Gobbinsite, a new zeolite mineral from Co. Antrim, N. Ireland

RAB NAWAZ

Department of Geology, Ulster Museum, Belfast

AND

JOHN F. MALONE

Department of Chemistry, Queen's University, Belfast

ABSTRACT. A chalky white, fibrous mineral, in the amygdales of Tertiary basalts from the Gobbins area, Co. Antrim, has been discovered to be a new mineral. It consists of fibrous clusters of lath-shaped crystals showing straight extinction with negative elongation. Its refractive index is ε 1.489, ω 1.494 (both \pm 0.003) and specific gravity is 2.194 (meas.), 2.147 (calc.). The mineral is tetragonal with $\varepsilon = c$ (elongation); a = 10.145, $c = 9.788 \,\text{Å}$. The strongest powder lines (in Å, intensity in brackets) are: 7.10, 4.10, 3.19(100); 3.10, 2.69(80); 5.07(50); 2.64(40). A spectrographic analysis shows major Si, Al, minor Ca, Na, Cu, and trace Fe. Two chemical and one probe analysis give the ideal formula Na₄(Ca,Mg,K₂)Al₆Si₁₀ O₃₂.12H₂O. The name gobbinsite (approved by the IMA Commission on New Mineral Names) is suggested after the locality. The type specimen (I7881) is preserved in the Ulster Museum.

Rotation and Weissenberg photographs of gobbinsite and garronite show doubled reflections, which are explained on the basis of submicroscopic twinning on (101). Relationship between gobbinsite and garronite is discussed and evidence is presented for the occurrence of minute amounts of a merlinoite-type mineral that forms regular intergrowths with gobbinsite and garronite.

Occurrence. Amygdaloidal basalt specimens collected from the scree and the cliff face of the coastal escarpment near Hills Port, south of the Gobbins area, contain a fibrous, chalky white mineral that has optical properties and an X-ray pattern distinctly different from any known naturally occurring zeolite mineral. The mineral occurs in roughly spherical vugs up to 5 mm diameter, either alone or in association with gmelinite of platy habit. In other specimens at this locality vugs in the basalt are filled with chabazite, gonnardite, or tetranatrolite

Physical and optical properties. Under the microscope gobbinsite consists of clusters of very fine lath-shaped or fibrous crystals showing straight

extinction and negative elongation. The crystals are elongated parallel to the c-axis. The refractive index parallel to length (ε) is 1.489 and across it (ω) is 1.494 (both ± 0.003). No cleavages were observed. The specific gravity of 2.194, determined on a 6.21 mg cluster using a torsion microbalance, is probably too high because of calcite and other impurities such as copper salts.

Chemical composition of gobbinsite. Spectrographic analysis was carried out on the same powder used for the X-ray diffraction pattern, with phillipsite from Dunseverick, Co. Antrim (No. 17882), as a comparative standard. The results were identical with respect to Si and Al (major), Fe (trace), and Cu, Na, and Ca (minor) but, while phillipsite showed a minor amount of K, gobbinsite showed none. Two wet chemical analyses of gobbinsite, both with carbonate impurity, are listed in Table I. After correcting for the impurity, both these analyses yield the simple formula for gobbinsite as Na₅Al₅Si₁₁O₃₂.11H₂O which is very similar to that of the synthetic Na-P(363) zeolite of Taylor and Roy (1964). However, the average of six electron probe analyses (Table I) shows a formula close to Na₄(Ca,Mg,Ba,Sr,K₂)Al₆Si₁₀O₃₂.10H₂O. The copper in both the wet analyses is considered as part of the carbonate impurity but is not considered in calculation of the impurity content represented by calcite alone: $d_{\text{mix.}} = 100/(\text{ct.}/d_{\text{ct.}} +$ gob./ $d_{gob.}$) where ct. and gob. are wt. % calcite and gobbinsite, $d_{ct.} = 2.72$, $d_{gob.} = 2.147$ and $d_{mix.} =$ 2.194. The gobbinsite density is calculated from $Na_4CaAl_6Si_{10}O_{32}.12H_2O.$

