

Chabazite-Mg: A new natural zeolite of the chabazite series

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ABSTRACT

Chabazite-Mg, $(\text{Mg}_{0.67}\text{K}_{0.52}\text{Ca}_{0.48}\text{Na}_{0.08}\text{Sr}_{0.03})_{\Sigma 1.78}[(\text{Al}_{3.16}\text{Si}_{8.89})_{\Sigma 12.05}\text{O}_{24}]\cdot 9.68\text{H}_2\text{O}$, is a new zeolite species of the chabazite series, occurring in basalts of the Karikás-tető area of Prága Hill, Veszprém County, Balaton Highland, Transdanubia, West Hungary. It crystallizes as single, colorless rhombohedra up to 0.4 mm in size. The streak is white and the luster is strong vitreous. Mohs' hardness is about 4. The observed density is 1.98(1) g/cm³ and the calculated density is 1.964(7) g/cm³. Chabazite-Mg is anisotropic, uniaxial (+), $\omega = 1.465(5)$, $\epsilon = 1.469(5)$ (546 nm). In its chemical composition, a predominance of Mg is observed among the extraframework cations. However, K and Ca are also very abundant, while Na and Sr levels are very low. The ratio Si/(Si+Al) is among the highest found in chabazite of hydrothermal genesis. Chabazite-Mg is rhombohedral, $R\bar{3}m$ space group, $a = 9.3433(5)$ Å, $\alpha = 94.894(4)^\circ$. The six strongest X-ray lines measured in the powder pattern [d in Å (I) (hkl)] are: 9.306 (60) (100), 5.537 (37) ($1\bar{1}\bar{1}$), 4.958 (25) (111), 4.315 (100) (20 $\bar{1}$), 2.924 (78) ($3\bar{1}\bar{1}$), 2.869 (41) (310). Single-crystal structure refinement of chabazite-Mg indicated that the extraframework occupation is distinct from other chabazite-series minerals. In particular, the Mg site (C3a) and one water site (W6a) are displaced from the threefold axis parallel to [111].

Keywords: Zeolite, chabazite, chemical composition, physical properties, structure refinement

INTRODUCTION

Chabazite, general formula $(\text{Ca}_{0.5}\text{Na,K,Sr,Mg})_4[\text{Al}_4\text{Si}_8\text{O}_{24}]\cdot 12\text{H}_2\text{O}$, is one of the most widespread natural zeolites and was one of the first zeolites to be studied, due to its excellent ion-exchange properties and its wide range of industrial and technological applications. Its genesis can be hydrothermal, for samples found in vugs and geodes of plutonic, volcanic, and metamorphic rocks, or sedimentary, when it is generated by alteration of glass in palagonitic basalts and pyroclastic rocks. Chabazite is rhombohedral, space group $R\bar{3}m$, with a_H and c_H unit-cell parameters ranging from 13.69 to 13.86 Å and 14.80 to 15.42 Å, respectively (Passaglia and Sheppard 2001). The chabazite framework (framework type CHA, Baerlocher et al. 2001) consists of parallel stacks of six-membered double rings ($d6R$) of tetrahedra in the sequence ABC. The resulting channel system is three-dimensional, and the channels are perpendicular to [001] (in the hexagonal setting) and are delimited by 8-membered rings (Dent and Smith 1958; Smith et al. 1963). In the rhombohedral symmetry, where only one tetrahedral site is present, the (Si, Al) distribution in this tetrahedron is disordered. However, Mazzi and Galli (1983) determined the space group $P\bar{1}$ for four chabazite samples and attributed the symmetry lowering to the presence of domains with ordered (Si, Al) distribution. Accurate determination of the positions of extraframework cations and water molecules in natural and cation-exchanged hydrated

chabazites was conducted by Alberti et al. (1982) and Calligaris et al. (1982) and more recently by Nakatsuka et al. (2007) and Zema et al. (2008).

Passaglia (1970) reported a thorough description of the chemical variability of natural chabazite showing that it is one of the most chemically variable zeolites, both as regards the exchangeable cations as well as the Si/Al ratio. This author also identified relationships between chemical composition and physical properties.

The "Recommended nomenclature for zeolite minerals: report of the subcommittee on zeolites of the IMA, Commission on New Minerals and Mineral Names" (Coombs et al. 1998) defined the chabazite series as consisting of three separate species: chabazite-Ca, chabazite-Na (Passaglia 1970), and chabazite-K (De Gennaro and Franco 1976). More recently, Pekov et al. (2000) reported a fourth new species, chabazite-Sr. Passaglia and Ferro (2002) described the new occurrence of three chabazite samples—strictly associated with the magnesian zeolite offretite—with unusually high levels of Mg and classified these zeolites as magnesian chabazite-Ca. In the same paper, the structure refinement of the sample from Mont Semiol, France, is discussed.

Here we describe a new species of the chabazite series, chabazite-Mg, with magnesium as the most abundant extraframework cation, recently found in the Karikás-tető area of Prága Hill, Hungary. The new mineral and name have been approved by the Commission on New Minerals and Mineral Names of the IMA. The name of the species chabazite-Mg follows the "Recommended nomenclature for zeolite minerals: report of

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the subcommittee on zeolites of the IMA" (Coombs et al. 1998) for the Mg-dominant member of the chabazite series. The type material is deposited in the collections of the Department of Mineralogy and Petrology, Hungarian Natural History Museum, Budapest (catalog no. Gyn./1742, 1743), and the Herman Ottó Museum, Miskolc, Hungary (catalog no. 2009.51.1).

