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Rietveld refinement of the crystal structure of the new zeolite mineral gobbinsite

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Abstract. The crystal structure of the new zeolite mineral gobbinsite, $Ca_{0.6}Na_{2.6}K_{2.2}Al_6Si_{10}O_{32} \cdot 12H_2O$, has been determined in the space group $Pmn2_1$ with $a = 10.108(1)$, $b = 9.766(1)$ and $c = 10.171(1)$ Å. The topology of the framework is the same as that of gismondine and can be described as a stacking of 2-dimensional arrays of double crankshaft chains. The structure was refined by the Rietveld technique using X-ray powder data, and converged with $R_F = 0.126$ and $R_{wp} = 0.136$ (statistically expected $R_e = 0.121$). Fifty soft restrictions on the bond distances and angles of the aluminosilicate framework atoms were included in the least-squares refinement as additional (geometric) observations. This facilitated the location of the non-framework cations and water molecules, and improved the stability of the refinement. As in the closely-related synthetic zeolite Na–P2, the pseudo-tetragonal axis of the gismondine-type framework is parallel to one of the near-equivalent unit cell dimensions (c-axis), not to the unique one as expected. The arrangement of cations within the zeolitic channels suggests an explanation for this distortion of the ideally tetragonal framework.

Introduction

The presence of the new zeolite mineral gobbinsite in Co. Antrim, N. Ireland, was reported recently by Dr. Rab Nawaz (Nawaz and Malone,

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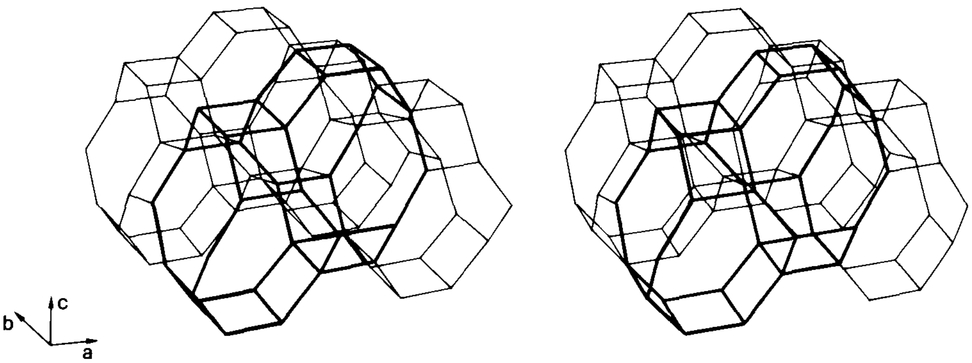

Fig. 1. A stereo view (Johnson, 1965) of the gismondine type aluminosilicate framework structure. Vertices correspond to T (Si or Al) atoms. The two cavities used for the more detailed drawing of the structure of gobbinsite shown in Figure 3 have been highlighted

1982). No single crystals were found, but a structure determination and refinement using X-ray powder diffraction techniques and the X-ray Rietveld System (Baerlocher, 1982) was considered feasible. Preliminary X-ray results indicated that gobbinsite may be a member of the gismondine or possibly the phillipsite family, and closely related to the synthetic zeolite Na – P2 (Barrer et al., 1959).

At the time, four zeolites with the gismondine-type framework structure (Figure 1) had been reported: gismondine (Fischer, 1963, and Fischer and Schramm, 1971), TMA-gismondine (Baerlocher and Meier, 1970), Na – P1 (Baerlocher and Meier, 1972), and amicite (Alberti and Vezzalini, 1979). These had been refined in the space group $P2_1/c$, $I4_1/amd$, $I\bar{4}$, and $I2$, respectively. Since then, Fälth has added Na – P2 and the space group $P2_12_12_1$ (Fälth and Hansen, 1983) to this list. No two have the same symmetry, but all have the same framework topology and 10 × 10 × 10 Å unit cell dimensions. Garronite is also proposed to have the gismondine-type framework structure (Gottardi and Alberti, 1974).

