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GEOCHEMISTRY

Uramarsite $(NH_4, H_3O)_2(UO_2)_2(AsO_4,PO_4)_2 \cdot 6H_2O$: A New Mineral of the Metaautunite Group[1]

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New mineral uramarsite, a hydrous ammonium uranylarsenate, was found in the supergene zone of the Bota-Burum molybdenite–pitchblende deposit (southern Kazakhstan), which is made up of carbonatized felsite porphyry and tuff breccia. In the supergene zone, the uranium mineralization is represented by arsenate uranite; the molybdenum mineralization, by U-bearing powellite and less abundant wulfenite. According to Kopchenova and Skvortsova [1], the close association of pitchblende with fine-grained molybdenite, arsenopyrite, and pyrite in primary ores defined the specifics of supergene mineralization. At the initial stage of supergene zone formation, arsenates of Al and Fe (mansfieldite and pharmacosiderite) were formed under acid conditions in the arsenopyrite-rich zones. Uranites (uranospinite, sodium uranospinite, metazeunerite, chistyakovaite, and uramarsite) were formed at the last stage. Researchers of the process of mineralization at the Bota-Burum deposit noted that the oxidation of pitchblende–sulfide mineralization is confined to the highly fractured zones in the hydrothermally altered felsic rocks [1]. The formation of ammonium uranite (uramarsite) is just related to these processes. The name of the new mineral reflects its chemical composition.

Although both uramarsite and chistyakovaite are crystallized after the same rock, they do not form solid solutions. Instead, they form a block-shaped pseudocrystal with sharp orthogonal boundaries between two phases.

Uramarsite forms imperfect platy crystallites (up to 2 mm in size), films, and less common flattened square crystals (up to 0.1 mm in size) with the major (001) and less common (010) forms. The mineral has a light green color and vitreous luster (dull in films). The UV luminescence is green (typical of uranyl ion). It is brittle, with perfect cleavage on {001} (less perfect on {010}) and stepped fracture. The hardness in the Mohs scale is 2.5.

The high porosity of the mineral hampers the determination of its density. The density measured by the sink-float method in heavy liquids depends on the particle size and systematically increases with decreasing particle size owing to opening of internal pores from 3.04 g/cm^3 for the largest fragments to 3.22 g/cm^3 for small particles. Based on the empirical formula and unit cell volume, the density is estimated at D_{calc} = 3.286 g/cm^3. Therefore, the limit value D_{meas} = 3.22 g/cm^3 seems to be underestimated. However, further decrease of particle size is impossible due to the influence of convection and surface tension.

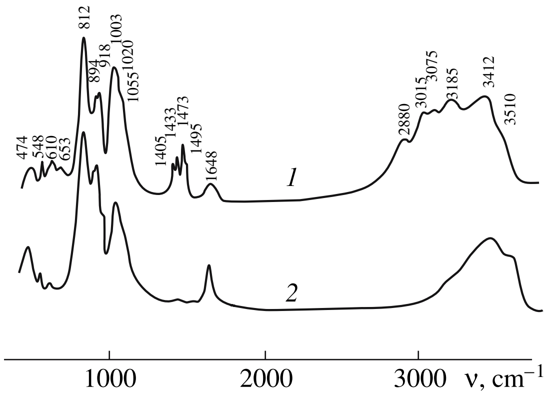

Fig. 1. IR spectra of uramarsite (*1*). The spectrum of metauranospinite (*2*) is shown for comparison.

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[1] New mineral uramarsite and its name were accepted by the Commission on New Minerals and Mineral Names of the All-Russia Mineralogical Society and approved by the Commission on New Minerals and Mineral Names of International Mineralogical Association on November 4, 2005 (IMA No. 2005-043).

