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DOMAIN STRUCTURE OF PIGEONITE AND CLINOENSTATITE

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ABSTRACT

Single crystals of pigeonite and clinoenstatite from different environments have been examined by the X-ray photographic and diffractometer methods. The reflections with $h+k$ odd are diffuse compared with those with $h+k$ even for the crystals from volcanic rocks, while all reflections are sharp for the crystals from plutonic rocks. The measurements of the spreading of the diffuse reflections with $h+k$ odd suggest that the spreading is closely related to composition and thermal history of the specimens.

The diffuse reflections are explained by a domain structure with an antiphase relation in which each domain is columnar along the c axis and has a shift of $(\mathbf{a}+\mathbf{b})/2$ from the contiguous ones. For pigeonite from the Isle of Mull, the statistical diameter of the columnar domains is estimated to be about 200 Å from the half widths of the diffuse reflections.

On the basis of the crystal structure of pigeonite, the domain structure is considered to be produced by rapid growth of a number of nuclei of pigeonite in a high-temperature phase with monoclinic symmetry. Clinoenstatite is, however, considered to have changed from protoenstatite or orthorhombic symmetry.

INTRODUCTION

In the ternary system $MgSiO_3$-$FeSiO_3$-$CaSiO_3$, the pyroxenes with less than 50 percent $CaSiO_3$ are generally divided into two groups: the Ca-rich and the Ca-poor. The Ca-poor pyroxenes found in nature are orthorhombic or monoclinic. Because of their importance in petrology, many experimental and field studies have been made on these two forms of the Ca-poor pyroxenes. Occurrences of the Ca-poor clinopyroxenes in nature strongly suggest that the clinopyroxenes are a high-temperature form or a quenched product of a high-temperature form (Hess, 1941; Poldervaart and Hess, 1951). However, recent experimental results have thrown a doubt on this interpretation (Sclar *et al.*, 1964; Akimoto *et al.*, 1966). Kuno (1966), summarizing the results of experimental and field studies on the Ca-poor pyroxenes, suggested that pigeonite is a high-temperature monoclinic form different from the monoclinic form synthesized at low temperatures and high pressures.

Morimoto (1956) and Bown and Gay (1957) found that the Ca-poor clinopyroxenes differ from the Ca-rich clinopyroxenes in space group. Bown and Gay (1957) termed the hkl reflections with $h+k$ even, given by both Ca-poor and Ca-rich clinopyroxenes, class (a) reflections, and those with $h+k$ odd, given only by the Ca-poor clinopyroxenes, class (b) reflections, and they reported that the class (b) reflections were slightly diffuse compared with the class (a) reflections in some pigeonites. They considered, in the same paper, that there was no obvious correlation of diffuseness either with the composition or with the probable thermal state separately. Their terminology of reflections is followed throughout this paper.

Morimoto, Appleman and Evans (1960) determined the structure of pigeonite $(Mg_{0.33}Fe_{0.57}Ca_{0.10})SiO_3$ from Asio, Japan and compared it with that of diopside. They confirmed the diffuse reflections of class (b) from the pigeonite and suggested an incipient exsolution of a diopsidic phase (called augite in this paper) in the pigeonite.

Although most crystals of pigeonite from volcanic rocks are microscopically homogeneous, they show reflections from augite in photographs taken by the X-ray single-crystal methods, indicating exsolution of augite (Morimoto, 1966). This fact suggested that the spreading of the class (b) reflections was not directly connected with the exsolution of augite in pigeonite. Bown and Gay (1960) reported that they did not observe any spreading of the class (b) reflections from pigeonite of the Skaergaard intrusion. This suggests a close relation between the spreading of the class (b) reflections of pigeonite and the thermal history.

In order to elucidate the phase relations of the Ca-poor clinopyroxenes, it was indispensable to understand the reason for the spreading of the class (b) reflections in some pigeonites on the basis of the accurate crystal structure of pigeonite. The refinement of the crystal structure was carried out for pigeonite from the Isle of Mull (Morimoto and Güven, 1968), which shows remarkably diffuse reflections of class (b).

The present investigation has been undertaken to study the spreading of the class (b) reflections of pigeonite crystals from various localities on the basis of the accurate crystal structure. The results of this study have provided a means for classifying the Ca-poor clinopyroxenes and a clue to their phase relations.

SPECIMEN DESCRIPTION

Single crystals of pigeonite and clinoenstatite from six different localities were used in this study (Table 1). The chemical compositions of the specimens are plotted in the area of the Di-Hd-En-Fs system (Fig. 1).

EXPERIMENTAL

All specimens of pigeonite and clinoenstatite were first examined by the precession and Weissenberg methods, in order to survey their general features, such as spreading of reflections, exsolution of augite and polysynthetic twinning on (100).

In all crystals examined, the class (a) reflections have generally much stronger intensities than the class (b) reflections, indicating that the $(\mathbf{a}+\mathbf{b})/2$ translation is a pseudosymmetry operation and that the lattice is approximately C-centered (Morimoto *et al.*, 1960; Morimoto and Güven, 1968).

