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UNIT CELL DIMENSIONS OF CLINOENSTATITE AND PIGEONITE IN RELATION TO OTHER COMMON CLINOPYROXENES.*

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ABSTRACT. The X-ray diffraction patterns of clinoenstatite and pigeonite are given and their similarity pointed out. The gradual change in unit cell dimensions from clinoenstatite to pigeonite, pigeonite through subcalcic augite, and augite to diopside, and finally from diopside to hedenbergite are demonstrated. All clinopyroxenes have the same structure as diopside. By measurement of unit cell dimensions and optical properties it seems probable that the chemical composition of clinopyroxenes may be fairly accurately determined.

INTRODUCTION

Of the monoclinic pyroxenes in the field clinoenstatite-diopside-hedenbergite-ferrosilite only the structure of diopside has been determined (Warren and Bragg, 1928). Of particular interest to petrologists is the structural relationship of clinoenstatite to the pigeonites and secondarily of this group to the more Ca-rich clinopyroxenes. The key to the problem seemed to lie in an understanding of the structure of clinoenstatite.

ACKNOWLEDGMENTS

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CLINOENSTATITE

The powder diffraction pattern of clinoenstatite using both Cu and Fe radiation was recorded. The diffraction lines were indexed assuming the same space group as had been determined

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1 Pigeonite-augite series measured by Kuno; clinoenstatite-diopside-hedenbergite series measured by Hess.

TABLE 1

Unit Cell Dimensions of Some Clinopyroxenes in Å

	1* Synthetic Clinoenstatite Mg_{100}	2 Pigeonite Usugoya-zawa Hakone volcano $Ca_8\ Mg_{64}\ Fe_{28}$	3 Pigeonite Yumoto Hakone volcano $Ca_7\ Mg_{45}\ Fe_{48}$	4 Diopside St. Lawrence Co. B. H. 1.23 $Ca_{49}\ Mg_{47}\ Fe_4$	5 Ferrosalite Ausable Quad. 1197a $Ca_{50}\ Mg_{17}\ Fe_{33}$	6 Hedenbergite Herault Calif. $Ca_{48}\ Mg_3\ Fe_{49}$
a	9.618	9.692	9.712	9.750	9.804	9.854
b	8.828	8.917	8.959	8.930	8.980	9.024
c	5.186	5.239	5.251	5.249	5.259	5.263
β	71°38½′	71°27′	71°27′	74°10′	74°46′	75°40′

Accuracy of cell dimensions probably better than ± .005 Å and β ± 6′.

*Calculated density..... 3.190 gm/cm³ at 23° or slightly lower than enstatite, 3.210 gm/cm³ at 23° C.

1 Synthetic, from Foster

2 Analysis, Kuno and Nagashima (1952)

3 Analysis, Kuno unpublished

4 Analysis, Hess (1949) #35

5 Analysis, Hess (1949) #16

6 Analysis, Hess (1949) #18

for diopside, C_{2h}^{6}. The unit cell dimensions resulting from these observations are given in table 1. The methods and constants used are the same as those given in Hess (1952).

On the basis of the above unit cell values, for clinoenstatite d_{hkl} values for about 100 planes were calculated and are compared to the observed values. In table 2 it can be seen that a good agreement has been obtained between calculated and observed values. The intensities of the observed lines also agree reasonably well with those observed for diopside. There are only six unidentified lines in the pattern and all but one are weak. All have relatively small 2θ values. The value d = 4.281 could possibly fit d_{011} and the value d = 4.052 could similarily be d_{210}. If so, these would be the only cases of an Okl plane with k odd or an hkO plane with h + k odd. The other four could not be indexed at all. Five of these six lines also appear in Atlas' (1952) table of d values for clinoenstatite. All of them could be attributed to enstatite impurities in the sample which seems to be the explanation.

The difference between our unit cell dimensions and those given by Atlas (1952) is related to the choice of which plane shall be designated as {001} and hence the value for β. The controlling factor in choosing this value is that the {001} be the analog of {001} in the diopside. In his choice Atlas seems to have been influenced by the value of β for clinoenstatite given in Winchell (1939)—$\beta = 87°36'$. This value probably came from Wright's and Larsen's measurement of a clinoenstatite crystal (Allen, White, Wright and Larsen, 1909) in which they gave β as 87°26′. The crystal face which Wright and Larsen measured was possibly $\{\bar{1}02\}$.

