

analysis, cited below, is in very close agreement with the established formula $Mn_2(Ca, Na)_3(AsO_4)_3$, with $Na:Ca = 1:2.18$; small amounts of Fe, Mg and Zn substitute for Mn.

MnO	MgO	FeO	ZnO	CaO	Na ₂ O	As ₂ O ₅	SiO ₂	H ₂ O—	Total
19.64	1.01	0.41	0.61	18.43	4.68	54.52	0.35	0.27	99.92

Contains traces of Pb, Cu, Ni, Co, Al. No Sb or P. Analyst, J. Ito, 1958.

The mineral has a honey yellow to orange yellow color, with specific gravity $4.21 \pm .02$ and an index of refraction of $1.770 \pm .002$ in white light. The unit cell dimension calculated from a sharp x-ray powder diffractometer pattern is $a 12.500 \pm .005$ Å. This value is in close agreement with that indicated by the graph relating MnO content and a obtained for the berzeliite-manganberzeliite series by Blix and Wickman (1959). The mineral is not fluorescent in either long or short-wave ultraviolet radiation. The specimens closely resemble the veinlets of granular, yellow to brown willemite sometimes found cutting the ore bodies at Franklin and Sterling Hill.

This species and its magnesium analogue berzeliite are known chiefly from their occurrences at Langban and at the Sjö mine, Sweden. The present occurrence is the first in the United States. The recognition of the mineral at Franklin is owing to the interest of two private mineral collectors, Roy W. Epting of Warwick, N. Y., and Stanley J. Schaub of Westfield, N. J., who noted an isotropic mineral that contained arsenic and manganese in specimens acquired from an old collection.

REFERENCE

- Blix, R. and F. E. Wickman (1959) A contribution to the knowledge of the mineral berzeliite. *Arkiv Mineral. Geol.* 2, 417-424.

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THE CRYSTAL STRUCTURE DETERMINATION OF THE ZEOLITE GISMONDITE. $CaAl_2Si_2O_8 \cdot 4H_2O$.

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EXPERIMENTAL PROCEDURE AND CRYSTALLOGRAPHIC DATA

A single-crystal fragment of gismondite was taken from a sample from Hohenberg near Buehne/Westfalia. A slightly modified Bond apparatus (Bond, 1951) was used to grind a sphere. Its average diameter was meas-

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ured to be 0.20₆ mm; the deviation from the ideal spherical shape was less than $\pm 0.02_4$ mm. Therefore, good absorption corrections could be applied to the diffraction intensities.

Fischer and Kuzel (1958)² have found gismondite to have monoclinic (not orthorhombic) symmetry and the following lattice parameters: $a=10.02$, $b=10.62$, $c=9.84$ Å, $\beta=92^\circ 25'$. The unit cell was found to contain four formula units and the probable space group was determined as $P2_1/c$.

X-ray diffraction intensities were measured with a single-crystal diffractometer of the equi-inclination type (Buerger, 1956, 1960; Hahn, 1960), using a scintillation counter and pulse-height discrimination.³ The crystal was mounted along the b -axis. Of 1953 independent reflections, 87 had intensities below the minimum observable value. Roughly scaled values of F_{obs} were obtained by means of a data-reduction program system for the IBM 650 computer (Fischer, 1959), employing Lorentz-polarization and spherical absorption corrections and Wilson's statistics for the scaling procedure. The $0k0$ intensities were obtained and suitably scaled by visual estimation from a precession photograph of the same crystal.

DETERMINATION OF THE STRUCTURE

The structure investigation started with some tests for an arrangement of tetrahedra in four- and eight-membered rings, as suggested by Joseph V. Smith, Chicago (priv. comm., 1961). Structure factors for two zones were calculated for the Si, Al atoms only, but attempted "refinement" by least-squares methods failed. (Smith's suggestion, however, was fully confirmed after the determination of the structure.)

A successful approach was based on the three-dimensional Patterson synthesis, which showed a number of multiple peaks caused by a predominant substructure. The strongest peaks were found to be at

$uvw = 0, 0, 0$	relative height	561,
$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$		309,
$0, \frac{1}{2}, \frac{1}{4}$		175,
$\frac{1}{2}, 0, \frac{1}{4}$		181.

These peaks correspond to those expected from a diamond structure after the transformation

$$\begin{aligned} \mathbf{a}_{d'} &= \frac{1}{2}(\mathbf{c}_d + \mathbf{a}_d) \\ \mathbf{b}_{d'} &= \mathbf{b}_d \\ \mathbf{c}_{d'} &= \frac{1}{2}(\mathbf{c}_d - \mathbf{a}_d), \end{aligned}$$

² An error occurred in the paper quoted above: The formula was given as $\text{Ca}[\text{Al}_2\text{Si}_2\text{O}_8] \cdot 1\text{H}_2\text{O}$ instead of $4\text{H}_2\text{O}$. The numbers given however, are correct.

