

CRYSTAL CHEMISTRY OF A LUNAR PIGEONITE

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ABSTRACT

A lunar pigeonite crystal from rock 10003,38 has broadened class (*b*) reflections ($h+k=2n+1$), similar to those observed by Morimoto and Tokonami for a pigeonite from Isle of Mull, Scotland. The broadening suggests the presence of a domain structure with domains about 100 Å in size. Least-squares refinement of the class (*b*) diffraction data reveals that the structure of the principal domains in the lunar pigeonite is close to that of a clinohypersthene with composition approximately $Mg_{0.54}Fe_{0.46}SiO_3$; the *M2* site is six-coordinated, and the domains are assumed to have very little Ca (0.04 atom per given formula unit, at most). The boundary regions between the domains are assumed to be Ca-rich, as suggested by Morimoto and Tokonami. Least-squares refinement of all the data or of the class (*a*) data alone ($h+k=2n$) produces a "statistical" structure, similar to that described by Morimoto and Güven for the Mull pigeonite. The "statistical" structure is considered to be an artifact produced by using normal data handling procedures in an abnormal situation. The most plausible explanation for its appearance is the presence of the "antiphase" domains postulated by Morimoto and Tokonami.

INTRODUCTION

A crystal structure refinement has been carried out for a lunar pigeonite crystal fragment from the type B igneous rock 10003,38; a preliminary account was given by Clark *et al.* (1970). The Apollo 11 type B rocks have been described by the National Aeronautics and Space Administration (1969), and the mineralogy of rock 10003 was further considered by Agrell *et al.* (1970) and Mason *et al.* (1970). Clinopyroxenes from rock 10003 have been studied by Ross *et al.* (1970*a, b*), Fernández-Morán *et al.* (1970), and Adams and McCord (1970). Using the various techniques of electron-microprobe, X-ray diffraction, and spectral reflection, these investigators all agreed on the presence of pigeonite.

In this paper we present the refinement results for the crystal structure of this lunar pigeonite, assuming the reader's knowledge of the pigeonite and clinoenstatite structures (Morimoto, Appleman, and Evans, 1960) and the pigeonite refinement by Morimoto and Güven (1968, 1970), the clinoferrosilite structural refinement (Burnham, 1967), the domain character of the pigeonite structure postulated by Morimoto and Tokonami (1969), and the orthopyroxene structural refinements by Ghose (1965), Burnham (1967), and Morimoto and Koto (1969). The nomenclature for clinopyroxenes proposed by Burnham *et al.* (1967) is used.

The results of the present study lead us to the conclusion that the lunar pigeonite, in addition to containing some augite exsolved on (001), has a domain structure. The data and our conclusions concerning the

chemical and structural nature of these domains are presented in the remainder of this paper, and a hypothetical crystallization sequence for the lunar pigeonite crystal is proposed.

EXPERIMENTAL WORK

Chemical Composition and Crystallography. We selected a crystal fragment of size approximately $0.09 \times 0.09 \times 0.15$ mm, of as nearly pure pigeonite as could be obtained by X-ray examination with the Buerger precession camera. The photographs of this crystal showed the presence of a minor amount of augite exsolved on (001). The cell constants for both pigeonite and the exsolved augite are given in Table 1, where the data for a terrestrial pigeonite are also listed. By comparison of relative intensities on the precession photographs (Ross, Papike, and Shaw, 1969), the amount of exsolved augite is estimated to compose somewhere between ten to 25 weight percent of the crystal.¹

TABLE 1. CELL PARAMETERS FOR LUNAR PIGEONITE AND AUGITE FROM ROCK 10003,38 COMPARED WITH THOSE OF PIGEONITE FROM THE ISLE OF MULL, SCOTLAND

Parameter	Lunar pigeonite This study ^a	Mull pigeonite Morimoto and Güven (1970)	Lunar augite exsolved on (001) This study ^a
a (Å)	9.678 ± 0.010	9.706 ± 0.002	9.731 ± 0.010
b (Å)	8.905 ± 0.010	8.950 ± 0.001	8.952 ± 0.010
c (Å)	5.227 ± 0.005	5.246 ± 0.001	5.244 ± 0.005
β (°)	108.71 ± 0.08	108.59 ± 0.01	106.00 ± 0.08
Cell volume (Å ³)	430.6	432.0 ± 0.2	439.1
Space group	$P2_1/c$	$P2_1/c$	$C2/c$

^a Errors estimated from precession film measurements, corrected for shrinkage.

After single-crystal diffraction data were collected for the pigeonite, the crystal was examined by A. E. Bence, SUNY, Stony Brook, using electron-microprobe scans with techniques and standards described by Bence and Albee (1968). The scans revealed an essentially homogeneous chemistry (Table 2) within the resolution of the electron microprobe.

Initially a formula was assigned to our pigeonite for use in the refinements by subtracting ten percent augite of composition assumed to be the same as that found by electron-microprobe analysis of a lunar augite from sample 10050,32 (Table 2). The lunar pigeonite is more magnesian than the terrestrial pigeonite from the Isle of Mull, Scotland (Table 2), for which the results of a modern crystal-structure refinement are available Morimoto and Güven, 1968; 1970).

Reflection broadening and domain size. The broadening of class (b) reflections², first reported

¹ A typical precession $h0l$ net of a lunar clinopyroxene crystal (rock 10003,38) containing about 50 percent pigeonite and 50 percent augite oriented on (001) is illustrated by Ross *et al.* (1970b, Fig. 1b).

² Following the nomenclature of Bown and Gay (1957), the class (a) reflections are those hkl with $h+k=2n$, and the class (b) reflections are those hkl with $h+k=2n+1$.

TABLE 2. ELECTRON MICROPROBE ANALYSIS AND FORMULA ASSIGNMENT FOR LUNAR PIGEONITE FROM ROCK 10003,38

Oxide	Wt. % ^a	Cation	Formula based on four cations			
			This study			Morimoto and Güven (1968)
			Average	Assumed augite ^b	Assigned pigeonite ^c	Pigeonite, Isle of Mull, Scotland ^d
CaO	5.37	Ca	0.218	0.735	0.163	0.16
Na ₂ O	0.03	Na	0.002	—	—	—
FeO	20.64	Fe	0.656	0.307	0.718	1.02
MnO	0.40	Mn	0.013	—	—	—
MgO	18.29	Mg	1.035	0.900	1.050	0.82
Cr ₂ O ₃	0.28	Cr	0.008	—	—	—
TiO ₂	1.03	Ti	0.029	0.058	0.026	—
		Al ^{VI}	0.039	—	0.043	—
Al ₂ O ₃	1.45					
		Al ^{IV}	0.026	0.106	0.017	—
SiO ₂	51.98	Si	1.974	1.894	1.983	2.00
Σ	99.47		4.000	4.000	4.000	4.00

^a Average of 6 traverses. Absence of Fe₂O₃ is assumed (Engel and Engel, 1970; Herr *et al.*, 1970; Herzenberg and Riley, 1970; Maxwell *et al.*, 1970).

^b Calculated as explained in the text by reference to the chemical composition of the most calcic portion of augite from rock 10050,32, crystal no. 6, analysis 46 (Ross *et al.*, 1970b, Table 1); Mn and Cr included with Fe, and Na with Ca.

^c Assuming 90% pigeonite and 10% augite as above.

^d Electron-probe microanalysis by F. R. Boyd, Geophysical Laboratory, Washington, D. C., which was in good agreement with a chemical analysis by Hallmond (1914).

by Bown and Gay (1957), was recently discussed in detail by Morimoto and Tokonami (1969), who studied the effect in pigeonite from the Isle of Mull, Scotland. Our observations of this phenomenon in the lunar pigeonite agree in general with the observations made by Morimoto and Tokonami for the Mull pigeonite. The broadening is not readily visible on precession photographs of the lunar pigeonite but is immediately apparent when 2θ scans are recorded on the single-crystal diffractometer charts and compared with similar scans for the class (*a*) reflections. We have not compared reflections from a standard crystal with the class (*a*) reflections of the lunar pigeonite; we refer to the class (*a*) reflections as "sharp" relative to the broader class (*b*) reflections only.

