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New nickel-uranium-arsenic mineral species from the oxidation zone of the Belorechenskoye deposit, Northern Caucasus, Russia: II. Dymkovite, $Ni(UO_2)_2(As^{3+}O_3)_2 \cdot 7H_2O$, a seelite-related arsenite

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Abstract: A new arsenite mineral species dymkovite, ideally $Ni(UO_2)_2(As^{3+}O_3)_2 \cdot 7H_2O$ (IMA no. 2010-087), was found at the Belorechenskoye deposit, Adygea Republic, Northern Caucasus, Russia. It is a supergene mineral associated with rauchite, annabergite, and goethite in cavities of a dolomite vein with primary uraninite (pitchblende), nickeline, and gersdorffite. Dymkovite forms long-prismatic, lath-shaped to acicular crystals ($\leq$0.5 mm long, $\leq$0.05 mm thick), which are elongated along [010]. They are combined in sprays or open-work, chaotic groups up to 1.5 mm across; crusts up to 2 × 2 mm^2 and up to 0.05–mm-thick also occur. Dymkovite crystals are transparent and bright yellow, whereas crusts are translucent and light yellow to light greenish-yellow. The luster is vitreous. The mineral is brittle, the Mohs' hardness is *ca.* 3. Cleavage was not observed. D_{calc} is 3.806 g cm^{-3}. Dymkovite is optically biaxial (−), $\alpha = 1.625(2)$, $\beta = 1.735(5)$, $\gamma = 1.745(3)$, $2V_{meas} = 20(10)^\circ$, $2V_{calc.} = 32^\circ$. Dispersion is strong, $r > v$. Pleochroism is strong: X = very pale yellowish-green, $Y \approx Z$ = light greenish yellow. In the IR spectrum, bands of $As^{3+}O_3$ anions are strong, whereas bands of $As^{5+}O_4$ anions are very weak. The average chemical composition (electron microprobe) is (in wt%): MgO = 1.11, FeO = 0.24, NiO = 5.40, ZnO = 0.23, As_2O_3 = 19.57, P_2O_5 = 0.58, UO_3 = 59.43, H_2O_{calc} = 13.44, total = 100.00. The empirical formula, calculated on the basis of 17 O *apfu,* is: $(Ni_{0.69}Mg_{0.26}Fe_{0.03}Zn_{0.03})_{\Sigma 1.01}U_{1.97}(As^{3+}_{1.88}P_{0.08})_{\Sigma 1.96}O_{9.94} \cdot 7.06H_2O$. Dymkovite is monoclinic, space group $C2/m$, $a = 17.99(3)$, $b = 7.033(7)$, $c = 6.633(9)$ Å, $\beta = 99.62(11)^\circ$, $V = 827(3)$ Å^3, $Z = 2$. The crystal structure was refined from single-crystal X-ray diffraction data ($R_1 = 0.063$). The structure is based upon the $[(UO_2)(As^{3+}O_3)]^-$ sheets formed by chains of edge-sharing $[UO_7]$ pentagonal bipyramids and $(As^{3+}O_3)$ triangular pyramids, which are linked through hydrogen bonds involving disordered $[Ni(H_2O)_6]^{2+}$ octahedra and additional H_2O molecules in the interlayer. The strongest lines of the powder X-ray pattern [d in Å (I)(hkl)] are: 8.93(100)(200), 4.463(34)(111, 400), 3.523(23)(020), 3.276(21)(220), 3.008(26)(11-2), 2.846(27)(112, 221, 31-2). Dymkovite is a Ni-dominant, almost arsenate-free analogue of seelite, $Mg(UO_2)_2[(As^{3+}O_3)_{1.4}(As^{5+}O_4)_{0.6}] \cdot 7H_2O$. The mineral is named in honor of the Russian mineralogist Yuriy Maksimovich Dymkov (b. 1926), a specialist in U mineralogy, the geology of U deposits, and problems of mineral formation, who was one of the first researchers of the U ores of the Belorechenskoye deposit.

Key-words: dymkovite, new mineral species, arsenite, seelite, crystal structure, oxidation zone, Belorechenskoye deposit, Adygea.

1. Introduction

In the first paper of the series (Pekov *et al*., 2012), we have described rauchite, $Ni(UO_2)_2(As^{5+}O_4)_2 \cdot 10H_2O$ (IMA no. 2010-037), a new arsenate member of the autunite group of minerals, discovered in the oxidation zone of the Belorechenskoye deposit, which is located in the upper reaches of the small river Syuk, a tributary of the Belaya river, 60 km to the south of the city of Maikop, Adygea Republic, Northern Caucasus, Russia. A brief description of the Belorechenskoye (formerly Dakhovskoye) deposit, prospected in different times for U and barite, is given in Pekov *et al*. (2012). A more detailed account of the deposit, including its secondary minerals, can be found in Pekov *et al*. (2010).

This paper contains a description and crystal-structure characterization of another new mineral species found at the same deposit, dymkovite, $Ni(UO_2)_2(As^{3+}O_3)_2 \cdot 7H_2O$, the nickel-uranyl arsenite closely related to seelite (Table 1).

