

**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) Å<sup>3</sup>, space group  $P4/mcc$ ,  $Z = 2$ ,  $D$  calc. 3.365 g/cm<sup>3</sup>, was refined to an  $R_1$  index of 2.9% based on 528 observed [ $F_o > 4\sigma F$ ] unique reflections measured with MoK $\alpha$  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, (SiO<sub>4</sub>) tetrahedra form a double four-membered ring: [Si<sub>8</sub>O<sub>20</sub>]. Eight-coordinated  $A$  and  $B$  polyhedra share common edges to form a (001) sheet. The sheets are connected through [Si<sub>8</sub>O<sub>20</sub>] 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)<sub>2</sub> (K<sub>1-x</sub>□<sub>x</sub>) Si<sub>8</sub>O<sub>20</sub> (H<sub>2</sub>O)<sub>n</sub>, and steacyite, Th (Na,Ca)<sub>2</sub> (K<sub>1-x</sub>□<sub>x</sub>) Si<sub>8</sub>O<sub>20</sub>,  $x \approx 0.5$ . The topology of silicate minerals with [Si<sub>8</sub>O<sub>20</sub>]<sup>8-</sup> units, including ekanite, Th Ca<sub>2</sub> Si<sub>8</sub>O<sub>20</sub>, and litidionite, Na<sub>2</sub> K<sub>2</sub> Cu<sub>2</sub> Si<sub>8</sub>O<sub>20</sub>, is discussed.

*Keywords:* arapovite, U<sup>4+</sup> silicate, crystal structure, [Si<sub>8</sub>O<sub>20</sub>] 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) Å<sup>3</sup>, groupe spatial  $P4/mcc$ ,  $Z = 2$ ,  $D$  (calc.) 3.365 g/cm<sup>3</sup>, 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 $\alpha$  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 (SiO<sub>4</sub>) forment un anneau double à quatre membres: [Si<sub>8</sub>O<sub>20</sub>]. 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 [Si<sub>8</sub>O<sub>20</sub>] 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)<sub>2</sub> (K<sub>1-x</sub>□<sub>x</sub>) Si<sub>8</sub>O<sub>20</sub> (H<sub>2</sub>O)<sub>n</sub>, et celle de la steacyite, Th (Na,Ca)<sub>2</sub> (K<sub>1-x</sub>□<sub>x</sub>) Si<sub>8</sub>O<sub>20</sub>,  $x \approx 0.5$ . Nous évaluons la topologie des minéraux silicatés ayant des modules [Si<sub>8</sub>O<sub>20</sub>]<sup>8-</sup>, y inclus l'ékanite, Th Ca<sub>2</sub> Si<sub>8</sub>O<sub>20</sub>, et la litidionite, Na<sub>2</sub> K<sub>2</sub> Cu<sub>2</sub> Si<sub>8</sub>O<sub>20</sub>.

(Traduit par la Rédaction)

*Mots-clés:* arapovite, silicate de U<sup>4+</sup>, structure cristalline, anneau double [Si<sub>8</sub>O<sub>20</sub>], 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 <sub>2</sub>	55.08	Si	8.00
UO <sub>2</sub>	18.17	ΣT	8.00
ThO <sub>2</sub>	7.75		
CaO	8.43	U <sup>4+</sup>	0.59
Dy <sub>2</sub> O <sub>3</sub>	0.35	Th	0.26
Sm <sub>2</sub> O <sub>3</sub>	0.23	Ca	0.10
Pr <sub>2</sub> O <sub>3</sub>	0.19	Dy	0.02
Na <sub>2</sub> O	2.39	Sm	0.01
Nd <sub>2</sub> O <sub>3</sub>	0.92	Pr	0.01
Ce <sub>2</sub> O <sub>3</sub>	0.56	ΣA	0.99
BaO	0.18		
K <sub>2</sub> 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: ThO<sub>2</sub>; Sr: strontianite; Ba: barite; U: UO<sub>2</sub>; 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 MoKα 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  $K + 0.48 \square$ .

