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Review of the hydrated oxides of U and Pb, with new X-ray powder data

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SUMMARY. New X-ray powder data are presented for vandendriesscheite, fourmarierite, masuyite, and wölsendorfite. Literature data on the known U–Pb hydrated oxides is reviewed, and suitable criteria for their distinction are set forth.

SEVEN hydrated oxides of lead and hexavalent uranium are known: curite (Schoep, 1921), fourmarierite (Buttgenbach, 1924), masuyite, vandendriesscheite, and richetite (Vaes, 1947), wölsendorfite (Protas, 1957), and the unnamed 'Mineral C' from the Wiseman mine, Mitchell County, North Carolina, briefly described by Frondel (1956).[1]

The samples in the mineralogical collection of the Musée royal de l'Afrique centrale from the uranium deposit of Shinkolobwe, Shaba (= Katanga), have been systematically re-examined in order to select the uranium–lead oxides. X-ray diffraction data on the selected specimens have been compared with data from the literature and their qualitative compositions checked; all the above species except richetite and 'Mineral C' were recognized.

Of the seven species, *richetite* has never been quantitatively analysed or adequately described, and material for a new study was not found; it should be readily distinguished from the others, as it occurs in thin black pseudohexagonal (monoclinic) plates, and the others are various shades of orange or red.

Curite, which is very common at Shinkolobwe, is easily distinguished by its acicular habit and its characteristic X-ray powder pattern (cf. Table V).

The present study therefore concentrated on the four species *vandendriesscheite*, *fourmarierite*, *masuyite*, and *wölsendorfite*; they are all orthorhombic, with related unit-cell dimensions and similar, though distinct, X-ray powder patterns. They are very similar, too, in habit and physical properties. Crystals are less than 1, or at most 2 mm in size, usually tabular on {001} with pseudohexagonal outline. and they also occur as microcrystalline aggregates or crusts. Such properties as refractive indices do not afford reliable criteria for differentiating the species—apart from the difficulty of determining indices in the range above 1·8, there are considerable variations in the values reported, possibly due to variations in the water content.

The best criterion for determining these four minerals is the X-ray powder pattern. Although their patterns display marked similarities, related to their similar pseudohexagonal pseudo-cell dimensions (Table V) there are several minor but typical differences between them. There is an appreciable decrease in pseudo-cell dimensions in the order vandendriesscheite–fourmarierite–masuyite–wölsendorfite, paralleling the decrease in U/Pb ratio (Table V). The strong or

[1] 'Mineral X', from Great Bear Lake, Canada, first described by C. Palache and H. Berman as a U-Pb oxide (Am. Mineral. **18**, 20 (1933)) and later regarded as $UO_3 . 2H_2O$ (C. Palache, ibid. **19**, 309 (1934)), has been identified as vandendriesscheite (Frondel, 1956).

TABLE I. *X-ray powder data for vandendriesscheite. Protas's Shinkolobwe specimen was RG 4413 of the Musée royal de l'Afrique centrale; Guillemin (1958) cites identical data for RG 2827*

