GEOCHEMISTRY =

Chistyakovaite, A New Mineral Al(UO₂)₂(AsO₄)₂(F,OH) · 6.5H₂O*

N. V. Chukanov¹, G. A. Sidorenko², I. S. Naumova², A. E. Zadov³, and V. I. Kuz'min³

Presented by Academician V. S. Urusov May 19, 2005

Received June 2, 2005

DOI: 10.1134/S1028334X06020310

New mineral, hydrous aluminum uranylarsenate, was found during detailed study of uranium mineral samples taken at the Bota-Burum deposit (southern Kazakhstan) by E.V. Kopchenova in the 1950s and stored at the Mineralogical Museum of the All-Russia Research Institute of Mineral Resources (VIMS). The mineral was termed *chistyakovaite* after the name of N. I. Chistyakova, a senior assistant at the VIMS and well-known specialist in the field of X-ray spectral analysis, who carried out a great number of microprobe analyses of uranium minerals. Chistyakovaite is the second (after arsenoshpathite) aluminum uranylarsenate found in nature.

The Bota-Burum deposit is restricted to the Devonian carbonatized felsite porphyries and their tuff breccias. Primary hydrothermal mineralization in this deposit is mainly represented by nasturan and sulfides with abundant arsenopyrite. Oxidation of arsenopyrite in the supergene zone produced a wide range of arsenates: sodium uranospinite, scorodite, mansfieldite, metazeunerite, trögerite, arseniosiderite, and others [1, 2].

Chistyakovaite forms imperfect, strongly flattened along $\{100\}$, yellow crystals (up to 2 mm across) and their intergrowths. The mineral is brittle, with perfect $\{100\}$ and imperfect $\{001\}$ cleavage, and stepped fracture. Its hardness in the Mohs scale is 2.5. The density, measured by microvolumetric method designed by M.M. Vasilevskii using a MP 4504 ultramicrobalance (Sartorius Co., Germany) and calibrated with a barometric capillary pipe, is 3.62(2) g/cm³ (average of five measurements). Under UV rays of a SVD-120 highpressure mercury lamp ($\lambda_{max} = 365$ nm), the mineral exhibits bright green luminescence. During heating in an argon atmosphere up to 850°C (sample 8.35 mg, heating rate 4°C/min), chistyakovaite losses 12.2 wt %. No gas is liberated during dissolution in HCl at room temperature.

Microscopic investigations showed that the mineral is optically colorless, biaxial, and negative with the following optical parameters: $\alpha = 1.557(2)$, $\beta = 1.580(1)$, $\gamma = 1.580(1); 2V_{\text{meas}} = -10(5)^\circ, -25^\circ < 2V_{\text{calc}} < 0^\circ.$ Orientation: $X = a; Z \approx b$. Dispersion is absent. The IR-spectrum of chistyakovaite pressed as a KBr pellet was recorded on a Specord 75IR two-beam spectrophotometer in the wavelength range of 400–4000 cm⁻¹. A pellet of pure KBr was placed under the beam for comparison. The obtained spectrum (Fig. 2) contains the following bands, cm⁻¹: 3475 sh (v-H₂O, v-OH⁻); 3360 s, 3130 sh (v-H₂O), 1665 sh, 1640 (δ -H₂O); 1480 w, 1397 w; 1055 sh, 1029 (v-PO₄³⁻); 940 s, 905 sh, 888 s $(v-UO_{2}^{2+})$; 814 s $(v-AsO_{4}^{3-})$; 743 s; 595, 580 sh, 505 sh $(\delta - PO_4^{3-}; Al - O \text{ bonds in octahedra}); 479^{**}$. The splitting of the δ -H₂O and v-UO₂²⁺ bands indicates that the mineral contains different types of water molecules and uranyl cations. A large shoulder at 3130 cm⁻¹ in the IR spectrum suggests that some water molecules form strong hydrogen bonds. The IR spectrum of chistyakovaite is unique and serves as an important diagnostic tool for the reliable identification of this mineral among

^{*} A new mineral, chistyakovaite, has been approved by the Commission on New Minerals and Mineral Names of the All-Russia Mineralogical Society (VMO) and approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association (IMA) on April 5, 2005.

