Mayenite supergroup, part II: Chlorkyuygenite from Upper Chegem, Northern Caucasus, Kabardino-Balkaria, Russia, a new microporous mineral with "zeolitic" H₂O

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Abstract: The new mineral chlorkyuygenite, $Ca_{12}Al_{14}O_{32}[(H_2O)_4Cl_2]$ ($\overline{I43}d$, a=12.0285(1)Å, V=1740.34(3)Å³), was discovered as an accessory mineral in Ca-humite zones of calcareous skarn xenoliths in ignimbrites of the Upper Chegem Caldera, Northern Caucasus, Kabardino-Balkaria, Russia. Rounded grains and crystals with tris-tetrahedral form of chlorkyuygenite up to 50µm and aggregates up to 100–150µm in size are enclosed in chegemite, reinhardbraunsite and srebrodolskite. Chlorkyuygenite also forms rims on wadalite crystals. Chegemite–fluorchegemite, reinhardbraunsite–kumtyubeite, rondorfite, hydroxylellestadite, lakargiite, perovskite, kerimasite, elbrusite, ettringite-group minerals, hydrocalumite, bultfonteinite, and minerals of the katoite–grossular series are associated with chlorkyuygenite. Larnite, spurrite and galuskinite are noted as relics in Ca-humites. Chlorkyuygenite is colourless, occasionally with a greenish or yellowish tint, and the streak is white. The mineral is transparent with strong vitreous lustre, it is isotropic, n = 1.672(1) (589 nm). The microhardness VHN load 50 g is 632(37) kg mm⁻², corresponding to $5-5\frac{1}{2}$ hardness according to the Mohs scale; the calculated density is 2.941 g cm⁻³. The calculated Gladstone-Dale's compatibility factor $1-(K_p/K_c) = -0.016$ is superior. The holotype specimen of chlorkyugenite from the chegemite zone is characterized by relatively constant composition corresponding to the crystal-chemical formula $Ca_{11.979}(Al_{12.986}\text{Fe}^{3+}_{0.823}\text{Si}_{0.179}\text{Ti}^{4+}_{0.033})_{\Sigma14.021}O_{32}$ [($H_{2}O)_{3.767}$ Cl_{2.234})_{\Sci}. In the Raman spectra of chlorkyuygenite the following characteristic main bands are distinguished: 202, 321, 511, 705, 776 and 881 cm⁻¹. A broad band with two maxima near 3400 and 3200 cm⁻¹ is observed in the OH region and it is related to H₂O in the structural cages of chlorkyuygenite. The molecular water is completely released from the mineral structure at about 550°C. Chlorkyuygenit

Key-words: chlorkyuygenite; new mineral; mayenite supergroup; crystal structure; Raman; skarn; xenolith; Caucasus; Russia.

Introduction

Chlorkyuygenite, initially named as "mayenite-Cl", was described in 2009 from large altered xenoliths in ignimbrites of the Upper Chegem Caldera, Northern Caucasus, Kabardino-Balkaria, Russia (Galuskin *et al.*, 2009). The composition of the mineral, $Ca_{12}Al_{14}O_{32}Cl_2$ as determined by electron-microprobe analyses, was characterized by low

analytical totals (~96 wt. %). For this reason we supposed that "mayenite-Cl" contains about 3 H₂O pfu (Galuskin *et al.*, 2009). The small crystal size was the reason of protracted search of suitable crystals for structural investigation. Only in 2012 did we manage to collect structural data for this mineral. This led to the approval of chlorkyuygenite (IMA2012-046) with the end-member crystal-chemical formula Ca₁₂Al₁₄O₃₂[(H₂O)₄Cl₂] by the Commission on New Minerals, Nomenclature and Classification, International Mineralogical Association (CNMNC IMA) under the name "kyuygenite" (Galuskin *et al.*, 2012a).

This paper, which is the second of a series of four (parts I-IV) on mayenite supergroup minerals, defines and describes the properties of the new mineral chlorkyuygenite. The mineral belongs to the mayenite group with the common crystal-chemical formula $X_{12}T_{14}O_{32}[W_6]$ and is isostructural with chlormayenite (Hentschel, 1964; Galuskin *et al.*, 2012b), but differing in that the structural cages of chlorkyuygenite are filled with H₂O as well as Cl.

