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## THE CRYSTAL STRUCTURE OF TRICLINIC WELOGANITE

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### ABSTRACT

The crystal structure of non-centrosymmetric triclinic ( $P1$ ) weloganite was solved by Patterson heavy-atom methods. The structure analysis and new chemical data give the chemical formula  $(\text{Sr}_{2.8}\text{Ca}_{0.2})\text{ZrNa}_2(\text{CO}_3)_6 \cdot 3\text{H}_2\text{O}$  with cell parameters,  $a = 8.966(1)$ ,  $b = 8.980(2)$ ,  $c = 6.730(1)\text{Å}$ ,  $\alpha = 102.72(2)^\circ$ ,  $\beta = 116.65(1)^\circ$ , and  $\gamma = 60.06(1)^\circ$ . The 2354 observed reflections used in the least-squares refinement yielded an  $R$  value of 0.043. The important anomalous dispersion correction for Sr and Zr leads to a unique enantiomorph. The six carbonate groups and three water molecules in weloganite are linked together by six cations with the coordinations 10 (for the three  $\text{Sr}^{2+}$ ), 9 (for the  $\text{Zr}^{4+}$ ) and 6 (for the two  $\text{Na}^+$ ). Each water molecule is hydrogen-bonded to two oxygens with average bond lengths of 2.79Å.

### RÉSUMÉ

La structure atomique de la weloganite triclinique ( $P1$ ) a été établie par l'usage des méthodes Patterson (atomes lourds). L'analyse structurale et de nouvelles données de chimie analytique montrent que la formule de la weloganite est  $(\text{Sr}_{2.8}\text{Ca}_{0.2})\text{ZrNa}_2(\text{CO}_3)_6 \cdot 3\text{H}_2\text{O}$ . Les paramètres de la maille cristalline sont  $a = 8.966(1)$ ,  $b = 8.980(2)$  et  $c = 6.730(1)\text{Å}$ ;  $\alpha = 102.72(2)^\circ$ ,  $\beta = 116.65(1)^\circ$  et  $\gamma = 60.06(1)^\circ$ . Les 2354 valeurs de  $F_{\text{obs}}$ , utilisées dans l'affinement conduisirent à une valeur de  $R = 0.043$ . La correc-

tion pour la dispersion anormale pour le Sr et le Zr est considérable; elle a permis de trouver la solution énantiomorphe unique. Les six groupements ( $\text{CO}_3$ ) et les trois molécules d'eau sont reliés par les six cations dans des coordinances de 10 (pour les trois  $\text{Sr}^{2+}$ ), de 6 (pour les 2  $\text{Na}^+$ ) et de 9 (pour le  $\text{Zr}^{4+}$ ). Chaque molécule d'eau présente des liaisons hydrogène à deux atomes d'oxygène; la longueur moyenne des liens  $[\text{H}_2\text{O}]\text{-}[\text{O}^{2-}]$  est de 2.79Å.

### INTRODUCTION

Weloganite was first described by Sabina *et al.* (1968) as a new Sr, Zr carbonate mineral from St. Michel, Montreal Island, Quebec. Later work by Gait & Grice (1971) on other material from this unique locality showed that weloganite contained considerable amounts of Na in addition to the previously-mentioned elements.

Sabina *et al.* (1968) reported the trigonal space group  $P3_12$  whereas Chen & Chao (1974) found that their weloganite was only pseudo-trigonal and that its true space group is triclinic,  $P1$  or  $P\bar{1}$ .

### EXPERIMENTAL

The chemical analyses of weloganite reported by Sabina *et al.* (1968) and Gait & Grice (1971) are given in Table 1. As these analyses showed major differences, a third was carried out at Ecole Polytechnique by Mr. V. Kubat and Mr. C. Dallaire. The  $\text{H}_2\text{O}$  analysis was done by the

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TABLE 1. CHEMICAL ANALYSES AND FORMULAE FOR WELOGANITE

Oxide	Sabina <i>et al.</i> (1968)	Gait & Grice (1971)	This study	Calc.*
SrO	41.0	34.5	36.18	36.06
CaO		1.49	1.14	1.39
ZrO <sub>2</sub>	19.4	13.78	15.26	15.31
Na <sub>2</sub> O		8.23	7.75	7.70
K <sub>2</sub> O		0.04	0.02	
CO <sub>2</sub>	32.2	30.5	30.70	32.82
H <sub>2</sub> O	6.6	9.66	7.85	6.72
SiO <sub>2</sub>		0.83	0.25	
Al <sub>2</sub> O <sub>3</sub>		0.08	N.D.	
Fe <sub>2</sub> O <sub>3</sub>		0.05	0.03	
MgO		0.02	-0.02	
H <sub>2</sub> O <sup>-</sup>			0.11	
Total	99.2	99.18	99.20	100.00
Chemical formulae for C = 6				
Sr <sup>2+</sup>	3.24	2.88	3.00	2.8
Ca <sup>2+</sup>		0.24	0.18	0.2
Zr <sup>4+</sup>	1.29	0.97	1.06	1
Na <sup>+</sup>		2.30	2.15	2
C <sup>4+</sup>	6	6	6	6
[H <sub>2</sub> O]	3.00	4.64	3.75	3
O <sup>2-</sup>	17.82	18.21	18.39	18

\*Calculation based on formula  $(\text{Sr}_{2.8}\text{Ca}_{0.2})\text{ZrNa}_2(\text{CO}_3)_6 \cdot 3\text{H}_2\text{O}$

Penfield technique, CO<sub>2</sub> by the Leco method and all other elements by x-ray fluorescence and atomic absorption techniques. The present analysis is in good agreement with that of Gait & Grice (1971) and hence was the basis for the formula used in the structure determination given in Table 1, column 4.

