

# A review of crystal chemistry of natural silicates of alkaline elements in the light of new structural data

N. V. ZUBKOVA\*, I. V. PEKOV AND D. YU. PUSHCHAROVSKY

Faculty of Geology, Moscow State University, Vorobiev Gory, 119991 Moscow, Russia

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## ABSTRACT

A review is presented here of the crystal chemistry of natural silicates of alkaline elements, mainly Na, with a focus on reporting recent data on the structural mineralogy of the new members of this chemical family and their crystal structures. The majority of the natural hydrous silicates of alkaline elements studied are characterized by a specific crystal-chemical feature – the presence of silanol groups Si–OH. The discovery of the two new minerals, chesnokovite and yegorovite, means that all the main topological types of the  $[\text{Si}_x\text{O}_y]$  complexes are represented in the crystal structures for this family.

**KEYWORDS:** alkaline silicate, mineral, crystal structure, chesnokovite, yegorovite, megacyclite, silanol group.

## Introduction

SILICATES containing only alkaline elements as large cations have been studied intensively due to their considerable importance for mineralogy, solid-state chemistry, chemical technology, etc. (Rieck, 1996; Kahlenberg, 2010). However, the minerals of this chemical family were unknown until 1967 (Eugster, 1967). The synthetic analogues of the natural layered Na silicates such as kanemite, magadiite, kenyaite, or makatite, have been used as precursors for the design of microporous and mesoporous materials (Vortmann *et al.*, 1999). They have pronounced ion-exchange properties and can be used as selective adsorbers, catalysts, etc. (Wolf and Schwieger, 1979; Corredor *et al.*, 2013; Takahashi and Kuroda, 2011; Krüger *et al.*, 2005). Here we present a review of the crystal chemistry of Na and K silicates with a focus on the structural mineralogy of the new members of this family.

So far 12 natural silicates of alkaline elements without other metal cations are known, and nine of them have been studied structurally. Sodium is

the only cation in ten of these minerals, whereas megacyclite contains Na with subordinate K and silinaite is a Na-Li silicate. It is noteworthy that the diversity of synthetic silicates with K and Na is much wider. To date >40 compounds have been characterized structurally. The above-mentioned minerals crystallize from aqueous solutions supersaturated by Na under different temperatures. They are found mainly in peralkaline (hyper-alkalic) pegmatites and hydrothermal bodies related to complexes of feldspathoid rocks and in sediments of soda lakes or of Na-rich hot springs (Khomyakov, 1995). The widest diversity of these minerals is related to the hypersodic pegmatites and hydrothermal bodies of two alkaline intrusions, namely Lovozero at Kola Peninsula, Russia, and Mont Saint-Hilaire in Québec, Canada (Pekov *et al.*, 2008). The remarkable feature of these minerals is that, while they have simple compositions and are few in terms of numbers of species, their crystal structures contain all of the known topological

\* E-mail: n.v.zubkova@gmail.com  
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TABLE 1. Structural characteristics of natural silicates of alkaline elements.

Mineral	Formula	Symmetry, space group	Complex of Si tetrahedra	Reference
Chesnokovite	$\text{Na}_2[\text{SiO}_2(\text{OH})_2] \cdot 8\text{H}_2\text{O}$	Orthorhomb., <i>Ibca</i>	Isolated tetrahedra $[\text{SiO}_2(\text{OH})_2]$	Pekov <i>et al.</i> (2007a)
Yegorovite	$\text{Na}_4[\text{Si}_4\text{O}_8(\text{OH})_4] \cdot 7\text{H}_2\text{O}$	Mon., <i>P2<sub>1</sub>/c</i>	Chains $[\text{Si}_4\text{O}_8(\text{OH})_4]$	Zubkova <i>et al.</i> (2009)
Megacyclite	$\text{K}_2\text{Na}_{16}[\text{Si}_{18}\text{O}_{34}(\text{O},\text{OH})_2(\text{OH})_{18}] (\text{H}_2\text{O})_{36}$	Mon., <i>P2<sub>1</sub>/c</i>	Rings $[\text{Si}_{18}\text{O}_{34}(\text{O},\text{OH})_2(\text{OH})_{18}]$	Yamnova <i>et al.</i> (1992) Zubkova <i>et al.</i> (2007)
Revdite	$\text{Na}_{16}[\text{Si}_4\text{O}_6(\text{OH})_5]_2[\text{Si}_8\text{O}_{15}(\text{OH})_6] (\text{OH})_{10} \cdot 28\text{H}_2\text{O}$	Mon., <i>C2</i>	Two types of bands: $[\text{Si}_4\text{O}_6(\text{OH})_5]$ and $[\text{Si}_8\text{O}_{15}(\text{OH})_6]$	Rastsvetayeva <i>et al.</i> (1992)
Kanemite	$\text{NaHSi}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$	Orthorhomb., <i>Pbcn</i>	Corrugated layers $[\text{Si}_4\text{O}_8(\text{OH})_2]$	Garvie <i>et al.</i> (1999) Vortmann <i>et al.</i> (1999)
Makatite	$\text{Na}_2[\text{Si}_4\text{O}_8(\text{OH})_2] \cdot 4\text{H}_2\text{O}$	<i>Pna2<sub>1</sub></i> (theoretical calculation)	Corrugated layers $[\text{Si}_4\text{O}_8(\text{OH})_2]$	Piekarz <i>et al.</i> (2009)
Silinaite	$\text{NaL}[\text{Si}_2\text{O}_5] \cdot 2\text{H}_2\text{O}$	Mon., <i>P2<sub>1</sub>/c</i>	Layers $[\text{Si}_4\text{O}_{10}]$	Annehed <i>et al.</i> (1982)
Natrosilite	$\text{Na}_2[\text{Si}_2\text{O}_5]$	Mon., <i>A2/n</i>	Corrugated layers $[\text{Si}_4\text{O}_{10}]$	Grice (1991)
Gramantite	$\text{Na}[\text{Si}_2\text{O}_4(\text{OH})] \cdot \text{H}_2\text{O}$	Mon., <i>P2<sub>1</sub>/a</i>	Interrupted framework $[\text{Si}_2\text{O}_4(\text{OH})]$	Pant (1968)
Magadite*	$\text{Na}[\text{Si}_7\text{O}_{13}(\text{OH})_3] \cdot 4\text{H}_2\text{O}$	Orthorhomb., <i>Fdd2</i>	Layers composed of tubular ribbons	Yamnova <i>et al.</i> (1989)
Kenyaite**	$\text{Na}_2\text{Si}_2\text{O}_4(\text{OH})_8 \cdot 6\text{H}_2\text{O}$	Mon. <i>B2/m</i> (?)	–	Garcés <i>et al.</i> (1988)
Ertixite**	$\text{Na}_2\text{Si}_4\text{O}_9$	Mon. (?) Cub. (?)	–	Eugster (1967) Rubo <i>et al.</i> (1985)

\* For magadite only the model including Si and O atoms was reported.

