

## The crystal structure of wardite<sup>1</sup>

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**SUMMARY.** Wardite,  $\text{NaAl}_3(\text{OH})_4(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ , has  $a = 7.03 \text{ \AA}$ ,  $c = 19.04 \text{ \AA}$ ; space group  $P4_12_12$  or  $P4_32_12$ . Its crystal structure was solved by a three-dimensional Patterson function computed using intensity data photographically collected by the Weissenberg method, and refined by successive Fourier maps and least-squares cycles to a  $R$  index 0.062 for 316 independent observed reflections.

The wardite structure is formed by layers of Al and Na coordination polyhedra sharing vertices and edges. These sheets, parallel to the  $a$  axes, are connected to each other in the  $c$  direction by  $\text{PO}_4$  tetrahedra and H-bonds. This structural feature accounts for the perfect  $\{001\}$  cleavage of wardite and explains the change that occurs in lattice parameters when Al is substituted by Fe in avelinoite. The relationships with the minerals of the trigonal families of crandallite, woodhouseite, and jarosite are also discussed.

WARDITE, first found by Davison (1896) in variscite nodules at Fairfield (Utah), occurs associated with millisite and crandallite, and was defined by Larsen and Shannon (1930) as a basic hydrated aluminum, sodium, and calcium phosphate. Pough (1937) described the morphology of the crystals and assigned them to the tetragonal system. Wardite was then discovered in pegmatitic rocks at Beryl Mountain, New Hampshire (Hurlbut, 1952), and assigned the formula  $\text{NaAl}_3(\text{OH})_4(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ . It is likely that calcium replaces sodium to some extent and this could account for the earlier analyses of the mineral. The existence of the mineral millisite,  $\text{NaCaAl}_6(\text{OH})_8(\text{PO}_4)_4 \cdot 3\text{H}_2\text{O}$ , which exhibits an X-ray pattern closely similar to wardite (Owens, Altschuler, and Berman, 1960) confirms the possible occurrence of a substitution Ca-Na in this mineralogical family. However, a partial analysis on Fairfield wardite by Gonyer (Hurlbut, 1952) does not reveal the presence of calcium. The first X-ray study of the mineral was undertaken in 1942 by Larsen, who determined the unit-cell dimensions and attributed to it the space group  $P4_1$  or  $P4_3$ . Heritsch (1955) redetermined the unit-cell parameters on crystals from Millstätter See (Austria) and fixed as correct the space group  $P4_12_12$  or the enantiomorphous one  $P4_32_12$ .

The present study concerns the crystallochemical investigations undertaken in our laboratory on phosphate minerals.

*Experimental.* A well-formed wardite crystal from a variscite nodule from the classical locality of Fairfield (Utah), with  $\{012\}$  dominant and with approximate dimensions  $0.15 \times 0.15 \times 0.30 \text{ mm}$  was chosen for X-ray study and was mounted with  $[100]$  as rotation axis. The lattice constants, obtained from Weissenberg photographs, are:

<sup>1</sup> Presented at the Eighth International Congress of Crystallography at Stony Brook, New York, U.S.A.

$a = 7.03 \pm 0.01$  Å;  $c = 19.04 \pm 0.01$  Å. The space group  $P4_12_12$  (or  $P4_32_12$ ) as determined by Heritsch (1955) was confirmed from systematic absences. The calculated density, assuming four units  $\text{NaAl}_3(\text{OH})_4(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  in the cell, is  $2.805 \text{ g cm}^{-3}$ , in agreement with the experimental value  $2.81 \text{ g cm}^{-3}$ , measured on crystals from Fairfield by Larsen and Shannon (1930).

Weissenberg multiple-film integrated photographs from the  $okl$  to the  $4kl$  layer were recorded using  $\text{Cu-K}\alpha$  radiation. The intensity data were measured with a micro-densitometer and, after Lorentz-polarization correction, were put on the same relative scale taking into account the symmetry related reflections occurring on different layers. A total of 565 independent diffraction effects were collected; of these, 249 were not observed and were given  $F_o$  values just below the estimated minimum observable intensity.

The linear absorption coefficient of wardite is  $\mu = 83.1 \text{ cm}^{-1}$  for the  $\text{Cu-K}\alpha$  radiation; the absorption correction was neglected, owing to the small dimensions of the crystal.

