# The crystal structures of clinoenstatite and pigeonite

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#### Auszug

Die Kristallstrukturen der monoklinen Pyroxene Klinoenstatit MgSiO<sub>3</sub> und Ferropigeonit (Ca,Mg,Fe)SiO<sub>3</sub> wurden auf Grund von Weissenberg-Aufnahmen um die *a*-, *b*- und *c*-Achse bestimmt und mittels zweidimensionaler Fourier-Analyse und der Methode der kleinsten Quadrate verfeinert. Die Atomabstände wurden auf 0,05 Å genau ermittelt, Die Abweichungen gegenüber der Diopsidstruktur werden erläutert und kristallchemisch begründet. Die Einfügung der kleinen zweiwertigen Kationen in die für den Diopsid charakteristischen einfachen SiO<sub>3</sub>-Ketten bedingt, daß die beiden Ketten der Elementarzelle kristallographisch verschieden werden, und damit den Übergang von C2/c beim Diopsid zu  $P2_1/c$ . Beim Ferropigeonit ist jedes der Metalle Ca und Mg einer der beiden Lagen M<sub>I</sub> und M<sub>II</sub> zugeordnet; Fe verteilt sich auf beide Lagen. Die größeren Metallatome bevorzugen die M<sub>I</sub>-Lagen: Die Koordinationszahl von M<sub>I</sub> ist im Diopsid acht, im Pigeonit sieben und im Klinoenstatit sechs, während diejenige von M<sub>II</sub> in allen drei Strukturen sechs beträgt. Die Pigeonitstruktur vermittelt zwischen den Strukturen von Diopsid und Klinoenstatit.

#### Abstract

The crystal structures of the two monoclinic pyroxenes clinoenstatite,  $MgSiO_3$ , and ferropigeonite,  $(Ca,Mg,Fe)SiO_3$ , have been determined from twodimensional x-ray diffraction data, and refined by Fourier and least-squares methods. Bond lengths have been determined with a standard error of 0.05 Å. Deviations in these structures from that of diopside have been elucidated and explained in terms of crystal-chemical principles. The introduction of small bivalent cations into the single-chain silicate structure characteristic of diopside is shown to result in the production of two crystallographically non-equivalent chains in the unit cell, with a corresponding change in the space group from C2/c to  $P2_1/c$ . In ferropigeonite complete order of Ca and Mg is found between the two metal positions,  $M_I$  and  $M_{II}$ , while Fe occupies both sites. Analysis of the coordination environments of the metal atoms in the clinoenstatite, pigeonite and diopside structures indicate that the larger atoms, where present, occupy the  $M_{I}$  positions preferentially; thus the coordination number of  $M_{I}$  is eight in diopside, seven in pigeonite and six in clinoenstatite, while the coordination number of  $M_{II}$  is six in all three structures. The pigeonite structure appears to be intermediate between those of diopside and clinoenstatite.

## Introduction

The determination of accurate crystal structures of rock-forming minerals of known chemical composition formed under various conditions has become an important field of investigation in mineralogy. From this viewpoint, many excellent crystallographic studies have been carried out on feldspars and amphiboles. A corresponding study of pyroxene structures, however, has not yet been made, in spite of recent developments in the petrological and experimental study of minerals of this group, and in spite of their relatively simple crystal structures compared with those of feldspars and amphiboles. This study has been undertaken as a part of a program to obtain crystallochemical knowledge of pyroxenes in general.

## Previous work on pyroxene structures

The natural pyroxenes fall into two classes: orthorhombic and monoclinic. The orthorhombic pyroxenes are known only in the composition range MgSiO<sub>3</sub>—FeSiO<sub>3</sub>, with less than 10 mol percent of CaSiO<sub>3</sub> (Kuno, 1954; HESS, 1952). WARREN and MODELL (1930) have made an x-ray analysis of hypersthene of composition (Fe<sub>.30</sub>Mg<sub>.70</sub>)SiO<sub>3</sub>. Ito (1950) has re-examined this structure using a hypersthene of composition (Fe<sub>.16</sub>Mg<sub>.84</sub>)SiO<sub>3</sub>, and discussed the relationship between monoclinic pyroxenes and orthorhombic pyroxenes. Protoenstatite, another orthorhombic form of MgSiO<sub>3</sub>, which forms synthetically at high temperatures, was described by THILO and ROGGE (1939), and FOSTER (1951), and its structure was analyzed by SMITH (1959). This paper is confined to a structure study of the monoclinic group of pyroxenes (clinopyroxenes).

WYCKOFF, MERWIN and WASHINGTON (1925) have shown that diopside, CaMgSi<sub>2</sub>O<sub>6</sub>; synthetic acmite, NaFeSi<sub>2</sub>O<sub>6</sub>; jadeite, NaAlSi<sub>2</sub>O<sub>6</sub>; hedenbergite, CaFeSi<sub>2</sub>O<sub>6</sub>; and various augites have similar structures and belong to the clinopyroxenes. Among these pyroxenes, diopside was the first mineral to be analyzed by x-ray diffraction methods (WARREN and BRAGG, 1928). WARREN and BISCOE (1931) have compared diopside, hedenbergite, augite, acmite, jadeite, clinoenstatite (MgSiO<sub>3</sub>), and spodumene (LiAlSi<sub>2</sub>O<sub>6</sub>), and concluded that all these substances are members of the monoclinic pyroxene group with 122

diopside as type structure. They have also shown that the structure of spodumene is slightly distorted as compared with diopside due to the small size of the Li atoms. MORIMOTO (1956), and BOWN and GAY (1957) have found that clinoenstatite and pigeonite,  $(Mg,Fe)_2Si_2O_6$ , belong to the space group  $P2_1/c$ , which is different from that of diopside, C2/c.

Although accurate measurement of unit cell dimensions of pyroxenes with various compositions has been made (HESS, 1952; KUNO and



Fig. 1. Composition diagram for the clinopyroxenes. Circles indicate composition of specimens studied in this work

HESS, 1953), no refinement of their structures such as is possible with modern techniques has been made and the minor structural variations among the different members of the series have not been investigated.

The relation between clinoenstatite, pigeonite and diopside

The most important pyroxenes found in nature occur in the ternary system MgSiO<sub>3</sub>—FeSiO<sub>3</sub>—CaSiO<sub>3</sub>, shown in Fig. 1, with less than 50 mol percent CaSiO<sub>3</sub>, although some replacement by other cations such as Al, Ti, Fe<sup>+3</sup>, etc. usually takes place. The monoclinic pyroxenes in this field may be divided into two different types. One is near the CaMgSi<sub>2</sub>O<sub>6</sub>—CaFeSi<sub>2</sub>O<sub>6</sub> join, with more than  $25^{0}/_{0}$  and less than  $50^{0}/_{0}$ CaSiO<sub>3</sub> component, and is typified by augite, diopside and hedenbergite. The other lies near the MgSiO<sub>3</sub>—FeSiO<sub>3</sub> join with less than  $15^{0}/_{0}$  CaSiO<sub>3</sub> component, typified by pigeonite and clinoenstatite. Some evidence of immiscibility between these two types has been observed in a region indicated by hatching in Fig. 1, in nature and in the laboratory (POLDERVAART and HESS, 1951; ATLAS, 1952; SCHAIRER and BOYD, 1957). The monoclinic pyroxenes of the pigeonite type, namely, clinoenstatite and pigeonite, have the space group  $P2_1/c$  and are distinct from the augite-type pyroxenes, which have a simpler structure in the space group C2/c.

