Mayenite supergroup, part I: Recommended nomenclature

Evgeny V. Galuskin[1,*], Frank Gfeller[2], Irina O. Galuskina[1], Thomas Armbruster[2], Radu Bailau[1] and Viktor V. Sharygin[3,4]

[1] Faculty of Earth Sciences, Department of Geochemistry, Mineralogy and Petrography, University of Silesia, Będzińska 60, 41–200 Sosnowiec, Poland
*Corresponding author, e-mail: evgeny.galuskin@us.edu.pl
[2] Mineralogical Crystallography, Institute of Geological Sciences, University of Bern, Freiestrasse 3, 3012 Bern, Switzerland
[3] V.S. Sobolev Institute of Geology and Mineralogy, Siberian Branch of the RAS, 3 prosp. Akad. Koptyuga, Novosibirsk, 630090, Russia
[4] Russia and Department of Geology and Geophysics, Novosibirsk State University, Pirogova Street 2, Novosibirsk 630090, Russia

Abstract: The mayenite supergroup, accepted by the IMA-CNMNC (proposal 13-C), is a new mineral supergroup comprising two groups of minerals isostructural with mayenite (space group No. 220, $I\bar{4}3d$, $a \approx 12$ Å) with the general formula $X_{12}T_{14}O_{32-x}(OH)_{3x}[W_{6-3x}]$: the mayenite group (oxides) and the wadalite group (silicates), for which the anionic charge over 6 W sites is -2 and -6, respectively. Currently only minerals dominated by end-members with x = 0 and the simplified formula $X_{12}T_{14}O_{32}[W_6]$ have been reported. The mayenite group includes four minerals: (1) chlormayenite, $Ca_{12}Al_{14}O_{32}[\square_4Cl_2]$; (2) chlorkyuygenite, $Ca_{12}Al_{14}O_{32}[(H_2O)_4Cl_2]$; (3) fluormayenite, $Ca_{12}Al_{14}O_{32}[\square_4F_2]$; and (4) fluorkyuygenite, $Ca_{12}Al_{14}O_{32}[(H_2O)_4F_2]$. The wadalite group comprises the two mineral species wadalite, with the end-member formula $Ca_{12}Al_{10}Si_4O_{32}[Cl_6]$, and eltyubyuite, with the end-member formula $Ca_{12}Fe^{3+}_{10}Si_4O_{32}[Cl_6]$. Current research on minerals and synthetic compounds indicates that minerals close to the composition of ideal end-members, such as $Ca_{12}Fe^{3+}_{10}Si_4O_{32}[F_6]$, $Ca_{12}Si_9Mg_5O_{32}[Cl_6]$ and $Ca_{12}Al_{14}O_{30}(OH)_6[\square_6]$, could be found in Nature.

A detailed re-examination of the type specimens of mayenite, originally described as $Ca_{12}Al_{14}O_{33}$, indicates that $Ca_{12}Al_{14}O_{32}[\square_4Cl_2]$ is its correct end-member formula. Consequently, we are redefining and renaming mayenite as chlormayenite, $Ca_{12}Al_{14}O_{32}[\square_4Cl_2]$, whereas the name mayenite would be reserved for a potential mineral with the end-member composition $Ca_{12}Al_{14}O_{32}[\square_5O]$. As a consequence, the mineral brearleyite, $Ca_{12}Al_{14}O_{32}[\square_4Cl_2]$, described in 2011 is identical with chlormayenite and is therefore discredited. By analogy with chlormayenite we changed the name of kyuygenite into chlorkyuygenite.

Key-words: mayenite supergroup nomenclature; mayenite group; wadalite group; chlormaynite; fluormayenite; chlorkyuygenite; fluorkyuygenite; eltyubyuite; brearleyite; calcium aluminate.

Introduction

Since 2010, five minerals related to mayenite, $Ca_{12}Al_{14}O_{32}[\square_5O]$ or $Ca_{12}Al_{14}O_{33}$, (Hentschel, 1964), and wadalite, $Ca_{12}Al_{10}Si_4O_{32}[Cl_6]$ or $Ca_{12}Al_{10}Si_4O_{32}Cl_6$ (Tsukimura *et al.*, 1993), have been described: brearleyite, $Ca_{12}Al_{14}O_{32}[\square_4Cl_2]$ (IMA2010-062; Ma *et al.*, 2011); eltyubyuite, $Ca_{12}Fe^{3+}_{10}Si_4O_{32}[Cl_6]$ (IMA2011-022; Galuskin *et al.*, 2013; Gfeller *et al.*, 2015); kyuygenite (chlorkyuygenite, see below), $Ca_{12}Al_{14}O_{32}[(H_2O)_4Cl_2]$ (IMA2012-046; Galuskin *et al.*, 2015a); fluormayenite, $Ca_{12}Al_{14}O_{32}[\square_4F_2]$ (IMA2013-019; Galuskin *et al.*, 2015b); and fluorkyuygenite, $Ca_{12}Al_{14}O_{32}[(H_2O)_4F_2]$ (IMA2013-043; Galuskin *et al.*, 2015b). Structural studies (Tsukimura *et al.*, 1993; Mihajlović *et al.*, 2004;

Galuskin *et al.*, 2012b, 2015a and 2015b; Gfeller *et al.*, 2015) show that all these minerals are closely related despite belonging to different classes (oxides and silicates), and thus naturally constitute a group. The structures of mayenite and related minerals resemble the structures of katoite–grossular solid solutions, but the minerals differ in that octahedral sites are not always present, so minerals isostructural with mayenite and wadalite were not taken into consideration when preparing the new garnet supergroup nomenclature (Grew *et al.*, 2013). All new mineral discoveries listed above required a classification of minerals with the mayenite-type structure. Thus, an informal working group was created with the aim solving this task. Subsequently, this group devised a nomenclature of the mayenite

supergroup, which was approved by CNMNC IMA in March 2014 (proposal 13-C; Williams *et al.*, 2014).

The present paper is the first part of the series of papers on the mayenite supergroup minerals. The second paper of this series describes the new mineral chlorkyuygenite (Galuskin *et al.*, 2015a), whereas the third paper provides 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 (Galuskin *et al.*, 2015b). In the fourth paper we present new X-ray single-crystal structure data for eltyubyuite (Gfeller *et al.*, 2015).

The synthetic analogue of mayenite is an important component of cement where it is known as calcium aluminate, $12CaO \cdot 7Al_2O_3$, long before its discovery as a mineral (Bussem & Eitel, 1936). The structure of mayenite, space group $I\bar{4}3d$, $a \approx 12$ Å, was first determined using synthetic material by Bussem & Eitel (1936). Unusual physical and chemical properties of mayenite are related to its large zeolite-like cages (Bartl & Scheller, 1970; Boysen *et al.*, 2007). The mayenite structure contains 32 framework oxygens linked to calcium and aluminium and a "free", 33rd oxygen disordered over the six cages and easily mobilized from one cage to another (Matsuishi *et al.*, 2009; Boysen *et al.*, 2010; Janek & Lee, 2010; Hayashi, 2011). Thus, synthetic mayenite, $Ca_{12}Al_{14}O_{32}[\square_5O]$, is actually an anion conductor. This migrating oxygen anion has the characteristics of a radical, which explains rapid hydration or hydroxylation in a humid environment (*e.g.* Raab & Pöllman, 2011). Kurashige *et al.* (2008) reported a unique case in which the oxygen in the cages was ordered and the symmetry reduced to $I\bar{4}2m$ in mayenite crystals grown by the Czochralski method. In chlorine-bearing mayenite (chlormayenite, see below), $Ca_{12}Al_{14}O_{32}[\square_4Cl_2]$, oxygen and one vacancy in the cages are replaced by two Cl^-, which are coordinated by two Ca^{2+} (Fig. 1).

In the main section of this paper we present: (1) a review of recent crystallographic studies leading to a new structural formula for mayenite and related minerals, (2) a redefinition of mayenite and discreditation of brearleyite based on a reinvestigation of the holotype specimen and additional samples from the type locality, (3) renaming of kyuygenite, and (4) basic concepts for the classification of mayenite and related minerals with practical guidelines for its application. In addition, we propose a mayenite supergroup comprising the mayenite group (oxides) and the wadalite group (silicates), consistent with the hierarchy of mineral groupings advocated by Mills *et al.* (2009).