TABLE I. Fractional atomic coordinates with their standard deviations in parentheses

| Atom  | $x/a$       | $y/b$      | $z/c$         | Atom | $x/a$      | $y/b$      | $z/c$      |
|-------|-------------|------------|---------------|------|------------|------------|------------|
| P     | 0.1427(7)   | 0.3659(7)  | 0.3488(2)     | O(3) | 0.2031(19) | 0.1771(19) | 0.3216(7)  |
| Al(1) | 0.3984(10)  | 0.1057(10) | 0.2581(3)     | O(4) | 0.0994(19) | 0.3532(19) | 0.4274(6)  |
| Al(2) | 0.1029(10)  | 0.1029(10) | 0             | O(5) | 0.1326(19) | 0.3537(19) | -0.0394(6) |
| Na    | 0.3733(14)  | 0.3733(14) | $\frac{1}{2}$ | O(6) | 0.1883(21) | 0.0294(21) | 0.1915(8)  |
| O(1)  | -0.0317(20) | 0.4279(20) | 0.3091(7)     | O(7) | 0.4083(18) | 0.3489(18) | 0.2173(6)  |
| O(2)  | 0.2960(19)  | 0.5112(19) | 0.3378(7)     |      |            |            |            |

*Structure determination and refinement.* The structure was solved and refined in the  $P4_12_12$  space group. No attempt to distinguish between the two enantiomorphic structures was made.

Since the multiplicity of the general position in the space group is eightfold, the sodium ion and one aluminium ion must lie in special positions on the diagonal two-fold axes. The approximate positions of these ions and those of phosphorus and of the other aluminium ion in the asymmetric unit were found by a three-dimensional Patterson function. The locations of oxygen atoms were then determined by crystallochemical considerations and by successive electron-density maps computed with the phases obtained from the partial structure. The atomic positions were roughly refined by successive Fourier maps, until the  $R$  index, defined as  $\sum ||F_o| - |F_c|| / \sum |F_o|$ , was 0.27 for all observed reflections.

At this stage the structure refinement was undertaken using the least-squares method. Reflections with intensities up to 4 times the minimum observable ( $F_{\text{min}}$ ) were assigned unit weight; more intense reflections were given a weight  $w = (F_o/4F_{\text{min}})^2$ . Unobserved reflections were excluded from the calculations. In the first step of the refinement, a block-diagonal programme written by Albano, Bellon, Pompa, and Scatturin (1963) was employed; further refinement with the full-matrix ORFLS programme by Busing and Levy, adapted by Stewart (1964), with anisotropic factors for all the atoms, brought the  $R$  index to 0.062 for all observed reflections.

Atomic coordinates with standard deviations are listed in table I. In table II are

TABLE II. *Anisotropic thermal parameters with standard deviations (in parentheses) and the equivalent isotropic temperature factors according to Hamilton. The anisotropic temperature factors are in the form:*

$$T = \exp \{-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})\}$$

| Atom  | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ | $B(\text{\AA})^2$ |
|-------|--------------|--------------|--------------|--------------|--------------|--------------|-------------------|
| P     | 0.0048(9)    | 0.0041(9)    | 0.0006(1)    | 0.0003(12)   | -0.0002(2)   | 0.0001(2)    | 0.88              |
| Al(1) | 0.0050(13)   | 0.0035(12)   | 0.0006(1)    | 0.0002(12)   | 0.0003(3)    | 0.0003(4)    | 0.85              |
| Al(2) | 0.0073(13)   | 0.0073(13)   | 0.0005(1)    | -0.0004(11)  | -0.0002(3)   | 0.0002(3)    | 1.20              |
| Na    | 0.0139(18)   | 0.0139(18)   | 0.0008(2)    | 0.0019(20)   | 0.0007(6)    | -0.0007(6)   | 2.22              |
| O(1)  | 0.0034(36)   | 0.0151(31)   | 0.0013(4)    | 0.0013(28)   | -0.0004(10)  | 0.0001(9)    | 1.85              |
| O(2)  | 0.0110(30)   | 0.0131(29)   | 0.0001(4)    | -0.0009(29)  | 0.0007(8)    | -0.0006(8)   | 1.64              |
| O(3)  | 0.0122(30)   | 0.0108(34)   | 0.0010(4)    | -0.0025(27)  | 0.0004(8)    | -0.0002(9)   | 2.00              |
| O(4)  | 0.0136(27)   | 0.0072(25)   | 0.0004(3)    | 0.0057(29)   | 0.0009(7)    | 0.0006(8)    | 1.56              |
| O(5)  | 0.0078(27)   | 0.0113(25)   | 0.0008(3)    | -0.0002(40)  | -0.0002(8)   | 0.0001(8)    | 1.64              |
| O(6)  | 0.0156(34)   | 0.0146(36)   | 0.0006(4)    | -0.0017(30)  | -0.0005(9)   | -0.0006(10)  | 2.27              |
| O(7)  | 0.0089(25)   | 0.0099(27)   | 0.0007(3)    | -0.0042(31)  | 0.0002(8)    | -0.0005(8)   | 1.58              |