The weloganite crystal used in the x-ray analysis was a sphere of radius 0.066 mm. Single-crystal data were collected using a Picker FACSII four-circle diffractometer. The refined cell dimensions for this crystal are given in Table 2. Using MoK $\alpha$  radiation, intensities were collected on one half of the sphere of reflection out to  $2\theta = 60^\circ$ . In this volume, there were 2662 reflections of which 2354 were observed. The intensities were collected using  $\theta/2\theta$  scans with a scanning speed of  $1^\circ 2\theta$  per minute and background counts of 20 seconds on either side of the peak. The X-Ray System of crystallographic computer programs (Stewart *et al.* 1972) with scattering curves by Cromer & Mann (1968) were used in this structure analysis. Intensities were corrected for Lorentz and polarization effects and for absorption ( $\mu = 103 \text{ cm}^{-1}$  for MoK $\alpha$  radiation).

#### STRUCTURE DETERMINATION AND REFINEMENT

The distribution of  $E$ -values suggested triclinic weloganite was centrosymmetric, but the

TABLE 2. SPACE GROUP, CELL DIMENSIONS AND CELL CONTENT FOR WELOGANITE

Space Group	$P\bar{1}$	
Cell Dimensions	$a=8.966(1)\text{\AA}$	$\alpha^*=0.14048\text{\AA}^{-1}$
	$b=8.980(2)$	$b^*=0.12852$
	$c=6.730(1)$	$c^*=0.16626$
	$\alpha=102.72(2)^\circ$	$\alpha^*=90.27^\circ$
	$\beta=116.65(1)$	$\beta^*=66.38$
	$\gamma=60.06(1)$	$\gamma^*=117.34$
Cell Volume	$V=419.60\text{\AA}^3$	
Cell Content	$(\text{Sr}_{2.8}\text{Ca}_{0.2})\text{ZrNa}_2(\text{CO}_3)_6 \cdot 3\text{H}_2\text{O}$	

positive result of a test for pyroelectricity strongly indicated that the mineral was non-centrosymmetric and space group  $P1$  was chosen.

A three-dimensional Patterson map showed eight major peaks excluding the origin. Initially it was impossible to determine which of these peaks were due to the center of symmetry inherent in a Patterson synthesis and which were a result of the heavy atoms in the atomic structure. In order to resolve this problem, structure factors were calculated for two trial structures in each of which we used pairs of atomic positions related by a center of symmetry in the Patterson map. The scattering curve of Sr<sup>2+</sup> was used for all input atomic positions and the coordinates for the first atom in each trial fixed the origin. For the first trial structure, atomic positions [1] (0.33, 0.33, 0.00) and [2] (0.67, 0.67, 0.00) refined to  $R = 0.38$ . The second trial structure was for the remaining three pairs of sites:

[3] (0.77, 0.00, 0.38), [4] (0.19, 0.00, 0.62)  
 [5] (0.10, 0.30, 0.35), [6] (0.80, 0.68, 0.64)  
 and [7] (0.41, 0.69, 0.35), [8] (0.50, 0.31, 0.64)

and these yielded an  $R = 0.41$ .  $\Delta F$  maps and changes in temperature factors from both of these syntheses were used to locate the 2 Na atoms at approximately sites [1] and [2] above and the 3 Sr atoms at sites [3], [5] and [7]. Zr was assigned to the large positive  $\Delta F$  at (0,0,0) and in subsequent least-square refinements the Zr atomic position was chosen to fix the origin.

Following the assignment of the above six cationic positions, 6 C<sup>4+</sup>, 10 O<sup>2+</sup> and 3 H<sub>2</sub>O positions were found using a series of structure factor calculations followed by  $\Delta F$  syntheses. The scattering curves for H<sub>2</sub>O and O are very similar and the initial decision as to the proper assigning of these sites was based on the observed coordinations. The six CO<sub>3</sub> groups could be readily recognized because of the trigonal configuration with the short 1.3 $\text{\AA}$  C-O bond length. The validity of choice for the H<sub>2</sub>O and O sites was checked by valence sums in the manner described by Donnay & Allman (1970); final bond-valence analysis obtained with refined interatomic distances is given in Table 7. When the  $\Delta F$  maps did not indicate any further atoms missing, the agreement factor was  $R = 0.072$  with each atom having an individual isotropic temperature factor.

To refine the weloganite structure, the Sr and Zr scattering curves were corrected for anomalous dispersion as this effect is quite marked with Mo radiation. The need for this correction was evident on the difference-synthesis map by the negative electron densities

