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Eltyubyuite, $Ca_{12}Fe^{3+}{}_{10}Si_4O_{32}Cl_6$ – the Fe^{3+} analogue of wadalite: a new mineral from the Northern Caucasus, Kabardino-Balkaria, Russia

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Abstract: Eltyubyuite (IMA2011-022), ideally $Ca_{12}Fe^{3+}{}_{10}Si_4O_{32}Cl_6$ *i.e.* the Fe^{3+} analogue of wadalite, $Ca_{12}Al_{10}Si_4O_{32}Cl_6$, was discovered in altered silicate-carbonate xenoliths in the diatreme facies of ignimbrites in the Upper Chegem caldera, Kabardino-Balkaria, Northern Caucasus, Russia. Eltyubyuite forms light-brown or yellow crystals with tetrahedral habit up to 10 μm across in rondorfite or larnite grains and commonly overgrows wadalite. Associated minerals are hydroxylellestadite, edgrewite-hydroxyledgrewite, chegemite-fluorchegemite, cuspidine, lakargiite, perovskite, kerimasite, srebrodolskite and dovyrenite. Eltyubyuite formed by contact metamorphism of calcareous sediments under sanidinite-facies conditions ($T > 800°C$, $P < 1$–2 kbar). Electron microprobe analysis (mean of 9 points) gave in weight% (s.d.): SiO_2 9.57(0.32), TiO_2 0.48(0.27), Al_2O_3 3.45(1.81), MgO 0.08(0.07), CaO 36.84(0.91), Fe_2O_3, Cl 9.60(0.48); O = Cl −2.13, Sum 98.26, and an empirical formula based on 26 cations, $Ca_{12.12}Mg_{0.04}Ti_{0.11}Fe_{9.41}Al_{1.26}Si_{2.98}O_{31.89}Cl_{5.04}$, which simplifies to $Ca_{12}(Fe^{3+},Al)_{11}Si_3O_{32}Cl_5$. Electron-back-scattered diffraction yields isometric symmetry, space group $I\bar{4}3d$ (no. 220), $a = 12.20(3)$ Å, $V = 1815.85(9)$ Å^3, $Z = 2$. Calculated density and refractive index are 3.349 g/cm^3 and 1.85, respectively. The main bands in Raman spectra of eltyubyuite are attributed to $[Fe^{3+}O_4]^{5-}$: 700–710 cm^{-1} (stretching vibrations), 460–470 cm^{-1} (bending vibrations), whereas bands <400 cm^{-1} are assigned to Ca-O and Ca-$[Fe^{3+}O_4]^{5-}$ vibrations. The mineral is named for the Balkarian village Eltyubyu, which is situated near the type locality. Eltyubyuite has subsequently been found in altered xenoliths within volcanic rocks of Eifel, Germany and Kel' Highland (volcano Shadil-Khokh), Southern Ossetia.

Key-words: eltyubyuite, mayenite, wadalite, calcium aluminium silicate, chlorine, new mineral, Raman, Caucasus, Eifel.

Introduction

The new mineral eltyubyuite (IMA2011-022), end-member $Ca_{12}Fe^{3+}{}_{10}Si_4O_{32}Cl_6$, was found as micrometre-sized inclusions in rondorfite and larnite grains from high-temperature skarns in xenoliths within ignimbrites of the Upper Chegem caldera, Northern Caucasus, Kabardino-Balkaria, Russia (Galuskin *et al.*, 2011a). It belongs to the mayenite supergroup, which comprises the mayenite (aluminates) and wadalite (silicates) groups, a proposed classification of which is currently in preparation (Galuskin *et al.*, 2012a) according to the recommendation of the CNMNC IMA (Mills *et al.*, 2009). Eltybyuite is the Fe^{3+}-analogue of wadalite, $Ca_{12}Al_{10}Si_4O_{32}Cl_6$ (Tsukimura *et al.*, 1993; Michajlović *et al.*, 2004). The proposed mayenite supergroup would include the following existing minerals: mayenite $Ca_{12}Al_{14}O_{33}$ (Hentschel, 1964), brearleyite $Ca_{12}Al_{14}O_{32}Cl_2$ (Ma *et al.*, 2011), wadalite (Tsukimura *et al.*, 1993), eltyubyuite and the recently discovered kyuygenite, $Ca_{12}Al_{14}O_{32}[(H_2O)_4Cl_2]_{\sum 6}$ (IMA2012-046; Galuskin *et al.*, 2013). Working out the mayenite supergroup classification has been slowed by the

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discovery of several new minerals currently under investigation – fluorine analogues of brearleyite and kyuygenite from pyrometamorphic rocks of the Hatrurim formation, Israel (Sharygin *et al*., 2013; Galuskin *et al*., unpublished data). In addition, re-investigation of mayenite in the holotype specimen (National Museum of Natural History, number 120045) and other specimens from the type locality of Eifel, Germany showed that it is in part the hydrated analogue of brearleyite (Galuskin *et al*., 2012a and b).