Structure and crystal-chemical formula of mayenite and related minerals

The structure of minerals of the mayenite supergroup is based on a tetrahedral framework $\{T_{14}O_{32}\}$, which forms six structural cages (Büssem & Eitel, 1936). Depending on the type of tetrahedrally coordinated cations in the
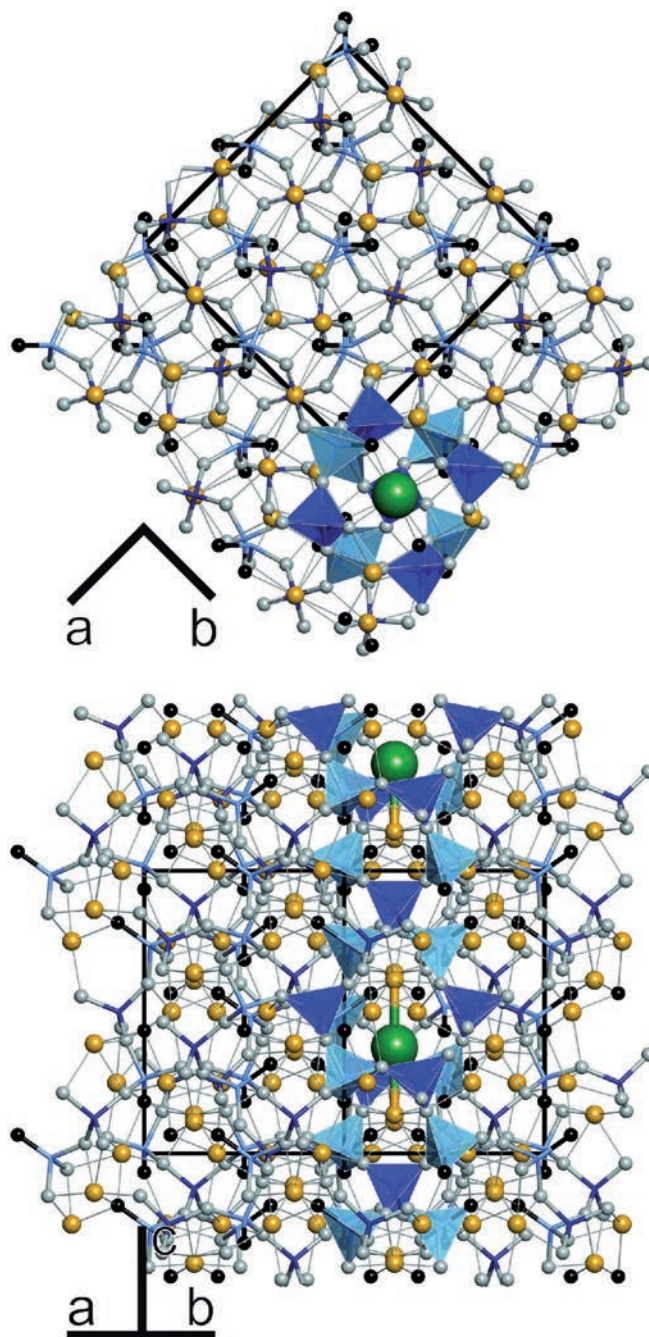

Fig. 1. Overall view of chlormayenite structure. Chlorine (green sphere) coordinated by two calcium cations (pale spheres). The two different types of aluminum tetrahedra are distinguished by light- and dark blue colour. Oxygen sites shared by two AlO_4 tetrahedra are grey whereas oxygen sites only bonded to one tetrahedron are in black.

framework ($T = Al^{3+}$, Fe^{3+}, Mg^{2+}, Si^{4+} Ti^{4+}), the negative framework charge ranges between –18 and –22. Each of the structural cages is occupied by two Ca^{2+} (+24), which results in an excess positive charge ranging between +2 (mayenite group) and +6 (wadalite group). The charge is balanced by anions at the central [*W*] site of the structural cages (Fig. 1).

A more general crystal chemical formula of minerals with the mayenite-type structure can be written as: $X_{12}\{^{IV}T1_{8-x}{}^{VI}T'1_x\}^{IV}T2_6O1_{24}O2_{8-x}(O2aH)_{3x}[W_{6-3x}]$ (Galuskin *et al.*, 2012a and 2012b), where x = 0–2, X is Ca polyhedral; $T1$ and $T'1$ (modified $T1$ site) are distorted tetrahedral and octahedral sites, respectively, centered by Al and other cations such as Fe^{3+}, Mg, Ti, Si . . . ; $T2$ is a regular tetrahedron filled by Al, Si and Fe^{3+}. The W site is confined to the centre of a structural cage $\sim$ 5 Å in diameter (Sakakura *et al.*, 2011). But this generalized formula is not practical to use for classifying minerals related to mayenite because of the large uncertainties in distinguishing the cation occupancies of the tetrahedral $T1$ and $T2$ sites. For example, Si in wadalite can occupy either $T1$ or $T2$ (Tsukimura *et al.*, 1993; Fujuta *et al.*, 2001; Mihajlović *et al.*, 2004). Instead we propose to use a simplified crystal chemical formula, $X_{12}T_{14}O_{32-x}(OH)_{3x}[W_{6-3x}]$, with the combined tetrahedral sites $T1$ and $T2$. In the absence of a direct determination of H_2O, formulae for mayenite and related minerals have been calculated from chemical analyses assuming 26 total cations, ^{O2a}OH as 3 × [(Σcation charge – 64) – (Cl + F + OH)] ≈ 3 × [2– (Cl + F + OH)] (only for a weakly hydroxylated phase; Galuskin *et al.*, 2012b), ^{W}OH from charge balance, and H_2O as 6 – (F + Cl + OH) [for a highly hydrated phase]. At present, only compositions dominated by end-members with x = 0, *i.e.*, $X_{12}T_{14}O_{32}[W_6]$ are known as minerals.

Renaming of mayenite as chlormayenite

Hentschel (1964) introduced mayenite as the calcium aluminate, $12CaO\cdot7Al_2O_3$ or $Ca_{12}Al_{14}O_{33}$, which he named for Mayen, a town near the type locality of Ettringer Bellerberg, Eifel, Germany, where mayenite occurs in altered calcsilicate xenoliths in volcanic rock. His proposed formula was based on analogy with the synthetic compound, which had been well studied as a component of cement clinker (*e.g.*, Büssem & Eitel, 1936). However, Hentschel (1964) admitted his wet-chemical analysis was unsatisfactory due the paucity and impurity of the analyzed material. Hentschel (1987) reported new analyses

containing several wt. % Cl and suggested that mayenite could be a solid solution between $Ca_{12}Al_{14}O_{33}$ and $Ca_{12}Al_{14}O_{32}Cl_2$. It is important to note that the oxide $Ca_{12}Al_{14}O_{33}$ is highly reactive in the presence of H_2O and decomposes rapidly by forming hydrates of calcium aluminates like $Ca_2AlO_5\cdot8H_2O$ or $CaAlO_4\cdot10H_2O$ (Raab & Pöllman, 2011). Thus, preservation of $Ca_{12}Al_{14}O_{33}$ at the type locality, given its association with ettringite $Ca_6Al_2(SO_4)_3(OH)_{12}(H_2O)_{26}$ and portlandite $Ca(OH)_2$ (Hentschel, 1987), seems highly unlikely.

We studied the holotype specimen No. M5026/86 from the Mineral Museum, University of Cologne, Germany and a type specimen, No. 120045, of mayenite and brownmillerite from the National Museum of Natural History, Washington, D.C., USA. Both are fragments of an altered carbonate xenolith from the Ettringer-Bellerberg volcano. In the holotype specimen M5026/86 mayenite occurs as grains up to 80–100 μm in size within a larnite zone containing abundant brownmillerite and rare ternesite crystals (Fig. 2). Secondary minerals include katoite–grossular, ettringite, and afwillite. In addition, mineral species discovered decades after mayenite (*e.g.,* jasmundite, lakargiite, srebrodolskite, shulamitite, ye'elimite) were found in other zones of this sample (*e.g.* Sharygin *et al.*, 2013).

Most of the type specimen No. 120045 is composed of a low-temperature mineral association (katoite–grossular, ettringite, afwillite, jennite, portlandite) with relics of brownmillerite and mayenite completely replaced by katoite–grossular. Mayenite up to 20 μm across is preserved only in grey fragments of rock together with spurrite, larnite, hydroxylellestadite, and brownmillerite (Fig. 3). Spurrite may indicate that specimen No. 120045 belongs to the central part of the mayenite-bearing xenolith.

