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The crystal structure of garronite

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ABSTRACT

The structures of the natural zeolite garronite, $NaCa_{2.5}Al_6Si_{10}O_{32}\cdot 13H_2O$, from Goble, Oregon, and Fara Vicentina, Italy, have been determined and refined by X-ray powder diffraction methods with the use of the full-profile Rietveld technique. The framework topology has the gismondine structure type (GIS), although the topological symmetry $I4_1/amd$ is lowered to $I\bar{4}m2$. Cell dimensions are Goble, $a = 9.9266(2)$, $c = 10.3031(3)$ Å; Fara Vicentina, $a = 9.8712(2)$, $c = 10.2987(3)$ Å. The space group assumed in the refinements accounts for the presence in the garronite powder pattern of reflections violating the d glide extinctions. Deviation from the maximum framework symmetry can be explained in terms of cation and H_2O arrangements in the zeolitic cavities.

INTRODUCTION

The natural zeolite garronite has been previously reported from a number of localities: Northern Ireland and Iceland (Walker, 1962; Nawaz, 1982), USSR (Feoktistov et al., 1969), France (Pongiluppi, 1976), Germany (Walenta, 1974; Hentschel, 1978), Hungary (Alberti et al., 1982), U.S.A. (Tealdi and Tschernich, 1984), Italy (Passaglia and Carnevali, personal communication). It is frequently associated with gismondine, gmelinite, mesolite, phillipsite, levyne, or other zeolites, and it is only known in rather compact radiating aggregates (Gottardi and Galli, 1985). The apparent impossibility of finding single crystals of garronite precluded structure solution for a long time, although analysis of the powder diffraction pattern and earlier comparative studies on the synthetic P zeolites (Barrer et al., 1959; Taylor and Roy, 1964) clearly indicated that garronite shares the framework topology of gismondine (Gottardi, 1979; Meier and Olson, 1987).

The ideal composition (Gottardi and Galli, 1985) corresponds to the chemical formula per unit cell: $NaCa_{2.5}Al_{6.0}Si_{10.0}O_{32.0}\cdot 13.0H_2O$. All characterization studies in the literature agree in assigning a tetragonal metric to the species, although peaks forbidden by space group $I4_1/amd$ have been observed (Gottardi and Galli, 1985, p. 325), and a domain structure model was postulated implying regions with Si,Al order and local monoclinic symmetry (Gottardi and Alberti, 1974). The garronite structure was therefore considered worth investigating by full-profile structure analysis techniques with powder diffraction data.

EXPERIMENTAL

Two specimens of garronite were selected for the present study on the basis of their phase purity: the sample from Goble, Oregon, U.S.A. (sample 16-10-38/gar/3 of the Mineral Collection, Institute of Mineralogy, University of Modena) is the same used by Gottardi and Galli (1985) to obtain X-ray powder diffraction data and thermal curves; the sample from a new locality, Fara Vicentina, Italy, is soon to be described (Passaglia and Carnevali, personal communication). The results of newly performed electron probe microanalyses were combined with thermal analysis data to yield the following chemical formulae: Goble, $K_{0.05}Na_{0.10}Ca_{2.71}Al_{5.87}Si_{10.20}O_{32.00}\cdot 14.12H_2O$; Fara Vicentina, $K_{0.05}Na_{0.06}Ca_{2.57}Sr_{0.11}Al_{5.63}Si_{10.40}O_{32.00}\cdot 13.79H_2O$. Both garronite samples therefore have slightly higher Ca/(Na + K) and Si/Al ratios compared with the chemical analysis of the type material from the Garron Plateau (Walker, 1962). High-Ca and low-Na,K contents were also found in garronite from Tardree (Northern Ireland, Nawaz, 1982). Based on the new analyses, it appears that the H_2O content in garronite is close to 14.0 H_2O molecules per cell and that Na-poor garronite is not uncommon.

Prior to X-ray diffraction analysis, the samples were repeatedly hand ground in an agate mortar. The diameter of the largest crystallites in the powder was below 15–20 μm, as measured by optical microscopy. Computation of approximate average particle size from the refined Lorentzian component of the peak profile function using the Scherrer equation (Scherrer coefficients between 1.0 and 1.5) gave values of 1.5–2.3 μm. The X-ray powder diffraction data were measured on a Philips PW-1050/81 instrument in the conventional Bragg-Brentano parafocusing geometry, using a flat-plate Plexiglas sample holder. Unfiltered Cu*Kα* radiation with a diffracted-beam pyrolitic graphite analyzer was employed, in a step-scan mode from 10 to 120° 2*θ* in steps of 0.02° and 10 s counting time for each step. The low-2*θ* region (10–17°), containing only one observed peak (101), was excluded during the refinement process because in this angular range not all the incident X-ray beam was striking the sample. The high background level from the sample holder present in the pattern of the Fara Vicentina garronite was caused by

