STUDIES OF URANIUM MINERALS (XIX): RUTHERFORDINE, DIDERICHITE, AND CLARKEITE[1,2]

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ABSTRACT

Rutherfordine, diderichite, and a synthetic uranyl carbonate obtained by heating UO_3 in H_2O under 15,000 psi CO_2 at 300° C. afforded identical *x*-ray powder patterns, and on analysis each yielded the formula $(UO_2)(CO_3)$. The name rutherfordine has priority. Two new localities are recorded for rutherfordine at Beryl Mountain, N. H., and Newry, Maine, where it occurs as a weathering product of uraninite in pegmatite. Rutherfordine occurs as crusts and aggregates of orthorhombic (?) fibers; biaxial positive, with $nX=1.720$–1.723, $nY=1.728$–1.730, $nZ=1.755$–1.760; Y along the fiber length.

Clarkeite is described from its second known locality, the Ajmer district, Rajputana, India, where it occurs as microcrystalline, chocolate-brown alteration product of uraninite in pegmatite. Analysis yielded the formula $(Na, Ca, Pb, Th, H_2O)_2U_2(O, H_2O)_7$; isostructural with $Na_2U_2O_7$ and CaU_2O_7. Specific gravity is 6.29, mean index of refraction 1.94–1.97.

RUTHERFORDINE

Four supposedly distinct uranyl carbonates have been described: rutherfordine, diderichite, sharpite, and studtite. The scant existing data for these minerals, summarized in Table 1, make further study desirable. About 20 specimens labeled rutherfordine from the original locality at Morogoro, Tanganyika, Africa, were available for study. Most of these specimens were found to consist variously of kasolite, uranophane, and hydrated lead uranyl oxides as alteration zones about cubes of uraninite, and only two contained a uranyl carbonate. The latter mineral was earthy to pulverulent in consistency, with a pale brownish-yellow to straw-yellow color and dull luster. Under the microscope the mineral appeared as minute fibers and lathlike subparallel aggregates; biaxial positive, with $nX=1.723$ (nearly colorless), $nY=1.730$ (pale yellow), $nZ=1.760$ (pale greenish yellow); extinction parallel, with Y along the elongation and Z perpendicular to the flattening. The mineral probably is orthorhombic. A new chemical analysis, made on material known to contain a small amount of kasolite, is close to the original analysis of Marckwald (1906). Both analyses, cited in Table 2, have been recalculated after deducting the Pb and Ca, as kasolite and uranophane, together with the H_2O^-, iron oxide, and residual Si or Ca.

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[1] Contribution from the Department of Mineralogy and Petrography, Harvard University, No. 360.

[2] Publication authorized by the Director, U. S. Geological Survey.

TABLE 1. DATA SUMMARIZED FROM THE LITERATURE ON THE NATURAL URANYL CARBONATES

	Rutherfordine	Diderichite	Sharpite	Studite
Symmetry	Orthorhombic?	Orthorhombic?	Orthorhombic?	Orthorhombic?
Habit	Aggregates of minute fibers	Fibrous crusts	Fibrous crusts	Fibrous crusts
Composition	$(UO_2)(CO_3)$?	Slightly hydrated uranyl carbonate	$(UO_2)(CO_3)\cdot H_2O$?	Hydrated uranyl carbonate with Pb
Analysis	Cited by Marckwald (1906)	Qualitative tests only	Cited by Mélon (1938)	Qualitative tests only
Color	Yellow	Yellow-green	Greenish yellow	Yellow
Specific gravity	4.82?	—	3.33	—
Indices of refraction	$nX=1.72\pm 0.01$	1.722–1.728	1.633, brownish	1.545
	$nY=$ —	1.728	—	1.555
	$nZ=1.80\pm 0.01$	1.728–1.74	1.72, greenish yellow	1.68
Other optic data		Y=elong.	Z=elong.	Z=elong.
		Biaxial positive	$Y\perp$flattening	Biaxial negative
		2V large		2V large
Thermal data	CO_2 lost over 300° C.		H_2O lost 200–275 ° C. CO_2 and H_2O at 325° C.	
Locality	Morogoro, Tanganyika	Katanga, Belgian Congo	Katanga, Belgian Congo	Katanga, Belgian Congo
References	Marckwald (1906) Larsen (1921)	Vaes (1947)	Mélon (1938)	Vaes (1947)

The ratios then are close to the formula $(UO_2)(CO_3)$, originally given for this mineral by Marckwald (1906) and later accepted by Mélon (1938) and others.