#### 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 <sup>3</sup> )	838.6(1)
Space group	<i>P4/mcc</i>
<i>Z</i>	2
Absorption coefficient (mm <sup>-1</sup> )	9.64
<i>F</i> (000)	799.0
<i>D</i> <sub>calc.</sub> (g/cm <sup>3</sup> )	3.365
Crystal size (mm)	0.120 x 0.100 x 0.080
Radiation/filter	MoK $\alpha$ /graphite
2 $\theta$ -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 Å<sup>3</sup>, *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,  $\alpha$  114.1(1),  $\beta$  99.5(1),  $\gamma$  105.6(1)°, *V* 456.8 Å<sup>3</sup>, *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 (Å<sup>2</sup>) FOR ARAPOVITE

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>23</sub>	<i>U</i> <sub>13</sub>	<i>U</i> <sub>12</sub>
<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)

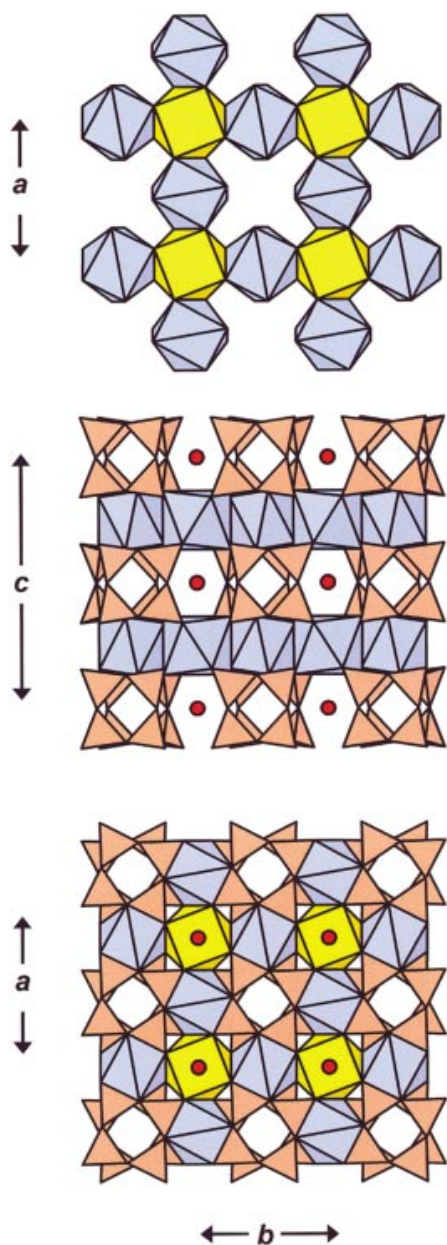


FIG. 1. The crystal structure of arapovite: (a) a sheet of [8]-coordinated *A* and *B* polyhedra; (b) the structure projected onto (100); (c) the structure projected onto (001); Si tetrahedra are orange, *A* and *B* polyhedra are yellow and blue, *C* atoms are shown as red circles.