Present study						Christ and Clark (1960)			Protas (1959)						Frondel (1958)			
RG. 2827a		RG. 6374c		RG. 6429c		HM 106. 523			Bois Noirs		Shinkolobwe		Synthetic		Shaba		Shaba	
d(Å)	*I*	*d*(Å)	*I*	*d*(Å)	*I*	d(Å)$_{mes}$	*I*	*hkl*	*d*(Å)	*I*	*d*(Å)	*I*	*d*(Å)	*I*	*d*(Å)	*I*	*d*(Å)	*I*
																	8·27	20
7·18	80	7·26	80	7·21	80	7·25	100	006	7·29	2F	7·34	F	7·22	F	7·41	100	7·31	100
						6·94	2	210										
						6·81	2	060							6·49	20	6·49	30
6·32	5d			6·21	5d	6·33	3	230										
						5·77	2	240									4·85	10
						4·71	2	236										
						4·53	10	246, 270			4·55	2f			4·58	20d		
4·48	5d	4·48	5d	4·46	5d	4·45	10	129									4·39	20
															4·27	10	4·14	10
															3·94	10	3·93	20
3·61	60	3·61	70	3·61	70	3·61	100	0. 0. 12	3·63	m	3·65	mF			3·61	90		
3·54	50	3·53	70	3·522	70	3·53	25b	2. 10. 0(*)	3·54	mF	3·53	mF	3·58	m			3·58	80
													3·50	mF				
																	3·37	10
3·19	100	3·18	100	3·17	100	3·17	75b	2. 10. 6(*)	3·18	3F	3·19	3F			3·22	100	3·19	90
						3·06	2	2. 4. 12					3·15	2F				
						3·01	2	470									3·00	10
						2·94	2											
2·799	5d	2·799	5	2·800	10	2·80	8b				2·78	2f	2·77	f	2·83	20		
						2·722	5										2·73	20
						2·660	2											
2·539	30	2·534	30	2·527	40	2·522	25		2·53	m	2·54	m	2·51	m	2·55	40	2·53	50
2·419	10	2·421	10	2·414	40	2·401	10				2·43	f			2·43	20	2·40	20
2·290	5d	2·290	10			2·29	3b				2·31	f	2·30	f	2·32	20	2·32	10
						2·18	3b											
2·066	5					2·058	5				2·05	mf	2·03	f	2·05	30	2·05	20
2·045	20	2·039	15	2·035	35	2·034	15		2·04	f								
2·001	30	1·996	25	1·990	50	1·985	40		2·00	mf	2·00	m	1·991	mf	2·01	40	1·989	70
1·965	10	1·961	10	1·959	15	1·961	5		1·960	f	1·966	mf	1·951	m				
						1·914	2										1·908	30
						1·877	2								1·886	10d		
1·817	15	1·816	5	1·812	30	1·800	10				1·823	2f			1·811	30		
						1·791	3										1·797	30
1·784	30	1·777	15	1·771	40	1·773	8		1·777	f			1·762	mf	1·783	30	1·773	50

(*) + other *hkl*-values.

TABLE II. *X-ray powder data for fourmarierite. ULB, Université libre de Bruxelles; UCL, Université Catholique de Louvain. The line at 7·24–7·31 Å is probably not due to fourmarierite (see text)*

Present study										Christ and Clark (1960)			Bignand (1955)		Guillemin (1958)		Protas (1959)			
UCL 849a		ULB B		RG. 2827c		RG. 6429b		RG. 11397a		USNM R 8396					RG. 4413		RG. 4413		Synthetic	
d(Å)	*I*	*d*(Å)	*I*	*d*(Å)	*I*	*d*(Å)	*I*	*d*(Å)	*I*	d(Å)$_{mes}$	I_{viz}	*hkl*	*d*(Å)	*I*	*d*(Å)	*I*	*d*(Å)	*I*	*d*(Å)	*I*
				8·66	10					8·55	1	111					8·54	mf	8·54	mf
7·24	40			7·27	40	7·31	40								7·34	F	8·18	f		
7·10	70	7·10	90	7·08	70	7·11	90	7·12	80	7·20	100	002	7·12	2F			7·14	2F	7·12	2F
6·41	10	6·37	10	6·39	20	6·37	20	6·39	15	6·42	3	210	6·36	f	6·36	f	6·43	m	6·43	m
																	5·32	2f		
						5·03	5			5·04	1	202					4·98	mf	4·96	mf
				4·82	10	4·81	5			4·82	3	131					4·79	mf	4·79	mf
4·36	15	4·33	30	4·35	30	4·34	50	4·36	15	4·36	2	113	4·31	f	4·34	f	4·35	m	4·33	m
4·13	5	4·08	5	4·13	5					4·13	2	040			4·11	3f	4·10	mf	4·10	mf
										4·00	3b	123								
3·89	5	3·89	10	3·91	10	3·89	10	3·91	10	3·90		321			3·91	2f	3·90	mf	3·88	mf
3·57	90	3·558	90b	3·567	80	3·57	100	3·562	100	3·58	50	004					3·59	mF	3·57	mF
										3·55	18	240					3·56	F		
3·50	40	3·494	30	3·505	60	3·51	20	3·523	50	3·50	6	400	3·53	2F	3·53	F			3·54	F
																	3·49	m	3·49	m
										3·28	1	313					3·26	2f	3·25	2f
3·167	100	3·151	100	3·169	100	3·165	100	3·169	100	3·178	50	242	3·16	F	3·16	3F	3·17	2F	3·16	2F
										3·143	12	402					3·14	m		
				3·088	5					3·095	2	412					3·08	mf	3·07	mf
										3·046	—	143								
										2·97	1	250					2·97	2f		
2·729	10	2·720	30	2·730	20	2·726	25	2·739	20	2·724	4	432	2·71	m	2·72	f	2·72	m	2·72	m
										2·70	1	044								
										2·65	1	153								
2·511	30			2·512	40	2·510	50	2·512	50	2·520	9	244	2·51	m	2·50	mf	2·51	mF	2·51	mF
		2·503	40							2·503	4	404								
2·382	10	2·382	10			2·388	15	2·383	10	2·389	4				2·39	2f	2·38	m	2·38	m
		2·358	5							2·340	1									
2·310	5	2·308	5	2·316	5	2·316	5	2·314	5	2·311	1				2·30	2f	2·31	m	2·30	m
2·226	5	2·218	5	2·224	5	2·225	10	2·227	10	2·229	2				2·21	2f	2·22	m	2·22	m
										2·181	2						2·17	2f		
						2·135	5			2·136	2				2·12	2f	2·13d	mf		
2·058	5	2·046	15	2·054	10	2·057	10	2·053	10	2·056	3				2·04	2f	2·05	m	2·05	m
2·027	10	2·024	15	2·029	15	2·028	20	2·029	10	2·030	4		2·02	mf	2·02	f	2·02	mF	2·02	mF
2·003	5	2·000	15	2·008	10	2·004	15	2·001	10	2·010	4						2·00	mf	2·00	mf
1·977	40	1·972	50	1·977	40	1·976	60	1·975	50	1·98	12b		1·96	F	1·972	m	1·972	F	1·972	F