Specimens with both new hydrous Ni-U-As-O minerals, rauchite and dymkovite, were collected in 2010 by one of the authors (V.V.L.) in Adit #1, the uppermost

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Table 1. Comparative data for dymkovite and seelite.

	Dymkovite	Seelite
Mineral formula	$Ni(UO_2)_2(As^{3+}O_3)_2 \cdot 7H_2O$	$Mg(UO_2)_2[(As^{3+}O_3)_{1.4}(As^{5+}O_4)_{0.6}] \cdot 7H_2O$
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/*m*	*C*2/*m*
Unit-cell data		
a, Å	17.99	18.19
b, Å	7.033	7.071
c, Å	6.633	6.670
β, °	99.62	99.70
V, Å^3	827	846
Z	2	2
Strongest reflections of the X-ray powder pattern:		
d, Å – *I*	8.93–100	9.02–100
	4.883–20	4.90–40
	4.463–34	4.48–80
	3.984–16	4.00–40
	3.523–23	3.53–40
	3.276–21	3.28–50
	3.008–26	3.01– 60
	2.846–27	2.849–60
Density, g cm^{-3}	3.81 (calc.)	3.70 (meas.), 3.60–3.71 (calc.)
Optical data		
α	1.625	1.602–1.610
β	1.735	1.730–1.737
γ	1.743	1.740–1.753
Optical sign, $2V_{meas}$	(–) 20°	(–) 30–41°
IR absorption bands, cm^{-1} (strong bands are marked in bold type)	**3310**	**3390**
	3210	**3220**
	1650	**1647**
	1017	980
	877	**875**
	800	**796**
	740	**735**
	663	640
	569	**565**
	474	**468**
Reference	this work	Bariand *et al*. (1993); Piret & Piret-Meunier (1994); our data on the IR spectrum

underground working at the deposit, in the supergene assemblage related to a slightly oxidized dolomite vein with a rich Ni, As, and U mineralization.

Dymkovite is named in honor of the Russian mineralogist Yuriy Maksimovich Dymkov (born 1926), a well-known specialist in U mineralogy, the geology of U deposits and problems of mineral formation, who works in the All-Russian Research Institute of Chemical Technology (VNIIKhT), Moscow. Yuriy Dymkov was one of the first researchers of the U ores of the Belorechenskoye deposit, and he published the first fundamental paper on their mineralogical composition and formation (Dymkov *et al*., 1970). Both the mineral data and the name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA no. 2010-087). The type specimen of dymkovite is deposited in the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, Russia, registration number 4065/1.

2. Occurrence and general appearance

Dymkovite was found in small cavities and cracks in pinkish, greenish or pale cream-colored dolomite with numerous nests of intimately intergrown uraninite (pitchblende), nickeline and gersdorffite. Pitchblende and nickeline together form concentric kidney-shaped or dendritic aggregates up to 2–3 cm in size. Gersdorffite overgrows nickeline, forming rims up to 1 mm thick or crusts of cubic or cubo-octahedral crystals ($\leq$0.5 mm across). Other primary minerals are represented by sphalerite, pyrite, millerite, dickite, calcite and quartz, which occur in minor amounts, mainly in cavities. The supergene minerals are rauchite (Pekov *et al*., 2012), dymkovite, annabergite and goethite (limonite).

Rauchite and dymkovite are closely associated with nickeline, gersdorffite and pitchblende, which must have served as sources of U, Ni, and As for the formation of

these secondary minerals. Dymkovite is the earliest As phase in the supergene mineral association.

Dymkovite forms long-prismatic, lath-shaped to acicular crystals, which are typically ≤0.2 mm long (rarely ≤0.5 mm) and ≤0.05 mm thick (Fig. 1a). They are elongated along [010] and terminated by the {010} pinacoids; faces of the ''prismatic'' zone {*h*0*l*} could not be indexed. The crystals are combined in sprays or open-work, chaotic groups up to 1.5 mm in size overgrowing dolomite and aggregates of pitchblende, nickeline, and gersdorffite (Fig. 1a, b, and 2a). Dymkovite also occurs as crusts (up to 2 × 2 mm^2 and ≤0.05 mm thick), composed of coarse, prismatic, acicular or hair-like individual crystals, on the surface of pitchblende-nickeline aggregates (Fig. 2b). Such