The problem of the stability relationships between the monoclinic pigeonite-type pyroxenes, the orthorhombic pyroxenes (hypersthenes) and protoenstatite has not yet been settled. When the FeSiO<sub>3</sub> component is less than about 30 mol percent, high-temperature x-ray and quenching experiments confirm the existence of three polymorphs, enstatite, protoenstatite and clinoenstatite (FOSTER, 1951), although only the enstatite form is known in nature. FOSTER and also ATLAS (1952) have assumed the following relations: protoenstatite-hightemperature form; enstatite-low-temperature form; and clinoenstatite-low-temperature, metastable form. Of the pyroxenes along the  $MgSiO_3$ -FeSiO<sub>3</sub> join with more than 30 mol percent FeSiO<sub>3</sub> component, the monoclinic form, pigeonite, and the orthorhombic form, hypersthene, have been found in nature (POLDERVAART and HESS, 1951). The mode of occurrence clearly shows that pigeonite is a hightemperature form and hypersthene is a low-temperature form (BOWEN and SCHAIRER, 1935; POLDERVAART and HESS, 1951).

On the basis of the pyroxene relationships so far known, our interest has been concentrated on the following two crystallographic problems: (1) the structural relations between diopside, pigeonite and clinoenstatite; and (2) the structural relations between the three polymorphs of  $MgSiO_3$ , i.e. enstatite, protoenstatite and clinoenstatite. Solution of the first problem will clarify the effect of different metal atoms on the silicate chain structure and on the stability relations of clinopyroxenes. This paper is only concerned with this problem. The structure analyses of clinoenstatite and ferropigeonite have been given in parts I and II respectively, and in part III we will discuss the relations among the structures of clinoenstatite, pigeonite and diopside. The structure refinement of enstatite is now in progress and a study of the second problem will be published in the near future.

The comparisons between our structure determinations of clinoenstatite and pigeonite with the diopside structure are based on the classic study made of diopside by WARREN and BRAGG (1928). Their trial-and-error analysis was subsequently augmented by Fourier synthesis studies, the first ever made in crystal structure analysis, 124

by BRAGG (1929). By modern standards, the Fourier series used are very poorly resolved, and we believe that the structure coordinates obtained earlier by WARREN and BRAGG (1928) are more reliable. These are the data we have used in this paper. Obviously, a redetermination of the diopside structure is urgently needed.

The present study is based only on two-dimensional data, consisting of three projections for each structure. The refinements have been carried by the method of least-squares analysis to close to the best possible stage, but the standard errors of the interatomic distances are still appreciable, about 0.05 Å for metal-oxygen and 0.07 Å for oxygen-oxygen distances. Such accuracy is sufficient for the main purpose of this work, namely, interpretation of changes of coordination and adjustments in silicate-chain dimensions which accompany substitutions of metal ions for one another. We believe that the structure of diopside as given by WARREN and BRAGG (1928) is also sufficiently accurate for this degree of interpretation. Studies of relationships among ionic charge, bond length and bond number must await a more accurate structure refinement, which can only be carried out in three dimensions.

# I. Structure analysis of clinoenstatite Experimental

The specimens of clinoenstatite used in these experiments were obtained by Dr. J. F. SCHAIRER of the Geophysical Laboratory, by heating Bishopville enstatite at  $1400 \,^{\circ}$ C for 24 hours. The chemical composition in weight percentages of this enstatite is: SiO<sub>2</sub> 59.97, MgO 39.33, and FeO 0.40, according to SMITH (1873). Clinoenstatite thus obtained always shows fine polysynthetic twinning on (100). As it was impossible to get single crystals free from twinning, it was necessary to use twinned crystals to measure the intensities.

The cell constants were obtained from the powder patterns using quartz and silicon as internal standards. The results are:  $a = 9.620 \pm 0.005$  Å,  $b = 8.825 \pm 0.005$ ,  $c = 5.188 \pm 0.005$ , and  $\beta = 108°20' \pm 10'$ . These values are in good agreement with those of synthetic clinoenstatite (KuNo and HESS, 1953). There are four chemical units of composition MgSiO<sub>3</sub> in the unit cell. The space group is  $P2_1/c$  ( $C_{2h}^5$ ). Throughout this paper, an unconventional monoclinic setting is used in which the positive senses of the a and c axes enclose an acute angle  $\beta$ , following the setting of axes in diopside by WARREN and BRAGG (1928).

Both standard and integrating-Weissenberg photographs were taken around the a, b, and c axes, using the multiple-film technique. The crystal used for the experiments was about  $0.2 \times 0.2 \times 0.5$  mm<sup>3</sup> in size.  $CuK\alpha$  radiation was used for the hk0 and h0l zones, and  $MoK\alpha$ radiation for the 0kl zone. The relative intensities were estimated visually from the standard Weissenberg photographs and by the photometer from the integrating-Weissenberg photographs. The values obtained by both methods are in agreement within  $5^{0}/_{0}$  for each reflection. Their average was taken as the observed relative intensity. The twinning on (100) affects the intensities of the h0l and 0kl reflections. On these photographs, the intensities of those reflections which are common to the two twinned lattices were corrected according to the relative intensities of the respective lattices as a whole. The relative intensities were corrected for Lorentz and polarization factors graphically. No correction was made for absorption, nor for extinction. After the relative intensities were adjusted to the same scale using the common reflections, they were converted to absolute values on the basis of the calculated structure factors of diopside, taking into consideration the difference of composition between diopside and clinoenstatite. These values were rescaled through the course of the work as each new set of structure factors was calculated. For the calculation of the structure factors, the scattering factor curves of BRAGG and WEST (1928) were used in the earlier stages of refinement and the curves of BERGHUIS et al. (1955) were used in the later stages.

# Structure analysis and refinement

The structure analysis of clinoenstatite was started from the known structure of diopside. Since reflections with h + k odd do not appear in diopside, we were not able to obtain the signs of these reflections from the diopside structure and the usual procedure of refinement did not give the structure of clinoenstatite. The signs of these reflections were determined in the following way.

The difference of the structure factors between diopside and clinoenstatite is most noticeable with the h0l reflections. The first step, therefore, was taken with the [010] projection, to find the deviation of the atoms in the clinoenstatite from those of the diopside structure. Contour maps (BRAGG and LIPSON, 1936) of the strongest reflections: 702, 304, 704, 306,  $10\overline{2}$  and  $30\overline{4}$ , which are not given by the diopside structure, were made. The assumption of the sign of  $10\overline{2}$ gave the possible area of the atomic displacement from the diopside structure by using the contour map of  $10\overline{2}$ . The other six contour maps of the strong reflections listed above restricted the possible area of the displacement of atoms, giving the sign of each reflection. These six h+k odd reflections were used for the first Fourier synthesis, together with all h+k even reflections, the signs of which were determined from the diopside structure given by WARREN and BRAGG. The resolution of atoms in this projection was not sufficiently good to locate the oxygen atoms, but new positions of Mg and Si atoms were determined. The coordinates of the oxygen atoms were estimated from geometrical consideration of the structure on the basis of the new Mg and Si positions. These coordinates were used for calculation of hk0, h0l and 0kl structure factors to obtain signs, and Fourier syntheses were again carried out for each projection. The atomic coordinates obtained from these electron density maps gave discrepancy factors

$$R = \Sigma \left| \left| F_o \right| - \left| F_c \right| \right| / \Sigma \left| F_o \right|$$

of about 30 percent.

On account of the difficulty of finding accurate positions of oxygen atoms, because of overlapping of atoms in the electron-density maps, the structure factors corresponding to a hypothetical structure consisting only of Mg and Si atoms were calculated. Fourier syntheses were then carried out using these values but subject to the same conditions of termination of series as are imposed in the Fourier syntheses by the observed structure factors. The resulting electron-density distributions were subtracted point by point from the experimentally determined ones, thereby giving projections free from the effects of Mg and Si atoms. The new coordinates of oxygen atoms obtained from these partial difference electron-density maps were used for the calculation of the structure factors together with the coordinates of metal atoms previously given. Starting from these new structure factors, the usual  $(F_o - F_c)$  synthesis was made twice, in which terms for reflections with  $F_{a} = 0$  were given half weight. In the process of these  $(F_{o} - F_{c})$  syntheses, different overall temperature factors were used for different projections. Finally, the coordinates were refined by the least-squares method with an individual isotropic temperature factor for each atom.