The above relationships can be demonstrated by tracing the variations of the various diffraction lines across the composition field of the clinopyroxenes to diopside. Diopside-hedenbergite pyroxenes have a good basal parting defining {001}, β for diopside being 74°10′. Augites and subcalcic augites have exsolution lamellae ll {001} and the β angle is close to 74°. It is only a small jump from Ca-poor augite to pigeonite which also has exsolution lamellae on {001} with β slightly smaller ($\beta = 71.5°$ from X-ray results). By X-ray diffraction patterns it is possible to trace the various lines from the pigeonites to clinoenstatite by which we arrive at our value for {001} and $\beta = 71° 38\frac{1}{2}'$. Atlas' value β is such that his {001} then

TABLE 2

C^6_{2h} hkl	Synthetic Clinoenstatite Calculated d (Å)	Synthetic Clinoenstatite Observed d (Å)	Relative Intensity	Pigeonite Yumoto Calculated d (Å)	Pigeonite Yumoto Observed d (Å)	Relative Intensity	Remarks
110	6.3460	6.36	5	6.4208	.....	..	
200	4.5643	.....	..	4.6037	4.616	15	
020	4.4140	4.413	15	4.4794	4.458	10	
111	4.3815	.....	..	4.4402	4.438	10	
...	.....	4.281	10	.....	.....	..	Impurity
...	.....	4.052	10	.....	.....	..	Impurity
...	.....	3.468	10	.....	3.603	10	Impurity
021	3.2861	3.2867	60	3.3299	3.3305	10	
220	3.1730	3.1743	70	3.2104	3.2101	60	
221	2.9806	2.9795	120	3.0205	3.0207	75	
311	2.8861	2.8874	5	2.9195	2.9080	60	
310	2.8768	2.8783	125	2.9035	2.9035	75	
130	2.8008	2.8026	10	2.8406	.....	..	
...	.....	2.7029	10	.....	.....	..	Impurity
131	2.5421	2.5418	45	2.5785	2.5783	45	
202	2.5235	2.5238	35	2.5561	.....	..	
112	2.4853	.....	..	2.5167	.....	..	
002	2.4610	2.4594	70	2.4892	2.4882	20	
$22\bar{1}$	2.4351	2.4358	25	2.4608	2.4591	20	
...	.....	2.3793	20	.....	2.4112	5	Impurity
$13\bar{1}$	2.3390	2.3380	10	2.3691	.....	..	
400	2.2822	2.2853	3	2.3019	2.3080	4	
312	2.2260	.....	..	2.2546	.....	..	
$31\bar{1}$	2.2131	2.2126	25	2.2327	2.2315	15	
040	2.2070	2.2080	25	2.2397	present*	5	
222	2.1908	.....	..	2.2201	2.2230	10	

* "Present" substituted for the d value where line too indefinite to measure or where interfered with by adjacent line.

TABLE 2 (cont.)

$C6_{2h}$ hkl	Synthetic Clinoenstatite Calculated d (Å)	Synthetic Clinoenstatite Observed d (Å)	Relative Intensity	Pigeonite Yumoto Calculated d (Å)	Pigeonite Yumoto Observed d (Å)	Relative Intensity	Remarks
022	2.1495	.....	..	**2.1758**	.....	..	
11$\bar{2}$	2.1419	2.1399	15	**2.1547**	.....	..	
331	2.1190	2.1190	55	2.1467	2.1457	30	
330	2.1153	2.1150	..	2.1403	.....	..	
421	2.0918	2.0923	5	2.1157	2.1167	15	
420	2.0272	.....	..	2.0473	.....	..	
402	2.0205	2.0183	10	2.0452	2.0449	30	
041	2.0119	2.0136	12	2.0425	2.0410	15	
240	1.9865	1.9885	**5**	**2.0140**	2.0120	4	
...	.....	1.9701	**5**	.....	.....	..	Impurity
132	1.9442	1.9419	2	1.9704	present	4	
241	1.9366	1.9376	10	1.9645	1.9630	8	
20$\bar{2}$	1.9274	1.9271	8	1.9459	.....	..	
511	1.8764	present	2	1.9856	.....	..	
422	1.8372	1.8469	5	1.8604	.....	..	
332	1.8123	.....	..	1.8368	.....	..	
33$\bar{1}$	1.8053	1.8095	2	1.8249	.....	..	
510	1.7879	1.7874	15	1.8038	1.8044	8	
22$\bar{2}$	1.7664	.....	..	see below			
13$\bar{2}$	1.7660	1.7648	15	1.7872	present	8	
24$\bar{1}$	1.7603	1.7626	15	1.7827 1.7848	1.7830	10	22$\bar{2}$ pigeonite
...	.....	.....	..				
150	1.7334	1.7333	20	1.7587	1.7592	10	
42$\bar{1}$	1.7133	1.7136	3	1.7292	present	4	
113	1.6801	.....	..	1.7007	.....	..	
151	1.6666	1.6614	5	1.6909	.....	..	
313	1.6526	.....	..	1.6740	present	4	
312	1.6439	.....	..	**1.6590**	1.6580	8	