\*\* The structure is unknown.

types of  $[\text{Si}_x\text{O}_y]$  complexes. Twelve natural silicates of alkaline elements with different types of silicate complexes in their structures are listed in Table 1. Ten minerals contain H-bearing groups and the presence of silanol groups, Si–OH, is a characteristic feature of these minerals unlike other natural silicates. Moreover, chesnokovite,  $\text{Na}_2[\text{SiO}_2(\text{OH})_2] \cdot 8\text{H}_2\text{O}$ , is the only mineral where the structure contains two OH groups in the vertices of each Si tetrahedron. Eight minerals contain only Na, Si, O and H as species-defining elements (see Table 1): chesnokovite,  $\text{Na}_2[\text{SiO}_2(\text{OH})_2] \cdot 8\text{H}_2\text{O}$ , yegorovite,  $\text{Na}_4[\text{Si}_4\text{O}_8(\text{OH})_4] \cdot 7\text{H}_2\text{O}$  (both are described below), magadiite,  $\text{NaSi}_7\text{O}_{13}(\text{OH})_3 \cdot 4\text{H}_2\text{O}$ , kenyaite,  $\text{Na}_2\text{Si}_{22}\text{O}_{41}(\text{OH})_8 \cdot 6\text{H}_2\text{O}$ , makatite,  $\text{Na}_2\text{Si}_4\text{O}_8(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ , kanemite,  $\text{NaHSi}_2\text{O}_4(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ , revdite,  $\text{Na}_{16}[\text{Si}_4\text{O}_6(\text{OH})_{512}][\text{Si}_8\text{O}_{15}(\text{OH})_6](\text{OH})_{10} \cdot 28\text{H}_2\text{O}$ , and grumantite,  $\text{NaSi}_2\text{O}_4(\text{OH}) \cdot \text{H}_2\text{O}$ . As mentioned above, despite the fact that their diversity has been known for a long time, the first natural representatives of this family were described <50 years ago. Magadiite and kenyaite were discovered in the soda-bearing sediments of Lake Magadi, Kenya (Eugster, 1967). Except kenyaite, all the members of this family have been found in late derivatives of peralkaline magmatic complexes and are most abundant in the Lovozero alkaline intrusion (Khomyakov, 1995; Pekov, 2000).

### Isolated Si-centred tetrahedra in chesnokovite

Chesnokovite is the first natural Na orthosilicate. It was discovered in an ussingite vein at Mt Kedykverpakhk in Lovozero (Pekov *et al.*, 2007a). Its empirical formula calculated according to the structural data on the basis of  $\text{O}_2(\text{OH})_2$  ( $Z = 8$ ) is:  $(\text{Na}_{1.96}\text{K}_{0.02})_{1.98}\text{Si}_{1.005}\text{O}_2(\text{OH})_2 \cdot 7.58\text{H}_2\text{O}$ . Chesnokovite is very unstable under room conditions: it decomposes readily to a loose aggregate of thermonatrite and opal. The decomposition accelerates with increased temperature and dry air, under elevated  $\text{CO}_2$  partial pressure. The poor quality of the chesnokovite crystals and the instability of the mineral prevented collection of single-crystal X-ray diffraction (XRD) data. The XRD powder pattern of the mineral showed that it is a natural analogue of a well known synthetic compound,  $\text{Na}_2[\text{SiO}_2(\text{OH})_2] \cdot 8\text{H}_2\text{O}$  (Jamieson and Dent

Glasser, 1966). Thus the structure of chesnokovite was studied using the Rietveld method (Zubkova *et al.*, 2006). The compound is orthorhombic, space group  $Ibca$ ,  $a = 11.7119(6)$ ,  $b = 16.973(1)$ ,  $c = 11.5652(6)$  Å, final  $R$ -values:  $R_p = 0.0577$ ,  $R_{wp} = 0.0777$ ,  $R_B = 0.0207$  and  $R_F = 0.0174$ . The crystal structure of chesnokovite (Fig. 1a) as well as its synthetic analogues (Jamieson and Dent Glasser, 1966; Schmid *et al.*, 1984) is based on the isolated tetrahedral anions  $[\text{SiO}_2(\text{OH})_2]^{2-}$  and chains of edge-sharing complex  $[\text{Na}(\text{H}_2\text{O})_6]^+$  cations running along  $[100]$  (Fig. 1b). Silicon- and Na-centred polyhedra are connected only by H bonding. Isolated  $[\text{SiO}_2(\text{OH})_2]$  tetrahedra are linked by H-bonds to form (010) pseudolayers as well as the chains of Na polyhedra.

Until now no minerals structurally related to chesnokovite have been discovered. It is characterized by the lowest value of the Si:Na ratio = 0.5 among natural aqueous Na silicates and the largest water content (55 wt.%  $\text{H}_2\text{O}$ ). For other alkaline silicates the  $\text{H}_2\text{O}$  content ranges from 11 to 33 wt.%.  $[\text{Si}_x\text{O}_y]$  complexes in all these minerals, except those of chesnokovite, are condensed (Table 1). The presence of only isolated  $\text{SiO}_4$  tetrahedra and the key role of the system of weak H-bonds determine the instability of chesnokovite under atmospheric conditions. Yegorovite and revdite with silicate chains and bands, respectively, as well as megacyclite with  $[\text{Si}_{18}\text{O}_{34}(\text{OH})_{18}(\text{O},\text{OH})_2]$  rings (see below) are also altered under atmospheric conditions but much more slowly. In dry air chesnokovite alters over the course of several hours and yegorovite in 1 month, whereas revdite and megacyclite take 5–6 months. Other minerals of the family with more condensed silicate anions are stable in air of normal humidity. This shows that the stability of aqueous Na silicates depends directly on the degree of the condensation of the  $[\text{Si}_x\text{O}_y]$  complexes in their structures (Pekov *et al.*, 2007a).

