

## Synthesis and Unit Cell Parameters of Ca-Mg-Fe Pyroxenes

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### Abstract

Within the pyroxene quadrilateral (the system  $\text{CaSiO}_3\text{-MgSiO}_3\text{-FeSiO}_3$ , with  $\text{CaSiO}_3$  (=Wo)  $\leq 50$  mol percent), clinopyroxenes can be synthesized for a wide range of compositions, although they may form metastably for compositions with intermediate or low calcium contents ( $30 > \text{Wo} > 10$ ; and  $\text{Wo} < 5$  percent). For most intermediate compositions, mixtures of oxides will crystallize to form clinopyroxene by repeated grinding and heating at temperatures just below the solidus, with total pressure 1 atm and partial pressure of oxygen within the furnace maintained at the iron-wüstite equilibrium. Compositions with  $100\text{Fe/Fe} + \text{Mg} > 70$  will crystallize clinopyroxenes only with hydrothermal or high-pressure methods. Clinoenstatite may be synthesized at low pressures and temperatures ( $900^\circ\text{C}$ ) in molten  $\text{MgCl}_2$ .

Orthopyroxenes can be synthesized with compositions along the En-Fs join, and with contents of calcium up to about 5 mol percent Wo. They will crystallize from mixtures of oxides at 1 atm for compositions with  $100\text{Fe/Fe} + \text{Mg} < 30$ ; for compositions with greater iron contents the requirement is pressure greater than 10 kbar.

Unit cell parameters of clinopyroxenes are satisfactorily expressed at third-order trend surfaces (except fourth-order for volume).  $a$  and  $V$  are smallest for clinoenstatite and largest for hedenbergite.  $b$  is sensitive mainly to changes in  $\text{Fe/Fe} + \text{Mg}$  content, whereas  $\beta$  is sensitive mainly to  $\text{CaSiO}_3$  content.  $c$  is virtually constant, 5.24 to 5.25 Å, over most of the quadrilateral, but decreases abruptly in the vicinity of clinoenstatite. There is a small positive excess volume of mixing between Ca-rich and Ca-poor clinopyroxenes of similar  $\text{Fe/Fe} + \text{Mg}$  across the quadrilateral.

Unit cell parameters of orthopyroxenes increase from enstatite to ferrosilite; only  $a$  and  $V$  show significant increases with  $\text{CaSiO}_3$  content. For Ca-free orthopyroxenes, volume varies linearly with composition, indicating that there is no excess volume of mixing.

### Introduction

Crystals of pyroxene in igneous and metamorphic rocks show a variability of composition, and textural evidence for polymorphic inversions, both of which are indicators of conditions that prevailed during the formation of the rock. For some years we have been attempting to specify the significance of these variations by determining the equilibrium phase relations of Ca-Mg-Fe pyroxenes. A first requirement for such studies is the synthesis of suitable starting materials. This paper describes those methods that we have found to be most successful. We make only brief reference to laboratory techniques, since these have been recently summarized in a volume edited by Ulmer (1971).

Compositions synthesized are shown in Figure 1.

It is emphasized that the conditions reported here are those of *synthesis* and do not necessarily reflect conditions of equilibrium. Indeed, prolonged heating of some compositions at the conditions of synthesis will ultimately yield a different phase or assemblage.

Unit-cell parameters reported here are for pure phases in the system  $\text{CaSiO}_3\text{-MgSiO}_3\text{-FeSiO}_3$ , and should be compared with those of natural pyroxenes only with extreme caution, if at all.

### Experimental Methods

There are several experimental methods for the synthesis of pyroxenes; the recipes are presented below. The choice of a method (or combination of two methods) is made to prevent the nucleation or persistence of other phases, such as pyroxenoids in the iron-rich region, olivine and orthopyroxene in the low-Ca region, or olivine in the En and Fs corners.

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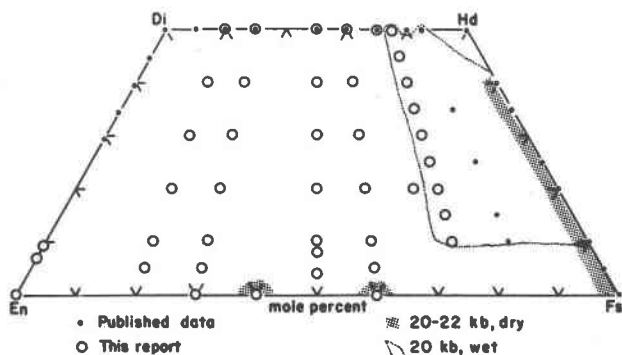


FIG. 1. The pyroxene quadrilateral showing clinopyroxene compositions synthesized in the present study (open circles) and published data (dots) used in calculating trend surfaces of the unit-cell parameters (Figure 2). Areas of synthesis at high pressures are shown by shading (1100–1200°C, 20–22 kb, dry) and by dotted outline (960–990°C, 20 kb, in presence of water-rich vapor). The remaining compositions were synthesized at one atmosphere, except for clinoenstatite, made in the presence of fused  $MgCl_2$  (this report), and compositions along the Di-Hd join (made hydrothermally by Rutstein and Yund, 1969). Sources of other published data are: Di-En join, Clark *et al.* (1962); Hd-Fs join, Lindsley *et al.* (1969);  $Wo_{0.5}En_{7.5}Fs_{92.5}-En_{15}Fs_{85}$  join, Smith and Finger (1971). Where identical compositions were made by more than one method, average values of unit-cell parameters were used in computing trend surfaces. Compositions are expressed in terms of molecular percentages of  $Wo$  ( $CaSiO_3$ ),  $En$  ( $MgSiO_3$ ), and  $Fs$  ( $FeSiO_3$ ). Two clinopyroxenes on the Di-En join at  $Wo_{7.0}$  and  $Wo_{9.4}$  were synthesized at 1365°C by J. Frank Schairer.

