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CRISTIAN BIAGIONI [(1)]

A NEW OCCURRENCE OF A Mg-RICH MEMBER OF THE CHABAZITE SERIES FROM TUSCANY (ITALY)

Abstract - C. BIAGIONI, *A new occurrence of a Mg-rich member of the chabazite series from Tuscany (Italy).*

The finding of a Mg-rich member of the chabazite series from vugs in metabasaltic rocks from the Ugione Valley, Monti Livornesi, Livorno, Tuscany, Italy, is reported here. This member of the chabazite series occurs as whitish pseudohexagonal (phacolitic habit) crystals, associated with "chlorite". Chemical analyses (EDS mode) gave the chemical formula $(Mg_{0.80}K_{0.55}Ca_{0.50})_{\Sigma 1.85}(Al_{3.07}Si_{8.91})_{\Sigma 11.98}O_{24}\cdot nH_2O$. Single-crystal X-ray diffraction allowed the refinement of the crystal structure of this sample. Unit-cell parameters (hexagonal setting) are a_H = 13.7979(4), c_H = 14.9364(5) Å, V_H = 2462.65(16) Å^3, space group $R\bar{3}m$. The crystal structure of this mineral was refined to R_1 = 0.0373 for 628 unique reflections with $F_o > 4\sigma(F_o)$ and 73 refined parameters. These data improve the knowledge about the zeolite minerals in Tuscany and allow to report the occurrence of a Mg-rich member of the chabazite series in the hydrothermal veins hosted within ophiolitic rocks.

Key words - zeolite, chabazite series, magnesium, crystal structure, ophiolite, Monti Livornesi, Tuscany

Riassunto - C. BIAGIONI, *Un nuovo ritrovamento di un termine ricco in Mg della serie della cabasite dalla Toscana (Italia).*

Viene descritto il ritrovamento di un membro ricco in Mg della serie della cabasite nelle cavità di rocce basaltiche affioranti nella valle dell'Ugione, Monti Livornesi, Livorno, Toscana, Italia. Questo membro della serie della cabasite forma cristalli biancastri, pseudoesagonali, di abito facolitico, associati a clorite. Analisi chimiche (in modalità EDS) hanno condotto alla formula $(Mg_{0.80}K_{0.55}Ca_{0.50})_{\Sigma 1.85}(Al_{3.07}Si_{8.91})_{\Sigma 11.98}O_{24}\cdot nH_2O$. Gli studi in diffrazione di raggi X con tecniche di cristallo singolo hanno consentito di raffinare la struttura di questo campione. I parametri della cella esagonale sono a_H = 13.7979(4), c_H = 14.9364(5) Å, V_H = 2462.65(16) Å^3, gruppo spaziale $R\bar{3}m$. La struttura è stata raffinata fino a un fattore di accordo R_1 = 0.0373 per 628 riflessi unici con $F_o > 4\sigma(F_o)$ e 73 parametri raffinati. Questi dati accrescono le conoscenze sulle zeoliti toscane e consentono di descrivere la presenza di un membro ricco in Mg della serie della cabasite nelle vene idrotermali ospitate nelle rocce ofiolitiche.

Parole chiave - zeolite, serie della cabasite, magnesio, struttura, ofioliti, Monti Livornesi, Toscana

INTRODUCTION

The occurrence of zeolite group minerals from Tuscany is known since the 19th century (e.g., D'Achiardi, 1873), when some species were described from two different kinds of occurrence. The first known occurrence was represented by ophiolitic rocks; in particular, several species were found during the exploitation of the Montecatini Val di Cecina copper mine (Biagioni *et al*., 2017, and references therein). The area around San Piero in Campo (Elba Island) is the most important representative of the second kind of occurrence, i.e., cavities within pegmatite (e.g., Orlandi & Pezzotta, 1996).