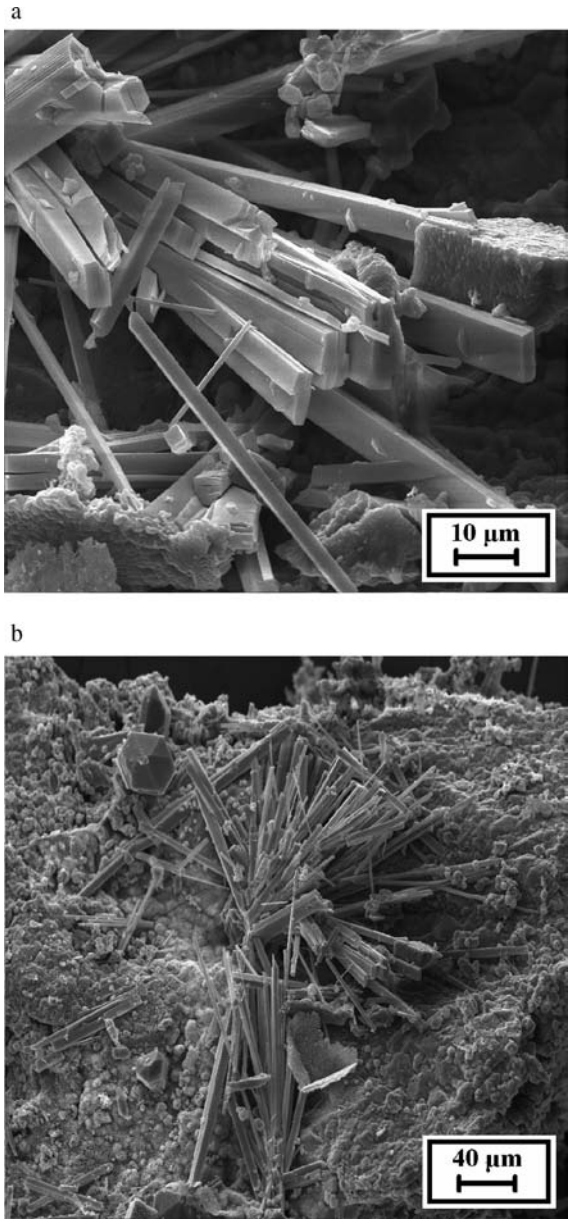

Fig. 1. Crystals of dymkovite (secondary electron images). (a) bundle of lath-shaped crystals. (b) groups of long-prismatic crystals with quartz on uraninite (pitchblende).

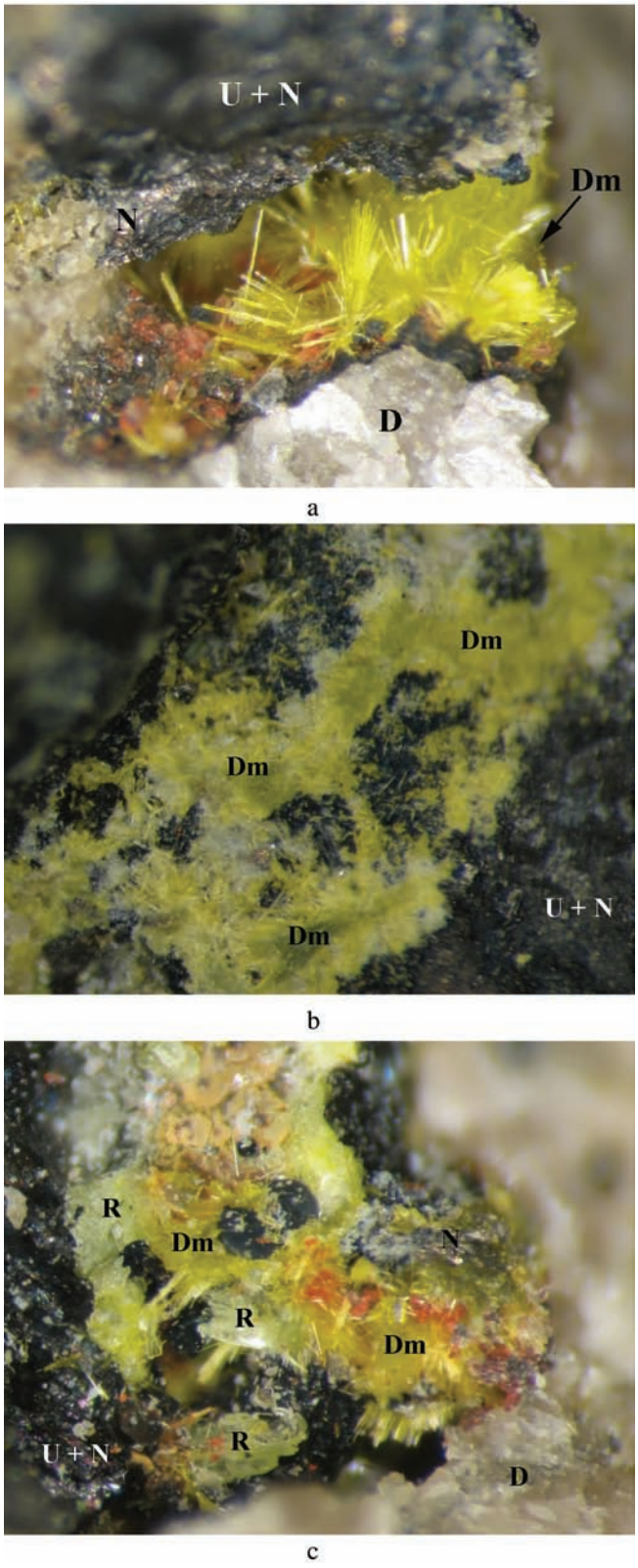

Fig. 2. Aggregates of dymkovite. (a) crystals and their bunches in cavity. Image width = 2.5 mm. (b) crusts on the surface of a nickeline-uraninite aggregate. Image width = 2.2 mm. (c) intimate intergrowths of dymkovite and rauchite. Image width = 2.4 mm.
Abbreviations: D – dolomite, Dm – dymkovite, N – nickeline, R – rauchite, U – uraninite (pitchblende). Photo: I.V. Pekov & A.V. Kasatkin.

crusts are especially typical of the porous zone on the borderline between concentric pitchblende-nickeline kidneys and the host dolomite. Intimate association of dymkovite and rauchite is common (Fig. 2c).