Chesnokov *et al*. (1996) described an anthropogenic phase ''demidovskite,'' $Ca_{18}Fe^{3+}{}_{15}AlSi_4O_{47}Cl_6$, space group, $I\bar{4}3d$, a = 12.20 Å, from Chelyabinsk coal dumps, Urals, Russia. Recalculation of their formula on a 26-cation basis gives approximately $Ca_{12}Fe^{3+}{}_{10.5}Al_{0.5}Si_3O_{32.5}Cl_3$, that is, ''demidovskite,'' appears to be equivalent to eltyubyuite.

The mineral is named for Eltyubyu, a famous historical Balkarian village, which is situated near the type locality. Type material is deposited in the collections of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, catalogue numbers 4027/1 (sample) and 4027/2 (thin-section). In this paper we present results of investigations of the new mineral eltyubyuite, approved by CNMNC IMA in June 2011.

Experimental techniques

The morphology and composition of mayenite-supergroup minerals were investigated using a Philips/FEI ESEM XL30/EDAX scanning electron microscope (Faculty of Earth Sciences, University of Silesia, Poland) and a CAMECA SX100 electron microprobe (Institute of Geochemistry, Mineralogy and Petrology, University of Warsaw, Poland). The following lines and standards were used for mayenite-group mineral analyses (CAMECA SX100, 15 kV, 10–20 nA, *ca.* 1 μm beam diameter): Ca$K\alpha$, Si$K\alpha$ – wollastonite; Al$K\alpha$ – orthoclase, Cl$K\alpha$ – tugtupite; F$K\alpha$ – fluorphlogopite; Fe$K\alpha$ – hematite; Mn$K\alpha$ – rhodochrosite; Ti$K\alpha$ – rutile; Mg$K\alpha$ – diopside; Na$K\alpha$ – albite.

Raman spectra of eltyubyuite from Northern Caucasus were recorded using a Dilor XY spectrometer (Bayerisches Geoinstitut, University of Bayreuth, Germany) equipped with a 1800 line mm^{-1} grating monochromator, a charge-coupled device (CCD), Peltier-cooled detector (1024×256) and an Olympus BX40 confocal microscope. The incident laser excitation was provided by a water-cooled argon laser source operating at 514.5 nm. The power at the exit of a 100x objective lens varied from 30 to 50 mW. Raman spectra were recorded in backscatter geometry in the range 100–4000 cm^{-1} with resolution of 2 cm^{-1}. Collection times of 20 s and accumulation of 5 scans were chosen. The monochromator was calibrated using the Raman scattering line of a silicon plate (520.7 cm^{-1}). Fitting of the Raman spectra was done by means of GRAMS software using a mixed Lorentzian + Gaussian function.

The small size of eltyubyuite crystals (<10 μm) required the use of single-crystal electron backscatter diffraction (EBSD) analysis to determine the crystal structure. The EBSD patterns were collected using an HKL EBSD system (HKL Technology Inc., Oxford Instruments Group) on a JEOL JSM-6480 scanning electron microscope (Institute of Materials Science, University of Silesia) using an accelerating voltage of 30 kV. Thin sections used for electron microprobe analyses were repolished using an Al_2O_3 suspension with a 20 nm particle size. To minimize charging, specimens were coated with a carbon layer several tens of nanometers thick. The calibration of the EBSD system was carried out using a Si single crystal at detector distances of 177 mm (normal working position) and 150 mm (camera retracted position). A Nordlys II camera with a resolution of 1344 × 1024 pixels was used. To improve the pattern quality, acquisition times of between 300 and 3000 ms and frame averaging were used. Depending on the detector distance and pattern collection time, up to 30 frames were averaged. The Channel5 software package (Oxford Instruments; Day & Trimby, 2004) was used for the interpretation of the EBSD patterns. For the 150 mm detector distance, only manual band detection was used as data reduction using the Hough transform was not effective. For the 177 mm detector distance, manual plus Hough (maximum 125 resolution) band detection was applied. In the match 54 reflectors and 7–11 bands were used.

