

## STUDIES OF URANIUM MINERALS (IX): SALÉEITE AND NOVACEKITE\*

CLIFFORD FRONDEL, *Harvard University, Cambridge, Massachusetts.*

### ABSTRACT

Novacekite, a new uranium mineral from Schneeberg, Saxony, has the composition  $\text{Mg}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot n\text{H}_2\text{O}$  and forms a probably complete series to the phosphate analogue, saléeite. Analyzed material with As:P~1:1 is tetragonal with  $a_0=7.12 \text{ \AA}$ ,  $c_0=20.14$  and gravity 3.3. Optically this material, like the other members of the series, has an anomalous biaxial negative character, with  $nY=nZ=1.620\text{--}1.623$  and  $2V 0^\circ$  to  $15^\circ$ . The unanalyzed but essentially pure end-component, also from Schneeberg, has  $a_0=7.16 \text{ \AA}$ ,  $c_0=20.19$ ; biaxial negative with  $nX=1.620$ ,  $nY=nZ=1.637$ ,  $2V 0^\circ$  to  $15^\circ$ ; gravity 3.6. An analysis is given of a new occurrence of saléeite,  $\text{Mg}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$ , at Mina da Quarta Seira, Sabugal, Portugal; tetragonal with  $a_0=7.01 \text{ \AA}$ ,  $c_0=19.84$ ; biaxial negative with  $nX=1.565$ ,  $nY=1.582$ ,  $nZ=1.585$ ,  $2V \sim 65^\circ$ ,  $r > v$ . Saléeite from Shinkolobwe, Belgian Congo, has  $a_0=7.02 \text{ \AA}$ ,  $c_0=19.81$ ;  $nX=1.554$ ,  $nY=nZ=1.571$ ,  $2V 0^\circ$  to  $10^\circ$ . Novacekite and saléeite closely resemble and are isostructural with fully-hydrated autunite. The indices of refraction vary with the content of zeolitic water within the limits of stability of the fully-hydrated phase.

### SALÉEITE FROM PORTUGAL

A description of the rare uranium mineral saléeite has been given in a preceding paper of this series.<sup>1</sup> A new occurrence of this mineral has been identified in a suite of secondary uranium minerals from Portugal. The locality is the Mina da Quarta Seira, Sabugal, Beira Province, Portugal. The mineral occurs as tiny, thin rectangular plates that are interleaved into a coherent but very porous aggregate. Many crystals are subparallel growths on {001} and none are measurable. The color is pale canary-yellow to straw-yellow. Other specimens from the same locality show deeply weathered pieces of granite or fine-grained pegmatite thickly incrustated with meta-autunite, sabugalite and minor amounts of phosphuranylite.

A chemical analysis of the mineral, cited in Column 3 of Table 2, shows that it conforms to the formula  $\text{Mg}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 9\text{H}_2\text{O}$ . A small amount of Pb and apparently also Al substitutes for Mg. The x-ray powder diffraction photograph indicates that this material, like the arsenatian saléeite with approximately  $10\text{H}_2\text{O}$  from Schneeberg described by Mrose,<sup>1</sup> is isostructural with fully-hydrated synthetic autunite as prepared by the method of Beintema.<sup>2</sup> The water content (approximately  $8\text{H}_2\text{O}$ ) and the optical properties of the original saléeite<sup>3</sup> from Shinkolo-

\* Contribution from the Department of Mineralogy and Petrography, Harvard University, No. 331.

<sup>1</sup> Mrose, M. E., *Am. Mineral.*, **35**, 525-530 (1950).

<sup>2</sup> Beintema, J., *Rec. Trav. Chim. Pays-Bas*, **57**, 155 (1938).