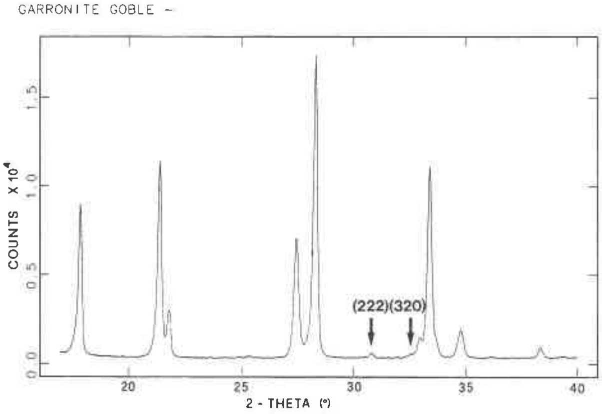

Fig. 1. Observed powder X-ray diffraction data for Goble garronite in the range 17.0–40.0°. The reflections violating the topological space group are indicated.

Table 1. Final Rietveld refinement parameters

		Goble	Fara Vicentina
Cell	*a* (Å)	9.9266(2)	9.8712(2)
	c (Å)	10.3031(3)	10.2987(3)
Parameters refined		70	78
Pseudo-Voigt profile	*U*	264.5(11.3)	50.8(3.5)
	W	16.7(0.6)	14.7(0.8)
	X	5.9(0.1)	5.8(0.2)
	Y	−2.4(0.7)	−7.4(0.4)
	Z	1.3(0.2)	0.4(0.1)
	asymmetry	7.76(0.07)	2.93(0.12)
Residual factors	R_p	0.097	0.087
	R_{wp}	0.127	0.119
	R_{exp}	0.047	0.032
	GOF	7.392	13.987
	R(Fsq)	0.111	0.188

the scarcity of the material available from this specimen. The powder was packed into the 0.2-mm-deep cavity of the holder, and care was taken to avoid large pressure on the material which could cause preferred orientation effects. The low packing efficiency of the Fara Vicentina sample, combined with the small linear absorption coefficient (μ = 83 cm^{-1}), might have caused errors in the observed intensities as a result of transparency effects. The 258 reflections simulated in the pattern were treated as $K\alpha_1,\alpha_2$ doublets in the fixed intensity ratio 2:1. The structure analysis and refinement procedures were performed using the generalized structure analysis system of programs (GSAS, Larson and Von Dreele, 1990). A total of 5149 data points were used in each refinement, the peak profiles were modeled using a pseudo-Voigt function, and a cosine Fourier series with six (Goble) and ten (Fara Vicentina) coefficients was used to fit the background. Correction for preferred orientation effects was attempted using the March model in the formulation of Dollase (1986). For both samples, refined coefficients relative to the 112 and 301 preferred orientation axes were in the range 0.98–1.03, indicating no significant preferred orientation effects, and there was no improvement of the agreement factors. The correction was therefore not applied during the last stages of the structure analysis. Final parameters for both refinements are listed in Table 1.

Structure analysis

Preliminary analysis of the observed powder histograms confirmed that all of the peaks could be indexed with tetragonal cell parameters close to a = 9.9, c = 10.3 Å and that some discrepancies are present with respect to the powder pattern reported by Gottardi and Galli (1985): the 311 reflection at 29.71° violating the *I* centering and the 114 reflection at 37.14° incompatible with the *d* glide in space group $I4_1/amd$ were not observed. However the 222 peak at 30.79° reported by Barrer et al. (1959) and by Gottardi and Galli (1985) is definitely present in both observed powder patterns and indicates the absence of the *d* glide. There is only one other reflection pointing to a symmetry lower than $I4_1/amd$: the 320 reflection at 32.48°. This reflection was observed by Gottardi and Galli (1985) as a very weak peak, although it had not been reported in any of the garronite powder patterns in the literature; it is present in both data sets, although it is barely above background. The 320 reflection violates the extinction conditions for body centering and indicates that the real lattice of garronite may be primitive. It is clearly beyond the limits of a structural refinement with powder data to discriminate among all the theoretically possible primitive space groups on the basis of one weak reflection. It was therefore deemed reasonable to restrict the analysis of the structural model to the limited number of tetragonal space groups derivative of the topological $I4_1/amd$ space group having a body-centered lattice and lacking the *d* glides. Figure 1 shows the observed data for the Goble garronite in the angular region 17.0–40.0° including the reflections of interest.

Preliminary least-squares refinement of the unit-cell parameters indicated that the two specimens have very similar *c* parameters, whereas the *a* parameters are significantly different. The garronite from Fara Vicentina has a smaller unit-cell volume [V = 1003.51(3) Å^3] than the Goble garronite [V = 1015.25(4) Å^3], despite the similar chemical content.

