Gobbinsite from Magheramorne Quarry, Northern Ireland

Gilberto Artioli

Dipartimento di Scienze della Terra, Università di Milano, via Botticelli 23, I-20133 Milano, Italy

AND

Harry Foy

19 Wynard Park, Belfast BT5 6XS, Northern Ireland

Abstract

The rare zeolite mineral gobbinsite has been found in vugs of altered basalts at the Magheramorne Quarry, Larne, Northern Ireland, intimately associated with phillipsite. The crystal chemistry of the sample ($Na_{4.3}Ca_{0.6}Si_{10.4}Al_{5.6}O_{32} \cdot 12H_2O$) is close to that reported for gobbinsite from the type locality. The crystal structure of the Magheramorne gobbinsite has been refined from X-ray powder diffraction data using the multiphase Rietveld full profile technique. The orthorhombic $Pmn2_1$ space group is confirmed. The refined cell parameters (a = 10.1027(5), b = 9.8016(5), and c = 10.1682(6) Å) are slightly different from those reported in the literature for the K-rich gobbinsite from Island Magee (a = 10.108(1), b = 9.766(1), and c = 10.171(1) Å), whose structure was also refined from powder data.

KEYWORDS: gobbinsite, zeolite, Rietveld refinement, crystal structure, Magheramorne Quarry

Introduction

GOBBINSITE is a rare zeolite mineral with the gismondine (GIS) framework type. To date it has been reported only from the type locality in the Gobbins area, Co. Antrim, Northern Ireland (Nawaz and Malone, 1982; Nawaz, 1983; McCusker et al., 1985), and from the Poudrette Quarry, Mont Saint-Hilaire, Quebec, Canada (Horváth and Gault, 1990). A recent review of the worldwide occurrences (Tschernich, 1992) also lists two other unpublished localities: at Aranga, North Island, New Zealand, and at Magheramorne, Larne, Northern Ireland. The gobbinsite from the latter locality refers to a personal communication of one of us (H.F.) and it is the object of the present description.

Occurrence

The gobbinsite at the Magheramorne Quarry is found as a rare filling of vugs and vesicles of amygdaloidal basalts. The cavities containing gobbinsite are composed of compact radiating masses, chalky-white or slightly pink in colour. All analysed vugs containing gobbinsite also contain a variable amount of intimately associated phillipsite. No cavity was found with gobbinsite alone. The other cavities in the altered basalt rock contain calcite and a variety of zeolite minerals (cowlesite, analcime, garronite, gmelinite, gonnardite, thomsonite and natrolite).

The content of a pinkish cavity showing the highest gobbinsite/phillipsite ratio, as determined from preliminary X-ray powder diffraction, was selected for the chemical analysis and the structure refinement.

Chemical composition

Four fragments of the radiating gobbinsite material were prepared for electron microprobe analysis. Two of the fragments were selected from the centre of the cavity, and the other two were extracted from wall material on opposite sides of the cavity, to check for possible segregation of

phillipsite. It is virtually impossible to distinguish the two minerals by colour, lustre or morphology, because of the intimate intergrowth.

Each of the gobbinsite fragments was analysed using an ARL-SEMQ instrument in the wavelength-dispersive mode. The electron beam was defocused to a sample spot size of about 10 μm, using a filament current of 0.20 μA and a voltage of 15 kV. Natural and synthetic silicates were used as standards. The water content resulting from the structure refinement (12.0 water molecules p.f.u.) was used to renormalize to 100% the chemical analyses listed in Table 1. The total weight loss of about 16.5 wt.% agrees with the thermal analysis reported for gobbinsite from the type locality (Gottardi and Galli, 1985). Each analysis in Table 1 is the mean of at least five spot analyses performed on each separate fragment.

No significant spatial variation of the potassium, sodium and aluminium content was observed, indicating a possible segregation of phillipsite. On the contrary, the material shows a remarkable chemical homogeneity and the results of the point analyses for all major elements listed in Table 1 indicate a very limited departure (within 15%) from the mean values.

There is a clear indication that gobbinsite and phillipsite are intermixed in the material used for the present study and the chemical analyses presented for the Magheramorne gobbinsite (columns 1–4, Table 1) are then to be considered mean analyses of gobbinsite with finely dispersed phillipsite fibres.

