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STABILITY OF IRON-RICH PYROXENE IN THE SYSTEM $CaSiO_3$–$FeSiO_3$–$MgSiO_3$

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ABSTRACT

Experiments have been made with synthetic pyroxenes on part of the join $Fs_{85}En_{15}$–Wollastonite in the pyroxene quadrilateral. Results at 15 kbar define parts of a miscibility gap between two clinopyroxenes and two fields of orthopyroxene plus clinopyroxene. The miscibility gap is symmetrical about a composition near the center of the join in the quadrilateral, and the solvus appears to have a critical temperature in the interval 915–950°C. Molar volume considerations suggest that this temperature is not sensitive to pressure. A field of orthopyroxene plus clinopyroxene lies between Wo_4 and Wo_{13} at 900–915°C and 15 kbar. Below 875°C, however, orthopyroxene coexists with Wo_{30} composition clinopyroxene, and consequently calcium-poor clinopyroxene ("pigeonite") cannot form below 875°C at 15 kbar. Results at 15 kbar together with an experiment at 30 kbar indicate that the minimum temperature for stability of calcium-poor clinopyroxene ("pigeonite") increases with increasing pressure. Experiments at lower pressures outline conditions at which pyroxenes on the join are not stable with respect to more calcic pyroxene, fayalitic olivine, and SiO_2 phase, and they outline part of the "forbidden zone" in the quadrilateral.

INTRODUCTION

Important elements of subsolidus phase relations in the system $CaSiO_3$–$FeSiO_3$–$MgSiO_3$ are (1) a field of two clinopyroxenes, reflecting a solvus or miscibility gap, and (2) fields of clinopyroxene plus orthopyroxene. These phase relations have been outlined on the enstatite–diopside join, the iron–free boundary of the pyroxene quadrilateral, by the experiments of Kushiro (1969), Boyd and Schairer (1964), and Davis and Boyd (1966). Textures and compositions of natural pyroxene assemblages indicate that a miscibility gap and fields of orthopyroxene plus clinopyroxene are present for compositions throughout the quadrilateral (*e.g.*, Hess, 1941; Barth, 1951). Experiments by Yoder *et al.* (1964), Turnock (1970), and Ross *et al.* (1971) have determined parts of these phase relations for pyroxenes of intermediate iron–magnesium contents. Phase relations on the hedenbergite–ferrosilite join have been studied by Lindsley and Munoz (1969) and Lindsley and Burnham (1970); their results did not provide unequivocal experimental evidence on the position of a clinopyroxene miscibility gap for iron–rich compositions. The experiments

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discussed here were undertaken to define this miscibility gap and to clarify phase relations of iron–rich pyroxenes.

Sufficiently iron–rich pyroxenes break down at low pressure to assemblages of more calcic pyroxene, fayalitic olivine, and an SiO_2 phase. Pressures necessary for pyroxene stability on the bounding magnesium–free and calcium–free joins of the quadrilateral have been outlined partly by Lindsley and Munoz (1969), Lindsley and Burnham (1970), and Smith (1971a). Results of several experiments to establish minimum pressures for stability of pyroxenes within the quadrilateral are reported here. Because phase relations of iron-rich pyroxenes reflect both temperature–sensitive pyroxene miscibility and pressure–sensitive pyroxene–olivine–silica relations, they may serve as indicators of both geologic pressures and temperatures.

Experiments were made with compositions on the part of the join $Fs_{85}En_{15}$–Wollastonite within the pyroxene quadrilateral (Figure 1). This join was chosen for several reasons. First, it lies partly within the "forbidden zone" of the pyroxene quadrilateral (Lindsley and Munoz, 1969), an area in which pyroxenes are not stable at low pressures relative to assemblages of more calcic pyroxene, olivine, and a silica phase. Second, compositions of some natural, terrestrial pyroxene pairs plot nearly on the join (*e.g.*, Smith, 1971b). Tielines connecting these pairs are approximately parallel to the join (Fig. 1) suggesting that subsolidus phase relations for coexisting pyroxene can be approximated by those in a binary system. This approximation has been made for the experimental results presented here, both for ease of presentation and because some pyroxenes in experimental products have been characterized only by their calcium contents. Finally, compositions of some of the late–forming pyroxene and magnesian pyroxferroite in lunar rocks plot very nearly on the join (*e.g.*, Boyd and Smith, 1971).

Pyroxenes were synthesized from six bulk compositions (Fig. 1) at 900–950°C and 20–23 kbar for use as starting materials for stability experiments. The four most calcic mixes yielded single phase clinopyroxenes, while the calcium–free mix yielded orthopyroxene. Mix of bulk composition $Wo_{10}En_{31.5}Fs_{58.5}$ yielded clinopyroxene with a trace of orthopyroxene. Synthesis methods and other experimental procedures are described in the appendix. X–ray data for the 200, $\bar{2}21$, 310, and $\bar{3}11$ reflections from the synthetic powders were used to construct determinative curves for wollastonite contents of clinopyroxenes in experimental products.