³ A more detailed description of the technique of intensity measurement will be given with the refinement of the structure.

where the subscripts d and d' of the elementary cell vectors refer to the old and new diamond cell, respectively. This transformation yields diamond-Patterson peaks with multiplicities of 16, 16, 8, 8 corresponding to the four peaks mentioned above. In gismondite, additional strong peaks with relative heights of 185 and below are found in the section P (u_0w), and corresponding ones in the section P ($u_{\frac{1}{2}}w$). Less strong, but still multiple, peaks occur in the section P ($u_{\frac{1}{4}}w$).

On the basis of this configuration, a trial structure was established consisting of only Si, Al atoms. No assumption was made about the distribution of the Si and Al atoms. The trial coordinates were as follows:

(Si, Al) ₁	$x \approx \frac{1}{12}$	$y \approx \frac{1}{8}$	$z \approx \frac{1}{6};$
(Si, Al) ₂	$\frac{5}{12}$	$\frac{1}{8}$	$\frac{1}{6};$
(Si, Al) ₃	$\frac{7}{12}$	$-\frac{1}{8}$	$\frac{1}{6};$
(Si, Al) ₄	$\frac{11}{12}$	$-\frac{1}{8}$	$\frac{1}{6}.$

To test this model, structure factors for the 74 h0l reflections with $\sin\theta$ between 0.3 and 0.8 were computed. They gave ab R-factor of 0.63. After some cycles of least-squares "refinement" R dropped to 0.50. After another least-squares computation, using 344 hkl reflections, 555 signs out of 789 hkl reflections were used for a first three-dimensional Fourier synthesis. This clearly showed 7 of the 8 oxygen atoms as well as four additional peaks which were interpreted as either H₂O molecules or a Ca atom. In a subsequent least-squares treatment, the f-curve for O²⁻ was assigned to these four atoms, and the temperature factors were allowed to vary in the third cycle. One of them turned out to be highly negative, thus indicating that atom to be Ca. After a second three-dimensional Fourier, the average distances between the Si, Al atoms and the oxygen atoms in the four tetrahedra were:

$$1.70 \text{ \AA}, \quad 1.61 \text{ \AA}, \quad 1.78 \text{ \AA}, \quad 1.66 \text{ \AA}.$$

Therefore, the second tetrahedron was assumed to contain a silicon and the third an aluminum atom. Consequently, in the next least-squares refinement different atomic scattering factors for Si, Al, (Si, Al), O, and Ca were employed. After three cycles, the R-factor was 0.16₀ based on all 1959 independent observations, and 0.15₄, based on all 1872 reflections with F_{obs.} above the minimum observable value. A third three-dimensional Fourier synthesis showed all the atoms clearly resolved. In addition, instead of the fourth H₂O molecule, two peaks appeared with about half the expected height of a water molecule. When the fourth H₂O molecule was divided between these two equipoints, the R-factor, based on all observed reflections, was reduced to 0.151. It was concluded, therefore, that this model of the structure is essentially correct. The atomic coordinates obtained from the last least-squares cycle and the third three-

TABLE 1. ATOMIC COORDINATES

	x	y	z
Si ₁	.415	.113	.182
Si ₂	.908	.870	.160
Al ₁	.097	.113	.170
Al ₂	.590	.867	.149
Ca	.720	.077	.354
O ₁	.078	.154	-.001
O ₂	.262	.075	.212
O ₃	.438	.145	.026
O ₄	.246	.407	.303
O ₅	.000	-.017	.215
O ₆	.044	.242	.261
O ₇	.463	.224	.276
O ₈	.511	-.005	.226
(H ₂ O) ₁	.257	.107	.505
(H ₂ O) ₂	.590	.127	.539
(H ₂ O) ₃	.911	.119	.501
$\frac{1}{2}(\text{H}_2\text{O})_4$.77	.21	.17
$\frac{1}{2}(\text{H}_2\text{O})_5$.74	.18	.89 _b

dimensional Fourier are listed in Table 1. Table 2 gives a preliminary list of the most important atomic distances. They should not be considered as very accurate. The standard errors of the Si-O and Al-O distances are about 0.02 Å, the others are certainly higher. The assignment of the Si and Al atoms among the four tetrahedra are based only on the distances.

