Calciomurmanite, $(Na, \Box)_2Ca(Ti, Mg, Nb)_4[Si_2O_7]_2O_2(OH, O)_2(H_2O)_4$, a new mineral from the Lovozero and Khibiny alkaline complexes, Kola Peninsula, Russia

INNA S. LYKOVA^{1,*,2}, IGOR V. PEKOV¹, NIKITA V. CHUKANOV^{1,3}, DMITRY I. BELAKOVSKIY², VASILIY O. YAPASKURT¹, NATALIA V. ZUBKOVA¹, SERGEY N. BRITVIN⁴ and GERALD GIESTER⁵

¹ Faculty of Geology, Moscow State University, Vorobievy Gory, 119991 Moscow, Russia *Corresponding author, e-mail: innalykova@mail.ru

² Fersman Mineralogical Museum RAS, 119071 Moscow, Russia

³ Institute of Problems of Chemical Physics RAS, Moscow Region 142432, Russia

⁴ Institute of Earth Sciences, St. Petersburg State University, 199034 St. Petersburg, Russia

⁵ Institute of Mineralogy and Crystallography, University of Vienna, 1090Vienna, Austria

Abstract: The new mineral calciomurmanite, $(Na, \Box)_2Ca(Ti, Mg, Nb)_4[Si_2O_7]_2O_2(OH, O)_2(H_2O)_4$, a Na-Ca ordered analogue of murmanite, was found in three localities at Kola Peninsula, Russia: at Mt. Flora in the Lovozero alkaline complex (the holotype) and at Mts. Eveslogchorr (the cotype) and Koashva, both in the Khibiny alkaline complex. Calciomurmanite is a hydrothermal mineral formed as a result of late-stage, low-temperature alteration (hydration combined with natural cation exchange) of a high-temperature, anhydrous phosphate-bearing titanosilicate, most likely lomonosovite and/or betalomonosovite, in the peralkaline (hyperagpaitic) rocks. The holotype sample is associated with microcline, aegirine, lorenzenite and fluorapatite, whereas the cotype sample occurs with microcline, aegirine, lamprophyllite, tsepinite-Ca and tsepinite-K. The mineral occurs as lamellae up to $0.1 \times 0.4 \times 0.6$ cm, sometimes combined in fan-shaped aggregates up to 3.5 cm. Calciomurmanite is pale brownish or purple; the streak is white. The lustre is nacreous on cleavage surface and greasy on broken surface across cleavage. The (001) cleavage is perfect, mica-like; the fracture is stepped. $D_{\text{meas}} = 2.70(3)$, $D_{\text{calc}} = 2.85 \text{ g cm}^{-3}$. The mineral is optically biaxial (-), $\alpha = 1.680(4)$, $\beta = 1.728(4)$, $\gamma = 1.743(4)$, $2V_{\text{meas}} = 58(5)^\circ$. The IR spectrum is reported. The chemical composition (wt%, electron-microprobe data, H₂O by the Alimarin method) is: Na₂O 5.39, K₂O 0.30, CaO 7.61, MgO 2.54, MnO 2.65, FeO 1.93, Al₂O₃ 0.85, SiO₂ 30.27, TiO₂ 29.69, Nb₂O₅ 6.14, P₂O₅ 0.27, H₂O 11.59, total 99.23. The empirical formula of the holotype sample, calculated on the basis of Si + Al = 4 apfu, is: Na1.34Ca1.04K0.05Mg0.49Mn0.29Fe0.21Nb0.36Ti2.85(Si3.87Al0.13) 24O16.40(OH)1.60(PO4)0.03(H2O)4.94. Calciomurmanite is triclinic, *P*-1, a = 5.3470(6), b = 7.0774(7), c = 12.146(1) Å, $\alpha = 91.827(4)$, $\beta = 107.527(4)$, $\gamma = 90.155(4)^{\circ}$, V = 438.03(8) Å³ and Z = 1. The strongest reflections of the X-ray powder pattern [d, Å(I)(hkl)] are: 11.69(100)(001), 5.87(68)(011, 002), 4.25(89) (-1-11, -111), 3.825(44)(-1-12, 003, -112), 2.940(100)(-1-21, -121), 2.900(79)(004, 120). The crystal structure was solved by direct methods from single-crystal low-temperature (200 K) X-ray diffraction data and refined to R = 0.0656 for the holotype and 0.0663 for the cotype. The structure is based on a three-sheet HOH block: an octahedral (O) sheet containing alternating chains of NaO₆ and TiO₆ octahedra and two heteropolyhedral (H) sheets consisting of Si₂O₇ groups, TiO₆ octahedra and CaO₈ polyhedra. H₂O molecules occupy two sites in the interlayer space.

Key-words: calciomurmanite, new mineral, murmanite, heterophyllosilicate mineral, titanosilicate, crystal structure, ion exchange, peralkaline rock, Lovozero alkaline complex, Khibiny alkaline complex.

Introduction

Among all natural layered titano- and niobosilicates (heterophyllosilicates), the bafertisite mero-plesiotype series (Ferraris & Gula, 2005) shows the greatest species diversity: it includes 37 minerals to date. Some of them belong to the epistolite group: epistolite, Na_4TiNb_2 $(Si_2O_7)_2O_2(OH)_2(H_2O)_4$, murmanite, $Na_4Ti_4[Si_2O_7]_2O_4$ $(H_2O)_4$, vuonnemite, $Na_{11}TiNb_2(Si_2O_7)_2(PO_4)_2O_3(F,OH)$, lomonosovite, Na₁₀Ti₄(Si₂O₇)₂(PO₄)₂O₄ (Back & Mandarino, 2008), betalomonosovite, Na₆Ti₄(Si₂O₇)₂ [PO₃(OH)][PO₂(OH)₂]O₂(OF) [known since 1962 and studied in detail (*e.g.* Gerasimovskiy & Kazakova, 1962; Rastsvetaeva, 1986; Yakubovich *et al.*, 2014) but validated as a mineral species only in 2015 (Sokolova *et al.*, 2015)], vigrishinite, Zn₂Ti_{4-x}(Si₂O₇)₂O₂(OH,F,O)₂ (H₂O,OH, \Box)₄, where *x* < 1 (Pekov *et al.*, 2013), zvya-ginite, NaZnNb₂Ti[Si₂O₇]₂O(OH,F)₃(H₂O)_{4+x}, where

x < 1 (Pekov *et al.*, 2014). In the present paper we describe the new species calciomurmanite, $(Na, \Box)_2Ca$ $(Ti,Mg,Nb)_4[Si_2O_7]_2O_2(OH,O)_2(H_2O)_4$, named as an analogue of murmanite with calcium instead of sodium in one of two non-equivalent large-cation sites in its structure.