Most clinopyroxenes in experimental products were too fine–grained for electron probe microanalysis. The compositions of these pyroxenes were assumed to lie near or on the join studied, and they were determined from powder X-ray diffraction data by reference to the determinative curves. Compositions of orthopyroxenes and a few of the more coarse-grained clinopyroxenes were measured with the electron probe; these compositions (values in Table 1) do plot very nearly on the join, supporting the assumption made for the more fine-grained material. Compositions of pyroxenes in the experimental products henceforth will be labeled only by their wollastonite contents; the approximation that they lie on the $Fs_{85}En_{15}$–Wollastonite join is implied by this notation.

All clinopyroxenes presumably had the same $C2/c$ (augite) structure at the temperatures of these experiments, since iron-rich pigeonite is apparently stable only below 700–800°C (Prewitt *et al.*, 1971). Prewitt *et al.* (1971) indicate that the low-temperature $P2_1/c$ (pigeonite) structure apparently transforms to the $C2/c$ (augite) structure at temperatures below 700°C for compositions as iron-rich as those on the join studied here, but that the observed transition temperature de-

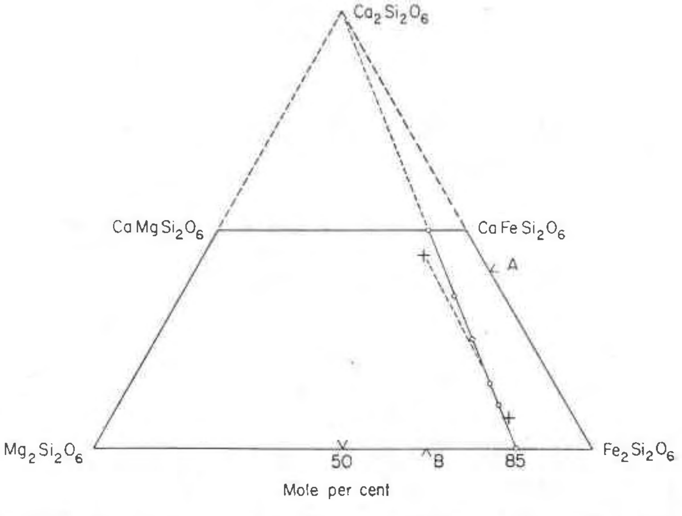

FIG. 1. Experiments were made with compositions on the portion of the join $Fs_{85}En_{15}$–Wollastonite shown by the solid line. Compositions of pyroxenes synthesized for starting materials for these experiments are plotted as circles. The crosses joined by dashed line represent compositions of a natural pyroxene pair, a calcium-poor host crystal with calcium-rich lamellae, from an olivine quartz monzonite (Smith, 1971b). A and B are limits of pyroxene stability at 900°C at low pressure on two bounding joins of the pyroxene quadrilateral (Lindsley and Munoz, 1969; Smith, 1971a).

TABLE 1

Homogenization and breakdown experiments made in solid-media, piston-cylinder apparatus on pyroxenes on the $Fs_{85}En_{15}$-Wollastonite join

Pyroxene starting material	Temperature (±15°C)	Pressure[a] (Kb)	Duration (hours)	Products[b]
Wo_{25}	915	16pi	213	Wo_{29}+cpx($Wo_{<25}$)
Wo_{25}	900	16pi	84	2cpx
Wo_{25}	890	16pi	192	$Wo_{15}+Wo_{31}$
Wo_{25}	875	15po	120	$Wo_{17}+Wo_{31}$
Wo_{15}	915	30pi	20	Wo_{30}+opx
Wo_{10}	905	16pi	120	$Ca_{12}Fe_{75}Mg_{13}$+opx($Ca_4Fe_{80}Mg_{16}$)
Wo_{10}	875	15po	168	Wo_{30}+opx($Ca_4Fe_{80}Mg_{16}$)
$Wo_{15}+Wo_{35}$	945	16pi	144	incomplete homogenization[c]
$Wo_{15}+Wo_{35}$	930	16pi	201	$Wo_{16}+Wo_{32}$
$Wo_{15}+Wo_{35}$	900	15po	145	$Wo_{17}+Wo_{34}$
opx(Wo_0)+Wo_{25}	915	16pi	142	$Ca_{13}Fe_{74}Mg_{13}$+opx($Ca_4Fe_{81}Mg_{15}$)
opx(Wo_0)+Wo_{25}	870	16pi	139	opx+Wo_{35}+residual Wo_{50}

[a] Experiments were made by the piston-out (po) or piston-in (pi) methods of Richardson, Bell, and Gilbert (1968).

[b] All products were clinopyroxene unless otherwise specified. Orthopyroxene compositions and clinopyroxene compositions for which Ca, Fe, and Mg are given were obtained by electron probe microanalysis. Other clinopyroxene compositions were determined by x-ray diffraction. The precision of the x-ray determinations, as evaluated by comparison of determinations using several x-ray peak positions, is plus or minus 1-2 percent wollastonite. The probe analyses are averages of data on a number of grains with a range of plus or minus 1-2 percent pyroxene endmember; accuracy of the probe analyses, as evaluated with internal standards, is better than this range. Compositions are in mole percent.

