

## The crystal structure of vuagnatite, $\text{CaAl}(\text{OH})\text{SiO}_4$

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### Abstract

The new orthorhombic mineral vuagnatite,  $\text{CaAl}(\text{OH})\text{SiO}_4$  ( $P2_12_12_1$ ,  $a = 7.055(6)$ ,  $b = 8.542(7)$ ,  $c = 5.683(5)\text{Å}$ ,  $Z = 4$ ) is isotypic with conichalcite,  $\text{CaCu}(\text{OH})\text{AsO}_4$ . From counter diffractometer data corrected for absorption [ $\mu(\text{MoK}\alpha) = 22.5\text{cm}^{-1}$ ] the structure was refined anisotropically to a final  $R$  value of 0.043 for 974 reflections ( $F > 3\sigma$ ). Vuagnatite is characterized by  $\text{AlO}_4(\text{OH})_2$  octahedra sharing edges to form chains linked by isolated  $\text{SiO}_4$  tetrahedra and  $\text{CaO}_7\text{OH}$  polyhedra. The Donnay-Allmann empirical method of recognizing  $\text{O}^{2-}$ ,  $(\text{OH})^-$ , and  $\text{H}_2\text{O}$  in crystal structures indicates the presence of only one hydroxyl group, creating a hydrogen bond between the tetrahedral oxygen O(2) and the octahedral oxygen O(5). The position of the hydrogen atom was confirmed from a difference Fourier synthesis and successfully refined. The bond distance O(5)–H (the hydroxyl group) is  $0.94(5)\text{Å}$  and the O(2)–O(5) distance is  $2.530(3)\text{Å}$  with a value of  $178(6)^\circ$  for the angle O(2)···H–O(5). Two oxygen atoms of each  $\text{AlO}_6$  octahedron are hydroxyl groups. The crystal chemical formula of vuagnatite is therefore  $\text{Ca}^{18}\text{Al}^{18}(\text{OH})\text{Si}^{4}\text{O}_4$ .

### Introduction

Vuagnatite,  $\text{CaAl}(\text{OH})\text{SiO}_4$ , is a new silicate mineral found in a metasomatic rodingite from Bögürtlencik Tepe in southwest Turkey. Its mineralogical data have been reported in the preceding article (Sarp *et al.*, 1976). This paper reports its crystal structure, with particular emphasis on determining the role of hydrogen, since by classical methods it was impossible in this material to quantify either the total water content or its role as  $(\text{OH})^-$  or  $\text{H}_2\text{O}$ .

### Experimental

Single crystals from crushed rock samples (containing predominantly hydrogarnet and chlorite (clinocllore) and minor amounts of prehnite and vesuvianite) were isolated and oriented for X-ray study by their optical ellipsoids on a spindle stage. Reciprocal-lattice explorer and Weissenberg films of four crystals indicated an orthorhombic unit cell. Systematic absences of the type  $h$  odd for  $h00$ ,  $k$  odd for  $0k0$  and  $l$  odd for  $00l$  lead uniquely to space group  $P2_12_12_1$ .

Intensities of an anhedronal crystal (approximately

$0.14 \times 0.10 \times 0.06$  mm) were measured on a Philips PW1100 computer-controlled four-circle diffractometer using  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71069\text{Å}$ ), graphite monochromator, in the  $\theta/2\theta$  scan mode. Data were collected in one octant of reciprocal space from  $\theta = 3$  to  $38^\circ$ . A total of 1084 nonequivalent reflections was measured out to  $\sin \theta/\lambda = 0.866\text{Å}^{-1}$  of which 974 had  $F_{\text{obs}}$  greater than  $3\sigma$ . Absorption correction was applied to the data using the program CAMEL JOCKEY (Flack 1974, 1975). For this, eight families of eight equivalent planes were additionally measured using the  $\psi$  scan method. The least-squares refinement, using the program LATTIX (Gvildys, 1965), of  $1/d$  values of 23 families of parallel planes yielded the following cell parameters (e.s.d.'s at the  $3\sigma$  level):  $a = 7.055(6)$ ,  $b = 8.542(7)$ ,  $c = 5.683(5)\text{Å}$ .

### Structure solution and refinement

Chemical formula, space group, and axial ratios  $a/b$  and  $c/b$  suggest an isotypy to the conichalcite [ $\text{CaCu}(\text{OH})\text{AsO}_4$ ] structure studied by Qurashi and Barnes (1963). The calculated powder pattern based on conichalcite atomic positions shows a close fit to the observed powder intensities<sup>2</sup> (Table 3, Sarp *et al.*,

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<sup>2</sup> Close also to those of a sample from Japan (A. Kato, 1975, private communication).

1976). Hence these atomic positions were used as starting values for a full-matrix refinement of the single crystal data by CRYLSQ (Stewart *et al.*, 1972). Atomic scattering factors for neutral atoms were used (Cromer and Mann, 1968), and anomalous dispersion corrections (*International Tables for X-ray Crystallography*, 1974) were applied. The system of weights used was  $w = 1/\sigma^2$  where  $\sigma$  is the standard deviation of  $F_{\text{obs}}$ .