TABLE 3. FINAL ATOMIC POSITIONS AND THERMAL PARAMETERS FOR WELOGANITE

Atom	x	y	z	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>12</sub>	U <sub>13</sub>	U <sub>23</sub>
Sr(1)	0.4679(3)	0.6565(2)	0.3769(4)	0.0100(3)	0.0084(3)	0.0086(7)	-0.0038(6)	0.0024(5)	0.0009(5)
Sr(2)	0.7769(3)	0.025(3)	0.3661(4)	0.0102(3)	0.0096(6)	0.0093(7)	-0.0049(5)	0.0042(6)	-0.0010(4)
Sr(3)	0.1204(3)	0.3442(3)	0.3763(4)	0.0115(6)	0.0103(3)	0.0105(7)	-0.0052(5)	0.0041(4)	-0.0008(5)
Zr	0	0	0	0.0064(6)	0.0052(7)	0.0058(6)	-0.0028(4)	0.0022(4)	-0.0002(4)
Na(1)	0.321(1)	0.336(1)	-0.014(1)	0.016(3)	0.022(4)	0.013(3)	-0.009(3)	0.001(3)	0.000(3)
Na(2)	0.661(1)	0.670(1)	-0.013(1)	0.015(3)	0.015(3)	0.010(3)	-0.009(3)	0.006(2)	-0.004(2)
C(1)	0.409(2)	0.000(2)	0.252(2)	0.009(2)					
C(2)	0.081(2)	0.675(2)	0.245(2)	0.011(2)					
C(3)	0.749(1)	0.325(1)	0.236(2)	0.006(2)					
C(4)	0.833(2)	0.308(2)	0.801(2)	0.013(2)					
C(5)	0.236(1)	0.799(1)	0.795(2)	0.007(2)					
C(6)	0.722(2)	0.900(2)	0.790(2)	0.012(2)					
O(1)	0.060(1)	-0.003(1)	0.248(2)	0.008(4)	0.019(5)	0.011(4)	-0.007(3)	0.003(3)	-0.004(4)
O(2)	0.415(1)	0.140(2)	0.289(2)	0.013(4)	0.010(4)	0.021(5)	-0.010(3)	0.007(4)	-0.003(4)
O(3)	0.538(1)	-0.143(1)	0.219(2)	0.009(4)	0.024(5)	0.016(5)	-0.007(5)	0.010(4)	-0.002(4)
O(4)	-0.060(1)	0.660(1)	0.253(2)	0.013(4)	0.017(5)	0.023(5)	-0.009(4)	0.004(4)	0.002(4)
O(5)	0.079(1)	0.824(1)	0.244(2)	0.003(3)	0.007(4)	0.008(4)	-0.004(3)	0.002(3)	-0.003(3)
O(6)	0.226(1)	0.535(1)	0.250(2)	0.014(4)	0.008(4)	0.018(5)	-0.005(3)	0.007(4)	-0.003(4)
O(7)	0.616(1)	0.320(1)	0.247(2)	0.014(4)	0.011(4)	0.018(5)	-0.008(3)	0.015(4)	-0.011(4)
O(8)	0.749(1)	0.464(1)	0.224(2)	0.015(4)	0.012(4)	0.016(5)	-0.007(4)	0.009(4)	-0.006(4)
O(9)	0.925(1)	0.179(1)	0.251(2)	0.016(4)	0.006(4)	0.009(4)	-0.002(3)	0.010(3)	0.000(3)
O(10)	0.763(1)	0.199(1)	0.735(1)	0.015(4)	0.008(4)	0.008(4)	-0.002(3)	-0.001(3)	-0.002(3)
O(11)	0.745(1)	0.456(1)	0.714(2)	0.018(4)	0.005(4)	0.017(5)	-0.002(3)	0.008(4)	0.004(4)
O(12)	0.999(1)	0.252(1)	0.360(1)	0.014(4)	0.016(4)	0.009(4)	-0.005(4)	0.000(3)	0.005(3)
O(13)	0.102(1)	0.952(1)	0.731(1)	0.011(4)	0.013(4)	0.012(4)	-0.006(3)	0.003(3)	0.001(4)
O(14)	0.358(1)	0.711(1)	0.713(2)	0.016(4)	0.015(4)	0.015(5)	-0.008(4)	0.005(4)	0.003(4)
O(15)	0.235(1)	0.741(1)	0.957(1)	0.011(4)	0.010(4)	0.004(4)	-0.004(4)	0.005(3)	0.000(3)
O(16)	0.608(1)	0.839(1)	0.793(2)	0.019(5)	0.023(5)	0.015(5)	-0.017(4)	0.006(4)	-0.005(4)
O(17)	0.857(1)	0.059(1)	0.727(2)	0.011(4)	0.012(4)	0.014(4)	-0.008(3)	0.004(3)	0.001(3)
O(18)	0.721(1)	1.005(1)	0.951(1)	0.018(4)	0.020(4)	0.004(4)	-0.015(4)	0.006(3)	-0.006(3)
W(1)	0.272(1)	0.132(1)	0.711(2)	0.018(4)	0.016(5)	0.020(5)	-0.010(4)	0.009(4)	0.000(4)
W(2)	0.022(1)	0.507(1)	0.700(2)	0.010(4)	0.013(4)	0.016(5)	-0.003(3)	0.006(4)	-0.001(4)
W(3)	0.400(1)	0.381(1)	0.717(2)	0.013(4)	0.012(4)	0.022(5)	-0.006(4)	0.008(4)	-0.005(4)

\*Anisotropic thermal parameters refer to the expression:  $T = \exp -2\pi^2 (U_{11}h^2 + U_{22}k^2 + U_{33}l^2 + 2U_{12}hk + 2U_{13}hl + 2U_{23}kl \dots)$

in the centers of the Zr and Sr atoms. When the anomalous dispersion correction was included in the least-squares refinement a curious feature arose on the  $\Delta F$  maps; on either side of each of the Zr and Sr atomic positions, there appeared a large negative electron density on one side and a positive peak of corresponding magnitude on the other side. This configuration was approximately parallel with the  $c$ -axis. These anomalies were interpreted as having arisen due to incorrect choice of enantiomorph. Changing all  $hkl$ 's to  $\bar{h}\bar{k}\bar{l}$ 's cleared the  $\Delta F$  map of this feature and reduced the  $R$  factor from 0.072 to  $R = 0.048$ .

Refinement was continued by using anisotropic temperature factors for all atoms. For some of the carbon atoms this led to negative values and it was decided to use isotropic temperature factors for all six of them. The final  $R$ -factor for the 2354 observed reflections was  $R = 0.043$ .

Table 3 gives the final atomic parameters and temperature factors, and Table 4\* the final observed ( $F_o$ ) and calculated ( $F_c$ ) struc-

ture factors for the triclinic weloganite structure. The structure as drawn by ORTEP (Johnson 1970) appears in Figure 1.