Occurrence at the type locality, Upper Chegem

Eltyubyuite was discovered in altered calc-silicate xenolith 1 (numbering of xenoliths after Gazeev *et al*., 2006, and Galuskin *et al*., 2009) in ignimbrites of the Upper Chegem caldera, Northern Caucasus, Kabardino-Balkaria, Russia. Gazeev *et al*. (2006) and Galuskin *et al*. (2008, 2009) described the geological features of the area between Lakargi and Vorlan peaks, where large (> 2–3 m) carbonate xenoliths were metamorphosed under sanidinite-facies conditions (T > 800°C and P < 1–2 kbar; Zharikov *et al*., 1998; Galuskin *et al*., 2009, 2012c). The Upper Chegem caldera is the type locality of 21 new minerals, discovered since 2007: *garnet-supergroup minerals*—bitikleite $Ca_3Sb^{5+}SnAl_3O_{12}$, usturite $Ca_3Sb^{5+}ZrFe^{3+}{}_3O_{12}$, dzhuluite $Ca_3Sb^{5+}SnFe^{3+}{}_3O_{12}$, toturite $Ca_3Sn_2Fe^{3+}{}_2SiO_{12}$, irinarassite $Ca_3Sn_2Al_2SiO_{12}$ and elbrusite $Ca_3U^{+6}{}_{0.5}Zr_{1.5}Fe_3O_{12}$ (Galuskina *et al*., 2010a and b, and c; 2011a and b; Grew *et al*., 2013); *perovskite-group minerals*—lakargiite $CaZrO_3$, megawite $CaSnO_3$ (Galuskin *et al*., 2008, 2011b); *humite-group minerals*—kumtyubyuite $Ca_5(SiO_4)_2F_2$, chegemite $Ca_7(SiO_4)_3(OH)_3$, fluorchegemite $Ca_7(SiO_4)_3F_2$, edgrewite $Ca_9(SiO_4)_4F_2$, hydroxyledgrewite $Ca_9(SiO_4)_4(OH)_2$ (Galuskina *et al*., 2009, 2012; Galuskin *et al*., 2009, 2012c); and *other minerals*: calcio-olivine γ-Ca_2SiO_4 (Zadov *et al*., 2008); rusinovite $Ca_{10}(Si_2O_7)_3Cl_2$ (Galuskin *et al*., 2011c); pavlovskyite $Ca_8(SiO_4)_2(Si_3O_{10})$

(Galuskin *et al*., 2012d); vorlanite $CaUO_4$ (Galuskin *et al*., 2011d); magnesioneptunite $KNa_2LiMg_2Ti^{4+}{}_2Si_8O_{24}$ (Zadov *et al*., 2011) and aklimaite $Ca_4[Si_2O_5(OH)_2](OH)_4 \cdot 5H_2O$ (Zadov *et al*., 2012).

Eltyubyuite is found as micrometre-sized inclusions in rondorfite, $MgCa_8(SiO_4)_4Cl_2$ (Fig. 1a), with an increased content of Fe and Al in the near-contact zone (endoskarn) consisting of a larnite-bearing contact breccia. Numerous inclusions of eltyubyuite, srebrodolskite $Ca_2Fe^{3+}{}_2O_5$ and perovskite up to 3–4 μm in size and of larnite (Fig. 1b) are concentrated in the external zones of rondorfite crystals (Fig. 1a,c). Zoned crystals with wadalite core and eltyubyuite rim are commonly present (Fig. 1b). Much rarer are relatively large eltyubyuite crystals about 10 μm in size occurring on the border of larnite and rondorfite crystals (Fig. 1c-f) in altered larnite zones, where the new calcium humite minerals – edgrewite-hydroxyledgrewite and fluorchegemite are noted (Galuskina *et al*., 2012; Galuskin *et al*., 2012c). Unfortunately, the relatively large eltyubyuite crystals are restricted to the borders of rondorfite and larnite grains and form flat grains up to 5–6 μm thickness (Fig. 1e), too thin to be used for X-ray single-crystal diffraction study.

