REEXAMINATION OF THE CRYSTAL STRUCTURE OF MELILITE

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Abstract

An accurate single-crystal investigation of an intermediate melilite has confirmed the structure found by Warren in 1930. Variations in O—O distances are explained by sharing of polyhedron edges. Variations in Si—O distances are not explained by cation-cation repulsion. There is a considerable deviation from Pauling's rule of electrostatic valence bonds. This deviation may be related to the variation in Si—O distances since the longer the distance the larger is the sum of electrostatic valence bonds. The Ca polyhedron is a fairly regular square antiprism. The Ca—O distances are in two groups at 2.4 Å and 2.7 Å, suggesting that the bonds have different characters. A discussion of the possible arrangements of Mg, Al, and Si atoms in the melilite series is given. Consideration of some new analyses on natural melilites confirms the accepted melilite formula and disproves Goldsmith's hypothesis of the necessity for OH′ replacing O″ in melilites.

Introduction

Melilite forms a continuous series between the end-members akermanite, $Ca_2MgSi_2O_7$, and gehlenite, $Ca_2Al_2SiO_7$. The composition of the natural melilites was extensively studied by Berman (1929) who found that the composition of the group could be well represented by $(Ca,Na)_2(Mg,Al,Si)_3O_7$ where (Ca,Na) is mainly Ca, $Mg<1.0$, and $Si<2.0$. Ferrous iron is also thought to substitute for the cations. Synthetic melilites have been produced in many experiments (see Goldsmith, 1948 for references), and their optical and morphological properties have been found to be similar to those of the natural melilites. Warren (1930) determined the crystal structure of a natural melilite from Capo di Bove, and Raaz (1930) determined the crystal structure of synthetic gehlenite. Apart from the necessary substitution of different cations, these structures are the same. The composition determined by Berman is confirmed by these two structure determinations. Andrews (1948) and Ervin and Osborn (1949) have independently measured the lattice parameters of the synthetic akermanite-gehlenite series and found regular changes throughout the whole series indicating complete solid solution. Warren and Trautz (1930) have shown that hardystonite, $Ca_2ZnSi_2O_7$, has the same structure as melilite.

It was thought that a redetermination of the melilite structure by the more accurate modern methods would be of interest for the following reasons: (*a*) the distribution of the Mg, Al, Si, atoms in the structure could be determined; (*b*) the coordination polyhedron of the Ca ion is variable in other crystals; (*c*) the possible distortion of the tetrahedra could be compared with the distortion found in the Si_2O_7 groups of tilleyite by Smith (1953*a*); and (*d*) the determination of accurate coordinates would provide a firm basis for the application of crystal-chemistry arguments to the possible substitutions in the melilites.

The natural melilite from Capo di Bove was chosen for analysis because Warren's crystals came from this locality.

PHYSICAL PROPERTIES AND COMPOSITION

The Capo di Bove melilite used in this work occurred as well crystallized tetragonal crystals showing only the (100) and (001) forms. The crystals were yellowish-brown and partly opaque. Some dark brown spots on the surface of the crystal indicated the presence of some impurity in small amounts; the main body of the crystal, however, was uniform.

Optical measurements, kindly carried out by W. S. MacKenzie of this Laboratory, gave: $\omega = 1.638 \pm 0.002$, $\epsilon = 1.634 \pm 0.002$, optically negative, $\omega - \epsilon = 0.004$.

Five analyses of Capo di Bove melilite have been made. These have been collected by Berman (1929) and are reproduced in Table 1. Analysis 2 differs considerably from the other four and it was provisionally disregarded. A mean of the other four was taken and when calculated to seven oxygen atoms the following formula was obtained:

TABLE 1. ANALYSES OF CAPO DI BOVE MELILITE

	I	II	III	IV	V
CaO	32.98	34.78	32.47	32.18	32.05
NaO	2.18	3.40	1.95	2.21	2.12
K_2O	1.49	0.68	1.46	1.45	1.51
MgO	6.33	5.87	6.44	6.41	6.71
Al_2O_3	6.47	10.93	6.42	7.56	8.61
SiO_2	40.14	41.09	39.27	39.20	38.34
Fe_2O_3	9.95	3.40	10.17	11.34	10.02
FeO	0.53	—	—	—	—

Analyses have been taken from Berman (1929).

$$Ca_{1.648}Na_{0.195}K_{0.089}Mg_{0.457}Al_{0.406}Si_{1.862}Fe_{0.417}O_7.$$

The assignment of atoms to the possible atomic sites in Warren's structure gave:

$[Ca_{1.648}Na_{0.195}K_{0.089}Fe_{0.068}]$	$[Mg_{0.457}Al_{0.268}Fe_{0.275}]$	$[Si_{1.862}Al_{0.138}]O_7$
Total 2 atoms	Total 1 atom	Total 2 atoms

with an excess of 0.084 atoms of Fe. The excess iron was a little disturbing; however, the crystal used in this work showed some brown impurities and a few weak extraneous reflections were observed on the Weissenberg photographs. It was thought that these impurities may have been some iron compound. The analysis was therefore recalculated neglecting iron oxide. The result was:

$[Ca_{1.752}Na_{0.207}K_{0.095}]$	$[Mg_{0.486}Al_{0.412}]$	$[Si_{1.980}Al_{0.020}]O_7$
Total 2.054 atoms	Total 0.898 atoms	Total 2 atoms

This also was unsatisfactory because the atomic sums are not integers. Later in the structure determination the composition was deduced from the *x*-ray measurements and from the refractive indices.

X-RAY MEASUREMENTS

The crystals are tetragonal with $a = 7.789 \pm 0.005$ Å, $c = 5.018 \pm 0.005$ Å, determined by the θ method (Weisz, Cochran and Cole, 1948) using Co K_{α_1} and Co K_{α_2} radiation ($\lambda_{\alpha_1} = 1.78890$ Å, $\lambda_{\alpha_2} = 1.79279$ Å). The corresponding values obtained by Warren are 7.74 Å and 5.02 Å, when his values are converted from KX units into Å. The axial ratio c/a obtained in this work is 0.6442, which compares well with the goniometric axial ratio, 0.6440. This is obtained from that of Des Cloiseaux (1862) after reindexing the parametral plane. The space group is $P\bar{4}2_1m$ or $P42_1$ as the only systematic absences are for reflections with h odd in $(h00)$. Warren discarded $P42_1$ as it was not possible to build a reasonable structure on this space group. There are two melilite units in the unit cell.

