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ARAPOVITE, $(U,Th)(Ca,Na)_2(K_{1-x}\square_x)Si_8O_{20}\cdot H_2O$ — NEW MINERAL

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New mineral, uranium analogue of turkestanite, arapovite, was found among alkaline rocks of Dara-i-Pioz (Tajikistan). The mineral is represented by zonal areas 0.1-0.3 mm width in turkestanite crystals from polylithionite-aegirine-microcline rock. It is associated with stillwellite-(Ce), sogdianite, zektzerite, pyrochlore, hyalotekite, tazhikite group minerals, albite, and quartz. The mineral has dark-green color; it is transparent in the thin sections. The hardness is 5.5-6.0 on Mohs' scale, Dexp. = 3.43(2), Dcalc. = 3.414 g/cm^3. The mineral is optically uniaxial, negative, no = 1.615(2); ne = 1.610(2). It is partially metamict. Crystal structure was studied by single-crystal method. The mineral is tetragonal, sp. gr. P4/mcc. Unit cell parameters are following: a = 7.6506(4), c = 14.9318(9)Å, V = 873.9(1)Å^3, Z = 2. Crystal structure refinement was made on annealed material by 528 independent reflexes with R1 = 2.9%. Unit cell parameters of annealed mineral are following: a = 7.5505(4), c = 14.7104(4)Å, V = 838.6(1)Å. The main lines on powder X-ray diagram are [d, Å, (I, %), (hkl)]: 7.57 (14) (010), 7.39 (12) (002), 5.34(23) (100), 5.28 (38) (012), 3.37 (100) (120), 3.31 (58) (014), 2.640 (64) (024), 2.161(45) (224). Chemical composition (electron microprobe method, wt %, H_2O — Penfield method) is following: SiO_2 53.99, UO_2 16.63, ThO_2 10.57, Ce_2O_3 0.55, La_2O_3 0.14, Pr_2O_3 0.05, Nd_2O_3 0.62, Sm_2O_3 0.11, Eu_2O_3 0.14, Gd_2O_3 0.03, Dy_2O_3 0.13, PbO 0.82, CaO 8.11, Na_2O 2.54, K_2O 4.52, H_2O^+ 1.80, total 100.76. The empiric formula of arapovite is $(U_{0.55}Th_{0.36}Pb_{0.03}Ce_{0.03}Nd_{0.03}La_{0.01}Sm_{0.01}Eu_{0.01}Dy_{0.01})_{1.04}(Ca_{1.29}Na_{0.73})_{2.02}(K_{0.85}\square_{0.15})_{1.00}Si_8O_{20.06}\cdot 0.89H_2O$. The ideal formula is $(U,Th)(Ca,Na)_2(K_{1-x}\square_x)Si_8O_{20}\cdot H_2O$. The IR-spectrum is given. The mineral was named after Yu.A. Arapov, geologist, petrographer, worked at Turkestan-Alay Range.
3 tables, 3 figures, 7 references

In the alkaline rocks of Verkhnii Dara-i-Pioz massif (Tajikistan), silicates with twinned sixfold, fourfold, and recently discovered threefold silica-oxide rings are widespread. In 1965 the thorium mineral was described among representatives with fourfold rings under the name «alkali-enriched crystalline ekanite» (Ginzburg *et al.*, 1965), which was finished studying later and was named turkestanite (Pautov *et al.*, 1997). Moreover, in the rocks of this massif silicate with similar properties, with prevalence of uranium and thorium, containing large amount of water and described under the name «uranium hydrate variety of ekanite — UH-ekanite» (Semenov, Dusmatov, 1975) was found. One more uranium-thorium silicate similar to «UH-ekanite» but differed by significant small content of water and different amount of alkalis was found by authors during subsequent study of Dara-i-Pioz massif. The further study of the mineral allows distinguishing it as independent mineral species, uranium analogue of turkestanite. The mineral was named in honor of Yu.A. Arapov (1907 – 1988), famous geologist, participant of Pamirs-Tajik expedition firstly noted green thorium silicate on Dara-i-Pioz, author of numerous works on geochemistry, mineralogy, petrography of Middle Asia.

Occurrence and mineral assemblage

Arapovite was found during study of alkaline rocks of Verkhnii Dara-i-Pioz massif, which were collected by authors (L.A. Pautov, A.A. Agakhanov, V.Yu. Karpenko) together with P.V. Khvorov in the moraine of Dara-i-Pioz glacier (Garm Region, Tajikistan).