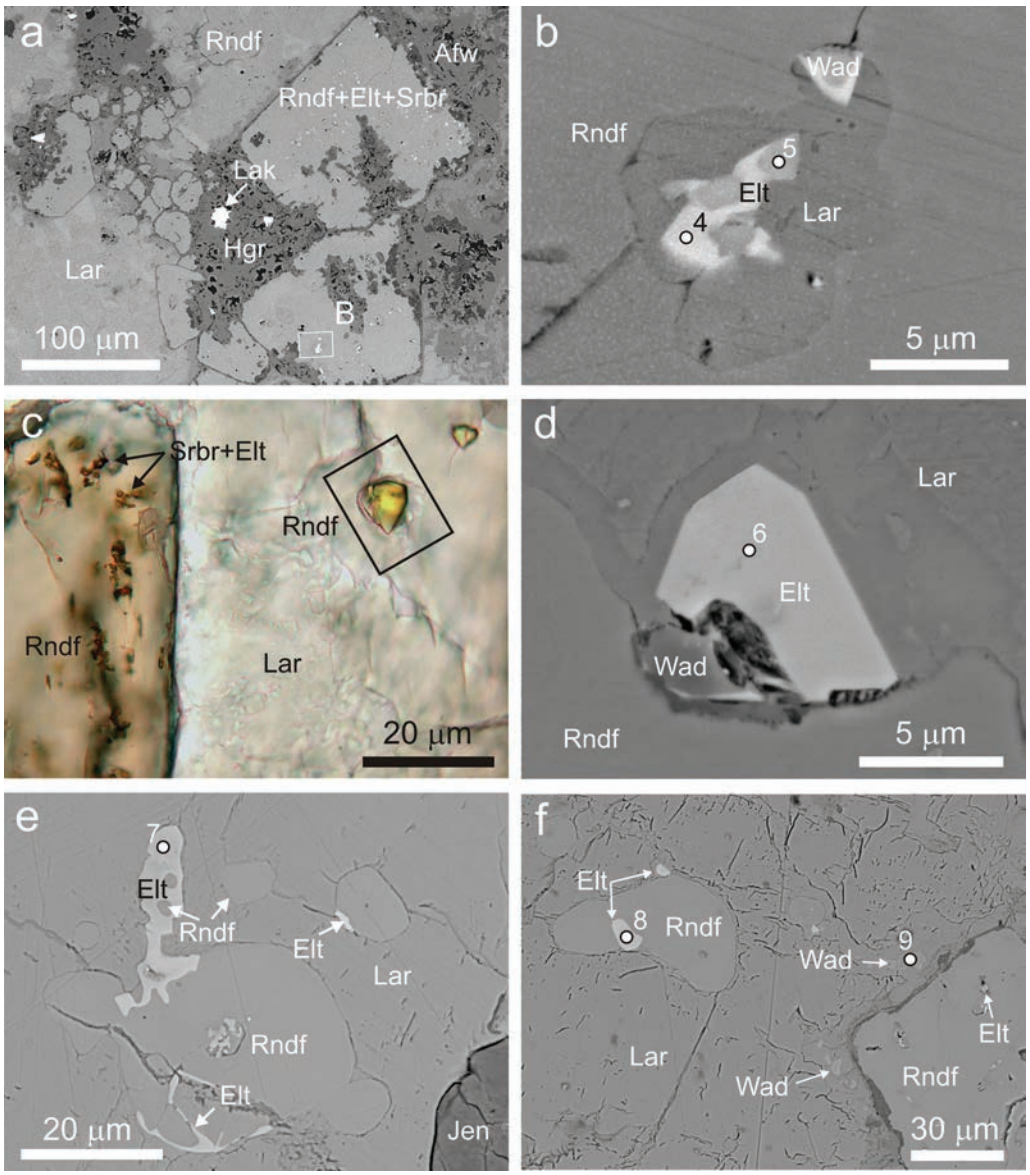

Fig. 1. (a) Backscattered electron (BSE) image of micrometer-sized inclusions of eltyubyuite and srebrodolskite (both light-grey) concentrated in external zones of rondorfite crystals. Fragment magnified in Fig. 1b is shown by frame; (b) BSE image of zoned inclusions with wadalite core and eltyubyuite rim; (c) Photomicrograph (plane polarised light) of grains of eltyubyuite and srebrodolskite < 1μm in size in external zone of rondorfite crystal and relatively large eltyubyuite crystal in larnite, fragment magnified in Fig. 1d is shown by frame; (d) BSE image of tetrahedral eltyubyuite crystal; (e) BSE image of the largest eltyubyuite crystal found in altered xenoliths of the Upper Chegem caldera; (f) BSE image of wadalite crystals in larnite in close proximity to contact with rondorfite, whereas eltyubyuite inclusions are in rondorfite. Elt – eltyubyuite, Lar – larnite, Srbr – srebrodolskite, Lak – lakargiite, Hgr – katoite-grossulare series, Rndf – rondorfite, Afw – afwillite, Wad – wadalite.

High-temperature minerals in rocks containing eltyubyuite are larnite, rondorfite, wadalite, hydroxylellestadite, edgrewite-hydroxyledgrewite, chegemite-fluorchegemite, cuspidine. Lakargiite, perovskite, kerimasite, srebrodolskite and dovyrenite are accessory minerals. Dovyrenite, $Ca_6Zr[Si_2O_7]_2(OH)_4$ had been reported only from skarns of the Dovyren massif, Pribaikalie, Russia (Galuskin *et al.*, 2007). Wadalite is widely distributed in altered larnite skarn zone; its concentration in larnite grains near their contacts with rondorfite crystals is noteworthy, whereas eltyubyuite, srebrodolskite and perovskite inclusions are enclosed in rondorfite (Fig. 1f). Bultfonteinite, hillebrandite, jennite, afwillite, zeophyllite, reinhardbraunsite, killalaite, trabzonite, grossular–katoite, hydrocalumite and minerals of the ettringite series are widespread, secondary low-temperature minerals.

We attribute the formation of the Fe^{3+} minerals eltyubyuite and srebrodolskite to oxidation of Fe^{2+} in rondorfite, an early formed mineral that in the eltyubyuite-bearing samples has a relatively high Fe content, up to 2–3 wt. % FeO substituting for Mg at an unusual tetrahedral site (Mihajlović *et al.*, 2004).