given the atomic thermal parameters with the average isotropic thermal parameters according to Hamilton (1959). A table of observed and calculated structure factors is deposited in the library of the Department of Mineralogy, British Museum (Natural History). For calculations the atomic scattering factors from *International Tables for X-ray Crystallography*, 1962 were used for  $\text{Al}^{3+}$ ,  $\text{Na}^+$ , P, and O.

#### Discussion of the structure

Bond distances and angles in wardite are listed with their standard deviations in table III, and the crystal structure is shown in fig. 1.

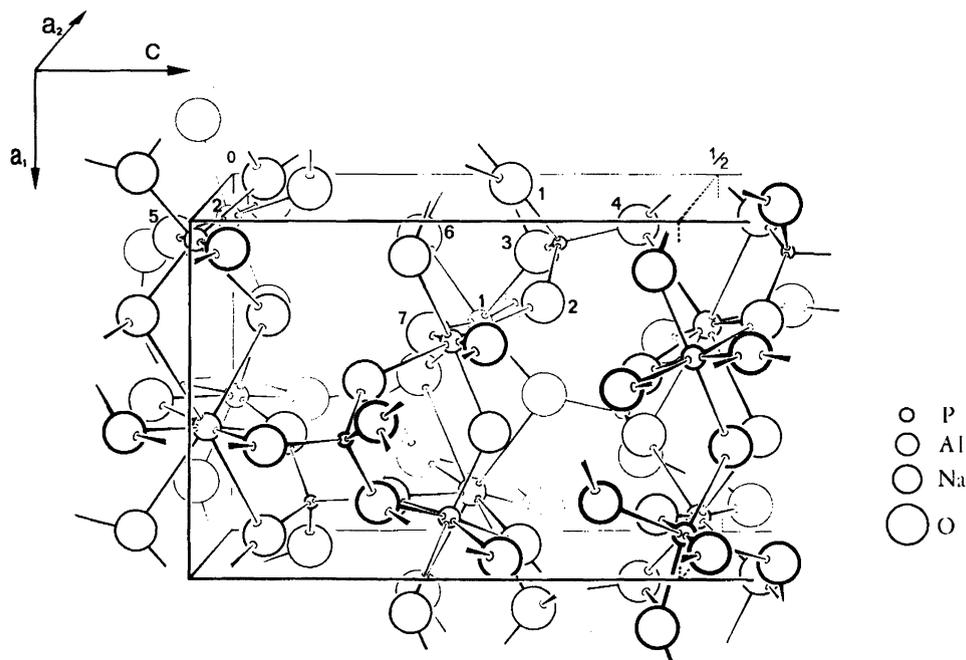


FIG. 1. Clinographic view of the wardite structure.

The two independent aluminum ions in the structure show octahedral coordination. Al(1) links six oxygen atoms with bond lengths in the range 1.84–2.02 Å (average value 1.90 Å). Al(2), on the twofold axis, is surrounded by six oxygen atoms at distances from 1.89 to 1.93 Å (average value 1.92 Å). These values are in agreement with those reported in the literature for aluminum in octahedral coordination.

The  $\text{Na}^+$  ion lies on the two-fold axis and is coordinated by eight oxygen atoms in an irregular polyhedron resembling a tetragonal prism. The Na–O distances are in the range 2.38–2.71 Å, with a mean distance of 2.54 Å. The sodium coordination number, eight, is rather unusual; however, a similar coordination around Na has been found in some chain silicates. Prewitt and Burnham (1966) in jadeite and Papike and Clark (1968) in glaucophane have shown the Na ions to be coordinated to eight