For our study of the lunar pigeonite reflections, we assumed that the broadening could be directly related to the small size of the domains. This assumption implies that the single crystal acts as a small mosaic diffraction grating in producing the class (*b*) reflections, each mosaic reflecting X-rays independently of the others. On this basis, we examined the 2θ -scan profiles of three class (*b*) reflections in the lunar pigeonite as follows. From the width of each of the three reflections, we subtracted a half-width measured for each of four standard class (*a*) reflections (Table 3). The resultant half-width values were then assumed to be due entirely to domain size, unaffected by either the type of instrument used to collect the data, or the diffraction geometry. The average domain thickness *t* perpendicular to

TABLE 3. DOMAIN THICKNESS^a ESTIMATED FOR CLINOHYPERSTHENE FROM LUNAR ROCK 10003,38

Class (b) <i>hkl</i>	Domain thickness <i>t</i> (Å), as estimated from selected class (a) <i>hkl</i> reflections				
	$\bar{6}02$	$\bar{7}12$	$\bar{6}22$	352	Average <i>t</i>
702	129	113	95	115	113
052	119	106	90	107	106
231	77	71	64	72	71

^a $t = 0.09\lambda/W_{1/2}$, where $W_{1/2} = 2(\sin \theta' - \sin \theta'')$, θ' and θ'' being respectively the value for high and low angle sides at half maximum intensity, $\lambda = 0.7107 \text{ \AA}$ (MoK α), and the constant 0.90 was evaluated from calculated diffraction profiles (see text).

each of the three *hkl* planes was calculated from the half-width $W_{1/2}$ of each reflection by using a variant of the Scherrer equation for line broadening: $t = 0.90\lambda/W_{1/2}$ (Ross, 1968), where λ is the X-ray wave length and $W_{1/2} = 2(\sin \theta' - \sin \theta'')$, θ' and θ'' being, respectively, the values of theta at the high and low angle sides of the reflection, at half maximum intensity. The constant, 0.90, was evaluated from calculated diffraction profiles obtained by taking the Fourier transform of various model graphite platelets of differing thicknesses. The thickness obtained from these calculations is given in Table 3. The values suggest that the domains are somewhat equant since the three reciprocal lattice vectors [702]*, [052]*, and [231]* are oriented quite differently in reciprocal space. There is some indication that the domains may be a little thinner perpendicular to the 231 plane.

An electron micrograph of a fragment of a pyroxene crystal from rock 10047,27 is shown in Figure 1. The crystal contains exsolution lamellae of "pigeonite" oriented parallel to (001) of the host. The lamellae vary in thickness from about 50 Å to 350 Å. Augite exsolution lamellae about 130 Å thick are seen in electron micrographs of pigeonite crystals from Apollo 12 rock 12021,103. Though these observations do not bear directly on the size of the clinohypersthene domains in the pigeonite from rock 10003, they do demonstrate that exsolution lamellae in lunar crystals can be sufficiently thin to cause line broadening.

Collection and Refinement of X-ray Diffraction Data. Intensity data for the lunar pigeonite were collected automatically on a normal-beam, equatorial diffractometer with Nb-filtered Mo X-radiation, and 2θ scan methods using a scintillation counter with background counts of 20 seconds at beginning and end points. Absorption corrections ($\mu = 34.7 \text{ cm}^{-1}$) were calculated, but were so slight overall that the uncorrected data were used in the refinements. Corrections for anomalous dispersion were applied, and details of the collection and refinement methods, including the scattering factors and computer programs used, are to be found in Clark, Appleman, and Papike (1969). A total of 1361 non-equivalent *hkl* reflections were available for the refinements. Of this number, 589 were considered "unobserved" because the $|F_0|$ was less than five times the standard deviation from the counting statistics. The refinements were initiated using the parameters obtained by Morimoto and Güven (1968) for the Mull pigeonite, with unit weights assigned to all reflections. Following six cycles of refinement for scale factor, positional parameters, individual isotropic temperature factors, and Mg/Fe occupancy in the *M* sites¹, the residual *R* dropped to

¹ Assuming fully occupied *M* sites, fixing Ca in *M2* and Ti and Al^{VI} in *M1* with values assigned from the probe analysis for these elements and, for total Fe total Mg (Table 2).

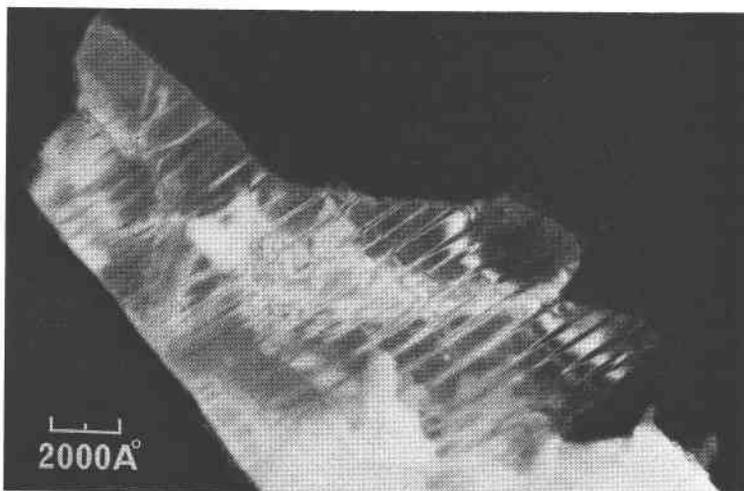


FIG. 1. Electron micrograph by E. J. Dwornik, U. S. Geological Survey, of a fragment of a lunar augite crystal from rock 10047,27, showing lamellae and domains (very light areas) of pigeonite. Although the lamellae generally trend parallel to (001) of the host they show a complex sub-structure, splitting into pairs, coalescing, and curving in various areas of the photograph. The lamellae vary in thickness and in some areas (right side of photograph) coalesce into larger domains, some as thick as 350 Å.

0.077 and the values listed in Table 4 in the column headed "All data" were in good agreement with those found for the Mull pigeonite.

The data were then divided into two classes, 673 class (a) reflections with 475 observed intensities, and 688 class (b) reflections with 297 observed intensities. Refinements were carried out separately for each data set, using first unit weights and then weights based on the counting statistics; the latter scheme gave better results and was used in the final cycles. For the class (a) data, the same parameters were refined in three cycles as for all the data, and the results are similar (Table 4). For the class (b) data, the unexpectedly good results, discussed below, led to some changes in procedure for the later cycles. The Mg/Fe occupancy was refined without including any other cations, for the following reasons. First, tests with and without the 0.16 atom of Ca in $M2$ showed that the refinements were insensitive to its presence. Second, although Ca commonly takes seven to nine coordinating oxygens, and rarely as few as six, the coordination of this $M2$ site was clearly sixfold. The additional oxygens completing the eightfold coordination of Ca in diopside are removed to beyond 3.0 Å in this structure. Third, a minimum Ca-O approach is close to 2.30 Å (MacGillavry and Rieck, 1962, p. 260), whereas here four of the six $M2$ -O distances are less than 2.20 Å. For these reasons, it was considered that very little Ca could be accommodated in such a site.

Using the class (b) data, three cycles of refinement were carried out omitting Ca, and without any chemical restriction other than that the total chemical content of $M1$ plus $M2$ be $Mg + Fe = 2.0$. The initially assigned equal distribution, $M1$ and $M2$ each 0.50 Mg plus 0.50 Fe, changed to yield values almost the same as those given in Table 4 for the class (b) data. This refinement exhibited no anomalies, produced reasonable temperature factors, also similar to those in Table 4 (class b data), and gave a total amount of Fe pres-

ent as 0.92 atom. When the average bond distances for each *M* site were used in the relationships between bond distance and ferrosilite content given by Morimoto and Koto (1969) for orthoenstatite, the resultant amount of total Fe was also 0.92 atom. Therefore the total amount of Fe was fixed at this value for the remaining refinements. Finally, three cycles were carried out fixing all parameters except the anisotropic temperature factors for O3 oxygens and the *M2* site. Anisotropic temperature factors could not be refined for all atoms because of the small number of data.

The final parameters are compared in Table 4 with those from the other refinements, and the anisotropic temperature factors and thermal ellipsoids are given in Table 5. A stereoscopic-pair view of the structure is given in Figure 2 for convenience in considering the structural details. The observed and calculated structure factors for the two classes of data are compared in Table 6¹. A final electron-density map based on all the observed data but using the parameters from the class (*b*) data refinement was calculated as a check, and had no unusual features. A difference Fourier calculated with class (*b*) data only was featureless, showing nothing more than ± 0.5 electrons per cubic Ångström. A subtraction Fourier was calculated from the class (*a*) data, and its interpretation is discussed below.

