Reinvestigation of the crystal structure of the zeolite gobbinsite: A single-crystal X-ray diffraction study

G. Diego Gatta,[1,2,*] William D. Birch,[3] and Nicola Rotiroti[1,2]

[1]Dipartimento di Scienze della Terra, Università degli Studi di Milano, via Botticelli 23, I-20133 Milano, Italy
[2]CNR-Istituto per la Dinamica dei Processi Ambientali, Milano, Italy
[3]Geosciences section, Museum Victoria, GPO Box 666, Melbourne, Victoria 3001, Australia

Abstract

The crystal structure of a natural Na-rich gobbinsite from Bundoora, a northern suburb of Melbourne, Victoria, Australia [$(Na_{4.97}K_{0.07}Ca_{0.48})_{\Sigma 5.52}(Al_{5.62}Si_{10.29})_{\Sigma 15.91}O_{32} \cdot 11.91H_2O$, $Z = 1$, $a = 10.1035(15)$, $b = 9.7819(10)$, $c = 10.1523(9)$ Å, and $V = 1003.37(20)$ Å^3, space group *Pmnb* (no. 62)], has been investigated by means of single-crystal X-ray diffraction, elemental CHN analysis, and electron microprobe analysis in the wavelength dispersive mode. For the first time, an anisotropic structural refinement has been performed on the basis of single-crystal X-ray diffraction data collected at 298 K, with: $R_1(F) = 0.0608$, 1362 unique reflections with $F_o > 4\sigma(F_o)$, and 114 refined parameters. The residuals in the final difference-Fourier maps are less than ± 0.6 $e^-/$Å^3. Previous structure solutions based on powder diffraction data were performed in the space group *Pmn*2$_1$, with a significantly different description of the channels' content. In this study, the Si/Al distribution in the tetrahedral framework is found to be highly disordered. A complex configuration of the extra-framework population occurs, with two possible and mutually exclusive sites for cations (Na and Ca) and five independent sites partially occupied by water molecules (W1, W2, W2′, W3, and W3′). The coordination shell of the Na site is represented by a distorted polyhedron with coordination number CN = 6 (4 framework O atoms + 2 H_2O molecules), with at least five possible mutually exclusive configurations, whereas the coordination shell of the Ca site is represented by a distorted polyhedron with CN = 7 (5 framework O atoms + 2 H_2O molecules), with at least two possible mutually exclusive configurations.

Keywords: Zeolite, gobbinsite, Bundoora (Victoria), crystal structure, single-crystal X-ray diffraction

Introduction

Gobbinsite is a rare natural zeolite with ideal composition: $Na_5[Al_5Si_{11}O_{32}] \cdot 12H_2O$ ($Z = 1$, Na:Ca:Mg:K variable, with Na greatly predominant; Coombs et al. 1997) or $(Na_2Ca)_2K_2Al_6Si_{10}O_{32} \cdot 12H_2O$ (The American Mineralogist Crystal Structure Database; Downs and Hall-Wallace 2003). The latter should be rewritten as $(Na_{2-2x}Ca_x)_2K_2Al_6Si_{10}O_{32} \cdot 12H_2O$. Gobbinsite usually occurs in amygdaloidal vugs of massive volcanic rocks (e.g., basalts), formed under hydrothermal postmagmatic conditions, usually in radiating aggregates of crystals and often associated with phillipsite, gmelinite, natrolite, and calcite (Nawaz and Malone 1982; Nawaz 1983; Gottardi and Galli 1985; Armbruster and Gunter 2001; Passaglia and Sheppard 2001). Samples with stacked triangular "chevrons," which give gobbinsite crystals a striated and "spiky" appearance, have also been reported.

Crystals of gobbinsite large enough for single-crystal X-ray diffraction experiments, and free of twinning or defects, have never been reported in the literature, forcing the use of X-ray powder diffraction for the structural solution and refinement. McCusker et al. (1985) solved the crystal structure of a K-rich gobbinsite from Island Magee, Antrim, Northern Ireland ($Ca_{0.6}Na_{2.6}K_{2.2}Al_6Si_{10}O_{32} \cdot 12H_2O$), from X-ray powder diffraction data. The authors indexed the diffraction pattern with an orthorhombic