TABLE 2. ATOMIC DISTANCES

Si ₁ -O ₂	1.63	Al ₁ -O ₁	1.73		
-O ₃	1.60	-O ₂	1.74	Ca-O ₄	2.41
-O ₇	1.56	-O ₅	1.75	-O ₈	2.55
-O ₈	1.63	-O ₆	1.73	-(H ₂ O) ₁	2.40
average	1.61	average	1.74	-(H ₂ O) ₂	2.35
				-(H ₂ O) ₃	2.40
				-(H ₂ O) ₄	2.4
Si ₂ -O ₁	1.60	Al ₂ -O ₃	1.74	-(H ₂ O) ₅	2.6
-O ₄	1.65	-O ₄	1.74		
-O ₅	1.59	-O ₇	1.78		
-O ₆	1.63	-O ₈	1.76		
average	1.62	average	1.74		

DISCUSSION OF THE STRUCTURE:¹

Figures 1 and 2 show the arrangement of the atoms in the unit cell. The structure consists of a three-dimensionally connected framework of SiO_4 - and AlO_4 -tetrahedra. These tetrahedra form three types of four-membered rings, one of which is nearly parallel to (010). The centers of gravity of these rings form a diamond arrangement stretched along the *a* and *c* axes by a factor of $\sqrt{2}$ (see determination of the structure). The two other types of four-membered rings are somewhat inclined to (100) and

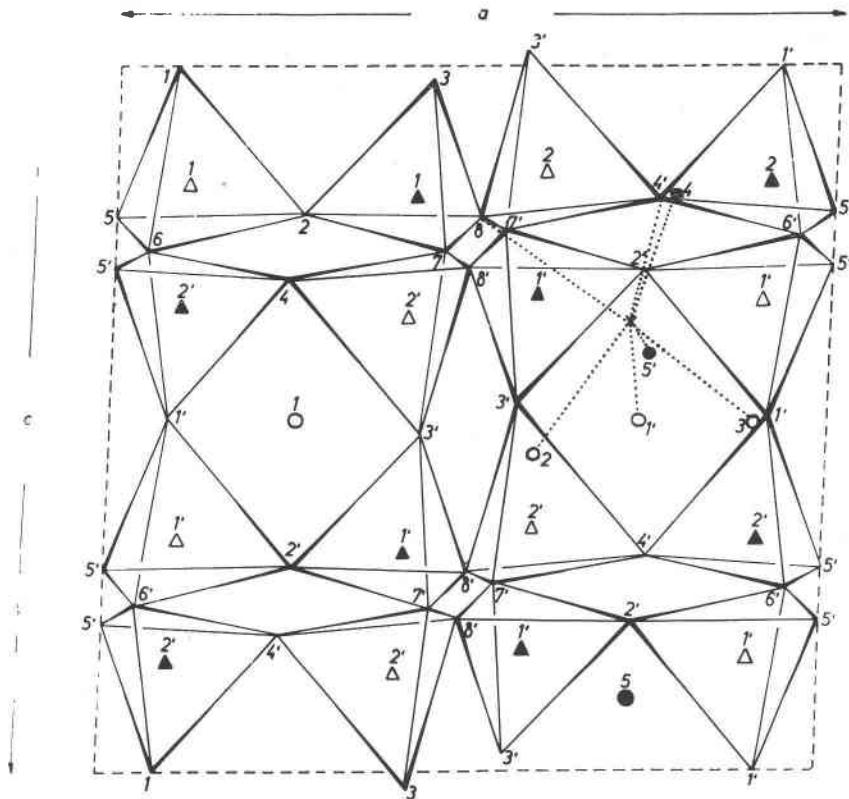


FIG. 1. Crystal structure of gismondite projected parallel the *b* axis. Full triangles: Si, open triangles: Al, crosses: Ca, open circles: H_2O , full circles: $\frac{1}{2}\text{H}_2\text{O}$. The oxygen atoms are located at the corners of the tetrahedra. The numbers indicate the labelling of the equi-points. Dashed numbers were used for symmetrically equivalent atoms.

¹ Only a short description of the structure will be given here. A more detailed discussion, as well as a list of observed and computed structure factors, will be presented in a separate paper on the structure refinement.