The structure analysis and all the preliminary refinement steps described below are for the Goble data set. A tentative refinement in space group $I4_1/amd$ (multiplicity of the general position 32) using one Si and two O tetrahedral atoms to model the framework converged rapidly (R_{wp} = 0.35) and produced reliable peak profile and background functions for subsequent attempts. Preliminary analysis of difference-Fourier maps clearly indicated strongly anisotropic or split sites for framework atoms and two extraframework sites corresponding to sites C and A/F of Mortier (1982, p. 33). The C site was assumed to contain H_2O since it is occupied by H_2O molecules in gismondine (Artioli et al., 1986), and the A/F sites, related by symmetry in the higher space group, were considered to be partially occupied cation sites and labeled Ca. The structural model was then refined in the following space groups with multiplicity of general position 16: $I\bar{4}m2$, $I4_122$, $I4_1/a$. Refinement in space group $I4_1/a$ was abandoned in the early stages because of poor convergence; furthermore, the framework atoms in this space group are not ordered since the tetrahedral sites are still in general positions and cannot be divided into subsets. The T site can be split into two subsets with multiplicity 8 in both remaining space groups. However, space group $I\bar{4}m2$ allows subsets only for framework O atom O1, retaining O2 in the general position, and space group $I4_122$ allows subsets for O2, maintaining multiplicity 16 for O1. Refinement of one Si site, three tetrahedral O sites, one cation (Ca), and one H_2O site (W1) converged rapidly to R_{wp} = 0.20 in both space groups. Trial refinement in subsequent cycles of isotropic and anisotropic temperature factors for all atoms and occupancy factors for extraframework species was made in the attempt to discriminate the best model between the two space groups. Space group $I\bar{4}m2$ was judged to give the best results based on the following observations: (1) Framework O atoms were poorly modeled in space group $I4_122$; O1 clearly needed to be modeled by an extremely anisotropic position or a split site with partial occupancy; in the O2 position, one of the sites still showed abnormally anisotropic behavior in spite of the subdivision into two subsets with multiplicity 8; in space group $I\bar{4}m2$ the refined temperature factors were reasonable for all three O positions, even for the O2 atom maintaining multiplicity 16. (2) The refined occupancy for the W1 site was very close to four atoms per cell in both space groups, in spite of the different multiplicity; this indicates that the eight sites present in space group $I4_122$ can be subdivided into two subsets of four positions, one of which is fully occupied in $I\bar{4}m2$. (3) Space group $I\bar{4}m2$ also allows modeling of different cation and H_2O molecules in adjacent cages; in particular, one cage with the W1 site occupied by H_2O molecules is surrounded by four cages where the W1 site is empty.

In spite of the indications favoring space group $I\bar{4}m2$, tentative refinements of the model were also attempted in the two body-centered tetragonal subgroups with general multiplicity 8: $I4_1$ and $I\bar{4}$. Subsets of framework atoms related in space groups with higher symmetry had to be refined in alternate cycles because of strong correlations. Neither of the two attempts led to improved models compared with the refinements in space groups with multiplicity 16, although they confirmed the need for subset positions for O1, the presence of the fully occupied W1 site with multiplicity 4, and the presence of site disorder around the Ca site.

The model structure was then refined in space group $I\bar{4}m2$. Refined temperature parameters were reasonable for all framework atoms, although their behavior was clearly anisotropic, especially for O11 and O12. After examination of the residual difference-Fourier maps, the extraframework species were all modeled both by isotropic split sites and also by anisotropic positions, except for W1, which showed a well-defined maximum in the Fourier map. Figure 2A shows, as an example, the residual electron density after removal of the Ca site from the structure model. This position is best modeled by two nearby cation sites (Ca1, Ca2), both located on the mirror plane. The other extraframework positions were refined as O atoms of H_2O, except for one site coordinated to five framework O atoms, which was considered a cation site