The *x*-ray powder spacing data are given in Table 3. These data are virtually identical with those given by Miller, Pray, and Munger (1949) for synthetic $(UO_2)(CO_3)$, and are identical with those afforded by a product[3] obtained by heating precipitated $UO_3\cdot nH_2O$ at 300° C. under 15,000 psi CO_2. An analysis of the latter substance, given in Table 2, affords the formula $(UO_2)(CO_3)$. This material was found to contain a small amount of U_3O_8 formed by thermal dissociation of the UO_3, accounting for the UO_2 reported in the analysis, together with a small amount of an unidentified impurity. The particle size of the material was too small for satisfactory optical study. It may be noted that the analyses of the natural and synthetic substances (Table 2) all show a small amount of water retained over 110° C. Although our data for rutherfordine are not based on a type specimen, the close correspondence in physical and chemical properties with the original description leaves little doubt but that they are representative of the mineral. The only discrepancy is with the description of a non-type specimen by Larsen

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[3] Prepared for us by Miss E. Berman and Dr. G. Kennedy, Harvard University, 1953.

TABLE 2. CHEMICAL ANALYSES OF URANYL CARBONATES

	1	2	3	4	5	6	7	8
UO_3	86.68	86.7	85.9	86.6	87.7	83.8	78.6	85.5
UO_2								2.6
CaO						1.1	0.2	
PbO						1.0	4.2	
Fe_2O_3						0.8	1.1	
SiO_2						0.8	1.8	
H_2O+		0.2	1.4	n.d.	0.5	0.7	1.9	0.5
H_2O-							0.6	0.0
CO_2	13.32	13.1	12.7	13.6	11.8	12.1	10.5	11.2
Total	100.00	100.0	100.0	100.2	100.0	100.3	98.9	99.8
Specific gravity			5.8	5.43	6.10		5.08	6.10

1. Theoretical weight percentages, $(UO_2)(CO_3)$.
2. Rutherfordine, Morogoro. Original analysis of Marckwald (1906), column 6, recalculated to 100 after deduction of Pb and Ca as kasolite and uranophane together with remaining CaO and FeO.
3. Rutherfordine, Morogoro. New analysis of R. Meyrowitz (column 7), recalculated after deduction of Pb and Ca as kasolite and uranophane together with remaining SiO_2, Fe_2O_3, and H_2O-.
4. Diderichite, Katanga. Analyst: R. Meyrowitz, 1954. Type material of Vaes. Contains a small but undetermined amount of H_2O.
5. Synthetic uranyl carbonate. Recalculated from the analysis of Meyrowitz (column 8) after deduction of UO_2 as U_3O_8.
6. Rutherfordine, Morogoro. Original analysis of Marckwald (1906). Fe reported as FeO.
7. Rutherfordine, Morogoro. Analyst: R. Meyrowitz, 1954. Known to contain some admixed kasolite.
8. Synthetic uranyl carbonate. Analyst: R. Meyrowitz, 1954. Known to contain some admixed U_3O_8.

TABLE 3. *X*-RAY POWDER DIFFRACTION SPACING DATA FOR RUTHERFORDINE

(CuKα/Ni)

I	*d(Å)*	*I*	*d(Å)*	*I*	*d(Å)*	*I*	*d(Å)*
10	4.60	2	2.41	2	1.874	2	1.435
8	4.29	3	2.32	3	1.734	3	1.388
6	3.90	4	2.15	1	1.658	1	1.373
9	3.21	5	2.05	1	1.603	1	1.346
4	2.64	1	1.95	1	1.588	1	1.318
1	2.51	2	1.914	2	1.510	1	1.275

(1921, p. 129), cited in Table 1. His value nX 1.72 agrees with ours, but his nZ 1.80 is much higher and probably was obtained on an admixed uranium oxide.

