# Chegemite Ca<sub>7</sub>(SiO<sub>4</sub>)<sub>3</sub>(OH)<sub>2</sub> – a new humite-group calcium mineral from the Northern Caucasus, Kabardino-Balkaria, Russia

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Abstract: The new mineral chegemite Ca<sub>7</sub>(SiO<sub>4</sub>)<sub>3</sub>(OH)<sub>2</sub> (*Pbnm*, *Z* = 4)1, *a* = 5.0696(1), *b* = 11.3955(1), *c* = 23.5571(3) Å; *V* = 1360.91(4) Å<sup>3</sup> – the calcium and hydroxyl analogue of humite – was discovered as a rock-forming mineral in high-temperature skarns in calcareous xenoliths in ignimbrites of the Upper Chegem volcanic structure, Northern Caucasus, Kabardino-Balkaria, Russia. The chegemite forms granular aggregates with grain sizes up to 5 mm and is associated with various high-temperature minerals: larnite, spurite, rondorfite, reinhardbraunsite, wadalite, lakargiite, and srebrodolskite, corresponding to the sanidinite metamorphic facies. The empirical formula of the holotype chegemite (mean of 68 analyses) is Ca<sub>7</sub>(Si<sub>0.997</sub>Ti<sub>0.003</sub>O<sub>4</sub>)<sub>3</sub>(OH)<sub>1.48</sub>F<sub>0.52</sub>. Chegemite is characterized by the following optical properties:  $2V_Z = -80(8)^\circ$ ,  $\alpha = 1.621(2)$ ,  $\beta = 1.626(3)$ ,  $\gamma = 1.630(2)$ ;  $\Delta = 0.009$ ; density  $D_{calc} = 2.892$  g/cm<sup>3</sup>. The crystal structure, including hydrogen positions, has been refined from single-crystal MoK $\alpha$  X-ray diffraction data to R = 2.2 %. Octahedral Ca–O distances are similar to those of  $\gamma$ -Ca<sub>2</sub>SiO<sub>4</sub> (calcio-olivine). As is characteristic of OH-dominant humite-group minerals, two disordered H positions could be resolved. The main bands in the FTIR-spectra of chegemite are at 3550, 3542, 3475, 927, 906, 865, 820, 800, 756, 705, 653, 561, 519 and 437 cm<sup>-1</sup>. Those in non-polarized Raman spectra are at 389, 403, 526, 818, 923.5, 3478, 3551 and 3563 cm<sup>-1</sup>. The X-ray diffraction powder-pattern (FeK $\alpha$ -radiation) shows the strongest lines {d [Å](*I*<sub>obs</sub>)} at: 1.907(10), 2.993(8), 2.700(8), 3.015(7), 2.720(7), 2.834(6), 3.639(5), and 3.040(5).

Key-words: chegemite, new mineral, humite-group, crystal structure, CSH, skarn, xenolith, Caucasus, Russia.

### 1. Introduction

Two new calcium minerals of the humite group have been approved by the *CNMNC IMA* at the end of 2008: chegemite  $Ca_7(SiO_4)_3(OH)_2$  (IMA2008–38) – the calcium and hydroxyl analogue of humite, and  $Ca_5(SiO_4)_2F_2$  (IMA2008–45) – the fluorine analogue of reinhardbraunsite, with the chondrodite structure-type (Galuskina *et al.*, in preparation). Both minerals were discovered in skarn xenoliths in ignimbrites of the Upper Chegem volcanic structure in the Northern Caucasus, Kabardino-Balkaria, Russia.

The humite group includes minerals with the common crystal-chemical formula  $nA_2SiO_4 \times A(F,OH)_2$ , where A = Mg,  $Fe^{2+}$ ,  $Mn^{2+}$ , Zn, Ca ... and n = 1, 2, 3, 4

(Jones *et al.*, 1969; Ribbe & Gibbs, 1971). Widespread fluorine-dominant magnesium minerals of this group are represented by the series norbergite Mg<sub>3</sub>(SiO<sub>4</sub>)(F,OH)<sub>2</sub> (n = 1), chondrodite Mg<sub>5</sub>(SiO<sub>4</sub>)<sub>2</sub>(F,OH)<sub>2</sub> (n = 2), humite Mg<sub>7</sub>(SiO<sub>4</sub>)<sub>3</sub>(F,OH)<sub>2</sub> (n = 3) and clinohumite Mg<sub>9</sub>(SiO<sub>4</sub>)<sub>4</sub>(F,OH)<sub>2</sub> (n = 4). The natural hydroxyl analogue of clinohumite is known as hydroxylclinohumite (Gekimyants *et al.*, 1999). The hydroxyl analogue of humite has been synthesized (Wunder *et al.*, 1995) but has not yet been defined as a mineral species. Reinhardbraunsite Ca<sub>5</sub>(SiO<sub>4</sub>)<sub>2</sub>(OH)<sub>2</sub> discovered in silicate-calcareous xenoliths from volcanites in the Eifel, Germany (Hamm & Hentschel, 1983; Kirfel *et al.*, 1983), is the only Ca-member of the humite group known to-date. A synthetic analogue of reinhardbraunsite, often called "calcio-chondrodite" (cement notation  $C_5S_2H$ ), is a component of cement materials (Hu *et al.*, 2006; Yanagisawa *et al.*, 2006; Richardson, 2008). Chegemite has no synthetic analogue. Monoclinic  $Mn_7(SiO_4)_3(OH)_2$  leucophoenicite has the same formula as orthorhombic manganhumite (and the same stoichiometry as chegemite) but the structures are different and, therefore, leucophoenicite (*e.g.*, Welch *et al.*, 2002) and manganhumite (*e.g.*, Francis & Ribbe, 1978) are considered to be dimorphs.

This paper presents a description of the new mineral chegemite and also reports on the rare minerals associated with it. The name chegemite derives from the Chegem River where the new mineral was discovered in the head-water tributary-area. The holotype sample of chegemite is deposited in the Fersman Mineralogical Museum in Moscow, Russia, with the number 3731/1 and the single grain used for structural investigation is deposited in the Museum of Natural History in Bern, Switzerland, with the number NMBE 39571.

#### 2. Methods of investigation

The morphology and composition of chegemite and associated minerals were investigated with an analytical scanning electron-microscope Philips XL30 ESEM/EDAX and a microprobe analyzer CAMECA SX100. The compositions of silicate minerals were measured at 15 kV and 10–20 nA. Perovskite-group minerals were examined at 15 kV and 40-50 nA and minerals of the ellestadite group at 10 kV and 40 nA with a widened beam up to 30 um. Natural and synthetic standards were employed. The following lines and standards were used for the analyses of the humite-group minerals: Ti $K\alpha$  – rutile; Ca $K\alpha$ , Si $K\alpha$  – wollastonite, diopside; MgK $\alpha$  – diopside; PK $\alpha$  – apatite; NaK $\alpha$  – albite; FeK $\alpha$ - Fe<sub>2</sub>O<sub>3</sub>, and radite; MnK $\alpha$  - rhodonite; ClK $\alpha$  - tugtupite;  $FK\alpha$  – synthetic fluorphlogopite;  $CrK\alpha$  – synthetic  $Cr_2O_3$ ,  $SK\alpha$  – barite. Recommendations on fluorine measurements (Ottolini et al., 2000) of Mg-humites were taken into consideration. Corrections were calculated using the PAP procedures suggested by CAMECA.

Reflectance infrared spectra were measured using a Bio-Rad FTS-6000 spectrometer equipped with an infrared microscope of the Bio-Rad UMA-500 type. The microscope had its own  $250 \times 250$  mm mercury cadmium telluride detector (MTC) cooled to 77 K using liquid nitrogen. The spectra were obtained in the range 6000- $700 \text{ cm}^{-1}$  with a resolution of 4 cm<sup>-1</sup>. The interferograms were recorded by accumulating 512 scans and a goldcovered microscope slide was used to obtain the background spectra. The infrared radiation reflected by a polished grain of chegemite  $(40 \times 160 \,\mu\text{m} \text{ on thin-section})$ was passed to the spectrometer. The reflection spectra were converted to standard absorption spectra using Fourier and Kramers-Krönig transformations. In addition, routine FTIR spectra of chegemite KBr pellets were collected using a Bio-Rad FTS-6000 spectrometer.