TABLE 1. CHEMICAL COMPOSITION, CELL DIMENSIONS AND SOME CHARACTERISTICS OF PIGEONITES AND CLINOENSTATITE[a]

No.	Locality	Composition (metal ion)	cell dimensions				Spreading of the class (b) reflections	Exsolution of augite		Polysynthetic twinning parallel (100)
			a(Å)	b(Å)	c(Å)	β(°)		parallel (001)	parallel (100)	
1	Mull	$Mg_{39}Fe_{52}Ca_9$	9.706(2)	8.950(1)	5.246(1)	108.59(1)	obs.	—	obs.	—
2	Asio	$Mg_{33}Fe_{57}Ca_{10}$	9.731(5)	8.953(5)	5.256(5)	108.5(2)	obs.	obs.	obs.	—
3	Usugoyazawa	$Mg_{65}Fe_{27}Ca_8$	9.70(1)	8.92(1)	5.24(1)	108.5(1)	obs.	obs.	obs.	—
4	Papua	$Mg_{90}Fe_{10}$	9.61(1)	8.83(1)	5.18(1)	108.4(1)	obs.[b]	—	—	obs.
5	Moore County	$Mg_{47.5}Fe_{47.5}Ca_5$	9.696(1)	8.942(1)	5.227(1)	108.75(1)	—	obs.	obs.	—
6	Skaergaard	$Mg_{45}Fe_{46}Ca_9$	9.69(1)	8.94(1)	5.23(1)	108.8(1)	—	obs.	—	—

[a] obs.: observed, —: not observed. The standard deviations, given between parentheses, are expressed in units of the last digit stated.

[b] Not observed on the photographs, but observed by the diffractometer measurement.

1. Pigeonite phenocrysts from andesite, Isle of Mull, Scotland (supplied by H. S. Yoder, Jr.): Hallimond (1914), Morimoto and Güven (1968).
2. Ferropigeonite phenocrysts from andesite, Asio, Japan (supplied by H. Kuno): Kuno (1968), Morimoto, Appleman and Evans (1960).
3. Pigeonite microphenocrysts from andesite (HK 47122401), Usugoyazawa, Hakone, Japan (supplied by H. Kuno): Kuno and Nagashima (1952), Kuno (1955).
4. Clinoenstatite phenocrysts from porphyritic volcanic rocks, the Cape Vogel Area, Papua (supplied by H. Kuno): Dallwitz, Green and Thompson (1966).
5. Pigeonite from meteorite, Moore County, North Carolina (supplied by H. S. Yoder, Jr.): Hess and Henderson (1949), Morimoto and Tokonami (1968).
6. Pigeonite from ferrogabbro 4430, the Skaergaard intrusion, East Greenland (supplied by G. M. Brown): G. M. Brown (1957), Morimoto and Tokonami (1969).

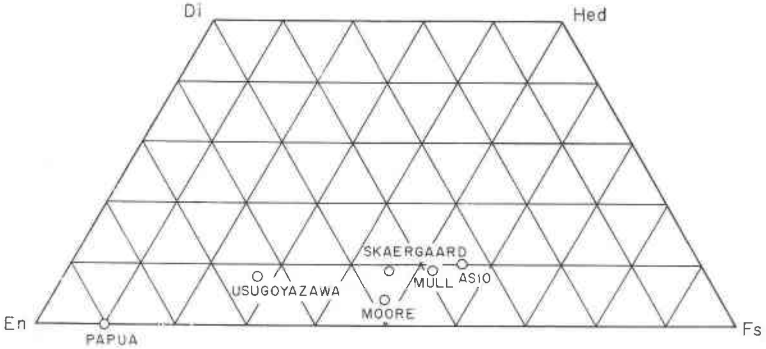

FIG. 1. Plot of chemical compositions of pigeonites and clinoenstatite used in the present study (see Table 1).

For pigeonites from volcanic rocks (Mull, Asio and Usugoyazawa), all class (b) reflections are diffuse compared with class (a) reflections; weak and sometimes diffuse reflections from exsolved augite are observed; no polysynthetic twinning is observed. For pigeonites from plutonic rocks (Moore County and Skaergaard), class (b) reflections are as sharp as class (a) reflections; sharp reflections from exsolved augite or hypersthene or both are always observed; no polysynthetic twinning is observed. For clinoenstatite from Papua, the diffuseness of the class (b) reflections is not appreciable on photographs; no exsolution of augite is observed; polysynthetic twinning parallel to (100) is common. These characteristics of all specimens examined are summarized and given with their cell dimensions (Table 1).