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[1] It was considered by the RMS KNMMN and approved by the IMA KNMMN on November 3, 2003

The mineralogy of the massif was considered in a number of publications (Dusmatov, 1968, 1971, etc.). Arapovite was found in the samples of rock composed mainly by microcline with subordinate amount of aegirine, polylithionite, bad-shaped crystals of stillwellite and turkestanite, small segregations of sogdianite and zektzerite replaced it. Rarely pyrochlore, hyalotekite, tazhikite group minerals, albite, and quartz were noted in this rock.

Arapovite was found in the form of small (0.1 – 0.3 mm) zones in large (up to 1 cm) bad-shaped crystals of turkestanite. Arapovite is spread both in central, and in edge zones of the crystals.

Physical properties

Arapovite has dark-green color; it is transparent in thin sections. In contrast to turkestanite arapovite has more deep green color connected to larger content of uranium. The luster is vitreous, pitchy. The cleavage and jointing are absent. The fracture is conchoidal. The hardness is 5.5 – 6 on Mohs' scale. Microindentation, VHN = 707 kgs/mm^2 (average value by 12 measurements with fluctuation of single measure from 682 to 766 kgs/mm^2) at load 100 g. The micro-indentation was measured by PMT-3 instrument calibrated on NaCl. The density of the mineral was determined by balancing of mineral grains in Clerichi solution; it is equal 3.43(2) g/cm^3. Arapovite is optically uniaxial, negative. Refractive indexes were measured by central screening method on rotated needle: $n_o = 1.615(2)$; $n_e = 1.610(2)$ (λ = 589 nm). The IR-spectrum of the mineral (Fig. 1) obtained by Specord-75IR (the sample was suspension on KBr base) has the following absorption bands: 3460, 1091 (shoulder), 1043, 797, 778, 590, 491 cm^{-1}; it is close to the IR-spectrum of turkestanite.

X-ray data

X-ray powder diagram of arapovite obtained by photomethod has small amount of diffusive lines (Tabl. 1) that is evidence of partially metamict state of the mineral. The following parameters of tetragonal unit cell were obtained by single-crystal study: a = 7.6506(4), c = 14.9318(9)Å, V = 873.9(1)Å^3, sp. gr. *P4/mcc*, *Z=2*. The mineral was annealed at 900°C during 3 hours in argon current for obtaining more detail X-ray powder diagram; after that the mineral gave clear X-ray diffractogram containing a lot of lines (Tabl. 1). X-ray powder diagram of arapovite is very close to data of turkestanite and steacyite by set of lines and their intensities.

The refinement of arapovite crystal structure was made on annealed material because of its partial metamict properties. The unit cell parameters of annealed mineral were decreased slightly; they are following: a = 7.5505(4), c = 14.7104(4)Å, V = 838.6(1)Å^3. The study was made with single-crystal diffractometer Bruker P4 (MoKα radiation, CCD detector). The crystal structure was refined with R_1 = 2.9% by 528 independent reflexes [$F_o > 4\sigma F_0$]. In the crystal structure of arapovite there is one tetrahedral site occupied entirely by Si with distance <Si – O> = 1.617 Å. Also there are two [8]-coordinated sites, A and B, occupied by (U,Th) and (Ca,Na) with distances <*A* – O> = 2.403 Å and <*B* – O> = 2.489 Å. Moreover, in the crys-

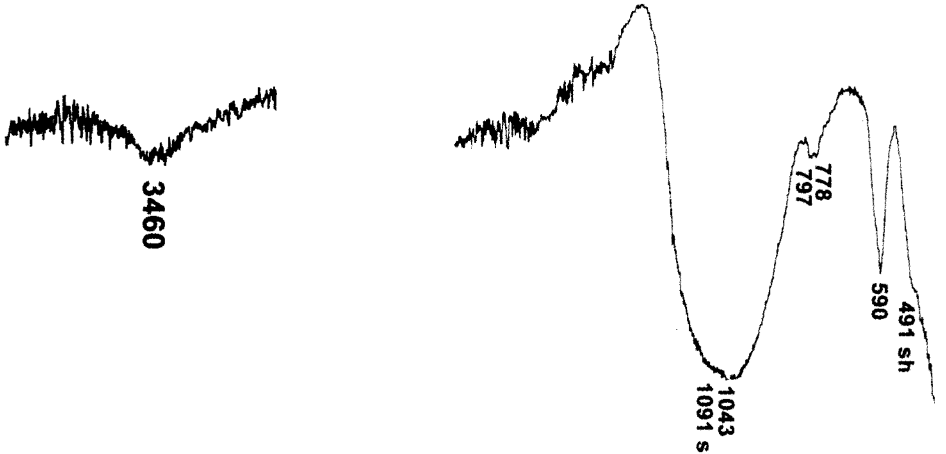

FIG. 1. The IR-spectrum of arapovite (Specord-75IR, the KBr tablet with mineral). Analyst Atali A. Agakhanov