Table 1A shows the method used for refinement at each stage, and the progress of the refinement as indicated by the usual discrepancy factor R. In calculating this factor, only those reflections with  $|F_o| > 0$  have been used. The observed intensities of the h0l and 0kl reflections

Stand	Mathad	hi	k0	h	01	07	kl	Commente
Stage	method	R	B	R	B	R	B	Comments
					$A.\mathrm{Cl}$	linoenst	atite	
I	$F_o$ synthesis	0.43		0.40				signs of $F_o$ were determined from the modified diopside structure; $f$ values of BRAGG and WEST (1928)
II	$F_o$ synthesis	.29		.28		0.30		
III	$F_o$ synthesis	.24		.23		.28	—	synthesis calculated with oxygen contributions only
IV	$(F_o - F_c)$ synthesis	.17	0.40	.22	0.70	.24	0.30	f values of BERGHUIS $et al.$ (1955)
V	$(F_o - F_c)$ synthesis	.15	.30	.21	.60	.15	.30	
VI	least-squares	.11	*	.17		.12	*	individual isotropic $B$ for each atom
	/				B.	Pigeon	ite	
I	${F}_{o}$ synthesis	0.45						same parameters as I of clinoenstatite; <i>f</i> values of BRAGG and WEST; metal atoms in complete disorder
II	$F_{o}$ synthesis	.35		0.25	—	0.37	—	metal atoms in ordered arrangement
III	$F_o$ synthesis	.27		.23		.25	—	synthesis calculated with oxygen contributions only
IV	$(F_o - F_c)$ synthesis	.22	0.63	.21	0.46	.24	0.80	f values of BERGHUIS et al. (1955)
V	$(F_o - F_c)$ synthesis	.16	.40	.18	.60	.16	.41	
VI	least-squares	.11	*	.15		.076	*	individual isotropic $B$ for each atom

Table 1. Details of the structure refinement of clinoenstatite and pigeonite

\* See Table 4.

are probably less accurate than those of the hk0 reflections because of the existence of twinning on (100) in the crystals used. The poorer agreement between  $F_o$  and  $F_c$  for the h0l and 0kl reflections may thus be accounted for. The final  $(F_o - F_c)$  maps along the b and c axes were calculated and are shown in Fig.2. The final atomic coordinates are given in Table 2. The values of  $F_o$  and  $F_c$  obtained for the structure which was finally adopted are given in Table 3A.

# Accuracy of the structure determination

The least-squares analyses of the three zones of data (in which the non-diagonal terms of the normal equations are neglected) give the following average standard errors of the position parameters in Ångström units: Mg 0.016, Si 0.013, and O 0.037. Thus, cationoxygen bond lengths have a maximum probable error of about 0.05 Å and oxygen-oxygen distances about 0.07 Å.

The individual isotropic temperature factors B are erratic in their distribution, and are subject to large standard errors. Thus, in the two refined projections, as shown in Table 4, the temperature factor for Mg ranges from zero to 0.45, with an average standard deviation of 0.25; for Si, B ranges from 0.11 to 0.84 with an average standard deviation of 0.21; and for O, B ranges from zero to 2.49 with an average standard deviation of 0.62. Without knowing the influence

	Cli	noensta	tite		Pigeonit	e	1	Diopside	
Atoms	x	y	z	x	y	z	x	$\begin{vmatrix} y \end{vmatrix}$	
M <sub>T</sub>	0.242	0.986	0.193	0.246	0.981	0.231	0.250	0.944	0.250
M <sub>II</sub>	.247	.347	.220	.251	.344	.236	.250	.333	.250
Sir	.457	.658	.294	.453	.661	.274	.461	.661	.236
Sin	.053	.661	.264	.049	.662	.252	(.039	.661	.264)
0, O	.362	.156	.320	.372	.168	.315	.372	.153	.361
$O_{I}'$	.124	.159	.112	.127	.166	.161	(.128	.153	.139)
O <sub>π</sub>	.377	.498	.298	.378	.506	.323	.392	.500	.319
$O_{TT}'$	.137	.518	.103	.125	.508	.147	(.108	.500	.181)
O <sub>III</sub>	.395	.775	.101	.395	.773	.070	.406	.731	0
ο <sub>π</sub> ,	.105	.813	.051	.108	.782	006	(.094	.769	0)

 

 Table 2. Final atomic parameters of clinoenstatite and pigeonite compared with those of diopside (WARREN and BRAGG, 1928)

\* The origin of the coordinates of diopside is displaced by (.25, .25, 0) from the origin given by WARREN and BRAGG (1928), to show the differences of coordinates among the three structures directly. The coordinates given in parentheses are crystallographically equivalent with those immediately above.

# ${\bf Table \, 3.} {\it Final \, observed \, and \, calculated \, structure \, factors \, for \, clinoenstatite \, and \, pigeonite$

