NEW DATA ON MEGACYCLITE

Natalia V. Zubkova
Geology Department, Lomonosov Moscow State University, Moscow nata_zubkova@rambler.ru

Igor V. Pekov
Geology Department, Lomonosov Moscow State University, Moscow
Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, Moscow

Nikita V. Chukanov
Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow oblast

Dmitriy V. Lisitsin
Federal State Establishment "Gem Museum", Moscow

Murtasali Kh. Rabadanov
Institute of Crystallography, Russian Academy of Sciences, Moscow

Dmitriy Yu. Pushcharovsky
Geology Department, Lomonosov Moscow State University, Moscow

The second and the third occurrences of megacyclite $KNa_8Si_9O_{18}(OH)_9 \cdot 19H_2O$ in two alkaline massifs of Kola Peninsula, Russia are described. This mineral occurs as abundant late hydrothermal veinlets up to 1.5 mm thick and rare prismatic individual crystals up to 1.5 cm long, hosted in a large peralkaline pegmatite in association with microcline, aegirine, sodalite, lamprophyllite, lomonosovite, shcherbakovite, villiaumite, delhayelite, phosinaite-(Ce), clinophosinaite, natisite, lovozerite, tisinalite, nacaphite, rasvumite, and revdite at Mt. Rasvumchorr, Khibiny massif. In the Lovozero massif, megacyclite have been found in the Palitra pegmatite at Mt. Kedykverpakhk as white and yellowish brown spherulites up to 2 mm in diameter together, with revdite and zakharovite with microcline and natrosilite in cavities. The chemical composition of megacyclite from Khibiny is as follows: wt %: 3.69 K_2O, 19.85 Na_2O, 42.74 SiO_2, 33.03 H_2O, total 99.31. The empirical formula calculated on the basis of $[Si_9(O,OH)_{27}]$ is as follows: $K_{0.99}Na_{8.11}Si_9O_{18.10}(OH)_{8.90} \cdot 18.75H_2O$. The IR-spectrum and X-ray powder diffraction pattern are reported. The crystal structure of megacylite has been refined to $R_{hkl} = 0.0339$ for 8206 unique reflections with $I > \sigma 2\ (I)$. The mineral is monoclinic, space group $P2_1/c$, $a = 24.8219(16)$, $b = 11.9236(8)$, $c = 14.8765(9)$ Å, $\beta = 94.486(5)°$; $V = 4389.5(5)$ Å^3. Structural formula is $K_2Na_{16}Si_{18}O_{34}(OH)_{18}[O_{0.75}(OH)_{0.25}]_2(H_2O)_{36}[(H_2O)_{0.75}(OH)_{0.25}]_2$ ($Z = 2$). The system of the hydrogen bonds is characterized in detail.

6 tables, 5 figures, 11 references

The hydrous silicate of potassium and sodium megacyclite was found earlier only in the peralkaline pegmatoid veins (mainly composed by potassic feldspar, fenaksite and delhayelite) at Mt. Rasvumchorr, Khibiny alkaline massif, Kola Peninsula, Russia. The mineral occurs as colorless anhedral grains up to 3 mm in size and aggregates up to 5 mm in size included in large individual crystals of fenaksite, and intimate intergrowths of megacyclite and revdite, $Na_{16}[Si_4O_6(OH)_5]_2[Si_8O_{15}(OH)_6](OH)_{10} \cdot 28H_2O$ (Khomyakov *et al.*, 1993). The large ring radical composed of 18 Si-tetrahedra is the most interesting feature of the mineral and is reflected in the mineral name (from the Greek *mega* — large, *kyklos* — ring) According to the X-ray study of a single crystal drawn from holotype material, megacyclite is monoclinic, space group $P2_1/c$, $a = 24.91$, $b = 11.94$, $c = 14.92$ Å, $\beta = 94.47°$, $V = 4426$ Å^3. The chemical composition determined with an electron microprobe is as follows, wt %: Na_2O 19.75, K_2O 3.62, SiO_2 43.42, total 66.79 мас.%. From the structure solution, the ideal formula of the mineral is $Na_8KSi_9O_{18}(OH)_9 \cdot 19H_2O$, $Z = 4$ (Yamnova *et al.*, 1992; Khomyakov *et al.*, 1993).

We have discovered two more occurrences of megacyclite in the Khibiny and neighbouring Lovozero alkaline massifs. In Khibiny, the mineral was found also at Mt. Rasvumchorr, but in a slightly different environment. Megacyclite occurs in a large peralkaline pegmatite in the quarry of the Tsentral'ny Mine. This pegmatite is hosted in urtite adjacent to the contact with the nepheline-apatite rock has been traced for more than 10 m along strike with a maximum thickness not less than 1 m. Three mineral assemblages corresponding to three sequential stages of crystallization were recognized within the pegmatite. Potassic feldspar, nepheline, sodalite, alkali pyroxene (aegirine-salite) and amphibole, eudialyte, lamprophyllite, ilmenite, and fluorapatite are the earliest minerals. The anhydrous and

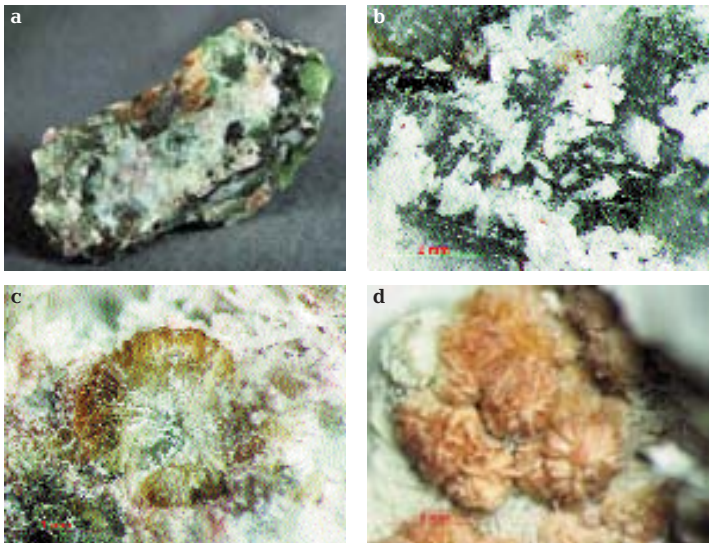


Fig. 1. Segregations of megacyclite: a,b — the Central mine, Mount Risvumchorr, Khibiny; c, d - the Palitra pegmatite, Mount Kedykverpakh, Lovozero. Fotos by S.I. Pekov (a), A.V. Kasatkin and I.V. Pekov(b—d).
a — white crust of megacyclite on the walls of fissure in peralkaline pegmatite (the sample was split along veinlet of megacyclite; tisinalite is brown; lomonosovite is dark brow; aegirine is green). Size of sample is 3 x 7 cm. Collection by D.V. Lisitsyn.
b — intergrowths of the megacyclite crystals encrusting the wall of crack. Collection by I.V. Pekov.
c — polychromatic (colorless core and amber-brown margins) spherulite in a matrix of revdite. Collection by V.G. Grishin.
d — segregation of light brown radiant intergrowths of megacyclite and revdite hosted by microcline in pocket. Collection by V.G. Grishin.

H_2O-low alkali-rich minerals green acicular aegirine (the major mineral of this assemblage), pectolite, magnesium astrophyllite, lomonosovite, shcherbakovite, barytolamprophyllite, villiaumite, fenaksite, delhayelite, phosinaite-(Ce), natisite (replaces ilmenite), zyrsinalite (rims and pseudomorphs after eudialyte), kazakovite, nakaphite (after fluorapatite), sidorenkite, djerfisherite, rusvumite, sphalerite and molybdenite crystallized during stage-2, which may be defined as "dry peralkaline". According to the presence of water-rich minerals with open structures, the stage-3 minerals were deposited from hydrothermal high-alkali fluids at temperatures not higher than 200—250°C. Some of "dry" peralkaline minerals are unstable in this environment and are replaced with water-bearing phases depleted in alkali cations and water-bearing: zyrsinalite with lovozerite, kazakovite with tisinalite, delhayelite with hydrodelhayelite and pectolite. Shafranovskite, ershovite, megacyclite, revdite, grumantite and poor-crystalline alkaline silicates with Mn and Ti are the other products of the hydrothermal stage, and fill small cavities and cracks.