Members of the epistolite group, mainly titanosilicates, are typical accessory or even rock-forming minerals of some peralkaline rocks and related pegmatites (Lovozero and Khibiny, Kola Peninsula, Russia; Ilìmaussaq, South Greenland, Denmark; Mont Saint-Hilaire, Québec, Canada). These minerals are considered as reliable indicators of the hyperagpaitic character of primary parageneses (Khomyakov, 1995).

Calciomurmanite was first discovered during the examination of layered titanosilicates from the collection of Viktor Ivanovich Stepanov (1924-1988), the most comprehensive private scientific mineral collection created in the former Soviet Union, donated by V.I. Stepanov in 1980s to the Fersman Mineralogical Museum of the USSR Academy of Sciences, Moscow (Pekov *et al.*, 2015). The new mineral was found in the specimen (catalogue number ST4994) from Mt. Flora, Lovozero alkaline complex, Kola peninsula, Russia, provided to V.I. Stepanov by Alexander Petrovich Khomyakov (1933-2012) in 1980 and originally labelled as "betalomonosovite". It is considered as the holotype specimen of calciomurmanite.

The cotype specimen from Mt. Eveslogchorr, Khibiny alkaline complex, Kola peninsula, Russia, belongs to the collections of the Bel'kov Museum of Geology and Mineralogy of the Geological Institute of Kola Science Center of Russian Academy of Sciences, Apatity, with catalogue number 3667. It was donated to the Museum by Yury Pavlovich Menshikov (1934-2013) and originally labelled as "murmanite".

Both the new mineral calciomurmanite and its name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA2014–103).

Occurrence and general appearance

In the holotype specimen from Mt. Flora, Lovozero, calciomurmanite occurs as irregular lamellae up to $0.1 \times 0.4 \times 0.6$ cm in size (Fig. 1), sometimes combined in up to 3 cm aggregates embedded in a rock mainly consisting of dark-green acicular aegirine and white microcline and containing lorenzenite, fluorapatite and minor calcite. The lamellae are slightly split and show microcracking. They are most likely homoaxial pseudomorphs after crystals of an unspecified epistolite-group titanosilicate, probably lomonosovite.

In the cotype specimen from Mt. Eveslogchorr, Khibiny, a 2×3.5 cm fan-shaped aggregate of calciomurmanite lamellae occurs in a hydrothermally altered peralkaline pegmatite together with microcline, aegirine, lamprophyllite, tsepinite-Ca and tsepinite-K.



Fig. 1. Lamellar calciomurmanite (the holotype from Mt. Flora, Lovozero) with microcline, aegirine and fluorapatite. Polished section, backscattered-electron (BSE) image.

Later, calciomurmanite was found in specimens collected by the senior author in 2008 in the Shcherbakovitovoe pegmatite at the Koashva open pit of the Vostochnyi apatite mine, Mt. Koashva, Khibiny. It occurs in the outer zone of the pegmatite as up to 0.5 cm lamellae forming chaotic and fan-shaped aggregates. The lamellae contain relics of yellow betalomonosovite. The new mineral is associated with aegirine, microcline, lamprophyllite and pectolite.

Physical properties and optical data

Calciomurmanite is pale brownish (Lovozero) or purple (Khibiny). The streak is white. The lustre is nacreous on the cleavage surface and greasy on broken surfaces. The mineral is non-fluorescent under ultraviolet rays or an electron beam. The Mohs hardness is 2.5-3. The (001) cleavage is perfect, mica-like; two other directions of distinct cleavage, nearly perpendicular to each other and both nearly perpendicular to (001), are observed under the microscope. The fracture is stepped. Density measured by floatation in heavy liquids (bromoform + dimethylformamide) is 2.70(3) g cm⁻³, the density calculated using the empirical formula of the holotype is 2.85 g cm^{-3} . This difference may be due to significant chemical variations typical for the mineral, especially in part of the (Ti,Mg,Nb,Mn,Fe) sites (see Chemical composition). The lower value of the measured density is also likely to relate to the lamellar morphology which favours floating.

In transmitted light calciomurmanite is colourless, nonpleochroic. It is optically biaxial (-), $\alpha = 1.680(4)$, $\beta = 1.728(4), \ \gamma = 1.743(4), \ 2V_{\text{meas}} = 58(5)^{\circ}$ and $2V_{\text{calc}} = 57^{\circ}$. No dispersion of the optical axes was observed. Orientation: Y and Z lie in the ab plane.

Infrared spectroscopy

The infrared (IR) absorption spectrum of calciomurmanite was obtained for a powdered sample mixed with anhydrous KBr and pelletized. The pellet was analyzed using an ALPHA FTIR spectrometer (Bruker Optics) at the resolution of 4 cm⁻¹, accumulating 16 scans. The IR spectrum of an analogous pellet of pure KBr was used as a reference.

Absorption bands and their assignments in the IR spectrum of calciomurmanite (Fig. 2) are $(cm^{-1}; s - cm^{-1})$ strong band, sh - shoulder): 3395, 3250sh (O-H stretching vibrations). 1644 (H-O-H bending vibrations of H₂O molecules), 1324 (Si – O^{-...}H⁺ bending vibrations), 1040sh, 975sh (Si-O stretching vibrations of Si-O-Si bridges in Si₂O₇ groups), 926s (Si-O stretching vibrations involving apical O atoms of Si₂O₇ groups), 800sh (bending vibrations of $M \cdots O$ -H, where M is a cation), 682 (O-Si-O bending vibrations), 523 (Ti…O stretching vibrations), 450, 410, 378 (lattice modes involving Si-O-Si bending vibrations).

A weak band at 1425 cm⁻¹ most probably corresponds to minor admixture of calcite.

Chemical composition

Chemical data for calciomurmanite were obtained using a Jeol JSM-6480LV scanning electron microscope equipped with an INCA-Wave 500 energy-

0.8 0.6 Absorbance 3395 0.4 1324 \$240 3377 475 0.2 638 2 0.0 1000 2000 3000 4000 Wavenumber, cm-1

Fig. 2. The IR spectra of the holotype calciomurmanite (1) and murmanite from the Severnyi (North) open pit, Umbozero mine, Mt. Alluaiv, Lovozero (2).

dispersive spectrometer (Laboratory of local methods of matter investigation, Faculty of Geology, Moscow State University). The standards used are: lorenzenite (Na, Si, Ti), MAD-10 Feldspar (K), wollastonite (Ca), diopside (Mg), rhodonite (Mn), orthopyroxene (Fe), SrSO₄ (Sr), hornblende (Al), GaP (P), Nb (Nb). The H₂O content was determined using the Alimarin method [modified Penfield method with selective sorption of H₂O on Mg(ClO₄)₂ from gaseous products obtained by heating the mineral at 1080 °C in an oxygen stream at ambient pressure].