"Chabazite" was first reported from this latter occurrence by Grattarola (1872); Sansoni (1880) gave chemical data, allowing the classification of this mineral as chabazite-Ca, following the current nomenclature of zeolite minerals (Coombs *et al*., 1997). In the Elba Island, further descriptions of "chabazite" were reported from Pomonte and Seccheto by Nannoni & Sammartino (1984, 1987) and from Cavoli by Orlandi & Pezzotta (1996). "Chabazite" has been found also in ophiolitic rocks. Nannoni & Sammartino (1979) reported the occurrence of rhombohedral crystals or phacolitic individuals, associated with natrolite, "phillipsite", prehnite, and "garnet", from the Poggio Corbolone area, in the northern sector of the Monti Livornesi; similar samples are shown in the Figure 13-3 of Bracci & Orlandi (1990). Sammartino (2008) reported other occurrences from the same area, i.e., from Monte Maggiore and from a basalt quarry close to Rosignano Marittimo. The same author described the occurrence of "chabazite" from the Ugione valley, in the southern part of the Poggio Corbolone area, along with another phase, tentatively identified as erionite/offretite (Sammartino, 2014). In addition, "chabazite" was reported from some ophiolitic outcrops along the Cecina Valley (i.e., Riparbella – Orlandi, 2005), in the Poggio del Cornocchio area (Betti *et al*., 2017), and along the Crevole stream, near Murlo (Betti & Pagani, 2000).

It is worth noting that no chemical data of "chabazite" from ophiolitic rocks were reported by all previous authors. In the framework of a systematic study of the mineralogy of Tuscany, we examined the crystal-chemistry of a sample of "chabazite" from the northern sector of the Monti Livornesi, finding high Mg content, suggesting the potential occurrence of chabazite-Mg. This species, belonging to the chabazite series, was first identified by Montagna *et al.* (2010) from basalts of the Karikás-tető area of the Prága Hill, West Hungary. Another potential occurrence of chabazite-Mg from the Island Magee,

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County Antrim, Ireland, was reported by Ryback *et al.* (1988). This finding from Tuscany may represent a potential third world-occurrence of chabazite-Mg. In this paper the crystal-chemical features of this Mg-rich member of the chabazite series are reported.

EXPERIMENTAL

The studied specimen was collected by the mineral amateur Franco Sammartino and briefly described in Sammartino (2014). The studied phase occurs as a pseudohexagonal crystal, showing a phacolitic habit, up to 1 mm across, white in color, associated with "chlorite". Chemical analyses were performed on an unpolished grain using a Philips XL30 scanning electron microscope equipped with an EDAX spectrometer operating in energy-dispersive mode (EDS). Emission lines were calibrated using the following standards: olivine (Mg, Si), albite (Al, Si), orthoclase (K, Al, Si), and diopside (Ca, Mg, Si). Sodium was below the detection limit. On the basis of 24 O atoms per formula unit (apfu), the chemical analyses gave the formula $(\mathrm{Mg}_{0.80}\mathrm{K}_{0.55}\mathrm{Ca}_{0.50})_{\Sigma 1.85}(\mathrm{Al}_{3.07}\mathrm{Si}_{8.91})_{\Sigma 11.98}\mathrm{O}_{24}\cdot n\mathrm{H}_2\mathrm{O}$. Owing to the low amount of available material, the H_2O content was not determined.