DISCUSSION OF RESULTS FROM THE CRYSTAL-STRUCTURE REFINEMENT

Atomic parameters and temperature factors. The parameters obtained from the refinements using all data, and class (*a*) data only, are in agreement with those obtained by Morimoto and Güven (1970) from refinement of all data for the Mull pigeonite. However, the separate refinement of the lunar pigeonite class (*b*) data shows significant differences from the others.

Considering first the refinement using all data, none of the positional parameters differ from those of the Mull pigeonite by more than seven standard deviations, and those few greater than three standard deviations are for atoms such as O3A, *M1* and *M2*, where shifts with changes in chemical composition might be expected. The refinement using only the class (*a*) data gives similar results with somewhat larger associated errors. However, these two refinements and that for the Mull pigeonite have in common some disturbing features. The standard deviations are appreciably higher than those found for parameters of *C2/c* intermediate-composition clinopyroxenes (Peacor, 1967; Clark, Appleman, and Papike, 1969), although the data were collected and refined similarly in two cases. The pigeonite temperature factors are generally larger than normal and exhibit curious imbalance for atoms having the same role in different chains, e.g., Mull pigeonite, O2A 0.93 Å², O2B 1.23 Å²; lunar pigeonite (all data), O3A 1.6 ± 0.1 Å², O3B 1.0 ± 0.1 Å². Such variations are well outside the limits of error and furthermore are physically un-

¹ To obtain a copy of Table 6, order NAPS Document #01379 from National Auxiliary Publications Service, c/o CCM Information Corporation, 909 Third Avenue, New York, New York 10022, remitting in advance \$2.00 for microfiche or \$5.00 for photocopies, payable to CCMIC-NAPS.

TABLE 4. COMPARISON OF ATOMIC PARAMETERS FROM VARIOUS REFINEMENTS OF DATA FOR A LUNAR PIGEONITE FROM ROCK 10003,38 AND A PIGEONITE FROM ISLE OF MULL, SCOTLAND

Atom	Parameter ^a	Mull pigeonite		Lunar pigeonite, This study	
		Morimoto and Güven (1970) ^b	All data	Class (a) data	Class (b) data ^c
M1	Mg	0.720 (7)	0.78	0.79	0.67
	Fe	0.280	0.15 (1)	0.14 (1)	0.33 (9)
	Ti (fixed)	—	0.03	0.03	—
	Al (fixed)	—	0.04	0.04	—
	<i>x</i>	0.2508 (4)	0.2503 (3)	0.2491 (9)	0.2506 (2)
	<i>y</i>	0.6548 (2)	0.6538 (3)	0.6540	0.6548 (6)
	<i>z</i>	0.2328 (8)	0.2283 (6)	0.2265 (14)	0.2300 (4)
	<i>B</i>	0.67	0.67 (6)	0.69 (8)	0.55 (6)
M2	Ca (fixed)	0.18	0.16	0.16	—
	Mg	0.060	0.27	0.26	0.41
	Fe	0.760	0.57	0.58	0.59
	<i>x</i>	0.2564 (3)	0.2560 (3)	0.2569 (5)	0.2564 (1)
	<i>y</i>	0.0183 (1)	0.0187 (2)	0.0189 (2)	0.0167 (3)
	<i>z</i>	0.2308 (6)	0.2269 (4)	0.2289 (10)	0.2246 (4)
	<i>B</i>	1.26	1.11 (4)	1.22 (6)	0.51 (3)
	SiA	<i>x</i>	0.0427 (3)	0.0431 (3)	0.0439 (6)
	<i>y</i>	0.3398 (5)	0.3408 (4)	0.3412 (7)	0.3399 (4)
	<i>z</i>	0.2797 (6)	0.2794 (5)	0.2786 (13)	0.2844 (5)
	<i>B</i>	0.62	0.74 (4)	0.71 (11)	0.40 (4)
SiB	<i>x</i>	0.5504 (3)	0.5508 (3)	0.5501 (6)	0.5520 (2)
	<i>y</i>	0.8367 (5)	0.8377 (3)	0.8371 (7)	0.8364 (4)
	<i>z</i>	0.2372 (6)	0.2367 (5)	0.2355 (12)	0.2368 (5)
	<i>B</i>	0.54	0.52 (4)	0.70 (10)	0.34 (4)
O1A	<i>x</i>	0.8659 (8)	0.8678 (8)	0.8712 (19)	0.8684 (7)
	<i>y</i>	0.3404 (13)	0.3377 (9)	0.3377 (21)	0.3373 (10)
	<i>z</i>	0.1715 (15)	0.1708 (14)	0.1715 (36)	0.1740 (12)
	<i>B</i>	0.62	0.72 (10)	0.74 (31)	0.57 (11)
O1B	<i>x</i>	0.3743 (8)	0.3739 (8)	0.3703 (20)	0.3755 (7)
	<i>y</i>	0.8342 (13)	0.8362 (9)	0.8358 (22)	0.8357 (9)
	<i>z</i>	0.1344 (15)	0.1332 (14)	0.1319 (37)	0.1296 (12)
	<i>B</i>	0.66	0.75 (10)	1.01 (35)	0.43 (11)
O2A	<i>x</i>	0.1220 (9)	0.1216 (8)	0.1177 (16)	0.1231 (8)
	<i>y</i>	0.4970 (10)	0.4991 (9)	0.5003 (16)	0.4977 (10)
	<i>z</i>	0.3306 (16)	0.3280 (15)	0.3260 (30)	0.3312 (13)
	<i>B</i>	0.93	0.90 (10)	0.85 (26)	0.78 (13)
O2B	<i>x</i>	0.6290 (8)	0.6307 (9)	0.6345 (16)	0.6314 (7)
	<i>y</i>	0.9877 (11)	0.9875 (9)	0.9874 (16)	0.9850 (9)
	<i>z</i>	0.3765 (17)	0.3771 (15)	0.3791 (32)	0.3814 (12)
	<i>B</i>	1.23	1.12 (12)	0.88 (26)	0.59 (12)
O3A	<i>x</i>	0.1037 (5)	0.1039 (10)	0.1034 (12)	0.1048 (6)
	<i>y</i>	0.2633 (6)	0.2659 (10)	0.2667 (13)	0.2683 (6)

TABLE 4. (Continued)

Atom	Parameter ^a	Mull pigeonite	Lunar pigeonite This study		
		Morimoto and Güven (1970) ^b	All data	Class (a) data	Class (b) data ^c
O3B	<i>z</i>	0.5779 (13)	0.5852 (18)	0.5815 (25)	0.5917 (9)
	<i>B</i>	0.95	1.62 (14)	1.39 (17)	1.12 (9)
	<i>x</i>	0.6053 (5)	0.6041 (8)	0.6034 (10)	0.6045 (5)
	<i>y</i>	0.7087 (6)	0.7079 (9)	0.7074 (11)	0.7047 (6)
	<i>z</i>	0.4773 (12)	0.4752 (15)	0.4739 (21)	0.4707 (9)
	<i>B</i>	0.93	1.04 (11)	0.80 (14)	1.05 (9)
Scale factor		—	0.609 (10)	0.603 (12)	0.714 (11)
R all data		—	0.134	0.098	0.152
observed only		0.036	0.077	0.071	0.039
R (wt.) all data		—	0.113	0.054	0.050
observed only		—	0.081	0.053	0.028
Std. error in F _{obs}		—	4.47	3.73	1.17
No. of data, all		1500	1361	673	688
observed only		507	772	475	297

^a *B* in (Å)². Values in parentheses are one standard deviation:

for 0.2296 (22) read 0.2296 ± 0.0022, for 0.2506(2) read 0.2506 ± 0.0002, etc.

$R = \sum (|F_o| - |F_c|) / \sum |F_o|$; $R \text{ (wt.)} = [\sum w(|F_o| - |F_c|)^2 / \sum F_o^2]^{1/2}$, where $w = 1$ unless otherwise noted.

^b Isotropic *B* values calculated from anisotropic refinements. Value given for number of all data is from Morimoto and Güven (1968).