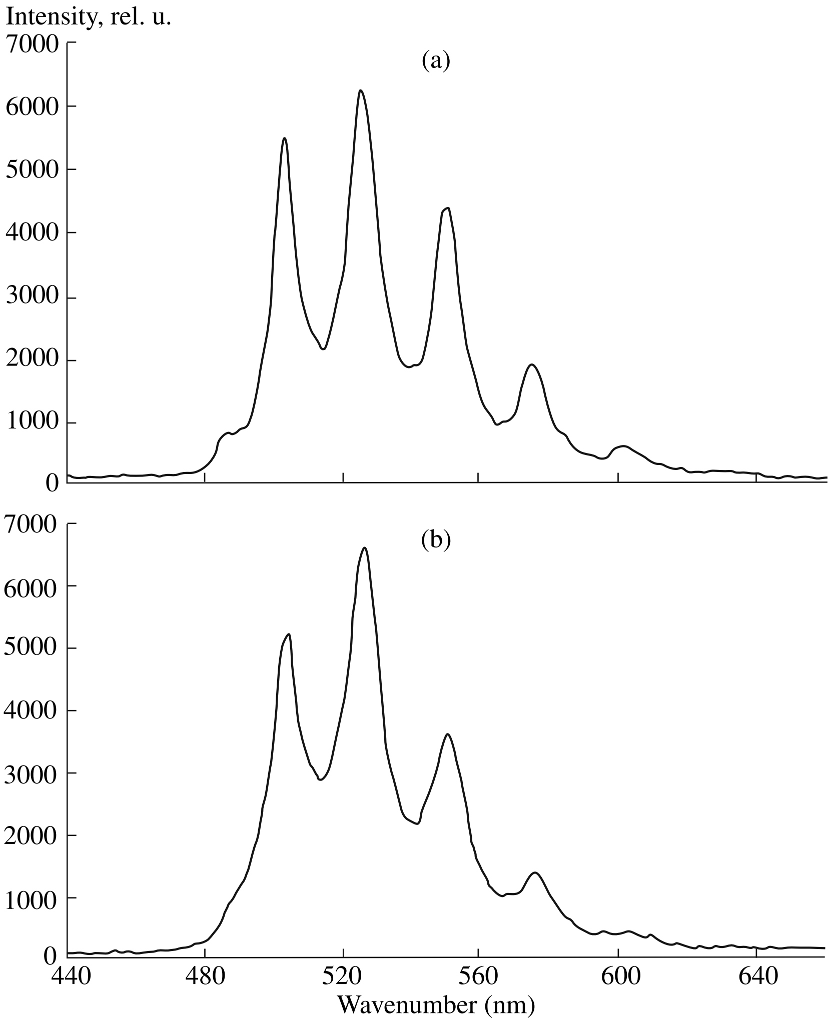

Fig. 2. Spectra of UV laser luminescence of uramarsite (a). The spectrum of chistyakovaite (b) is shown for comparison.

In immersion oils, the mineral forms slightly elongated orthogonal colorless plates. The uramarsite is optically biaxial and negative: $\alpha = 1.562(2)$; $\beta \approx \gamma = 1.593(2)$; $2V < 5°$. Dispersion is absent. The optical orientation is as follows: $X = c$, $Y \approx b$. Extinction along the long edge is straight.

As is evident from Fig. 1, the IR absorption spectra recorded using a SPECORD 75IR spectrophotometer have the following bands, cm^{-1} (*s* and *w* designate the strong and weak bands, respectively; *sh*, the shoulder): 3510 sh, 3412 s (stretching vibrations of the water molecules); 3185 s, 3075 s, 3015 s (stretching vibrations of ammonium ion); 2880 (stretching vibrations of probably oxonium); 1648 (bending vibrations of water molecules); 1495sh, 1473, 1433, 1405 (bending vibrations of ammonium ion); 1055 sh, 1020 sh, 1003 s (stretching vibrations of phosphate anions); 935 sh, 918 s, 894 s (stretching vibrations of uranyl ion); 812 s (stretching vibrations of arsenate anions); and 653 w, 610, 548, 474 (bending vibrations of anion groups). The absence of bands in the 1800–2600 cm^{-1} range indicates that the mineral does not contain As–OH and P–OH acid groups. The splitting of the band ascribed to bending vibrations into four components unambiguously indicates the different positions of these ions in the uramarsite structure. The presence of oxonium in the mineral is confirmed by the increased width of the H–O–H band of bending vibrations as compared to those in other minerals of the metaautunite group. Ions UO_2^{2+} occupy at least three nonequivalent local sites, which correspond to three bands in the region 890–940 cm^{-1}. The splitting of the band of antisymmetric stretching vibrations of UO_2^{2+} ions can be related with hydrogen bonding to different donors (NH_4^+, H_2O, and H_3O^+).

The laser luminescence spectrum of uramarsite in the visible region is distinguished from the typical uranite spectra by the presence of an additional weak band with a maximum at $\lambda = 485$ nm (Fig. 2), which confirms the existence of different states of UO_2^{2+} in this mineral.

