

Equilibria in the Mg-rich part of the pyroxene quadrilateral

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ABSTRACT. Pyroxene phase relations in the Mg-rich corner of the pyroxene quadrilateral, at 1 atmosphere, have been reinvestigated. Experimental studies on sixteen selected compositions in the systems CMS and CFMS were undertaken in the temperature range 1100–1400 °C. The results of this study clarify our understanding of the pyroxene stability relations at low pressure. In particular, the demonstration that there is a high-temperature stability field of orthoenstatite denies the existence of a stable (or real) invariant point defined by the reactions $OE = PE + DI$, $PE + DI = PI$, and $OE + DI = PI$, in the system $CaMgSi_2O_6$ – $Mg_2Si_2O_6$. New phase relations, consistent with the experimental findings of this and other studies, for the Mg-rich corner of the pyroxene quadrilateral are presented. These new phase relations may be of use in interpreting the origin of volcanic rocks containing magnesian pigeonite.

A THOROUGH understanding of the phase relationships of pyroxenes is essential to the interpretation of many igneous (and other) rocks. Establishing the equilibrium phase relations for pyroxenes involves not only experimental work but careful observation of the natural phase assemblages (Huebner, 1980). The occurrence of clinoenstatite (CE) in some high-Mg andesites (Jenner, 1981, 1982) is an excellent example of the interplay necessary between experimental and natural pyroxene studies. The crystallization of protoenstatite (PE) (clinoenstatite precursor: Tilley *et al.*, 1964; Dallwitz *et al.*, 1966; Nakamura, 1971; Huebner, 1980) over a limited compositional range and its replacement by orthopyroxene at a particular composition (cf. Dallwitz *et al.*, 1966; Komatsu, 1980; Jenner, 1982) suggested that it may be possible to constrain the extrusion temperatures and to limit the conditions of parental magmas to the high-Mg andesites using knowledge of the stability relations of protoenstatite and orthopyroxene. Conversely, observed relations in high-Mg andesites have been important in deducing

possible equilibrium phase relations in the pyroxene quadrilateral (Nakamura, 1971).

Recent uncertainty concerning the nature of the phase relations in the Mg-rich portion of the pyroxene quadrilateral (Huebner, 1980; Longhi and Boudreau, 1980) and the limited amount of data available on protoenstatite stability has necessitated a re-examination of phase relations on the enstatite–diopside join and in the system CaO – FeO – MgO – SiO_2 (CFMS).

Previous work and the nature of the controversy

Atlas (1952) studied phase equilibria in the system $MgSiO_3$ – $CaMgSi_2O_6$ and also the polymorphism of $MgSiO_3$. Much of his work in the system $MgSiO_3$ – $CaMgSi_2O_6$ was redone as part of a more comprehensive study by Boyd and Schairer (1964); however his determination of the orthopyroxene–protopyroxene transition temperature (985 ± 10 °C) in the pure $MgSiO_3$ system has been confirmed by Anastasiou and Siefert (1972) and Smyth (1974).

The stability fields of Ca-poor pyroxenes in the system $Mg_2Si_2O_6$ – $CaMgSi_2O_6$ are limited by the reactions schematically presented in fig. 1 (Warner, 1975; Mori and Green, 1975) and are related to the stability fields of orthoenstatite (OE), protoenstatite, and Ca-free high-temperature clinopyroxene ('pigeonite') in the system $Mg_2Si_2O_6$. The position of the invariant point A in $CaMgSi_2O_6$ – $Mg_2Si_2O_6$ is estimated as 1.6 kbar and 1280 °C (Warner, 1975; Mori and Green, 1975). This *P*–*T* location is subject to considerable uncertainty arising chiefly from inadequacies in conventional experimental techniques at low pressures and high temperatures. The location of invariant point A' is not well constrained. The univariant reaction $OE = PE$ ($Mg_2Si_2O_6$) passes through 1 bar, 985 °C (see above) and the reaction $PE = PI$ (pigeonite) may pass through 1 bar, 1400 °C if the experiments in the $Mg_2Si_2O_6$ – $LiScSi_2O_6$ system can be extrapolated to pure $Mg_2Si_2O_6$ (Takeuchi, 1978).