The average chemical composition (seven spot analyses) of the holotype sample of calciomurmanite (wt%, ranges are in parentheses) is: Na_2O 5.39 (4.79 - 6.54), $K_2O 0.30 (0.22 - 0.43)$, CaO 7.61 (7.34 - 8.03), MgO 2.54 (1.79 - 3.05), MnO 2.65 (2.27 - 2.97), FeO 1.93 $(1.58 - 2.09), Al_2O_3 0.85 (0.49 - 1.04), SiO_2 30.27$ (28.82 - 32.13), TiO₂ 29.69 (27.60 - 31.32), Nb₂O₅ $6.14 (5.53 - 7.14), P_2O_5 0.27 (0.17 - 0.63), H_2O(meas.)$ 11.59, total 99.23. It corresponds to the following empirical formula, calculated on the basis of Si + Al = 4 atoms per formula unit (*apfu*), with the OH^{-}/O^{2-} ratio calculated by charge balance:

Na_{1.34}Ca_{1.04}K_{0.05}Mg_{0.49}Mn_{0.29}Fe_{0.21}Nb_{0.36}Ti_{2.85} $(Si_{3,87}Al_{0,13})_{\Sigma 4}O_{16,40}(OH)_{1,60}(PO_4)_{0,03}(H_2O)_{4,94}$

The measured H₂O content is higher than the value obtained from the structure refinement (see below); this is most likely caused by a slight hydration, typically with partial amorphization, of some grains of calciomurmanite due to their hydrothermal and/or supergene alteration; it is confirmed by the decreased Si/Ti ratio and lower totals in some analyses.

The formula $NaCa(Ti_3Mg_{0.5}Nb_{0.5})[Si_2O_7]_2O_{2.5}(OH)_{1.5}$ (H₂O)₄ requires Na₂O 4.18, CaO 7.83, MgO 2.72, SiO₂ 32.43, TiO₂ 32.33, Nb₂O₅ 8.96, H₂O 11.55, total 100.00 wt%.

Typical electron-microprobe analyses of calciomurmanite from all known localities are given in Table 1. The table includes the data on a sample from Mt. Rischorr, Khibiny, reported by Selivanova (2012) as "murmanite" that shows the highest calcium content in the murmanitelike phases: 9.45 wt.% CaO = 1.35 apfu Ca. We believe that this analysis corresponds to calciomurmanite. All studied samples are chemically inhomogeneous and demonstrate significant variations in contents of subordinate constituents substituting Ti, namely Mg, Nb, Mn, and Fe. This causes, in particular, some differences in density and refractive indices for different particles even within the holotype sample of the new mineral. For instance, the calculated density varies from 2.76 to 2.87 g cm⁻³ and the Gladstone-Dale compatibility index, if D(calc.) is used, varies from 0.033 (excellent) to 0.079 (fair) while its value calculated using D(meas.)for the holotype is 0.021 (excellent).

Calciomurmanite forms a continuous solid-solution series with murmanite (according to 32 electron microprobe analyses; Fig. 3) in which the Ca content varies from 0.17 to 1.35 apfu.



Table 1. Chemical	composition of o	calciomurmanite	from the I	Lovozero a	nd Khibiny	alkaline	complexes,	Kola p	eninsula,	Russia	(1-7)
murmanite from Lo	ovozero (8) and p	products of its re-	action with	h 1N CaCl	2 aqueous s	olution (9	<i>P-10</i>).				

	1	2	3	4	5	6	7	8	9	10
					wt. %					
Na ₂ O	5.39	5.04	3.97	1.21	6.03	8.87	5.71	11.43	4.51	6.80
$K_2 O$	0.30	0.40	0.79	1.26	0.91	0.64	0.54	0.50	0.30	0.41
CaO	7.61	8.03	6.94	6.17	8.57	6.90	9.45	4.18	5.02	6.31
SrO	-	-	1.64	2.12	-	-	0.16	-	-	-
MgO	2.54	2.57	1.01	0.65	0.45	0.22	0.54	0.45	0.52	0.33
MnO	2.65	2.67	2.78	3.29	2.92	2.90	1.41	2.01	1.57	1.16
FeO	1.93	1.71	1.48	1.48	2.52	1.77	2.61	2.42	2.88	3.19
Al_2O_3	0.85	0.99	0.38	0.70	0.23	0.06	0.36	-	0.28	0.24
SiO ₂	30.27	30.89	28.77	28.15	30.75	29.65	29.61	30.22	28.12	28.46
TiO_2	29.69	27.60	24.62	23.26	30.43	27.49	27.66	27.33	26.69	30.00
ZrO_2	-	-	-	-	-	-	0.17	-	-	-
Nb_2O_5	6.14	6.08	12.30	14.38	6.61	10.94	4.37	5.93	5.37	6.85
P_2O_5	0.27	0.63	0.41	0.30	1.78	1.12	1.28	1.58	-	-
Total	87.64	86.61	85.09	82.97	91.20	90.56	83.87	86.06	76.02	83.76
			ator	ns per formu	la unit (based	d on Si+Al =	4)			
Na	1.34	1.22	1.05	0.32	1.51	2.32	1.47	2.93	1.23	1.83
Κ	0.05	0.06	0.14	0.22	0.15	0.11	0.09	0.08	0.05	0.07
Ca	1.04	1.07	1.02	0.91	1.18	1.00	1.35	0.59	0.76	0.94
Sr	-	-	0.13	0.17	-	-	0.01	-	-	-
Mg	0.49	0.48	0.21	0.13	0.09	0.04	0.11	0.09	0.11	0.07
Mn	0.29	0.28	0.32	0.39	0.32	0.33	0.16	0.22	0.18	0.14
Fe	0.21	0.18	0.17	0.17	0.27	0.20	0.29	0.27	0.34	0.38
Al	0.13	0.15	0.06	0.12	0.03	-	0.06	-	0.05	0.04
Si	3.87	3.85	3.94	3.88	3.97	4.00	3.94	4.00	3.95	3.96
Ti	2.85	2.59	2.54	2.42	2.95	2.79	2.77	2.72	2.82	3.14
Zr	-	-	-	-	-	-	0.01	-	-	-
Nb	0.36	0.34	0.76	0.90	0.38	0.67	0.26	0.35	0.34	0.43
Р	0.03	0.07	0.05	0.03	0.19	0.13	0.14	0.18	-	-

Localities: 1-2 - Mt. Flora, Lovozero (holotype), 3-4 - Mt. Eveslogchorr, Khibiny (cotype), 5-6 - Shcherbakovitovoe pegmatite, Koashva open pit, Mt. Koashva, Khibiny; 7 - Mt. Rischorr, Khibiny; 8 - Severnyi open pit, Mt. Alluaiv, Lovozero; 9-10 - products of reactions of murmanite (8) with 1N CaCl₂ aqueous solution at 90 °C for 1 hour (9) and 24 hours (10). Dash means 'below detection limit'. Sources: 7 - Selivanova (2012): tentatively assigned by us to calciomurmanite on the basis of chemical composition; others – our data.