We did not attempt to fully investigate the holotype mayenite, but instead compared holotype mayenite with the mayenite from the type locality, for which composition and structural data were obtained (Galuskin *et al.*, 2012b). Raman spectra of these mayenite samples are practically identical (Fig. 4). The empirical crystal chemical formula of holotype mayenite (M5026/86), $Ca_{11.996}(Al_{13.572}Fe^{3+}_{0.418}$ $Si_{0.007}Mg_{0.006})_{\Sigma14.003}(O_{31.375}\square_{0.625})_{\Sigma32}(\square_{4.124}$ (OH)$_{1.876})$ $_{\Sigma6}[Cl_{1.375}\square_{4.625}]_{\Sigma6}$ (Table 1, analysis 1), and type mayenite
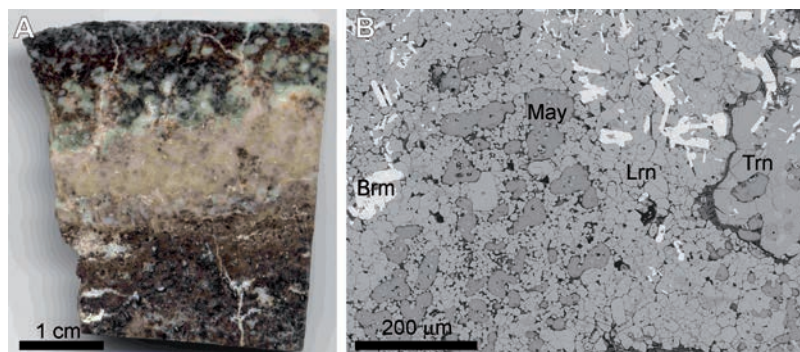

Fig. 2. A. Holotype specimen M5026/86, Mineral Museum, University of Cologne, Germany. Greenish zone (upper fragment of specimen) is enriched in chlormayenite crystals up to 100 μm in size; B. Backscattered-electron image of the polished mount prepared from the greenish zone. Lrn - larnite, May - chlormayenite, Brm - brownmillerite, Trn - ternesite.
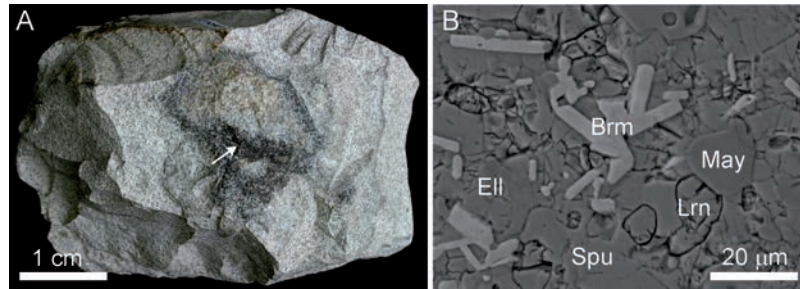
Fig. 3. A. Type specimen No. 120045, National Museum of Natural History, Washington, D.C., USA. Grey fragments of rock are enriched in chlormayenite crystals less than 20 µm in size; B. Backscattered-electron image of the polished mount prepared from the grey fragment of rock indicated by the arrow in Fig. 2A (BSE), Ell - hydroxylellestadite, Lrn - larnite, May – chlormayenite, Brm - brownmillerite, Spu - spurrite.
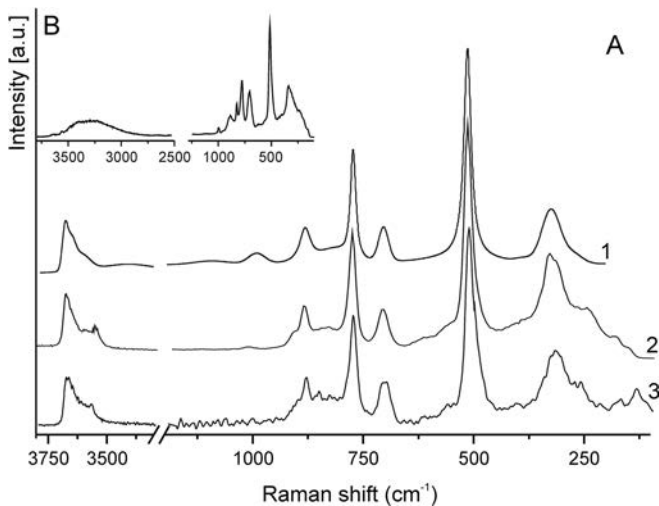

Fig. 4. A. Raman spectra of chlormayenite from Eifel: 1–type-locality chlormayenite (Bernd Ternes' [cf. 4/5] sample), 2–holotype chlormayenite (M5026/86), 3–type chlormayenite (120045). B. Raman spectrum of chlorkyuygenite from Upper Chegem Caldera. Spectrum 1 was obtained using Dilor XY Raman spectrometer (514 nm), spectrum 2, 3 and chlorkyuygenite spectrum were obtained using WITec confocal CRM alpha 300 Raman microscope (532 nm). a.u. – arbitrary units.

(No. 120045), $(Ca_{12.069}Mn^{2+}_{0.004})_{\Sigma 12.073}(Al_{13.324}Fe^{3+}_{0.562}$ $Mg_{0.022}Si_{0.015}\,Ti^{4+}_{0.004})_{\Sigma 13.931}(O_{31.249}\square_{0.751})_{32}\,(\square_{3.747}$ $(OH)_{2.253})_{\Sigma 6}\,[Cl_{1.172}\square_{4.828}]_{\Sigma 6}$ (Table 1, analysis 2), are very close to the composition of type-locality mayenite (Bernd Ternes' sample), $Ca_{12}(Al_{13.513}Fe^{3+}_{0.465}\,Mg_{0.012}$ $Si_{0.007}Ti^{4+}_{0.003})_{\Sigma 14}\,(O_{31.323}\square_{0.677})_{32}(\square_{3.972}(OH)_{2.028})_{\Sigma 6}$ $[Cl_{1.323}\square_{4.680}]_{\Sigma 6}$ (Galuskin *et al.*, 2012b). The compositions of holotype, type and type-locality mayenite may be described as sum of two main end-members, respectively, 69 %, 59 % and 62.5 %, $Ca_{12}Al_{14}O_{32}[\square_4Cl_2]$, 31 %, 41 % and 37.5 % $Ca_{12}Al_{14}O_{30}(OH)_6(\square_6)$; the end-member $Ca_{12}Al_{14}O_{32}[\square_4Cl_2]$, therefore, is dominant. There is no need for the end-member $Ca_{12}Al_{14}O_{32}[\square_5O]$ [IMA_Master_List (2014–03)] proposed by Hentschel (1964, 1987) to explain compositional variations of mayenite in specimens from the type locality, including the

holotype and type material, *i.e.*, Hentschel's (1987) suggestion that mayenite belongs to an anhydrous solid solution between $Ca_{12}Al_{14}O_{32}[\square_5O]$ and $Ca_{12}Al_{14}O_{32}[\square_4Cl_2]$ could not be confirmed (Galuskin *et al.*, 2012b).

Instead, our investigations have shown that hydroxyl plays an important role in mayenite from the type locality (Galuskin *et al.*, 2012b). Mayenite apparently formed initially as the anhydrous phase $Ca_{12}Al_{14}O_{32}[\square_4Cl_2]$, but was subsequently partially hydroxylated to form solid solutions between $Ca_{12}Al_{14}O_{32}[\square_4Cl_2]$ and $Ca_{12}Al_{14}O_{30}(OH)_6(\square_6)$. This conclusion is supported by the discovery of mayenite close to the end-member $Ca_{12}Al_{14}O_{32}[\square_4Cl_2]$ as inclusions in jasmundite, $Ca_{11}(SiO_4)_4O_2S$, from an altered carbonate xenolith in volcanic rocks of the Caspar quarry near Mayen, Eifel district, Germany (Table 1, analysis 3, Bernd Ternes' sample). The component $Ca_{12}Al_{14}O_{30}(OH)_6(\square_6)$ is characterized by a coordination change of Al from tetrahedral to octahedral, associated with additional OH groups. Charge balance is attained by the presence of OH^-, which is evident in Raman spectra (Fig. 4).