Starting mixtures of pyroxene compositions were made from reagent-grade chemicals. Water adsorbed by these chemicals must be accounted for prior to weighing, either by drying or by correction for the water content as determined by weight-loss analysis. For drying,  $CaCO_3$  requires 4 hours at 400°C,  $Fe_2O_3$  1–2 hours at 800°C,  $SiO_2$  8 hours at 1250°C, and  $MgO$  18 hours at 1250°C. (Fe sponge, when used, is not dried, but must be analyzed for oxygen as described below.) The dried materials are cooled and stored in a desiccator, and preferably weighed out in a desiccated balance, since especially  $Fe_2O_3$  and  $MgO$  pick up water from the atmosphere. An alternative method is to determine the water content of 10 grams of material, after drying as described above, and then to weigh out *unheated* material in amounts corrected for water content. This latter method can be used only if the resulting mixture is to be heated in an open system to allow escape of the adsorbed water.

Almost all the pyroxenes reported here are iron-

bearing, and their synthesis requires the maintenance of iron in the ferrous state, either by imposing an appropriate partial pressure of oxygen or by reacting stoichiometric mixtures in a closed system.

The following outline of methods is not intended to be a comprehensive review, nor do we claim that the methods presented are all original. Rather, these are the methods that we have found to be successful.

#### Method 1: Controlled-Gas Quench Furnace, One Atmosphere

Synthesis of iron-bearing pyroxenes at one atm pressure requires a quench furnace with gas-mixing atmosphere control. The atmosphere within the furnace should be kept at the iron-wustite oxygen pressure by passing a gas mixture [ $CO + CO_2$  or  $H_2 + CO_2$  at  $P_{total} = 1$  atm (Nafziger *et al.*, 1971)] through the furnace. The starting material is a mixture of  $CaCO_3$ ,  $MgO$ ,  $Fe_2O_3$ , and  $SiO_2$ . Excess iron in the mix over the stoichiometric amount is required because there are losses of iron, both to the platinum container and to vapor. A platinum foil envelope is preferable to a heavier crucible in order to minimize iron loss; it should be prepared by heating at 1200°C in the controlled atmosphere with some iron oxide or iron silicate in it so as to impregnate the platinum with iron (the thinner the metal, the easier this is). We have found that for mixes weighing 4 grams, in platinum foil containers weighing 0.4 gram, the optimum excess is one wt percent of the iron oxide content desired. The chemicals should be ground (under liquid) for 1 hour. After evaporation of the liquid, the mix is loaded into the crucible. The first heating is for 4 hours at 900°C. Four or five additional heating cycles are required, with grinding between each cycle; the temperature of these heatings is 1200°, with the following qualifications: (1) for compositions with  $100 Fe/Fe + Mg > 50$ , the temperature must be lower (1150°) to prevent melting; (2) for compositions close to hedenbergite, the temperature must be reduced to a value lower than the temperature of transition to pyroxenoid (960° at the Mg-free compositions); Methods 4 and 5 produce larger crystals and less unreacted material for these compositions.

The product pyroxenes are clear, colorless, up to 60  $\mu m$  across. Phase impurities may be inclusions of cristobalite or olivine, or both, and interstitial glass, in amounts less than 1 percent. Iron losses to the crucible and to vapor may cause errors of

$\pm 1$  relative wt percent of the desired weight of FeO. Our results confirm the findings of Bowen *et al.* (1933, pp. 213–214) that the ratio of Si to divalent cations is very close to unity for pyroxenes: a slight excess of FeO results in pyroxene plus minor olivine, whereas a slight deficiency in FeO yields pyroxene plus minor cristobalite.

#### *Method 2: Synthesis in Sealed, Evacuated Silica-Glass Tubes*

The major drawback to the one-atmosphere method is the probability of losing some iron, as described above; it is impossible to add exactly the right amount of excess iron to compensate for this effect. Synthesis of pyroxenes in sealed, evacuated silica-glass tubes avoids this problem, and also obviates the need for a controlled atmosphere in the furnace. A drawback is the requirement that the starting mix be stoichiometric with respect to oxygen as well as the other elements prior to sealing in the silica-glass tubes. More specifically, iron must be added as the component "FeO", and any CaCO<sub>3</sub> used in the starting mix must be decarbonated prior to sealing the evacuated capsules.

The carbonate problem is overcome by pre-reacting equimolar mixtures of CaCO<sub>3</sub> and SiO<sub>2</sub> so that the calcium can be weighed in as CaSiO<sub>3</sub>. Adding iron as the component "FeO" is more difficult inasmuch as wüstite is difficult to prepare and is non-stoichiometric. Hence, it is necessary to use materials that will yield "FeO" upon reaction.

We have found that the most satisfactory method is to weigh out Fe<sub>2</sub>O<sub>3</sub> and metallic Fe sponge to give the desired composition. Fe sponge is easier to weigh to a calculated value and easier to mix with other constituents than are Fe pellets, but because of its high specific surface area the sponge contains significant oxygen as coatings and inclusions of oxide. Even if the oxide is removed by reduction in hydrogen immediately prior to weighing, atmospheric oxidation during and after weighing is sufficient to throw the mix off the desired composition. We have found it best to analyze the unreduced sponge for its oxygen content and to make appropriate allowances in the proportions of hematite and sponge used. For the analysis, the sponge is well mixed, and 2 to 5 grams are weighed into a silica-glass boat, which is then placed in a silica-glass combustion tube. After the tube is flushed with dry hydrogen, it is held in a furnace at approximately 700°C for 15 to 30 minutes and then cooled rapidly

in an air stream while hydrogen continues to pass over the sponge. The oxygen content of the Fe sponge, as indicated by the weight loss, is checked against the weight gain (due to H<sub>2</sub>O) of a U-tube containing magnesium perchlorate (the ratio of the weight changes is close to the theoretical 8/9 value). The sample of sponge on which the analysis is performed is then discarded, at least insofar as its use as a starting material is concerned. Replicate determinations of the oxygen content are desirable.

The oxygen content of the remaining sponge is reckoned as Fe<sub>2</sub>O<sub>3</sub>; the amounts of sponge and hematite needed to yield "FeO" are adjusted accordingly. We have found that the following procedure obviates the need for frequent oxygen analyses of the Fe sponge: The sponge is purchased well in advance of the time it is to be used and is stored for at least a year over activated alumina in a vacuum desiccator. A portion is then withdrawn for analysis, and the remaining sponge is ready for use. Subsequent analyses show little further change in composition of the sponge over periods of a year or more. Sponge stored in this fashion typically contains excess oxygen corresponding to 0.2 to 0.7 wt percent Fe<sub>2</sub>O<sub>3</sub>. The procedure is admittedly cumbersome, but is the only one with which we are familiar that permits precise addition of stoichiometric "FeO" to a mix.