Megacyclite is one of the latest phases and occurs as dense branching veinlets. At the type locality (Khomyakov *et al.*, 1993), this K,Na-silicate occurs in insignificant amount, whereas here, it is common: monomineralic veinlets are locally more than 10 cm long and up to 1.5 mm thick. Splitting the rock along these veinlets provides specimens with colorless or white crusts of megacyclite (Fig. 1) up to 5 x 7 cm in size. These veinlets are composed of elongated (less frequent isometric) lammelae without pronounced faces, reaching 1—1.5 mm in maximum dimension, occasionally 2—3 mm, and usually distorted. As a rule, these veinlets comprise subparallel lamellar segregations in which individual crystals of megacyclite are oriented normal or oblique to the selvages. Two other morphological types of megacyclite have been observed: (1) euhedral crystals as rhomb-like lamellae and plates up to 0.5 mm (goniometric study was not done due to the low quality of the crystal faces) covering the walls of small fissures, and (2) rosettes occurring in fissures and composed of coarse colorless crystals up to 0.2—1.5 cm in size; these are the largest individual crystals of the mineral.

In the Lovozero massif, megacyclite has been identified in the large peralkaline Palitra pegmatite developed by the underground working at Mt. Kedykverpakhk and has been recently described in detail by Pekov (2005). Megacyclite occurs in small cavities as inclusions in microcline and natrosilite. It is intimately associated with revdite, locally zakharovite, and earlier aegirine, villiaumite, serandite, nordite-(Ce), vuonnemite, potassic arfvedsonite and sphalerite. Megacyclite occurs as compact spherulites up to 1.5—2 mm in diameter, which are locally present as clusters included in a sugar-like matrix of revdite

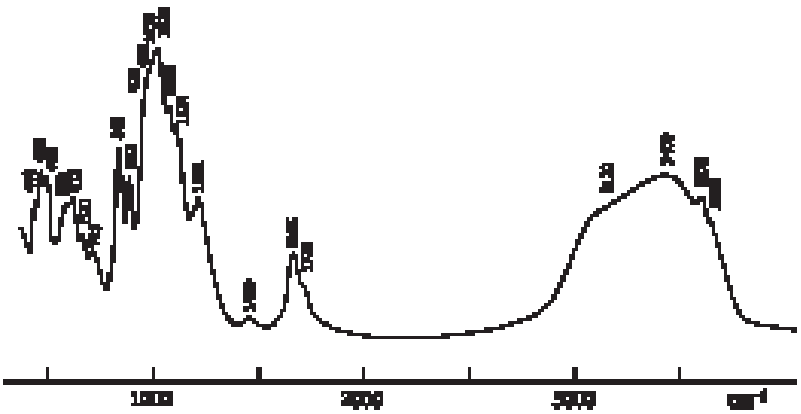


Fig. 2. IR spectrum of megacyclite.

or in crusts overgrown microcline. These spherulites are white, jonquil, or yellowish brownish on the surface and are composed of individual lamellar or columnar crystals.

According to local environment and intimate association with minerals unstable in the presence of surface water (villiaumite, natrosilite and revdite), megacyclite is endogenic rather than supergene. It seems to crystallize from residual fluid enriched in Na and K and derived from earlier peralkaline minerals during alteration. Megacyclite is one of the low-temperature phases in these pegmatites. It formed at temperatures not higher than 100 – 130°C, where the mobility of Ti, Zr, Fe and Al is already low, even in high-alkali media. Conditions of formation of such hydrothermal rocks are described by Lovskaya *et al.* (2002).

Individual crystals of megacyclite have mica-like cleavage and vitreous luster. In most cases, they are colorless and water clear. During extended interaction with dry air, megacyclite becomes opaque and white. However, its X-ray diffraction pattern and IR-spectrum were not modified. Optical properties of our samples are practically identical to those of the type material described by Khomyakov *et al.* (1993). Density of the Khibiny sample measured by A.E. Zadov by heavy liquids is 1.89(1) g/cm^3.

The chemical composition was studied with a Camebax MBX/Link AN 10000 at an accelerating voltage 15.7 kV, current 1.5 nA, analyst A.N. Nekrasov. The low current and the defocused beam (10 x 10 μm) avoided damage of the sample during analysis. The water content in our sample from Khibiny was determined by the Alimarin method: a ground sample was heated up to 1000°C and the released water was trapped in an adsorption tube filled with $Mg(ClO_4)_2$, analyst A.S. Astakhova. The average chemical composition is as follows (wt %, range of contents in parentheses, 6 analyzed points): 3.69 (3.5 – 4.0) K_2O, 19.85 (19.1 – 20.1) Na_2O, 42.74 (41.3 – 43.8) SiO_2, 33.03 H_2O, total 99.31. Other elements with $Z > 8$ are below detection limit. The empirical formula calculated on the basis of $[Si_9(O,OH)_{27}]$ is as follows: $K_{0.99}Na_{8.11}Si_9O_{18.10}(OH)_{8.90}\cdot 18.75H_2O$, very close to the ideal formula $KNa_8Si_9O_{18}(OH)_9\cdot 19H_2O$. The ideal chemical composition calculated from this formula is (wt %): 3.74 K_2O, 19.69 Na_2O, 42.94 SiO_2, 33.63 H_2O, total 100.00. For the Lovozero specimen, the following electron microprobe data were obtained (wt %): 3.8 K_2O, 19.5 Na_2O, 43.5 SiO_2, total 66.8.

In contrast to the authors of the original description of megacyclite, we had sufficient material to allow collection of much higher quality infrared and X-ray powder diffraction data.

In Khomyakov *et al.* (1993), only the set of maximum frequencies of bands in the IR-spectrum was published, whereas the spectral curve was not given and virtually no interpretation of the spectrum was given.

The IR-spectrum of our Kihibiny sample (Fig. 2) (in KBr disc, measured on a Specord 75 IR spectrophotometer) contains characteristic absorption bands of water (3300 – 3700 cm^{-1} stretching vibrations, 1665 cm^{-1} = bending vibrations). Most water molecules form hydrogen bonds and appear in the spectrum as a

