Canadian Mineralogist
Vol. 13, pp. 22-26 (1975)

X-RAY CRYSTALLOGRAPHY OF WELOGANITE

T. T. CHEN AND G. Y. CHAO
Department of Geology, Carleton University, Ottawa, Ontario K1S 5B6

ABSTRACT

Single-crystal *x*-ray studies of weloganite showed that the mineral is triclinic, $P1$ or $P\bar{1}$, with a = 8.988(1), b = 8.988(1), c = 6.730(1)Å, α = 102.84(1), β = 116.42(2) and γ = 59.99(1)°. Weloganite has a pronounced rhombohedral subcell which resembles in geometry that of rhombohedral carbonates. It also displays a pseudo-monoclinic cell that corresponds to the cell reported by other authors for the monoclinic polytype of weloganite. Twinning by $[103]_{120°}$ is very common, with twin obliquity $\omega = 0$ and twin index $n = 3$. The twin cell is trigonal and is identical to the cell originally assigned to weloganite. The ideal chemical formula for weloganite is proposed as $Na_2Sr_3Zr(CO_3)_6 \cdot 3H_2O$ with $Z = 1$ for the triclinic cell.

INTRODUCTION

Weloganite, a hydrated carbonate of Na, Sr and Zr from St. Michel, Montreal Island, Quebec, was originally described by Sabina *et al.* (1968). The symmetry of weloganite was considered to be trigonal $P3_{1,2}$ with a = 8.96 and c = 18.06Å. The cell contained two units of $Sr_5Zr_2C_9H_8O_{31}$. The authors noted the discrepancy that, between crossed nicols, nearly all cleavage (basal) fragments gave an off-centred biaxial interference figure with $2V$ about 15°. The mineral was later restudied by Gait & Grice (1971) who reported a monoclinic polytype with $C2/c$, $C2$ or Cc symmetry and a = 8.95, b = 15.54, c = 37.09Å and β = 103°45′. The *x*-ray powder diffraction patterns of the two polytypes were indistinguishable. The relationships between the two polytypes were given as $a_M = a_T$, $b_M = 2a_T\sin 60°$, and $c_M = 2c_T$ cosec(180°-β). Based on a new analysis the chemical formula of weloganite was revised to $(Sr_{1.36}Na_{1.08}Zr_{0.45}Ca_{0.11})(CO_3)_3 \cdot 2H_2O$ with $Z = 24$ for the monoclinic cell and $Z = 6$ for the trigonal cell.

Our interests in weloganite began when an unknown mineral from Mont St. Hilaire was brought to our attention and shown to be an yttrium analogue of weloganite. The crystals of this yttrium mineral were composed of parallel intergrowths of a large number of individuals that were too small to be separated for single-crystal *x*-ray studies. It was hoped that once the cell geometry of weloganite was established the cell parameters of the unknown yttrium mineral might be derived from the powder diffraction data by its isomorphous relationship to weloganite.

The problems of weloganite may be outlined as follows:

(1) The space group $P3_{1,2}$ is one of the few in which no minerals and only a few chemical compounds are found, as Sabina *et al.* (1968) correctly pointed out.

(2) If the published chemical analyses and space group symmetry (Sabina *et al.* 1968; Gait & Grice 1971) are correct they would require the positional disorder of Sr, Na and Zr atoms which crystal-chemically are drastically different.

(3) The *x*-ray precession photographs of the so-called trigonal polytype showed peculiar extra-space-group systematic extinctions with reflections of the type h-k = $3n$ absent when $h+l$ and $k+l$ are not equal to $3n$.

(4) The relative intensities of many weak reflections on the precession photographs appeared to be variable from crystal to crystal.

(5) The deviation of the acute bisectrix by more than 5° from the normal to the basal cleavage, consistently observed on grains lying on the cleavage plane, suggests that the symmetry of weloganite cannot be higher than monoclinic.