Like chesnokovite, the synthetic aqueous Na silicates  $\text{Na}_2[\text{SiO}_2(\text{OH})_2] \cdot 4\text{H}_2\text{O}$  (Jost and Hilmer, 1966; Schmid and Felsche, 1985),  $\text{Na}_2[\text{SiO}_2(\text{OH})_2] \cdot 7\text{H}_2\text{O}$  (Dent Glasser and Jamieson, 1976) and  $\text{Na}_2[\text{SiO}_2(\text{OH})_2] \cdot 5\text{H}_2\text{O}$  (Jamieson and Dent Glasser, 1967; Williams and Dent Glasser, 1971) contain double protonated isolated Si-centred tetrahedra. Monoprotonated isolated  $[\text{SiO}_3(\text{OH})]$  tetrahedra were found in the structure of  $\text{Na}_3[\text{SiO}_3(\text{OH})] \cdot \text{H}_2\text{O}$  (Schmid and Felsche, 1990). Two modifications of  $\text{Na}_3[\text{SiO}_3(\text{OH})] \cdot 2\text{H}_2\text{O}$  also contain the same units (Schmid *et al.*, 1979, 1981). In

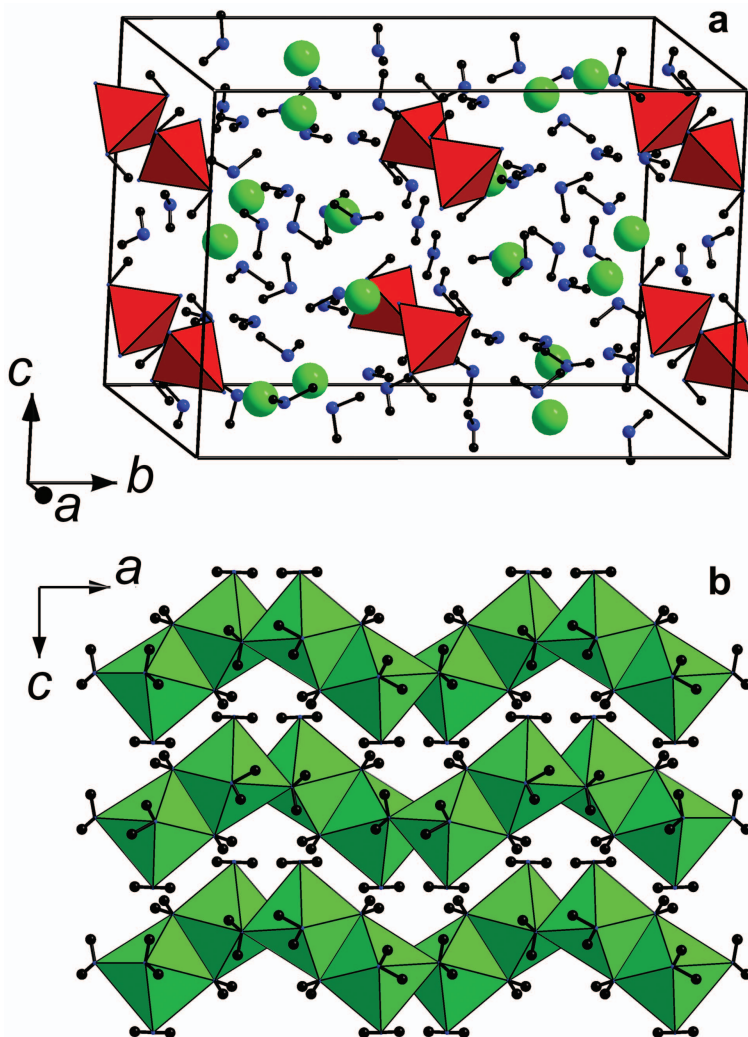


FIG. 1. (a) Crystal structure of chesnokovite and (b) its chains of Na-centred polyhedra. SiO<sub>4</sub> tetrahedra are red, Na cations are green circles (green polyhedra in (b)), O atoms are small blue circles, H atoms are small black circles.

Na<sub>3</sub>[SiO<sub>3</sub>(OH)]·5H<sub>2</sub>O two of these tetrahedra are connected via H-bonds to form the Si<sub>2</sub>O<sub>6</sub>(OH)<sub>2</sub> groups (Smolin *et al.*, 1973). The anhydrous synthetic silicates Na<sub>4</sub>SiO<sub>4</sub> (Barker and Gadd, 1981) and K<sub>4</sub>SiO<sub>4</sub> (Bernet and Hoppe, 1990) also contain isolated Si-centred tetrahedra. In the structures of Na<sub>6</sub>Si<sub>2</sub>O<sub>7</sub> (Kahlenberg *et al.*, 2010) and K<sub>6</sub>Si<sub>2</sub>O<sub>7</sub> (Jansen, 1982) the Si<sub>2</sub>O<sub>7</sub> dimers were found. It should be noted that these compounds belong to the family of sorosilicates of alkaline cations and also include Li<sub>6</sub>Si<sub>2</sub>O<sub>7</sub> (Völlenkle *et al.*, 1969), Rb<sub>6</sub>Si<sub>2</sub>O<sub>7</sub> and Cs<sub>6</sub>Si<sub>2</sub>O<sub>7</sub> (Hoch and Röhr, 2001).