Water content. The average of six probe analyses of gobbinsite gives a water content, by difference, of 13.55% or 9.41 molecules. This value, however, is too low because a 6.21 mg cluster, on which the specific gravity of 2.194 was determined, lost 17.9%

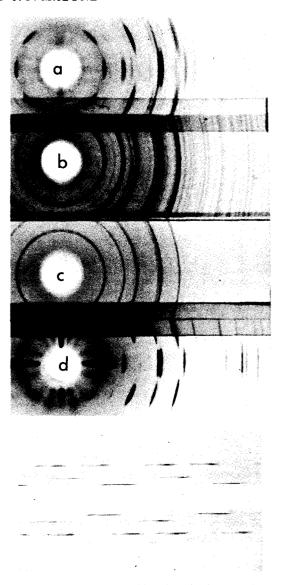
TABLE I. Wet chemical and microprobe analyses of gobbinsite

	1	1 <i>a</i>	2	2 <i>a</i>	3
SiO ₂	57.12	52.17	48.5	51.15	49.21
Al_2O_3	22.48	20.52	20.0	21.09	23.64
Fe_2O_3	0.60	0.55	0.3	0.32	0.04
MgO	n.d.		0.47	0.50	1.00
CuO	0.06		0.1	_	n.d.
SrO	n.d.	_	n.d.	_	0.36
CaO	7.98	1.00	2.05	0.66	1.58
BaO	n.d.	_	n.d.		0.12
Na ₂ O	11.73	10.71	9.5	10.02	9.85
K_2O	n.d.		0.93	0.98	0.66
CO_2			1.20		
H_2O		15.04	14.5	15.29	[13.55]
Total	99.97	100.00	97.55	100.00	100.00
	Cat	ions on the	basis of 3	32 oxygens	
Si		10.93		10.79	10.25
Al		5.07		5.24	5.80
Fe		0.09		0.05	0.01
Mg				0.16	0.31
Sr		_			0.04
Ca		0.22		0.14	0.35
Ba				****	0.01
Na		4.35		4.10	3.98
K		_		0.26	0.18
H ₂ O		10.51		10.79	9.41

n.d. = not determined.

weight when heated to 1000 °C for a half hour. Assuming a small calcium and copper carbonate impurity content this weight loss suggests that the probable water content is 11 or 12H₂O. The latter gives a calculated specific gravity of 2.147 commensurate with the Na-rich nature of this mineral.

X-ray data. The X-ray powder diffraction pattern of gobbinsite (Table II) was recorded using a camera of 114.86 mm diameter and Cu- $K\alpha$ radiation and was indexed by comparing the powder film with a fibre rotation photograph (fig. 1) from a small cluster of gobbinsite crystals with common elongation. This axis was labelled as c and its repeat distance was measured from the fibre photograph. The fibre diagram (fig. 1) reveals twinning (see below), which can also be seen on the Weissenberg hk0 photograph (fig. 2). The unit cell dimensions,



Figs. 1 and 2: Fig. 1 (top). (a) Gobbinsite fibre rotation photograph about the needle axis. (b) Gobbinsite powder pattern with very weak diffraction lines due to merlinoite-type impurity. (c) Garronite powder pattern. (d) Garronite fibre rotation photograph about the needle axis. Specimen G1, Walker (1962), used for both c and d. Fig. 2 (bottom). The hk0 Weissenberg photograph of gobbinsite showing the doubling due to twin structural intergrowths.

a = 10.08, c = 9.80 Å measured from the Weissenberg film, were refined from ten powder lines to be a = 10.145, c = 9.788 Å.

The gobbinsite unit cell has a > c and indexing is on this basis. It is fairly certain that 0k0 reflections

^{1.} Wet chemical analysis of anhydrous material by chemistry Department, Queen's University, Belfast. The wt. loss was 17.9% at $1000\,^{\circ}$ C after $\frac{1}{2}$ hr heating.

