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REFINEMENT OF THE CRYSTAL STRUCTURE OF PIGEONITE

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ABSTRACT

The crystal structure of pigeonite, $(Mg_{0.39}Fe_{0.52}Ca_{0.09})SiO_3$, from the Isle of Mull has been refined to a residual of 0.036 for three-dimensional counter-measured intensities.

This crystal was refined with space group $P2_1/c$ and has cell dimensions $a=9.706\pm0.002$ Å, $b=8.950\pm0.001$ Å, $c=5.246\pm0.001$ Å, $\beta=108.59\pm0.01°$. The reflections with $h+k=2n+1$ are slightly diffuse compared with the reflections with $h+k=2n$.

The site occupancies of metal atoms in the two crystallographically different positions have been determined on the basis of the refinement of scattering factors of the atoms at the two sites and of the total chemical composition. One position has almost regular octahedral coordination of oxygen atoms around it and is occupied by 0.73 Mg and 0.27 Fe. The other position is in a rather irregular polyhedron coordinated by seven oxygen atoms and is occupied by 0.05 Mg, 0.77 Fe, and 0.18 Ca.

The structure of pigeonite can be interpreted as an average structure of clinoferrosilite and diopside. Large temperature factors in this structure may be due to the positional disorder of atoms arising from solid solution rather than thermal disorder. The coordination of seven oxygen atoms around metal atoms is considered to be an average of six oxygen atoms around Mg and Fe and of eight oxygen atoms around Ca.

INTRODUCTION

Morimoto (1956) and Bown and Gay (1957) found that pigeonite has space group $P2_1/c$, unlike diopside, which has space group $C2/c$. The crystal structures of clinoenstatite and pigeonite, $(Mg_{0.34}Fe_{0.56}Ca_{0.10})SiO_3$, were determined from two-dimensional photographic data by Morimoto, Appleman, and Evans (1960) and were compared with that of diopside (Warren and Bragg, 1928). Their results indicate many interesting features for pigeonite, such as (1) ordered distribution of Mg, Fe, and Ca atoms in two crystallographically different positions, $M1$ and $M2$[1]; and (2) coordination of seven oxygen atoms around $M2$, which is coordinated by eight oxygen atoms in the diopside structure. Since their study the crystal structures of many pyroxenes have been refined by

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[1] In the structure determination for clinoenstatite and Asio pigeonite, MI and MII were used to express the positions for larger cations and smaller cations, respectively (Morimoto, Appleman, and Evans, 1960). MI and MII as used in the earlier paper are referred to in the present paper as $M2$ and $M1$, respectively, in accordance with the new usage of Burnham *et al.* (1968). Readers should keep this in mind when referring to the earlier paper on pigeonite.

modern X-ray crystallographic techniques (Prewitt and Burnham, 1966; Clark and Papike, 1967; Peacor, 1967; Clark, Appleman, and Papike, 1969). The structure of clinoferrosilite was also refined and was found to be essentially the same as that of clinoenstatite (Burnham, 1966*c*). Both structures have six-coordination around $M2$.

The purpose of this study was to refine the crystal structure of pigeonite and to elucidate the effect of the isomorphous replacement of metal atoms on the clinopyroxene structures. For this purpose, our efforts have been concentrated on (1) the distribution of Ca, Fe, and Mg atoms in the $M1$ and $M2$ positions, (2) the coordination of oxygen atoms around $M1$ and $M2$, and (3) the effect of the isomorphous replacement of metal atoms on the temperature factors in the structure.

TABLE 1. CELL DIMENSIONS OF MULL PIGEONITE, AND, FOR COMPARISON, ASIO PIGEONITE, SYNTHETIC CLINOENSTATITE AND SYNTHETIC CLINOFERROSILITE[a]

	Mull pigeonite	Asio pigeonite (Morimoto *et al.*, 1960)	Clinoenstatite, synthetic (Stephenson *et al.*, 1966)	Clinoferrosilite, synthetic (Burnham, 1965)
a (Å)	9.706 (2)	9.733 (5)	9.6065 (11)	9.7085 (8)
b (Å)	8.950 (1)	8.956 (5)	8.8146 (7)	9.0872 (11)
c (Å)	5.246 (1)	5.248 (5)	5.1688 (6)	5.2284 (6)
β (deg)	108.59 (1)	108.55 (16)	108.335 (9)	108.432 (4)
V (Å^3)	432.0 (2)	433.8	415.46 (9)	437.6 (1)

[a] Standard deviations, σ, given in parentheses.

SPECIMEN DESCRIPTION

Crystals of pigeonite from several localities were examined by single-crystal X-ray methods. Most crystals were found to have exsolution of augite parallel to (001) or (100) of pigeonite (Morimoto, 1966; Morimoto and Tokonami, 1969*a*). Pigeonite crystals from the Isle of Mull and Asio are practically homogeneous, with faint exsolution. Pigeonite crystals from Asio (Kuno, 1969) were used for the structure determination by Morimoto, Appleman, and Evans (1960). The pigeonite used for the structure refinement in the present study is from the Isle of Mull and was kindly supplied by Dr. H. S. Yoder, Jr. It shows diffuseness for reflections with $h+k=2n+1$.

