

**THE CRYSTAL STRUCTURE OF ARAPOVITE, $U^{4+} (Ca,Na)_2 (K_{1-x}\square_x) [Si_8 O_{20}]$,
 $x \approx 0.5$, A NEW MINERAL SPECIES OF THE STEACYITE GROUP
FROM THE DARA-I-PIOZ MORAINÉ, TIEN-SHAN MOUNTAINS, TAJIKISTAN**

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ABSTRACT

The crystal structure of arapovite, ideally $U^{4+} (Ca,Na)_2 (K_{1-x}\square_x) [Si_8 O_{20}]$, $x \approx 0.5$, tetragonal, a 7.5505(4), c 14.7104(9) Å, V 838.6(1) Å³, space group $P4/mcc$, $Z = 2$, D calc. 3.365 g/cm³, was refined to an R_1 index of 2.9% based on 528 observed [$F_o > 4\sigma F$] unique reflections measured with MoK α radiation on a Bruker $P4$ diffractometer with a 1K CCD area detector. In the crystal structure of arapovite, there is one tetrahedrally coordinated site solely occupied by Si, with $\langle Si-O \rangle = 1.617$ Å. There are two [8]-coordinated sites, A and B , occupied by ($U^{4+}_{0.59} Th_{0.26} Ca_{0.10} REE_{0.04}$) and ($Ca_{1.23} Na_{0.68} REE_{0.08} Ba_{0.01}$), with $\langle A-O \rangle = 2.403$ and $\langle B-O \rangle = 2.490$ Å. There is one [12]-coordinated site, C , partly occupied by K ($K_{0.52} \square_{0.48}$), with $\langle C-O \rangle = 3.103$ Å. In the crystal structure of arapovite, (SiO₄) tetrahedra form a double four-membered ring: [Si₈O₂₀]. Eight-coordinated A and B polyhedra share common edges to form a (001) sheet. The sheets are connected through [Si₈O₂₀] groups to form a framework; C atoms are situated in large cages within the framework. The topology of the arapovite structure is identical to that of turkestanite, Th (Ca,Na)₂ (K_{1-x}□_x) Si₈O₂₀ (H₂O)_n, and steacyite, Th (Na,Ca)₂ (K_{1-x}□_x) Si₈O₂₀, $x \approx 0.5$. The topology of silicate minerals with [Si₈O₂₀]⁸⁻ units, including ekanite, Th Ca₂ Si₈O₂₀, and litidionite, Na₂ K₂ Cu₂ Si₈O₂₀, is discussed.

Keywords: arapovite, U⁴⁺ silicate, crystal structure, [Si₈O₂₀] double ring, Dara-i-Pioz, Tajikistan.

SOMMAIRE

Nous avons affiné la structure cristalline de l'arapovite, dont la formule idéale est $U^{4+} (Ca,Na)_2 (K_{1-x}\square_x) [Si_8 O_{20}]$, $x \approx 0.5$, tétragonale, a 7.5505(4), c 14.7104(9) Å, V 838.6(1) Å³, groupe spatial $P4/mcc$, $Z = 2$, D (calc.) 3.365 g/cm³, jusqu'à un résidu R_1 de 2.9% en utilisant 528 réflexions distinctes observées [$F_o > 4\sigma F$] et mesurées avec rayonnement MoK α et un diffractomètre Bruker $P4$ muni d'un détecteur à aire 1K de type CCD. Dans la structure de l'arapovite, il y a un site à coordination tétraédrique uniquement occupé par le Si, avec $\langle Si-O \rangle = 1.617$ Å. Il y a deux sites à coordination [8], A et B , qu'occupent ($U^{4+}_{0.59} Th_{0.26} Ca_{0.10} TR_{0.04}$) et ($Ca_{1.23} Na_{0.68} TR_{0.08} Ba_{0.01}$), avec $\langle A-O \rangle = 2.403$ et $\langle B-O \rangle = 2.490$ Å. Il y a un site à coordination [12], C , partiellement rempli par le K ($K_{0.52} \square_{0.48}$), avec $\langle C-O \rangle = 3.103$ Å. Dans cette structure, les tétraèdres (SiO₄) forment un anneau double à quatre membres: [Si₈O₂₀]. Les polyèdres à huit coins renfermant A et B partagent des arêtes communes pour former un feuillet (001). Ces feuillets sont connectés grâce aux groupes [Si₈O₂₀] pour former une trame; les atomes de C occupent des cages volumineuses dans cette trame. La topologie de la structure de l'arapovite est identique à celle de la turkestanite, Th (Ca,Na)₂ (K_{1-x}□_x) Si₈O₂₀ (H₂O)_n, et celle de la steacyite, Th (Na,Ca)₂ (K_{1-x}□_x) Si₈O₂₀, $x \approx 0.5$. Nous évaluons la topologie des minéraux silicatés ayant des modules [Si₈O₂₀]⁸⁻, y inclus l'ékanite, Th Ca₂ Si₈O₂₀, et la litidionite, Na₂ K₂ Cu₂ Si₈O₂₀.

