STUDIES OF URANIUM MINERALS (VIII): SABUGALITE, AN ALUMINUM-AUTUNITE*

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ABSTRACT

Sabugalite is a new member of the autunite group with the composition $HAl(UO_2)_4(PO_4)_4 \cdot 16H_2O$. Analyses are cited of material from the Mina da Quarta Seira, Sabugal, Beira province, and from Kariz, Minho province, in Portugal; a third occurrence is noted from Bendada in Beira province. Sabugalite is a secondary mineral found associated with meta-autunite, saléeite and phosphuranylite. It occurs as crusts of yellow platy crystals with perfect cleavage {001}. Hardness $2\frac{1}{2}$; gravity 3.20. Air dried sabugalite optically has an anomalous biaxial negative character with $nX=1.564$–1.565 (colorless), $nY=1.581$–1.583 (yellow), $nZ=1.582$–1.584 (yellow), and $2V=0°$ to moderate. *X*-ray study indicates a tetragonal cell with $a_0=6.96$ Å, $c_0=19.3$; $a_0:c_0=1:2.773$; cell contents $HAl(UO_2)_4(PO_4)_4 \cdot 16H_2O$. Sabugalite is isostructural with fully-hydrated autunite, $Ca_2(UO_2)_4(PO_4)_4 \cdot 16H_2O$, with $Al''' + H' = 2Ca''$. Sabugalite breaks down between 68° and 101° to a new phase isostructural with the artificial meta-II hydrate of autunite and does not form an intermediate meta-I hydrate with halved cell contents as does fully-hydrated autunite. The water content of the fully-hydrated and meta-II hydrates of sabugalite varies zeolitically with accompanying variation in the indices of refraction.

The new uranium mineral here described under the name sabugalite has the composition $HAl(UO_2)_4(PO_4)_4 \cdot 16H_2O$ and is isostructural with fully-hydrated autunite, $Ca_2(UO_2)_4(PO_4)_4 \cdot 16H_2O$. The mineral has been recognized on specimens from three different localities in a suite of uranium minerals from Portugal acquired in 1932 with the collection of the Portuguese mineralogist A. d'O. Bello. Sabugalite very closely resembles autunite and like that species is of secondary origin. A specimen from the Mina da Quarta Seira, Sabugal, Beira province, shows a thick crust of sabugalite on a brecciated mass of milky quartz and feldspar. Other specimens from this place contain meta-autunite, saléeite and phosphuranylite as crusts upon deeply altered granitic or pegmatitic rock. Material from Kariz in Minho province shows brecciated milky quartz and kaolinized feldspar apparently of pegmatitic origin that is thickly coated with sabugalite admixed with and underlain by meta-autunite. A specimen from Bendada, Beira province, shows a thin coating of sabugalite intergrown with meta-autunite and perhaps also saléeite on a slab of quartzose and limonitic vein material.

Sabugalite has a bright yellow to lemon yellow color. It typically occurs as densely aggregated crusts of very thin platy crystals up to about one millimeter on edge. The mineral is probably tetragonal in crystallization. Individual plates are square or lath-like in shape and are bounded laterally by very narrow and indistinct faces of {100} and {*h0l*}. A few

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relatively perfect crystals under the microscope were observed to have their corners truncated at 45° by tiny faces of {*hkl*}. The plane of flattening, {001}, is uneven or warped and subparallel growths joined on this surface are very common. Morphological measurements could not be obtained. The plates are somewhat flexible and have a perfect cleavage parallel to {001}. The hardness is $2\frac{1}{2}$ and the specific gravity, measured by suspension in heavy liquids, is approximately 3.20.

Optical Properties and Fluorescence. Samples of sabugalite air dried at room temperature are biaxial negative with 2V somewhat variable but usually moderately large. Some flakes were noted, especially in the material from Kariz, to be sensibly uniaxial or to have an optic angle of only a few degrees. The departure from uniaxiality in this probably tetragonal species is believed due, as in other members of the autunite group,[1] to variation in the content of zeolitic water within the limits of stability of the phase. The plates ordinarily extinguish uniformly. A few plates showed a mottled extinction but none were observed to exhibit the sectoral structure with varying optical orientation therein such as has been described[1] in other members of the autunite group. The X (or E) vibration direction is perpendicular to the flattening. It is curious to find in lath-like {001} plates that Z always is parallel to the elongation. This is true not only of sabugalite but also of zeunerite, saléeite and autunite. The optical data for natural sabugalite are listed in Table 1. Optical data on artificial dehydration products of sabugalite are cited beyond in Table 6.