TABLE 2 (cont.)

$C6_{2h}$ hkl	Synthetic Clinoenstatite Calculated d (Å)	Synthetic Clinoenstatite Observed d (Å)	Relative Intensity	Pigeonite Yumoto Calculated d (Å)	Pigeonite Yumoto Observed d (Å)	Relative Intensity	Remarks
042	1.6429	1.6431	15	1.6650†	.....	..	
441	1.6167	.....	..	see below			
531	1.6082	.....	50	1.6266	1.6265	45	
223	1.6081	1.6086		1.6289	present	..	
...	.....	.....		1.6376	present	..	441 pigeonite
15$\bar{1}$	1.6052	1.6068		1.6275	present	..	
440	1.5863	1.5879	6	1.6052	.....	..	
530	1.5514	.....	..	1.5674	present	8	
023	1.5379	.....	..	1.5561	.....	..	
51$\bar{1}$	1.5354	.....	..	1.5484	present	10	
350	1.5271	1.5273	20	1.5474	1.5470	10	
602	1.5270	1.5257	20	1.5440	.....	..	
600	1.5214	1.5229	20	1.5346	1.5350	8	
442	1.4903	1.4875	30	1.5103	.....	..	
513	1.4744	1.4769	10	1.4708	.....	..	
060	1.4713	1.4715	40	1.4931	1.4935	45	
40$\bar{2}$	1.4599	1.4590	3	1.4725	.....	..	
	Miscellaneous other lines measured						
260	.....	.....	..	1.4203	1.4202	15	
53$\bar{1}$	1.3777	1.3782	50	1.3910	1.3912	45	
800	.....	.....	..	1.1509	1.1507	10	
660	1.0577	1.0582	3	1.0702	present	8	
513	1.0490	1.0481	20	1.0668	1.0660	8	
750	1.0491			1.0603	1.0600	10	
840	1.0136	1.0128	5	.....	.....	..	

† A few pigeonite d values are listed out of numerical sequence so that they appear opposite the equivalent hkl for clinoenstatite. Clinoenstatite measured with Cu radiation pigeonite with Fe radiation.