¹a. Calculated from analysis 1, together with the loss on ignition, deducting $10.2\,\%$ calcite and Cu carbonate, and adjusting to $100\,\%$

^{2.} Wet analysis by V. K. Din and A. J. Easton (BMNH).

²a. Calculated from analysis 2 by deducting CaO and CuO equivalent to the observed CO₂ and adjusting to 100%.

^{3.} Microprobe analysis, G. Vezzalini analyst (Modena).

TABLE II. X-ray powder pattern of gobbinsite

hkl	d _{calc.} (Å)	dobs. (Å)	I	hkl	$d_{\mathrm{calc.}}(\mathrm{\AA})$	d _{obs.} (Å)	1	hkl	$d_{\mathrm{calc.}}(\mathrm{\AA})$	$d_{\mathrm{obs.}}(\mathrm{\AA})$	1	hkl	$d_{\mathrm{calc.}}(\mathrm{\AA})$	$d_{\mathrm{obs.}}(\mathrm{\AA})$	I
110	7.17 }	711	100b	331	2.322		_	522	1.757	_		226	1.485	_	_
101	7.04 }	7.11	1000	114	2.316	2.317	10	503	1.722	1.722	30	613	1.484	1.483	10
111*	5.78	5.78	20	420	2.267		_	225	1.718	_	_	425	1.482	_	****
200*	5.07	5.056	50	402	2.251	2.256	15	600	1.690	1.686	25	306	1.469	1.470	5
002	4.894	4.893	30	421	2.209	_	_	442	1.683		_	316	1.454	1.453	5
102*	4.407	4.409	25	204	2.204	2.206	25	315	1.671	_	_	444	1.446	1.445	10
211*	4.115	4.116	100	412	2.197	-	_	610	1.667	1.667	10	632	1.444	_	
112*	4.042	4.027	20	214	2.153	2.153	25	424	1.663		_	543	1.425	1.422	10
202	3.520	3.515	10	332	2.148		_	611	1.643	1.641	5	711	1.419	_	_
212*	3.326	3.326	30	442	2.057	2.057	20	532	1.639	_	_	640	1.406	1.406	10
310*	3.207)		***	510	1.989	_	-	006	1.631	1.631	15	720	1.393	_	_
301	3.195	3.201	100	431	1.986	1.986	25	325	1.607	_		641	1.392	_	
103*	3.106	3.106	80	304	1.982		_	620	1.603	1.604	10b	604	1.391	1.390	10
311	3.047	3.040	10	413	1.964	1.965	10	602	1.597		_	702	1.389	_	_
113	2.970	2.968	10 <i>b</i>	511	1.949	_	_	540	1.584	_		712	1.376	_	
222	2.892	2.887	5	314	1.945	1.945	5	621	1.582	1.582	5	406	1.372	1.373	25
302	2.781)		_	333	1.928		_	612	1.578		_	703	1.324	_	_
203	2.744	2.757	5	105	1.922	1.922	10	541	1.563	_	_	445	1.322	1.321	10b
321	2.703			423	1.862	1.863	10	504	1.561	1.561	15	317	1.282	_	
312	2.682	2.699	9 80 <i>b</i>	521	1.849		_	405	1.549	1.548	5	723	1.281	1.281	20
213*	2.648	2.651	40	324	1.846	1.845	20	514	1.543		_	506	1.271	1.271	10
400*	2.535	2.539	25	512	1.842	_	_	533	1.535	1.536	5	800	1.268		_
004	2.447	_	_	205	1.826	1.824	2	415	1.532		_	327	1.252	1.252	10
402	2.438	2.435	20	215	1.797		_	335	1.514		_	733	1.233	_	_
330	2.390	_	_	440	1.792	1.793	20	630	1.512	1.512	10	545	1.231	1.232	5
411	2.385	_		441	1.763	1.762	25	631	1.494	1.493	10		1.218	1.218	5
104	2.379	2.379	20	404	1.761	_		524	1.492	_	_	446+		1.203	5

^{*} Reflections used for least squares refinement giving a = 10.145, $c = 9.788 \,\text{Å}$; b = Broad.

are absent when k is odd; all others (except 00l) have no restrictions. The 00l is seen to be absent when l=2n+1 but it is not absolutely certain whether l odd are absent accidentally. This leads to the possible space groups of gobbinsite as $P4_22_12$, $P42_12$, or $P\overline{4}2_1m$; the first is the more probable.