In the first paper of this series we present a recommended nomenclature for the mayenite supergroup, and also redefine mayenite and discredit brearleyite (Galuskin *et al.*, 2015a). In the third paper descriptions of the two new minerals fluormayenite and fluorkyuygenite from holotype specimens collected at the Jabel Harmun, Judean Mts., Palestinian Autonomy and from the Hatrurim Basin, Negev Desert, Israel, respectively, are given (Galuskin *et al.*, 2015b), whereas in the fourth paper we present new X-ray singlecrystal structure data for eltyubyuite (Gfeller *et al.*, 2015).

The original name of chlorkyuygenite (kyuygenite) was given for the locality situated close to the Kyuygen-Kaya Mountain. This mountain is at the northern part of the Upper Chegem caldera, reaching a height of 3743 m above sea level. The name Kyuygen-Kaya is translated from the Balkarian as "burnt mountain top", thus also reflecting the conditions of chlorkyuygenite formation in pyrometamorphic rocks. The prefix ,,chlor" reflects the composition of the mineral. Type material is deposited in the mineralogicollections of the Naturhistorisches cal Museum, Bernastrasse 15, CH-3005 Bern, Switzerland under the registration number NMBE 41538 and in the Fersman Mineralogical Museum in Moscow, Russia, with the number 3731/1 (this specimen is also the holotype for chegemite).

Methods of investigation

Crystal morphology and chemical composition of chlorkyuygenite and associated minerals were examined using an optical microscope, an analytical scanning electron microscope Philips XL30 ESEM/EDAX (Faculty of Earth Sciences, University of Silesia) and an electron microprobe CAMECA SX100 (Institute of Geochemistry, Mineralogy and Petrology, University of Warsaw). Electron probe microanalyses (EPMA) of chlorkyuygenite were performed at 15 kV and 20 nA using the following lines and standards: wollastonite – CaK α , SiK α ; periclase – MgK α ; orthoclase – AlK α ; Fe₂O₃ – FeK α ; YAG – YL α ; rutile – TiK α ; ClK α – tugtupite.

Single-crystal X-ray studies of chlorkuygenite from Upper Chegem caldera were carried out using a SuperNova Dual diffractometer with a mirror monochromator (CuK α = 1.54184 Å) and Atlas CCD detector (Aligent Technologies) at the Institute of Physics, University of Silesia, Poland. The structure was solved by direct methods, with subsequent analyses of difference-Fourier maps, and refined with neutral atom scattering factors using SHELX97 (Sheldrick, 2008). The occupancy of the *W* site was refined with Cl and O (resembling H_2O) scattering factors assuming full occupancy. The Al, Fe occupancy at *T1* was also refined.

Reflectance infrared spectra were measured using a Bio-Rad FTS-6000 spectrophotometer equipped with a Bio-Rad UMA-500 infrared microscope (Institute of Physics, University of Silesia, Poland). The microscope has its own 250×250 mm mercury cadmium telluride detector cooled to 196° C using liquid nitrogen. Spectra were obtained in the range 6000–700 cm⁻¹ with a resolution of 4 cm⁻¹. They were recorded by accumulating 256 scans and a gold covered microscope slide was used to obtain the background. Reflection spectra were converted to standard absorption spectra using Fourier and Kramers-Krönig transformations.

The Raman spectra of chlorkyuygenite were recorded using a WITec confocal CRM alpha 300 Raman microscope (Institute of Physics, University of Silesia, Poland) equipped with an air-cooled solid-state laser operating at 532 nm and a CCD detector which was cooled to -58° C. The laser was coupled to the microscope via a single-mode optical fibre with a diameter of 50 µm. The scattered radiation was focused onto a multi-mode fibre and a monochromator. A dry Olympus MPLAN (50x/0.76NA) objective was used. The integration time for a single spectrum was 10 s. The spectra were collected in the range between $4000-120 \text{ cm}^{-1}$ with the spectral resolution of 3 cm^{-1} . The monochromator of the spectrometer was calibrated using the Raman scattering line produced by a silicon plate (520.7 cm^{-1}) . Temperature Raman spectra were collected with the use of THMS600 heating stage (Linkam Scientific Instruments) with the temperature accuracy of $\pm 10^{\circ}$ C/min.

Mineral association and description of chlorkyuygenite

Chlorkyuygenite was found in the Ca-humite zone of the largest skarn carbonate–silicate xenolith no. 1 (>20 m in diameter) in ignimbrites of the Upper Chegem Caldera, Northern Caucasus, Kabardino-Balkaria, Russia. A geological overview of the Upper Chegem Caldera and a detailed description of the zonal structure of xenolith no. 1 are given by Gazeev *et al.* (2006) and Galuskin *et al.* (2009). In the unique xenoliths of the Upper Chegem Caldera more than 20 new minerals were discovered during 2006–2012. Among them five Ca-humite minerals, six minerals of the garnet supergroup, two of the perovskite group, two of the mayenite supergroup and others (Galuskin *et al.*, 2013).