(Traduit par la Rédaction)

Mots-clés: arapovite, silicate de U⁴⁺, structure cristalline, anneau double [Si₈O₂₀], Dara-i-Pioz, Tajikistan.

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INTRODUCTION

Arapovite, $U^{4+} (Ca,Na)_2 (K_{1-x}\square_x) [Si_8 O_{20}]_x$, $x \approx 0.5$, is a new mineral species from the moraine of the Dara-i-Pioz glacier, the Alai mountain ridge, Tien-Shan Mountains, northern Tajikistan (Agakhanov *et al.* 2004). Arapovite is the seventh silicate with a double-ring module $[Si_n O_{2.5n}]$ described from the Dara-i-Pioz moraine. There are three types of double rings of tetrahedra known for silicates. A three-membered double ring $[Si_6 O_{15}]$ has been recently described in moskvinitite-(Y), $Na_2 K Y Si_6 O_{15}$, from the same locality (Sokolova *et al.* 2003). Four-membered $[Si_8 O_{20}]$ double-rings occur in three minerals with the general formula $^{[8]A} [^{[8]B}_2]^{[12]C} [Si_8 O_{20}] (H_2O)_n$, where $A = Th, REE$; $B = Ca, Na$; $C = K, \square$ (vacancy): steacyite, $Th (Na,Ca)_2 (K_{1-x}\square_x) Si_8 O_{20} (H_2O)_n$ (Richard & Perrault 1972, Perrault & Szymański 1982), iraqite-(La), $REE (Na,Ca)_2 (K_{1-x}\square_x) Si_8 O_{20} (H_2O)_n$ (Livingstone *et al.* 1976), and turkestanite, $Th (Ca,Na)_2 (K_{1-x}\square_x) Si_8 O_{20} (H_2O)_n$, $x = 0.5$ (Kabalov *et al.* 1998); the crystal structure of iraqite-(La) has not yet been refined. Six-membered double-rings, ideally $[Si_{12} O_{30}]$, occur in the 18 minerals of the milarite group with the general formula $^{[6]A}_2 [^{[9]B}_2]^{[12]C} [^{[18]D} [^4]T(2)_3 [^4]T(1)_{12} O_{30}]$, where $T(1) = Si, Al$; $T(2) = Li, Be, B, Mg, Al, Si, Mn^{2+}, Zn$; $A = Al, Fe^{3+}, Sn^{4+}, Mg, Zr, Fe^{2+}, Ca, Na, Y, REE$; $B = Na, H_2O, K, \square$; $C = K, Na, Ba, \square$; $D = \square$ (Forbes *et al.* 1972, Hawthorne *et al.* 1991). Here, we report the crystal structure and crystal chemistry of arapovite.

TABLE 1. CHEMICAL COMPOSITION (wt. %) AND UNIT FORMULA* (*apfu*) FOR ARAPOVITE

SiO ₂	55.08	Si	8.00
UO ₂	18.17	ΣT	8.00
ThO ₂	7.75		
CaO	8.43	U ⁴⁺	0.59
Dy ₂ O ₃	0.35	Th	0.26
Sm ₂ O ₃	0.23	Ca	0.10
Pr ₂ O ₃	0.19	Dy	0.02
Na ₂ O	2.39	Sm	0.01
Nd ₂ O ₃	0.92	Pr	0.01
Ce ₂ O ₃	0.56	ΣA	0.99
BaO	0.18		
K ₂ O	2.78	Ca	1.23
Σ	97.03	Na	0.68
		Nd	0.05
		Ce	0.03
		Ba	0.01
		ΣB	2.00
		K	0.52
		ΣC	0.52
		O	20

* The structural formula calculated on the basis of 8 Si *apfu*.

ELECTRON-MICROPROBE ANALYSIS

The chemical composition of arapovite (Table 1) was established on annealed material with a Cameca SX 100 electron microprobe operating in wavelength-dispersion mode with an accelerating voltage of 15 kV, a specimen current of 15 nA, a beam size of 20 μm and counting times on peak and background of 20 and 10 s, respectively. The following standards and crystals were used for *K, L* or *M* X-ray lines: Na: albite; Si, Ca: diopside; Al, K: orthoclase; Th: ThO₂; Sr: strontianite; Ba: barite; U: UO₂; Pb: PbTe. Data were reduced using the X-PHI procedure (Merlet 1992).