¹ Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Noginskii raion, Moscow oblast, 142432 Russia

² All-Russia Research Institute of Mineral Resources, Staromonetnyi per. 31, Moscow, 119017 Russia

³ NPO Regenerator, Skladochnaya ul. 6, 127018 Moscow, Russia

^{**} Letter designations: (s) strong band, (w) weak band; (sh) shoulder, (v) stretching vibrations; (δ) deformation vibrations



Fig. 1. Aggregate of chistyakovaite crystals (polished section, BSE image).



Fig. 2. IR spectrum of chistyakovaite.

arsenate members of the autunite and meta-autunite groups.

Chemical composition of the mineral was studied by the SAED method on a JXA-8100 microprobe (JEOL, Japan). A defocused microprobe beam was used to avoid sample destruction. The Al, U, As, and P contents were measured in seven points under the following conditions: V = 20 kV, I = 10 nA, and beam size 50 µm. Fluorine was analyzed at V = 15 kV, I = 70 nA, and beam size 50–60 µm. The microprobe was calibrated using the following standards: microcline (for Al), UO₂ (for U), InAs (for As), GaP (for P), and SrF₂ for (F). Average contents of major components are as follows, wt %:* Al_2O_3 4.99 (±0.1), UO₃ 58.34 (±0.3), As_2O_5 21.40 (±0.15), P_2O_5 1.23 (±0.1), F 1.1 (±0.1); H_2O (based on thermogravimetric data) 12.2 ± 0.1, and $-O = F_2 - 0.46$; total 98.80.

The empirical formula of chistyakovaite calculated adjusted to $(AsO_4,PO_4)_2$ with the consideration of valence balance is as follows: Al_{0.96}(UO₂)_{2.00}[(AsO₄)_{1.83}(PO₄)_{0.17}][F_{0.57}(OH)_{0.31}] · 6.50H₂O. Simplified formula is Al(UO₂)₂(AsO₄)₂(F,OH) · 6.5H₂O.

^{*} Measurement errors are shown in parentheses.