TABLE 1. OPTICAL DATA FOR AIR DRIED SABUGALITE

	Mina da Quarta Seira	Kariz	Bendada	Pleochroism
*n*X or *n*E	1.564	1.564	1.565	Colorless
n*Y*	1.582	1.581–1.583	1.581–1.582	Pale yellow
n*Z* or *n*O	1.584	1.583	1.582	Pale yellow
2V	moderate	small to moderate	0° to moderate	

Air dried sabugalite fluoresces a bright lemon yellow in both long-wave and short-wave ultraviolet radiation although somewhat more intensely in the long wave-lengths. Slightly dehydrated material obtained by heating fresh sabugalite to temperatures of 44° or 68° also fluoresces lemon-yellow but somewhat less intensely, and the meta-II hydrate obtained

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[1] Beintema, J., *Rec. Trav. Chim. Pays-Gas*, **57,** 155 (1938); Hallimond, A. F., *Minerol. Mag.*, **17,** 326 (1916); **19,** 43 (1920); Rinne, J. F., *Cbl. Min.*, 618, 709 **(1901).**

by heating to 135° is very weakly fluorescent; in both cases the fluorescence is slightly stronger in long-wave than in short-wave radiation. This variation in intensity of fluorescence with water content also is shown by the analogous hydrates of zeunerite[2] and autunite.

X-Ray Crystallography. X-ray powder photographs of sabugalite are very similar to those of fully-hydrated saléeite, $Mg_2(UO_2)_4(PO_4)_4 \cdot 16H_2O$, and resemble but are distinct from those of both fully-hydrated autunite and meta-autunite. The photographs yielded by the substance unfortunately are of poor quality. *X*-ray rotation and Weissenberg films taken on cleavage flakes also were rather unsatisfactory. Usable photographs could not be obtained about [001] due to the very thin and warped nature of the crystals. Rotation photographs taken about the horizontal axes showed much continuous streaking along the layer-lines, together with crystal disorientation effects due to subparallel growth, and these features were repeated on the Weissenberg resolutions. The single-crystal photographs were indexed in terms of a tetragonal cell with $a_0 = 6.96$ Å and $c_0 = 19.3$. The powder photograph also can be indexed in terms of this cell (Table 2), but with some uncertainty due partly to diffuseness of the lines. The principal difficulty is in the interpretation of the faint line with $d = 5.59$. This line approximates to (102) in the cell stated, but then is the only reflection present with $h+k+l$ odd and is contrary to the extinction requirements in the space group of fully-hydrated autunite, $I4/mmm$, with which substance sabugalite is presumed to be isostruc-

TABLE 2. X-RAY POWDER SPACING DATA FOR SABUGALITE

Indexing for cell with $a_0 = 6.96$ Å, $c_0 = 19.3$, obtained from single-crystal measurements, Cu/Ni

hkl	*d*(calc.)	*d*(meas.)	*I*	*hkl*	*d*(calc.)	*d*(meas.)	*I*
002	9.650	9.69	10	220	2.461	2.452	2
101	6.548	6.56	1	222	2.384	2.389	2
102	5.644	5.59	1	303	2.183	2.188	6
004	4.825	4.86	9	310	2.201		
112	4.384	4.39	4	323	1.792	1.792	1
200	3.480	3.47	8	400	1.740	1.726	1
114	3.345	3.36	1	330	1.640	1.641	½
006	3.216	3.22	½	404	1.637		
211	3.072	3.06	½	420	1.556	1.552	1
204	2.822	2.818	1	510	1.364	1.364	1

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[2] Frondel, J. W., *Am. Mineral.*, **36**, 249–255 (1951).

trual. It also may prove that sabugalite is actually orthorhombic and only pseudo-tetragonal. The pattern can not be completely indexed in terms of a cell with $a_0 = 6.96$ Å and c_0 halved to 9.65. This point is of some importance since the 19.3 Å period is characteristic of the fully-hydrated phases in the autunite group, while the meta-I hydrates have a cell with an identical a_0 but with c_0 halved. The x-ray data indicates that sabugalite has the structure of the fully-hydrated phase. A comparison of the unit cell dimensions of sabugalite and some other members of the autunite group is given in Table 3.