Raman spectra of chegemite crystals were recorded using a LabRam System spectrometer (Jobin-Yvon-Horiba) at room temperature. Argon-ion laser light of 514.5 nm was used to excite the spectra. The power at the sample was below 20 mW. To eliminate the Rayleigh line, the scattered light was passed through a holographic notch filter with a cut-off at 200 cm<sup>-1</sup>. The Raman spectra were recorded in 0° geometry in the range 100–4000 cm<sup>-1</sup> with a spectral resolution of  $3.5 \text{ cm}^{-1}$ . The collection time was 60 s and 4–10 scans were accumulated. The monochromator was calibrated with a silicon plate (520.7 cm<sup>-1</sup>).

An X-ray powder pattern of the chegemite was recorded using Philips: X'Pert PW 3710 and PRO MRD PW 3040/60 powder diffractometers (filtered FeK $\alpha$ -radiation, 45 kV, 30 mA, 0.01° step, 100–1000 s/point).

A single crystal of chegemite was mounted on a Bruker Apex II three-circle CCD diffractometer using graphite monochromated MoKa X-radiation for diffraction intensity data-collection. Preliminary lattice parameters and an orientation matrix were obtained from three sets of frames and refined during the integration of the intensity data. Diffraction data were collected with  $\omega$  scans at different  $\phi$ settings ( $\phi$ - $\omega$  scan) using the program SMART (Bruker, 1999). Data were processed using SAINT (Bruker, 1999). An empirical absorption correction using SADABS (Sheldrick, 1996) was applied. Reflection statistics and systematic absences were consistent with a space group of type Pbnm (No. 62) already known for humite. The standard setting of this space group is *Pnma* but, in accordance with refinements on humite (Ribbe & Gibbs, 1971), the *Pbnm* setting was preferred. In addition, we used the same atom-labelling scheme as Ribbe & Gibbs (1971). Structural refinement was performed using SHELXL-97 (Sheldrick, 1997). Scattering factors for neutral atoms were employed. Positions of the hydroxyl-group hydrogen atoms were derived from difference-Fourier syntheses. Subsequently, hydrogen positions were refined at a fixed value of  $U_{iso} = 0.05 \text{ Å}^2$  and O-H distances were restrained to 0.95(2) Å. Data collection and refinement details are summarized in Table 5.

### **3.** Occurrence, mineral association and results of chegemite investigations

Chegemite was discovered in 2007 in altered calcareoussilicate xenolith 1 (numbering of xenoliths after Gazeev *et al.*, 2006) in ignimbrites of the Upper Chegem volcanic structure, Northern Caucasus, Kabardino-Balkaria, Russia (Fig. 1). Xenolith 1, which extends more than 10 m in cross-section (geographical position:  $43.2^{\circ}$  N  $43.1^{\circ}$  E), is also the type locality for lakargiite CaZrO<sub>3</sub> (Galuskin *et al.*, 2008) and the new mineral Ca<sub>5</sub>(SiO<sub>4</sub>)<sub>2</sub>F<sub>2</sub> (Galuskina *et al.*, in preparation). Calcio-olivine was detected in xenolith 3 which is located a few metres away from xenolith 1 (Fig. 1). Calcio-olivine from this occurrence has also been accorded mineral status by *CNMNC IMA* (Gobechiya *et al.*, 2008;



Fig. 1. Geological map of the Upper Chegem volcanic structure (after Gazeev *et al.*, 2006, with simplifications). Inset map shows location of Kabardino-Balkaria. Legend: 1–5: Formations of different ages belonging to the volcanic structure basement. 1,2 – structural zone of the Greater Caucasus Mountain Range: 1 – crystalline schist and gneiss, 2 – granite gneiss; 3 – Permian conglomerate, sandstone and argillaceous slate; 4,5 – Jurassic terrigenous carbonaceous formations: 4 – argillite, slitstone and sandstone, 5 – limestone. 6–10: Neogene-Quaternary formations. 6 – rhyolite and rhyodacite ignimbrites, 7 – horizon of tuff and lavas in ignimbrites, 8 – granodiorite, 9 – glacial sediments of Mindel Glaciation, 10 – Post-Mindel Glaciation andesite lavas. 11 – Quaternary glacial, alluvial and proluvial sediments. 12 – xenolith localization and number, shown without scale; 13 – mountain peaks above 3000 m.

Zadov *et al.*, 2008). Geological descriptions of the area in the environs of the Lakargi and Vorlan peaks (Fig. 1) where the large (>1 m) sanidinite-facies carbonate xenoliths were discovered are provided by Gazeev *et al.* (2006) and Galuskin *et al.* (2008).

The central part of xenolith 1 (visible thickness 2–3 m) is composed of bluish-grey marble with relict banding. Dark gray massive spurite-calcite rocks are developed at the southern part of the xenolith. A few outcrops, 1–1.5 m in size, along the west and north-west contact are composed of white, yellowish, reddish rocks. Ca-minerals of the humite group, *i.e.* chegemite and/or reinhardbraunsite or  $Ca_5(SiO_4)_2F_2$  are prominent in these rocks. Small fragments of lightly coloured spurite rock, up to 50 cm in size, with pink spots of reinhardbraunsite and yellow egg-like segregations of rondorfite are considerably less common. Wadalite, rondorfite, hydroxylellestadite, and lakargiite are widespread in different rock types within xenolith 1. Perovskite, srebrodolskite and garnet of close to kimzeyite composition are rare constituents. Among secondary lowtemperature minerals, calcium hydrosilicates (hillebrandite, afwillite), minerals of the ettringite group, hydrocalumite, and hydrogarnets are more common.

The contact with the hosting ignimbrite is exposed on the eastern side of xenolith 1 where the rocks are weakly altered by secondary low-temperature processes. A cuspidine zone (1–2 cm thick) with rustumite and fine-grained hydrogrossular pseudomorphs after a mineral with orthogonal cross-section (gehlenite?) is observed along the contact. Wollastonite coronas (<100  $\mu$ m) overgrow quartz phenocrystals within the ignimbrite.

Relics of larnite and magnesioferrite are characteristic in cuspidine-, chegemite- and  $Ca_5(SiO_4)_2F_2$  bearing rocks. Bultfontainite is also common in cuspidine- and  $Ca_5(SiO_4)_2F_2$  bearing rocks. Brucite grains with periclase relics, associated with calcite, are found in the spurite rock.

Chegemite composed of up to 85 % Ca<sub>7</sub>(SiO<sub>4</sub>)<sub>3</sub>(OH)<sub>2</sub> end-member component is a rock-forming mineral in xenolith 1 (Fig. 2A-C Table 1). The size of commonly cracked chegemite grains typically does not exceed 200-300 µm in maximum dimension. Titanium is the main impurity in the chegemite, reaching 1.3 wt% TiO<sub>2</sub> (Table 1, analysis 5). Xenomorphic and ovoid relics of larnite, spurrite, hydroxylellestadite and inclusions of isometric wadalite crystals with zones of a potential new mineral of the mayenite group (simplified formula: Ca<sub>12</sub>Al<sub>14</sub>O<sub>32</sub>Cl<sub>2</sub>  $\times$  3H<sub>2</sub>O) occur within the chegemite grains (Fig. 2A, B, Table 2). Lakargiite and srebrodolskite inclusions are also occasionally detected within chegemite grains (Fig. 2A, Table 3). Minerals of the mayenite group are replaced by hydrogrossular (katoite) (Fig. 2B, Table 2), which also forms rims on reinhardbraunsite (Fig. 2C, Table 2). Rounded relics of chegemite with thin rims of a calcium hydrosilicate are enclosed in large grains of reinhardbraunsite (Fig. 2C, Table 1). The main properties establishing chegemite as a new mineral were determined on specimens from xenolith 1, the type locality for the mineral.

A new occurrence of chegemite was discovered during fieldwork in 2008 on the slope of Mt. Vorlan about 1 km to the northwest of xenolith 1 (Fig. 1). It is a skarned carbonate-silicate xenolith more than 5 m across labelled as xenolith number 7. The contact of this xenolith with the hosting ignimbrite is marked by an almost 1 m thick cuspidine rock with fluorite. A light-yellow rock with dark-pink spots underlies the fluorite-cuspidine zone. The pink patches proved to be monomineralic aggregates of chegemite reaching 30 cm in maximum extension comprising individual chegemite grains up to 5 mm in size (Fig. 2D, Table 1).