[c] X-ray determinative methods could not distinguish whether one inhomogeneous clinopyroxene was formed or whether two clinopyroxenes, separated by a maximum of 8 percent wollastonite, remained. Partial x-ray data on reactants and products are shown in Figure 3.

pends on the sensitivity of the X-ray method used. All peaks in the diffractometers traces made at room temperature of clinopyroxene powders on the $Fs_{85}En_{15}$–Wollastonite join were consistent with $C2/c$ symmetry, even for calcium-poor clinopyroxenes, though the traces were carefully examined for peaks diagnostic of a $P2_i/c$ space group. These diagnostic reflections ($h + k = 2n + 1$) may have been too weak to observe. The name pigeonite has traditionally implied clinopyroxene both with about 10 mole percent wollastonite and with the $P2_1/c$ structure. Since clinopyroxenes of the appropriate wollastonite content presumably did not have this structure at the temperatures of these experiments, the term pigeonite will always be placed in quotation marks when applied to these experimental products.

PYROXENE EQUILIBRIA AT 15 KILOBARS

Pyroxene stability relations were determined at 15–16 kbar pressure by hydrothermal experiments carried out in solid-media, piston-cylinder apparatus (see Appendix). These pressures were sufficient to stabilize the iron-rich pyroxene. The presence of water was necessary to ensure reasonable reaction rates. The experimental results (Fig. 2)

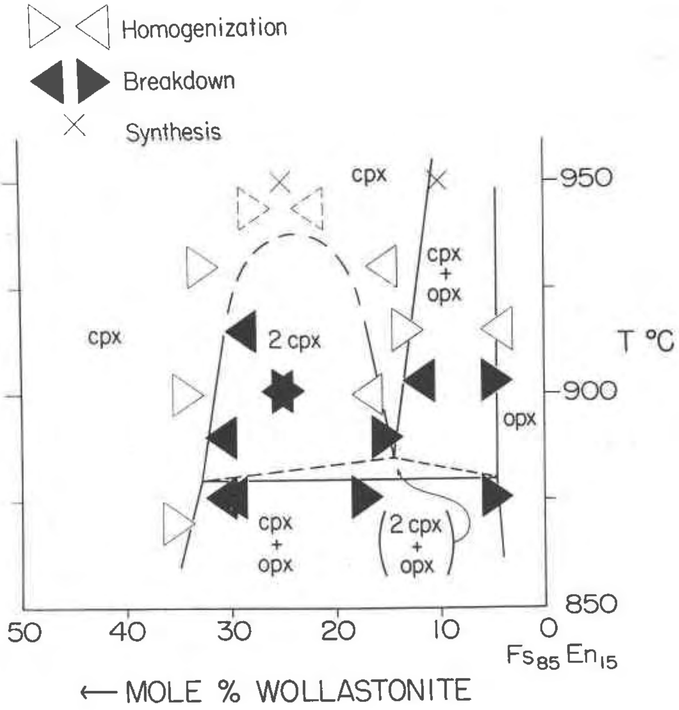

FIG. 2. Results of hydrothermal experiments at 15–16 kilobars in a solid-media, piston-cylinder apparatus. Most clinopyroxene compositions were obtained by X-ray diffraction techniques. Orthopyroxene and some clinopyroxene compositions (Table 1) were obtained by electron probe microanalysis. Experimental techniques and results are described in the appendix. The dashed triangles at 945°C represent the results of an experiment in which homogenization was not complete but separate pyroxenes could not be distinguished; the separation of this pair of triangles represents the maximum compositional difference possible in the experimental products. The small field of two clinopyroxenes plus orthopyroxene near 880°C must be present since the join is not binary; it was not defined by the products of these experiments.