Table 1. **X-ray powder diffraction data of megacyclite**

$I_{meas.}$	$I_{calc.}$	$d_{meas.}$	$d_{calc.}$	*h k l*
3	13	24.61	24.746	1 0 0
10	31	12.41	12.373	2 0 0
2	5	9.27	9.293	0 1 1
6	6	8.84	8.843	-1 1 1
5	15	8.23	8.249	3 0 0
31	35	7.394	7.415	0 0 2
	1		7.261	2 1 1
7	5	7.276	7.261	-1 0 2
32	36	6.944	6.955	1 0 2
	4		6.325	-3 1 1
7	8	6.283	6.297	0 1 2
1	3	6.171	6.186	4 0 0
2	8	6.123	6.152	2 0 2
35	33	5.957	5.962	0 2 0
22	19	5.786	5.796	1 2 0
2	3	5.749	5.742	-3 0 2
1	2	5.535	5.532	0 2 1
1	2	5.487	5.491	4 1 0
5	7	5.355	5.371	2 2 0
	1		5.365	1 2 1
1	2	5.248	5.270	-4 1 1
2	8	5.030	5.037	4 1 1
2	4	4.951	4.944	-4 0 2
1	1	4.892	4.852	3 1 2
15	18	4.633	4.646	0 2 2
1	1	4.605	4.608	-1 2 2
	2		4.577	4 0 2
12	23	4.517	4.526	1 2 2
14	35	4.452	4.460	-5 1 1
40	69	4.275	4.282	5 1 1
1	4	4.176	4.185	-4 2 1
1	1	4.130	4.136	-3 2 2
	1		4.124	6 0 0
2	3	3.972	3.975	5 0 2
	2		3.966	3 2 2
1	1	3.834	3.840	-6 1 1
31	38	3.798	3.808	-4 1 3
3	5	3.739	3.743	-5 2 1
14	8	3.714	3.728	1 2 3
4	2	3.690	3.708	0 0 4
	5		3.703	6 1 1
	1		3.700	-2 2 3
5	15	3.632	3.636	5 2 1
	1		3.631	4 2 2
19	16	3.617	3.625	1 0 4
3	8	3.570	3.577	2 2 3
1	2	3.536	3.540	0 1 4
2	3	3.504	3.503	0 3 2
	3		3.490	6 0 2
10	11	3.480	3.484	-5 1 3
36	23	3.464	3.469	1 1 4
1	3	3.373	3.379	3 2 3
1	2	3.361	3.359	-7 1 1
	2		3.339	2 1 4
	1		3.338	2 3 2
5	4	3.331	3.332	-4 2 3
	5		3.293	-7 0 2
8	8	3.285	3.292	-4 3 1
3	4	3.243	3.252	7 1 1
	1		3.241	5 1 3
7	7	3.168	3.177	-6 1 3
	3		3.177	-4 1 4
	3		3.162	-6 2 2
9	11	3.142	3.148	0 2 4
100	100	3.089	3.098	1 2 4
33	42	3.056	3.064	-5 3 1
9	17	2.999	3.004	5 3 1
	2		3.004	2 2 4
40	40	2.976	2.981	0 4 0
	4		2.979	-8 1 1
13	12	2.949	2.956	6 1 3
	2		2.948	-3 3 3
28	29	2.930	2.938	-8 0 2
	21		2.933	5 2 3
4	5	2.914	2.922	0 4 1
	3		2.907	-1 4 1
9	6	2.895	2.898	2 4 0
	1		2.897	1 4 1
	1		2.878	3 2 4
1	2	2.877	2.871	-6 0 4
1	3	2.852	2.852	-8 1 2
8	15	2.820	2.826	-4 3 3
3	8	2.796	2.803	3 4 0
	2		2.791	-6 1 4
3	7	2.776	2.782	6 3 1
3	3	2.763	2.766	0 4 2
1	2	2.733	2.734	-8 2 1
1	1	2.706	2.702	7 1 3
	6		2.685	4 4 0
23	14	2.674	2.679	9 1 0
	7		2.678	1 3 4
	2		2.672	-9 1 1
7	7	2.651	2.658	-4 4 1
	2		2.656	6 0 4
18	26	2.641	2.646	-9 0 2
2	3	2.620	2.627	4 4 1
	1		2.617	2 3 4
1	7	2.566	2.570	5 3 3
1	1	2.528	2.537	4 1 5
10	17	2.495	2.500	5 4 1
3	4	2.464	2.472	-8 0 4
6	5	2.434	2.441	1 0 6
	17	2.414	2.421	-8 1 4
9	3		2.420	6 3 3
6	7	2.405	2.410	5 1 5
9	12	2.385	2.391	1 1 6
2	2	2.374	2.377	0 3 5
2	2	2.348	2.352	1 3 5
1	4	2.336	2.342	2 1 6
2	4	2.312	2.317	9 2 2
	3		2.307	-5 4 3
9	7	2.297	2.302	1 4 4
8	11	2.275	2.281	6 1 5
	1		2.275	-2 2 6
	3		2.275	5 2 5
	1		2.271	-3 5 1
9	3	2.268	2.270	0 5 2
	2		2.267	-4 3 5
5	3	2.253	2.259	1 2 6
	1		2.256	1 5 2
	2		2.210	-7 4 2
4	3	2.207	2.210	-4 5 1
5	5	2.188	2.191	4 5 1
2	4	2.158	2.165	6 2 5
	1		2.153	7 1 5
1	2	2.134	2.141	10 2 2
	1		2.136	-5 5 1
1	3	2.114	2.116	5 5 1
	1		2.113	10 1 3
	2		2.101	10 3 0
2	7	2.090	2.092	-8 4 2
	1		2.083	-2 1 7
2	1	2.079	2.078	-11 1 3
1	5	2.067	2.072	-7 1 6
5	8	2.054	2.060	-3 1 7
	1		2.056	-6 5 1
1	2	2.027	2.034	6 5 1
1	2	2.020	2.025	-4 4 5
	1		2.020	10 2 3
1	3	2.004	2.009	-8 0 6
9	11	1.989	1.992	1 5 4
10	11	1.975	1.979	-9 4 2
1	2	1.942	1.946	5 5 3
	1		1.932	-12 1 3
3	3	1.913	1.918	7 3 5
	1		1.914	12 2 1
	2		1.904	10 4 0
2	2	1.900	1.904	-8 2 6
	1		1.901	-5 2 7
2	7	1.883	1883	-13 1 1
7	8	1.876	1.879	6 5 3
	1		1.864	-11 3 3
2	1	1.857	1.855	-2 0 8
1	3	1.828	1.832	-3 5 5
2	5	1.812	1.816	-13 2 1
	1		1.815	-4 0 8
	2		1.813	2 0 8
3	5	1.802	1.804	-4 5 5
	5		1.781	-4 6 3
10	8	1.776	1.778	10 3 4
	1		1.752	-14 1 1
3	2	1.748	1.752	-1 6 4
	2		1.751	0 6 4
	3		1.745	-13 2 3
10	9	1.740	1.743	1 6 4
	2		1.740	-12 1 5
	3		1.734	2 2 8
	4		1.719	-13 3 1
	5		1.716	-8 5 4
7	1	1.712	1.712	5 5 5
	1		1.712	-3 4 7
	4		1.712	5 6 3
1	2	1.693	1.698	-14 2 1
	2		1.697	-7 0 8
	1		1.691	-4 4 7
1	1	1.688	1.687	-12 2 5
	3		1.680	-7 1 8
	4		1.664	6 5 5
4	9	1.659	1.660	6 3 7
2	1		1.648	-8 0 8
	3	1.646	1.641	-14 2 3
4	4	1.629	1.633	-3 6 5
	2		1.625	-3 1 9

Table 2. **Crystal data and X-ray single-crystal measurement parameters for megacyclite**

Formula	$K_2Na_{16}Si_{18}O_{34}(OH)_{18}[O_{0.75}(OH)_{0.25}]_2(H_2O)_{36}[(H_2O)_{0.75}(OH)_{0.25}]_2$
Unit-cell parameters, Å	a = 24.8219(16), b = 11.9236(8), c = 14.8765(9), β = 94.486(5)o
Space group; Z	$P2_1/c$; 2
Unit-cell volume of unit cell V, Å^3	4389.5(5)
Calculated density ρ, g/cm^3	1.905
Extinction coefficient μ, мм$^{-1}$	0.573
Formula weight	1259.21
F_{000}	2592
Crystal size, mm	0.24 x 0.45 x 0.32
Difractometer	Xcalibur S (CCD)
Radiation; wave length, Å	Mo$K\alpha$ λ = 0.71073
Range for data collection θ, °	3.68, 57.79
Scanning intervals	$-54 \le h \le 57$; $-17 \le k \le 17$; $-32 \le l \le 32$
Total reflections	130583
Number of reflections with $I > \sigma(I)$	39442
Number of inequivalent reflections with $I > \sigma(I)$	10773
Number of inequivalent reflections with $I > 2\sigma(I)$	8206
Number of refined parameters	761
R_F [$I > 2\sigma(I)$]	0.0339
$wR(F^2)$ [$I > 2\sigma(I)$]	0.0598
GOF	0.973
$\Delta\rho_{max}/\Delta\rho_{min}$, e/Å^3	0.502/-0.388

strong broad band with a maximum at 3400 cm^{-1}. The weak narrow band at 3575 cm^{-1} corresponds to stretching of O-H fragments of H_2O groups where the H is not involved in hydrogen bonding. The total intensity of this band is about 1% of the intensity of band at 3400 см$^{-1}$, indicating an insignificant content of free OH-groups (really, taking into account a decreasing transition probability coefficient, it can be conclude that the amount of such groups rather more than 1%).