The space group is $P2_1/c$. The cell dimensions were determined by least-squares refinement by Burnham's (1962) program, and the data were measured on precision back-reflection Weissenberg photographs. The results, based on 32 independent measurements, are compared with the cell dimensions of clinoenstatite, clinoferrosilite, and pigeonite from Asio (Table 1).

The chemical composition of Mull pigeonite was determined to be $En_{39}Fs_{52}Wo_9$ by Hallimond (1914). To confirm this composition and determine the extent of compositional variation in different specimens, examination by the electronprobe microanalyzer was carried out by Dr. F. R. Boyd at the Geophysical Laboratory. The composition obtained was $En_{41}Fs_{51}Wo_8$, in good agreement with Hallimond's result. As several crystals gave nearly the same composition by electron probe, and several other crystals examined by X-rays gave the same cell dimensions, within the limit of experimental error, it is reasonable to assume that all crystals of Mull pigeonite have essentially the same chemical composition. As described later, the chemical composition obtained by Hallimond and by electron probe has been confirmed by our site-occupancy refinement. The calculated density for the chemical formula, $(Mg_{0.39}Fe_{0.52}Ca_{0.09})SiO_3$, is 3.44 g/cm^3; the measured value is 3.30 g/cm^3 (Hallimond, 1914).

INTENSITY MEASUREMENT

The integrated intensities were measured on the Supper-Pace automatic single-crystal diffractomater at the Geophysical Laboratory with Nb-filtered $MoK\alpha$ radiation (0.7107 Å) The instrument employed a Th-activated NaI scintillation detector associated with a pulse-height analyzer adjusted to accept 90 percent of the diffracted radiation. The intensity-collection and data-processing procedures are the same as those described by Burnham (1966*b*).

A single crystal, $0.2\times0.03\times0.05$ mm in size, elongated along the c axis, was used for the intensity data. The intensities of 1532 reflections from the zeroth to sixth layer around the c axis were recorded. All reflections with $\sin\theta<0.75$ and values of Υ greater than 14° were measured in each layer. The intensity data were converted to observed structure factors by applying the standard Lorentz and polarization corrections, and the absorption correction was made by computing the transmission factor by means of the GNABS subroutine (Burnham, 1966*a*), with a linear absorption coefficient of 42.47 cm^{-1}.

If the computed values of integrated intensity are less than 2σ, where σ represents the estimated standard deviation computed from counting statistics (Cetlin and Abrahams, 1963), the intensity is assumed to be below the minimum observable value. Since pigeonite has a pseudo C-centered lattice, the $h+k=2n+1$ reflections are generally weak, resulting in many reflections with integrated intensities lower than the minimum observable value. Furthermore, several reflections were determined inaccurately because of diffuseness and had to be discarded. Thus only 507 reflections could be used for the refinement, of which 367 have $h+k=2n$ and 140 have $h+k=2n+1$. The test reflections were measured after every twenty reflections in each layer. The standard deviation $\langle s\rangle$ of the mean value (I_{obs}) of the n measurements of the test reflection, calculated by the formula $\surd\sum^{n}(I_{obs}-\langle I_{obs}\rangle)^2/n(n-1)$, is about 0.2–0.4 percent of the mean value. The values of F_0-F_c calculated by the final parameters are within the range expected from the standard deviation $\langle s\rangle$ for the test reflections (Table 2).

STRUCTURE REFINEMENT

Full matrix least-squares refinement of the structure of pigeonite was carried out on the IBM 7094 with the use of a program written by C. T. Prewitt in 1962 and modified by Burnham. The function minimized in the least-squares refinement is $\sum 1/(\delta)^2||F_0|-|F_c||^2$. The modified program used an analytical expression for scattering curves of Mg^{2+}, Fe^{2+}, Ca^{2+}, Si^{4+}, and O^{-2} (Prewitt and Burnham, 1966).

Refinement was initiated using the atomic coordinates of Asio pigeonite from Morimoto, Appleman, and Evans (1960), with the following isotropic temperature factors: 0.5 for Mg, Fe, and Ca, 0.4 for Si, and 0.6 for oxygen atoms. For the distribution of metal atoms, it was assumed that Mg and Ca are completely ordered in the $M1$ and $M2$ positions, respectively. This assumption resulted in a starting distribution of 0.78 Mg and 0.22 Fe in $M1$ and 0.82 Fe and 0.18 Ca in $M2$ on the basis of the total chemical composition given by Hallimond. This initial structure gave $R(\sum||F_0|-|F_c||/\sum|F_0|)=0.158$ for 507 reflections. Calculated structure factors were scaled to the observed ones using one scale factor.

The first three cycles of least squares on F's were carried out varying only the atomic coordinates and the scale factor. In the next three cycles, the isotropic temperature factors were allowed to vary. After six cycles of refinement, the *R* value for 507 observed reflections reduced to 0.068. At this stage of refinement, twelve reflections were rejected for which the effects of background to the intensity were not accurately estimated. The site occupancies of metal atoms in *M*1 and *M*2 were then varied by changing the ratios Mg:Fe and Fe:Ca for *M*1 and *M*2, respectively, together with the scale factor, atomic coordinates, and isotropic temperature factors. Three cycles of refinement further reduced the *R* value to 0.045. Finally the isotropic temperature factors were converted to the anisotropic form, and after three cycles of refinement, varying the scale factor, atomic coordinates, metal distribution factors, and anisotropic temperature factors, no further change of parameters took place. The final residual is 0.037 for 495 reflections and 0.038 for 507 reflections.