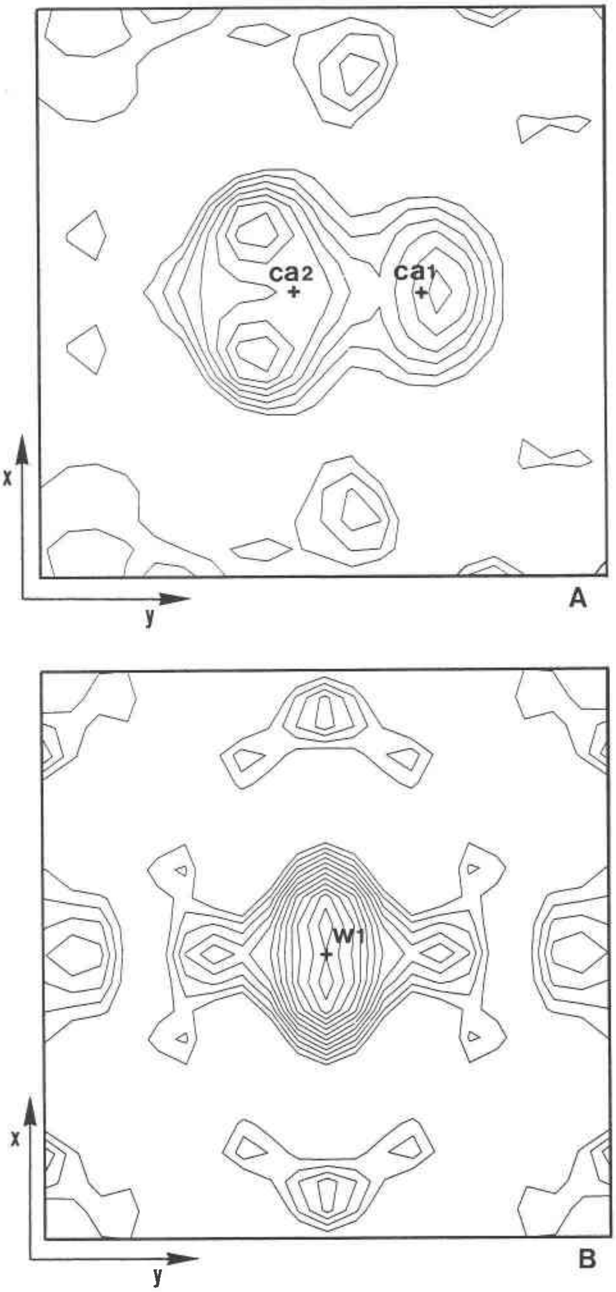

Fig. 2. Difference-Fourier map around (**A**) the Ca site for the Goble garronite; the center of the map has coordinates (0.00,0.25,0.14), the plotted region is 6.0 Å on a side, electron density intervals of 0.08 e/Å^3; (**B**) the W1 site for the Fara Vicentina garronite; the center of the map has coordinates (0.00,0.00,0.12), the plotted region is 6.0 Å on a side, electron density intervals of 0.20 e/Å^3.

TABLE 2. Refined parameters for garronite

Site	Occu-pancy	Multi-plicity	x	y	z	U (Å)
			Goble			
T1	1.0	8	0.1607(3)	0.1607(3)	½	0.039(3)
T2	1.0	8	0.3421(3)	0.1579(3)	¼	0.051(4)
O11	1.0	8	0.1746(3)	0	0.5351(5)	0.034(7)
O12	1.0	8	0.3078(3)	0	0.2192(6)	0.032(7)
O2	1.0	16	0.2922(5)	0.2488(3)	0.1244(2)	0.085(5)
Ca1	0.197(8)	8	0	0.352(2)	0.094(2)	0.110(6)
Ca2	0.155(6)	8	0	0.238(7)	0.107(4)	0.110(6)
Na	0.10(1)	8	0	0.281(4)	0.223(4)	0.08(3)
W1	1.0	4	0	0	0.159(1)	0.117(7)
W2	0.14(2)	8	0.105(2)	0.395(2)	¼	0.026(6)
W2b	0.24(2)	16	0.161(3)	0.433(3)	0.234(4)	0.026(6)
W3	0.39(2)	8	0	0.173(3)	0.981(3)	0.21(2)
			Fara Vicentina			
T1	1.0	8	0.155(4)	0.155(4)	½	0.025(3)
T2	1.0	8	0.340(5)	0.160(4)	¼	0.018(3)
O11	1.0	8	0.15(2)	0	0.55(1)	0.029(8)
O12	1.0	8	0.30(1)	0	0.23(2)	0.020(7)
O2	1.0	16	0.291(6)	0.26(1)	0.127(8)	0.084(7)
Ca1	0.262(5)	8	0	0.407(2)	0.080(2)	0.04(1)
Ca2	0.174(6)	8	0	0.206(3)	0.086(2)	0.049(7)
W1	0.59(2)	4	0	0	0.124(1)	0.03(2)
W1b	0.19(2)	4	0	0	0.22(1)	0.14(1)
W2	0.59(5)	16	0.157(1)	0.433(3)	0.228(2)	0.043(4)

Note: U (Å) are U_{iso} for extraframework atoms and U_{eq} for framework atoms in both refinements and for Ca1 and W1 in the Fara Vicentina garronite. T sites were modeled by $Si_{0.65}, Al_{0.35}$. Thermal parameter constraints for the Goble garronite were U_{iso}(Ca1) = U_{iso}(Ca2) and U_{iso}(W2) = U_{iso}(W2b). Occupancy factor of W1 in the Goble garronite refined to 1.06(2) and was reset to 1.0.

and refined as an Na atom. Occupancy parameters and isotropic temperature factors for all extraframework atoms were freely refined in separate cycles, and only the thermal factors of split sites were constrained. The cell content resulting from the refinement is consistent with the chemical analysis: the refined occupancy factors of the two close Ca sites sum to 2.82 Ca atoms per cell, compared with 2.71 atoms from the electron microprobe analysis; the Na site has a low occupancy of 0.80 atoms per cell, a value higher than the total number of monovalent cations in the cell (Na + K = 0.15), indicating that about 80% of the scattering power of the site is due to O atoms of H_2O. Adding the H_2O value estimated for the Na site to the occupancy factors refined for the other four H_2O sites, we obtain a total of 12.73 H_2O molecules per cell, to be compared with 14.12 H_2O molecules per formula unit resulting from the thermogravimetric analysis. The difference might be caused by a slight bias in the refinement of the occupancy factors or by the presence of weakly bonded H_2O molecules in the cavities not detectable in the residual difference-Fourier maps.