On the basis of these results mayenite should be redefined as $Ca_{12}Al_{14}O_{32}[\square_4Cl_2]$ and renamed chlormayenite. More generally, we propose to add a prefix to indicate anion composition, at the same time retaining the root name for the town near the type locality. By analogy, the mayenite-group mineral from Hatrurim, Israel, with the end-member formula $Ca_{12}Al_{14}O_{32}[\square_4F_2]$, is named fluormayenite (see below). The root name mayenite without a prefix should be reserved for a mineral with the composition $Ca_{12}Al_{14}O_{32}[\square_5O]$ if such be found. Changing the formula for mayenite as a mineral species could lead to confusion when information is exchanged between mineralogists and other scientists. In addition, the root name mayenite is appropriate as a group name for oxides isostructural with $Ca_{12}Al_{14}O_{32}[\square_5O]$ and chlormayenite.

Chesnokov & Bushmakin (1995) were the first to use the name ''chlormayenite,'' which they applied to an anthropogenic phase formed in burned dumps of the Chelaybinsk coal Basin, Russia. However, their simplified crystal chemical formula $(Ca_{13}Al_{14}(SiO_4)_{0.5}O_{32}Cl_2)$ for this phase, calculated from wet chemical analysis, is erroneous. Recalculation of Chesnokov *et al.*'s data, supported by

Table 1. Chemical composition of mayenite-supergroup minerals: type chlormayenite, Eifel (1 - M5026/86, 2 - No. 120045), chlormayenite inclusions from jasmundite, Jebel Harmun (3), fluormayenite, Eifel (4), fluorkyuygenite, Hatrurim Basin (5), chlormayenite, Hatrurim Basin (6), high chlorine chlormayenite, Hatrurim Basin (7), chlorine fluormayenite, Hatrurim Basin (8), high chlorine chlormayenite, Eifel (9) and antropogenic F-analogue of eltyubyuite, Chelyabinsk coal basin (10), wt.%.

	1			2			3			4			5			6	7	8	9	10		
	mean 40	s.d.	range	mean 11	s.d.	range	mean 14	s.d.	range	mean 12	s.d.	range	mean 14	s.d.	range				mean 3	mean 32	s.d.	range
SiO_2	0.03	0.02	<0.02–0.06	0.06	0.03	0.03–0.12	0.02	0.02	<0.02–0.07	0.04	0.02	0.02–0.08	0.89	0.4	0.44–1.41	0.35	0.06	0.36	0.72	11.06	0.5	9.92–11.84
TiO_2	<0.02		<0.02–0.06	0.02	0.02	<0.02–0.06	0.01	0.01	<0.02–0.04	<0.01			0.04	0.03	<0.02–0.12			<0.02	0.06	<0.02		
Al_2O_3	47.78	0.4	46.9–48.6	46.60	0.6	45.7–47.4	46.50	0.4	45.9–47.4	48.85	0.2	48.2–49.1	45.00	0.3	44.4–45.4	48.13	48.14	45.56	41.01	44.56	0.9	42.7–47.0
Fe_2O_3	2.31	0.3	1.76–2.84	3.08	0.3	2.61–3.50	2.06	0.2	1.77–2.37	1.51	0.1	1.32–1.75	2.10	0.4	1.59–2.68	0.87	2.28	1.97	6.88	0.08	0.1	<0.06–0.60
MnO	<0.06		<0.02–0.06	0.02	0.02	<0.06–0.06	0.02	0.02	0.02–0.08	<0.06			<0.06					<0.06				
MgO	0.02	0.02	<0.02–0.06	0.06	0.02	0.02–0.09	<0.01			0.11	0.02	0.08–0.15	<0.01			0.03	0.03	<0.01	0.02	0.06	0.1	<0.01–0.52
CaO	46.45	0.3	45.5–47.1	46.43	0.6	45.5–47.3	46.39	0.4	45.8–47.0	47.57	0.1	47.4–47.8	44.64	0.3	44.0–45.2	46.0	46.9	44.4	43.60	37.24	0.6	35.8–38.6
SrO	<0.06			<0.07			<0.06			<0.05			<0.05			0.11	0.11	<0.06		n.m.		
Na_2O	<0.02			<0.02			<0.01			0.08	0.01	0.06–0.10	<0.01			<0.02	0.11	0.02		<0.02		
SO_3	<0.03			<0.03			<0.03			0.08	0.03	0.04–0.12	<0.04			0.07	0.08	0.06		0.24	0.1	0.06–0.49
P_2O_5	<0.03			<0.03			<0.03			<0.03			<0.03			0.13	<0.04	<0.04		n.m.		
Cl	3.37	0.2	3.05–3.80	2.85	0.1	2.64–3.02	4.14	0.4	3.45–4.74	0.11	0.01	0.09–0.12	<0.03			4.04	1.98	3.97	6.91	0.02	0.02	<0.02–0.07
F	<0.12			<0.13			<0.10			2.13	0.2	1.84–2.45	2.38	0.3	1.84–2.84	0.24	1.18	0.30	0.64	10.83	0.5	10.03–11.59
H_2O	1.17			1.39			0.19			0.51			4.71			0.44	0.52	4.73	1.83	4.57		
$-O = F + Cl$	0.76			0.64			0.93			0.92			1.00			1.01	0.94	1.02				
	100.36			99.87			98.40			100.06			98.76			99.4	100.4	100.4	98.01	99.52		
Formulas calculated for total cations = 26																						
Ca	11.996			12.069			12.180			12.037			12.031			11.946	11.968	11.986	12.023	12.229		
Sr																	0.008					
Na										0.037						0.015	0.051	0.010				
X	**11.996**			**12.069**			**12.180**			**12.073**			**12.031**			**11.962**	**12.027**	**11.996**	**12.023**	**12.229**		
Al	13.572			13.324			13.429			13.596			13.340			13.755	13.524	13.529	12.440	10.277		
Fe^{3+}	0.418			0.562			0.380			0.268			0.397			0.159	0.409	0.374	1.333			
Si	0.007			0.015			0.005			0.009			0.224			0.085	0.014	0.091	0.185	3.390		
Ti				0.004			0.002						0.008						0.012			
Mn^{2+}				0.004			0.004													0.021		
Mg	0.006			0.022																0.027		
S^{6+}										0.039						0.013	0.011	0.011	0.008	0.055		
P										0.014						0.027	0.014					
T	**14.003**			**13.931**			**13.820**			**13.927**			**13.969**			**14.038**	**13.973**	**14.004**	**13.977**	**13.771**		
Cl	1.375			1.172			1.719			0.044						1.660	0.800	1.695	3.014	0.010		
F										1.591			1.893			0.184	0.890	0.239	0.521	10.498		
H_2O^*													3.796					3.882				
OH^{**}													0.310					0.185				
W	**1.375**			**1.172**			**1.719**			**1.635**			**6.000**			**1.844**	**1.689**	**6.001**				
OH^{***}	1.876			2.253			0.312			0.795			0.310			0.712	0.834	0.185				

Footnotes: * H_2O wt.% calculated from OH^* pfu (calculated on charge balance) and H_2O^{**} pfu [calculated as $6 - (Cl + OH)$] or from OH^{***} pfu (calculated as $3 \times [(\sum \text{cation charge} - 64) - (Cl + F + OH)]$) (see Galuskin *et al.*, 2012b); n.d. – not detected; n.m. – not measured. All Fe is given as Fe_2O_3.

our unpublished analytical results of Cl-bearing minerals from the burned dumps of the Chelyabinsk coal Basin (samples were kindly supplied by M. Murashko), confirms that this anthropogenic phase is analogous to Si- and Mg-bearing chlormayenite.

Renaming of kyuygenite

By analogy with chlormayenite ($Ca_{12}Al_{14}O_{32}[\square_4Cl_2]$), fluormayenite ($Ca_{12}Al_{14}O_{32}[\square_4F_2]$) and fluorkyuygenite ($Ca_{12}Al_{14}O_{32}[(H_2O)_4F_2]$), the name of kyuygenite, $Ca_{12}Al_{14}O_{32}[(H_2O)_4Cl_2]$, found in xenoliths within ignimbrites of the Upper Chegem Caldera, Kabardino-Balkaria, Russia, is changed to chlorkyuygenite. Its full description is presented in the accompanying paper (Galuskin *et al.*, 2015a).