3. Physical properties and optical characteristics

Crystals of dymkovite are transparent and bright yellow, whereas crusts are translucent and light yellow to light greenish-yellow. The streak is pale yellow. The luster is vitreous. Dymkovite is nonfluorescent in both ultraviolet and cathode rays. It is brittle, the Mohs' hardness is *ca.* 3. Cleavage and parting were not observed, and the fracture is uneven. The calculated density is 3.806 g cm^{-3} (using the empirical formula). The density could not be measured because of both paucity of available material and lack of heavy liquids of necessary density. The mineral is radioactive.

Dymkovite is optically biaxial (−), $\alpha = 1.625(2)$, $\beta = 1.735(5)$, $\gamma = 1.745(3)$, $2V$ (meas.) = 20(10)°, $2V$ (calc.) = 32°. Dispersion is strong, $r > v$. Orientation: $Y \approx b$. The pleochroism is strong: X = very pale yellowish-green, $Y \approx Z$ = light greenish yellow; the absorption scheme is: $Z \geq Y > X$.

4. IR spectroscopy

Dymkovite powder was mixed with anhydrous KBr, pelletized, and analyzed using a Bruker Alpha spectrophotometer. Polystyrene and gaseous NH_3 were used as frequency standards; the precision of the frequency measurement is ±1 cm^{-1}; the mean resolution for the range 400–1600 cm^{-1} is 0.8 cm^{-1}. Because of scarcity of pure material, the IR spectrum of dymkovite (Fig. 3) was measured on a sample contaminated by dolomite (its characteristic band with a maximum at 1436 cm^{-1}, marked with an asterisk, corresponds to the C-O stretching vibrations).

Absorption bands in the IR spectrum of dymkovite and their assignments (cm^{-1}; s – strong band, w – weak; vw – very weak, br – broad) are: 3310s/br, 3210s/br (O-H-stretching vibrations of H_2O molecules); 1650s (H-O-H bending vibrations of H_2O molecules); 1017w (P-O stretching vibrations of admixed PO_4^{3-} anions), 877s (asymmetric U-O stretching vibrations of UO_2^{2+} cations); 800vw, 740vw (As-O stretching vibrations of admixed $As^{5+}O_4^{3-}$ anions); 663w, 569s (As-O stretching vibrations of arsenite anions, $As^{3+}O_3^{3-}$); 474s (As-O stretching vibrations of arsenite anions combined with Ni-O stretching vibrations).

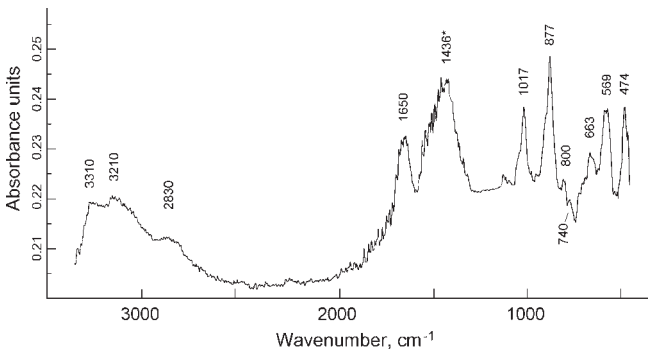

Fig. 3. IR spectrum of dymkovite. Band with maximum at 1436 cm^{-1} (marked with an asterisk) corresponds to admixed dolomite.

The IR spectrum of dymkovite is similar to that of seelite, $Mg(UO_2)_2[(As^{3+}O_3)_{1.4}(As^{5+}O_4)_{0.6}]\cdot 7H_2O$, the structurally related arsenite mineral with significant arsenate admixture. The IR spectrum of seelite, unlike that of dymkovite, contains strong IR absorption bands of arsenate ions with maxima at 796 and 735 cm^{-1} (Table 1), which confirms significant role of arsenate anion, and it does not contain bands of the phosphate ion. The IR spectrum of dymkovite shows significant predominance of admixed PO_4 over $As^{5+}O_4$.