OCCURRENCE

Chabazite-Mg was found in the basalt cavities of the Karikás-tető quarry of Prága Hill (geographical coordinates: 46°56'N, 17°15'E), near Bazsi, Veszprém County, Balaton Highland, Transdanubia, West Hungary. Karikás-tető is the central and highest part of a ~5 km long, southwest to northeast trending ridge of ~3.5 Ma old basalt rocks, belonging to a sill and dyke complex (Kovács-Pálffy et al. 2007). The basalt quarry lies WSW of the Karikás-tető (the summit region of Prága Hill), in the Tátika Group of the Keszthely Mts. The basalt bodies intrude neogene (Miocene to Pliocene) siliciclastic sediments (siltstone, sandstone, silt, and sand). The sills are irregular in shape and their lateral extent is highly variable. Along the margin of the coherent lava body, the host sediment is thermally affected in a decimeter- to meter-wide zone. Near the contact zone cavities occur filled with hydrothermal minerals. Cavities are usually ovoid and rarely elongated in shape, varying greatly in size. Most are up to 5 cm with some up to 15 cm. Cavities larger than 15 cm are very rare. The miarolitic minerals (e.g., apatite, augite, feldspars, and magnetite) were crystallized first on the cavity walls, followed by hydrothermal minerals. Two different parageneses of the cavity-filling hydrothermal minerals are present in the quarry. The first contains mainly fibrous zeolites (e.g., natrolite, gonnardite, thomsonite-Ca) accompanied by analcime, gismondine, aragonite, calcite, and smectite. In the upper part of the quarry, a contact zone was found (along the basalt-sand boundary), where mainly carbonates (aragonite, calcite) occur, along with very few zeolites (phillipsite, chabazite-Mg). Here all cavities and fractures are lined with pale green to pale brown saponite about 1–2 mm thick (Kovács-Pálffy et al. 2007; Kónya 2009). The minerals closely associated with chabazite-Mg are saponite, aragonite, and phillipsite. Chabazite-Mg was formed

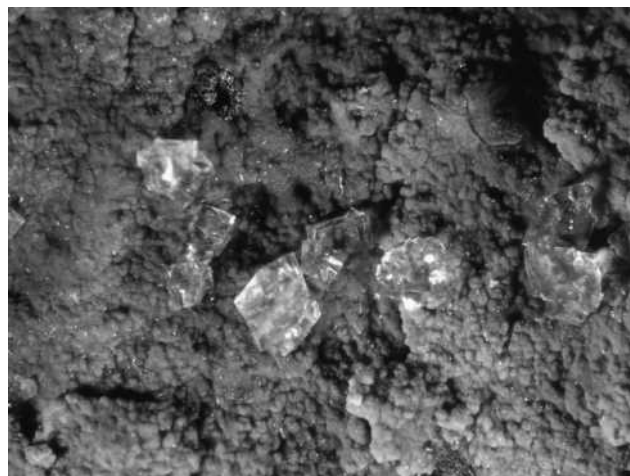


FIGURE 2. Microphotograph of colorless chabazite-Mg on saponite crust. Size of the crystals: 1–2 mm.

by hydrothermal alteration of feldspar and volcanic glass, in a closed system with Mg-rich solutions. Figure 1 shows minute chabazite-Mg crystals on a bed of saponite.

APPEARANCE AND PHYSICAL PROPERTIES

Chabazite-Mg occurs as single, colorless rhombohedra up to 0.4 mm in size, dominated by rhombohedra faces (10 $\bar{1}$ 1). Aggregates of intergrown crystals up to 1–2 mm in thickness are quite common (Figs. 1 and 2). The streak is white. The luster is strong vitreous. The mineral is non-fluorescent. Mohs' hardness is about 4. The crystals are quite brittle. Cleavage was not observed, fracturing is rough. The density, 1.98(1) g/cm³, was measured using the sink-float method (acetone-bromoform mixture). This value is close to the calculated density, 1.964(7) g/cm³. Optically, chabazite-Mg is anisotropic, uniaxial (+), $\omega = 1.465(5)$, $\epsilon = 1.469(5)$ (546 nm). Pleochroism was not detected.

Density and refractive indices are low when compared with the values of other chabazites reported in literature (Passaglia 1970), but consistent with the chemical composition reported in the next section. In effect, the Compatibility Index $1 - (K_p/K_c)$ (Mandarino 1979) used as a measure of the compatibility of refractive index, density, and chemical composition is –0.031 (excellent) and 0.023 (excellent) on the basis of calculated and measured density values, respectively.