The broad shoulder at 3120 см$^{-1}$ is attributed to O-H-stretching fragments of Si-OH, "weak-acid hydroxyls". The shoulder at 1720 cm^{-1} is not characteristic of H_2O molecules. Usually, the bands in the range of 1700 – 1760 cm^{-1} are assigned to oxonium ions (Yukhnevich, 1973; Wilkins *et al.*, 1974). Taking into account the acid nature of the Si-OH groups, the existence of equilibrium $Si\text{-}OH^{+\delta} + H_2O \leftrightarrow Si\text{-}O^{-\delta'} + H_3O^+$ in megacyclite to form short-lived oxonium ions may be assumed. In the case of megacyclite, this equilibrium should be shifted left, because according to the frequency of SiO-H stretching vibrations (3120 cm^{-1}), cyclic anion of megacyclite may be considered as residual of very weak acid.

The weighted average frequency of Si-O stretching vibrations <ν> (range 840 – 1230 cm^{-1}) is shifted more than 30 cm^{-1} to higher values from ~980 cm^{-1}, which is typical of silicates with simple isolated rings of Si-tetrahedra (Chukanov, 1995). According to our data, the increasing of <ν> during protonation of the Si-O anion is characteristic of most acidic silicates, including rosenhanite, chesnokovite, afwilite and hydroxyl members of the lovozerite group.

The IR-spectrum of megacyclite from Lovozero is identical to that from Khibiny.

X-ray powder diffraction pattern of our sample of megacyclite from Khibiny was recorded with a STOE - STADI MP powder diffractometer using a Ge(111) curved monochromator, linear position-sensitive detector, and Cu$K\alpha$ radiation. Calculation of the theoretical XRD powder pattern (software package WinXPOW, 2005) in accord with experiments (Table 1).

Table 3. **Atom coordinates, equivalent atom displacements, and site occupancy in the structure of megacyclite**

Atom	x	y	z	U_{eq}/U_{iso}*	Atom	x	y	z	U_{eq}/U_{iso}*
K	0.91382(2)	0.14525(5)	0.72291(3)	0.03881(13)	O(25)	0.09694(5)	0.16394(11)	0.70337(8)	0.0215(3)
Na(1)	0.34232(3)	0.12237(7)	0.34597(5)	0.02689(19)	O(26)	0.52769(7)	0.18390(14)	0.76158(13)	0.0272(4)
Na(2)	0.44824(3)	0.13180(7)	0.82325(5)	0.0289(2)	H(26a)	0.5282(11)	0.164(2)	0.7162(18)	0.054(10)*
Na(3)	0.55939(3)	0.12869(7)	0.28837(6)	0.0324(2)	H(26b)	0.5536(10)	0.1526(19)	0.7832(15)	0.033(8)*
Na(4)	0.22742(3)	0.13972(6)	0.86258(5)	0.02652(19)	O(27)	0.63890(7)	0.18017(14)	0.23162(12)	0.0264(4)
Na(5)	0.78914(3)	0.12064(7)	0.25418(5)	0.02935(19)	H(27a)	0.6627(9)	0.1479(19)	0.2508(15)	0.027(8)*
Na(6)	0.67336(3)	0.13710(7)	0.76626(6)	0.0324(2)	H(27b)	0.6405(9)	0.166(2)	0.1835(16)	0.036(8)*
Na(7)	0.11812(3)	0.11694(7)	0.40322(6)	0.0354(2)	O(28)	0.19670(6)	0.16976(14)	0.33956(13)	0.0266(4)
Na(8)	0.01282(4)	0.05626(9)	0.11570(6)	0.0446(3)	H(28a)	0.2213(9)	0.1435(18)	0.3683(15)	0.028(7)*
Si(1)	0.297439(19)	0.17493(4)	0.54092(3)	0.01369(11)	H(28b)	0.2008(11)	0.157(2)	0.2943(18)	0.052(10)*
Si(2)	0.71951(2)	0.17838(4)	0.44664(3)	0.01423(11)	O(29)	0.30838(6)	0.19508(14)	0.80967(12)	0.0255(4)
Si(3)	0.400360(19)	0.17567(4)	0.01732(3)	0.01369(11)	H(29a)	0.3297(9)	0.1563(19)	0.8418(15)	0.034(7)*
Si(4)	0.61727(2)	0.18088(4)	0.97530(3)	0.01496(11)	H(29b)	0.3114(11)	0.181(2)	0.7653(19)	0.063(11)*
Si(5)	0.50792(2)	0.18194(4)	0.49761(3)	0.01547(11)	O(30)	0.94346(5)	0.14092(11)	0.48509(9)	0.0243(3)
Si(6)	0.19635(2)	0.18284(4)	0.06553(3)	0.01437(11)	O(31)	0.45601(5)	0.23503(11)	0.99030(9)	0.0271(3)
Si(7)	0.81558(2)	0.17287(4)	0.92411(3)	0.01483(11)	O(32)	0.12566(6)	0.00013(11)	0.59820(9)	0.0285(3)
Si(8)	0.14334(2)	0.11673(4)	0.64686(3)	0.01471(11)	O(33)	0.41257(8)	0.06048(14)	0.68015(11)	0.0318(4)
Si(9)	0.88173(2)	0.11110(4)	0.46350(3)	0.01564(11)	H(33a)	0.4321(11)	0.085(2)	0.6483(18)	0.055(10)*
O(1)	0.71992(5)	0.10119(12)	0.35537(9)	0.0191(3)	H(33b)	0.3768(12)	0.077(2)	0.6651(18)	0.067(9)*
H(1)	0.7150(9)	0.0333(18)	0.3548(14)	0.028(7)*	O(34)	0.75341(7)	0.19701(15)	0.70393(12)	0.0290(4)
O(2)	0.27993(5)	0.09279(12)	0.45507(9)	0.0200(3)	H(34a)	0.7550(10)	0.182(2)	0.6552(17)	0.043(9)*
H(2)	0.2728(11)	0.026(2)	0.4583(18)	0.066(10)*	H(34b)	0.7731(9)	0.1575(18)	0.7254(15)	0.021(7)*
O(3)	0.16938(5)	0.10964(12)	0.98044(9)	0.0192(3)	O(35)	0.62623(8)	0.06541(14)	0.62515(12)	0.0348(4)
H(3)	0.1672(10)	0.039(2)	0.9860(17)	0.059(9)*	H(35a)	0.5896(11)	0.082(2)	0.6129(16)	0.052(8)*
O(4)	0.29887(5)	0.11160(11)	0.63522(8)	0.0203(3)	H(35b)	0.6392(13)	0.093(3)	0.590(2)	0.077(13)*
O(5)	0.61265(6)	0.10717(13)	0.88171(9)	0.0217(3)	O(36)	0.55876(5)	0.23442(12)	0.98791(10)	0.0351(4)
H(5)	0.6071(11)	0.043(2)	0.8851(18)	0.060(10)*	O(37)	0.74524(7)	0.05079(13)	0.11455(10)	0.0286(4)
O(6)	0.38321(6)	0.09797(12)	0.92889(9)	0.0215(3)	H(37a)	0.7666(11)	0.075(2)	0.0840(17)	0.053(9)*
H(6)	0.3776(11)	0.031(2)	0.9326(18)	0.061(9)*	H(37b)	0.7074(11)	0.074(2)	0.0944(16)	0.060(8)*
O(7)	0.75123(5)	0.20640(10)	0.92225(9)	0.0205(3)	O(38)	0.30555(8)	0.05356(14)	0.20507(11)	0.0300(4)
O(8)	0.51367(6)	0.10963(11)	0.58735(8)	0.0275(3)	H(38a)	0.3247(11)	0.078(2)	0.1746(17)	0.051(10)*
O(9)	0.19976(5)	0.11501(10)	0.15772(8)	0.0194(3)	H(38b)	0.2697(12)	0.075(2)	0.1889(17)	0.066(9)*
O(10)	0.40724(5)	0.10633(11)	0.10854(8)	0.0233(3)	O(39)	-0.00211(8)	0.24854(15)	0.62662(13)	0.0426(5)
O(11)	0.82367(5)	0.09931(12)	0.83298(9)	0.0198(3)	H(39a)	0.9833(13)	0.215(3)	0.581(2)	0.104(14)*
H(11)	0.8171(9)	0.0367(18)	0.8338(15)	0.032(7)*	H(39b)	0.0262(14)	0.215(3)	0.639(2)	0.108(15)*
O(12)	0.35638(5)	0.22273(11)	0.51836(9)	0.0235(3)	O(40)	0.08499(7)	0.20186(14)	0.87558(12)	0.0295(4)
O(13)	0.50322(6)	0.10376(13)	0.40678(9)	0.0278(4)	H(40a)	0.0913(10)	0.185(2)	0.8190(19)	0.060(9)*
H(13)	0.4965(11)	0.041(2)	0.4101(18)	0.061(10)*	H(40b)	0.1067(11)	0.172(2)	0.9051(18)	0.059(10)*
O(14)	0.74530(5)	0.11403(11)	0.53314(8)	0.0216(3)	O(41)	0.03014(7)	0.04650(16)	0.41017(11)	0.0303(4)
O(15)	0.83506(5)	0.10594(11)	0.01271(8)	0.0222(3)	H(41a)	0.0334(9)	-0.0070(19)	0.4371(15)	0.029(8)*
O(16)	0.84737(5)	0.20972(10)	0.40773(8)	0.0205(3)	H(41b)	0.0046(10)	0.082(2)	0.4368(16)	0.051(8)*
O(17)	0.65669(5)	0.21333(11)	0.45761(9)	0.0246(3)	O(42)	0.87103(8)	0.14303(16)	0.18903(13)	0.0352(4)
O(18)	0.25601(5)	0.21879(10)	0.03407(9)	0.0210(3)	H(42a)	0.8969(11)	0.113(2)	0.1981(17)	0.050(10)*
O(19)	0.16028(5)	0.20192(10)	0.56640(8)	0.0188(3)	H(42b)	0.8651(9)	0.134(2)	0.1413(16)	0.035(8)*
O(20)	0.41959(7)	0.18052(14)	0.28331(13)	0.0273(4)	O(43)	0.96867(8)	0.00773(16)	0.24304(12)	0.0379(4)
H(20a)	0.4443(10)	0.145(2)	0.3088(16)	0.039(8)*	H(43a)	0.9485(9)	-0.041(2)	0.2583(15)	0.038(8)*
H(20b)	0.4181(11)	0.163(2)	0.2375(18)	0.050(10)*	H(43b)	0.9844(10)	0.021(2)	0.2860(11)	0.051(10)*
O(21)	0.19890(6)	0.09026(12)	0.71178(9)	0.0231(3)	O(44)	0.51857(8)	0.05720(14)	0.14594(12)	0.0343(4)
H(21)	0.2250(9)	0.0995(19)	0.6896(14)	0.030(7)*	H(44a)	0.5338(13)	0.083(3)	0.111(2)	0.083(13)*
O(22)	0.63775(6)	0.10804(11)	0.06030(9)	0.0288(3)	H(44b)	0.4816(11)	0.073(2)	0.1367(16)	0.056(8)*
O(23)	0.09260(7)	0.09683(14)	0.21876(11)	0.0309(4)	O(45)	0.97420(8)	0.18565(17)	0.87773(13)	0.0448(5)
H(23a)	0.1210(11)	0.094(2)	0.1956(17)	0.058(9)*	H(45a)	0.9658(12)	0.235(3)	0.912(2)	0.093(13)*
H(23b)	0.0898(12)	0.176(3)	0.215(2)	0.089(11)*	H(45b)	0.0075(12)	0.192(2)	0.8738(17)	0.059(9)*
O(24)	0.85386(6)	0.08407(12)	0.55810(9)	0.0253(3)	O(46)	0.94217(7)	0.02574(19)	0.00379(15)	0.0680(6)
H(24)	0.8199(9)	0.0927(18)	0.5588(14)	0.032(7)*	H(46a)	0.9136(5)	0.0501(19)	0.0070(16)	0.043(8)*