The iron sponge is added to the other components only after they have been ground together for several hours under alcohol in an agate mortar. To minimize oxidation of the iron sponge, the complete mixture is then ground for as short a time—usually 1 to 2 hours—as will yield a homogeneous mix. It is imperative that there be a minimum of liquid during the final stages of grinding—that is, the mix should be a thick slurry—to insure homogeneity. Most of the alcohol can then be driven off using a heat lamp. To prevent reaction with the silica-glass tubing, the charge is enclosed in silver or silver-palladium foil before insertion into the tube, one end of which has been sealed. The remaining alcohol adsorbed by the mix is then driven off by heating the charge to approximately 700°C for one hour with the open end of the tube on line to a vacuum system. (Failure to follow this drying procedure may result in an explosion when the sealed capsule is placed in a furnace.) Otherwise, the technique is standard for silica-glass tube work (Kullerud, 1971, pp. 290–293). Approximately 2 to 2½ grams of mix can be conveniently reacted in

TABLE 1. INDEXED POWDER DATA AND UNIT-CELL PARAMETERS FOR THREE SYNTHETIC CLINOPYROXENES

h k l	$W_{0.25}En_{18.8}Fs_{56.2}$ (x=75, y=25)		$W_{0.30}En_{19}Fs_{21}$ (x=30, y=30)		$W_{0.10}En_{63}Fs_{27}$ (x=30, y=10)	
	obs	calc	obs	calc	obs	calc
2 0 0	4.680	4.681	--	--	--	--
0 2 1	3.352	3.356	3.332	3.338	3.312	3.314
2 2 0	3.241	3.248	3.218	3.225	3.196	3.197
-2 2 1	3.017	3.014	3.001	2.999	3.004	3.007
-----						
3 1 0	2.946	2.949	2.930	2.935	2.899	2.895
-3 1 1	2.910	2.911	2.901	2.901	2.899	2.909
-1 3 1	2.590	2.586	2.571	2.568	2.564	2.565
0 0 2	2.510	2.512	2.510	2.511	2.480	2.479
-----						
2 2 1	2.510	2.509	--	--	2.451	2.451
-2 3 1	--	--	--	--	2.401	2.400
3 1 1	2.286	2.287	2.277	2.278	2.224	2.226
1 1 2	2.197	2.200	--	--	--	--
-----						
0 2 2	2.197	2.195	--	--	--	--
3 3 0	--	--	2.150	2.150	--	--
-3 3 1	2.150	2.150	2.138	2.137	2.137	2.137
-4 2 1	2.120	2.119	2.111	2.110	2.109	2.108
-----						
0 4 1	2.059	2.057	2.042	2.041	2.036	2.032
-4 0 2	2.028	2.026	2.023	2.023	2.036	2.038
-1 3 2	--	--	1.968	1.968	--	--
1 5 0	1.770	1.771	1.755	1.755	1.749	1.749
-----						
-5 3 1	1.632	1.634	1.625	1.625	1.621	1.621
-2 2 3	1.627	1.626	1.624	1.624	1.621	1.622
-1 3 3	1.503	1.504	1.500	1.500	1.492	1.491
0 6 0	1.503	1.503	1.488	1.489	1.484	1.485
-----						
5 3 1	1.421	1.419	1.413	1.412	1.386	1.386
-7 1 2	1.337	1.337	1.333	1.333	1.336	1.336
0 6 2	1.290	1.290	1.281	1.281	1.274	1.274

a, Å	b, Å	c, Å	β, deg	V, Å <sup>3</sup>	V̄, cm <sup>3</sup> /mole	Source*
9.771(6)	9.762	9.735(5)	9.738	9.685(6)	9.679	
9.019(3)	9.013	8.934(2)	8.932	8.910(3)	8.901	
5.244(3)	5.250	5.244(3)	5.246	5.228(4)	5.226	
106.65(4)	106.98	106.74(4)	106.96	108.52(5)	108.50	
442.7(5)	442.0	436.75(4)	436.5	427.8(6)	426.6	

\*\* See Table 3.

a capsule 7 mm in inner diameter, 9 mm in outer diameter, and 8 to 9 cm long.

Reaction temperatures are limited by the melting temperature of the foil used to separate the charge from the silica-glass tube: 960°C for pure silver; higher temperatures for silver-palladium foil, the exact value depending on the composition of the alloy (Muan, 1963). These metals are used despite their low melting temperatures because the solubility of iron in them is negligible. To compensate for the rather low temperatures, run durations of 1 to 2 weeks are needed; even that time may be insufficient to produce a single-phase pyroxene, and it is commonly necessary to repeat the heating after grinding the partly-reacted material. We have employed this technique mainly to prepare intermediate starting materials for use in synthesis at high pressures of pyroxenes with 100 Fe/Fe + Mg greater than 70.

This sealed-silica-glass-tube technique yields products that are stoichiometric with respect to CaO,

MgO, and FeO; but grinding in the agate mortar and possible contamination from the silica-glass tube by vapor transport at high temperature tend to increase the SiO<sub>2</sub> content slightly above the desired value. The net result is a pyroxene of the desired composition plus a small amount—less than 1 percent—of free silica. This excess silica would be undesirable in melting experiments, but it is essentially inert with respect to sub-solidus reactions. It