Larnite relics and abundant inclusions of rondorfite replaced by calcium hydrosilicates with magnesium impurities occur within chegemite grains (Fig. 2E, Tables 1 and 2). The yellow part of the rock with the pink chegemite spots comprises a hydrogarnet-bultfontainite-ettringite groundmass with abundant calcium hydrosilicates. Here, another potential new mineral CaUO<sub>4</sub> (Table 3), rare lakargiite crystals, and



Fig. 2. Xenolith 1 (A–C): (A) Chegemite with larnite relics and srebrodolskite, lakargiite, spurrite and "Cl-mayenite" inclusions, (B) Chegemite with inclusions of zoned wadalite crystals with external zones of "Cl-mayenite" partially substituted by hydrogarnet, (C) Reinhardbraunsite grains with chegemite inclusions. Xenolith 7 (D–F): (D) Pink chegemite in skarn, (E) Chegemite with rondorfite inclusions and larnite relics, (F) Larnite grain with characteristic twinning replaced by chegemite partially substituted by fluorine reinhardbraunsite. (A–C), (E) BSE images. (F) Transmitted light, crossed nicols. (5) shows field of microprobe analyses points from 12 to 15 in Table 1. 1–17 – microprobe analyses points, see Tables 1–3.

					Xenol	ith 1					Xenoli	ith 7 cent	re of rock bloc	ks			Xenolith 7 rim	of rock b	ocks		
Z	Mean 68	1 s.d.	Range	1 2	6.2	4 9	5 7	6 12	7 8	8	Mean 19	9 s.d.	Range	10	Mean 48	11 s.d.	Range	12 15	13 15	14 15	15 15
P2O5 wt%	n.d.	0 43	0 1 30	0.04	.b.n	n.d.	n.d.	n.d.	n.d.	.b.n	0.01	0.02	0-0.07	0.04	n.d.	100	0 0 03	n.d.	n.d.	n.d.	n.d.
SiO,	0.49 29.76	0.35	0-1-20 28.97-30.36	0.02 30.25	0.04 29.70	29.31	1.30 29.30	30.30	0.19 28.35	0.00 28.34	0.04 29.36	0.19	020-0.05 29.05-29.59	0.74 29.45	29.90	0.04	28.85–30.36	30.18	cu.u 29.97	28.51	п.ч. 28.24
$Fe_2O_3$	0.02	0.03	0-0.13	n.d.	n.d.	0.08	0.06	n.d.	n.d.	n.d.	0.03	0.04	0-0.10	0.05	0.01	0.03	0-0.10	n.d.	n.d.	n.d.	n.d.
$Cr_2O_3$	n.d.			n.d.	n.d.	n.d.	n.d.	n.d.	0.03	n.d.	n.d.			n.d.	0.00	0.01	0-0.07	n.d.	n.d.	0.05	n.d.
MgO	n.d.			0.02	0.02	0.02	0.03	n.d.	n.d.	n.d.	0.01	0.01	0-0.04	0.03	0.03	0.02	0-0.07	0.03	0.02	n.d.	0.04
CaO MaO	65.67 5.d	0.32	65.35-66.33	66.01 ترط	65.62	66.08 n d	65.43 " d	66.17 " d	66.32 " d	66.11 5 d	65.10 n.d	0.72	63.68–65.78	65.32 n d	66.01	0.24	65.41–66.53	66.08 ترط	65.51 0.00	66.15 n.d	66.22 5 d
Na <sub>2</sub> O	n.d.			n.d.	n.d.	n.d.	0.02	n.d.	n.d.	n.d.	n.d.			n.d.	0.01	0.01	0-0.03	0.03	n.d	n.d.	0.03
CI	n.d.			n.d.	n.d.	0.06	n.d.	n.d.	n.d.	0.05	n.d.			n.d.	0.03	0.03	0-0.11	0.05	0.07	0.06	n.d.
Н	1.64	0.35	1.03 - 2.52	1.27	1.50	2.52	1.03	1.67	1.53	2.03	2.48	0.12	1.97 - 2.92	2.36	3.12	0.20	2.57-3.49	3.22	2.58	4.51	2.51
$H_2O$	2.23	0.19	1.83 - 2.58	2.40	2.40	1.80	2.60	2.26	3.51	3.35	1.83	0.25	1.59 - 2.08	1.88	1.49	0.10	1.35 - 1.79	1.51	1.77	2.07	3.18
= 0 =	0.70			0.54	0.64	1.08	0.44	0.72	0.65	0.87	0.77			1.00	1.32			1.36	1.09	1.92	1.06
г + С																					
Total	99.11			99.47	99.44	99.82	99.33	99.73	99.28	99.09	98.69			98.87	99.34			99.81	98.95	99.54	99.16
Ca Ma2+	7			L	6.99	L	6.99	L	5	5	L			7	7.02			L	7	4.99	S
Yeite	L			Г	6 00	L	6 00	L	v	v	Ľ			٢	7.07			L	10.0	1 00	v
Si	00 6			- 11	200	, 01	0.0	3 00	1 00	000	7 05			, 07	20.7			00 6	10.0	, F c	) (
$\mathrm{Ti}^{4+}$	0.01			r	0.06	0.08	0.10	00.0	0.01	00.7	0.05			0.06	07.7			0.01		0.01	1
$Fe^{3+}$						0.01															
Zsite	ŝ			б	3.01	ŝ	3.01	б	0	7	б			ŝ	2.98			ŝ	2.99	2.01	0
НО	1.48			1.60	1.55	1.19	1.69	1.47	1.66	1.54	1.23			1.25	0.99			0.99	1.17	1.01	1.43
F	0.52			0.40	0.47	0.79	0.33	0.53	0.34	0.45	0.77			0.75	0.97			1.00	0.81	1.01	0.57
G						0.01				0.01								0.01	0.01	0.01	
OH-Hm %	74			80	76.5	60	85	73.5	83	LL	61.5			62.5	50.5			49.5	59	49.75	71.5
F–Hm %	26			20	23.5	39.5	15	26.5	17	22.5	38.5			37.5	49.5			50	40.5	49.75	28.5
1-6, 9-13 - Fig. 2; OF	- chegem	ite [for chegen	mula calcul <sup>§</sup> nite Ca <sub>7</sub> (SiC	ated on O4)3(OF	10 catic	ons and 1 einhardl	4(O+OH braunsite	+F)]; 7, 8 Ca <sub>5</sub> (SiO <sub>4</sub>	, 14, 15 - ) <sub>2</sub> (OH) <sub>2</sub>	- reinh: end-m	ardbraunsi embers; H	te [fon 7-Hm	mula calcula – F-analogu	ated on 7 ate of ch	7 cations : negemite	and 10( Ca <sub>7</sub> (Si	O + OH + O $O_4)_3F_2 \text{ or } 1$	F)]; <i>N</i> -	analysi neral C	s numb a <sub>5</sub> (SiO	er on 4)2F2
end-memb	STS.	)											)		)						

Table 1. Composition of calcium humite-group minerals from the Caucasus.

Table 2. Minerals associated with chegemite.

Ν	1 4	2 <sup>*</sup> 17	3 2	4 10	5 11	6 3	7 9	8 14	9	10	11 <sup>*</sup> 16
SO <sub>3</sub> wt.%	0.09	n.d.	n.d.	n.d.	n.d.	0.04	2.02	3.04	18.90	0.08	n.d.
$P_2O_5$	0.07	0.03	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.45	0.25	n.d.
As <sub>2</sub> O <sub>5</sub>	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.61	n.d.	n.d.
TiO <sub>2</sub>	0.03	0.02	0.05	0.51	0.19	0.19	0.16	0.37	n.d.	0.04	0.07
SiO <sub>2</sub>	26.75	34.63	34.27	11.46	0.66	0.61	16.73	16.12	16.83	29.83	30.27
$Al_2O_3$	n.d.	n.d.	n.d.	30.81	42.95	42.92	20.53	24.14	n.d.	0.77	0.74
Fe <sub>2</sub> O <sub>3</sub>	0.02	n.d.	n.d.	3.49	3.96	4.21	3.59	0.10	n.d.	0.04	0.03
CaO	62.71	64.86	65.29	42.85	43.50	43.65	40.02	41.38	55.18	56.49	57.00
MgO	n.d.	n.d.	n.d.	0.93	n.d.	n.d.	0.65	0.26	n.d.	4.35	4.23
Na <sub>2</sub> O	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.20	0.26
Cl	n.d.	n.d.	n.d.	10.39	5.84	5.25	n.d.	n.d.	1.20	8.84	8.51
F	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.55	0.57	0.32	0.16	n.d.
$H_2O_{**}^{**}$				0.24	3.73	3.53	14.40	14.84	1.32		
$\text{CO}_2^{**}$	9.77								1.95		
-O = F + Cl				2.31	1.30	1.17	0.23	0.24	0.40	2.04	1.89
Total	99.50	99.54	99.61	98.43	99.53	99.23	98.42	100.58	98.36	99.01	99.22
Calculated on:											
Cations	7	3	3							13	13
Anions and normalized on:				12 Ca	12 Ca	12 Ca	3 Ca	3 Ca	10 Ca		
Na										0.05	0.07
Ca	5	2	2.01	12	12	12	3	3	10	8.00	8.01
Mø	-	_		0.37			0.07	0.03		0.85	0.83
Al				9.65	13.04	12.98	1.69	1.93		0.12	0.11
Fe <sup>3+</sup>				0.70	0.77	0.81	0.19				
Cr <sup>3+</sup>				0.01							
Ti <sup>4+</sup>				0.10	0.04	0.04	0.01	0.02			0.01
Si	1.99	1	0.99	2.99	0.17	0.16	1.17	1.09	2.85	3.94	3.97
$P^{5+}$									0.07	0.03	
As <sup>5+</sup>									0.23		
$S^{6+}$	0.01					0.01	0.11	0.15	2.40	0.01	
$C^{4+}$	1.01								0.45		
ОН				0.42	0.28	0.05	6.72	6.69	1.49		
F							0.12	0.12	0.17	0.07	
Cl				4.60	2.55	2.28			0.34	1.98	1.89
H <sub>2</sub> O					3	3					