Chistyakovaite	Threadgoldite	Arsenouranospathite (hydrated species)	Arsenouranospathite (partially dehydrated species)	
$\begin{array}{c} Al(UO_2)_2(AsO_4)_2F \cdot \\ \cdot \ 6.5H_2O \end{array}$	$\begin{array}{c} Al(UO_2)_2(PO_4)_2(OH) \cdot \\ \cdot 8H_2O \end{array}$	$\begin{array}{c} H_{0.5}Al_{0.5}(UO_{2})_{2}(AsO_{4})_{2}\cdot\\ \cdot 20H_{2}O\end{array}$	$\begin{array}{c} H_{0.5}Al_{0.5}(UO_{2})_{2}(AsO_{4})_{2}\cdot\\ \cdot 10H_{2}O\end{array}$	
<i>P2/m, P2</i> or <i>Pm</i>	$Cc \text{ or } C2/c \qquad P4_2/n?$		Tetragonal?	
19.99	20.25	7.16	7.15	
9.79	9.85	7.16	7.15	
19.62	19.75	30.37	20.52	
110.7	111.4	90	90	
8	8	2	2	
9.34 (100), 9.14 (100), 4.93(18), 4.87(20), 4.76(27), 4.69(17), 3.55(14.5)	9.43(100), 5.35(50), 4.93(40), 4.10(40), 3.729(40), 3.474 (80), 3.366 (60), 2.197(60)	14.62(100), 7.62(100), 5.03(80), 3.59(60), 3.49(90), 3.24(40)	10.54(100), 5.13(60), 3.54(100), 3.17(50), 2.25(50)	
1.557	1.573 (Calculations)	≪1.538	1.564	
1.580	1.583	1.538	1.594	
1.580	1.588	1.542	1.596	
10	70	52	28	
3.62	3.4	2.52 (Calculations)	3.20 (Calculations)	
Present paper	[5]	[4]	[4]	
	Chistyakovaite Al(UO ₂) ₂ (AsO ₄) ₂ F \cdot \cdot 6.5H ₂ O P2/m, P2 or Pm 19.99 9.79 19.62 110.7 8 9.34 (100), 9.14 (100), 4.93(18), 4.87(20), 4.76(27), 4.69(17), 3.55(14.5) 1.557 1.580 1.580 1.580 10 3.62 Present paper	ChistyakovaiteThreadgolditeAl(UO2)2(AsO4)2F · · 6.5H2OAl(UO2)2(PO4)2(OH) · · 8H2O $P2/m, P2$ or Pm Cc or $C2/c$ 19.9920.259.799.8519.6219.75110.7111.4889.34 (100), 9.14 (100), 4.93(18), 4.87(20), 4.76(27), 4.69(17), 3.55(14.5)9.43(100), 5.35(50), 4.93(40), 4.10(40), 3.729(40), 3.474 (80), 3.366 (60), 2.197(60)1.5571.573 (Calculations)1.5801.5831.5801.58310703.623.4Present paper[5]	ChistyakovaiteThreadgolditeArsenouranospathite (hydrated species)Al(UO2)2(AsO4)2F · · $6.5H2O$ Al(UO2)2(PO4)2(OH) · · $8H2O$ $H_{0.5}Al_{0.5}(UO2)2(AsO4)2 ·· 20H2OP2/m, P2 or PmCc or C2/cP42/n?19.9920.257.169.799.857.1619.6219.7530.37110.7111.4908829.34 (100), 9.14 (100),4.93(18), 4.87(20),3.55(14.5)9.43(100), 5.35(50),3.366 (60), 2.197(60)14.62(100), 7.62(100),5.03(80), 3.59(60),3.49(90), 3.24(40)1.5571.573 (Calculations)\leqslant1.5381.5801.5831.5381.5801.5831.5381.5801.5831.5421070523.623.42.52 (Calculations)Present paper[5][4]$	

Table 1. Comparative data on chistyakovaite and related minerals

Note: According to structural data [6], the space group of threadgoldite is Cc.

Correctness of the obtained chemical composition, refractive indices, and mineral density is supported by a good compatibility index from the Gladstone–Dale relationship (using coefficients from [3]: $1 - K_p/K_c = 0.00$ for D_{meas} ; $1 - K_p/K_c = 0.01$ for D_{calc}).

Fissuring and the microblock structure of chistyakovaite did not allow us to study its crystalline structure (Fig. 1).

According to the powder XRD pattern obtained on a DRON-1 diffractometer with CuK_{α} irradiation (Table 1), the new mineral is monoclinic and characterized by the following properties: sp. gr. *P2/m*, *P2* or *Pm* (systematic extinctions are absent); unit cell parameters: a =19.99(1) Å, b = 9.79(1) Å, c = 19.62(2) Å, $\beta =$ 110.7(2)°; V = 3592(6) Å³; Z = 8, d = 3.585 g/cm³.

The family of natural aluminum uranylphosphates is rather diverse and includes at least ten mineral species: furongite, moreauite, mundite, phuralumite, ranunculite, sabugalite, threadgoldite, triangulite, upalite, and uranospathite. Most of them were first found in Kobokobo (Kivu, Congo). At the same time, only one mineral species (arsenouranospathite) first reported from the Menzenschwand deposit (Schwarzwald Mountains, Germany) had been known thus far among the family of aluminum uranylarsenates. The mineral occurs as two varieties with different unit cell parameters and physical properties (hydrated and partially dehydrated modifications) [4].

Chistyakovaite is isostructural or homeotypical to threadgoldite in terms of unit cell parameters and stoichiometry (Al : U : (As + P) = 1: 2 : 2), [5, 6]. However, the former is an arsenate mineral and is distinguished by an insignificant isomorphic impurity of P, relatively high F content, and lower water content. The comparative characteristics of chistyakovaite and some cognate minerals are given in Table 2.