medium lines 200, 002, and 111 (indices for the pseudo-cell) are particularly useful for discrimination, and are listed, together with some other useful lines, in Table V.

Frondel's '*Mineral C*' contains small amounts of many oxides other than lead and uranium, including 2 % BaO; how far these are essential is uncertain. Its refractive index (1·77–1·82) and X-ray powder pattern (strongest lines 3·46 Å (10), 3·09 (10), 1·916 (6), 1·730 (6)) suggest that it could possibly be an impure barian vandendriesscheite, but this is mere speculation.

TABLE III. *X-ray powder data for masuyite and for a synthetic product 'apparenté à la masuyite' (Protas, 1959)*

Present study				Christ and Clark (1960)			Guillemin (1958)		Chervet (1960)		Protas (1959)		Frondel (1958)	
RG. 2840d		RG. 6441		HM. 106. 524			RG. 2832		Shinkolobwe		Synthetic		Shaba	
d(Å)mes	*I*vis	*d*(Å)mes	*I*vis	*d*(Å)mes	*I*	*hkl*	*d*(Å)	*I*	*d*(Å)	*I*	*d*(Å)	*I*	*d*(Å)	*I*
													8·53	10
7·10	80	7·10	80	7·08	100	006	7·10	F	7·10	2F	7·06	2F	7·10	100
													6·43	20
6·05	15	6·06	15				5·99	3f	6·05	f	6·08	2f		
									5·87	f				
									4·60	2f	4·56	2f	4·80	10
4·38	5	4·40	5	4·36	6				4·38	2f	4·36	2f	4·35	40
				4·30	6									
							3·88	3f					3·92	20
		3·56	20	3·56	35	0. 0. 12			3·54	F			3·54	80
3·528	80	3·52	80	3·52	70	660	3·50	F	3·52	F				
3·481	80	3·48	40	3·48	21	12. 0. 0			3·49	F	3·49	3F		
									3·45	F				
				3·16	12	666			3·14	3F	3·14	3F	3·15	90
3·132	100	3·127	100d	3·12	50	12. 0. 6	3·11	2F	3·10	3F	3·09	3F		
									3·02	f			2·97	10
2·764	20	2·761	15				2·77	f	2·78	m	2·78	m	2·74	30
							2·60	3f						
				2·51	6	12. 0. 12					2·53	m	2·51	50
2·486	40	2·486	30	2·484	12	6·6·12	2·48	mf	2·49	m				
				2·38	4								2·38	20
2·364	10	2·365	5	2·36	9	0. 0. 18	2·37	mf						
2·281	30	2·274	20	2·27	4		2·28	f						
2·168	10	2·168	10				2·18	2f						
				2·12	4									
				2·008	18	0. 12. 0	2·00						2·06	10
2·019	40	2·018	40			18. 6. 0								
				1·973	9								1·984	40
1·952	50	1·952	40	1·95	17b		1·936	mf						
1·853	5b						1·844	2f					1·908	30
				1·79	4								1·784	40d
1·774	10	1·775		1·766	12									
1·753	25	1·755	10b	1·745	9									
1·739	10	1·741					1·741	mf						
				1·72	4								1·727	20

Vaes (1947) described masuyite as a hydrated oxide of Pb and U, but Cuttita (in Frondel, 1958) gave the formula $UO_3 . 2H_2O$. A qualitative X-ray fluorescence analysis was therefore made of all four species studied, and confirmed the presence of lead in all four and of calcium in wölsendorfite.