unit cell, with $a = 10.108(1)$, $b = 9.766(1)$, and $c = 10.171(1)$ Å. The reflection conditions led to the space group *Pmn*2$_1$. Their refined structural model ($R_F = 0.126$, $R_{wp} = 0.136$) showed a tetrahedral framework with the same topological configuration as gismondine [GIS-framework type, Baerlocher et al. (2001)], and as found also in garronite (Gottardi and Alberti 1974; Artioli 1992), amicite (Alberti and Vezzalini 1979; Alberti et al. 1979) and other synthethic zeolites (e.g., Na-P2, SAPO-43; McCusker et al. 1985; Hansen et al. 1990; Baerlocher et al. 2001; and references therein). Such a framework is built up by two secondary building units (i.e., 4- and 8-membered rings of tetrahedra) and can be described as a stacking of two-dimensional arrays of double crankshaft chains. The topological symmetry is tetragonal, space group $I4_1/amd$, with idealized unit-cell constants: $a = 9.8$ and $c = 10.2$ Å (Baerlocher et al. 2001). The gobbinsite tetrahedral framework (GIS-type) shows two main systems of channels: 8-membered ring channels parallel to the a axis (hereafter 8mR[100]) and 8-membered ring channels parallel to the b axis (hereafter 8mR[010]) (Fig. 1). The Rietveld structure refinement of Na-rich gobbinsite from Magheramorne, Larne, Northern Ireland ($Na_{4.3}Ca_{0.6}Si_{10.4}Al_{5.6}O_{32} \cdot 12H_2O$, $a = 10.1027(5)$, $b = 9.8016(5)$, and $c = 10.1682(6)$ Å, space group *Pmn*2$_1$, $R_p = 0.105$, $R_{wp} = 0.136$) was later reported by Artioli and Foy (1994), on the basis of the structural model of McCusker et al. (1985). A slightly different configuration for the extra-framework cations

* E-mail: diego.gatta@unimi.it

was found, ascribable to the different chemistry.

However, the structural model derived by powder-diffraction data leads to some unusual polyhedral configurations of the extra-framework cations: a low coordination number (CN) of the K site, with CN = 4 (2 O atoms of the tetrahedral framework + 2 water molecules), and of the Na site, with CN = 5 (3 O atoms of the tetrahedral framework + 2 water molecules; McCusker et al. 1985).

A recent finding of single crystals of gobbinsite from Melbourne, Victoria, Australia, gave us the opportunity to re-investigate the crystal structure and crystal chemistry of this zeolite by means of single-crystal X-ray diffraction, electron microprobe analysis in the wavelength dispersive mode (EMPA-WDS), and elemental CHN analysis. The structural reinvestigation is aimed mainly at providing new insights into the configuration of the complex extra-framework populations and establishing a structural model including anisotropic displacement parameters (adp's).

SAMPLE DESCRIPTION AND MINERALOGY

The gobbinsite crystals were collected in a basalt quarry (Boral Quarry) at Bundoora, a northern suburb of Melbourne, Victoria, Australia, in 1989. The quarry has since been closed. During its operation, it exposed four flows of tholeiitic basalt, totaling up to 32 m in thickness, occupying a former creek valley (now Darebin Creek). The sources of the flows are volcanoes in the lava field to the north of Melbourne, where activity has been dated between about 4.5 and 0.8 million years ago (Croker 1984; Gray and McDougall 2009). The gobbinsite occurred in a vesicular zone close to a distinctive flow boundary about 18 m below the surface. This zone was particularly rich in zeolites, in particular chabazite-Na, phillipsite-Na, gonnardite, natrolite, and thomsonite-Ca (Vince 1989; Birch 1989). Only a few specimens were collected at the time, as without closer inspection the gobbinsite resembles aggregates of phillipsite crystals.

The gobbinsite crystals form aggregates up to 4 mm across. They are water clear, with a wedge-like habit and lustrous faces that show evidence for lamellar twinning. Crystals are complexly interpenetrating and in some clusters show an apparent epitaxial relationship with a phillipsite crystal or with platy twinned aggregates of thomsonite (Fig. 2). Compared to several gobbinsite samples from different localities that we analyzed, gobbinsite from Victoria gave the most suitable sub-millimetric crystals for this study (i.e., absence of inclusions, twinning-free crystals, high-quality X-ray diffraction).