^c Statistical weights based on counting statistics were used, so w in $R \text{ (wt.)}$ is $1/\sigma^2_F$. Anisotropic temperature refinements were made for O3A, O3B, *M2* only (Table 5); equivalent isotropic *B* values are given here for those atoms.

reasonable. The temperature factor for the *M2* site, despite the presence of less than 0.20 atom of Ca, remains high at about 1.2 Å², a value comparable to those found for sites having major Ca or Na (Clark, Appleman, and Papike, 1969) but about double the value usually associated with sites containing major Mg or Fe.

However, the results for the refinement using only the class (*b*) data give a substantially lower residual *R*. Some of the positional parameters for several atoms differ appreciably from those found in refinements using other data sets. The temperature factors tend to equalize for atoms having a similar role in the different chains, notably for O2A, O2B and O3A, O3B. Although the *B* values of the O3 oxygen atoms do remain high at about 1.0 Å², such a result is physically reasonable because these are the oxygen atoms linking the tetrahedra into chains. Particularly noteworthy is the temperature factor obtained for the *M2* site, 0.51 ± 0.03 Å², which agrees well with values generally reported for six-coordinated

TABLE 5. ANISOTROPIC TEMPERATURE FACTOR TENSOR VALUES AND THERMAL ELLIPSOIDS FOR O3A, O3B AND M2 IN LUNAR CLINOHYPERSTHENE^a

Atom	Tensor values ($\times 10^4$)					
	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O3A	22 (6)	54 (8)	95 (16)	0 (6)	16 (9)	33 (9)
O3B	22 (6)	44 (8)	110 (15)	7 (5)	22 (8)	26 (9)
M2	17 (2)	18 (2)	38 (4)	3 (1)	6 (3)	4 (2)

	Thermal ellipsoids		
	O3A	O3B	M2
Axis 1, rms amplitude (\AA)	0.08 (1)	0.09 (1)	0.066 (4)
angle ($^\circ$) with <i>a</i>	120 (39)	175 (11)	81 (10)
<i>b</i>	118 (8)	86 (68)	110 (10)
<i>c</i>	32 (16)	68 (95)	34 (12)
Axis 2, rms amplitude (\AA)	0.10 (1)	0.10 (1)	0.080 (4)
angle ($^\circ$) with <i>a</i>	148 (39)	91 (107)	49 (15)
<i>b</i>	83 (18)	55 (12)	-132 (13)
<i>c</i>	102 (36)	140 (63)	123 (12)
Axis 3, rms amplitude (\AA)	0.16 (1)	0.15 (1)	0.093 (4)
angle ($^\circ$) with <i>a</i>	98 (7)	85 (9)	42 (15)
<i>b</i>	29 (6)	36 (9)	49 (14)
<i>c</i>	61 (6)	59 (8)	97 (8)

^a Errors in parentheses are one standard deviation; for 22 (6) read 0.0022 ± 0.0006 , etc. Rms means root mean square. Temperature factor form: $\exp\{-\sum_{i=1}^3 \sum_{j=1}^3 h_i h_j \beta_{ij}\}$

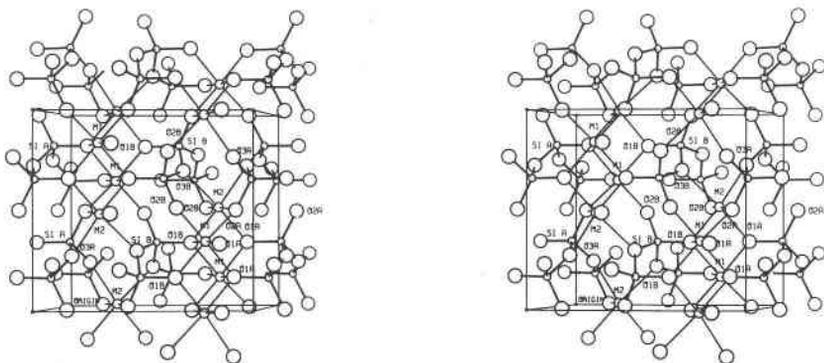


FIG. 2. Stereoscopic-pair view of the clinohypersthene structure, *a* horizontal, *b* vertical, +*c* towards viewer. Outline of one unit cell is shown; selected atoms are labelled. Coordination around M2 can be followed at a labelled M2. Drawing produced by ORTEP (Johnson, 1965).

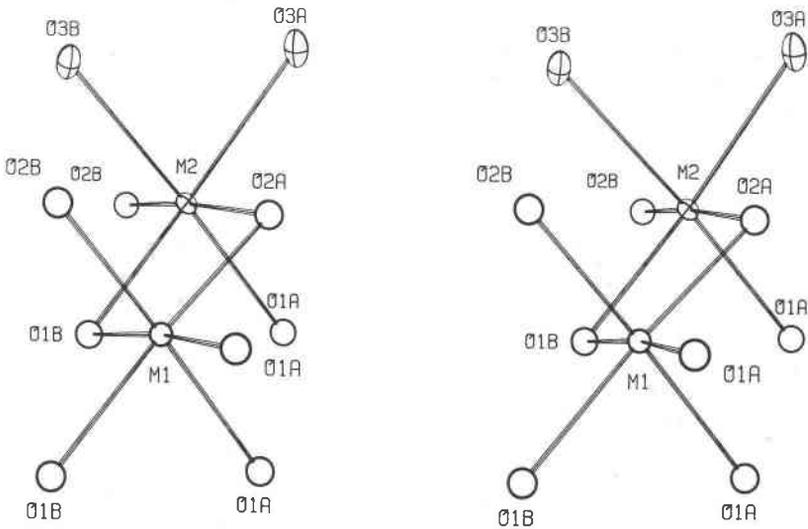


FIG. 3. Stereoscopic-pair view of the coordination octahedra *M1* and *M2* in clinohypersthene showing the thermal ellipsoids for O3 oxygens and the *M2* cation; orientation is nearly the same as in Fig. 2. Drawing produced by ORTEP (Johnson, 1965).

M2 sites containing Mg/Fe: hypersthene, $0.43 \pm 0.03 \text{ \AA}^2$ (Ghose, 1965); clinoferrosilite, $0.54 \pm 0.03 \text{ \AA}^2$ (Burnham, 1967); orthoenstatite, $0.77 \pm 0.07 \text{ \AA}^2$ (Morimoto and Koto, 1969). This low value is in striking contrast to the values around 1.2 \AA^2 found from refinements using other data sets.

The anisotropic temperature factor refinements for O3A, O3B, and *M2* proceeded smoothly. As Figure 3 illustrates, the two oxygen atoms have similar thermal ellipsoids, both resembling prolate spheroids, and the thermal ellipsoid for *M2* is virtually a sphere. There is little evidence available to determine what values the axes of thermal ellipsoids can be expected to have for oxygen atoms in an ordered structure. In a comparison of six ordered clinopyroxene structures, values from 0.04 to 0.13 \AA were found (Prewitt and Burnham, 1966; Clark *et al.* 1969, Table 19). The present values are about one-third higher (Table 5), but it is difficult to assess the significance of this difference. Oxygen atoms in other, ordered structures with no compositional complications are found to have thermal ellipsoids of similar magnitudes. Examples are few but one is provided in the sheet structure of fabianite, $\text{CaB}_5\text{O}_5(\text{OH})$, where rms amplitudes of 0.08 to 0.14 \AA are found for the axes of thermal ellipsoids of oxygen atoms (Konnert *et al.* 1971). In the absence of further evidence, about all that can be said about the oxygen thermal ellipsoids

TABLE 7. BOND DISTANCES AND ANGLES^a FOR THE SILICATE TETRAHEDRA OF A LUNAR CLINOHYPERSTHENE FROM ROCK 10003,38

Atoms	Distance (Å)		Oxygen atoms of O-Si-O angle	Angle (°)	
	A chain	B chain		A chain	B chain
Si-O1	1.605 (7)	1.618 (6)	O1, O2	118.3 (5)	117.5 (4)
Si-O2	1.583 (9)	1.593 (8)	O1, O3	110.7 (3)	107.1 (4)
ave., 4 non-br.		1.600	O1, O3'	108.7 (3)	106.3 (3)
Si-O3	1.651 (5)	1.652 (6)	O2, O3	109.8 (3)	104.6 (3)
Si-O3'	1.637 (5)	1.667 (5)	O2, O3'	111.2 (4)	110.4 (4)
ave., 4 br.		1.652	O3, O3'	106.4 (2)	111.0 (2)
ave. of 4	1.619	1.632			
ave. of 8		1.626	O3-O3'-O3''	165.7 (5)	145.5 (5)
Si-Si'	3.065 (4)	3.032 (4)	Si-O3-Si'	137.5 (4)	132.0 (3)

^a Errors in parentheses are one standard deviation: for 1.605 (7) read 1.605 ± 0.007 Å *etc.* Abbreviations as follows: non-br., non-bridging oxygen atoms; br., bridging oxygen atoms.

in lunar pigeonite is that the values are not indicative of major disordering or appreciable thermal motion. As for the *M2* site in lunar pigeonite, the values of its thermal ellipsoid provide no evidence for any disordering, because they are quite similar to those observed for the six-coordinated *M1* site in *C2/c* ordered clinopyroxenes and are actually less than those for the *M2* site in such clinopyroxenes (Prewitt and Burnham, 1966; Clark *et al.* 1969, Table 19). Clearly, further evidence on this point is needed for meaningful discussion.