The first lattice constant determinations of gobbinsite suggested a tetragonal unit cell, but initial attempts to refine the data with a gismondine-type framework structure (ideal space group $I4_1/amd$) in several tetragonal subgroups failed. Lowering the symmetry to orthorhombic while preserving pseudotetragonal cell dimensions did not meet with any greater success. These difficulties were found puzzling and worthy of further investigation.

Experimental section

The sample of gobbinsite came from the Two-Mouth Cave, Island, Magee, Co. Antrim. Mr. Norman Moles did three electron probe analyses. The average of these, based on 32 oxygen atoms, yielded the mole ratios

9.93 Si:6.17 Al:0.59 Ca:2.50 Na:2.11 K. This differs significantly from the type material analysis (Nawaz and Malone, 1982) in having more K and Al and less Na and Si. The H_2O content is 16.2%, which corresponds to 12 molecules per unit cell.

Data collection and reduction: A well-ground powder sample was pressed into a plastic, flat-plate sample holder (2 × 3 cm) and mounted vertically on a PAD-I diffractometer (Baerlocher and Moeck, 1975). Scanning electron micrographs showed crystallites with no discernible morphology and indicated no tendency towards preferred orientation. The step scan data collection procedure, the background correction, and the standard peak profile function calculation are described elsewhere (Baerlocher, 1984 and McCusker and Baerlocher, 1984). Details pertinent to this particular investigation are given in Table 1. The lattice constants were refined using all but the low-angle data, and then the $2\,\theta$-correction variables were refined and applied to the experimental data.

Structure determination

Unit cell and space group information obtained from a very small untwinned crystal of gobbinsite (Nawaz, 1983) and the preliminary results on the structure of Na – P2 by Dr. Fälth (Fälth and Hansen, 1983) helped us overcome our initial difficulties with this structure determination. The space group $Pmn2_1$ with the unit cell dimensions $a = 10.108(1)$, $b = 9.766(1)$ and $c = 10.171(1)$ Å with the pseudo-tetragonal axis parallel to c (and not to the short b axis as initially assumed) emerged as the most probable one.

The X-ray Rietveld System (XRS-82) (Baerlocher, 1982) was used for the refinement. Fifty soft constraints in the form of bond distance and angle restrictions were placed on the framework atoms (listed as 'prescribed' values in Table 3). These geometric observations facilitated the location of the non-framework cations and water molecules, and improved the stability of the refinement. As structure solution progressed, these constraints were given less and less weight, but they could not be removed completely. In the final cycles of refinement, the common weight factor for these restrictions was reduced to 2. Nine profile parameters (three for the lattice constants, two for the $2\,\theta$-correction, and four for the $2\,\theta$-dependence of the peak width and peak asymmetry) were varied during the course of refinement.

Atomic scattering factors of partially-ionized T (reflecting the 10:6 Si:Al ratio) and O^- atoms were used for the framework positions, and Na^+, K^+ and O^0 for the non-framework ones. No anomalous dispersion or absorption correction was applied.

Least-squares refinement was initiated in the space group $Pmn2_1$ with coordinates from a DLS refinement (Baerlocher et al., 1977) of the gismondine-type framework structure. Subsequent difference Fourier syntheses revealed the locations of several non-framework atoms. Two of these, Na(1) and K(1) (see Table 2), could be identified as cations: Na(1) because of its approach distances to framework oxygens, and K(1) because of its population parameter and its coordination environment. The presence of disordered H_2O molecules in the zeolitic channels made the identification of the other positions less definitive, so all were refined as water. The water electron density is only approximated by these H_2O positions, and they should not be taken as an accurate description of the actual arrangement of H_2O molecules within the zeolite. Since the interpretation of the non-framework sites was incomplete, no restrictions were placed on the population parameters, even though some are impossibly high. To keep the number of variables to a minimum, only three temperature factors (one each for T-atoms, O-atoms, and non-framework atoms) were used.

Final refinement converged with the error indices $R_F = 0.126$ and $R_{wp} = 0.136$ (Table 1). All parameter shifts in the last cycles of refinement were less than their corresponding e.s.d.'s. The final difference Fourier showed no significant peaks.

Crystallographic details are summarized in Table 1, final parameters in Table 2, and selected bond distances and angles in Table 3. The profile is shown in Figure 2 and the cation positions in Figure 3.