Chlorkyuygenite is a typical accessory mineral of the Cahumite zones, which are located between the spurrite and larnite zones (Galuskin *et al.*, 2009). Ca-humite zones are assumed to have been formed as a result of fluorine metasomatism of the primary spurrite and galuskinite zones of the skarn. Spurrite, $Ca_5(SiO_4)_2CO_3$, was replaced by minerals of the reinhardbraunsite—kumtyubeite series, $Ca_5(SiO_4)_2$ [(OH),F]₂). Galuskinite, $Ca_7(SiO_4)_3CO_3$, was replaced by minerals of the chegemite–fluorchegemite series, Ca₇(SiO₄)₃[(OH),F]₂ (Galuskin *et al.*, 2012c). All new Cahumite minerals were found for the first time in xenolith no.1. Chlorkyuygenite was only observed in reinhardbraunsite–kumtyubeite and chegemite–fluorchegemite zones. In the larnite zone, containing also Ca-humite minerals of the edgrewite–hydroxyledgrewite series, Ca₉(SiO₄)₃[F,(OH)]₂, only minerals of the wadalite group are present (Galuskin *et al.*, 2012c, 2013). Rare grains of chlorkyuygenite were also detected in the chegemite zone of xenolith no. 9 (see geological scheme in Galuskin *et al.*, 2009). Xenoliths of the Upper Chegem Caldera are the second locality for galuskinite, which was first described from skarn xenoliths of the Birkhin Massif, Baikal (Lazic *et al.*, 2011, 2012).

Rounded grains and well developed crystals of chlorkyuy-genite, 20–30 μm in size but occasionally reaching 50 μm , as

well as aggregates of chlorkyuygenite grains up to 100-150 µm form inclusions in chegemite, reinhardbraunsite and srebrodolskite (Fig. 1A-C). The form of chlorkyuygenite crystals corresponds to a tris-tetrahedron {211} (Fig. 1C). Chlorkyuygenite in Ca-humite zones forms outer rims on wadalite crystals (Fig. 1D). In addition to Ca-humite minerals of the chegemite-fluorchegemite and reinhardbraunsite-kumtyubeite series, the following hightemperature skarn minerals are associated with chlorkyuygenite: rondorfite, fluor- and hydroxylellestadite, lakargiite, perovskite, kerimasite, elbrusite, and low-temperature secondary minerals such as minerals of the ettringite group, hydrocalumite, bultfonteinite and minerals of the katoite-grossular series. Larnite, spurrite and galuskinite are noted as relics in Ca-humites (Fig. 1A).



Fig. 1. Backscattered electron images of chlorkyuygenite in altered xenolith of the Upper Chegem Caldera, Northern Caucasus. A Rounded crystal of chlorkyuygenite and their aggregates in chegemite with larnite, fluorellestadite, spurrite and galuskinite inclusions; **B** relatively big crystals of chlorkyuygenite in chegemite and smaller crystals in srebrodolskite; white rectangle encloses area enlarged in Figure 1 **C**; **C** tristetrahedron of chlorkyuygenite; **D** zonal crystals with wadalite core and chlorkyuygenite rim; **E** wadalite crystals from calcite-spurrite zone with epitactic growths of chlorkyuygenite; **F** chlorkyuygenite relics in brucite marble. Chkg - chlorkyuygenite, Chg - chegemite, Lar - larnite, Hcl - hydrocalumite, Spu - spurrite, Gal - galuskinite, Etr - ettringite, Ell - fluorellestadite, Srb - srebrodolskite, Wad - wadalite, Kat - katoite, Rhb - renhardbrausite, Rnd - rondorfite, Cal - calcite, Brc - brucite.

In the spurrite zone wadalite occurs as abundant finegrained aggregates. In a few places, tetrahedral wadalite crystals with epitactic chlorkyuygenite are observed in calcite between spurrite grains (Fig. 1E). Such crystals are altered to katoite–grossular with formation of pseudomorphs resembling the known tetrahedral "achtarandite" pseudomorphs, which more probably formed after mayenite-like minerals (Lyachovich, 1954; Galuskin *et al.*, 1995; Galuskina *et al.*, 1998, 2001; Galuskin, 2005).