CHEMICAL COMPOSITION

Chemical analysis of chabazite-Mg was performed on four crystalline aggregates with an ARL-SEMQ electron microprobe, operating in the wavelength dispersive (WDS) mode. Standards used were Amelia albite for Al and Na, microcline for Si and K, P140 synthetic olivine for Mg and Fe, and paracelsian, AN70 synthetic glass, and Sr-anorthite for Ba, Ca, and Sr, respectively. X-ray counts were converted into oxide weight percentages using the PROBE correction program (Donovan 1995). For most zeolites, in particular those with large channels, the electron bombardment and vacuum conditions in the microprobe sample chamber can cause loss of H₂O and extraframework cation migration. To minimize these effects, a beam current of 10 nA and a defocused beam of 25 μ m were used. The water content could not

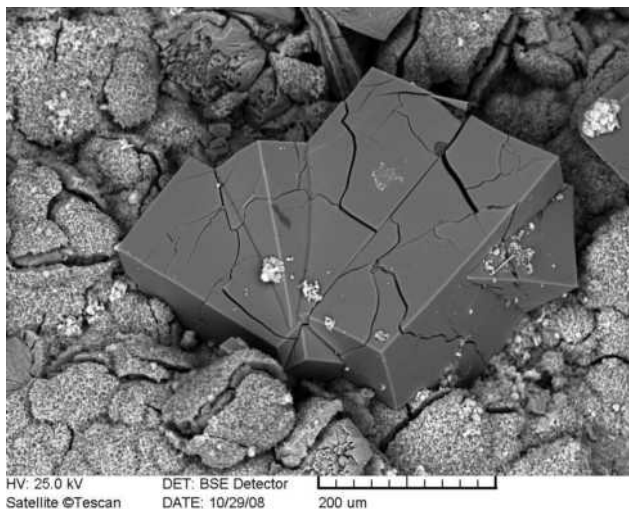


FIGURE 1. SEM image of chabazite-Mg on saponite.

be directly determined because of the very small amount of material available, but, as reported in the following sections, it was calculated from the results of the crystal-structure analysis and used to normalize the microprobe analysis to 100%, to correct for the undetermined loss of zeolitic water under the electron beam. Only 17 point analyses, with balance error $E\% < 10\%$ (Passaglia 1970), were considered reliable, averaged, and reported in Table 1. The empirical formula (based on 24 framework O atoms) is $(\text{Mg}_{0.67}\text{K}_{0.52}\text{Ca}_{0.48}\text{Na}_{0.08}\text{Sr}_{0.03})_{\Sigma 1.78}[(\text{Al}_{3.16}\text{Si}_{8.89})_{\Sigma 12.05}\text{O}_{24}] \cdot 9.68 \text{ H}_2\text{O}$. The simplified, charge-balanced formula is $(\text{Mg}_{0.7}\text{K}_{0.5}\text{Ca}_{0.5}\text{Na}_{0.1})[\text{Al}_3\text{Si}_9\text{O}_{24}] \cdot 10\text{H}_2\text{O}$.

Different crystals show slightly different chemical composition, although Mg is always the most abundant extraframework cation. As shown by the high standard deviation value (Table 1), the main variability is observed, among the extraframework cations, for K. In particular, the K value is positively related to the Al content, while the Mg content is nearly constant.

Chemical formulae of chabazite species are reported for comparison in Table 2. Besides the different extraframework content, substantial differences in the Si/Al ratio are evident. In particular, chabazite-Mg is the species with the highest Si/(Si+Al) ratio (0.74), while chabazite-Sr has the lowest (0.61). This result is consistent with the data reported by Passaglia and Ferro (2002) for magnesian chabazite-Ca samples, where the Si/(Si+Al) ratio ranges from 0.65 to 0.75.

X-RAY CRYSTALLOGRAPHY

Powder data

The X-ray powder diffraction pattern of chabazite-Mg (Table 3) was obtained from a synchrotron experiment carried out at the BM01A beamline of the ESRF (Grenoble, France), using a Debye-Scherrer geometry and a MAR 345 IP detector. NIST SRM 660a was used for the calibration of sample to detector

TABLE 1. Chemical analysis and unit-cell content (on the basis of 24 O atoms) of chabazite-Mg

Oxide wt%	apfu
SiO ₂	56.0(7)
Al ₂ O ₃	16.9(4)
Fe ₂ O ₃	0.02(2)
MgO	2.85(7)
K ₂ O	2.5(4)
CaO	2.8(2)
Na ₂ O	0.27(5)
SrO	0.3(1)
BaO	0.02(3)
H ₂ O	18.30
E%*	6.48
Si/(Si+Al)	0.74
Si	8.89(9)
Al	3.16(9)
Fe	—
Mg	0.67(2)
K	0.52(9)
Ca	0.48(3)
Na	0.08(2)
Sr	0.03(1)
Ba	—
H ₂ O	9.68
M/D†	0.51
Point analyses	17

Notes: Standard deviations are given in parentheses; oxides weight percentages were normalized to 100% according to the water content obtained from structural refinement.

* Passaglia et al. (1970).

† M = Na + K; D = Mg + Ca + Sr.

distance, beam center, and non-orthogonality of detector. The wavelength used in the experiment was 0.7355 Å; the detector distance was 230 mm and the exposure time 300 s. The powdered sample was carefully packed inside a 0.3 mm capillary. A one-dimensional diffraction pattern was obtained in the 2θ range 1.5–37° by integrating the two dimensional image with the program FIT2D (Hammersley et al. 1996).