N - number of analyses on Fig.1; in total: 1-0.06 wt.% ZnO, 4-0.06 wt.% Cr<sub>2</sub>O<sub>3</sub>.

1 – spurrite  $Ca_5(SiO)_{1.99}(S^{6+}O_4)_{0.01}(CO_3)_{1.01} \approx Ca_5(SiO_4)_2(CO_3)$ .

2 - larnite Ca2SiO4.

 $\begin{array}{l} 2 - \text{larmite } Ca_2\text{SiO}_4. \\ 3 - \text{larmite } Ca_2\text{SiO}_4. \\ 4 - \text{wadalite } Ca_1\text{c}(\text{Al}_{0.65}\text{Fe}^{3+}\text{0.70}\text{Si}_{2.99}\text{Mg}_{0.37}\text{Ti}^{4+}\text{0.10}\text{Cr}^{3+}\text{0.01})_{\Sigma13.82}\text{O}_{31.52}(\text{OH})_{0.42}\text{Cl}_{4.60} \approx \text{Ca}_{12}\text{Al}_{11}\text{Si}_{3}\text{O}_{32}\text{Cl}_{5}. \\ 5 - \text{``mayenite-Cl'`} Ca_12(\text{Al}_{13.04}\text{Fe}^{3+}\text{0.77}\text{Si}_{0.17}\text{Ti}^{4+}\text{0.04})_{\Sigma14.02}\text{O}_{31.72}(\text{OH})_{0.28}\text{Cl}_{2.55} \times 3\text{H}_2\text{O} \approx \text{Ca}_{12}\text{Al}_{14}\text{O}_{32}\text{Cl}_{2} \times 3\text{H}_2\text{O}. \\ 6 - \text{``mayenite-Cl'`} Ca_12(\text{Al}_{12.98}\text{Fe}^{3+}\text{0.81}\text{Si}_{0.16}\text{Ti}^{4+}\text{0.04}\text{O}_{5}^{6+}\text{0.01})_{\Sigma14}\text{O}_{31.98}(\text{OH})_{0.05}\text{Cl}_{2.28} \times 3\text{H}_2\text{O} \approx \text{Ca}_{12}\text{Al}_{14}\text{O}_{32}\text{Cl}_{2} \times 3\text{H}_2\text{O}. \\ 7 - \text{katoite } Ca_3(\text{Al}_{1.93}\text{Mg}_{0.03}\text{Ti}^{4+}\text{0.02})_{\Sigma19}(\text{Si}_{1.09}\text{S}^{6+}\text{0.15})_{\Sigma12}24[(\text{OH})_{6.69}\text{O}_{5.19}\text{F}_{0.12}]_{\Sigma12} \approx \text{Ca}_3\text{Al}_2(\text{SiO}_4)(\text{H}_4\text{O}_{4})_2. \\ 8 - \text{katoite } Ca_3(\text{Al}_{1.69}\text{Fe}^{3+}\text{0.19}\text{Mg}_{0.07}\text{Ti}^{4+}\text{0.01})_{\Sigma19}\text{6}(\text{Si}_{1.17}\text{S}^{6+}\text{0.11})_{\Sigma1.28}[(\text{OH})_{6.72}\text{O}_{5.16}\text{F}_{0.12}]_{\Sigma12} \approx \text{Ca}_3\text{Al}_2(\text{SiO}_4)(\text{H}_4\text{O}_{4})_2. \\ 9 - \text{hydroxylellestadite } Ca_{10}[\text{SiO}_4]_{2.85}[\text{SO}_4]_{2.40}[\text{CO}_3]_{0.45}[\text{ASO}_4]_{0.23}[\text{PO}_4]_{0.07}(\text{OH}_{1.49}\text{Cl}_{0.34}\text{F}_{0.17}) \approx \text{Ca}_{10}(\text{SiO}_4)_3(\text{SO}_4)_3(\text{OH})_2. \\ 10 - \text{rondorfite } (\text{Ca}_{8.01}\text{Na}_{0.07})_{\Sigma8.08}(\text{Mg}_{0.83}\text{Ca}_{0.08}\text{Al}_{0.08}\text{Ti}^{4+}\text{0.01})_{\Sigma0.92}(\text{Si}_{3.97}\text{Al}_{0.03})_{\Sigma4}\text{O}_{16.01}\text{Cl}_{1.97} \approx \text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2. \\ 11 - \text{rondorfite } (\text{Ca}_{8.00}\text{Na}_{0.05})_{\Sigma8.05}(\text{Mg}_{0.85}\text{Al}_{0.10}))_{\Sigma0.95}(\text{Si}_{3.94}\text{P}_{0.03}\text{S}^{6+}\text{0.01}\text{Al}_{0.02})_{\Sigma4}\text{O}_{16.01}\text{Cl}_{1.98}\text{F}_{0.07} \approx \text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2. \\ 11 - \text{rondorfite } (\text{Ca}_{8.00}\text{Na}_{0.05})_{\Sigma8.05}(\text{Mg}_{0.85}\text{Al}_{0.10}))_{\Sigma0.95}(\text{Si}_{3.94}\text{P}_{0.03}\text{S}^{6+}\text{0.01}\text{Al}_{0.02})_{\Sigma4}\text{O}_{16.01}\text{Cl}_{1.98}\text{F}_{0.07} \approx \text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2. \\ 12 - \text{rondorfite } (\text{Ca}_{8.00}\text{Na}_{0.05})_{\Sigma8.$ 

<sup>\*</sup>Xenolith 7.

<sup>\*</sup>calculated on charge balance.

larnite grains replaced on the periphery by chegemite, and As-CO<sub>3</sub>-bearing hydroxylellestadite are noted. In addition, chegemite is replaced by reinhardbraunsite (Fig. 2F, Table 1). Ti-bearing chegemite from the central part of the dark-pink patches contains nearly 40 % of the fluorine end-member whereas, in chegemite rims on larnite, the content of this end-member increases up to 50 % (Table 1) Reinhardbraunsite substituting for chegemite shows a tendency to increase in OH end-member content from 50 to 72 % towards the crystal rim (Table 1).

Chegemite is colourless and transparent in thin section. The colour in massive samples varies from pink, yellowpink to white. The streak is white. It forms irregular grains, in rare cases individual crystals with rhombic cross-section. Twins, probably on (110), are occasionally noted. The cleavage is imperfect on (010) and the fracture is

Table 3.	Oxide	minerals	associated	with	chegemite.

