

NATROAUTUNITE

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A new mineral is described, hydrated sodium uranyl phosphate, found in one of the granodiorite ranges of the USSR. The mineral belongs to the group of uranium micas and is similar in properties to autunite.

In 1953 a mineral very similar to autunite in external appearance was discovered in one of the granodiorite ranges of the USSR. It consists of lemon-yellow or lettuce-yellow elongated or square thin tabular plates with perfect (001) cleavage and less perfect (100) cleavage. The plates, which form scales and fanlike aggregates, and sometimes radiating bundles (Fig. 1), are brittle. Hardness 2-2.5. The luster at the (001) cleavage planes is nacreous, and glassy in other directions.

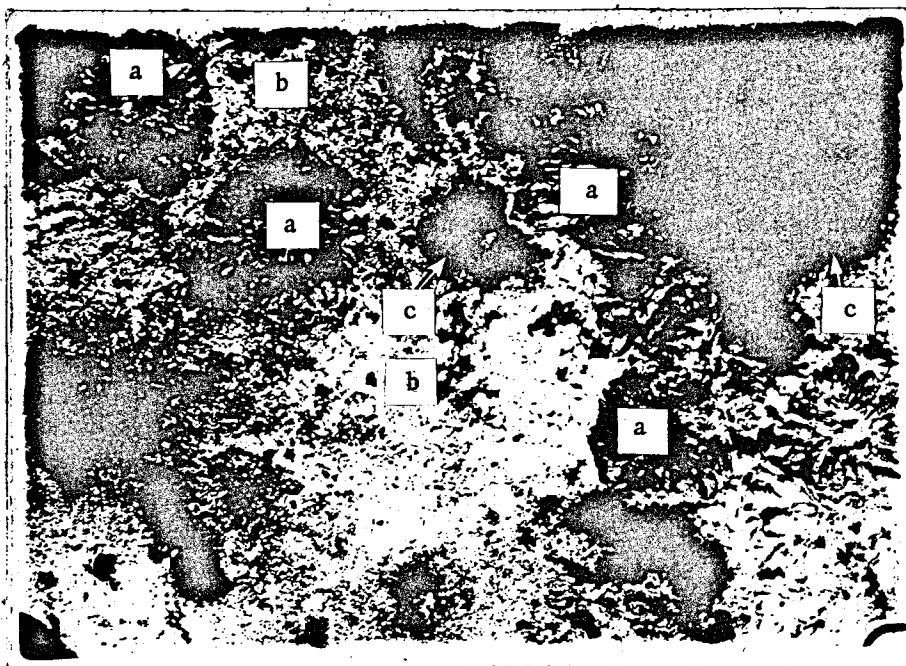


Fig. 1. a) Natroautunite formation ($\times 5$); b) kaolinite; c) limonite.

The mineral is readily soluble in acids, giving greenish yellow solutions. When heated in a sealed tube it gives off water, becoming straw-yellow and loose. It gives a distinct reaction for uranium with borax and phosphate.

The mineral exhibits a bright greenish yellow luminescence under ultraviolet light. The luminescence

spectrum and microphotogram of natroautunite are very similar to those of autunite (Fig. 2). Examination under the immersion microscope shows clearly defined square crystals of greenish yellow and pale yellow color; the interference color is pale yellow.

