

Chesnokovite, $\text{Na}_2[\text{SiO}_2(\text{OH})_2] \cdot 8\text{H}_2\text{O}$, the First Natural Sodium Orthosilicate from the Lovozero Alkaline Pluton, Kola Peninsula: Description and Crystal Structure of a New Mineral Species¹

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Abstract—Chesnokovite, a new mineral species, is the first natural sodium orthosilicate. It has been found in an ussingite vein uncovered by underground mining at Mt. Kedykverpakhk, Lovozero alkaline pluton, Kola Peninsula, Russia. Natrolite, sodalite, vuonnemite, steenstrupine-(Ce), phosinaite-(Ce), natisite, gobbinsite, viliaumite, and natrosilite are associated minerals. Chesnokovite occurs as intergrowths with natrophosphate in pockets up to $4 \times 6 \times 10$ cm in size consisting of chaotic segregations of coarse lamellar crystals (up to $0.05 \times 1 \times 2$ cm in size) flattened along [010]. The crystals are colorless and transparent. The aggregates are white to pale brownish yellowish, with a white streak and a vitreous luster. The cleavage is perfect parallel to (010) and distinct to (100) and (001). The fracture is stepped. The Mohs' hardness is 2.5. The measured density is 1.68 g/cm^3 ; the density calculated on the basis of an empirical formula is 1.60 g/cm^3 and 1.64 g/cm^3 on the basis of an idealized formula. The new mineral is optically biaxial, positive, $\alpha = 1.449$, $\beta = 1.453$, $\gamma = 1.458$, $2V_{\text{meas}} = 80^\circ$, and $Z = b$. The infrared spectrum is given. The chemical composition (Si determined with electron microprobe; Na, K, and Li, with atomic emission analysis; and H_2O , with the Alimarin method) is as follows, wt %: 21.49 Na_2O , 0.38 K_2O , 0.003 Li_2O , 21.42 SiO_2 , 54.86 H_2O , total is 98.153. The empirical formula calculated on the basis of $\text{O}_2(\text{OH})_2$ is as follows: $(\text{Na}_{1.96}\text{K}_{0.02})_{\Sigma 1.98}\text{Si}_{1.005}\text{O}_2(\text{OH})_2 \cdot 7.58\text{H}_2\text{O}$. The simplified formula ($Z = 8$) is $\text{Na}_2[\text{SiO}_2(\text{OH})_2] \cdot 8\text{H}_2\text{O}$. The new mineral is orthorhombic, and the space group is *Ibca*. The unit-cell dimensions are: $a = 11.7119$, $b = 19.973$, $c = 11.5652 \text{ \AA}$, and $V = 2299.0 \text{ \AA}^3$. The strongest reflections in the X-ray powder pattern [d , Å (I , %)(hkl)] are: 5.001(30)(211), 4.788(42)(022), 3.847(89)(231), 2.932(42)(400), 2.832(35)(060), 2.800(97)(332, 233), and 2.774(100)(341, 143, 114). The crystal structure was studied using the Rietveld method, $R_p = 5.77$, $R_{wp} = 7.77$, $R_B = 2.07$, and $R_F = 1.74$. The structure is composed of isolated $[\text{SiO}_2(\text{OH})_2]$ octahedrons and the chains of edge-shared $[\text{Na}(\text{H}_2\text{O})_6]$ octahedrons. The Si and Na polyhedrons are linked only by H-bonds, and this is the cause of the low stability of chesnokovite under atmospheric conditions. The new mineral is named in memory of B.V. Chesnokov (1928–2005), an outstanding mineralogist. The type material of chesnokovite is deposited in the Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow.

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INTRODUCTION

The specific family of minerals containing only Na, Si, O, and H as the major components is recognized among natural silicates. Until now, six minerals from this family have been described: 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 $\text{Na}_{16}[\text{Si}_4\text{O}_6(\text{OH})_5]_2[\text{Si}_8\text{O}_{15}(\text{OH})_6](\text{OH})_{10} \cdot 28\text{H}_2\text{O}$, and grumantite $\text{NaSi}_2\text{O}_4(\text{OH}) \cdot \text{H}_2\text{O}$. Despite the diversity of synthetic hydrous sodium silicates, minerals of this

family were described for the first time only 40 years ago after the discovery of magadiite and kenyaite in the soda-bearing sediments of Lake Magadi, Kenya (Eugster, 1967). A few years later, makatite and kanemite also found in the sediments of African soda lakes were described by Sheppard et al. (1970) and Johan and Maglione (1972). Other findings in a similar environment showed that hydrous sodium silicates are characteristic of alkali carbonate supergene, foremost, the sedex-type mineral assemblages. Subsequently, the members of this family were described from a quite different setting. Makatite and new minerals—revdite and grumantite—were found in the salt mineralization of the late, low-temperature derivatives of hyperalkaline igneous rocks in the Lovozero alkaline pluton, Kola Peninsula, Russia (Khomyakov et al., 1980a, 1980b,

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1987). Nowadays, hydrous sodium silicates are also known from other alkaline complexes all over the world: Khibiny, Kola Peninsula; Mont Saint-Hilaire and Saint-Amable, Quebec, Canada; Aris, Namibia; etc. Except for kenyaite, all members of this family have been identified in peralkaline massifs and are most abundant in Lovozero. Makatite, kanemite, revdite, and grumantite, which occur in this pluton, replace anhydrous natrosilite $\text{Na}_2\text{Si}_2\text{O}_5$ that is unstable under the late hydrothermal and supergene conditions or fill cavities and fissures as segregations within pegmatite and hydrothermal bodies (Khomyakov, 1990; Pekov, 2001).

A new mineral, the first natural sodium orthosilicate, is described in this paper. This mineral was discovered in the hydrothermal assemblages of the Lovozero pluton and named *chesnokovite* in memory of Boris Valentinovich Chesnokov (1928–2005), an outstanding Russian mineralogist who worked at the Institute of Mineralogy, Ural Division, Russian Academy of Science, in Miass, Chelyabinsk oblast. Chesnokov, a scientist of worldwide reputation and with a wide scope of interests, made a great contribution to the theory of mineralogy; the ontogeny of minerals; the mineralogy of ore deposits, granitic pegmatites, and metamorphic rocks; in latter decades, he actively developed techogenic mineralogy. The late derivatives of alkaline rocks mainly from the miaskite province of the Il'meny and Vishnevyy Mountains in the southern Urals were one of the objects of his studies. In particular, Chesnokov et al. (1982) first described sulfate-type salt mineralization in alkaline intrusions.

The type material of chesnokovite is deposited in the Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow. The registration number is 3419/1.