Because of minute exsolution lamellae of augite in the crystal, the effect of extinction should be very small. The influence of the anomalous dispersion is also negligible for atomic coordinates or temperature factors (Prewitt and Burnham, 1966). Thus no corrections for extinction and anomalous dispersion were made.

TABLE 2. COMPARISON OF OBSERVED AND CALCULATED *F* VALUES FOR THE TEST REFLECTIONS

Layer	*hkl*	Number of observations	F_o	$\langle s\rangle$	F_c	F_o-F_c
0	750	29	202.82	0.21	203.03	−0.21
1	$\bar{2}81$	12	213.88	0.33	213.98	−0.10
2	$\bar{7}52$	13	181.64	0.16	181.98	−0.34
3	$\bar{2}83$	12	166.23	0.26	−165.72	−0.51
4	404	11	151.52	0.23	151.09	0.43
5	135	9	129.76	0.27	−129.07	−0.69
6	$\bar{3}66$	4	92.70	0.65	− 93.90	1.20

The final results of the least-squares refinement show that the site occupancies of metal atoms are 0.73 Mg and 0.27 Fe for *M*1 and 0.75 Fe and 0.25 Ca for *M*2. In order to meet the total chemical composition, on the basis of the site occupancy of *M*1 obtained by least squares, the *M*2 site must have 0.05 Mg, 0.77 Fe, and 0.18 Ca. Fortuitously, this metal distribution gives the same total scattering factor as that by the distribution of 0.75 Fe and 0.25 Ca, which was obtained by the least-squares method for *M*2. Since the result of the refinement confirmed the assumption that Ca atoms occupy only the *M*2 site the structure factors were computed with the site occupancies for *M*1 (0.73 Mg, 0.27 Fe) and *M*2 (0.05 Mg, 0.77 Fe, 0.18 Ca). The *R* value is 0.036 for 507 observed reflections.

The final parameters and the individual anisotropic temperature factors are listed with their estimated standard deviations (Table 3). The observed and calculated structure factors are on deposit.[1]

In order to determine the standard deviations of the site occupancies fo metal atoms

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[1] To obtain a copy of Table 4, order NAPS Document # 01052 from National Auxiliary Publications Service, c/o CCM Information Corporation, 909 Third Avenue, New York, New York 10022; remitting $2.00 for microfiche or $5.00 for photocopies, in advance payable to CCMIC-NAPS.

TABLE 3. FINAL ATOMIC COORDINATES, ANISOTROPIC TEMPERATURE FACTORS, AND EQUIVALENT ISOTROPIC TEMPERATURE FACTORS FOR ATOMS IN PIGEONITE[a]

Atom (Equipoint)	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B (equiv.)
$M1$	0.2508 (4)	0.6548 (2)	0.2328 (8)	0.0017 (2)	0.0016 (2)	0.0078 (9)	0.0001 (5)	0.0013 (3)	0.0001 (9)	0.67
$M2$	0.2564 (3)	0.0183 (1)	0.2308 (6)	0.0028 (1)	0.0045 (2)	0.0114 (7)	0.0005 (2)	0.0007 (2)	0.0005 (5)	1.26
Si*A*	0.0427 (3)	0.3398 (5)	0.2797 (6)	0.0017 (3)	0.0015 (3)	0.0069 (9)	−0.0001 (3)	0.0010 (4)	−0.0012 (6)	0.62
Si*B*	0.5504 (3)	0.8367 (5)	0.2372 (6)	0.0014 (3)	0.0016 (3)	0.0052 (9)	−0.0004 (3)	0.0008 (4)	0.0006 (6)	0.54
O1-*A*	0.8659 (8)	.3404 (13)	0.1715 (15)	0.0011 (7)	0.0023 (8)	0.0067 (23)	−0.0004 (8)	0.0003 (10)	−0.0013 (18)	0.62
O2-*A*	0.1220 (9)	0.4970 (10)	0.3306 (16)	0.0041 (8)	0.0013 (9)	0.0076 (25)	−0.0002 (7)	0.0032 (12)	−0.0008 (13)	0.93
O3-*A*	0.1037 (5)	0.2633 (6)	0.5779 (13)	0.0014 (5)	0.0030 (7)	0.0121 (26)	−0.0006 (5)	0.0008 (10)	0.0023 (10)	0.95
O1-*B*	0.3743 (8)	0.8342 (13)	0.1344 (15)	0.0023 (7)	0.0016 (8)	0.0056 (25)	0.0003 (8)	0.0017 (11)	−0.0007 (17)	0.66
O2-*B*	0.6290 (8)	0.9877 (11)	0.3765 (17)	0.0022 (8)	0.0045 (11)	0.0139 (32)	−0.0018 (7)	0.0033 (13)	−0.0033 (16)	1.23
O3-*B*	0.6053 (5)	0.7087 (6)	0.4773 (12)	0.0010 (5)	0.0038 (7)	0.0106 (27)	−0.0005 (5)	0.0003 (10)	0.0024 (9)	0.93