EXPERIMENTAL METHODS

Quantitative electron microprobe analyses (EMPA-WDS) of a large crystal of gobbinsite (~2 mm^3) were obtained using a Cameca SX50 instrument at the School of Earth Sciences at the University of Melbourne. Analytical conditions were 15 kV and specimen current of 25 nA, with counting times of 20 s on the peaks and 5 s on the backgrounds. A slightly defocused beam ($\varnothing$ 5 μm) was used to minimize loss of water. Standards used were jadeite (Na), wollastonite (Ca, Si), corundum (Al), and synthetic KTaO$_3$ (K). The results were corrected for matrix effects using a conventional ZAF routine. The crystal was found to be homogeneous within the analytical error. A 0.9 mg crystal fragment of gobbinsite was used for the elemental CHN determination with a Carlo Erba 1106 automatic analyzer in the Research School of Chemistry, Australian National University. The calculated amount of water (deduced on the basis of the H wt%) was 16.47 wt%. The general chemical formula, obtained by averaging 10 point analyses in EMPA-WDS, combined with the CHN results and calculated on the basis of 32 O atoms, is the following:

$(Na_{4.97}K_{0.07}Ca_{0.48})_{\Sigma5.52}[Al_{5.62}Si_{10.29}]_{\Sigma15.91}O_{32}\cdot11.91H_2O$ ($Z = 1$) [$E(\%) = -6.3$; Passaglia 1970].

A single crystal, free of defects and twinning under the polarized microscope, was selected for the X-ray diffraction experiment. Diffraction data were collected at 298 K using an Xcalibur Oxford Diffraction diffractometer equipped with a CCD detector and graphite-monochromated Mo$K\alpha$ radiation, operating at 50 kV and 40 mA. Intensity data were collected using a combination of ω and φ scans, to maximize the reciprocal space coverage and redundancy, with a fixed exposure time per frame (15 s/frame) and a crystal-detector distance of 80 mm. Further details pertaining to the data collection are given in Table 1. The diffraction patterns confirmed a metrically orthorhombic lattice with $a = 10.1035(15)$, $b = 9.7819(10)$, $c = 10.1523(9)$ Å, and $V = 1003.37(20)$ Å^3, according to the previous experimental findings. The reflection conditions were found to be consistent with the space group $Pmnb$. No evidence of non-merohedric twinning was observed. Lorentz-polarization and analytical absorption corrections, by Gaussian integration based upon the physical description of the crystal (CrysAlis, Oxford Diffraction 2007), were performed. The discrepancy factor between symmetry-related diffraction intensities (Laue class mmm) was $R_{int} = 0.0597$ (Table 1).

STRUCTURAL REFINEMENT

The single-crystal X-ray diffraction data of gobbinsite were first processed with the program E-STATISTICS, implemented in the WinGX package (Farrugia 1999). Wilson plot, normal-
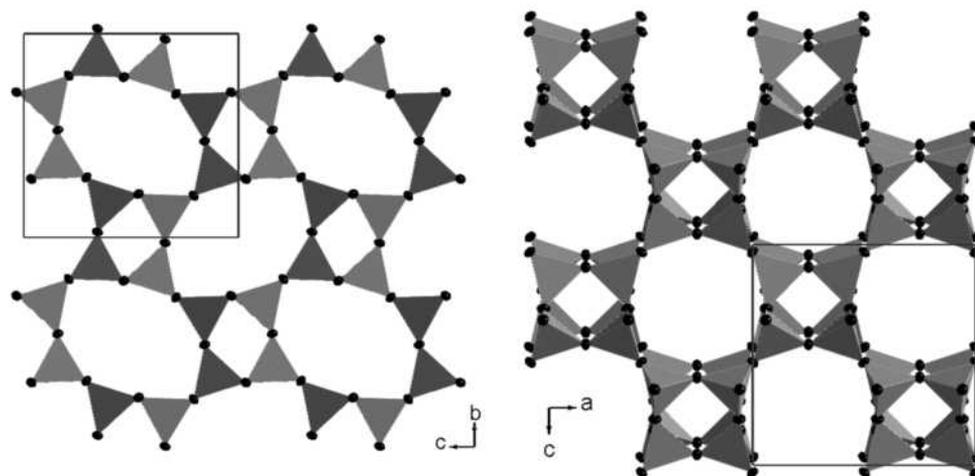
FIGURE 1. Tetrahedral framework of gobbinsite viewed down [100] and [010]. The two main channel-systems are: 8mR[100] and 8mR[010].
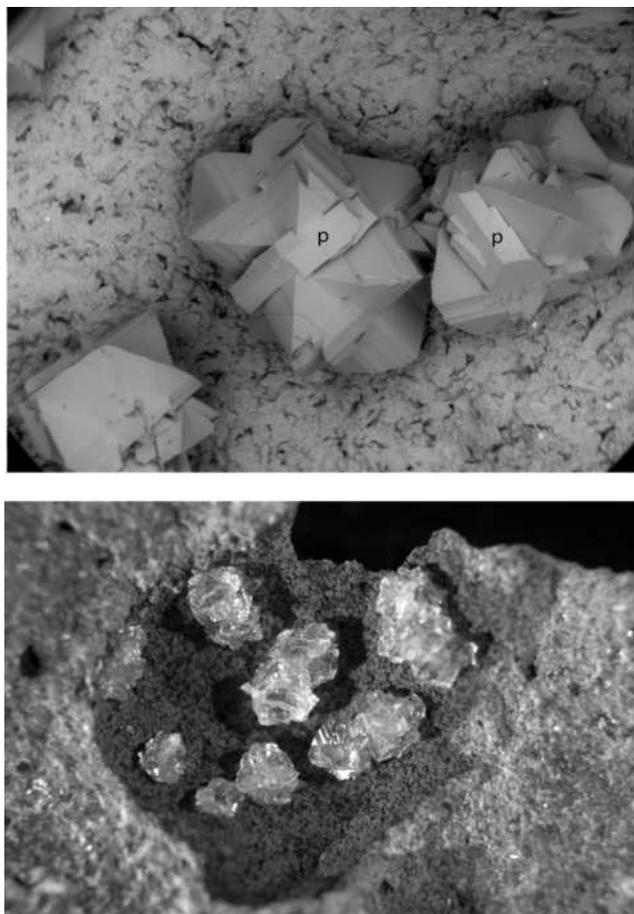
FIGURE 2. (top) SEM-BSE image of clusters of twinned gobbinsite crystals from Bundoora, Victoria. Central cluster is 2.5 × 2 mm. Note tabular phillipsite crystal (p) central to clusters. **(bottom)** The same clusters of gobbinsite crystals as found in an amygdaloidal vug of tholeiitic basalt. Museum Victoria specimen M39238.