X-ray diffraction study was performed on the same unpolished grain used for chemical analysis. Data were collected using a Bruker Smart Breeze diffractometer operating at 50 kV and 30 mA and equipped with an air-cooled CCD detector. Graphite-monochromatized Mo*K*α radiation was used. The detector-to-crystal working distance was set to 50 mm. Intensity data were integrated and corrected for Lorentz, polarization, background effects, and absorption using the package of software *Apex* 2 (Bruker AXS Inc., 2004). The studied sample is trigonal, space group $R\bar{3}m$, with unit-cell parameters (hexagonal setting) a_H = 13.7979(4), c_H = 14.9364(5) Å, V = 2462.65(16) Å^3, Z = 3. In the rhombohedral setting, the unit-cell parameters are a_R = 9.3941(2) Å, α = 94.512(1)°. The crystal structure was refined in the hexagonal setting using *Shelxl*-2018 (Sheldrick, 2015), starting from the atomic coordinates given by Montagna *et al.* (2010) in the rhombohedral setting and recasting them in the hexagonal setting. Neutral site scattering factors were taken from the *International Tables for Crystallography* (Wilson, 1992). The following scattering curves were used: K *vs* □ at the *C*(2) site, Mg *vs* □ at the *C*(3) site, Ca *vs* □ at the *C*(4) site, O at the O framework sites, and O *vs* □ at the H_2O site. The Si:Al ratio at the *T* site was fixed on the basis of chemical data. The isotropic refinement converged to R_1 = 0.212, with high U_eq values for extraframework cations and H_2O molecules. This suggested the necessity to refine the site occupancy factors (s.o.f.) at cation sites as well as at the H_2O sites, lowering the R_1 to 0.189. In addition, the occurrence of twinning according to a two-fold axis along [120] was suggested by the software PLATON. The addition of the twin matrix $[\,0\ 0\ \bar{1}\mid 1\ 1\ 0\mid 0\ 0\ \bar{1}\,]$ [twin ratio 0.524(3)] lowered the R_1 value to 0.136. The U_eq values of some H_2O molecules reported by Montagna *et al.* (2010) remained too high and they were removed. In addition, the *C*(3) site was removed owing to its high U_eq value and its position, as well as those of further H_2O molecules, was found in the difference-Fourier map. All atom positions, apart those corresponding to the Ow(3) site, were refined anisotropically. After several cycles of anisotropic refinement, the refinement converged to R_1 = 0.0373 for 628 unique reflections with $F_\mathrm{o} > 4\sigma(F_\mathrm{o})$ and 73 refined parameters. Details of data collection and crystal structure refinement are given in Table 1. Fractional atomic coordinates, site occupancies, and displacement parameters are reported in Table 2, whereas Table 3 shows interatomic distances shorter than 3.1 Å for cation sites. For the sake of comparison with the crystal structure of chabazite-Mg (Montagna *et al.*, 2010), the same site labels were used; the differences will be discussed in the following section.

Table 1. Crystal data and summary of parameters describing single-crystal X-ray data collection and refinement for the Mg-rich member of the chabazite series.

Crystal data	
Crystal size (mm)	0.18 × 0.15 × 0.12
Cell setting, space group	Hexagonal, $R\bar{3}m$
a (Å)	13.7979(4)
c (Å)	14.9364(5)
V (Å^3)	2462.65(16)
Z	3
Data collection and refinement	
Radiation, wavelength (Å)	Mo*K*α, λ = 0.71073
Temperature (K)	293(2)
Maximum observed 2θ (°)	56.83
Measured reflections	12449
Unique reflections	748
Reflections $F_\mathrm{o} > 4\sigma(F_\mathrm{o})$	628
R_int after absorption correction	0.0595
$R\sigma$	0.0232
Range of h, k, l	$-18 \le h \le 18$ $-18 \le k \le 18$ $-19 \le l \le 19$
R_1 [F_o>4σF_o]	0.0373
R_1 (all data)	0.0478
wR_2 (on F_o^2)	0.0938
Goodness of fit	1.134
Number of least-squares parameters	73
Maximum and minum residual peak (e/Å^3)	0.63 [at 3.04 Å from O(4)] -0.31 [at 1.21 Å from O(3)]

Table 2. Sites, Wyckoff position, site occupancy factors (s.o.f.), fractional atomic coordinates, and isotropic (*) or equivalent isotropic displacement parameters (Å^2) for the Mg-rich member of the chabazite series.

Site	**Wyckoff position**	**s.o.f.**	***x/a***	***y/b***	***z/c***	U_{eq}
T	36*i*	$Si_{0.75}Al_{0.25}$	-0.33351(6)	-0.43865(5)	0.43861(3)	0.0132(2)
O(1)	18*f*	$O_{1.00}$	0.2607(2)	0	0	0.0381(7)
O(2)	18*g*	$O_{1.00}$	-0.01424(19)	-1/3	1/6	0.0286(6)
O(3)	18*h*	$O_{1.00}$	-0.21347(13)	-0.4269(3)	0.4675(2)	0.0337(7)
O(4)	18*h*	$O_{1.00}$	-0.09927(13)	-0.1986(3)	0.1269(2)	0.0341(7)
C(2)	6*c*	$K_{0.22(6)}$	0	0	0.222(5)	0.066(13)
C(3)	6*c*	$Mg_{0.342(12)}$	0	0	0.4056(5)	0.056(4)
C(4)	18*h*	$Ca_{0.140(6)}$	0.1160(4)	0.2320(7)	0.4666(6)	0.049(3)
Ow(1)	9*e*	$O_{1.00}$	0	½	0	0.123(3)
Ow(2)	36*i*	$O_{0.50}$	-0.0294(13)	-0.1591(10)	0.3520(13)	0.201(7)
Ow(3)	36*i*	$O_{0.241(16)}$	0.152(3)	0.118(3)	0.530(2)	0.20(2)*
Ow(6)	18*h*	$O_{0.29(5)}$	0.009(3)	0.019(6)	0.247(4)	0.085(13)