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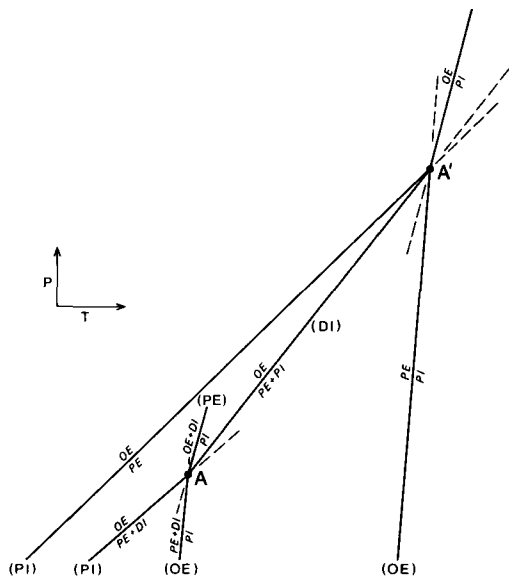


FIG. 1. Schematic P - T projection of inferred invariant and univariant pyroxene phase equilibrium relationships for the systems $Mg_2Si_2O_6$ and $Mg_2Si_2O_6$ - $CaMgSi_2O_6$ (after Warner, 1975). A' is the invariant point in the Ca-free system and A is the invariant point in the Ca-bearing system. (DI) joins the two invariant points and the phases become less calcic as they approach A' .

Phase relations in the pyroxene quadrilateral presented by Nakamura (1971) (see fig. 2) are consistent with the phase relations depicted in fig. 1, assuming the 1 atm. P -axis passes below invariant point A . That the 1 atm. P -axis would pass below A is inherent in the interpretation of experimental results by Warner (1975) and is consistent with the relations on the $Mg_2Si_2O_6$ - $CaMgSi_2O_6$ join as depicted by Boyd and Schairer (1964), Kushiro (1972), and Warner (1975; for $P < 1.5$ kbar).

Longhi and Boudreau (1980) re-investigated the system forsterite (Fo)-diopside (Di)-silica (SiO_2) at one atmosphere and suggested that there is an orthoenstatite liquidus field in this system. Foster and Lin (1975) had also noted the existence of an OE liquidus field in the same system. Longhi and Boudreau (1980) and Huebner (1980) presented reviews of the work by Yang and Foster (1972), Yang (1973), and Kushiro (1972), and concluded that these authors had also found evidence for the existence of an OE liquidus field; however misidentification of some of the low-Ca pyroxene phases had led to this field being overlooked.

Based on the interpretation of results from the liquidus studies Longhi and Boudreau (1980) and Huebner (1980) have suggested that the topology

of the $Mg_2Si_2O_6$ - $CaMgSi_2O_6$ join at 1 atm. should be that shown in fig. 3. Longhi and Boudreau (1980) interpreted the OE field to extend from the liquidus to 1375 °C (see fig. 3A), and to account for the existence of a high- and low-temperature OE field proposed that there was a bow-like shape for the PE+OE two-phase fields. Huebner (1980) proposed that two lines of evidence suggested that at low pressure OE is continuously stable from low temperature (< 1000 °C) to the solidus (see fig. 3B). These are: (i) PE does not appear to be stable in the presence of augite at pressures > 2 kbar; and (ii) when natural magnesian orthopyroxenes are heated in the presence of augite, no protopyroxene was detected.

The topology of the $Mg_2Si_2O_6$ - $CaMgSi_2O_6$ join at 1 atm. as depicted in fig. 3A is inconsistent with a Schreinemaker's analysis of the pyroxene relations presented in fig. 1. The topology depicted in fig. 3B is inconsistent with a Schreinemaker's analysis of the pyroxene relations presented in fig. 1, if the invariant point A is real. However, if the invariant point A is metastable or unreal the phase relations at pressure $> A$ and $< A'$ are consistent with the topology of the $Mg_2Si_2O_6$ - $CaMgSi_2O_6$ join as depicted in fig. 3B (cf. Warner, 1975; for $P > 1.5$ kbar).

Present study

Experimental techniques. Sixteen mixes were prepared by mechanical mixing of clinoenstatite (CE), enstatite (OE), diopside (DI), and hypersthene (HY) Mg_{52} . Proportions of the end members were selected to produce (i) mixes of Mg-numbers 85,90,95 with 0,1,4 wt. % CaO; (ii) mixes of Mg-number 98 with 1,2,6 wt. % CaO; and (iii) mixes of Mg_{100} with 4,6,8,15 wt. % Di. Note that 1 wt. % CaO is equivalent to approximately 4 wt. % Di. During all stages of preparation mixes were ground to dryness under acetone a minimum of three times, in an agate mortar. Particle size in the resulting mixes was generally less than 10 microns, with 10–20 μm particles forming less than 5–20% of the mix.

Prior to the preparation of the mixes the pure phases were prepared from oxides, carbonate, or metal AR grade reagents. Details of the synthesis of the pure phases are given below.

Clinoenstatite was prepared by sintering a 1 g pellet of $MgSiO_3$ at 1300 °C/1 atm. in a Pt crucible, for 48 hours. Minor amounts of quartz and olivine were present, as indicated by a routine X-ray diffractometer tracing. 300 mg of pure orthoenstatite was made by running CE at 15 kbar/1150 °C for 6 hours in large capacity $Ag_{50}Pd_{50}$ capsules (3 mm diameter).