ized structure factors (E) and their statistics of the distributions were carried out. The structure of gobbinsite was found to be centrosymmetric at 67.3% likelihood. Similarly, the Sheldrick's $|E^2-1|$ criterion (Sheldrick 1997) also indicated the presence of the inversion center, as $|E^2-1| = 0.868$. The diffraction data were then processed with the program ASSIGN-SPACEGROUP (in WinGX, Farrugia 1999). This software compares the equivalent reflections under all possible Laue classes, providing a valuable check on the supposed Laue symmetry and suggesting the most likely space group. For gobbinsite, two possible space groups (both belonging to the mmm Laue class) were selected: $P2_1nb$ and $Pmnb$.

A structural refinement including adp's of the gobbinsite was then performed using the SHELX-97 software (Sheldrick 1997), starting from the atomic coordinates of the tetrahedral framework of McCusker et al. (1985) but rearranged in the space group $Pmnb$. Further cycles of least-square refinement allowed the location of all the maxima found in the difference-Fourier function of the electron density. Neutral atomic scattering factors for Na, Ca, Al, Si, and O were taken from the *International Tables for Crystallography* (Wilson and Prince 1999). A scattering curve based on tetrahedral sites partially occupied by

Al and Si (as shown by the refined tetrahedral bond distances, Tables 2 and 3) did not significantly improve the figure of merit of the refinement. An unusually complex configuration of the extra-framework content was found, significantly different from those reported in the previous powder diffraction studies: (1) one sodium site (Na, Table 2) and one calcium site (Ca, Table 2), both partially occupied and mutually exclusive (~1.24 Å apart, Fig. 3), were located; (2) five independent sites, all with partial occupancy, were assigned to water molecules (W1, W2, W2′, W3, and W3′; Table 2). The W2 and W3 sites are split into two sub-sites (i.e., W2 and W2′, ~1.22 Å apart; W3 and W3′, ~1.38 Å apart) (Figs. 3 and 4; Table 2). Protons were not located.

With this structural model, the convergence was achieved and the variance–covariance matrix did not show any significant correlation between the refined parameters. At the end of refinement, the residuals in the difference-Fourier maps of the electron density were less than ±0.6 e^-/Å^3, with an agreement factor $R_1(F) = 0.0608$ based on 1362 unique reflections with $F_o > 4\sigma(F_o)$ and 114 refined parameters (Table 1). Atomic positions and anisotropic displacement parameters are reported in Table 2. Bond distances are listed in Table 3. Tetrahedral bond angles and other further structural parameters are in Table 4.