A crystal showing (001) and (100) faces was selected and cut with a razor-blade until it had a cross-section of 0.43×0.47 mm. perpendicular to the *y*-axis. The intensities of the $(h0l)$ reflections were then recorded on multiple packs of film placed in a Weissenberg camera. MoK_α radiation was used and reflections were recorded from planes of spacing greater than 0.44 Å. The range of intensity was about 1500 to 1, and absorbing copper foil giving a step-down ratio of 3:1 from film to film was used. The intensities were measured visually by comparison with a calibrated intensity scale, and the Lorentz and polarization factors were applied by the method of Cochran (1948). As the crystal had a nearly uniform cross-section, no correction was made for differential absorption. The remaining correction factors (except for extinction) should be functions of $\sin\theta$ and were found later in the structure determination. A rough correction for extinction was also made later in the structure determination.

DETERMINATION OF THE ATOMIC COORDINATES

Structure amplitudes for the $(h0l)$ reflections were calculated from the atomic coordinates given by Warren (these are given in Table 2). The space group $P\bar{4}2_1m$ is non-centrosymmetric; however, by a suitable choice

TABLE 2. ATOMIC COORDINATES DETERMINED BY WARREN

Atom	*x*	*y*	*z*
Ca	0.33	0.17	0.51
Si	0.14	0.36	0.95
Mg	0.00	0.00	0.00
O_1	0.50	0.00	0.19
O_2	0.14	0.36	0.26
O_3	0.08	0.18	0.81

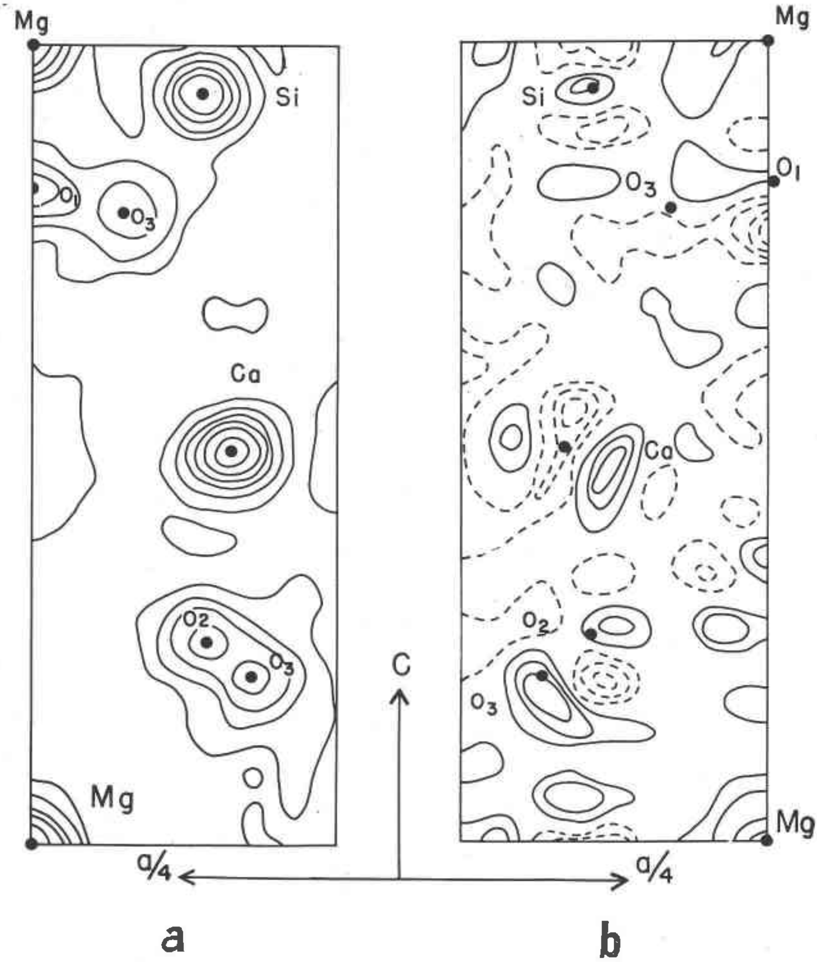

FIG. 1 (*a*) *y*-axis projection of the F_0-synthesis. Contours at arbitrary units of 50 around O atoms and 100 around other atoms. (*b*) *y*-axis projection of the F_0-F_c synthesis. Contours at units of 10 on the same scale as that of (*a*).

of position for the origin of the unit cell, the *y*-axis projection becomes centrosymmetric. The empirical atomic-scattering curves given by Bragg and West (1929) were used in the calculations. Weighted means of these atomic-scattering curves were used in order to take account of the atomic substitution in the melilite. As shown earlier in the paper, there was some doubt as to the composition of the melilite. There was, therefore, some doubt as to the scattering factors. Whether or not Fe″ is present makes little difference to the scattering factors for the "Ca" and "Si" atoms. The scattering factor for the "Mg" atom, however, varies greatly with the percentage of "Fe" in the structure as shown in columns *a* and *b* of Table 5. For convenience, the "Si" scattering factor was also used for the "Mg" atom in the preliminary calculations.

There was fair agreement between the observed and calculated structure amplitudes. An F_0-synthesis was computed (Fig. 1*a*) and more accurate atomic coordinates were obtained. The structure amplitudes were recalculated for the new coordinates and they then agreed slightly better with the observed structure amplitudes. After changing the "Mg" scattering factor, good agreement was obtained. The observed structure amplitudes were placed on an absolute scale by comparison of the observed and calculated structure amplitudes in the following way. The ratio of the mean values of the observed and calculated structure amplitudes for seven ranges of $\sin\theta$ was plotted against $\sin\theta$ on a graph. The best curve was drawn between the points to reduce the statistical fluctuations, and values from the graph were used to put the observed structure amplitudes on an absolute scale and also to correct for the factors varying with $\sin\theta$. An (F_0-F_c) synthesis was computed in order to refine further the atomic coordinates (Cochran, 1951). As the three strongest structure amplitudes were definitely affected by extinction (see Table 3), they were not included in the (F_0-F_c) synthesis.