We have identified rutherfordine on the basis of x-ray patterns and qualitative chemical tests from two additional localities. It occurs abundantly at Beryl Mountain, N. H., as dense to earthy pseudomorphs after uraninite in pegmatite, associated with schoepite, vandendriesscheite, and uranophane. It also occurs as an alteration of uraninite at Newry, Maine. At both localities the mineral forms earthy, yellow to straw-yellow aggregates of extremely small particle size, and appears to be a weathering product. Certain specimens of yellow to orange "gummite" from the Ruggles and Palermo pegmatites, both in New Hampshire, also were found to effervesce slightly in dilute HCl, but rutherfordine could not be identified in them with certainty.

Rutherfordine, synthetic $(UO_2)(CO_3)$ and diderichite (see beyond) were not observed to fluoresce under either short- or long-wave ultraviolet radiation. This conflicts with the observation of Bültemann (1954), who found rutherfordine from Morogoro to fluoresce strongly in yellow-green.

DIDERICHITE

An authentic specimen of diderichite from the type locality at Katanga, Belgian Congo, was kindly given to us by Dr. J. F. Vaes, of the Union Minière du Haut Katanga, who described the mineral in 1947. The x-ray powder pattern proved to be identical with that of rutherfordine and a chemical analysis, cited in Table 2, is very close to the formula $(UO_2)(CO_3)$. The mineral occurs as crusts of fibers and laths. These are biaxial positive, with $nX = 1.720$ (pale yellow), $nY = 1.728$ (yellow), $nZ = 1.755$ (greenish yellow), with 2V large. They also have parallel extinction, with Y along the elongation and Z perpendicular to the flattening. These data agree with those of Vaes (1947) and with our data for rutherfordine. We consider that diderichite is identical with rutherfordine. The latter name has priority.

SHARPITE AND STUDTITE

No new data have been obtained for either sharpite or studtite. The type specimens of sharpite were destroyed during the Second World War,[4] and other specimens do not appear to be extant. A specimen labeled studtite from the type locality at Katanga was available for study, but despite careful examination no mineral closely answering the

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[4] Private communication, Professor H. Brasseur, University of Liège, 1954.

description of this species was found on it. The optical properties of both sharpite and studtite, cited in Table 1, are distinct from those of rutherfordine and the other known carbonates of uranium.

CLARKEITE

Clarkeite, hitherto known only from the Spruce Pine district, N. C., has been identified as an alteration product of uraninite in pegmatite in the Ajmer district, Rajputana, India. The specimens, striking in appearance, consist of fractured and in part kaolinized masses of white feldspar containing crystals of uraninite as much as an inch in diameter. The uraninite crystals are zonally altered, and show a small, embayed core of black uraninite, a surrounding zone of deep chocolate-brown clarkeite with a waxy luster, a succeeding zone of bright orange-red microcrystalline fourmarierite, and an outer pale yellowish-green zone composed chiefly of uranophane. In some specimens the residual core of uraninite is lacking, and in others the crystals have been completely altered to uranophane. A zoned specimen from Rajputana apparently of this nature is mentioned by Krishnan (1948), and details of the uraninite from this region are given by Crookshank (1948).

The clarkeite is dense and microcrystalline. The color in transmitted light is deep brownish yellow, the mean index of refraction, slightly variable, is between 1.94 and 1.97, and the specific gravity is 6.29. The *x*-ray powder pattern is virtually identical with that obtained from the analysis sample of the original material from Spruce Pine described by Ross, Henderson, and Posnjak (1931). *X*-ray powder data for the latter mineral and for synthetic clarkeite are given by Gruner (1954).