MODE OF OCCURRENCE AND GENERAL DESCRIPTION

Samples with the oncoming new mineral were collected in September 2005 by I.V. Pekov and V.V. Levitsky from a recently uncovered part of the Kedykverpakhk-22 vein (the numeration of veins is continued from Pekov (2001)) in an underground working mine at Mount Kedykverpakhk (Kedykverpakhk area of the Karnasurt Mine) located in the northwestern Lovozero pluton.

The vein field that embraces more than 30 hyperalkaline bodies was uncovered during underground mining at Mount Kedykverpakhk. These bodies are distinguished by specific geological, geochemical, and mineralogical features and drastically differ in the formation condition from "normal" pegmatites, which also occur at this locality. The hyperalkaline veins were described in more detail by Pekov (2006). They are 1–15-cm thick and extend for hundreds of meters filling the NW- and NWN-trending systems of subvertical fissures. The veins crosscut a malignite unit enriched in loparite (so-called layer II-4), the overlying foyaite and

urtite units, and pinch downward no more than 0.5 m below the malignite unit and locally within this unit itself. Ussingite and/or natrolite are major vein-forming minerals. Well-defined features of crystallization in the free space of the fissure—the growth of mineral individuals from the selvage to the center, the geometric selection at the vein margins, and the chains of residual cavities in the axial zone—are characteristic of these bodies. Almost 70 mineral species were identified in the described vein complex (Pekov, 2006). Practically all minerals contain sodium as a species-forming component, occasionally in a great amount (>15–20 vol %). In general, ultrasodium specialization is characteristic of the veins; in contrast to the Lovozero pegmatites, the Na/K ratio ranges within $n \cdot 10^3$ – $n \cdot 10^4$. Unlikely for pegmatites, the described bodies are devoid of nepheline, the early generation of feldspars (microcline and albite are late here and negligible in amount), amphiboles, and zirconium minerals; aegirine occurs in a very small amount, whereas OH- and especially H_2O -bearing minerals are abundant. The abundance of natrolite indicates the hydrothermal origin of the described veins. In contrast to pegmatites, they are considered to be derivatives of a geochemically open system and were formed as products of the crystallization of ultrasodium fluid (solution) that reacted with country rocks. The appearance of this fluid was probably related to the release of components (largely, the most mobile H_2O , Na, and F) from micropores of rocks into the opening fissures (Pekov, 2006).

The Kedykverpakhk-22 vein is 6–8-cm thick and extends for more than 500 m. Natrolite and substantially ussingite + subordinate natrolite segments a few meters long alternate within the vein. Chesnokovite was found in one of the ussingite intervals, where the vein crosscuts urtite above the unit of loparite malignite.

In addition to ussingite, the early minerals in this interval are natrolite, sodalite, vuonnemite, steenstrupine-(Ce), phosinaite-(Ce), serandite, and natisite. The latter five minerals occur in selvages. The complex of later minerals with a predominance of salt species is hosted in numerous lens-shaped cavities developed in the axial zone encrusted with ussingite crystals. In turn, the salt mineralization can be divided into two substages, the products of which crystallized in-sequence at different temperatures. Anhydrous salt minerals—villiaumite NaF, natrosilite $\text{Na}_2\text{Si}_2\text{O}_5$, minor olympite $\text{Na}_5\text{Li}(\text{PO}_4)_2$, and sidorenkite $\text{Na}_3\text{Mn}(\text{PO}_4)(\text{CO}_3)$ —were formed during the early substage; the partial replacement of phosinaite-(Ce) with vitusite-(Ce) appeared to occur during this hyperalkaline substage as well. Finally, the assemblage of salt minerals highly enriched in water including revdite (partially complete pseudomorphs after natrosilite, less frequently, separate pods), chesnokovite $\text{Na}_2[\text{SiO}_2(\text{OH})_2] \cdot 8\text{H}_2\text{O}$, and natrophosphate $\text{Na}_7(\text{PO}_4)_2\text{F} \cdot 19\text{H}_2\text{O}$ were deposited during the late hydrothermal substage; alkali zeolite, gobbinsite, $(\text{Na},\text{K})_5[\text{Al}_5\text{Si}_{11}\text{O}_{32}] \cdot 12\text{H}_2\text{O}$, with highly

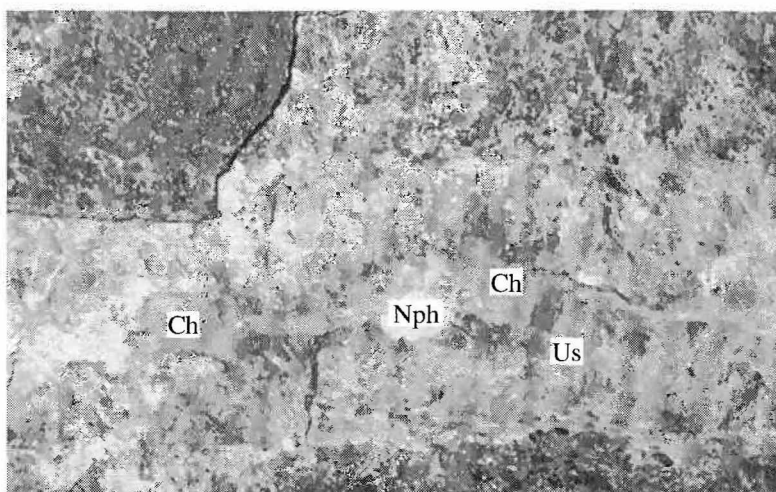


Fig. 1. Pods of chesnokovite (Ch) with natrophosphate (Nph) in ussingite (Us). The Kedykverpakhk-22 vein crosscutting urtite, photo in situ. The width of the photograph is 23 cm. Photo by I.V. Pekov.

disordered Al and Si (as follows from the IR spectrum), probably, also pertains to this substage.

Chesnokovite occurs as pods up to $4 \times 6 \times 10$ cm in size completely filling the cavities (Fig 1). Some of these pods are monomineralic, whereas inclusions of natrophosphate are observed elsewhere. Segregations of chesnokovite are composed of chaotic aggregates of poorly shaped lamellar crystals flattened along [010] and usually split to varying degrees. Pinacoid {010} is the main form; the lateral faces are not developed. Twinning is not observed. Separate crystals vary from several μm to $0.05 \times 1 \times 2$ cm in size.

It should be added that the pods of hydrous sodium silicate, which are not visually discernible from those in vein Kedykverpakhk-22, were observed by Pekov in the two other ussingite veins uncovered by underground mining at Mount Kedykverpakhk. Judging by the nature of alteration (see below) of the samples collected that year, these pods were composed of chesnokovite.