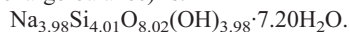
Thus, the discovery of sufficient amounts of chesnokovite with double protonated [SiO<sub>2</sub>(OH)<sub>2</sub>] tetrahedra predicts the probable existence of natural representatives of other structure types characteristic of synthetic Na silicates but exotic for minerals. For example, several synthetic polymorphs of Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> have been studied and a review of the crystal chemistry of anhydrous Na silicates is given by Kahlenberg (2010). Crystal structures of the majority of these compounds contain [Si<sub>2</sub>O<sub>5</sub>]-layers whereas the γ-form is based on an interrupted framework (Kahlenberg *et al.*, 2003). Another type of interrupted framework is

the basis of  $\text{Na}_2\text{Si}_3\text{O}_7$  (Kahlenberg *et al.*, 2002). In nature only natrosilite,  $\beta\text{-Na}_2\text{Si}_2\text{O}_5$ , is known. In contrast with supergene conditions of soda lakes, Na silicates in the derivatives of alkaline magmatic complexes are formed over a wide temperature range that significantly increases their diversity.

Chesnokovite could be considered as a sensitive indicator of formation conditions due to its structural features, chemical properties and behaviour upon heating. The synthetic analogue of chesnokovite crystallizes from an aqueous solution at 20°C and the formation of the mineral probably occurs at a temperature <50°C (if pressure is considered as an additional parameter the temperature could be higher, but in any case <70–80°C) (Pekov *et al.*, 2007a).

### Tetrahedral chains in yegorovite

The discovery of another new Na silicate yegorovite,  $\text{Na}_4[\text{Si}_4\text{O}_8(\text{OH})_4]\cdot 7\text{H}_2\text{O}$ , with tetrahedral chains filled the gap in the list of  $[\text{Si}_x\text{O}_y]$  complexes in the structures of these minerals (Zubkova *et al.*, 2009; Pekov *et al.*, 2010). Yegorovite was found in the Palitra peralkaline pegmatite on Mt. Kedykverpakhk, Lovozero. Its empirical formula (calculated on the basis of  $(\text{O},\text{OH})_{12}$  with the  $\text{OH}/\text{H}_2\text{O}$  ratio calculated by charge balance) is:



A single-crystal XRD study of yegorovite showed that the mineral is monoclinic, space group  $P2_1/c$ ,  $a = 9.8744(4)$ ,  $b = 12.3981(5)$ ,  $c = 14.8973(7)$  Å,  $\beta = 104.675(5)^\circ$  and  $Z = 4$ . The structure was solved and refined to the final  $R_F = 0.0745$  for 1977 independent reflections with  $I > 2\sigma(I)$ . All H atoms were localized and refined isotropically. Yegorovite is a representative of a new structure type. Its crystal structure (Fig. 2a) is unique and the mineral has no close relatives among natural and synthetic compounds (Zubkova *et al.*, 2009). The structure of yegorovite is based on the zig-zag chains  $[\text{Si}_4\text{O}_8(\text{OH})_4]_\infty$  running along the  $a$  axis with a period of four tetrahedra. One of the vertices of each Si-centred tetrahedron is an OH group. Four crystallographically nonequivalent Na atoms occupy six-fold polyhedra of two types:  $[\text{NaO}(\text{OH})_2(\text{H}_2\text{O})_3]$  and  $[\text{NaO}(\text{OH})(\text{H}_2\text{O})_4]$ . They are linked to each other by common vertices and edges to form corrugated (001) layers consisting of three-, four-, five- and eight-membered rings of Na polyhedra (Fig. 2b). Each layer is connected from both sides to the chains of the  $\text{SiO}_4$ -

tetrahedra and the neighboring Na,Si mixed layers are linked by a system of H bonds.

The  $[\text{Si}_4\text{O}_8(\text{OH})_4]$  tetrahedral chains in yegorovite are topologically similar to those found in pyroxenes but slight tilting of tetrahedra and the arrangement of the H atoms of OH groups in the vertices of tetrahedra lead to an increase in the chain periodicity from two to four. According to Liebau (1985), the unbranched tetrahedral chain in the structure of yegorovite could be presented as  $\{\text{uB}1_\infty\}[\text{Si}_4\text{O}_8(\text{OH})_4]^{4-}$ .

Yegorovite is the only natural representative of silicates of alkaline elements with single chains. Among synthetic Na silicates, single chains were described in the anhydrous Na silicate  $\text{Na}_2\text{SiO}_3$  (McDonald and Cruickshank, 1967). Double chains containing four-membered rings of Si tetrahedra that could be described as being built by the condensation of *zweier* single chains were found in the high-pressure phase  $\text{NaKSi}_2\text{O}_5\text{-II}$  (Rakić *et al.*, 2003a). In  $\text{Na}_6\text{Si}_8\text{O}_{19}$  the Si,O layers can be obtained by the condensation of four different *zweier* single chains of Si tetrahedra (Krüger *et al.*, 2005). Another way that the single chains  $[\text{Si}_2\text{O}_6]$  can connect to form layers is described in  $\text{K}_4\text{Si}_8\text{O}_{18}$  (Schweinsberg and Liebau, 1974). A chain built by four-membered rings of Si-centred tetrahedra was found in the micro-porous compound Mu-29,  $\text{Na}_{32}\text{Si}_{64}\text{O}_{128}(\text{OH})_{32}$  (Sassi *et al.*, 2003). In revdite,  $\text{Na}_{16}[\text{Si}_4\text{O}_6(\text{OH})_5]_2[\text{Si}_8\text{O}_{15}(\text{OH})_6](\text{OH})_{10}\cdot 28\text{H}_2\text{O}$ , two types of bands formed by four-membered tetrahedral rings were described (Rastsvetaeva *et al.*, 1992). The bands of the first type with the formula  $[\text{Si}_4\text{O}_6(\text{OH})_5]$  are similar to those found in vlasovite,  $\text{Na}_2\text{Zr}[\text{Si}_4\text{O}_{11}]$  (Voronkov and Pyatenko, 1962) and synthetic  $\text{Li}_2\text{Mg}_2[\text{Si}_4\text{O}_{11}]$  (Czank and Bissert, 1993) while the bands of the second type  $[\text{Si}_8\text{O}_{15}(\text{OH})_6]$  can be considered as doubled vlasovite-like bands and could be compared with doubled bands formed by four-membered rings of Si tetrahedra in the structures of modulated  $\text{K}_4(\text{NbO})_2[\text{Si}_8\text{O}_{21}]$  (Rastsvetaeva *et al.*, 1994) and  $\text{Cs}_4(\text{NbO})_2[\text{Si}_8\text{O}_{21}]$  (Crosnier *et al.*, 1990). Layers consisting of the bands of five-membered tetrahedral rings were found in  $\text{Na}[\text{Si}_4\text{O}_8(\text{OH})]\cdot 4\text{H}_2\text{O}$  (Vortmann *et al.*, 1997). Layers formed by six-membered tetrahedral rings with a different configuration are observed in kanemite (Garvie *et al.*, 1999; Vortmann *et al.*, 1999), makatite (Annehed *et al.*, 1982), silinaite (Grice, 1991), natrosilite (Pant, 1968) and its synthetic analogue  $\beta\text{-Na}_2\text{Si}_2\text{O}_5$  (Grund, 1954) as well as in synthetic  $\alpha\text{-}$  (Pant and Cruickshank,