Diopside was prepared by sintering a pellet at 1300 °C/1 atm. in a Pt crucible for 48 hours. The mix was well crystallized and no other phases were observed in the X-ray diffraction pattern. 300 mg of this DI was run at 10 kbar/1150 °C for 5 hours in a large capacity $Ag_{50}Pd_{50}$

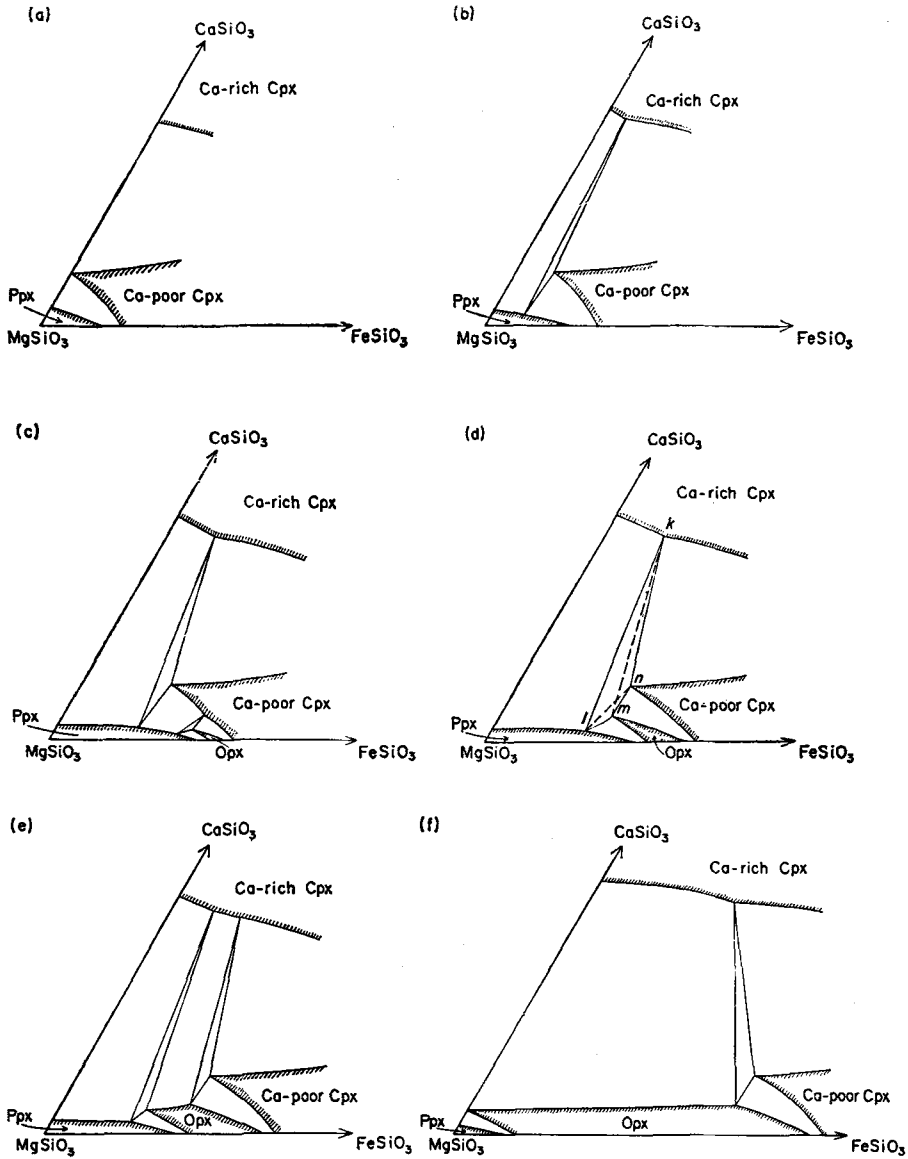


FIG. 2. Possible isothermal sections on the Mg-rich part of the pyroxene quadrilateral. Temperature falls successively from (a) to (f). (Reprinted from fig. 4 (p. 273) of Nakamura (1971), with permission from the author.)

capsule to provide material for seeds, chemical analysis, and as a check on the 1 atm. product.

Hypersthene was prepared using a three-stage procedure. First, MgO , Fe_2O_3 , and SiO_2 were dried for 3 hours at 600°C . Fe metal was then mixed in, and a pellet made. The resultant mix was run in an evacuated SiO_2 tube for 3 days at 1000°C , along with a pellet of 1.5 g of Fe metal to ensure no oxidation took place. The resulting product was poorly crystalline and very fine grained. 300 mg of well crystallized hypersthene was made at 20 kbar/

1050°C by running the 1 atm. HY for 4.5 hours in $\text{Ag}_{50}\text{Pd}_{50}$ capsules.