It should be noted that we found a mineral chemically similar to chistyakovaite, but with a higher F content in the oxidation zone of the Menzenschwand deposit (Schwarzwald Mountains, Germany), in the form of tiny fissured elongated-tabular crystals up to 1 mm long. This mineral associates with uranophane, studite, uranospathite, sabugalite, and kasolite. Microprobe analysis showed that the sample from the Menzenschwand deposit has the following composition (wt %): Al₂O₃ 5.77, UO₃ 59.73, As₂O₅ 22.79, P₂O₅ 1.69, F 1.82, $-O = F_2 - 0.78$, total 91.02. The empirical formula can be written as follows: Al_{1.02}(UO₂)_{2.00}[(AsO₄)_{1.79}(PO₄)_{0.21}][F_{0.86}(OH)_{0.20}] · *n*H₂O. Unfortunately, the small amount of matter and imper-

DOKLADY EARTH SCIENCES Vol. 407 No. 2 2006

	1		5				
I _{meas}	d _{meas} , Å	$d_{\rm calc},$ Å	hkl	I _{meas}	$d_{\rm meas}$, Å	$d_{\text{calc}}, \text{\AA}$	hkl
4	16.36	16.290	-101	4.5	2.45	2.452	-308
100	9.34	9.350	200			2.449	603
100	9.14	9.177	002	8.5	2.338	2.337	800
18	4.93	4.930	-402	4	2.317	2.316	-633
1	4.90	4.895	020			2.314	-527
20	4.87	4.880	212	13	2.281	2.294	008
		4.873	-104			2.272	043
27	4.76	4.748	-313			2.270	-608
17	4.69	4.697	311	1	2.170	2.171	631, -409
		4.688	-121			2.169	416
		4.675	400	1	2.074	2.076	-245
10	4.57	4.588	004			2.075	-609
7	3.87	3.870	-105			2.073	-826
		3.864	-322	4.5	1.877	1.879	-351
12	3.84	3.850	320			1.878	-546, -918
		3.848	-223			1.877	038, 606
14.5	3.55	3.547	-315	4.5	1.873	1.873	-836, 641
4	3.50	3.504	510	5	1.866		
		3.494	-421	1	1.857		
4.5	3.31	3.329	-324	4.5	1.852		
		3.302	322	4	1.830		
9	3.105	3.101	502, -611, -216	4.5	1.820		
2	3.03	3.029	-232	1	1.762		
		3.028	-523	2.5	1.713		
5.5	2.80	2.797	-333	3	1.556		
		2.796	-307	2.5	1.536		
1	2.63	2.631	233	1	1.484		
		2.629	620	3	1.454		

Table 2. XRD powder diffraction data on chistyakovaite

fectness of the crystals hampered detailed study of the aluminum uranylarsenate from Germany.

Standard samples of chistyakovaite are stored in the collection of E.V. Kopchenova at the Mineralogical Museum of the All-Russia Research Institute of Mineral Resources, Moscow (inventory no. 350/59) and in the Fersman Mineralogical Museum, Moscow (inventory no. 3286/1).

ACKNOWLEDGMENTS

We are grateful to N.I. Chistyakova for microprobe analyses of studied minerals.

REFERENCES

- 1. E. V. Kopchenova and K. V. Skvortsova, Dokl. Akad. Nauk SSSR **114**, 634 (1957).
- 2. G. A. Sidorenko, N. V. Chukanov, and I. S. Naumova, Zap. Vseross. Mineral. O-va, No. 6, 88 (2004).
- 3. J. A. Mandarino, Can. Mineral. 19, 441 (1981).
- 4. K. Walenta, Miner. Mag. 42, 117 (1978).
- 5. M. Deliens and P. Piret, Bull. Miner. 102, 338 (1979).
- 6. P. Piret, J. R. Declercq, and D. Wauter–Stoop, Acta Cryst. **35**, 3017 (1979).