Table 3. Interatomic distances (Å) lower than 3.1 Å for cation sites in the Mg-rich member of the chabazite series.

T	– O(1)	1.6356(10)	*C*(2)	– O(4) ×3	2.77(4)
	– O(3)	1.6395(11)		– *C*(3)	2.74(7)
	– O(4)	1.6435(11)		– Ow(2) × 6	2.80(5)
	– O(2)	1.6436(10)		– Ow(6) × 6	0.43(7)*
	average	1.6406			
			C(4)	– Ow(3) × 2	1.12(4)*
C(3)	– *C*(2)	2.74(7)		– Ow(3) × 2	2.09(4)*
	– *C*(3)	2.821(16)		– Ow(1)	2.330(9)
	– *C*(4) × 3	2.918(9)		– Ow(2) × 2	2.473(18)
	– Ow(3) × 6	2.14(3)		– O(3)	2.529(9)
	– Ow(2) × 6	2.176(12)		– O(2) × 2	2.812(5)
	– Ow(6) × 3	2.38(5)		– *C*(3)	2.918(9)
	– Ow(3) ×6	2.66(3)		– Ow(2) × 2	2.93(2)
				– *C*(4) × 2	2.946(11)

Note: the symbol * indicates too close sites to be simultaneously occupied.

DESCRIPTION OF THE CRYSTAL STRUCTURE

The framework of chabazite series minerals (framework type CHA; Baerlocher *et al.*, 2001) is formed by the stacking, along the **c** axis, of six-membered double rings of (Si,Al)-centered tetrahedra in the sequence ABC. In this way, a three-dimensional channel system, perpendicular to [0001] and delimited by eight-membered rings of tetrahedra, can be distinguished.

Silicon and aluminum are disordered at the unique *T* site. The average *T*–O bond distance is 1.641 Å. Taking into account the ideal $^{[IV]}$Si–O and $^{[IV]}$Al–O distances of 1.624 and 1.757 Å, respectively, calculated on the basis of the bond parameters of Brese & O'Keeffe (1991), such an average bond length should correspond to the *T*-site population ($Si_{0.87}Al_{0.13}$), to be compared with that of the chemical analysis, i.e., ($Si_{0.75}Al_{0.25}$). It is worth noting that the studied sample has a Si/(Al+Si) atomic ratio of 0.74, identical with that found in chabazite-Mg by Montagna *et al.* (2010) and in agreement with the high values reported for Mg-rich chabazite-Ca samples (Passaglia & Ferro, 2002). In agreement with Passaglia (1970), who observed that the unit-cell parameter *c* increases with the Al content, the studied sample, having a low Al content, has a *c* parameter (*c* = 14.936 Å) shorter than that found in other Al-richer samples (e.g., *c* = 15.040 and 15.165 Å in chabazite-Ca and chabazite-Na, respectively – Passaglia, 1970), and longer than that reported in chabazite-Mg (*c* = 14.872 Å – Montagna *et al.*, 2010).