Fig. 3. Na and Ca contents (apfu, calculated on the basis of 4 Si +Al) for the members of the murmanite–calciomurmanite solidsolution series from peralkaline pegmatites within the Lovozero and Khibiny complexes (based on 32 electron-microprobe analyses). (online version in colour)

X-ray crystallography and crystal structure

X-ray powder diffraction data (Table 2) for calciomurmanite were collected with a Rigaku R-AXIS Rapid II single-crystal diffractometer equipped with a cylindrical image plate detector using Debye-Scherrer geometry (d = 127.4 mm; CoK α radiation). Unit-cell parameters refined from the powder data are: a = 5.349(9), b = 7.08(1), c = 12.15(2) Å, $\alpha = 91.85(3)$, $\beta = 107.72$ (3), $\gamma = 90.17(3)^{\circ}$ and V = 438.1(5) Å³.

Single-crystal X-ray diffraction studies of both holotype and cotype of calciomurmanite were carried out using a Bruker Kappa X8 APEX diffractometer equipped with a CCD detector (λ MoK α = 0.71073). Several sets of phi- and omega-scans with 2° scan-width were measured up to 60° 2 θ (full sphere) at *T* = 200 K with a crystal– detector distance of 35 mm. The absorption was corrected by evaluation of multi-scans.

The crystal structures were solved by direct methods and refined by full-matrix least-squares techniques on F^2 in the space group *P*-1 using the SHELX-97

Table 2. X-ray powder-diffraction data of calciomurmanite.

I _{obs}	$d_{\rm obs}$	I_{calc}^{*}	$d_{ m calc}$ **	h k l
100	11.69	100	11.575	001
15	7.08	2	7.073	010
68	5.87	24, 36	5.946, 5.788	011, 002
18	4.586	6	4.556	0-12
89	4.251	17, 9	4.241, 4.232	-1-11, -111
16	4.139	4	4.111	110
44	3.825	13, 20, 3	3.865, 3.858, 3.811	-1-12, 003, -112
14	3.668	3	3.651	-103
16	3.580	5	3.588	111
14	3.461	5	3.437	0-13
15	3.359	3, 2	3.357, 3.350	102, 021
10	3.077	5, 4	3.066, 3.065	1-12, 0-22
47	2.940	1, 10	2.943, 2.937	-1-21, -121
79	2.900	39, 26	2.894, 2.889	004, 120
26	2.752	28	2.742	1-21
26	2.681	15, 1	2.680, 2.676	121, -114
39	2.659	6, 1, 15	2.664, 2.653, 2.646	-201, 0-23, -202
9	2.571	3, 1	2.570, 2.556	-1-23, 1-13
26	2.509	8, 2, 11	2.511, 2.504, 2.502	-123, 113, -203
4	2.367	2	2.366	-2-13
14	2.292	4, 2, 7, 5	2.315, 2.291, 2.285, 2.284	005, -1-15, -204, -1-24
8	2.223	1, 1, 1, 1	2.224, 2.223, 2.214, 2.210	-124, 0-15, 211, 0-32
6	2.085	1, 4	2.082, 2.081	-132, -220
9	2.057	6, 3	2.055, 2.052	220, -2-23
3	1.981	3	1.982	033
6	1.934	3	1.929	006
6	1.879	2, 6	1.878, 1.867	0-16, 124
6	1.829	6, 1	1.826, 1.823	-206, 115
9	1.784	1, 2	1.788, 1.778	-2-25, -2-16
16	1.770	4, 7	1.771, 1.768	-231, 040
4	1.729	1, 2	1.734, 1.729	-107, -126
3	1.720	2, 3	1.720, 1.719	230, 0-26
3	1.706	1, 1	1.708, 1.704	-233, -3-11
6	1.659	1, 1, 2, 2, 1	1662, 1.657, 1.657, 1.654, 1.653	-3-14, -310, -314, 007, 125
4	1.636	1, 4	1.643, 1.630	2-14, -207
15	1.597	7	1.594	-322
13	1.588	7, 4	1.590, 1.587	-3-22, 043
6	1.571	4	1.576	-1-27
7	1.541	1, 3	1.546, 1.538	142, -127
3	1.503	3, 2	1.503, 1.500	205, 224
5	1.474	1, 1, 5, 2, 1	1.479, 1.470, 1.469, 1.469, 1.469	2-15, -2-41, -242, 036, -325
4	1.457	1, 1, 1, 1, 4	1.460, 1.458, 1.458, 1.452, 1.451	-2-36, 321, 135, 233, -2-43
5	1.414	1, 1, 1, 3	1.415, 1.414, 1.411, 1.411	050, -3-33, 117, -1-28
4	1.375	1, 2, 1, 2	1.378, 1.376, 1.376, 1.371	-128, -137, 0-37, 2-42
5	1.339	2, 3	1.338, 1.336	-228, -403
5	1.318	1, 1	1.323, 1.314	216, -308
4	1.221	1, 1	1.225, 1.222	-229, 2-51
3	1.214	3	1.214	-2-47

*for the calculated pattern, only reflections with intensities ≥ 1 are given;

** for the unit-cell parameters calculated from single-crystal data.

program package (Sheldrick, 2008). The crystal structure of the holotype was refined to R = 0.0656 on the basis of 2127 unique reflections with $I > 2\sigma(I)$, and that of the cotype to R = 0.0663 [2148 independent reflections with $I > 2\sigma(I)$, Table 3]. Atom coordinates and equivalent displacement parameters, site occupancies and bond valence sums (BVS) for both samples are given in Table 4, selected interatomic distances in Tables 5 and 6. The crystal-structure models obtained are similar to each other. Unless otherwise stated, the description given below refers to the crystal structure of the holotype sample.

The crystal structure of calciomurmanite, as well as of other heterophyllosilicates belonging to the bafertisite series, is based on a three-sheet *HOH* block (Ferraris & Gula, 2005; Fig. 4–6). The central octahedral (O) sheet is formed by alternating chains of the

Table 3. Crystal data, data collection information and structure refinement details for the holotype (1) and cotype (2) samples of calciomurmanite.