The shape or intensity distribution of each diffuse reflection of class (b) was examined with the Mull pigeonite by taking many precession photographs of different orientations because the Mull pigeonite shows the most remarkable spreading of the class (b) reflections among the pigeonites examined. It was found that the diffuse reflections have a similar disk-like shape regardless of their indices. They are always diffuse in the plane perpendicular to the c direction, that is, in the a^* b^* plane, and the spreading along the a^* direction is almost the same as or is slightly greater than that along the b^* direction. Spreading along the c direction is not appreciable in comparison with that of the class (a) reflections. In a precession photograph (010) * of the Mull pigeonite (Fig. 2), class (b) reflections spread along the a^* direction are observed together with regular class (a) reflections. Weak reflections from augite, exsolved parallel to (100) of the pigeonite, are also observed.

In order to study the spreading of the class (b) reflections more precisely, the intensity profiles of selected reflections from pigeonites and clinoenstatite described above were measured with a scintillation counter and a pulse-height analyzer on the Supper single-crystal diffractometer, based on the Weissenberg geometry. Small crystals were mounted with the c axis as a rotation axis and were studied with Mo$K\alpha$ ($\lambda = 0.7108$ Å) and Co$K\alpha$ ($\lambda = 1.790$ Å) radiations. The ω-scan method was used at the equi-inclination positions with continuous scanning at the speed of 0.5°/min.

The profiles of reflections obtained by the ω-scan method represent the projection of the intensity in a direction transverse to the radial reciprocal lattice vector (Alexander and Smith, 1962). When reflections spread in disk-like shape in the plane perpendicular to the rotation axis c, their observed profiles in higher levels must be corrected for the inclination angle, μ, of the diffractometer to estimate the spreading. However, when l is small and

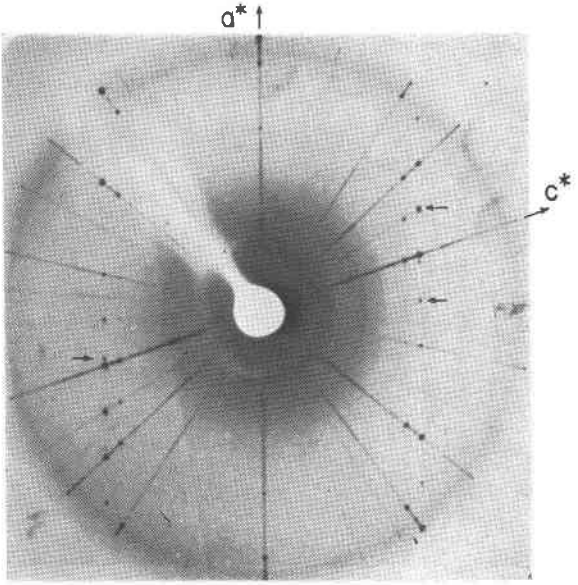

FIG. 2. Precession photograph $(010)_0^*$ of the Mull pigeonite (specimen No. 1). Cu-radiation (unfiltered), 15mA, 40KV, 10 hours. Diffuse reflections of class (b) elongated along the a^* direction are shown by arrows on the right. The reflection from the exsolved augite is shown by an arrow on the left.

cos μ is close to one, the correction is small and the profiles of *0kl* approximately represent spreadings of the reflections parallel to the a^* direction, those of *h0l* parallel to the b^* direction and those of *hkl* along directions between the a^* and b^* directions.

To investigate dependency of the shape of the diffuse reflections on indices in more detail, many reflections with different indices were examined for a crystal of Mull pigeonite (Table 2). The profiles of $\bar{2}31$ and $\bar{7}02$ obtained with Mo*Kα* are shown together with the profiles of their reference reflections, which will be explained below (Fig. 3). After confirming that the spread of a diffuse reflections is circular or ellipsoidal in the plane perpendicular to *c* and constant in shape, regardless of indices or wave length of X rays, for one crystal (Table 2), reflections 052 and $\bar{7}02$ were selected for the measurement of the spread of reflections along the a^* and b^* directions for each crystal.

The experimental procedures were simplified as follows. Each single crystal was first adjusted by the photographic method to have the *c* axis as a rotation axis, and the cell dimensions were obtained from the photographs. Then the crystal was mounted on the diffractometer and precisely adjusted by using the strong 600 and 060 reflections; after completion of the adjustment, the μ angle was changed to the equi-inclination position for the second layer and the profiles of 052 and $\bar{7}02$ were measured; each of them was compared with its two reference reflections, which are the nearest higher and lower reflections of class (a) in the setting angle of the counter, γ (Arndt and Willis, 1966): $\bar{3}52$ and $\bar{6}22$ for 052, and $\bar{7}12$ and $\bar{1}52$ for $\bar{7}02$. This comparison enables corrections to be made for spreading caused by experimental instruments, crystal mosaicity and diffraction geometry.