tal structure of arapovite there is [12]-coordinated C-site occupied partially by potassium with distance <*C*−O> = 3.103Å. In the crystal structure of arapovite SiO_4 tetrahedra form twinned fourfold rings $[Si_8O_{20}]^{8-}$. The [8]-coordinated A- and B-polyhedra with mutual edges form the layers (001). These layers are joined in framework by $[Si_8O_{20}]$ groups (Fig. 3). The C atoms are located in the large holes of the framework. The topology of arapovite crystal structure is identical to that of turkestanite, $Th(Ca,Na)_2(K_{1-x}\square_x)Si_8O_{20}\cdot nH_2O$ (Kabalov *et al.*, 1988) and steacyite, $Th(Na,Ca)_2(K_{1-x}\square_x)Si_8O_{20}$ (Richard and Perrault, 1972).

Table 1. X-ray powder data of arapovite

1		*2*				
$I_{exp.}$	$d_{exp.}$	$I_{exp.}$	$d_{exp.}$	$I_{calc.}$	$d_{calc.}$	*hkl*
7	7.76	14	7.57	33	7.551	0 1 0
		12	7.39	58	7.355	0 0 2
8	5.40	23	5.34	26	5.339	1 0 0
		38	5.28	67	5.269	0 1 2
		3	4.33	10	4.321	1 1 2
10	3.41	100	3.37	100	3.372	1 2 0
8	3.37	58	3.31	80	3.306	0 1 4
3	3.10	9	3.07	15	3.069	1 2 2
		8	3.03	8	3.029	1 1 4
		15	2.672	16	2.670	2 2 0
9	2.67	64	2.640	55	2.634	0 2 4
2	2.56	21	2.515	18	2.517	0 3 0
1	2.52	15	2.493	13	2.487	1 2 4
		4	2.391	5	2.388	1 3 0
		1	2.334	3	2.332	0 1 6
		1	2.227	1	2.228	1 1 6
2	2.189	45	2.161	34	2.160	2 2 4
		11	2.080	10	2.077	2 3 1
		6	2.063	8	2.056	0 2 6
1	2.02	29	2.016	23	2.014	2 3 2
1	2.00	14	1.989	17	1.984	1 2 4
		8	1.888	13	1.888	0 4 0
		5	1.841	12	1.838	0 0 8
1	1.829	21	1.821	20	1.820	2 3 4
		11	1.808	13	1.806	2 2 6
		6	1.781	8	1.7770	1 4 2
		7	1.761	8	1.756	0 3 6
		16	1.689	11	1.688	2 4 0
1	1.647	30	1.644	19	1.646	2 4 2
		18	1.618	13	1.615	1 2 8
		4	1.537	14	1.534	2 4 4
		11	1.514	4	1.514	2 2 8
		7	1.483	14	1.485	0 3 8
		2	1.443	8	1.444	0 1 10
				6	1.440	3 3 6
		12	1.400	5	1.402	2 5 0
				3	1.397	0 5 4
		7	1.373	2	1.371	0 2 10

Note:

1 — non-annealed arapovite. URS-50IM, FeKa, Mn filter, RKD 57.3 camera, the lines on the debayegram are diffusive; 2 — annealed arapovite, diffractometer DRON-4, CuKa, the counter speed is 1 grad/min, graphite monochromator, quartz was the inner standard. Analyst A.A. Agakhanov