	1 <sup>a</sup>	2 <sup>a</sup>	3 <sup>a</sup>	4 <sup>b</sup>	5 <sup>b</sup>	6 <sup>c</sup>
UO <sub>3</sub> wt.%	0.19	n.d.	n.d.	n.d.	n.d.	84.40
$Nb_2O_5$	1.08	1.27	1.20	n.d.	0.05	n.d.
ThO <sub>2</sub>	0.22	0.49	0.52	n.d.	n.d.	n.d.
HfO <sub>2</sub>	0.81	0.71	0.73	n.d.	n.d.	n.d.
$SnO_2$	21.96	29.73	30.03	0.30	0.52	n.d.
$ZrO_2$	41.76	33.39	33.86	0.14	0.24	n.d.
TiO <sub>2</sub>	0.98	1.05	0.91	2.12	1.61	n.d.
SiO <sub>2</sub>	0.12	n.d.	n.d.	0.10	0.15	n.d.
$La_2O_3$	n.d.	0.15	0.15	n.m.	n.m.	n.d.
$Ce_2O_3$	0.19	0.22	0.18	n.m.	n.m.	n.d.
Fe <sub>2</sub> O <sub>3</sub>	2.67	2.62	2.67	46.97	44.97	n.d.
$Cr_2O_3$	n.d.	n.d.	n.d.	0.05	0.10	n.d.
$Sc_2O_3$	0.08	0.05	0.03	n.d.	n.d.	n.d.
$Al_2O_3$	0.05	n.d.	n.d.	5.38	7.26	n.d.
CaO	30.33	29.09	29.35	43.19	43.49	16.55
MnO	n.d.	n.d.	n.d.	0.35	0.26	n.d.
SrO	0.08	n.d.	n.d.	n.d.	n.d.	n.d.
MgO	n.d.	n.d.	n.d.	0.86	0.70	n.d.
Total	100.52	98.77	99.63	99.46	99.35	100.95
Calculated on 2 <sup>3</sup>	<sup>a</sup> and 4 <sup>b</sup> cations					
Ca	0.994	0.987	0.988	2.023	2.025	1.000
Mn				0.013	0.010	
Th	0.002	0.004	0.004			
Sr	0.001					
La <sup>3+</sup>		0.002	0.002			
$Ce^{3+}$	0.002	0.003	0.002			
Xsite	0.998	0.996	0.996	2.036	2.035	1.000
Zr	0.622	0.516	0.519	0.003	0.005	
$\mathrm{Sn}^{4+}$	0.267	0.376	0.376	0.005	0.009	
Ti <sup>4+</sup>	0.023	0.025	0.022	0.070	0.053	
$U^{6+}$			0.001			1.000
Sc	0.002	0.001	0.001			
Cr <sup>3+</sup>				0.002	0.003	
Nb <sup>5+</sup>	0.015	0.018	0.017		0.001	
Si	0.004			0.005	0.007	
Hf	0.007	0.006	0.007			
Al	0.002			0.277	0.372	
Fe <sup>3+</sup>	0.061	0.063	0.063	1.546	1.471	
Mg				0.056	0.045	
Ysite	1.002	1.004	1.004	1.964 <sup>d</sup>	1.965 <sup>d</sup>	1.000
Charge	5.966	5.976	5.973	9.991	9.999	8.000

<sup>a</sup>Lakargiite.

<sup>c</sup>CaUO<sub>4</sub>.

 $^{d}Y + Z$  sites.

conchoidal. The micro-hardness VHN<sub>50</sub> = 306–349 kg/mm<sup>2</sup> (9 measurements with a mean of 315 kg/mm<sup>2</sup>) corresponding to Mohs' scale of 5.5–6. Holotype chegemite (Table 1, analysis 2) from xenolith 1 gave the following optical data:  $\alpha = 1.621(2), \beta = 1.626(3), \gamma = 1.630(2); \Delta = 0.009, 2V_Z,$ meas = -80(8)°; 2V<sub>Z, calc</sub> = -83°. Pink chegemite from xenolith 7 is characterized by  $\alpha = 1.630(2); \beta = 1.636(2);$  $\gamma = 1.640(2), \Delta = 0.010; 2V_Z,$  meas = -81(5)° and 2V<sub>Z, calc</sub> = -78°. The measured density of the chegemite from xenolith 7 is 2.86(1) g/cm<sup>3</sup>. The optical orientation of chegemite is: X = a, Y = b, Z = c. Gladstone-Dale's compatibility factors range from -0.007 (superior) for chegemite from xenolith 1 (using calculated density) to -0.055 (good) for chegemite from xenolith 7 (using measured density).

FTIR spectroscopic data were measured for chegemite from both xenoliths. A non-polarized reflectance spectrum adapted following the Kramers-Krönig method (Andermann *et al.*, 1965) was obtained for a 40 × 160 µm grain of chegemite from xenolith 1 (Fig. 3) with abundant inclusions of spurrite, a wadalite-like phase and larnite. A standard (KBr pellet) transmission spectrum (Fig. 4) was routinely recorded for chegemite from xenolith 7. The following FTIR bands (cm<sup>-1</sup>) were found (strong bands are underlined): 3565, 3558, <u>3550</u>, <u>3542</u>, 3535, 3525, 3487, <u>3475</u>, 1011; 960, <u>927</u>; 906, 889; 865; 838, 820, 800, 756, 718, 705, 653, 640, 610,

<sup>&</sup>lt;sup>b</sup>Srebrodolskite.

<u>561</u>, <u>519</u>, 500, 443, <u>437</u> and 417. A slight shift of the main bands observed in the FTIR spectrum of chegemite from xenolith 1 probably reflects the different experimental procedures (Fig. 3 and 4).

The following bands  $(\text{cm}^{-1})$  were resolved (strong bands are underlined) in non-polarized Raman spectra of the chegemite (Fig. 5): 226, 273, 293, 311, 323, <u>389</u>, 403, <u>526</u>, 549, 766, 774, <u>818</u>, 845, 893, <u>923.5</u>, <u>3478</u>, 3532, <u>3551</u> and <u>3563</u>. Slights shifts of bands below 600 cm<sup>-1</sup> are attributed to an orientation effect (Fig. 5). The Raman spectra of chegemite are very similar to the spectra of reinhardbraunsite (Fig. 5).

Raman and FTIR spectra of chegemite are also similar to the spectra of humite- and olivine-group minerals (Piriou & McMillan, 1983; Chopelas, 1991; Mohanan *et al.*, 1993; Lin *et al.*, 2000; Frost *et al.*, 2007a and b).



Fig. 3. FTIR reflection spectrum, transformed by the Kramers-Krönig method, measured for a chegemite grain from xenolith 1 in the regions: (a)  $1100-700 \text{ cm}^{-1}$ , (b)  $3650-3400 \text{ cm}^{-1}$ .



Fig. 4. FTIR spectrum of chegemite from xenolith 7 determined by the standard method (KBr pellet) in the regions: (a)  $1100-400 \text{ cm}^{-1}$ , (b)  $3600-3400 \text{ cm}^{-1}$ .

There are two broad bands near  $3550-3560 \text{ cm}^{-1}$  and one at  $3480 \text{ cm}^{-1}$  in the OH region of the FTIR and Raman spectra of chegemite and reinhardbraunsite. The complexity of the OH related part of the spectrum is due to two different hydrogen positions H1 and H2 in humite-group structures (this study; Abbott *et al.*, 1989; Berry & James, 2001, 2002; Kuribayashi *et al.*, 2008).

Abundant impurities of reinhardbraunsite, ettringite, spurrite, hydrogrossular, mayenite-group minerals and of hydrocalumite within the chegemite from xenolith 1 prevented collection of a detailed powder diffraction pattern. Nevertheless, using the 21 strongest reflections, unit-cell parameters could be refined: (*Pbnm*, *Z* = 4) *a* = 5.071(3), *b* = 11.388(3), *c* = 23.579(3) Å; *V* = 1361.7(4) Å<sup>3</sup>. These values compare closely with the values obtained from the single-crystal investigation: *a* = 5.0696(1), *b* = 11.3955(1), *c* = 23.5571(3) Å; *V* = 1360.92(4) Å<sup>3</sup> (Table 5). In contrast, high-quality diffraction data obtained for the chegemite from xenolith 7 (Table 4) converge at: *a* = 5.0697(2), *b* = 11.3975(6), *c* = 23.531(1) Å; *V* = 1359.65(2) Å<sup>3</sup>.

Chegemite can be easily identified using a combination of optical, Raman and qualitative EDS compositional data. Chegemite is distinguished from optically similar calcioolivine by the presence of a fluorine peak in EDS spectra, and also from its polymorph larnite, which shows thin lamellar twinning. Chegemite is distinguished by a greater  $2V_z$  (-78 to -83°) from chemically similar reinhardbraunsite and from Ca<sub>5</sub>(SiO<sub>4</sub>)<sub>2</sub>F<sub>2</sub> (2V<sub>z</sub>  $\approx$  -45 to -60°). The potential new mineral Ca<sub>7</sub>(SiO<sub>4</sub>)<sub>3</sub>F<sub>2</sub>, the fluorine analogue of chegemite, and also Ca<sub>5</sub>(SiO<sub>4</sub>)<sub>2</sub>F<sub>2</sub> (Galuskina *et al.*, in preparation), have only one FTIR and Raman band characteristic of one OH-group whereas chegemite is characterized by the presence of two strong bands in the OH region.