Three different crystals of Mull pigeonite were examined to study the variation of the spreading of the class (b) reflections. Although they do show some differences, the dif-

TABLE 2. WIDTHS OF SOME CLASS (b) REFLECTIONS OF THE MULL PIGEONITE (SPECIMEN NO. 1), WIDTHS OF DIFFUSE REFLECTION (CORRECTED) EXPRESSED IN DEGREES (Δ) AND IN RECIPROCAL ÅNGSTROM (Γ)

Reflections	Reference reflections	Mo$K\alpha$		Co$K\alpha$	
		Δ 0.01°	Γ 0.0001 Å^{-1}	Δ 0.01°	Γ 0.0001 Å^{-1}
$\bar{2}31$	221 131	60	38	61	39
$\bar{4}31$	$\bar{2}41$ 331	40	34	59	49
$\bar{5}21$	241 421	40	37	42	39
$\bar{7}02$	$\bar{1}52$ $\bar{7}12$	38	40	39	45
052	$\bar{3}52$ $\bar{6}22$	—	—	41	44
362	602 172	32	44	—	—
$\bar{2}33$	$\bar{1}33$	68	41	—	—
$\bar{5}23$	$\bar{2}43$	44	32	—	—

ferences are much smaller than those observed among specimens from different localities (Table 3). Thus we can consider that the widths of the diffuse reflections are nearly constant for specimens from the same locality.

The profiles of 052 and $\bar{7}02$ and of their reference reflections obtained from the Mull pigeonite (specimen No. 1) are compared with those from the Moore County pigeonite (specimen No. 6) and the Papua clinoenstatite (Fig. 4). In this figure, the profiles of different reflections were adjusted to give them almost the same peak heights. Because the Moore County pigeonite has two kinds of exsolution of augite parallel to (100) and (001) (Morimoto and Tokonami, 1969), the class (a) reflections of the pigeonite are superposed to those of exsolved augite and are slightly more diffuse than the class (b) reflections, which have no corresponding reflections from the augite. Crystals from other localities were also investigated (Table 3).

RESULTS

The diffuse reflections must be explained as due to imperfections in the structure; the sharp reflections indicate that the lattice is maintained throughout the crystal. According to the theory of the Fourier transform,

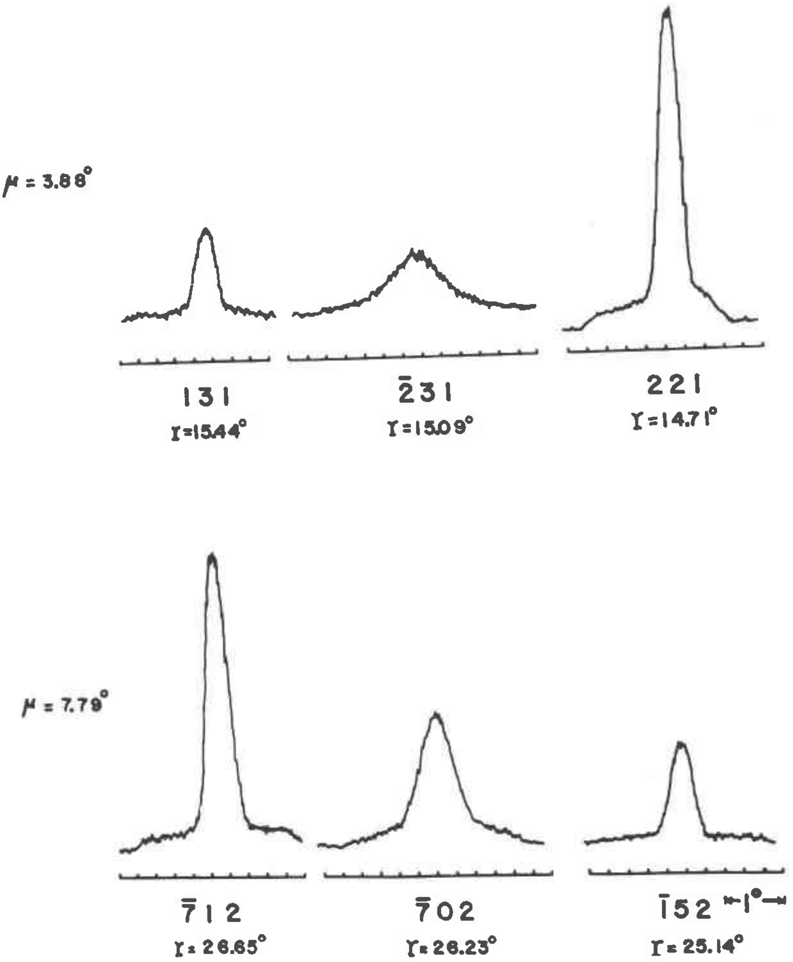

FIG. 3. Intensity profiles of $\bar{2}31$ and $\bar{7}02$ of the Mull pigeonite (specimen No. 1) taken with Mo$K\alpha$. Their reference reflections of class (a) are also shown.

the crystal must have two regions, both of which have the normal primitive lattice but one of which is translated by $(\mathbf{a}+\mathbf{b})/2$ with respect to the other. In other words, the crystal consists of two kinds of domains, in an antiphase relation. The experimental fact for pigeonites that the diffuse reflections of class (b) have a similar shape spreading perpendicular to the *c* direction, indicates that the domains have columnar shapes parallel to the *c* direction.