It is well-known that the extra-framework species (both cations and H_2O molecules) may be difficult to be confidently assigned, owing to the partial occupancy of each site (e.g., Nakatsuka *et al.*, 2007 and references therein). In the studied sample, three extra-framework cation sites have been located, labeled *C*(2), *C*(3), and *C*(4). The *C*(2) site is on the three-fold axis and displays a trigonal prismatic coordination, being bonded to three framework oxygen atoms and to three H_2O molecules hosted at the Ow(2) site. The average bond distance, 2.78 Å, can be compared with the average distance observed in chabazite-Mg, 2.75 Å (Montagna *et al.*, 2010), supporting the preferential occurrence of K at this position. Actually, as shown in Table 3, there are six H_2O molecules at bond distance from *C*(2), but only one half can be occupied, in order to avoid too short Ow(2)–Ow(2) distances. *C*(2) is excessively close to Ow(6) [only 0.43(7) Å] and consequently these two sites are mutually exclusive. Similarly, the *C*(3) site is at relatively short distances from both *C*(2) and *C*(4) sites, suggesting – consistently with their s.o.f. – that these positions are alternately occupied. The *C*(3) site lies on the three-fold axis, but it is displaced ~ 2.75 Å with respect to the *C*(2) position. It is coordinated by H_2O molecules only. In chabazite-Mg, this site is slightly displaced from the three-fold axis. However, in the present sample, the crystal structure refinement suggested that a better description of the electron density could be achieved placing the site on the triad axis. According to Montagna *et al.* (2010), this site hosts Mg in octahedral coordination, in agreement with previous studies on Mg-rich chabazite-Ca (Passaglia & Ferro, 2002) and other Mg-zeolites (e.g., Vaughn, 1966; Galli, 1975). Taking into account the short distances between H_2O molecules, an octahedral coordination with three Ow(2) and three Ow(3) H_2O molecules may be proposed for the studied sample, with average bond length of 2.16 Å. Such a distance is definitely longer than that found in an ideal Mg-centered octahedron (i.e., ~ 2.10 Å). However, the large displacement parameters shown by H_2O molecules and, in particular, by the Ow(3) site, may suggest that shorter distances actually occur when the *C*(3) site is occupied by Mg. A seventh possible bond with Ow(6), at a longer distance [2.38(5) Å], occurs too. The *C*(4) site is located along the walls of the chabazite cage, as in chabazite-Mg (Montagna *et al.*, 2010). It forms too short distances with two Ow(3) atoms [at 1.12(4) Å]; likely, also other two distances *C*(4)–Ow(3) cannot be considered as bond distances, since their value [2.09(3) Å] seems to be too short for a site mainly occupied by Ca^{2+}. Consequently, the *C*(4) site shows a six-fold coordination, with bond distances ranging between 2.330(9) and 2.812(5) Å, and average bond distance of 2.572 Å. An additional bond at 2.93(2) Å with Ow(2) increases the coordination number to seven, allowing the description of this coordination polyhedron as a distorted pentagonal dipyramid. Likely, this site is mainly occupied by Ca^{2+}, although the occurrence of minor K^+ cannot be excluded.

The H_2O molecules show some differences with respect to chabazite-Mg. Indeed, whereas Ow(1) and Ow(6) correspond to W1 and W6 sites of Montagna *et al.* (2010), Ow(2) and Ow(3) have different coordinates and W4 of chabazite-Mg was not found. This is not surprising, taking into account the weak bonding interaction between H_2O molecules and the chabazite framework, as well as their disordered nature. Oxygen atoms belonging to H_2O molecules show several O···O distances in the typical range of H-bonds. Unfortunately, owing to the disordered nature of H_2O molecules, H atoms were not located, and the possible H-bond system will not be discussed here. However, it is interesting to observe that the O···O distances between oxygen atoms of the H_2O molecules and those belonging to the chabazite framework are usually longer than ~ 2.9 Å, thus suggesting that these H-bonds are weak. On the contrary, some relatively short O···O distances between H_2O molecules (i.e., ~ 2.6 Å) may indicate the occurrence of strong H-bonds.