#### A. Clinoenstatite

Ъ	k	1	P <sub>e</sub>	P.,	b k l	. P <sub>c</sub>	Po	h k l	۳ <sub>с</sub>	Po	Ъ	<b>k</b> 1	۶ ¢	۶.
2	0	0	- 70	58	950	i 30	38	091	12		0 1	0 6	21	19
3	0	0	- 8	6	10 5 0	7	8	0 10 1	50	48	0 1	16	21	23
¥.	0	0	24	19	060	171	173	0 11 1	- 8		0	1 7	- 21	19
5	0	0	5	6	160	4		0 12 1	16	14	0	27	- 7	
6	0	0	-124	117	260	- 28	23	0 0 2	-201	207	0	37	- 24	
7	0	0	- 5		360	- 5		0 1 2	- 4		0	47	- 6	
8	0	0	82	89	460	50	48	0 2 2	- 51	53	0	57	- 17	
9	0	0	0	6	5 6 0	- 2	1.0	0 5 2	- 0	11	0	07 77	- 9	
10		0	- 75	90	7 6 0		49	0 4 2	33	35	0	1 1 8 7	- 12	
1	1	0	- 22	رد د	7 0 0 8 6 0	35	41	0 6 2	-148	150	0	08		31
- -	+	õ	104	101	960	6	••	072	- 5	-9-	0	18	9	16
ر ۲	1	0	- 4	•••	10 6 0	- 70	62	082	- 12	15	0	28	2	
5	1	0	39	44	170	10	11	0 9 2	5	-	0	38	- 1	
6	1	0	1		270	6	6	0 10 2	34	38	0	48	- 4	
7	1	o	51	58	370	2		0 11 2	17	19	0	58	- 23	25
8	1	0	- 3		470	- 1		0 12 2	- 49	45	0	68	23	25
9	1	0	- 19	17	570	53	48	013	- 19	20	0	78	- 1	
10	1	0	- 0		670	2		023	6		0	88	2	
11	1	0	15	14	770	27	22	0 3 3	- 22	21				
0	2	0	- 3	10	870	- 8		043	- 44	42	1	0 0	1	
1	2	0	3		970	11	11	0 5 3	- 6	13	2	0 0	- 71	63
2	2	0	- 89	90	080	9 19	22	063	- 17	21	3	0 0	- 8	6
3	2	0	- 5		180	- 5		073	- 20	19	4	00	28	21
4	2	0	48	40	280	- 29	25	083	- 23	20	5	00	5	0
5	2	0	9	7	3 8 0	1		0 9 3	5	74	-	0 0 0 0	-128	129
6	2	0	- 12	12	4 8 0			0 10 3	- ))	)1	/ 9	00	- /	08
7	2	0	- 8		580	17	19	0 11 3	- 72	22	0	00	, 03 1 6	,0 6
8	2	0	55	41	7 8 0		10	0 0 4		115	10	00	- 85	99
10	2 2	ñ	- 13	14	, 80	23	26	0 1 4	28	28	11	0 0	- 8	
11	2	õ	- 6	••	0 9 0	0		0 2 4	- 9		0	0 2	-202	197
1	3	0	- 5	9	1 9 0	21	10	034	- 9	9	1	02	- 26	24
2	3	0	3	6	290	- 4		0 4 4	- 16	18	2	02	12	42
3	3	0	- 35	38	390	0		054	- 26	22	3	02	8	12
4	3	0	- 1		490	- 6		064	69	61	4	02	-125	120
5	3	0	19	20	590	19	17	074	- 2		5	02	- 22	32
6	3	0	2		690	6		084	3		6	02	123	118
7	3	0	15	20	0 10 0	- 33	27	094	- 2		7	02	52	63
8	3	0	- 5		1 10 0	4		0 10 4	- 26	27	8	02	- 61	75
9	3	0	13	15	2 10 0	- 12	11	0 11 4	- 23	20	9	02	- 10	12
10	3	0	1		3 10 0	0		0 12 4	20	21	10	02	11	109
11	3	0	- 15	15	4 10 0	- 23	20	0 1 5	28		19	0 2 0 2	_ 2	
0	4	0	1	52	0 11 0			0 2 5	23	20		0 4	111	111
1	4 1.	0	 - 17	66	9 11 0	, -, А		0 4 5	- 5	12	1	04	25	17
2 1	4	0	- •/		3 11 0	_ 48	60	0 5 5	24	23	2	04.	24	20
ر ا	7	0	- 31	36	,	0		0 6 5	19	17	3	04	- 59	71
5	4	0	12	13	0 2 0	- 1	8	075	12	12	4	04	121	134
6	4	0	- 20	26	0 4 0	33	34	085	19		5	04	22	17
7	4	0	- 6		060	174	176	0 9 5	11		6	04	-110	87
8	4	0	45	36	0 8 0	25	24	0 10 5	26	22	7	04	- 46	42
9	4	0	3		0 10 0	- 29	28	0 0 6	- 50	52	8	04	19	12
10	4	0	27	22	0 12 0	54	48	016	- 14	9	9	0 4	24	12
1	5	0	97	93	0 1 1	17	11	026	1		10	04	- 50	57
2	5	0	~ 0		021	~ 33	45	036	1		11	0 4	- 27	24
3	5	0	- 75	65	0 3 1	- 20	18	0 4 6	12		12	04	26	
- 4	5	0	- 3		041	66	64	056	28	27	0	06	- 47	42
5	5	0	- 14	24	0 5 1	27	21	066	- 34	31	1	u to n ∠	- 18	17
6	5	0	3		0 6 1	27	30	076	- 0		2	0 0 1 4	1/	11
7	5	0	-108	112	071	- 14		0 8 6	- 3		· ر ۱	 n .	11 	51 69
8	5	0	2		0 8 1	2		0 9 6	4		• •	- 0	- 0)	

**13**0

# Table 3. (Continued)

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2	0 2	2 1	15	125	-8	02	- 30	39	4 0 4	07	0)			
								B. Pig	conite					t Geografia
	-						_	-	· · · · ·	P	P	5 K I	P	F
h	k 1	. F	c	F.	Ъ	k 1	P <sub>c</sub>	. Fo	h k i	r <sub>c</sub>	r <sub>o</sub>	<u>п к 1</u>	f c	<b>*</b> •
•			6		10	10	24	23	3 11 0	- 33	30	0 11 3	- 9	
2	00	-		4.0	10	- 0	55	57	2			0 12 3	- 12	10
3	00	, -	14	12	-	50	, , ,	11	0 2 0	- 2t	28	0 13 3	- 13	17
4	00	) -	23	20	2	50	- 0	50	0 2 0	- 14	12	0 14 3		
5	0 0	) –	2		3	50	- 01	50	0 4 0	160	156	0 15 3	,	
6	0 0	) –	75	69	4	50	- 9	5	0 0 0	100	100	0 15 3	- 16	14
7	0 (	) -	19	19	5	50	- 39	34	0 8 0	19	10	0 10 5	- 10	37
8	0 0	)	46	47	6	50	13		0 10 0	- 40	30	0 0 4	57	
9	0 (	3	11		7	50	- 73	80	0 12 0	50	62	0 1 4	4)	40
10	0 0	o	59	51	8	50	. 9		0 14 0	19		0 2 4	- 14	10
1	1 (	- 0	8	16	9	50	18	20	0 16 0	- 33	35	034	- 6	-
2	1 (	5	4	9	10	50	16	14	0 1 1	21	25	044	- 35	28
3	1 (	3	94	90	0	60	150	150	0 2 1	- 56	60	054	- 36	40
4	1 (	o -	3		1	60	15	16	0 3 1	- 39	42	064	39	41
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، م		- 1 –	 9		5	60	- 15	15	071	- 2		0 10 4	- 21	17
0		- -	13	20	6	60	- 38	35	0 8 1	- 38	32	0 11 4	- 23	22
7			10	15	7	6 0	- 15	17	0 9 1	- 1		0 12 4	19	20
10			12	11	8	6.0	19	20	0 10 1	36	35	0 13 4	- 3	
11	11		14	11		6.0	15	10	0 11 1	- 5		0 14 4	. 4	
0	2 0		-	27	9	60	51	56	0 12 1	18	10	0 1 5	33	31
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4	2 (	D	18	17	3	70	25	25	0 15 1		17	0 5 5	25	24
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8	2 (	0	25	26	7	70	17	21	0 2 2	- 10	11	0 0 5		10
9	2 (	0	4		8	70	- 11	12	0 3 2	- 13	19	0 9 5	0	10
10	2	0 -	7		9	70	7	14	0 4 2	39	57	0 10 5	-	. 20
11	2	0 –	11	10	0	80	14	17	0 5 2	53	48	011 2	19	20
1	3	0 -	16	17	1	80	- 14	16	0 6 2	- 94	86	0 12 5		• 4
2	3 4	0	20	16	2	80	- 27	27	072	- 0	4	0 0 6	- 21	10
3	3 -	0 -	17	18	3	80	2		082	- 18	17	0 1 6	÷ 25	27
4	3 1	0 -	1		4	80	12	15	0 9 2	2		0 2 6	19	14
5	3	0	11	14	5	80	17	17	0 10 2	39	36	036	- 3	
6	3	0 -	9	5	6	80	_ 6		0 11 2	33	33	046	13	23
7	ź	- 0	20	20	7	80	- 0		0 12 2	- 42	45	056	27	26
	7	° –	 L		8	80	17	15	0 13 2	6		066	- 11	10
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11	•	• -		7	י י	00	- 11	16	0 1 3	- 33	29	0 10 6	5 12	15
0	4	· -	14	14	2			16	0 2 3	23	23	0 11 6	5 23	21
1	4	u –	10	12	2	y U	- 0		0 3 3	- 25	14	0 12 6	5 - 6	11
2	4	0 -	38	35	0	90	- 2		0 4 3	- 43	42	0 1 3	7 - 16	15
3	4	0	2		0	10 0	- 54	>>	0 = 7	_ 96		0 2	7 8	
4	4	0 -	26	27	1	10 0	8		ر ز ب + ۲ م		- /	0 3	7 2	10
5	4	0	26	21	2	10 0	- 18	16			01	0 4 1	- 7 0	
6	4	0 -	1		3	10 0	0		0 7 3	- 21	41	0 T	7 _ 16	14
7	4	0	7		4	10 0	- 16	17	083	- 1			, - 10	. 1
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9	4	0 -	6		2	11 0	8		0 10 3	- 22	24	U 7	, - 9	1