If the intensity distribution of the diffuse reflections of a pigeonite is obtained in the plane perpendicular to the *c* direction, it will give accurate

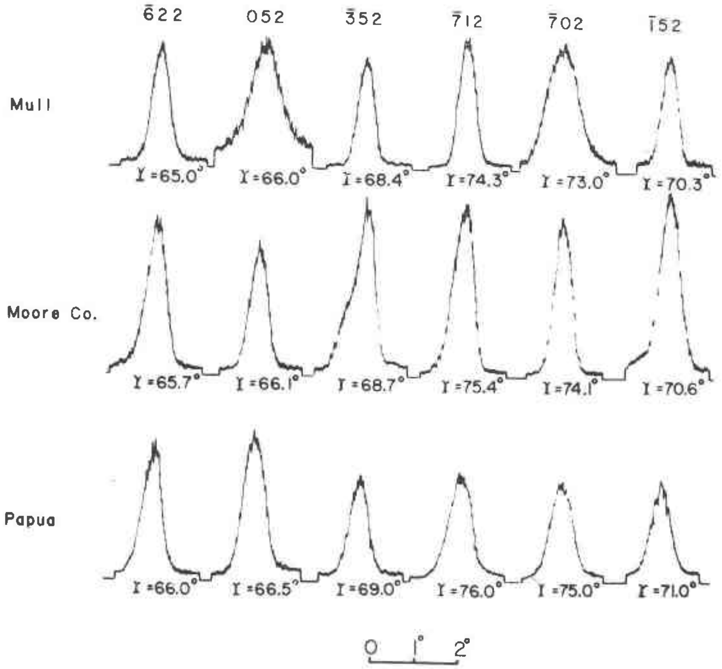

FIG. 4. Comparison of the intensity profiles of 052 and $\bar{7}02$ and their reference reflections for the Mull and Moore County pigeonites and for the Papua clinoenstatite. Intensity profiles adjusted to give almost the same peak height. All profiles taken with Co$K\alpha$.

TABLE 3. WIDTHS OF 052 AND $\bar{7}02$, REPRESENTED BY Δ° AND Γ Å^{-1}, PROBABILITIES OF DOMAIN BOUNDARIES ALONG THE *a* AND *b* DIRECTIONS AND APPARENT DOMAIN SIZES OF PIGEONITES AND CLINOENSTATITE

Specimen	Δ(×0.01°)		Γ(×0.0001 Å^{-1})		Probability		Apparent domain size
	052	$\bar{7}02$	052	$\bar{7}02$	α	β	
Mull No. 1	41	39	44	45			
No. 2	46	28	49	33			
No. 3	38	31	40	36			
Mull (mean)	42±4	33±6	45±4	38±7	0.06±0.01	0.05±0.01	~200 Å
Asio	15	12	16	14	0.02	0.02	~500 Å
Usugoyazawa	28	16	30	19	0.04	0.03	~300 Å
Papua	10>	10>	10>	10>	0.02>	0.02>	700 Å<
Moore County	−4[a]	−10[a]	0	0	0	0	—
Skaergaard	0	0	0	0	0	0	—

[a] The class (a) reflections are wider than the class (b) reflections because of superposition of reflections from the exsolved augite on the class (a) reflections.

information on the domain structure. However, the experimental procedures described in the last section gave only profiles of intensity projected on the direction approximately perpendicular to the radial reciprocal lattice vectors and we had to interpret the experimental results on the basis of a simple model.

Consider a structure consisting of columnar domains elongated parallel to the c direction, in which there are probabilities of finding the domain boundaries, α and β, for the unit translations, a and b, respectively. On the assumption of perfect random distribution of the domain boundaries, a mathematical treatment was carried out for a two-dimensional system, based on that of Wilson (1949). The intensity distribution I $(h+u,\ k+v,\ l+w)$ around the reciprocal lattice point hkl with $h+k$ odd is obtained as follows,

$$I(h+u,\ k+v,\ l+w) = \left| F(hkl) \right|^2 \cdot \frac{M\alpha}{\alpha^2 + \pi u^2} \cdot \frac{N\beta}{\beta^2 + \pi v^2} \cdot P \cdot \delta(w),$$

where u, v and w are small fractions, positive or negative, M, N and P represent the numbers of unit translations along the a, b and c directions respectively for the crystal examined and $\delta(w)$ represents the delta function.

This equation means that the profiles of the diffuse reflections projected on the a^* and b^* directions have the Cauchy-type distribution and that their half widths are $2\alpha/\pi$ and $2\beta/\pi$ along the a^* and b^* directions respectively. In fact, the observed profiles of the diffuse reflections for pigeonite are approximately of the Cauchy type, supporting the model discussed above. Therefore, we were able to determine the values of α and β for different pigeonites on the basis of the half widths obtained, as shown below.