OPTICAL OBSERVATIONS

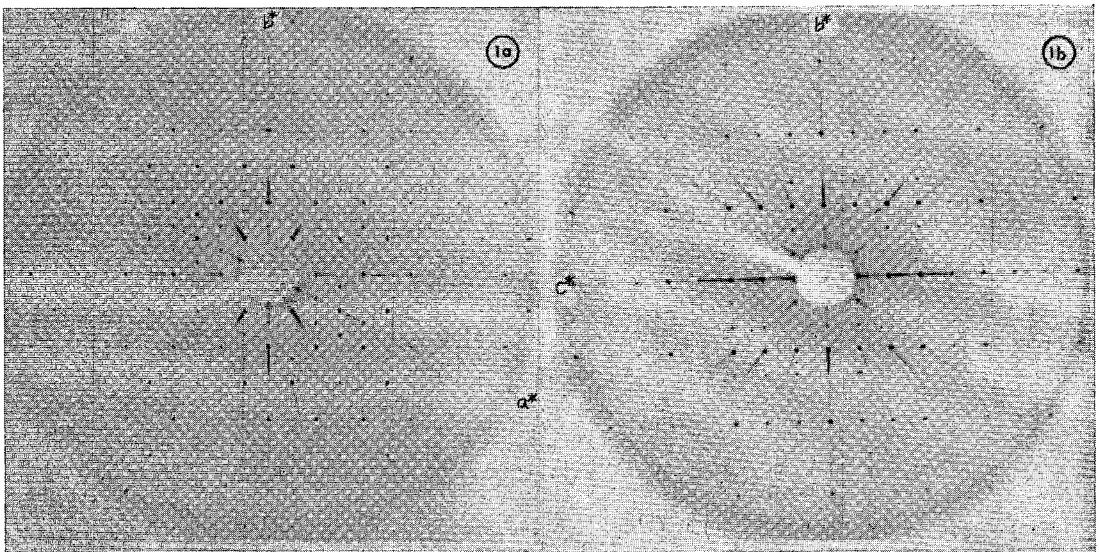
Prior to *x*-ray single-crystal studies weloganite was examined optically using both immersion mounts of crushed grains and thin sections of large crystals. Both colourless and yellow varieties were examined. The biaxial characteristics of weloganite reported by Sabina *et al.* (1968) were confirmed.

In the immersion mounts two types of grains were noted. Type I grains, although free of twin lamellae, either did not show sharp extinctions or showed no extinctions at all between crossed nicols. For the type I grains $2V$ ranged from 10 to 15°. Type II grains were characterized by sharp and homogeneous extinction between crossed nicols and considerably larger $2V$ (about 20°). Type I was by far the more common.

One thin section of a large crystal cut parallel to the basal cleavage showed a distinct core in the form of a nearly perfect equilateral triangle surrounded by material showing relatively coarse twin lamellae and patchy extinctions. Along the well-defined boundaries there was, at places, a thin veneer of very fine-grained pyrite. The core material gave extinctions that were sharper but not homogeneous over the whole area. $2V$ was very small, about 2 to 5°, or nearly uniaxial in contrast to the $2V$ of 10 to 15° for the surrounding material. Both the rim and the core, however, gave identical powder diffraction patterns.

X-Ray Crystallography

Many crystal fragments were selected from the immersion mounts, after careful examination under the polarizing microscope, for single-crystal x-ray diffraction studies. Precession photographs of type II grains consistently showed triclinic diffraction symmetry corresponding to