TABLE 2. CLINOPYROXENE UNIT-CELL DIMENSIONS USED IN COMPUTING TREND SURFACES

x	y	a, Å	b, Å	c, Å	β, deg	V, Å <sup>3</sup>	V̄, cm <sup>3</sup> /mole	Source*
0 0	9.590	8.812	5.159	108.15	414.3	31.19		
0 7	9.650	8.840	5.180	108.45	419.2	31.56		
0 9.4	9.653	8.848	5.202	108.41	421.5	31.73		
0 29.2	9.714	8.903	5.250	107.27	433.8	32.66	(1)	
0 34.3	9.723	8.908	5.250	106.78	435.0	32.75	(1)	
0 39.4	9.731	8.916	5.250	106.39	436.5	32.86	(1)	
0 44.6	9.739	8.919	5.250	106.15	438.2	32.99	(1)	
0 50	9.7485	8.931	5.249	105.85	439.6	33.10	(1),(2)	
10 50	9.762	8.936	5.249	105.75	441.0	33.21	(2)	
20 5	9.652	8.872	5.206	108.55	422.6	31.82		
20 10	9.655	8.876	5.201	108.46	422.8	31.83		
20 20	9.718	8.902	5.239	107.85	431.4	32.48		
20 30	9.734	8.921	5.244	106.73	436.1	32.83		
20 40	9.745	8.935	5.246	106.23	438.6	33.02		
20 50	9.771	8.947	5.250	105.68	442.0	33.28	(2)	
30 0	9.645	8.878	5.193	108.58	421.4	31.73		
30 5	9.662	8.893	5.210	108.61	424.2	31.94		
30 10	9.684	8.907	5.227	108.51	427.6	32.19		
30 20	9.707	8.919	5.249	108.22	431.6	32.50		
30 30	9.745	8.939	5.244	106.69	437.6	32.95		
30 40	9.757	8.943	5.246	106.05	439.9	33.12		
30 50	9.7755	8.955	5.251	105.67	443.1	33.36	** (2)	
40 0	9.649	8.900	5.199	108.59	423.2	31.86		
50 5	9.662	8.931	5.218	108.71	426.5	32.11		
50 8	9.689	8.930	5.232	108.53	429.2	32.32		
50 10	9.703	8.947	5.238	108.57	431.1	32.46		
50 20	9.727	8.942	5.255	108.10	434.4	32.71		
50 30	9.741	8.953	5.248	106.67	438.5	33.01		
50 40	9.767	8.956	5.249	105.97	441.4	33.24		
50 50	9.7955	8.9725	5.252	105.49	445.4	33.54	** (2)	
60 0	9.667	8.961	5.216	108.69	428.0	32.22		
60 5	9.684	8.958	5.227	108.62	429.7	32.35		
60 10	9.712	8.978	5.244	108.49	433.7	32.65		
60 20	9.731	8.984	5.258	107.82	437.6	32.95		
60 30	9.752	8.981	5.249	106.63	440.5	33.17		
60 40	9.781	8.982	5.244	105.87	443.2	33.37		
60 50	9.813	8.982	5.251	105.32	445.5	33.54	(2)	
70 20	9.740	8.998	5.251	107.77	438.2	32.99		
70 50	9.821	8.992	5.251	105.18	447.6	33.70	(2)	
75 10	9.732	9.015	5.258	108.38	437.7	32.95		
75 15	9.744	9.021	5.256	108.06	439.2	33.07		
75 20	9.749	9.018	5.247	107.40	440.0	33.13		
75 25	9.771	9.019	5.244	106.65	442.7	33.33		
75 30	9.767	9.015	5.242	106.44	442.7	33.33		
75 35	9.791	9.001	5.242	106.02	444.0	33.43		
75 40	9.797	9.002	5.243	105.70	445.2	33.52		
75 45	9.814	9.002	5.249	105.46	447.0	33.65		
75 50	9.821	9.002	5.251	104.98	448.4	33.76		
80 50	9.832	9.002	5.251	105.02	448.6	33.78	(2)	
85 10	9.740	9.046	5.259	108.20	440.2	33.14	(3)	
85 15	9.746	9.055	5.255	107.70	441.8	33.27	(3)	
85 25	9.772	9.038	5.245	106.75	443.4	33.38	(3)	
85 35	9.800	9.030	5.244	105.92	446.3	33.60	(3)	
85 50	9.836	9.014	5.248	104.92	449.6	33.85	(2),(3)	
100 0	9.709	9.087	5.228	108.43	437.6	32.95	(4)	
100 5	9.724	9.092	5.226	108.14	439.1	33.06	(4)	
100 10	9.745	9.083	5.225	107.30	441.5	33.24	(4)	
100 20	9.765	9.081	5.231	106.69	444.3	33.46	(4)	
100 25	9.781	9.072	5.232	106.30	445.6	33.55	(4)	
100 35	9.8095	9.050	5.238	105.61	447.9	33.72	** (4)	
100 40	9.821	9.042	5.242	105.38	448.8	33.79	(4)	
100 50	9.840	9.024	5.2495	104.68	450.8	33.94	(2),(4)	

x =  $\frac{Fe \times 100}{Fe + Mg}$  =  $\frac{Fs \times 100}{Fs + En}$ ; y =  $\frac{Ca \times 100}{Ca + Fe + Mg}$  = Wo (mole percent)

Molar volume, V̄, is calculated on the basis of 8 R(SiO<sub>3</sub>) per unit cell.

\* No reference given, new data of this report, with following ranges of standard deviations: a, 0.003 to 0.010; b, 0.002 to 0.007; c, 0.002 to 0.006; β, 0.02 to 0.08; V, 0.3 to 0.9; V̄, 0.02 to 0.07.

(1) Clark, Schairer, and de Neufville (1962). Compositions converted from weight percent.

(2) Rutstein and Yund (1969).

(3) Smith and Finger (1971).

(4) Lindsley, Munoz, and Finger (1969).

\*\* Mean of published values and new data.

