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*WITH THE AID OF CHEMISTS AT HOME AND ABROAD*

BY

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EXAMINATION OF THE NORTH CAROLINA  
URANIUM MINERALS.

BY F. A. GENTH.

Prof. W. C. Kerr describes the occurrence of uranium minerals in Mitchell County, North Carolina, as follows:\* "A new locality, the Flat Rock mine, recently visited, has yielded the following in immediate association, viz. uraninite, gummite, uraconite, and, as incrustations on the outside of the latter, and of the fragments of rock adjacent, torbernite and autunite. These minerals occur only in one part of the mica-bearing portion of a very large granite vein, and are found in irregular nodules and rounded masses, some with a nucleus of uraninite of  $\frac{1}{2}$  to  $\frac{3}{4}$  inch, enveloped with a heavy layer of gummite, outside of which is a pale, yellow, earthy coating from  $\frac{1}{4}$  to  $\frac{1}{2}$  of an inch thick, which is uranochre or uraconite. One lump, the largest, weighs just a pound, and in all, I obtained between 3 and 4 pounds. The quantity of pitchblende, remaining unaltered is very small, and by far the greater part of the mass of the nodules, probably nine-tenths, is gummite; and the smaller ones are nearly or entirely changed to uraconite."

Through the kindness of Prof. Kerr I have recently come into possession of specimens of this highly interesting occurrence, which fully agree with the description above quoted. As his mineralogical determinations, however, were not supported by chemical analysis, and, especially as the composition of gummite is very doubtful, I thought that an investigation of the uranium minerals from this locality would be desirable.

I regret that of the uraninite no material for analysis could be obtained. One of my specimens of gummite, however, still contains one or two small fragments of uraninite; the larger one has a brownish black color, on the margin changing into brownish and, by degrees, into the pure gummite. It is also penetrated by small veins, showing the gradual alteration of the uraninite.

\* *Am. Journ. Sc.* [3] xlv, 496.

## Uranotil.—E. Boricky.

The analysis of the pale yellow coating surrounding the gummite shows that it is a variety of *uranotil*, and *not uranochre* or *uranoconite*. The original uranotil has been found in cavities of quartz, associated with fluorite at Wælsendorf in Bavaria, in lemon-yellow, rhombic needles of a specific gravity of 3.95. For comparison I will give below Boricky's analysis of it.

The North Carolina variety is apparently amorphous; massive, compact. H = 2.5. Sp. gr. = 3.834. Lustre waxy to dull; color from pale straw-yellow to lemon-yellow; streak pale straw-yellow; opaque; fracture uneven.

B. B. in a tube yields water and becomes brownish yellow; with fluxes the uranium reactions. Easily soluble in chlorhydric acid; on evaporation yields a jelly of silicic acid.

The analyses gave, after deducting a small quantity of quartz, mica and feldspar:

			Mean.	Boricky.	Calculated.
SiO <sub>2</sub>	= 13.55 ... 13.88 ...	13.72 ... 13.78 ...	13.95		
Al <sub>2</sub> O <sub>3</sub> & Fe <sub>2</sub> O <sub>3</sub>	= traces ... traces ...	traces ...	0.51 ...	.....	
UO <sub>2</sub>	= 66.76 ... 66.59 ...	66.67 ... 66.75 ...	66.98		
PbO	= 0.74 ... 0.45 ...	0.60 ...	...	...	...
BaO	= 0.28	0.28 ...	...	...	...
SrO	= 0.13	0.13 ...	...	...	...
CaO	= 6.23 ... 7.11 ...	6.67 ... 5.27 ...	6.51		
P <sub>2</sub> O <sub>5</sub>	= not det'd 0.29 ...	0.29 ... 0.45 ...	...		
H <sub>2</sub> O	= not det'd 12.02 ...	12.02 ... 12.67 ...	12.56		
		100.82	100.38	99.43	100.00

Rammelsberg\* gives for uranotil the formula  $\text{Ca}_7(\text{UO}_2)_6\text{Si}_6\text{O}_{18} + 15\text{H}_2\text{O}$ . My analyses agree far better with the following formula  $\text{Ca}_5(\text{UO}_2)_6\text{Si}_6\text{O}_{21} + 18\text{H}_2\text{O}$ , as will be seen from the above calculated analysis. It forms an incrustation upon gummite and results from its alteration, sometimes (as has been observed by Prof. Kerr) changing the entire mass of the latter and yielding nodules of pure uranotil; mostly, however, converting not only the outside of the gummite into uranotil, but penetrating its whole mass, so that even the purest particles contain already a large percentage of it, as will be seen from the analyses of the gummite.

\* Mineralchemie, 692.

Gummite.