Concentrations of REE elements were determined titrimetrically after chromatographic partition on unannealed material. On the basis of 8 Si *apfu* (atoms per formula unit), the following chemical formula for arapovite was obtained: $(U^{4+}_{0.59} Th_{0.26} Ca_{0.10} Dy_{0.02} Sm_{0.01} Pr_{0.01})_{\Sigma 0.99} (Ca_{1.23} Na_{0.68} Nd_{0.05} Ce_{0.03} Ba_{0.01})_{\Sigma 2.00} (K_{0.52} \square_{0.48})_{\Sigma 1.00} Si_8 O_{20}$, with an ideal formula of $U^{4+} (Ca,Na)_2 (K_{1-x}\square_x) [Si_8 O_{20}]_x$, $x \approx 0.5$.

COLLECTION OF X-RAY DATA AND STRUCTURE REFINEMENT

The highly metamict natural crystals of arapovite gave an indistinct X-ray-diffraction pattern, and it was impossible to refine the structure. Arapovite was annealed for 3.5 hours up to 1100°C in air. Single-crystal X-ray-diffraction data for an annealed single crystal of arapovite were collected with a Bruker P4 diffractometer equipped with MoK α X-radiation and a 1K CCD detector. Integrated intensities of 8780 reflections with $10 < h < 10$, $10 < k < 10$, $20 < l < 20$ were collected up to $2\theta = 60.08^\circ$ using 60 s per frame. The refined cell-parameters (Table 2) were obtained from 4657 reflections ($I > 10 \sigma I$). An empirical absorption correction (SADABS, Sheldrick 1998) was applied.

The crystal structure of arapovite was refined to the final R_1 index of 2.9% using atom coordinates of turkestanite (Kabalov *et al.* 1998) as the initial model and the SHELXTL 5.1 system of programs (Sheldrick 1997). Scattering factors for neutral atoms were taken from the International Tables for X-ray Crystallography (1992). Site occupancies were refined for the *A, B* and *C* sites with the scattering curves of U, Ca and K. Details of the X-ray data collection and structure refinement are given in Table 2. Residual weak maxima [two maxima of 3.4 *e* and 1.1 *e* located 0.75 Å and 1.74 Å from the *U* site, respectively, and one maximum of 1.1 *e* located 0.87 Å from the *K* site] were present in difference-Fourier maps calculated at the final stages of refinement. Final atom-parameters for arapovite are given in Table 3, selected interatomic distances are presented in Table 4, refined site-scattering values are given in Table 5, and a bond-valence analysis is shown in Table 6. Structure factors may be obtained from The

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DESCRIPTION OF THE CRYSTAL STRUCTURE

Cation coordination

There is one *Si* site, tetrahedrally coordinated by O atoms and fully occupied by Si with an $\langle Si-O \rangle$ distance of 1.617 Å. The shortest *Si-O* distance, $Si-O(3) = 1.577(3)$ Å, involves a bond to a non-bridging O atom (Table 6), whereas all other O atoms are bonded to two Si atoms. There are two sites, *A* and *B*, coordinated by eight O atoms with $\langle A-O \rangle$ and $\langle B-O \rangle$ distances of 2.403 and 2.490 Å, respectively. The total refined scattering at the *A* and *B* sites is 79.4(4) and 37.1(3) *epfu* (electrons per formula unit) and the analogous scattering calculated from the unit formula (Tables 1, 5) is 82.2 and 37.4 *epfu*, respectively. Thus the *A* and *B* site-populations were assigned as 0.59 $U^{4+} + 0.26 Th + 0.10 Ca + 0.02 Dy + 0.01 Sm + 0.01 Pr$ and 1.23 $Ca + 0.68 Na +$

0.05 $Nd + 0.03 Ce + 0.01 Ba$, following the unit formula (Table 1). There is one *C* site coordinated by twelve O atoms, with a $\langle C-O \rangle$ distance of 3.103 Å. The [12]-coordinated *C* site is partly occupied by K: 0.52 K + 0.48 □.

Structure topology

Eight (SiO_4) tetrahedra share corners to form a four-membered double-ring of the form $[Si_8O_{20}]$. The (AO_8) and (BO_8) polyhedra share edges to form a sheet parallel to (001) (Fig. 1a). In the sheet, each *A* polyhedron shares common edges with four *B* polyhedra, and each *B* polyhedron shares common edges with two *A* polyhedra, the ratio *A* : *B* being 1 : 2. These sheets are linked in the *c* direction by $[Si_8O_{20}]$ double-rings, forming a mixed-polyhedron framework (Fig. 1b). Large cages of the framework occlude [12]-coordinated *C* sites (Fig. 1c). The *C* cations are situated at the same level along the *c* direction as the $[Si_8O_{20}]$ double-rings. The topology of the arapovite structure is identical to that of steacyite (Richard & Perrault 1972) and turkestanite (Kabalov *et al.* 1998).