TABLE 3. UNIT CELL DIMENSIONS OF SOME MINERALS OF THE AUTUNITE GROUP

	Sabugalite	Saléeite[a]	Autunite[b]
Space group		$I4/mmm$	$I4/mmm$
Cell contents	$HAl(UO_2)_4(PO_4)_4 \cdot 16H_2O$	$Mg_2(UO_2)_4(PO_4)_4 \cdot 16H_2O$	$Ca_2(UO_2)_4(PO_4)_4 \cdot 16H_2O$
a_0	6.96Å	7.01	7.00
c_0	19.3	19.84	20.67
$a_0:c_0$	1:2.773	1:2.830	1:2.952

(*a*) By powder method on analyzed material from Mina da Quarta Seira, Sabugal, Portugal.

(*b*) Beintema (1937).

Chemistry. Complete chemical analyses were made of the sabugalite from the Mina da Quarta Seira in Beira province and from Kariz in Minho province. These are cited in Table 4. The material from Mina da Quarta Seira was treated in heavy liquids, which removed traces of quartz and meta-autunite, and the analysis sample was entirely homogeneous under the microscope. Meta-autunite is quite easily distinguished because of its higher indices of refraction. The material from Kariz was rather intimately intergrown with meta-autunite and this proved very difficult to remove from the sample because its gravity in part overlapped that of the sabugalite. The first sample of this material prepared by treatment in heavy liquids afforded on partial analysis CaO 0.84, P_2O_5 13.91, As_2O_5 2.71. A second sample, ground more finely and fractionated closely in the heavy liquids, gave the analytical results cited in Table 4. This sample was estimated optically to contain about 5 per cent of meta-autunite, and the amount of CaO found in the analysis roughly corresponds to this figure. The Ca hence has been disregarded in the calculation of the formula. The material from Bendada in Beira

TABLE 4. ANALYSES OF SABUGALITE

Analysis 1: Mina da Quarta Seira, Beira.

Weight per cent		Molecular quotient	Atomic quotient		Experimental cell contents (×1802/100)	Theoretical cell contents	Theoretical weight per cent	
Al_2O_3	2.65	.0260	Al	.052	0.94	1	Al_2O_3	2.87
UO_3	65.22	.2280	U	.228	4.11	4	UO_3	64.41
P_2O_3	16.08	.1133	P	.226	4.08	4	P_2O_5	15.99
H_2O	15.93	.8842	H	1.768	31.9	33	H_2O	16.73
Total	99.88		O	2.213	39.9	40	Total	100.00

Analysis 2: Kariz, Minho.

Weight per cent		Molecular quotient	Atomic quotient		Experimental cell contents (×1802/100)	Theoretical cell contents	Theoretical weight per cent	
CaO	0.36							
Al_2O_3	3.20	.0314	Al	.063	1.13	1		
UO_3	65.01	.2273	U	.227	4.08	4		
P_2O_5	14.02	.0987	P	.197	$\left.\begin{matrix}3.55\\0.42\end{matrix}\right\}3.97$	4		
As_2O_5	2.70	.0117	As	.023				
H_2O	[14.71]							
Total	[100.00]							

1. Sabugalite. Mina da Quarta Seira, Sabugal, Beira province, Portugal. Analysis by F. A. Gonyer, 1950. Following elements sought and found absent: Ca, Mg, Ba, Cu, Fe, Mn, As. The theoretical weight per cent cited corresponds to the formula $HAl(UO_2)_4(PO_4)_4 \cdot 16H_2O$.
2. Sabugalite. Kariz, Minho province, Portugal. Analysis by F. A. Gonyer, 1950. With MgO trace. CaO due to admixed meta-autunite. A direct water determination on material probably containing a slightly larger amount of meta-autunite gave 16.78 per cent.

province was a mixture of at least three components of about the same specific gravity, including meta-autunite and apparently also saléeite, and a reasonably pure analysis sample could not be obtained. Chemical tests of this material proved the presence of Ca, Mg and Al in addition to U and P.

The unit cell contents of the two analyzed samples, calculated directly from the measured molecular weight of the cell, 1802, indicates that the formula of the mineral is

$$HAl(UO_2)_4(PO_4)_4 \cdot 16H_2O.$$

A small amount of As substitutes for P in the material from Kariz, with As:P = 1.17:10. The average of the two analyses is somewhat closer to the formula than either analysis alone. The agreement in any case is satisfactory, especially in view of the isostructural relation to autunite, $Ca_2(UO_2)_4(PO_4)_4 \cdot 16H_2O$, indicated by the x-ray work. This relation may be discussed in some detail in view of the interesting composition of the substance and of the question of the existence of a meta-I hydrate of sabugalite analogous to meta-autunite.