The resulting atomic positions did not lie on appreciable gradients of electron density, thus showing that the atomic coordinates were correct. However, exactly on the positions occupied by the "Ca," "Si," and "Mg" atoms, there were small but significant peaks. These showed that the atomic scattering factors had been wrongly estimated. The necessary alterations in the atomic scattering factors were calculated and the structure amplitudes were recalculated using the new scattering factors. A further (F_0-F_c) synthesis was calculated and is shown in Fig. 1*b*. It contained only small peaks which did not indicate any appreciable change in the atomic coordinates or in the atomic scattering factors. The refinement, therefore, was judged to be complete. The fluctuation of electron density over regions not close to the atoms is about $2e/A^2$. There is a small peak on the silicon atom of $2e/A^2$ indicating a possible

TABLE 3. CALCULATED AND OBSERVED STRUCTURE AMPLITUDES

h	*l*	F_0	F_c	*h*	*l*	F_0	F_c	*h*	*l*	F_0	F_c	*h*	*l*	F_0	F_c
0	0	—		1	1	14.8	14.0	8	0	9.2	12.4	9	1	4.8	7.6
	1	26.0	18.0		2	31.2	34.0		1	31.6	34.4		2	x	0.4
	2	32.0	27.6		3	17.2	17.6		2	16.4	12.8		3	x	$\overline{0}.4$
	3	37.2	$\overline{38}.4$		4	11.2	10.4		3	27.2	25.2		4	8.4	$\overline{7}.2$
	4	54.8*	69.2		5	3.6	9.2		4	x	00.0		5	x	4.4
	5	8.4	$\overline{6}.4$		6	19.6	17.2		5	5.6	8.8		6	x	$\overline{3}.6$
	6	19.6	14.0		7	8.0	5.6		6	5.6	$\overline{5}.6$		7	6.0	5.2
	7	30.0	$\overline{30}.0$		8	3.4	3.6		7	8.8	8.0		8	x	$\overline{4}.8$
	8	7.6	11.2		9	9.2	$\overline{6}.0$		8	6.0	$\overline{5}.6$		9	x	4.0
	9	25.6	$\overline{18}.0$		10	x	0.0		9	x	2.0		10	x	$\overline{4}.4$
	10	7.2	9.6		11	5.6	$\overline{5}.2$		10	7.6	$\overline{4}.8$				
	11	10.1	$\overline{9}.6$									11	1	x	$\overline{1}.6$
				3	1	33.6	39.6	10	0	16.8	$\overline{16}.4$		2	10.4	$\overline{7}.6$
2	0	12.0	$\overline{16}.0$		2	10.8	$\overline{12}.4$		1	9.2	11.6		3	13.2	$\overline{14}.0$
	1	41.2	42.8		3	34.4	$\overline{38}.4$		2	15.2	$\overline{14}.0$		4	10.0	$\overline{9}.2$
	2	11.2	$\overline{11}.2$		4	37.2	$\overline{37}.6$		3	9.2	10.0		5	8.4	$\overline{9}.2$
	3	27.6	24.8		5	7.6	$\overline{6}.4$		4	4.4	$\overline{5}.6$		6	10.0	$\overline{6}.4$
	4	7.2	$\overline{6}.8$		6	16.4	$\overline{14}.8$		5	21.6	22.0		7	5.6	$\overline{5}.6$
	5	27.2	26.8		7	x	$\overline{0}.8$		6	6.8	4.0		8	x	0.8
	6	3.2	2.8		8	8.8	$\overline{8}.4$		7	15.2	17.6				
	7	20.0	18.4		9	8.0	7.2		8	x	2.0	13	1	x	3.6
	8	x	.8		10	x	$\overline{2}.4$		9	18.8	16.0		2	6.4	6.0
	9	10.0	12.0		11	10.4	9.8		10	x	2.8		3	x	1.2
	10	x	.4										4	x	2.4
	11	11.6	9.2	5	1	15.6	$\overline{18}.0$	12	0	21.2	23.2		5	x	0.4
					2	11.6	$\overline{9}.2$		1	11.2	$\overline{14}.4$		6	8.8	7.2
4	0	43.6*	$\overline{60}.4$		3	2.0	$\overline{1}.2$		2	14.0	16.4				
	1	14.8	11.6		4	2.8	1.6		3	11.2	$\overline{14}.4$	15	1	x	2.4
	2	12.4	$\overline{14}.0$		5	10.4	$\overline{11}.2$		4	17.2	21.6		2	5.2	3.6
	3	20.0	17.6		6	9.2	$\overline{6}.4$		5	x	$\overline{4}.4$		3	6.8	6.8
	4	15.2	$\overline{16}.8$		7	5.6	$\overline{4}.8$		6	20.8	20.0		4	x	3.6
	5	29.2	28.8		8	6.4	5.2		7	x	$\overline{4}.8$				
	6	14.0	10.8		9	x	.8		8	13.2	15.6				
	7	27.6	28.0		10	x	2.0								
	8	5.6	6.0					14	0	14.8	12.0				
	9	27.2	19.2	7	1	x	$\overline{2}.0$		1	16.4	19.2				
	10	7.2	6.0		2	19.6	18.2		2	10.0	6.0				
	11	14.8	11.6		3	22.8	26.0		3	13.2	13.2				
					4	22.4	22.4		4	x	2.4				
6	0	55.2*	74.4		5	6.4	10.0		5	x	6.4				
	1	x	$\overline{6}.8$		6	16.4	15.2								
	2	42.8	45.6		7	8.0	6.8	16	0	x	$\overline{1}.6$				
	3	12.8	$\overline{12}.8$		8	5.6	6.0		1	12.0	13.6				
	4	36.0	38.0		9	9.6	$\overline{5}.6$		2	x	$\overline{2}.4$				
	5	14.0	$\overline{16}.0$		10	x	$\overline{1}.2$		3	7.6	11.2				
	6	20.4	20.8												
	7	15.2	$\overline{15}.2$												
	8	11.2	14.0												
	9	17.6	$\overline{12}.8$												
	10	7.6	10.0												

* Affected considerably by extinction.
x Too weak to be recorded.

small increase in the atomic scattering factor. There is a negative peak flanked by two positive peaks at the Ca atom, indicating anisotropic temperature vibration with the largest vibration approximately parallel to the (001) plane. There are small peaks near to the positions occupied by the oxygen atoms. All the peaks near to the atomic positions are of approximately the same height as peaks far from the atoms and therefore are of doubtful significance. No adjustments have been made for these possible changes.