The starting model for the refinement of the Fara Vicentina structure used the atomic coordinates of framework atoms from the final refinement of the Goble garronite. After convergence of the framework model and refinement of background and peak profile parameters, extraframework atom positions were located by analysis of difference-Fourier maps. In the corresponding cage of Fara Vicentina garronite that is occupied by W1 in Goble garronite, there clearly appeared to be a split position (labeled W1/W1b), the two sites having different partial occupancies. The Ca sites were found to be very close to the Ca1 and Ca2 sites in the Goble garronite. No electron density was detected in the Na and W3 sites. Both the W1 and Ca1 sites showed residual electron density out of the mirror plane in the Fourier map and were therefore modeled with anisotropic thermal parameters. Figure 2B

TABLE 3. Selected bond lengths (Å) and angles (°) for the Goble garronite

T1-O2 ×2	1.634(3)	O11-T1-O11	102.2(3)	T1-O11-T1	152.8(6)
T1-O11 ×2	1.642(3)	O11-T1-O2 ×2	109.7(2)	T2-O12-T2	146.9(3)
mean	1.638	O11-T1-O2 ×2	113.9(2)	T1-O2-T2	145.9(3)
		O2-T1-O2	107.6(3)		
		mean	109.5		
T2-O12 ×2	1.635(3)	O12-T2-O12	116.0(3)		
T2-O2 ×2	1.654(3)	O12-T2-O2 ×2	108.0(2)		
mean	1.645	O12-T2-O2 ×2	109.0(3)		
		O2-T2-O2	106.5(3)		
		mean	109.4		
Ca1-W2b ×2	3.03(4)	W1-W3	2.51(3)		
Ca1-O2 ×2	3.094(7)	W1-O12 ×2	3.118(4)		
Ca1-W2 ×2	3.15(2)	W1-W1	3.28(2)		
Ca1-O12	3.26(2)				
Ca2-W2 ×2	2.39(5)	W2-W2b ×2	2.67(3)	W2b-W2b ×2	2.47(4)
Ca2-W1	2.43(7)	W2-O2 ×2	2.70(2)	W2b-O2	2.51(3)
Ca2-W2b ×2	2.83(6)	W2-W2	2.94(4)	W2b-W2	2.67(3)
Ca2-O2 ×2	2.909(6)	W2-W2b ×2	3.14(3)	W2b-O11	2.70(4)
Ca2-W3 ×2	3.06(6)	W2-O11 ×2	3.29(2)	W2b-O2	2.82(4)
				W2b-W2	3.14(3)
Na-O11	2.71(4)	W3-W3 ×2	2.46(4)		
Na-W3	2.71(5)	W3-O12	2.46(3)		
Na-W1	2.87(4)	W3-W1	2.51(3)		
Na-O2 ×2	3.04(2)	W3-O2 ×2	2.95(2)		
Na-O2 ×2	3.09(1)				
Na-W2b ×2	3.26(4)				

shows the difference-Fourier map around the W1 site. In the cage with empty W1 sites, a well-defined position was found for W2, corresponding to the split W2/W2b sites in the Goble garronite refinement, and a minor peak appeared at coordinates (0½0). This peak is in a special position with high symmetry and was considered to be a Fourier artifact. Although it could be refined as an O atom of H_2O having low occupancy (0.05) and high thermal parameters, it was excluded from the refinement. In the last stages of the refinement, anisotropic thermal parameters were used for framework atoms. The total occupancy of extraframework atoms from the Fara Vicentina garronite refinement indicates about 3.5 Ca atoms and 12.5 H_2O molecules per cell. The H_2O content appears to be underestimated with respect to the value measured from thermal analysis, as in the case of the Goble garronite. On the other hand, the total cation occupancy of the Ca1 and Ca2 sites is much higher than indicated by the chemical analysis, even accounting for the possibility that the Na, K, or Sr atoms might occupy the same site. These discrepancies might be caused by the lower quality of the data for the Fara Vicentina sample with respect to the Goble garronite. Transparency effects and strong correlation among the refined coefficients of the background and the profile functions and the thermal factors might significantly bias the refined structural parameters. Nonetheless, in the Fara garronite the mean T-O distances [T1-O = 1.62(8); T2-O = 1.68(8) Å] are significantly different from those in the Goble garronite, possibly indicating a partial ordering of the framework Al atoms on the T2 site. The Si,Al partial ordering, coupled with the increased occupancy of the W2 H_2O site influencing the T1-O11-T1 angle (139.65°), might be the cause of the framework distortion and the origin of the difference in cell volume observed between the two samples. Despite the fact that such speculations have to be taken with caution because of the poor accuracy of the Fara Vicentina data, there is little doubt that the general structure model derived for the Goble garronite, in terms of the framework topology, the space group assignment, and the content of the zeolitic cavities, is in full agreement with the results of the Fara Vicentina refinement.

Table 2 reports final positional, site occupancy, and temperature parameters for all refined atoms; Table 3 lists selected distances and angles for framework and cavity atoms in the Goble garronite; and Figure 3 shows the profiles of observed and calculated data for both refinements. The following discussion of the structure geometry is based on the results of the Goble garronite refinement.