Unit-cell parameters were refined using the GSAS package (Larson and Von Dreele 1996) and the EXPGUI graphical interface (Toby 2001) with the Rietveld method. Initial unit-cell parameters were taken from Zema et al. (2008) and the refinement was performed in the space group $R\bar{3}m$. Lattice parameters

TABLE 3. X-ray powder diffraction data for chabazite-Mg

<i>l</i> / <i>h</i>	<i>d</i> _{meas}	<i>d</i> _{calc} *	<i>hkl</i>	<i>l</i> / <i>h</i>	<i>d</i> _{meas}	<i>d</i> _{calc} *	<i>hkl</i>	<i>l</i> / <i>h</i>	<i>d</i> _{meas}	<i>d</i> _{calc} *	<i>hkl</i>
60	9.306	9.307	1 0 0	8	1.861	1.861	5 0 0	1	1.382	1.382	24 5
14	6.888	6.889	1 0 1	1	1.845	1.845	5 1 1	1	1.378	1.378	50 5
5	6.311	6.311	0 1 1	5	1.837	1.837	2 3 3	4	1.359	1.359	32 6
37	5.537	5.537	1 1 1	5	1.806	1.806	4 2 3	1	1.357	1.357	43 5
25	4.958	4.957	1 1 1	2	1.797	1.797	5 1 1	1	1.346	1.346	60 4
5	4.653	4.653	2 0 0	15	1.795	1.795	1 3 4	1	1.344	1.344	34 4
100	4.315	4.316	2 0 1				5 1 0	1	1.341	1.341	63 0
10	3.977	3.977	2 1 1	1	1.788	1.788	0 3 4	6	1.331	1.331	62 2
20	3.856	3.856	1 1 2	3	1.783	1.783	3 2 4	1	1.329	1.330	23 6
38	3.550	3.550	2 1 1	1	1.775	1.775	4 2 2	2	1.327	1.327	61 4
12	3.444	3.444	2 0 2	12	1.767	1.767	5 1 2	7	1.326	1.326	63 3
9	3.230	3.230	2 1 2	2	1.739	1.739	2 3 4	2	1.321	1.321	52 5
13	3.156	3.155	0 2 2	14	1.722	1.722	4 0 4	2	1.309	1.309	70 2
3	3.102	3.102	3 0 0	3	1.719	1.719	1 3 4	1	1.307	1.307	71 2
			1 2 2	3	1.693	1.693	5 2 2	1	1.307	1.307	63 1
2	3.023	3.023	3 0 1	4	1.684	1.685	5 2 1	1	1.295	1.295	24 5
78	2.924	2.925	3 1 1	5	1.653	1.652	3 3 3	3	1.281	1.281	54 4
4	2.886	2.886	1 2 2	7	1.644	1.644	5 1 3				72 2
41	2.869	2.869	3 1 0	2	1.637	1.638	2 2 5	1	1.271	1.271	15 5
3	2.829	2.829	3 1 1	4	1.634	1.634	3 3 4	1	1.264	1.264	44 5
5	2.768	2.768	2 2 2	1	1.627	1.627	5 1 3	2	1.263	1.263	70 3
1	2.692	2.692	3 0 2	2	1.621	1.621	5 2 1	3	1.262	1.262	05 5
7	2.662	2.662	3 1 1	2	1.587	1.587	1 4 4	1	1.259	1.259	53 5
16	2.603	2.604	3 1 2	2	1.580	1.580	5 2 3				71 3
6	2.569	2.569	2 1 3	2	1.578	1.578	0 4 4	3	1.250	1.250	72 0
20	2.483	2.483	0 2 3	7	1.552	1.552	6 0 1	1	1.246	1.246	63 4
1	2.472	2.472	1 2 3	4	1.520	1.520	5 0 4	1	1.242	1.242	04 6
2	2.356	2.356	3 2 2	1	1.513	1.513	2 3 5	1	1.240	1.240	72 2
4	2.332	2.332	3 2 1	3	1.512	1.512	6 0 2	1	1.237	1.237	61 5
4	2.305	2.305	2 2 3	1	1.509	1.509	6 1 0	1	1.232	1.231	15 5
4	2.296	2.296	3 0 3	3	1.484	1.484	5 3 3	2	1.223	1.224	43 6
3	2.272	2.272	4 1 1	1	1.479	1.479	3 4 4	1	1.212	1.212	14 6
1	2.204	2.204	4 1 1	1	1.476	1.476	4 3 3	2	1.207	1.207	62 5
2	2.158	2.158	4 0 2	2	1.462	1.462	6 2 2	1	1.204	1.204	72 3
2	2.121	2.121	4 1 2	2	1.451	1.451	5 2 4	1	1.200	1.200	70 4
1	2.104	2.104	4 1 1	2	1.446	1.446	3 3 5	5	1.192	1.192	73 1
2	2.092	2.092	3 2 2	3	1.438	1.439	4 2 5	1	1.185	1.185	54 5
12	2.083	2.084	4 1 2	4	1.430	1.430	6 1 3	1	1.183	1.183	63 3
9	2.059	2.059	3 2 3	4	1.414	1.414	6 2 2	1	1.172	1.172	72 4
1	2.012	2.012	4 2 0	3	1.413	1.413	6 1 3	2	1.169	1.169	45 5
5	1.988	1.989	4 2 2	3	1.413	1.413	5 3 2	1	1.169	1.169	81 1
2	1.944	1.944	4 0 3	1	1.404	1.404	1 4 5	2	1.163	1.163	80 0
3	1.922	1.922	4 2 1	6	1.395	1.395	6 2 1	2	1.152	1.152	53 6
4	1.910	1.911	4 1 3				0 4 5				
2	1.896	1.897	3 1 4	2	1.390	1.390	6 2 3				

Note: By *hkl* from rhombohedral setting.

