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## FOUR STAGES IN THE ALTERATION OF THE VILLENEUVE URANINITE

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During the winter of 1927 Dr. W. F. Ferrier in the course of rearranging the old mineral collection of the Geological Survey, which has been packed away in boxes for many years, came across a fine specimen labelled "Uraninite with Gummite L 31 R 1 of Villeneuve, Ottawa Co., Que." This unquestionably is the uraninite referred to in *G. S. C. Annual Report* for 1886, p. 10T by G. Christian Hoffman, then chemist and mineralogist to the Survey, who in December 1886 reported the receipt of this specimen weighing nearly a pound and noted that it was the first "pitchblende" found in Canada. The Lake Superior "coracite," an altered uraninite had been found long before this, however,

The specimen still weighs over 370 grams after removing some material for analysis and it evidently is only a comparatively small part of an originally much larger mass, thus substantiating a tradition which has been handed down to the effect that during the time of Hoffman a mass of uraninite the size of a cannon ball and weighing about 50 pounds was found in the Villeneuve mine. From the form of the specimen and the arrangement of the altered material one can readily believe that the original mass was roughly spherical and quite possibly 5 or 6 inches in diameter.

This uraninite is of particular interest because it shows four well marked zones of varying materials due to progressive alteration. Zone A, the part which evidently was nearest the centre of the original mass, naturally is the least altered and has a Sp. Gr. = 9.144, H = 6, colour steely black, lustre more or less metallic, and uneven

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fracture. Zone B, representing the next stage of alteration, has a Sp. Gr. = 7.779, H = 4.5, colour pitch black, lustre nonmetallic, fracture conchoidal. Zone C is composed of a beautiful bright "flame-scarlet" (Ridgway)<sup>1</sup> coloured substance with a Sp. Gr. = 5.273, H = 3.5, waxy lustre, and brittle conchoidal fracture. It has an index greater than 1.75 and is mostly anisotropic but does not appear to be entirely homogeneous. Zone D, representing the extreme stage of alteration, comprises an irregular layer seldom more than 1 mm. thick which evidently was the outside of the original uraninite mass in contact with the rocky matrix. On its outer surface it bears partly embedded scales of altered muscovite. A certain amount of D penetrates into C along fractures, etc., but D is plainly a more advanced alteration than C. The material of D is physically much like that of C but slightly softer. H = 3+, Sp. Gr. not determined, colour buff yellow to apricot yellow (Ridgway), lustre waxy, brittle, with a conchoidal fracture. It is anisotropic with index less than 1.75.

Although the Villeneuve uraninite, probably a part of this very mass, was analyzed by Hillebrand<sup>2</sup> it appeared to the writer that this specimen offered a unique opportunity to obtain valuable data as to the effect of alteration on the lead ratio of uraninite. Here we have a single mass showing the whole sequence of alteration products all in place in their relative order and conveniently arranged in zonal fashion in sufficient quantity to permit obtaining samples for examination. Quantities of A, B, and C sufficient for chemical analyses were readily obtainable without injuring the appearance of the specimen, but to secure enough of D it would have been necessary to sacrifice the whole outer layer, so no analysis of this substance was made.

The main chemical determinations were made on 2 gram portions in the case of A and B, and on a single 1 gram lot of C. The sample of C as prepared for analysis was estimated to contain perhaps 25 per cent of D which it was impracticable to attempt to remove, as too much of C would have been lost.

The analyses yielded the following results:

<sup>1</sup> Color Standards and Nomenclature.

<sup>2</sup> *Am. J. Sc.*, **42**, 390, 1891. Dr. Hillebrand states in part—No. 111 is an analysis of uraninite from the Villeneuve Mica mines, township of Villeneuve, Ottawa Co., Quebec. To Mr. G. C. Hoffman of the Can. Geol. Survey, who first recognized and reported this occurrence, I am indebted for the material analyzed.



The analyses throw considerable light on the changes which may take place accompanying alteration. It is evident that in the case of the Villeneuve uraninite the percentages of Pb,  $UO_3$ , Th, Ca,  $SiO_2$ , and  $H_2O$  increase with increasing alteration, while total U,  $UO_2$  and rare earths decrease. It also appears that the ratio of cerium group earths to yttrium and erbium earths decreases as alteration progresses. The lead ratio fortunately increases only slightly so long as the mineral remains black due to an appreciable  $UO_2$  content, but once the  $UO_2$  is entirely oxidized uranium is lost much faster than lead and the lead ratio rises to a large and entirely misleading value. This observation appears to supply the answer to the question whether to include the decomposition products, which arises when analyzing altered uraninites for age determinations. It is evident that all red and yellow decomposition products should be excluded, and probably results nearer the truth would be obtained if the material was given a preliminary digestion with hydrochloric acid to remove the more soluble alteration products. Much the same results as these were obtained by the writer some years ago in connection with the Cardiff township uraninite.<sup>3</sup> In fact it is now apparent that the analyses of this mineral represented in Table II by Todd<sup>4</sup> and the writer<sup>5</sup> show more or less similar effects amongst which the augmentation of the lead ratio with increasing alteration is notable. The percentage of  $UO_2$  relative to  $UO_3$  in any uraninite gives an accurate index of the degree to which the mineral has altered, so that it may be seen that Todd's specimen was the least altered, followed in order by the "Ellsworth Hard XL" and the "Ellsworth massive much altered." The results are not strictly comparable because these were three entirely different specimens and the writer has found that single crystals from the same occurrence may vary slightly in composition. However, even so, it is clear enough that alteration of the Cardiff uraninite is accompanied by an increase in the Pb and Th, and a decrease in the total U content with also a decrease in the total rare earths. The effect on the CaO content is not certain. Further evidence of the effect of alteration in causing higher lead ratio is

<sup>3</sup> *G. S. C. Sum. Rept.* 1923, Part CI, p. 20 CI.