The position of Ca, Al, Si, and O were refined using initially isotropic, then anisotropic temperature factors. Although secondary extinction was not evident, refinement of the appropriate parameter at the isotropic stage was tried. This resulted in no change in  $R$  value (weighted and unweighted), and therefore it was omitted from further refinements. At both stages a difference Fourier map was calculated which showed residual electron density at the atomic sites. Nevertheless on both maps a peak with definite volume and electron density characteristic of a hydrogen atom was located. This position near oxygen O(5) on the Al octahedron corresponds to the hydrogen position postulated by Qurashi and Barnes (1963) in conchalcite. The hydrogen position deduced from the Fourier maps was refined with an isotropic temperature factor while the other atoms were refined with anisotropic temperature factors. The refinement converged smoothly.

To determine the absolute configuration, a further refinement was carried out with the signs of the  $z$  coordinates inverted for all atoms. Application of the

TABLE 2. Vuagnatite. Interatomic distances (Å) within the polyhedra<sup>†</sup>

|         |          |      |         |          |      |
|---------|----------|------|---------|----------|------|
| Si-O(1) | 1.691(2) | **'A | Ca-O(1) | 2.495(2) | ***K |
| -O(2)   | 1.615(2) | '/'B | -O(2)   | 2.482(3) | +/'L |
| -O(3)   | 1.637(2) | **'C | -O(2')  | 2.328(2) | +/'M |
| -O(4)   | 1.640(3) | **'D | -O(3)   | 2.507(2) | +/'N |
| ave.    | 1.646    |      | -O(3')  | 2.455(2) | +/'P |
|         |          |      | -O(4)   | 2.505(2) | +/'Q |
|         |          |      | -O(4')  | 2.417(2) | +/'R |
| Al-O(1) | 1.944(2) | +/'E | -O(5)   | 2.330(2) | **/S |
| -O(1')  | 2.053(2) | +/'F |         |          |      |
| -O(3)   | 1.934(3) | +/'G | ave.    | 2.440    |      |
| -O(4)   | 1.914(3) | +/'H |         |          |      |
| -O(5)   | 1.846(2) | +/'I | H -O(2) | 1.59(5)  | +/'  |
| -O(5')  | 1.834(2) | +/'J | -O(5)   | 0.94(5)  | **'  |
| ave.    | 1.921    |      |         |          |      |

<sup>†</sup>E.s.d.'s in parentheses refer to the last significant figure. Corner shared is symbolized: + with SiO<sub>4</sub> tetrahedron, \* with AlO<sub>4</sub>(OH)<sub>2</sub> octahedron, ' with CaO<sub>7</sub>OH polyhedron and / with hydrogen bond. Letters refer to the bond vectors in Fig. 1

Hamilton  $R$ -factor test (Hamilton, 1965) favored the positive  $z$  configuration at the 0.005 significance level, so this was adopted.

The final  $R(=\Sigma|\Delta F|/\Sigma|F_{\text{obs}}|)$  was 0.043, and the maximum shift/error was 0.02 except for hydrogen (0.1 in  $x$ ). The final difference Fourier map showed ripples of electron density which were most marked at the Ca site, where they extended parallel to the  $a$  direction across the whole cell (maximum density 1.5 e/Å<sup>3</sup>). The possibility of systematic errors ( $|F_{\text{obs}}| > |F_{\text{calc}}|$ ) in the  $0k0$  reflections arising from the irregular shape of the crystal suggested a trial run without these reflections (C. H. MacGillavry, 1975,

TABLE 1. Vuagnatite. Atomic positional and thermal parameters\*

| Atom      | $x$       | $y$       | $z$       | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|-----------|-----------|-----------|-----------|----------|----------|----------|----------|----------|----------|
| Ca        | 0.3627(1) | 0.6646(1) | 0.0282(1) | 81(2)    | 51(2)    | 47(2)    | 2(1)     | 3(2)     | 0(2)     |
| Al        | 0.2610(1) | 0.9951(2) | 0.7429(2) | 76(3)    | 43(4)    | 24(4)    | -3(2)    | -4(3)    | 7(3)     |
| Si        | 0.6198(1) | 0.8095(1) | 0.5120(2) | 62(3)    | 48(4)    | 23(3)    | 3(2)     | 1(2)     | 0(3)     |
| O(1)      | 0.4293(2) | 0.9287(2) | 0.4909(4) | 76(7)    | 37(9)    | 47(9)    | 9(5)     | -8(6)    | -3(7)    |
| O(2)      | 0.7885(3) | 0.9314(3) | 0.5699(4) | 75(7)    | 88(11)   | 60(9)    | -16(6)   | -1(7)    | 11(8)    |
| O(3)      | 0.6468(3) | 0.7106(3) | 0.2677(4) | 89(7)    | 59(9)    | 30(8)    | 11(7)    | -5(6)    | -4(7)    |
| O(4)      | 0.6133(3) | 0.6934(3) | 0.7417(4) | 103(8)   | 61(11)   | 18(8)    | 9(6)     | 4(6)     | 0(7)     |
| O(5) (OH) | 0.3955(2) | 0.9356(3) | 0.0043(4) | 66(6)    | 50(9)    | 41(9)    | -10(5)   | -6(6)    | 8(8)     |
| H         | 0.514(7)  | 0.984(7)  | 0.032(10) | 34(16)   |          |          |          |          |          |

\* Space group:  $P2_12_12_1$   $Z = 4$ , all atoms in general point position 4a  
 Anisotropic temperature factor expressed as  $T = \exp(-2\pi^2 \sum_i \sum_j U_{ij} a_i a_j)$  where  $a_1 = ha^*$ ,  $a_2 = kb^*$ , etc.,  $U_{ij}$  is  $\times 10^4$ . Isotropic temperature factor expressed as  $T = \exp(-2\pi^2 U s^2)$ , where  $s = 1/d_{hkl}$ ,  $U$  is  $\times 10^3$ . E.s.d.'s in parentheses refer to last significant figures.

private communication). Although the  $R$  value decreased by 0.001, the topography persisted.