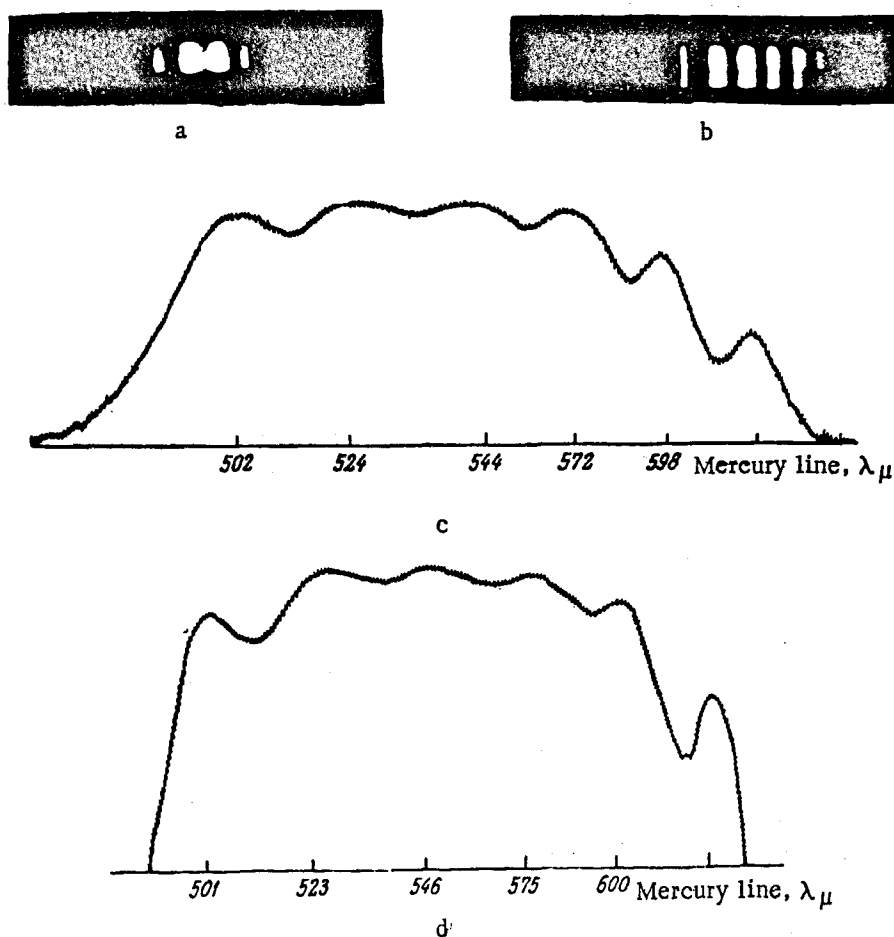


Fig. 2. a) Luminescence spectrum of natroautunite; b) luminescence spectrum of autunite; c) microphotogram of natroautunite; d) microphotogram of autunite (Taken by Senior Assistant of the IGEM, Acad. Sci. USSR, E. S. Rudnitskaya).

The freshly mined crystals are uniaxial, optically negative, $N_0 = 1.578$, $N_e = 1.559$, weakly pleochroic, bright yellow along N_0 , pale yellow along N_e . After the crystals have been kept for two days at 35-40° the refractive indices increase to 1.585 for N_0 and 1.564 for N_e .

It is seen that the optical properties of natroautunite are very similar to the optical properties of autunite as given in the literature [1-3].

Spectroscopic analysis carried out in the spectroscopy laboratory of IGEM (Institute of the Geology of Ore Deposits, Mineralogy, Geochemistry, and Petrography) showed that the mineral contains large amounts of uranium and phosphorus, several percent of sodium, up to 1% iron, and small amounts of calcium, aluminum, and silicon.

On the basis of these results, the following scheme was devised for chemical analysis of two samples of natroautunite.

The weighed sample was treated with perchloric acid. Silicic acid was filtered off and determined in the usual way. For precipitation of iron, aluminum, and uranium phosphates, ammonia free from carbon dioxide was used. The precipitate was filtered off, washed, dissolved in sulfuric acid, and treated with cupferron after preliminary reduction of the uranium with sodium hydrosulfite. Uranium and iron were precipitated, while

phosphorus and aluminum remained in solution. The precipitate was ignited and fused with potassium bisulfate, dissolved in sulfuric acid, and again treated with cupferron after oxidation of uranium to the hexivalent state. The precipitated iron was ignited and weighed as Fe_2O_3 . A test for titanium was performed.

The filtrate which contained phosphorus and aluminum was treated with nitric acid to decompose the cupferron present, and divided into aliquot portions. One was analyzed for phosphorus (precipitation as magnesium phosphate and ignition to pyrophosphate) and the other for aluminum (colorimetric arsenazo method).