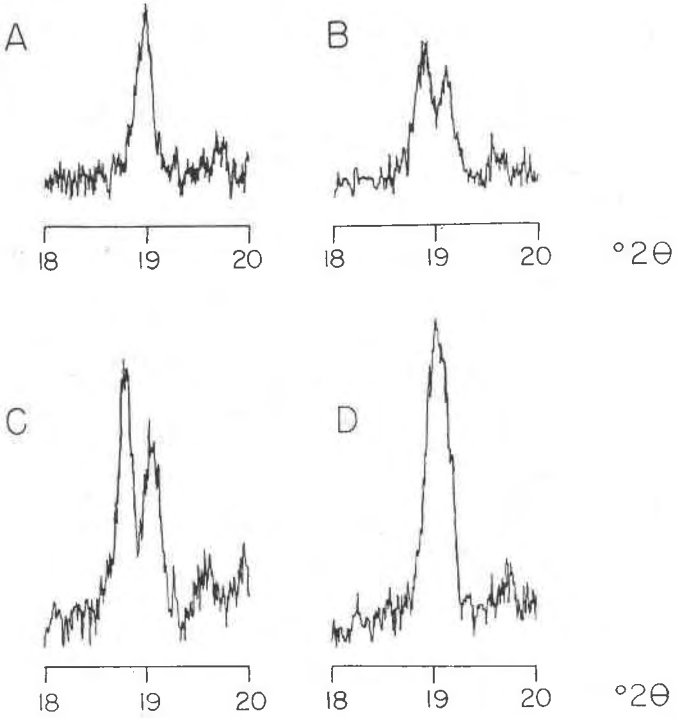

FIG. 3. Diffractometer traces of the (200) reflections of starting materials and products of selected experiments outlining the clinopyroxene miscibility gap on the join $Fs_{85}En_{15}$–Wollastonite. CuKα radiation. (A) Single-phase clinopyroxene, $Wo_{25}En_{11.25}Fs_{63.75}$. (B) Products of an experiment at 875°C starting with Wo_{25} clinopyroxene. Two clinopyroxenes, Wo_{17} and Wo_{31}, are present. (C) Mixture of two clinopyroxenes ($Wo_{15}En_{12.75}$ $Fs_{72.25}$ and $Wo_{35}En_{9.75}Fs_{55.25}$) in approximately equal proportions, used as a starting material. (D) Product of a homogenization experiment at 945°C, starting with the clinopyroxene mixture illustrated by the diffractometer trace shown in (C). Homogenization was not complete, as shown by the width of the (200) peak and by examination of other reflections. The results of all experiments are presented in Table 1 (Appendix).

establish parts of a clinopyroxene miscibility gap and two orthopyroxene plus clinopyroxene fields.

The clinopyroxene miscibility gap separates relatively calcium-poor and calcium-rich phases, presumably with the same *C*2/*c* (augite) structure at the temperatures of these experiments. Compositions of products of homogenization and breakdown experiments were determined from X-ray diffraction data; examples of X-ray data for reactants and products are shown in Figure 3. The compositional data indicate that the miscibility gap is approximately centered on the join (Fig. 2); some data suggest that the composition of critical mixing may actually be slightly less calcic than the central Wo_{25} composition (perhaps Wo_{22}). Wo_{25} clinopyroxene broke down to two pyroxenes at 915°C, indicating the critical temperature of the solvus exceeds this value. A mixture of Wo_{15} and Wo_{35} clinopyroxene was largely but incompletely homogenized at 945°C (Fig. 3), indicating that the critical temperature cannot substantially exceed 945°C. Synthesis of single phase Wo_{25} pyroxene at 950°C supports this conclusion. The data strongly suggest that the critical temperature lies between 915 and 950°C at 15 kbar. The synthesis experiment at 950°C does not necessarily represent equilibrium, however, and it is possible that the critical temperature might lie slightly above this value.[1]

A narrow field of orthopyroxene plus clinopyroxene ("pigeonite") was bracketed by homogenization and breakdown experiments in the temperature range 900–915°C. Compositions of both phases, as determined by electron probe microanalysis for Ca, Fe, and Mg (Table 1), indicate that the field lies between Wo_4 and Wo_{13}. At 875°C, however, orthopyroxene (Wo_4) coexists with much more calcic clinopyroxene (Wo_{30}), indicating that the field of orthopyroxene plus "pigeonite" has intersected the calcium-poor limb of the solvus curve. A three–phase assemblage of orthopyroxene, calcium–poor clinopyroxene, and calcium–rich clinopyroxene must be stable in a small temperature interval at or above 875°C; the interval would contract to a single temperature if the join were truly binary. Since orthopyroxene coexists with calcic pyroxene (augite) at lower temperatures, calcium–poor clinopyroxene ("pigeonite") cannot form stably below 875°C at 15 kbar for these iron–rich compositions.

Extrapolation of Results to Other Pressures

The experimental data at 15–16 kbar must be extrapolated to lower pressures before they can be used to interpret pyroxene assemblages formed in the crust of the earth. The variation of molar volume as a function of calcium content for pyroxenes on the join can be applied in interpreting how the phase relations will be affected by pressure. Molar volumes of the six pyroxenes synthesized for starting material are plotted in Figure 4.

The effect of pressure upon the critical temperature of the clinopy-

[1] Circumstances precluded further experiments, but D. H. Lindsley kindly carried out one further homogenization experiment at 955°C and 16 kbar on a mixture of Wo_{15} and Wo_{35} clinopyroxene (bulk composition Wo_{25}) provided by the author. Homogenization was complete, indicating that Wo_{25} composition does lie in a field of one clinopyroxene at 955°C and 16 kbar.

roxene miscibility gap can be evaluated by considering the excess volume of mixing for clinopyroxenes of intermediate calcium content (*e.g.*, Bell and Davis, 1969). Molar volumes, measured at room temperature and atmospheric pressure, appear to be a linear function of composition for the five synthetic clinopyroxenes. The excess volume of mixing under these conditions is zero or negligible. The linear fit suggests that pressure will have little effect upon the critical temperature of the clinopyroxene miscibility gap and that the solvus curve obtained at 15 kbar can be extrapolated to low pressures without serious error. The linear dependence of molar volume upon composition might not be satisfied at conditions other than 1 atm and room temperature, but data are not available to evaluate this possibility.