Seeds of high-pressure OE and HY were added to the Mg_{85-95} mixes in amounts such that the seeds were 10% OE and 30% HY contents respectively of the mixes. In the Mg_{85-95} runs all the DI was from the high-pressure synthesis. The remainder of the components in the Mg_{85-95} compositions and all components in other compositions were from 1 atm. sintered oxide mixes.

Run conditions. Fe-bearing runs were performed in

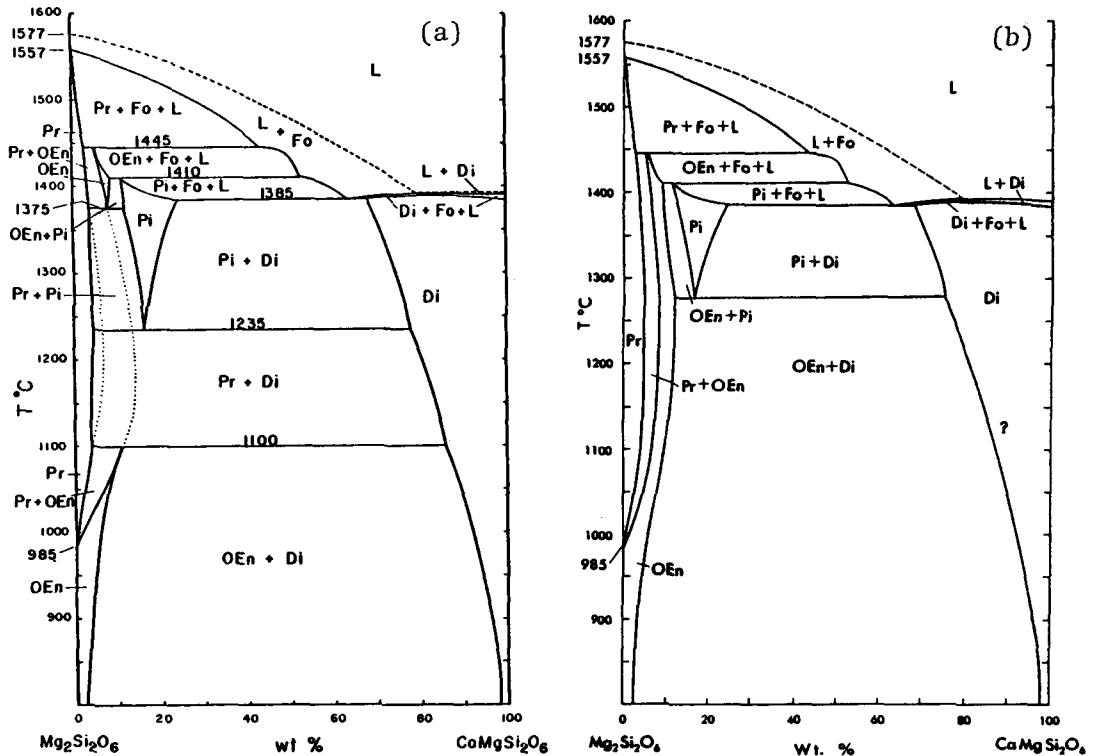


Fig. 3. Temperature-composition diagram for the system $Mg_2Si_2O_6$ - $CaMgSi_2O_6$ at 1 bar. (a) Phase topology depicted by Longhi and Boudreau (1980). (b) Phase topology suggested by Huebner (1980). (Reprinted from fig. 7 (p. 235) of Huebner (1980), by permission of the Mineralogical Society of America.)

spec-pure Fe capsules sealed in evacuated SiO_2 tubes. OE-DI mixes were run in Pt capsules, which had been sealed by welding at the base and crimping at the top, in open SiO_2 tubes. Runs were made in either a 1 inch or $\frac{3}{4}$ inch 1 atm. furnace. A harness of Pt wire capable of holding three SiO_2 tubes, each containing up to three capsules, made it possible to run up to nine mixes at a time. The position of the hot 'spot' was checked before each run and temperature variation due to thermal gradients in the assembly and calibration is within $\pm 5^\circ C$. The runs were drop quenched into a beaker of water.

Examination of run products. Each run was examined using three techniques: the optical microscope, SEM-microprobe, and X-ray powder camera. Optical mounts were made of crushed run products placed in refractive index oil. Emphasis in the optical work was on the detection of twinning, cracking, crystal morphology, and overall texture. The size and/or morphology of some phases, usually orthopyroxene, made it possible, in some runs, to positively associate chemical composition (from the probe) with optical properties.