#### DISCUSSION OF THE STRUCTURE

The triclinic structure of weloganite is very strongly pseudo-trigonal. This is evident not only from the cell parameters with  $a \approx b$  and  $\gamma \approx 60^\circ$  or  $120^\circ$ , but also from the structural arrangement of the six carbonate groups, three water molecules, and the coordination symmetry about each of the six cations; all of this will be discussed in the following paragraphs. The structure is dominated by six carbonate groups. Each carbonate group is very close to being planar and the usual equilateral triangles of oxygen atoms about each carbon are only slightly distorted (Table 5). The oxygen atoms in the structure lie in three planes parallel to (001) at heights of 0.25, 0.72 and 0.95  $c$ . In the plane at height 0.72  $c$  there are also three water molecules.

The three carbonate groups centered by carbon atoms C(1), C(2), and C(3) at a height of approximately 0.25 of the  $c$ -repeat are coplanar with the  $a$ - $b$  plane and have roughly 3-fold symmetry around the Na(1) site. In Table 5 it can be seen that there is one C-O distance longer than the other two in each of these groups (C(1)-O(1), C(2)-O(5), C(3)-O(9));

\*Table 4 has been deposited with the Depository of Unpublished Data. Copies may be obtained on request to: Depository of Unpublished Data, National Science Library, National Research Council of Canada, Ottawa, Ontario, Canada.

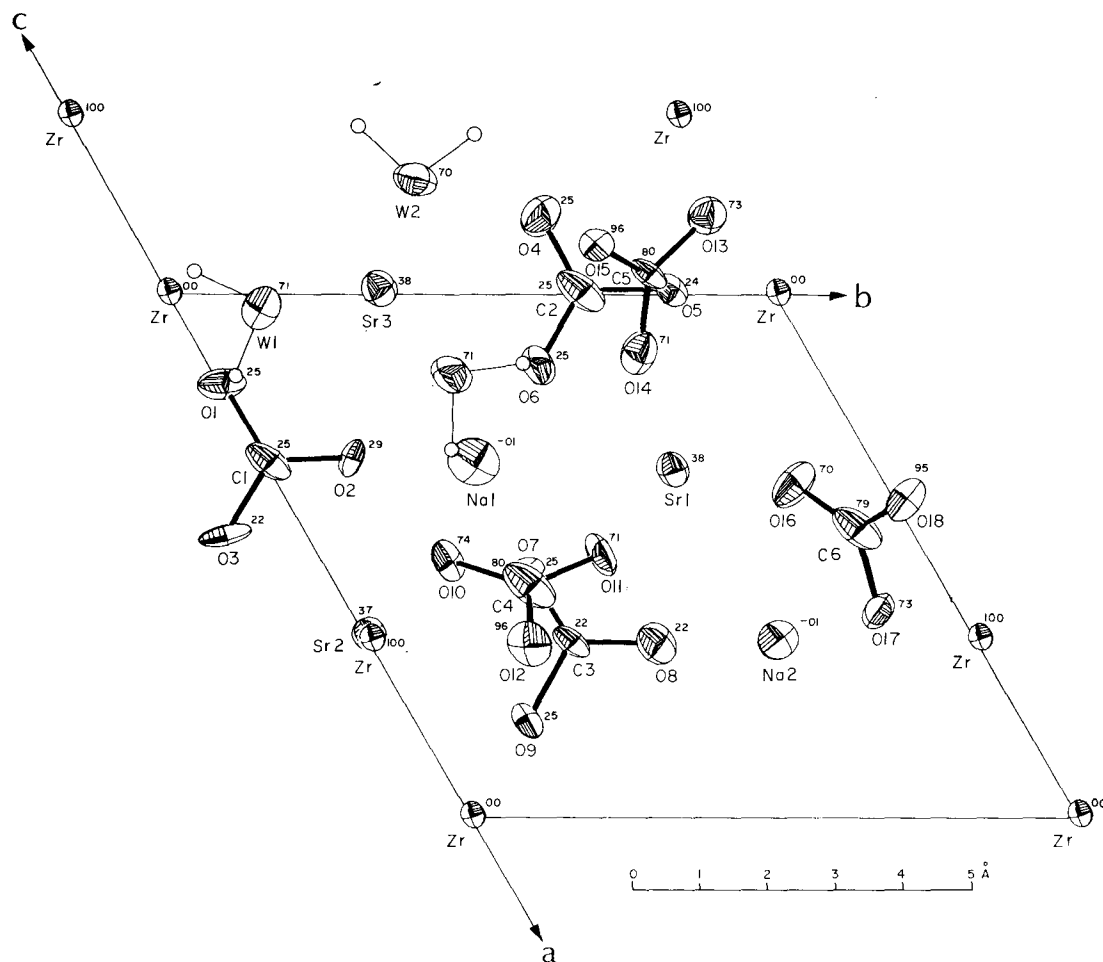


FIG. 1. ORTEP drawing of the triclinic structure of weloganite. The view is down  $c^*$ : elevations of each atom above the base (001) in fractional coordinates  $\times 100$ . The hydrogen atoms as located by valence sums and linear O-H-O bonds have been added to the water ( $W$ ) molecules.

this distortion is probably attributable to each of these oxygens being bonded to zirconium as well. The good {001} cleavage could be explained in terms of this carbonate plane in addition to the plane of oxygen atoms and water molecules at a height of approximately  $0.75c$ .

