CLARKEITE; A NEW URANIUM MINERAL

Clarence S. Ross, E. P. Henderson and E. Posnjak*

Occurrence and Association

The pegmatites in the vicinity of Spruce Pine, North Carolina, have probably yielded more uraninite, and related uranium minerals than any other locality in the eastern United States. During mining operations for mica and feldspar, uraninite, gummite, uranophane and antunite have been found. These minerals seem to occur with mica in albitized areas of the pegmatite, and associated with the variety of zircon known as cyrtolite, and with monazite.

Many specimens of uranium ores from Spruce Pine have been observed to contain a dark brown to brownish black material which seemed to have definite optical properties that distinguished it from the associated gummite. Most of this material was intimately intergrown with gummite, or uranophane, but one specimen in a lot secured from Spruce Pine several years ago, and one from the Roebling collection of the National Museum were so pure that very careful hand picking yielded material suitable for analysis. This material has been found to be a new mineral with distinct, chemical, optical and X-ray properties, which it is proposed to call *clarkeite* after Professor Frank Wigglesworth Clarke.

The uranium minerals of Spruce Pine make strikingly beautiful specimens. In some there is a central core of black, sub-metallic uraninite. This is surrounded by a zone of dark reddish brown clarkeite; this by brilliant orange-red gummite; and the whole by an outer zone of bright yellow uranophane. The various zones vary in width but in the larger specimens they may be several centimeters wide.

Physical and Chemical Properties (E.P.H.)

Clarkeite is massive, without cleavage, has a conchoidal fracture and a hardness of 4 to 4.5. The specific gravity is 6.39. The color is very dark brown in the hand specimen and reddish brown to orange brown in microscopic grains. The luster is slightly waxy and the streak is lighter in color than the mineral and more of a yellowish brown. The following analyses were made on selected material from two specimens:

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Table I

Analyses of Clarkeite, E. P. Henderson, Analyst

	Analysis No. 1			*Analysis No. 2*[a]		
MgO	0.28	.0069				
CaO	2.84	.0506		1.10	.0196	
PbO	3.71	.0106	.1341	3.70	.0162	
K_2O	0.48	.0051		1.42	.0151	.0932
Na_2O	3.44	.0555		2.61	.0421	
BaO	None			0.04	.0002	
UO_3	81.72	.2857	.2857	82.76	.2894	.2894
Fe_2O_3	0.18			0.50		
Al_2O_3	0.92					
Rare Earths	2.62			1.12		
H_2O	3.36	.1865	.1865	5.22[b]	.2886	.2886
SiO_2	0.50	.0082		0.30		
Insol.	0.14			1.20		
Total	100.19			99.97		

[a] Duplicate analyses were made.

[b] H_2O at 110° was 0.64 and +110° was 4.58.

Analysis No. 1 was made upon the material found in the Roebling collection; analysis No. 2 was made upon the specimen that was first observed to be distinct from gummite.

The chemical formula calculated from analysis No. 2 is $RO \cdot 3UO_3 \cdot 3H_2O$. Alkalies are the essential RO constituents and sodium predominates over potassium. Analysis No. 1 is closely similar to No. 2, the only essential difference being a slight excess of calcium in the former. The quantity of lead and of alkalies is nearly the same in the two analyses, and the uranium contents agree very closely. Both analyses contain only small quantities of iron and aluminum oxides but there is a difference in the water content.

Under the microscope a greater proportion of opaque impurities (probably uraninite) were revealed in sample No. 1 than in No. 2, but the latter probably contained slightly more included gummite. A comparison of the analysis of uraninite and a so-called gummite from Spruce Pine, North Carolina, is shown in Table No. II. From these analyses it can be seen that a slight excess of uraninite or gummite, say less than 5 per cent, would not be noticeable in the analytical results.

TABLE II

ANALYSES OF URANINITES AND GUMMITES FROM NORTH CAROLINA

	Uraninite		*Gummite*
	X	XI	3
UO_3	50.83	44.11	77.99
UO_2	39.31	46.56	
ThO_2	2.78	3.04	1.06
CeO_2	0.26		
$(La, De)_2O_3$	0.50		
$(Y, Er)_2O_3$	0.20		
Fe_2O_3	trace		0.29
Al_2O_3	—	—	0.86
PbO	4.20	4.53	5.28
CaO	0.85	0.23	0.90
MgO	0.30	0.30	none
Na_2O			0.51
K_2O			0.86
H_2O	1.21	undet.	8.90
N	0.37	undet.	
SiO_2	0.08	0.13	1.97
BaO	—	—	2.16
Insol.	0.10	0.06	0.08
	100.99	98.91	100.86

Analyses X and XI of uraninites, Spruce Pine, by W. F. Hillebrand.[1]
Analysis 3 by E. P. Henderson.