5. Chemical data

The chemical composition of dymkovite was determined by electron microprobe (in wavelength-dispersive mode) with a Camebax SX 50 instrument, operating at a voltage of 15 kV and a beam current of 30 nA. The electron beam was rastered on an area of 5 × 5 μm^2 to minimize sample damage. The following standards were used: olivine (Mg), Fe_2O_3 (Fe), NiO (Ni), ZnO (Zn), $KTiPO_5$ (P), tilasite (As), UO_2 (U). Contents of Na, K, Ca, Sr, Ba, Pb, Mn, Co, Cu, Al, V, Si, S, F and Cl are generally below detection limits; in some points CaO, CoO, or CuO contents are up to 0.1 wt%.

The H_2O content was not measured because of scarcity of pure material, but its presence was confirmed by IR spectroscopy. The amount of H_2O determined from structural data (see below) shows good agreement with the deficiency of the average chemical composition obtained by electron microprobe analysis.

The average (12 analyses) chemical composition of dymkovite (in wt%; ranges are in parentheses) is: MgO = 1.11 (0.4–1.7), FeO = 0.24 (0.0–0.4), NiO = 5.40 (4.5–7.4), ZnO = 0.23 (0.0–0.4), As_2O_3 = 19.57 (18.7–21.3), P_2O_5 = 0.58 (0.4–0.9), UO_3 = 59.43 (57.8–60.7), H_2O_{calc} = 13.44, and total = 100.00. The H_2O content was calculated by difference. Arsenic was considered as only As^{3+} (based on both structural and IR spectroscopy data); the insignificant content of As^{5+} reflected in very weak bands corresponding to the arsenate ion in the IR spectrum (see above) was ignored.

The empirical formula of dymkovite, calculated on the basis of 17 O *apfu*, is $(Ni_{0.69}Mg_{0.26}Fe_{0.03}Zn_{0.03})_{\Sigma 1.01}U_{1.97}(As^{3+}_{1.88}P_{0.08})_{\Sigma 1.96}O_{9.94}\cdot 7.06H_2O$.

The simplified, end-member formula is $Ni(UO_2)_2(As^{3+}O_3)_2\cdot 7H_2O$, corresponding to (in wt%): NiO 7.70, UO_3 58.93, As_2O_3 20.38, H_2O 12.99, and a total of 100.00.

6. X-ray crystallography

Single-crystal X-ray studies of dymkovite were carried out using a Bruker SMART APEX CCD diffractometer. The mineral is monoclinic, space group $C2/m$, $a = 17.91(2)$, $b = 6.985(9)$, $c = 6.594(9)$ Å, $\beta = 99.89(2)^\circ$, $V = 813(2)$ Å^3, $Z = 2$. The a:b:c ratio is 2.558:1:0.943.

X-ray powder diffraction data of dymkovite were collected using a STOE IPDS II diffractometer equipped with an image-plate detector, using the Gandolfi method (Mo$K\alpha$-radiation; detector-to-sample distance: 200 mm). Data are given in Table 2 (for d_{calc}, only reflections with intensities ≥ 1 are included). Monoclinic unit-cell parameters refined from the powder data are: $a = 17.99(3)$, $b = 7.033(7)$, $c = 6.633(9)$ Å, $\beta = 99.62(11)^\circ$, $V = 827(3)$ Å^3.

The difference between unit-cell dimensions and density values of dymkovite obtained from the single-crystal ($V = 813$ Å^3, $D_{calc} = 3.910$ g cm^{-3}) and powder ($V = 827$ Å^3, $D_{calc} = 3.806$ g cm^{-3}) X-ray diffraction data is probably caused by slight dehydration of the sample under the X-ray beam during the long-time single-crystal experiment. For this reason, we have used unit-cell dimensions obtained from powder data for the density calculation. The correctness of this assumption is confirmed by the very low value of the Gladstone–Dale compatibility index: $1 - (K_P/K_c) = 0.003$ (superior).

Table 2. X-ray powder diffraction data for dymkovite.

I_{obs}	d_{obs}	I_{calc}	d_{calc}	$h\ k\ l$
100	8.93	100	8.869	200
8	6.57	3, 6	6.540, 6.538	001, 110
7	5.77	13	5.742	20-1
17	4.883	20	4.888	201
34	4.463	12, 43	4.489, 4.434	111, 400
16	3.984	18	3.966	31-1
23	3.523	24	3.517	020
8	3.424	10	3.415	401
21	3.276	30	2.269	220
26	3.008	32	2.999	11-2
27	2.846	12, 7, 20	2.855, 2.855, 2.828	112, 221, 31-2
12	2.763	16	2.755	420
5	2.542	6	2.539	601
12	2.474	5, 11	2.503, 2.466	312, 51-2
5	2.371	6	2.362	71-1
2	2.269	1.5	2.263	620
6	2.211	3, 3	2.217, 2.205	800, 13-1
4	2.183	2, 1.5	2.180, 2.175	003, 131
9	2.107	2, 4, 2	2.107, 2.107, 2.100	11-3, 33-1, 40-3
6	2.064	1, 7	2.070, 2.059	31-3, 621
5	2.032	4	2.031	113
3	2.005	4	2.001	801
10	1.916	2, 9, 1	1.923, 1.914, 1.914	53-1, 13-2, 60-3
10	1.873	2, 4, 3, 5	1.876, 1.875, 1.873, 1.867	820, 132, 313, 33-2
3	1.802	2, 1	1.803, 1.797	42-3, 712
7	1.758	4, 3	1.764, 1.758	332, 040
4	1.722	4	1.713	73-1
2	1.685	3	1.682	513
1	1.659	2	1.658	20-4
3	1.636	3, 2	1.644, 1.635	10.0.1, 440
1	1.599	1	1.599	73-2
1	1.569	1	1.573	133
1	1.543	1	1.534	60-4
1	1.536	2	1.533	82-3
3	1.497	2	1.500	22-4
1	1.444	2, 1	1.446, 1.442	641, 93-2
1	1.418	2	1.414	62-4
1	1.393	2	1.393	533
1	1.378	1	1.378	840
3	1.337	2	1.338	11.3.-1
2	1.328	1, 1	1.331, 1.329	12.0.-3, 913
2	1.296	2, 1	1.295, 1.295	15-2, 12.2.1
2	1.284	1, 1	1.283, 1.282	152, 733
2	1.244	1, 1	1.245, 1.241	12.2.-3, 55-2