[a] Standard deviations, σ, given in parentheses.

for $M1$ and $M2$, the occupancy refinements were carried out by Finger's RFINE program (L. W. Finger, unpublished). The fractional occupancy of Ca in $M2$ was fixed at 0.18. The fractional occupancy of Mg in $M1$ was varied subject to the condition that the sum of the fractional occupancies for Mg was equal to 0.78 in accordance with the total composition. The results are 0.720 ± 0.007 Mg, 0.280 ± 0.007 Fe for $M1$; and 0.060 ± 0.007 Mg, 0.760 ± 0.007 Fe, 0.18 Ca for $M2$, confirming the results obtained above.

DISCUSSION OF THE STRUCTURE

The variance-covariance matrix of the refined parameters and the standard deviations of the cell dimensions were used as input data for the crystallographic function and error program (ORFEE) (Busing, Martin, and Levy, 1964) to compute bond lengths and angles (Tables 4[1] and 5) and the rms components of each atom along the principal axes of its ellipsoid (Table 6). The rms displacements along interatomic vectors were also calculated (Table 7).

The structure, which is essentially the same as that obtained earlier

TABLE 4. INTERATOMIC DISTANCES IN PIGEONITE STANDARD DEVIATIONS, σ, GIVEN IN PARENTHESES

Atom Pair	Distance, Å, (σ)
Si*A* tetrahedron:	
Si—O1*A*	1.627 (8)
Si—O2*A*	1.585 (10)
Si—O3*A*	1.636 (7)
Si—O3*A*′	1.650 (7)
Mean Si*A*—O	1.625
O1*A*—O2*A*	2.742 (9)
O1*A*—O3*A*	2.686 (10)
O1*A*—O3*A*′	2.675 (9)
O2*A*—O3*A*	2.497 (11)
O2*A*—O3*A*′	2.658 (10)
O3*A*—O3*A*′	2.634 (1)
Mean O—O	2.649
Si*A* chain:	
Si*A*—Si*A*′	3.077 (5)
Si*B* tetrahedron:	
Si—O1*B*	1.620 (8)
Si—O2*B*	1.609 (11)
Si—O3*B*	1.665 (7)
Si—O3*B*′	1.660 (7)
Mean Si*B*—O	1.639
O1*B*—O2*B*	2.759 (9)
O1*B*—O3*B*	2.653 (9)
O1*B*—O3*B*′	2.637 (11)
O2*B*—O3*B*	2.688 (10)
O2*B*—O3*B*′	2.578 (12)
O3*B*—O3*B*′	2.725 (3)
Mean O—O	2.673
Si*B* chain:	
Si*B*—Si*B*′	3.048 (5)
*M*1 octahedron:	
*M*1—O1*A*	2.158 (11)
*M*1—O1*A*′	2.062 (10)
*M*1—O1*B*	2.162 (9)
*M*1—O1*B*′	2.068 (10)
*M*1—O2*A*	2.057 (10)
*M*1—O2*B*	2.086 (9)
Mean *M*1—O	2.099
*M*2 polyhedron:	
*M*2—O1*A*	2.143 (10)
*M*2—O1*B*	2.156 (10)
*M*2—O2*A*	2.093 (10)
*M*2—O2*B*	2.006 (10)
*M*2—O3*A*	2.430 (6)
*M*2—O3*B*	2.614 (7)
*M*2—O3*B*′	2.968 (6)
*M*2—O3*A*′	(3.470 (6))
Mean *M*2—O	2.344

(Morimoto, Appleman, and Evans, 1960), is projected on (100) along the direction of *a** (Fig. 1) and on (001) along the direction of *c* (Fig. 2).

There are two crystallographically different kinds of single silicate chain in the structure. The Si*A* chain is more fully extended along the *c* axis (O3*A*–O3*A*′–O3*A*″ = 170°) than the Si*B* chain (O3*B*–O3*B*′–O3*B*″ = 149°) but is not as fully extended as the chain in jadeite, (O3–O3′–O3″ = 175°) (Fig. 3). Thus the Si*B* chain is more kinked than the Si*A* chain. The same situation has been found in clinoenstatite and clinoferrosilite.