X-ray camera patterns were obtained on needles made up of finely ground run products and gum tragacanth. An 11.54 cm Straumanis camera and Fe-tube were used. Identification of the phases was achieved in large part

by comparison with films on standards of known composition. Standards used were: (a) natural CE separated from a high-Mg andesite from Cape Vogel, PNG; (b) synthetic OE and DI (conditions of origin described above); and (c) natural OE and DI (Mg_{92}) from a spinel lherzolite xenolith from Mt. Porndon, Victoria (N. Ortez, pers. comm., 1980). CE and Mg-rich pigeonite (PI) have indistinguishable X-ray powder patterns. PE was identified on the basis of the pattern given in Atlas (1952).

Probe mounts of run products were made either of small fragments or, in the case of some Ca-poor runs, a slurry of powder in resin had to be prepared first. A JEOL 50X-A SEM-microprobe with an EDAX energy dispersive system was used. Calibration of the system is described by Griffin (1979). High-pressure DI, OE, and HY were used to double check the calibration.

PE is recognized by either the presence of its distinctive X-ray pattern or in the more general case by the presence of its lower temperature multiply-twinning inversion product CE. As noted, CE and PI have identical powder X-ray patterns (at least in the lines observable with our concentrations and techniques); therefore a combination of microprobe and XRD techniques is required. Thus observations and interpretations are related as follows:

- (a) very low CaO phase +
(CE or PI)
1-2% CaO phase (EPMA)
OE (X-ray) } CE+OE
- (b) 1-2% CaO phase +
OE
2% CaO phase (EPMA)
(CE or PI) (X-ray) } PI+OE

In (a) CE is interpreted to be present and implies that PE+OE were originally present. PE+OE assemblages may also be identified by the presence of a very low Ca-bearing phase plus a PE X-ray pattern.

Results

Attainment of equilibrium. One of the major difficulties hampering interpretation of the pyroxene phase relations in the Mg-rich portion of the pyroxene quadrilateral is that of knowing when equilibrium has been attained (Huebner, 1980). Subsolidus runs are particularly notorious for their slow reaction rates (Huebner and Turnock, 1980; Boyd and Schairer, 1964). Internal consistency, phase homogeneity, and results consistent with our knowledge of crystal chemistry are the major criteria which we have adopted in this study in recognizing or presuming the attainment of equilibrium (see also Huebner and Turnock, 1980). Run times for experiments were selected on the basis of previous experience in subsolidus (metamorphic) phase equilibrium studies (S. Harley, pers. comm., 1980). Experiments at 1300°C were run for 4 and 7 days with identical results being obtained.

Two series of Fe-bearing runs failed to meet the equilibrium requirements noted above. One series at 1100°C was run for 4 weeks; however original mix heterogeneities were present and these led to the development of quartz and olivine. These products were larger than anything in the original mix and presumably grew at the expense of the poorly crystalline hypersthene. Pure diopside and enstatite seeds were also noted.

A series of runs at 1200°C (2 weeks run time) showed phase homogeneity; however the results were inconsistent with those from higher temperature experiments in this study (see below) and also with the experiments of Longhi and Boudreau (1980), and the interpretation of Huebner (1980) (see above). In particular the three-phase assemblage PI-OE-PE was suggested to be present, based on X-ray, optical, and probe examination of the run products. This association would mark the CFMS univariant reaction OE+DI=PE+PI, which implies (fig. 2C, D) that the stability field of OE contracts to more Fe-rich Ca-poor bulk compositions. This conclusion is inconsistent with the presence of OE in Mg-rich bulk com-

positions in experiments at higher temperatures (see below).

Interpretation of the 1370°C and 1400°C runs in the Fe-free experiments was hampered by the presence of disequilibrium assemblages in some runs. For example, the 4% and 6% Di runs at 1400°C contain the assemblage CE (inverted PE)+OE, which with the increasing Di content would be expected to give way to OE and/or OE+PI. The 8% Di (1400°C) run however contains OE+CE+PI. A possible interpretation of this observation is that CE persists metastably in the presence of a high Ca-bearing phase, i.e. PI. This is consistent with the observation that OE increases in abundance from the 4% to 6% run and then decreases abruptly in the 8% Di run.

An attempt was made to reverse the reaction PI=DI+OE. Some of the run product from the 1370°C/15% Di run, which was homogeneous PI, was loaded in another capsule and run at 1280°C for 4 days along with an equivalent composition made up from 1 atm. sintered oxide mixes. Conditions for the run were estimated from our work and that of Warner (1975). The PI from the 1370°C run remained 'stable' at the lower temperature, while the sintered oxide mix showed signs of obvious disequilibrium, i.e. unreacted diopside seeds remained, and olivine and quartz appeared. According to Huebner (1980) (see also fig. 3B) the reaction PI=DI+OE occurs at about 1270°C ± 10°C and the close proximity of our runs to this reaction position may account in part for the lack of success.