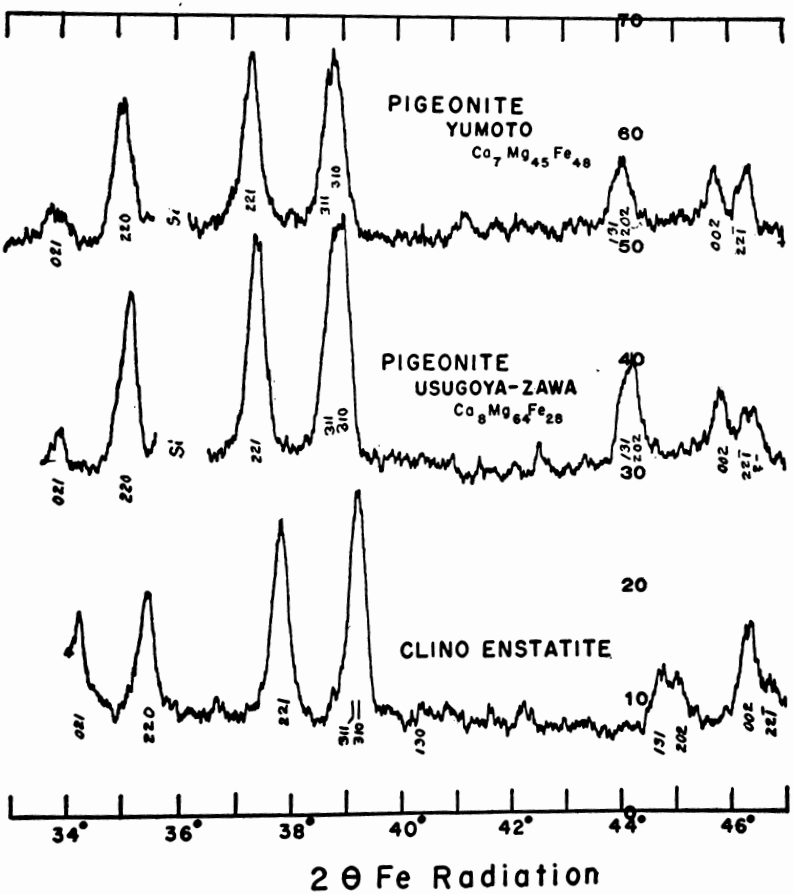

Fig. 1. Records of X-ray powder diffraction patterns of clinoenstatite and pigeonites.

becomes exactly our $\{10\bar{2}\}$ morphological plane by calculation. Our {001} undoubtedly is the analog of {001} in diopside, and ours we believe is the unit cell which should be chosen to be consistent with diopside.

PIGEONITES

For comparison with clinoenstatite the main lines of pigeonite from Yumoto Hakone volcano are given in table 2. There are two unidentified lines in the pattern corresponding to unidentified lines in the clinoenstatite pattern. Both lines are weak. The

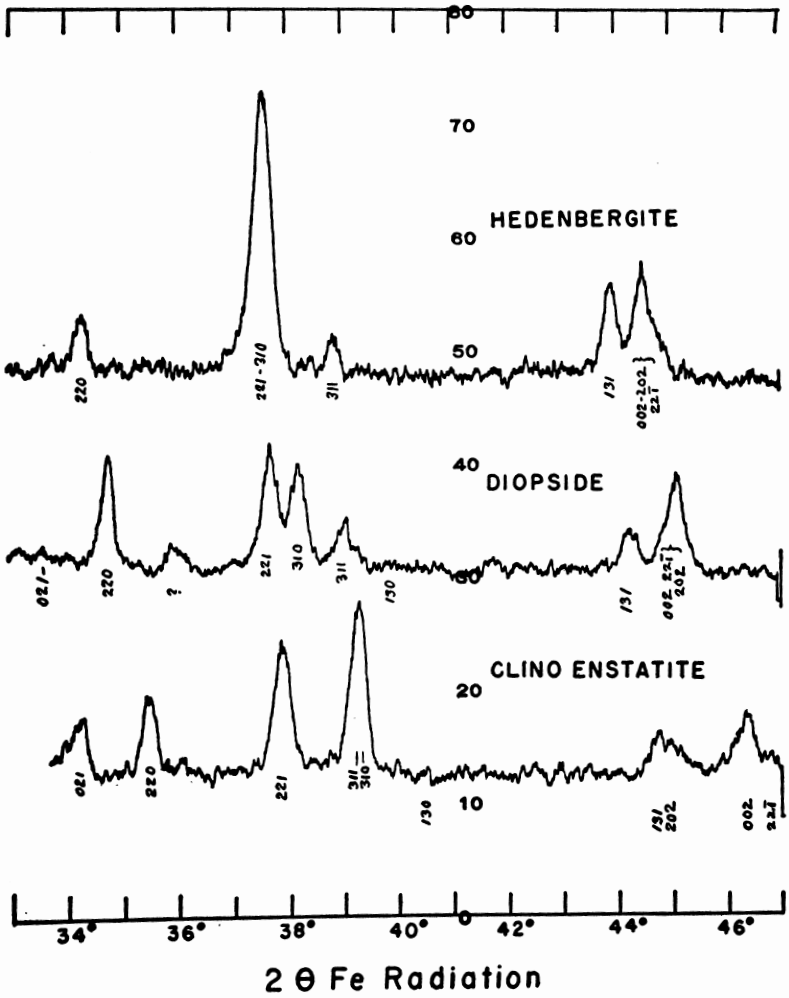

Fig. 2. Records of X-ray powder diffraction patterns of clinoenstatite, diopside, and hedenbergite.