TABLE 2. MISCELLANEOUS REFINEMENT DATA FOR ARAPOVITE

<i>a</i> (Å)	7.5505(4)
<i>c</i>	14.7104(9)
<i>V</i> (Å ³)	838.6(1)
Space group	<i>P4/mcc</i>
<i>Z</i>	2
Absorption coefficient (mm ⁻¹)	9.64
<i>F</i> (000)	799.0
<i>D</i> _{calc.} (g/cm ³)	3.365
Crystal size (mm)	0.120 x 0.100 x 0.080
Radiation/filter	MoK α /graphite
2 θ -range for data collection (°)	60.08
<i>R</i> (int) (%)	7.3
Reflections collected	8780
Independent reflections	649
$F_o > 4\sigma F_o $	528
Refinement method	Full-matrix least squares on F^2 , fixed weights $\propto 1/\sigma F_o ^2$
Goodness of fit on F^2	1.064
Final $R_{(obs)}$ (%) [$F_o > 4\sigma F_o $]	$R_1 = 2.9$
<i>R</i> indices (all data) (%)	$R_1 = 4.3$ $wR_2 = 7.6$ GoF = 1.064

RELATED MINERALS

Other minerals with $[Si_8O_{20}]$ units

Two minerals contain a silicate unit of different bond-topology but the same stoichiometry as that in arapovite: ekanite, $Th Ca_2 [Si_8O_{20}]$, *a* 7.483(3), *c* 14.893(6) Å, *V* 833.9 Å³, *Z* = 2, space group *I422* (Szymański *et al.* 1982), and litidionite, $Na_2 K_2 Cu_2 [Si_8O_{20}]$, *a* 9.800(10), *b* 8.010(10), *c* 6.970(10) Å, α 114.1(1), β 99.5(1), γ 105.6(1)°, *V* 456.8 Å³, *Z* = 2, space group *P1* (Pozas *et al.* 1975). The $[Si_8O_{20}]$ units in these minerals are a sheet and a chain, respectively. The sheet in the crystal structure of ekanite consists of four- and eight-membered rings of tetrahedra (Fig. 2a). Polyhedra containing [8]-coordinated Th and Ca form a sheet identical to that in the structure of arapovite (Fig. 1a). In the crystal structure of ekanite, $[Si_8O_{20}]$ sheets and sheets of Th and Ca polyhedra alternate along the *c* direction (Fig. 2b). Figure 2c shows a general view of the mixed framework in the crystal structure of ekanite,

TABLE 3. FINAL ATOM POSITIONS AND DISPLACEMENT PARAMETERS (Å²) FOR ARAPOVITE

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
<i>A</i>	0	0	1/4	0.0097(2)	0.0071(2)	0.0071(2)	0.0149(3)	0	0	0
<i>B</i>	0	1/2	1/4	0.0141(6)	0.0134(9)	0.0124(9)	0.0165(9)	0	0	0
<i>C</i>	0	0	0	0.0339(13)	0.0288(18)	0.0288(18)	0.0442(32)	0	0	0
Si	0.2594(2)	0.3354(2)	0.10846(7)	0.0107(3)	0.0093(6)	0.0097(6)	0.0132(6)	0.0001(4)	0.0008(4)	0.0001(4)
O(1)	-0.2362(6)	0.6845(8)	0	0.0229(11)	0.0263(27)	0.0295(28)	0.0129(20)	0	0	0.0000(22)
O(2)	0.4538(4)	0.2567(5)	0.1361(2)	0.0172(8)	0.0105(16)	0.0191(17)	0.0221(16)	0.0036(13)	0.0004(12)	0.0005(12)
O(3)	-0.1026(4)	0.2508(4)	0.3357(2)	0.0157(7)	0.0130(16)	0.0138(15)	0.0202(14)	-0.0026(13)	0.0037(13)	-0.0001(12)