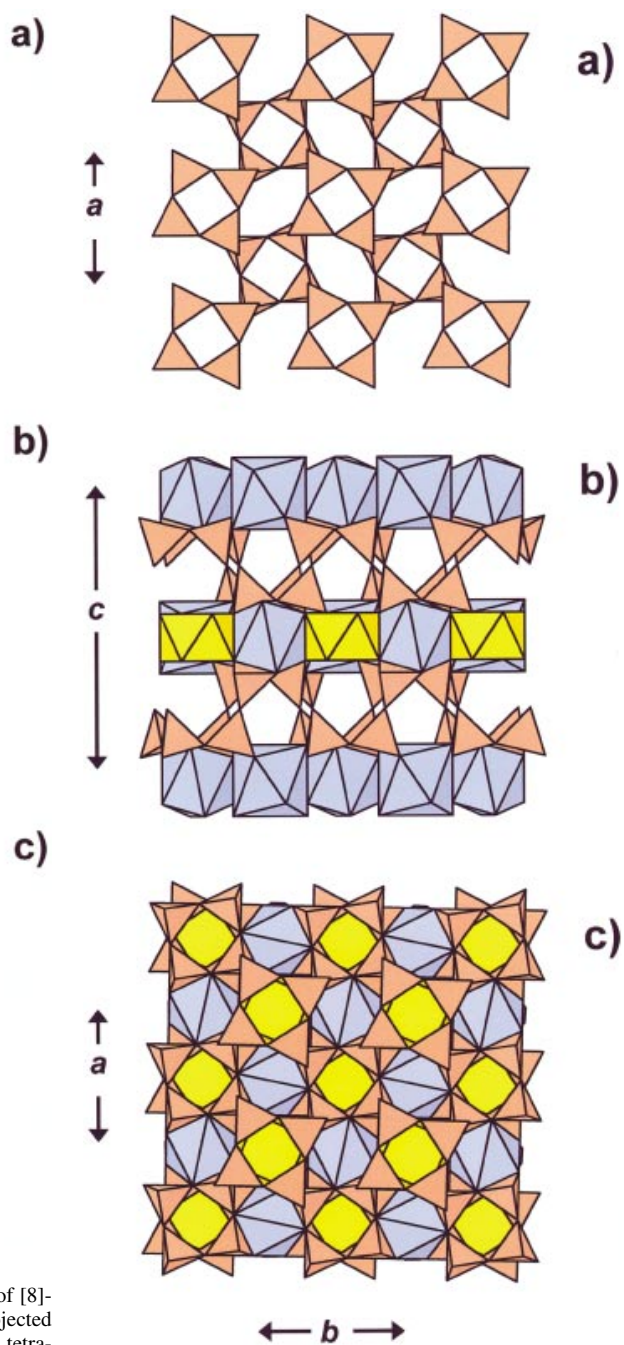


FIG. 2. The crystal structure of ekanite: (a) the Si-O sheet; (b) the structure projected onto (100); (c) the structure projected onto (001); Si tetrahedra are orange, [8]-coordinated Ca and Th polyhedra are blue and yellow, respectively.

formed through linkage of (SiO<sub>4</sub>) tetrahedra and [8]-coordinated polyhedra.

The chain [Si<sub>8</sub>O<sub>20</sub>]<sup>8-</sup> 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 (SiO<sub>4</sub>) tetrahedra and (CaO<sub>5</sub>) and (NaO<sub>7</sub>) polyhedra share common vertices to form a mixed-polyhedron framework (Fig. 3c).

#### Distribution of minerals of (Si<sub>n</sub>O<sub>2.5n</sub>) stoichiometry

There are twenty-three minerals that contain double rings of tetrahedra of the form [Si<sub>n</sub>O<sub>2.5n</sub>], 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 [Si<sub>8</sub>O<sub>20</sub>] units, and four minerals have [Si<sub>8</sub>O<sub>20</sub>] double-rings. The 18 minerals of the milarite-group have six-membered [Si<sub>12</sub>O<sub>30</sub>] double-rings in their crystal structure. There is only one mineral with the same stoichiometry as milarite, but with a different topology: miserite, K<sub>2</sub>Ca<sub>10</sub>(Y,REE)<sub>2</sub>[Si<sub>2</sub>O<sub>7</sub>]<sub>2</sub>[Si<sub>12</sub>O<sub>30</sub>](OH)<sub>2</sub>F<sub>2</sub>, contains a chain of the form [Si<sub>12</sub>O<sub>30</sub>] (Scott 1976). A unit of the form [Si<sub>6</sub>O<sub>15</sub>] occurs in nine minerals. A three-membered double-ring occurs in the crystal structure of moskvinit-(Y), Na<sub>2</sub>K(Y,REE)[Si<sub>6</sub>O<sub>15</sub>]. A chain of the form [Si<sub>6</sub>O<sub>15</sub>] occurs in the crystal structures of five minerals. An extended (or elpidite) chain was described in crystal structures of elpidite, Na<sub>2</sub>Zr[Si<sub>6</sub>O<sub>15</sub>](H<sub>2</sub>O)<sub>3</sub> (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 <sub>b</sub> -O(1)-Si <sub>c</sub>	163.6(4)	C-O(1) x4	2.976(6)
Si-O(2)-Si <sub>d</sub>	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

