

l'atome d'étain, ce qui n'est pas le cas pour les composés fluorohalogénés où seul le fluor participe à cet environnement pour les phases riches en fluor, c'est-à-dire Sn_2ClF_3 (Donaldson *et al.*, 1977), Sn_3BrF_5 (Donaldson *et al.*, 1977; Vilminot, Granier & Cot, 1978) et Sn_2IF_3 (Vilminot *et al.*, 1978a). Le seul fait d'obtenir une solution solide laissait prévoir un tel résultat. La faible différence des rayons ioniques et des électronégativités des ions Cl^- et Br^- peut expliquer ce comportement. Ce même résultat est confirmé par l'étude du binaire SnCl_2 - SnBr_2 qui met en évidence l'existence de deux solutions solides, de type SnCl_2 et SnBr_2 respectivement (Thevet *et al.*, 1979).

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The Crystal Structure of Amicite, a Zeolite

BY A. ALBERTI AND G. VEZZALINI

Istituto di Mineralogia e Petrologia della Università di Modena, Via S. Eufemia 19, I-41100 Modena, Italy

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Abstract

Amicite, $\text{K}_4\text{Na}_4[\text{Al}_8\text{Si}_8\text{O}_{32}]\cdot 10\text{H}_2\text{O}$, is monoclinic, pseudotetragonal, with $a = 10.226$ (1), $b = 10.422$ (1), $c = 9.884$ (1) Å, $\beta = 88^\circ 19' (1)'$, space group $I2$. The topology of its framework is the same as that of garronite, gismondine and synthetic zeolite P and the structure can be described as formed by two untwisted double-crankshaft chains developed in two perpendicular directions. The Si/Al and Na/K distributions are ordered and consequently the symmetry is lowered from the topological symmetry of $I4_1/amd$ to the real symmetry $I2$.

Introduction

Amicite, cell formula $\text{K}_4\text{Na}_4[\text{Al}_8\text{Si}_8\text{O}_{32}]\cdot 10\text{H}_2\text{O}$, was recently described as a new mineral by Alberti, Hentschel & Vezzalini (1979). It was found closely associated with merlinoite in a basaltic rock at Höwenegg in Hegau, southern West Germany.

The mineral is closely related to garronite, gismondine and synthetic zeolite P . It is monoclinic, pseudo-

tetragonal, with $a = 10.226$, $b = 10.422$, $c = 9.884$ Å, $\beta = 88^\circ 19'$, space group $I2$.

Experimental

The study was carried out on a fragment approximately $0.06 \times 0.11 \times 0.15$ mm. The intensity data were collected on a Philips PW 1100 diffractometer (Mo $K\alpha$ radiation) at the Istituto di Mineralogia, Università di Perugia. 2667 intensities, referred to a triclinic cell with $a = 8.741$, $b = 8.739$, $c = 9.900$ Å, $\alpha = 123^\circ 14'$, $\beta = 123^\circ 15'$, $\gamma = 73^\circ 17'$, were collected. From these unit-cell data a monoclinic I centered cell with $a = 10.234$, $b = 10.429$, $c = 9.900$ Å, $\beta = 88^\circ 21'$ can be derived by the transformation matrix 111/-110/001. This monoclinic symmetry was confirmed by comparison of the equivalent reflections. 1439 independent reflections corresponding to 12% of the Mo $K\alpha$ limiting sphere were obtained. No systematic absences, with the exception of the hkl reflections with $h + k + l = 2n + 1$, were found, indicating $I2/m$, $I2$ and Im as probable space groups for amicite. 1245 reflections with $I > 3\sigma(I)$ were used in the refinement.

The chemical formula (Alberti *et al.*, 1979) is $K_{3.75}Na_{3.61}Ca_{0.05}[Al_{7.86}Si_{8.24}O_{32}] \cdot 9.67H_2O$.