PHYSICAL AND OPTICAL PROPERTIES

The crystals of chesnokovite are colorless and transparent, whereas the segregations are white or light brownish, yellowish, and translucent. The streak is white, with a muddy vitreous luster. Fluorescence is not observed. Chesnokovite is brittle, with a cleavage in three perpendicular directions: perfect on (010) and distinct on (100) and (001). The fracture is stepped and conchoidal on cross chips of thick plates. The Mohs' hardness is 2.5. The density measured with equilibration in heavy liquids is 1.68 (2) g/cm^3 ; the density calculated on the basis of the empirical formula is 1.60 g/cm^3 and that calculated on the basis of an idealized formula is 1.64 g/cm^3 .

The new mineral is optically biaxial, positive, $\alpha = 1.449$ (2), $\beta = 1.453$ (2), $\gamma = 1.458$ (3), $2V_{\text{meas}} = 80$ (5) $^\circ$, $2V_{\text{calc}} = 84$ $^\circ$. Dispersion of the optic axes is not detected. Under a microscope, chesnokovite is colorless and is nonpleochroic. Extinction is parallel to the cleavage directions. Section *XY* of the optic indicatrix lies in the {010} cleavage face and, accordingly, $Z = b$.

The compatibility index of the chemical composition and properties calculated from the Gladstone–Dale equation (Mandarino, 1981) is 0.029 (excellent) for the measured density, -0.021 (excellent) and 0.005 (superior) for the density calculated from the empirical and idealized formulas, respectively.

INFRARED SPECTROSCOPY

The infrared spectrum of chesnokovite (Fig. 2) in a KBr disk with the powder of the mineral was measured on a Specord 75 IR dual-beam spectrophotometer. The spectrum of the pure KBr disk was deducted during recording in the automatic mode. The checking experiment (spectrum of the chesnokovite suspension in vaseline oil within the range $300\text{--}400$ cm^{-1}) confirmed that the mineral sample was not dehydrated during quick grinding with KBr.

The IR spectrum of chesnokovite is characterized by very strong bands of stretching (range $3200\text{--}3700$ cm^{-1}) and bending (range $1580\text{--}1680$ cm^{-1}) vibrations of water molecules forming hydrogen bonds of different strengths. Bands in the range 2200 to 3200 cm^{-1} correspond to stretching vibrations of weak-acid Si–OH groups.

The origin of the weak band at 1450 cm^{-1} is uncertain. It can be attributed to both an insignificant impurity of the presumably new-formed carbonate (no more than 1 vol %, taking into account the high extinction

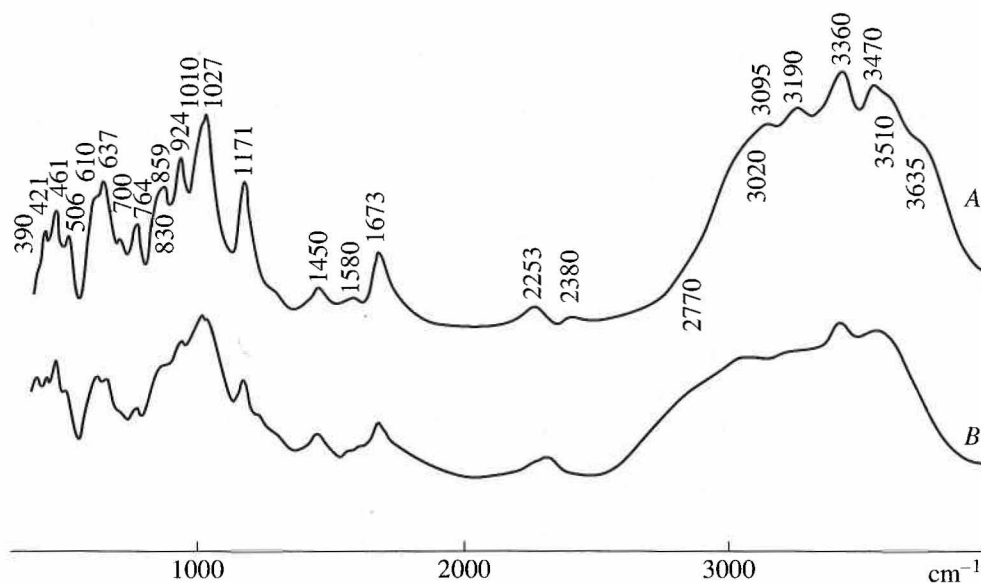


Fig. 2. IR spectra of (A) chesnokovite and (B) its synthetic analogue (B).

index of such bands) or isolated H^+ cations with acid groups Si–OH as a donor.

The absorption maximums within the ranges 400–510 and 850–930 cm^{-1} result from the vibrations of isolated SiO_4 tetrahedrons. Strong bands within the range 1000–1200 cm^{-1} (absorption maximums 1010, 1027, and 1171 cm^{-1}), which are untypical of orthosilicates without protoned SiO_4 tetrahedrons, are probably caused by Si–OH groups. This suggestion is confirmed by the presence of strong bands at 1042 and 1191 cm^{-1} in the IR spectrum of suolunite $Ca_2[Si_2O_5(OH)_2] \cdot H_2O$, a sorosilicate mineral, where two of the six nonbridge vertices of the Si_2O_7 group are occupied by hydroxyl ions; strong bands at 1042 and 1191 cm^{-1} are recorded.

The IR spectrum of synthetic $Na_2[SiO_2(OH)_2] \cdot 8H_2O$ measured under similar conditions contains the same set of bands, as well as that of chesnokovite, but is distinguished by a worse resolution: the absorption maximums are observed against the background of diffuse bands of a poorly crystallized component (Fig. 2).

The IR spectrum of chesnokovite markedly differs from the spectra of other minerals, including hydrous sodium silicates, and can be used as a reliable diagnostic feature.

CHEMICAL COMPOSITION AND CHEMICAL PROPERTIES

The microprobe analysis of chesnokovite meets difficulties due to the high concentration of water: the stable reproducibility of the analytical results was obtained only for Si with a Camebax MBX/ Link AN 10000 EDS at an accelerating voltage of 15 kV, a current of 3 nA, and a raster analysis area of $10 \times 10 \mu m$

(analyst A.N. Nekrasov). It was established that only the K contents from elements with an atomic number higher than oxygen can be measured with an electron microprobe in the new mineral. Concentrations of Na, K, and Li were measured with the atomic emission method (analyst S.P. Purusova). The water content was determined with the Alimarin method: a ground sample was heated up to 1000°C and the released water was entrapped in an adsorption tube filled with $Mg(ClO_4)_2$ (analyst A.S. Astakhova). During this experiment, the absence of CO_2 was monitored by a tube filled with ascarite, an asbestos material saturated with NaOH. The absence of borate and organic groups in the mineral was confirmed by IR spectroscopy.