Table 1. Diffractogram of uramarsite

I	d_{meas}, Å	d_{calc}, Å	*hkl*	*I*	d_{meas}, Å	d_{calc}, Å	*hkl*
100	9.27	9.15	001	1	1.866	1.864	124
3	5.69	5.65	011	8	1.823	1.823	133
0.5	5.07	5.08	110	7	1.713	1.713	141
25	4.58	4.575	002	1	1.635	1.631	025
20	3.86	3.860	012	2	1.616	1.613	134
3	3.59	3.595	020	2	1.600	1.608	240
5	3.33	3.346	021	2.5	1.514	1.514	143
1	3.03	3.034	121	4	1.483	1.485 1.481	225 333
13	2.80	2.808	013	4	1.458		
4	2.60	2.615	113	2	1.415		
20	2.28	2.287 2.274	004 130	0.5	1.395		
4	2.18	2.180	014	4	1.277		
6	2.076	2.086	114	2	1.259		

No gas is released during dissolution of uramarsite in hydrochloric acid.

The chemical composition of the mineral was studied by the SAED method. A defocused microprobe beam was used to avoid sample destruction. Concentrations of U, As, P, and Na were measured in eight points using EDS LINK under the following conditions: $V = 20$ kV, $I = 5$nA, and beam size 50 μm. The microprobe was calibrated using the following standards: UO_2 for U, InAs for As, GaP for P, and albite for Na. The control determinations were carried out using EDS LINK AN 10000 under milder conditions: $V = 15.7$ kV, $I = 1.0$–1.5 nA.

The NH_4 content was determined by the ionometric method following the technique described in [2]. The ammonia was extracted from solution and measured using an ammonium-selective electrode in a gas-sensitive cell. The average contents of components are as follows (wt %, standard deviation is given in parentheses): Na_2O 0.3 (±0.2), UO_3 61.8 (±0.5), As_2O_5 15.0 (±1.2), P_2O_5 5.9 (±0.5), $(NH_4)_2O$ 3.2; total 86.2%. K, Ca, Sr, Ba, Pb, Zn, Cu, Mg, Fe, Si, S, and Cl were not found. The H_2O content (based on difference) is 13.8%.

The empirical formula of uramarsite calculated for $(AsO_4, PO_4)_2$ with consideration of valence balance and IR data (see above) is as follows ($Z = 1$):

$$[(NH_4)_{1.15}(H_3O)_{0.72}Na_{0.09}]_{\Sigma 1.96}(UO_2)_{2.02}[(AsO_4)_{1.22}(PO_4)_{0.78}]_{\Sigma 2.00} \cdot 6.1H_2O.$$

Taking into account the absence of characteristic bands of the As–OH and P–OH groups in the IR spectrum coupled with the presence of H_3O ion bands at 2880 cm^{-1}, the "excess" hydrogen in the empirical formula is assigned to oxonium groups. The simplified formula of uramarsite is $(NH_4, H_3O)_2(UO_2)_2(AsO_4, PO_4)_2 \cdot 6H_2O$. The end ammonium arsenate member $(NH_4)_2(UO_2)_2(AsO_4)_2 \cdot 6H_2O$ has the following composition (wt %): $(NH_4)_2O$ 5.41, UO_3 59.46, As_2O_5 23.89, H_2O 11.24, total 100.00%.

The correctness of the obtained chemical composition, refractive indices, and mineral density is supported by a good compatibility index from the Gladstone–Dale relationship ($1 - K_p/K_c = 0.000$ for D_{meas} and 0.020 for D_{calc}).

The study of monocrystal uramarsite was not carried out because of the absence of appropriate crystals. Pseudomonocrystal aggregates represent a combination of randomly oriented blocks.

Table 1 presents the powder XRD pattern (diffractometer DRON-3, CuK_α radiation, silica as standard). In spite of the absence of perfect monocrystals suitable for study of the crystalline structure, uramarsite yields a distinct powder diffraction pattern with a resolved (α_1–α_2) doublet at high reflection angles, indicating an ordered structure but small size of coherent scattering domains. Based on the XRD pattern, uramarsite is a tetragonal mineral with the following unit cell parameters: $a = 7.19(1)$ Å, $c = 9.15(2)$ Å, and $V = 473(2)$ Å^3 ($Z = 1$). The systematic absence of reflections with odd $h + k$ at $l = 0$ attests to space group $P4/nmm$.