Chemical composition

The chemical composition of arapovite was performed by electron microprobe instrument JCXA-50A (JEOL) equipped by energy-dispersive spectrometer under accelerating voltage 20 kV and electron microprobe current 3 nA. The standards were following: microcline USNM143966 (Si, K), synthetic UO_2 (U), synthetic ThO_2 (Th), $LaPO_4$ (La), $CePO_4$ (Ce), NdP_5O_{14} (Nd), PrP_5O_{14} (Pr), SmP_5O_{14} (Sm), EuP_5O_{14} (Eu), $GdPO_4$ (Gd), Dy_2O (Dy), crocoite (Pb), anorthite USNM137041 (Ca), omphacite USNM110607 (Na). The concentrations were calculated with use of ZAF-correction. Six mineral grains were analyzed (Fig. 2). The water was determined by Penfield method from micro-weight (20 mg). The results of analyses are in the Tabl. 2. The empiric formula of arapovite calculated on 8 atoms of Si by analyses results is following: $(U_{0.55}Th_{0.36}Pb_{0.03}Ce_{0.03}Nd_{0.03}La_{0.01}Sm_{0.01}Eu_{0.01}Dy_{0.01})_{1.04}(Ca_{1.29}Na_{0.73})_{2.02}(K_{0.85}\square_{0.15})_{1.00}Si_8O_{20.06}\cdot 0.89H_2O$. The ideal formula of arapovite is: $(U,Th)(Ca,Na)_2(K_{1-x}\square_x)Si_8O_{20}\cdot H_2O$. The coincidence index is $(1-K_p/K_c) = 0.031$ (excellent).

Comparison with similar minerals

Arapovite, $(U,Th)(Ca,Na)_2(K_{1-x}\square_x)Si_8O_{20}\cdot H_2O$, is U^{4+}-analogue of turkestanite, $Th(Ca,Na)_2(K_{1-x}\square_x)Si_8O_{20}\cdot nH_2O$, and U^{4+}-Ca-analoge of steacyite, $Th(Na,Ca)_2(K_{1-x}\square_x)Si_8O_{20}$ (Tabl. 3). There is the continual isomorphous series between arapovite and turkestanite. Apparently, the presence of isomorphous series between arapovite, steacyite, and iraqite is possible, however, the intermediate phases weren't found in these series. The existence of arapovite as phase where C-site occupied predominantly by potassium is caused (according to valence balance) by that A-site of 4-valent cations is also occupied by some amount of

Table 2. Chemical composition of arapovite and «uranium hydrate ekanite (UH-ekanite)»

	*Arapovite**							*«UH-ekanite»***
	1	*2*	*3*	*4*	*5*	*6*	*average*	
SiO_2	54.25	53.62	54.27	53.86	54.10	53.86	53.99	48.00
UO_2	20.49	14.64	17.33	16.66	16.31	14.37	16.63	22.80
ThO_2	4.98	14.26	9.46	9.36	13.40	11.99	10.57	5.50
Ce_2O_3	0.71	0.19	0.56	0.80	0.22	0.83	0.55	
La_2O_3	0.20	0.10	0.14	0.13	0.06	0.18	0.14	
Pr_2O_3	0.00	0.13	0.19	0.00	0.00	0.00	0.05	
Nd_2O_3	0.76	0.45	0.92	0.73	0.32	0.55	0.62	
Sm_2O_3	0.19	0.05	0.23	0.05	0.12	0.01	0.11	
Eu_2O_3	0.47	0.06	0.00	0.28	0.00	0.00	0.14	
Gd_2O_3	0.03	0.00	0.00	0.14	0.00	0.00	0.03	
Dy_2O_3	0.13	0.29	0.35	0.00	0.01	0.02	0.13	
PbO	0.72	0.70	0.70	0.78	1.04	0.98	0.82	
CaO	8.48	8.11	8.45	8.09	7.31	8.21	8.11	8.24
Na_2O	2.29	2.24	2.52	3.24	2.49	2.47	2.54	0.70
K_2O	4.87	4.30	4.66	4.28	4.56	4.43	4.52	1.50
H_2O^+	1.80	1.80	1.80	1.80	1.80	1.80	1.80	13.76
Total	100.38	100.95	101.57	100.20	101.74	99.70	100.76	100.50
				Formula calculated on Si = 8				
Si^{+4}	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
U^{+4}	0.67	0.49	0.57	0.55	0.54	0.47	0.55	0.85
Th^{+4}	0.17	0.48	0.32	0.32	0.45	0.41	0.36	0.21
Ce^{+3}	0.04	0.01	0.03	0.04	0.01	0.05	0.03	
La^{+3}	0.01	0.01	0.01	0.01	0.00	0.01	0.01	
Pr^{+3}	0.00	0.00	0.01	0.00	0.00	0.00	0.00	
Nd^{+3}	0.04	0.02	0.05	0.04	0.02	0.03	0.03	
Sm^{+3}	0.01	0.00	0.01	0.00	0.01	0.00	0.01	
Eu^{+3}	0.02	0.00	0.00	0.01	0.00	0.00	0.01	
Gd^{+3}	0.00	0.00	0.00	0.01	0.00	0.00	0.00	
Dy^{+3}	0.01	0.01	0.02	0.00	0.00	0.00	0.01	
Pb^{+2}	0.03	0.03	0.03	0.03	0.04	0.04	0.03	
Ca^{+2}	1.34	1.30	1.33	1.29	1.16	1.31	1.29	1.47
Na^{+1}	0.66	0.65	0.72	0.93	0.71	0.71	0.73	0.23
K^{+1}	0.92	0.82	0.88	0.81	0.86	0.84	0.85	0.32
H^{+1}	1.77	1.79	1.77	1.78	1.78	1.78	1.78	15.30
O^{-2}	20.65	21.00	21.01	20.99	20.91	20.90	20.95	27.50