Discreditation of brearleyite

Ma *et al.* (2011) introduced the new species brearleyite, $Ca_{12}Al_{14}O_{32}Cl_2$, as "the Cl analogue of mayenite ($Ca_{12}Al_{14}O_{33}$)" from a refractory inclusion from the Northwest Africa 1934 CV3 carbonaceous chondrite, *i.e.*, the distinction between brearleyite and mayenite as defined by Hentschel (1964) was the presence of 2Cl and one less O per formula unit. However, our reexamination of the holotype mayenite clearly demonstrates the presence of Cl and that the dominant component is $Ca_{12}Al_{14}O_{32}Cl_2$ ($Ca_{12}Al_{14}O_{32}[\square_4Cl_2]$) and, consequently, brearleyite is no longer a Cl analogue of mayenite, but identical to it. Despite the incompleteness of the original analysis, mayenite was sufficiently well described by Hentschel (1964) that its validity is not in question, and thus has priority over brearleyite. According to IMA-CNMNC procedures and guidelines (Nickel & Grice, 1998; Hatert *et al.*, 2012), a mineral may be discredited if it can be shown to be identical to another one that has priority. Consequently, brearleyite was discredited in favour of the name derived from mayenite, chlormayenite.

Mayenite from other localities

Gross (1977) reported mayenite from pyrometamorphic rocks of the Hatrurim formation, Israel, the second occurrence of this mineral, and assigned the formula $Ca_{12}Al_{14}O_{33}$. Reinvestigation of this mayenite showed it is its fluorine analogue, $Ca_{12}Al_{14}O_{32}[\square_4F_2]$ ($I\overline{4}3d$, $a = 11.9894(2)$ Å; Table 1, analysis 4), a new mineral species (fluormayenite, see Galuskin *et al.*, 2015b) and the natural analogue of a synthetic phase (Williams, 1973; Qijun *et al.*, 1997). Alteration of the fluorine analogue yielded a second new mineral – fluorkyuygenite, $Ca_{12}Al_{14}O_{32}[(H_2O)_4F_2]$ ($I\overline{4}3d$, $a \approx 12$ Å, Galuskin *et al.*, 2015b; Table 1, analysis 5). Our latest investigations show that chlormayenite

($Ca_{12}Al_{14}O_{32}[\square_4Cl_2]$, end-member up to 83 %, Table 1, analysis 6) and chlorkyuygenite ($Ca_{12}Al_{14}O_{32}[(H_2O)_4Cl_2]$), end-member up to 85 %, Table 1, analysis 7) are also present in pyrometamorphic rocks of the Hatrurim Formation, but in limited quantities, as are phases with intermediate composition between chlormayenite and fluormayenite (Table 1, analysis 8).

Chlormayenite (mayenite) was also reported in altered xenoliths in alkali basalt from Klöch, Styria, Austria and its formula given as $Ca_{12}Al_{14}O_{33}$ (Exel, 1993). However, compositional data indicate that it contains up to 2.5 wt.% Cl (Heritsch, 1990, and our data).

Synthetic analogues of mayenite

The name "mayenite" has been used by physicists, chemists and technologists to refer to synthetic phases with composition $Ca_{12}Al_{14}O_{33}$ (Matsuishi *et al.*, 2003; Boysen *et al.*, 2007, 2009, 2010; Palacios *et al.*, 2007, 2008; Hosono *et al.*, 2009; Sakakura *et al.*, 2011; Tolkacheva *et al.*, 2011). The halogen-bearing compounds $Ca_{12}Al_{14}O_{32}Cl_2$ and $Ca_{12}Al_{14}O_{32}F_2$ have been synthesized (Williams, 1973; Qijun *et al.*, 1997; Ju *et al.*, 2006; Iwata *et al.*, 2008; Sun *et al.*, 2009) and were the main object of numerous studies in different fields from optic physics (transparent semiconductors) to cement, ceramics and sorbents technology, which has resulted in hundreds of publications (*e.g.*, Hosono *et al.*, 2007; Sushko *et al.*, 2007a; Iwata *et al.*, 2008; Li *et al.*, 2009). The compound $Ca_{12}Al_{14}O_{33}$ is very reactive in the presence of water (Park, 1998; Strandbakke *et al.*, 2009), so it is likely that in most geologic environments anhydrous mayenite is stabilized by halogens.

The crystal structure of synthetic mayenite is considered as a tetrahedral framework $\{Al_{14}O_{32}\}^{22-}$ enclosing six structural cages each occupied by two Ca^{2+}. The excess positive (2^+) charge is balanced by partial occupancy of the *W* site, which is located between the Ca sites at the centre of the cages. The *W* site may be occupied by negatively charged particles or ions: electrons e^-, O_2^-, O_2^{2-}, O^-, S^{2-}, OH^-, N_x^-, F^-, Cl^-, Au^- (Posch *et al.*, 2004; Sango, 2006; Hosono *et al.*, 2007; Palacios *et al.*, 2007; Sushko *et al.*, 2007b; Li *et al.*, 2009; Matsuishi *et al.*, 2009; Boysen *et al.*, 2010; Janek & Lee, 2010) as well as uncharged molecules like H_2O (Galuskin *et al.*, 2015a and 2014b). The first synthetic wadalite had the composition $Ca_{12}Al_{10.6}Si_{3.4}O_{32}Cl_{5.4}$ (Feng *et al.*, 1988). The synthetic analogues of wadalite $Ca_{12}Al_{10}Si_4O_{32}Cl_6$ and $Ca_{12}Al_{10}Si_4O_{32}O_3$ are also known (Fujita *et al.*, 2003, 2005; Sato *et al.*, 2006).

Unit-cell volume, density, and refractive index are compared for synthetic and natural mayenite related species (Table 2). It is striking that all values determined by Hentschel (1964) for his original mayenite are significantly different from those for $Ca_{12}Al_{14}O_{33}$ and chlorkyuygenite (Galuskin *et al.*, 2013, 2015a). Instead,

Table 2. Physical properties of some mayenite related compounds.

Formula	$Ca_{12}Al_{14}O_{33}$	$Ca_{12}Al_{14}O_{32}Cl_2$	"Mayenite" original	Chlormayenite, type locality	Chlorkyuygenite, type locality
Cell volume A^3	1719.1 (m)	1732.1 (m)	1736.7 (m)	1741.9 (m)	1740.3 (m)
Density g/cm^3	2.70 (m)	2.79 (c)	2.85 (m)	2.77 (c)	2.95 (c)
Refractive index	1.604 (m)		1.643 (m)		1.672 (m)
References	Boysen et al. (2007); Kühl (1958)	Iwata et al. (2008)	Hentschel (1964)	Galuskin et al. (2012b)	Galuskin et al. (2015a)

Note: (m) = measured, (c) = calculated

Chlorkyuygenite: $Ca_{11.98}(Al_{12.99}Fe^{3+}_{0.82}Si_{0.18}Ti^{4+}_{0.03})_{\Sigma14.02} (O_{31.91}(OH)_{0.09})_{\Sigma32}[(H_2O)_{3.57}Cl_{2.33}]_{\Sigma6}$

Chlormayenite, type locality: $Ca_{12}(Al_{13.513}Fe^{3+}_{0.465}Mg_{0.012}Si_{0.007}Ti^{4+}_{0.003})_{14} (O_{31.323}\square_{0.677})_{\Sigma32}(\square_{3.972}(OH)_{2.028})_{\Sigma6} [Cl_{1.323}\square_{4.680}]_{\Sigma6}$

Hentschel's (1964) values agree with those obtained on $Ca_{12}Al_{14}O_{32}Cl_2$ and type-locality mayenite by Galuskin et al. (2012b).

New nomenclature

We propose to base the classification of the mayenite supergroup on the positive charge of the framework, balanced by anions at the W site, i.e., the boundary between the mayenite and wadalite groups is a total charge of 4 over 6 W sites (Figs. 5 and 6; Table 3). End-members of the mayenite group would have a total charge of 2 over 6 W sites, whereas end-members of the wadalite group would have a total charge of 6 over 6 W sites. The boundary corresponds to 2 Si atoms per formula unit (apfu) at the T sites (Fig. 6). In a given group, mineral species would be distinguished on the basis of the anion dominant at the W site, whether Cl, F (+ OH or O). Further distinction of mineral species in the mayenite group is based on the presence of H_2O versus vacancy at W.

In the original description of wadalite, the end-member crystal-chemical formula $Ca_6Al_5Si_2O_{16}Cl_3$ was proposed (Tsukimura et al., 1993; Ishii et al., 2010; IMA List of Minerals - March 2014). Taking into consideration the proposed general formula of minerals of the mayenite supergroup, the wadalite formula should be doubled to $Ca_{12}Al_{10}Si_4O_{32}[Cl_6]$.