7. Crystal structure

More than a hemisphere of diffraction data were collected using Mo$K\alpha$-radiation and frame widths of 0.5° in ω, with 90 s used to acquire each frame. The unit-cell dimensions were refined using least-squares techniques (Table 3). The data were reduced and corrected for Lorentz, polarization, absorption and background effects using the Bruker programs SAINT and XPREP (Bruker AXS, Inc., 2001, 2003). A semi-empirical absorption-correction based upon the intensities of equivalent reflections was done by modeling the crystal as an ellipsoid. The Bruker SHELXTL Version 5 system of programs was used for the determination and refinement of the structures (Sheldrick, 2008). The structure was solved by direct methods, which gave the positions of the As, Ni and U atoms. Oxygen atoms were located in difference-Fourier maps calculated following least-squares refinements of the partial-structure models. The structures were refined on the basis of F^2 for all unique data. The final refinement included the atomic positional parameters of all atoms, with an allowance for anisotropic displacement of all atoms except half-occupied H_2O sites, and included a weighting scheme of the structure factors. The final atom coordinates and displacement parameters are listed in Table 4. Selected cation–anion bond lengths and anion-anion distances that may be responsible for hydrogen bonds are given in Table 5.

Dymkovite is structurally related to seelite, $Mg(UO_2)_2[(As^{3+}O_3)_{1.4}(As^{5+}O_4)_{0.6}]\cdot 7H_2O$ (Piret & Piret-Meunier, 1994) (Table 1). These minerals belong to the family of compounds with structures characterized by uranyl-based layers with the uranophane anion topology (Burns *et al.*, 1996; Burns, 2005; Locock, 2007). The structure of dymkovite is based upon the $\{(UO_2)(As^{3+}O_3)\}^-$ layers formed by chains of edge-sharing $[UO_7]$ pentagonal bipyramids and $(As^{3+}O_3)$ triangular pyramids (Fig. 4b). The layers are parallel to (100) and are linked through hydrogen bonds involving disordered $[(Ni,Mg)^{2+}(H_2O)_6]^{2+}$ octahedra in the interlayer (Fig. 4a). The anion topology of the uranyl arsenite layer in dymkovite (Fig. 4c) consists of pentagons (occupied by U), triangles (occupied by As), and squares (empty). The uranophane topology is known for its isomeric variations arising from possibility of orientation of tetrahedral anions (occupying triangles of the topology) either up (**u**) or down (**d**) relative to the plane of the layer (Krivovichev, 2008). The isomer observed in the structure of dymkovite is the simplest one and can be designated as (**ud**), where symbols **u** and **d** indicate orientation of the As-Ψ group (Ψ = lone pair of electrons) either ''up'' or ''down:'' respectively (the $As^{3+}O_3$ triangular pyramid may be viewed as a $As^{3+}O_3\Psi$ tetrahedron with the lone pair of electrons at its apical corner). The isomer observed in dymkovite is the most common one in mineral structures and has been observed in seelite, α-uranophane, boltwoodite,

Table 3. Crystallographic data and refinement parameters for dymkovite.

Crystal data	
Simplified formula	$(Ni_{0.6}Mg_{0.4})(UO_2)_2(As^{3+}O_3)_2\cdot 7H_2O$
Temperature	293 K
Radiation, wavelength	Mo$K\alpha$, 0.71073 Å
Crystal system	monoclinic
Space group	*C*2/*m*
Unit-cell dimensions *a*, *b*, *c* (Å), β (°)	17.91(2), 6.985(9), 6.594(9), 99.89(2)
Unit-cell volume (Å^3)	813(2)
Z	2
Calculated density (g/cm^3)	3.910
Absorption coefficient (mm^{-1})	24.702
Crystal size (mm^3)	0.03 × 0.01 × 0.01
Data collection	
θ range	2.31 – 28.00°
h, *k*, *l* ranges	–23→ 23, –9→ 9, –8→ 8
Total reflections collected	4528
Unique reflections (R_{int})	1062 (0.222)
Unique reflections $F > 4\sigma(F)$	717
Structure refinement	
Refinement method	Full-matrix least-squares on F^2
Weighting coefficients *a*, *b*	0.0001, 0
Extinction coefficient	0.0005(2)
Data/restraints/parameters	1062/0/62
R_1 [$F > 4\sigma(F)$], wR_2 [$F > 4\sigma(F)$],	0.057, 0.108
R_1 all, wR_2 all	0.090, 0.118
Goodness-of-fit on F^2	0.927
Largest diff. peak and hole, e Å^{-3}	2.620, –2.585

Table 4. Coordinates, site-occupancies and displacement parameters ($Å^2$) of atoms in the structure of dymkovite.