TABLE 4. ATOMIC COORDINATES AS FRACTIONS OF THE LATTICE PARAMETERS

Atom	x	y	z
Ca	0.3355	(0.5−x)	0.5073
Si	0.1396	(0.5−x)	0.9412
Mg	0.0000	0.0000	0.0000
O_1	0.5000	(0.5−x)	0.1804
O_2	0.1450	(0.5−x)	0.2583
O_3	0.0820	0.1820	0.7909

TABLE 5. ATOMIC SCATTERING CURVES USED IN THE STRUCTURE-FACTOR CALCULATIONS

Sin θ/λ	Ca	Si	Mg	O	a	b
0.0	19.0?	13.3?	10.7?	10.0?	10.7?	17.0?
0.1	16.2	11.6	9.4	8.0	9.4	13.8
0.2	13.1	9.8	7.8	5.8	7.8	11.3
0.3	10.5	8.3	6.5	3.7	6.5	9.3
0.4	8.5	6.8	5.2	2.5	5.2	7.6
0.5	7.2	5.6	4.1	1.7	4.1	6.2
0.6	6.0	4.6	3.2	1.1	3.2	5.1
0.7	5.1	3.6	2.5	0.7	2.5	4.2
0.8	4.3	3.0	1.9	0.5	1.9	3.5
0.9	3.7	2.5	1.5	0.4	1.5	2.9
1.0	3.1	2.0	1.2	0.3	1.2	2.5
1.1	2.6	1.6	1.0	0.2	1.0	2.1
1.2	2.3	1.4	0.9	0.1	0.9	1.8

The final reliability factor $\Sigma|F_0-F_c|/|F_0|$ is 0.13, neglecting the three planes affected considerably by extinction. The observed and calculated structure amplitudes are given in Table 3, the atomic coordinates in Table 4, the atomic scattering factors in the first four columns of Table 5. The random errors in the atomic coordinates were estimated by the method of Cruickshank (1949) using the following modifications. The profiles of the atomic peaks were taken from the F_0-synthesis and the errors in the observed electron density were found directly from the final (F_0-F_c) synthesis, at regions between the atoms. The random errors in the atomic coordinates are given in Table 6 and the calculated interatomic distances together with their standard errors are given in Table 7.

TABLE 6. RANDOM PROBABLE ERRORS OF THE ATOMIC COORDINATES

Atom	Error
Ca	0.003_3 Å
Si	0.004_4 Å
O	0.015_0 Å

TABLE 7. INTERATOMIC DISTANCES AND THEIR PROBABLE ERRORS

Atom	Distance (Å)	Error (Å)
$Si—O_1$	1.65_4	0.00_8
$Si—O_3$	1.64_3	0.01_6
$Si—O_2$	1.59_2	0.01_6
$O_3—O_3'$	2.60_0	0.02_1
$O_3—O_2$	2.74_9	0.01_9
$O_3—O_1$	2.56_2	0.01_5
$O_2—O_1$	2.72_0	0.01_8
$Mg—O_3$	1.87_6	0.01_5
$Ca—O_3$	2.43_8	0.01_5
$Ca—O_3'$	2.71_2	0.01_5
$Ca—O_2$	2.44_2	0.01_5
$Ca—O_2'$	2.68_7	0.01_5
$Ca—O_1$	2.44_4	0.01_1

The analysis deduced from the observed structure amplitudes and the chemical analyses give:

$$(Ca_{1.7}Na_{0.2}K_{0.1})\ (Mg_{0.5}Al_{0.4})\ (Si_{2.0}Al_{small})O_7 \text{ (to nearest 0.1)}$$

with variations possible for the substitutions Na↔Ca, Mg↔Al↔Si as these substitutions have little effect on the structure amplitudes. There can be little if any Fe in the structure, for the presence of the heavily scattering Fe atoms would considerably affect the structure amplitudes. The mean atomic scattering factors for the "Mg" atom with Fe present and with Fe absent are given in columns *a* and *b* of Table 5. The observed scattering factor is given under Mg in Table 5 and was found to be so close to column *a* that identical figures are given. The presence of one-tenth of the Fe given in the analyses 1, 3, 4, and 5 of Table 2 would give a significant peak on the (F_0-F_c) synthesis. Analysis 2 contains less iron but even this is too much. The deficiency of (Mg+Al) in the second group is a little disturbing. Better agreement with the *x*-ray data would be obtained if extra Mg were to replace Al but this would make the composition differ even more from the chemical analyses.

As with other mineral series, the refractive indices of melilite are a function of composition. Data on the pure Ak—Ge series (synthetic) are given by J. R. Goldsmith (1948*a*). At 55 per cent Ak the crystals are uniaxial with $\omega=\epsilon=1.65$. The effect of replacement of Ca by Na is not given for the Ak—Ge series except for the end-member, Ge. For this member, the effect is to reduce ω and ϵ and to make the crystal optically more negative. Assuming that the replacement by Na has the same effect throughout the series, then for the composition deduced from the structure factors and the chemical analyses of Capo di Bove melilite, the refractive indices should be reduced from 1.65 and the crystal should become negative. The values of $\omega=1.638$, $\epsilon=1.634$, found by MacKenzie are in rough agreement with the *x*-ray value in indicating a composition near 60 per cent Ak and some replacement by Na. Comparison of the values of *a* and *c* with those obtained by Andrews (1948) and Ervin and Osborn (1949) gives akermanite percentages of 75 and 85 (Andrews) and 65 and 100 (Ervin and Osborn). The presence of Na and other substituents complicates these deductions also.

All indications, however, show that this melilite is nearer to the Ak end of the melilite series with about 60 per cent Ak and some substitution by Na.