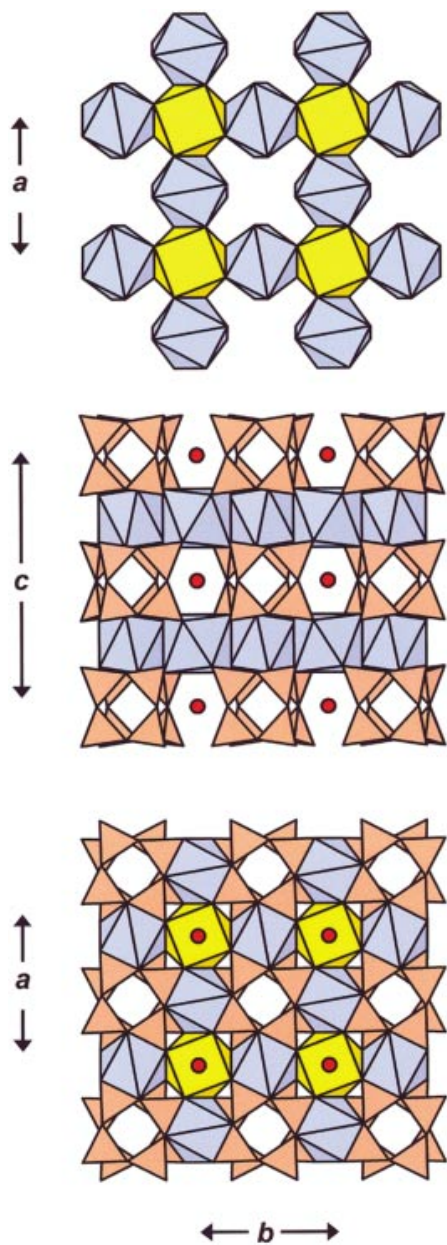


FIG. 1. The crystal structure of arapovite: (a) a sheet of [8]-coordinated *A* and *B* polyhedra; (b) the structure projected onto (100); (c) the structure projected onto (001); Si tetrahedra are orange, *A* and *B* polyhedra are yellow and blue, *C* atoms are shown as red circles.

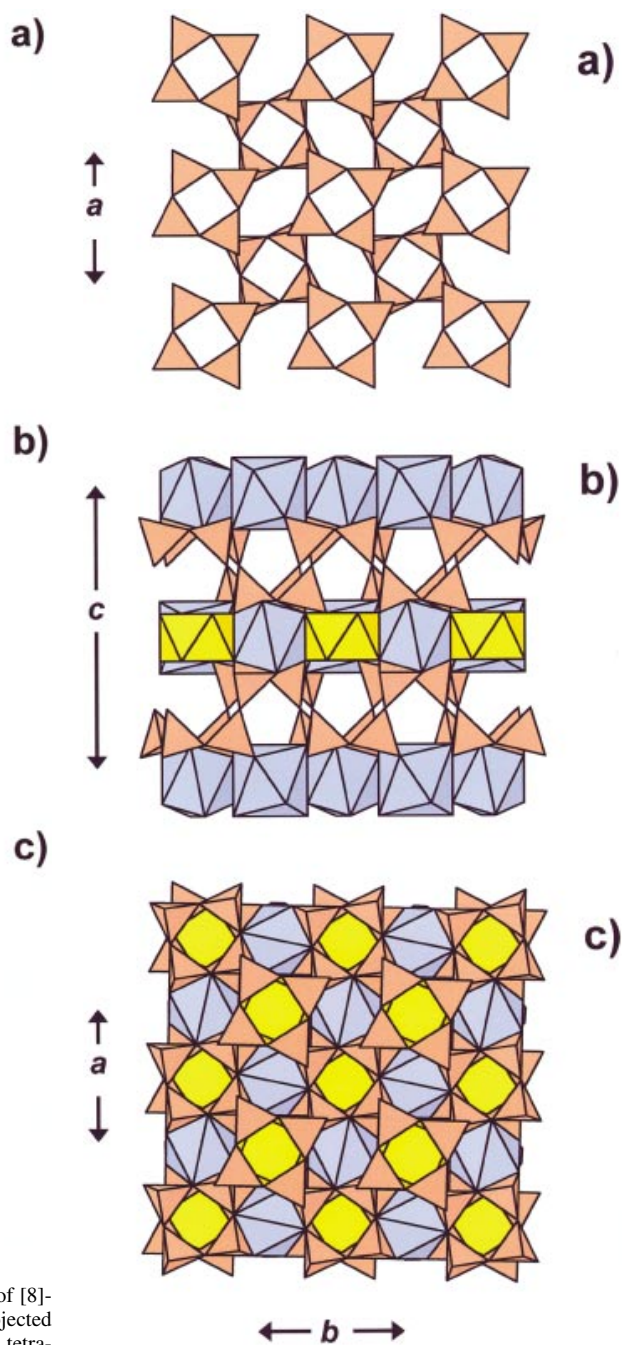


FIG. 2. The crystal structure of ekanite: (a) the Si-O sheet; (b) the structure projected onto (100); (c) the structure projected onto (001); Si tetrahedra are orange, [8]-coordinated Ca and Th polyhedra are blue and yellow, respectively.

formed through linkage of (SiO₄) tetrahedra and [8]-coordinated polyhedra.