The other three carbonate groups centered by carbon atoms C(4), C(5), and C(6) at an average height of 0.80 of the  $c$ -repeat are not coplanar with the  $a$ - $b$  plane. In each of these groups two of the oxygens are at a height of about 0.72 whereas the other is about 0.95. The planes described by these three carbonate groups would correspond to the {1011} planes of the pseudo-trigonal cell with  $c = 18\text{\AA}$ . Furthermore, these three groups are in ap-

proximately 3-fold symmetry centered about the Sr(1) site.

A survey of all O-O (or  $W$ ) distances for O (or  $W$ ) not bonded to the same cation gave only six values smaller than  $3.2\text{\AA}$ : these are  $W(1)\text{-O}(13)$ ,  $W(1)\text{-O}(16)$ ,  $W(2)\text{-O}(11)$ ,  $W(2)\text{-O}(17)$ ,  $W(3)\text{-O}(10)$  and  $W(3)\text{-O}(14)$ . This made the interpretation of hydrogen bonding rather straight-forward. Table 6 gives the coordination of water molecules. Each of the water molecules is bonded to the Sr(3) and Na(1) cations and is hydrogen-bonded to two oxygen atoms. Water-oxygen bond lengths vary from  $2.75$  ( $W2\text{-O}17$ ) to  $2.86$  ( $W1\text{-O}16$ ) with the average for the six bonds being  $2.79\text{\AA}$ . Also of interest in Table 6 are the bond angles surrounding each water molecule; the averages

TABLE 5. BOND DISTANCES AND ANGLES FOR WELOGANITE (standard deviations in parentheses)

Bond distances (Å)		Bond angles (degrees)		Bond distances (Å)		Bond angles (degrees)		
Sr(1) - O(5)	2.79(1)	O(5) - Sr(1) - O(6)	49.1(3)	Na(1) - O(2)	2.54(2)	O(2) - Na(1) - O(6)	78.1(5)	
O(6)	2.63(1)	O(1)	59.2(4)	O(6)	2.35(1)	O(2)	77.3(5)	
O(7)	2.75(1)	O(7)	68.9(3)	O(7)	2.38(1)	O(6)	80.2(5)	
O(8)	2.76(1)	O(8)	47.5(4)	W(1)	2.36(1)	W(1)	W(2)	76.0(4)
O(11)	2.62(1)	O(3)	68.3(4)	W(2)	2.41(1)	W(1)	W(3)	77.2(6)
O(14)	2.71(1)	O(3)	48.2(3)	W(3)	2.41(2)	W(2)	W(3)	75.5(5)
O(16)	2.66(1)	O(11)	69.9(4)	mean	2.408	mean		77.5
O(1)	2.76(1)	O(16)	69.9(3)	Na(2) - O(8)	2.30(2)	O(8) - Na(2) - O(4)	52.9(5)	
O(3)	2.73(2)	O(16)	68.4(5)	O(4)	2.37(1)	O(8)	O(3)	65.3(6)
O(15)	2.64(1)	O(15)	124.3(3)	O(3)	2.25(1)	O(4)	O(3)	80.2(5)
mean	2.705	mean	67.4	O(11)	2.42(1)	O(11)	O(14)	78.8(4)
Sr(2) - O(2)	2.66(1)	O(2) - Sr(2) - O(3)	48.6(3)	O(14)	2.39(1)	O(11)	O(16)	77.1(5)
O(3)	2.73(1)	O(2)	71.6(4)	O(16)	2.43(2)	O(14)	O(16)	77.5(5)
O(7)	2.59(1)	O(3)	69.1(3)	mean	2.360	mean		80.6
O(9)	2.76(1)	O(7)	49.3(3)	C(1) - O(1)	1.34(2)	O(1) - C(1) - O(2)	119(1)	
O(10)	2.72(1)	O(9)	59.5(3)	O(2)	1.25(2)	O(1)	O(3)	116(1)
O(4)	2.62(1)	O(4)	48.7(4)	O(3)	1.27(2)	O(2)	O(3)	123(2)
O(5)	2.77(1)	O(10)	60.1(3)	mean	1.29	mean		120
O(13)	2.74(1)	O(10)	61.0(3)	C(2) - O(4)	1.27(2)	O(4) - C(2) - O(5)	117(1)	
O(17)	2.64(1)	O(13)	60.2(4)	O(5)	1.34(2)	O(4)	O(6)	123(2)
O(18)	2.61(1)	O(2)	95.0(3)	O(6)	1.27(1)	O(5)	O(6)	120(2)
mean	2.684	mean	62.35	mean	1.29	mean		120
Sr(3) - O(1)	2.81(1)	O(1) - Sr(3) - O(2)	48.4(4)	C(3) - O(7)	1.26(2)	O(7) - C(3) - O(8)	123(1)	
O(2)	2.60(1)	O(1)	59.6(3)	O(8)	1.27(2)	O(7)	O(9)	129(1)
O(4)	2.72(1)	O(2)	70.6(4)	O(9)	1.34(1)	O(8)	O(9)	127(1)
O(6)	2.73(2)	O(4)	48.3(4)	mean	1.29	mean		120
O(8)	2.69(1)	O(4)	69.7(4)	C(4) - O(10)	1.31(2)	O(10) - C(4) - O(11)	122(1)	
O(9)	2.75(1)	O(8)	48.2(3)	O(11)	1.27(2)	O(10)	O(12)	115(1)
O(12)	2.62(1)	O(9)	71.4(3)	O(12)	1.29(1)	O(11)	O(12)	123(2)
W(1)	2.67(1)	W(1)	68.5(3)	mean	1.29	mean		120
W(2)	2.59(1)	W(1)	68.5(4)	C(5) - O(13)	1.29(1)	O(13) - C(5) - O(14)	124(2)	
W(3)	2.62(1)	W(2)	69.0(4)	O(14)	1.27(2)	O(13)	O(15)	113(1)
mean	2.680	mean	62.2	O(15)	1.32(2)	O(14)	O(15)	122(1)
Zr - O(1)	2.17(1)	O(1) - Zr - O(5)	78.5(5)	mean	1.29	mean		120
O(5)	2.16(1)	O(1)	78.4(4)	C(6) - O(16)	1.25(2)	O(16) - C(6) - O(17)	124(1)	
O(9)	2.21(1)	O(5)	78.4(4)	O(17)	1.32(2)	O(16)	O(18)	124(2)
O(15)	2.30(1)	O(9)	118.6(4)	mean	1.29	mean		120
O(12)	2.34(1)	O(15)	118.0(4)	C(6) - O(17)	1.29(2)	O(17) - C(6) - O(18)	122(1)	
O(18)	2.34(1)	O(12)	119.5(4)	mean	1.29	mean		120
O(13)	2.25(1)	O(12)	74.8(4)					
O(10)	2.26(1)	O(13)	73.5(5)					
O(17)	2.26(1)	O(10)	74.2(4)					
mean	2.254	mean	90.4					