In Tables I to IV the new X-ray powder data (Cu-$K\alpha$ radiation, 114·6 mm diameter camera) are presented and in Table V the unit cell and optical data for the four species are collected and compared with those of curite, and their distinctive X-ray powder lines set out.

Discussion

Vandendriesscheite. The new X-ray powder data agree well with those of Christ and Clark (the latter include many weak lines not recorded elsewhere, presumably due to longer exposure),

TABLE IV. *X-ray powder data for wölsendorfite*

Present study								Protas (1957)			Protas (1959)				Frondel (1958)		Chervet (1960)	
RG. 2225a		RG. 2768		RG. 2832		RG. 6428		ASTM 12–159			950 F		CV 58 A		Wolsendorf		Margnac 909	
d(Å)	*I*	*d*(Å)	*I*	*d*(Å)	*I*	*d*(Å)	*I*	*d*(Å)	*I*	*hkl*	*d*(Å)	*I*	*d*(Å)	*I*	*d*(Å)	*I*	*d*(Å)	*I*
		7·86	10												7·86	20		
																	7·46	40
6·90	40	6·96	50	6·96	50	6·96	40	6·93	60	020	6·93	F	6·83	F	6·83	40	6·87	60
5·99	5	6·01	5	6·08	10			6·02	30	200,120	5·99	mf	5·99	mf			5·97	20
																	3·74	20
		3·516	30			3·523	20	3·51	40	002,040								
3·44	90b	3·46	90	3·48	100	3·464	90	3·47	80	320,301	3·46	3F	3·42	3F	3·45	90	3·44	90
								3·13	60	041,022								
3·09	100	3·10	100	3·10	100	3·105	100b	3·09	100	321	3·10	2F	3·08	2F	3·09	100	3·09	100
2·734	30	2·740	10b	2·752	15	2·731	5	2·75	30	420,401	2·74	*m*	2·72	mf	2·73	40	2·72	30
2·438	20	2·456	25	2·460	25	2·455	20	2·45	30b	341,322	2·45	m	2·43	m	2·44	60	2·44	40
		2·309	10	2·319	5													
2·270	20	2·264	15	2·274	10	2·266	10	2·25	30	412	2·26	m	2·25	mfd	2·26	50	2·26	40
								2·14	5b	152,213	2·16	2f			2·15	20		
															2·09	20		
2·010	30	2·008	20	2·013	30	2·008	20	2·01	30		2·008	mF	2·003	mF			2·00	50
1·987	25	1·990	20	1·989	5	1·984	10	1·998	5						1·996	60		
		1·943	15	1·926	70	1·922	70				1·932	F					1·921	50
1·907	60												1·902	F	1·907	80	1·907	50
1·892	10	1·898	5	1·901	5			1·89	30b		1·896	f						
				1·832	5						1·829	2fd						
1·812	10												1·806	2f	1·817	20	1·811	20
		1·766	5															
1·734	30	1·737	40	1·741	50	1·737	60	1·74	30b		1·740	mF	1·728	*m*	1·729	70	1·731	60
1·718	20												1·710	m				
1·694	5	1·698	5	1·697	10	1·694	10	1·699	20		1·694	mf	1·686	mf	1·687	20		
1·677	10	1·677	15	1·679	10	1·677	10	1·681	20		1·676	mf	1·667	mf	1·669	20	1·669	10
1·655	10			1·658	5			1·658	20		1·656	mf	1·648	mf	1·645	30	1·652	20

The indices quoted are based on Protas's unit cell; Toussaint (1961) determined *c* as 6·85 Å, which leads to a more likely indexing of the strong line at 3·47 Å as 002, the line at 3·51 Å being 040.

and with Protas's natural samples. Protas's synthetic material is also in general agreement, but gave distinctly lower spacings throughout. Frondel's data, however, include a number of lines not recorded by other observers and other lines are displaced, while the doubtlet 3·61, 3·53 Å is replaced by a single line at 3·61 or 3·58 Å.