The chain [Si₈O₂₀]⁸⁻ in the crystal structure of litidionite is a combination of four- and eight-membered rings (Fig. 3a). Polyhedra containing [5]-coordinated Ca and polyhedra containing [7]-coordinated Na share common edges to form chains along [001] (Figs. 3b, c). The (SiO₄) tetrahedra and (CaO₅) and (NaO₇) polyhedra share common vertices to form a mixed-polyhedron framework (Fig. 3c).

Distribution of minerals of (Si_nO_{2.5n}) stoichiometry

There are twenty-three minerals that contain double rings of tetrahedra of the form [Si_nO_{2.5n}], where $n = 3, 4$ and 6. There are also eleven minerals that have similar stoichiometries but bond topologies not involving silicate rings. As described above, six minerals have nonring [Si₈O₂₀] units, and four minerals have [Si₈O₂₀] double-rings. The 18 minerals of the milarite-group have six-membered [Si₁₂O₃₀] double-rings in their crystal structure. There is only one mineral with the same stoichiometry as milarite, but with a different topology: miserite, K₂Ca₁₀(Y,REE)₂[Si₂O₇]₂[Si₁₂O₃₀](OH)₂F₂, contains a chain of the form [Si₁₂O₃₀] (Scott 1976). A unit of the form [Si₆O₁₅] occurs in nine minerals. A three-membered double-ring occurs in the crystal structure of moskvinit-(Y), Na₂K(Y,REE)[Si₆O₁₅]. A chain of the form [Si₆O₁₅] occurs in the crystal structures of five minerals. An extended (or elpidite) chain was described in crystal structures of elpidite, Na₂Zr[Si₆O₁₅](H₂O)₃ (Cannillo *et al.* 1973) and epididymite,

TABLE 4. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN ARAPOVITE

Si-O(1)	1.612(1)	A-O(3) x8	2.403(3)
Si-O(2)	1.635(4)		
Si-O(2)a	1.643(3)	B-O(2) x4	2.586(3)
Si-O(3)	<u>1.577(3)</u>	B-O(3) x4	<u>2.393(3)</u>
<Si-O>	1.617	<B-O>	2.490
Si _b -O(1)-Si _c	163.6(4)	C-O(1) x4	2.976(6)
Si-O(2)-Si _d	143.5(2)	C-O(3) x8	<u>3.167(3)</u>
		<C-O>	3.103

a: y, -x+1, z; b: -x, -y+1, -z; c: -x, -y+1, z; d: -y+1, x, z

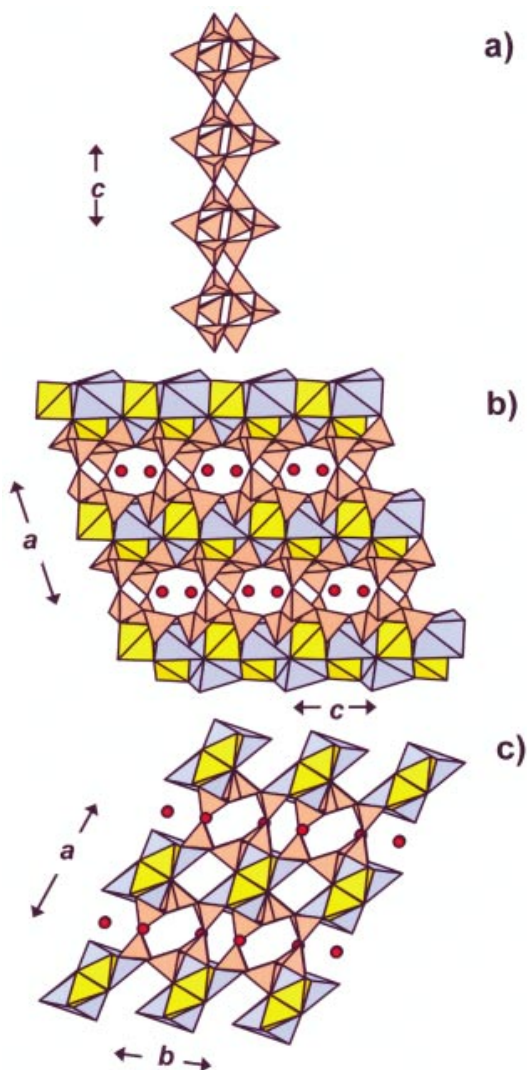


FIG. 3. The crystal structure of litidionite: (a) the Si-O chain; (b) the structure viewed down the b axis; (c) the structure viewed down the c axis. The [5]-coordinated Ca polyhedra are yellow, the [7]-coordinated Na polyhedra are blue, the Si tetrahedra are orange, and the K atoms are shown as red circles.