Notice: Positions of H atoms are given as coordinates of the electron density maximums resulted from these atoms

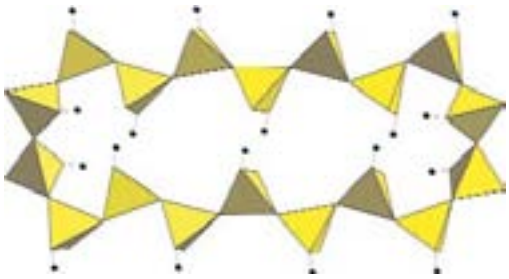


Fig. 3. Silicate ring in the structure of megacyclite (H atoms of OH groups on the apices of Si tetrahedra are shown as circles).

The crystal structure of megacyclite was refined using a single crystal selected from the new Khibiny material. Three-dimensional set of reflections was collected with a Xcalibur S CCD single-crystal diffractometer at room temperature. The crystal data are given in Table 2.

The crystal structure was determined by direct methods in the $P2_1/c$ using the SHELX-97 software package (Sheldrick, 1997). The final R_{hkl} is 0.0339 for 8206 unique reflections with $I > 2\sigma(I)$ in comparison with the refinement of the mineral structure to $R = 0.048$ for 2860 unique reflections with $I > 1.96\ \sigma(I)$ published by Yamnova *et al.* (1992). The final atom coordinates and parameters of equivalent atom displacements are listed in Table 3, interatomic distances, in Table 4, and characteristic of H-bonds, in Table 5.

As a result, the structural formula $K_2Na_{16}Si_{18}O_{34}(OH)_{18}[O_{0.75}(OH)_{0.25}]_2(H_2O)_{36}[(H_2O)_{0.75}(OH)_{0.25}]_2$ has been refined and it is close both to the empirical formula of megacyclite calculated from the electron microprobe data and the formula given by Yamnova *et al.* (1992). Calculation of the bond valences for anions in the structure (Brese & O`Keeffe, 1991) is given in Table 6.

As previously shown by Yamnova *et al.* (1992), Si-O rings consist of 18 tetrahedra and of composition $[Si_{18}O_{34}(OH)_{18}[O_{0.75}(OH)_{0.25}]_2]^{17.5-}$ are present in the structure of megacyclite (Fig. 3). The partial replacement of one oxygen atom [O(30)] by an OH-group is the only difference of our data from that previously reported (Yamnova *et al.*, 1992). This replacement is confirmed by calculated local valency balance (Table 6). Sum of the bond valences for O(30) is 1.72 vu, allowing the presence of both O and OH at this position. The deficiency of negative charge resulted from this replacement is compensated by the partial substitution of one of water molecule [O(46)] by an OH-group, that is also confirmed by the calculation of valency balance the sum of which for this position is 0.27. In addition, only one hydrogen atom H(46a) is allocated near to the position of oxygen atom O(46), rather than two. In our case, the position corresponding to the second hydrogen atom for O(46) reported by Yamnova *et al.* (1992) is present in the difference synthesis as an extremely weak maximum (0.31 e/Å^3) and its introduction into the structure model. Taking into account allocation of the other 46 hydrogen atoms, the above data suggest the following replacement $[(H_2O)_{0.75}(OH)_{0.25}]$.