β angle for two pigeonites measured was found to be near $71\frac{1}{2}°$. Figure 1 is a graphic presentation of records from $2\theta = 34°$ to $2\theta = 47°$ (Fe radiation Mn filter) for clinoenstatite, pigeonite from Yumoto and pigeonite from Usugoya-Zawa, Hakone volcano. This permits visual comparison of the variation of the positions and intensities of the peaks with changing composition.

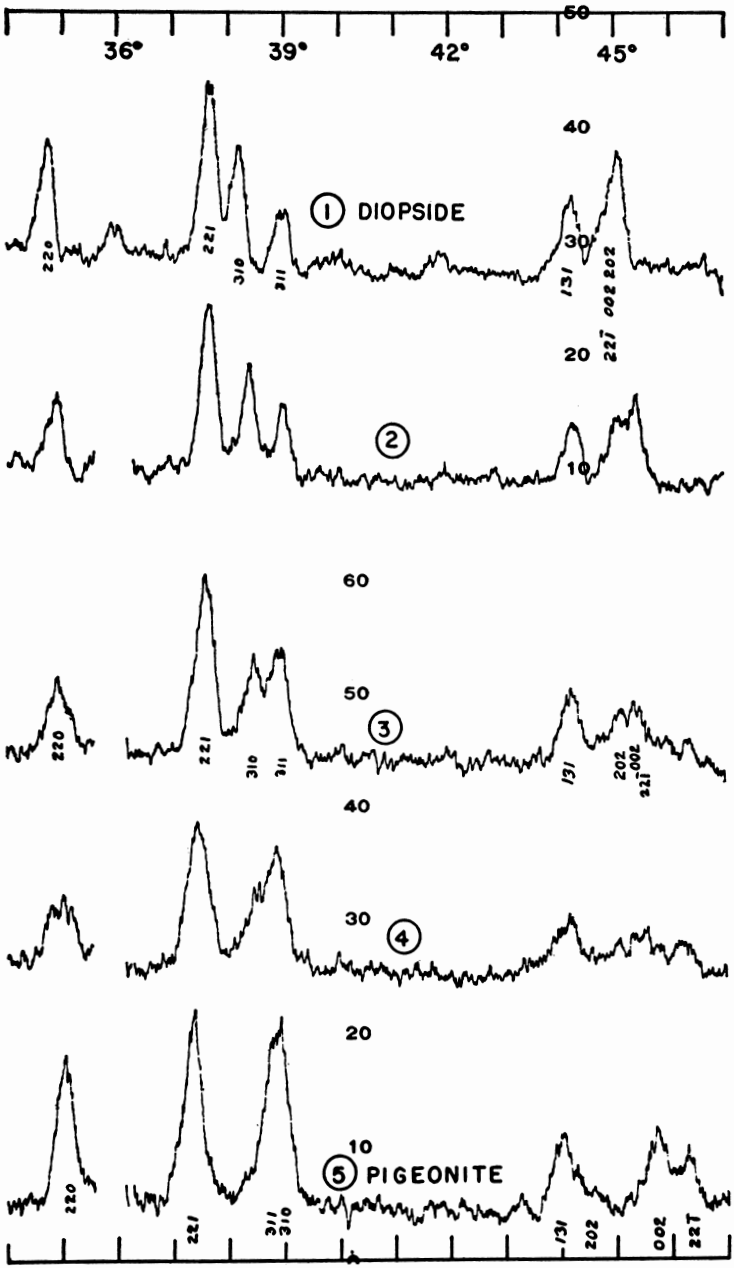

Fig. 3. Records of X-ray powder diffraction patterns from St. Lawrence diopside through augite and subcalcic augite to Yumoto pigeonite. Compositions shown in figure 6.

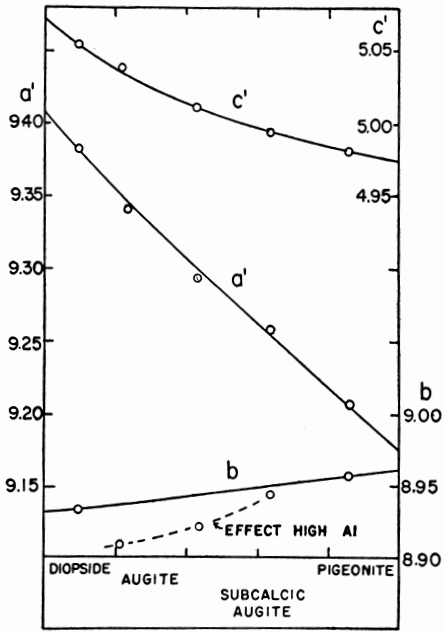

Fig. 4. Variations in unit cell dimensions from Yumoto pigeonite to St. Lawrence diopside.