TABLE 5. REFINED SITE-SCATTERING VALUES ($epfu$) AND ASSIGNED SITE-POPULATIONS ($apfu$) FOR ARAPOVITE

Refined site-scattering	Site population	Calculated site-scattering	<X-O> _{calc} * (Å)	<X-O> _{obs} (Å)
A 79.4(4)	0.59 U ⁴⁺ + 0.26 Th + 0.10 Ca + 0.02 Dy + 0.01 Sm + 0.01 Pr	82.2	2.28	2.40
B 37.1(4)	1.23 Ca + 0.68 Na + 0.05 Nd + 0.03 Ce + 0.01 Ba	37.4	2.49	2.49
C 9.1(1)	0.52 K + 0.48 □	9.9	3.02	3.10

*Calculated by summing constituent ionic radii; values from Shannon (1976)

TABLE 6. BOND-VALENCES* (vu) FOR ARAPOVITE

	A	B	C	Si	Σ
O(1)			0.041 ¹⁴	1.027 ²	2.095
O(2)		0.186 ¹⁴		0.966 0.946	2.098
O(3)	0.450 ⁸	0.277 ¹⁴	0.023 ¹⁸	1.128	1.878
Σ	3.603	1.853	0.348	4.067	

* Bond-valence curves are from Brown (1981)

$\text{Na}_2\text{Be}_2[\text{Si}_6\text{O}_{15}](\text{H}_2\text{O})$ (Pobedimskaya & Belov 1956). A kinked (or tuhualite) chain was described in the crystal structures of tuhualite, $(\text{Na},\text{K})\text{Fe}^{2+}\text{Fe}^{3+}[\text{Si}_6\text{O}_{15}]$ (Merlino 1969), zektzerite, $\text{NaLiZr}[\text{Si}_6\text{O}_{15}]$ (Ghose & Wan 1978), and emeleusite, $\text{Na}_2\text{LiFe}^{3+}[\text{Si}_6\text{O}_{15}]$ (Johnsen *et al.* 1978). A sheet of the form $[\text{Si}_6\text{O}_{15}]$, with of 4-, 6- and 8-membered rings of tetrahedra, occurs in crystal structures of armstrongite, $\text{CaZr}[\text{Si}_6\text{O}_{15}](\text{H}_2\text{O})_{2.5}$ (Kashaev & Sapozhnikov 1978), dalyite, $\text{K}_2\text{Zr}[\text{Si}_6\text{O}_{15}]$ (Fleet 1965), and davanite, $\text{K}_2\text{Ti}^{4+}[\text{Si}_6\text{O}_{15}]$ (Gebert 1983).

Figure 4 shows the distribution of minerals of $(\text{Si}_n\text{O}_{2.5n})$ stoichiometry. Where $n = 3$, double-rings are rare and the structure topology is dominated by other connectivities. Where $n = 4$, there is a similar number of double-rings as other connectivities. Where $n = 6$, double-rings dominate the topology of the structure, and other connectivities are rare.