TABLE III. *Interatomic distances and angles in wardite.* (I) =  $x, y, z$ ;  
 (II) =  $y, x, 1-z$ ; (III) =  $\frac{1}{2}+x, \frac{1}{2}-y, \frac{3}{4}-z$ ; (IV) =  $1-y, -x, \frac{1}{2}-z$ ;  
 (V) =  $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{4}-z$ ; (VI) =  $\frac{1}{2}-x, \frac{1}{2}+y, \frac{5}{4}-z$ ; (VII) =  $\frac{1}{2}-y, \frac{1}{2}+x, \frac{1}{4}+z$ ;  
 (VIII) =  $-\frac{1}{2}+y, \frac{1}{2}-x, -\frac{1}{4}+z$ ; (IX) =  $\frac{1}{2}-y, -\frac{1}{2}+x, \frac{1}{4}+z$ ; (X) =  $y, x, -z$ ;  
 (XI) =  $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{5}{4}-z$

*Bond lengths*

|                  |               |                  |                   |                    |               |
|------------------|---------------|------------------|-------------------|--------------------|---------------|
| Al(1)(I)-O(3)(I) | 1.90 ± 0.01 Å | Al(2)(I)-O(5)(I) | 1.93 ± 0.01 Å × 2 | P(I)-O(1)(I)       | 1.51 ± 0.02 Å |
| -O(7)(I)         | 1.88 0.01     | -O(2)(V)         | 1.93 0.01 × 2     | -O(2)(I)           | 1.50 0.02     |
| -O(6)(I)         | 2.02 0.02     | -O(7)(V)         | 1.89 0.01 × 2     | -O(3)(I)           | 1.49 0.02     |
| -O(4)(III)       | 1.90 0.01     | Na(I)-O(4)(I)    | 2.38 ± 0.02 × 2   | -O(4)(I)           | 1.53 0.02     |
| -O(1)(IV)        | 1.84 0.02     | -O(6)(VII)       | 2.57 0.02 × 2     | O(6)(I)-O(2)(VIII) | 2.64 ± 0.02   |
| -O(5)(V)         | 1.88 0.02     | -O(1)(VII)       | 2.49 0.02 × 2     | -O(5)(IX)          | 2.83 0.02     |
|                  |               | -O(3)(VII)       | 2.71 0.02 × 2     |                    |               |

*Bond angles*

|                             |              |                             |               |
|-----------------------------|--------------|-----------------------------|---------------|
| O(3)(I) -Al(1)(I)-O(7)(I)   | 92°49' ± 38' | O(4)(I) -Na(I)-O(4)(II)     | 104°00' ± 70' |
| -O(6)(I)                    | 86°35' 39'   | -O(6)(VII)                  | 90°52' 31'    |
| -O(4)(III)                  | 94°59' 37'   | -O(6)(XI)                   | 165°05' 35'   |
| -O(1)(IV)                   | 175°06' 42'  | -O(1)(VII)                  | 65°43' 30'    |
| -O(5)(V)                    | 87°55' 37'   | -O(1)(III)                  | 84°30' 30'    |
| O(7)(I) -Al(1)(I)-O(6)(I)   | 90°33' 37'   | -O(3)(VII)                  | 103°43' 33'   |
| -O(4)(III)                  | 95°48' 38'   | -O(3)(III)                  | 113°10' 25'   |
| -O(1)(IV)                   | 86°53' 38'   | O(6)(VII) -Na(I)-O(6)(XI)   | 74°17' 65'    |
| -O(5)(V)                    | 172°37' 38'  | -O(1)(VII)                  | 100°59' 34'   |
| O(6)(I) -Al(1)(I)-O(4)(III) | 173°21' 42'  | -O(1)(III)                  | 117°46' 30'   |
| -O(1)(IV)                   | 88°32' 39'   | -O(3)(VII)                  | 61°02' 29'    |
| -O(5)(V)                    | 82°10' 37'   | -O(3)(III)                  | 70°35' 29'    |
| O(4)(III)-Al(1)(I)-O(1)(IV) | 89°53' 39'   | O(1)(VII) -Na(I)-O(1)(III)  | 131°21' 73'   |
| -O(5)(V)                    | 91°26' 37'   | -O(3)(VII)                  | 55°25' 28'    |
| O(1)(IV)-Al(1)(I)-O(5)(V)   | 91°44' 39'   | -O(3)(III)                  | 171°35' 35'   |
|                             |              | O(3)(VII) -Na(I)-O(3)(III)  | 118°23' 64'   |
| O(5)(I) -Al(2)(I)-O(5)(X)   | 87°18' ± 74' | O(1)(I) -P(I)-O(2)(I)       | 108°33' ± 47' |
| -O(2)(V)                    | 85°55' 33'   | -O(3)(I)                    | 108°28' 47'   |
| -O(2)(VII)                  | 92°04' 36'   | -O(4)(I)                    | 110°13' 46'   |
| O(7)(V)                     | 174°35' 37'  | O(2)(I) -P(I)-O(3)(I)       | 110°45' 47'   |
| -O(7)(VII)                  | 90°43' 36'   | -O(4)(I)                    | 108°37' 45'   |
| O(2)(V) -Al(2)(I)-O(2)(VII) | 177°13' 83'  | O(3)(I) -P(I)-O(4)(I)       | 110°11' 46'   |
| -O(7)(V)                    | 89°07' 36'   |                             |               |
| -O(7)(VII)                  | 92°49' 33'   | O(2)(VIII)-O(6)(I)-O(5)(IX) | 120°24' ± 40' |
| O(7)(V) -Al(2)(I)-O(7)(VII) | 91°41' 75'   |                             |               |