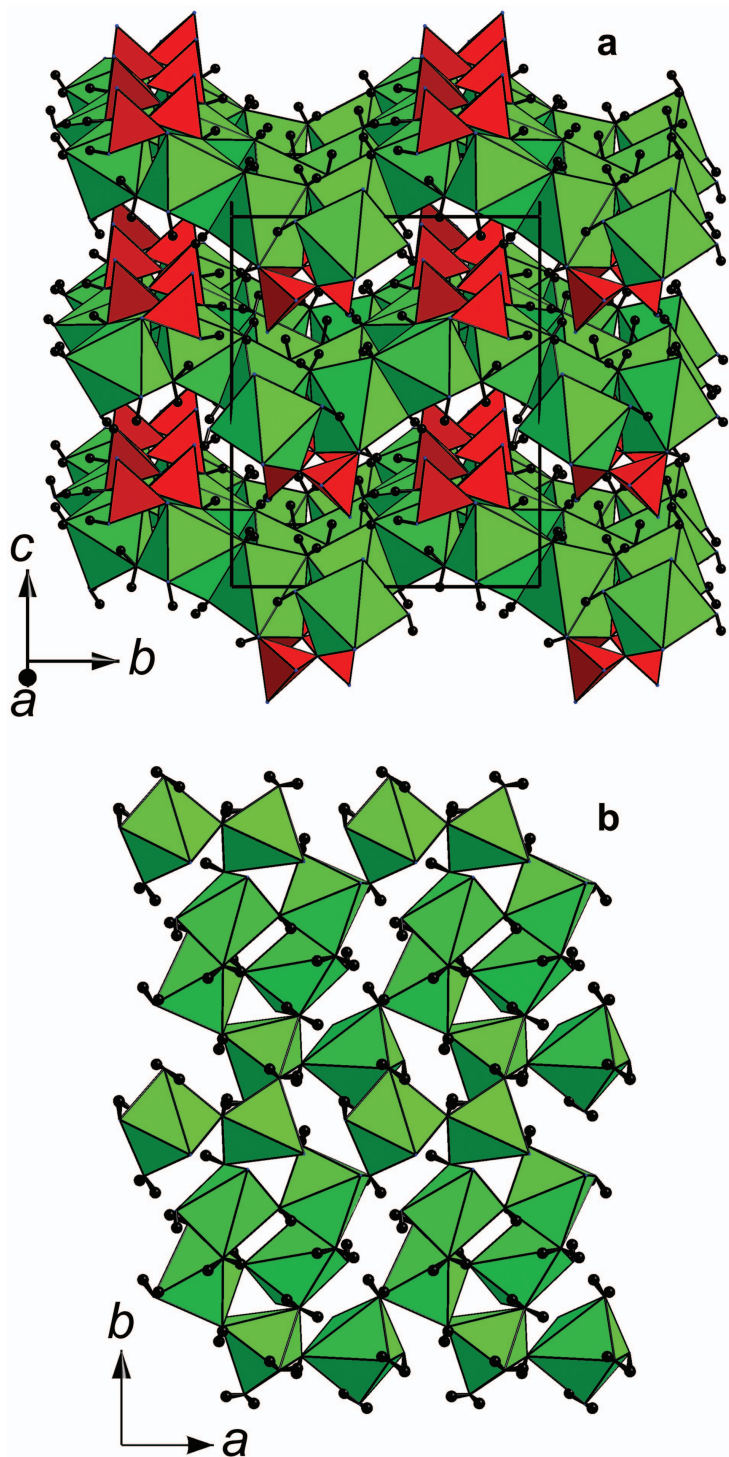


FIG. 2. (a) Crystal structure of yegorovite in  $bc$  projection and (b) the corresponding corrugated layers of Na polyhedra.  $\text{SiO}_4$  tetrahedra are red, Na-centred polyhedra are green, H atoms are small black circles.

1968),  $\kappa$ - (Rakić *et al.*, 2003b),  $\varepsilon$ - (Fleet and Henderson, 1995a) and  $\delta$ - (Kahlenberg *et al.*, 1999) forms of  $\text{Na}_2\text{Si}_2\text{O}_5$ , in the high-pressure phase C- $\text{Na}_2\text{Si}_2\text{O}_5$  (Rakić *et al.*, 2002), in  $\text{Na}_{1.84}\text{K}_{0.16}\text{Si}_2\text{O}_5$  (Rakić *et al.*, 2003b),  $\text{Na}_{1.55}\text{K}_{0.45}\text{Si}_2\text{O}_5$  (Rakić and Kahlenberg, 2001a) and  $\text{KHSi}_2\text{O}_5$  (Le Bihan *et al.*, 1971; Malinovskii and Belov, 1979). In  $\text{NaKSi}_2\text{O}_5$  and high-pressure  $\text{Na}_{0.67}\text{K}_{1.33}\text{Si}_2\text{O}_5$  the tetrahedral layers contain four-, six- and eight-membered rings (Rakić and Kahlenberg, 2001b; Rakić *et al.*, 2003a). For the hypothetical model of the magadiite structure sheets of six-membered rings of Si tetrahedra with blocks of five-membered rings on both sides of the sheet were assumed. Moreover it was suggested that these layers can be partially condensed into an interrupted 3D framework (Garcés *et al.*, 1988).