Atomic positional and thermal parameters are given in Table 1. Interatomic distances and angles calculated using the program BONDLA (Stewart *et al.*, 1972) are shown in Table 2 and 3 and Figures 1 and 3 in both articles, based on ORTEP drawings (Johnson, 1970). The final observed and calculated structure factors are available as Table 7.<sup>3</sup>

## Discussion of the structure

### Description of the structure

Schematically the backbone of the structure is composed of Al octahedral chains. The Al atom has approximate coordinates of  $1/4, 1, 3/4$ . Its coordinating oxygens O(3) and O(4) have similar  $z$  coordinates, whereas O(1) and O(5)  $\equiv$  (OH)<sup>-</sup> are at  $z \approx 1/2$  (Fig. 2). The screw axis at  $1/4, 1, z$  repeats Al, O(3), and O(4) at  $z \approx 1/4$ , and O(1) and O(5) at  $z \approx 0$  and 1. Hence successive octahedra share O(1)–O(5) edges [2.569(3)Å]. These AlO<sub>4</sub>(OH)<sub>2</sub> octahedra form a chain parallel to the  $c$  axis with alternating O(3) and O(4) apices. This chain in position  $A$  is centered on Al atoms at roughly  $1/4, 1, z$ . The screw axis at  $z, 3/4, 1/2$  repeats this chain in position  $B$  centered on Al atoms at approximately  $3/4, 1/2, z$ .

The chains are cross-linked by SiO<sub>4</sub> tetrahedra and CaO<sub>7</sub>(OH) polyhedra. A tetrahedron around the Si atom at (0.62, 0.81, 0.51) links three chains via O(1) to chain  $A$ , via O(3) and O(4) to chain  $B$ , and to an  $A$  chain at  $5/4, 1, z$  by a hydrogen bond O(2) ... H–O(5) which is the shortest O–O distance in the structure [2.530(3)Å] (see Fig. 3 in both articles). The tetrahedra share two edges with the Ca polyhedra: O(1)–O(2) = 2.574(3) and O(2)–O(4) = 2.571(3)Å. The Ca polyhedra link two Al chains by sharing one edge of each of four octahedra, two in each chain. The Ca polyhedra share O(2) apices in  $b$ , and form zig-zag chains in the  $a$  direction by sharing O(3)–O(4) = 3.002(3) edges (Fig. 3, Sarp *et al.*, 1976). These common edges are distinctly longer than the SiO<sub>4</sub> edge O(4)–O(3) = 2.708(3)Å that relays it in  $c$  (Fig. 2). Hence the Al chains are cross-linked successively in the  $a$  direction but alternately in  $b$  and  $c$  by two isolated tetrahedra and two Ca polyhedra.