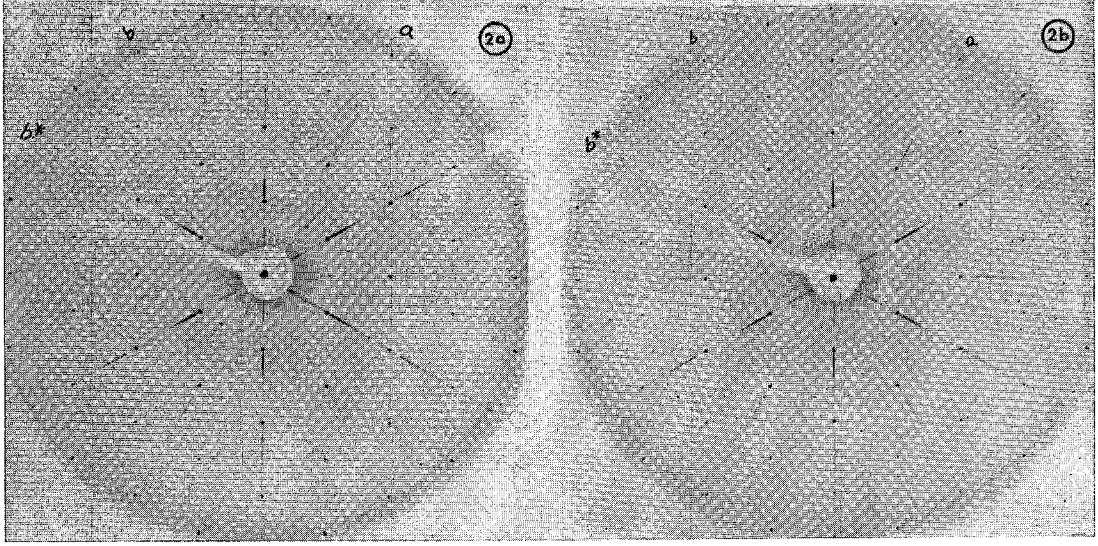


FIG. 1. Precession photographs (0-level, $\mu = 30°$, Mo$K\alpha$ radiation) of a single crystal of weloganite showing (a) the a^*-b^* net and (b) the b^*-c^* net with a pseudo-mirror plane normal to b^*.

FIG. 2. [103] - precession photographs (0-level, $\mu = 30°$, Mo$K\alpha$ radiation) of weloganite (a) single crystal and (b) crystal twinned by $[103]_{120°}$ resulting in trigonal symmetry. Pseudo-rhombohedral symmetry is evident in both (a) and (b) from the strong reflections.

space groups $P1$ or $P\bar{1}$ (Figs. 1 and 2). The parameters of the triclinic cell presented in Table 1 are results of least-squares refinement using powder diffraction data. The cell, although not a reduced one, was chosen because the relationship between the present cell and the trigonal cell of Sabina *et al.* (1968) may be described in simple terms ($a_{\text{tric}} = a_{\text{trig}}$, $b_{\text{tric}} = -b_{\text{trig}}$ and $c^*_{\text{tric}} = -3c^*_{\text{trig}}$) and it brings out clearly the pseudo-symmetry of the mineral ($a=b$ $\gamma=60°$ and $\alpha^*=90°$). Due to the high pseudo-symmetry of the lattice there are two equally acceptable choices for the reduced cell, which may be derived from the present cell by the transformations $101/\bar{1}10/00\bar{1}$ and $\bar{1}0\bar{1}/010/001$. The parameters of both reduced cells are compared in Table 1 with those of the chosen cell.

TABLE 1. CELL PARAMETERS OF WELOGANITE

	Adopted Cell	Reduced Cells	
		(1)	(2)
a	8.988(1)Å	8.500Å	8.500Å
b	8.988(1)	8.987	8.988
c	6.730(1)	6.730	6.730
α	102.84 (1)°	102.87°	102.84°
β	116.42 (2)	108.74	108.74
γ	59.99 (1)	110.63	110.67
V	421.62Å^3	421.62Å^3	421.62Å^3
a*	0.13988(2)Å^{-1}	0.1398Å^{-1}	0.1399Å^{-1}
b*	0.12848(2)	0.1285	0.1285
c*	0.16592(4)	0.1696	0.1695
α*	90.01(1)°	67.73°	67.74°
β*	66.71(1)	64.01	64.01
γ*	117.35(1)	62.67	62.64

Transformation matrix from adopted cell to reduced cell (1) = $101/\bar{1}10/00\bar{1}$ and to (2) = $\bar{1}0\bar{1}/010/001$.

The weloganite lattice has a nearly ideal rhombohedral sub-cell with $a_{\text{rhom}} = \frac{1}{2} a_{\text{trig}}/\sin 60° = \frac{1}{2} a_{\text{tric}}/\sin 60° = 5.161$Å and $c_{\text{rhom}} = c_{\text{trig}} = 17.901$Å. This sub-cell is evident from the fact that reflections that do not conform to the requirement of rhombohedral symmetry are either absent or very weak (Fig. 2a). The geometry of the rhombohedral sub-cell resembles that of the cells of the rhombohedral carbonates such as calcite ($a = 4.9898$ and $c = 17.060$Å; Andrews 1950) and barium calcium carbonate, $(Ca_{0.6}Ba_{0.4})CO_3$, ($a = 5.09$ and $c = 17.88$Å; Donnay 1963, p. 801). This suggests that the structure of weloganite is probably derivable from the structure of the rhombohedral carbonates.