Occurrences in the Shadil-Khokh volcano and the Eifel

In 2010 one from the authors (Viktor Gazeev) of the eltyubyuite discovery found xenoliths up to 3 m across with rondorfite in andesite-dacite lava of Shadil-Khokh volcano, Kel' Highland, Southern Ossetia, on the southern flank of the Greater Caucasian Mountain Range (Gazeev *et al.*, 2012). During field work in this area in the summer of 2012 we collected samples from this xenolith. Tetrahedral eltyubyuite crystals were found in a thin vein (~3 mm) enriched with magnetite, magnesioferrite, srebrodolskite, harmunite and cuspidine (Fig. 2a; analysis 11, Table 1) cutting larnite-rondorfite rock with subordinate wadalite and fluorellestadite. Harmunite, $CaFe_2O_4$, is a new mineral described recently in pyrometamorphic larnite rocks of the Hatrurim formation in Jabel Harmun, Palestinian Autonomy, Israel (Galuskina *et al.*, 2013).

Eltyubyuite was found in xenoliths enriched with rondorfite and fluorellestadite from volcanic rocks of Bellerberg, Eifel district, Rhineland-Palatinate, Germany, where it forms overgrowths on mayenite–wadalite crystals (Fig. 2b; analysis 12, Table 1). In addition to minerals of the mayenite supergroup, kerimasite, magnetite, magnesioferrite, srebrodolskite and Mn-bearing harmunite were identified.

Optical and physical properties of type material

Unfortunately, we were not able to measure standard physical properties of eltyubyuite because of small crystal size. Eltyubyuite ranges from yellow to light-brown and brown in transmitted light under the optical microscope, its refractive index is higher than the refractive indices of larnite (1.71–1.73), which is confirmed by theoretical calculations of refractive index on the base of Gladstone-Dale relation for the grain shown in Fig. 1d: $n = 1.85$ (analysis 3, $Fe_2O_3 = 38.26$ wt. %, Table 1). The calculated density is 3.349 g cm^{-3} for analysis 1 in Table 1.

Chemical composition

Eltyubyuite forms a partial solid solution with wadalite (Table 1, Fig. 3). There is extensive Al ↔ Fe^{3+} isomorphism, whereas Cl and Si contents remain approximately constant, which allows an empirical crystal-chemical formula to be given for the wadalite-eltyubyuite solid solution as $Ca_{12}(Fe^{3+}, Al)_{11}Si_3O_{32}Cl_5$. A compositional gap in solid solution (Fig. 3) is manifested by overgrowths of eltyubyuite on wadalite cores (as illustrated in Fig. 1b, with $X_{Fe} = Fe/(Al + Fe)$ around 0.10 in wadalite core and 0.85 in the rim). This compositional gap does not imply the existence of a miscibility gap. By analogy with wadalite, for which compositions close to the end-member $Ca_{12}Al_{10}Si_4O_{32}Cl_6$ (analysis 7, Table 1) exist, we give the

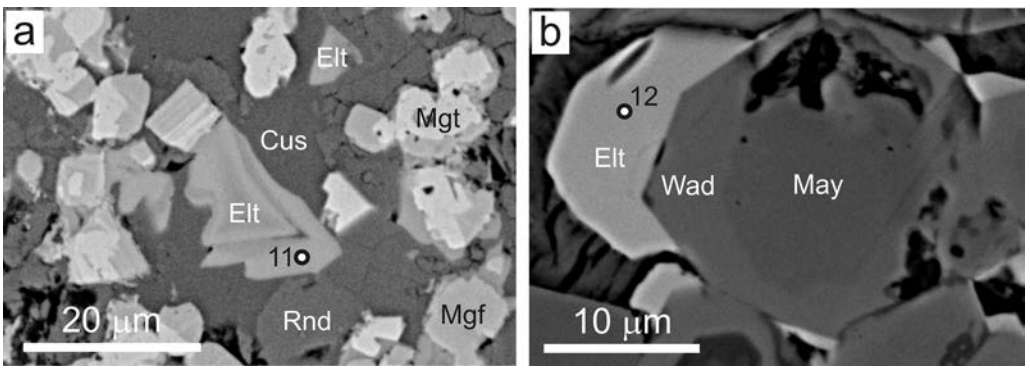

Fig. 2. (a) BSE image of tetrahedral crystal of eltybyuite in magnetite-magnesioferrite vein from rondorfite rock from Shadil-Khokh xenolith; (b) BSE image of pseudo-tris-octahedral crystal of mayenite-wadalite (combination of two tris-tritetrahedra {211} and {21$\bar{1}$}) with eltybyuite epitaxial overgrowth from Eifel xenolith. Elt – eltyubyuite, Cus – cuspidine, Mgf – magnesioferrite, Mgt – magnetite, Rnd – rondorfite, Wad – wadalite, May – mayenite.