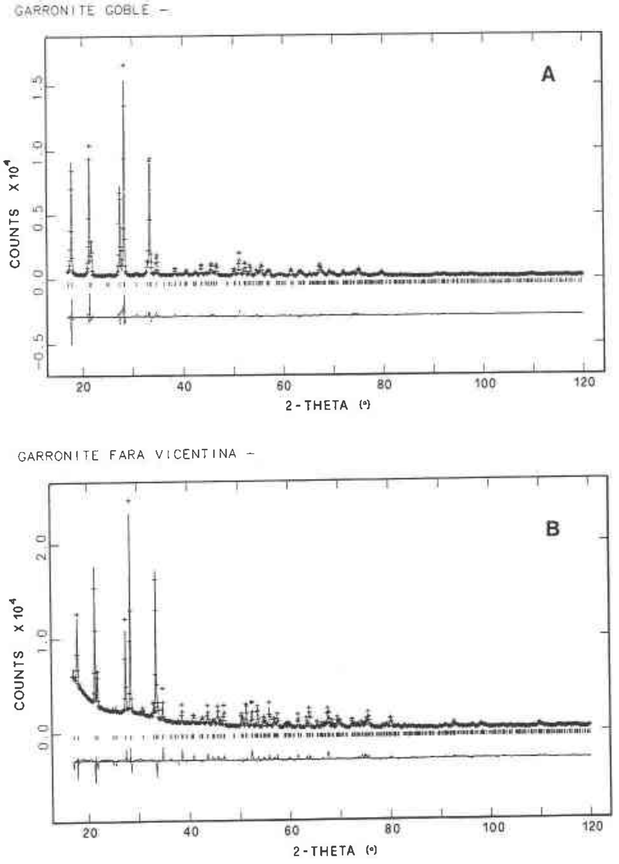

Fig. 3. Observed and calculated powder diffraction patterns for the Goble (A) and Fara Vicentina (B) garronite samples. The crosses are the observed data, and the solid line is the calculated profile. Vertical bars mark Bragg reflection positions, and the bottom curve is the plot of the difference between observed and calculated profiles.

DISCUSSION

The gismondine-type framework (GIS) is commonly described by doubly connecting the basic crankshaft chains composed of four-membered rings of tetrahedra like those in the feldspar structures (see, for example, Gottardi and Galli, 1985, p. 14). This metrically pseudocubic framework topology has been reported for three natural zeolites (amicite, Alberti and Vezzalini, 1979; gismondine, Artioli et al., 1986; and gobbinsite, McCusker et al., 1985) and a variety of synthetic analogues (zeolite Na-P: Baerlocher and Meier, 1972; Hansen et al., 1990; Håkansson et al., 1990; TMA-gismondine: Baerlocher and Meier, 1970; beryllium silicon gismondine: Ueda and Koizumi, 1972; magnesium aluminophosphate: Pluth et al., 1989). The gismondine-type framework is very flexible both from the geometrical point of view, because of the possible distortion of the T-O-T bridges between perpendicular crankshaft chains, and from the chemical point of view, because it can easily accommodate different Si/Al ratios in the framework tetrahedra. The Si,Al atoms can be disordered or ordered over the tetrahedral sites, in the latter case producing a topochemical symmetry lower than the topological one (Gottardi, 1979). An ordered Si,Al distribution allows a limited substitutional range for the extraframework cations (Vezzalini and Oberti, 1984), whereas framework Si,Al disorder, combined with a variable Al content of the tetrahedral sites, makes it possible to accommodate different cation species by means of small geometrical distortions of the cavities. A consequence of

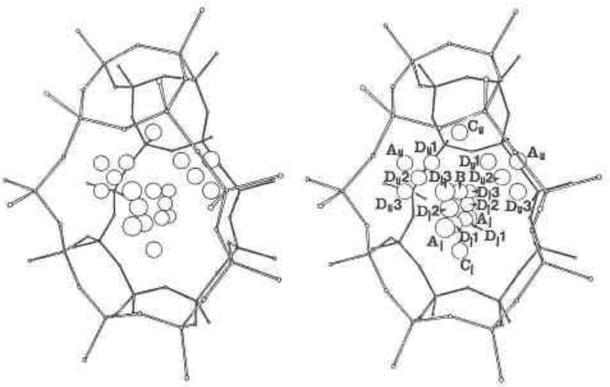

Fig. 4. Stereo Ortep plot of possible extraframework sites in the gismondine-type structures. The positions are referred to the topological $I4_1/amd$ symmetry and described in Table 4.

the interaction between framework Si,Al order and extraframework atoms is that, on the one hand, gismondine and amicite, having complete tetrahedral order, both show completely occupied cation positions of low multiplicity and also display monoclinic symmetry, the lowest symmetry among all reported structures with the same framework. On the other hand, the high-silica variety of zeolite Na-P (Håkansson et al., 1990), showing a disordered distribution of the Al atoms on tetrahedral sites and a statistical occupancy of the Na atoms in a general position in the cavity, exhibits the space group compatible with the maximum topological symmetry ($I4_1/amd$). All other reported species with the gismondine-type framework contain mixed extraframework cations (gobbinsite: Na,K; garronite: Ca,Na) or disordered Si,Al distribution or both and consequently show real or pseudo symmetries intermediate between the gismondine symmetry and the topological one.