oxygen atoms by six short and two longer bonds. The values given by these authors are respectively: averaged shorter distances, 2.377 and 2.398 Å; longer distances, 2.741 and 2.798 Å. Prewitt and Burnham found similar coordination in richterite, riebeckite, and pectolite.

The tetrahedral phosphate group is quite regular. P-O bond lengths have an average value 1.51 Å in the range 1.49-1.53 Å. A close regularity occurs in the O-P-O angles too (range 108° 28'-110° 45').

Among the interatomic distances, the occurrence of two contacts between oxygen

atoms not belonging to the same coordination polyhedron, with values 2.64 and 2.83 Å, led us to attribute these distances to hydrogen bonds.

The distinction between oxygen atoms, hydroxyl groups, and water molecules was made on the basis of Pauling's electrostatic valence rule: better agreement in the charge balance is reached if we consider O(6) as a water molecule and O(5) and O(7) as hydroxyl groups. The charge balance is reported in table IV.

TABLE IV. Balance of electrostatic valences for oxygen atoms

| Atom | Al                     | Na            | P             | -H...                  | ...H-         | -H | Total             |
|------|------------------------|---------------|---------------|------------------------|---------------|----|-------------------|
| O(1) | $\frac{1}{2}$          | $\frac{1}{8}$ | $\frac{5}{4}$ | —                      | —             | —  | $2 - \frac{1}{8}$ |
| O(2) | $\frac{1}{2}$          | —             | $\frac{5}{4}$ | —                      | $\frac{1}{4}$ | —  | 2                 |
| O(3) | $\frac{1}{2}$          | $\frac{1}{8}$ | $\frac{5}{4}$ | —                      | —             | —  | $2 - \frac{1}{8}$ |
| O(4) | $\frac{1}{2}$          | $\frac{1}{8}$ | $\frac{5}{4}$ | —                      | —             | —  | $2 - \frac{1}{8}$ |
| O(5) | $2 \times \frac{1}{2}$ | —             | —             | —                      | $\frac{1}{2}$ | 1  | $2 + \frac{1}{2}$ |
| O(6) | $\frac{1}{2}$          | $\frac{1}{8}$ | —             | $2 \times \frac{1}{4}$ | —             | —  | $2 + \frac{1}{4}$ |
| O(7) | $2 \times \frac{1}{2}$ | —             | —             | —                      | —             | 1  | 2                 |

The crystal structure of wardite consists of sheets of coordination polyhedra around Na and Al ions parallel to the (001) plane and at  $z/c = 0, \frac{1}{4}, \frac{1}{2}, \frac{3}{4}$ . In these sheets the Al(1) octahedron shares two opposite vertices with the octahedra around Al(2) and two opposite edges with the Na polyhedra. Each Al(2) octahedron shares four vertices with four different Al(1) octahedra, which, together with the two oxygen atoms, gives a *trans* configuration. The Na coordination polyhedron shares four different edges with four Al(1) octahedra.

A view of a single sheet projected along [001] is shown in fig. 2. These sheets are linked together by  $\text{PO}_4$  tetrahedra and by hydrogen bonds.

#### Relationships to other groups of minerals.

Wardite is closely related by its chemical formula and also, in certain cases, by paragenetic conditions, to a large group of minerals belonging to the trigonal system, including certain phosphates and arsenates such as crandallite, goyazite, florencite, and dussertite, some sulphate-phosphates and sulphate-arsenates such as woodhouseite, svanbergite, hidalgite, and certain sulphates such as alunite and jarosite.