TABLE 5. INTERATOMIC ANGLES IN PIGEONITE

Atoms	Angles, degrees, (σ)	Atoms	Angles, degrees, (σ)
Si*A* tetrahedron:		Si*B* tetrahedron:	
O1*A*—Si*A*—O2*A*	117.2 (6)	O1*B*—Si*B*—O2*B*	117.4 (6)
O1*A*—Si*A*—O3*A*	110.8 (4)	O1*B*—Si*B*—O3*B*	107.7 (4)
O1*A*—Si*A*—O3*A*′	109.4 (4)	O1*B*—Si*B*—O3*B*′	107.0 (5)
O2*A*—Si*A*—O3*A*	101.7 (4)	O2*B*—Si*B*—O3*B*	110.4 (4)
O2*A*—Si*A*—O3*A*′	110.5 (4)	O2*B*—Si*B*—O3*B*′	104.1 (4)
O3*A*—Si*A*—O3*A*′	106.5 (3)	O3*B*—Si*B*—O3*B*′	110.1 (3)
Si*A* chain:		Si*B* chain:	
Si*A*—O3*A* —Si*A*′	138.9 (4)	Si*B*—O3*B* —Si*B*′	132.9 (4)
O3*A*—O3*A*′—O3*A*″	169.6 (5)	O3*B*—O3*B*′—O3*B*″	148.5 (5)

In all tetrahedra the Si—O bonds to chain-linking or bridging oxygens (O3*A* and O3*B*) are significantly longer than those to other nonbridging oxygens; the distances for Si—O3*A* and for Si–O3*B* are 1.643 and 1.663 Å, respectively, compared with 1.606 and 1.615 Å for Si–O1*A* and Si–O2*B*, respectively. The deviations of the bond angles at Si from the tetrahedral value are similar for the Si*A* and Si*B* tetrahedra. The angle O1–Si–O2 is 117° for each chain, compared with 106.5° for O3*A*–Si–O3*A* and 110° for O3*B*–Si–O3*B*. These deviations are also shown by the O–O distances of the Si tetrahedra. The O1*A*–O2*A* and O1*B*–O2*B* distances are 2.742 and 2.759 Å, respectively, compared with O3*A*–O3*A*′ and O3*B*–O3*B*′ distances of 2.634 and 2.725 Å, respectively. These distortions of the SiO_4 tetrahedra are in complete agreement with those in other metasilicates (MacDonald and Cruickshank, 1967), supporting the picture that the nonbridging oxygen atoms are more negatively charged than the bridging oxygen atoms.

The Si–Si distances are 3.076 Å for the Si*A* chain and 3.048 Å for the Si*B* chain. These values are in good agreement with those for other monoclinic pyroxenes and are considered to be characteristic of the single silicate chains of the pyroxene type.

METAL POLYHEDRA AND CATION ORDERING

Both *M*1 and *M*2 are in general positions in pigeonite compared to those in special positions on the two-fold axes in jadeite and diopside. The deviations in the *x* and *z* coordinates of *M*1 and *M*2 from the special position, (*a*/4, *c*/4), are (0.007, 0.090 Å) and (0.062, 0.101 Å), respectively. They are rather small, as discussed in the structure refinement of clinoferrosilite (Burnham, 1966c), compared with the deviations of other atoms.

TABLE 6. MAGNITUDE AND ORIENTATION OF PRINCIPAL AXES OF THERMAL ELLIPSOIDS

Atom, axis	rms displacement, A, (σ)	Angle (°) with respect to:		
		$+a$ (σ)	$+b$ (σ)	$+c^*$ (σ)
$M1, r_1$	0.079 (11)	60±42	30±42	92±28
r_2	0.087 (10)	30±42	120±42	88±30
r_3	0.099 (6)	90±18	88±37	2±38
$M2, r_1$	0.102 (4)	136±5	105±6	50±5
r_2	0.131 (4)	54±12	74±22	40±6
r_3	0.138 (3)	113±14	23±16	93±19
SiA, r_1	0.067 (11)	89±25	32±11	58±11
r_2	0.085 (7)	13±20	84±19	101±25
r_3	0.102 (8)	102±18	59±11	146±11
SiB, r_1	0.064 (11)	128±22	45±11	110±30
r_2	0.079 (7)	57±34	86±23	147±33
r_3	0.095 (8)	55±18	46±11	64±24
O1A, r_1	0.061 (28)	138±36	67±30	57±24
r_2	0.088 (21)	49±38	54±38	61±35
r_3	0.108 (22)	98±29	44±32	133±27
O2A, r_1	0.065 (26)	80±23	28±41	64±35
r_2	0.089 (21)	118±27	62±32	139±14
r_3	0.134 (13)	150±13	94±14	61±13
O3A, r_1	0.070 (17)	151±19	61±20	88±20
r_2	0.094 (14)	109±26	130±19	46±12
r_3	0.145 (11)	169±9	53±12	44±12
O1B, r_1	0.063 (30)	63±25	47±30	55±32
r_2	0.091 (24)	83±81	133±45	44±58
r_3	0.100 (18)	152±29	75±71	67±67
O2B, r_1	0.069 (24)	156±20	66±17	86±20
r_2	0.105 (19)	108±25	124±15	140±12
r_3	0.164 (15)	75±8	44±10	130±11
O3B, r_1	0.063 (18)	161±8	77±15	76±19
r_2	0.094 (14)	87±21	130±13	40±14
r_3	0.148 (11)	71±8	43±11	53±11

The $M1$ site is coordinated octahedrally by six oxygen atoms, with $M1$–O distances that depart a maximum of 0.06 Å from the mean, 2.099 Å. These $M1$ octahedra form "chains" parallel to the silicate chains by

Table 7. rms Displacements (Å) Along the Interatomic Vector, and the Interatomic Distances (Å)