* Calculated on the basis of the unit-cell parameters obtained by powder pattern [$a_R(\text{Å}) = 9.3727(3)$, $\alpha_R(^{\circ}) = 94.609(2)$].

TABLE 2. Chemical formulae and unit-cell parameters—in hexagonal setting—of the species of chabazite series

	Formulae	Ref.	<i>a</i> _H (Å)	<i>c</i> _H (Å)	<i>V</i> _H (Å ³)
Chabazite-Ca	(Ca _{1.86} Na _{0.03} K _{0.26} Mg _{0.02} Sr _{0.03})Al _{3.94} Si _{8.03} O ₂₄ ·13.16 H ₂ O	Passaglia (1970) n.13*	13.790(5)	15.040(4)	2476.89
Chabazite-Na	(Na _{3.11} K _{1.05} Ca _{0.19} Mg _{0.06} Sr _{0.05})Al _{4.53} Si _{7.40} O ₂₄ ·11.47 H ₂ O	Passaglia (1970) n.1*	13.863(3)	15.165(3)	2523.99
Chabazite-K	(K _{2.06} Na _{0.98} Ca _{0.46} Mg _{0.10} Sr _{0.01})Al _{4.37} Si _{7.60} O ₂₄ ·11.42 H ₂ O	De Gennaro et al. (1976)	13.849(3)	15.165(3)	2518.89
Chabazite-Sr	(Sr _{1.08} Ca _{0.92} K _{0.68} Na _{0.30} Ba _{0.02})Al _{4.62} Si _{7.28} O ₂₄ ·11.06 H ₂ O	Pekov et al. (2000)	13.715(6)	15.09(1)	2458.17
Chabazite-Mg	(Mg _{0.67} K _{0.52} Ca _{0.48} Na _{0.08} Sr _{0.03})Al _{3.16} Si _{8.89} O ₂₄ ·9.68 H ₂ O	This work	13.7773(8)	14.8724(6)	2444.77

* As reported by Coombs et al. (1998).

were refined in the range $3^\circ \leq 2\theta \leq 36.8^\circ$. The background was fitted with a Chebyshev polynomial function with 24 polynomial coefficients. The pseudo-Voigt profile function proposed by Thomson et al. (1987) was applied using one Gaussian and two Lorentzian coefficients.

All observed peaks are consistent with the $R\bar{3}m$ space group. In Table 2, unit-cell parameters of chabazite-Mg—in the hexagonal setting—are reported along with those of the other chabazite species for comparison. In the crystallochemical study of chabazites, Passaglia (1970) observed that the unit-cell parameter c (in the hexagonal setting) increases with the Al content. In agreement with this study, the c_H of chabazite-Mg is the smallest among the chabazite species, as expected on the basis of the lowest Al content, and its unit-cell volume is the smallest.

Structure analysis

Single-crystal data collection was carried out using a Bruker X8-Apex diffractometer equipped with a CCD detector. Operating conditions were 50 kV and 30 mA. The Bruker SMART system was used for preliminary crystal lattice determination and X-ray data collection. A total of 2140 frames (resolution: 512×512 pixels) were collected at seven different goniometer settings, using a scan width of 0.3° , exposure time of 20 s/frame, and a sample to detector distance of 4 cm. For each setting, only one of the four goniometer circles was moved, while the other three were fixed. A complete set of data up to $40.86^\circ 2\theta$ was measured. The Bruker program SAINT+ was used for data reduction and background and Lorentz-polarization corrections. The semi-empirical absorption correction of Blessing (1995) was applied using the program SADABS (Sheldrick 2003).

The unit-cell parameters calculated from powder data are larger than those obtained from the single-crystal experiment (Table 4). This result can be explained by the observed chemical variability in different crystals of chabazite-Mg. In particular, the microprobe analyses performed on the crystal used for X-ray diffraction data collection gave a balance error greater than 10% and were not included in the mean chemical analysis. However, the Mg content was very similar to the other “good” point analyses, while the K and Al contents were among the lowest found for the analyzed crystals. In agreement with results of Passaglia (1970)—with the observation that the chabazite c cell parameter (in the hexagonal setting) increases with Al content—the unit-cell parameters of chabazite-Mg were certainly obtained from a crystal with lower K and Al contents than the mean of the crystals used for the powder pattern. In general, the unit-cell volume of chabazite-Mg is among the smallest reported for chabazite species.

The systematic extinctions were consistent with the space group $R\bar{3}m$, thus indicating that the prevalence of Mg among

TABLE 4. Lattice parameters obtained by single-crystal and powder data in rhombohedral and hexagonal setting

Single-crystal		Powder	
a_R (Å)	9.3433(5)	a_R (Å)	9.3727(3)
α_R (°)	94.894(4)	α_R (°)	94.609(2)
V_R (Å ³)	806.17(5)	V_R (Å ³)	814.93(7)
c_H (Å)	13.7655(7)	a_H (Å)	13.7773(8)
c_H (Å)	14.7378(7)	c_H (Å)	14.8724(6)
V_H (Å ³)	2418.51	V_H (Å ³)	2444.77

Notes: Standard deviations are given in parentheses.

the extraframework cations does not affect the original chabazite symmetry. Consequently, structural refinement was carried out in the space group $R\bar{3}m$ using SHELXL-97 (Sheldrick 1998), starting from the atom coordinates reported by Zema et al. (2008). The neutral atomic scattering curves were taken from the *International Tables for X-ray Crystallography* (Ibers and Hamilton 1974). Equivalent reflections were averaged and the resulting internal agreement factors are reported in Table 5.