for these angles are: O-W-O 98°, Sr-O-Na 94°, Sr-W-O on either side 122° and 111°, and Na-W-O angles on either side 120° and 113°. The environment of W(3), representative of all three water molecules, is shown in Figure 2.

In Figure 2 it can be seen that the water molecule has a very rough tetrahedral coordination in this structure. If the hydrogen bonds are linear, the H-O-H bond angle within the water molecule would be 98° while the angle between the two "lone pairs of electrons", now involved in bonding to the Sr(3) and Na(1) atoms, is about 93°. These two angles are considerably less than 109.5°, the ideal tetrahedral angle, and the other angles of approximately 121° and 111° are somewhat larger.

Although the average H-O-H bond angle in weloganite (98°) is quite different from that in ice (105°), the H-O bond length is probably very similar. In ice, O-O bond lengths are 2.76Å and in weloganite the average W-O distance involved in hydrogen bonding is 2.79Å, which is very similar. Thus, if the hydrogen bonding is linear in weloganite, we might expect the O-H bond length to be close to, but slightly smaller than its 1.01Å length in ice (Lippincott & Schroeder 1955). We have assigned approximate positions for the hydrogen atoms assuming a distance of 1.0Å to the donor atom and a linear O-H-O bond (Table 6).

The three Sr atomic sites in the weloganite structure have similar environments. Any calcium in the structure would likely occupy these sites, but the least-squares refinement did not clearly indicate any preference for Ca in any one of the three sites. The 10-fold coordination observed for Sr<sup>2+</sup> is not unusual

TABLE 6. BOND DISTANCES AND ANGLES WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES FOR WATER MOLECULES

Bond distance (Å)		Bond angle (°)		
W(1) - O(13)	2.77(2)	O(13) - W(1) - O(16)	96.7(5)	
O(16)	2.86(1)	Sr(3)	Na(1)	93.4(5)
Sr(3)	2.67(1)	Sr(3)	O(13)	122.9(4)
Na(1)	2.36(1)	Sr(3)	O(16)	109.8(6)
		Na(1)	O(13)	120.3(7)
		Na(1)	O(16)	114.6(5)
W(2) - O(11)	2.79(2)	O(11) - W(2) - O(17)	98.4(5)	
O(17)	2.75(1)	Sr(3)	Na(1)	94.3(4)
Sr(3)	2.59(1)	Sr(3)	O(11)	113.0(5)
Na(1)	2.41(1)	Sr(3)	O(17)	122.1(6)
		Na(1)	O(11)	109.5(6)
		Na(1)	O(17)	120.1(5)
W(3) - O(10)	2.76(2)	O(10) - W(3) - O(14)	97.7(6)	
O(14)	2.79(2)	Sr(3)	Na(1)	93.4(5)
Sr(3)	2.62(1)	Sr(3)	O(10)	121.2(5)
Na(1)	2.41(2)	Sr(3)	O(14)	110.5(4)
		Na(1)	O(10)	120.6(5)
		Na(1)	O(14)	114.2(5)

## PROPOSED HYDROGEN POSITIONS

Assuming a linear O-H-O bond and a 1.0Å distance between the hydrogen atom and the donor oxygen.

	x	y	z
H(1)	0.21	0.07	0.72
H(2)	0.39	0.02	0.71
H(3)	0.92	0.49	0.71
H(4)	0.96	0.64	0.71
H(5)	0.53	0.31	0.72
H(6)	0.38	0.50	0.71

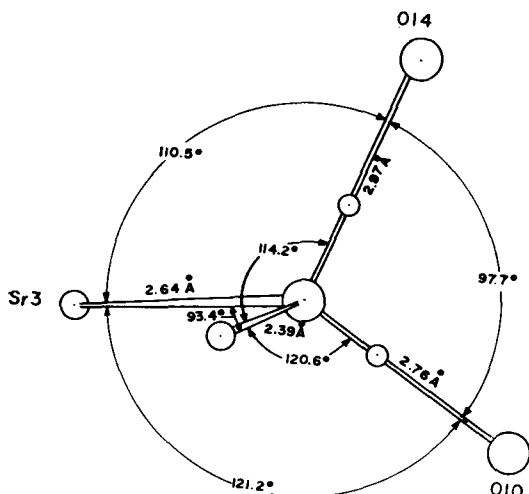


FIG. 2. The tetrahedral coordination of  $W(3)$  water molecule viewed down  $c[001]$ .

and the average Sr-O bond length of  $2.69\text{\AA}$  is close to the  $2.70\text{\AA}$  calculated using Shannon & Prewitt's (1969) atomic radii of  $1.38\text{\AA}$  for  $O^{2-}$  surrounded by four cations and  $1.32\text{\AA}$  for  $Sr^{2+}$  in 10-fold coordination.