Since the profiles of both diffuse and sharp reflections are approximately of the Cauchy type, the widths of diffuse reflections, $\Delta°$ for 052 and $\bar{7}02$, corrected for spreading by experimental instruments, crystal mosaicity and diffraction geometry, were obtained simply by subtracting the mean half widths of two sharp reference reflections nearest to the diffuse reflections in γ, from the half widths of the diffuse reflections. The widths of the diffuse reflections were finally expressed by the reciprocal lattice units, Γ Å^{-1} by the following relation on the assumption that Υ is approximately equal to 2θ,

$$\Gamma = \frac{2}{\lambda} \cdot \sin\left(\frac{\gamma}{2}\right) \cdot \frac{\pi}{180} \Delta$$

where λ is the wavelength of the X rays and Γ and Δ are expressed in reciprocal ångströms and degrees respectively. It is clear (Table 3) that all crystals from volcanic rocks show the diffuse reflections of class (b), while those from plutonic rocks do not.

Based on the equation for the intensity of diffuse reflections, the numbers of domain boundaries, α and β for the unit translations a and b (Table 3), are obtained from the observed values of Γ for 052 and $\bar{7}02$ as follows,

$$\alpha = \left(\pi \times \frac{\Gamma_{052}}{a^*}\right)/2$$

$$\beta = \left(\pi \times \frac{\Gamma_{\bar{7}02}}{b^*}\right)/2$$

where Γ_{052} and $\Gamma_{\bar{7}02}$ represent Γ for 052 and $\bar{7}02$. For the Mull pigeonite, they are both about 1/20, indicating that domain boundaries of antiphase domains occur statistically every 20 unit cells along the a and b directions. If we define apparent domain size by the mean of $1/(\alpha \times a^*)$ and $1/(\beta \times b^*)$, it comes out about 200 Å for the Mull pigeonite. The apparent domain sizes are also listed for pigeonites and clinoenstatite from volcanic rocks (Table 3).

DOMAIN STRUCTURE OF PIGEONITE

The crystal structure of pigeonite, determined by using the integrated intensities (Morimoto *et al.*, 1960; Morimoto and Güven, 1968), represents a statistically averaged structure, which has no direct connection with the spreading of the class (b) reflections. In this structure, there are two similar but crystallographically different silicate chains. Chains of one kind (SiA chains in the structure of the Mull pigeonite, Morimoto and Güven, 1968) form layers parallel to (100) (called layers A), which alternate regularly with other layers (layers B) consisting of the second kind of chains (SiB chains) (Fig. 5).

Since the SiA chains do not differ much from the SiB chains in shape, the structure of pigeonite can be considered to have approximately a C-centered lattice. The metal atoms are partly ordered in the M1 and M2 positions. For the Mull pigeonite, the site occupancies are 0.73 Mg and 0.27 Fe for the M1 position and 0.05 Mg, 0.77 Fe and 0.18 Ca for the M2 position. The mutual replacements of Mg, Fe and Ca in the M1 and M2 positions must cause local modifications in the structure: the atoms surrounding Mg and Fe form a clinoenstatite or clinoferrosilite-like arrangement while those surrounding Ca form a diopside-like arrangement. The resultant structure is the statistical mean of these modifications. The apparent atomic temperature factors obtained in the structure of the

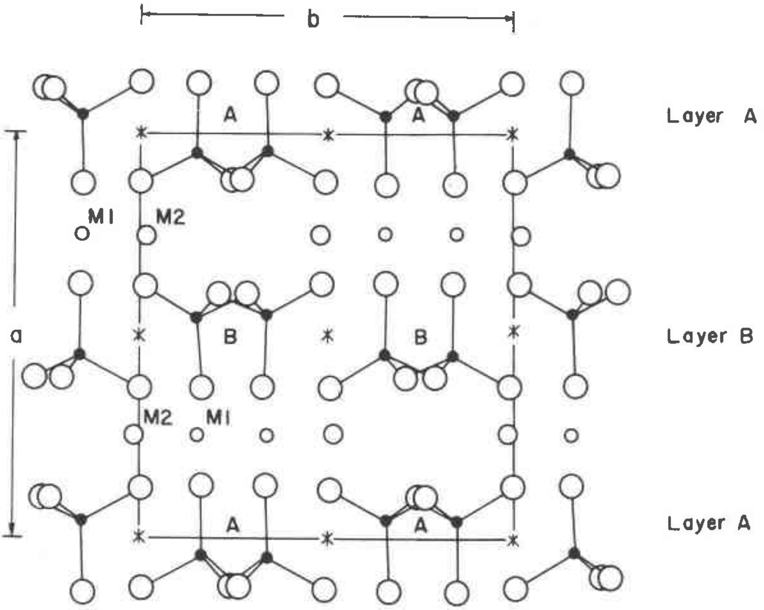

FIG. 5. Structure of pigeonite projected on (001), showing the pseudo-*C*-centered lattice. A: SiA chains, B: SiB chains.

Mull pigeonite have extraordinarily large values, compared with those found in other pyroxenes where there is no solid solution. These large values are considered to represent the local modifications brought about by the mutual replacement of metal atoms and by the domain structure.