Table 1. Chemical composition of eltyubyuite and wadalite.

wt.%	1	s.d.	Range	2	3	4	5	6	7	8	9	10	11	12
TiO_2	0.48	0.27	0.18–0.88	0.24	0.45	0.26	0.25	0.64	0.11	0.27	0.76	0.25	0.56	0.21
SiO_2	9.57	0.32	9.22–10.05	10.07	9.77	10.49	15.35	10.27	8.83	10.15	8.72	14.25	10.06	9.44
Al_2O_3	3.45	1.81	1.60–6.86	3.62	11.51	4.31	27.50	11.15	5.49	10.13	28.45	28.69	2.23	1.49
Fe_2O_3	40.37	1.90	37.36–43.08	40.57	30.52	39.52	4.81	30.30	39.21	31.71	10.98	4.09	42.54	43.69
MgO	0.08	0.07	0.01–0.20	0.07	n.d.	n.d.	0.41	n.d.	n.d.	n.d.	n.d.	n.d.	0.03	0.06
CaO	36.84	0.91	35.85–38.03	37.72	38.52	37.03	41.92	38.26	37.23	37.82	41.93	41.83	35.02	36.23
MnO	n.d.			n.d.	n.d.	n.d.	0.23	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Na_2O	n.d.			0.00	n.d.	0.03	0.04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
SO_3	n.d.			n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.05
Cl	9.60	0.48	8.84–10.08	9.12	9.66	9.50	11.77	9.99	9.18	9.95	8.82	12.39	9.70	9.98
	100.39			101.41	100.43	101.14	102.28	100.60	100.06	100.02	99.65	101.50	100.15	101.14
$-O = Cl$	2.13			2.03	2.15	2.11	2.62	2.22	2.04	2.21	1.96	2.75	2.15	2.25
	98.26			99.38	98.28	99.03	99.66	98.38	98.02	97.81	97.69	98.75	98.00	98.90
Formulae for 26 cations														
Ca	12.222			12.280	12.206	12.102	11.994	12.155	12.233	12.157	12.162	12.073	11.799	12.136
Na						0.018	0.021							
Mn^{2+}							0.052							
X	12.222			12.280	12.206	12.120	12.066	12.155	12.233	12.157	12.162	12.073	11.799	12.136
Fe^{3+}	9.407			9.277	6.792	9.071	0.967	6.760	9.048	7.158	2.236	0.829	10.063	10.276
Al	1.259			1.296	4.012	1.549	8.655	3.898	1.985	3.581	9.075	9.108	0.827	0.548
Si	2.963			3.060	2.889	3.200	4.099	3.044	2.708	3.044	2.359	3.839	3.163	2.951
Ti^{4+}	0.112			0.055	0.100	0.060	0.050	0.143	0.026	0.060	0.155	0.051	0.133	0.048
Mg	0.037			0.032	0.001		0.163				0.013	0.100	0.014	0.029
S^{6+}														0.012
Z	13.778			13.720	13.794	13.880	13.934	13.845	13.767	13.843	13.838	13.927	14.201	13.864
Cl	5.038			4.697	4.841	4.911	5.327	5.021	4.769	5.057	4.048	5.656	5.171	5.288
O (calc)	31.889			32.053	31.971	32.106	32.287	32.006	31.856	31.945	32.146	32.031	32.155	31.791

1–eltyubyuite small inclusions in rondorfite, Fig. 1a, mean of $n = 9$ analyses; 2–eltyubyuite inclusion on the larnite-rondorfite boundary, $n = 5$; 3–big eltyubyuite crystal used for Raman investigation, Fig. 1d, $n = 5$; 4, 5–zoned eltyubyuite (4) and wadalite (5) crystals on Fig. 1b; 6–eltyubyuite crystal in Fig. 1d; 7–eltyubyuite crystal in Fig. 1e; 8–eltyubyuite crystal in Fig. 1f, 9–wadalite crystal in Fig. 1f; 10–wadalite crystal from xenolith number 3 with composition close to wadalite end-member; 11–eltyubyuite from Southern Ossetia, Fig. 2a; 12–eltyubyuite from Eifel, Germany, Fig. 2b; n.d. – not detected