As shown by Beintema,[1] the crystal structure of autunite consists of (PO_4) tetrahedra and deformed (UO_6) octahedra that are linked by the sharing of corners into two-dimensional sheets on {001}. The U-O coordination group is deformed in such way that two oxygen atoms are more closely associated with the U^6 ion, giving rise to the so-called uranyl ion $(UO_2)^2$. The water molecules and the Ca ions (or Mg, Ba, Cu, Fe″ in other members of the group) occupy relatively large cavities between the layers. The unit cell contents are $Ca_2(UO_2)_4(PO_4)_4 \cdot 16\text{-}20H_2O$. The Ca ions occupy the two-fold positions in (a) of I4/mmm. When the water content is reduced below about $16H_2O$ by heating or desiccation, the structure breaks down to that of a new phase, meta-autunite-I. On further dehydration, the meta-I phase breaks down into a still lower hydrate, meta-autunite-II, the structure of which is unknown. The principal difference between the structure of the meta-I phase and that of fully-hydrated autunite is in the way in which the $(UO_6)(PO_4)$ layers are stacked. During the transformation to the meta-I phase, the individually unchanged layers are moved over a distance $[\frac{1}{2}\frac{1}{2}0]$ with respect to each other. The geometry of this change maintains the a-axis period, but halves the c-axis period, the initial body-centered cell transforming into two primitive cells of the meta-I phase. The symmetry remains tetragonal. The new cell contents are then $Ca(UO_2)_2(PO_4)_2 \cdot 6H_2O$. The new space-group $P4/nmm$, however, affords only a two-fold position for the single Ca ion and this ion is believed to be distributed statistically over half of the available positions. The ready base-exchange of the inter-layer cations and the zeolitic dehydration phenomena within the limits of stability of the phase are both consequences of the relatively open layer-type structure. In the meta-I phase, the Ca can be replaced by direct crystallization or by base-exchange by twice the number of monovalent ions such as Na, K, NH_4 or H. The monovalent cations then wholly occupy the two-fold positions. The latter ions can not be obtained in crystals of the fully-hydrated structure-type, however, because space is lacking for a sufficient number to be introduced to effect valence compensation with the $(UO_6)(PO_4)$ layers. Treatment of fully-hydrated autunite in strong solutions of base-exchangeable monovalent cations results in a conversion to the meta-I hydrate.

In the present instance, sabugalite appears to belong to the fully-hydrated phase rather than the meta-I phase. The calculated unit cell contents conform to the autunite-type but with one trivalent Al ion in place of the two divalent Ca ions of autunite. It is presumed that the Al ion is distributed statistically over the two-fold position taken by the Ca in autunite, and that valence compensation is effected by the concomitant presence of one H′ ion, with $Al''' + H' = 2Ca''$. If this interpretation is correct, it appears that sabugalite should not form a meta-I hydrate isostructural with meta-autunite since the halving of the cell volume thus brought about would admit only halved Al‴ and H′ ions. Dehydration data for sabugalite described beyond indicate that this substance does not form a meta-I hydrate but breaks down directly from the fully hydrated phase to the meta-II phase.

Dehydration Data. Samples of fresh, air-dried sabugalite were heated to essentially constant weight at temperatures of 44°, 68°, 101°, 117°, 135° and 165° C. No change in the *x*-ray powder pattern was found in the samples heated at 44° and 68°, although there was a small loss of water and an increase in the indices of refraction. The samples heated at 135° and 165°, however, afforded an entirely new pattern which proved on direct comparison to be virtually identical with that of the meta-II hydrate of autunite. The spacing data for this pattern are listed in Table 5. The samples heated at 101° and 117° proved to represent mixtures of the meta-II phase and still undecomposed remnants of the fully-hydrated phase. The temperature of breakdown of the fully-hydrated to the meta-II phases thus is between 68° and 101°. The pattern of the fully hydrated phase after heating at 44° and 68° was identical with that of the unheated material. The pattern afforded by the still undecomposed remnants of this phase in samples heated at 101° and 117° showed a marked diffuseness of the line at $d = 4.86$, although the few other lines remaining of the pattern were relatively sharp, and there was a progressive decrease in the spacing of the innermost, most intense line of the

TABLE 5. *X*-RAY POWDER SPACING DATA FOR THE META-II HYDRATE OF SABUGALITE. Cu/Ni (in Å). Heated at 135°.

d(meas.)	*I*	*d*(meas.)	*I*
8.51	10	2.21	1
5.5–4.3	diffuse region	2.17	1
3.51	7	2.02	2
3.23	5	1.91	1
2.99	6	1.87	1
2.84	2	1.74	1

pattern. At room temperature, 44° and 68° this line of the fully-hydrated phase had d essentially constant at 9.70; at 101° $d=9.12$, 117° $d=8.63$, 135° $d=8.51$, 165° $d=8.16$. No pairing of lines was observed in this region that could be attributed to admixture, and the (002) reflection of the sabugalite apparently passes continuously into the meta-II pattern. The two phases may be structurally related, with their (001) layers parallel, and the spacings of (011) in the meta-II phase vary with the content of zeolitic water (?) held between the layers.