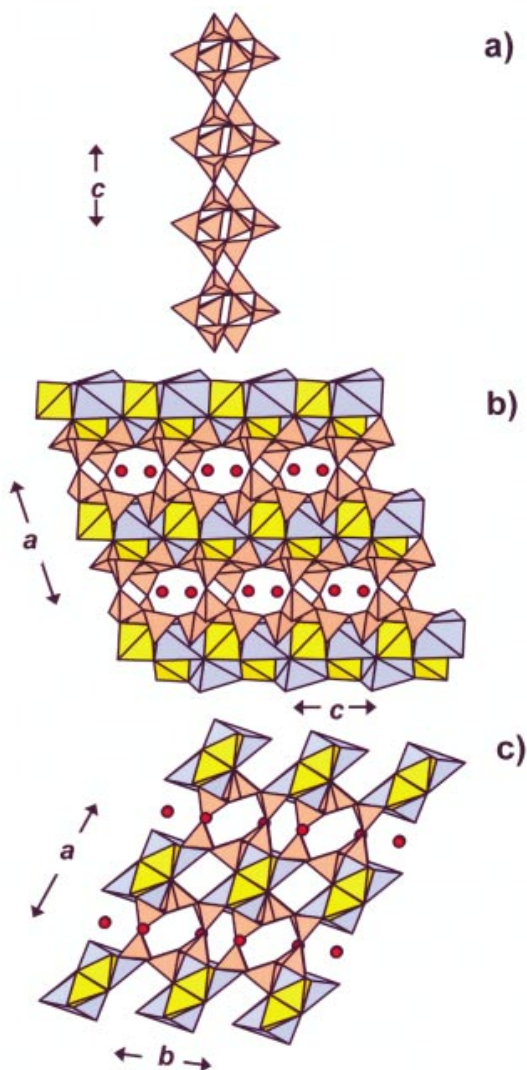


FIG. 3. The crystal structure of litidionite: (a) the Si-O chain; (b) the structure viewed down the  $b$  axis; (c) the structure viewed down the  $c$  axis. The [5]-coordinated Ca polyhedra are yellow, the [7]-coordinated Na polyhedra are blue, the Si tetrahedra are orange, and the K atoms are shown 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> <sub>calc</sub> * (Å)	<X-O> <sub>obs</sub> (Å)
A 79.4(4)	0.59 U <sup>4+</sup> + 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	$\Sigma$
O(1)			0.041 <sup>14</sup>	1.027 <sup>2</sup>	2.095
O(2)		0.186 <sup>14</sup>		0.966 0.946	2.098
O(3)	0.450 <sup>8</sup>	0.277 <sup>14</sup>	0.023 <sup>18</sup>	1.128	1.878
$\Sigma$	3.603	1.853	0.348	4.067	

\* Bond-valence curves are from Brown (1981)

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

Figure 4 shows the distribution of minerals of (Si<sub>n</sub>O<sub>2.5n</sub>) 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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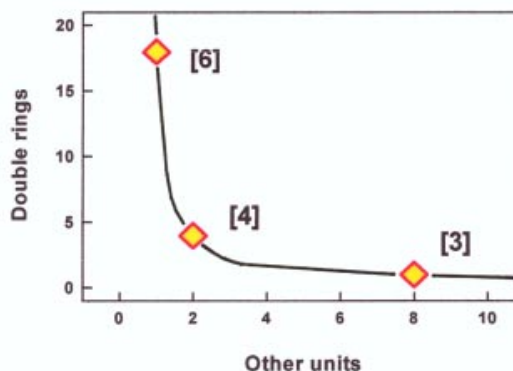


FIG. 4. The distribution of minerals of (Si<sub>n</sub>O<sub>2.5n</sub>) stoichiometry;  $n$  is shown in square brackets.

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