Sample	1	2
Space group, Z	<i>P</i> -1, 1	<i>P</i> -1, 1
a, Å	5.3470(6)	5.3459(6)
<i>b</i> , Å	7.0774(7)	7.0972(8)
<i>c</i> , Å	12.1456(13)	12.0933(14)
α, °	91.827(4)	92.915(4)
β, °	107.527(4)	107.130(4)
γ, °	90.155(4)	90.186(4)
$V, Å^3$	438.03(8)	437.83(9)
λ (MoKa) (Å), T (K)	0.71073, 200(2)	
Diffractometer	Kappa X8 APEX	CCD
Reflections collected	10695	11697
Unique reflections, R_{int}	2127, 0.0457	2148, 0.0634
Reflections with $I > 2\sigma(I)$	1895	1650
Number of refined parameters	167	166
R1	0.0656	0.0663
$wR2_{all}(F^2)$	0.1443	0.1388
GoF	1.264	1.169
$\Delta \rho_{max}$ / $\Delta \rho_{min}$ (e/Å ³)	1.309/-0.951	1.224/-0.951

Na-centred and Ti(2)-centred octahedra (Fig. 5a). The O sheet is sandwiched between two identical heteropolyhedral (H) sheets consisting of the tetrahedral disilicate groups Si₂O₇, the Ti(1)-centred octahedra and the hexagonal dipyramids centred by Ca (Fig. 6a). The Ti(1) site contains small admixture of Nb; the Ti(2)-site contains admixtures of Nb and lighter cations with lower valencies: Mg, Mn and Fe. Both Ca and Na sites are partially vacant, with occupancies of 58% and 72%, respectively (50% and 52% for the cotype; Tables 4).

There are eight anion sites O(1-8) occupied solely by O^{2-} and one site O(9) bridging Ti(2)-O-Ti(2) in the *O* layers with a mixed occupancy of O^{2-} and OH⁻. For O(9) BVS = 1.56 vu (valence units; 1.53 vu for the cotype: Table 4) which prevents an unambiguous determination of the prevalent anion in this site, but the O: OH ratio calculated from the charge balance for different chemical analyses shows that the O(9) site is OH-dominant.

In the interlayer space, between the *HOH* blocks, two H_2O sites $O_w(10)$ and $O_w(11)$ are located and form the vertices of the Ti(1)- and Ca-centred polyhedra, respectively (Tables 3–5; Fig. 4). The $O_w(10)$ site is fully occupied whereas $O_w(11)$ contains vacancies.

The H₂O content found from the structure data is $(H_2O)_{3.56}$ *pfu* for the holotype specimen (additionally, small amount of H₂O molecules can present in the interlayer space: see below) and $(H_2O)_{3.86}$ for the cotype specimen. However, the H₂O content determined by direct measurement using the Alimarin method is higher, as discussed above. Thus, the anionic part of the simplified formula is considered as $O_{16}(OH,O)_2(H_2O)_4$.

In the holotype, two low-occupancy large-cation sites in the interlayer space were found, A and B,

with a refined number of electrons (e_{ref}) of 3.5 and 1.0, respectively. We believe that they contain the largest cations, K and possibly Sr (their presence in the mineral is confirmed by the electron-microprobe data). The occurrence of H₂O molecules in these sites is also not excluded. Either the *A* or the *B* site could be occupied only if both the O_w(11) and Ca sites are vacant. One low-occupancy large-cation site *A* is located in the interlayer space of the cotype specimen.

The simplified formula is, taking into account the structure data: $(Na, \Box)_2Ca(Ti,Mg,Nb)_4[Si_2O_7]_2O_2(OH,O)_2(H_2O)_4$.

Discussion

Relationship with other minerals species

Calciomurmanite, $(Na,\Box)_2Ca(Ti,Mg,Nb)_4[Si_2O_7]_2O_2$ $(OH,O)_2(H_2O)_4$, is chemically and structurally related to murmanite, Na₄Ti₄[Si₂O₇]₂O₄(H₂O)₄ (Table 7). It is a Na-Ca ordered murmanite-type heterophyllosilicate with selective occupancy of the large-cation site in the heteropolyhedral H sheet by Ca, and of the largecation site in the octahedral O sheet by Na, whereas in murmanite these positions are both occupied by species-defining Na (Fig. 4 to 6). Calcium is a typical admixture in the Na site in the H sheet of murmanite and it was never reported in the O sheet (Khalilov, 1989; Cámara et al., 2008). Bond-valence calculations show that in the O sheet $[Ti_2Na_2O_2]$ of murmanite the O²⁻ anions are saturated, in terms of bond valence, mainly from Ti⁴⁺, therefore the substitution of the univalent cation Na⁺ for a divalent cation would inevitably lead to a local excess of positive charge on them, a strong violation of Pauling's second rule. Thus, a divalent cation cannot occupy, as major constituent, the large-cation site in the murmanite-type O sheet. This restricts the calcium amount in murmanite-type minerals and allows a mineral with Na:Ca = 1:1 in the idealized formula – calciomurmanite – but not a hypothetic phase with 2 Ca apfu, a formal Ca-dominant analogue of murmanite.

Calciomurmanite is chemically similar to kolskyite, $(Ca)Na_2Ti_4(Si_2O_7)_2O_4(H_2O)_7$ (Cámara *et al.*, 2013), however the structural features of the HOH blocks of these minerals are essentially different. In kolskyite, a titanosilicate related to kazanskyite, Ba TiNbNa3Ti (Si₂O₇)₂O₂(OH)₂(H₂O)₄ (Cámara et al., 2012), and nechelyustovite, (Ba,Na)₂{(Na,Ti,Mn)₄[(Ti,Nb)₂O₂Si₄ O_{14} (OH,O,F)₂ (H₂O)₄₅ (Németh *et al.*, 2009), the large-cation site in the H sheet is vacant and Ca is located in the interlayer space, in positions corresponding to the low-occupancy A sites in calciomurmanite. The presence of both Ca and much H₂O (seven H_2O molecules *pfu* instead of four in murmanite) in the interlayer causes significant increase of the c unit-cell parameter and of d_{00l} spacings in the powder X-ray diffraction pattern of kolskyite in comparison with murmanite and calciomurmanite (Table 7).