Data on the water content and optical properties of the heated samples are summarized in Table 6. Optically, none of the samples were

TABLE 6. DEHYDRATION DATA FOR SABUGALITE (MINA DA QUARTA SEIRA)

Sample	Phase	Optical Properties				Per cent loss of original H_2O
		nX	nY	nZ	2V	
Unheated. Airdried.	Fully-hydrated	1.564	1.582	1.584	mod.	0
Heated at 44°	Fully-heated		1.591	1.594	mod.	3.4
Heated at 68°	Fully-hydrated	1.575	1.596	1.597	small	20
Heated at 101°	Mixture					57
Heated at 117°	Mixture					63
Heated at 135°	Meta-II	1.592	1.604	1.618	large	82
		to	to	to		
Heated at 165°	Meta-II	1.596	1.608	1.623	large	91
Cooled from 135° and		Part:	1.577 <	1.59	large	
			to	to		
held over water.	Meta-II	Mostly:	1.581	1.587	large	
			to	to		
		Part:	> 1.59 ~	1.602	large	

entirely homogeneous, including those which gave x-ray patterns indicating the presence of one phase only. The variation is believed to be due to minor differences in zeolitic water content between different grains in material that had not been heated sufficiently long to reach equilibrium. The optical data given represent the values afforded by the great bulk of the sample in each case. The indices of the fully-hydrated phase are seen to increase with decreasing content of zeolitic water within the limit of stability of the phase. When samples of this phase heated at 44° and 68° are held in a moist atmosphere at room temperature the indices decrease to practically the original values with no accompanying change in the x-ray pattern. Unheated sabugalite when placed in water at room temperature decreases very slightly in indices and the x-ray pattern does not change. Heated samples of the meta-II phase when placed in a moist atmosphere at room temperature decrease markedly in indices (Table 6) but the *x*-ray pattern remains that of the meta-II phase. The breakdown between the fully-hydrated and meta-II phases thus is not reversible. The samples heated at 135° and 165° showed a considerable variation in indices, with most of the grains in the range cited.

The dehydration phenomena of sabugalite are similar to those of autunite except that a meta-I hydrate is not found in sabugalite. Fully-hydrated autunite breaks down into the meta-I hydrate near room temperature, depending on the humidity, and the change is reversible. The meta-I hydrate in turn breaks down irreversibly into the meta-II hydrate at about 80°. Fully-hydrated zeunerite behaves similarly.[2] The indices of refraction of the fully-hydrated, meta-I and meta-II phases of autunite and zeunerite all vary with the content of zeolitic water within the stability range of the phase itself. The fact that samples of sabugalite do not change in *x*-ray pattern when immersed in water at room temperature indicates that the phase represented is already the fully-hydrated one as indicated by the unit cell dimensions. The observation is not critical, however, because different samples of the meta-I phase of both torbernite and zeunerite rehydrate to the fully-hydrated phase with markedly different ease and some samples apparently do not reconvert at all.

The dehydration data of Beintema[1] indicates that the fully hydrated phase of autunite, $Ca_2(UO_2)_4(PO_4)_4 \cdot nH_2O$, is stable with $n > 10\frac{1}{2}H_2O$, the meta-I phase with n from $2\frac{1}{2}$ to $6\frac{1}{2}H_2O$ and the meta-II phase with n from 0 to about $6H_2O$. The data for sabugalite are comparable.

Synthesis. Efforts to synthesize sabugalite have been unsuccessful. In one set of experiments, solutions of uranyl nitrate and aluminum chloride in molar ratios up to U:Al = 1:2.5 were precipitated by the calculated amount of H_3PO_4. These gave products identical with hydrogen-autunite, $H_2(UO)_2(PO_4)_2 \cdot 8H_2O$. It may be noted that hydrogen-autunite also precipitates in place of autunite from solutions containing Ca when the acidity is high. Efforts to obtain sabugalite by reaction of a saturated solution of aluminum acetate in acetic acid with uranyl acetate and ammonium hydrogen phosphate gave negative results, as did an effort to base-exchange washed hydrogen-autunite with a 1N water solution of aluminum chloride.

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