Atom	rms	Atom	rms	Distance	Atom	rms	Atom	rms	Distance
O1*A*	0.068	Si*A*	0.085	1.627	*M*1	0.081	O1*A*	0.093	2.158
	0.087	*M*1	0.098	2.062		0.098	O1*A*′	0.087	2.062
	0.093	*M*1′	0.081	2.158		0.087	O1*B*	0.095	2.162
	0.089	*M*2	0.137	2.143		0.098	O1*B*′	0.090	2.068
O2*A*	0.085	Si*A*	0.077	1.585		0.087	O2*A*	0.096	2.057
	0.096	*M*1	0.087	2.057		0.081	O2*B*	0.103	2.086
	0.114	*M*2	0.113	2.093	*M*2	0.137	O1*A*	0.089	2.143
O3*A*	0.103	Si*A*	0.101	1.636		0.126	O1*B*	0.069	2.156
	0.088	Si*A*′	0.077	1.650		0.113	O2*A*	0.114	2.093
	0.097	*M*2	0.117	2.430		0.113	O2*B*	0.136	2.006
	0.140	(*M*2)	0.130	3.470		0.117	O3*A*	0.097	2.430
O1*B*	0.098	Si*B*	0.078	1.620		0.136	O3*B*	0.139	2.614
	0.090	*M*1	0.098	2.168		0.134	O3*B*′	0.125	2.968
	0.095	*M*1′	0.087	2.162		0.130	O3*A*′	0.140	3.470
	0.069	*M*2	0.126	2.156	Si*A*	0.085	O1*A*	0.068	1.627
O2*B*	0.084	Si*B*	0.079	1.609		0.077	O2*A*	0.085	1.585
	0.103	*M*1	0.081	2.086		0.101	O3*A*	0.103	1.636
	0.136	*M*2	0.113	2.006		0.077	O3*A*′	0.088	1.650
O3*B*	0.105	Si*B*	0.088	1.665	Si*B*	0.078	O1*B*	0.098	1.620
	0.072	Si*B*′	0.073	1.660		0.079	O2*B*	0.084	1.609
	0.139	*M*2	0.136	2.614		0.088	O3*B*	0.105	1.665
	0.125	*M*2′	0.134	2.968		0.073	O3*B*′	0.072	1.660

sharing a common edge (O1*A*–O1*B*) with a length of 2.825 Å (Fig. 1). It is of interest to compare the mean *M*1–O distance with that for orthopyroxenes (Morimoto and Koto, 1969). The expected value for the *M*1 site with 0.73 Mg and 0.27 Fe in orthopyroxenes is 2.090 Å. We cannot decide at present whether the slight expansion of the *M*1 octahedron in pigeonite is due to characteristics of the structure of clinopyroxenes or due to the existence of cations other than Mg or Fe in the *M*1 site.

The *M*2 site is coordinated irregularly as in other pyroxenes. The long bond distances *M*2–O3*A* (2.430 Å) and *M*2–O3*B* (2.614 Å) produce a large distortion in the *M*2 polyhedron. The distances *M*2–O3*A*′ (3.470 Å) and *M*2–O3*B*′ (2.968 Å) are characteristic of this structure: the corresponding distances are greater than 3 Å in clinoenstatite and clinoferrosilite (Burnham, 1966c), and less than 3 Å in diopside and jadeite. Thus the *M*2 site is considered to be coordinated by six oxygen atoms in clinoenstatite and clinoferrosilite and by eight oxygen atoms in diopside and jadeite. In the structure of pigeonite, a seven-fold coordination of *M*2 is apparently observed as in the structure of pigeonite from Asio (Miromoto, Appleman, and Evans, 1960).

Each $M2$ polyhedron shares one edge ($O2A$–$O3A$) with a Si-A tetrahedron and two edges ($O2B$–$O3B$) and $O3B$–$O3B'$) with SiB tetrahedra (Fig. 2). The shared-edge length with the SiA tetrahedron is 2.497 Å, and those with the SiB tetrahedron are 2.688 Å for $O2B$–$O3B$ and 2.725 Å for $O3B$–$O3B'$.

The Pauling's electrostatic balance rule (Pauling, 1960) fails for all oxygen atoms in the structure. When we consider that $M1$ and $M2$ are coordinated by six and seven oxygen atoms, respectively, the charge balance on oxygen atoms is estimated as follows: $-1/21$ for $O1A$ and $O1B$ (bonded to Si, two $M1$, and $M2$), $-8/21$ for $O2A$ and $O2B$ (bonded to Si, $M1$, and $M2$), $+2/7$ for $O3A$ (bonded to two Si and M2), and $+4/7$ for $O3B$ (bonded to two Si and two $M2$).