Discussion

The gismondine-type aluminosilicate framework structure has been described in detail previously (Fischer, 1963, Meier and Olson, 1978). A skeletal diagram is shown in Figure 1. It has a two-dimensional, interconnecting 8-ring channel system. This structure can also be described as a stacking of two-dimensional arrays of double crankshaft chains parallel [100] and [010]. This allows for a flexibility in the framework which is manifested in the different symmetries observed. The twinning in gobbinsite (Nawaz and Malone, 1982; Nawaz, 1983) is readily explained on the basis of this framework structure (Baerlocher and Meier, 1972). Ordering of the Si and Al atoms was not apparent, but cannot be ruled out.

The framework was refined using geometric observations. Since this is not a common practice some comments may be appropriate. When these soft constraints were removed unacceptable interatomic distances resulted with no improvement in the R-values. This may be due to the presence of pseudosymmetry and/or to the fact that the X-ray data alone could not support the refinement of 64 structural parameters. However, the refined model must be a correct approximation to the structure, since the requirements of both the X-ray and the geometric data were fullfilled. The sensitivity of the X-ray data to the correct structure is evident from our previous experience and also from unsuccessful attempts to refine the

Table 1. Experimental and crystallographic data

Temperature (°C)	25(2)
Profile 2 θ range (°2 θ)	8.2–95.0
Stepscan increment (°2 θ)	0.02
Radiation	Cu$K\alpha_1$
Standard peak for peakshape function (*hkl*, 2 θ)	020, 18.1
Peak range (no. full width at half height)	10
Space group	$Pmn2_1$
a(Å)	10.108(1)
b(Å)	9.766(1)
c(Å)	10.171(1)
No. steps (N)	4038
No. contributing reflections	518
No. geometric observations [g(pred.)]	50
No. structural parameters (P1)	64
No. Profile parameters (P2)	9
$R_{wp} = \{\Sigma w[y(obs)-y(calc)]^2/\Sigma w\ y^2(obs)\}^{1/2}$	0.136
$R_e = [(N-P1-P2)/\Sigma w\ y^2(obs)]^{1/2}$	0.121
$R_F = \Sigma\lvert F(obs)-F calc)\rvert/\Sigma F(obs)$	0.126
$R_{wg} = \{\Sigma w[g(pred) - g(calc)]^2/\Sigma w\ g^2(pred)\}^{1/2}$	0.027
$\chi^2 = (R_{wp}/R_e)^2$	1.26

structure in $P222_1$ and $P2_12_12_1$. Geometric refinements in both space groups yielded reasonable interatomic distances and angles, but no satisfactory fit of the X-ray data could be obtained.

The Na(1) ions are located in 8-rings perpendicular to the *a*-axis, where each is coordinated to three framework oxygens [O(3), O(7) and O(8)] and two non-framework oxygens [$H_2O(1)$ and $H_2O(3)$] in a distorted trigonal bipyramidal manner. Because of their approach distances to Na(1) and their population parameters, there is little doubt that $H_2O(1)$ and $H_2O(3)$ are water positions. A bridging arrangement parallel to the *a*-axis linking Na^+ ions in opposite 8-rings through water molecules at both $H_2O(1)$ and $H_2O(3)$ must occur because the Na(1) position is more than half occupied. It is probably because of this bridging function that these two water positions are so well-defined.

The K(1) ions are also located in 8-rings, but in ones perpendicular to the *b*-axis. Each cation is coordinated to two O(6) and one O(5) framework oxygens, and to one $H_2O(3)$ molecule. The coordination to other non-framework oxygens is not clear, since the atomic identities and probably the positions of $H_2O(2)$, $H_2O(4)$ and $H_2O(5)$ are less certain. From its location and its population parameter, it appears likely that the $H_2O(4)$ position contains the unlocated Ca^{2+} ions as well as water. Similarly, the $H_2O(2)$ position may include the remaining K^+ ions. Since $H_2O(5)$ is more than 3.4 Å from its nearest framework oxygen, it could be an average of several water positions.

