.722	106
vw			2.713	024
	2	2.602		
	1	2.512		
	2	2.442		
	2	2.377		
	1	2.243		
	1	2.221		
	1	2.189		
	2	2.102		
	3	2.068		
	6	2.000		
	1	1.966		
	3	1.944		
	3	1.880		
	plus additional lines, all with I (powder) ≤ 2			

After alteration of the single crystal was observed in the present study, another *x*-ray powder pattern of spindle no. 8596 was taken in January, 1959. This pattern is strikingly different from the original one and yields data that apparently have not been previously reported. Most of the observed lines can be indexed from the single-crystal data for wyartite II, and in Table 4 observed data are listed together with all calculated interplanar spacings for $d \geq 2.700$. The wyartite II data also permit indexing of the lines previously unaccounted for on the original pattern, and these lines are identified in Table 3. A few lines corresponding to the presence of wyartite I still occur on the more recent pattern, and in

Table 4 these lines are identified. Approximate intensities for single-crystal reflections, listed in Tables 3 and 4, were estimated visually from precession films to verify indexing of the powder patterns. The powder diffraction data for wyartite I and for wyartite II are distinctive from those reported for ianthinite and epi-ianthinite (Frondel, 1958; Guillemin and Protas, 1959).

At present the nature of the alteration that has occurred in wyartite is unknown, although it is undoubtedly connected, at least in part, with the oxidation of U^{+4} to U^{+6} and formation of the $[O\text{-}U\text{-}O]^{+2}$ uranyl ion. Some dehydration may also be taking place. It is not yet certain whether the alteration process is complete or will continue, so the crystal and the powder spindle will be kept under observation and any future developments of interest will be reported.

Acknowledgments

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I am grateful to several colleagues at the U. S. Geological Survey for assistance in the course of this study. Mary E. Mrose made available the crystals supplied by Dr. C. Guillemin, took *x*-ray powder pattern no. 14253, and provided helpful discussion. Other *x*-ray powder patterns were taken by F. A. Hildebrand who also prepared powder spindle no. 8596. Calculations of interplanar spacings were carried out by D. E. Appleman on a digital computer. C. L. Christ and H. T. Evans, Jr., contributed valuable suggestions in the course of numerous discussions.

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