Atom	Occupancy	x	y	z	U_{iso}
U	U	0.24091 (6)	0	0.12781 (11)	0.0338 (3)
As	As	0.20792 (15)	1/2	0.3255 (3)	0.0425 (6)
Ni	$Ni_{0.60\ (3)}Mg_{0.40\ (3)}$	0	0	1/2	0.049 (2)
O1	O	0.3415 (10)	0	0.212 (2)	0.051 (4)
O2	O	0.1415 (9)	0	0.044 (2)	0.047 (4)
O3	O	0.2225 (9)	0	0.4596 (19)	0.043 (4)
O4	O	0.2407 (8)	0.6738 (13)	0.1790 (13)	0.050 (3)
H_2O1	$O_{0.50}$	0.0906 (15)	0.181 (3)	0.521 (3)	0.066 (6)
H_2O2	$O_{0.50}$	−0.0218 (18)	0.139 (6)	0.743 (4)	0.104 (11)
H_2O3	$O_{0.50}$	0.060 (3)	0.198 (7)	0.692 (6)	0.160 (16)
H_2O4	$O_{0.50}$	0	1/2	0.185 (8)	0.132 (19)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U	0.0546 (6)	0.0170 (4)	0.0326 (4)	0	0.0157 (3)	0
As	0.0579 (15)	0.0382 (13)	0.0347 (10)	0	0.0174 (11)	0
Ni	0.039 (3)	0.046 (4)	0.064 (4)	0	0.011 (3)	0
O1	0.039 (3)	0.046 (4)	0.064 (4)	0	0.011 (3)	0
O2	0.052 (10)	0.048 (10)	0.052 (9)	0	0.010 (8)	0
O3	0.053 (10)	0.035 (9)	0.055 (8)	0	0.011 (9)	0
O4	0.050 (9)	0.041 (8)	0.038 (7)	0.000 (4)	0.010 (7)	0.000 (7)

Table 5. Selected interatomic distances (Å) in the structure of dymkovite.

U-O2	1.771 (16)	$O1^{\cdots}H_2O3$	2.76 (5)
U-O1	1.792 (17)	$O1^{\cdots}H_2O4$	2.87 (7)
U-O3	2.268 (13)	$O1^{\cdots}H_2O1$	2.97 (3)
U-O4	2.304 (9) 2×	$O2^{\cdots}H_2O3$	2.88 (5)
U-O4	2.430 (9) 2×	$O2^{\cdots}H_2O2$	2.92 (4)
<U-O>	2.19	$O3^{\cdots}H_2O1$	2.77 (3)
		$H_2O1^{\cdots}H_2O2$	2.70 (4)
As-O4	1.717 (10) 2×	$H_2O1^{\cdots}H_2O3$	2.81 (6)
As-O3	1.719 (14)	$H_2O1^{\cdots}H_2O3$	2.96 (5)
<As-O>	1.718	$H_2O1^{\cdots}H_2O2$	2.96 (5)
		$H_2O2^{\cdots}H_2O4$	2.59 (4)
Ni-H_2O2	1.97 (3) 2×	$H_2O2^{\cdots}H_2O3$	2.82 (6)
Ni-H_2O1	2.04 (3) 4×	$H_2O2^{\cdots}H_2O3$	2.86 (5)
<Ni-H_2O>	2.00	$H_2O4^{\cdots}H_2O3$	2.56 (6)

sklodowskite, cuprosklodowskite, and kasolite [see Krivovichev (2008) for details and references].

8. Discussion

Dymkovite is closely related to seelite in its symmetry, unit-cell dimensions, X-ray powder pattern, and the majority of physical properties (Table 1). Unlike seelite, dymkovite contains no detectable amount of arsenate anions. In our opinion, it is possible that seelite was an initially arsenate-free arsenite phase, like dymkovite, and the appearance of AsO_4^{3-} could be the result of partial post-crystallization oxidation of As^{3+} to As^{5+} by oxygen from the air or meteoric water. It is of note that seelite was previously reported as an arsenate with the ideal composition $Mg(UO_2)_2(AsO_4)_2{\cdot}4H_2O$ (Bachet *et al.*, 1991). Only during a detailed reinvestigation it was found that seelite is an arsenite with significant admixture of arsenate and that the formula of the mineral can be described better as $Mg(UO_2)_2[(As^{3+}O_3)_{1.4}(As^{5+}O_4)_{0.6}]{\cdot}7H_2O$ (Bariand *et al.*, 1993; Piret & Piret-Meunier, 1994). Thus, dymkovite is a Ni-dominant, almost arsenate-free analogue of seelite.