TABLE 3. Vuagnatite. Polyhedron edge lengths (Å) and polyhedral angles\*

|            |         |           |            | Edge shared with    |                     |                     |
|------------|---------|-----------|------------|---------------------|---------------------|---------------------|
|            |         |           |            | [SiO <sub>4</sub> ] | [AlO <sub>6</sub> ] | [CaO <sub>7</sub> ] |
| O(1) - Si  | - O(2)  | 2.574 (3) | 102.2 (1)° | -                   | -                   | 1                   |
|            | - O(3)  | 2.727 (3) | 110.1 (1)° | -                   | -                   | -                   |
|            | - O(4)  | 2.785 (3) | 113.5 (1)° | -                   | -                   | -                   |
| O(2) - Si  | - O(3)  | 2.740 (3) | 114.8 (1)° | -                   | -                   | -                   |
|            | - O(4)  | 2.571 (3) | 104.4 (1)° | -                   | -                   | 1                   |
| O(3) - Si  | - O(4)  | 2.708 (3) | 111.5 (1)° | -                   | -                   | -                   |
|            |         |           |            | ave. 2.684          | ave. 109.4°         |                     |
| O(1) - Al  | - O(3)  | 2.696 (3) | 88.1 (1)°  | -                   | -                   | -                   |
|            | - O(4)  | 2.741 (3) | 90.5 (1)°  | -                   | -                   | 1                   |
|            | - O(5)  | 2.569 (3) | 85.3 (1)°  | -                   | 1                   | -                   |
|            | - O(5') | 2.928 (3) | 101.5 (1)° | -                   | -                   | -                   |
| O(1') - Al | - O(3)  | 2.871 (3) | 92.1 (1)°  | -                   | -                   | 1                   |
|            | - O(4)  | 2.794 (3) | 89.5 (1)°  | -                   | -                   | -                   |
|            | - O(5)  | 2.777 (3) | 90.7 (1)°  | -                   | -                   | -                   |
| O(3) - Al  | - O(5)  | 2.569 (3) | 82.5 (1)°  | -                   | 1                   | -                   |
|            | - O(5') | 2.700 (3) | 91.1 (1)°  | -                   | -                   | -                   |
| O(4) - Al  | - O(5)  | 2.650 (3) | 89.3 (1)°  | -                   | -                   | 1                   |
|            | - O(5') | 2.695 (3) | 91.5 (1)°  | -                   | -                   | 1                   |
|            |         |           |            | ave. 2.717          | ave. 90.0°          |                     |
| O(1) - Ca  | - O(2)  | 3.334 (3) | 84.1 (1)°  | -                   | -                   | -                   |
|            | - O(2') | 2.574 (3) | 64.4 (1)°  | 1                   | -                   | -                   |
|            | - O(3') | 2.871 (3) | 70.9 (1)°  | -                   | 1                   | -                   |
|            | - O(4') | 2.741 (3) | 67.8 (1)°  | -                   | 1                   | -                   |
| O(2) - Ca  | - O(3') | 2.952 (3) | 73.4 (1)°  | -                   | -                   | -                   |
|            | - O(4)  | 2.571 (3) | 62.1 (1)°  | 1                   | -                   | -                   |
| O(2') - Ca | - O(2)  | 3.122 (3) | 80.9 (1)°  | -                   | -                   | -                   |
|            | - O(3)  | 3.290 (4) | 85.7 (1)°  | -                   | -                   | -                   |
|            | - O(4)  | 3.773 (3) | 102.6 (1)° | -                   | -                   | -                   |
|            | - O(4') | 3.768 (3) | 105.1 (1)° | -                   | -                   | -                   |
| O(3) - Ca  | - O(4)  | 3.002 (3) | 73.6 (1)°  | -                   | -                   | 1                   |
|            | - O(4') | 3.392 (3) | 87.1 (1)°  | -                   | -                   | -                   |
|            | - O(5)  | 2.650 (3) | 66.3 (1)°  | -                   | 1                   | -                   |
| O(3') - Ca | - O(4)  | 3.852 (3) | 101.9 (1)° | -                   | -                   | -                   |
|            | - O(4') | 3.002 (3) | 76.1 (1)°  | -                   | -                   | 1                   |
| O(4) - Ca  | - O(5)  | 3.013 (3) | 78.0 (1)°  | -                   | -                   | -                   |
|            | - O(5)  | 2.695 (3) | 67.6 (1)°  | -                   | 1                   | -                   |
| O(4') - Ca | - O(5)  | 2.978 (3) | 77.7 (1)°  | -                   | -                   | -                   |
|            |         |           |            | ave. 3.088          | ave. 79.2°          |                     |
| O(2) - H   | - O(5)  | 2.530 (3) | 178 (6)°   | -                   | -                   | -                   |

\*E.s.d.'s in parentheses refer to last significant figure

### Location and confirmation of the (OH)<sup>-</sup> group

In the preliminary stages of this investigation the question arose about the role of water in the structure and its quantity, since by microprobe analysis it is impossible to quantify the water content or its form as (OH)<sup>-</sup> or H<sub>2</sub>O.

This type of structure precludes the presence of more than one (OH)<sup>-</sup> group simply on crystal chemical grounds. Furthermore, since vuagnatite is isotypic with conicalcite, H<sub>2</sub>O cannot be present in the structure. This is substantiated by the fact that no electron density which could be interpreted as mo-

<sup>3</sup> To obtain a copy of Table 7, order Document No. Am-76-028 from the Business Office, Mineralogical Society of America, Suite 1000 lower level, 1909 K Street, N.W., Washington, D.C. 20006. Please remit \$1.00 in advance for the microfiche.

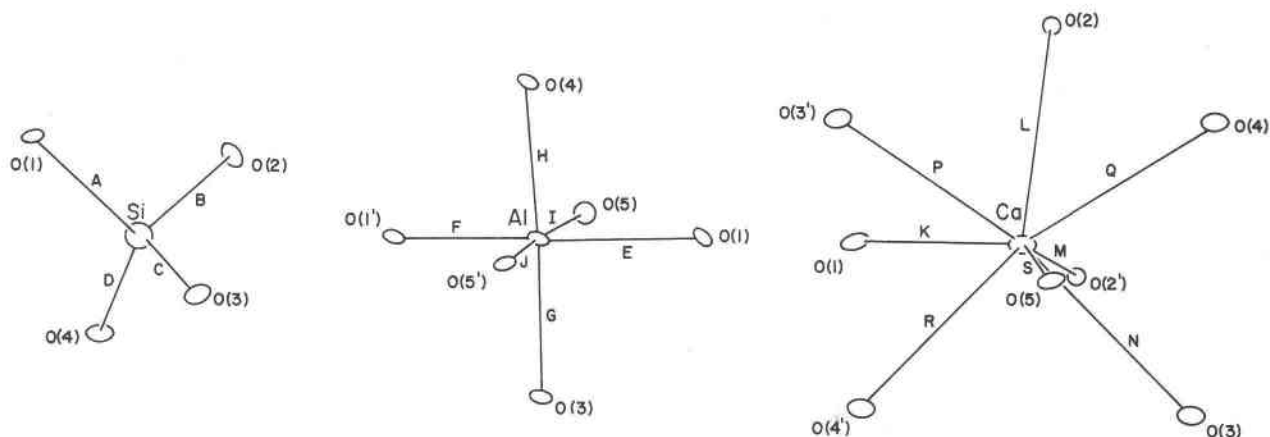


FIG. 1. Vuagnatite. Schematic bond diagram of the three coordination polyhedra. Letters refer to the bond vectors listed in Table 2.