Table 3	(Continued)
$\mathbf{T}$ and $\mathbf{O}$ .	CONVENCE

										•			•					· ·
ł	1	k	1	F <sub>c</sub>	r <sub>o</sub>	h	k	1 P	r Fo	h	k	1	r <sub>c</sub>	P.,	h	k 1	Pc	';; <b>₽</b> ₀
C	)	8	7	15		7	0	o – :	21 21	1	0	4	4	11	7	06	28	27
C	)	9	7	1	17	8	0	0 1	7 48	2	0	4	28	18	ī	02	83	75
c	1	0	7	- 0		9	0	0	6 22	3	0	4	- 80	90	2	02	67	75
c	,	0	8	- 9		10	0	0 - 3	56 54	4	0	4	57	73	3	02	- 35	29
G	)	1	8	25	22	11	0	0 –	7	5	Ó	4	29	14	4	02	- 63	51
C	)	2	8	- 11		0	0	2 -13	21 113	6	0	4 .	- 12	30	5	02	~ 19	19
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Q	)	5	8	- 36	28	3	0	2 - 3	13 12	9	0	4	- 10	11	8	02	10	5
0	) (	6	8	- 8		4	0	2 - 6	56 73	10	0	4	- 13	20	9	02	13	14
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2	. (	0	0	- 6		8	0	2 - 1	8 27	2	0	6	- 28	11	3	04	84	57
3	; (	0	0	- 13	10	9	0	2	1 7	3	0	6	51	54	4	04	33	35
4	, (	0	0	- 26	27	10	0	2 3	57 41	. 4	0	6	- 4	24	5	04	- 19	14
5		0	D	- 0	5	11	0	2	36	5	0	6	- 6		5	04	- 28	24
6		0 1	D	- 73	77	0	0	4 3	32 37	6	0	6	2	11	7	04	- 0	

on the data of absorption and twinning in the crystal, it is felt that no great significance can be attached to this distribution of temperature factors. The same observation may be made about the final residual maps of Fig. 2, which do not show any interpretable features, especially in regard to anisotropic thermal motions.

Atoma	(	Clinoen	statite			Pigeonite				
Atoms	$B_{hk0}$	$\varepsilon_B$	B <sub>0kl</sub>	$\varepsilon_{B}$	B <sub>hk0</sub>	$\varepsilon_{B}$	B <sub>0kl</sub>	$\varepsilon_B$		
Mr	0.43	0.26	0.07	0.26	1.32	0.17	0.64	0.09		
$M_{TT}$	.45	.26	.00	.20	1.09	.22	.62	.11		
Sit	.41	.23	.25	.17	.49	.34	.75	.17		
$Si_{II}$	.84	.27	.11	.17	.73	.37	.80	.16		
Or	.96	.62	.26	.47	.81	.71	1.53	.60		
$\hat{0_{I'}}$	1.24	.66	.47	.50	.00	.56	1.19	.55		
0 <sub>11</sub>	2.49	.80	.73	.57	.86	.93	.91	.47		
$O_{II}'$	.86	.60	.47	.60	1.44	1.03	.73	.48		
Om	.65	.68	.75	.65	.00	.59	1.02	.51		
O <sub>III</sub> ′	.00	.47	.80	.77	.00	.62	.94	.58		
R	0.11		0.12		0.11		0.07			

Table 4. Isotropic temperature factors obtained by the least-squares method

# II. Structure analysis of pigeonite Experimental

The crystals used for the structure analysis are taken from ferropigeonite specimens kindly donated by Professor H. Kuno. He collected them from andesite-dacite dikes near the Asio Mine, Japan,

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and d	lescribed	$\mathbf{the}$	chemical	composit	tion as	follows	(personal	communi	-
catio	n, 1959):								

Weightp	er cent		Mole ratio	)S
$\overline{\mathrm{SiO}_2}$	48.36	Si	1.933	
$Al_2O_3$	0.41	Al	0.018	1.99
$\rm Fe_2O_3$	1.36	$\mathrm{Fe^{+3}}$	0.041	
FeO	<b>32.86</b>	$\mathrm{Fe^{+2}}$	1.097	
$TiO_2$	0.39	Ti	0.011	
MnO	0.84	Mn	0.028	2.01
MgO	11.34	Mg	0.675	
CaO	4.58	Ca	0.195 )	
$Na_2O$	$\mathbf{tr}$			
$K_{2}O$	$\mathbf{tr}$	CaSiO	3 : MgSiC	)3 :
$H_{2}O(+)$	0.15	FeSiO	3 (includi	ng
H <sub>2</sub> O ()	$\mathbf{tr}$	MnSiC	D <sub>3</sub> )	
$P_2O_5$	0.04	= 10	: 34 : 56*	:
	$\overline{100.33}$			

Crystals of about  $0.3 \times 0.3 \times 0.5 \text{ mm}^3$  were used for the standard and integrating-Weissenberg photographs as in the case of clinoenstatite, and  $\text{Cu}K\alpha$ ,  $\text{Fe}K\alpha$  and  $\text{Mo}K\alpha$  radiations were used. There was no twinning in these crystals. The cell constants were determined by the powder method using silicon as a standard substance. They are:  $a = 9.731 \pm 0.005$  Å,  $b = 8.953 \pm 0.005$ ,  $c = 5.256 \pm 0.005$  and  $\beta = 108°33' \pm 10'$ . The space group is  $P2_1/c$  ( $C_{2h}^5$ ), the same as that of clinoenstatite. There are eight formula units of  $\text{Ca}_{0.10}\text{Mg}_{0.34}\text{Fe}_{0.56}\text{SiO}_3$ in the unit cell. Intensities were obtained in the same way as for clinoenstatite. The intensities were corrected for Lorentz and polarization factors and scaled by comparison with calculated structure factors in the usual way. The structure refinement was carried out in almost the same way as for clinoenstatite.

#### Refinement

The atomic coordinates obtained for clinoenstatite by the use of contour maps of strong h0l reflections were used for the first structure-factor calculation of pigeonite. Completely disordered distribution of metal atoms Mg, Fe and Ca over the available positions was assumed in this calculation. Using the signs of the calculated structure factors,

<sup>\*</sup> This table represents a revision of an earlier analysis by KUNO (personal communication), in which these ratios were determined to be 12:26:62. All of our structure factor calculations for ferropigeonite are based on these earlier ratios. We have not repeated the calculations using the improved ratios, because the difference is not great enough to affect the structure determination.

the electron-density maps projected along [100], [010] and [001] were calculated. It was obvious from the difference in peak heights on these maps that some ordered distribution of metal atoms is present in the structure.



Fig. 2. Final  $(F_o - F_c)$  syntheses for clinoenstatite projected (a) along the a axis and (b) along the c axis. Contour intervals: for (a) 1 electron/Å<sup>2</sup>; for (b) 0.5 electron/Å<sup>2</sup>. The zero contours are omitted, negative contours dashed.