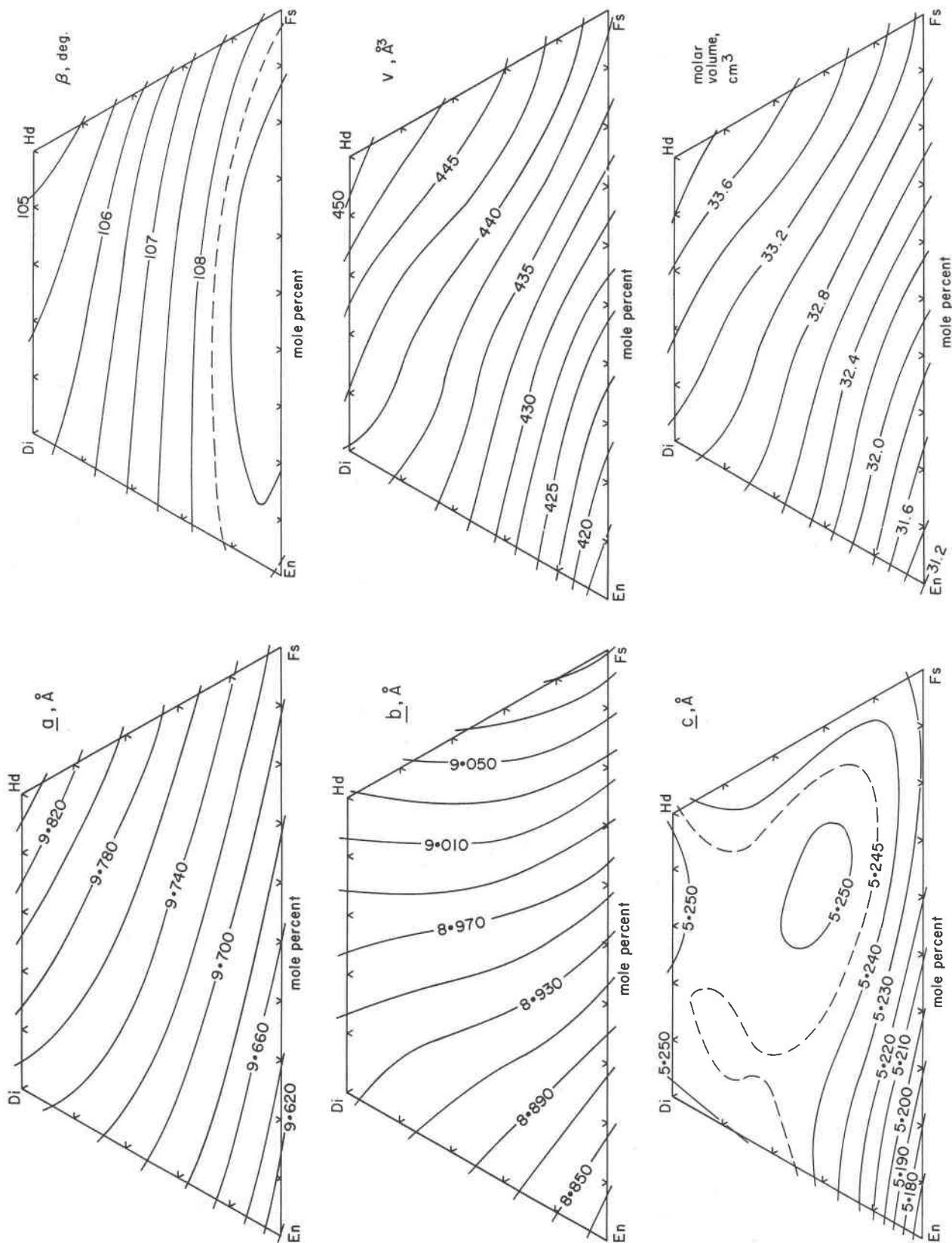


FIG. 1. Contours on trend surfaces showing variation of unit-cell parameters for the synthetic Ca-Mg-Fe clinopyroxenes in Figure 1. Trend surfaces for  $a$ ,  $b$ ,  $c$ , and  $\beta$  are third order; those for  $V$  and molar volume are fourth order. Contour intervals are:  $a$ , 0.02 Å;  $b$ , 0.02 Å;  $c$ , 0.01 Å (but note the extra contour for 5.245 Å shown as a dashed line);  $\beta$ , 0.5° (but note the extra contour for 108.25° shown as a dashed line);  $V$ , 2.5 Å<sup>3</sup>; molar volume, 0.2 cm<sup>3</sup>/mole, based on  $z = 8$  RSiO<sub>3</sub> per unit cell.

is an actual advantage in high-pressure hydrothermal experiments, where a small amount (less than 1 percent) of excess silica is needed to saturate the vapor phase.

#### *Method 3: Synthesis of Clinoenstatite in MgCl<sub>2</sub> Flux*

Clinoenstatite, MgSiO<sub>3</sub>, can be synthesized metastably at very low pressure from a stoichiometric mix of MgO and silica glass held at 900°C in the presence of dry MgCl<sub>2</sub> salt. Such syntheses have been successful in runs lasting from 16 to 30 days. The mix is dried *in vacuo* and immediately loaded into a gold capsule welded at one end. Several such capsules are then placed in an air-tight glove box along with a supply of (anhydrous) MgCl<sub>2</sub>. The glove box is flushed with extra-dry nitrogen and the interior water content is maintained at the level of P<sub>2</sub>O<sub>5</sub> desiccant. The capsules are loaded with dry chloride salt; the open end is crimped; and the capsules sealed in evacuated silica-glass capsules (Kullerud, 1971, pp. 290-293) with the added precaution that their contents must not be exposed to the atmosphere. Thorough drying of the MgCl<sub>2</sub> is essential; a successful method using anhydrous HCl vapor is given by Grover (1972, pp. 259-261).

At 900°C, the vapor pressure of MgCl<sub>2</sub> is appreciable, and some silica-glass tubes exploded upon heating. In practice it is useful to test the capsules in a pre-heated furnace. The vapor seems to reach "equilibrium" with the chloride liquid in less than a minute, so that if no explosion occurs in the first few minutes, the capsule can be transferred to a second furnace for final reaction. When the capsules are opened, the chloride is removed by dissolving it in dilute HCl.

The clinoenstatite crystals produced by this method are relatively large (many are as large as 75 to 100 $\mu$ ); most are roughly equant or only moderately elongate. The crystals are generally clear, although some may be mottled, and most display sharp, well-developed polysynthetic twinning. The method could be extended to Fe- and Ca-bearing pyroxenes if the distribution coefficients of Ca, Mg, and Fe between silicate and chloride were known.

#### *Method 4: Hydrothermal Synthesis at Intermediate Pressures (1 to 2 kbar)*

Synthesis of clinopyroxenes at 1 to 2 kbar under hydrothermal conditions are described by Rutstein and Yund (1969) and Nolan (1969).

#### *Method 5: The Synthesis of Pyroxenes at High Pressures (10 to 20 kilobars)*

Synthesis of pyroxenes at high pressures has been extremely useful in the iron-rich portions of the quadrilateral. Lindsley and Munoz (1969, pp. 320-321) describe the dry synthesis of pyroxenes at 20 to 22 kilobars and temperatures from 1100 to 1200°C in iron capsules. We have since found that hydrothermal synthesis at high pressure yields more complete reaction and larger crystal size. To prevent escape of hydrogen released by thermal dissociation of water, silver capsules must be used.