Interatomic Distances and Angles. Bond lengths and angles and selected interatomic distances and angles have been calculated from the parameters obtained in the refinement of class (*b*) data. The results for the silicate tetrahedra are given in Table 7, and for the *M1* octahedron, in Table 8. These values are comparable to those obtained by Morimoto and Güven for the Mull pigeonite, allowing for the difference in chemical composition of the *M1* site. The characteristic features common to chain silicates are evident here: the short Si-O2 distances, the longer Si-O distances for the bridging O3 oxygen atoms, and the increased O1-Si-O2 angle of the non-bridging oxygens. There is considerable difference in the O3-O3'-O3'' angle between the two chains, the *A* chain (165.7°) resembling in this respect the chains of *C2/c* intermediate-composition clinopyroxenes (Clark *et al.*, 1969), whereas the *B* chain (145.5°) is much more twisted. A similar difference between *A* and *B* chains was found in the Mull pigeonite (Morimoto and Güven, 1968; 1970) and in clinoferrosilite (Burnham, 1967).

TABLE 8. OCTAHEDRAL M-O DISTANCES AND ANGLES^a IN A LUNAR CLINOHYPERSTHENE FROM ROCK 10003,38

Oxygen atom of <i>M1-O</i>	Location of oxygen atom			Distance (Å)
	<i>x</i>	<i>y</i>	<i>z</i>	
O1A	0.1316	0.6627	-0.1740	2.057 (7)
O1A'	0.1316	0.8373	0.3260	2.142 (9)
O1B	0.3755	0.6643	0.6296	2.052 (7)
O1B'	0.3755	0.8357	0.1296	2.176 (8)
O2A	0.1231	0.4977	0.3312	2.044 (9)
O2B	0.3686	0.4850	0.1186	2.087 (8)
				ave. 2.093

Oxygen atoms of O- <i>M1-O</i> angle	Angle (°)	Oxygen atoms of O- <i>M1-O</i> angle	Angle (°)
1A, 1A'	92.8 (3)	1B, 1B'	91.4 (3)
1A, 1B'	84.2 (3)	1B, 2A	88.4 (3)
1A, 2A	95.9 (3)	1B, 2B	96.7 (3)
1A, 2B	85.1 (3)	1B', 2B	94.2 (3)
1A', 1B	85.2 (3)	2A, 2B	90.4 (5)
1A', 1B'	83.0 (4)	1B', 2A	175.5 (4)
1A', 2A	92.5 (3)	1A, 1B	175.3 (5)
		1A', 2B	176.6 (3)

^a Errors in parentheses are one standard deviation: for 2.057 (7) read 2.057 ± 0.007 Å. *M1* contents, 0.67 Mg, 0.33 Fe (from site occupancy refinements).

A linear relationship between mean *M1-O* distance and Mg/Fe occupancy for the *M1* site in orthopyroxenes has been given by Morimoto and Koto (1969), and using that equation, occupancies of 0.69 Mg and 0.31 Fe²⁺ are found for the lunar pigeonite. These values agree with the final results of the site occupancy refinement, 0.67 Mg and 0.33 Fe²⁺, within the rather large error (Table 4). A similar linear relationship can be obtained for the *M1* site in clinopyroxenes by taking as end points the bond distances for diopside and clinoferrosilite (see Clark *et al.* 1969, p. 43). Using the notation of Morimoto and Koto (1969), this relationship is

$$r[M(1) - O] = 2.077 + 0.060X$$

where *r* is the mean *M1-O* distance, and *X* is the mole percent ferrosilite. The values obtained from this equation for the lunar pigeonite are 0.73 Mg and 0.27 Fe²⁺, again in agreement with the site occupancy refinement, within the errors.

The $M2$ coordination in the lunar pigeonite is definitely sixfold and is illustrated together with the $M1$ octahedron in Figure 3. The $M2$ octahedron containing Mg in orthoenstatite (Morimoto and Koto, 1969) and the one containing Fe^{2+} in clinoferrosilite (Burnham, 1967) are remarkably similar to the mixed (Mg,Fe)-octahedron ($M2$) of the present structure (Table 9). Only pyroxenes with eight-coordinated $M2$ sites are known to have the $C2/c$ (diopside type) structure. Since 1960 when Morimoto, Appleman, and Evans discussed the effect of introducing small bivalent cations such as Mg and Fe^{2+} into the clinopyroxene structure, numerous investigators have agreed that the resultant reduction of the $M2$ site from eightfold to sixfold coordination produces distortions in the silicate chains that cause the symmetry changes observed: either to monoclinic $P2_1/c$ or to orthorhombic $Pbca$.

The longest $M2$ -O distance observed for the six coordinating oxygens in lunar pigeonite is 2.557 ± 0.006 Å. This value is higher than the 2.453 ± 0.009 Å in orthoenstatite (Morimoto and Koto, 1969), but slightly lower than the 2.587 ± 0.006 Å in clinoferrosilite (Burnham, 1967). In the lunar pigeonite the next approach by an oxygen to $M2$ is 3.021 ± 0.006 Å by O3B', whereas SiA approaches at 2.851 Å (see discussion below). Although O3B' has been considered part of a sevenfold coordination polyhedron in pigeonite (Morimoto, Appleman, and Evans, 1960; Morimoto and Güven, 1970), we believe that it is too far away to be part of the primary coordination scheme. The $M2$ site has primary coordination of either six or eight oxygen atoms, but not seven.

With the refinements now available the differences between the $M2$ sites in the $C2/c$ and $P2_1/c$ structures produced by this coordination change can be followed in detail, and reference to a labelled $M2$ in Figure 2 illustrates the discussion. The refinement of diopside (Clark, Appleman, and Papike, 1969, see Fig. 3) shows that edges of four tetrahedra are shared with the large $M2$ polyhedron: two equivalents, O2C2-O3C1 and O2D2-O3D1, each 2.570 ± 0.002 Å, and two other equivalents, O3C1-O3C2 and O3D1-O3D2, each 2.644 ± 0.003 Å. The octahedron coordinating the $M2$ site in pigeonite has only one edge shared with a tetrahedron, and this is the O2A-O3A edge, corresponding to diopside O2D2-O3D1, but shortened in pigeonite to 2.492 ± 0.009 Å. As a result, there is a close $M2$ -SiA approach of 2.851 ± 0.009 Å. Because only one O3 from each chain coordinates the pigeonite $M2$, there are no O3-O3 tetrahedral edges shared with the $M2$ octahedron. The remaining possible shared tetrahedral edge, corresponding to diopside O2C2-O3C1, is O2B-O3B' in pigeonite, not O2B-O3B which is not a tetrahedral edge.¹ The tetrahedral

¹ Morimoto and Güven (1970) say that each $M2$ polyhedron shares "two edges (O2B-O3B and O3B-O3B') with SiB tetrahedra". They are including O3B' in the coordination

angles involved reflect these changes. The shared edges in diopside have associated O-Si-O angles reduced from the normal tetrahedral value to 103.5° and 104.2° ; in pigeonite, the retained shared edge (*A* chain) has a tetrahedral angle of 100.1° , but the released, and now unshared, edge has the normal tetrahedral angle of 109.6° . Similar effects are also observed in the *M2* octahedra and O-Si-O angles of orthoenstatite and clinoferrosilite.