The orange-colored mineral from the Flat Rock mine has been called gummite, from its resemblance to that from European localities. It occurs in amorphous, compact, nodular masses.  $H = 3$ . Sp. gr. = 4.840. Lustre faintly resinous to dull; color reddish yellow to deep orange red; streak orange yellow; opaque; fracture subconchoidal to uneven.

B. B. yields water and turns reddish brown; upon charcoal with sodium carbonate yields metallic lead, with fluxes gives the reactions of uranium. Easily soluble in acetic acid.

Below I give the analyses of the purest, deep orange red material, after deducting a minute quantity of quartz, feldspar and mica. For comparison I add the only analysis which is known of gummite, that from Johann-Georgenstadt in Saxony, by Kersten:

				Johann-Georgen-		
				Mean.	stadt.	Kersten.
SiO <sub>2</sub>	=	4.49 ...	4.83 ...	4.58 ...	4.63	... 4 26
Al <sub>2</sub> O <sub>3</sub>	=	0.67 ...	0.40	} [4.59] }	0.53	Mn <sub>2</sub> O <sub>3</sub> 0.05
BaO	=	0.98	1.12		1.08	As, Fl traces.
SrO	=	0.05			...	...
CaO	=	1.96 ...	2.14		...	2.05 ... 6.00
PbO	=	5.48 ...	5.58 ...	5.64 ...	5.57	... ..
UO <sub>3</sub>	=	[75.71]...	75.50 ...	74.39 ...	75.20	... 72.00
P <sub>2</sub> O <sub>5</sub>	=	0.12 ...	0.07 ...	0.16 ...	0.12	... 2.30
H <sub>2</sub> O	=	not det'd	10.43 ...	10.64 ...	10.54	... 14.75
				100.07	99.72	99.36

The opinion of chemists as to the composition of gummite is very much divided. Kersten thought it to be a combination of phosphate of lime with uranic hydrate, the composition of which he expressed by the formula  $3CaO, P_2O_5 + 4U_2O_3, 9H_2O$ . Berzelius considered it as a mixture of basic phosphate and basic silicate of uranic oxide and lime. Hausmann takes it to be principally the hydrate of uranic oxide. Rammelsberg expresses the same opinion, but believes that the analyses of gummite, together with those of eliasite and pittinitite, represent mixtures, and that from their analyses no rational composition can be derived. Hermann, on the other hand, considers these and other uranium minerals, in which silicic acid has been

found, even uraninite, as definite compounds of the formula:  $4RO, SiO_2 + 4(4R_2O_3, SiO_2) + mH_2O + nX$ . The accessory molecule X being wanting in pittinitite, and in the other species represented by  $R(AsS)$  in uranochalcite, by  $4RO, U_2O_5$  in uraninite, by  $CaO, CO_2$  in eliasite, by  $3CaO, P_2O_5$  in phosphor-gummite, and by  $3CaO, (PV)_2O_5$  in vanadin-gummite. Hermann's views are as untenable as those of the others. Nearest to the truth, in my opinion, comes Paterra, who holds that silicic acid and phosphoric acid are not essential, and that gummite is principally a lime-uranate,  $CaO, 2U_2O_5 + 6H_2O$ , analogous in composition to the artificial uran-yellow.

Gummite is the result of an alteration of uraninite, and it seems to me that both pittinitite and eliasite are intermediate between the two, containing more or less of either. But I have already pointed out the fact that the gummite from North Carolina is a mechanical mixture, and that uranotil penetrates the whole mass. The gradual change from gummite into uranotil can be observed on every specimen from this locality.

If we calculate from the  $SiO_2$  in the gummite the requisite constituents of uranotil, making up the minute deficiency of  $CaO$  by its equivalent of  $BaO$ , we get:

$SiO_2$	=	4.63
$CaO$	=	2.05
$BaO$	=	0.30
$H_2O$	=	4.17

33.38 per cent. of uranotil.

The  $PbO$  and  $BaO$  may be most rationally considered as being present in the form of  $\bar{M}(UO_2)_2O_3 + 6H_2O$ ; we get therefore

$PbO$	=	5.57
$UO_3$	=	14.39
$H_2O$	=	2.70

22.66 per cent. of lead-uranate; and

$BaO$	=	0.78
$UO_3$	=	2.93
$H_2O$	=	0.55

4.26 per cent. of barium-uranate.

There remain 35.65 per cent. of  $\text{UO}_3$ , which is evidently present as uranic hydrate, requiring 4.45 per cent. of water.