In brucite marble within the central part of xenolith no. 1, rounded grains of chlorkyuygenite, which are intensively altered to katoite, are noted occasionally (Fig. 1F).

The holotype specimen of chlorkyuygenite from the chegemite zone is characterized by relatively constant composition corresponding to the crystal-chemical formula $Ca_{11.979}(Al_{12.986}Fe^{3+}_{0.823}Si_{0.179}Ti^{4+}_{0.033})_{\Sigma14.021}O_{32}$ [(H₂O)_{3.767}Cl_{2.234}]_{$\Sigma6$}, which can be simplified to $Ca_{12}(Al_{13}Fe^{3+}_{0.8}Si_{0.2})_{\Sigma14}O_{32}[(H_2O)_{3.8}Cl_{2.2}]$. In regard to end-members, it consists of 95 % $Ca_{12}Al_{14}O_{32}[(H_2O)_4Cl_2]$ (chlorkyuygenite) and 5 % $Ca_{12}(Al_{10}Si_4)_{\Sigma14}O_{32}[Cl_6]$ (wadalite) (Table 1, analysis 1). Wadalite in the crystal cores has the composition: $Ca_{12.026}(Al_{9.820}Fe^{3+}_{0.688}Si_{3.002}Mg_{0.363}Ti^{4+}_{0.101})_{\Sigma13.974}O_{32}[Cl_{4.612}(H_2O)_{1.287}(OH)_{0.101}]_{\Sigma6}$ (Table 1, analysis 2) and it is characterized by relatively

high Mg and Ti contents. The composition of this wadalite contains a chlorkyuygenite $(Ca_{12}Al_{14}O_{32}[(H_2O)_4Cl_2])$ component and the theoretical end-member $Ca_{12}Mg_5Si_9O_{32}Cl_6$ (Table 1, analysis 2).

Chlorkyuygenite is colourless, occasionally with a greenish or yellowish tint, and its streak is white. It is transparent with strong vitreous lustre, and isotropic, n = 1.672(1) (589 nm). The microhardness VHN load 50 g of chlorkyuygenite was measured together with that of the chlormayenite holotype specimen from the Eifel provided by the Mineralogical Museum, (kindly University of Cologne). A slight decrease in microhardness is noted for chlorkyuygenite (632(37) kg mm⁻², n = 11) compared to chlormavenite (764(8) kg mm⁻², n = 10). The Mohs hardness of kyuygenite is $5-5\frac{1}{2}$, that of chlormayenite 5¹/₂–6. Fracture of chlorkyuygenite is irregular, conchoidal; cleavage and parting are not observed. The calculated density based on the empirical formula of the holotype specimen is 2.941 g cm⁻³. The calculated Gladstone-Dale's compatibility factor $1 - (K_p/K_c) =$ -0.016 is superior.

Minerals of the mayenite supergroup in calcite–spurrite rocks are represented by chlorkyuygenite–wadalite solidsolution. Tris-tetrahedral crystals found in calcite (Fig. 1E)

Ta	bl	e	1.	C	hemi	ical	compos	sitio	ı of	ch	lor	kyu	ygeni	ite	and	wac	lal	ite.
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		С	a-humite zone		Spur	rite zone	Marble	
		1		2	3	4	5	
	mean 27	s.d.	range	mean 4	mean 3	mean 2	mean 3	
SiO ₂ wt.%	0.70	0.1	0.53-0.92	11.46	5.01	9.36	0.79	
TiO ₂	0.17	0.03	0.10-0.24	0.51	0.96	1.38	0.18	
Al_2O_3	43.00	0.5	42.1-44.1	31.80	36.10	27.80	45.20	
Fe ₂ O ₃	4.27	0.3	3.86-4.81	3.49	5.74	9.85	0.37	
Y_2O_3	< 0.08			< 0.08	< 0.08	< 0.08	1.94	
MgO	< 0.03			0.93	0.07	0.74	< 0.03	
CaO	43.70	0.3	43.1-44.2	42.90	42.10	41.70	42.40	
Cl	5.13	0.1	4.88-5.66	10.39	7.78	9.74	5.80	
H ₂ O	4.42			1.54	2.81	1.72	4.04	
$-\mathbf{O} = \mathbf{Cl}$	1.16			2.34	1.76	2.20	1.31	
Total	100.23			100.67	98.82	100.09	99.41	
Ca	11.989			12.035	11.991	12.056	11.702	
Y							0.266	
X	11.989			12.035	11.991	12.056	11.968	
Al	12.976			9.813	11.310	8.841	13.722	
Si	0.179			3.001	1.332	2.526	0.203	
Fe ³⁺	0.823			0.688	1.148	2.000	0.072	
Ti ⁴⁺	0.033			0.100	0.192	0.280	0.035	
Mg				0.363	0.028	0.298	0.000	
Z	14.011			13.965	14.009	13.944	14.032	
Cl	2.226			4.610	3.505	4.454	2.532	
OH**				0.093				
H_2O^*	3.774			1.297	2.495	1.546	3.468	
W	6.000			6.000	6.000	6.000	6.000	
Chlorkyuygenite	95 %			32 %	62 %	38 %	86 %	
Wadalite	5 %			60 %	38 %	57 %	6 %	
$Ca_{12}Mg_5R^{4+}{}_9O_{32}Cl_6$				8 %		6 %		
$Y_4Ca_8R^{3+}{}_{14}O_{32}Cl_6$							8 %	
$R^{3+} = Al, Fe^{3+} (Al >>$	> Fe^{3+}); $R^{4+} = Si$, Ti ⁴⁺ (Si >	> Ti ⁴⁺); Cl = Cl, 0	OH (Cl >> OH)				