The domain structure derived in the last section must now be explained on the basis of the statistical structure. Each domain in pigeonite has the statistical structure with constant site occupancies for the M1 and M2 positions, but is out of phase by $(\mathbf{a}+\mathbf{b})/2$ from the surrounding ones. The antiphase relation of the domain structure can be schematically shown (Fig. 6) by representing the pseudo-C-centered lattice of pigeonite projected on (001) by black and white lattice points. The phase shift of $(\mathbf{a}+\mathbf{b})/2$ between domains is possible in the pigeonite structure with A and B representing the SiA and SiB chains respectively (Fig. 7a) in the following two ways: mistakes in alternate stacking of layer A and layer B causing the phase shift along (100), and changes of layer A to layer B or vice versa in each layer causing the phase shift along (010) (Fig. 7b). Because the SiA and SiB chains are not much different as mentioned above, these mistakes take place not by any actual translation of $(\mathbf{a}+\mathbf{b})/2$ but by slight displacements of the atoms in the chains.

The shift of $(\mathbf{a}+\mathbf{b})/2$ between the domains produces bands with a C-

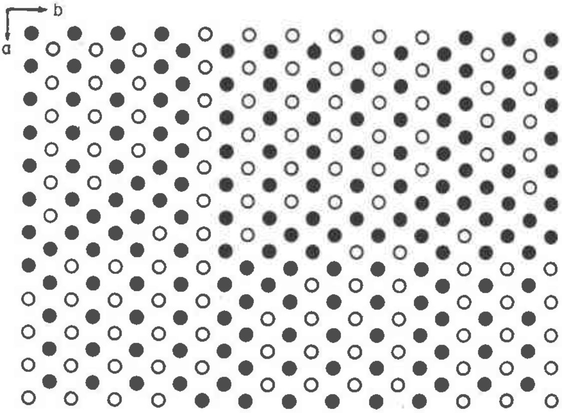

FIG. 6. Domain structure of pigeonite projected on (001), showing antiphase relation with a shift of $(a+b)/2$. Pseudo-C-centered lattice shown by black and white lattice points. The bands of the black lattice points represent domain boundaries.

centered lattic along the domain boundaries (bands of black lattice points, Fig. 6). Because the *C*-centered lattice is likely to accept Ca atoms as in the diopside structure, it is natural to consider that Ca atoms are preferred to Mg or Fe atoms and build a diopside-like structure at the domain boundaries. The SiA chains are closer in shape to the chains in the diopside structure than the SiB chains (Morimoto and Güven, 1968), and are considered to predominate at the domain boundaries. Thus the black lattice points represent the SiA chain groups in Figure 6. Because the diopside-like structure has a slightly larger cell volume than the structure inside the domains, some disturbances occur in the lattice of the crystal. However, the observed reflections of class (a) of pigeonite are sharp, indicating the lattice, to a first approximation, is perfect through-

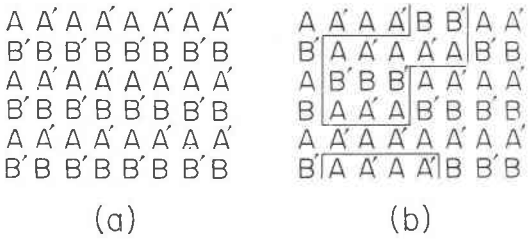

FIG. 7. (a) Pseudo-C-centered lattice of pigeonite projected on (001). (b) Domain structure of pigeonite projected on (001). The SiA chains are represented by A and A′, and the SiB chains by B and B′. An antiphase relation with a shift of $(a+b)/2$ among domains is observed in (b).

out the crystal including the domain boundaries. Therefore, the domain boundaries must be narrow so that their volume can be neglected compared with that of the domains. Such domain boundaries may be one of the reasons for the extraordinarily large temperature factors encountered in the structure of the Mull pigeonite.

Thus pigeonite crystals from volcanic rocks are considered to consist of columnar domains with the statistical structure of pigeonite arranged parallel to the *c* direction with a mean diameter of a few tens of unit cells, which are connected by films of a diopside-like structure with a thickness of a few unit cells.

As observed in the precession photograph $(010)_0^*$ of the Mull pigeonite (Fig. 2), most crystals of pigeonite from volcanic rocks contain exsolved augite crystallites large enough to give sharp reflections, even though the crystals look microscopically homogeneous. The exsolved augite is generally in one or two orientations, approximately parallel to (100) or (001) of the host pigeonite (Morimoto, 1966). Streaks connecting the reflections of pigeonite to those of the exsolved augite are occasionally observed. Since the reflections from the exsolved augite are very weak in intensity compared with those from the host pigeonite, the augite must be very small in total volume compared with the host. Since the orientations of the exsolved augite crystallites are different from those of the domain boundaries with the diopside-like structure, the exsolution of augite cannot have any direct relation to the formation of the domain structure.