Uranium was determined in a separate sample by P. A. Volkov's method [4]. The principle of the method is that uranium is reduced by sodium hydrosulfite to the quadrivalent state. The precipitate is dissolved in 33% sulfuric acid and titrated with potassium dichromate solution.

If not enough material is available, uranium can be determined in the cupferron solution.

Calcium and magnesium were determined in the filtrate after R^{3+} precipitation by the usual gravimetric methods: calcium as the oxalate, magnesium as the pyrophosphate.

Potassium and sodium were determined by the Smith method.

Hygroscopic water (H_2O^-) was determined by drying a sample to constant weight at 105-110°, and bound water (H_2O^+) was determined by the Penfield method.

The results of two chemical analyses of natroautunite are given in Table 1.

TABLE 1

	I			II			III		
	%	Molecular amounts	Molecular ratios	%	Molecular amounts	Molecular ratios	%	Molecular amounts	Molecular ratios
UO_3	61.9	0.209	1.91	62.53	0.215	2.1	62.18	0.218	2
P_2O_5	15.56	0.109	1.00	14.69	0.104	1.0	15.43	0.109	1
Na_2O	5.62	0.09	0.83	6.88	0.111	1.06	6.74	0.109	1
CaO	1.2	0.021	0.19	0.14	—	—	—	—	—
SiO_2	1.6	0.027	0.25	—	—	—	—	—	—
CO_2	0.24	0.006	0.006	—	—	—	—	—	—
MgO	0.43	0.01	0.01	—	—	—	—	—	—
Al_2O_3	0.32	0.03	0.03	—	—	—	—	—	—
Fe_2O_3	0.97	0.006	0.006	—	—	—	—	—	—
H_2O^+ 4.05	13.07	0.728	6.66	14.84	0.824	7.9	15.65	0.87	8
H_2O^- 9.02									
Total	100.91			99.08			100.00		

Note: I and II) native natroautunite (I - analysis performed by Junior Assistant, IGEM Acad. Sci. USSR O. V. Krutetskaya; II - uranium, phosphorus, and water determined by Senior Laboratory Assistant, IGEM Acad. Sci. USSR V. I. Litenkova, sodium and calcium by O. V. Krutetskaya); III) theoretical composition for $\text{Na}_x(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$.

In the first analysis there is not enough sodium for the formula $\text{Na}_x(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$. This is possibly because the analyzed sample contained some impurity.

The analytical results for the second sample, more carefully taken, correspond fairly exactly to the formula $\text{Na}_x(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$. Only the water content is somewhat lower, which is probably the result of loss in a dry atmosphere, as for most micas.

The possibility of isomorphous substitution of sodium by calcium in the first sample is not excluded.

Published analytical data on native autunite [1 - 3] show absence of sodium, but Fairchild [5] showed that in artificial autunites sodium readily replaces calcium.

TABLE 2

Photographic Conditions: Cu Radiation, Camera Diameter 57.9 mm, Specimen Diameter 0.6 mm