A further structure refinement was performed in the non-centrosymmetric space group $P2_1nb$. However, the refinement in the centrosymmetric space group $Pmnb$ was superior.

DISCUSSION

For the first time, the occurrence of gobbinsite in basalt from Bundoora, Victoria, Australia, is reported. The present and the previous experimental findings on gobbinsite show a very wide range in composition, with 35% < [Na/(Na+K+Ca)] < 90%, which probably reflects different genetic environments and/or post-formational processes, as recently reported for other zeolites

TABLE 1. Details of data collection and refinement of gobbinsite

T (K)	298
Crystal size (μm^3)	160 × 120 × 50
a (Å)	10.1035(15)
b (Å)	9.7819(10)
c (Å)	10.1523(9)
V (Å^3)	1003.37(20)
Space group	$Pmnb$ (no. 62)
Radiation	Mo$K\alpha$
Detector type	CCD
Crystal-detector distance (mm)	80
Scan type	ω/φ
Scan width (°)	0.4
Exposure time (s)	15
2θ max (°)	70
	$-13 \leq h \leq 12$
	$-15 \leq k \leq 15$
	$-16 \leq l \leq 16$
Redundancy	3.5
No. measured reflections	20653
No. unique reflections	1943
No. unique reflections with $F_o > 4\sigma(F_o)$	1362
No. refined parameters	114
R_{int}	0.0597
R_σ	0.0749
R_1 (F) with $F_o > 4\sigma(F_o)$	0.0608
$wR_2(F^2)$	0.0617
GooF	1.585
$\Delta(F^2)/\sigma(F^2)$	<4.2
Extinction coefficient	0.0026(6)
Residuals (e^-/Å^3)	−0.45/+0.53

Note: $R_{int} = \Sigma|F_o^2 - F_o^2(\text{mean})|/\Sigma [F_o^2]$; $R_\sigma = \Sigma[\sigma(F_o^2)]/\Sigma[F_o^2]$; $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; $w = 1/[\sigma^2(F_o^2) + (0.012*P)^2]$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{0.5}$; $P = [\text{Max} (F_o^2, 0) + 2*F_c^2]/3$.

TABLE 2. Refined positional and thermal displacement parameters (Å^2) of gobbinsite

Site (Wyck.)	x	y	z	Site Occupancy	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}/U_{iso}
T1 (8d)	0.40570(6)	0.13813(5)	0.35438(4)	1.0	0.0114(3)	0.0123(2)	0.0125(2)	0.00146(18)	−0.0017(2)	−0.0004(2)	0.0121(1)
T2 (8d)	0.40577(6)	−0.17927(5)	0.40411(4)	1.0	0.0110(3)	0.0116(2)	0.0124(2)	−0.00130(18)	−0.0009(2)	−0.0004(2)	0.0117(1)
O1 (8d)	0.44147(14)	−0.02673(12)	0.34254(13)	1.0	0.0292(10)	0.0178(7)	0.0295(7)	0.0037(6)	0.0023(7)	−0.0007(6)	0.0255(4)
O2 (8d)	0.50124(13)	0.21335(13)	0.46586(12)	1.0	0.0262(10)	0.0242(8)	0.0256(6)	−0.0028(6)	−0.0086(6)	−0.0009(6)	0.0253(4)
O3 (8d)	0.43921(15)	0.20512(13)	0.20920(13)	1.0	0.0393(11)	0.0251(8)	0.0230(7)	0.0074(6)	0.0006(6)	0.0023(7)	0.0291(4)
O4 (4c)	1/4	0.16485(19)	0.39755(17)	1.0	0.0189(13)	0.0339(12)	0.0317(10)	−0.0045(9)	0	0	0.0282(5)
O5 (4c)	1/4	−0.1873(2)	0.45158(17)	1.0	0.0175(13)	0.0348(12)	0.0328(10)	0.0044(9)	0	0	0.0284(5)
Na (8d)	0.0753(2)	0.5486(2)	0.6519(2)	0.592(5)	0.0586(18)	0.116(2)	0.0462(15)	0.0319(12)	0.0169(11)	0.0101(12)	0.074(1)
Ca (8d)	0.0447(7)	0.5065(6)	0.5408(6)	0.154(3)	0.163(9)	0.071(4)	0.061(5)	0.016(3)	−0.014(4)	−0.022(4)	0.098(4)
W1 (4c)	3/4	−0.4058(10)	0.2289(6)	0.54(1)	0.039(5)	0.269(15)	0.088(5)	0.091(7)	0	0	0.132(6)
W2 (4c)	3/4	−0.1176(13)	0.3039(8)	0.47(1)	0.070(6)	0.194(14)	0.058(6)	0.018(6)	0	0	0.107(6)
W2′ (4c)	3/4	−0.2013(9)	0.2151(10)	0.51(1)	0.059(6)	0.143(9)	0.092(7)	−0.037(6)	0	0	0.098(4)
W3 (4c)	3/4	0.1263(9)	0.0802(8)	0.54(1)	0.125(7)	0.150(9)	0.112(7)	0.008(6)	0	0	0.129(5)
W3′ (4c) anis	3/4	0.0333(8)	−0.0225(8)	0.67(2)	0.76(4)	0.069(6)	0.084(6)	0.004(4)	0	0	0.305(14)
W3′ (4c) iso	3/4	0.0358(10)	−0.0219(11)	0.54(2)	–	–	–	–	–	–	0.146(7)