There are two crystallographically different positions for metal atoms in the structure of pigeonite as in diopside. One, called the  $M_{I}$  position, is considered to be suitable for larger metal atoms, such as Ca in diopside, and the other, called the  $M_{II}$  position, is associated





Fig. 3. Final  $(F_o - F_c)$  syntheses for pigeonite projected (a) along the *a* axis and (b) along the *c* axis. Contour intervals, 1 electron/Å<sup>2</sup>; zero contour omitted, negative contours dashed

with smaller atoms such as Mg in diopside. Four likely arrangements for the metal atoms in pigeonite of composition  $Ca_{0.10}Mg_{0.34}Fe_{0.56}SiO_3$  were considered as follows:

Case	$\mathbf{M}_{\mathbf{I}}$	M <sub>II</sub>	Assumption	Ratio of electron density (M <sub>I</sub> /M <sub>II</sub> )
(1)	$Ca_{20}Fe_{80}$	$Mg_{68}Fe_{32}$	Complete order of Ca and Mg	1.50
(2)	$\mathrm{Ca_{20}Fe_{50}Mg_{30}}$	$Mg_{38}Fe_{62}$	Complete order of Ca only	1.00
(3)	$\mathrm{Ca_{10}Mg_{34}Fe_{56}}$	$Ca_{10}Mg_{34}Fe_{56}$	Complete disorder of Ca, Mg and Fe	1.00
(4)	$\mathrm{Ca_{20}Mg_{68}Fe_{12}}$	$\mathrm{Fe}_{100}$	Complete order of Ca, Mg and Fe	0.59

The electron-density ratio obtained from the peak heights at the  $M_{II}$  and  $M_{II}$  positions is found to be 1.40, which is closest to case (1). The ordered distribution of metal atoms reduced the discrepancy factor of the *h0l* reflections from 0.45 to 0.35. The electron-density maps showing only oxygen atoms were constructed by subtraction of the calculated contributions of metal and Si atoms from the observed structure factors. The further refinement process has been carried out in the same way as in clinoenstatite, and is shown in Table 1. In that table, only the reflections with  $|F_o| > 0$  were considered in calculation of the discrepancy factors.

In Fig. 3, the final  $(F_o - F_c)$  maps along the *b* and *c* axes are shown. The final coordinates are given in Table 2. Table 3 *B* shows the values of  $F_o$  and  $F_c$  obtained from the structure which was finally adopted<sup>\*</sup>.

Accuracy of the structure determination

The least-squares estimates of the standard errors of the atomic coordinates are comparable to the results obtained for clinoenstatite. Again, little significance can be attributed to the individual temperature factors calculated. The residual maps shown in Fig.3 also show no special features. These maps, together with the low discrepancy factors obtained in the parameter refinements confirm the correctness of the assumption that was made regarding the distribution of metal atoms over the sites  $M_I$  and  $M_{II}$ .

# III. Discussion of the structures

The structures of clinoenstatite and pigeonite are projected along [010] in Fig.4 and compared with that of diopside. In Fig.5, the projections along [001] for the three structures are given on the

\* See footnote, p. 132.



Fig. 4. Crystal structures of clinoenstatite, pigeonite and diopside projected along the b axis. Numbers represent heights of atoms above the plane of the a and c axes in hundredths of the b length.

assumption that they have exactly the same unit cell. It is clear from these figures that the difference in the atomic coordinates is greatest along the c axis, except for the  $M_I$  atoms. The interatomic distances and interbond angles in these structures calculated from the final parameters are given in Table 5. The results show in detail the configuration of the single silicate chain, in clinoenstatite and pigeonite, which is the characteristic feature of the pyroxene group. Further, the



Fig. 5. Comparison of atomic positions in clinoenstatite, pigeonite and diopside based on a common unit cell projected along the *c* axis

coordination environments of the metal atoms are defined, and the effect of these atoms on the crystal chemistry of the pyroxene structures in general is clarified. We will discuss in detail the structures found for clinoenstatite and pigeonite and compare them with that of diopside.

#### Metal atoms

The  $M_I$  positions in diopside are occupied by Ca atoms and coordinated by eight oxygen atoms, and the  $M_{II}$  positions by Mg atoms having a coordination of six oxygen atoms.  $M_I$  positions are regarded

# Table 5. Interatomic distances and interbond angles of clinoenstatite, pigeonite and diopside

Atoms	Clinoenstatite	Pigeonite	Diopside
Si $-$ O ( $\pm$ 0.05 Å)			
$Si_{T} - O_{T}$	1.65	1.62	1.56
$\dot{Si_{I}} = O_{II}$	1.61	1.55	1.59
Si <sub>T</sub> —O <sub>III</sub>	1.67	1.69	1.60
Si <sub>T</sub> -O <sub>III</sub>	1.63	1.59	1.65
Av. $Si_I - O$	1.64	1.61	1.60
$Si_{II} - O_{I}'$	1.62	1.63	1.56
$Si_{II} - O_{II}$	1.58	1.58	1.59
Si <sub>II</sub> -O <sub>III</sub> '	1.70	1.68	1.65
$Si_{II} - O_{III}$	1.74	1.63	1.60
Av. Si <sub>II</sub> —O	1.66	1.63	1.60
M = O(+ 0.04  Å)			
$M_{-\Omega}$	2 1 2	2 20	2.36
$M_1 \cup I$ $M_2 - O_2'$	2.12 2.02	2.12	2.36
MO.	2.02	2.12	2.36
MO.r.'	2.00 2.05	2.13	2.36
M <sub>1</sub> On M-On	2.33	2.35	2.55
M <sub>1</sub> Om M.—O	(3,73)	(3.48)	2.74
$M_{-}O_{m'}$	2 29	(0.10) 2.76	2.74
MO···	(3, 26)	2.84	2.55
$A_{\rm V} M_{\rm c}$	2.15	2.01 2.36	2.50
	2.10	2.00	
$M_{II}$ — $O_I$	2.17	2.09	2.16
$M_{II} - O_I$	2.02	2.15	2.06
$M_{II} - O_{I}'$	2.21	2.11	2.16
$M_{II}$ — $O_{I}$	2.00	2.18	2.06
$M_{II}$ -O <sub>II</sub>	1.96	2.05	2.12
$M_{II}$ — $O_{II}$	2.04	2.06	2.12
Av. $M_{II}$ —O	2.07	2.11	2.12
$\Omega - \Omega (+ 0.07 \text{ Å})$			
in Si-tetrahedron			
0 - 0	2.80	2.72	2.61
$0_1 - 0_1$	2.35	2.57	2.66
$\Omega_1 = \Omega_{111}$	2.74	2.69	2.55
$O_{II} = O_{III}$	2.63	2.00	2.63
$O_{11} = O_{11}$	2.50	2.40	2.59
	2.00	2.40	2.63
	2.00	2.00	2.0 <del>4</del> 9.61
Av. 0–0	2.09	2.03	2.01

#### A. Interatomic distances in Ångström units

Atoms	Clinoenstatite	Pigeonite	Diopside
O - O (+ 0.07  Å)			
in Sin tetrahedron			
$O_{\mathbf{r}'} - O_{\mathbf{r}'}$	2.77	2.73	2.61
$O_1' - O_{11}'$	2.61	2.70	2.55
$O_{I}' - O_{III}'$	2.71	2.64	2.66
$O_{II}' - O_{III}'$	2.70	2.60	2.63
$O_{II}' - O_{III}'$	2.65	2.59	2.59
O <sub>III</sub> 'O <sub>III</sub> '	2.82	2.69	2.64
Av. 0–0	2.71	2.66	2.61
	B. Interbond angl	es	
$O-Si-O(\pm 2^\circ)$			1
$O_{I} - Si_{I} - O_{II}$	116.8°	118.7°	111.7°
$O_{I} - Si_{I} - O_{III}$	114.0°	106.4°	111.7°
$O_{I} - Si_{I} - O_{III}$	110.9°	109.1°	107.6°
$O_{II} - Si_{I} - O_{III}$	106.4°	99.7°	106.2°
$O_{II} - Si_I - O_{III}$	107.0°	113.7°	110.9°
$O_{III}$ $-Si_I$ $-O_{III}$	105.7 °	$108.3^\circ$	108.8°
Av. $O-Si_{\Gamma}-O$	110.1°	$109.3^\circ$	109.5°
	190.1°	116.9°	111.7°
$O_{I} = O_{II} = O_{II}$	103 1 °	112.0°	107.6°
$O_{I} = O_{II} = O_{III}$	109.5°	105.8°	111.7°
$O_1 = S_{11} = O_{111}$	108.8°	107.4°	110.9°
$O_{\rm II} = S_{\rm II} = O_{\rm III}$	107.0°	106.0°	106.2°
$O_{\rm II} = S_{\rm II} = O_{\rm III}$	110.1°	108.6°	108.8°
$Av. O-Si_{II}-O$	109.8°	109.5°	109.5°
$Si-O-Si(\pm 2^{\circ})$			140.00
$\operatorname{Si}_{I} - \operatorname{O}_{III} - \operatorname{Si}_{I}$	136.8°	139.1 °	140.8°
$Si_{II} - O_{III} - Si_{II}$	125.1 °	$135.3\degree$	140.8°

Table 5A (Continued)

as occupied by the univalent cations or by larger bivalent cations, and  $M_{II}$  by the smaller bivalent cations.