The gummite from the Flat Rock mine is therefore a mechanical mixture of:

Uranic hydrate	= $\text{H}_2(\text{UO}_2)_2\text{O}_3 + \text{H}_2\text{O}$	= 40.10 %
Uranotil	= $\text{Ca}_3(\text{UO}_2)_6\text{Si}_6\text{O}_{21} + 18\text{H}_2\text{O}$	= 33.38
Lead-uranate	= $\text{Pb}(\text{UO}_2)_2\text{O}_3 + 6\text{H}_2\text{O}$	= 22.66
Barium-uranate	= $\text{Ba}(\text{UO}_2)_2\text{O}_3 + 6\text{H}_2\text{O}$	= 4.26
		100.40

The analyses of pittinitite and eliasite admit of no calculation as they appear to have too many foreign substances present, and as the amount of uranous oxide which they evidently contain has not been determined; if we take the analysis of gummite from Johann-Georgenstadt, we find it probably to be a mixture of calcium-uranate, with uranotil, a uranium-phosphate (phosphuranylite) and uranic hydrate. These calculations give the following amounts:

SiO <sub>2</sub>	=	4.26	
UO <sub>3</sub>	=	20.45	
CaO	=	1.99	
H <sub>2</sub> O	=	3.84	
			30.54 per cent. of uranotil.

CaO	=	4.01	
UO <sub>3</sub>	=	41.25	
H <sub>2</sub> O	=	7.73	
			52.99 per cent. of calcium-uranate.

P <sub>2</sub> O <sub>5</sub>	=	2.30	
UO <sub>3</sub>	=	4.68	
H <sub>2</sub> O	=	1.75	
			8.73 per cent. of phosphuranylite.

UO <sub>3</sub>	=	5.62	
H <sub>2</sub> O	=	0.70	
			6.32 per cent. of uranic hydrate.

The gummite from Johann-Georgenstadt has therefore probably the following composition, corresponding with Kersten's analysis :

Uranic hydrate	=	$H_2(UO_2)_2O_2 + H_2O$	=	6.32 %
Uranotil	=	$Ca_2(UO_2)_2Si_2O_{11} + 18H_2O$	=	30.54
Phosphuranylite	=	$(UO_2)_2P_2O_8 + 6H_2O$	=	8.73
Calcium-uranate	=	$Ca(UO_2)_2O_8 + 6H_2O$	=	52.99
				98.58

*Phosphuranylite.*—A new species.

Rhombic (?). Under the microscope very minute rectangular scales with pearly lustre can be distinguished. In pulverulent incrustations upon quartz, feldspar and mica. Color deep lemon-yellow.

B. B. in the tube yields water and becomes reddish brown while hot, brownish yellow after cooling; readily soluble in nitric acid, yielding with ammonium molybdate a yellow precipitate; contains *no* arsenic acid.

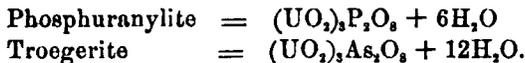
As this mineral is very rare, only a very minute quantity could be obtained which was free from autunite; this being in the form of a thin coating upon quartz, both together had to be taken as material for analysis.

0.6705 grams contained 0.5617 grams quartz—the analysis was therefore made with 0.1088 grams of material. This was slightly mixed probably with cerussite, which was visible under the microscope in the form of very small colorless particles. In the first column I give the results of the analysis, in the second the percentage of the phosphate, excluding the lead oxide, and in the third the calculated percentage, corresponding to the formula given below.

				Calculated.
UO <sub>2</sub>	=	71.73	... 76.71	... 77.56
PbO	=	4.40	... ..	...
P <sub>2</sub> O <sub>5</sub>	=	11.30	... 12.08	... 12.75
H <sub>2</sub> O	=	10.48	... 11.21	... 9.69
		97.91		

It will be seen from this analysis that the uranium and phosphorus are present exactly in the ratio of 3 : 2, and that

the composition of phosphuranylite may be expressed by a formula analogous to that of troegerite, but containing only half the amount of water:



Prof. Kerr mentions torbernite as one of the uranium minerals from the Flat Rock mine, and he sent me some uranite, which had a deep green color and resembled it very closely; but the chemical examination of one of the darkest green crystals showed that it contained only lime, and not a trace of copper oxide, and that the uranite from this locality is therefore only autunite.

UNIVERSITY OF PENNSYLVANIA, W. Philadelphia, April 12, 1879.

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*CONTRIBUTIONS FROM THE CHEMICAL  
LABORATORY OF HARVARD  
COLLEGE.*

No. I.

RESEARCHES ON THE SUBSTITUTED BENZYL  
COMPOUNDS.\*

BY C. LORING JACKSON.

INTRODUCTION.

The existence of the benzyl compounds was first established by Cannizaro,† in 1853; for, although Liebig and Wöhler,‡ in their classical research on the benzoyl compounds, obtained benzylalcohol as a secondary product from the action of potassic hydrate on benzaldehyde, they merely spoke of it as an oily liquid, and did not determine its composition or properties. It was also Cannizaro who, in 1855,§ showed that

\* Presented to the American Academy of Arts and Sciences. Communicated by the author.

† *Ann. der Chemie*, 88, p. 129. ‡ *Ib.*, 3, p. 249. § *Ib.*, 96, p. 246.