The structural formula of the studied sample, as derived through the crystal structure refinement, is $[^{C(2)}K_{0.44}{}^{C(3)}Mg_{0.68}{}^{C(4)}Ca_{0.84}](Al_3Si_9)O_{24}{}^{Ow(1)}(H_2O)_3{}^{Ow(2)}(H_2O)_6{}^{Ow(3)}(H_2O)_{2.89}{}^{Ow(6)}(H_2O)_{1.74} = (Ca_{0.84}Mg_{0.68}K_{0.44})_{\Sigma 1.96}(Al_3Si_9)O_{24}{\cdot}13.63H_2O$. Such a formula is not charge-balanced, showing an excess of positive charges (+0.48). In addition, Ca appears to be the dominant cation. Actually, owing to the similar site scattering of K ($Z = 19$) and Ca ($Z = 20$), and the disordered nature of the extra-framework cation positions, it is not possible to distinguish between these two elements and the excess of positive charges may be simply due to the incorrect assignment of K and Ca. Consequently, it can be simply stated that the sum of (Ca + K) is larger than the amount of Mg, in agreement with chemical data, although Mg is underestimated with respect to EDS data. What is important is the comparison between the refined site scattering with that calculated on the basis of chemical data. The crystal structure refinement shows that the site scattering at the aggregate site [*C*(2) + *C*(3) + *C*(4)] is 33.3 electrons per formula unit (epfu), that can be compared with the calculated value of 30.0 epfu based on the results of the chemical analysis.

DISCUSSION

The crystal-chemical investigation of the specimen from the Monti Livornesi suggests the possible occurrence of chabazite-Mg in this area. However, since chemical analyses were performed on an unpolished sample and using EDS mode (instead of more accurate WDS mode on a polished grain), and some discrepancies were observed between chemical and structural data (possibly due to some chemical inhomogeneity of the studied grain), a more cautious classification of this mineral has to be preferred and indeed it is simply indicated as a Mg-rich member of the chabazite series. Notwithstanding this shortcoming, the studied specimen represents the first Mg-rich zeolite identified from the ophiolitic rocks occurring in Tuscany. It is worth noting that some Mg-zeolites were reported in the 19th century, to be later discredited due to further studies. Indeed, on the basis of the chemical analyses performed by Emilio Bechi, Meneghini (1852) described three new species from the Montecatini Val di Cecina copper mine: "picroanalcime", "picrothomsonite", and "savite". Bechi found up to ~ 10 wt% MgO in "picroanalcime", but later Bamberger (1882) demonstrated that Mg does not occur in this phase that could be correctly classified as analcime. Similarly, Manasse (1906) showed that the Mg content found by Bechi in "picrothomsonite" was due to chlorite inclusions in thomsonite. Finally, the finding of "savite", closely related to natrolite (Sella, 1858; D'Achiardi, 1873) gave rise to a scientific debate, because several mineralogists did not accept that a monovalent cation, like Na^+, could be replaced by divalent Mg^{2+}. In this case, Mattirolo (1886) clearly showed that the high Mg content was due to the occurrence of inclusions of Mg-rich phases.

The finding and crystal-chemical study of a Mg-rich chabazite in vugs from metabasalts belonging to the ophiolitic sequence was likely due to the action of Mg-rich hydrothermal fluids and it may suggest the potential presence of other interesting and rare Mg-rich zeolites in this kind of occurrence. On this basis, a reexamination of the old zeolite specimens from the Montecatini Val di Cecina mine, as well as samples from other localities, using a combination of micro-chemical and X-ray diffraction methods, seems to be mandatory. This study suggests another take-home message. The first description of a chabazite series mineral from the ophiolitic rocks occurring in Tuscany dates to the end of the 1970s (Nannoni & Sammartino, 1979). Since then, other identifications have been reported, but no chemical data were given. This shortcoming precluded the correct classification of these chabazite specimens and, very likely, the first identification of chabazite-Mg, that was described only recently (Montagna *et al.*, 2010). Every time that a mineralogist is dealing with a complex mineral (like zeolites), a full set of chemical and structural data is necessary to achieve an accurate characterization of the studied material. For instance, during the preliminary analyses of the studied specimen, a possible identification as offretite or erionite was suggested by the results of EDS chemical data (this is the reason for the erroneous report of Sammartino, 2014). Finally, X-ray diffraction data allowed a more correct classification of this chabazite series mineral. The only way to improve our knowledge of mineral crystal-chemistry and to find unexpected (but in some cases predictable) mineral species in the studied localities is a diligent and meticulous study using appropriate analytical techniques.

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