The most important substitutions in minerals of the mayenite supergroup are the following:

(1) $^T(Al,Fe^{3+}) + {}^W\square \Leftrightarrow {}^TSi^{4+} + {}^W(Cl^-,F^-)$, which relates chlormayenite and fluormayenite, with wadalite and its Fe^{3+} analogue, eltyubyuite. This substitution is expressed as a linear array of compositions between Si = 0, Cl = 2 and Si = 4 and Cl = 6 (Fig. 5).
(2) $^TAl^{3+} \Leftrightarrow {}^TFe^{3+}$, which relates wadalite and eltyubyuite (Fig. 6).
(3) $^W\square \Leftrightarrow {}^WH_2O$, which relates chlormayenite and fluormayenite with chlorkyuygenite and fluorkyuygenite, respectively
(4) The substitution $F^- \Leftrightarrow Cl^-$ is most distinctly displayed in the minerals of the chlormayenite–fluormayenite series from pyrometamorphic rocks of the Hatrurim Formation (Table 1, analysis 8). The significant difference between the ionic radii of fluorine and chlorine results in a small shift of Ca towards F, as reported by Galuskin et al. (2015b).

Other substitutions could also be relevant for distinguishing mineral species in the mayenite supergroup, but to date have not yielded any additional mineral species:

(5) $2^T(Al^{3+}, Fe^{3+}) \Leftrightarrow {}^TMg^{2+} + {}^T(Si^{4+}, Ti^{4+})$, which most often is noted in wadalite-group minerals. Maximum Mg contents reach 2 apfu, and Si $\approx$ 6 apfu, i.e., the formula becomes $Ca_{12}(Mg_2Al_6Si_6)O_{32}[Cl_6]$, which significantly exceeds the Si content in the wadalite end-member (Figs. 5 and 6). Nonetheless, Mg-bearing wadalite is not a distinct species because the two T sites are to be considered together for classification purposes. If the individual occupancies of the $T1$ and $T2$ sites were considered the basis of classification, the structures would have to be refined, and occupancies of individual T sites measured in each specimen in order to name it. The formula of an Al-free member of the wadalite group, where all Al is substituted by Mg and Si, is $Ca_{12}(Si_9Mg_5)O_{32}[Cl_6]$. On first consideration, such a composition appears not to be stable as a mayenite-supergroup mineral because Mg would be expected to occupy the relatively large and more distorted tetrahedra $T1$ (8 apfu) and Si, the relatively small, nearly ideal tetrahedra $T2$ (6 apfu) (Fujita et al., 2001), so that the maximum Mg content would be $Ca_{12}{}^{T1}(Al_6Mg_2)^{T2}(Si_6)O_{32}[Cl_6]$. Only two of the analyses of wadalite in our compilation contain more than 6 Si apfu (Figs. 5 and 6), suggesting the upper limit on Si is 6 apfu in minerals of the wadalite group. However, the latest experimental data on synthesis of high-Mg wadalite have revealed that tetrahedra can change their functions in the mayenite structure, such that $T1$ accepts smaller cations and $T2$ larger cations (Gfeller, unpublished data). Gfeller (unpublished data) synthesized phases with the compositions between $Ca_{12}{}^{T1}(Si_8)^{T2}(Mg_{4.5}Al_{1.5})O_{32}[Cl_{5.5}\square_{0.5}]$ and $Ca_{12}{}^{T1}(Si_8)^{T2}(Mg_4Al_2)O_{32}[Cl_6]$. This suggests potential existence of a new mineral belonging to the wadalite group with a composition between $Ca_{12}(Si_6Al_6Mg_2)O_{32}[Cl_6]$ and $Ca_{12}(Si_8Al_2Mg_4)O_{32}[Cl_6]$, leading to a new mineral species in the wadalite group with a theoretical end-
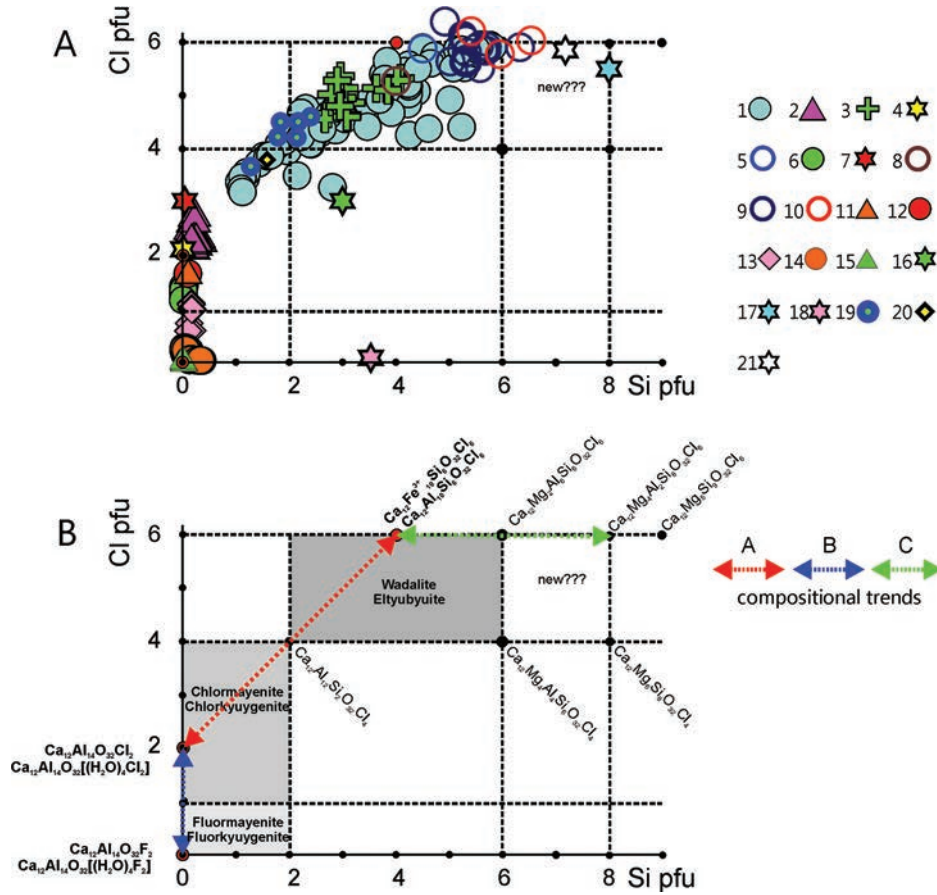
Fig. 5. Analyses of the mayenite-supergroup minerals (A) and compositional trends (B) projected in Si–Cl apfu diagrams. 1, 2, 3–wadalite, chlorkyuygenite and eltyubyuite analyses from Upper Chegem caldera (Galuskin *et al.*, 2009; Bailau *et al.*, 2012; our unpublished data); 4–brearleyite (Ma *et al.*, 2011); 5–wadalite, Eifel (Mihajlović *et al.*, 2004); 6–holotype chlormayenite, Eifel (Galuskin *et al.*, 2012b, our unpublished data); 7 - high chlorine chlormayenite, Eifel; 8–holotype wadalite (Tsukimura *et al.*, 1993); 9–wadalite, Mexico (Kanazawa *et al.*, 1997); 10–wadalite from Allende chondrite (Ishii *et al.*, 2010); 11–15–chlorkyuygenite, chlormayenite, fluormayenite and fluorkyuygenite (our data), Hatrurim formation; 16–anthropogenic ''demidovskite'', Chelyabinsk coal basin (Chesnokov *et al.*, 1996); 17–Frank Gfeller's synthetic phase; 18–anthropogenic F-rich phase close to eltyubyuite, Chelyabinsk coal basin (Sharygin, 2014); 19–anthropogenic mayenite-wadalite, Oslavany, 20–anthropogenic mayenite, Zastavka (Hršelová *et al.*, 2013) and 21–adrianite (Ma *et al.*, 2014b). Compositional trend: A – chlormayenite–wadalite (eltyubyuite); B – chlormayenite (chlorkyuygenite) – fluormayenite (fluorkyuygenite); C – wadalite – potentially new mineral ''Mg-wadalite'' (Gfeller, unpublished data).

Table 3. Mayenite-supergroup minerals.