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REFERENCES

- AGAKHANOV, A.A., PAUTOV, L.A., UVAROVA, YU.A., SOKOLOVA, E. & HAWTHORNE F.C. (2004): Arapovite – a new mineral from the Dara-i-Pioz, Tien Shan. *Zap. Vser. Mineral. Obshchest.* **133**(?), (in press).
- BROWN, I.D. (1981): The bond-valence method: an empirical approach to chemical structure and bonding. *In* Structure and Bonding in Crystals II (M. O'Keeffe & A. Navrotsky, eds.). Academic Press, New York, N.Y. (1-30).
- CANNILLO, E., ROSSI, G. & UNGARETTI, L. (1973): The crystal structure of elpidite. *Am. Mineral.* **58**, 106-109.
- FLEET, S.G. (1965): The crystal structure of dalyite. *Z. Kristallogr.* **121**, 349-368.
- FORBES, W.C., BAUR, W.H. & KHAN, A.A. (1972): Crystal chemistry of milarite-type minerals. *Am. Mineral.* **57**, 463-472.
- GEBERT, W., MEDENBACH, O. & FLÖRKE, O.W. (1983): Darstellung und Kristallographie von $\text{K}_2\text{TiSi}_6\text{O}_{15}$ Isotyp mit Dalyit $\text{K}_2\text{ZrSi}_6\text{O}_{15}$. *Tschermaks. Mineral. Petrogr. Mitt.* **31**, 69-79.
- GHOSE, S. & WAN, CHE'NG (1978): Zektzerite, $\text{NaLiZrSi}_6\text{O}_{15}$: a silicate with six-tetrahedral-repeat double chains. *Am. Mineral.* **63**, 304-310.
- HAWTHORNE, F.C., KIMATA, M., ČERNÝ, P., BALL, N., ROSSMAN, G.R. & GRICE, J.D. (1991): The crystal chemistry of the milarite-group minerals. *Am. Mineral.* **76**, 1836-1856.
- INTERNATIONAL TABLES FOR X-RAY CRYSTALLOGRAPHY (Vol. C) (1992): Kluwer Academic Publishers, Dordrecht, The Netherlands.
- JOHNSEN, O., NIELSEN, K. & SOTOFTE, I. (1978): The crystal structure of emeleusite, a novel example of Sechser-Doppelkette. *Z. Kristallogr.* **147**, 297-306.
- KABALOV, YU.K., SOKOLOVA, E.V., PAUTOV, L.A. & SCHNEIDER, J. (1998): Crystal structure of a new mineral turkestanite: a calcium analogue of steacyite. *Crystallogr. Rep.* **43**, 584-588.
- KASHAEV, A.A. & SAPOZHNIKOV, A.N. (1978): Crystal structure of armstrongite. *Sov. Phys. Crystallogr.* **23**, 539-542.
- LIVINGSTONE, A., ATKIN, D., HUTCHINSON, D. & AL-HERMEZI, H.M. (1976): Iraqite, a new rare-earth mineral of the ekanite group. *Mineral. Mag.* **40**, 441-445.
- MERLET, C. (1992): Quantitative electron probe microanalysis. New accurate $\phi(\rho Z)$ description. *Mikrochim. Acta* **12**, 107-115.
- MERLINO, S. (1969): Tuhualite crystal structure. *Science* **166**, 1399-1401.

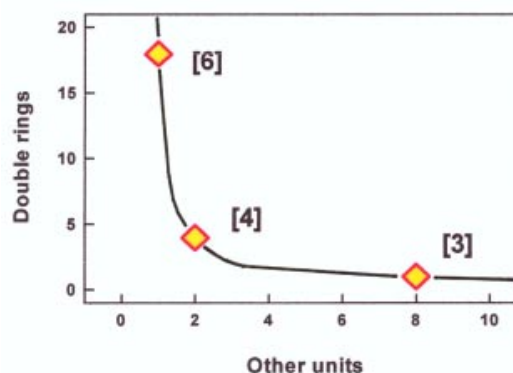


FIG. 4. The distribution of minerals of $(\text{Si}_n\text{O}_{2.5n})$ stoichiometry; n is shown in square brackets.

- PERRAULT, G. & SZYMAŃSKI, J.T. (1982): Steacyite, a new name and a re-evaluation of the nomenclature of "ekinite"-group minerals. *Can. Mineral.* **20**, 59-63.
- POBEDIMSKAYA, E.A. & BELOV, N.V. (1956): The crystal structure of epididymite. A new type of infinite silicoxygenous chains (bands). *Dokl. Akad. Nauk SSSR* **129**, 900-903 (in Russ.).
- POZAS, J.M.M., ROSSI, G. & TAZZOLI, V. (1975): Re-examination and crystal structure analysis of litidionite. *Am. Mineral.* **60**, 471-474.
- RICHARD, P. & PERRAULT, G. (1972): Structure cristalline de l'ekinite de St.-Hilaire, P.Q. *Acta Crystallogr.* **B28**, 1994-1999.
- SCOTT, J.D. (1976): Crystal structure of miserite, a Zoltai type-5 structure. *Can. Mineral.* **14**, 515-528.
- SHANNON, R.D. (1976): Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr.* **A32**, 751-767.
- SHELDRIK, G.M. (1997): *SHELX-97: Program for the Solution and Refinement of Crystal Structures*. Siemens Energy and Automation, Madison, Wisconsin.
- _____ (1998): *SADABS User Guide*. University of Göttingen, Göttingen, Germany.
- SOKOLOVA, E., HAWTHORNE, F.C., AGAKHANOV, A.A. & PAUTOV, L.A. (2003): The crystal structure of moskvinite-(Y), Na₂ K (Y,REE) [Si₆O₁₅], a new silicate mineral with [Si₆O₁₅] three-membered double-rings from the Dara-i-Pioz moraine, Tien-Shan Mountains, Tajikistan. *Can. Mineral.* **41**, 513-520.
- SZYMAŃSKI, J.T., OWENS, D.R., ROBERTS, A.C., ANSELL, H.G. & CHAO, G.Y. (1982): A mineralogical study and crystal-structure determination of non-metamict ekanite, ThCa₂Si₈O₂₀. *Can. Mineral.* **20**, 65-75.

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