 $\label{eq:Footnote: H2O wt.\% calculated from H2O* pfu [calculated as 6-(Cl+OH)] and OH** pfu (calculated on charge balance).$

are represented by wadalite, $Ca_{12.053}(Al_{8.847}Fe^{3+}_{1.999}Si_{2.524}Ti^{4+}_{0.280}Mg_{0.297})_{\Sigma_{13.947}}O_{32}[(H_2O)_{1.540}Cl_{4.460}]_{\Sigma_6}$, in which the chlorkyuygenite end-member content is 38 % (Table 1, analysis 4). Chlorkyuygenite with the composition $Ca_{11.990}(Al_{11.307}Fe^{3+}_{1.149}Si_{1.332}Ti^{4+}_{0.193}Mg_{0.029})_{\Sigma_{14.010}}O_{32}$ [(H₂O)_{2.484} Cl_{3.516}]_{\Sigma_6} growing epitactically on wadalite contains 38 % of wadalite end-member (Table 1, analysis 3).

Chlorkyuygenite from the central brucite marble of xenolith no. 1 shows a relatively high Y content: $(Ca_{11.696} Y_{0.266})_{\Sigma11.962}(Al_{13.724}Fe^{3+}_{0.072}Si_{0.203}Ti^{4+}_{0.035})_{\Sigma14.034}O_{32}$ [(H₂O)_{3.473}Cl_{2.530}]_{$\Sigma6$}; in this case Y substitutes in the chlorkyuygenite structure according to the theoretical end-member (Y₄Ca₈)Al₁₄O₃₂[Cl₆] (Table 1, analysis 5).

Structure and molecular spectroscopy data of chlorkyuygenite

The crystal structure of chlorkyuygenite was refined in space group $I\overline{4}3d$ (a = 12.0285(1) Å, V = 1740.34(3) Å³) using single-crystal XRD data collected on a crystal $30 \times 30 \times 20 \ \mu\text{m}^3$ in size (Tables 2–5). The chlorkyuygenite structure corresponds to the one of chlormayenite Ca₁₂Al₁₄O₃₂[\Box_4 Cl₂] ($I\overline{4}3d$, Z = 2, a = 12.0320(4) Å, V = 1741.86(1) Å³; Galuskin *et al.*, 2012b), from which it is distinguished by H₂O molecules filling the empty structural cages (W sites). The tetrahedral framework of chlorkyuygenite {Al₁₄O₃₂}^{22–} encloses six structural cages, each occupied by two Ca²⁺, leading to an excess of positive charges of 2+ which is balanced by incorporation of Cl⁻ at two out of six W sites. Chlorine is linearly coordinated by two Ca cations (Fig. 2). Site scattering at W is compatible with

Table 2. Parameters for X-ray data collection and crystal-structure refinement of chlorkyuygenite.