Structure determination and refinement

The similarities between the powder patterns of amicitite and the other minerals of the phillipsite group, related to their cell dimensions ($a \approx b \approx c \approx 10 \text{ \AA}$, $\beta \approx 90^\circ$ for the *I* centered cell), suggested the hypothesis that the framework of amicitite could correspond to one of the possible structures based on the 4.8^2 net (Smith, 1978) but not necessarily to the framework of gismondine. As the centrosymmetry tests used in the *MULTAN* program (Germain, Main & Woolfson, 1971) provided results between centrosymmetry and noncentrosymmetry, the Harker *h0l* section and *0k0* line of the Patterson function were examined, and indicated the space group *I2* as the most probable. The solution, which is associated with the highest combined figure of merit of the *MULTAN* program in this space group, gives for amicitite a framework analogous to that of gismondine, which was confirmed by the Patterson map, and supplied the starting parameters of the framework atoms.

A combination of a three-dimensional Fourier synthesis (to locate cations and water molecules) and least-squares techniques, with weight assigned according to counting statistics and variable occupancy factors for non-framework cations and water molecules, converged by isotropic thermal refinement to an *R* value of 4.1%. Refinement with anisotropic thermal parameters further reduced the residual indices

to final values of $R = 2.6\%$, $wR = 3.3\%$, with an *R* value for observed and non-observed reflections of 3.5%.* Since at the end of the refinement the occupancy factors of Na, K, *W*(1), *W*(2) and *W*(3) differed only slightly from unity, they were fixed at 100% in the last cycle of refinement. No absorption correction was applied since Mo *K* α radiation ($\mu = 0.96 \text{ mm}^{-1}$) and a very small crystal were used. Because of the negligible values of f' and f'' for the atoms involved (Cromer, 1965), no correction for anomalous scattering was made. The atomic scattering curves used for Si^{4+} , Al^{3+} , O^{2-} , Na^+ , and K^+ were from Cromer & Mann (1968) while the atomic scattering curve for H_2O was taken from Hajdu (1972).

The unit-cell parameters obtained from the refinement of the powder data (Alberti *et al.*, 1979) were used in the refinement of the structure. These parameters, $a = 10.226(1)$, $b = 10.422(1)$, $c = 9.884(1) \text{ \AA}$, $\beta = 88^\circ 19(1)'$, with space group *I2*, are in agreement with the values obtained from the single-crystal diffractometer.

The positional and thermal parameters are given in Table 1, interatomic distances and bond angles in Tables 2 and 3.

The X-ray refinement shows a total of 11.06 water molecules, which is somewhat higher than the 9.67 water molecules given by thermogravimetric analysis.

Discussion of the structure

The framework can be described on the basis of the 4.8^2 net and untwisted *UDD* crankshafts (Schläfli symbol 4^36^28); it is formed by two double-crankshaft chains oriented in two perpendicular directions and therefore has tetragonal symmetry (Smith, 1978). As a consequence, a gismondine-like cage is obtained, which is formed by six four-membered rings and four eight-membered rings. Two sets of channels delimited by eight-membered rings run parallel to the *a* and *c* axes.

A skeletal diagram of this framework is shown in Fig. 3 of Baerlocher & Meier (1972). A projection of the structure in the (010) plane is shown in Fig. 1, while the gismondine cages are shown in Fig. 2.

In amicitite the distribution of Si/Al cations is extensively ordered with a Si/Al ratio close to 1.0. The Na and K are well ordered in two completely filled sites. Na is six-coordinated if we consider 2.90 Å too large a distance for the Na–*W*(4) coordination, while K is seven-coordinated, including both framework oxygens and water molecules (see Fig. 1); average distances are 2.52 and 2.89 Å respectively. As shown in Fig. 2, K