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$\begin{array}{c c c c c c c c c c c c c c c c c c c $,			•• •		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Site	x	У	Z	$U_{ m eq}$	s.o.f./site composition ¹	BVS ⁵
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Ti(1)	0.4129(2)	0.33480(16)	0.23563(10)	0.0162(4)	[23.2] Ti _{0.94} Nb _{0.06}	4.28
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		0.41369(19)	0.32320(14)	0.23553(10)	0.0166(4)	[25.7] Ti _{0.80} Nb _{0.20}	4.24
	Ti(2)	0.2726(2)	0.88223(15)	0.50619(9)	0.0158(4)	[23.3] Ti _{0.42} Mg _{0.21} Mn _{0.15} Nb _{0.14} Fe _{0.08}	3.45
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		0.2692(2)	0.88252(16)	0.50588(10)	0.0181(4)	[23.7] Ti _{0.52} Mn _{0.16} Mg _{0.13} Nb _{0.12} Fe _{0.07}	3.50
	Si(1)	0.9236(3)	0.0576(2)	0.26061(15)	0.0121(4)	1	4.13
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		0.9218(4)	0.0468(2)	0.25796(16)	0.0155(4)	1	4.11
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Si(2)	0.9464(3)	0.6295(2)	0.27748(15)	0.0134(4)	1	4.23
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		0.9438(4)	0.6201(2)	0.27615(17)	0.0176(5)	1	4.31
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Ca	0.3866(5)	0.8375(4)	0.2014(2)	0.0247(9)	[11.6] Ca _{0.580(8)}	0.96
$ \begin{array}{llllllllllllllllllllllllllllllllllll$		0.3863(6)	0.8254(4)	0.2026(3)	0.0267(11)	[10.1] Ca _{0.504(7)}	0.93
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Na	0.7225(9)	0.6049(6)	0.4887(4)	0.0290(16)	[7.8] Na _{0.712(14)}	0.80
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		0.7085(11)	0.6015(8)	0.4863(5)	0.027(2)	[5.7] Na _{0.518(13)}	0.58
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O(1)	0.1393(10)	0.1442(9)	0.2101(4)	0.0305(13)	1	1.96
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		0.140(1)	0.1326(9)	0.2083(5)	0.0364(15)	1	1.92
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	O(2)	0.6389(10)	0.1396(8)	0.2010(4)	0.0287(12)	1	1.91
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		0.6391(10)	0.1293(9)	0.1995(5)	0.0344(14)	1	1.88
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O(3)	0.0023(9)	0.9298(6)	0.5989(4)	0.0159(9)	1	1.88
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		0.0046(9)	0.9356(7)	0.6009(4)	0.0242(11)	1	1.90
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O(4)	0.9030(12)	0.8349(7)	0.2187(4)	0.0291(12)	1	2.13
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		0.9035(12)	0.8219(7)	0.2181(5)	0.0353(14)	1	2.14
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O(5)	0.6686(11)	0.5273(9)	0.2368(5)	0.0371(15)	1	1.97
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		0.6684(11)	0.5190(9)	0.2352(5)	0.0388(15)	1	1.96
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O(6)	0.0522(10)	0.6645(7)	0.4164(4)	0.0245(11)	1	1.93
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		0.0447(12)	0.6609(7)	0.4155(5)	0.0355(14)	1	1.80
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O(7)	0.1617(11)	0.5290(9)	0.2312(5)	0.0343(14)	1	2.00
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		0.1645(11)	0.5170(9)	0.2330(5)	0.0404(15)	1	1.97
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	O(8)	0.5328(9)	0.3008(7)	0.3921(4)	0.0203(10)	1	1.98
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		0.5335(10)	0.2951(7)	0.3906(4)	0.0248(11)	1	1.98
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	O(9)	0.5024(8)	0.8964(6)	0.4121(4)	0.0155(9)	1	1.56
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		0.5043(10)	0.8911(7)	0.4121(4)	0.0229(11)	1	1.53
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$O(10) = H_2O$	0.2821(12)	0.3574(8)	0.0451(5)	0.0349(14)	1	0.34
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		0.2829(12)	0.3457(9)	0.0439(5)	0.0408(15)	1	0.33
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$O(11) = H_2O$	0.2538(14)	0.7409(11)	0.0104(6)	0.0337(19)	[6.4] 0.779(19)	0.19
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		0.2542(15)	0.7420(13)	0.0152(9)	0.061(3)	[7.4] 0.928(12)	3.26
$B \qquad \begin{array}{cccc} 0.343(8) & 0.807(6) & 0.103(4) & 0.065(16)^2 & [2.7] \text{ K}_{0.072(12)} \\ 0.290(7) & 0.862(5) & 0.072(3) & 0.034(8)^2 & [1.0]^{3,4} \text{ K}_{0.05} \end{array}$	A	0.2050(17)	0.6419(14)	-0.0624(8)	0.0337(19)	$[3.5]^3$ Sr _{0.093(3)}	
<i>B</i> 0.290(7) 0.862(5) 0.072(3) 0.034(8) ² $[1.0]^{3,4}$ K _{0.05}		0.343(8)	0.807(6)	0.103(4)	$0.065(16)^2$	$[2.7]_{K_{0.072(12)}}$	
	В	0.290(7)	0.862(5)	0.072(3)	$0.034(8)^2$	$[1.0]^{3,4} K_{0.05}$	

Table 4. Atom fractional coordinates, equivalent thermal displacement parameters (U_{eq} , Å²), site occupancy factors (s.o.f.) and bond-valence sums (BVS) in the structures of the holotype (upper line) and cotype (lower line) samples of calciomurmanite.

¹We consider the site occupancies based on the e_{ref} values (given in square brackets) and electron-microprobe data, taking also into account coordination polyhedra character and interatomic distances.² U_{iso} .³ Low-occupancy A and B sites most probably contain large cations, possibly Sr and K. However, the presence of H₂O molecules in these sites is not excluded.⁴ Values were fixed on the last stages of the refinement.⁵ BVS have been formally calculated taking into account s.o.f. Parameters are taken from (Brese & O'Keeffe, 1991). The low-occupancy A and B sites were not taken into account because of their insignificant contribution.

Genetic features of calciomurmanite

The genesis of calciomurmanite is still ambiguous. Calciomurmanite and murmanite are related in terms of structure, chemistry, and occurrence and we believe that their mode of formation could be similar. We assume two plausible mechanisms of formation of calciomurmanite.

Murmanite is considered to be a product of hydrothermal or supergene alteration (with sodium-phosphate leaching and hydration) of the high-temperature, anhydrous phosphate-bearing titanosilicates lomonosovite, $Na_{10}Ti_4(Si_2O_7)_2(PO_4)_2O_4$, and/or betalomonosovite, $Na_6Ti_4(Si_2O_7)_2[PO_3(OH)][PO_2(OH)_2]O_2(OF)$. Murmanite forms homo-axial pseudomorphs after these minerals and no convincing evidence is known that murmanite can crystallize directly from a melt, solution or gas (Borneman-Starynkevich, 1946; Khomyakov, 1995). Calciomurmanite could be a product of the same process, the topotactic replacement of a hypothetic epistolitegroup titanosilicate with formula $(Na, \Box)_2Ca(Ti,Mg,Nb)_4$ $[Si_2O_7]_2O_2(OH,O)_2(Na_3PO_4)_2$. However, no such primary P-rich heterophyllosilicate mineral containing much Ca in the *HOH* block is known in nature.