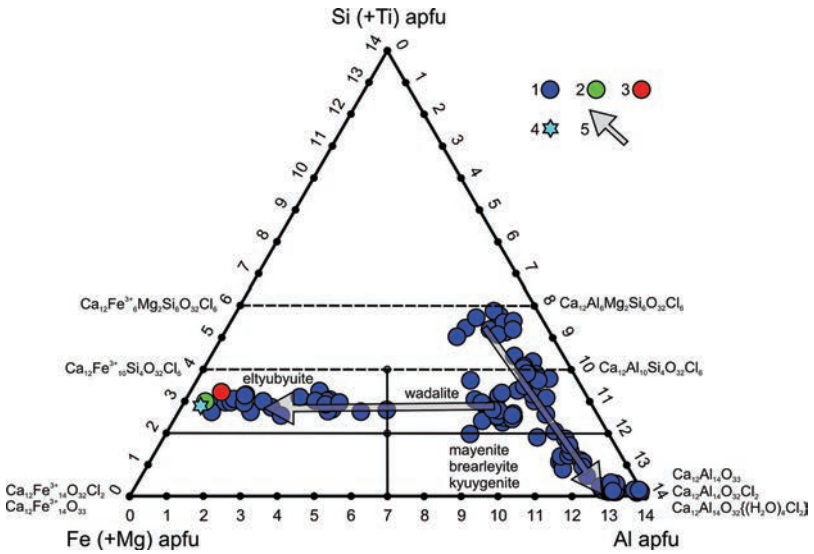

Fig. 3. Plot on a Fe(+Mg)-Si(+Ti)-Al diagram of point analyses of minerals of the mayenite supergroup from xenoliths of the Upper Chegem caldera (1), the Shadil-Khokh volcano (2) and Eifel (3) as well as of ''demidowskite'' (4); 5–arrow showing compositional trends.

end-member crystal-chemical formula of eltyubyuite as $Ca_{12}Fe^{3+}{}_{10}Si_4O_{32}Cl_6$.

Two compositional trends (Fig. 3) are characteristic for minerals of the mayenite supergroup from altered xenoliths in ignimbrites of the Upper Chegem caldera: (1) at relatively constant Fe/Al ratio from wadalite with 5–6 Si and up to 2 Mg per formula unit to Si-poor wadalite, and then to the nominally Si-free phase, kyuygenite, which corresponds compositionally to hydrated brearleyite; (2) at relatively constant Si content from wadalite to eltyubyuite.

Crystallographic properties of type material

Structural data for eltyubyuite were obtained using EBSD because of the small size of the crystals. Fitting of the EBSD patterns (Fig. 4) was performed using structural data of both the anthropogenic analogue of eltyubyuite, ''demidovskite'', $I\bar{4}3d$, a = 12.20 Å (Chesnokov *et al.*, 1996) and wadalite, a = 12.014–12.034 Å, $I\bar{4}3d$ (Tsukimura *et al.*, 1993; Michajlović *et al.*, 2004). The fit yields isometric symmetry, space group $I\bar{4}3d$, (no. 220), $a = 12.20(3)$ Å, $V = 1815.85(9)$ Å^3, $Z = 2$ (MAD = 0.26°). Calculated powder XRD data for eltyubyuite (Cu$K\alpha$, Debye-Scherrer geometry, POWDER CELL program calculation, Kraus & Nolze, 1996), together with observed data for wadalite (Michajlović *et al.*, 2004) and ''demidovskite'' (Chesnokov *et al.*, 1996) are listed in Table 1S (supplementary material, freely available online from the journal GSW website at http://eurjmin.geoscienceworld.org).

Raman spectra of type material

Raman spectra were obtained of eltyubyuite with maximum Fe^{3+} content (spectrum 2, Fig. 5; Fig. 1b, point 4) and

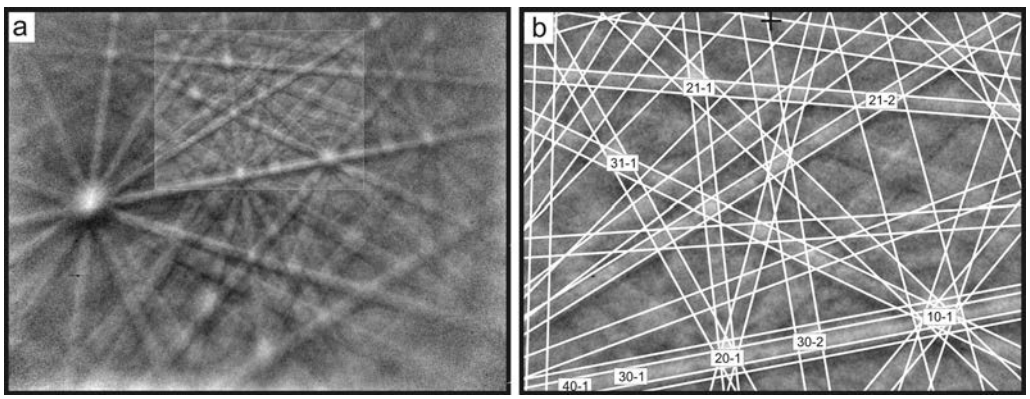

Fig. 4. (a) Electron backscattered diffraction pattern of eltyubyuite for detector distance 177 mm, inset shows Kikuchi lines for detector distance 150 mm, performed at point 4 (Fig. 1b); (b) Fitting result of diffraction patterns of eltyubyuite for detector distance 150 mm.