Being closely associated minerals (Fig. 2c) with the same combination of species-defining elements (Ni, U, As, O, H), dymkovite and rauchite show some differences in the contents of admixed constituents, especially of Mg and P. Dymkovite is more depleted in P than rauchite. The Mg content of dymkovite varies significantly, exhibiting a Mg:Ni atom-ratio range from 0.08 to 0.98, whereas, in rauchite, this ratio varies from 0.08 to 0.45. Moreover, one point of electron microprobe analysis within a light greenish-yellow crust of dymkovite coating a pitchblende-nickeline kidney yielded a composition that was characterized by predominance of Mg over Ni in atomic proportion and the following absolute values (in wt%): MgO = 2.09, FeO = 0.13, CoO = 0.14, NiO = 3.43, ZnO = 0.20, As_2O_3 = 20.63, P_2O_5 = 0.45, UO_3 = 59.76, H_2O_{calc} = 13.17, total = 100.00 (H_2O content calculated by difference). The empirical formula calculated on the basis of 17 O *apfu* is: $(Mg_{0.49}Ni_{0.44}Zn_{0.02}Co_{0.02}Fe_{0.02})_{\Sigma 0.99}\ U_{1.98}(As^{3+}{}_{1.98}P_{0.06})_{\Sigma 2.04}O_{10.05}{\cdot}6.95H_2O$. This composition formally corresponds to the Ni-rich variety of seelite, whereas neighboring points in the same sample showed the dymkovite composition with Ni > Mg. Thus, we conclude that (1) seelite is present at Belorechenskoye, and (2) a continuous isomorphous series between seelite and dymkovite exists in nature.

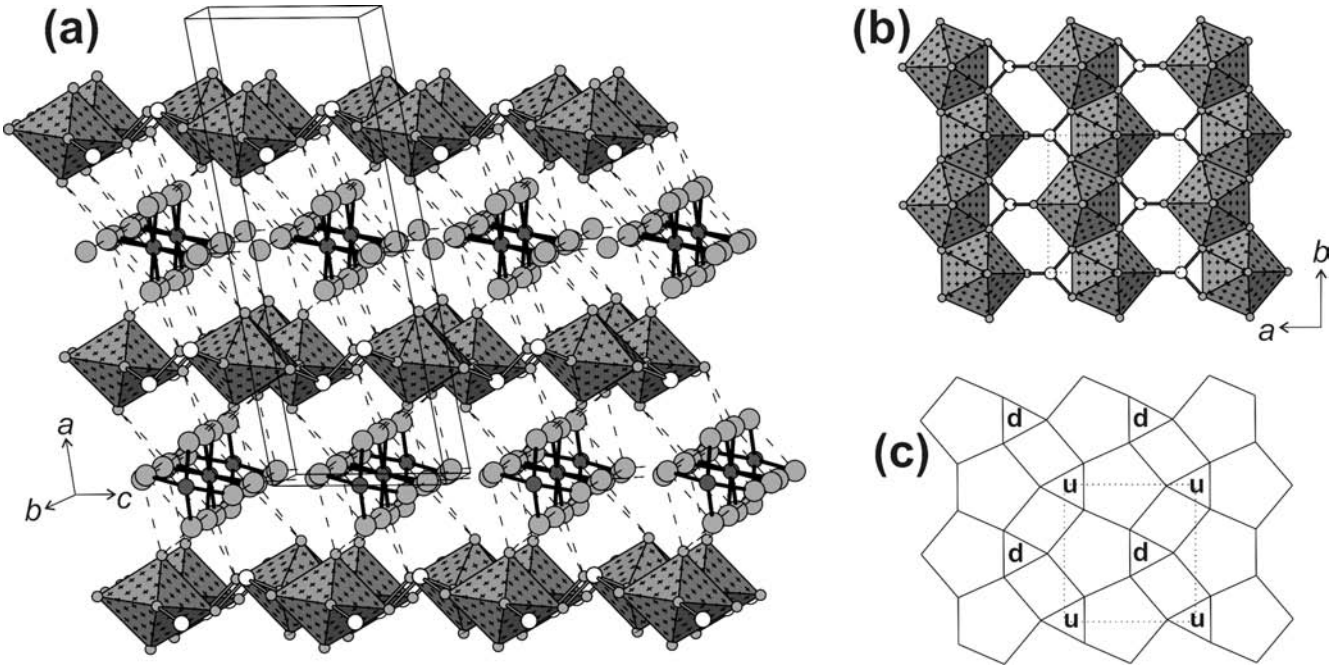

Fig. 4. The crystal structure of dymkovite. (a) projection, (b), top view of the uranyl arsenite layer, and (c) uranophane anion topology with the **u** and **d** symbols in the triangles showing orientations of arsenite groups up and down relative to the plane of the layer, respectively.

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