The chemical composition of chesnokovite determined using a combination of the above methods is as follows (wt %; range of contents in parentheses): 21.49 (20.65–22.33) Na_2O , 0.38 (0.31–0.45) K_2O , 0.003 (0.002–0.004) Li_2O , 21.42 (20.0–22.9) SiO_2 , 54.86 H_2O , where the total is 98.153. This composition corresponds to the following empirical formula calculated in line with the structural data on the basis of $O_2(OH)_2$: $(Na_{1.96}K_{0.02})_{1.98}Si_{1.005}O_2(OH)_2 \cdot 7.58H_2O$. The simplified formula ($Z = 8$) is $Na_2[SiO_2(OH)_2] \cdot 8H_2O$. The theoretical chemical composition calculated from this formula is, wt %: 21.81 Na_2O , 21.14 SiO_2 , 57.05 H_2O , where the total is 100.00.

During the heating of chesnokovite sample in air (derivatograph, analyst L.V. Mel'chakova), a quick weight loss (48.5%) is recorded within the range of 50 to 120°C and then gives way to a slow weight loss (more 5.5%) upon heating up to 800°C. Thus, the amount of molecular water (7.58 molecules per formula) calculated on the basis of the measurement with the Penfield method is consistent with thermogravimet-

ric data: 48.5% weight loss within the range 50–210°C corresponds to 7.59 H₂O molecules.

The lower measured content of water in comparison with the theoretical estimation probably results from the partial dehydration of the sample during preparation at room temperature, as indicated by the incomplete sum of analysis, the best fit of the measured density to the density calculated on the basis of the empirical formula, and the lowest value of the compatibility index of the composition and properties calculated from the Gladstone–Dale equation for the idealized formula.

The new mineral slowly dissolves in dilute HCl without gas emission, yielding clots of a silica gel. A long stay in cold water results in the soaking of its segregations, probably owing to a partial decomposition under the effect of dissolved atmospheric CO₂ or hydrolytic breakdown.

Chesnokovite is a highly unstable mineral in a room environment. At a normal atmospheric humidity and CO₂ concentration, lumps 0.5–1 cm in size are irreversibly altered after 2–3 days, whereas the powder becomes altered in a few hours. The alteration is manifested in the dehydration and carbonation; as a result, chesnokovite transforms to a loose aggregate of thermonatrite and opal, probably, in line with the following scheme: $\text{Na}_2[\text{SiO}_2(\text{OH})_2] \cdot 8\text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O} + \text{SiO}_2 \cdot n\text{H}_2\text{O} + (8 - n)\text{H}_2\text{O} \uparrow$. The decomposition accelerates with an increasing temperature, dry air, and its enrichment in CO₂. According to our observations, cores of large chesnokovite segregations remain unaltered under a thermonatrite–opal crust in humid and cold air of a mine for several months. Thus, the solid encapsulation of chesnokovite samples is required to retain this mineral, including collections. Preferably, such encapsulation should be carried out immediately during the course of sampling.

X-RAY CRYSTALLOGRAPHY

The single-crystal X-ray diffraction analysis of the new mineral failed because of the mineral's imperfection and instability in air. Analysis of the X-ray powder pattern (Table 1) demonstrates that chesnokovite is a natural analogue of the well-known synthetic compound Na₂SiO₃ · 9H₂O, or more precisely, taking into account the structural parameters, Na₂[SiO₂(OH)₂] · 8H₂O (Jamieson and Dent Glasser, 1966).

The X-ray diffraction pattern of chesnokovite was recorded with a STOE STADI MP powder diffractometer using a Ge(111) curved monochromator and a linear position-sensitive detector. The crystal structure of the new mineral was studied using the Rietveld method on the basis of the powder data set. Crystal data as well as the basic parameters of the experiment and refinement of the chesnokovite crystal structure are presented in Table 2, while the atom coordinates and isotropic displacement parameters are given in Table 3. The program Wyrriet, version 3.3 (Schneider, 1989) was used

for data processing. The structure of the synthetic compound Na₂[SiO₂(OD)₂] · 8D₂O, space group *Ibca* (Schmidt et al., 1984), a deuterated analogue of chesnokovite, was accepted as the initial model for refinement. The profiles were fitted using a pseudo-Voigt function. At the initial stage, the structure model was fixed, and the scale factor, zero point, unit-cell parameters, peak asymmetry ($2\theta < 50^\circ$), and peak-widths at half-height were refined using graphic modeling of the background throughout the refinement until the *R* factors ceased to change. At the next stage, the atom coordinates and isotropic displacement parameters were refined. At the last stage, the hydrogen atoms were added to the structural model. The coordinates of these atoms were taken from the structure of Na₂[SiO₂(OD)₂] · 8D₂O (Schmidt et al., 1984) and corresponded to the location of the D atoms. The displacement parameters of H atoms were fixed and only their coordinates were refined. The refinement resulted in the following final reliability factors: $R_p = \Sigma|I_{\text{meas}} - I_{\text{calc}}|/\Sigma I_{\text{meas}} = 5.77$, $R_{wp} = [\Sigma w|I_{\text{meas}} - I_{\text{calc}}|^2/\Sigma w]^{1/2} = 7.77$, $GOF = \{\Sigma[w|I_{\text{meas}} - I_{\text{calc}}|^2]/(N_{\text{meas}} - N_{\text{calc}})\}^{1/2} = 1.78$, $R_b = \Sigma|I'_{\text{meas}} - I'_{\text{calc}}|/\Sigma I'_{\text{meas}} = 2.07$, $R_f = \Sigma|F_{\text{meas}} - F_{\text{calc}}|/\Sigma F_{\text{meas}} = 1.74$, and the Durbin–Watson statistics $DWD = 0.85$ (Hill and Flack, 1987). In these expressions, I'_{meas} and I'_{calc} are the measured and calculated integral intensities of the Bragg reflections, and I_{meas} and I_{calc} are the measured and calculated intensities, respectively. Figure 3 demonstrates a good fit between the experimental and calculated X-ray diffraction patterns of chesnokovite.