Notes: The anisotropic displacement factor exponent takes the form: $-2\pi^2[(ha^*)^2U_{11} + \cdots + 2hka^*b^*U_{12}]$. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor. For the T1 and T2 sites, the scattering curve of silicon was used. For the Na site, the scattering curve of sodium was used, whereas for the Ca site the scattering curve of calcium was adopted. The scattering curve of oxygen was use for W1, W2, W2′, W3, and W3′ sites. Atomic coordinates and site occupancy of the W3′ site are provided with isotropic and anisotropic displacement factors. The reasons of the large thermal factors for the W1 and W3′ sites, and of the high site occupancy factor of the W3′ site, are discussed in the text.

TABLE 3. Relevant bond distances (Å) in the gobbinsite structure

		"a"	"b"	"c"	"d"	"e"
T1-O3	1.6482(13)	Na-O1	2.371(2)	a	b	c	d	e
T1-O4	1.6538(8)	Na-O2	2.722(2)	a	b	c	d	e
T1-O1	1.6570(13)	Na-O3 (I)	2.896(3)	a	b	c	d	e
T1-O2	1.6595(13)	Na-O3 (II)	3.112(2)	a	b	c	d	e
⟨T1-O⟩	1.6546	Na-W1	2.555(5)			c		e
T2-O5	1.6478(8)	Na-W2	2.440(6)	a			d	
T2-O3	1.6481(13)	Na-W2′	2.400(6)		b	c		
T2-O2	1.6543(13)	Na-W3	2.564(6)	a				
T2-O1	1.6575(13)	Na-W3′	2.625(5)		b		d	e
⟨T2-O⟩	1.6519							
		Ca-O1	3.242(6)	a	b			
		Ca-O2 (I)	2.776(5)	a	b			
		Ca-O2 (II)	3.003(5)	a	b			
		Ca-O3 (I)	2.888(5)	a	b			
		Ca-O3 (II)	3.200(6)	a	b			
		Ca-W3	2.480(9)	a				
		Ca-W3′ (I)	2.207(7)		b			
		Ca-W3′ (II)	2.994(7)	a	b			