Twinning. The rotation and Weissenberg photographs of gobbinsite about the fibre axis show doubled reflections similar to those noted by Pabst (1971) for natrolite. The doubling (see Table III and fig. 3) can be explained on the basis of an intergrowth akin to twinning on (101). This is to be expected since the axial ratio is very close to unity. As a result of twinning rotation about the fibre axis provides both h and l indices of the reflections and thus indexing the powder pattern is made easy. The plausible structure at the twin boundary is that of merlinoite (Passaglia et al. 1977) or a related mineral (see below) that occurs as an impurity in gobbinsite and garronite.

Distinction from other zeolites. Gobbinsite belongs to the gismondine, phillipsite, merlinoite, garronite, and synthetic Na-P group of minerals, which have one dimension c. 10 Å and the other two either c. 10 Å or c. 14 Å $\sqrt{(2 \times 10^2)}$. Chemically it differs from merlinoite and phillipsite, in which K is usually an essential constituent, and from gismondine and garronite, which have major Ca. Its chemical composition and X-ray diffraction

pattern are the same as the Na-P (tetragonal form) of Barrer et al. (1959a) and Taylor and Roy (1964). Garronite is tetragonal but its structure is based on a body-centred lattice (see below) rather than the primitive lattice of gobbinsite. Optically, garronite, gismondine, and harmotome have higher refractive indices, whereas merlinoite, amicite, and phillipsite of comparable refractive index have positive elongation.

TABLE III. The doubled reflections of gobbinsite and garronite due to twinning on (101)

Gobbinsite			Garronite*			
d Å	h,l	hkl	d Å	h,l	hkl	
7.11	0,1	110,011	7.13	0,1	011	
5.056	0,2	200	4.95	0,2	002	
4.893	0,2	002	4.15	1,2	211	
4.409	0,2	012	4.07	1,2	112	
4.116	1,2	211	3.240	0,1	130	
4.027	1,2	112	3.140	0,3	013	
3.515	0,2	022	2.674	1,3	123	
3.326	1,2	122	2.573	0,4	400	

^{*}Pattern of Ca-Pt(363) from Taylor and Roy (1964) indexed on the basis of a > c, a = 10.246, c = 9.896 Å. Due to twinning each hkl is split into two reflections for which h and l are given.

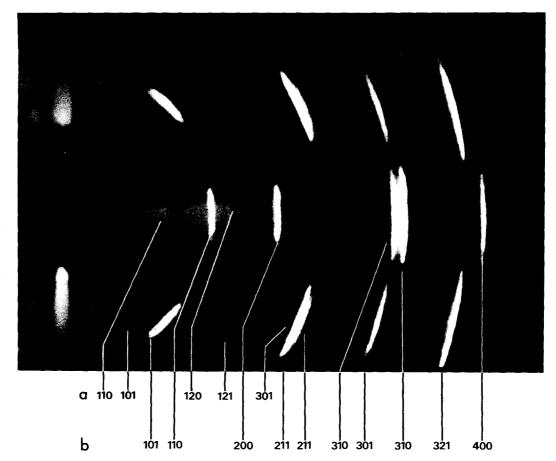


Fig. 3. Same as Fig. 1d but overexposed to show (a) merlinoite-like phase and (b) garronite twin doubling of reflections.

The name gobbinsite is proposed after the name of the locality and the type material is incorporated in the Ulster Museum mineral collection.