### Tetrahedral rings in megacyclite

The only representative of Na and K containing hydrous silicates is the rare mineral megacyclite,

ideally  $\text{K}_2\text{Na}_{16}\text{Si}_{18}\text{O}_{36}(\text{OH})_{18}\cdot 38\text{H}_2\text{O}$ . It was first found in the peralkaline pegmatoid veins, which consist mainly of potassic feldspar, fenaksite and delhayelite, at Mt Rasvumchorr in the Khibiny alkaline complex, Kola (Khomyakov *et al.*, 1993), and its crystal structure was solved by Yamnova *et al.* (1992). Later, the present authors found two more localities for megacyclite, in Khibiny (a large peralkaline pegmatite uncovered within the Tsentral'nyi Mine at Mt Rasvumchorr) and Lovozero (the Palitra pegmatite at Mt Kedykverpakhk). The sample from the first of these was studied structurally (Zubkova *et al.*, 2007). Megacyclite is one of the lowest temperature phases in these pegmatites. The chemical composition of megacyclite from the Tsentral'nyi Mine in Khibiny corresponds to the empirical formula (calculated on the basis of the silicate component  $[\text{Si}_9(\text{O},\text{OH})_{27}]\text{K}_{0.99}\text{Na}_{8.11}\text{Si}_9\text{O}_{18.10}(\text{OH})_{8.90}\cdot 18.75\text{H}_2\text{O}$  close to the idealized formula.

Our single-crystal XRD data showed that megacyclite is monoclinic, space group  $P2_1/c$ ,  $a = 24.8219(16)$ ,  $b = 11.9236(8)$ ,  $c = 14.8765(9)$  Å

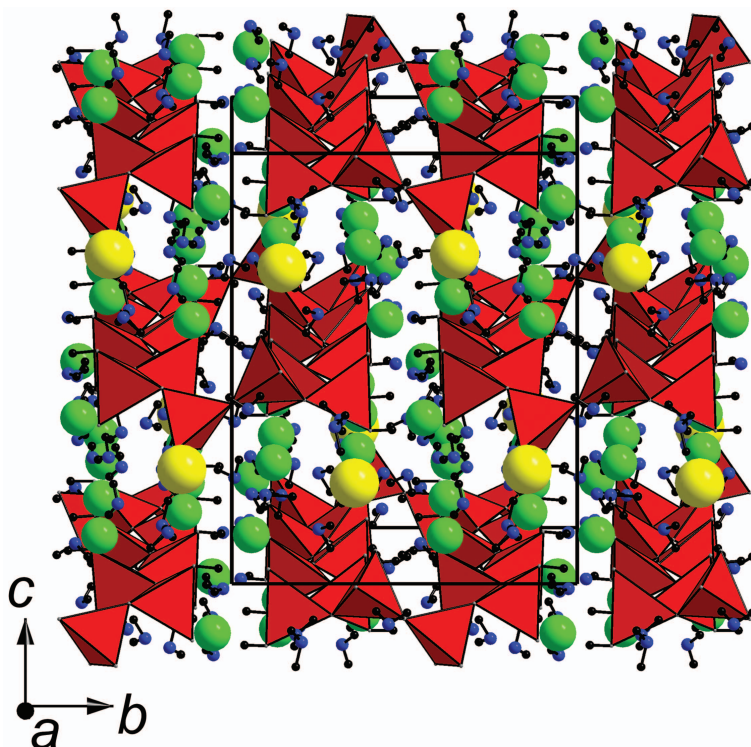
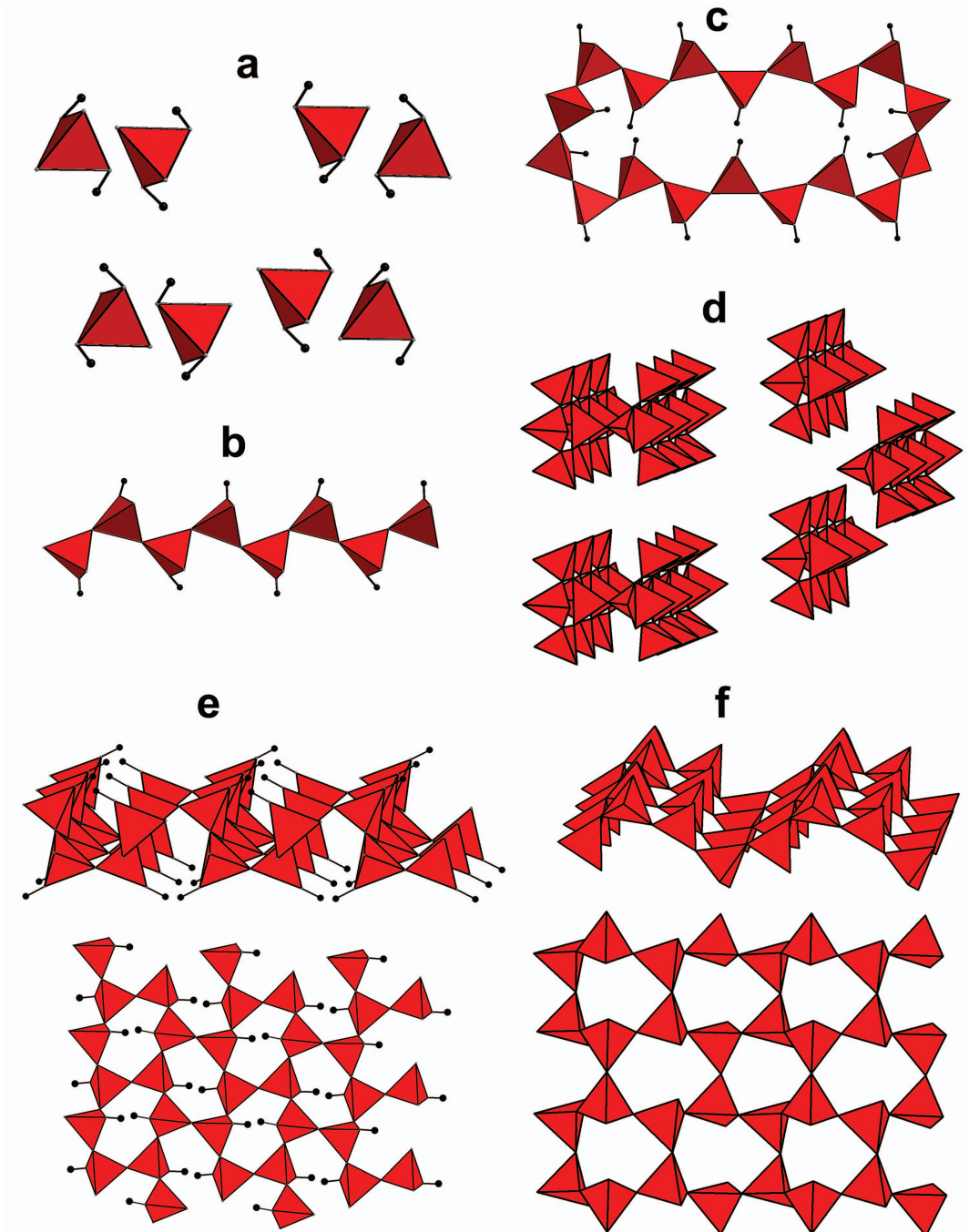