<sup>3</sup> Thoreau, J., and Vaes, J. F., *Bull. soc. belge géol.*, **42**, 96 (1932).

bwe, Belgian Congo, suggests that this particular material corresponds to the meta-I hydrate of autunite. Two specimens of saléeite from Shinkolobwe, one originally from the collection of A. Schoep and obtained through the U. S. National Museum, and the other loaned through the courtesy of Professor P. F. Kerr of Columbia University, were checked in this regard and both were found to have the structure of the fully-hydrated phase. The Shinkolobwe and Portuguese material has practically identical tetragonal cell dimensions (see Table 1).

Under the microscope, the saléeite from Portugal appears as rectangular plates with the corners sometimes truncated at 45°. The mineral is

TABLE 1. OPTICAL PROPERTIES AND UNIT CELL DIMENSIONS  
IN THE SALÉEITE-NOVACEKITE SERIES

Name	Saléeite	Saléeite	Saléeite	Arsenatian saléeite	Phosphatian novacekite	Novacekite
Locality	Shinkolobwe <sup>a</sup>	Shinkolobwe <sup>b</sup>	Portugal	Schneeberg <sup>c</sup>	Schneeberg	Schneeberg
Anal. No.	2	(Qual. only)	3	4	5	(Qual. only)
P:As ratio	No As	No As	No As	1:0.22	1:1.01	Trace of P
<i>n</i> X or <i>n</i> E	1.559	1.554	1.565	1.559		1.620
<i>n</i> Y	1.570	1.571	1.582	1.574	1.620-1.623	1.637
<i>n</i> Z or <i>n</i> O	1.574	1.571	1.585	1.574	1.620-1.623	1.637
2V	61°	0°-10°	65°	0°	0°-15°	0°-15°
Disp.	<i>r</i> > <i>v</i>		<i>r</i> > <i>v</i>		<i>r</i> > <i>v</i>	<i>r</i> > <i>v</i>
<i>a</i> <sub>0</sub>		7.02 Å	7.01	7.05	7.12	7.16
<i>c</i> <sub>0</sub>		19.81	19.84	19.87	20.14	20.19
<i>a</i> <sub>0</sub> : <i>c</i> <sub>0</sub>		2.823	2.830	2.819	2.829	2.820

All members of the series are pleochroic with X (or O) =nearly colorless, Y =pale yellow, Z = (or E) pale yellow.

<sup>a</sup> Thoreau and Vaes (1932).

<sup>b</sup> New data on specimen from U. S. National Museum.

<sup>c</sup> Mrose (1950). Original single-crystal measurements reported as *a*<sub>0</sub>=6.98, *c*<sub>0</sub>=19.813; present data from powder film of original sample.

biaxial negative, with 2V about 65° and with X perpendicular to the flattening. The plates extinguish uniformly and do not have a mosaic structure of varying optical orientation such as is shown by the original Shinkolobwe material. The optical properties of air dried saléeite from its known occurrences are given in Table 2, beyond, together with those of the isostructural arsenate, novacekite, described in the following section. The unheated saléeite from Portugal when kept in moist air at room temperature for 30 days decreased slightly in indices of refraction, with *n*Y=1.578 and *n*Z=1.581. A sample when heated in air at 92° C for 48 hours was found to have lost water with an accompanying increase in indices to *n*X=1.592, *n*Y=1.603, *n*Z=1.614 and 2V large. After

standing at room temperature in a moist atmosphere for 40 days the indices returned almost to the original values.

#### NOVACEKITE, AND THE SALÉEITE—NOVACEKITE SERIES

In the course of examination of a small suite of secondary uranium minerals from Schneeberg, Saxony, that were suspected to consist of uranospinite or troegerite, two specimens were found of a mineral that has proved to be a new hydrated magnesium uranyl arsenate member of the autunite group. The name novacekite is proposed for this species after the Czech mineralogist Radim Nováček (1905–1942)<sup>4</sup>, who made important contributions to the knowledge of the mineralogy of uranium.