## 4. Single-crystal structural investigation of chegemite

The crystal structure of chegemite (Tables 5-9) corresponds to the humite structure-type (Ribbe & Gibbs, 1971). The framework of the chegemite structure is composed of zigzag chains of four symmetry-independent Ca octahedra M(1,2,3,4) linked by two types of isolated Sitetrahedra (Fig. 6). Average Ca–O distances vary between 2.36 Å (M4) and 2.40 Å (M2). These distances are very similar to those in calcio-olivine  $\gamma$ -Ca<sub>2</sub>SiO<sub>4</sub>,  $\langle$ Ca1–O $\rangle$  =  $2.35 \text{ Å}, \langle \text{Ca2-O} \rangle = 2.39 \text{ Å}$  (Gobechiya *et al.*, 2008) and in reinhardbraunsite  $Ca_5(SiO_4)_2(OH,F)_2$ ,  $\langle Ca1-O \rangle =$ 2.37 Å,  $\langle Ca2-O \rangle = 2.38$  Å, and  $\langle Ca3-O \rangle = 2.34$  Å (Kirfel et al., 1983). A projection of a polyhedral structure model of chegemite along [100] (Fig. 6) is indistinguishable from a corresponding drawing for humite (Ribbe & Gibbs, 1971) with the only obvious difference being that the volume of chegemite is 34 % greater than that of humite due to the difference in octahedral ionic radii, 0.72 Å for Mg versus 1.00 Å for Ca (Shannon, 1976).

A special feature of the chegemite structure is the strongly anisotropic smearing of O8 related to positional and chemical disorder. O8 is to 75 % occupied by O and to



Fig. 5. Raman spectra of chegemite (1 – separated grain, 2 – grain in thin-section) and reinhardbraunsite (3 – separated grain) in the regions: (a) 1200–200 cm<sup>-1</sup>, (b) 3700–3300 cm<sup>-1</sup>.

h	k	l	$d_{\rm obs}$	I <sub>obs</sub>	$d_{\rm cal}$	I <sub>cal</sub>	h	k	l	$d_{\rm obs}$	I <sub>obs</sub>	$d_{\rm cal}$	I <sub>cal</sub>
0	0	4	5.88272	19	5.88270	35	2	2	4	2.15504	62	2.15465	62
0	2	0	5.69875	23	5.69779	36	1	1	10	2.09791	112	2.09782	79
0	2	1	5.53864	181	5.53776	137	1	5	1	2.07094	18	2.07058	22
0	2	2	5.12879	150	5.12809	160	1	5	2	2.04729	13	2.04694	11
1	1	0	4.63102	8	4.63112	11	1	5	3	2.00961	59	2.00928	62
1	1	2	4.31008	3	4.30930	12	1	2	10	1.99879	82	1.99868	44
1	0	3	4.25772	83	4.25707	140	1	0	11	1.97078	21	1.97083	17
0	2	4	4.09312	236	4.09276	266	1	5	4	1.96020	40	1.95989	35
1	1	3	3.98851	105	3.98789	156	1	1	11	1.94208	121	1.94200	79
0	0	6	3.92181	81	3.92180	75	2	0	8	1.92017	35	1.91993	35
1	2	1	3.73961	85	3.7389	140	2	2	7	1.90720	1000	1.90693	1000
1	1	4	3.63930	540	3.63883	574	2	4	0	1.89388	318	1.89351	344
1	2	2	3.60551	7	3.60487	11	1	3	10	1.86083	74	1.86070	88
1	0	5	3.44912	27	3.44876	39	2	4	3	1.84097	218	1.8406	165
1	2	3	3.41087	22	3.41032	23	1	5	6	1.83680	22	1.83661	54
1	1	5	3.30126	59	3.30091	73	0	6	4	1.80768	377	1.80740	235
1	2	4	3.18470	36	3.18425	30	1	1	12	1.80380	60	1.80570	20
1	3	0	3.0404	530	3.03965	500	1	6	1	1.77375	12	1.77344	12
1	3	1	3.01516	667	3.01460	640	1	5	7	1.76817	150	1.76794	115
1	1	6	2.99311	777	2.99284	586	2	4	5	1.75695	13	1.75665	16
1	3	2	2.94307	22	2.94302	41	1	3	11	1.74949	135	1.74938	136
0	0	8	2.94136	130	2.94135	95	0	2	13	1.72514	58	1.72511	71
0	2	7	2.89536	362	2.89523	290	0	4	11	1.71072	193	1.71061	160
0	4	0	2.84937	70	2.84890	64	2	4	6	1.70515	50	1.70516	63
1	3	3	2.83473	565	2.83427	548	1	5	8	1.69773	26	1.69753	33
1	0	7	2.80162	10	2.80143	10	0	0	14	1.68078	349	1.68077	314
1	1	7	2.72063	724	2.72043	690	3	1	1	1.66741	50	1.66705	42
1	3	4	2.70086	759	2.70046	526	0	6	7	1.65380	320	1.65358	400
0	4	3	2.67814	210	2.67774	195	1	3	12	1.64787	30	1.64778	30

Table 4. X-ray powder diffraction pattern of chegemite from xenolith 7.

Table 4. Continued

h	k	l	$d_{\rm obs}$	Iobs	$d_{\rm cal}$	$I_{\rm cal}$	h	k	l	$d_{\rm obs}$	I <sub>obs</sub>	$d_{\rm cal}$	$I_{\rm cal}$
1	3	5	2.55370	123	2.55336	110	3	1	3	1.63490	48	1.63456	62
2	0	0	2.53483	63	2.53427	106	2	5	4	1.62870	19	1.62841	11
1	2	7	2.51422	324	2.51399	335	1	4	11	1.62092	19	1.62080	24
1	4	0	2.48393	462	2.48348	223	3	2	1	1.61633	16	1.61598	19
1	1	8	2.47020	29	2.48289	240	3	1	4	1.60795	33	1.60763	50
2	1	0	2.47411	37	2.47384	87	1	3	13	1.55529	51	1.55521	58
2	1	1	2.4610	13	2.46028	22	1	7	0	1.54687	165	1.54996	120
0	4	5	2.43743	11	2.43713	15	3	3	1	1.54072	31	1.54040	33
2	1	2	2.42140	8	2.42090	14	3	1	6	1.53775	45	1.53747	34
1	3	6	2.40279	62	2.40251	75	3	3	3	1.51496	33	1.51465	43
2	1	3	2.35974	55	2.35928	55	3	1	7	1.49676	52	1.49650	55
0	4	6	2.30491	62	2.30493	51	3	3	4	1.49344	55	1.49315	46
2	1	4	2.28082	37	2.28040	52	1	5	11	1.49090	50	1.49076	22
2	1	5	2.19011	9	2.18974	10	0	6	10	1.47807	56	1.47792	64

Table 5. Parameters for X-ray data collection and crystal-structure refinement.

Crystal data	Chegemite
Unit cell dimensions (Å)	a = 5.0696(1)
	b = 11.3955(1)
	c = 23.5571(3)
Volume (Å <sup>3</sup> )	1360.92(4)
Space group	<i>Pbnm</i> (No. 62)
Ż	4
Chemical formula	Ca <sub>7</sub> (SiO <sub>3</sub> ) <sub>4</sub> (OH <sub>1.5</sub> F <sub>0.5</sub> )
$\mu (mm^{-1})$	3.057
Intensity measurement	
Crystal shape	prism
Crystal size (mm)	0.16  imes 0.16  imes 0.05
Diffractometer	APEX II SMART
X-ray radiation	Mo $K\alpha \lambda = 0.71073$ Å
X-ray power	50 kV, 30 mA
Monochromator	Graphite
Temperature	293 K
Detector to sample distance	5.95 cm
Measurement method	Phi and omega scans
Rotation width	$0.5^{\circ}$
Total number of frames	2180
Frame size	$512 \times 512$ pixels
Time per frame	30 s
Max. $\theta$ -range for data collection	32.76
Index ranges	$-7 \le h \le 7$
	$-16 \le k \le 16$
	$-34 \le l \le 34$
No. of measured reflections	19,563
No. of unique reflections	24,00
No. of observed reflections $(I > 2\sigma(I))$	1,949
Refinement of the structure	
No. of parameters used in refinement	122 + 2 restraints
R <sub>int</sub>	0.0322
R <sub>o</sub>	0.0215
$R1, 1 > 2\sigma(1)$	0.0230
R1, all data	0.0316
$wR2$ (on $F^2$ )	0.0600
GooF	1.076
$\Delta \rho_{\min} \left(-e. A^{-3}\right)$	-0.45 close to Ca3
$\Delta \rho_{\rm max}$ (e. A <sup>-3</sup> )	0.76 close to H2