Unit cell dimensions (Å)	12.0285(1)
Volume $(Å^3)$	1740.34(3)
Space group	$I\overline{4}3d$
Ζ	2
Crystal size (mm)	$0.03 \times 0.03 \times 0.02$
Diffractometer	SuperNova
X-ray radiation	Mo <i>K</i> α , $\lambda = 0.71073$ Å
Monochromator	graphite
Temperature	293 K
Max 20	52.74°
Index ranges	$-13 \le h \le 15$
	$-15 \le k \le 9$
	$-14 \le l \le 15$
No. of measured reflections	5312
No. of unique reflections	300
No. of parameters used in refinement	29
R _{int}	0.0227
R_{σ}	0.0078
$R1, I > 2\sigma(I)$	0.0116
R1, all data	0.0114
$wR2$ (on F^2)	0.0301
GooF	1.062
$\Delta \rho_{\min} \left(e \dot{A}^{-3} \right)$	-0.17 close to Al1
$\Delta \rho_{\rm max} \left(e \ {\rm \AA}^{-3} \right)$	0.17 close to Ca1

a random distribution of 2 Cl⁻ and 4 H₂O (Table 3, Fig. 2). The disordered character of Cl and H₂O within the cages did not allow for determination of the proton (H) sites.

It is not possible to distinguish Si and Al on the basis of electron density and the Si content is too low to be derived from the shortening of *T*-O bond lengths. An approximate Si content can be calculated on the basis of

Table 3. Atom coordinates and isotropic equivalents (Å²) of anisotropic atom displacement parameters of chlorkyuygenite.

Site	Species	x	у	Z	$U_{ m eq}$	Occ.
Ca <i>l</i>	Ca	0.14823(3)	0	0.25	0.01311(15)	1
T1	Al	0.26765(3)	0.26765(3)	0.26765(3)	0.0077(2)	0.903(3)
	Fe	0.26765(3)	0.26765(3)	0.26765(3)	0.0077(2)	0.097(3)
<i>T2</i>	Al	0.125	0.5	0.25	0.0074(2)	1
01	0	0.30513(9)	0.21402(9)	0.40002(9)	0.0203(3)	1
02	0	0.18464(8)	0.18464(8)	0.18464(8)	0.0147(4)	1
W	Cl	0.375	0	0.25	0.0298(6)	0.397(8)
	O (H ₂ O)	0.375	0	0.25	0.0298(6)	0.603(8)

Table 4. Anisotropic displacement parameters (Å²) for chlorkyuygenite.

Site	U_{11}	<i>U</i> ₂₂	<i>U</i> ₃₃	U_{23}	U_{13}	U_{12}
Cal	0.0140(2)	0.0156(2)	0.0098(2)	0.00203(17)	0.000	0.000
Tl	0.0077(2)	0.0077(2)	0.0077(2)	0.00009(13)	0.00009(13)	0.00009(13)
T2	0.0064(3)	0.0079(3)	0.0079(3)	0.000	0.000	0.000
01	0.0167(6)	0.0242(6)	0.0199(6)	0.0138(4)	-0.0067(4)	-0.0096(4)
02	0.0147(4)	0.0147(4)	0.0147(4)	-0.0018(4)	-0.0018(4)	-0.0018(4)
W	0.0158(8)	0.0368(8)	0.0368(8)	0.000	0.000	0.000

Table 5. Selected interatomic distances (Å) in chlorkyuygenite.

Ca <i>l</i>	O1	$2.3837(10) \times 2$
	O2	2.3964(8) ×2
	O1	$2.6069(13) \times 2$
	W	2.7277(4)
TI	O2	1.7294(18)
	O1	$1.7761(11) \times 3$
<i>T</i> 2	O1	$1.7414(9) \times 4$

charge balance: $Ca_{12}(Al_{12.86}Fe_{0.78}Si_{0.38})_{\Sigma 14}O_{32}$ [(H₂O)_{3.62} Cl_{2.38}]. This formula is close to the simplified formula $Ca_{12}(Al_{13}Fe^{3+}_{0.8}Si_{0.2})_{\Sigma 14}O_{32}$ [(H₂O)_{3.8}Cl_{2.2}], which has been obtained from our EPMA data.

Because chlorkyuygenite occurs only in small amounts, X-ray powder diffraction data have been calculated from the refined crystal structure (Table 6).

The following characteristic main bands have been identified in the Raman spectra of chlorkyuygenite



Fig. 2. A Chlorkyuygenite structure: an overall view, Al1 (light-blue) and Al2 (blue) tetrahedra and central W site (green spheres) coordinated by two Ca (brown spheres) are shown. **B** Ball model of cage in chlorkyuygenite structure, \sim 1/3 of W sites is occupied by Cl (green sphere) atoms and \sim 2/3–by H₂O (not shown), axis $\overline{4}$ is parallel to Ca-Cl-Ca vector.