Most of our syntheses have been performed at 20 kbars total pressure and at a temperature of approximately 960 to 990°C, which is just below the melting temperature of the silver capsule at that pressure. Because the system is essentially closed with respect to oxygen, a stoichiometric mix must be used as starting material. The most satisfactory mix for this purpose is one that has been pre-reacted in sealed silica glass tubes from the initial starting chemicals. The pre-reacted mix is tightly packed into a silver capsule together with about 5 wt percent water, ½ to 1 wt percent oxalic acid, and approximately ½ wt percent excess silica to saturate the vapor phase. The silver capsule is closed with a tightly fitting lid, and the rim of the capsule is hammered down over the lid to provide a seal. The capsule is then ready for insertion in standard piston and cylinder high-pressure apparatus (for example, Boyd and England, 1963). The oxalic acid decomposes at pressure and temperature to a mixture of water, carbon dioxide and carbon monoxide. Our experience has shown that this mixture effectively maintains conditions inside the capsule well within the fayalite stability field; even if some oxidation of the iron component has taken place during grinding, this gas mixture effectively reduces the iron back to the ferrous state.

Runs of several hours duration yield well-crystallized pyroxenes with less than 1 percent olivine and quartz. For CaSiO<sub>3</sub> compositions equal to or greater than 10 percent, single-phase clinopyroxene is produced. For compositions less than 5 percent, a single-phase orthopyroxene is the result. Compositions between 5 and 10 percent give a mixture of ortho- and clino-pyroxene. The clinopyroxenes are nearly equant but elongated in the *c* direction, and typically have lengths of 25 to 50 microns. The orthopyroxenes are more elongate, with lengths

up to 200 microns. Approximately 0.4 to 0.5 g of material may be produced in a silver capsule  $\frac{1}{2}$  inch long by  $\frac{1}{4}$  inch in diameter (12.7 millimeters by 6.35 millimeters diameter), with a bore of 0.210 inches (5.33 mm) in a piston and cylinder device with an 0.750-inch (19.05 mm) bore.

### Synthesis of Clinopyroxene

Clinopyroxenes can be synthesized for almost every composition in the pyroxene quadrilateral. Some of the products are apparently metastable under the conditions of synthesis; for example, (1) metastable one-phase clinopyroxenes will grow with compositions within the probable two-phase region ( $30 > Wo > 10$ ); and (2) clinopyroxenes will grow with compositions of  $Wo < 5$  percent, at temperatures and pressures at which orthopyroxenes are probably stable.

Samples were accepted as homogeneous single phases when the contents of unreacted olivine, silica, and glass were less than one percent as determined optically and when the X-ray powder patterns showed sharp peaks for reflections known to be sensitive to changes in composition. These criteria were confirmed by electron microprobe analysis of several samples.

TABLE 3. COEFFICIENTS FOR TREND-SURFACE EQUATIONS\* RELATING COMPOSITION AND UNIT-CELL PARAMETERS FOR CLINOPYROXENES

	a(Å)	b(Å)	c(Å)	s(deg)	v(Å <sup>3</sup> )
c <sub>1</sub>	9.602	8.814	5.150	108.2	414.5
c <sub>2</sub>	$1.182 \times 10^{-3}$	$1.592 \times 10^{-3}$	$1.245 \times 10^{-3}$	$1.569 \times 10^{-2}$	$2.496 \times 10^{-1}$
c <sub>3</sub>	$5.819 \times 10^{-3}$	$4.071 \times 10^{-3}$	$6.783 \times 10^{-3}$	$5.729 \times 10^{-2}$	$6.738 \times 10^{-1}$
c <sub>4</sub>	$-1.816 \times 10^{-6}$	$1.398 \times 10^{-5}$	$3.945 \times 10^{-6}$	$-1.769 \times 10^{-5}$	$-3.194 \times 10^{-3}$
c <sub>5</sub>	$-2.287 \times 10^{-5}$	$-2.304 \times 10^{-5}$	$-6.725 \times 10^{-5}$	$-1.102 \times 10^{-3}$	$-5.006 \times 10^{-3}$
c <sub>6</sub>	$-8.889 \times 10^{-5}$	$-5.915 \times 10^{-5}$	$-1.569 \times 10^{-4}$	$-4.502 \times 10^{-3}$	$9.813 \times 10^{-3}$
c <sub>7</sub>	$8.445 \times 10^{-9}$	$-2.278 \times 10^{-8}$	$-9.022 \times 10^{-8}$	$-1.378 \times 10^{-6}$	$7.625 \times 10^{-5}$
c <sub>8</sub>	$3.112 \times 10^{-8}$	$-1.343 \times 10^{-7}$	$1.949 \times 10^{-7}$	$3.669 \times 10^{-6}$	$-1.344 \times 10^{-5}$
c <sub>9</sub>	$3.612 \times 10^{-7}$	$-3.124 \times 10^{-9}$	$6.364 \times 10^{-7}$	$1.015 \times 10^{-5}$	$2.364 \times 10^{-5}$
c <sub>10</sub>	$6.342 \times 10^{-7}$	$5.098 \times 10^{-7}$	$1.250 \times 10^{-6}$	$4.861 \times 10^{-5}$	$-5.054 \times 10^{-4}$
c <sub>11</sub>	---	---	---	---	$-4.627 \times 10^{-7}$
c <sub>12</sub>	---	---	---	---	$3.556 \times 10^{-7}$
c <sub>13</sub>	---	---	---	---	$-8.099 \times 10^{-7}$
c <sub>14</sub>	---	---	---	---	$1.348 \times 10^{-6}$
c <sub>15</sub>	---	---	---	---	$4.775 \times 10^{-6}$

\* These have the form:

$$z = c_1 + c_2x + c_3y + c_4x^2 + c_5xy + c_6y^2 + c_7x^3 + c_8x^2y + c_9xy^2 + c_{10}y^3 + c_{11}x^4 + c_{12}x^3y + c_{13}x^2y^2 + c_{14}xy^3 + c_{15}y^4$$

$$\text{where } x = \frac{\text{Fe} \times 100}{\text{Fe} + \text{Mg}}, \quad y = \frac{\text{Ca} \times 100}{\text{Fe} + \text{Mg} + \text{Ca}}$$

and z is the unit-cell parameter.