25 % by F. O8 lies on a triangular plane with  $2 \times Ca4$ and  $1 \times Ca3$  in the corners. The disorder, represented by anisotropic displacement parameters (Table 7, Fig. 7), is most pronounced perpendicular to the triangular plane. In the  $Ca_7(SiO_4)_3(OH)_2$  chegemite end-member, O8 acts simultaneously as donor and acceptor of a hydrogen bond. The chegemite structure has a centre of inversion halfway between two adjacent O8 sites (Fig. 7). Thus, on a statistical basis, H1 between the two O8 sites can only be 50 %occupied (Fig. 7). If both H1 sites were to be occupied (H1 occupancy = 100 %), the two centrosymmetric H1 counterparts would be in too-close proximity. For stoichiometric reasons, the OH end-member must have 2 OH pfu. However, with H1 50 % occupied, it only contributes to 1 OH pfu. If O8a (Fig. 7) acts as acceptor of a hydrogen bond from O8b (O8b-H1···O8a), O8a will also be hydroxylated but the alternate O8a-H2 vector points almost opposite to the weak O8a…H1 interaction (Fig. 7). This additional hydrogen bond system can be described as O8a-H2····O7 (Fig. 7). Disordered hydrogen bonds are characteristic of the OH end-members of all humite-group minerals as has been confirmed by neutron powder diffraction for synthetic deuterated hydroxylclinohumite (Berry & James, 2001) and hydroxyl-chondrodite (Lager et al., 2001).

The good quality of our diffraction data invited a test of whether the smeared O8 position could be resolved into two sub-sites (O8' and O8"). Subsequently, a refinement was attempted with individual O8' and O8" sites having a common isotropic displacement parameter and a constraint that the occupancies of both sub-sites sum up to one. Such a sub-site refinement involves one parameter less than the anisotropic O8 model but it converged to slightly better *R* values [w*R*2 (on  $F^2$ ) = 0.0591 and *R*1, I > 2 $\sigma$ (I) = 0.0224]. In the new model, O8' and O8" are 0.4 Å apart. O8' is on the plane formed by the triangle with 2 × Ca4 and 1 × Ca3 at the apices [Ca4–O8': 2.268(4) Å and 2.327(4) Å, Ca3-O8': 2.272(4) Å]. O8" is displaced from the triangular plane and shifted towards the inversion centre. Corresponding distances between O8" and Ca are significantly greater

Atom	Occup.	x	у	Z	$U_{ m eq}$
Cal	1.0	0.50376(5)	0.37818(2)	0.176543(11)	0.00886(8)
Ca2	1.0	-0.50687(7)	0.65807(3)	1/4	0.00771(9)
Ca3	1.0	-0.00244(5)	0.59346(2)	0.111399(11)	0.00850(8)
Ca4	1.0	0.50746(5)	0.36064(2)	0.027895(12)	0.00915(7)
Si1	1.0	-0.07130(10)	0.47112(5)	1/4	0.00608(11)
Si2	1.0	0.07409(7)	0.27988(3)	0.107074(14)	0.00620(9)
01	1.0	-0.7511(3)	0.47020(12)	1/4	0.0094(3)
O2	1.0	-0.2981(3)	0.83850(11)	1/4	0.0083(3)
O3	1.0	-0.20219(19)	0.53681(8)	0.19476(4)	0.00867(19)
04	1.0	0.7539(2)	0.27935(9)	0.10590(4)	0.0094(2)
05	1.0	0.20452(19)	0.41215(8)	0.10440(4)	0.00884(19)
06	1.0	0.29695(19)	0.71759(8)	0.16372(4)	0.00896(19)
O7	1.0	0.20452(19)	0.21020(8)	0.05265(4)	0.00905(19)
O, F8	1.0	0.7518(2)	0.53095(10)	0.03410(5)	0.0214(3)
H1	0.44	0.912(6)	0.502(4)	0.019(2)	0.050 (fix)
H2	0.44	0.619(7)	0.540(4)	0.0593(16)	0.050 (fix)

Table 6. Atomic coordinates and isotropic displacement parameters  $(U_{eq.})$  for chegemite.

Table 7. Anisotropic displacement parameters for chegemite.

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Cal	0.00768(14)	0.01069(15)	0.00821(14)	-0.00192(9)	-0.00120(9)	-0.00048(9)
Ca2	0.00827(19)	0.00673(18)	0.00813(18)	0.000	0.000	0.00048(12)
Ca3	0.00964(15)	0.00691(15)	0.00895(14)	0.00051(9)	0.00066(9)	-0.00077(9)
Ca4	0.00957(15)	0.00944(15)	0.00843(13)	0.00022(9)	0.00127(9)	-0.00042(9)
Si1	0.0047(2)	0.0067(2)	0.0069(2)	0.000	0.000	0.00016(18)
Si2	0.00551(18)	0.00669(18)	0.00640(17)	-0.00006(12)	-0.00011(12)	-0.00003(13)
01	0.0071(6)	0.0111(7)	0.0100(6)	0.000	0.000	0.0001(5)
O2	0.0082(6)	0.0078(6)	0.0089(6)	0.000	0.000	0.0001(5)
03	0.0093(5)	0.0090(5)	0.0077(4)	0.0011(3)	-0.0001(4)	0.0008(3)
04	0.0066(5)	0.0103(5)	0.0112(4)	-0.0002(3)	-0.0006(3)	-0.0002(3)
05	0.0088(5)	0.0077(5)	0.0100(4)	-0.0006(3)	-0.0002(3)	0.0004(4)
06	0.0086(5)	0.0099(5)	0.0084(4)	0.0013(3)	-0.0003(4)	0.0001(4)
07	0.0087(5)	0.0096(5)	0.0089(4)	-0.0018(3)	0.0004(3)	-0.0001(3)
08	0.0259(6)	0.0109(5)	0.0274(6)	0.0030(5)	-0.0193(5)	-0.0042(5)

[Ca4–O8": 2.3265(17) Å and 2.3316(19) Å, Ca3–O8": 2.3475(18) Å]. In accordance with the smaller ionic radius of  $F^-$  (1.30 Å) compared to  $O^{2-}$  (1.36 Å) for three-fold coordination (Shannon, 1976), fluorine scattering factors were assigned to O8', now named F8. A distance restraint  $(0.95(2) \text{ \AA})$  between O8" and the two proton sites (H1 and H2) was applied to obtain physically meaningful O-H distances (Lager et al., 1987). The occupancy refinement (Table 9) converged at 0.72(1) for O8'' and 0.28(1) for F8. This is in good agreement with the results of the chemical analyses. The sub-site refinement yielded the following O···O distances for the various hydrogen-bond systems: O8"-H1...O8" 2.847; O8"-H1...F8 3.229 Å; O8"-H2...O7 3.200 Å. According to the correlations between O-H stretching frequencies and O-H···O hydrogen bond lengths (Libowitzky, 1999), the low frequency band at ca. 3480  $cm^{-1}$  in the Raman and FTIR spectra is related to O8''-H1...O8" whereas the weaker hydrogen bonds O8"-H1...F8 and O8"-H2...O7 are related to the bands near  $3550-3560 \text{ cm}^{-1}$ .

In both chegemite (this paper) and humite (Ribbe & Gibbs, 1971) M1O<sub>6</sub> and M2O<sub>6</sub> octahedra show considerably stronger angular distortion than M3O<sub>6</sub> and M4O<sub>6</sub> octahedra. Differences in bond-length distortion are much less pronounced and even corresponding octahedra in chegemite and humite have similar bond length distortions. However, if the bond angle variance is applied as a measure of polyhedral distortion (Table 10), variances for corresponding octahedra in chegemite are almost twice as high as those in humite. On the other hand SiO<sub>4</sub> tetrahedra in chegemite are less distorted in their O-T-O angles than those in humite (Table 10). The different distortion behaviour in chegemite and humite is related to a cation-size effect (Ca versus Mg). Within a larger CaO<sub>6</sub> octahedron oxygen atoms have a higher flexibility in their arrangement without coming too close to each other whereas the humite structure (Ribbe & Gibbs, 1971) is much more based on a hexagonal closepacked anion (O,F) arrangement giving rise to more ideal octahedral geometry. As the CaO<sub>6</sub> moieties are the flexible links in the chegemite structure SiO<sub>4</sub> tetrahedra are less

Atom	-Atom	[Å]	Atom	-Atom	[Å]
Cal	01	2.4008(10)	Si1	O1	1.6232(14)
	O2	2.3293(9)		O2	1.6500(14)
	O3	2.3821(10)		$O3 \times 2$	1.6414(9)
	O4	2.3763(10)	Mean		1.6398
	O5	2.3108(9)			
	O6	2.4008(10)	Si2	O4	1.6232(11)
Mean		2.3667		O5	1.6471(10)
				O6	1.6470(9)
Ca2	01	2.4732(14)		07	1.6471(10)
	O2	2.3125(14)	Mean		1.6411
	$O6 \times 2$	2.36221(9)			
	$O3 \times 2$	2.4472(10)	08	H1	0.950(18)
Mean		2.4021	O8	H2	0.903(19)
Ca3	O3	2.3018(9)			
	O4	2.4759(10)			
	O5	2.3231(10)	O8	O8	3.071
	O6	2.4133(10)	08	O7	3.116
	O7	2.4424(10)			
	O8	2.3184(11)			
Mean		2.3792			
Ca4	O4	2.4075(10)			
	O5	2.4394(9)			
	O7	2.2913(9)			
	O7	2.3744(10)			
	O8	2.3071(11)			
	O8	2.3209(11)			
Mean		2.3568			

Table 8. Selected bond distances (Å) and angles (°) for chegemite.