Discussion of the Structure

This work has confirmed the structure obtained by Warren and testifies to the accuracy of his determination. The use of modern, more accurate, techniques has produced more accurate coordinates than those of Warren, but this was to be expected. The structure obtained by Raaz (1930) for synthetic gehlenite has the same atomic positions as those in melilite.

The *z*-axis projection of the melilite structure is shown in Fig. 2. The melilite structure consists essentially of twisted sheets of tetrahedra linked parallel to (001). The sheets are held together by calcium-oxygen linkages. As the tetrahedral binding in the sheets should be stronger than the calcium-oxygen binding between the sheets, the strongest cleavage should be parallel to (001). The weakest binding in the sheets probably is across the (110) planes, as these planes leave intact most of the tetrahedral bonds. In accord with these deductions a moderate cleavage parallel to (001) and a poor cleavage parallel to (110) are recorded for the various melilites.

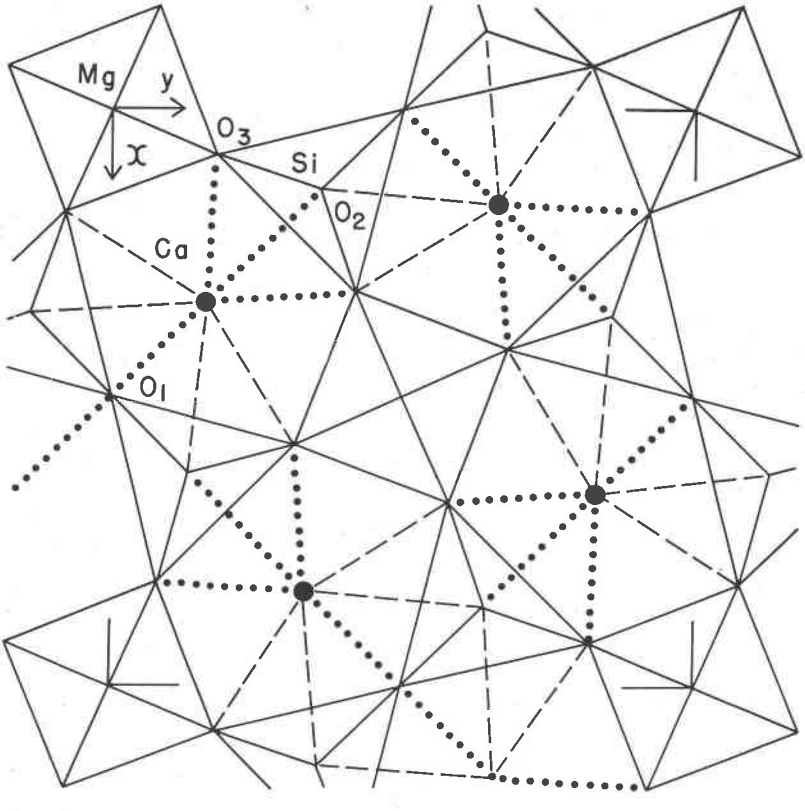

FIG. 2. *z*-axis projection of the melilite structure. The tetrahedra are outlined by unbroken lines. The broken lines show long Ca—O distances and the heavy dotted lines show short Ca—O distances.

There is little doubt that all the melilites have the same structure apart from the atomic substitution. The arrangement of Mg, Al, and Si atoms in the tetrahedra is of interest for they may be distributed in various ways inside the tetrahedra. It is unlikely that Mg and Si share the same tetrahedron because of the difference in ionic radii. Substitution between Al and Si is well known in the feldspars, and substitution between Al and Mg is possible because the ionic radii are not greatly different. For akermanite, $Ca_2MgSi_2O_7$, the Mg atom would be expected to occupy the tetrahedron at the origin of the unit cell (for convenience, this will be called tetrahedron 1) and the 2 Si atoms would be expected to occupy the other two tetrahedra which are equivalent (for convenience, these tetrahedra will be called 2 and 3). In gehlenite, $Ca_2Al_2SiO_7$, substitution between Al and Si is possible in all the tetrahedra. The two extreme cases of ordering are: (*a*) 1 Al in tetrahedron 1 and (1 Al and 1 Si) in tetrahedrons 2 and 3; (*b*) 1 Si in tetrahedron 1 and 2 Al in tetrahedrons 2 and 3. For case (*a*), there would be only statistical satisfaction of the space group symmetry but this does not rule out the possibility. Intermediate stages of ordering are possible.

If only the two extreme cases of ordering are considered, the possible arrangement of atoms through the whole Ak—Ge series is shown in Fig. 3. If no substitution between Mg and Si can occur, the distribution is as shown by the full lines with Al linearly replacing Mg, while the corresponding change of Al for Si occurs in the other tetrahedron. However, it would be expected that the other gehlenite structure would be more stable as each tetrahedron then contains only one type of atom. If this structure is really the more stable one, there is probably a change in the mode of substitution somewhere in the series as indicated by the dotted lines. It is possible that the ordering of the atoms in melilite changes with time, and therefore the synthetic melilites may differ from the natural melilites.

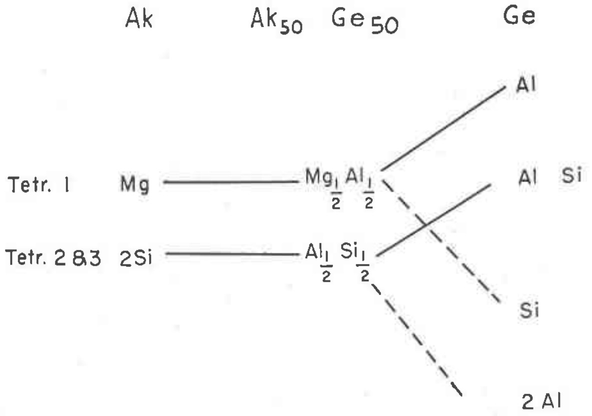

FIG. 3. Possible substitution in the Ak—Ge series.