Column 5 of Table 1 is a tentative recalculation of a possible chemical analysis of gobbinsite, using the relative weight proportion of the two minerals derived from the Rietveld scale factors (gobbinsite:phillipsite = 85:15). The back calculation was applied to the grand mean of the chemical analyses of the four separate fragments using a theoretical formula of a K-rich phillipsite ($K_2Na_{0.3}Ca_{2.1}Si_{9.5}Al_{6.4}O_{32} \cdot 12H_2O$, phillipsite of Casal Brunori, analysis no. 3 of Galli and Loschi Ghittoni, 1972). The recalculated formula assumes

TABLE 1. Electron probe microanalyses of Magheramorne gobbinsite

	1	2	3	4	5
SiO_2	47.29	47.42	47.79	47.80	48.44
Al_2O_3	22.93	22.26	22.57	22.27	22.15
Na_2O	8.76	9.13	8.29	8.97	10.21
K_2O	0.94	0.97	1.34	1.25	0.09
CaO	3.34	3.48	3.23	2.90	2.27
MgO	0.03	0.02	0.02	0.02	0.02
BaO	0.01	0.04	0.06	0.10	0.05
FeO	0.03	0.04	0.02	0.01	0.03
SrO	0.06	0.06	0.05	0.07	0.06
H_2O	16.62	16.58	16.63	16.61	16.68
	100.00	100.00	100.00	100.00	100.00
Si	10.23	10.29	10.34	10.36	10.44
Al	5.85	5.69	5.75	5.69	5.62
Na	3.68	3.84	3.48	3.77	4.27
K	0.26	0.27	0.37	0.34	0.03
Ca	0.77	0.81	0.75	0.67	0.52
Mg	0.01	0.01	0.01	0.01	0.01
Ba	–	–	0.01	0.01	–
Fe	0.01	0.01	–	–	–
Sr	0.01	0.01	0.01	0.01	0.01
H_2O	12.00	12.00	12.00	12.00	12.00
E%	6.09	−1.12	7.01	3.27	4.73

Note:
Columns 1–4 are the results of the analyses on gobbinsite-phillipsite mixtures.
Column 5 is the recalculated analysis for pure gobbinsite assuming a gobbinsite:phillipsite ratio of 85:15 (see text for details). Balance error (E%) has the usual meaning.

TABLE 2. Data collection and final Rietveld refinement parameter

instrument	Philips PW 1050/81
2θ range	$10-140°$
step size	$0.02°$
$n.$ points	6501

cell:

a	$10.1027(5)$ Å
b	$9.8016(5)$ Å
c	$10.1682(6)$ Å

$n.$ contributing independent reflections:

gobbinsite	1090
phillipsite	2083

$n.$ refined parameters: 78

residual factors:

R_p	0.105
R_{wp}	0.136
GOF	10.72
R_{exp}	0.042

that most K in the material is located in the phillipsite.

However, even disregarding the tentative recalculation, the overall chemical analyses clearly show that the studied material is remarkably richer in Na and poorer in K than the gobbinsite used in the previous structure refinement (McCusker *et al.*, 1985), and that the crystal chemistry of the Magheramorne gobbinsite is close to that of the original material from Hills Port (Nawaz and Malone, 1982).

Structure refinement

X-ray powder diffraction data were collected on a conventional source using a flat-plate Bragg-Brentano geometry, and graphite monochromatized Cu-K_α radiation. Details of the data collection are listed in Table 2.

Because of the strong pseudosymmetry present in the crystal structures of the gismondine group (Alberti and Vezzalini, 1979; McCusker *et al.*, 1985; Artioli, 1992) a careful analysis of the Bragg peaks present in the observed X-ray diffraction pattern was performed by comparison with the simulated profiles relative to all subgroups of the topologic $I4_1/amd$ space group (Gottardi, 1979). Diffraction peak splitting clearly indicate orthorhombic symmetry, and among the possible orthorhombic subgroups the $Pmn2_1$ space group

used in the previous structure study (McCusker *et al.*, 1985) was found to correctly describe the average diffraction symmetry of the Magheramorne gobbinsite.

The structure refinement was performed using the multiphase Rietveld technique and the GSAS computer program package (Larson and Von Dreele, 1993). The phillipsite structure as resulting from single crystal refinement (Rinaldi *et al.*, 1974) was inserted as a minor phase and its structure was held fixed during the least-squares refinement. Only the peak profile parameters, the lattice constants, one overall temperature factor, and the site occupancy parameters of the K and Ca cations were allowed to vary in the final cycles.