The average *M2*-O bond distance has been related to Mg/Fe occupancy of the *M2* site in orthopyroxenes by Morimoto and Koto (1969). Using that relationship and the average lunar pigeonite *M2*-O distance, 2.213 Å, the *M2* site would contain 0.33 Mg and 0.67 Fe²⁺. The site occupancy refinements gave 0.41 Mg and 0.59 Fe²⁺, again in agreement within the rather large errors. However, a similar linear relationship can be developed including the possibility of Ca-O contributions, provided a few further assumptions are made, as follows. For the average six-coordinated *M2*-O distance we take Ca-O from diopside, 2.425 Å (Clark, Appleman, and Papike, 1969), Mg-O from orthoenstatite, 2.158 Å (Morimoto and Koto, 1969), and Fe²⁺-O from clinoferrosilite, 2.224 Å (Burnham, 1967). Using the average 2.213 Å value (Table 9) for the lunar pigeonite, we can calculate the number of atoms of Ca and Fe²⁺ that might be present in *M2* by fixing the amount of Mg and assuming the site fully occupied. If we take the minimum amount of Mg as 0.26 atom (Table 4) and the maximum as 0.41, we find, respectively, 0.03 and 0.08 atom of Ca. This method seems to provide a reasonable estimate of the limits of Ca that might be considered present in the *M2* site.

Such a low Ca content is in agreement with the values obtained from electron-microprobe analyses of coexisting inverted pigeonite and augite host from the Bushveld intrusion (Boyd and Brown, 1969). The inverted pigeonite host which had exsolved augite contains 0.06 Ca atom per formula unit based on six oxygens. The lamellae of clinohypersthene exsolved from the augite host contain 0.03 atom of Ca per formula unit.

Interpretation of the results of the crystal-structure refinement. The lunar pigeonite we are studying is a single crystal, but we know from the broadening of the class (*b*) reflections that the crystal is composed of small mosaic domains. The satisfactory refinement of the class (*b*) data taken together with the resultant structural features suggest that the structure

polyhedron; the octahedron we are considering omits O3B'. The coordinates of the O2B and O3B' atoms coordinating *M2* at the *x*, *y*, *z* of Table 4 are: O2B, *x*=0.3686, *y*=0.0150, *z*=0.6186; O3B', *x*=0.3955, *y*=0.2954, *z*=0.5293, so these two are in the same tetrahedron, but O3B at *x*=0.3955, *y*=0.2046, *z*=0.0293 is not. Therefore, for the octahedron, the only edge shared with a tetrahedron is O2A-O3A. Inspection of the labelled *M2* site (Fig. 2) illustrates the situation.

TABLE 9. COMPARISON OF *M2* OCTAHEDRA FOR LUNAR CLINOHYPERSTHENE FROM ROCK 10003,38, A PIGEONITE FROM ISLE OF MULL, SCOTLAND, AN ORTHOENSTATITE FROM THE BISHOPVILLE METEORITE, AND A SYNTHETIC CLINOFERROSILITE

Oxygen atom of <i>M2</i> -O	Distance (Å) ^a			
	Mull pigeonite	Lunar clinohypersthene	Bishopville orthoestatite	Synthetic clinoferrrosilite
	Morimoto and Güven (1970)	This study	Morimoto and Koto (1969)	Burnham (1967)
O1A	2.143 (10)	2.168 (8)	2.102 (9)	2.159 (7)
O1B	2.156 (10)	2.130 (8)	2.081 (9)	2.136 (6)
O2A	2.093 (10)	2.051 (7)	2.035 (10)	2.032 (5)
O2B	2.006 (10)	1.996 (7)	1.984 (10)	1.985 (5)
O3A	2.430 (6)	2.376 (6)	2.292 (9)	2.444 (5)
O3B	2.614 (7)	2.557 (6)	2.453 (9)	2.587 (6)
average of 4 shortest	2.099	2.086	2.050	2.078
average of 6	2.240	2.213	2.158	2.224
O3B'	2.968 (6)	3.021 (6)	3.109	3.107
Octahedral edges				
O1A-O1B	2.826	2.861 (10)	2.800 (10)	2.851
O1A-O2A	2.959	2.952 (11)	2.910 (13)	2.909
O1A-O2B	2.789	2.802 (10)	2.757 (11)	2.856
O1A-O3A	3.761	3.700 (11)	3.577 (12)	3.742
O1B-O2A	2.886	2.856 (11)	2.804 (11)	2.914
O1B-O2B	3.029	3.032 (10)	2.977 (13)	3.025
O1B-O3B	3.419	3.341 (10)	3.201 (11)	3.391
O2A-O3A	2.497	2.492 (9)	2.500 (12)	2.537
O2A-O3B	3.116	3.085 (10)	3.037 (12)	3.078
O2B-O3A	3.771	3.649 (10)	3.529 (12)	3.636
O2B-O3B	3.680	3.594 (9)	3.441 (13)	3.593
O3A-O3B	2.940	2.945 (7)	2.884 (12)	2.986
Average	3.139	3.109	3.035	3.126
Oxygens of O- <i>M2</i> -O				
		Angles (°)		
O1A, O1B	82.2	83.4 (4)	84.1 (3)	83.2
O1A, O2A	88.6	88.8 (3)	89.4 (4)	87.8
O1A, O2B	84.4	84.5 (3)	84.8 (4)	87.0
O1A, O3A	110.5	108.9 (2)	108.9 (4)	108.6
O1B, O2A	85.6	86.2 (3)	85.9 (4)	88.7
O1B, O2B	93.4	94.5 (3)	94.2 (3)	94.4
O1B, O3B	91.1	90.5 (2)	89.4 (3)	91.3
O2A, O3A	66.6	68.0 (3)	70.3 (4)	68.3
O2A, O3B	82.1	83.3 (3)	84.6 (3)	82.7
O2B, O3A	116.2	112.8 (3)	111.0 (4)	109.9
O2B, O3B	104.8	103.6 (3)	101.2 (3)	102.8
O3A, O3B	71.2	73.2 (2)	74.8 (3)	72.8
Average	89.7	89.8	89.9	89.8
O1A, O3B	168.9	170.3 (2)	171.5	169.1
O2A, O2B	173.0	173.1 (3)	174.2	173.6
O1B, O3A	148.3	150.5 (2)	152.3	153.2

^a Errors in parentheses are one standard deviation; for 2.143 (10) read $2.143 \pm 0.010 \text{ \AA}$, etc. Distances and angles not given in reference were calculated during present study using coordinates in reference.

of the domains is essentially that of a clinohypersthene with chemical composition close to $Mg_{0.54}Fe_{0.46}SiO_3$. For a formula based on six oxygens, the amount of Ca present is limited to 0.05 ± 0.03 atoms, according to the evidence just presented. With this information in mind, we next examine the "antiphase" domain model proposed by Morimoto and Tokonami (1969) for pigeonites.

DOMAIN MODEL FOR PIGEONITES

Morimoto and Tokonami (1969) suggested that at high temperatures there exists a pyroxene phase of pigeonite composition with a *C*-centered lattice. On cooling, this phase transforms to pigeonite with $P2_1/c$ symmetry. Transformation between a $C2/c$ pyroxene and one with $P2_1/c$ symmetry has since been observed experimentally (Smyth, 1969; Prewitt, Papike, and Ross, 1970; Prewitt, Papike, and Bence, oral comm., transformation observed in lunar pigeonite, 1970).

In the X-ray patterns of Isle of Mull pigeonite, Morimoto and Tokonami observed and analyzed diffuse class (*b*) reflections. They propose that such reflections are diffuse in pigeonite because of the occurrence of two sets of domains, both having identical primitive lattices but displaced, one with respect to another, by the translation $(\mathbf{a}+\mathbf{b})/2$. They refer to these as "antiphase" domains. Such a translation, as they point out, shifts an *A*-type silicate chain into the position of a *B*-type chain. Because the configurations of the two types of chains are similar, the translational mistake does not appreciably perturb the crystal structure. However, as they show (Morimoto and Tokonami, 1969, Fig. 6), the shift does produce bands with a *C*-centered lattice along the domain boundaries. From their analysis of the class (*b*) reflections, they conclude that the domain boundaries occur statistically every 20 unit cells along the *a* and *b* directions. They suggest that Ca tends to concentrate at the domain boundaries, which are considered sufficiently narrow to be of negligible volume compared with the primitive domains, and which therefore make a negligible contribution to the observed reflections.