The weloganite lattice also possesses a pseudo-mirror plane perpendicular to b^*_{tric} (Figs. 1b and 2a), giving rise to a pseudo-monoclinic symmetry. The pseudo-monoclinic cell has $a = a_{\text{tric}} = 8.988$, $b = 2b_{\text{tric}} \sin 60° = 15.567$, $c^* = \frac{1}{2} c^*_{\text{trig}}$ or $c = 36.865$Å and $\beta = 103.8°$, corresponding exactly to the monoclinic cell reported by Gait & Grice (1971).

The powder patterns of weloganite obtained with materials used in this study are identical to that given by Sabina *et al.* (1968). The indexing of the powder pattern based on the present triclinic cell is presented in Table 2, which includes indices only of those reflections that make substantial contributions to the powder diffraction lines as judged from precession and Weissenberg x-ray photographs.

TABLE 2. X-RAY POWDER DIFFRACTION DATA OF WELOGANITE*

hkℓ	dcalc(Å)	dobs(Å)	I	hkℓ	dcalc(Å)	dobs(Å)	I
010	7.784	7.786	3	$24\bar{2}$	2.012		
100	7.149	7.143	3	$2\bar{2}\bar{2}$	2.012	2.012	7
001	6.027	6.022	5	420	2.012		
$10\bar{1}$	5.898	5.901	1	003	2.010		
011	4.766	4.766	½	$33\bar{3}$	1.966		
$01\bar{1}$	4.765			$30\bar{3}$	1.966		
120	4.362			$03\bar{2}$	1.966		
$2\bar{1}\bar{1}$	4.361	4.362	8	032	1.966	1.966	7
$1\bar{1}0$	4.361			301	1.966		
$12\bar{1}$	4.024			331	1.966		
$1\bar{1}\bar{1}$	4.024	4.022	4	241	1.909		
$2\bar{1}0$	4.024			$42\bar{3}$	1.908	1.907	7
101	3.909	3.906	1	$2\bar{2}1$	1.908		
111	3.909			$54\bar{2}$	1.691		
121	3.188			$51\bar{2}$	1.691		
$1\bar{1}1$	3.187	3.187	5	$1\bar{4}0$	1.691	1.691	4
$21\bar{2}$	3.187			150	1.691		
002	3.013	3.013	5	$4\bar{1}\bar{1}$	1.691		
211	2.818			$45\bar{1}$	1.691		
$1\bar{1}\bar{2}$	2.817	2.817	10	$21\bar{4}$	1.677		
$12\bar{2}$	2.817			$1\bar{1}3$	1.677	1.676	4
$33\bar{1}$	2.595			$51\bar{3}$	1.590		
030	2.594	2.594	7	$1\bar{4}1$	1.590		
$30\bar{1}$	2.594			151	1.590		
330	2.384			$4\bar{1}0$	1.590	1.589	6
$30\bar{2}$	2.383			033	1.589		
$03\bar{1}$	2.383	2.382	6	$03\bar{3}$	1.588		
031	2.383			302	1.588		
300	2.383			$30\bar{4}$	1.588		
$21\bar{3}$	2.239			540	1.538		
$1\bar{1}2$	2.239			$4\bar{1}\bar{3}$	1.537		
122	2.239	2.233	7	$1\bar{4}\bar{2}$	1.537	1.538	4
$22\bar{1}$	2.230			$15\bar{2}$	1.537		
$24\bar{1}$	2.230			510	1.537		
$42\bar{1}$	2.230			$3\bar{3}\bar{1}$	1.498		
$2\bar{2}0$	2.180	2.181	2	$36\bar{1}$	1.498	1.497	3
240	2.180			$63\bar{2}$	1.498		
$3\bar{1}0$	2.032			$36\bar{3}$	1.341	1.341	1
$1\bar{1}\bar{3}$	2.019	2.024	1	$3\bar{3}\bar{3}$	1.341		
212	2.019			Plus many more lines			

*CuK$_\alpha$ radiation, λ = 1.5418Å, 114.6 mm camera, Si standard. Intensities estimated visually.