The starting parameters for the framework atoms of gobbinsite were from McCusker *et al.* (1985). Soft constraints on the Si,Al−O distances were imposed in the starting stages of the refinement to avoid divergence.

Pseudo-Voigt peak profile functions were used for both phases, and a cosine real Fourier series with six coefficients was used to model the background profile. Five isotropic atomic displacement parameters were used for gobbinsite: one for the tetrahedral Si,Al atoms, one for the framework oxygens, one for the extra-framework water molecules and two for the extra-framework cation sites. The refined T−O distances indicate no significant ordering of Al on the tetrahedral sites: they were treated as fully occupied by Si and Al in the fixed proportion 10.4:5.6. The extra-framework atom positions were identified on the difference Fourier maps. The position facing the upper 8-ring in the cavity (site D_u1 in the notation of Artioli, 1992) is considered a cation position because of its distances from the framework oxygens. It is assigned to Na and it corresponds to the Na(1) position of McCusker *et al.* (1985). The site was found to be a very diffuse position, appearing in the difference Fourier maps as a broad maximum, and it was modelled in the final cycles by two cation sites (labelled Na1 and Na2). Another position in the cavity near the centre of the lower 8-ring (site A_l of Artioli, 1992) is assigned to Ca cations because of the large residual peak density in the Fourier maps: this site corresponds to the K(1) position of McCusker *et al.* (1985), it shows a rather sharp peak in the difference Fourier maps, and it is labelled Ca1.

The total electron density refined on the three cation sites is in excess with respect to the cation content of the material as resulting from the electron probe analysis. This over-estimation is likely to be an artifact of the profile refinement, probably due to correlation with the atomic displacement parameters. It was decided to fix

TABLE 3. Final atomic coordinates, isotropic atomic displacement parameters and site occupancy factors for the Magheramorne gobbinsite

site	mult.	x	y	z	occupancy	U_{iso}[1]
t1	4	0.1545(7)	0.4289(8)	0.8003(9)	1.00[2]	0.040(1)
t2	4	0.1526(8)	0.1063(8)	0.758(1)	1.00[2]	0.040(1)
t3	4	0.3406(8)	0.0778(8)	0.0[3]	1.00[2]	0.040(1)
t4	4	0.3408(7)	0.3825(9)	0.047(1)	1.00[2]	0.040(1)
o1	4	0.168(2)	0.2705(8)	0.752(2)	1.00	0.045(2)
o2	2	0.0	0.454(2)	0.837(2)	1.00	0.045(2)
o3	4	0.306(2)	0.469(1)	0.188(1)	1.00	0.045(2)
o4	4	0.254(1)	0.451(2)	0.926(1)	1.00	0.045(2)
o5	2	0.0	0.067(2)	0.797(2)	1.00	0.045(2)
o6	4	0.189(2)	0.033(1)	0.618(1)	1.00	0.045(2)
o7	4	0.253(1)	0.040(1)	0.867(1)	1.00	0.045(2)
o8	4	0.305(2)	0.2249(8)	0.062(2)	1.00	0.045(2)
o9	2	0.5	0.079(2)	0.965(2)	1.00	0.045(2)
o10	2	0.5	0.398(2)	0.016(2)	1.00	0.045(2)
na1	4	0.253(2)	0.257(2)	0.363(2)	0.62(2)[4]	0.093(9)
na2	4	0.369(2)	0.240(2)	0.333(2)	0.38(2)[4]	0.093(9)
ca1	2	0.5	0.118(3)	0.102(3)	0.47(4)	0.11(1)
w1	2	0.5	0.096(2)	0.603(3)	1.08(5)	0.094(4)
w2	2	0.0	0.319(3)	0.090(4)	1.14(4)	0.094(4)
w3	2	0.0	0.316(2)	0.390(2)	2.07(5)	0.094(4)
w4	4	0.330(2)	0.287(1)	0.544(2)	1.70(3)	0.094(4)
w5	2	0.5	0.533(3)	0.156(2)	1.67(4)	0.094(4)

Notes:
[1] atomic displacement parameter ($\mathring{A}^2$) defined as: $e^{-(8\pi^2 U \cdot \sin^2\theta/\lambda^2)}$
[2] tetrahedral sites treated as: $Si_{10.4}Al_{5.6}$
[3] fixed to define cell origin along the z axis
[4] combined occupancy constrained to 4.0 Na atoms p.f.u.

the cation site occupancy factors to values close to the Na and Ca chemical content.