Table 1. Atomic coordinates and B_{eq} (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq} *
Si(1)	0.1523 (1)	−0.0133	0.3261 (1)	0.46
Si(2)	0.1534 (1)	0.2615 (1)	0.8263 (1)	0.40
Al(1)	0.1546 (1)	0.2491 (2)	0.1546 (1)	0.43
Al(2)	0.1582 (1)	0.0027 (2)	0.6512 (1)	0.44
O(1)	0.0010 (3)	−0.0471 (3)	0.3037 (3)	1.21
O(2)	−0.0030 (2)	0.2956 (3)	0.2047 (3)	1.14
O(3)	0.2031 (3)	0.1401 (3)	0.7354 (3)	0.96
O(4)	0.1810 (3)	0.0304 (3)	0.4785 (3)	1.18
O(5)	0.1712 (3)	0.2264 (3)	0.9833 (3)	1.13
O(6)	0.1989 (3)	0.1018 (3)	0.2263 (3)	1.00
O(7)	0.2620 (3)	0.3610 (3)	0.2184 (3)	1.09
O(8)	0.7558 (3)	0.3812 (3)	0.2177 (3)	0.73
Na	0.4312 (2)	0.2559 (2)	0.6716 (2)	2.53
K	0.3071 (1)	−0.0040 (2)	0.9692 (1)	2.09
<i>W</i> (1)	0.3435 (3)	0.2507 (5)	0.4539 (3)	2.65
<i>W</i> (2)	0.4779 (3)	0.0682 (4)	0.2179 (4)	2.76
<i>W</i> (3)	0	0.3191 (5)	$\frac{1}{2}$	2.70
<i>W</i> (4)†	$\frac{1}{2}$	0.4729 (9)	$\frac{1}{2}$	2.35

* Obtained from the anisotropic temperature factors after Hamilton (1959).

† Occupancy 0.53 (1).

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34709 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Interatomic distances (Å) and angles (°) within the framework of amicite*

Si(1) tetrahedron		Si(2) tetrahedron		Al(1) tetrahedron		Al(2) tetrahedron	
Si(1)—O(1)	1.608 (3)	Si(2)—O(2)	1.616 (3)	Al(1)—O(2)	1.741 (3)	Al(2)—O(1)	1.753 (3)
Si(1)—O(4)	1.609 (3)	Si(2)—O(3)	1.624 (3)	Al(1)—O(5)	1.714 (3)	Al(2)—O(3)	1.726 (3)
Si(1)—O(6)	1.616 (3)	Si(2)—O(5)	1.609 (3)	Al(1)—O(6)	1.756 (3)	Al(2)—O(4)	1.740 (3)
Si(1)—O(7)	1.630 (3)	Si(2)—O(8)	1.607 (3)	Al(1)—O(7)	1.734 (3)	Al(2)—O(8)	1.752 (3)
O(1)—O(4)	2.685 (4)	O(2)—O(3)	2.662 (4)	O(2)—O(5)	2.873 (4)	O(1)—O(3)	2.891 (4)
O(1)—O(6)	2.646 (4)	O(2)—O(5)	2.667 (4)	O(2)—O(6)	2.901 (4)	O(1)—O(4)	2.917 (4)
O(1)—O(7)	2.610 (4)	O(2)—O(8)	2.622 (4)	O(2)—O(7)	2.802 (4)	O(1)—O(8)	2.744 (4)
O(4)—O(6)	2.603 (4)	O(3)—O(5)	2.620 (4)	O(5)—O(6)	2.753 (4)	O(3)—O(4)	2.800 (4)
O(4)—O(7)	2.679 (4)	O(3)—O(8)	2.591 (4)	O(5)—O(7)	2.892 (4)	O(3)—O(8)	2.757 (4)
O(6)—O(7)	2.601 (4)	O(5)—O(8)	2.649 (4)	O(6)—O(7)	2.779 (4)	O(4)—O(8)	2.950 (4)
O(1)—Si(1)—O(4)	113.2 (2)	O(2)—Si(2)—O(3)	110.5 (2)	O(2)—Al(1)—O(5)	112.5 (1)	O(1)—Al(2)—O(3)	112.4 (2)
O(1)—Si(1)—O(6)	110.3 (2)	O(2)—Si(2)—O(5)	111.6 (1)	O(2)—Al(1)—O(6)	112.1 (1)	O(1)—Al(2)—O(4)	113.3 (2)
O(1)—Si(1)—O(7)	107.4 (2)	O(2)—Si(2)—O(8)	108.9 (2)	O(2)—Al(1)—O(7)	107.5 (2)	O(1)—Al(2)—O(8)	103.1 (1)
O(4)—Si(1)—O(6)	107.6 (2)	O(3)—Si(2)—O(5)	108.3 (2)	O(5)—Al(1)—O(6)	105.0 (2)	O(3)—Al(2)—O(4)	107.8 (2)
O(4)—Si(1)—O(7)	111.6 (2)	O(3)—Si(2)—O(8)	106.6 (1)	O(5)—Al(1)—O(7)	114.0 (1)	O(3)—Al(2)—O(8)	104.8 (1)
O(6)—Si(1)—O(7)	106.5 (2)	O(5)—Si(2)—O(8)	110.9 (1)	O(6)—Al(1)—O(7)	105.5 (1)	O(4)—Al(2)—O(8)	115.2 (1)