In Table 4 and Figure 4, a simplified labeling scheme of the extraframework sites in gismondine-type zeolites allows comparison of the occupancy of the positions in the different structures. To make it possible to compare sites with different multiplicity, all positions are referred to the topological space group, with an arbitrary distinction between the upper and lower part of the cage. Furthermore sites lying in adjacent cages in a lower space group (as in garronite and gobbinsite) have been ideally located in the same cage unit, maintaining the distinction between upper and lower parts of the cage. Finally, all deviations out of the topological mirror plane have been removed, and the sites displaced from the center of the

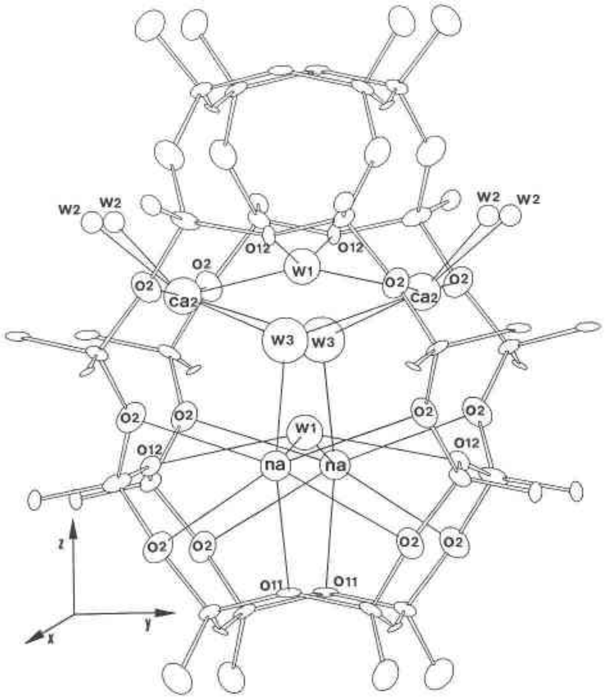

Fig. 5. Ortep plot of the possible configuration of extraframework species in the cage unit of the Goble garronite containing the W1 O site. Ellipsoids at 30% probability level.

TABLE 4. Comparison of extraframework positions in zeolites of the gismondine type

			Du				Dl						
	Au	Cu	1	2	3	B	1	2	3	Cl	Al	Space group	Ref.
	A	C	E	D	B		H	G			F		1
Gismondine	—	W1	W2	W3	Ca	—	—	W6	—	W5	W4	$P2_1/c$	2
Gobbinsite	—	W1	Na	W4	—	W3	W5	W2	—	—	K	$Pmn2_1$	3
Amicite	—	W4	—	K/W1	—	W3	—	Na/W2	—	—	—	$I2$	4
Na-P	W1	W3	—	Na/W4	W2	—	—	Na/W4	W2	W3	W1	$I4_1/amd$	5
Na-P1	—	I	IV	V	II/III	—	IV	V	II/III	I	—	$I\bar{4}$	6
Garronite	Ca2	W1	Ca1	W2/W3	Na	—	Ca1	W2/W3	Na	W1	Ca2	$I\bar{4}m2$	7
Garronite	Ca2	W1	Ca1	W2	—	—	Ca1	W2	—	W1	Ca2	$I\bar{4}m2$	8

Note: Cation and H_2O molecule site labels conform to those in the referenced publications. Displacements out of the topological mirror planes were ignored. Location of the extraframework sites is as follows (see also Fig. 4): Au = center of upper eight-membered ring, Cu = center of niche formed by the upper crankshaft chain, Du = sites facing the upper eight-membered ring, shifted from Au, Du1 = shifted only in the plane parallel to crankshafts, Du2 = shifted toward the center of the cage, Du3 = shifted only in the direction perpendicular to crankshafts, B = center of the gismondine cage, Dl = sites facing the lower eight-membered ring, shifted from Al, Dl1 = shifted only in the plane parallel to crankshafts, Dl2 = shifted toward the center of the cage, Dl3 = shifted only in the direction perpendicular to crankshafts, Cl = center of niche formed by the lower crankshaft chain, Al = center of lower eight-membered ring. References: 1 = Mortier (1982), 2 = Artioli et al. (1986), 3 = McCusker et al. (1985), 4 = Alberti and Vezzalini (1979), 5 = Håkansson et al. (1990), 6 = Baerlocher and Meier (1972), 7 = this study, Goble garronite, 8 = this study, Fara Vicentina garronite.

eight-membered ring of tetrahedra (site D) were characterized by shift vectors having components parallel (site D1), perpendicular (site D3), or both (site D2) with respect to the axes of the topological crankshaft chains of tetrahedra. For comparison, the site labels of Mortier (1982) are also reported.