No.	Natroautunite			Synthesized autunite (E. N. Leonova)			Synthesized hydrogen autunite (E. N. Leonova)		
	<i>l</i>	d_{α}	(<i>hkl</i>)	<i>l</i>	d_{α}	(<i>hkl</i>)	<i>l</i>	d_{α}	(<i>hkl</i>)
1	5	8.57	001	6	8.46	001	5	8.45	001
2	4	5.40	101	3	5.41	110. 101	4	5.77	110
3	5	4.32	002	1	4.91		6	4.30	111
4				5	4.168	002			
5	2	4.03		2	4.00		1	3.85	
6	10	3.67	102	10	3.65	102	3	3.71	102
7	5	3.49	200	4	3.51	200	10	3.56	200
8	7	3.23	112	6	3.25	120	10	3.28	112. 201
9	5	2.94	121	4	2.93	121	8	2.97	121
10				2	2.77	003			
11	8	2.675	103	8	2.62	103	5	2.69	103
12	4	2.54	122	3	2.53	122	4	2.57	122
13	3	2.46	113	3	2.46	113	4	2.49	113
14	4	2.36	221	2	2.40	221	7	2.39	221
15				2	2.34				
16				3	2.27	301			
17	3	2.20	130	4	2.23	130			
18				3	2.16	131			
19	3	2.16	004	7	2.11	123. 004	3	2.19	004
20	6	2.12	123				2	2.14	123
21	5	2.05	104. 302	5	2.04	104	6	2.09	104
22	5 b	1.984	114	7	1.96	230	4	2.00	114
23	2	1.889	231	1	1.90	231	4	1.908	231
24	3	1.845	204	5	1.81	303. 204	3	1.854	222
25	4	1.816	303						
26	3	1.768	124		1.78		4	1.79	124
27				5 b		400			
28	3	1.746	133. 400		1.76		2	1.745	400
29	3	1.711	005	4	1.70	005	3	1.729	
30	7	1.639	115	10	1.59	115	4	1.655	115
31	4	1.614	224				2	1.62	
32	2	1.576	304	3	1.58	304			
33	8 b	1.566	205. 134	8	1.53	134. 303	5	1.574	303
34	3	1.461		1	1.49				
35	3	1.449	006	1	1.487		2	1.468	006
36	4	1.420	106				1	1.435	106
37							2	1.407	
38	2	1.386		5	1.385		6	1.380	
39	7	1.364		6	1.35				
40	4	1.322		2	1.34		1	1.330	
41	3	1.298							
42	1	1.282							
43	2	1.259		4	1.260		2	1.267	
44		1.240					2	1.243	
45	2 b	1.214					2	1.224	
46		1.200					1	1.204	
47	2 b	1.187		6	1.19		1	1.193	
48	6 b	1.166		2	1.159				
49		1.156							
49	1	1.141		3	1.136				
50	3	1.111		1	1.115				
51	3	1.097					1	1.110	
52							1	1.099	
							1	1.086	
53	5	1,074		5	1,074				
54	3	1,048					6	1,046	
55							1	1,039	
56	1	1,024		2	1,024				
57	5	0,985		1	1,008				
58				3	0,988				
59	2	0,967							
60	5	0,950							
61				3	0,902				
62				1	0,88				
63	3	0,858		1	0,87				

A comparison of x-ray powder pattern data (Table 2) for native natroautunite and artificial hydrogen and calcium autunites synthesized by Junior Scientific Assistant of IGEM, Acad. Sci. USSR E. N. Leonova (data not published) shows that they have related structures. All the x-ray patterns were analyzed for tetragonal syngony by means of Hull charts by N. I. Organova. Indices of the nOO , $n2nO$, $2n2nO$ types were not found. This indicates that all the autunites studied belong to the $p4/nmm$ space group. The unit cell dimensions of the samples studied were also similar (Table 3).

Calculations show that the samples belong to the meta group. By analogy with calcium metautunite reported in the literature [1, 2] it may be concluded that the unit cell of metanatroautunite contains one molecule of $Na_2(UO_2)_2(PO_4)_2 \cdot 8H_2O$.

TABLE 3

	Natroautunite	Synthesized calcium autunite	Synthesized hydrogen autunite
<i>a</i>	6.97Å	7.04Å	7.07Å
<i>c</i>	8.69Å	8.46Å	8.80Å
<i>c/a</i>	1.245	1.20	1.245

On this assumption the calculated density of the mineral was 3.89 g/cc. Experimental determination of the density, carried out by V. S. Amelina, gave 3.584 g/cc.

This discrepancy probably cannot be attributed only to porosity of the sample. It is probably associated with variable contents of water in autunites. The decrease in the amount of water in metautunites by comparison with autunites is accompanied by an increase in density. As the material was powdered when prepared

for the x-ray photography, some water could have been lost from the lattice, leading to the discrepancy between the calculated and experimental densities.

It is seen from the foregoing that natroautunite is very similar to autunite in properties (color, crystal form, type of luminescence, structure, optical properties), and differs from it only in chemical composition.

Received February 25, 1957

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