Another mechanism is considered more probable for the formation of calciomurmanite. The precursor of calciomurmanite could also be lomonosovite or betalomonosovite. In that case, sodium-phosphate leaching and

calciomurmanite.					calcion	nurmanite.					
	Ti(1) octahe	edron		Ti(2) octahedron			Ti(1) octahedron			Ti(2) octah	edron
Ti(1)	-O(8) -O(7) -O(5) -O(1) -O(2)	1.838(4) 1.915(5) 1.924(5) 1.935(5) 1.955(5)	Ti(2)	-O(8) -O(9) -O(9) -O(6) -O(3)	$\begin{array}{c} 1.903(5) \\ 1.917(5) \\ 2.014(4) \\ 2.015(5) \\ 2.104(4) \end{array}$	Ti(1)	-O(8) -O(7) -O(5) -O(1) -O(2)	1.816(5) 1.913(5) 1.943(5) 1.933(5) 1.948(5)	Ti(2)	-O(8) -O(9) -O(9) -O(6) -O(3)	1.913(5) 1.928(5) 2.037(5) 2.037(6) 2.093(5)
	-O(10)	2.217(5)		-O(3)	2.133(4)		-O(10)	2.229(6)		-O(3)	2.132(5)
<ti< td=""><td>(1)–O></td><td>1.964</td><td><ti< td=""><td>(2)–O></td><td>2.014</td><td><ti< td=""><td>(1)–O></td><td>1.964</td><td><ti(< td=""><td>2)–O></td><td>2.023</td></ti(<></td></ti<></td></ti<></td></ti<>	(1)–O>	1.964	<ti< td=""><td>(2)–O></td><td>2.014</td><td><ti< td=""><td>(1)–O></td><td>1.964</td><td><ti(< td=""><td>2)–O></td><td>2.023</td></ti(<></td></ti<></td></ti<>	(2)–O>	2.014	<ti< td=""><td>(1)–O></td><td>1.964</td><td><ti(< td=""><td>2)–O></td><td>2.023</td></ti(<></td></ti<>	(1)–O>	1.964	<ti(< td=""><td>2)–O></td><td>2.023</td></ti(<>	2)–O>	2.023
a. (1)	Si(1) tetrahe	edron	a. (a)	Si(2) tetrahe	dron		Si(1) tetrahe	dron		Si(2) tetrah	edron
Si(1)	-O(1) -O(2) -O(3) -O(4) (1) O	$\begin{array}{c} 1.590(5) \\ 1.596(5) \\ 1.631(4) \\ 1.634(5) \\ 1.613 \end{array}$	Si(2)	-O(5) -O(7) -O(6) -O(4)	$\begin{array}{c} 1.582(5) \\ 1.586(5) \\ 1.621(5) \\ 1.627(5) \\ 1.604 \end{array}$	Si(1)	-O(1) -O(2) -O(3) -O(4)	1.593(5) 1.596(5) 1.632(5) 1.638(5)	Si(2)	-O(5) -O(7) -O(6) -O(4)	1.567(5) 1.590(6) 1.622(6) 1.614(6)
~51	Na octabec	1.015	-31(2)-0> 1.004 Ca polyhedron		<si(1)–o> 1.615</si(1)–o>		<si(2)–o></si(2)–o>		1.598		
Na <n< td=""><td>-O(6) -O(8) -O(6) -O(9) -O(8) -O(3) Va-O></td><td>2.238(7) 2.353(6) 2.395(6) 2.446(6) 2.480(6) 2.810(6) 2.454</td><td>Ca <c< td=""><td>-O(11) -O(9) -O(2) -O(1) -O(7) -O(5) -O(4) -O(4) a-O> B collaboda</td><td>2.293(8) 2.467(5) 2.526(6) 2.560(6) 2.578(7) 2.639(7) 2.657(6) 2.706(6) 2.553</td><td>Na <n< td=""><td>Na octahed -O(6) -O(8) -O(6) -O(9) -O(8) -O(3) Va-O></td><td>ron 2.254(8) 2.336(7) 2.436(8) 2.418(7) 2.457(8) 2.898(8) 2.467</td><td>Ca <c< td=""><td>Ca polyhe -O(11) -O(9) -O(2) -O(1) -O(7) -O(5) -O(4) -O(4) a-O></td><td>dron 2.215(12) 2.443(6) 2.549(7) 2.559(7) 2.580(7) 2.630(7) 2.657(6) 2.716(7) 2.54</td></c<></td></n<></td></c<></td></n<>	-O(6) -O(8) -O(6) -O(9) -O(8) -O(3) Va-O>	2.238(7) 2.353(6) 2.395(6) 2.446(6) 2.480(6) 2.810(6) 2.454	Ca <c< td=""><td>-O(11) -O(9) -O(2) -O(1) -O(7) -O(5) -O(4) -O(4) a-O> B collaboda</td><td>2.293(8) 2.467(5) 2.526(6) 2.560(6) 2.578(7) 2.639(7) 2.657(6) 2.706(6) 2.553</td><td>Na <n< td=""><td>Na octahed -O(6) -O(8) -O(6) -O(9) -O(8) -O(3) Va-O></td><td>ron 2.254(8) 2.336(7) 2.436(8) 2.418(7) 2.457(8) 2.898(8) 2.467</td><td>Ca <c< td=""><td>Ca polyhe -O(11) -O(9) -O(2) -O(1) -O(7) -O(5) -O(4) -O(4) a-O></td><td>dron 2.215(12) 2.443(6) 2.549(7) 2.559(7) 2.580(7) 2.630(7) 2.657(6) 2.716(7) 2.54</td></c<></td></n<></td></c<>	-O(11) -O(9) -O(2) -O(1) -O(7) -O(5) -O(4) -O(4) a-O> B collaboda	2.293(8) 2.467(5) 2.526(6) 2.560(6) 2.578(7) 2.639(7) 2.657(6) 2.706(6) 2.553	Na <n< td=""><td>Na octahed -O(6) -O(8) -O(6) -O(9) -O(8) -O(3) Va-O></td><td>ron 2.254(8) 2.336(7) 2.436(8) 2.418(7) 2.457(8) 2.898(8) 2.467</td><td>Ca <c< td=""><td>Ca polyhe -O(11) -O(9) -O(2) -O(1) -O(7) -O(5) -O(4) -O(4) a-O></td><td>dron 2.215(12) 2.443(6) 2.549(7) 2.559(7) 2.580(7) 2.630(7) 2.657(6) 2.716(7) 2.54</td></c<></td></n<>	Na octahed -O(6) -O(8) -O(6) -O(9) -O(8) -O(3) Va-O>	ron 2.254(8) 2.336(7) 2.436(8) 2.418(7) 2.457(8) 2.898(8) 2.467	Ca <c< td=""><td>Ca polyhe -O(11) -O(9) -O(2) -O(1) -O(7) -O(5) -O(4) -O(4) a-O></td><td>dron 2.215(12) 2.443(6) 2.549(7) 2.559(7) 2.580(7) 2.630(7) 2.657(6) 2.716(7) 2.54</td></c<>	Ca polyhe -O(11) -O(9) -O(2) -O(1) -O(7) -O(5) -O(4) -O(4) a-O>	dron 2.215(12) 2.443(6) 2.549(7) 2.559(7) 2.580(7) 2.630(7) 2.657(6) 2.716(7) 2.54
A <	A polyned -O(10) -O(7) -O(2) -O(5) -O(1) -O(10) -O(10) A-O>	2.404(11) 2.630(11) 2.632(11) 2.662(11) 2.664(10) 2.675(11) 2.687(11) 2.62	B < 1	-O(2) -O(1) -O(4) -O(10) -O(10) -O(2) -O(1) -O(10) B-O>	2.79(4) 2.84(4) 3.12(4) 3.32(4) 3.39(4) 3.45(4) 3.51(4) 3.53(4) 3.24	A <.	A polyheda -O(2) -O(1) -O(4) -O(10) A-O>	ron 2.78(4) 2.95(4) 3.07(4) 3.19(4) 3.00			