The first specimen was labelled uranospinite, which is the calcium uranyl arsenate member of the autunite group. It comprised a small piece of deeply altered, quartzose and limonite vein material that was coated and veined by secondary uranium minerals. The so-called uranospinite was present as a small area, apparently a filled cavity, of a platy, cleavable mineral of a straw-yellow color. This was subsequently identified as novacekite. The substance closely resembles saléeite in general appearance. It forms lamellar and sub-parallel aggregates of small plates with a perfect basal cleavage. The specific gravity is 3.6. Small irregular flakes of zeunerite were present around the borders of the mass of novacekite and represent the first deposition on the cavity walls. Small groups of crystals of zeunerite were present elsewhere on the specimen together with tufted crusts of uranophane and an impregnation of a golden-yellow, earthy uranium mineral that has not been identified. The amount of novacekite available on the specimen was insufficient for a quantitative analysis. A careful qualitative chemical examination of hand picked samples was made by Mr. F. A. Gonyer. This proved the substance to be a hydrated uranyl arsenate, with a strong trace of phosphate, but with calcium absent and with magnesium present in its place. The mineral is the arsenate analogue of saléeite and is isostructural therewith as shown by *x*-ray study described beyond.

The second specimen found of this mineral, from the Roebling collection of the U. S. National Museum, also was labelled uranospinite. This specimen comprised a small, friable mass of vein material, light brown in color and composed largely of limonite and quartz. The mass is somewhat fractured and the cavities are lined or filled completely by indistinct straw-yellow to lemon-yellow crystals of novacekite. Euhedral crystals are thick tabular on {001} and are rectangular in shape with rounded {*h*0*l*} forms and are not measurable. There is a perfect cleavage

<sup>4</sup> A memorial of Nováček is given by Čech: *Věstník Stát. Geol. Ústavu Republiky Českoslov.*, 20, 23 (1945).

on {001}. The luster is weak, inclining to waxy. The hardness is  $2\frac{1}{2}$  and the specific gravity 3.25. The veinlets are bordered by green crystals of zeunerite, which formed earlier than the novacekite, as in the first specimen described, and some of the novacekite crystals show intergrown cores of zeunerite in parallel orientation. The zeunerite has  $n_O=1.637$ ,  $n_E$  1.620, and is not quite uniaxial ( $2V=0^\circ$  to about  $8^\circ$ ). Sufficient novacekite was available on the specimen for a complete analysis (column 5, Table 2). This proved the material to be a hydrated magnesium uranyl arsenate-phosphate, conforming to the autunite formula-type, with arsenate and phosphate substituting mutually almost in equal amounts.

*X-Ray Crystallography and Optical Properties.* The x-ray powder patterns of the two samples of novacekite described above differ from those of the pure saléeite from Portugal and Shinkolobwe, and of the arsenatian saléeite from Schneeberg (Columns 2, 3, 4 in Table 1) only in having slightly greater cell sizes. The tetragonal cell dimensions obtained from the powder patterns are cited in Table 2.

Optically, both samples of the Schneeberg novacekite are biaxial negative with  $2V$  ranging from nearly  $0^\circ$  up to about  $15^\circ$ . The phosphatian novacekite of analysis 5 in Table 2 shows mottled extinction with at times a parquet-structure on a fine scale. There was some variation in indices between different grains in both samples. The values cited in Table 1 represent the great bulk of the sample in the two cases. The variation in indices is doubtless due to variation in the content of zeolitic water within the stability range of the fully-hydrated phase. This feature and the appearance of biaxial characters within this range as a function of water content also occurs in other members of the autunite group, and in the meta-I hydrates as well, and has been discussed in light of the crystal structure by Beintema.<sup>2</sup>

Both the indices of refraction and the unit cell dimensions in general increase with increase in the ratio of As to P, as would be expected, but the variation shown is somewhat irregular. This can be ascribed to differences in the water content of the several samples that are independent of the As:P ratio. A more regular relation between indices and composition presumably would be obtained if all of the samples were hydrated to the same degree.