Garronite—twinning, orientation, and possible space group. Mandarino (1963) quoting a private communication from Barrer et al. (1959b) says that the garronite powder pattern may be indexed on two sets of tetragonal cells, a > c and c > a, preferably the latter, since agreed by Taylor and Roy (1964). None of these studies, however, is based on single crystal data. Garronite shows twinning, as gobbinsite, on (101) and its rotation pattern contains doubled reflections, which have to be indexed (Table III) on the basis of a > c to account for observed h and l. Garronite thus has the same orientation as gobbinsite.

This indexing shows that for hkl, h+k+l=2n. The possible space group is therefore one of the following: I4/mmm, I422, I4mm, I4m2, I4/m, I4, or $I\overline{4}$. Gottardi and Alberti (1974) have suggested that

the framework of garronite may be based on $14_1/amd$ but the present indexing does not lead to this space group.

Merlinoite-type impurity mineral. This mineral occurs in both gobbinsite and garronite (fig. 3) in regular intergrowths such that their c-axes coincide and are parallel to their elongation. The reflections corresponding to this impurity mineral, Table IV, can be indexed on the basis of an orthorhombic unit cell close to a = 14.22, b = 14.29, c = 9.83 Å. This indexing and unit cell are similar to but not the same as those of the new zeolite mineral merlinoite (Passaglia et al., 1977) nor the same as two synthetic zeolites, the orthorhombic form of the Na-P group (Barrer et al., 1959a), and the phase K-M (Barrer and Baynham, 1956).

Passaglia et al. (1977) suggest that merlinoite and the above synthetic phases are synonymous but the powder line at 5.6 Å (201) in the latter patterns is incompatible with the space group of

TABLE IV. Partial X-ray powder pattern of a merlinoite-like phase*

 d Å	I	hkl	
10.13	2	110	
8.13	5	101	
6.41	5	120	
5.37	5	121	
4.277	5	301	

^{*} Pattern obtained from the gobbinsite film (fig. 1b).

merlinoite (*Immm*). The powder pattern of the impurity mineral is remarkably similar to that of the synthetic phase Ba-H(1) (Taylor and Roy, 1964). In particular the powder line at 6.41 Å (120) is common to both but does not occur in either merlinoite or the synthetic zeolites Na-P and K-M. Furthermore it is not compatible with the merlinoite space group. Taylor and Roy (1964) have suggested close resemblance between the powder patterns of the Ba-H(1) phase and the monoclinic harmotome; therefore the impurity mineral is distinct from harmotome and must remain a problem for the time being.

Acknowledgements. Thanks are due to Drs Hey, Gottardi, and Kato for arranging the analyses to be made at British Museum (NH) and Modena University and to V. K. Din, A. J. Easton, and G. Vezzalini for performing the analyses. Mr Foy kindly brought the mineral to our notice.

REFERENCES

Barrer, R. M., and Baynham, J. W. (1956) The hydrothermal chemistry of the silicates. Part VII. Synthetic potassium aluminosilicates. J. Chem. Soc. 2882-91 [M.A. 13-449].

— Bultitude, F. W., and Kerr, I. S. (1959b) Some properties of, and structural scheme for, the Harmotome zeolites. Ibid. 1521-8.

Gottardi, G., and Alberti, A. (1974) Domain structure in garronite: a hypothesis. *Mineral. Mag.* 39, 898-9.

Mandarino, J. A. (1963) Garronite abstract, New Mineral Names (by M. Fleischer) Am. Mineral. 48, 711-12.

Pabst, A. (1971) Natrolite from the Green River Formation, Colorado, showing an intergrowth akin to twinning. Ibid. 56, 560-9.

Passaglia, E., Pongiluppi, D., and Rinaldi, R. (1977) Merlinoite, a new mineral of the zeolite group. *Neues Jahrb. Mineral.*, *Monatsh.* 355-64.

Taylor, A. M., and Rustum Roy (1964) Zeolite studies IV. Na-P zeolites and the ion-exchanged derivatives of tetragonal Na-P. Am. Mineral. 49, 656-82.

Walker, G. P. L. (1962) Garronite, a new zeolite, from Ireland and Iceland. *Mineral. Mag.* 33, 173-86.

[Manuscript received 25 June 1981; revised 22 August 1981]