Polyhedra of eight non-equivalent Na atoms and one K atom in the structure of megacyclite form a framework (Fig. 4). In contrast to Yamnova *et al.* (1992), we have assigned larger coordination numbers to most cations: six Na atoms are [6]-coordinated, two are [5]-coordinated and K is [7]-coordinated. An overview of the crystal structure of megacyclite is shown in Figure 5.

The major differences of our results from data reported by Yamnova *et al.* (1992) are related to the allocation of several hydrogen atoms and description of the hydrogen bond system in the structure. The position of H(3) reported by Yamnova *et al.* (1992) that should correspond to atom H(39b) according to our data does not result in an O(39)−H(3) distance of 2.541Å (Yamnova *et al.*, 1992). The atom coordinates of H(45) and H(46) given in the first description of the megacyclite structure are entirely consistent with the position of the Si(1) atom (Yamnova *et al.*, 1992). These discrepancies are probably related to the errata in the referred article. In our case, these hydrogen atoms (H(13) and H(40a), respectively) are allocated with different coordinates and are characterized by the following distances to the corresponding oxygen atoms O(13)−H(13) = 0.77(3) and O(40)−H(40a) = 0.89(3)Å. The H(1) atom coincides with H(44) (Yamnova *et al.*, 1992). However, in our case, this atom is slightly displaced and the O(44) − H(1)[H(44a)] ··· O(22) hydrogen bond is not observed. The presence of such a "free" hydrogen atom is confirmed by IR-spectroscopy (see above). The O(5)−H(5)

Table 4. **Interatomic distances (Å) in the structure of megacyclite**

K seven-vertex polyhedron		Na(1) six-vertex polyhedron		Na(2) six-vertex polyhedron		Na(3) six-vertex polyhdron	
K - O(45)	2.6913(19)	Na(1) - O(20)	2.3039(18)	Na(2) - O(26)	2.3239(17)	Na(3) - O(27)	2.2902(18)
- O(42)a	2.770(2)	- O(2)	2.3560(15)	- O(6)	2.3737(16)	- O(13)	2.3495(17)
- O(24)	2.8613(15)	- O(38)	2.3665(18)	- O(33)	2.3966(18)	- O(26)d	2.3921(19)
- O(39)b	2.897(2)	- O(29)d	2.3808(18)	- O(20)a	2.4084(19)	- O(33)c	2.3958(18)
- O(11)	2.9260(15)	- O(35)c	2.3989(19)	- O(44)c	2.4307(19)	- O(44)	2.4305(19)
- O(23)c	3.0220(18)	- O(12)	2.8267(16)	- O(31)	2.7665(16)		
- O(41)c	3.3932(19)						
<K - O>	2.937	<Na(1) - O>	2.439	<Na(2) - O>	2.450	<Na(1) - O>	2.372

Na(4) six-vertex polyhedron		Na(5) six-vertex polyhedron		Na(6) five-vertex polyhedron		Na(7) six-vertex polyhedron	
Na(4) - O(29)	2.3111(18)	Na(5) - O(42)	2.3347(19)	Na(6) - O(38)c	2.3641(18)	Na(7) - O(28)	2.3209(18)
- O(21)	2.3734(16)	- O(1)	2.3825(15)	- O(34)	2.3678(19)	- O(40)d	2.3367(18)
- O(3)	2.3819(15)	- O(37)	2.4171(18)	- O(27)a	2.3823(18)	- O(41)	2.3496(18)
- O(37)c	2.3875(17)	- O(34)d	2.4431(19)	- O(5)	2.3985(16)	- O(24)c	2.5488(16)
- O(28)a	2.4121(18)	- O(21)c	2.5777(16)	- O(35)	2.474(2)	- O(19)	2.7599(15)
- O(18)e	2.7600(15)	- O(16)	2.8140(15)			- O(23)	2.7780(18)
<Na(4) - O>	2.438	<Na(5) - O>	2.495	<Na(6) - O>	2.397	<Na(7) - O>	2.516

Na(8) six-vertex polyhedron		Si(1)-tetrahedron		Si(2)-tetrahedron		Si(3)-tetrahedron	
Na(8) - O(43)f	2.334(2)	Si(1) - O(4)	1.5910(13)	Si(2) - O(14)	1.5892(13)	Si(3) -O(10)	1.5869(13)
- O(46)f	2.350(2)	- O(12)	1.6295(13)	- O(17)	1.6346(13)	- O(31)h	1.6301(13)
- O(39)d	2.364(2)	- O(18)a	1.6302(13)	- O(7)d	1.6381(13)	- O(12)d	1.6315(13)
- O(46)g	2.382(2)	- O(2)	1.6408(15)	- O(1)	1.6411(14)	- O(6)h	1.6378(14)
- O(23)	2.4558(18)						
- O(45)c	2.903(2)						
<Na(8) - O>	2.465	<Si(1) - O>	1.623	<Si(2) - O>	1.626	<Si(3) - O>	1.622

Si(4)-tetrahedron		Si(5)-tetrahedron		Si(6)-tetrahedron		Si(7)-tetrahedron	
Si(4) - O(22)e	1.5847(14)	Si(5) - O(8)	1.5863(14)	Si(6) - O(9)	1.5887(13)	Si(7) - O(15)e	1.5837(13)
- O(36)	1.6108(14)	- O(31)d	1.6218(13)	- O(3)h	1.6370(14)	- O(16)a	1.6346(13)
- O(17)a	1.6303(13)	- O(36)d	1.6238(14)	- O(19)d	1.6406(13)	- O(11)	1.6401(14)
-O(5)	1.6430(15)	- O(13)	1.6381(16)	- O(18)	1.6445(13)	- O(7)	1.6448(13)
<Si(4) - O>	1.617	<Si(5) - O>	1.617	<Si(6) - O>	1.628	<Si(7) - O>	1.626

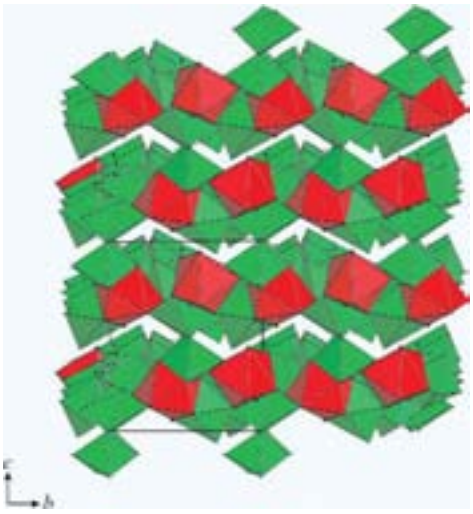
Si(8)-tetrahedron		Si(9)-tetrahedron	
Si(8) - O(25)	1.5816(13)	Si(9) - O(30)	1.5813(13)
- O(32)	1.6123(14)	- O(32)c	1.6152(14)
- O(19)	1.6492(13)	- O(16)	1.6394(13)
- O(21)	1.6511(15)	- O(24)	1.6479(14)
<Si(7) - O>	1.624	<Si(9) - O>	1.621

Notice: **a**: x, -y+1/2, z+1/2; **b**: x+1, y, z; c: -x+1, -y, -z+1; **d**: x, -y+1/2, z-1/2; **e**: x, y, z+1; **f**: x-1, y, z; **g**: -x+1, -y, -z; **h**: x, y, z-1