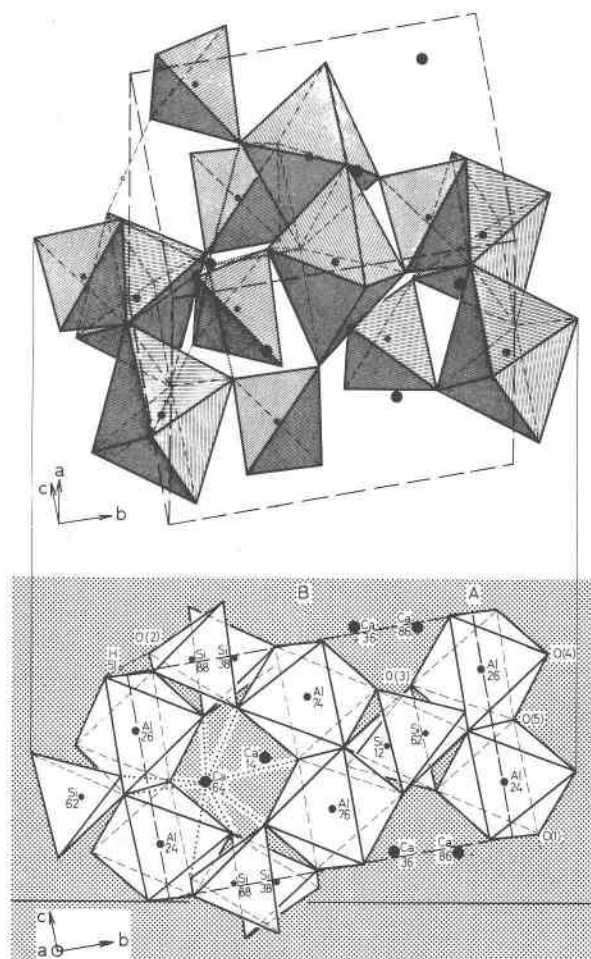


FIG. 2. Vuagnatite. The lower part of the figure shows the structure projected down the  $a$  axis, heights in  $100x$ . The upper part shows the corresponding clinographic projection (tilt angle about  $10^\circ$ ). For clarity, only one hydrogen position is shown.

lecular water was found on a difference Fourier map. The peaks found on the two difference Fourier maps near the position of O(5) were assumed to be the correct site of the hydrogen atom. To check the oxygen assignment of this proton, the modified version of the Donnay and Allmann (1970) valence summation procedure (Donnay and Donnay, 1973) was applied. The method is based on Pauling's principle of local neutralization of charge (Pauling, 1929) and provides a means of distinguishing  $O^{2-}$  from  $OH^{1-}$  and  $H_2O$  in nonmolecular structures.

It can be concluded from the bond valence summations in Table 4 (5th column) that O(1), O(3), and O(4) are nonhydroxyl groups, but O(2) and O(5) have valence sums much less than would be expected if they were  $O^{2-}$ . These values suggest that either O(5) is the oxygen atom of the hydroxyl group and donates a hydrogen bond to O(2), or else O(2) is the OH group, and hydrogen bonds to O(5). To account for the hydrogen bond, a correction term of 0.30 v.u. corresponding to the distance  $O(2)-O(5) = 2.530\text{\AA}$  has been added or subtracted from O(2) and O(5) (Table 4). Actually the valence summation procedure does not allow the differentiation between the two cases; however the results from the difference Fourier syntheses, which agree with the first of the two solutions, confirm the usefulness of this method.

The location of the hydrogen atom in vuagnatite on a difference Fourier map, its successful refinement to give reasonable interatomic bond lengths (Table 2 and 3; and the  $O-H \cdots O$  distance between the two oxygens which does not form an edge of an Si, Al, or Ca polyhedron, is clearly the shortest O-O distance in the whole structure), and the Donnay and Allmann calculation are sufficient confirmation of its existence

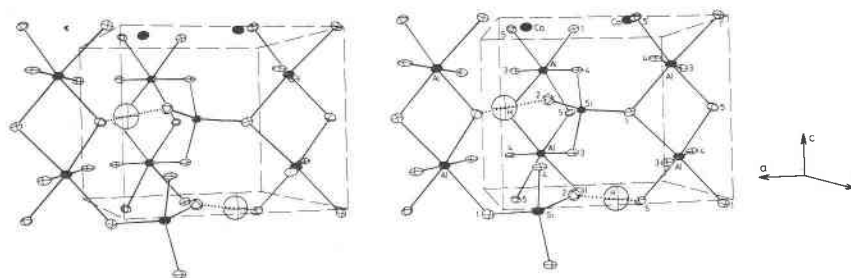


FIG. 3. Vuagnatite. Stereoscopic view down the *b* axis, atoms represented by their 75 percent ellipsoids of vibration. Unattached ellipsoids are Ca atoms. Numbers refer to oxygen atoms defined in Tables 2 and 3.

and correct positioning in the structure. The crystal chemical formula is therefore  $\text{Ca}^{(8)}\text{Al}^{(6)}(\text{OH})\text{Si}^{(4)}\text{O}_4$ . Thus the mineral can be described as a basic nesosilicate.