Note:

* — electron microprobe analyses. H_2O — Penfield method (analysts A.A. Agakhanov, V.Yu. Karpenko).

** — wet chemistry method. Analyst A.V. Bykova (the total 99.50 was given in the original) (Semenov, Dusmatov, 1975).

Table 3. Comparative description of arapovite, turkestanite, steacyite

	Arapovite	*Turkestanite*	*Steacyite*
Chemical formula	$(U,Th)(Ca,Na)_2(K_{1-x}\square_x)Si_8O_{20}\cdot H_2O$	$Th(Ca,Na_2(K_{1-x}\square_x)\ Si_8O_{20}\cdot nH_2O$	$Th(Na,Ca)_2(K_{1-x}\square_x)Si_8O_{20}$
Space group	*P4/mcc*	*P4/mcc*	*P4/mcc*
a, Å	7.65	7.59	7.58
c, Å	14.93	14.82	14.77
Z	2	2	2
The strong lines of X-ray powder diagram: $d_{exp.}(I)$	7.57(14) 7.39(12) 5.34(23) 5.28(38) 3.37(100) 3.31(58) 2.6(64) 2.161(45)	7.59(23) 7.40(20) 5.36(40) 5.31(70) 3.40(100) 3.34(65) 2.65(59) 2.175(25)	7.60(14) 7.42(11) 5.37(15) 5.3(45) 3.38(100) 3.32(55) 2.64(41) 2.00(26)
Density, g/cm³	3.43	3.36	302
Optic characteristics	uniaxial (-)	uniaxial (-)	uniaxial (-)
n_o	1.615	1.611	1.573
n_e	1.610	1.606	1.572