Note: Five possible and mutually exclusive configurations for the Na-polyhedron (labeled as "a," "b," "c," "d," and "e") and two for the Ca-polyhedron (labeled as "a" and "b") are reported (see text for details).
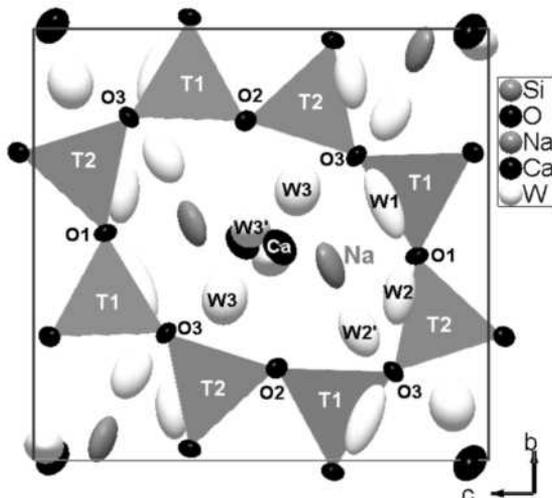
FIGURE 3. Configuration of the extra-framework population in gobbinsite, as viewed down [100], based on the structural refinement of this study. Thermal ellipsoid probability factor: 50%.
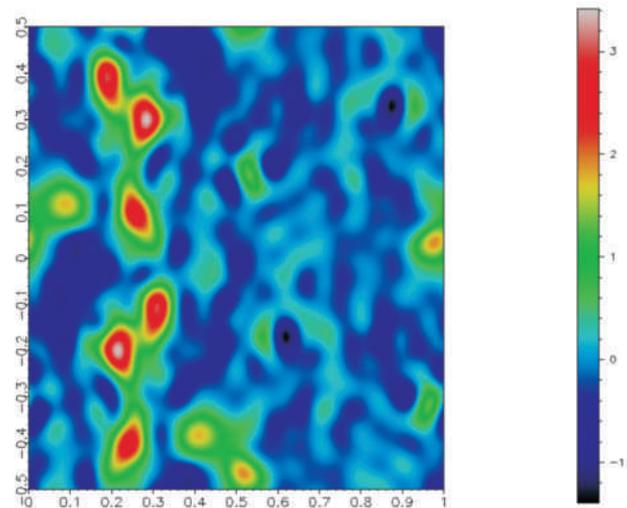
FIGURE 4. Difference Fourier maps of the electron density ($e^-/Å^3$) of gobbinsite at $x = 3/4$ based on refinement without the water molecule sites, showing five intense positive residual peak at $y \sim -0.40$ and $z \sim 0.22$ (ascribable to W1), $y \sim -0.12$ and $z \sim 0.30$ (ascribable to W2), $y \sim -0.20$ and $z \sim 0.21$ (ascribable to W2′), $y \sim 0.13$ and $z \sim 0.08$ (ascribable to W3), and $y \sim 0.03$ and $z \sim -0.02$ (ascribable to W3′). Map orientation: z positive to the right.

(Passaglia and Sheppard 2001; Gatta et al. 2009, and references therein). The gobbinsite investigated in this study is enriched in sodium, with [Na/(Na+K+Ca)] ~ 90%. Its composition differs significantly from that of gobbinsite from Island Magee, Antrim, Northern Ireland [with Na/(Na+K+Ca) ~ 37%, McCusker et al. 1985], but it is similar to that of gobbinsite from Magheramorne, Larne, Northern Ireland [with Na/(Na+K+Ca) ~ 88%, Artioli and Foy 1994]. On this basis, a general chemical formula for this zeolite can be written as:

$$(Na,K,0.5Ca)_{5+x}(Al_{5+x}Si_{11-x})O_{32} \cdot 12H_2O \quad (Z = 1).$$

The structural refinement based on single-crystal X-ray diffraction data showed that the previous powder diffraction

TABLE 4. Tetrahedral bond angles (°) in the gobbinsite structure and "free diameters" (↔, Å) (Baerlocher et al. 2001) of the channel systems

O3-T1-O4	111.69(9)	8mR[100]	
O3-T1-O2	108.11(7)	O3↔O3	5.746(2)
O3-T1-O1	106.09(7)	O3↔O3	3.371(2)
O4-T1-O2	107.61(8)	$\varepsilon_{8mR[100]}$	0.59
O4-T1-O1	112.37(9)		
O1-T1-O2	110.74(7)		
O3-T2-O5	111.56(9)	8mR[010]	
O3-T2-O2	107.59(7)	O5↔O4	4.164(3)
O3-T2-O1	108.05(7)	O3↔O3	3.680(2)
O5-T2-O2	107.43(8)	$\varepsilon_{8mR[010]}$	0.88
O5-T2-O1	111.15(9)		
O2-T2-O1	111.02(7)		

Note: ε is the "ellipticity ratio," defined as the ratio between the shortest and the longest free diameter; the lower the ellipticity ratio, the higher the ellipticity of the channel (Gatta et al. 2003, 2004).

refinements of natural gobbinsite provided a correct description of the framework topology and the structural homology with gismondine [GIS framework type, McCusker et al. (1985); Artioli and Foy (1994); Baerlocher et al. (2001)]. We cannot exclude that the different symmetry found by McCusker et al. (1985) (i.e., $Pmn2_1$) would be due to the different crystal chemistry of the K-rich gobbinsite from Island Magee. However, the crystal chemistry of Na-rich gobbinsite from Magheramorne described by Artioli and Foy (1994) is similar to that of gobbinsite from Bundoora reported in this study.