The 10 ligands surrounding each  $Sr^{2+}$  cation could be roughly contained within a hexagonal dipyrmaid. Figure 3, representing the coordi-

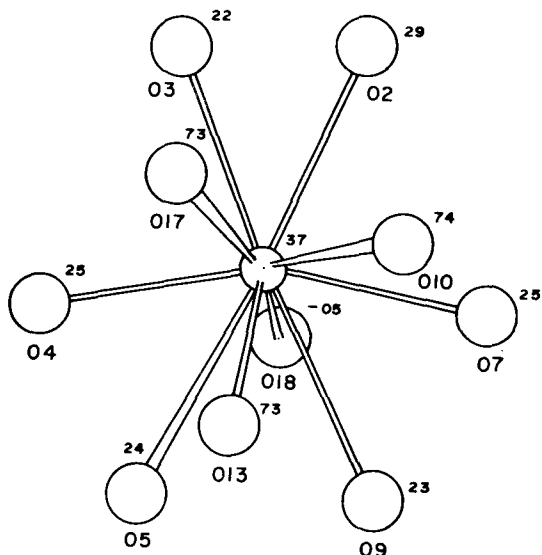


FIG. 3. The 10-fold coordination of  $Sr(2)$ . Numbers indicate the atom number and the elevation above the reference plane (001). View along the  $c^*$ -axis direction.

nation for the  $Sr(2)$  atom, is representative of all three. Note the six oxygen atoms at elevation  $0.25c$  describing a roughly hexagonal plane, the  $Sr(2)$  atom at elevation  $0.37c$ , the upper apical oxygen atom at elevation  $0.95c$ , and the three lower oxygens at  $0.73c$ . This coordination has approximately  $C_{3v}$  symmetry and it is expected that the  $\sigma$  bonds would occupy the five  $4d$ , one  $5s$ , three  $5p$ , and one  $6s$  orbitals.

Both Na atomic sites in the weloganite structure have 6-fold coordination, but the configuration and bond lengths about each differ. About the Na(1) site are three water molecules below, and three oxygens above the Na atom in a trigonal prism arrangement with  $D_{3h}$  symmetry. The average Na(1)-O distance is  $2.41\text{\AA}$ , which is close to the calculated value of  $2.40\text{\AA}$  (Shannon & Prewitt 1969), whereas the Na(2)-O distance is  $2.36\text{\AA}$ , which is considerably shorter. The six oxygens around the Na(2) cation have a slightly distorted octahedral arrangement with  $O_h$  symmetry. The ligand repulsion in the trigonal prism would be greater than that for the octahedron, and this would explain the shorter and hence more stable bonds observed for the Na(2) atomic site.

Due to the small ionic radius of  $Zr^{4+}$  ( $0.80\text{\AA}$ ) the 9-fold coordination that is observed in weloganite is unusual. Although the ionic radius is small for this high a coordination, the noble-gas formalism would in fact predict nine ligands as the stable configuration about a  $Zr^{4+}$  ion: *i.e.* five  $\sigma$  bonds in  $4d$ , one in  $5s$ , and three in  $5p$ , adding 18 electrons to the 36 of the  $Zr^{4+}$  ion gives a total of 54 electrons which is the number for xenon.

The nine oxygen atoms around the  $Zr^{4+}$  atomic site are distributed at three elevations:  $0.25c$ ,  $0.73c$  and  $0.96c$  (Fig. 4). The arrangement has approximately  $D_{3h}$  symmetry. The average Zr-O bond distance of  $2.25\text{\AA}$  is reasonable since the predicted bond length from Shannon & Prewitt (1969) for  $Zr^{4+}$  in 8-fold coordination is  $2.22\text{\AA}$ , which is slightly smaller, as expected.

Bond-valence summations are presented in Table 7. They bear out the location of hydrogen bonding in this structure. All summations for the oxygen atoms are centered on a valence of 2.00, with variations from 1.87 for O(15) to 2.15 for O(13). Considering the chemical uncertainties associated with this mineral, and more particularly the high water content, we are satisfied that the distribution of valences as per Table 7 bears out the essential correctness of this structure.

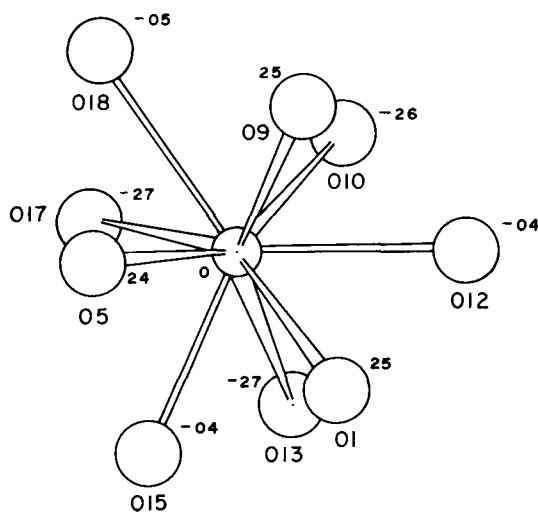


Fig. 4. The 9-fold coordination of Zr. Numbers indicate the atom numbers and the elevation above the reference plane (001). View along the  $c^*$ -axis direction.