A small positive volume of mixing for clinopyroxenes on the magnesium–free hedenbergite–ferrosilite join was reported by Lindsley, Munoz, and Finger (1969). Their data were also obtained by measure-

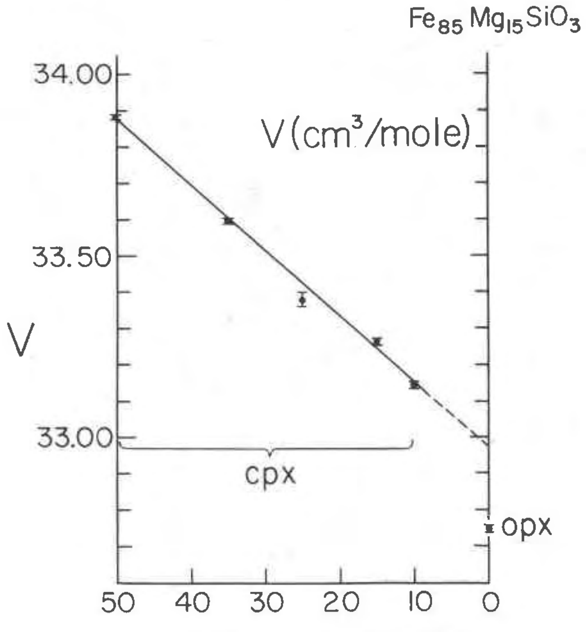

FIG. 4. Molar volume–composition relations for pyroxenes synthesized on the join $Fs_{85}En_{15}$–Wollastonite. Molar volume data for clinopyroxenes and the best-fit straight line are from Smith and Finger (1971). The orthopyroxene volume was calculated from X-ray diffraction data by the procedures of Smith and Finger. The error bars are estimated standard deviations and reflect precision only.

ments at room temperature and atmospheric pressure. The difference between their results and those obtained here could be real and related either to the compositional difference between the joins or to the generally higher temperatures of pyroxene synthesis of Lindsley *et al.* Alternatively, at least part of the apparent difference between the volume–composition relations for the two joins may simply be an artifact, arising from the fact that the volume data of Lindsley *et al.* represent a wider range of pyroxene composition. The least calcic clinopyroxene for which a molar volume was obtained on the $Fs_{85}En_{15}$–Wollastonite join was Wo_{10}. Molar volumes for pyroxenes more calcic than Wo_{10} on the hedenbergite–ferrosilite join could be plotted as an almost linear function of composition (Lindsley *et al.*, 1969, Fig. 7). The calculated curvature of the molar volume–composition relation on the magnesium-free join in part reflects the fact that volumes for Wo_0 and Wo_5 clinopyroxenes were included in the statistical treatment of Lindsley *et al.* Both these pyroxenes presumably had pigeonite structures at room temperatures, rather than the augite structures of pyroxenes participating in the unmixing reaction. Prewitt *et al.* (1971) determined that the volume expansion of pigeonite with increasing temperature is greater than that of the more calcic augite coexisting with it. An exact evaluation of any excess volume of mixing should utilize pyroxenes of a wide range of calcium contents, but such an evaluation may be possible only at temperatures near the critical temperature of the solvus.

The extent of the fields of orthopyroxene plus clinopyroxene and the minimum temperature for formation of calcium-poor clinopyroxene ("pigeonite") appear to be sensitive to pressure. The molar volume of an orthopyroxene–clinopyroxene mixture is less than that of a single clinopyroxene of equivalent bulk composition, as is evident from the volume–composition relations in Figure 4. Since an increase in pressure should favor the lower volume assemblage, the fields of orthopyroxene plus clinopyroxene should expand with increasing pressure. To test this possibility, an experiment was carried out on single-phase clinopyroxene of Wo_{15} composition at 915°C and 30 kbar. Reversed reactions clearly show that this composition lies within the single clinopyroxene stability field at 15 kbar (Fig. 2). At 30 kbar it broke down to more calcic clinopyroxene (Wo_{30}) and orthopyroxene, indicating an extension of the field of augite plus orthopyroxene to higher temperatures and an increase in the minimum temperature for stability of "pigeonite". No further experiments were made at 30 kbar, but phase relations on this join at 30 kbar may resemble those reported for the hedenbergite–ferrosilite join at 20 kbar by Lindsley and Munoz (1969), in which a broad field of orthopyroxene plus clinopyroxene apparently completely overlaps a metastable clinopyroxene miscibility gap.