*Deformation of polyhedra*

The variations in cation-oxygen bond lengths in the structure can be explained by Baur's extended electrostatic valence rule (Baur, 1970, 1971). Three

models were tried, one with the hydrogen charge assigned to O(5), a second with a 5/8:3/8 distribution to O(5) and O(2) respectively (based on the results of the Donnay and Allmann calculation), and a third with a 5/6:1/6 distribution in accordance with the Baur (1970) postulation. The latter two models gave results closest to the observations and are summarized in Table 5. It can be deduced from this table that in general the 5/8:3/8 distribution is the better of

TABLE 4. Vuagnatite. Coordination bond lengths (Å, left values) and estimated bond valences (v.u., right values)

|  | Ca             |                  | Al             |                  | Si       |                  | $\sum_{\nu}^{\text{cation}}$ | 1st possibility   |                  | 2nd possibility                 |                  |
|--|----------------|------------------|----------------|------------------|----------|------------------|------------------------------|---|------------------|---------------------------------|------------------|
|  | Distance       | Valence          | Distance       | Valence          | Distance | Valence          |                              | $\sum_{\nu}^{\text{corrected}}$   | anion            | $\sum_{\nu}^{\text{corrected}}$ | anion            |
|  |                |                  |                |                  |          |                  |                              | for H-bonding   | chem.            | for H-bonding                   | chem.            |
| O(1)   | 2.495          | 0.232            | 1.944<br>2.053 | 0.456<br>0.301   | 1.691    | 0.905            | 1.894                        | 1.89  | O <sup>2-</sup>  | 1.89                            | O <sup>2-</sup>  |
| O(2)   | 2.328<br>2.482 | 0.288<br>0.236   |                |                  | 1.615    | 1.065            | 1.589                        | 1.89  | O <sup>2-</sup>  | 1.29                            | OH <sup>1-</sup> |
| O(3)   | 2.455<br>2.507 | 0.244<br>0.228   | 1.934          | 0.475            | 1.637    | 1.017            | 1.964                        | 1.96  | O <sup>2-</sup>  | 1.96                            | O <sup>2-</sup>  |
| O(4)   | 2.417<br>2.505 | 0.256<br>0.229   | 1.914          | 0.503            | 1.640    | 1.010            | 1.998                        | 2.00  | O <sup>2-</sup>  | 2.00                            | O <sup>2-</sup>  |
| O(5)   | 2.330          | 0.286            | 1.834<br>1.846 | 0.642<br>0.619   |          |                  | 1.547                        | 1.25  | OH <sup>1-</sup> | 1.85                            | O <sup>2-</sup>  |
| $\sum_{\nu}^{\text{anion}}$                    |                | 1.999            |                | 2.996            |          | 3.997            | $\Delta\nu_{\text{rms}}$     | 0.13  |                  | 0.15                            |                  |
| N.F.   |                | 0.997            |                | 0.987            |          | 0.999            | $\sum_{\nu}^{\text{cation}}$ | is the sum of bond valences emanating from anion summed over the bonded cations |                  |                                 |                  |
| cation chemistry                               |                | Ca <sup>2+</sup> |                | Al <sup>3+</sup> |          | Si <sup>4+</sup> | $\sum_{\nu}^{\text{anion}}$  | is the sum of bond valences reaching anion                                      |                  |                                 |                  |
| $\bar{L}$                                      | 2.440          |                  | 1.921          |                  | 1.646    |                  | $\Delta\nu_{\text{rms}}$     | root-mean-square deviation  |                  |                                 |                  |
| $L_{\text{max}}$                               | 3.25           |                  | 2.26           |                  | 2.13     |                  | N.F.                         | normalization factor applied to $\sum_{\nu}^{\text{anion}}$                     |                  |                                 |                  |
| $P = \frac{\bar{L}}{L_{\text{max}} - \bar{L}}$ | 3.01           |                  | 5.67           |                  | 3.40     |                  | $\bar{L}$                    | is the mean of the observed cation-anion distances in a given polyhedron        |                  |                                 |                  |
| $\nu_i$  | 2/8            |                  | 3/6            |                  | 4/4      |                  | $L_{\text{max}}$             | is the sum of the 'maximum radii' for cation and anion                          |                  |                                 |                  |
|  |                |                  |                |                  |          |                  | $\nu_i$                      | is the ratio of formal cation valence to coordination number                    |                  |                                 |                  |

TABLE 5. Vuagnatite. Comparison of observed and predicted cation-oxygen bond lengths