Table 3. *Cations, oxygens and water molecules: distances less than 3.10 Å*

Na polyhedron		K polyhedron	
Na—O(1)	2.547 (4)	K—O(3)	2.978 (3)
Na—O(3)	2.685 (4)	K—O(5)	2.775 (3)
Na—O(8)	2.537 (3)	K—O(6)	2.955 (3)
Na—W(1)	2.356 (4)	K—O(8)	2.821 (3)
Na—W(1)	2.585 (4)	K—W(1)	3.069 (4)
Na—W(2)	2.438 (4)	K—W(2)	2.929 (4)
Na—W(4)	2.901 (7)	K—W(3)	2.724 (4)
W(1) polyhedron		W(2) polyhedron	
W(1)—O(4)	2.841 (5)	W(2)—O(2)	2.956 (4)
W(1)—O(7)	2.747 (5)	W(2)—O(6)	2.874 (4)
W(1)—W(4)	2.859 (8)	W(2)—Na	2.438 (4)
W(1)—Na	2.356 (4)	W(2)—K	2.929 (4)
W(1)—Na	2.585 (4)		
W(1)—K	3.069 (4)		
W(3) polyhedron		W(4) polyhedron	
W(3)—O(2)	2.930 (3) [×2]	W(4)—O(1)	3.010 (3) [×2]
W(3)—K	2.724 (4) [×2]	W(4)—W(1)	2.859 (8) [×2]
		W(4)—Na	2.901 (7) [×2]

occludes the channels parallel to [100] and Na those parallel to [001]. The water molecules occupy four independent sites, three of them completely filled.

Relationships among the gismondine-type structures

The framework of the gismondine-type structures has topological symmetry $I4_1/am\bar{d}$; this is probably the space group of garronite (Gottardi & Alberti, 1974) and the topological symmetry of gismondine (Fischer & Schramm, 1970), amicite and synthetic zeolite *P* (Baerlocher & Meier, 1972). If we consider an ordered distribution of Si/Al, as present in gismondine and amicite, the space group lowers to $Fddd$ with *c*

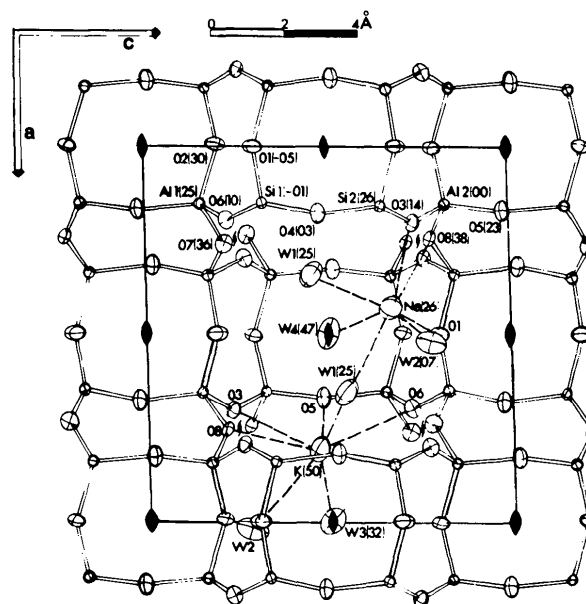


Fig. 1. Projection of the structure of amicite parallel to (010). Numbers in parentheses give the heights of the atoms in hundredths of *b*. Cations and water molecules are reported only once to show their coordination. Ellipsoids enclose 70% probability (ORTEP, Johnson, 1965).