As was mentioned above, uramarsite is weakly biaxial. At the same time, X-ray data do not indicate lowering of symmetry that could be responsible for

Table 2. Comparative data on uramarsite, uramphite, and their synthetic analogues

Characteristics	Uramarsite (present paper)	Synthetic uranylarsenate of ammonium [3]	Uramphite [9]	Synthetic ammonium uranylphosphate [10]
Simplified formula	$(NH_4,H_3O)_2(UO_2)_2$ $(AsO_4,PO_4)_2 \cdot 6H_2O$	$(NH_4)_2(UO_2)_2$ $(AsO_4)_2 \cdot 6H_2O$	$(NH_4)_2(UO_2)_2$ $(PO_4)_2 \cdot 6H_2O$	$(NH_4)_2(UO_2)_2$ $(PO_4)_2 \cdot 6H_2O$
Symmetry	Tetragonal, *P*4/*nmm*	Tetragonal	Tetragonal	Tetragonal
a, Å	7.19	7.21	No data	7.01
c, Å	9.15	8.85*		9.05
Z	1	1		1
Strong lines in the powder diffraction pattern *d*, Å (*I*, %)	9.27 (100)	9.26 (100)	3.78 (100)	9.02 (100)
	4.58 (25)	5.72 (70)	3.24 (70)	5.49 (70)
	3.86 (20)	4.54 (60)	2.75 (80)	4.33 (70)
	2.80 (13)	3.86 (90)	2.22 (90)	3.80 (100)
	2.28 (20)	3.36 (80)	2.12 (80)	3.52 (70)
	1.823 (8)	2.80 (70)	1.696 (90)	3.26 (90)
		2.28 (70)		2.76 (80)
		2.22 (70)		
Optical parameters:				No data
α or N_e	1.562	1.601	1.564	
β	1.593		1.585	
γ or N_o	1.593	1.611	1.585	
–2V, deg	<5	0	3	
D, g/cm^2	3.286**	3.47**	3.7	3.26

Note: (*) According to (Mrose, 1953), c = 8,85 Å; however, X-ray data on $(NH_4)_2(UO_2)_2(AsO_4)_2 \cdot 6H_2O$ (Mrose, 1953) corresponds to $c \approx 9.1$ Å ($D_{calc} \approx 3.38$ g/cm^3).
(**) Calculated values.

biaxiality. In general, the anomalous optical biaxiality of minerals having high (tetragonal, trigonal, and even cubic) symmetry is a widespread phenomena repeatedly observed even in the structurally studied crystals. In our case, the optical anomaly is presumably related to microtensions produced during dehydration of the highly hydrous protophase. This inference also follows from the microporosity and block structure of the uramarsite crystals, as well as from the fact that transition of uranites from the highly hydrous state into metaphase owing to low-temperature dehydration is a widespread phenomena. Although synthetic ammonium uranites are described as phases with three water molecules, this fact does not rule out the existence of more hydrous analogues, especially given the preliminary air drying of the studied precipitates prior to X-ray investigations.

Uramarsite pertains to the metaautunite group and represents the arsenate analogue of uramphite. In the aforementioned holotype sample of a new mineral, As is partially substituted for P; ammonium, for oxonium ion.

The arsenate analogue of ammonium uranite was repeatedly synthesized. Its crystallochemical formula $(NH_4)(UO_2)(AsO_4) \cdot 3H_2O$ could be classed with a synthetic As-bearing analogue of uramphite. In particular, the synthetic arsenate end member of the uramphite–uramarsite series is described in [3, 4]. Data on synthetic uranylarsenate of ammonium, oxonium, and potassium (with metatorbernite structure), including their solid solutions, as well as consideration for hydrogen bonds and effective ionic radii, suggest the possibility of existence of continuous isomorphic series of these compounds, including those with a general formula $(NH_4)_{1-y}(H_3O)_y(UO_2XO_4) \cdot 3H_2O$, where X = P or As (Ross and Evans, 1964, 1965).

According to [3], synthetic ammonium arsenate uranite has a tetragonal unit cell with a *c* parameter two times greater than that of uramarsite. Similar doubling of the unit cell was detected for synthetic analogues of uramphite [6, 7] and other synthetic uranites with a univalent interlayer cation [8]. At the same time, the powder XRD data on uramarsite do not indicate the doubling of parameter *c*. Structural data on synthetic uranites suggest that the minimum tetragonal unit cell determined from diffractometric data on uramarsite represents a subcell. However, it is important to keep in mind that the doubling of the cell and transition to P4/ncc space group are only suggested by some very weak reflections in the powder pattern. Thus, the problem of the true unit cell of uramarsite remains open until the solution of its crystal structure.

Ammonium minerals are rather widespread in the lithosphere, although they typically do not form large accumulations. There are 42 minerals with NH_4^+ as a species-forming component. However, only one ammonium mineral of uranium (uramphite), the phosphate analogue of uramarsite, has been found thus far [9]. Thus, uramarsite is the second ammonium mineral of U.

The comparison of uramarsite and related phases is shown in Table 2.

The holotype sample of uramarsite is stored at the Fedorovskii All-Russia Research Institute of Mineral Resources (inventory no. 350/59/zel).

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