TWINNING

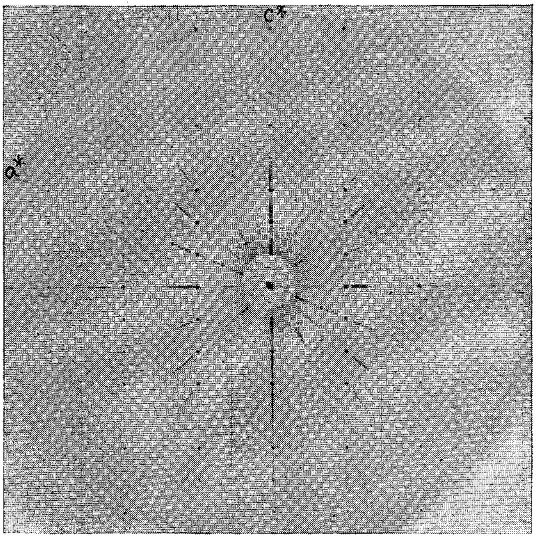
Weloganite may represent an ideal textbook illustration of twinning of crystals in the triclinic system. The twinning condition for triclinic crystals requires that the following ratios must approach rational numbers (*International Tables for X-Ray Crystallography*, **II**, 1959, p 106):

$$a^2 : b^2 : c^2 : bc\cos\alpha : ca\cos\beta : ab\cos\gamma.$$

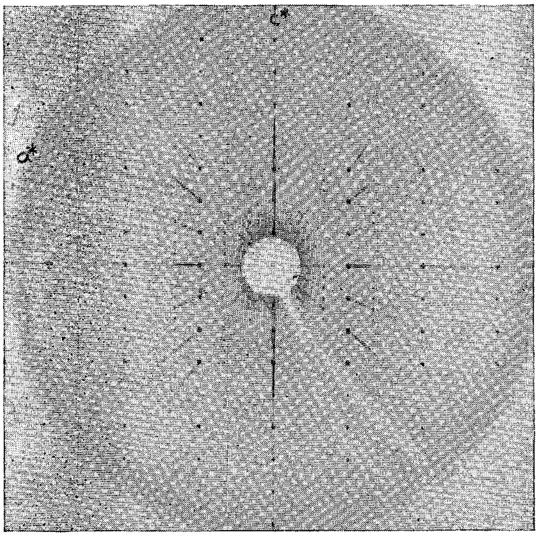
This condition is beautifully met for weloganite as the required ratios are:

$$6.013 : 6.013 : \tfrac{1}{3} \times 10.114 : 1.000 : 2.003 : 3.007.$$

In fact, all type I grains selected from the immersion mounts and fragments removed from the core material in the thin section were found to be twinned. The twin law may be stated as $[103]_{120°}$ or $[001]^*_{120°}$ with twin obliquity $\omega=0$ and twin index $n=3$. It falls in the class of twin by twin-lattice symmetry (TLS) according to the simplified classification of twins by Donnay & Donnay (1974). The complete twin symmetry is 3. The twinned cell corresponds exactly to the trigonal cell reported by Sabina *et al.* (1968) with the same type of peculiar extra-space-group systematic extinctions with $h-k=3n$ absent when $h+l$ and $K+l$ are not equal to $3n$. The 0-level [103] precession photograph of a twinned crystal is shown in Figure 2b which is to be compared with that of the untwinned crystal (Fig. 2a).