From a structural point of view wardite and these trigonal minerals show some analogies but also some remarkable differences. In order to compare the crystal

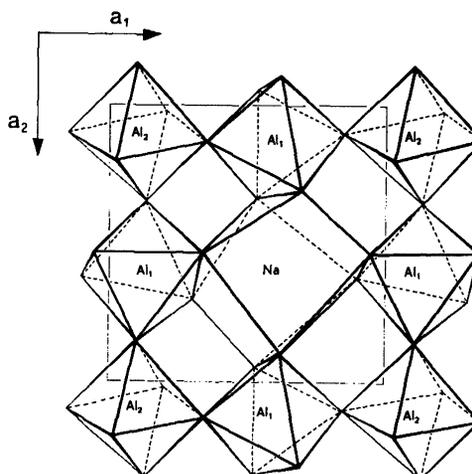


FIG. 2. A single sheet of coordination polyhedra in wardite.

structure of wardite with the atomic arrangement occurring in the trigonal family, the crystal structure of woodhouseite,  $\text{CaAl}_3(\text{PO}_4)(\text{SO}_4)(\text{OH})_6$  (Pabst, 1947), may be considered.

In both structures there are sheets formed by Al-coordination octahedra sharing vertices and this common feature accounts for the presence of perfect cleavage normal to the  $c$  axis. However, in wardite, these sheets are formed by tetragonal meshes constituted by eight Al-coordination polyhedra, while in woodhouseite the resulting motif is rather complex with hexagonal and triangular meshes. The larger size of the

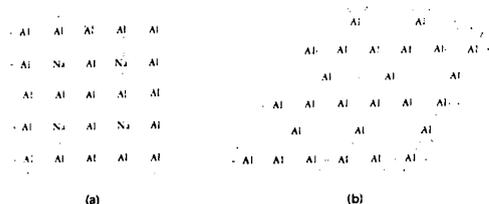


FIG. 3. The layer motifs in wardite (a) and in woodhouseite (b).

meshes in the crystal structure of wardite allows the Na ions to occupy the central sites of these meshes, while in woodhouseite calcium ions are located between two adjacent Al layers and contribute, together with sulphur and phosphorus, in connecting different sheets. The layer motives of wardite and woodhouseite are sketched in fig. 3 (a) and (b) respectively.

*Relative cell dimensions of the wardite family.* Pallite,  $\text{Ca}(\text{Al,Fe})_3(\text{PO}_4)_2(\text{OH})_6 \cdot \text{H}_2\text{O}$ , with  $a$  7.0,  $c$  19.2 Å (Capdecombe and Pulou, 1954), and millisite,  $\text{NaCaAl}_6(\text{PO}_4)_4(\text{OH})_6 \cdot 3\text{H}_2\text{O}$ , with  $a$  7.00,  $c$  19.07 Å (Owens, Altschuler, and Berman, 1960), are related to wardite by replacement of all and of half the  $\text{Na}^+$  respectively by  $\text{Ca}^{2+}$ , with a balancing replacement of  $\text{H}_2\text{O}$  by  $\text{OH}^-$ ; and this replacement will be seen to have very little effect on the cell dimensions. In avelinoite,  $\text{NaFe}_3(\text{PO}_4)_2(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ ,  $a$  7.32,  $c$  19.40 Å (Lindberg, 1957), however, the replacement of  $3\text{Al}^{3+}$  by  $3\text{Fe}^{3+}$  results in an expansion of  $a$  by 4.1 % and of  $c$  by 1.9 %.

This expansion is in reasonable agreement with that to be expected if we take the Al–O link as 1.91 Å and the Fe–O link as 2.00 Å and assume no rearrangement in the sheets: the calculated increases are 4.7 % in  $a$  and 2.3 % in  $c$ , suggesting that there is a slight rearrangement of the structure to accommodate the larger  $\text{Fe}^{3+}$ .

Brophy, Scott, and Snellgrove (1962) found an increase of 4.5 % in the  $a$ -dimension when the Al of alunite,  $\text{NaAl}_3(\text{SO}_4)_2(\text{OH})_6$ , is replaced by Fe in jarosite; this agrees better with the calculated expansion for a close-packed  $Me$ -O sheet, perhaps because of the smaller dimensions of the meshes in alunite and the impossibility of even a slight rearrangement (alunite and jarosite have the same structure as woodhouseite; cf. fig. 3).

*Acknowledgements.* We are grateful to the Centro Nazionale Universitario di Calcolo Elettronico of Pisa University for computer facilities.

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[Manuscript received 30 May 1969]