Table 6 gives the distribution of metal atoms between the  $M_I$  and  $M_{II}$  positions, the coordination numbers of the metal atoms, and the average atomic distances from the metal atoms to the neighboring oxygen atoms. These data are consistent with the assumption that metal atoms Ca, Fe and Mg are in almost completely ordered distribution between the  $M_I$  and  $M_{II}$  positions, with the larger atoms (Ca) occupying the  $M_I$  position by preference. If enough larger atoms are not available, smaller atoms (Fe, Mg) occupy this position and the coordination

······		Atoms	Coordi- nation number	Average M—O distance	Displacement of atoms*		
					a	b	с
 Clinoenstatite	MI	Mg	6	$2.15~{ m \AA}$	0.08	0.38	0.30
	M <sub>II</sub>	$\widetilde{\mathrm{Mg}}$	6	2.07	.03	.13	.16
Pigeonite	MI	$Ca_{0.20}Fe_{0.80}$	7	2.36	.04	.33	.10
•	$M_{II}$	$\mathrm{Mg}_{0.68}\mathrm{Fe}_{0.32}$	6	2.11	.01	.10	.07
Diopside	MI	Ca	8	2.50			
(WARREN and	M <sub>II</sub>	${ m Mg}$	6	2.12			
Bragg, 1928)							

Table 6. The nature of the metal atoms in clinoenstatite, pigeonite and diopside

\* Deviations from the diopside metal positions, given in Ångström units in the a, b, and c directions.

tends to decrease from eight to six. The coordinations of the  $M_I$  and  $M_{II}$  positions are shown in Fig. 4 with dotted lines for  $M_{II}$  and dashedand-dotted lines for  $M_I$ . In comparison with other oxygen atoms the  $O_{III}$  and  $O_{III}$  atoms are always slightly farther from the  $M_I$  positions, making the coordination of  $M_I$  irregular. The  $M_{II}$  position is evidently occupied by the smaller divalent atoms (Mg or Fe) and has nearly regular octahedral coordination in all three structures.

It is interesting to compare the distribution of metal atoms in clinopyroxenes obtained here with the similar situation that exists in the amphiboles. Most amphiboles are represented by the general formula  $X_{2-3}Y_5Z_8O_{22}(OH, F)_2$ , where X is Na, K or Ca; Y is Mg,  $Fe^{+2}$ ,  $Fe^{+3}$  etc; and Z is Si or Al. The general formula of pyroxenes may be written as XYZ<sub>2</sub>O<sub>6</sub> in the same way. In some amphiboles either Mg or Fe atoms accompany Ca atoms in the X positions in the structures, as in the structure of clinopyroxenes. The results of WHITTAKER (1949) on crocidolite and of ZUSSMAN (1955) on actinolite suggest that the Mg atoms enter the X positions, which correspond to the  $M_{I}$ positions in clinopyroxene structure, in preference to iron, in contrast to the case of clinopyroxenes. According to a recent study by GHOSE (1960) the structure refinement of the amphiboles grunerite and cummingtonite gives a metal atom distribution similar to that of pigeonite, with the Fe atoms rather than Mg occupying preferentially the X positions not filled by Ca. As far as the ionic radii are concerned,  $Fe^{+2}$  atoms would be expected to occupy the large space of the X or  $M_{\tau}$  positions.

Both  $M_I$  and  $M_{II}$  sites are on the two-fold axes in the diopside structure. In clinoenstatite and pigeonite these sites are in general positions, since the two-fold axes are absent in these structures. Metal atoms at the  $M_I$  and  $M_{II}$  positions in diopside are exactly superposed in the projection on (010), but in pigeonite and clinoenstatite they show some separation in this projection. The deviations of the coordinates of the  $M_I$  and  $M_{II}$  positions in clinoenstatite and pigeonite from those of diopside are also given in Table 6 in Ångström units. The deviation of both  $M_I$  and  $M_{II}$  positions is greater in clinoenstatite than in pigeonite. Also, the deviation of the  $M_I$  position is greater than that of  $M_{II}$  in both clinoenstatite and pigeonite. The displacement of the metal atoms is easily understood as the result of two effects which tend to compensate each other: first, the tendency of the metal atoms to assume regular octahedral coordination; and second, the relative rigidity of the silicate chain.

### Single silicate chains

Although the structures of clinoenstatite and pigeonite are built up from the single silicate chains found in diopside, a number of differences in the details of the chain structure are revealed by this analysis.

The silicate chains in the three clinopyroxenes are projected perpendicular to (100) in Fig. 6, where the Si atoms are taken to lie in the plane of the paper, and the heights of oxygen atoms are represented in Ångström units. There is only one kind of chain in diopside (Fig. 6E) because all chains must be crystallographically equivalent. There are, on the other hand, two crystallographically different kinds of chains in clinoenstatite and pigeonite. Fig. 6A and B are chains of clinoenstatite and C and D are those of pigeonite. A fact of interest is the constant distance of  $3.05 \pm 0.02$  Å between neighboring Si atoms belonging to the same chain in all three structures, regardless of the kind of metal atoms present. The difference in the shapes of the chains results from a slight rotations of SiO<sub>4</sub> tetrahedra around the axis passing through the Si and  $O_I$  atoms, without changing the relative position of Si atoms. The rotations of SiO<sub>4</sub> tetrahedra belonging to two crystallographically different chains in the same structure have opposite senses.

The main effect of the metal atoms on the single silicate chains can be observed in the change of relative position of silicate chains along the c axis together with the change of relative position of atoms



Fig. 6. Silicate chains in the structures of clinoenstatite, pigeonite and diopside projected on the (100) plane. Numbers represent distances in Ångström units above and below (negative) a plane passed through the silicon atoms.

in the chain itself, to give appropriate coordination of oxygen atoms to the metal atoms as shown in Fig. 4. The changes both of the shape and of the relative position of the chains are greater in clinoenstatite than in pigeonite when compared with diopside.

# Conformity to PAULING's rule of valency sums

It is interesting to examine to what extent PAULING'S rule is obeyed in the structure of clinoenstatite and pigeonite, in connection with the interatomic distances. The valency sums were calculated for each oxygen atom in the usual way for clinoenstatite and pigeonite as given in Table 7. PAULING'S rule is apparently not satisfied completely. The deviation from the expected valency sums may be reduced to some