In the initial stages of structure refinement, only framework atoms were inserted in the model and refined with anisotropic displacement parameters, with the Si/Al ratio constrained on the basis of chemical data. The extraframework cations and water molecules were localized using difference Fourier map, inserted in the model, and then refined. These positions agree closely with those found by Alberti et al. (1982) and hence were labeled following these authors. All these extraframework sites are partially occupied (Table 6). Two new sites, labeled C3a

TABLE 5. Details on single-crystal data collection and refinement of chabazite-Mg

a_R (Å)	9.3433(5)
α_R (°)	94.894(4)
V_R (Å ³)	806.17(5)
Space group	$R\bar{3}m$
T_{min}/T_{max}	0.908
θ range (°)	3.25–40.86
Index ranges	$-16 \leq h \leq 17, -16 \leq k \leq 16, -16 \leq l \leq 15$
Reflections measured	57552 (13766 after merging identical reflections)
R_{int}^*	0.0313 (1842 unique reflections)
$R_1^\dagger$	0.0571 (1584 refl. with $I > 4\sigma$)
R_{all}	0.0640
wR_2	0.1709
GOF [‡]	1.085
Refined parameters	67
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0895 P)^2 + 0.88 P]$, where $P = (F_o^2 + 2F_c^2)/3$
(shift/e.s.d.)max	0.000

Notes: Standard deviations are given in parentheses.

$$^* R_{int} = \sum |F_o^2 - \overline{F_o^2}| / \sum F_o^2$$

$$^\dagger R_1 = \sum \|F_o\| - \|F_c\| / \sum \|F_o\|$$

$$^\ddagger GOF = S = \sqrt{\sum w(F_o^2 - F_c^2)^2 / (n - p)}$$

where n is the number of reflections and p is the total number of parameters refined.

TABLE 6. Atomic coordinates (rhombohedral setting), site occupancy, and displacement factors for chabazite-Mg

Site	x/a	x/b	x/c	Occ.	U_{eq}
T-12i	0.10679(4)	0.33406(4)	0.87926(4)	1	0.0148(1)
O1-6f	0.2583(2)	-0.2583(2)	0	1	0.0441(6)
O2-6g	0.1544(2)	-0.1544(2)	0.5	1	0.0321(4)
O3-6h	0.2560(2)	0.2560(2)	0.8998(3)	1	0.0405(6)
O4-6h	0.0313(2)	0.0313(2)	0.3312(3)	1	0.0346(4)
C2-2c	0.2380(7)	0.2380(7)	0.2380(7)	0.26(2)	0.047(3)
C3a-6h	0.425(1)	0.350(2)	0.425(1)	0.11(1)	0.085(9)
C4-6h	0.5843(9)	0.5843(9)	0.221(2)	0.058(4)	0.041(3)
W1-3d	0	0.5	0.5	0.48(4)	0.13(1)*
W2-6h	0.258(3)	0.258(3)	0.524(4)	0.24(2)	0.16(3)*
W3-12i	0.151(3)	0.419(2)	0.511(3)	0.29(1)	0.19(2)*
W4-6g	0.375(2)	-0.375(2)	0.5	0.34(2)	0.20(3)*
W6a-6h	0.289(3)	0.289(3)	0.232(2)	0.21(2)	0.072(8)*

Notes: Standard deviations are given in parentheses. Multiplicity and Wyckoff letter are reported for each site. U_{eq} = equivalent displacement parameters = $1/3[U_{11} + U_{22} + U_{33} + 2(U_{12} + U_{13} + U_{23})\cos\alpha]$ (Hamilton 1959).

* U_{iso} = isotropic displacement parameters.

and W6a, were found slightly displaced out of the threefold axis and near the C3 and W6 positions—here empty—reported by Alberti et al. (1982). Moreover, the W3 position shows slightly different coordinates from literature chabazites, but is relatively close to those reported by Alberti et al. (1982) for the Sr-exchanged chabazite. On the basis of cation-framework oxygen atom distances and of the cation distribution in extraframework sites proposed by Alberti et al. (1982), Ca was assumed to occupy the C4 site and K the C2 site. Magnesium was located in C3a considering the short distances from the water molecules (Table 7).

Anisotropic temperature factors were used for framework atoms and for extraframework cation sites. Conversely, because of the high number and closeness of partially occupied sites, isotropic temperature factors were used for the water O atoms. The final difference-Fourier map was featureless. In Table 6, atomic coordinates (in the rhombohedral setting), displacement, and site occupancy factors for chabazite-Mg are reported.

The C4 site is located along the walls of the chabazite cage about 2.2 Å away from the plane of the 8-ring window (Fig. 3).