FIG. 3. Crystal structure of megacyclite in  $bc$  projection.  $\text{SiO}_4$  tetrahedra are red, Na cations are big green circles, K cations are big yellow circles, O atoms are small blue circles, H atoms are small black circles.

and  $\beta = 94.486(5)^\circ$  (final  $R_F = 0.0339$  for 8206 independent reflections with  $I > 2\sigma(I)$ ) and mainly confirmed the data by Yamnova *et al.* (1992). The refinement gave the following structural formula of megacyclite from the Tsentral'nyi Mine:

$\text{K}_2\text{Na}_{16}\text{Si}_{18}\text{O}_{34}(\text{O},\text{OH})_2(\text{OH})_{18}(\text{H}_2\text{O})_{36}(\text{H}_2\text{O},\text{OH})_2$ . In mega-cyclite from its type locality and in our sample the structure contains 18-membered rings of Si-centred tetrahedra but in our case their composition is  $[\text{Si}_{18}\text{O}_{34}(\text{O},\text{OH})_2]$





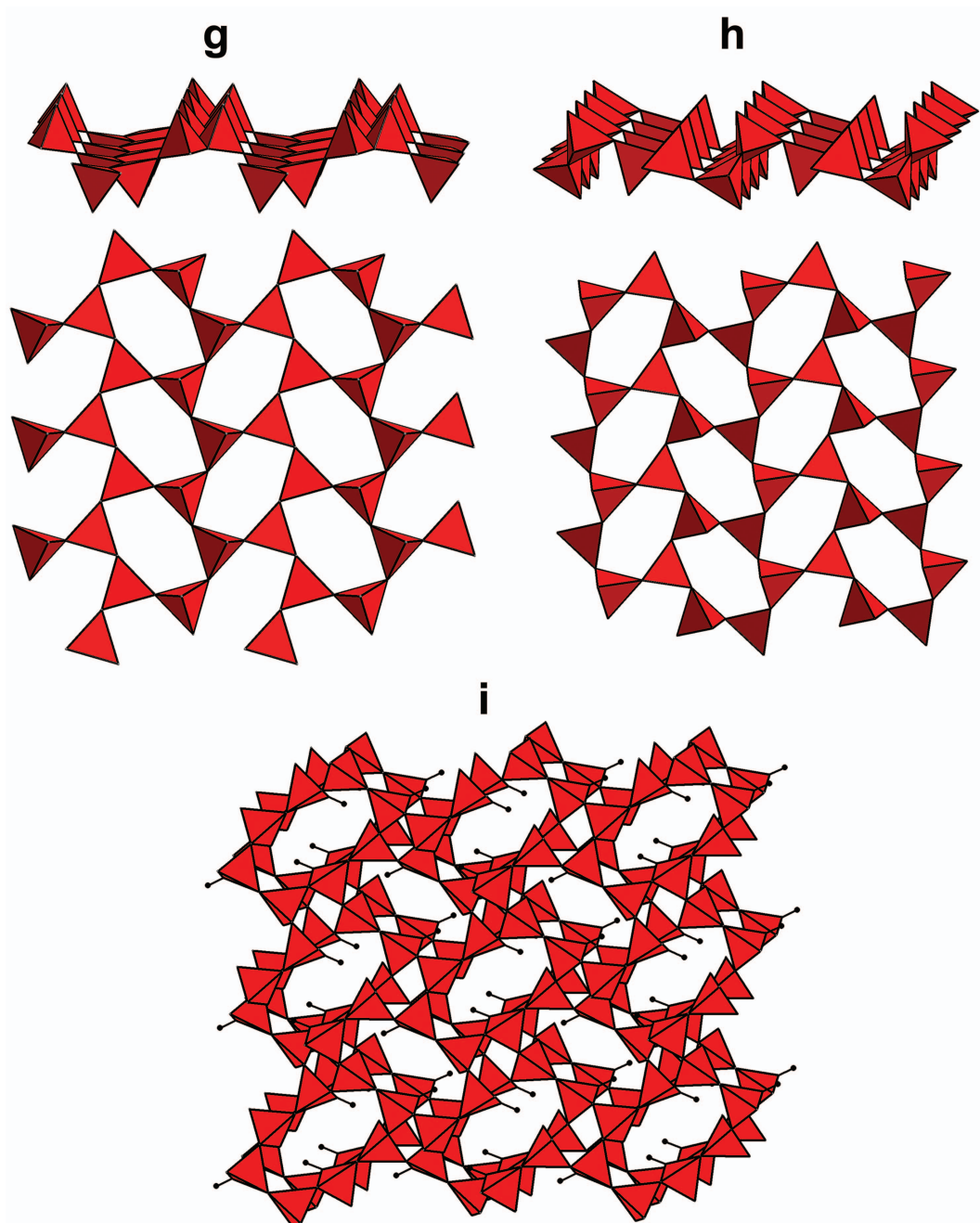


FIG. 4 (*this and facing page*). [Si<sub>x</sub>O<sub>y</sub>] complexes in the structures of natural silicates of alkaline elements: (a) chesnokovite (Pekov *et al.*, 2007a), (b) yegorovite (Zubkova *et al.*, 2009), (c) megacyclite (Zubkova *et al.*, 2007), (d) revdite (Rastsvetaeva *et al.*, 1992), (e) kanemite (Garvie *et al.*, 1999), (f) makatite (Annehed *et al.*, 1982), (g) silinaite (Grice, 1991), (e h) natrosilite (Pant, 1968), (i) grumantite (Yamnova *et al.*, 1989). All tetrahedral layers are given in two projections. H atoms are shown as small black circles.