The remaining five major Fourier peaks were assigned to water oxyens and their occupancy factors refined to values close to or larger than one. A few other minor Fourier peaks were tentatively refined as water molecules, but resulted in negative site occupancy factors. The overall water content resulting from the five fully occupied sites corresponds to 12 water molecules p.f.u although it can not be ruled out that some extra water molecules are present, either disordered over multiple sites in the cavity, or located on the cation sites.

The refined cation positions closely match the cation sites of McCusker et al. (1985), as do the water sites W2, W3 and W4. On the other hand the W1 and W5 water mlecule positions are remarkably shifted with respect to the corresponding sites in the previous refinement. The two water molecules appear to be removed from the centre of the cavity, and closer to the Ca1

cation position in the centre of the 8-ring. The shift might be caused by the different chemical content of the cation site.

The detailed parameters of the Rietveld refinement are listed in Table 2; the final atomic coordinates, the isotropic displacement parameters, and the site occupancy factors are listed in Table 3. The observed, calculated and difference powder diffraction profiles are shown in Fig. 1.

The Rietveld refined scale factors allowed the accurate estimate (Hill, 1992; Bish and Post, 1993) of the average weight proportions of gobbinsite and phillipsite in the studied material: the ratio between the two crystalline phases is close to 85:15.

Conclusions

Gobbinsite occurrs at the Magheramorne Quarry, Larne, Northern Ireland, in close association with phillipsite. The combination of multiphase Rietveld refinement and electron microprobe analysis show that the crystal chemistry of the
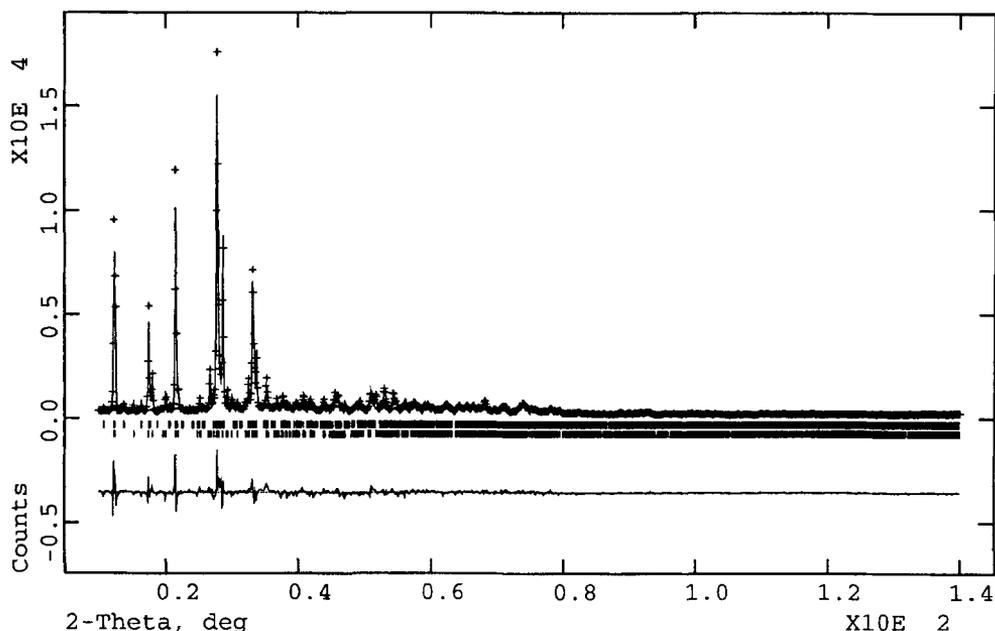
FIG. 1. Observed, calculated and difference profiles for the Magheramorne gobbinsite. Lower Bragg peak marks are for gobbinsite, upper marks are for phillipsite.

Magheramorne gobbinsite is near the one reported for the type material from Hills Port (Nawaz and Malone, 1982), and that the space group and structure interpretation of McCusker *et al.* (1985) can be applied to gobbinsite samples from other localities.

Acknowledgements

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