Table 6. Calculated powder diffraction data for chlorkyuygenite (Cu $K\alpha_1 = 1.540598$, Debye-Scherrer geometry, I > 1.00). Data were calculated using PowderCell 2.4 (Kraus & Nolze, 1996).

h	k	l	$d_{ m hkl}$	I _{rel.}	h	k	l	$d_{ m hkl}$	I _{rel.}
2	1	1	4.9106	31	6	5	1	1.5276	3
2	2	0	4.2527	2	7	3	2		2
3	1	0	3.8038	1	8	0	0	1.5036	6
3	2	1	3.2148	15	7	4	1	1.4806	7
4	0	0	3.0071	38	7	5	0	1.3983	4
4	2	0	2.6897	100	7	4	3		5
3	3	2	2.5645	8	7	5	2	1.3620	3
4	2	2	2.4553	46	8	4	0	1.3448	5
5	1	0	2.3590	11	9	1	0	1.3283	2
4	3	1		2	8	4	2	1.3124	8
5	2	1	2.1961	21	6	5	5	1.2971	1
5	3	0	2.0629	4	6	6	4	1.2822	4
6	1	1	1.9513	1	9	3	0	1.2679	1
5	3	2		10	7	5	4		2
5	4	1	1.8560	1	8	5	3	1.2151	1
6	3	1	1.7735	3	9	4	1		3
4	4	4	1.7362	10	10	2	0	1.1795	2
7	1	0	1.7011	5	7	6	5	1.1469	1
5	4	3		1	8	7	1	1.1266	1
6	4	0	1.6681	26	10	4	0	1.1168	4
5	5	2	1.6369	5	8	6	4		4
6	3	3		2	10	3	3	1.1073	1
6	4	2	1.6074	30	10	4	2	1.0981	4



Fig. 3. Raman spectrum of chlorkyuygenite.

(cm⁻¹): 202 (O–Ca–O vibration), 321 (v_2 Al–O), 511 (v_4 Al–O), 705, 776 (v_1 Al–O) and 881(v_3 Al–O) (Fig. 3). These bands are also the main bands in Raman spectra of synthetic mayenite and chlorinated mayenite, as well as in the spectra of «brearleyite» and chlormayenite (Sun *et al.*, 2009; Ma *et al.*, 2011; Tolkacheva *et al.*, 2011; Galuskin *et al.*, 2012b). A broad band composed of two maxima near 3400 and 3200 cm⁻¹ is observed in the OH region. This band is related to H–O-stretching vibrations in H₂O [see, for example, Obukhovsky *et al.* (2011)].

A FTIR reflection spectrum on few small chlorkyuygenite crystals was also recorded (Fig. 4). The main bands located at 780 cm⁻¹ (v₁ Al–O) and 847 cm⁻¹ (v₃ Al–O) are observed in the same position as in the spectrum of synthetic mayenite (Tolkacheva *et al.*, 2011). Weak bands in the region of H₂O-bending and OH-stretching vibrations are also noted (Fig. 4).

We collected temperature-dependent Raman spectra on chlorkyuygente grains (about 20 μ m in size) enclosed in chegemite (Fig. 5). The strongly broadened 2750–3600 cm⁻¹ band due to stretching vibrations of H₂O at room temperature changes at 400°C to a spectrum with one prominent maximum near 3400 cm⁻¹. At ~550°C water is completely released from the chlorkyuygenite structure. A contribution of chegemite surrounding chlorkyuygenite



Fig. 4. FTIR reflection spectrum of chlorkyuygenite, transformed by the Kramers-Krönig method. In inset fragment of the spectrum marked by grey.



Fig. 5. Raman spectra of chlorkyuygenite obtained at different temperatures. At the bottom of figure the chegemite spectrum is shown, bands of which are observed in chlorkyuygenite spectra (stars).

could not be avoided in the collected spectra. Bands at about 820 cm⁻¹ (stretching vibration of Si–O) and 3485 and 3560 cm⁻¹ (stretching vibrations of O–H) are characteristic of chegemite. These bands do not change up to 600°C, which is the maximum temperature of this experiment.