The number of independent sites belonging to the tetrahedral framework in space group $Pmn2_1$ is 14 (McCusker et al. 1985), whereas in space group $Pmnb$ is reduced by half (i.e., 7, Table 2). The structural model of gobbinsite here described in the centrosymmetric space group $Pmnb$ is consistent with that of the synthetic (isotypic) Na-P2 zeolite by single-crystal X-ray diffraction refinement [$Na_4Al_4Si_{12}O_{32}\cdot14H_2O$, GIS-framework type, space group $Pnma$, a = 9.868(2), b = 10.082(2), c =10.098(2) Å, and V = 1004.6(3) Å; Hansen et al. (1990)]. In our study, the Si/Al distribution in the two independent tetrahedral sites is highly disordered (with <T1-O> = 1.6546 Å and <T2-O> = 1.6519 Å, Table 3). Similar findings were reported in the previous powder investigations (McCusker et al. 1985; Artioli and Foy 1994) and also for the synthetic Na-P2 zeolite (Hansen et al. 1990). The "free diameters" of the two systems of channels have been calculated according to Baerlocher et al. (2001). The two channels show a different elliptical distortion, as deduced by the different ellipticity ratios: $\varepsilon_{8mR[100]}$ ~0.59 and $\varepsilon_{8mR[010]}$ ~0.88 (see Fig. 1 and Table 4 for details). In other words, the 8mR[100] channel is strongly deformed, whereas the 8mR[010] is much more circular.

Our data show a complex configuration of the extra-framework population, with two possible and mutually exclusive sites for cations (Na and Ca, Table 2) and five independent sites partially occupied by water molecules (W1, W2, W2′, W3, and W3′, Table 2). The coordination shell of the Na site is represented by a distorted polyhedron with coordination number CN = 6 (4 framework O atoms + 2 H_2O molecules), with at least five possible mutually exclusive configurations, labeled as "a," "b," "c," "d," and "e" in Table 3. The coordination shell of the Ca site is represented by a distorted polyhedron with CN = 7 (5 framework O atoms + 2 H_2O molecules), with at least two possible mutually

exclusive configurations labeled as "a" and "b" in Table 3. As the Na and Ca sites are mutually exclusive (i.e., Na–Ca distance ~1.24 Å), the sum of the two site occupancy factors (S) must be lower than 100%. Using the scattering curve of sodium alone at the Na site, the refined S(Na site) is 59.2(4)%, whereas that of the Ca site using the calcium scattering curve is S(Ca site) = 15.4(3)% (Table 2). Using the scattering curve of oxygen alone, the sum of the site occupancy factors of the W2 and W2′ (split) sites is lower than 100% [i.e., S(W2) + S(W2′) = 47(1)% + 51(1)%, Table 2]. An excess in occupancy is observed for the W3 and W3′ sites, if W3′ is refined anisotropically [i.e., S(W3) + S(W3′) = 54(1)% + 67(2)%, Table 2]; whereas, if W3′ displacement is modeled as isotropic, the sum of the occupancies approaches 100% within 3σ [i.e., S(W3) + S(W3′) = 54(1)% + 54(2)%, Table 2]. The virtual excess in the occupancy factors at the W3 and W3′ sites, and the significantly large anisotropy of the displacement ellipsoid of the W3′ site, can be ascribed to a potential local disorder around the refined center of gravity of the electron distribution of the two sites, as shown by the configuration of the electron density in the difference-Fourier map in Figure 4.

The chemical unit formula based on the structural refinement using the aforementioned scattering curves is: $Na_{4.74}Ca_{1.23}(Al,Si)_{16}O_{32}\cdot10.90\ H_2O$. This gives lower amounts of sodium and water, and higher amounts of calcium, than those obtained by chemical analysis, suggesting a partial disordering of the two cations and water molecules among the channel sites (i.e., Na, Ca, W1, W2, W2′, W3, and W3′), as the total number of electrons of the extra-framework sites calculated on the basis of the structural refinement compared to that obtained on the basis of the chemical analysis differ only by 1.9%, respectively $\Sigma e_{(Na,Ca,W1,W2,W2',W3,W3')}^- = 163.9e^-$ and $\Sigma e_{(Na,Ca,Wtot)}^- = 160.9e^-$. In other words, a small fraction of water molecules would share the Na and Ca sites along with sodium and calcium, respectively, or sodium would partially occupy the Ca site or some of the water molecules sites as well (e.g., W3′). A partial disorder in the distribution of cations would also explain some significantly high displacement parameters of some extra-framework sites (e.g., W1 and W3′). The partial occupancy of all the extra-framework sites made the use of mixed scattering curves impossible during refinement, thus inhibiting the direct refinement of multiple elements in one site.

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