Table 5. **Hydrogen bonds in the structure of megacyclite**

D-H	d(D-H), Å	D-H···A	d(D-A), Å	∠(D-H···A)°	H-D-H	∠(H-D-H)°
O(1)-H(1)	0.82(2)	O(1)-H(1)···O(4)a	2.5855(19)	173.75		
O(2)-H(2)	0.82(3)	O(2)-H(2)···O(14)a	2.5537(19)	177.13		
O(3)-H(3)	0.84(3)	O(3)-H(3)···O(15)a	2.5752(19)	174.55		
O(5)-H(5)	0.78(3)	O(5)-H(5)···O(10)a	2.599(2)	178.58		
O(6)-H(6)	0.81(3)	O(6)-H(6)···O(22)a	2.5187(19)	176.87		
O(11)-H(11)	0.76(2)	O(11)-H(11)···O(9)a	2.6268(19)	176.86		
O(13)-H(13)	0.77(3)	O(13)-H(13)···O(8)a	2.581(2)	174.73		
O(20)-H(20a)	0.81(2)	O(20)-H(20a)···O(13)	2.815(2)	158.42	H(20a)-O(20)-H(20b)	106(3)
O(20)-H(20b)	0.71(3)	O(20)-H(20b)···O(10)	2.741(2)	174.74		
O(21)-H(21)	0.76(2)	O(21)-H(21)···O(4)	2.8217(19)	174.78		
O(23)-H(23a)	0.81(3)	O(23)-H(23a)···O(9)	2.885(2)	167.04	H(23a)-O(23)-H(23b)	94(2)
O(23)-H(23b)	0.94(3)	O(23)-H(23b)···O(25)b	2.864(2)	170.30		
O(24)-H(24)	0.85(2)	O(24)-H(24)···O(14)	2.7148(19)	167.60		
O(26)-H(26a)	0.72(3)	O(26)-H(26a)···O(8)	2.735(2)	168.80	H(26a)-O(26)-H(26b)	99(3)
O(26)-H(26b)	0.79(2)	O(26)-H(26b)···O(5)	2.809(2)	157.50		
O(27)-H(27a)	0.74(2)	O(27)-H(27a)···O(1)	2.782(2)	153.36	H(27a)-O(27)-H(27b)	99(2)
O(27)-H(27b)	0.74(2)	O(27)-H(27b)···O(22)	2.688(2)	171.48		
O(28)-H(28a)	0.78(2)	O(28)-H(28a)···O(2)	2.740(2)	171.30	H(28a)-O(28)-H(28b)	106(3)
O(28)-H(28b)	0.71(3)	O(28)-H(28b)···O(9)	2.790(2)	170.96		
O(29)-H(29a)	0.83(2)	O(29)-H(29a)···O(6)	2.724(2)	167.12	H(29a)-O(29)-H(29b)	108(3)
O(29)-H(29b)	0.69(3)	O(29)-H(29b)···O(4)	2.772(2)	162.58		
O(33)-H(33a)	0.76(3)	O(33)-H(33a)···O(8)	3.015(2)	156.55	H(33a)-O(33)-H(33b)	115(3)
O(33)-H(33b)	0.92(3)	O(33)-H(33b)···O(4)	2.914(2)	178.65		
O(34)-H(34a)	0.75(2)	O(34)-H(34a)···O(14)	2.719(2)	165.70	H(34a)-O(34)-H(34b)	101(2)
O(34)-H(34b)	0.73(2)	O(34)-H(34b)···O(11)	2.750(2)	153.27		
O(35)-H(35a)	0.94(3)	O(35)-H(35a)···O(8)	2.856(2)	177.70	H(35a)-O(35)-H(35b)	104(3)
O(35)-H(35b)	0.72(3)	O(35)-H(35b)···O(17)	3.192(2)	162.75		
O(37)-H(37a)	0.78(3)	O(37)-H(37a)···O(15)	2.868(2)	166.36	H(37a)-O(37)-H(37b)	113(2)
O(37)-H(37b)	1.00(3)	O(37)-H(37b)···O(22)	2.811(2)	176.53		
O(38)-H(38a)	0.74(3)	O(38)-H(38a)···O(10)	3.065(2)	158.07	H(38a)-O(38)-H(38b)	112(3)
O(38)-H(38b)	0.94(3)	O(38)-H(38b)···O(9)	2.764(2)	179.55		
O(39)-H(39a)	0.84(4)	O(39)-H(39a)···O(30)	2.731(2)	173.78	H(39a)-O(39)-H(39b)	105(3)
O(39)-H(39b)	0.81(3)	O(39)-H(39b)···O(25)	2.815(2)	161.88		
O(40)-H(40a)	0.89(3)	O(40)-H(40a)···O(25)	2.641(2)	172.52	H(40a)-O(40)-H(40b)	106(3)
O(40)-H(40b)	0.76(3)	O(40)-H(40b)···O(3)	2.742(2)	173.07		
O(41)-H(41a)	0.75(2)	O(41)-H(41a)···O(30)a	2.773(2)	169.25	H(41a)-O(41)-H(41b)	103(2)
O(41)-H(41b)	0.88(3)	O(41)-H(41b)···O(30)c	2.741(2)	171.42		
O(42)-H(42a)	0.74(3)	O(42)-H(42a)···O(43)	2.969(3)	171.06	H(42a)-O(42)-H(42b)	102(3)
O(42)-H(42b)	0.72(2)	O(42)-H(42b)···O(15)	2.740(2)	170.18		
O(43)-H(43a)	0.81(2)	O(43)-H(43a)···O(25)a	2.771(2)	176.68	H(43a)-O(43)-H(43b)	102(3)
O(43)-H(43b)	0.739(10)	O(43)-H(43b)···O(41)d	2.851(2)	176.32		
O(44)-H(44a)	0.73(3)				H(44a)-O(44)-H(44b)	112(3)
O(44)-H(44b)	0.93(3)	O(44)-H(44b)···O(10)	2.837(2)	175.58		
O(45)-H(45a)	0.81(3)	O(45)-H(45a)···O(30)e	2.757(2)	175.99	H(45a)-O(45)-H(45b)	107(3)
O(45)-H(45b)	0.84(3)	O(45)-H(45b)···O(40)	2.760(3)	175.07		
O(46)-H(45a)	0.771(9)	O(46)-H(46a)···O(15)	2.838(2)	176.49		

Notice: D — donor, A — acceptor **a:** -x+1, -y, -z+1; **b:** x, -y+1/2, z-1/2; **c:** x-1, y, z; **d:** x+1, y, z; **e:** x, -y+1/2, z+1/2



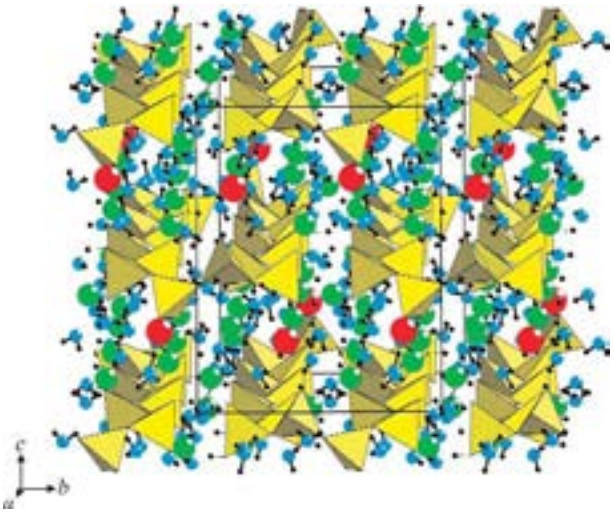


Fig. 4. The quasi-framework formed by Na-polyhedra (green) and K-polyhedra (red) in the structure of megacyclite; small black circles are H atoms.