The assemblage of calcic pyroxene plus calcium–poor pyroxene ("pigeonite") plus orthopyroxene will be stable at a particular pressure and temperature for given pyroxene compositions. Since the minimum temperature for formation of calcium–poor pyroxene is markedly affected by pressure for these iron-rich compositions, the occurrence of the three–phase assemblage may be useful as a geobarometer when calibrated with suitable experimental data. Bonnichsen (1969) has inferred from textural evidence that iron–rich pigeonite was a stable crystallization product during metamorphism of an iron formation at maximum temperatures of 700–750°C. The metamorphism, in the contact aureole of the Duluth gabbro, presumably took place at relatively low pressures. The metamorphic pyroxenes have Fe/(Fe + Mg) ratios in the range 0.70 to 0.75. Since these pigeonites are more magnesian than compositions on the $Fs_{85}En_{15}$–Wollastonite join, they should break down to orthopyroxene plus augite at higher temperatures than the "pigeonite" studied here. The 700–750°C temperature is significantly lower, however, than the minimum temperature of 875°C for formation of "pigeonite" at 15 kbar. The difference is compatible with the pressure sensitivity deduced from the data above, and it emphasizes the potential for application of the assemblage as a geobarometer.

PYROXENE–OLIVINE–QUARTZ EQUILIBRIA

The "forbidden zone" in the pyroxene quadrilateral (Lindsley and Munoz, 1969) is outlined by the intersection of a volume in pressure–temperature–composition space with the plane of the quadrilateral. Pyroxenes in the system $CaSiO_3$–$FeSiO_3$–$MgSiO_3$ are not stable within this volume. The volume decreases with increasing pressure at constant temperature, and the "forbidden zone" disappears at the pressure at which pure ferrosilite is stabilized.

Several experiments have been made to explore the extent of the zone within the quadrilateral at subsolidus temperatures. Clinopyroxenes with compositions, of Wo_{10}, Wo_{15}, and Wo_{35} on the join broke down to more calcic pyroxene, fayalitic olivine, and silica in experiments at 1000°C in evacuated silica–glass tubes. Wo_{15}, Wo_{25}, and Wo_{35} clinopyroxene reacted to yield clinopyroxene, fayalitic olivine, and quartz in hydrothermal experiments at 800°C, 1 kbar, and controlled oxygen fugacity[1]. Olivine in the experimental products contained 90–

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[1] Oxygen fugacities in these hydrothermal experiments and those in the gas-media apparatus were buffered with assemblages of fayalite, magnetite, and quartz.

95 percent fayalite, as determined by X-ray diffraction using synthetic iron-rich olivines (Smith, 1971) as standards. Wo_{10} and Wo_{15} clinopyroxenes reacted to yield more calcic pyroxene, olivine, and quartz in hydrothermal experiments carried out at 925°C and 3.5 kbar in an internally-heated gas-media apparatus.

Minimum pressures for clinopyroxene stability at temperatures near 925°C deduced from these data and from the experiments of Lindsley and Munoz (1969), Lindsley and Burnham (1970), and Smith (1971a) on bounding joins of the quadrilateral area are plotted in Figure 5. A minimum pressure of 3.5 kbar at 925°C is necessary for stability of clinopyroxenes less calcic and more iron-rich than the Wo_{15} composition on the join studied; the minimum pressure increases with iron content. The effect of temperature on these minimum pressures has not been studied for compositions within the quadrilateral. The "forbidden zone" expands and minimum pressures increase with increasing temperature on the bounding enstatite–ferrosilite join (Smith, 1971a). In contrast, the "forbidden zone" contracts with increasing temperature along the ferrosilite–hedenbergite join (Lindsley and

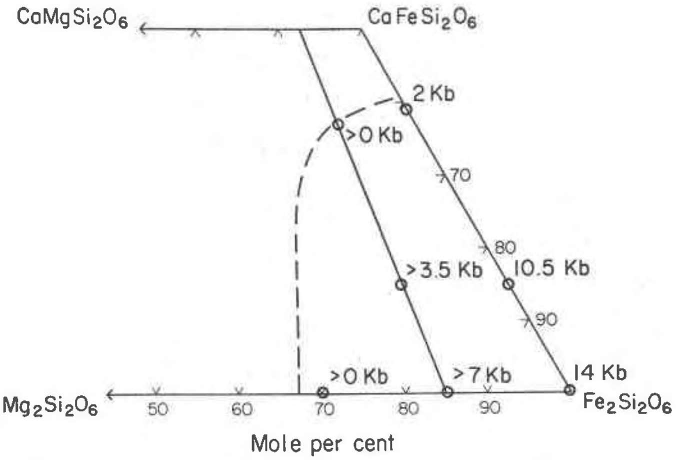

FIG. 5. Minimum pressures for the stability of iron-rich pyroxenes at 925°C. Results on the hedenbergite–ferrosilite join are from Lindsley and Munoz (1969) and Lindsley and Burnham (1970). Values on the enstatite–ferrosilite join are from Smith (1971a). The "greater than" symbols indicate that the minimum pressures may be greater than the values shown. The dashed line outlines the approximate area of the "forbidden zone" within which pyroxene is not stable at 925°C and one atmosphere pressure. The shape of the actual boundary of the area will be more complex than the smooth curve shown here, since it will reflect equilibria of both orthopyroxene and clinopyroxene with olivine plus silica.