CRYSTAL STRUCTURE

The crystal structure of chesnokovite, as well as its synthetic analogue (Jamieson and Dent Glasser, 1966; Schmidt et al., 1984), is composed of isolated tetrahedral anions [SiO₂(OH)₂]²⁻ (two vertices of each tetrahedron are occupied by O-atoms and two others by OH-groups) and edge-shared chains of polyatomic cations [Na(H₂O)₆]⁺ running along [100]. The interatomic distances in the tetrahedron vary from 1.553(10) Å [with atom O(2) = O] to 1.658 (10) Å [with atom O(1) = OH]. Distances within the octahedron Na(H₂O)₆ range within 2.335(9)–2.498(10) Å. Si- and Na-polyhedrons are linked only by H-bonds. Isolated tetrahedrons [SiO₂(OH)₂] linked to one another by hydrogen bonds form pseudosheets perpendicular to axis *b* (Fig. 4) providing the layered structure of the chesnokovite structure and perfect cleavage on {010}.

COMPARATIVE CRYSTAL CHEMISTRY

Minerals with a structure allied to chesnokovite are unknown. The first natural sodium orthosilicate has a unique feature for minerals, that is, two OH-groups in the vertices of an isolated Si-tetrahedron. The appear-

Table 1. X-ray powder diffraction data for chesnokovite

I_{meas}	I_{calc}	d_{meas}	d_{calc}	hkl	I_{meas}	I_{calc}	d_{meas}	d_{calc}	hkl
11	23	8.507	8.4865	020	11	6	2.003	2.0192	541
						7		2.0010	145
16	23	5.925	5.9078	121	3	8	1.998	1.9994	424
3	6	5.794	5.7826	002	1	2	1.991	1.9918	082
30	41	5.001	4.9932	211	3	4	1.971	1.9693	363
42	51	4.788	4.7787	022	1	1	1.955	1.9520	600
2	6	4.251	4.2432	040	2	3	1.941	1.9403	372
1	1	4.126	4.1146	202	4	4	1.917	1.9174	354
89	100	3.847	3.8383	231	4	6	1.913	1.9125	611
6	10	3.776	3.7714	141	1	1	1.882	1.8797	026
2	2	3.398	3.3908	321	1	2	1.853	1.8512	444
2	2	3.368	3.3622	123	13	18	1.837	1.8349	174
19	29	3.168	3.1635	213	4	4	1.825	1.8222	631
42	58	2.932	2.9280	400	9	1	1.813	1.8105	543
5	5	2.899	2.8913	004	11	14	1.810	1.8097	514
35	45	2.832	2.8288	060	5	7	1.803	1.8017	345
97	20	2.800	2.8087	332	1	2	1.785	1.7826	561
			2.7985	233					
			2.7882	341	1	3	1.776	1.7739	291
100	17	2.774	2.7722	143					
	58		2.7694	124					
5	4	2.741	2.7368	024	2	4	1.772	1.7701	165
11	13	2.680	2.6752	161	5	6	1.734	1.7324	613
4	1	2.615	2.6122	402	3	1	1.715	1.7180	480
	4		2.6101	323					
1	3	2.596	2.5925	204	4	6	1.711	1.7105	084
2	3	2.542	2.5370	431	2	1	1.651	1.6776	374
2	4	2.520	2.5145	134	3	5	1.648	1.6469	482
1	1	2.483	2.4794	224	3	2	1.617	1.6174	572
1	0.5	2.376	2.3893	044	7	3	1.615	1.6157	525
10	10	2.342	2.3421	352	9	8	1.612	1.6100	406
	7		2.3362	253					
6	8	2.306	2.3036	343	2	6	1.595	1.5929	066
6	4	2.302	2.3020	314	2	1	1.551	1.5498	185
7	11	2.249	2.2470	361	3	5	1.549	1.5495	653
4	6	2.220	2.2161	521	3	3	1.508	1.5075	671
17	3	2.196	2.1964	172	1	1	1.487	1.4860	615
	19		2.1922	125					
6	7	2.156	2.1535	512	1	1	1.479	1.4769	484
1	1	2.147	2.1493	334	4	4	1.457	1.4556	574
1	3	2.138	2.1342	215	1	1	1.423	1.4226	565
5	17	2.122	2.1216	080	1	3	1.418	1.4181	295
20	26	2.035	2.0344	460	1	2	1.400	1.3992	466
6	3	2.023	2.0269	532					

Table 2. Crystal data of chesnokovite and experimental data on the refinement of its crystal structure

Formula	$\text{Na}_2[\text{SiO}_2(\text{OH})_2] \cdot 8\text{H}_2\text{O}$
Space group; Z	<i>Ibca</i> ; 8
Unit-cell dimensions, Å	$a = 11.7119(6)$, $b = 16.973(1)$, $c = 11.5652(6)$
Volume of unit cell, Å ³	2299.0(2)
$a : b : c$	0.6900 : 1 : 0.6814
D_{calc} , g/cm ³	1.64
μ , mm ⁻¹	0.328
Radiation, wavelength, Å	$\text{CuK}\alpha_1$; 1.54056
2 θ range, degree	8.00–105.48
Number of reflections	661
Number of refined parameters	67
R_p	5.77
R_{wp}	7.77
R_B	2.07
R_F	1.74

ance of $[\text{SiO}_2(\text{OH})_2]^{2-}$ anion instead of a common $[\text{SiO}_4]^{4-}$ is evidently caused by the necessity to maintain a general and local valence balance at a very low-charge cation fraction made up only of two Na^+ ions for one Si-tetrahedron.

Among natural hydrous sodium silicates, chesnokovite is distinguished by the lowest value of $\text{Si}/\text{Na} = 0.5$ and the largest content of H_2O (54.9 wt % against a theoretical 57 wt %), whereas in makatite, revdite, kanemite, grumantite, magadiite, and kenyaite, the water content ranges from 11 to 33 wt %. In contrast to chesnokovite, Si-tetrahedrons in the above minerals are not isolated and make up a condensed double-chain, layer, and framework structural motifs (Fig. 5) (see below). The kenyaite structure is unknown, but according to $\text{Si}/\text{Na} = 11$, this mineral must have a high-condensed (Si–O) motif. Only chesnokovite of all sodium hydrous

silicates is highly unstable in air owing to the extremely loose structure supported by the system of H-bonds, which are easily broken during a reaction even with such a weak acid as carbonic (carbonation) and by heating (dehydration). Other natural hydrous silicates are more stable due to the presence of bridge Si–O–Si bonds in infinite (Si–O) radicals. Revdite, which has a chain (Si–O) motif, is transformed under atmospheric conditions over several years and to an insignificant degree, whereas makatite, kanemite, grumantite, and magadiite with higher condensed (Si–O) motifs are stable in air. Thus, the stability of sodium hydrous silicates is directly related to the degree of (Si–O)-radical condensation.