a



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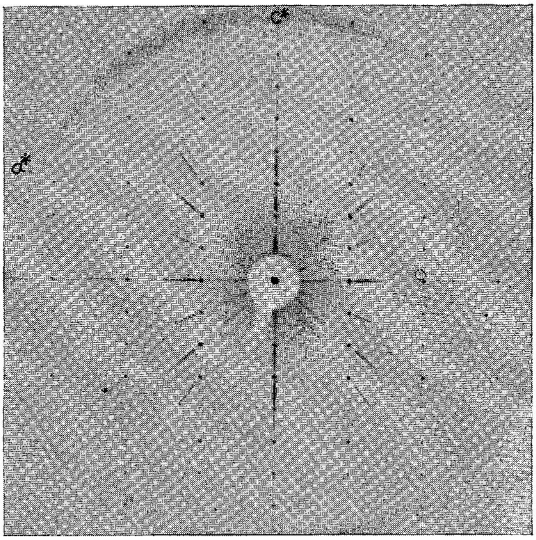

c

FIG 3. *b*-precession photographs (0-level, $\mu = 30°$, Mo$K\alpha$ radiation) of weloganite (a) single crystal, (b) twinned crystal and (c) twinned crystal displaying diffuse streaks along c^*.

It is interesting to note that pronounced diffuse streaks along c^* or the twin axis, [103], were observed on precession photographs of some twinned crystals (Fig. 3c). However, they were not observed for all twinned crystals (Fig. 3b) and were never observed for untwinned crystals (Fig. 3a). Similar diffuse streaks were observed and described by Gait & Grice (1971) as "streaking" of reflections and were interpreted as due to stacking disorder along the c^* direction. Although stacking disorder could not be completely ruled out, the development of the diffuse streaks may be adequately explained, without introducing stacking disorder, by twinning of individuals of submicroscopic thickness repeating along [103]. The adjacent twin individuals, if small enough to diffract *x*-rays coherently, would act as antiphase domains and produce diffuse streaks similar to the effect of stacking disorder. The submicroscopic size of the twin individuals is testified by the fact that many fragments of weloganite crystals that showed no twin lamellae under polarizing microscope with high magnification (500×) were nevertheless found by *x*-ray diffraction to be twinned.

CHEMICAL FORMULA

Recalculation of the chemical analysis of weloganite reported by Gait & Grice (1971) on the basis of 6 oxygen atoms (excluding CO_2 and H_2O) per formula gave $Na_{2.22}K_{0.01}Sr_{2.79}Ca_{0.22}Zr_{0.94}(CO_3)_{5.72}O_{0.28}\cdot 4.49H_2O$ or ideally $Na_2Sr_3Zr(CO_3)_6\cdot$ 4-5H_2O. Several new analyses of the water content by the Penfield method gave 6.78 and 6.80% (Jambor, private communication, 1974), 6.9 and 6.9% (analyst: V. Boyko). The consistency of results of these independent analyses suggests that the water content (9.66%) reported by Gait & Grice is probably in error. If the new values are accepted, the ideal formula of weloganite becomes $Na_2Sr_3Zr(CO_3)_6\cdot 3H_2O$. This formula is confirmed by results of a preliminary crystal structure analysis (Grice, private communication, 1974). Assuming $Z = 1$, the density of weloganite calculated from the ideal formula using the volume of the triclinic cell is 3.208 g/cm^3 which compares favorably with the measured values 3.22 (Sabina *et al.* 1968) and 3.20 g/cm^3 (Gait & Grice 1971).

ACKNOWLEDGEMENTS

We wish to thank Drs. J. L. Jambor and J. D. Grice for making available to us the single crystal *x*-ray diffraction photographs of weloganite used in their studies and for their permission to quote their unpublished materials. We would also like to thank Mr. V. Boyko for his analyses of H_2O. This work is supported by research grant A5113, from the National Research Council of Canada (to G.Y.C.).

REFERENCES

ANDREWS, K. W. (1950): An *x*-ray examination of a sample of pure calcite and of solid-solution effects in some natural calcite. *Mineral. Mag.* **29**, 85.

DONNAY, G. & DONNAY, J. D. H. (1974): Classification of triperiodic twins. *Can. Mineral.* **12**, 422-425.

DONNAY, *J. D. H. (Ed.)* (1963): *Crystal Data, Determinative Tables.* 2nd Edit. Amer. Crystall. Assoc.

GAIT, R. I. & GRICE, J. D. (1971): Some observations on weloganite. *Can. Mineral.* **10**, 912 (abstr.).

SABINA, A. P., JAMBOR, J. L. & PLANT, A. G. (1968): Weloganite, a new strontium zirconium carbonate from Montreal Island, Canada. *Can. Mineral.* **9**, 468-477.

Manuscript received August 1974, emended September 1974.