<u>.</u>	Clinoenstatite			Pigeonite			Diopside		
Oxygen atoms	Neighbors	Valencies	Total	Neighbors	Valencies	Total	Neighbors	Valencies	Total
01-	$\begin{array}{c} \mathrm{Si_{I}}\\ \mathrm{M_{I}}\\ \mathrm{2M_{II}} \end{array}$	$ \begin{array}{c} 1\\1/3\\1/3\\1/3\\1/3\end{array} $	2	$\begin{array}{c} \mathrm{Si}_{\mathrm{I}} \\ \mathrm{M}_{\mathrm{I}} \\ \mathrm{2M}_{\mathrm{II}} \end{array}$	$ \begin{array}{c} 1\\2/7\\ 1/3\\ 1/3 \end{array} $	$1^{20}/_{21}$	Si Ca 2Mg	$1\\1/4\\ {1/3\\1/3}$	111/12
О <sub>п</sub> —	Si <sub>I</sub> M <sub>I</sub> M <sub>II</sub>		1²/3	$egin{array}{c} { m Si_I} \ { m M_I} \ { m M_{II}} \end{array}$	$\left. \begin{array}{c} 1 \\ 2/7 \\ 1/3 \end{array} \right\}$	$1^{13}/_{21}$	Si Ca Mg	$1\\1/4\\1/3$	17/12
O <sub>III</sub> —	$egin{array}{c} { m Si}_{{ m I}} \\ { m Si}_{{ m I}} \\ { m M}_{{ m I}} \end{array}$	$ \begin{array}{c}1\\1\\1/3\end{array} $	$2^{1}/_{3}$	$egin{array}{c} {\rm Si}_{{\mathfrak l}} \ { m Si}_{{\mathfrak l}} \ { m M}_{{\mathfrak l}} \end{array}$	$\left. \begin{array}{c} 1 \\ 1 \\ 2/7 \end{array} \right\}$	$2^{2}/_{7}$	Si Si 2Ca	$1 \\ 1 \\ \{1/4 \\ 1/4 \\ 1/4 \end{bmatrix}$	$2^{1}/_{2}$
0 <sub>t′</sub>	$egin{array}{c} { m Si}_{ m II} \ { m M}_{ m I} \ { m M}_{ m II} \end{array}$	$\begin{array}{c}1\\1/3\\1/3\\1/3\\1/3\end{array}$	2	$egin{array}{c} { m Si}_{ m II} \ { m M}_{ m I} \ { m M}_{ m II} \end{array}$	$\begin{array}{c}1\\2/7\\1/3\\1/3\end{array}$	1 <sup>20</sup> / <sub>21</sub>		(1/*)	
О <sub>11′</sub> —	${f Si_{II}}\ {f M_{I}}\ {f M_{II}}$	$egin{array}{c} 1 \\ 1/3 \\ 1/3 \end{bmatrix}$	$1^{2}/_{3}$	Sim Mr Mr	$egin{array}{c} 1 \\ 2/7 \\ 1/3 \end{bmatrix}$	1 <sup>13</sup> /21			
О <sub>Ш'</sub> —	$\begin{array}{c} \mathrm{Si}_{\mathrm{II}} \\ \mathrm{Si}_{\mathrm{II}} \\ \mathrm{M}_{\mathrm{I}} \end{array}$	$\begin{pmatrix} 1\\ 1\\ 1/3 \end{pmatrix}$	· 21/3	$egin{array}{c} { m Si}_{ m II} \\ { m Si}_{ m II} \\ 2{ m M}_{ m I} \end{array}$	$egin{array}{c} 1 \\ 1 \\ \{ 2/7 \\ 2/7 \} \end{array}$	24/7			

 Table 7. The valency sums of oxygen atoms in clinoenstatite, pigeonite and diopside

extent by taking account of the lengthening of the atomic distances between  $Si_{II}$  and  $O_{III}$  atoms, and between  $O_{III}$ ,  $O_{III}$  and  $M_I$  atoms, reducing the bond number of these links. While some differences are found in the various Si—O distances as shown in Table 5, they are hardly greater than the estimated standard errors, and we do not feel that we can interpret these distances in this way at present. The same situation would be expected in the diopside structure, though no accurate structure determination is yet available to enable us to test the point in that case, either.

# Distribution of cations in pigeonite

The chemical composition of natural pigeonite shows that Ca atoms are present usually to the extent of about 9 atomic percent and at most 15 percent of all metal atoms in the structure. The maximum amounts of Fe and Mg atoms in the natural pigeonite are each limited to less than  $70^{\circ}/_{0}$  of all metal atoms in the structure. As Ca and Mg atoms have a tendency to occupy respectively the M<sub>I</sub> and M<sub>II</sub> positions preferentially, the distribution of metal atoms in pigeonite can be defined as follows: M<sub>I</sub> = (Ca<sub>20</sub> Fe<sub>80-x</sub>Mg<sub>x</sub>); M<sub>II</sub> = (Mg<sub>100-y</sub> Fe<sub>y</sub>), where always either x = 0 or y = 0, and x and y can have maximum values of 40 and 60 respectively. If the value of x is over 40, the pyroxene approaches the clinoenstatite-type and apparently is metastable. If the value of y becomes more than 60, the pyroxene is not stable at any temperature and changes to olivine and silica.

The results of the structure analyses indicate that the structure of pigeonite is intermediate between those of clinoenstatite and diopside, giving seven-fold coordination to the  $M_I$  position instead of eight as in diopside, or six as in clinoenstatite. Ca, Fe and Mg atoms are evidently distributed randomly in the  $M_I$  position. It is possible, however, to give the results of the analysis of pigeonite another interpretation, namely, that the seven-fold coordination of the  $M_I$  position is the average effect of local eight coordination around Ca atoms and six coordination around Fe or Mg atoms. The same interpretation can be applied to the deviations of the  $M_I$  and  $M_{II}$  positions in pigeonite from those in diopside; that the deviations are the average of the deviation of the Mg atoms and the normal positions of Ca atoms. At the present stage, it is not possible to decide which interpretation is better, especially because of poor resolution of the electron density in the (010) projection. Bown and GAY (1957) have reported that the h+k odd reflections of some pigeonites were observed to be diffuse. We have not considered the diffuseness of reflections in estimating the intensity, although some h+k odd reflections are slightly diffuse in our photographs. This diffuseness of reflections in pigeonite could be explained on the basis of the local adjustments of coordination about the metal atoms as suggested in the last section, or by incipient exsolution into Ca rich regions and Fe, Mg rich regions.

At high temperatures, it is possible that the amount of Ca atoms in clinopyroxenes is between 15 and 30 mol percent of all metal atoms, covering the gap between augite and pigeonite (KuNO, 1955). This clinopyroxene, however, exsolves to augite and pigeonite on cooling by the diffusion of metal atoms. Thus the  $M_I$  positions in the pigeonite contain Ca atoms to the extent of less than  $30^{\circ}/_{0}$  and those of the augite contain more than  $50^{\circ}/_{0}$  Ca atoms (MORIMOTO and ITO, 1959).

# The structural relationship of clinopyroxenes

Although the crystal structure of clinopyroxenes is principally built up of single silicate chains, we have seen that a slight change in these chains takes place depending on the kinds of metal atoms in the structures. The changes in clinopyroxene structures can conveniently be classified into the following three cases, taking the diopside structure as standard: (1) displacement of the silicate chains; (2) distortion of the silicate chains, and (3) displacement of the metal atoms.

The clinopyroxenes of the compositions along the diopsidehedenbergite join are examples of case (1). Although the clinopyroxenes on this join have practically a constant translation along the c axis, which is the direction of the silicate chains, the distance between the silicate chains changes to allow appropriate space for metal atoms of various sizes. This results in a slight change of the cell constants other than the c translation (Kuno and Hess, 1953).

When displacement of the silicate chains is not enough to give space for metal atoms, a distortion of silicate chains takes place as in spodumene. Various augites also show the effect of case (2). The clinopyroxenes of the above two cases have one kind of silicate chain and have all metal atoms on the two-fold axes, corresponding to the space group C2/c. These are the augite-type pyroxenes.

Change of the position or distortion of the silicate chain is inadequate to compensate for the introduction of small bivalent cations such as 146

Fe or Mg atoms into the  $M_I$  positions. The Fe or Mg atoms become displaced from the special position characteristic of the diopside structure, producing two kinds of silicate chains. Thus the space group becomes  $P2_1/c$ . The clinopyroxenes with compositions adjacent to the enstatite-ferrosilite join are examples of case (3) corresponding to this situation. These, the pigeonite-type pyroxenes, are no longer stable in nature and exist in a metastable state, or transform to orthopyroxenes, which are stable at low temperature, exsolving Ca atoms from the structures to form augite-type pyroxenes.

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