coincident with but *a* and *b* at 45° to the corresponding tetragonal axes and $a \approx b \approx a_{\text{tet}}/\sqrt{2}$. If an *I* centered cell is considered, for better comparison with the space group of garronite, the symmetry can be described as $I2/c$ (Gottardi, 1979). In this space group the multiplicity of the general positions is eight, whereas the multiplicity of all the special positions is four. These special positions lie either on the twofold axes [at the center of the four-membered rings parallel to (010)] or at $\bar{1}$ [at the center of the four-membered rings not

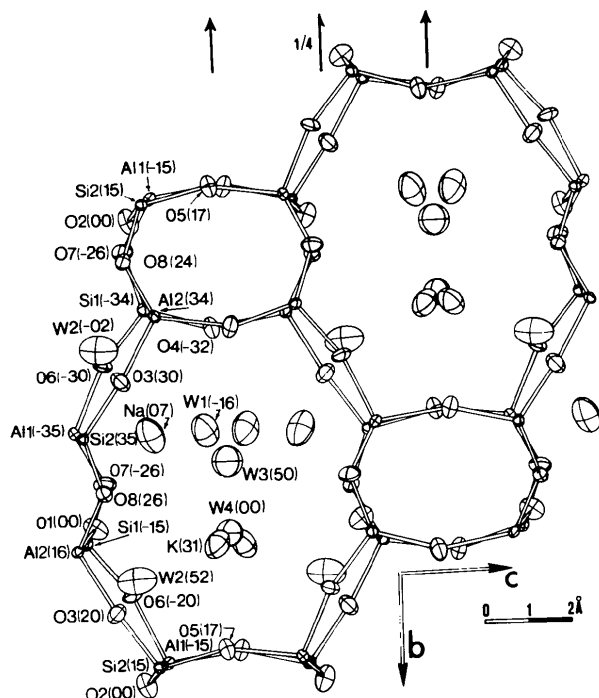


Fig. 2. Projection of two gismondine cages of amicitze along the direction perpendicular to (100). Numbers in parentheses give the heights of the atoms in hundredths of a . Ellipsoids enclose 70% probability (ORTEP, Johnson, 1965).

parallel to (010) and at the center of the eight-membered rings]. If we assume that four Ca atoms in gismondine occupy only a fourfold site and that Na and K in amicitze are ordered in two distinct fourfold sites, then all these atoms must lie in special positions for this space group. Obviously the $\bar{1}$ sites at the center of the four-membered ring must be excluded because the gap would be too small to accommodate the cations mentioned. In the other special positions the resulting coordinations are not satisfactory for the cations involved, so that the cations must occupy general positions. This implies a lowering of the symmetry to space groups where the multiplicity of the general positions is four. These possible space groups are $P2_1/c$, $I2$ and Ic ; the first is the space group of gismondine, the second that of amicitze, whereas for the third no phase is known at present. Two sites occupied

by Na in amicitze are comparable with those occupied by Ca in gismondine, while the other two differ because of the different symmetries of the two minerals. The sites occupied by K in amicitze are similar to those occupied by two water molecules [$W(2)$ and $W(3)$] in gismondine.

The synthetic zeolite P seems to have, at least in the variant Na- $P1$ (Baerlocher & Meier, 1972), a disordered Si/Al distribution; but it is worth noting that its Si/Al ratio is as high as 1.66. It is possible that a synthetic Na- P phase with a Si/Al ratio = 1 has an ordered Si/Al distribution [as occurs in zeolite Na- A (Gramlich & Meier, 1971)] and hence space group $I2/c$ (or even $Fddd$). The crystal structure analysis of a Na-exchanged amicitze or gismondine would clarify some of these points.

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