In garronite, adjacent cages have a different content of extraframework species. The main difference is related to the presence of the fully occupied W1 site. In one cage, both W1 sites above and below the $\bar{4}m2$ special position at the center of the cavity (W1-W1 distance 3.28 Å) are energetically stabilized by simultaneous coordination to the Ca2 and Na cation sites and by H bridges to the O12 framework O atoms (W1-O12 = 3.12 Å) and from the W3 O atom (W1-W3 = 2.51 Å). The possible configuration in the gismondine cage unit containing W1 is shown in Figure 5. The Na site is displaced from the center of the framework eight-membered ring, and it is bonded to five framework O atoms and several H_2O sites. Although this position is partially occupied by a very low Na content, the distances to the framework atoms (Na-O11 = 2.71, Na-O2 = 3.04,3.09 Å) and to the H_2O in the same cavity (Na-W3 = 2.71, Na-W1 = 2.87 Å) and in the adjacent cavity (Na-W2b = 3.26 Å) are quite compatible with an H-bonded H_2O molecule in the same site, acting as a H-bond donor for the framework O atoms (O2, O11) and as an H-bond acceptor from W1, W2b, and W3. The minimum Na-Na distance is 3.12 Å; therefore, both Na sites in the same cage could theoretically be occupied by Na or H_2O at the same time. This situation is similar to the arrangement found for the K and W1 sites in amicite. Obviously the short distances from the Na site to the other cation positions around the center of the same eight-membered ring (Na-Ca1 = 1.51, Na-Ca2 = 1.27 Å) preclude simultaneous occupation of the Ca and Na sites, and the same is true for the two Ca positions (Ca1-Ca2 = 1.14 Å). However, the Ca2 sites, which are very close to the center of the other two eight-membered rings of the same cage, might be partially filled and are bonded to two framework O atoms (Ca2-O2 = 2.91 Å) and five H_2O sites (Ca2-W2 = 2.39, Ca2-W1 = 2.43, Ca2-W3 = 3.06 Å). Following the label scheme in Table 4, when site D_u3 is occupied by Na or H_2O, then sites A_u and D_u1 are empty, site D_u2 is occupied by H_2O W3, and site A_l might be occupied by Ca2, with sites D_l1 and D_l3 empty and site D_l2 occupied by H_2O W2 (or W2b) in the next cage.

The other cage unit present in the structures does not show any residual electron density around the position corresponding to the W1 site that is in the center of the niche formed by the crankshaft chain. In this cage, the only extraframework species are in the Ca1 and W2,W2b positions. Occupancy of the Ca1 site is incompatible with simultaneous occupancy of Ca2 and Na sites positioned opposite the same eight-membered ring. The cation in this position is weakly bonded to three framework O atoms (Ca1-O2 = 3.09, Cal-O12 = 3.25 Å) and to two O atoms of H_2O molecules (either W2 at 3.15 Å or W2b at 3.03 Å). The alternative W2 and W2b sites are occupied by an O atom of H_2O firmly bonded to two framework O atoms (W2-O2 = 2.70, W2b-O2 = 2.51 Å). H bonds with other W2,W2b sites that are possibly occupied at the same time (W2-W2b = 2.67, W2-W2 = 2.94, W2b-W2b = 2.47 Å) and weak interactions with the Ca1 cation site might explain the geometry of this split position, which could be modeled equally well by one extremely anisotropic O atom of H_2O. Figure 6 shows the possible arrangements in the cages where the W1 site is unoccupied.

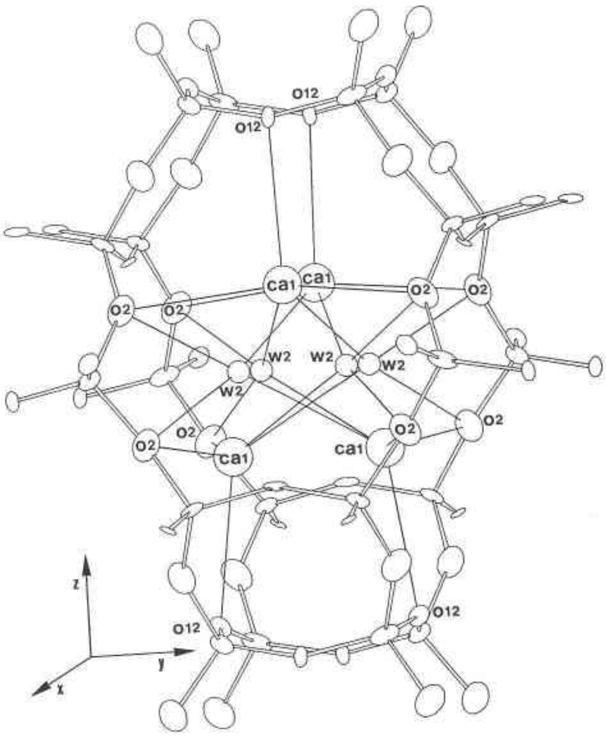

Fig. 6. Ortep plot of the possible configuration of extraframework species in the cage unit of the Goble garronite lacking the W1 site. Ellipsoids at 30% probability. Alternative site W2b close to the H_2O site W2 is not shown for clarity.

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