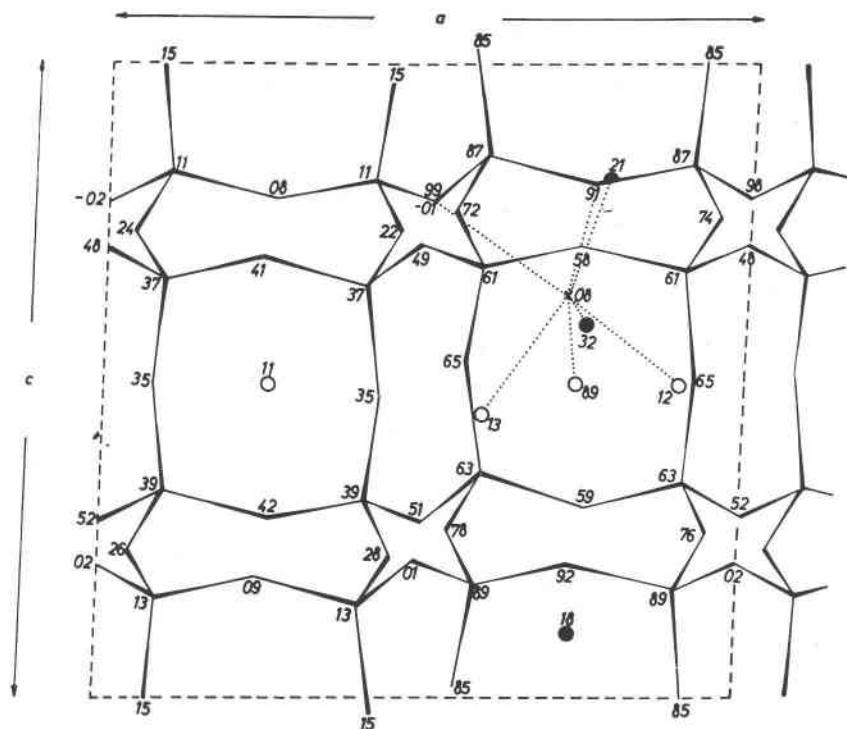


FIG. 2. Same projection as Fig. 1. The (100,y)-coordinates of the atoms are given together with Si-O and Al-O bonds (full lines), and Ca-O and Ca-H₂O bonds (dotted lines).

(001) respectively and are of the UUDD-type (*cf.* J. V. Smith, 1962). The symmetry of the framework is pseudo-tetragonal, if Al and Si are considered to be equal. In this case, the 2_1 -axes would become pseudo- 4_1 -axes. 8-membered rings define the aperture of channels parallel to [100] and [001]. Within these, the Ca atoms and H₂O molecules are located.

If Si and Al are completely ordered (which has to be tested by the refinement of the structure), the Si and Al tetrahedra alternate in all possible chains throughout the structure, as should be expected from Pauling's rules. The Si-O and Al-O distances, averaged for each tetrahedron, do not indicate considerable disorder (taking into account that the present standard deviation of these distances is about 0.02 Å).

The cross-sections of the channels parallel [100] and [001] are shown in Figs. 3 and 4. It can be seen that the channels are nearly elliptical with open diameters of about 3 and 4 Å, the latter about parallel the b -axis. At the intersection of these channels, a cavity is formed containing a cluster of Ca surrounded by 3 "full" plus two "half" H₂O molecules. In addition

to these, Ca is coordinated to the oxygen atoms 4 and 8 of the framework (Figs. 1, 2 and Table 2), giving a total average coordination number of six. The distances to the oxygens, especially to O₈, are somewhat higher than those to the "full" H₂O, indicating that those bondings are less strong. (The positions of (H₂O)₄ and (H₂O)₅ are not as well determined as the other ones.) O₄ and O₈ have, on the other hand, the highest sum of distances (3.39 Å each) to the central atoms Si and Al of the two tetrahedra they belong to (the average sum for the other six oxygens is 3.34 Å). One may judge from this, that the Si₂-O₄-Al₂ and Si₁-O₈-Al₂ bonds are weakened by the existence of the O₄-Ca and O₈-Ca bonds.

An interesting feature of the structure is this: All the atoms but one could be located at normal crystallographic equipoints. This does not hold for one H₂O, which populates two equipoints statistically. There is