|         | $P_o$ (A) | $P_o$ (B) | $d_o$ | $d_c$ (A) | $\Delta$ (A) | $d_c$ (B) | $\Delta$ (B) |         | $P_o$ (A) | $P_o$ (B) | $d_o$ | $d_c$ (A) | $\Delta$ (A) | $d_c$ (B) | $\Delta$ (B) |
|---------|-----------|-----------|-------|-----------|--------------|-----------|--------------|---------|-----------|-----------|-------|-----------|--------------|-----------|--------------|
| Ca-O(1) | 2.25      | 2.25      | 2.495 | 2.527     | 0.032        | 2.536     | 0.041        | Al-O(1) | 2.25      | 2.25      | 1.944 | 1.971     | 0.027        | 1.955     | 0.011        |
| Ca-O(2) | 1.875     | 1.667     | 2.328 | 2.403     | 0.075        | 2.344     | 0.016        | Al-O(2) | 2.25      | 2.25      | 2.053 | 1.971     | 0.082        | 1.955     | 0.098        |
| Ca-O(2) | 1.875     | 1.667     | 2.482 | 2.403     | 0.079        | 2.344     | 0.138        | Al-O(3) | 2.0       | 2.0       | 1.934 | 1.911     | 0.023        | 1.895     | 0.038        |
| Ca-O(3) | 2.0       | 2.0       | 2.455 | 2.444     | 0.011        | 2.454     | 0.001        |         |           |           |       |           |              |           |              |
| Ca-O(3) | 2.0       | 2.0       | 2.507 | 2.444     | 0.063        | 2.454     | 0.053        | Al-O(4) | 2.0       | 2.0       | 1.914 | 1.911     | 0.003        | 1.895     | 0.019        |
| Ca-O(4) | 2.0       | 2.0       | 2.417 | 2.444     | 0.027        | 2.454     | 0.037        | Al-O(5) | 1.875     | 2.083     | 1.834 | 1.881     | 0.047        | 1.915     | 0.081        |
| Ca-O(4) | 2.0       | 2.0       | 2.505 | 2.444     | 0.061        | 2.454     | 0.051        | Al-O(5) | 1.875     | 2.083     | 1.846 | 1.881     | 0.035        | 1.915     | 0.069        |
| Ca-O(5) | 1.875     | 2.083     | 2.330 | 2.403     | 0.073        | 2.481     | 0.151        |         |           |           |       |           |              |           |              |
|         |           |           |       |           |              |           |              | Si-O(1) | 2.25      | 2.25      | 1.691 | 1.665     | 0.026        | 1.670     | 0.021        |
|         |           |           |       |           |              |           |              | Si-O(2) | 1.875     | 1.667     | 1.615 | 1.631     | 0.016        | 1.617     | 0.002        |
|         |           |           |       |           |              |           |              | Si-O(3) | 2.0       | 2.0       | 1.637 | 1.643     | 0.006        | 1.617     | 0.010        |
|         |           |           |       |           |              |           |              | Si-O(4) | 2.0       | 2.0       | 1.640 | 1.643     | 0.003        | 1.647     | 0.007        |

Letters in parentheses refer to the Donnay and Allmann model (A) and the Baur model (B).

$P_o$  sum of bond strengths (v.u.) received by an oxygen atom

$d_o$  observed cation-oxygen distance (Å)

$d_c$  predicted cation-oxygen distance (Å) according to Baur (1971)

$\Delta$  modulus of the difference between observed and calculated distances (Å)

the two models, although the Baur model is in closer agreement with the  $SiO_4$  observed distances. The deviations of the predicted values from the observed are in some cases somewhat larger than might be expected by this method. However the overall trend in variations is consistent with the principle.

All three types of coordination polyhedra are distorted. Apart from the variations in the cation-oxygen bond lengths, such distortions can be further explained to a certain extent by Pauling's principle of shared edges (Pauling, 1929). The Ca polyhedron<sup>4</sup> and the tetrahedron conform to this principle, since their shared edges are shorter than their unshared edges (Table 3). Indeed, for the tetrahedron, the difference between the average length of shared edges and that of unshared edges is 0.168 Å, which is quite close to the expected 0.15 Å contraction of a shared edge (Baur, 1972). However, for the octahedron, this difference is only 0.068 Å, an indication of contradictions. Comparison to the mean O-O distance (2.717) shows that for shared edges the Al-Al edge is 5 percent shorter, whereas the Ca-Al edge O(1')-O(3) = 2.871(3) is 6 percent longer. This lengthening may denote adjustment stresses due to polyhedral misfit (Baur, 1972). As for the unshared

edges: O(1)-O(5') = 2.928(3) is even 8 percent longer than the mean, whereas O(4)-O(5') = 2.610 Å shows a 4 percent contraction which may be due to a combined effect: short Al-O(5') distance [1.834(2) Å] and torsion of the octahedron [O(5)-Al-O(5') = 173.2(1)° and O(3)-Al-O(4) = 175.9(1)°]. Next nearest neighbor effects are probably the reason for these discrepancies in the octahedron edge lengths.

#### Temperature factors

Because the  $U_{11}$  values tend to be much larger than the other values (Table 1), the corresponding thermal ellipsoids are elongated in the  $a$  direction (Table 6 and Fig. 3, Johnson, 1970) except for O(1), O(2), and O(5). For the latter two, the maximum elongation is approximately perpendicular to the hydrogen bond. As temperature factors tend to compensate for systematic errors, it is important to estimate the latter.

Since the anhedron crystal (longest dimension  $b$ ) was mounted on the diffractometer in a random orientation, systematic multiple diffractions are absent. A statistical absorption correction had to be used because of the crystal's reentrant angle (examples of discrepancies of  $R$  values for Laue-equivalent reflections before and after corrections: 8 to 2 percent for 681, 5 to 5 percent for 251, and 6 to 3 percent for 332). The  $\Delta F$  maps are not featureless. On both types of sections that contain the  $a$  axis, ripples of residual electron density parallel to  $a$  appear at the atomic sites, implying a "rod-like" distribution in three dimensions. Hence doubts arise not only about the  $0k0$  reflections ( $R = 15.4\%$ ) but also about the  $0kl$  reflections ( $R = 8.7\%$ ,  $0k0$  and  $00l$  reflections excluded).