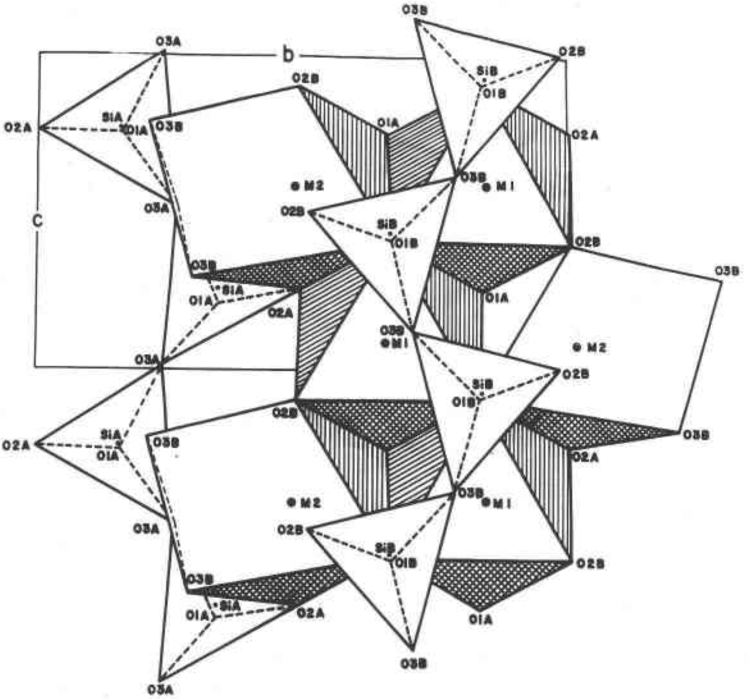

FIG. 1. Structure of pigeonite projected on (100) along the direction of a^*.

The variation in bond distances of similar nature can be reasonably explained on the basis of the differences in charge balance on the oxygen atoms. The surplus charge on $O3A$ and $O3B$, responsible for long distances from these oxygens to Si and $M2$, compensates for the negative

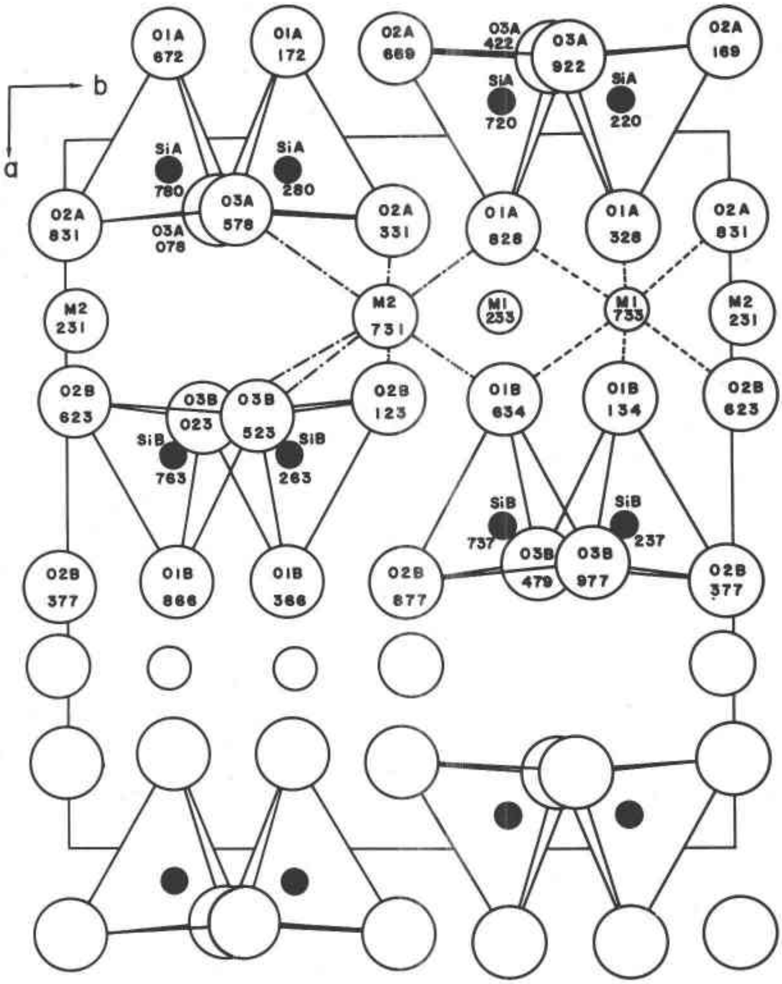

FIG. 2. Structure of pigeonite projected on (001) along the direction of *c*.

charge on O2*A* and O2*B*, in the form of short distances of these oxygens to Si, *M*1, and *M*2.

TEMPERATURE FACTORS

The equivalent isotropic temperature factors (Table 3) are of extraordinarily large values in this structure compared with those found in other pyroxenes where there is no solid solution. Therefore, the large values of the temperature factors in pigeonite are considered to reflect