Table I. Results of "equilibrium" 1 atmosphere pyroxene experiments

T(°C)	Mix (wt.%)	Products ⁺	Composition [*]			
			CaO (range)	n		
1400 (96 hours)	96EN-4DI	CE	0.62	(0.48-0.82)	27	
		OE	1.21	(1.20-1.22)	3	
	94EN-6DI	CE	0.64	(0.51-0.83)	17	
		OE	1.54	(1.27-1.68)	17	
	92EN-8DI	CE	0.66	(0.56-0.77)	26	
		OE	1.40	(0.95-1.87)	5	
		PI	2.30	(2.0-2.6)	14	
	1370 (96 hours)	94EN-6DI	OE	0.97	(0.83-1.17)	12
			PI	2.91	(2.68-3.24)	21
		92EN-8DI	OE	0.94	(0.73-1.20)	9
PI			3.03	(2.58-3.25)	21	
85EN-15DI		PI	4.07	(3.78-4.38)	10	
		Mgs ₉₀ -4DI	CE	Mgs ₉₅ 0.73	(0.68-0.80)	5
		OE	Mgs ₉₅ 1.50	(1.38-1.68)	12	
		Mgs ₉₀ -8DI	OE	Mgs ₉₅ 1.66	(1.64-1.72)	8
		PI	Mgs ₉₅ 2.23	(2.18-2.30)	11	
		Mgs ₉₀ -24DI	PI	Mgs ₉₅ 5.11	(4.68-5.65)	12
1300 (168 hours)	Mgs ₉₀ -0% CaO	PE	Mgs ₉₂		10	
		OE	Mgs ₉₂ 1.1	(0.96-1.15)	14	
		PI	Mgs ₉₂ 3.60	(3.32-4.16)	30	
	Mgs ₉₀ -0% CaO	PE	Mgs ₉₇		10	
		OE	Mgs ₉₇ 0.9	(0.74-1.18)	39	
		PI	Mgs ₉₇ 3.57	(3.4-3.82)	19	
	Mgs ₉₀ -1% CaO	OE	Mgs ₉₅ 0.86	(0.74-1.12)	11	
		PI	Mgs ₉₅ 3.50	(3.34-3.77)	8	

⁺ identification based on X-ray, probe and optical examination.
^{*} average CaO in wt. %
 n = number of analyses.

Bulk composition. It was difficult to check the bulk composition of an individual run because of the disaggregated texture of most of the runs. Fe loss to Pt capsules was a minor problem as indicated in Table I. Ca content of the mixes was dependent on the thorough mixing and reaction of the diopside component to the mix. In general Ca contents appear to be slightly lower than expected in almost all runs, an observation attributed to persistence of diopside seeds. The difficulties in knowing the reacting composition of the mix would be a problem if we were dependent on only X-ray and optical analysis. However, with use of the microprobe we can determine the phase compositions and use these results to plot in the quadrilateral, rather than having to rely on an assumed bulk composition.

Results from experiments which met the criteria for having attained equilibrium are given in Table I and selected analysis of products are given in Table II. Details for specific run compositions or temperatures are given below.

Mg₁₀₀-1400°C. The 4% and 8% Di runs were characterized by 20-30 μm sized crystals. Orthopyroxenes in the 6% Di run however ranged from 60-120 μm and may enclose low-Ca (PE or CE) crystals. The orthopyroxene X-ray pattern is clearly developed in the 6% Di run, while intensity differences in the 2.93-3.02 and 3.27-3.35d (Å) lines point to its presence in the 4% and 8% Di runs. The X-ray patterns confirm the existence of the CE/PI phase in addition to OE and do not show PE. Microprobe analyses combined with the XRD data thus indicate the presence of OE and CE (after PE). The CE

in these runs does not show transverse cracks or well-developed multiple twinning.

Mg₁₀₀-1370°C. Grain size in the 6% Di run is predominantly less than 10 μm; however orthopyroxenes form approximately 20 μm sized prismatic crystals with parallel extinction. The 8% and 15% runs have an overall grain size of 10-20 μm. Pigeonite grains appear to have a more regular or less diffuse multiple and simple twinning than clinoenstatite.

Mg₉₈-1370°C. Average grain size increases from 10-20 μm in 4% Di runs through 20 μm in 8% Di to 40-50 μm in the 24% Di run. Twinning is not well developed in any of the runs and many grains have indeterminate extinction. The orthopyroxene is somewhat lath-shaped.

1300°C. In general grain size increases from 10-20 μm in Ca-free runs to 30-50 μm in 4% CaO runs. Protoenstatite is the low Ca-bearing phase, as determined by the X-ray pattern and lack of twinning. The orthopyroxene is equigranular and has a well-defined X-ray pattern. Orthopyroxene is not obvious in the optical mounts having no distinctive morphology. Pigeonites have well-developed twinning.