Saléeite free from arsenate fluoresces a bright lemon-yellow in both short-wave and long-wave ultraviolet radiation. The phosphatian novacekite of analysis 5 and the essentially pure arsenate end-composition fluoresce a dull green. The intensity of the fluorescence in all instances is somewhat less in short-wave than in long-wave radiation.

*Chemistry.* The available analyses of saléeite and novacekite are listed

in Table 2. The saléeite from Shinkolobwe and Portugal represents the pure phosphate compound. The Schneeberg material of analysis 4 is an arsenatian variety of saléeite with P:As=1:0.22; the material of analysis 5 is a phosphatian variety of novacekite with P:As=1:1.01. A series involving mutual substitution of As and P in the formula  $Mg(UO_2)_2(P,AsO_4)_2 \cdot nH_2O$  thus extends from the pure phosphate end up to at least P:As=1:1. While material with larger amounts of arsenate has not been analyzed, qualitative tests show the existence in nature of the essentially pure arsenate end-member and the series probably is

TABLE 2. CHEMICAL ANALYSES OF SALÉEITE AND NOVACEKITE

	1.	2.	3.	4.	5.	6.
CuO					1.73	
PbO			0.21			
MgO	4.40	5.01	4.04	4.31	3.41	4.01
Al <sub>2</sub> O <sub>3</sub>			0.37			
UO <sub>3</sub>	62.41	64.07	63.05	60.32	59.74	56.96
P <sub>2</sub> O <sub>5</sub>	15.50	14.44	14.97	11.98	6.87	
As <sub>2</sub> O <sub>5</sub>			nil	4.50	11.23	22.88
H <sub>2</sub> O	17.69	16.48	17.42	[18.89]	[17.02]	16.15
Total	100.00	100.00	100.06	[100.00]	[100.00]	100.00
G		<3.3		3.27	3.3	3.6

1.  $Mg(UO_2)_2(PO_4)_2 \cdot 9H_2O$ . Theoretical composition.
2. Saléeite. Shinkolobwe, Belgian Congo. Mollet analysis of original material cited by Thoreau and Vaes (1932). Recalculated to 100 after deducting 2.79 per cent insoluble.
3. Saléeite. Sabugal, Portugal. H. J. Hallowell analysis, 1949.
4. Arsenatian saléeite. Schneeberg, Saxony. Gonyer analysis cited by Mrose (1950).
5. Phosphatian novacekite. Schneeberg, Saxony. Gonyer analysis, 1949. Recalculated to 100 per cent after deduction of insoluble SiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub>.
6.  $Mg(UO_2)_2(AsO_4)_2 \cdot 9H_2O$ . Theoretical composition.

complete. The species name saléeite and novacekite are here applied to the halves of the series with P>As and As>P, respectively, in atomic per cent.

The novacekite of analysis 5 contains some Cu in substitution for Mg, with Cu:Mg=1:3.9, and indicates a series extending toward zeunerite. Qualitative tests on various specimens of uranospinite in the Harvard collection indicates that Mg is sometimes present in significant amounts in substitution for Ca and a partial series at least extends between this species and novacekite.

*Synthesis of Novacekite.* A rather flocculent precipitate found by qualitative test to be magnesium uranyl arsenate was obtained by reac-

tion at room temperature of water solutions of magnesium chloride, uranyl acetate and ammonium acid arsenate in the molar ratio of 1:2:2. The material gave a very diffuse powder pattern and was too fine grained for optical study. The precipitate was then heated at 50° in the mother solution for several weeks. The product gave a definite pattern that was similar to that of meta-autunite and which presumably represents the meta-I hydrate of novacekite. Optical data could not be obtained. Uranospinite is easily obtained in crystals by similar means.