Table 2. Positional, thermal and population parameters for gobbinsite

Atom	Point symmetry	x	y	z	U[a]	Population[b]	Multiplicity
T(1)	1	0.156(1)	0.432(2)	−0.191(2)	2.6(1)	4	4
T(2)	1	0.154(2)	0.110(2)	−0.242(2)	2.6(8)	4	4
T(3)	1	0.345(2)	0.073(2)	0	2.6(8)	4	4
T(4)	1	0.348(2)	0.389(2)	0.048(3)	2.6(8)	4	4
O(1)	1	0.186(3)	0.275(2)	−0.241(3)	2.3(2)	4	4
O(2)	m	0	0.441(5)	−0.162(5)	2.3(2)	2	2
O(3)	1	0.200(4)	0.538(3)	−0.309(3)	2.3(2)	4	4
O(4)	1	0.254(3)	0.459(3)	−0.061(3)	2.3(2)	4	4
O(5)	m	0	0.074(5)	−0.197(5)	2.3(2)	2	2
O(6)	1	0.198(4)	0.048(3)	−0.394(3)	2.3(2)	4	4
O(7)	1	0.254(3)	0.046(3)	−0.138(2)	2.3(2)	4	4
O(8)	1	0.312(3)	0.226(2)	0.059(3)	2.3(2)	4	4
O(9)	m	0.5000	0.073(5)	−0.026(4)	2.3(2)	2	2
O(10)	m	0.5000	0.414(5)	0.009(5)	2.3(2)	2	2
Na(1)	1	0.247(5)	0.228(6)	0.284(8)	11.6(2)	2.6(2)	4
K(1)	m	0.5000	−0.071(4)	0.615(4)	11.6(2)	1.7(1)	2
H_2O(1)	m	0.5000	0.243(8)	0.321(8)	11.6(2)	2.2(1)	2
H_2O(2)	m	0	0.395(5)	0.146(5)	11.6(2)	2.9(2)[c]	2
H_2O(3)	m	0	0.314(1)	0.306(1)	11.6(2)	1.8(2)	2
H_2O(4)	1	0.341(6)	0.271(5)	0.559(6)	11.6(2)	5.1(1)[c]	4
H_2O(5)	m	0.5000	0.338(6)	0.600(7)	11.6(2)	2.9(2)[c]	2

[a] Thermal parameters are given × 10^2 Å^2. Numbers in parenthesis are the esd's in the units of the least significant digit given. Those parameters without esd's were held fixed in least-squares refinement

[b] Population parameters are given as the number of atoms or ions per unit cell

[c] High values are probably due to the presence of K^+ or Ca^{2+} ions in addition to H_2O at these positions (see text)

Table 3. Selected interatomic distances (Å) and angles (deg)

T–O	prescribed	1.656(10)	
	min/max	1.59/1.72	
	average	1.65(3)	
O–T–O	prescribed	109.47(1.00)	
	min/max	104/115	
	average	109.4	
T–O–T	prescribed	145(12)	
	min/max	139/161	
	average	148	
Na(1)–O(3)	2.53(7)	$H_2O(1)$–O(2)	3.09(9)
Na(1)–O(7)	2.79(7)	$H_2O(1)$–O(5)	3.10(9)
Na(1)–O(8)	2.38(8)		
Na(1)–$H_2O(1)$	2.59(5)	$H_2O(2)$–O(2)	3.17(7)
Na(1)–$H_2O(3)$	2.64(6)	$H_2O(2)$–O(3)	3.14(4)
K(1)–O(5)	3.17(7)	$H_2O(3)$–O(10)	3.37(12)
K(1)–O(6)	3.27(5)		
K(1)–$H_2O(2)$	3.19(6)	$H_2O(4)$–O(1)	2.57(7)
K(1)–$H_2O(3)$	3.07(11)	$H_2O(4)$–O(6)	2.66(7)