Fig. 5. The crystal structure of megacyclite. SiO_4 tetrahedra are yellow, K atoms are shown as red circles, Na as green circles, O atoms of water molecules are blue, H atoms are small black circles.

··· O(10) hydrogen bond recorded in our case is absent in the description of the megacyclite structure reported by Yamnova *et al.* (1992), and despite practically entire coincidence of hydrogen atomic coordinates (H(5) atom in our case corresponds to H(2) in referred article), the O(5) — H(2)[H(5)] ··· O(28) hydrogen bond with the O(5)-O(28) distance of 2.602(8) Å given in the first description of the structure does not correspond to the distance O(5)-O(28) that is more than 6.8 Å. Furthermore, in our case, the bifurcated hydrogen bonds are not observable.

Since discovery of megacyclite, the 18-membered elliptic rings of ~19 Å in diameter containing in its structure are still the largest among the ring silicates. However, they are less than the ring components of tetrahedral frameworks of zeolites of different composition. Practically simultaneously with the discovery of megacyclite, a synthetic gallophosphate named cloverite (due to similarity of the zeolite cavity outlines to the leaves of clover). In its structure, 20-membered rings with a diagonal of 29—30 Å (Estermann *et al.*, 1991) that exceeds the usual sizes of pores in microporous compounds (2.5—20 Å). A framework containing 20-membered elliptical rings was identified in the structure of aluminophosphate zeolite JDF-20 with the following composition: $[Al_5P_6O_{24}H]^{2-}$ $2[N(C_2H_5)_3H]^+$ $2H_2O$ (Jones *et al.*, 1993). The gallophosphate zeolite NTHU-1, in the framework of which channels are formed by 24-membered rings, has been synthesized by Lin *et al.* (2006). These wide channels can comprise atoms of five transition metals that define peculiar fluorescent and magnetic properties of this compound. Against the background, silicogermanate zeolite ITQ-33 (abbreviation of Spanish name of Institute of Chemical Technology, Valencia, Spain) with pores outlined by 18- and 10-member rings does not appeared so effective, although the inner surface of its tetrahedral framework and its catalytic properties are great (Corma *et al.*, 2006). The above examples indicate extensive opportunities to synthesize novel materials with large tetrahedral structure components, which define their catalytic, ion-exchange, and sorption properties.

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Table 6. **Calculation of bond valences for megacyclite**

	K	Na(1)	Na(2)	Na(3)	Na(4)	Na(5)	Na(6)	Na(7)	Na(8)	Si(1)	Si(2)	Si(3)	Si(4)	Si(5)	Si(6)	Si(7)	Si(8)	Si(9)	Σ*	Contribution of hydrogen bonds **	Σ
O(1)[OH]						0.21					0.95								1.16	-0.30(O4) 0.19(O27)	1.05
O(2)[OH]		0.22								0.95									1.17	-0.32(O14) 0.21(O28)	1.06
O(3)[OH]					0.21										0.96				1.17	-0.31(O15) 0.21(O40)	1.07
O(4)										1.09									1.09	0.30(O1) 0.18(O21) 0.19(O29) 0.15(O33)	1.91
O(5)[OH]							0.20						0.95						1.15	-0.29(O10) 0.18(O26)	1.04
O(6)[OH]			0.21									0.96							1.17	-0.35(O22) 0.21(O29)	1.03
O(7)											0.96					0.94			1.90		1.90
O(8)														1.10					1.10	0.30(O13) 0.21(O26) 0.13(O33) 0.16(O35)	1.90
O(9)															1.10				1.10	0.27(O11) 0.16(O23) 0.19(O28) 0.20(O9)	1.92
O(10)												1.10							1.10	0.29(O5) 0.21(O20) 0.12(O38) 0.17(O44)	1.89
O(11)[OH]	0.12															0.96			1.08	-0.27(O9) 0.20(O34)	1.01
O(12)		*0.06*								0.99		0.98							2.03		2.03
O(13)[OH]				0.23										0.96					1.19	-0.30(O8) 0.18(O20)	1.07
O(14)											1.10								1.10	0.32(O2) 0.22(O24) 0.22(O34)	1.86
O(15)																1.11			1.11	0.31(O3) 0.16(O37) 0.21(O42) 0.17(O46)	1.96
O(16)						*0.06*										0.97		0.96	1.99		1.99
O(17)											0.97		0.98						1.95	0.10(O35)	2.05
O(18)					*0.07*					0.98					0.95				2.00		2.00
O(19)								*0.07*							0.95		0.93		1.95		1.95
O(20)[H_2O]		0.26	0.19																0.45	-0.18(O13) -0.21(O10)	0.06
O(21)[OH]					0.21	0.12											0.93		1.26	-0.18(O4)	1.08
O(22)													1.11						1.11	0.35(O6) 0.23(O27) 0.18(O37)	1.87
O(23)[H_2O]	0.09							*0.07*	0.17										0.33	-0.16(O9) -0.16(O25)	0.01
O(24)[OH]	0.14							0.13										0.94	1.21	-0.22(O14)	0.99
O(25)																	1.12		1.12	0.16(O23) 0.18(O39) 0.26(O40) 0.19(O43)	1.91
O(26)[H_2O]			0.24	0.20															0.44	-0.21(O8) -0.18(O5)	0.05
O(27)[H_2O]				0.27			0.21												0.48	-0.19(O1) -0.23(O22)	0.06
O(28)[H_2O]					0.19			0.24											0.43	-0.21(O2) -0.19(O9)	0.03
O(29)[H_2O]		0.21			0.25														0.46	-0.21(O6) -0.19(O4)	0.06
O(30)[O,OH]																		1.12	1.12	0.21(O39) 0.19(O41) 0.21(O41) 0.20(O45)	1.72
O(31)			0.07									0.98		1.00					2.05		2.05
O(32)																	1.03	1.02	2.05		2.05
O(33)[H_2O]			0.20	0.20															0.40	-0.13(O8) -0.15(O4)	0.12
O(34)[H_2O]						0.18	0.21												0.39	-0.22(O14) -0.20(O11)	-0.03
O(35)[H_2O]		0.20					0.16												0.36	-0.16(O8) -0.10(O17)	0.00
O(36)													1.04	1.00					2.04		2.04
O(37)[H_2O]					0.20	0.19													0.39	-0.16(O15) -0.18(O22)	0.05
O(38)[H_2O]		0.22					0.22												0.44	-0.12(O10) -0.20(O9)	0.12
O(39)[H_2O]	0.13								0.22										0.35	-0.21(O30) -0.18(O25)	-0.04
O(40)[H_2O]								0.23											0.23	-0.26(O25) -0.21(O3) 0.20(O45)	-0.04
O(41)[H_2O]	*0.03*							0.23											0.26	-0.19(O30) -0.21(O30) 0.17(O43)	0.03
O(42)[H_2O]	0.18					0.23													0.41	-0.14(O43) -0.21(O15)	0.06
O(43)[H_2O]									0.24										0.24	0.14(O42) -0.19(O25) -0.17(O41)	0.02
O(44)[H_2O]			0.18	0.18															0.36	-0.17(O10)	0.19
O(45)[H_2O]	0.22								*0.05*										0.27	-0.20(O30) -0.20(O40)	-0.13
O(46)[H_2O, OH]									0.21	0.23									0.44	-0.17(O15)	0.27
Σ			0.91	1.17	1.09	1.08	1.13	0.99	1.00	0.97	1.12	4.01	3.98	4.02	4.08	4.06	3.96	3.98	4.01	4.04	

Notice: * Sum excepting hydrogen bonds.
** Oxygen atoms, which are donors (negative values) and/or acceptor (positive values) are in parentheses; values of valence contributions og oxygen and water molecules located at the longest distances in the Na and K polyhedra are in italic

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