Discussion

Originally it was assumed that "zeolitic" water may be trapped in the structural cages of synthetic mayenite, which is released upon heat treatment without influencing the tetrahedral framework structure (Jeevaratnam et al., 1962). Subsequent investigations, however, showed that H₂O reacts with O^{2} to form hydroxylated mayenite $Ca_{12}Al_{14}O_{32}[\Box_4(OH)_2]$ (Bartl & Scheller, 1970; Havashi et al., 2005). Chlorkyuygenite Ca₁₂Al₁₄O₃₂[(H₂O)₄Cl₂] and fluorkyuygenite $Ca_{12}Al_{14}O_{32}[(H_2O)_4F_2]$ (Galuskin *et al.*, 2015b) are the first known phases with "zeolitic" water in the mayenite group.

Bands on chlorkyuygenite Raman spectra in the 2700–3600 cm⁻¹ region indicate H₂O (Fig. 3). Bands in FTIR spectra above 1600 cm⁻¹ characteristic of H₂O-bending vibrations are very weak. Intensities of bands from H-O-stretching vibrations (3000–3800 cm⁻¹) are poorly defined and very low (Fig. 4).

Spectroscopic studies indicate that the total EPMA analytical deficiency is associated with the presence of H_2O molecules, which occupy the *W* sites in structural cages (Table 1). This hypothesis is corroborated by structural data showing that the *W* site is fully occupied by 3.62(2) O + 2.38(2) Cl. This result is very close to the data obtained by calculation of the H_2O content as (6 – Cl): 3.77 $H_2O + 2.23$ Cl (Table 1, analysis 1).

Structural study of synthetic $Ca_{12}Al_{14}O_{32}[\Box_4(OH)_2]$, fluorkyuygenite $Ca_{12}Al_{14}O_{32}[(H_2O)_4F_2]$, fluormayenite $Ca_{12}Al_{14}O_{32}[\Box_4F_2]$ and heated chlormayenite $Ca_{12}Al_{14}O_{32}[\Box_4F_2]$ shows that the presence of



Fig. 6. Diagram of minerals belonging to the mayenite supergroup. 1–compositional trends; 2–holotype chlorkyuygenite, 3–mayenite supergroup minerals from Upper Chegem Caldera, 4–endmembers of known minerals of the mayenite supergroup.

a small anion such as OH^- or F^- at the *W* site is accompanied by a shift of adjacent Ca cations. In the case of vacancies or Cl^- at *W*, such a Ca displacement is not observed (Hayashi *et al.*, 2008, 2014; Galuskin *et al.*, 2012b, 2015b and our unpublished data). H₂O at the *W* site in chlorkyuygenite (Ca₁₂Al₁₄O₃₂[(H₂O)₄Cl₂]) results in a slight shift of Ca towards *W* compared to empty cages in clormayenite (Galuskin *et al.*, 2012b). The Ca – Ca separation in chlormayenite amounts to 5.71 Å, whereas chlorkyuygenite shows a Ca – Ca distance of 5.46 Å.

Donor-acceptor distances between H₂O and O1 and O2 on the cage walls are longer than 3.25 Å in chlorkyuygenite. This may indicate very weak hydrogen bonds (Libowitzky, 1999). Changes of the shape of Raman bands in the region of 3000–4000 cm⁻¹ (Fig. 5) between 27 and 600°C indicate mobility of water molecules leading to dehydration of the structure of chlorkyuygenite.

In the Si–Fe–Al classification diagram the points representing chlorkyuygenite and chlormayenite merge in the same field (Fig. 6). There is problem in distinguishing chlorkyuygenite and chlormayenite on the basis of EPMA data pointing to intermediate compositions, especially phases with a high content of the $Ca_{12}Al_{14}O_{30}(OH)_6[\Box]_6$ end-member (Galuskin *et al.*, 2015b). Chlorkyuygenite that is close to ideal composition can be readily identified.

As shown by temperature-dependent Raman spectroscopy, above 550° C zeolitic H₂O is completely released from chlorkyuygenite (Fig. 5). This temperature is considerably below the formation temperature of primary skarn minerals in Upper Chegem xenoliths. Chegemite, larnite, spurrite, galuskinite, lakargiite, and srebrodolskite, associated with chlorkyuygenite, were formed between 600 and 900°C (Galuskin *et al.*, 2009, 2012c). We assume that chlorkyuygenite initially crystallized as chlormayenite, which later was altered under influence of volcanic gases containing water vapour according to the reaction $Ca_{12}Al_{14}O_{32}[\Box_4Cl_2] + 4H_2O \rightarrow Ca_{12}Al_{14}O_{32}[(H_2O)_4Cl_2].$

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