Analyses No. 3, Table II, was made on a specimen from the Wiseman mica mine, Mitchell County, North Carolina, (Specimen U.S.N.M., No. 86120) that was typical of material commonly known as gummite. This appeared homogeneous to the unaided eye, but a microscopic examination showed that it was a fine-grained aggregate, the complete homogeneity of which was questionable. This analysis was made in order to compare a typical specimen of gummite with clarkeite and to test the character of the material used in the X-ray diffraction patterns. Hillebrand in discussing the North Carolina uraninites says:

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[1] Hillebrand, W. F., *Amer. Jour. Sci.*, (V) **40,** 384, 1890; also *U. S. Geol. Surv., Bull.* **78,** 1891.

The material was analyzed mainly to learn if rare earths enter into its composition. No. X represents the composition of the purest sample available and No. XI of the residue after extraction of the yellow oxidation products by very weak HCl. No really unaltered uraninite appears to have been found in North Carolina.

There is but little doubt that the opaque specks found in the clarkeite are uraninite for dilute mineral acids dissolve the clarkeite rather readily leaving behind minute dark specks which are decomposed on continued boiling. A visual estimation of the percentage quantity of the uraninite in the analyzed specimen of clarkeite would be somewhere in the neighborhood of 1 or 2 per cent.

ANALYTICAL PROCEDURE. Although no new or unusual methods were used for this analysis it may be advisable to briefly outline the general analytical procedure.

Clarkeite dissolves readily in mineral acids, hydrochloric acid being used in the sample decomposed for analysis. The mineral can be dissolved in very dilute acid (1 part acid to 4 parts water), and a small residue of supposed uraninite remained insoluble although by continued boiling the dark spots were decomposed and a granular white sandy residue remained, after which this residue was filtered and the ignition weighed and reported as insoluble.

The solution or filtrate from insoluble portions was evaporated to dryness and SiO_2 determined in the usual manner. Sulfuric acid was added to the silica filtrate and the solution evaporated and fumed, the lead being thus precipitated as $PbSO_4$.

Any barium present would be precipitated and separated from the solution along with the lead as a sulfate. The lead sulfate was dissolved off the filter paper by a solution of ammonium acetate and next converted into lead chromate and weighed; the remaining residue left on the filter paper being insoluble in ammonium acetate was ignited and weighed as $BaSO_4$ and later qualitatively tested by a flame test.

The uranium was twice precipitated with ammonia and then on the third precipitation enough ammonium carbonate was added to the ammonia to dissolve the uranium. The insoluble material was filtered off and the rare earths present were removed before iron and aluminum were determined.

The uranium, after the ammonium carbonates had been completely decomposed was reprecipitated with ammonia, filtered and weighed as U_3O_8. This uranium precipitate was redissolved in nitric acid, evaporated to dryness and redissolved in water and the rare earths removed by adding oxalic acid.

Rare earths divide themselves into two groups, one being soluble in ammonium carbonate and hence must be recovered from the uranium oxide, while the other being insoluble remained with the iron and aluminum oxides.

In each case it was found that a larger portion of the rare earths were soluble in ammonium carbonate. The direct determinations are given in the following table.

RELATIVE DISTRIBUTION OF RARE EARTHS BETWEEN UO_3 AND R_2O_3.

Rare earths recovered from	Analysis 1	Analysis 2
R_2O_3	0.48	0.34
UO_3	2.14	0.78

No attempt was made to separate these rare earths, so if thorium is present it is included as a rare earth. The other constituents were determined by well-known methods and need no comment.

The age of clarkeite was not calculated because there is evidence to show that the ratios between uranium and lead are considerably disturbed during the alteration of uraninites. H. V. Ellsworth[2] has recently shown how the lead uranium ratios on highly oxidized uranium minerals may give misleading or erroneous values.

OPTICAL PROPERTIES (C.S.R.)

The following table gives the optical properties of Clarkeite and those of gummite for comparison:—

TABLE III

OPTICAL PROPERTIES OF CLARKEITE AND GUMMITE

	Color in thin section	Cleavage	Pleochroism	Indices of refraction			Birefringence	Dispersion	Axial angle	Optical character
				α	β	γ				
Clarkeite Spruce Pine No. 1	Orange	None	Slightly deeper orange	1.997	2.098	2.108	.211	$\rho<\nu$ weak	30°—50°	(−)
Gummite Spruce Pine	Yellow	None	None	1.742	1.762	1.776	.034	$\rho<\nu$	60°	(−)

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[2] *American Mineralogist*, Vol. **15**, No. 10, p. 455.