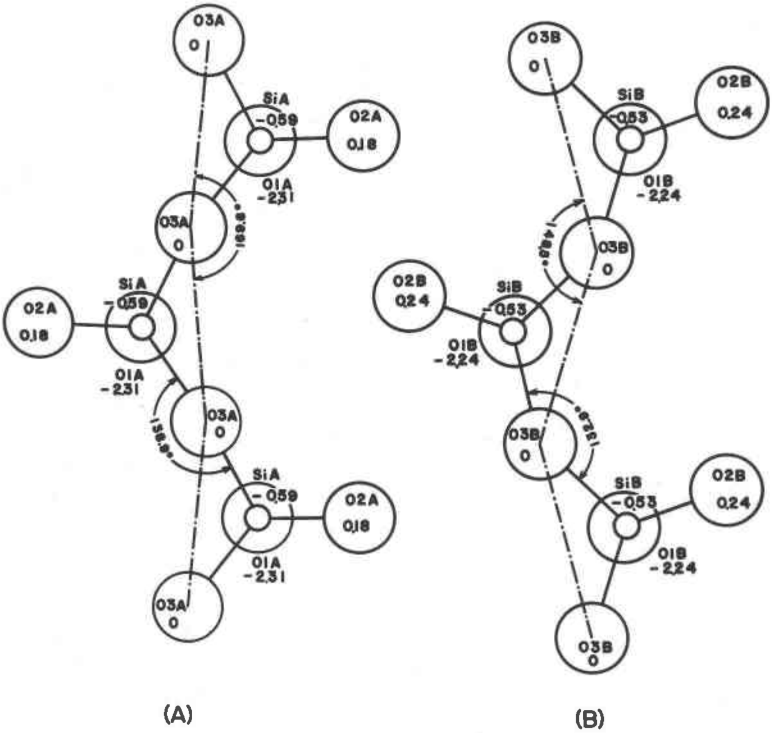

FIG. 3. Silicate chains in the structure of pigeonite projected on (100). Numbers represent distances in ångström units above and below (negative) a plane passed through the O3 oxygen atoms.

positional disorder of atoms arising from solid solution rather than thermal disorder in the structure.

In order to visualize the positional disorder of atoms, stereoscopic drawings of the crystal structure showing the vibration ellipsoids of atoms (Fig. 4) were obtained by using Johnson's (1965) ORTEP program. The rms displacements are significantly anisotropic and large for $M2$, O2A, O3A, O2B, and O3B. The direction of displacements of oxygen atoms is approximately toward the $M2$ site. The *rms* displacements of $M2$ toward O3B, O3B', and O3A' are also large (Table 6).

These rms displacements are well explained by considering that the structure of pigeonite is a statistical average of two kinds of structure representing atomic arrangements around Mg or Fe atoms, on the one hand, and around Ca atoms, on the other hand, both associated with $M2$. As discussed in the structure refinement, the $M2$ site is occupied by divalent metal atoms with the site occupancy 0.05 Mg, 0.77 Fe, and 0.18 Ca.

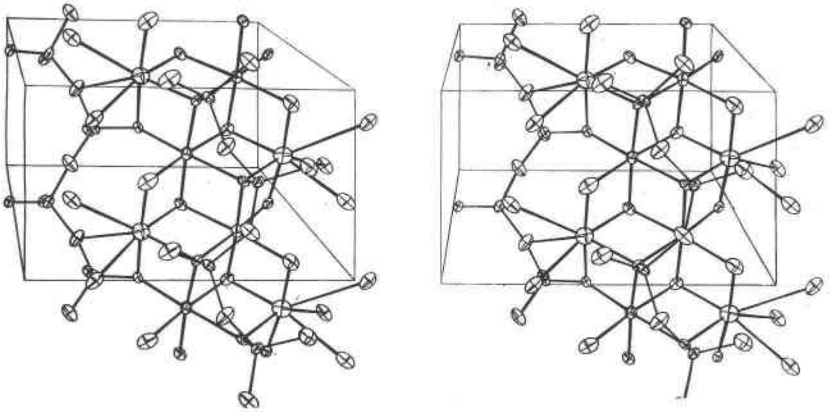

FIG. 4. Stereoscopic drawing of the crystal structure of pigeonite showing the atomic thermal ellipsoids. The ellipsoids enclose 85 percent of the probability distribution, as their axes are equal to 2.3 times the rms displacements. The crystal setting is conventional: origin at the lower left back corner of the cell, +**c** vertical, +**a** sloping toward the observer, +**b** horizontal and to the right. The line of sight is rotated by an angle of 3° toward the left and inclined downward at an angle of 5°.

The atoms surrounding the $M2$ sites, occupied by Mg or Fe aroms are arranged as in the clinoenstatite or clinoferrosilite structure, whereas those surrounding the $M2$ sites occupied by Ca atoms are arranged as in the diopside structure. Since clinoenstatite and clinoferrosilite have very little difference in structure, the structure of pigeonite is considered to be an average structure of clinoferrosilite- and diopside-like structure. The seven-fold coordination of $M2$ in pigeonite, therefore, is considered to be a statistical average between six-fold coordination for Mg and Fe and eight-fold coordination for Ca.

Our structure determination is based on the assumption of the absence of domains and therefore cannot tell us anything of their possible presence. The diffuse reflections with $h+k=2n+1$ of the Mull pigeonite, on the other hand, indicate that this pigeonite consists of domains of the same composition but in antiphase relation (Morimoto and Tokonami, 1969*b*). It is possible that the positional disorder of atoms in the domain boundaries slightly increases their temperature factors. Nevertheless the interpretation given in this paper for all temperature factors is considered to be essentially correct because the volume of the domain boundaries is negligible compared with that of the domains.

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