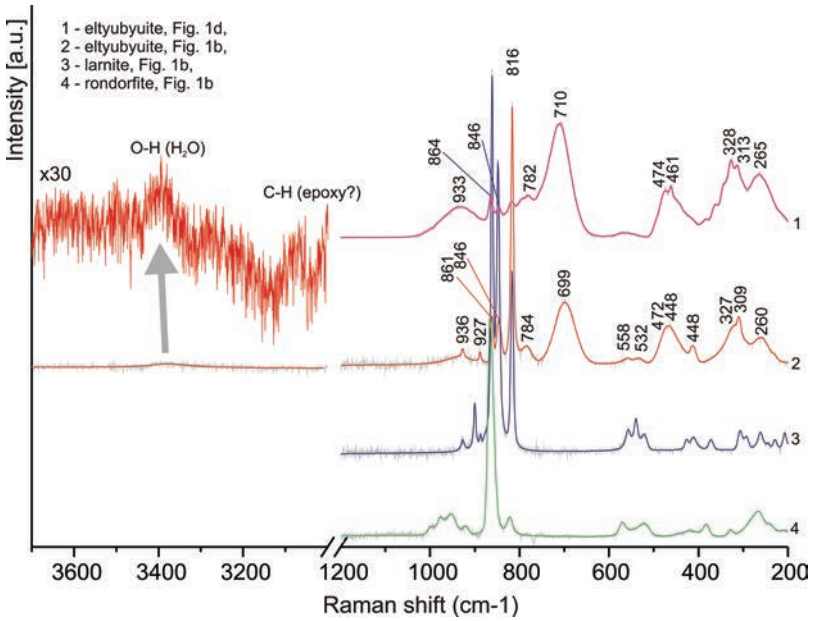

Fig. 5. Raman spectra of eltyubyuite and associated minerals.

high Al content (spectrum 1, Fig. 5; Fig. 1d, point 6). We used confocal regime during Raman spectroscopy study, but we were not successful in completely eliminating the effect of surrounding minerals, so there are bands from larnite and rondorfite above 800 cm^{-1} in the spectra of eltyubyuite (Fig. 5). The main bands in the eltyubyuite spectra are attributed to $[FeO_4]^{5-}$: 700–710 cm^{-1}–stretching vibrations, 460–470 cm^{-1}–bending vibrations. Bands at less than 400 cm^{-1} are attributed to vibrations of Ca-O and Ca-$[FeO_4]$. A weak band near 770–780 cm^{-1} corresponds to Al-O stretching vibrations in $[AlO_4]^{5-}$; a band in this position is prominent in the mayenite spectra (Galuskin *et al*., 2012c). Very weak bands in the OH region are occasionally noted on the Raman spectra of eltyubyuite (Fig. 5).

Relationship to other minerals in the mayenite supergroup

The general crystal-chemical formula of mayenite-supergroup minerals can be given as: $X_{12}({}^{IV}T1_{8\text{-}x}{}^{VI}T'1_x){}^{IV}T2_6O1_{24}O2_{8\text{-}x}(O'2H)_{3x}\{W_{6\text{-}3x}\}$, where x= 0–2, *X* is the Ca polyhedral site; *T1* and *T'1* (modified *T1* site) are distorted tetrahedral and octahedral sites, respectively, centred by Al and other cations such as Fe^{3+}, Mg, Ti, Si, Fe^{2+}. . .; *T2* is a regular tetrahedron filled by Al, Si and Fe^{3+} (Galuskin *et al*., 2012a and b). The *W* site is confined to the centre of a structural cage ∼ 5Å in diameter (Sakakura *et al*., 2011). At present all known minerals of the mayenite supergroup correspond to the formula with x = 0: $X_{12}{}^{IV}T1_8{}^{IV}T2_6O1_{24}O2_8\{W_6\}$, which simplifies to $X_{12}T_{14}O_{32}\{W_6\}$(Galuskin *et al*., 2012a): mayenite (=brearleyite) $Ca_{12}Al_{14}O_{32}\{Cl_2\square_4\}$(Hentschel, 1964; Ma *et al*., 2011; Galuskin *et al*., 2012a and b), kyuygenite $Ca_{12}Al_{14}O_{32}\{Cl_2(H_2O)_4\}$ (Galuskin *et al*., 2013), wadalite $Ca_{12}(Al_{10}Si_4)O_{32}Cl_6$ (Tsukimura *et al*., 1993; Mihajlović *et al*., 2004), eltyubyuite $Ca_{12}(Fe^{3+}{}_{10}Si_4)O_{32}Cl_6$ (Galuskin *et al*., 2011a). The end-member $Ca_{12}Al_{14}O_{30}(OH)_6$, which corresponds to a general formula with x = 2: $X_{12}({}^{IV}T1_6{}^{VI}T'1_2){}^{IV}T2_6O1_{24}\,O2_6(O'2H)_6$, which simplifies to $X_{12}T_{14}O_{30}(OH)_6$, constitutes up to 38 mol% of mayenite from Eifel, Germany (Galuskin *et al*., 2012b).

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