Discussion

The results of the 1300-1400°C experiments of this study in the systems CMS and CFMS indicate that *orthopyroxene is a stable phase in this temperature range* and that its stability field extends from the Mg₂Si₂O₆-CaMgSi₂O₆ join (CMS) into the CFMS pyroxene quadrilateral. The phase relations schematically given in fig. 4 are consistent with the experimental results and with the interpretation that the *P* = 1 atm. axis passes above the invariant

Table II. Representative analyses of pyroxenes from 1 atmosphere CMS and CFMS experiments

T, °C	1300	1300	1300	1300	1300	1300	1370	1370
CaO% (mix)	1	4	1	4	1	4	1	1
Mg no.	85	85	90	90	95	95	98	98
SiO ₂	55.58	56.03	57.07	56.49	58.21	57.37	59.25	59.25
FeO	10.65	10.21	8.51	8.19	5.38	5.29	3.51	3.72
MgO	31.82	29.68	33.15	31.21	34.83	33.21	36.57	35.57
CaO	0.84	3.46	0.89	3.59	1.14	3.57	0.68	1.46
Mg no.	84.19	83.83	87.4	87.19	92	91.81	94.87	94.46
Ca:Mg:Fe	1.6/82.9/15.6	6.6/78.3/15.1	1.7/86.12.4	6.7/81.4/12	2.1/90.1/7.8	6.6/85.7/7.7	1.3/93.7/5.1	2.7/91.9/5.4
T, °C	1370	1370	1370	1370	1370	1370	1370	1370
CaO% (mix)	2	2	6	1.5	1.5	2	2	3.75
Mg no.	98	98	98	100	100	100	100	100
SiO ₂	58.95	58.87	58.57	60.18	59.87	60.28	59.27	59.89
FeO	3.56	3.48	3.06					
MgO	35.87	35.41	33.44	38.77	37.27	38.50	36.72	36.27
CaO	1.62	2.23	4.93	0.83	2.86	0.95	2.93	3.84
Mg no.	94.75	94.79	95.11	100	100	100	100	100
Ca:Mg:Fe	3/92/5	4.1/90.9/5	9.1/86.4/4.4	1.5/98.5	5.2/94.8	1.7/98.3	5.4/94.6	7.1/92.9
T, °C	1400	1400	1400	1400	1400	1400	1400	1400
CaO% (mix)	1	1	1.5	1.5	2	2	2	2
Mg no.	100	100	100	100	100	100	100	100
SiO ₂	59.9	59.75	60.05	60.11	59.97	59.48	59.62	
MgO	39.46	38.72	38.52	39.27	39.42	37.82	38.76	
CaO	0.64	1.22	1.42	0.63	0.61	2.39	1.62	
Mg no.	100	100	100	100	100	100	100	
Ca:Mg:Fe	1.2/98.8	2.2/97.8	2.6/97.4	1.1/98.9	1.1/98.9	4.3/95.7	2.9/97.1	

point *A* in fig. 1. Referring to fig. 4, the temperature for the change from T1 to T2, i.e. the intersection of the PI stability field with the CMS boundary, is not fixed in this study since the three-phase assemblage OE+DI+PI was not encountered. Results from the study of Huebner and Turnock (1980) indicate that the change from phase relations in T1 to those in T2 may take place at temperatures of 1230–1300 °C and a temperature of 1275 °C is indicated in fig. 3B. The reaction $OE = PE + PI$ (fig. 1) will not be reached before melting takes place in either CMS or CFMS, and this reaction cannot therefore be used to construct possible phase relations beyond T2 (Huebner and Turnock, 1980; Longhi and Boudreau, 1980).

The experimental results and interpretation offered here are in agreement with those suggested by Huebner (1980) both for the $CaMgSi_2O_6$ – $Mg_2Si_2O_6$ join (fig. 3B) and the solidus phase topology in the Mg-rich portion of the pyroxene quadrilateral (see his fig. 21a). This interpretation