The lattice parameter measurements on the synthetic Ak—Ge series by Andrews (1948) and Ervin and Osborn (1949) show a continuous change with composition. Measurements of the refractive indices of the synthetic Ak—Ge series by Goldsmith (1948*a*) also show a continuous change with composition. The first ordering reaction gives a completely smooth substitution of the atoms and would explain the continuous curves. For the second ordering reaction, the substitution of the atoms may or may not be a continuous function of composition according to the exact nature of the substitution. If only Al replaces the Mg at the akermanite end of the series and then there is a sharp change with the Si moving into tetrahedron 1, there should be a discontinuity in the lattice parameters. However, if there is a gradual change in the substitution of Si for (Mg, Al) there will be no discontinuity but there may be a change of slope in the graph of the lattice parameter, or refractive index, against composition. As there is no discontinuity either in the lattice parameters or refractive indices and no appreciable discontinuity in the first derivative, it is not possible to decide between the two forms of ordering.

It should be possible to determine the ordering of the Mg, Al and Si atoms by accurate determinations of the sizes of the tetrahedra by means of single crystal *x*-ray methods. The expected Si—O, Al—O, and Mg—O distances are respectively about 1.6 Å, 1.75 Å, and 1.9 Å. The mean cation-oxygen distances found in this work are $1.87_6 \pm 0.01_5$ Å for tetrahedron 1, and $1.63_3 \pm 0.01_1$ Å in tetrahedra 2 and 3. The melilite from Capo di Bove, therefore, shows a definite separation of the Si from the Mg and Al, as would be expected. The Capo di Bove melilite is not represented on the Ak—Ge series because of the substitution of Na and K. If only the Mg:Al ratio is considered, the nearest point on the Ak—Ge series is at about 60 per cent Ak, 40 per cent Ge. It is extremely likely that all the other natural melilites at the Ak end of the Ak—Ge series have the same segregation of the silicon atoms.

The only other melilite, the coordinates of which have been worked out, is synthetic gehlenite (Raaz, 1930). Raaz could not determine the ordering of the atoms because the technique for measuring interatomic distances was not sufficiently accurate. He considers that the arrangement of 1 Si in tetrahedron 1 and 2 Al in tetrahedra 2 and 3 is more likely, from space group considerations, and gives that as his determined structure.

Further accurate single crystal work is necessary to determine the ordering in the melilites. Accurate determination of both the natural and synthetic gehlenite would fix the ordering in this end-member of the series.

The melilites have commonly been regarded as belonging to the pyrosilicates with a Si/O ratio of 2/7. The Si:O ratio is not always a good criterion for the classification of silicate structures. A better criterion, sometimes, is one expressing the linking of the tetrahedra in the structure. This may be obtained by taking the $X:O$ ratio where X represents all the cations in the centers of the oxygen tetrahedra. For the melilites, X is Si, Al and Mg (with possible other substitutions). This ratio is 3:7 for the melilites and lies between the values of 1:2 for the feldspars and 2:5 for the micas. The $X:O$ ratio remains constant throughout the Ak—Ge series, whereas the Si:O ratio varies from 2:7 at Ak to 1:7 in Ge. The Si_2O_7 group in the Ak structure and the possible Al_2O_7 group in the Ge structure are best regarded as ordering of the cations in a more complex linking of tetrahedra.

From the geometrical point of view, the following substitutions are possible:

(1) Ca, Na, K
(2) Mg, Al, Fe'', Fe''', Mn, Ti, Zn
(3) Si, Al

Berman (1929) has calculated the analyses of 23 melilites. He assumes that there are 70 oxygen atoms in the structure and adds up the (Ca, etc.) in one group and the (Mg, etc., Si, etc.) in another group. If the ideal formula of the melilites holds true then these two groups add up to 20 and 30 respectively. Figure 4 is a histogram of the results. For group 1, the mean is 19.5 and apart from one result at 17.2 the analyses are con-

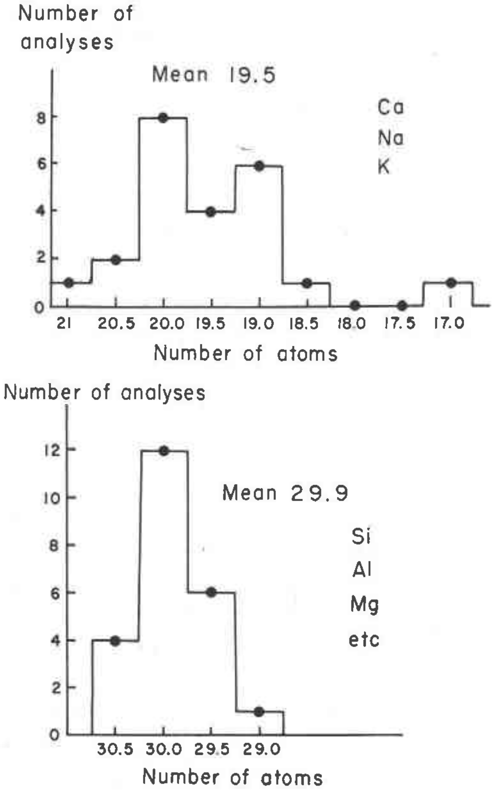

FIG. 4. Histograms of the analyses used by Berman.

fined to a spread of about 1. The 17.0 result must be regarded with some suspicion. In group 2, the mean is 29.9 and the spread of the results is confined to 1. There is little doubt from these results, as Berman stated, that melilite has the formula (Ca, etc.)$_2$ (Mg, etc.; Si, etc.)$_3$O$_7$. In only one analysis is the silicon greater than 20 (viz., 20.7). This confirms the segregation of the silicon from the other elements deduced from the geometrical considerations of the crystal structure.

Berman (1929) points out that the sum of (Ca, etc.) is lower than the ideal value of 20.0. Goldsmith (1948) points out that the sum of (Mg, etc.)