The diversity of synthetic sodium silicates, including their structures, is much wider than that of natural analogues. From two modifications of $\text{Na}_2\text{Si}_2\text{O}_5$, only the β form, natrosilite, has been found in nature (Timoshenkov et al., 1975). This modification differs from α - $\text{Na}_2\text{Si}_2\text{O}_5$ by the number of similarly oriented tetrahedrons in six-member rings that make up sheets: in α - $\text{Na}_2\text{Si}_2\text{O}_5$, three tetrahedrons “look” to one side, and three, to the opposite side, whereas in β - $\text{Na}_2\text{Si}_2\text{O}_5$, the ratio of distinctly oriented tetrahedrons is 4 : 2 (Pant, 1968; Pant and Cruickshank, 1968). Three additional phases— $\text{Na}_4\text{Si}_2\text{O}_6$ (McDonald and Cruickshank, 1967), $\text{Na}_4\text{Si}_6\text{O}_{14}$ (Jamieson, 1967), and $\text{Na}_6\text{Si}_8\text{O}_{19}$ —are known among artificial anhydrous sodium silicates. The latter compound was synthesized more than 40 years ago; however, its structure was determined only recently (Kruger et al., 2005).

Most natural and synthetic sodium silicates have highly condensed (Si–O) complexes. These are unidimensional chains in the structure of $\text{Na}_4\text{Si}_2\text{O}_6$ (McDonald and Cruickshank, 1967) and two types of nonbonded tetrahedral ribbons in revdite (Rastsvetaeva et al., 1992). An extremely rare (Si–O) complex consisting of doubled chains combined are transformed into a ribbon similar to that of caysichite and composed of four-member rings, as was recently established for the structure of synthetic $\text{NaSi}_2\text{O}_4(\text{OH})$ (Sassi et al., 2003). Bilateral networks of natrosilite-type six-mem-

Table 3. Atom coordinates and isotropic displacement parameters of chesnokovite

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}	Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}
Si	0.3770(16)	0.0	0.25	0.028(3)	H(2)	0.09(3)	0.035(14)	0.49(2)	0.1
Na	0.1244(10)	0.1817(6)	0.4143(6)	0.038(3)	H(3)	0.04(2)	0.013(15)	0.39(2)	0.1
O(1)	0.2898(14)	0.0540(12)	0.1696(12)	0.039(6)	H(4)	0.05(2)	0.138(17)	0.209(19)	0.1
O(2)	0.4469(12)	0.0541(12)	0.3319(12)	0.030(5)	H(5)	0.17(2)	0.134(15)	0.205(19)	0.1
O(3)	0.119(2)	0.0379(10)	0.4339(14)	0.033(5)	H(6)	0.37(2)	0.133(12)	0.093(17)	0.1
O(4)	0.1122(18)	0.1649(10)	0.2061(12)	0.025(5)	H(7)	0.40(2)	0.167(11)	−0.027(16)	0.1
O(5)	0.4140(14)	0.1755(12)	0.0536(12)	0.044(6)	H(8)	0.38(2)	0.159(13)	0.365(18)	0.1
O(6)	0.3215(12)	0.1905(12)	0.3848(16)	0.047(8)	H(9)	0.35(2)	0.238(14)	0.339(18)	0.1
H(1)	0.27(2)	0.016(9)	0.11(2)	0.1					

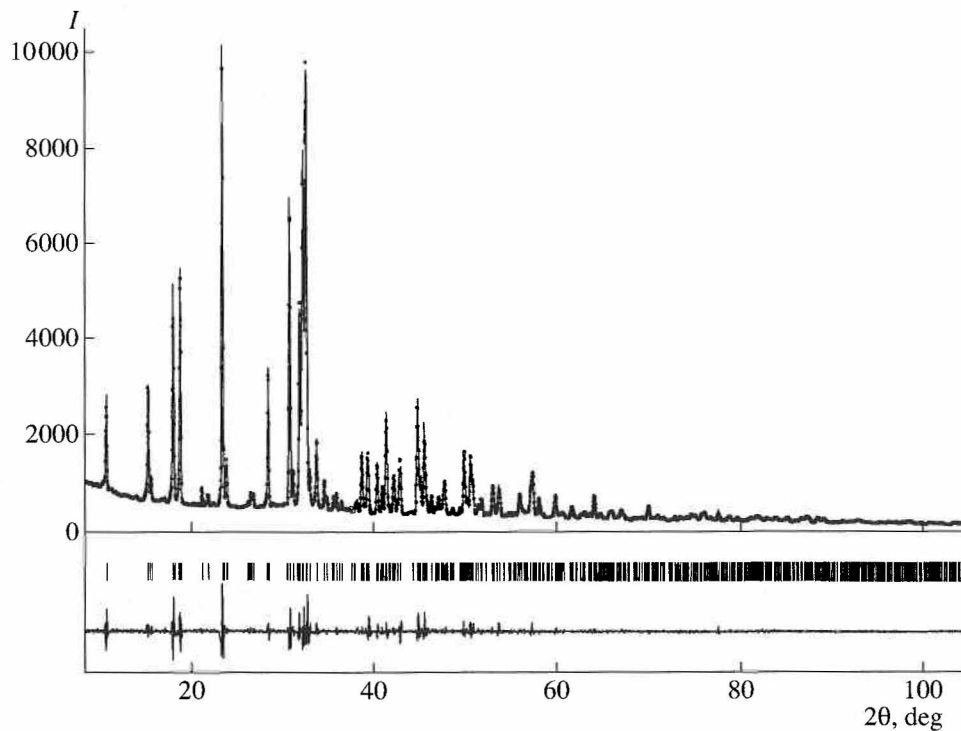


Fig. 3. Experimental and calculated (dashes) X-ray powder diffraction patterns of chesnokovite. Vertical dashes show the location of reflections in the calculated powder pattern, and the curve in the lower part of the figure is the difference curve of the intensities of the experimental and calculated X-ray powder patterns.

ber rings occur in the structures of makatite (Annehed et al., 1982) and kanemite (Garvie et al., 1999), and two-dimensional (Si–O) complexes were established in the structures of magadiite (Garces et al., 1988) and $\text{Na}_4\text{Si}_6\text{O}_{14}$ (Jamieson, 1967). A relatively insignificant change in the composition of the latter compound due to the incorporation of 0.5 water molecules per formula results in the formation of the $\text{Na}_2\text{Si}_3\text{O}_7 \cdot \text{H}_2\text{O}$ phase with open microporous framework containing ten-membered rings (Matijasic et al., 2000). A new type of (Si–O) sheets composed of five-, six-, and eight-membered rings was identified in the structure of $\text{Na}_5\text{Si}_8\text{O}_{19}$ (Kruiger et al., 2005). Finally, the broken (Si–O) framework composed of spiral chains with a period of four tetrahedrons in the structure of grumantite (Yamnova et al., 1989) demonstrates the highest condensation among the structures of sodium silicates.