The synthesis of clinopyroxenes with a 1 atm quench furnace is successful for a broad range of compositions, as shown in Figure 1. However, other methods must be used for extreme compositions (Fig. 1). In the hedenbergite corner, lower temperatures or higher pressures will prevent the formation of the pyroxenoid called wollastonite solid solution by Bowen, Schairer, and Posnjak (1933). Clinopyroxenes with compositions in this corner may be synthesized by the hydrothermal method (Rutstein and Yund, 1969; Nolan, 1969), or at high pressures.

In the ferrosilite corner, there is a forbidden zone of compositions in which olivine plus silica (plus Ca-rich clinopyroxene, for  $Wo > 5$  percent) is stable at low pressures instead of single-phase pyroxene. The extent of this zone for various pressures is described by Smith (1971). High pressures (Method 5) are required to synthesize clinopyroxenes in this corner. Synthesis at high pressures of clinopyroxenes with  $Wo < 10$  must be performed under dry conditions (Lindsley and Munoz, 1969) to prevent nucleation of orthopyroxene.

Clinoenstatite has been synthesized by several methods (see Boyd and Schairer, 1964). The molten chloride method, described above (Method 3) produces clear, 100  $\mu\text{m}$  crystals.

### Synthesis of Orthopyroxene

Orthopyroxenes can be synthesized for compositions with  $Wo < 5$  percent. Orthoenstatite can be synthesized hydrothermally; optimum conditions were 800°C, 1 kbar, and 2 weeks. Mg-rich orthopyroxenes, 100 Fe/Fe + Mg < 30, may be grown at 1 atm (Method 1), but for more iron-rich compositions high-pressure (Method 5) is required.

### Unit Cell Parameters

Unit-cell parameters were determined for the pyroxenes synthesized in this study. X-ray powder diffractometer tracings, with CaF<sub>2</sub> ( $a = 5.4626$  Å) internal standard, were made over the range 18 to 76° 2 $\theta$  (CuK $\alpha_1$  radiation,  $\lambda = 1.54051$  Å) at scan speed of 0.5 degree 2 $\theta$  per minute. These tracings were measured by comparing them to a template on which were marked values of  $d$  and also the lines for the CaF<sub>2</sub> standard. Peaks on the tracing were measured with the closest standard peak aligned with the corresponding line of the template.

The peaks were indexed by comparison with the calculated patterns for diopside, pigeonite, clino-



enstatite, hypersthene, and ferrosilite, as given by Borg and Smith (1968). Examples of patterns indexed and measured by the above method are in Table 1.

At least 20 indexed peak measurements were used in each least-squares refinement of a unit cell, after the method of Burnham (1965a). The unit cell data for clinopyroxenes are in Table 2, and calculated trend surfaces are presented in Figure 2. Trend surface equations of order one to five were calculated and the choice of order giving the best fit to the data was made on the basis of maximum correlation coefficient and minimum standard deviation. The third order surfaces provided the best fit for  $a$ ,  $b$ ,  $c$ , and  $\beta$ ; and the fourth order for  $V$  (Table 3).

The use of trend surfaces implies an assumption that the unit-cell parameters vary smoothly with composition; any discontinuities in the data, if present, would be masked by the calculated surfaces. The assumption appears reasonable; for the most part the residuals between the calculated values and the original data are less than the uncertainties in the latter, and most of the exceptions appear to reflect random variations. However, larger residuals (0.1 to 0.3 percent) in  $\beta$  are restricted to compositions in the range  $Wo = y = 20$  to 30, and in  $a$ ,  $c$ , and  $V$  to those in the range  $Wo = y = 10$  to 20. The latter range probably contains the transition interval between the augite ( $C2/c$ ) and pigeonite ( $P2_1/c$ ) structures at room temperature, and the discrepancies may reflect small differences in  $a$ ,  $c$ , and  $V$  between the two structures.

These trend surfaces can be used to estimate the compositions of synthetic Ca-Mg-Fe clinopyroxenes to within 2 to 5 mole percent. We emphasize that the data are not directly applicable to natural pyroxenes, since other elements in the latter may affect unit-cell parameters.

The cell parameters for orthopyroxenes are listed in Table 4 and are shown in Figure 3; the data for pure ferrosilite are from Burnham (1965b). The curves in this figure are calculated for Ca-free compositions (the join En-Fs), using curvilinear least-squares regression analysis. Best fits were obtained using a third order equation for  $a$ , second order for  $b$  and  $c$ , and first order for  $V$ . Most of the Ca-bearing orthopyroxenes coexist with a few percent of augitic clinopyroxene, and hence are slightly less calcic than indicated in Table 4. Nevertheless, the data are sufficient to show that, for constant Fe/Fe + Mg, the addition of calcium significantly

TABLE 4. COMPOSITIONS AND UNIT-CELL PARAMETERS OF ORTHOPYROXENES\*

$x$	$y$	$a, \text{\AA}$	$b, \text{\AA}$	$c, \text{\AA}$	$V, \text{\AA}^3$	$\bar{V}, \text{cm}^3/\text{mole}$
0	0	18.223	8.815	5.169	830.4	31.26
10	0	18.235	8.841	5.187	836.3	31.48
20	0	18.251	8.847	5.195	838.8	31.58
40	0	18.289	8.911	5.208	848.8	31.95
50	0	18.310	8.931	5.219	853.5	32.13
60	0	18.321	8.958	5.219	856.6	32.24
75	0	18.362	9.000	5.234	864.9	32.56
80	0	18.370	9.011	5.245	868.2	32.68
90	0	18.402	9.053	5.233	871.7	32.81
100	0	18.431	9.080	5.238	876.7	33.00
0	1.1	18.235	8.815	5.175	831.8	31.31
20	5**	18.257	8.858	5.195	840.2	31.63
30	5**	18.293	8.879	5.207	845.8	31.84
50	4**	18.350	8.936	5.234	858.2	32.31
60	5**	18.365	8.963	5.229	860.8	32.40
75	5**	18.417	9.030	5.233	870.2	32.76
100	2	18.453	9.081	5.241	878.2	33.06
100	4	18.473	9.076	5.242	878.9	33.09