(OH)<sub>18</sub>], unlike the data of Yamnova *et al.* (1992) where the composition of the ring is [Si<sub>18</sub>O<sub>36</sub>(OH)<sub>18</sub>]. Partial substitution of one O atom by an OH group causes a deficiency in negative charge that is compensated by partial replacement of one H<sub>2</sub>O molecule by an OH group. These substitutions are confirmed by bond-valence calculations and unambiguous localization of only one H atom in the H<sub>2</sub>O molecule (the position of the second H atom belonging to this H<sub>2</sub>O molecule is apparently partially occupied because of partial OH → H<sub>2</sub>O substitution and could not be localized). Thus, the differences between the data for the two studied samples of megacyclite are in the positions of H atoms and the system of H-bonds (Zubkova *et al.*, 2007). Polyhedra centred by Na and K cations form the cationic framework. Eight crystallographically independent Na atoms occupy six six-fold and two five-fold polyhedra whereas the K cation is at the centre of a seven-fold polyhedron. The crystal structure of megacyclite is shown in Fig. 3.

Since its discovery, megacyclite with 18-membered elliptical tetrahedral rings with a large diameter, ~19 Å, still remains the compound with the largest isolated Si<sub>6</sub>O rings among cyclosilicates. At the same time the size of this ring is much smaller than that of the ring elements of zeolite frameworks of different compositions.

Among K-Na silicates, synthetic K<sub>2</sub>SiO<sub>3</sub> is a cyclosilicate with three-membered rings of tetrahedra (Werthmann and Hoppe, 1981). The crystal structure of KHSiO<sub>3</sub> is based on four-membered rings (Hilmer, 1964; 1965; Dent Glasser *et al.*, 1984).

Among natural silicates of alkaline elements only grumantite contains an interrupted framework built by SiO<sub>4</sub> tetrahedra (Yamnova *et al.*, 1989). Interrupted tetrahedral frameworks were also described in the above-mentioned compounds γ-Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> and Na<sub>2</sub>Si<sub>3</sub>O<sub>7</sub>. A microporous framework with ten-membered tetrahedral rings was found in the structure of Na trisilicate Mu-11, Na<sub>2</sub>Si<sub>3</sub>O<sub>7</sub>·H<sub>2</sub>O (Matijasic *et al.*, 2000). A three-dimensional defect cristobalite-type framework is the basis of the K<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> structure (de Jong *et al.*, 1998).

High-pressure synthetic compounds with Si atoms occupying both tetrahedral and octahedral sites form a specific family. In particular, Na<sub>2</sub><sup>VI</sup>Si<sup>IV</sup>Si<sub>2</sub>O<sub>7</sub> contains a framework built by isolated Si octahedra and Si<sub>2</sub>O<sub>7</sub> pyrogroups (Fleet and Henderson, 1995b) with the composite building unit M<sub>2</sub>T<sub>4</sub> (where M is octahedrally

coordinated and T is tetrahedrally coordinated Si) similar to those found in the microporous zirconosilicates khibinskite, K<sub>2</sub>ZrSi<sub>2</sub>O<sub>7</sub>, keldyshite, (Na,H)<sub>2</sub>ZrSi<sub>2</sub>O<sub>7</sub> and parakeldyshite, Na<sub>2</sub>ZrSi<sub>2</sub>O<sub>7</sub> (Pekov *et al.*, 2007b). The crystal structure of K<sub>2</sub><sup>VI</sup>Si<sup>IV</sup>Si<sub>3</sub>O<sub>9</sub> (Swanson and Prewitt, 1983) is close to that of wadeite, K<sub>2</sub>ZrSi<sub>3</sub>O<sub>9</sub>, and contains a framework built by isolated Si octahedra and three-membered rings of SiO<sub>4</sub> tetrahedra. Six-membered rings of Si tetrahedra linked with Si octahedra form a framework described in the structure of Na<sub>8</sub><sup>VI</sup>Si<sup>IV</sup>Si<sub>6</sub>O<sub>18</sub>] (Fleet, 1998). In this compound the topology of the framework is close to those in lovozerite-group minerals. In Na<sub>6</sub><sup>VI</sup>Si<sub>3</sub><sup>IV</sup>Si<sub>9</sub>O<sub>27</sub>] the framework consists of nine-fold rings of Si tetrahedra and isolated octahedra occupied by Si cations (Fleet, 1996). These nine-fold rings are topologically similar to those found in the eudialyte-group minerals and in the phase Na<sub>2</sub>(Na,Ca)<sub>3</sub>Zr<sub>3</sub>[Si<sub>9</sub>O<sub>27</sub>] obtained from natural catapleiite, (Na<sub>1.4</sub>Ca<sub>0.3</sub>)<sub>Σ1.7</sub>Zr<sub>1.0</sub>Si<sub>3.0</sub>O<sub>9</sub>·2H<sub>2</sub>O, by annealing at 1000°C (Ksenofontov *et al.*, 2013).

## Conclusions

The majority of hydrous representatives of the family of natural silicates of alkaline elements studied structurally (except silinaite, NaLi[Si<sub>2</sub>O<sub>5</sub>]·2H<sub>2</sub>O) are characterized by a specific, important crystal chemical feature: the presence of silanol groups. This is a rarity for other natural silicates. Thus, these minerals obey Pauling's second rule and avoid the local excess of negative charge on the non-bridging O vertices of SiO<sub>4</sub> tetrahedra due to the presence of only univalent Na and K cations.

The discoveries of chesnokovite and yegorovite closes the gaps in the list of [Si<sub>x</sub>O<sub>y</sub>] complexes in the structures of alkaline silicate minerals. Consequently, all the main topological types of silicate complexes, from isolated tetrahedra to framework, are now known within this family. All the types of tetrahedral anions found in these minerals are shown in Fig. 4.

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