Thus the crystals of pigeonite from volcanic rocks generally consist of three different parts: the domains with pigeonite structure, the domain boundaries with diopside-like structure, and the exsolved augite. Since the volumes of the domain boundaries and the exsolved augite are very small compared with that of the domains, the total composition given to pigeonite represents an approximate composition of the domains with the statistical structure.

TRANSITION OF PIGEONITE AND CLINOENSTATITE

Observations on different pigeonites and clinoenstatite indicate that the domain structure is closely related to the rate of cooling and possibly to the chemical composition. The domain structure is most reasonably explained by considering that it was formed in the process of transition from high-temperature phases to pigeonite or clinoenstatite.

Let us consider the process of formation of pigeonite in volcanic rocks. A large number of pigeonite nuclei appeared in the high-temperature phase and grew to domains by rapid cooling. This high-temperature phase had a structure with a *C*-centered lattice, in which all silicate chains were crystallographically equivalent. Two crystallographically different kinds of chains, SiA and SiB, appeared during the transition to pigeonite. Because the original silicate chains could equally change to the SiA or SiB chains, an antiphase relation with a shift $(\mathbf{a}+\mathbf{b})/2$ took place among the domains of pigeonite, elongated in the direction of the chains. If two domains of the same phase grew to make contact with each other, they coalesced into one domain, while between two antiphase domains, an antiphase domain boundary was produced. The domain structure could be retained by the formation of the Ca-rich domain boundaries and rapid cooling, both of which suspended further growth of domains by preventing the displacement and diffusion of metal atoms in the pigeonite structure. As reported by Bown and Gay (1957), heating of the Mull pigeonites at 1000°C for two days is not sufficient to eliminate the domain structure.

Pigeonites from Moore County and Skaergaard were also formed by transition from the high-temperature phase. The domains, even if they appeared, grew by slow cooling until the spreading of the class (b) reflections cannot be detected by the X rays.

If the high-temperature phase was orthorhombic, the nucleation of pigeonite of monoclinic symmetry must have been equally possible in two orientations, mirror images of each other in (100), and resulted in fine polysynthetic twinning on (100) of pigeonite. Since the domain structure is observed in single crystals of pigeonites from volcanic rocks and no polysynthetic twinning on (100) is observed in pigeonites from either volcanic or plutonic rocks, the high-temperature phase is considered to be monoclinic.

Because extensive migration of Ca and other metal atoms was necessary for the exsolution of augite in the Ca-poor pyroxenes, the exsolution of augite must have taken place in the high-temperature phase prior to its transition to pigeonite, in which the domain structure is still retained. The exsolution of augite observed in pigeonites from not only plutonic rocks but also volcanic rocks follows monoclinic symmetry, sharing (001) or (100) or both with the host. If the high-temperature phase was orthorhombic, the exsolution must have taken place with orthorhombic symmetry. The orientations of the exsolved augite in pigeonites also support the monoclinic symmetry of the high-temperature form.

Thus all the observed results on pigeonites seem to support the existence of a high-temperature phase with a *C*-centered monoclinic lattice, from which pigeonites were directly derived. However, this does not necessarily mean that the structure of the high-temperature phase consists of only one kind of silicate chain as in the diopside structure. In fact, it seems difficult for the structure of clinopyroxenes to have only one kind of silicate chain even at high temperatures when most of the metal atoms are Mg and Fe atoms, because one kind of silicate chain results in a structure with spaces too large for Fe and Mg atoms, as in the diopside structure (Morimoto and Koto, 1968). However, we can consider the case where the domains become smaller in the domain structure of pigeonite so that the class (b) reflections become more diffuse and finally disappear in the background. In this case the SiA and SiB chains have local order but complete distant disorder, in the terminology suggested by Megaw and quoted by Smith and Mackenzie (1961), and the two chains are considered to be crystallographically equivalent. The high-temperature phase of pigeonite must have such a disordered arrangement of two kinds of chains resulting in a C-centered lattice. It is probable that this high-temperature phase can make a wide solid solution with augite. Exsolution of augite can be easily formed through diffusion of metal atoms in this structure when the solid solution becomes unstable.

For clinoenstatite from Papua, the polysynthetic twinning on (100) is commonly observed, indicating a transition from the orthorhombic high-temperature phase, protoenstatite. In this transition, crystallographically equivalent silicate chains in protoenstatite (Smith, 1959) changed to two different kinds of chains and the domain structure appeared in each individual of the twinned clinoenstatite. However, because of deficiency of Ca atoms, the movement of the domain boundaries must have been easier than in pigeonite and the domains were able to grow. This is seen in the limited spreading of the class (b) reflections in clinoenstatite from Papua (Table 3).

The existence of a protohypersthene with orthorhombic symmetry was not indicated in this study, other than that of protoenstatite for clinoenstatite from Papua. It is, however, possible that the high-temperature phase of monoclinic symmetry has another higher-temperature phase of orthorhombic symmetry. The observation of protohypersthene from the Moore County pigeonite in the presence of liquid by Yoder *et al.* (1963) suggests a possibility of protohypersthene.

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