TABLE 8. SOME MELILITE ANALYSES

	1 Melilite Sugar loaf series, Honolulu		2 Melilite Mt. Elgon, Uganda		3 Gehlenite Fassathal, Tyrol		4 Gehlenite Luna County, New Mexico		5 Melilite Iron Hill, Colorado		Mean
	Wt.%	Atoms	Wt.%	Atoms	Wt.%	Atoms	Wt.%	Atoms	Wt.%	Atoms	
SiO_2	42.81	19.42	42.86	19.58	30.09	13.59	32.60	14.80	43.27	19.66	
Al_2O_3	6.59	3.52	5.02	2.70	21.67	11.53	18.10	9.69	6.44	3.45	
Fe_2O_3	1.90	0.65	0.26	0.09	1.36	0.46	0.95	0.32	0.97	0.33	
FeO	3.06	1.16	2.99	1.14	2.14	0.81	0.92	0.35	2.32	0.88	
MnO	0.08	0.03	0.08	0.03	0.04	0.01	0.02	0.01	0.16	0.06	
MgO	7.48	5.05	9.20	6.26	3.87	2.60	6.91	4.67	7.90	5.35	
CaO	33.27	16.16	34.90	17.08	38.36	18.55	40.08	19.49	34.76	16.92	
Na_2O	3.75	3.30	3.68	3.26	0.75	0.66	0.18	0.16	3.59	3.16	
K_2O	0.33	0.19	0.42	0.25	0.16	0.09	0.21	0.12	0.20	0.11	
TiO_2	0.12	0.05	0.06	0.02	tr		0.00		tr		
ZnO	n.d.		n.d.		n.d.		n.d.		n.d.		
P_2O_5	n.d.		n.d.		0.00		0.00		0.00		
H_2O^+	0.43	1.30	0.22	0.67	1.64	4.94	0.48	1.46	0.28	0.85	
H_2O^-	0.00		0.00		0.00		0.00		0.00		
Sum	99.82		99.69		100.08		100.45		99.89		
Sum Ca, etc.		19.65		20.59		19.30		19.77		20.19	19.90
Sum Si, etc.		29.88		29.82		29.00		29.84		29.73	29.65
Sum Ca, etc. Sum Si, etc.	If neglect H_2O										20.16 30.04

Analyst: H. B. Wiik, Finland.

is very close to 30 (actually 29.9) and therefore the errors in the analyses should be small and the deficiency of (Ca, etc.) is real. If the poor result be neglected at 17.2, the deficiency of (Ca, etc.) is reduced a little from 0.5 atoms to 0.4 atoms, but it is still appreciable. In a series of heating experiments he attempted to explain the substitution of Na for Ca. He heated $Na_2Si_3O_7$ with Ak—Ge mixtures and found that for Ge, 3.85 per cent by weight of Na_2O entered the structure whereas no Na_2O entered the Ak.

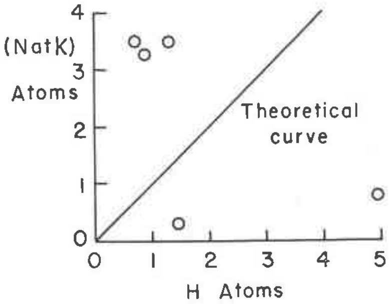

FIG. 5. Graph of (Na+K) and H atoms for some melilite analyses.

In effect he was making the substitution Ca→Na together with (Mg, Al)→Si. This amount of Na_2O was not sufficient to explain the Na_2O in the natural melilites. He suggested that the only reasonable way of replacing Ca by Na is by making the corresponding replacement O'' to OH'. Unfortunately, nearly all the analyses considered by Berman do not contain water, presumably because it was not determined, and no test could be made of this hypothesis. By courtesy of K. J. Neuvonen, some further analyses of natural melilites, made by H. B. Wiik of the Geological Survey of Finland, have been placed at my disposal. These are reproduced in Table 8. The melilites vary from the akermanite end to the gehlenite end. The analyses show considerable amounts of H_2O^+ water (i.e., water not removed by heating to 100° C.). The analyses were computed to 70 oxygen atoms (including water). The mean (Ca, etc.) is 19.90 atoms which is very close to 20. The mean (Si, etc.) is 29.65, which is rather low. These results differ from the analyses considered by Berman as they have a closer agreement for (Ca, etc.) and a poorer agreement for (Si, etc.). On Goldsmith's theory of the OH replacement there should be a relation between the proportions of Na and H atoms. Figure 5 is a graph of this. If the presence of Na is caused solely by the presence of H_2O then the graph points should fall on the straight line. This is definitely not true. However, it is still possible that some of the Na is explained by the H_2O and the rest explained by other mechanisms.

However, analysis 3 has 4.94 H atoms and only 0.75 atoms of (Na+K); analysis 4 has 1.46 H atoms and only 0.28 atoms of (Na+K). There is no doubt, therefore, that Goldsmith's hypothesis does not explain these melilite analyses and another explanation of the role of H_2O is needed. It is still possible that it does occur in the structure as OH' groups, in which case, the most probable position of the OH groups is at the only unshared corner of the tetrahedra, O_2. Megaw (1949) has shown that in afwillite OH groups form some of the corners of the silicon tetrahedra, but it is the only known structure in which this has been found with certainty. The unshared corner of the melilite tetrahedron has insufficient valence bonds for an O'' ion on the basis of Pauling's rule of electrostatic valence bonds (see later). It is not very unlikely, therefore, that an OH group could go into the structure at this point. However, if the chemical analyses are recalculated with the water neglected, slightly better agreement for the sum of (Ca, etc.) and (Mg, Si, etc.) is obtained. The old totals are 19.90 and 29.65, and the new ones, 20.16 and 30.04. The significance of the water in the melilite analyses must be regarded as uncertain; apart from the role of H_2O, the melilite analyses are well explained on a geometrical basis of atomic substitution. Goldsmith's failure to produce a synthetic melilite containing sufficient Na_2O is not explained.

The detailed shapes of the polyhedra in this melilite structure are of interest. As mentioned earlier, the segregation of the (Mg, Al) from the Si was deduced from the sizes of the tetrahedra. There are only two independent O—O distances in the MgO_4 tetrahedra; these have similar lengths of 3.11 and 3.04 Å, showing that the tetrahedron is almost regular in shape.