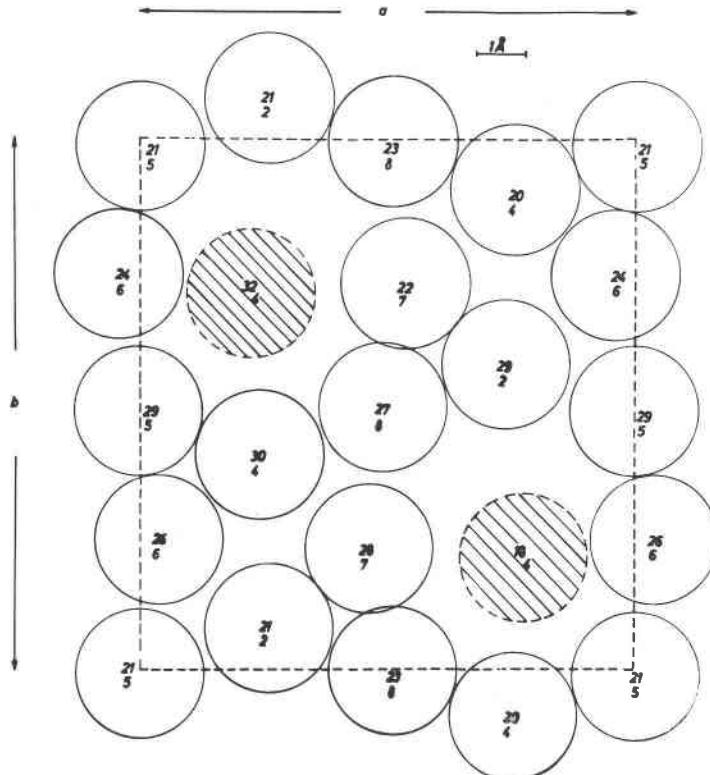


Fig. 3. Section $xy\frac{1}{4}$ through the structure (cross-section of channels parallel [001]). Oxygen atoms: full circles "half" H₂O: dashed circles, shaded. In each atom, the lower number indicates the labelling of the equipoint the upper number gives the 100-fred coordinate perpendicular to the plane of drawing.

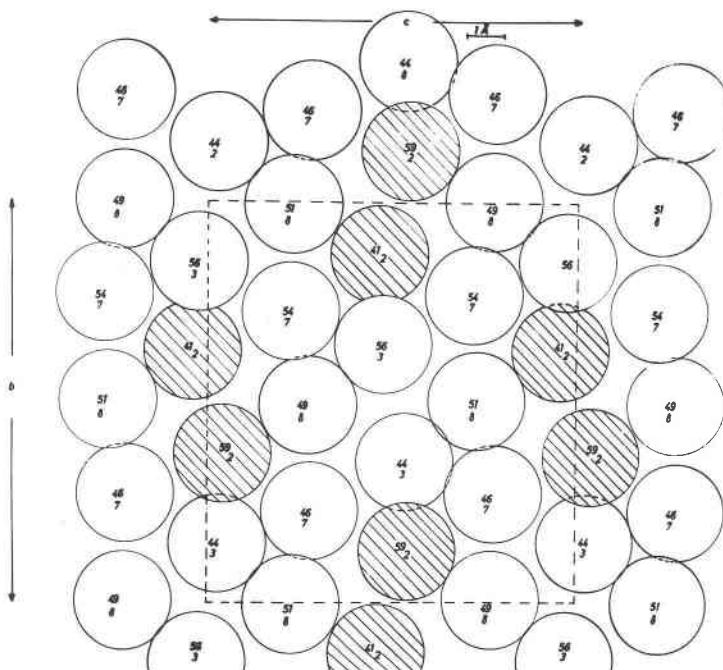


FIG. 4. Section $\frac{1}{2}yz$ through the structure (cross-section of channels parallel [100]). "Full" H_2O : full circles, shaded. "Half" H_2O : dashed circles, shaded. All the other designations as in Fig. 3.

space enough in the channels for a fifth H_2O . The sample used for this investigation, however, was completely stable with respect to its H_2O -content under normal laboratory conditions for a long time. Two years after the first very accurate intensity measurements, some F's specifically sensitive to these "half" H_2O and taken from the same crystal could not be found to have changed. It must be assumed, therefore, that either the Ca atom does, in this specific configuration, not call for a higher coordination number, or that the arrangement of H_2O in this structure is a very stable one itself. This might be due to hydrogen bonds. A decision about these ideas will be possible on the basis of more accurate atomic distances and anisotropic temperature vibration studies after the detailed refinement of this structure.

If gismondite is partly or fully dehydrated, the Ca atoms loose the important part of their coordination. J. V. Smith found (1962) in dehydrated chabazite that both Ca positions and details of the framework are considerably changed. A similar study, together with G. Pieper, is in progress on this mineral with its well-known Si-Al-distribution.

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CRYSTAL DATA FOR SYNTHETIC $\text{Cu}_{5.5\text{x}}\text{Fe}_x\text{S}_{6.5\text{x}}$ (IDAITE)

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A synthetic phase corresponding to the general formula $\text{Cu}_{5+\text{x}}\text{FeS}_{6+\text{x}}$ was first reported by Merwin and Lombard (1937). Roseboom and Kul-