Like chesnokovite and its synthetic analogue $\text{Na}_2[\text{SiO}_2(\text{OH})_2] \cdot 8\text{H}_2\text{O}$, only $\text{Na}_2[\text{SiO}_2(\text{OH})_2] \cdot 4\text{H}_2\text{O}$ (Jost and Hilmer, 1966) and $\text{Na}_2[\text{SiO}_2(\text{OH})_2] \cdot 7\text{H}_2\text{O}$ (Dent Glasser and Jamieson, 1976) contain biprotonated isolated Si-tetrahedrons among a wide series of hydrous sodium silicates. As in the case of chesnokovite, in $\text{Na}_2[\text{SiO}_2(\text{OH})_2] \cdot 4\text{H}_2\text{O}$, a complicated system of H-bonds combines these tetrahedrons in pseudosheets. Monoprotonated tetrahedrons $[\text{SiO}_3(\text{OH})]$ in the structure of $\text{Na}_3[\text{SiO}_3(\text{OH})] \cdot \text{H}_2\text{O}$ curl around screw axis 2_1 and a spiral pseudochain owing to the hydrogen bonds (Schmidt and Felscher, 1990). While the number of

crystalhydrate water molecules increases to 2 per formula unit, this type of one-dimensional chain is retained; however, two orthorhombic $\text{Na}_3[\text{SiO}_3(\text{OH})] \cdot 2\text{H}_2\text{O}$ modifications arise. They differ in the crystallization temperature and unit-cell dimensions, but have the same space group (Schmidt et al., 1979, 1981). Compound $\text{Na}_3[\text{SiO}_3(\text{OH})] \cdot 5\text{H}_2\text{O}$ with monoprotonated tetrahedrons $[\text{SiO}_3(\text{OH})]$ is more hydrated. In this compound, pairs of Si-tetrahedrons are linked by H-bonds into the $\text{Si}_2\text{O}_6(\text{OH})_2$ groups (Smolin et al., 1973). In the structure of the synthetic phase $\text{Na}_2\text{SiO}_3 \cdot 6\text{H}_2\text{O}$, Na-octahedrons form sheets with orthotetrahedrons $[\text{SiO}_3(\text{OH})]$ “hanged” by one (OH) vertex (Williams and Dent Glasser, 1971). The original (Si–O) complex that comprises the layers consisting of five-membered ring ribbons was described in the structure of the microporous $\text{Na}[\text{Si}_4\text{O}_8(\text{OH})] \cdot 4\text{H}_2\text{O}$ compound (Vortmann et al., 1997).

As can be seen from this overview, the structures of sodium silicates, especially synthetic, are highly diverse, and finding a sufficient amount of chesnokovite containing isolated biprotonated tetrahedrons $[\text{SiO}_2(\text{OH})_2]$ indicates the probable existence of other natural species of similar structural types.

GENETIC FEATURES

Chesnokovite may be regarded as a sensitive indicator of formation conditions. The structure, chemical

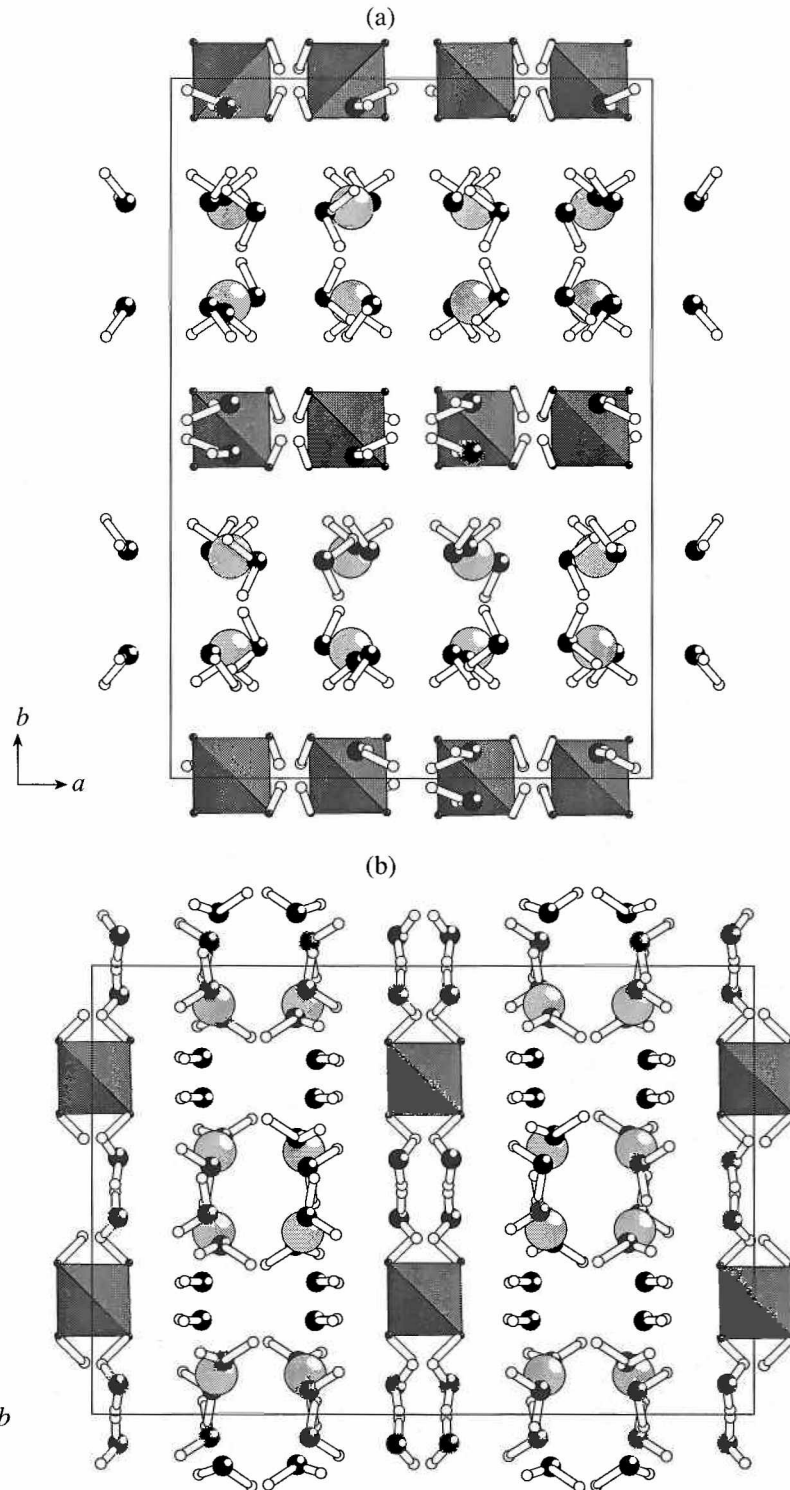


Fig. 4. Crystal structure of chesnokovite: (a) ab and (b) bc projections. Si tetrahedra and Na atoms are dark gray and light gray, respectively. O atoms in water molecules and in the vertices of the Si tetrahedra are large and small solid circles, respectively. H atoms are open circles.