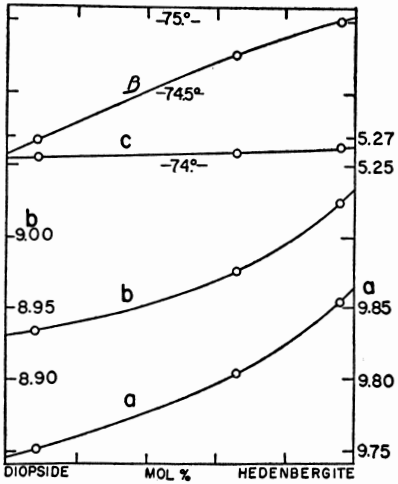

Fig. 5. Variations in unit cell dimensions in the series diopside-hedenbergite.

OTHER CLINOPYROXENES

Figures 2, 3, 4 and 5 similarly portray the changes across the field from pigeonite to diopside and diopside to hedenbergite. With this much information an approximate diagram may be drawn to show variations in unit cell dimensions for the whole clinopyroxene field (fig. 6). It is evident from this figure that determination of chemical composition of the major constituents Mg, Fe and Ca is possible by X-ray analysis. The effects on the unit cell of Al^{+3}, Fe^{+3}, Ti^{+4} and Na^{+1} will have to be determined before precision can be expected from such determinations. When such an investigation has been completed it may be possible to estimate not only the amounts of major constituents but also the four minor constituents by combining X-ray and

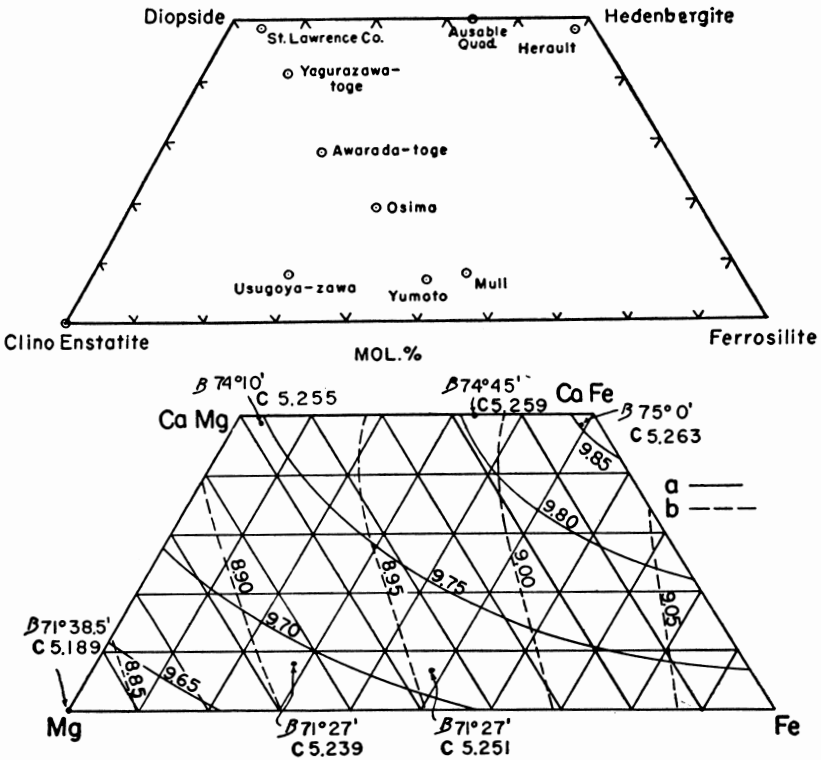

Fig. 6. Upper diagram shows compositions of clinopyroxenes used in investigation, and lower diagram the variations in unit cell dimensions.

optical methods. Figure 6 even in its present form is convenient for a first approximation in indexing clinopyroxene X-ray diffraction patterns.

It may be expected that with refinement of the X-ray data, effects related to the environment at the time of crystallization and to the post-crystallization history may become evident as in the case of the orthopyroxenes.

The results embodied in this paper support the conclusion of Wyckoff, Merwin and Washington (1925) that the structures of all clinopyroxenes are similar.

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