Mayenite supergroup	T site	W site	Formula	Simplified formula
Mayenite group ($W_{charge} = -2$)				
1. chlormayenite	Al_{14}	$\square_4Cl_2$	$Ca_{12}Al_{14}O_{32}[\square_4Cl_2]$	$Ca_{12}Al_{14}O_{32}Cl_2$
2. fluormayenite	Al_{14}	$\square_4F_2$	$Ca_{12}Al_{14}O_{32}[\square_4F_2]$	$Ca_{12}Al_{14}O_{32}F_2$
3. chlorkyuygenite	Al_{14}	$(H_2O)_4Cl_2$	$Ca_{12}Al_{14}O_{32}[(H_2O)_4Cl_2]$	
4. fluorkyuygenite	Al_{14}	$(H_2O)_4F_2$	$Ca_{12}Al_{14}O_{32}[(H_2O)_4F_2]$	
Wadalite group ($W_{charge} = -6$)				
5. wadalite	$Al_{10}Si_4$	Cl_6	$Ca_{12}Al_{10}Si_4O_{32}[Cl_6]$	$Ca_{12}Al_{10}Si_4O_{32}Cl_6$
6. eltyubyuite	$Fe^{3+}_{10}Si_4$	Cl_6	$Ca_{12}Fe^{3+}_{10}Si_4O_{32}[Cl_6]$	$Ca_{12}Fe^{3+}_{10}Si_4O_{32}Cl_6$

member formula $Ca_{12}(Si_9Mg_5)O_{32}[Cl_6]$. About 40 % of this end-member has been reported in wadalite from the Allende chondrite (Kanazawa *et al.*, 1997; Ishii *et al.*, 2010) and from the Caucasus (Bailau *et al.*, 2012; our unpublished data; Figs. 5 and 6).

(6) $O^{2-} + Cl^-/F^- \Leftrightarrow 3(OH)^-$, was first reported to explain partial hydroxylation of chlormayenite and fluormayenite (Galuskin *et al.*, 2012b, 2015b). Fully hydroxylated mayenite is a possible new mineral with the formula $Ca_{12}Al_{14}O_{30}(OH)_6[\square_6]$, which has 0
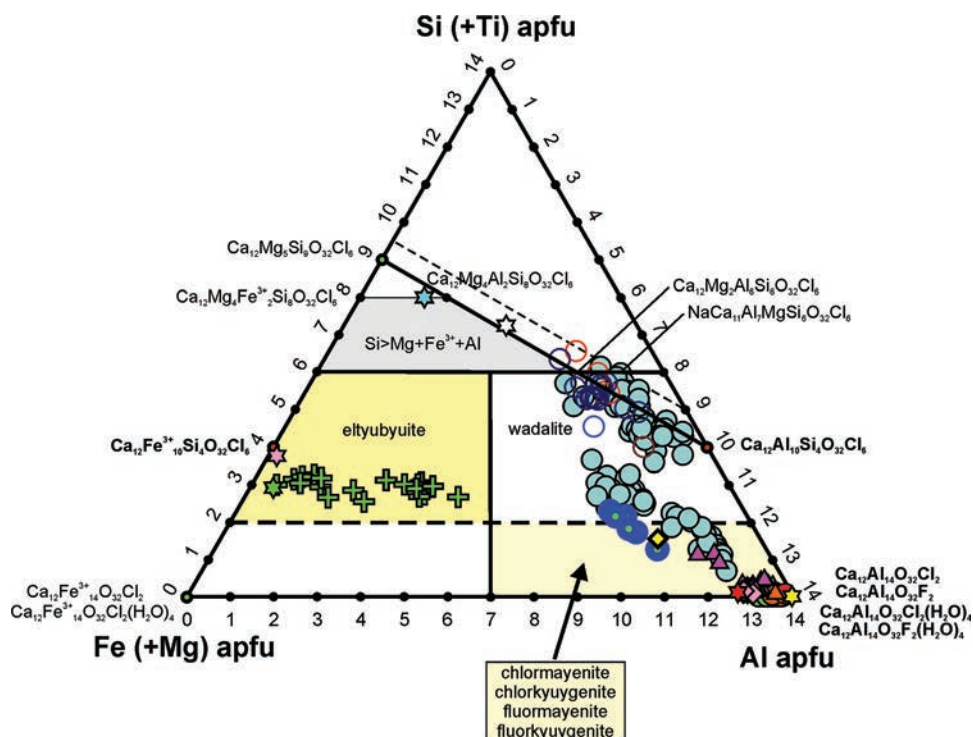
Fig. 6. Analyses of the mayenite-supergroup minerals projected in the Fe(+Mg)–Al–Si apfu diagram, symbols as in Fig. 5.

charge at W, because the OH groups are not at the centre of the cage, but replace O2 and coordinate $T1$ (Galuskin *et al.*, 2012b).

(7) Hydroxylation of chlormayenite and fluormayenite is possible by the substitutions $Cl^- \Leftrightarrow OH^-$ and $F^- \Leftrightarrow OH^-$, which have been reported in synthetic phases (Ruszak *et al.*, 2007). The resulting composition would be $Ca_{12}Al_{14}O_{32}[\square_4(OH)_2]$. These phases might be found as alteration products of water-free minerals of the mayenite group.

Hydroxyl groups, corresponding to the two types of hydration in mayenite-group minerals, differ in band position in the OH region on Raman spectra: OH groups incorporated by $O^{2-} + Cl^- \Leftrightarrow 3(OH)^-$ yield a band at about 3670 cm^{-1}, whereas OH groups incorporated by $Cl^- \Leftrightarrow OH^-$ and $F^- \Leftrightarrow OH^-$ give a band at about 3570 cm^{-1} (Fig. 4; Galuskin *et al.*, 2012b, 2015a and 2015b).

(8) There are other substitutions introducing halogen in excess of 2 (Cl, F) in end-members of the mayenite group and 6 (Cl, F) in end-members of the wadalite group. For example, chlormayenite from a xenolith enriched in rondorfite from the Caspar quarry near Mayen, Germany (collected by Bernd Ternes) has the composition $Ca_{12}Al_{12.5}Fe^{3+}_{1.5}O_{31.25}Cl_3F_{0.5}$ (Table 1, an. 9), and an anthropogenic F-analogue of eltyubyuite from a burned dump of the Chelyabinsk basin, Russia has the composition $Ca_{12}Fe^{3+}_{10.5}Si_{3.5}O_{29.5}F_{10.5}$ (Table 1, an. 9; Sharygin, unpublished data). The excess halogens might be substituting for oxygens. Possibly the mechanism for

substitution of oxygen is similar to no. 5 above for partially hydrated chlormayenite (see above and Galuskin *et al.*, 2012b).

Investigations of isomorphic substitutions at the X(Ca) site in minerals of the mayenite supergroup show that Ca is dominant in all natural phases studied to date, although an Sr analogue of $Sr_{12}Al_{14}O_{33}$ has been synthesized (Hayashi *et al.*, 2008). Minor Na, Sr, Y have been reported as rare impurities in minerals of the mayenite supergroup (Kanazawa *et al.*, 1997; Galuskin *et al.*, 2009; Bailau *et al.*, 2012). Sodium could be incorporated by the substitution $Na^+ + Al^{3+} \Leftrightarrow Ca^{2+} + Mg^{2+}$ in Mg-bearing wadalite (Fig. 6).

Minor end-members noted among the minerals of the mayenite supergroup and also synthetic and not strictly natural phases are given in Table 4. The data suggest that minerals close to the composition of the ideal end-members $Ca_{12}Fe^{3+}_{10}Si_4O_{32}[F_6]$, $Ca_{12}Si_9Mg_5O_{32}[Cl_6]$ and $Ca_{12}Al_{14}O_{30}(OH)_6[\square_6]$ could be found in Nature.

Adrianite

After our mayenite supergroup nomenclature was approved by CNMNC IMA in March 2014 (proposal 13-C; Williams *et al.*, 2014), adrianite, $Ca_{12}(Al_4Mg_3Si_7)O_{32}Cl_6$, was approved in July 2014 as a new mineral species in the wadalite group (IMA 2014–028; Ma *et al.*, 2014a), and a brief description of the mineral was published as an abstract (Ma *et al.*, 2014b). Adrianite is reported to occur in grains 2–6