It is probable that clarkeite has been previously assumed to be impure gummite but the data given in Table III show that the optical properties of gummite and clarkeite are distinct. The determination of the optical properties of gummite were made on a very small portion of beautiful material with orange red color, resinous luster, and conchoidal fracture that showed complete homogeneity. Unfortunately, however, the sample was too small for chemical or X-ray studies. Examination of less perfect material showed slight variations from the values given, but in no specimen did the optical properties approach those of clarkeite. It is to be noted that the optical data on gummite given here does not correspond with those recorded in the literature, and it is evident that gummite needs to be re-examined whenever adequate amounts of suitable material can be secured.

X-RAY PROPERTIES (E.P.)

X-ray powder photographs using K_α radiation of molybdenum were taken of the two samples of clarkeite and for comparison also of the supposed mineral gummite (U.S.N.M. No. 86120). In all the specimens examined, the analysis of which is shown in tables I and II considerable general blackening of the films took place and the

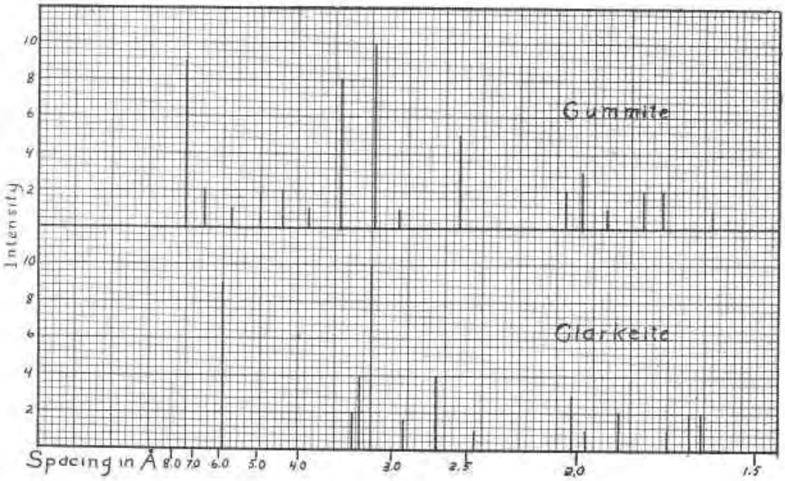

FIG. 1. X-Ray diffraction Pattern of Clarkeite and Gummite.

diffraction lines were broad, indicating the minuteness in size of the individual crystals. While possibly not all the material is crystalline, the reflections obtained showed clearly that the two samples of clarkeite were essentially identical and different from those obtained from the specimen of gummite. This is shown in Fig. 1 where the spacings and the estimated relative intensities of the lines observed on the films are given. While undoubtedly they do not represent the complete X-ray spectra of these substances and some of the lines may later be accounted for by some impurities present in these specimens, the powder photographs leave no doubt that the two uranium minerals represent different species.

Genetic Relations (C.S.R.)

Uraninite is the primary uranium mineral in the pegmatites at Spruce Pine, but its association with albitic areas and muscovite indicates that it was formed early in the post-pyrogenic stages of pegmatite formation. Clarkeite is a direct alteration product of uraninite since it surrounds uraninite and commonly contains residual grains of it. Gummite is later than clarkeite, since it surrounds and sends veinlets into the clarkeite. Uranophane surrounds gummite and veinlets of it cut the gummite and clarkeite.

The secondary minerals—clarkeite, gummite and uranophane—occur in fresh unweathered pegmatites and are clearly not the result of weathering processes, and it seems evident that their formation occurred during the late hydrothermal stages of pegmatite formation. Clarkeite seems to have formed from the action of hot sodic solutions on uraninite. It seems probable that the formation of clarkeite was related to the alteration of microcline to albite, an alteration that is marked in all pegmatites bearing rare minerals. At a later stage the solutions changed in composition until the clarkeite was unstable in their presence.

The compositions of clarkeite and gummite indicate that the solutions that caused the alteration of uraninite to clarkeite were alkali bearing. By the time gummite formed they had ceased to be alkalic but held notable amounts of silica so that the resulting mineral contained essential silica. At a later stage in the hydrothermal alteration process, the gummite and to a less extent clarkeite were altered to uranophane, with a higher calcium, silica and water content than either clarkeite or gummite.

SUMMARY

A mineral occurring at Spruce Pine, North Carolina, has distinctive chemical, optical and X-ray properties, and it is proposed to call this mineral clarkeite. The chemical formula is $RO \cdot 3UO_3 \cdot 3H_2O$ and the essential RO constituent is sodium.

Gummite, an associated mineral, has optical properties distinct from those of clarkeite, but differing from those given in the literature and so gummite should be re-investigated.

Clarkeite is a hydrothermal alteration product of uraninite, and gummite and uranophane are later products of the same process.