Although Morimoto and Tokonami say in some sections of their paper that the domains have "the statistical structure of pigeonite" (Morimoto and Tokonami, 1969, p. 737), they say elsewhere (*ibid.*, p. 734) "the atoms surrounding Mg and Fe form a clinoenstatite or clinoferrosilite-like arrangement while those surrounding Ca form a diopside-like arrangement". They go on to say "The resultant structure is the statistical mean of these modifications." On the basis of the present refinement of class (*b*) data for the lunar pigeonite, we suggest that the "resultant structure" obtained by refinement of all data (or of class (*a*) data alone, since the results are essentially equivalent) is an artifact. This point is amplified in

the next section of this paper. The true situation is revealed by the refinement of the class (*b*) data. The structure of the principal domains in the lunar pigeonite crystal is close to that of a clinohypersthene; the boundary regions can be assumed to be Ca-rich, probably with Ca coordinated by eight oxygen atoms. Morimoto and Güven (1968, 1970) did not separate the data for the refinement of the Mull pigeonite, so there is no information available on the results of a separate class (*b*) refinement for that pigeonite. However, the close agreement between refinements for all the data of both the Mull and lunar pigeonites indicates that the results of a class (*b*) refinement for the Mull pigeonite would be similar to those for the lunar pigeonite. We suggest, therefore, that the Mull pigeonite domains are very probably also of essentially clinohypersthene structure.

We can estimate the relative amounts of the clinohypersthene domains and Ca-rich boundary regions in the lunar pigeonite crystal by using the observed scale factors as follows. Let K be the true scale factor relating counts per second to electrons for this crystal in this X-ray diffraction experiment, disregarding the augite. We can write

$$K |F_{\text{obs}}| = r |F_{\text{calc}}(I)| + (1 - r) |F_{\text{calc}}(II)|,$$

where I stands for the clinohypersthene domains, II for the Ca-rich regions, and r is the mole percent of clinohypersthene in the crystal. For the class (*b*) reflections, we assume that $F_{\text{calc}}(II) = 0$, so $K |F_{\text{obs}}| = r |F_{\text{calc}}(I)|$. Therefore $(K/r) |F_{\text{obs}}| = |F_{\text{calc}}(I)|$ and we can write

$$K/r = k(b),$$

where $k(b)$ is the scale factor obtained from the refinement of the class (*b*) data alone. It follows that

$$r = K/[k(b)].$$

Substituting the values given in Table 4, we find $r = 0.609/0.714$ or 85 percent. As the domains are about 100 Å in size (Table 3), the boundary regions making up the remaining 15 percent cannot each be more than a very few unit cells, at most.

THE "STATISTICAL" STRUCTURE OF PIGEONITE

Why does refinement of all data or of class (*a*) data produce an "average" or "statistical" structure? We have considered several possible reasons, as follows. First, there might be two distinct phases with identical cell dimensions, one $P2_1/c$ and one $C2/c$, both contributing to the class (*a*) reflections but only the $P2_1/c$ phase to the class (*b*) reflections. X-ray photographs of some lunar clinopyroxenes do show evidence for incomplete unmixing (Ross *et al.*, 1970*a, b*). The diffuse streaking between

the reciprocal lattice spots of host and lamellar phases suggests that small "islands" or possibly "domain boundaries" of more calcium-rich clinopyroxene persist within the host pyroxene, and residual calcium may cause depression of the inversion temperature ($C2/c$ to $P2_1/c$) to a value below that of the quench temperature. If the Ca-rich regions tend to maintain $C2/c$ symmetry, they would contribute to the class (a) reflections but not to the class (b) reflections. However, as we have just shown, these regions must be extremely small, with negligible contributions. Furthermore, there would be interference between the diffraction from two such phases, and it is also difficult to assume a true Ca-rich phase (such as the $C2/c$ one would be) which would not have the cell constants normally found for such clinopyroxenes. Despite certain attractive features, this hypothesis does not seem tenable.

Prior to reaching this conclusion, we tested the hypothesis by calculating a subtraction Fourier for the class (a) data, the coefficients being the differences between the observed structure factors, appropriately scaled, and the calculated structure factors for the refined parameters of clinohypersthene. It was assumed that an electron-density map of the second phase, appropriately scaled, would result, and the map does in fact have this general appearance. The peak heights are approximately one-tenth of those observed on an electron-density map. The $M2$ y position, in particular, is appreciably shifted away from the clinohypersthene value, corresponding to a six-coordinated site, towards that found for diopside which has an eight-coordinated site. However, the subtraction map can also be considered to represent the differences between the "average" structure and that of the clinohypersthene (H. T. Evans, Jr., oral comm., 1970), and this seems the most satisfactory explanation of its features.

Second, there might be appreciable contributions to the intensity of the class (a) reflections by the augite exsolved on (001). However, its cell parameters (Table 1), particularly the β value, preclude superposition of reflections except at low angles. Careful monitoring of the reflections during collection was made with this possibility in mind, and questionable reflections were eliminated from the data set. Therefore, the presence of augite should not be affecting the refinement.

Third, the differences between the A and B chains in the $P2_1/c$ structure might be so slight that the structure, considered as consisting of two sub-cells, is fundamentally so very nearly $C2/c$ that the data cannot distinguish the sub-cells. If this were the case, routine least-squares refinement of any isostructural $P2_1/c$ clinopyroxene might be expected to produce a "statistical" structure. Fortunately, a synthetic clinoferrosilite structure has been refined (Burnham, 1967), so that direct comparison without complications produced by compositional disorder can be

made. The positional parameters for clinoferrosilite are in general similar to those obtained for the Mull pigeonite (Morimoto and Güven, 1968; 1970), although the clinoferrosilite $M2$ site is six-coordinated. However, the temperature factors for the clinoferrosilite atoms agree well with those obtained by Clark, Appleman, and Papike (1969) for fully ordered $C2/c$ clinopyroxenes, in striking contrast to those obtained for the "statistical" pigeonite. Therefore the results for the "statistical" pigeonite cannot be due to a simple close correspondence between $P2_1/c$ and $C2/c$ structures.

We are thus led to the conclusion that the most plausible explanation presently available for the observed "statistical" structure is the presence in pigeonite of domains and associated boundary regions, proposed by Morimoto and Tokonami (1969). Within each domain the structure is close to that of a clinohypersthene and the class (*b*) data result from this structure. The strong class (*a*) reflections, which dominate a data set of all data, are produced by coherent diffraction from the entire crystal, and these data thus yield an "out-of-focus" picture of the structure when routine least-squares refinements are carried out. We reject the reality of the "statistical" structure for the various reasons already given, and emphasize that it exhibits anomalies not found from refinements of data for intermediate-composition clinopyroxenes with $C2/c$ symmetry, as previously noted. Obviously, further studies of various pigeonites, particularly of some exhibiting no observable broadening of the class (*b*) reflections, should be made with the evidence of the present study in view.

CRYSTALLIZATION OF THE LUNAR PIGEONITE

A consistent and rather simple physical explanation of the process that produced the present state of this lunar pigeonite crystal can be given, following the present study and based on our current knowledge of pyroxene crystal chemistry, high-temperature inversions, and exsolution phenomena. Each step can be assumed to take place under given, but unknown, temperature and pressure conditions.

First, a $C2/c$ pigeonite saturated with respect to calcium crystallized at temperatures around 1100° to 1200°C. Second, as cooling progressed, the pigeonite, in order to maintain internal equilibrium, unmixed thin lamellae of $C2/c$ augite on (001). At a particular composition on the pigeonite solvus the $C2/c$ pigeonite inverted to the $P2_1/c$ structure-type. As cooling continued to the quench temperature, domains of the $P2_1/c$ pigeonite became further depleted in calcium, thus obtaining a chemical composition close to that of clinohypersthene, $(Mg,Fe)SiO_3$.

ACKNOWLEDGEMENTS

This research was carried out in cooperation with the National Aeronautics and Space Administration. We appreciate the assistance of Prof. A. E. Bence, J. J. Papike and C. T.