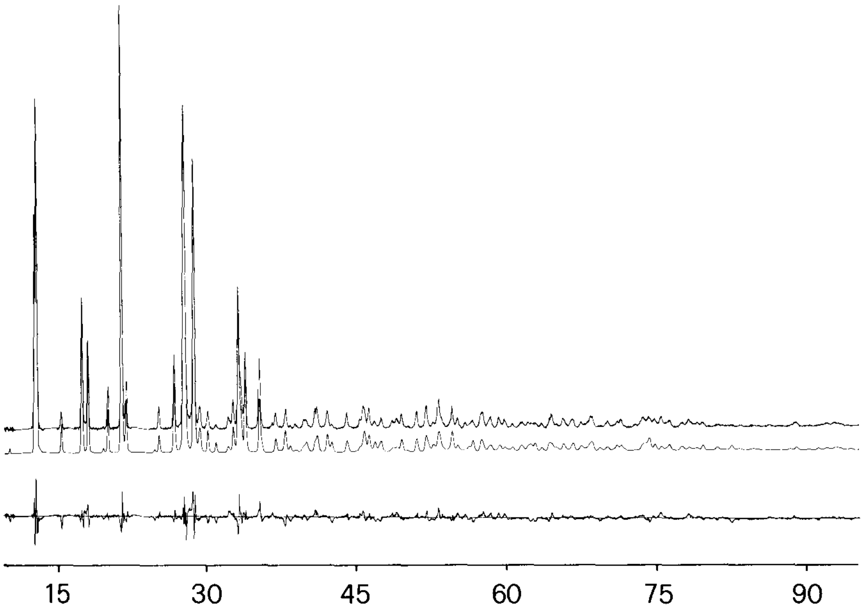

Fig. 2. Observed (upper), calculated (middle) and difference (lower) profiles for gobbinsite

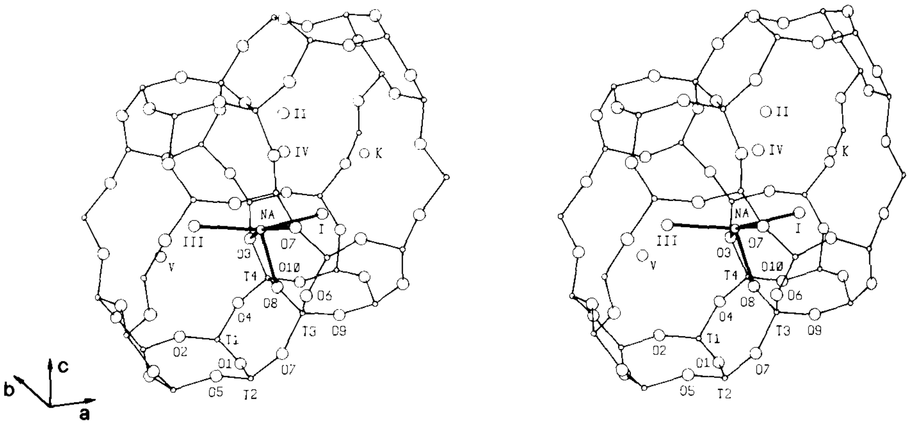

Fig. 3. A stereo view (Johnson, 1965) of the gobbiniste framework structure and the non-framework atom sites. Those positions refined as H_2O are labelled with Roman numerals

The K(1) ions occupy alternating 8-rings perpendicular to the *b*-axis, whereas the Na(1) ions and possibly Ca^{2+} ions at $H_2O(4)$ occupy more than half of those perpendicular to the *a*-axis. Since they have no crystallographically required order, these Na^+ and Ca^{2+} ions must be considered to occupy the 8-rings randomly. That is, some adjacent 8-rings perpendicular to the *a*-axis are occupied simultaneously by Na^+ and/or Ca^{2+} ions, while only alternate 8-rings perpendicular to the *b*-axis are occupied (by K^+ ions). The result of this arrangement of cations is an expansion of the framework structure along *a* and a contraction along *b*. This reduces the ideal framework symmetry from tetragonal to orthorhombic. A similar situation was found in the synthetic zeolite Na–P2 (Fälth and Hansen, 1983). In that structure, solved by single-crystal methods in the space group $P2_12_12_1$, only Na^+ ions are present, and they are located in the channels parallel to the longer unit cell dimension. In amicite (Alberti and Vezzalini, 1979) the Na^+ and K^+ are located in similar positions but in *all* the 8-rings. The cations are ordered, with Na^+ in one direction and K^+ in the other. As expected, the direction containing the 8-rings fully-occupied with K^+ is the longer axis.

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