Atom	Occupancy	x	у	Z	$U_{ m iso}$
O8″	0.72(1)	0.7673(5)	0.52940(16)	0.03067(11)	0.0130(3)
F8	0.28(1)	0.7135(11)	0.5348(3)	0.0424(2)	0.0130(3)
H1	0.36	0.929(8)	0.505(6)	0.011(3)	0.05 fixed
H2	0.36	0.626(9)	0.533(5)	0.060(2)	0.05 fixed

Hydrogen bonds (Å): O8"-H1…O8": 2.847(7); O8"-H1…F8: 3.229(9); O8"-H2…O7: 3.200(3); O8"-H1: 0.98(2); O8"-H2: 0.99(2).

distorted than in humite. Average <Si–O> bond lengths in humite are *ca*. 0.012 Å shorter than in chegemite. This is probably also related to the closer anion packing in humite compared to chegemite.

### 5. Genesis of chegemite

The mineral association in the skarns of the Upper Chegem volcanic structure and the geological position of sedimentary carbonate rocks suggest the possible source of the xenoliths in the subvolcanic magma chamber at a depth of ~1.5 km. This hypothesis is supported by skarn formation at high temperatures (750–1000 °C) and low fluid pressures (~ 30 MPa) sharply decreased during magma ascent and volcanic eruption. The CO<sub>2</sub> fugacity also dropped sharply from  $\sim 20$  MPa to a fraction of kPa. The high temperatures of magma and lava combined with oxidation processes at low CO<sub>2</sub> fugacity led to decarbonatation and the formation of numerous high-calcium minerals characteristic of the sanidinite metamorphic facies and Korzhinskii's larnite-merwinite depth facies (Zharikov & Smulovich, 1969; Pertsev, 1977; Korzhinski, 1940; Zharikov *et al.*, 1998; Mihajlović *et al.*, 2004; Gazeev *et al.*, 2006; Callegari & Pertsev, 2007). Rapid changes in the conditions of mineral formation in the xenoliths led to incomplete reactions and to earlier mineral parageneses being commonly overgrown by secondary assemblages.

High CaO-content minerals in the contact-metasomatic rocks (skarns) formed in carbonate xenoliths show zoning characterized by increasing CaO and decreasing SiO<sub>2</sub> and



Fig. 6. [100] projection of the polyhedral structure model of chegemite. Four symmetry independent  $CaO_6$  octahedra are labelled M1 to M4. SiO<sub>4</sub> tetrahedra are black with light grey outlines. (OH, F) sites are indicated by black circles with white rims. The structure consists of two staggered olivine-like slabs separated by a boundary (along [010]) with (OH, F).

Al<sub>2</sub>O<sub>3</sub> contents from the xenolith-ignimbrite contacts inwards towards their marble cores. The thermal stability and paragenesis of CaO-rich minerals are constrained by CO<sub>2</sub> in the fluid. The volcanic and/or subvolcanic skarn formation is evidenced by numerous high-calcium minerals reflecting the strong chemical activity of CaO. A simplified scheme of primary skarn zonation in xenoliths in the ignimbrites of the Upper Chegem volcanic structure involves the following sequence: wollastonite  $\rightarrow$  rankinite (fully replaced in xenoliths 1 and 7 but preserved in xenoliths 3 and 5) + larnite  $\pm$  rondorfite  $\pm$  gehlenite  $\rightarrow$  larnite + spurrite  $\pm$  rondorfite  $\pm$  wadalite  $\rightarrow$  spurrite + calcite  $\pm$ rondorfite  $\pm$  wadalite-group minerals.

The internal zones of the skarned xenoliths, which remain close to the boundary with relic marble at the core of xenolith



Fig. 7. (OH, F) disorder in chegemite displayed with a model using anisotropic atomic displacement parameters (50 % probability) connected by bonds. (a) The structure of chegemite has an inversion centre midway between two adjacent O8 sites relating opposite moieties. In this disorder model, the two H1 sites are too close to each other to allow simultaneous occupancy. The sketches (b) to (d) show local situations of the hydrogen-bond systems contributing to the observed average disorder in (a).

Table 10. Bond angle variance for MO <sub>6</sub> octahedra and
SiO <sub>4</sub> tetrahedra in chegemite (this study) and humite.

Polyhedron	Chegemite	Humite
M1 octahedron	$(215^{\circ})^2$	$(105^{\circ})^2$
M2 octahedron	$(185^{\circ})^2$	$(99^{\circ})^{2}$
M3 octahedron	$(146^{\circ})^2$	$(75^{\circ})^2$
M4 octahedron	$(125^{\circ})^2$	$(62^{\circ})^2$
Si1 tetrahedron	$(24^{\circ})^2$	$(38^{\circ})^2$
Si2 tetrahedron	$(22^{\circ})^{2}$	$(43^{\circ})^2$

Source: Ribbe & Gibbs (1971).

1, are characterized by the appearance of calcite and the disappearance of larnite and calcio-olivine, which are incompatible with calcite. They are further characterized by the association spurrite–calcite–hydroxylellestadite–wada-lite–rondorfite and the irregular development of periclase partially or completely replaced by low-temperature brucite.

Outer skarn zones close to the contact with the volcanites contain larnite, cuspidine after larnite, calcio-olivine and spurrite, gehlenite replaced by hydrogrossular, hydroxylellestadite with, commonly, significant As impurity, rondorfite, wadalite, magnesioferrite, perovskite and lakargiite. Rare cuspidine–rustumite and cuspidine–fluorite zones (xenolith 7) may occur on the contact with the ignimbrite. These outer zones do not contain chegemite or other calcium analogous of the humite group; nor is chegemite present in internal spurrite zones with hydroxylellestadite and calcite.

In general, chegemite occurs in intermediate skarn zones comprising spurrite and larnite, with hydroxylellestadite, rondorfite and wadalite. It formed there at the expense of larnite and spurrite. Reinhardbraunsite, and its fluorine analogue  $Ca_5(SiO_4)_2F_2$ , occurring in the central part of the skarn reflect the replacement of earlyformed spurrite, larnite and chegemite at decreasing temperatures and CO<sub>2</sub> pressures combined with increasing F and OH activities (Fig. 2A, F). The earlier chegemite is replaced by distinctive poikiloblasts of reinhardbraunsite with inclusions of chegemite of different optical orientation (Fig. 2C).

The coexisting humite-group Ca-minerals have rather similar OH/F ratios (Table 1). Two parageneses can be distinguished: (1) reinhardbraunsite–chegemite with OH/ F > 1 and (2) Ca<sub>5</sub>(SiO<sub>4</sub>)<sub>2</sub>F<sub>2</sub> – F-analogue of chegemite with OH/F < 1 (Galuskina *et al.*, in preparation). F-dominant, Ca-rich humite-group minerals form earlier and at higher temperature than their OH-dominant counterparts. Possibly, the F-dominant species formed at the same time as the cuspidine that developed after larnite in the outer skarn zone.

Acknowledgements: We express our thanks to Ray L. Frost, Satoshi Matsubara and Massimo Nespolo (Associate Editor) for the constructive reviews and comments. Financial support for this project was provided by the grant RFBR project 08-05-00181(Russia) and MSHE grants N 307 3531 33 and 2 PO4D 01730 (Poland). Pádhraig Kennan helped with the English.

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Received 10 March 2009 Modified version received 2 May 2009 Accepted 25 May 2009