TABLE 7. Chabazite-Mg interatomic distances (Å) lower than 3.1 Å

T-O1	1.6290(9)	W2-C2	2.65(4)
T-O2	1.6400(8)	W2-C3a (x2)	2.04(5)
T-O3	1.6321(8)	W2-C3a	2.83(4)
T-O4	1.6403(8)	W2-C4	2.90(4)
Mean	1.6353	W2-C4 (x2)	3.10(3)
		W2-W3 (x2)	1.88(4)*
C2-O4 (x3)	2.856(6)	W2-W3 (x2)	2.86(4)
C2-C3a (x3)	2.46(2)*	W2-W4 (x2)	2.50(3)
C2-W2 (x3)	2.65(4)	W2-W6a (x2)	2.23(4)*
C2-W6a (x3)	0.65(3)*	W2-W6a	2.80(4)
C3a-C2	2.46(2)*	W3-O1	3.10(3)
C3a-C3a (x2)	1.04(4)*	W3-C3a	2.08(4)
C3a-C3a (x2)	3.00(3)	W3-C3a	2.86(3)
C3a-C4	2.46(2)*	W3-C3a	3.07(3)
C3a-W2 (x2)	2.04(5)	W3-C4	1.69(2)*
C3a-W2	2.82(4)	W3-W1	1.66(3)*
C3a-W3 (x2)	2.08(4)	W3-W2	1.88(4)*
C3a-W3 (x2)	2.86(3)	W3-W2	2.86(4)
C3a-W3 (x2)	3.08(3)	W3-W3	1.26(5)*
C3a-W4 (x2)	1.92(2)	W3-W3	3.06(4)
C3a-W4 (x2)	2.34(3)	W3-W4	2.30(3)*
C3a-W4 (x2)	2.69(3)	W3-W4	2.73(3)
C3a-W6a	1.92(3)	W3-W6a	2.52(4)
C3a-W6a (x2)	2.12(3)	W3-W6a	3.04(4)
C4-O2 (x2)	2.739(6)	W4-O2	3.04(2)
C4-O3	2.44(1)	W4-C3a (x2)	1.92(2)
C4-C3a	2.46(2)*	W4-C3a (x2)	2.34(3)
C4-C4 (x2)	3.08(1)	W4-C3a (x2)	2.69(3)
C4-W1	2.20(1)	W4-C4 (x2)	1.72(2)*
C4-W2	2.90(4)	W4-W2 (x2)	2.50(3)
C4-W2 (x2)	3.10(3)	W4-W3 (x2)	2.30(3)*
C4-W3 (x2)	1.69(2)*	W4-W3 (x2)	2.73(3)
C4-W4 (x2)	1.72(2)*	W4-W4 (x2)	1.72(3)*
		W4-W4 (x2)	2.98(3)
W1-C4 (x2)	2.20(1)	W6a-O3 (x2)	3.08(2)
W1-W3 (x4)	1.66(3)*	W6a-O4 (x2)	3.00(2)
		W6a-C2	0.65(3)*
		W6a-C3a	1.92(3)
		W6a-C3a (x2)	2.12(3)
		W6a-W2 (x2)	2.23(4)*
		W6a-W2	2.80(4)
		W6a-W3 (x2)	2.52(3)
		W6a-W3 (x2)	3.04(3)
		W6a-W6a (x2)	0.78(5)*

Notes: Standard deviations are given in parentheses.

* These pairs of sites are too close to be simultaneously occupied (see text).

It coordinates two O2, one O3, one W1, and three W2 (Table 7; Fig. 4) in a distorted pentagonal bipyramid. The excessively short distances from the W3 and W4 water molecules rule out the simultaneous occupation of these sites.

The C2 site is located along the threefold axis, near the 6-ring of *d6R*, and is coordinated by three O atoms O4 and by three W2 water molecules in a triangular prism (see Table 7; Fig. 5). The excessively short distance from the W6a water molecule rules out the simultaneous occupation of these sites.

In chabazite, Na and Ca usually occupy the C3 site on the threefold axis (Alberti et al. 1982; Calligaris et al. 1982; Zema et al. 2008), while in magnesian chabazite-Ca C3 is occupied by Mg (Passaglia and Ferro 2002). In chabazite-Mg, C3 is empty and Mg is sited at C3a, near the center of the chabazite cage. This site has a distorted octahedral coordination with six water molecules (one W2, one W3, three W4, and one W6a) (Table 7; Fig. 6). This coordination is the only one possible for the C3 site as a consequence of the excessively short distances between the water molecules. The octahedral coordination is characteristic of Mg and has also been reported in magnesian chabazite-Ca (Passaglia and Ferro 2002) and in other zeolites like mazzite (Galli 1975) and ferrierite (Vaughn 1966). The C3a position has excessively short distances from the C2 and C4 sites for simultaneous occupancy (Table 7).

The W1 site is at the center of the 8-ring window and has occupancy of 0.5, much lower than that found in literature