Table 4. Possible end-members and known synthetic phases

Mayenite supergroup	Simplifiedformula	X_{12}	T_{14}	O_{32-x}	OH/F_{3x}	W_{6-2x}	Maximum of end-member	Synth.
Mayenite group ($W_{charge} = -2$, x = 0)								
$Ca_{12}Al_{14}O_{32}[\square_5O]$	$Ca_{12}Al_{14}O_{33}$	Ca_{12}	Al_{14}	O_{32}		$\square_5O$	??	Yes
$Ca_{12}Al_{14}O_{32}[\square_4(OH)_2]$	$Ca_{12}Al_{14}O_{32}(OH)_2$	Ca_{12}	Al_{14}	O_{32}		$\square_4(OH)_2$	$\sim$5% in chlor- and fluormayenite	Yes
$Ca_{12}Fe^{3+}_{14}O_{32}[\square_4(OH)_2]$	$Ca_{12}Fe^{3+}_{14}O_{32}(OH)_2$	Ca_{12}	Fe^{3+}_{14}	O_{32}		$\square_4(OH)_2$	< 1% in chlormayenite	No
$Ca_{12}Fe^{3+}_{14}O_{32}[\square_4Cl_2]$	$Ca_{12}Fe^{3+}_{14}O_{32}Cl_2$	Ca_{12}	Fe^{3+}_{14}	O_{32}		$\square_4Cl_2$	10% in chlormayenite	No
$Ca_{12}Fe^{3+}_{14}O_{32}[\square_4F_2]$	$Ca_{12}Fe^{3+}_{14}O_{32}F_2$	Ca_{12}	Fe^{3+}_{14}	O_{32}		$\square_4F_2$	2% in fluormayenite	No
$Ca_{12}Fe^{3+}_{14}O_{32}[(H_2O)_4Cl_2]$		Ca_{12}	Fe^{3+}_{14}	O_{32}		$(H_2O)_4Cl_2$	< 2% in chlorkyuygenite	No
$Ca_{12}Fe^{3+}_{14}O_{32}[(H_2O)_4F_2]$		Ca_{12}	Fe^{3+}_{14}	O_{32}		$(H_2O)_4F_2$	<2% in fluorkyuygenite	No
$Ca_{12}Fe^{3+}_{14}O_{32}[(H_2O)_4(OH)_2]$		Ca_{12}	Fe^{3+}_{14}	O_{32}		$(H_2O)_4(OH)_2$	<2% in chlorkyuygenite	No
$Ca_{12}Al_{14}O_{32}[(H_2O)_4(OH)_2]$		Ca_{12}	Al_{14}	O_{32}		$(H_2O)_4(OH)_2$	$\sim$14% in fluorkyuygenite	No
$Sr_{12}Al_{14}O_{32}[\square_4Cl_2]$	$Sr_{12}Al_{14}O_{32}Cl_2$	Sr_{12}	Al_{14}	O_{32}		$\square_5Cl_2$	<1% in chlormayenite	Yes
Wadalite group ($W_{charge} = -6$, x = 0)								
$Ca_{12}Fe^{3+}_{10}Si_4O_{32}[F_6]$	$Ca_{12}Fe^{3+}_{10}Si_4O_{32}F_6$	Ca_{12}	$Fe^{3+}_{10}Si_4$	O_{32}		F_6	<2% in eltyubyuite	No
$Ca_{12}Mg_5Si_9O_{32}[Cl_6]^*$	$Ca_{12}Mg_5Si_9O_{32}Cl_6$	Ca_{12}	Si_9Mg_5	O_{32}		Cl_6	$\sim$ 40% in wadalite	Yes
$\{Y_4Ca_8\}Al_{14}O_{32}[Cl_6]$	$Y_4Ca_8Al_{14}O_{32}Cl_6$	Y_4Ca_8	Al_{14}	O_{32}		Cl_6	$\sim$10 % in chlorkyuygenite	No
Ungrouped ($W_{charge} = 0$, x = 2)								
$Ca_{12}Al_{14}O_{30}(OH)_6\square_6$	$Ca_{12}Al_{14}O_{30}(OH)_6$	Ca_{12}	Al_{14}	O_{30}	$(OH)_6$	$\square_6$	$\sim$ 40% in chlormayenite	No
$Ca_{12}Al_{14}O_{30}F_6\square_6$	$Ca_{12}Al_{14}O_{30}F_6$	Ca_{12}	Al_{14}	O_{30}	F_6	$\square_6$	$\sim$3% in fluormayenite???	No
?????								
$\sim Ca_{12}Fe^{3+}_{10}Si_4O_{30}F_{10}^{**}$		Ca_{12}	$Fe^{3+}_{10}Si_4$			$O_{30}F_{10}$	anthropogenic phase	No

*synthetic phase $Ca_{12}Al_2Mg_4Si_8Cl_6$ (Gfeller, unpublished data)
** anthropogenic phase (Sharygin, 2014)

μm in size, with monticellite, grossular, wadalite, and hutcheonite in secondary alteration areas along cracks between primary melilite, spinel and Al,Ti-diopside in the core area of the Allende CV3 meteorite. The structure was not refined; electron backscatter diffraction data were fitted using the wadalite structure $I\bar{4}3d$ with the unit-cell dimensions: $a = 11.981$ Å, $V = 1719.8$ Å3, and $Z = 2$ (Feng *et al.*, 1988). An averaged electron microprobe analysis is (wt%): CaO 41.49, SiO$_2$ 27.49, Al$_2$O$_3$ 12.42, MgO 7.34, Na$_2$O 0.41, Cl 13.03, -O = Cl –2.94, total 99.24; this analysis yields the empirical formula $(Ca_{11.69}Na_{0.21})(Al_{3.85}Mg_{2.88}Si_{7.23})O_{32}Cl_{5.80}$, ideally $Ca_{12}(Al_4Mg_3Si_7)O_{32}Cl_6$, which Ma & Krot (2014b) inferred to be the end-member formula. This composition is plotted in our classification diagrams (Figs. 5 and 6). However, this formula is not a proper end-member, because there is no way to apportion Al, Mg and Si between $T1$ and $T2$ so that only one site has two occupants and no site has more than two, *e.g.*, $Ca_{12}{}^{T1}(Al_4Mg_3Si)^{T2}(Si_6)O_{32}[Cl_6]$ or $Ca_{12}{}^{T1}(Al_3Mg_3)^{T2}(Si_7Al)O_{32}[Cl_6]$ (see discussion above in the chapter "New nomenclature" concerning the $2^T(Al^{3+}, Fe^{3+}) \Leftrightarrow {}^TMg^{2+} + {}^T(Si^{4+}, Ti^{4+})$ substitution). Pending the availability of information on T-site occupancies, it is not possible to specify the relationship of adrianite to other minerals in the mayenite supergroup.

Summary of conclusions, actions and recommendations

– The general formula for the mayenite supergroup is simplified to $X_{12}T_{14}O_{32-x}(OH)_{3x}[W_{6-3x}]$, with the two tetrahedral sites $T1$ and $T2$ considered as a single unit. Distinctions between the mineral species are based on charge at the W site and on cations at the two T sites considered together. We distinguish two groups in the mayenite supergroup, they differ in charge at the W site: the mayenite group ($W = -2$) and the wadalite group ($W = -6$).

– Minerals in the mayenite supergroup are isostructural with the synthetic phase mayenite ($Ca_{12}Al_{14}O_{32}[\square_5O]$).

– Re-examination of the holotype mayenite (Eifel, Germany) showed that it has the end-member formula $Ca_{12}Al_{14}O_{32}[\square_4Cl_2]$, and is thus renamed as chlormayenite, whereas mayenite is retained as a group name.

– Brearleyite, also given as $Ca_{12}Al_{14}O_{32}Cl_2$ or $Ca_{12}Al_{14}O_{32}[\square_4Cl_2]$, is thus identical to chlormayenite. The name mayenite has priority, and thus the name brearleyite is discredited in favour of the name derived from mayenite, chlormayenite.

– Kyuygenite ($Ca_{12}Al_{14}O_{32}[(H_2O)_4Cl_2]$) is renamed as chlorkyuygenite.

- Re-examination of mayenite from the Hatrurim formation, Israel revealed the presence of fluorine analogues of chlormayenite, fluormayenite ($Ca_{12}Al_{14}O_{32}[\square_4F_2]$) and of chlorkyuygenite, fluorkyuygenite ($Ca_{12}Al_{14}O_{32}[(H_2O)_4F_2]$), respectively.
- The mayenite group includes chlormayenite ($Ca_{12}Al_{14}O_{32}[\square_4Cl_2]$), fluormayenite ($Ca_{12}Al_{14}O_{32}[\square_4F_2]$), chlorkyuygenite ($Ca_{12}Al_{14}O_{32}[(H_2O)_4Cl_2]$), and fluorkyuygenite ($Ca_{12}Al_{14}O_{32}[(H_2O)_4F_2]$).
- The wadalite group includes wadalite ($Ca_{12}Al_{10}Si_4O_{32}[Cl_6]$) and eltyubyuite ($Ca_{12}Fe^{3+}_{10}Si_4O_{32}[Cl_6]$).
- Analysis of possible isomorphic substitutions and data on synthetic and anthropogenic phases suggests the possibility of three additional new mineral species.

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