Fourmarierite. The line at 7·24–7·31 Å in the present data is probably not due to fourmarierite itself, but to another, unidentified mineral present as a pale yellow outer zone on many of the platy crystals; it was not observed on ULB B, which does not give this line, and was not

TABLE V. *Summary of data for the* U–Pb *oxides*

		Vandendriesscheite	Fourmarierite	Masuyite	Wölsendorfite		Curite
Unit cell	*a*	14·07 Å*	14·00 Å*	41·93 Å*	11·95 Å‡	11·90 Å§§	12·50 Å†
	b	40·85	16·47	24·22	13·99	13·98	13·01
	c	43·33	14·39	42·61	7·02	6·85	8·40
Pseudo-cell (ortho-hexagonal)		7·04 (*a*/2) 4·08 (*b*/10) 7·22 (*c*/6)	7·00 (*a*/2) 4·12 (*b*/4) 7·20 (*c*/2)	6·99 (*a*/6) 4·04 (*b*/6) 7·10 (*c*/6)	7·00 3·98 7·02	6·99 (*b*/2) 3·97 (*a*/3) 6·85	— — —
Formula		$PbO.7UO_3.12H_2O$†	$PbO.4UO_3.4H_2O$*	$3PbO.8UO_3.10H_2O$‖	(Pb, Ca)O.$2UO_3.2H_2O$‡		$2PbO.5UO_3.4H_2O$†
Refractive indices	α	1·780*; 1·7ū 1·785, 1·790†	1·863*; 1·865†; 1·85‖	1·785†	2·05 α' on (001)‡		2·05†; 2·06‖
	β	1·850*; 1·810, 1·824, 1·840, 1·882†, 1·884¶	1·885*; 1·900†; 1·92‖	1·895*; 1·90†; 2·11 2·15¶	—		2·07, 2·08†; 2·06, 2·21‖; 2·12††
	γ	1·860*; 1·820, 1·828, 1·845, 1·890†; 1·884¶	1·890*; 1·904†; 1·94‖	1·915*; 1·917†	2·09 γ' on (001)‡		2·12†; 2·15‖; 2·12††
$2V_\alpha$		Med., r > v†	Large, r > v‖	50°, r > v†	—		Large, r > v‖
Pleochroism	α	Colourless†	Colourless‖, **	Pale yellow†	—		—
	β	Golden yellow	Pale yellow	Deep gold	—		—
	γ	Golden yellow	Deep yellow	Deep gold	—		—
Orientation		α ‖ [010]† β ‖ [100]	α ‖ [100]‖,** β ‖ [001]	α ‖ [010]† β ‖ [001]	— —		γ ‖ [001]‖
Diagnostic X-ray lines		3·6 s 002 3·18 vs 111 2·80 w 2·42 mw	3·57 vs 002 3·51 ms 200 3·16 vs 111 6·4 w 2·73 w 2·51 m	3·56 m 002 3·52 s 110 3·48 ms 200 3·13 vs 111	3·46 vs 002 3·10 vs 111 6·9 s		3·51 vs ‡‡ 3·36 s 3·11 s 6·22 vs

* Christ and Clark, 1960.
‡ Protas, 1957, 1959.
‖ Larsen and Berman, 1934.
** Buttgenbach, 1924.
‡‡ Bignand, 1955.
† Frondel, 1958.
§ Protas in Chervet, 1960.
¶ Vaes, 1947.
†† Billiet, 1926.
§§ Toussaint, 1961.

observed by Christ and Clark, with whose data the present agree well otherwise—better than with those of Protas. The data of Guillemin differ mainly in the first strong line (7·34 Å as against 7·11–7·20) and the absence of a line at 3·56–3·60 Å, which is also absent in the generally line-poor data of Bignand. The data cited by Frondel (1958) for fourmarierite are clearly those of wölsendorfite, which had only just been described when his work was published.

Masuyite. The present data agree well with those of Christ and Clark and of Chervet. Frondel's data are very different, and his specimen was probably fourmarierite. Guillemin's data are a puzzle: the weak line at 3·88 Å suggests fourmarierite, but few other lines fit; the weak line at 2·60 Å does not appear on any other pattern; many of the other lines could equally well be due to masuyite or to wölsendorfite, and material from the same specimen appears to be wölsendorfite (present study, Table IV).

Wölsendorfite. All the available data are closely similar, with one minor discrepancy: a line appears at medium strength at 1·94–1·92 Å in some data and one at 1·907–1·902 Å in others, but only Chervet's Margnac II specimen has both these lines.

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