<sup>4</sup> The  $CaO_4OH$  polyhedron is described as a square antiprism in conicalite. In vuagnatite neither "square" face [O(5), O(4), O(2), and O(3')] and [O(4'), O(3), O(2'), and O(1)] has coplanar atoms, and the "face" diagonal O(2')-O(4') = 3.768(3) is within one e.s.d. of the longest edge O(2')-O(4) = 3.773(3) Å. Hence the subdivision of square faces into two triangles yields twelve triangular faces which evoke the dodecahedron ( $D_{2d}$ ) found in grossular (Muetterties and Wright, 1976, p. 142).

$F_{\text{obs}}$  is not systematically bigger than  $F_{\text{calc}}$  for  $h00$  ( $R = 4.8\%$ ) or for  $00l$  ( $R = 3.4\%$ ). Therefore the large  $U_{11}$  values are probably partly compensating this residual density, and their physical meaning at least is doubtful.

### Relations between structure and physical properties

In comparison with other silicates of similar compositions, the vuagnatite structure's compactness entails relatively high values both for its density ( $3.42 \text{ g cm}^{-3}$ ) and its refractive indices ( $\alpha = 1.700, \beta = 1.725, \gamma = 1.730$ ) (Sarp *et al.*, 1976). Indeed, the volume per oxygen atom is only  $17.1(5)\text{\AA}^3$ , smaller than that of forsterite (h.c.p. assemblage of oxygens). These properties relate to hydrogen bonding which, in decreasing O-O distances, increases compactness and oxy-

gen polarizability (three of the shortest O-O distances in the structure are approximately parallel to  $a$ , the direction of  $\gamma$ , see Fig. 3 in both articles).

The dominant morphology deduced by Sarp from thin-section study (other small faces not shown on Fig. 2, Sarp *et al.*, 1976) is prismatic parallel to  $c$ , the direction of the Al octahedral chains. A more complete discussion of the relation between structure and morphology may be proposed by the group working with Professor Pabst, who are studying bigger, euhedral, California crystals (Pabst *et al.*, 1976). Interestingly they confirm (with other experimental techniques, R. C. Erd and A. Pabst, 1975, private communication) the conclusion of the present work as to the quantity and  $(\text{OH})^-$  form of water in vuagnatite.

It would be interesting to see if a comparison of the parageneses in Turkey, California (at least three localities), Japan, and Guatemala will throw further light on the crystallization conditions of this dense structure.

TABLE 6. Vuagnatite. Dimensions and orientations of thermal ellipsoids\*

| Atom | Rms vib.   | Angle to $\underline{a}$ | Angle to $\underline{b}$ | Angle to $\underline{c}$ |
|------|------------|--------------------------|--------------------------|--------------------------|
| Ca   | 0.068 (1)  | 85 (1)                   | -90 (16)                 | - 5 (13)                 |
|      | 0.071 (2)  | -87 (5)                  | 3 (15)                   | -89 (15)                 |
|      | 0.090 (1)  | 10 (6)                   | 87 (3)                   | 85 (3)                   |
| Al   | 0.047 (2)  | -86 (1)                  | 72 (4)                   | -18 (5)                  |
|      | 0.067 (3)  | 82 (7)                   | 19 (6)                   | 73 (3)                   |
|      | 0.087 (3)  | 9 (7)                    | -83 (5)                  | -84 (4)                  |
| Si   | 0.048 (3)  | 89 (3)                   | 90 (5)                   | - 1 (5)                  |
|      | 0.069 (2)  | -79 (8)                  | 11 (8)                   | 90 (4)                   |
|      | 0.079 (2)  | 11 (8)                   | 79 (8)                   | 89 (4)                   |
| O(1) | 0.059 (3)  | -79 (2)                  | 12 (14)                  | 84 (18)                  |
|      | 0.067 (4)  | -75 (15)                 | 87 (14)                  | -15 (20)                 |
|      | 0.089 (8)  | -18 (12)                 | -78 (5)                  | 76 (10)                  |
| O(2) | 0.074 (3)  | 71 (2)                   | 64 (7)                   | -33 (5)                  |
|      | 0.082 (1)  | -37 (1)                  | -69 (4)                  | -61 (1)                  |
|      | 0.101 (10) | -60 (1)                  | 34 (4)                   | 77 (7)                   |
| O(3) | 0.054 (4)  | 86 (3)                   | 84 (8)                   | 7 (9)                    |
|      | 0.075 (3)  | -71 (10)                 | 19 (11)                  | -86 (5)                  |
|      | 0.096 (7)  | -19 (11)                 | -72 (8)                  | 84 (7)                   |
| O(4) | 0.042 (6)  | 87 (5)                   | -89 (10)                 | - 3 (10)                 |
|      | 0.077 (6)  | -79 (5)                  | 11 (9)                   | -89 (11)                 |
|      | 0.103 (5)  | 12 (7)                   | 79 (6)                   | 87 (2)                   |
| O(5) | 0.060 (2)  | -88 (2)                  | 61 (6)                   | -29 (6)                  |
|      | 0.069 (4)  | 58 (11)                  | 41 (11)                  | 66 (1)                   |
|      | 0.086 (10) | 32 (12)                  | -63 (6)                  | -74 (9)                  |

\* Principal vibrations (root-mean-square) in  $\text{\AA}$  cited for each atom; angles in degrees. Approximate errors, calculated from the e.s.d.'s of the  $U_{ij}$ 's are in parentheses.

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