<sup>4</sup> T. L. Walker, *Contributions to Canadian Mineralogy*, 1924, University of Toronto Studies, No. 17.

<sup>5</sup> *Loc. cit.*

TABLE II  
ANALYSES OF URANINITES FROM ARENDAL, NORWAY, BY W. F. HILLEBRAND AND  
FROM CARDIFF TP., HALIBURTON COUNTY, ONTARIO, BY TODD  
AND BY ELLSWORTH.

	TODD Cardiff Hard XL	ELLSWORTH Cardiff Hard XL	ELLSWORTH Cardiff, massive, much altered	HILLEBRAND Arendal less altered	HILLEBRAND Arendal much altered
PbO . . . . .	10.40	10.95	11.05	10.95	10.54
(Pb) . . . . .	(9.65)	(10.19)	(10.25)	(10.16)	(9.78)
UO <sub>2</sub> . . . . .	45.18	39.10	13.55	44.18	24.18
UO <sub>3</sub> . . . . .	24.90	32.40	52.04	26.80	41.71
(Total U) . . . . .	(60.56)	(61.44)	(55.26)	(61.27)	(56.05)
(As U <sub>3</sub> O <sub>8</sub> ) . . . . .		(72.44)	(65.15)		
ThO <sub>2</sub> . . . . .	11.40	10.60	13.56	3.48	3.00*
(Th) . . . . .	(10.02)	(9.32)	(11.92)	(3.06)	(2.64)
(Th=U equiv.) . . . . .	(3.81)	(3.54)	(4.53)	(1.16)	(1.00)
(Ce, La, Di) <sub>2</sub> O <sub>3</sub> . . . . .	1.82	1.88	1.26	0.67	0.67*
(Yt, Er) <sub>2</sub> O <sub>3</sub> . . . . .	2.74	2.14	1.87	9.05	9.76
Fe <sub>2</sub> O <sub>3</sub> . . . . .	0.58	0.43	0.47	0.24	0.03
MnO . . . . .	0.04	0.03	0.03		
Al <sub>2</sub> O <sub>3</sub> , etc. . . . .		0.09	0.11		
CaO . . . . .	0.28	1.01	0.27	0.61	1.06
MgO . . . . .	0.19	0.08	0.07	0.04	0.10
SiO <sub>2</sub> . . . . .	0.43	0.19	0.58	0.50	0.90
H <sub>2</sub> O . . . . .	0.61	0.65	1.60	undet.	1.23
He, etc. . . . .	0.35	0.31			
Insol. . . . .		0.15	0.67	1.19	1.10
CO <sub>2</sub> } . . . . .					
SO <sub>4</sub> } . . . . .			1.29		
P <sub>2</sub> O <sub>5</sub> } . . . . .					
		100.01	98.42		
Sp. Gr. . . . .	9.082	9.062	7.178		
Pb/U+0.38 Th . . . . .	0.150	0.157	0.171	0.163	0.171

\* ThO<sub>2</sub> and Ce group not separated. The value for ThO<sub>2</sub> given is a close approximation obtained by subtracting figure for Ce group in XVIII from total ThO<sub>2</sub>+Ce group in XVII. In view of some apparent irregularities which became noticeable when these tables were compiled, *i.e.*, the small amount of CaO in the Ellsworth altered sample, compared with the relatively large amount in the Ellsworth hard XL sample it was thought to be worth while to re-analyze these for Th, rare earths, and CaO, since, fortunately, enough of the original ground samples remained. This was done during 1927 and the new results, which however differ but inappreciably from the old, have been used here. It was found further, that the values for the Ce and Yt groups had been transposed in the published analyses of the "Ellsworth altered Cardiff" sample.

to be seen in the case of Hillebrand's<sup>6</sup> two analyses of the Arendal, Norway, uraninite (Table II). One sample as indicated by the greater  $\text{UO}_3$  content was evidently much more altered than the other and yields a considerably higher lead ratio.

From the evidence of the examples cited it is seen that the lead ratios of greatly altered uraninites containing up to 15%  $\text{UO}_2$  may need scaling down to the extent of 0.01 or more. The question then arises whether all uraninites which have a  $\text{UO}_2$  content greater than would be produced by autoxidation<sup>7</sup> alone do not yield lead ratios which are slightly too high. The amount of  $\text{UO}_3$  due to autoxidation alone would not exceed 15 or 20 per cent for the uraninites considered here, so that  $\text{UO}_3$  in excess of this must be the result of normal external alteration. The amount of the normal external alteration thus calculated may afford a rough index of the reduction in the lead ratio necessary to give exact results. It may well be that uraninites containing 10 to 20%  $\text{UO}_3$  in excess of that due to oxidation should have their lead ratios scaled down by 0.002 to 0.005 to represent more correctly the true values. Evidently only a very small, practically negligible, correction of this sort is necessary for well preserved specimens but when dealing with considerably altered uraninites it might well be taken into account.

It is interesting to note that the effect of alteration on uraninite as just cited is exactly the opposite of the effect on complex titano-tantalo-columbates, which appear to lose lead to a greater degree than uranium.

<sup>6</sup> *U. S. Geol. Survey, Bulletin* **78**, 1891, p. 67.

<sup>7</sup> H. V. Ellsworth, *Radioactive Minerals as Geological Age Indicators*. This Journ., Feb. 1925, pp. 137, 144.