*Occurrence of Uranium Arsenates and Phosphates.* The composition of the secondary uranium minerals formed by the alteration of uraninite in the zone of weathering is influenced by the nature of the primary minerals immediately associated with the uraninite. At Schneeberg, the presence of abundant arsenides of cobalt, nickel, and iron in the veins has resulted in the formation of uranyl arsenates in the oxidized zone. The known arsenates of uranium, zeunerite ( $\text{Cu}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot n\text{H}_2\text{O}$ ), uranospinite ( $\text{Ca}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot n\text{H}_2\text{O}$ ), novacekite ( $\text{Mg}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot n\text{H}_2\text{O}$ ), troegerite ( $\text{H}_2(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot n\text{H}_2\text{O}$ ), and walpurgite ( $\text{Bi}_4(\text{UO}_2)(\text{AsO}_4)_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ ) all were first described from Schneeberg and the three last named species are known only from this place. The bismuth content of walpurgite and of the bismuth-uranium oxide uranosphaerite, the latter also known only from Schneeberg, has been derived from the association of native bismuth with the Co-Ni minerals. A number of secondary arsenates containing Ca, Co, Ni, Fe or Bi also occur at Schneeberg, among them erythrite, annabergite, roselite, pharmacosiderite, pharmacolite, agricolite and atelestite. Zeunerite occurs in very minor amounts at Tintic, Utah, where its arsenate content has been derived by the oxidation of enargite. In contrast to the relations at Schneeberg, the uraninite from hydrothermal veins containing sulfides but with little or no arsenides typically affords on oxidation the uranyl sulfates uranopilite, zippeite, johannite ( $\text{Cu}(\text{UO}_2)_2(\text{SO}_4)_2(\text{OH})_2 \cdot 6\text{H}_2\text{O}$ ), and also torbernite ( $\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ ), the copper content of the two latter minerals coming from sulfides such as chalcopyrite. The uraninite of pegmatites and of fluorite deposits of the Wölsendorf type generally affords uranyl phosphates and silicates, such as autunite, phosphuranylite, uranophane, and beta-uranophane, in which the principal divalent cation is calcium. In these deposits, and in the uraninite-quartz-fluorite veins such as those of Portugal, sulfides are lacking and the cations, usually calcium but sometimes magnesium and aluminum, the latter appearing in sabugalite ( $\text{HAl}(\text{UO}_2)_4(\text{PO}_4)_4 \cdot 16\text{H}_2\text{O}$ ), are probably derived locally in the zone of weathering from the alteration of the wall-rock or from fluorite or apatite. Torbernite does not occur in significant amounts in deposits of the latter type due to the general absence of primary copper-containing sul-

fides. Lead, however, sometimes is present, as in parsonsite, kasolite, and dewindtite, but probably is of radiogenic origin. The phosphate content of the secondary uranium minerals in these occurrences and probably also in the sulfide veins apparently is derived from associated apatite. This certainly is true of the pegmatite occurrences. The origin of the abundant phosphate in the oxidized uranium veins of the Belgian Congo is not clear, but probably has come from the dolomitic limestones of the country rock via meteoric solutions. In the absence of both phosphate and arsenate, the uraninite of sulfide veins alters chiefly to johannite, as in Gilpin County, Colorado, and to other sulfates, but these minerals are only sparsely developed due to their relatively high solubility. The uranyl carbonates, including schroekingite, bayleyite, andersonite, and swartzite, also are relatively soluble compounds and typically develop as efflorescences in the upper part of the oxidized zone. Oxidation at Great Bear Lake is only superficial and the principal secondary minerals are oxides of uranium and of uranium and lead with very minor amounts of zippeite, uranopilite, and traces of johannite. Uranium arsenates have not been reported here, although the primary minerals include arsenides of cobalt, nickel, and iron, but annabergite occurs in small amounts. The hydrated hexavalent uranium oxides in general represent the first stage of alteration of uraninite and antedate the formation of the secondary phosphates, arsenates, and silicates.

*Manuscript received January 26, 1951*