\*As in Table 2,  $x = \frac{\text{Fe} \times 100}{\text{Fe} + \text{Mg}} = \frac{\text{Fs} \times 100}{\text{Fs} + \text{En}}$ ;  $y = \frac{\text{Ca} \times 100}{\text{Ca} + \text{Fe} + \text{Mg}} = \text{Wo}$  (mole percent). However, molar volume,  $\bar{V}$ , is calculated on the basis of 16 R(SiO<sub>3</sub>) per unit cell. The unit-cell parameters for Ca-free orthopyroxenes are given by  $z = b_0 + b_1x + b_2x^2 + \dots + b_nx^n$ .

where	$b_0$	$b_1$	$b_2$	$b_3$
$a$	18.221	$1.5814 \times 10^{-3}$	$-1.0184 \times 10^{-6}$	$6.1850 \times 10^{-8}$
$b$	8.8152	$1.9544 \times 10^{-3}$	$7.0400 \times 10^{-6}$	---
$c$	5.1715	$1.2085 \times 10^{-3}$	$-5.2815 \times 10^{-6}$	---
$V$	830.4	$4.6109 \times 10^{-1}$	---	---

\*\*Indicates samples that contains small amounts of augitic clinopyroxene.

increases  $a$  and  $V$ , but has no detectable effect on  $b$  and  $c$  in orthopyroxenes.

There is no significant difference in molar volume between Ca-free orthopyroxenes and Ca-free clinopyroxenes. Based on these data obtained at room temperature and pressure, it appears that the orthopyroxene-clinopyroxene inversion should be virtually independent of hydrostatic pressure. (Possible differences in thermal expansion or compressibility or both might invalidate this conclusion.)

The trend surface for clinopyroxene volume is convex upward along any section taken at constant Fe/Fe + Mg. This indicates the existence of a small but real positive excess volume of mixing. (Although Ca-poor pyroxenes typically have larger Fe/Fe + Mg values than do coexisting Ca-rich pyroxenes, the



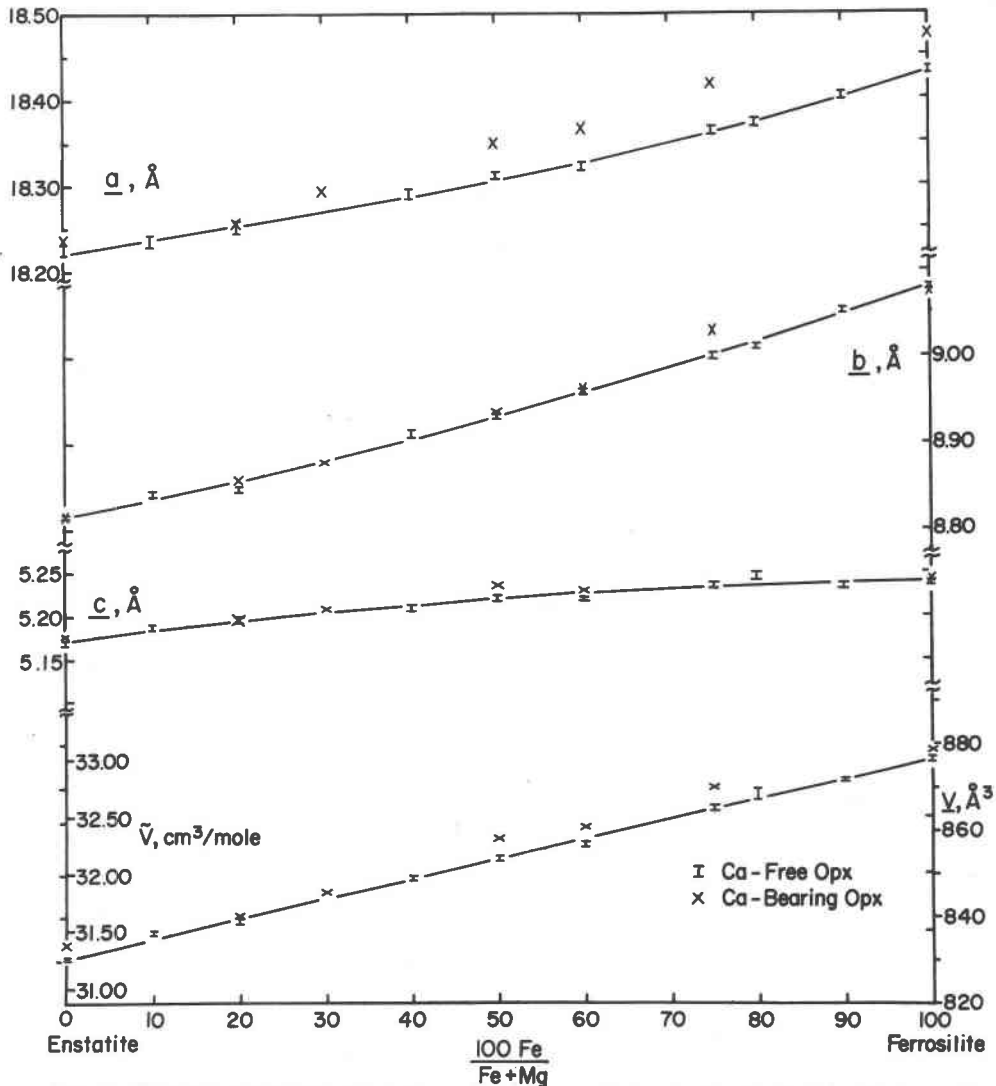


FIG. 3. Unit-cell parameters for orthopyroxenes on and close to the En-Fs join. Curves were calculated on the basis of Ca-free samples only. Compositions of Ca-bearing orthopyroxenes (shown by x) are projected from Wo onto the join. Wo contents are 1.1 mole percent for the Fe-free sample, 4 to 5 mole percent for the rest. Note that the bottom curve gives unit-cell volume (outer scale) and molar volume (inner scale; based on  $z = 16 \text{ RiSo}_3$  per unit cell). Conversion factor is:  $V(\text{cm}^3/\text{mole}) = 0.037645 V(\text{\AA}^3)$ .

differences are relatively small, and the generalization is still valid.) Again with the proviso that neither thermal expansion nor compressibility effects eliminate the volume of mixing, this suggests that increasing pressure will very slightly expand the two-pyroxene (augite plus Ca-poor pyroxene) field at constant temperature.

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