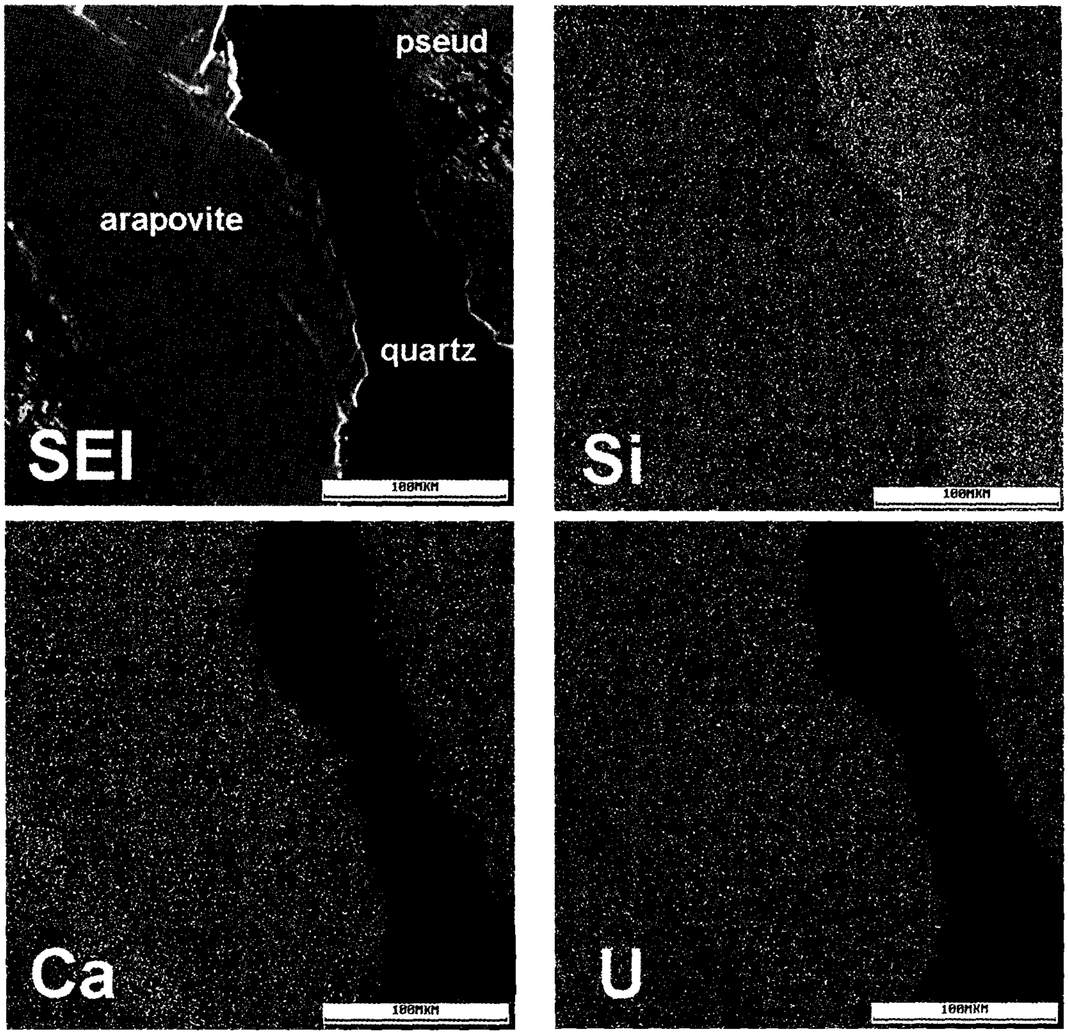

FIG. 2. The intergrowth of arapovite with quartz and the pseudomorph after arapovite. The image in SEI regime and in X-ray characteristic radiation of mentioned elements

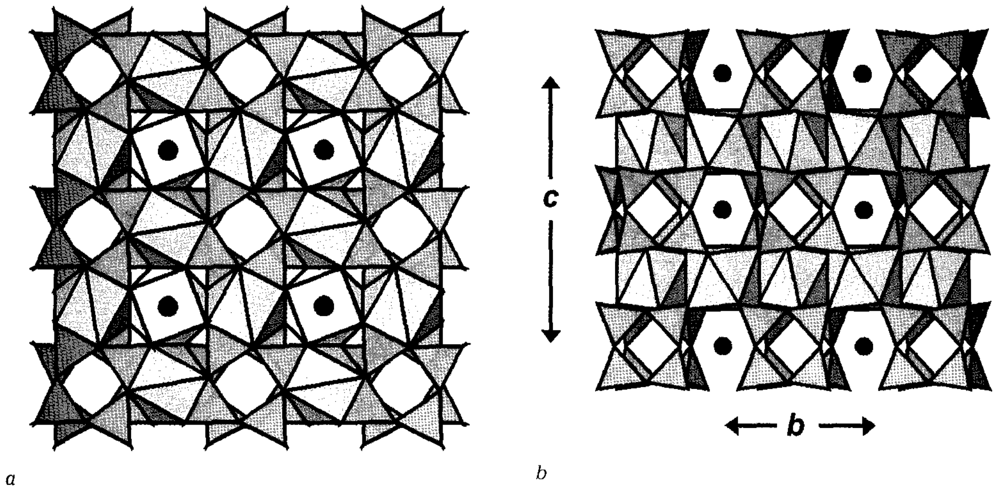

FIG. 3. Crystal structure of arapovite: a) projection on (001); b) projection on (100). Si tetrahedra are orange, A and B [8]-coordinated polyhedra are yellow and blue correspondingly, C atoms are shown as red circles

ions with smaller valence (Pb, REE), and B-site is occupied not only by calcium but also sodium. It isn't excluded that the presence in the nature of the end member with formula $UCa_2Si_8O_{20}$ is possible, however it isn't clear that this phase will have the crystal structure of arapovite or turkestanite type. The possibility of the presence in the nature the vacancy-dominant phase by C-site is confirmed by finding of «uranium hydrate variety of ekanite» (Semenov, Dusmatov, 1975), which chemical composition can be recalculated on following formula (Si = 8): $(U_{0.85}Th_{0.21})_{1.06}(Ca_{1.47}Na_{0.23})_{1.70}(\square_{0.68}K_{0.32})_{1.00}Si_8(O,OH)_{20}\cdot nH_2O$. Unfortunately, this phase remains while structurally unstudied.

The sample with arapovite was given to the Fersman Mineralogical Museum RAS (Moscow).

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