Table 5. Selected interatomic distances (Å) for the holotype Table 6. Selected interatomic distances (Å) for the cotype



Fig. 4. General view of the crystal structures of calciomurmanite (a) and murmanite (b: drawn after Cámara et al., 2008). Unit cells are outlined. (online version in colour)



Fig. 5. The O sheet in the structures of calciomurmanite (a) and murmanite (b: drawn after Cámara et al., 2008). (online version in colour)



Fig. 6. The H sheet in the structures of calciomurmanite (a) and murmanite (b: drawn after Cámara et al., 2008). (online version in colour)

Table	7.	Comparative	data c	on calciomur	manite. m	nurmanite	and	kolskvite.

Mineral	Calciomurmanite	Murmanite	Kolskyite	
Simplified formula	(Na,□) ₂ Ca(Ti,Mg,Nb) ₄ [Si ₂ O ₇] ₂ O ₂ (OH, O) ₂ (H ₂ O) ₄	$Na_4Ti_4[Si_2O_7]_2O_4(H_2O)_4$	$(Ca\Box)Na_2Ti_4(Si_2O_7)$ $_2O_4(H_2O)_7$	
Content of <i>H</i> sheet	$(Ti,Mg,Mn,Nb)_2(Ca,\Box)_2O_2[Si_2O_7]_2$	$Ti_2Na_2O_2[Si_2O_7]_2$	$Ti_2 \square_2 O_2 [Si_2 O_7]_2$	
Content of O sheet	$(Ti,Nb)_2(Na,\Box)_2(OH,O)_2$	Ti ₂ Na ₂ O ₂	Ti ₂ Na ₂ O ₂	
Content of interlayer space	$(H_2O)_4$	$(H_2O)_4$	$Ca(H_2O)_7$	
Crystal system	Triclinic	Triclinic	Triclinic	
Space group	P-1	<i>P</i> -1	<i>P</i> -1	
a, Å	5.3470(6)	5.3875(6)	5.387(1)	
b, Å	7.0774(7)	7.0579(7)	7.091(1)	
<i>c</i> , Å	12.1456(13)	12.176(1)	15.473(3)	
α, °	91.827(4)	93.511(2)	96.580(4)	
β, °	107.527(4)	107.943(4)	93.948(4)	
γ, °	90.155(4)	90.093(2)	89.818(3)	
V, Å ³	438.03(8)	439.55(2)	585.8(3)	
Z	1	1	1	
Strongest reflections of the X-ray powder	11.69 - 100	11.56 - 90	15.161 - 100	
pattern: $d, Å - I$	5.87 - 68	5.81 - 90	2.810 - 19	
•	4.25 - 89	4.22 - 100	3.069 - 12	
	3.825 - 44	3.762 - 60	2.938 - 10	
	2.940 - 47	2.867 - 100		
	2.900 - 79			
Density, g/cm ³	2.70 (meas.)	2.76 – 2.84 (meas.)	2.51 (calc.)	
Optical data:				
a	1.680	1.682-1.735	1.669	
β	1.728	1.765-1.770	1.701	
γ	1.743	1.807-1.839	1.720	
Optical sign, 2V(meas.)	(-) 58°	(-) 57–64°	(-) 74°	
Reference	This study	Khalilov, 1989; Cámara <i>et al.</i> , 2008	Cámara et al., 2013	



Fig. 7. Holotype calciomurmanite: elemental X-ray ($K\alpha$) maps for P (a) and Ca (b) obtained using the EDS mode. Bright Ca- and P-rich areas correspond to inclusions of fluorapatite. Polished section, field of view 130 μ m.

hydration were combined with natural cation exchange resulting in partial replacement of Na⁺ for Ca²⁺. These processes could have been occurring simultaneously or, more likely, successively.

Lomonosovite and betalomonosovite show invariable chemical composition with only small admixture of Ca. Unlike them, murmanite is characterized by variable chemical composition with common admixtures of Ca, K and sometimes Sr (Fig. 3; Selivanova, 2012). That was the reason for us to assume that murmanite could be a cation-exchanger and to check its ionexchange properties. Our experiments with aqueous solutions of salts of various metals (K, Rb, Cs, Sr, Ag, Cu, Ni, Zn) under mild conditions (<100 °C) confirmed this assumption and demonstrated that the degree of exchange can be high (Lykova et al., 2013a, 2013b, 2015a, 2015b). Moreover, the recently described titanosilicate mineral vigrishinite, Zn₂Ti_{4-x} $(Si_2O_7)_2O_2(OH,F,O)_2(H_2O,OH,\Box)_4$, was shown to be a product of natural ion exchange of Na⁺ for Zn²⁺ in murmanite (Pekov et al., 2013; Lykova et al., 2015b).

Experiments with 1N CaCl₂ solution at 90 °C show that murmanite undergoes ion exchange with Ca: the content of Ca reaches up to 0.76 *apfu* in 1 hour and 0.94 *apfu* in 24 hours, starting from 0.59 *apfu* Ca in the untreated murmanite (Table 1). Although the mineral shows only weak ion-exchange properties for Ca in our experiments, the intensification of the reaction under different conditions (at first, higher temperature) seems very probable.

The formation of calciomurmanite by replacement of a phosphate-bearing titanosilicate involving a hydrothermal solution enriched by Ca^{2+} is confirmed by the common presence of fluorapatite micro-inclusions scattered inside the lamellae of the new mineral (Fig. 7). Fluorapatite could have been formed involving the phosphorus mobilized from a primary phosphate-bearing titanosilicate during its alteration by a late-stage hydrothermal solution. The presence of small amounts of P (0.2–1.8 wt. % P_2O_5 , Table 1) in all studied samples of calciomurmanite, most probably as relics of PO₄ groups in the interlayer space, is an additional indirect argument for this "genetic model". Relics of the P-bearing titanosilicate

betalomonosovite found in lamellae of calciomurmanite from Mt. Koashva, Khibiny, give us direct evidence. The Ca content of this sample of calciomurmanite reaches $1.18 \ apfu$, whereas it is significantly lower in betalomonosovite ($0.41-0.55 \ apfu$); this indicates the involvement of a Ca-enriched hydrothermal solution in calciomurmanite formation.

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