A chemical analysis of the Rajputana material is cited in Table 4. The analysis is close to the ratio $Na_2O \cdot CaO \cdot PbO \cdot 8UO_3 \cdot 6H_2O$. Gruner (1954), however, has shown that clarkeite is a diuranate isostructural with $Na_2U_2O_7$ and CaU_2O_7. Water is present in the natural material and in some synthetic preparations but is not essential to the structure. Both the Rajputana and Spruce Pine materials are solid solutions between $Na_2U_2O_7$, CaU_2O_7, and PbU_2O_7 in which the cation vacancies are occupied by neutral H_2O molecules and in which valence compensation is effected by a concomitant substitution of (OH) or H_2O for O. Our analysis of the Rajputana material conforms to the formula

$$(Na_{0.53}Ca_{0.26}Pb_{0.25}Th_{0.06}U_{0.02}H_2O_{0.88})_2U_2(O_{6.87}OH_{0.13})_7$$

or to

$$(Na_{0.53}Ca_{0.26}Pb_{0.25}Th_{0.06}U_{0.02}H_2O_{0.88})_2U_2(O_{6.93}H_2O_{0.07})_7.$$

The calculated weight percentages for the latter formula are given in Table 4.

TABLE 4. CHEMICAL ANALYSIS OF CLARKEITE FROM RAJPUTANA

	1	2	3
Na_2O	2.4	2.3	2.3
CaO	2.1	2.1	2.1
PbO	8.0	8.0	7.9
UO_2	0.8	0.8	0.8
UO_3	82.0	80.2	79.9
ThO_2	2.3	2.4	2.4
H_2O+	2.4	4.2	4.2
H_2O-			1.3
Insol.			0.2
Total	100.00	100.0	101.1
Specific gravity			6.29

1. Theoretical weight percentages for the derived formula $(Na_{0\cdot53}Ca_{0\cdot26}Pb_{0\cdot25}Th_{0\cdot06}U_{0\cdot02}H_2O_{0\cdot88})_2U_2(O_{6\cdot93}H_2O_{0\cdot07})_7$.
2. Analysis 3 recalculated to 100 after deduction of insoluble and H_2O-.
3. Clarkeite, Rajputana. Analyst: R. Meyrowitz, 1953.

The above interpretation may have to be modified in light of work by Wamser et al. (1952), who indicate that the supposed compound $Na_2U_2O_7$ actually has the composition $Na_6U_7O_{24}$. They find that air dried material contains $16H_2O$ and that there is no change in *x*-ray pattern when the water is completely driven off by heating to 130°.

ANALYTICAL METHODS

The methods employed were guided by semiquantitative spectrographic analyses of the samples by C. S. Annell, U. S. Geological Survey. Quadrivalent uranium was determined by dissolving the mineral in 1:3 H_2SO_4 and titrating with approximtaely 0.03 N potassium permanganate that had been standardized against a known uranium solution. Sexivalent uranium was calculated by difference after total uranium had been determined by reduction in a Jones reductor and titrating with standard potassium permanganate, using the same sample employed for the determination of quadrivalent uranium; lead was removed as the sulfate prior to the reduction of the dilute solution. The alkaline earths were determined as the sulfates after separation as the sulfates from a 85 per cent ethyl alcohol solution. The alkalies were determined as the sulfates; the alkali pyrosulfate formed on ignition was converted to the normal sulfate by heating with successive small samples of ammonium carbonate in a covered dish to constant weight. Lead was separated as the sulfide and determined as the sulfate. The R_2O_3 group was precipitated by CO_2-free ammonium hydroxide. Qualitative spectrographic analyses were made of the total alkali, total alkaline earth, and total R_2O_3 precipitates. In the carbonate analyses, the CO_2 and H_2O were determined by a modified microcombustion train of the type used for determination of C and H in organic compounds. The samples were decomposed by ignition at 900° C. in a stream of oxygen. In the clarkeite analyses the H_2O was calculated from the loss on ignition. H_2O^- was determined by dehydrating the sample to constant weight at 110° C. The iron was determined using o-phenanthroline. A standard iron curve was prepared using solutions that contained approximately the same amount of uranium contained in the aliquot of solution used for the determination of iron. The thorium was calculated by difference using the R_2O_3 value. The samples employed in the separate determinations ranged in weight from 20 to 100 mg.

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