The triclinic weloganite crystal structure derived here can be readily "expanded" into the trigonal cell described by Sabina *et al.* (1968) with  $a = b = 8.96\text{\AA}$  and  $c = 18.1\text{\AA}$  in space group  $P3_1 2$ . This is done by retaining the present triclinic  $a$  and  $b$  axes and taking three consecutive triclinic cells along the triclinic  $c^*$  axis ( $1/c^*$  for triclinic weloganite equals  $6.01\text{\AA}$ ). This tripling of the cell volume gives the trigonal cell contents,  $\text{Sr}_9\text{Zr}_3\text{Na}_6(\text{CO}_3)_{18} \cdot 9\text{H}_2\text{O}$ . Figure 5 shows only the Sr, Zr and Na sites of the tripled triclinic cell and for convenience the orientation of Figure 1 has been retained ( $\gamma = 60^\circ$  and not the usual  $120^\circ$

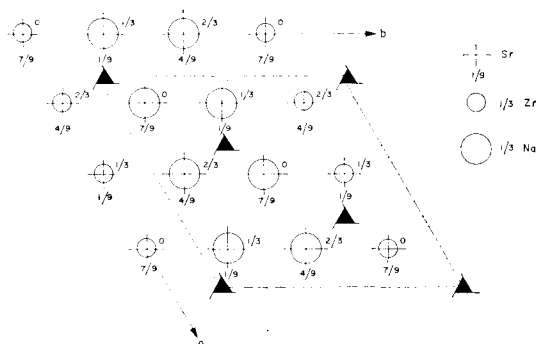


FIG. 5. Expansion of the triclinic cell of weloganite into a theoretical trigonal cell (outlined) by taking three consecutive triclinic cells along  $c^*$ . Only the metal positions are shown.

for the trigonal system). With this simplified structure it is possible to choose several cells with space-group symmetry close to that of either  $P3_1$  or  $P3_2$ ; one such cell for  $P3_1$  is outlined in Figure 5. Within the outlined cell the Sr sites and the carbonate groups centered by C1, C2 and C3 (not shown) need no changes to convert from the triclinic to a trigonal structure. The Na and Zr sites need no positional changes, but require ordering about the 3 axes. The positions of the carbonate groups centered by C4, C5 and C6 in the triclinic cell need only small positional changes to be compatible with the location of the 3 screw axes shown in Figure 5. These 3 sites give the only indication of preference of the  $P3$  enantiomorph over the  $P\bar{3}$  structure. The addition of the trigonal screw axes in the structure creates possible additional water molecule sites and this could explain the observed variance in water analyses (Table 1), depending on how much of each polymorph is in the bulk sample.

Although the authors acknowledge the fact there is a great deal of twinning in weloganite as reported by Chen & Chao (1974), it is felt that there is a distinct possibility of a trigonal weloganite polymorph and this is being presently investigated.

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TABLE 7. BOND DISTANCES AND ESTIMATED BOND VALENCES

	X Sr 1	X Sr 2	X Sr 3	IX Zr	VI Na 1	VI Na 2	III C 1	III C 2	III C 3	III C 4	III C 5	III C 6	Zc v	dev. P bonds	Eq. total
IV O 1	2.76 (0.18)		2.61 (0.16)	2.17 (0.55)			1.34 (1.20)						2.09		2.09
IV O 2		2.66 (0.21)	2.60 (0.23)		2.54 (0.13)		1.25 (1.43)						2.00		2.00
IV O 3	2.73 (0.19)	2.73 (0.18)				2.25 (0.19)	1.27 (1.58)						1.94		1.94
IV O 4		2.62 (0.22)	2.72 (0.19)			2.37 (0.16)		1.27 (1.39)					1.96		1.96
IV O 5	2.79 (0.17)	2.77 (0.17)		2.16 (0.57)				1.34 (1.20)					2.11		2.11
IV O 6	2.63 (0.23)		2.73 (0.18)		2.35 (0.18)			1.26 (0.41)					2.00		2.00
IV O 7	2.75 (0.18)	2.59 (0.24)			2.38 (0.18)				1.26 (1.41)				2.01		2.01
IV O 8	2.76 (0.18)		2.69 (0.20)			2.30 (0.18)			1.27 (1.39)				1.95		1.95
IV O 9		2.76 (0.17)	2.75 (0.18)	2.21 (0.50)					1.34 (1.20)				2.05		2.05
III O 10			2.72 (0.19)	2.26 (0.44)					1.31 (1.27)				1.90	0.18	2.08
III O 11	2.62 (0.23)					2.42 (0.15)			1.27 (1.39)				1.77	0.17	1.94
III O 12			2.62 (0.22)	2.34 (0.35)					1.29 (1.33)				1.90		1.90
III O 13		2.74 (0.18)		2.25 (0.45)						1.29 (1.34)			1.97	0.18	2.15
III O 14	2.71 (0.20)					2.39 (0.16)				1.27 (1.40)			1.76	0.17	1.93
III O 15	2.64 (0.22)			2.30 (0.39)						1.32 (1.26)			1.87		1.87
III O 16	2.66 (0.22)					2.43 (0.15)					1.25 (1.43)		1.80	0.14	1.94
III O 17		2.64 (0.22)		2.26 (0.44)						1.32 (1.24)			1.90	0.19	2.09
III O 18		2.61 (0.23)		2.34 (0.35)						1.29 (1.32)			1.90		1.90
W 1			2.67 (0.20)		2.36 (0.18)								0.38	-0.18 -0.14	0.06
W 2			2.59 (0.23)		2.41 (0.16)								0.39	-0.17 -0.19	0.03
W 3			2.62 (0.22)		2.41 (0.16)								0.38	-0.18 -0.17	0.03
I	2.705	2.684	2.680	2.254	2.408	2.360	1.287	1.290	1.290	1.290	1.293	1.287			
Eqv	2.00	2.01	2.01	4.04	0.99	0.99	4.01	4.00	4.00	3.99	4.00	3.99			36.03

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