Prewitt, State University of New York, Stony Brook: Prof. Bence carried out the electron-probe analysis and gave permission to use the results; they also permitted our use of their information on pigeonite inversions in the lunar material, and provided useful suggestions throughout the progress of this study. Drs. Nobuo Morimoto and Masayasu Tokonami, Osaka University, Japan, kindly sent us preprints of papers and valuable critical comments on an early version of this manuscript. Our indebtedness to the extensive research of Dr. Morimoto is evident. The manuscript has also been critically read by Dr. F. R. Boyd, Jr., Geophysical Laboratory, Washington, D. C., Prof. C. W. Burnham, Harvard University, and Dr. Howard T. Evans, Jr., U. S. Geological Survey, all of whom made useful comments. Dr. E. J. Dwornik, U. S. Geological Survey, took the electron micrograph of Fig. 1 and gave permission for its use here. We are especially grateful to the Apollo 11 astronauts and all others associated with the Apollo 11 program for making available rock 10003,38.

REFERENCES

- ADAMS, JOHN B. AND THOMAS B. MCCORD (1970) Remote sensing of lunar surface mineralogy: Implications from visible and near-infrared reflectivity of Apollo 11 samples. *Geochim. Cosmochim. Acta Suppl.* **1** 3, 1937-1945.
- AGRELL, S. O., J. H. SCOON, I. D. MUIR, J. V. P. LONG, J. D. C. MCCONNELL, AND A. PECKETT (1970) Observations on the chemistry, mineralogy and petrology of some Apollo 11 lunar samples. *Geochim. Cosmochim. Acta Suppl.* **1** 1, 93-128.
- BENCE, A. E., AND A. L. ALBEE (1968) Empirical correction factors for the electron microanalysis of silicates and oxides. *J. Geol.* **76**, 382-403.
- BOWN, M. G., AND P. GAY (1957) Observations on pigeonite. *Acta Crystallogr.* **10**, 440-441.
- BOYD, FRANCIS R., AND G. MALCOLM BROWN (1969) Electron-probe study of pyroxene exsolution. *Mineral. Soc. Amer. Spec. Pap.* No. **2**, 211-216.
- BURNHAM, CHARLES W. (1967) Ferrosilite. *Carnegie Inst. Wash. Year Book* **65**, 285-290.
- , JOAN R. CLARK, J. J. PAPIKE, AND C. T. PREWITT (1967) A proposed crystallographic nomenclature for clinopyroxene structures. *Z. Kristallogr.* **125**, 109-119.
- CLARK, JOAN R., DANIEL E. APPLEMAN, AND J. J. PAPIKE (1969) Crystal-chemical characterization of clinopyroxenes based on eight new structure refinements. *Mineral. Soc. Amer. Spec. Pap.* No. **2**, 31-50.
- , MALCOLM ROSS, DANIEL E. APPLEMAN, J. J. PAPIKE, AND A. E. BENCE (1970) Fe/Mg distribution in a lunar pigeonite [abstr.]. *Trans. Amer. Geophys. Union* **51**, 436.
- ENGEL, A. E. J., AND CELESTE G. ENGEL (1970) Lunar rock compositions and some interpretations. *Science* **167**, 527-528.
- FERNÁNDEZ-MORÁN, H., STEFAN S. HAFNER, MITSUO OHISUKI, AND DAVID VIRGO (1970) Mössbauer effect and high-voltage electron microscopy of pyroxenes in type B samples. *Science* **167**, 686-688.
- GHOSE, SUBRATA (1965) Mg^{2+} - Fe^{2+} order in an orthopyroxene, $Mg_{0.93}Fe_{1.07}Si_2O_6$. *Z. Kristallogr.* **122**, 81-99.
- HALLIMOND, A. F. (1914) Optically uniaxial augite from Mull. *Mineral. Mag.* **17**, 97-99.
- HERR, W., U. HERPERS, B. HESS, B. SKERRA, AND R. WOEFLE (1970) Determination of manganese-53 by neutron activation and other miscellaneous studies on lunar dust. *Science* **167**, 747-749.
- HERZENBERG, C. L., AND D. L. RILEY (1970) Analysis of first returned lunar samples by Mössbauer spectrometry. *Geochim. Cosmochim. Acta Suppl.* **1** 3, 2221-2241.
- JOHNSON, CARROLL K. (1965) ORTEP: A FORTRAN thermal-ellipsoid plot program for crystal structure illustrations. *U. S. Clearinghouse Fed. Sci. Tech. Info. Doc.* **ORNL 3794**, Revised.
- KONNERT, JUDITH A., JOAN R. CLARK, AND C. L. CHRIST (1971) Crystal structure of

- fabianite, $\text{CaB}_3\text{O}_6(\text{OH})$, and comparison with the structure of its synthetic dimorph. *Z. Kristallogr.* **132**, (in press).
- MACGILLAVRY, C. H., AND G. D. RIECK (1962) *International Tables for X-Ray Crystallography*, Vol. 3. The Kynoch Press, Birmingham.
- MASON, B., K. FREDRIKSSON, E. P. HENDERSON, E. JAROSEWICH, W. G. MELSON, K. M. TOWE, AND J. S. WHITE, JR. (1970) Mineralogy and petrography of lunar samples. *Science* **167**, 656-659.
- MAXWELL, J. A., L. C. PECK, AND H. B. WIIK (1970) Chemical composition of Apollo 11 lunar samples 10017, 10020, 10072 and 10084. *Geochim. Cosmochim. Acta Suppl.* **1** **2**, 1369-1374.
- MORIMOTO, NOBUO, AND NECIP GÜVEN (1968) Refinement of the crystal structure of pigeonite, $(\text{Mg}_{0.39}\text{Fe}_{0.52}\text{Ca}_{0.09})\text{SiO}_3$. *Carnegie Inst. Wash. Year Book* **66**, 494-497.
- AND ——— (1970) Refinement of the crystal structure of pigeonite. *Amer. Mineral.* **55**, 1195-1209.
- , AND KICHIRO KOTO (1969) The crystal structure of orthoenstatite. *Z. Kristallogr.* **129**, 65-83.
- , AND MASAYASU TOKONAMI (1969) Domain structure of pigeonite and clinoenstatite. *Amer. Mineral.* **54**, 725-740.
- , DANIEL E. APPELMAN AND HOWARD T. EVANS, JR. (1960) The crystal structures of clinoenstatite and pigeonite. *Z. Kristallogr.* **114**, 120-147.
- NATIONAL AERONAUTICS AND SPACE ADMINISTRATION (1969) Apollo 11 preliminary science report. Chapter 5, Preliminary examination of lunar samples. *U. S. Clearinghouse Fed. Sci. Tech. Info. Doc. NASA SP-214*, 123-142.
- PEACOR, D. R. (1967) Refinement of the crystal structure of a pyroxene of formula $\text{M}_1\text{M}_{11}(\text{Si}_{1.5}\text{Al}_{0.5})\text{O}_6$. *Amer. Mineral.* **52**, 31-41.
- PREWITT, C. T. AND CHARLES W. BURNHAM (1966) The crystal structure of jadeite, $\text{NaAlSi}_2\text{O}_6$. *Amer. Mineral.* **51**, 956-975.
- PREWITT, C. T., J. J. PAPIKE, AND MALCOLM ROSS (1970) Cummingtonite: A reversible nonquenchable transition from $P2/m$ to $C2/m$ symmetry. *Earth Planet. Sci. Lett.* **8**, 448-450.
- ROSS, MALCOLM (1968) X-ray diffraction by non-ideal crystals of biotite, muscovite, montmorillonite, mixed-layer clays, graphite and periclase. *Z. Kristallogr.* **126**, 80-97.
- , A. E. BENICE, E. J. DWORNIK, JOAN R. CLARK, AND J. J. PAPIKE (1970a) Lunar clinopyroxenes: Chemical composition, structural state, and texture. *Science* **167**, 628-630.
- , ———, ———, AND ——— (1970b) Mineralogy of the lunar clinopyroxenes, augite and pigeonite. *Geochim. Cosmochim. Acta Suppl.* **1** **1**, 839-848.
- , J. J. PAPIKE, AND K. WIER SHAW (1969) Exsolution textures in amphiboles as indicators of subsolidus thermal histories. *Mineral. Soc. Amer. Spec. Pap. No. 2*, 275-299.
- SMYTH, J. R. (1969) High temperature single-crystal X-ray studies of natural orthopyroxenes. *Earth Planet. Sci. Lett.* **6**, 406-407.

Manuscript received, November 5, 1970; accepted for publication, January 21, 1971.