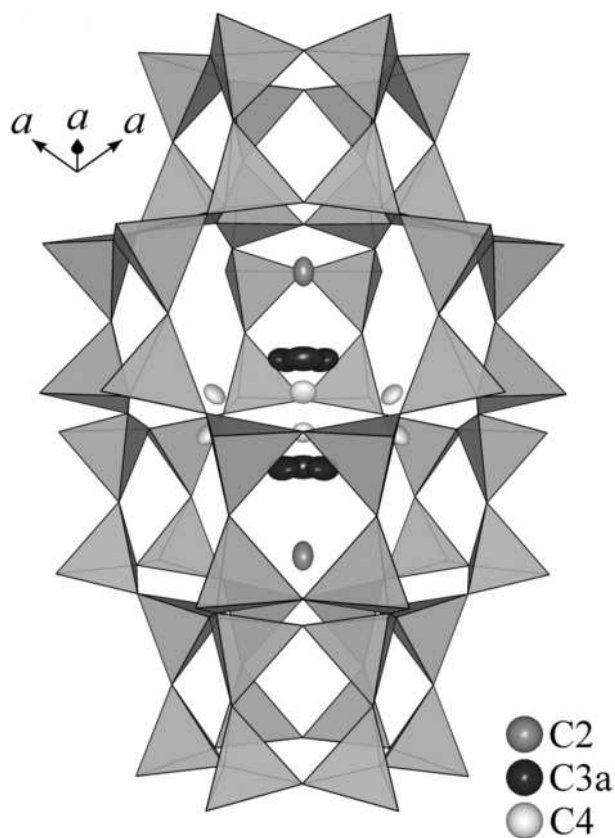


FIGURE 3. Crystal structure of chabazite-Mg. Extraframework cations are represented as displacement ellipsoids drawn at 50% probability level.

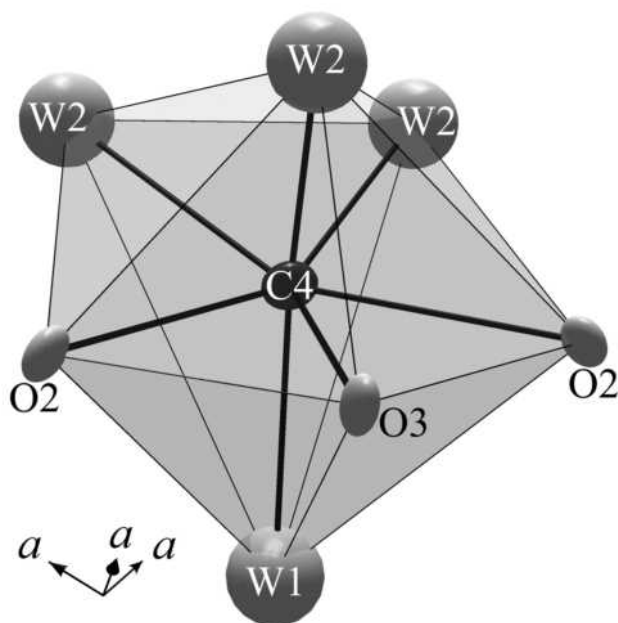


FIGURE 4. Coordination polyhedron of the C4 site. Atoms are represented as displacement ellipsoids drawn at 30% probability level.

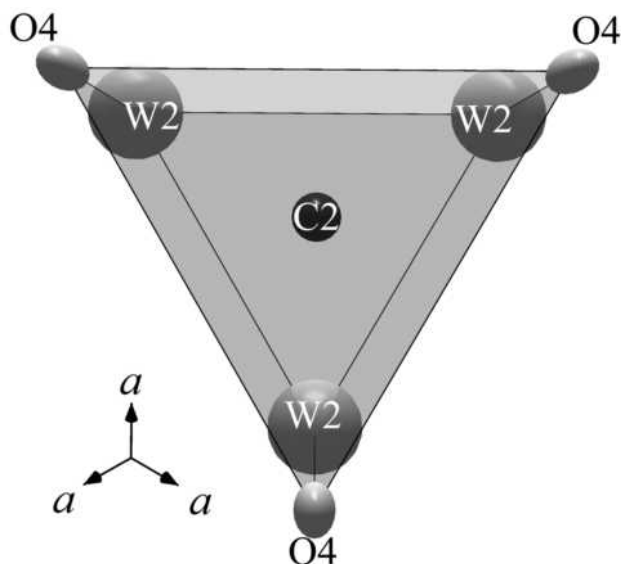


FIGURE 5. Coordination polyhedron of the C2 site. Atoms are represented as displacement ellipsoids drawn at 30% probability level.

(Alberti et al. 1982; Calligaris et al. 1982; Zema et al. 2008; Passaglia and Ferro 2002). The excessively short distance from W3 rules out simultaneous occupation of the two sites. The other water sites are inside the large chabazite cage, with occupancies ranging between 0.2 and 0.3. The large distances between water sites and framework O atoms—greater than 3.00 Å (Table 7)—suggest that all these hydrogen bonds are very weak. Strong hydrogen bonds are instead observed between W2···W4, W3···W4, and W3···W6a.

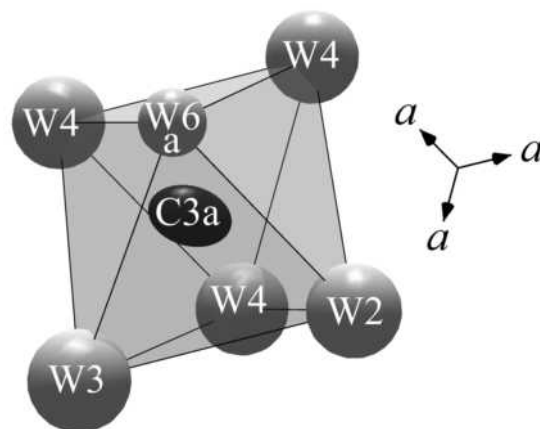


FIGURE 6. Coordination polyhedron of the C3a site. Atoms are represented as displacement ellipsoids drawn at 30% probability level.

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