Munoz, 1969). In each case the limiting compositions for pyroxene stability change only three to four mole percent ferrosilite for each one hundred degree change of temperature. The effect of temperature upon minimum pressures for pyroxene stability within the quadrilateral is unlikely to be large, because the effects of temperature on the "forbidden zone" at the boundary joins are not large and are of opposite sense.

Compositions of magnesian pyroxferroite in lunar rock 12021 (Boyd and Smith, 1971) plot between Wo_{10} and Wo_{15} on the join, well within the "forbidden zone". The pyroxenoid was not observed in the products of any of the experiments discussed above. This is *negative* evidence that magnesian pyroxferroite is not stable with respect to either clinopyroxene or a pyroxene–olivine–silica assemblage at low pressures from 800 to 1000°C. Lindsley and Burnham (1970) showed that magnesium–free pyroxferroite is not stable below 9.5 kbar. Lindsley, Papike, and Bence (1972) confirmed that magnesian pyroxferroite is not stable at 950° to 990°C and very low pressures in evacuated silica–glass tubes.

COMPARISONS WITH OTHER EXPERIMENTAL RESULTS

Experiments by Kushiro (1969) indicate that the critical temperature of the clinopyroxene miscibility gap must exceed 1650°C at 20 kbar on the enstatite–diopside join. The decrease in temperature with iron–enrichment from a value greater than 1650°C to a value in the 915–950°C range defined here is consistent with the phase relations long inferred by petrologists from observations of natural pyroxene assemblages (*e.g.*, Barth, 1951). Lindsley and Munoz (1969) did not observe a two–clinopyroxene field in experiments at 20 kbar on the hedenbergite–ferrosilite join; they did observe an inflection in the clinopyroxene boundary curve of a field of orthopyroxene plus clinopyroxene, however, and they advanced two possible explanations for the inflection. Their preferred interpretation implied the existence of a clinopyroxene miscibility gap symmetrical about Wo_{25} composition with a critical temperature of 870°C at 20 kbar. The results obtained here support this interpretation.

The clinopyroxene miscibility gap has been investigated over a range of compositions by Ross, Huebner, and Dowty (1971). They made homogenization experiments on single crystals of lunar clinopyroxenes with exsolution lamellae at 1 atmosphere pressure. One of these host–lamellae pairs—$Wo_{24}Fs_{65}En_{11}$ with $Wo_{14}Fe_{70}En_{16}$ lamellae —nearly plots on the $Fs_{85}En_{15}$–Wollastonite join. Ross *et al.* found that this pair homogenized at 960°C, establishing that the bulk composition of the host pyroxene plus lamellae plots on or above the solvus curve at this temperature and 1 atmosphere pressure. The miscibility gap outlined by the lamellae–host pair apparently is centered about a less calcic composition than the gap outlined at 15 kbar. The difference may not be real. Compositions of Ross *et al.* were by necessity derived from unit cell dimensions determined by X–ray using a nomogram derived from clinopyroxenes on other joins in the quadrilateral. The effects of minor element contents and lattice strain on the cell dimensions of finely intergrown, natural pyroxenes are not yet completely understood. Part of the difference between the two solvus positions may simply reflect the different methods of obtaining compositions. Since clinopyroxene compositions bracketing the solvus in this study were measured by comparison with other synthetic clinopyroxenes on the same join, the miscibility gap outlined in Figure 2 may be more accurately located than the one obtained from the study of natural host–lamellae pairs. However, there may be a real difference in the positions of the gaps reflecting either the difference in pressure between the two sets of experiments or the presence of minor elements such as Al and Ti in the lunar pyroxenes.

The experimental data at 15 and 30 kbar indicate that the maximum temperature for stability of orthopyroxene plus augite and the minimum temperature for formation of "pigeonite" decrease with decreasing pressure. These changes may reflect a shift of the field of orthopyroxene plus "pigeonite" to less calcic compositions and lower temperatures at lower pressures. The field, which is shown in Figure 2, presumably terminates on the calcium-free boundary in a small temperature interval considerably above 950°C at 15 kbar. Ross, Huebner, and Dowty (1971) found that a natural orthopyroxene (En_{14}) nearly on the $Fs_{85}En_{15}$–Wollastonite join transforms to clinopyroxene at 1 atmosphere at 955°C, a temperature apparently in the orthopyroxene field at 15 kbar. This transformation takes place in an orthopyroxene–"pigeonite" field, and the apparent difference between the 1 atmosphere and 15 kbar results does indicate that this field includes less calcic compositions and is at lower temperatures at 1 atmosphere. Lindsley and Munoz (1969) determined that the transformation temperature for pure ferrosilite decreased with decreasing pressure. They noted that this decrease would presumably cause a contraction of the orthopyroxene–"pigeonite" field within the quadrilateral, as suggested by the contrast between the 15 kbar and 30 kbar results.