The two Si tetrahedra are related by a plane of symmetry and each tetrahedron also has a plane of symmetry passing through it. The distances in the Si tetrahedra are: $Si—O_1$, $1.65_4 \pm 0.00_8$; $Si—O_2$, $1.59_2 \pm 0.01_6$; $Si—O_3$, $1.64_3 \pm 0.01_6$ (twice); $O_3—O_2$, $2.74_9 \pm 0.01_9$ (twice); $O_1—O_2$, $2.72_0 \pm 0.01_8$; $O_3—O_3$, $2.60_0 \pm 0.02_1$; $O_1—O_3$, $2.56_2 \pm 0.01_5$ Å (twice). The mean Si—O distance of $1.63_4 \pm 0.01$ Å compares well with the sum of the theoretical ionic radii 1.60 Å for Si—O and the values 1.60 ± 0.01 for Si—O in afwillite (Megaw, 1952), 1.61 ± 0.02 for Si—O in tilleyite (Smith, 1952*a*), 1.642 for $Si_{3/4}Al_{1/4}—O$ in sanidinized orthoclase (Cole, Sorum, and Kennard, 1949); and $1.69_6 \pm 0.02$ Å for $Si_{1/2}Al_{1/2}—O$ in paracelsian (Smith, 1952*b*) when account is taken of the possible substitution of the Si by the larger Al ion in melilite. Pauling (1929) discusses the deformation of coordination polyhedra, and states: (*a*) shared edges are shortened while unshared edges are correspondingly lengthened, and (*b*) electrostatic repulsion increases the separation of neighbouring cations. A detailed study of the cation-cation forces does not explain the variation of

Si—O distances. A possible explanation of this variation is given later. The variation of the O—O distances is explained by the sharing of edges; for the three short distances of 2.60 and 2.56 (twice) Å are for shared edges, and the three long distances of 2.75 (twice) and 2.72 Å are for unshared edges. In tilleyite, $Ca_5 \cdot Si_2O_7 \cdot 2CO_3$ (Smith, 1952*a*) the variations of Si—O and O—O distances in the structure were explained by Pauling's statements.

The coordination polyhedron of the Ca ion is distorted. The Ca ion has eight neighbors at distances of $2.43_8 \pm 0.01_5$ (twice); $2.44_2 \pm 0.01_5$; $2.44_4 \pm 0.01_5$; $2.71_2 \pm 0.01_5$ (twice); and $2.68_7 \pm 0.01_5$ Å (twice). This striking segregation into two groups of distances suggests that the Ca—O bonds are of two kinds. The shorter distances should correspond to stronger ionic bonds than the longer distances. Assuming that only the shorter distances correspond to bonds, the application of Pauling's rule of electrostatic valence bonds gives the following counts: O_1, 2.9; O_2, 1.4_5; O_3, 2.0_5 (assuming a composition of $Ca_{1.7}Na_{0.2}K_{0.1}Mg_{0.6}Al_{0.4}Si_{2.0}O_7$). There is a considerable deviation from the ideal value of 2.0 for O_1 and O_2. Assuming that all Ca—O bonds involve an equal transfer of electrons, we get the following valence counts: O_1, 2.4_5; O_2, 1.7_0; O_3, 2.0_5. The deviation is now only half as much. Only if the shorter bonds are completely neglected is it possible to get a valence balance: O_1, 2.0; O_2, 1.9; O_3, 2.0_5. It is probable that the Ca—O bonds are not truly ionic and have a considerable homopolar character. Pauling's rule would not then be expected to hold exactly. The deviation is, however, rather large. It is possible that the deviation is related to the variation in the Si—O distances as shown below.

Distance	1.59_2	1.64_3	1.65_4 Å
Valence bonds	1.4_5	2.0_5	2.9

The shorter the Si—O distance, the stronger should be the bond between the Si and O atoms and vice versa. This could balance the deficiency or excess in the sum of electrostatic valence bonds. The values given are in accord with this hypothesis.

It is well known that Ca polyhedra are irregular and numbers of oxygen neighbors from 6 to 9 have been recorded in different structures. Although the Ca—O distances in melilite are somewhat irregular, the polyhedron has a fairly regular shape, approximating the square Archimedean antiprism. Figure 6 is a representation of the Ca polyhedron on a stereographic projection. The O—Ca—O angles vary from 59° to 83°, the mean being 73°. The mean deviation of the O—Ca—O angles from the value of 73° is only 6°, showing that the steric coordination is undoubtedly a fairly regular square antiprism with 8-coordination. As men-

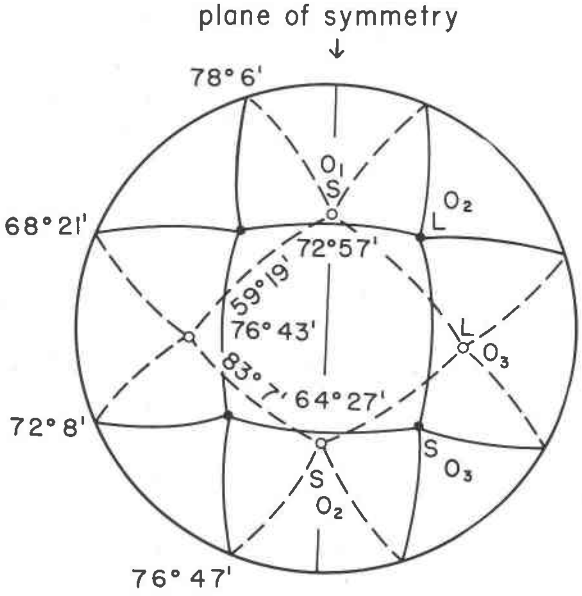

FIG. 6. The Ca polyhedron. S and L denote short and long Ca—O distances.

tioned earlier there is some doubt as to the exact electrostatic coordination because of the variation in the Ca—O distances and because of the deviation from Pauling's rule. Similar variations have been found in the recently determined structures of afwillite (Megaw, 1952) and tilleyite (Smith, 1952*a*). In these structures, there are 6 or 7 oxygen neighbors at varying angles and distances; it is also difficult to determine the electrostatic coordination. These variations are to be expected, for the main factor governing the packing of a silicate is the strong bond in the silicon tetrahedra. The steric hindrance between these strong tetrahedral groups usually prevents the formation of regular polyhedra around the Ca ions, for it is usually not possible to arrange the tetrahedra in such a way that the oxygen atoms lie at the corners of other regular polyhedra. The ideal coordination number of Ca is about 8, corresponding to a cube or a square antiprism. The observed variations from these ideal polyhedra are considerable and sometimes lead to difficulty in applying the geometrically based rules of Pauling. However, when the difficulties of packing together polyhedra of different sizes and shapes are considered, it is surprising that Pauling's rules explain so well the packing of crystal structures.

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