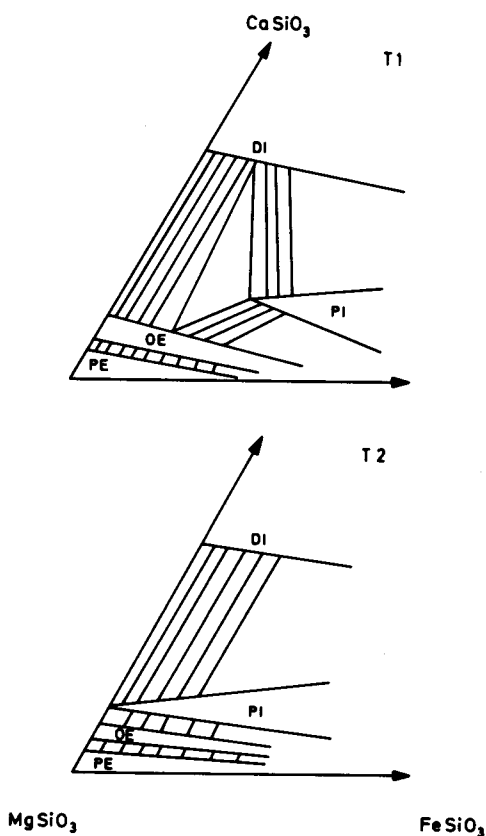


FIG. 4. Probable isothermal sections in the Mg-rich part of the pyroxene quadrilateral based on results of this study. Temperature in T2 higher than T1.

implies that invariant point *A* in fig. 1 is imaginary and hence also the reactions, among others, $PE + DI = PI$ (Nakamura, 1971; Mori and Green, 1975) and $OE = PE + DI$ (Atlas, 1952), do not occur in real P, T space.

Experimental evidence for the existence of the reaction $OE = PE + DI$ comes from three studies, those of Atlas (1952), Boyd and Schairer (1964), and Warner (1975). Warner (1975) investigated the position of the invariant line $OE = PE + DI$ at 1 kbar and 1240 °C; however he noted that the results are difficult to interpret since the assemblages he obtained in different runs are incompatible. Boyd and Schairer (1964) failed to locate the solvus boundary in the OE-rich side of the system OE+DI at temperatures of 1000–1250 °C because of reaction rates. Hydrothermal runs in the lower part of this temperature range were unsuccessful and they noticed that the presence of a flux in dry runs created problems. Atlas (1952) did a number of runs using LiF flux and glasses on the OE-rich side of the OE+DI join. His results are equivocal in many respects, for instance, he reported $CE + DI + OE$ at 12.5% Di and 1135 °C in an experiment for 12 days; however, a run at 15% Di/1130 °C for 7 days gave $CE + PE + DI$ and at 20% Di/1140 °C for 12 days only $CE + DI$ are reported. Atlas (1952) noted a slight inflection in the OE–DI solvus at 1050–1100 °C and he suggested that along with his experimental results this implied the presence of the reaction $OE = PE + DI$. Note that Boyd and Schairer also choose to interpret their runs in this manner.

The experimental evidence for the existence of the reaction $OE = PE + DI$ is certainly equivocal and the phase relations on the Mg-rich side of the OE–DI join are subject to interpretation. It is interesting to note that if the above reaction is accepted then the PE and/or CE phase would need to contain 5–12% Di (~1.2–3% CaO). This is difficult to reconcile with the chemistry of naturally occurring clinoenstatite in high-Mg andesites and the demonstration that the occurrence of clinoenstatite is sensitive to the Ca content (normative $Di/Di + Hy$) of the magma (Jenner, 1982). Based on the experimental results from this study it would seem that the lack of evidence for OE in the temperature range 1000–1235 °C is probably due to the persistence of metastable CE, in a manner similar to that observed in the 1400 °C experiments noted earlier.

Conclusions

Experimental studies in the systems CMS and CFMS have indicated that orthopyroxene is a stable phase at least up to 1400 °C. These results

are consistent with the results from liquidus experiments in the forsterite–diopside–silica and anorthite–diopside–enstatite–silica systems at 1 atm. (Yang, 1973; Kushiro, 1972; Longhi and Boudreau, 1980; Huebner, 1980). The results can be interpreted to imply that orthoenstatite is a stable phase from $< 1000^{\circ}\text{C}$ to $> 1400^{\circ}\text{C}$ in the system CMS. This is consistent with the suggestion of Huebner (1980) and suggests that the explanation offered by Longhi and Boudreau (1980) for the existence of two separate temperature stability fields of orthopyroxene is unnecessary.

The experiments also demonstrate the existence of orthopyroxene along the MgSiO_3 – FeSiO_3 join.

The experimental results were unfortunately not of great value in ascertaining the temperature of eruption of high-Mg andesites. The assemblage present in these rocks is not sufficient to pinpoint a point at which the liquid of high-Mg andesites intersects the pyroxene solidus. Compositional rather than temperature control determines the appearance of clinoenstatite in high-Mg andesites (Jenner, 1982). However, the phase relations depicted in fig. 3 and their extensions to CFMS (fig. 4) may be of use in interpreting the origin of volcanic rocks which are richer in CaO, and either lack or contain magnesian pigeonite. These relations would then help in deciding on the water content/liquidus temperature for second-stage lavas found in some ophiolite complexes (cf. Duncan and Green, 1980a, b; Cameron, 1980).

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