Few other experimental studies of pigeonite stability have been reported. Minimum temperatures for formation of "pigeonite" decrease with iron enrichment from about 1450°C at 20 kbar on the enstatite–diopside join (Kushiro, 1969) to about 875°C at 15 kbar on the join studied here. Brown (1968) determined that the minimum temperature for stability of a natural pigeonite on the join $Fs_{47}En_{53}$–Wollastonite changed from about 1140° at 20 kbar to about 1000°C at 1 atm. Kushiro and Yoder (1970) suggested that the minimum temperature for stability of iron–free pigeonite may decrease from near 1480°C at 20 kbar to near 1400°C at 12.5 kbar. Minimum temperatures for the formation of "pigeonite" therefore apparently decrease with decreasing pressure for compositions throughout the pyroxene quadrilateral.

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Discussions with D. H. Lindsley were valuable in early stages of the investigation. H. S. Yoder, Jr., carried out several experiments in his internally heated gas–media apparatus. F. R. Boyd, B. Hensen, I. Kushiro, and H. S. Yoder, Jr., constructively criticized drafts of this manuscript. The study was undertaken while I held a postdoctoral fellowship at the Geophysical Laboratory of the Carnegie Institution of Washington.

APPENDIX

Oxide mixes of pyroxene composition were made using the procedures and materials of Smith (1971) and Lindsley and Munoz (1969). The initial mixes were wrapped in $Ag_{80}Pd_{20}$ foil and reacted in H_2–CO_2 gas mixtures at oxygen fugacities lower than those of the wustite–magnetite buffer and temperatures from 900 to 1025°C. These products were then reacted with 10mg H_2O and excess silica to saturate the fluid phase in silver capsules in a large-volume piston–cylinder apparatus at temperatures from 900 to 950°C and pressures of 20 to 23 kbar. The final products, minor quartz with the rest greater than 99 percent pyroxene by visual estimate, served as starting materials for stability experiments.

Experiments in solid–media piston–cylinder apparatus were made in silver capsules with lmg H_2O plus a trace of excess silica. Initial experiments were made at 15 kbar by piston–out techniques; subsequent experiments were made at 16 kbar by piston–in techniques, as water seemed to be retained better with the more simple pressure cycle. The experience of Richardson, Bell, and Gilbert (1968) indicates that a greater pressure correction must be made for piston–in experiments, and the 15 and 16 kbar experiments probably produced nearly equivalent pressure on the silver capsules. No corrections were made for the effects of pressure on the Pt–$Pt_{90}Rd_{10}$ thermocouples. Experiments under "wet" conditions for a minimum of several days duration were necessary to define the miscibility gap. The experiments of Turnock (1970) did not define this gap, apparently because they were "dry" and of shorter duration. Results of experiments in the piston–cylinder apparatus are presented in Table 1.

Results at lower pressures are presented in Table 2. Hydrothermal experiments at 1 kbar were made in standard cold–seal apparatus (Tuttle, 1949). Hydrothermal experiments at 3.5 and 5 kbar were made by H. S. Yoder, Jr., in an internally heated, gas–media apparatus (Yoder, 1950).

Experiments in the piston–cylinder apparatus were not buffered with respect to oxygen fugacity, but the clinopyroxenes most probably contain only minor

TABLE 2

Experiments at lower pressures to study the breakdown of single-phase clinopyroxenes[a]

Clinopyroxene starting material	Temperature ±10°C	Pressure (Kb)	Duration (hours or days)	Products[b]
Wo_{35}	800	1	27d	cpx+ol(Fa_{94})+SiO_2
Wo_{25}	800	1	32d	cpx+ol+SiO_2
Wo_{15}	800	1	40d	cpx+ol(Fa_{91})+SiO_2
Wo_{15}	925	3.5	6h	cpx+ol+SiO_2
Wo_{10}	925	3.5	6h	cpx+ol+SiO_2
Wo_{15}	925	5	8h	cpx+ minor mgt
Wo_{35}	1000	evac.	32d	cpx+ol+SiO_2
Wo_{25}	1000	evac.	62d	cpx+ol+SiO_2
Wo_{15}	1000	evac.	32d	cpx+ol+SiO_2
Wo_{10}	1000	evac.	32d	cpx+ol+SiO_2

[a] Starting materials were single-phase clinopyroxenes on the $Fs_{85}En_{15}$-Wollastonite join. Experiments at 800°C were made in standard cold-seal apparatus; those at 925°C were made in internally-heated gas-media apparatus. Experiments at 1000°C were made in evacuated silica-glass tubes.

[b] Olivine compositions were obtained by x-ray diffraction study and comparison with the iron-rich olivines synthesized by Smith (1971).

ferric iron. The experience and discussions of Lindsley and Munoz (1969) and Smith (1971) suggest that major oxidation generally is not a problem with such experiments in silver capsules. Reaction products with more than a trace of magnetite were discarded. Experiments in cold-seal and internally heated apparatus were buffered with respect to oxygen fugacity by assemblages of fayalite–magnetite–quartz.

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