properties, and behavior upon heating demonstrate that this mineral is very responsive to such parameters of a mineral-forming environment as temperature and CO_2

activity, which apparently should be very low. In the Kedykverpakhk-22 vein, carbonates are absent (only sporadic grains of carbonate-phosphate sidorenkite

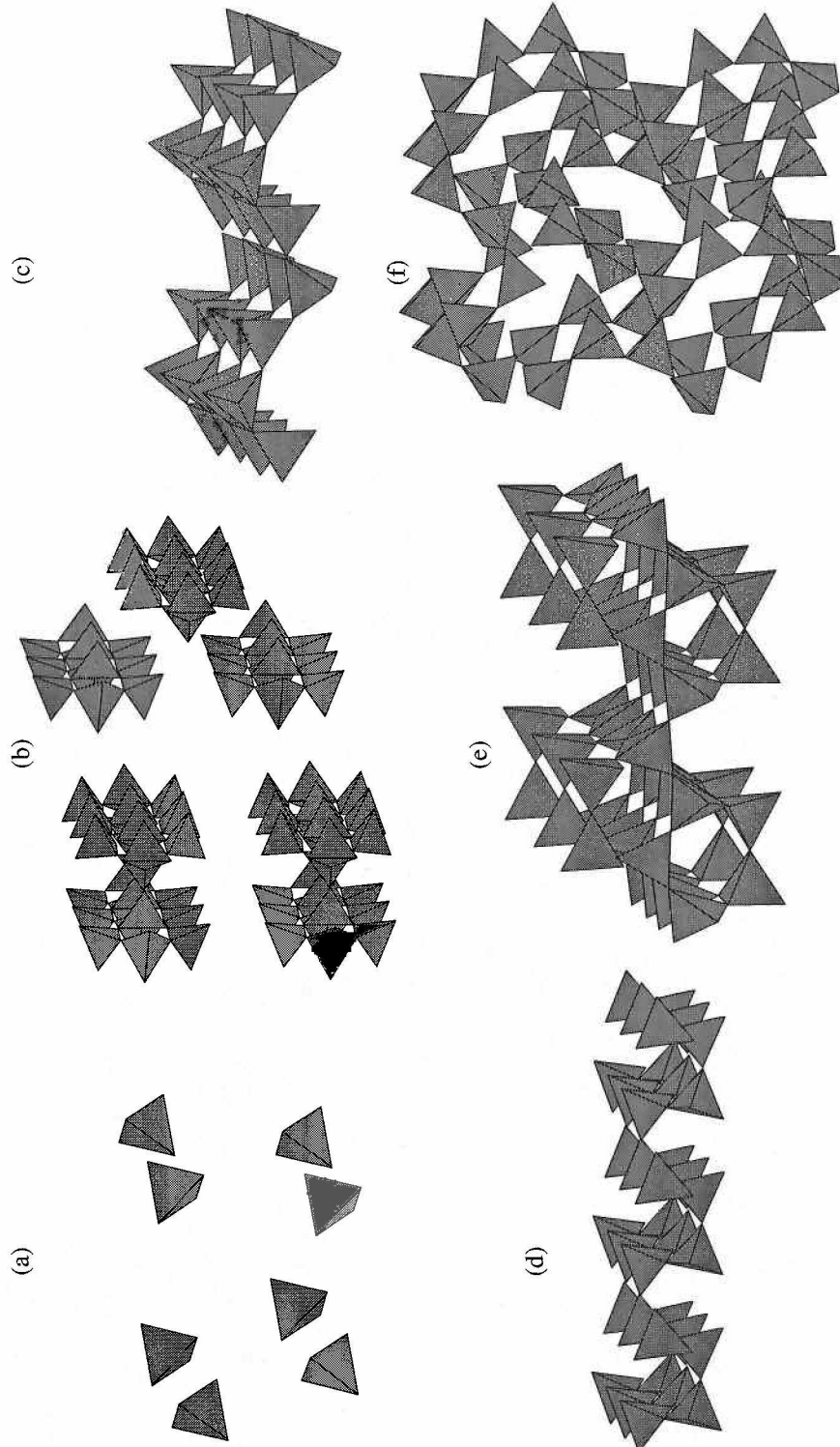


Fig. 5. Different types of (Si-O) complexes in the structures of natural sodium hydrous silicates: (a) isolated tetrahedrons in chesnokovite; (b) two types of isolated tetrahedral bands in revdite (Rastsvetaeva et al., 1992); (c) layers in makatite (Annehed et al., 1982); (d) layers in kanemite (Garvie et al., 1999); (e) layers composed of tubular ribbons in magadiite (Graces et al., 1998); and (f) broken framework in grumanite (Yamnova et al., 1989).

were observed), and no chesnokovite occurs where they are noted. The ready transformation of chesnokovite to thermonatrite and opal testifies that its association with carbonates seems forbidden. The formation of chesnokovite probably occurs at a temperature no higher than 50°C (taking into account the pressure, this estimate may increase, but in any case, unlikely exceeds 70–80°C). An analogue of chesnokovite was synthesized by crystallization from an aqueous solution at 20°C (Schmidt et al., 1984).

Natron $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ containing 63 wt % H_2O is known to crystallize from sodium-carbonate systems at a low temperature (<32°C). This mineral occurs in derivatives of peralkaline rocks, where it is regarded as both supergene (Dorfman et al., 1969) and hypogene (Khomyakov et al., 1990). Chesnokovite probably crystallizes under similar conditions from fairly cold solutions enriched in Na and strongly depleted in CO_2 .

The occurrence of chesnokovite in veins hosted in massive intrusive rocks at a great depth supports an hypogene rather than supergene origin of this mineral. Chesnokovite is assumed to crystallize during the final stage of evolution of an ultrasodium hydrothermal system at the very end of cooling of the upper part of the Lovozero pluton or after the cessation of this process.

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