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STABILITY OF THE ASSEMBLAGE IRON-RICH ORTHOPYROXENE-OLIVINE-QUARTZ

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ABSTRACT. Experiments to determine the relative stability of orthopyroxene and the compositionally equivalent assemblage of olivine plus quartz were carried out with synthetic phases in the system Mg_2SiO_4–Fe_2SiO_4–SiO_2 at temperatures from 600° to 1100°C and pressures up to 19 kb. Maximum limits of iron enrichment in orthopyroxene stable at pressures of 1 kb or lower are $Fs_{80}En_{20}$ at 600° and 700°C, $Fs_{75}En_{25}$ at 800°C, and $Fs_{70}En_{30}$ at 900° and 1000°C. Actual limits are somewhat less iron-rich. These compositions bound part of the area in the pyroxene quadrilateral in which calcium-poor pyroxenes are unstable relative to olivine plus quartz plus a calcic pyroxene. Appropriate temperatures and minimum pressures for the stability of pure orthoferrosilite are 750°C and 12 kb, 900°C and 14 kb, and 1100°C and 16 kb. Results at 900°C and intermediate pressures may be used as an approximate geobarometer for the three-phase assemblage in magmatic rocks. Data from natural assemblages and calculations based on a calculated free energy for the reaction of fayalite plus quartz to ferrosilite are used together with the experimental data to estimate the approximate Fe-Mg partition between olivine and orthopyroxene in the three-phase assemblage.

INTRODUCTION

At sufficiently iron-rich compositions, orthopyroxene is not stable relative to the compositionally equivalent assemblage of iron-rich olivine plus silica at low pressure, as shown by the pioneering experiments of Bowen and Schairer (1935) on the system MgO–"FeO"–SiO_2. Pressure stabilizes orthopyroxene relative to olivine plus quartz, however, and at high pressures the pure iron pyroxene end member, orthoferrosilite, is formed (Lindsley, Davis, and MacGregor, 1964; Akimoto, Fujisawa, and Katsura, 1964). At pressures lower than those required to stabilize pure orthoferrosilite, the three-phase assemblage orthopyroxene–olivine–silica occurs in the system Mg_2SiO_4–Fe_2SiO_4–SiO_2 (fig. 1). The orthopyroxene in this assemblage has the most iron-rich composition stable at a given pressure and temperature. This limiting orthopyroxene composition defines part of the boundary of the "forbidden zone" of the pyroxene quadrilateral (Lindsley and Munoz, 1969), a zone in which calcium-poor pyroxenes are not stable at low pressures relative to assemblages of more calcium-rich pyroxene, olivine, and quartz.

The experiments reported here were designed to outline the stability limits of the orthopyroxene–olivine–silica field over the range of pressures and temperatures at which these iron-rich silicates are likely to have crystallized in the Earth's crust. The data redefine part of the boundary of the pyroxene "forbidden zone," and they serve as a basis for experimental investigations of the stability of the more complex iron-rich pyroxenes containing calcium. Because iron contents of orthopyroxene and olivines coexisting together with silica systematically increase with pressure at a given temperature, the experimental results may be useful as a geobarometer for some crustal rocks. Calculations based on these data define activity ratios for olivine and orthopyroxene solid solutions

in the three-phase assemblage; the calculations can be used to check activity-composition relations and partition data determined by other experiments.

EXPERIMENTAL RESULTS

Results of experiments conducted with a solid-media, piston-cylinder apparatus in the limiting system Fe_2SiO_4–SiO_2 are shown in figure 2. Procedures and techniques for these and other experiments and tables of experimental results are cited in the appendix. The fayalite-quartz-orthoferrosilite boundary drawn in figure 2 is at somewhat lower pressures and has a lower slope than the boundary determined by Lindsley (1965). All but one of Lindsley's (1965) experiments defining the breakdown of pyroxene to fayalite plus quartz were at temperatures of 1000°C or higher, and at these high temperatures the correspondence between the two boundary curves is good. At 800°C, however, the boundary determined here lies 2 kb below that of Lindsley. Part of the discrepancy may be attributed to the fact that the boundary here was bracketed by modified piston-out reactions (Richardson, Bell, and Gilbert, 1968), whereas the direction of piston movement was not specified in the experiments of Lindsley (1965). The comparisons of W. Johannes and others (in preparation) have emphasized the uncertainties involved in pressure determinations in solid-media, piston-cylinder apparatus. Even so, the determinations reported here and those of Lindsley (1965) were made with the same furnace-cell design in the same apparatus, and part of the discrepancy remains unexplained. Water was added to the reactants in all low-temperature experiments, and the low-temperature field of clinoferrosilite found by Lindsley (1965) in "dry" experiments was not observed.

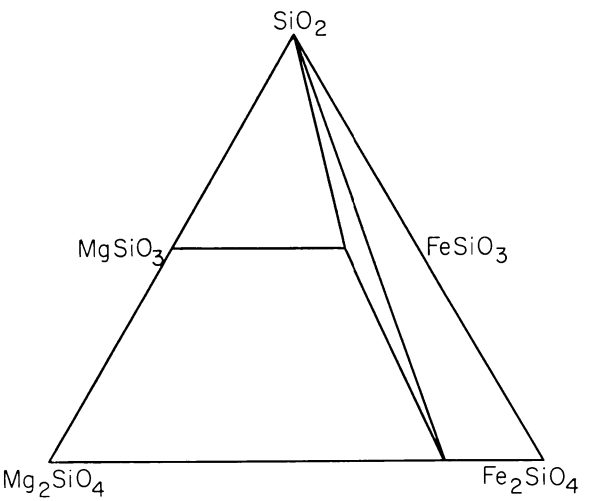

Fig. 1. Phase stability fields in the system Mg_2SiO_4–Fe_2SiO_4–SiO_2 at low pressure.

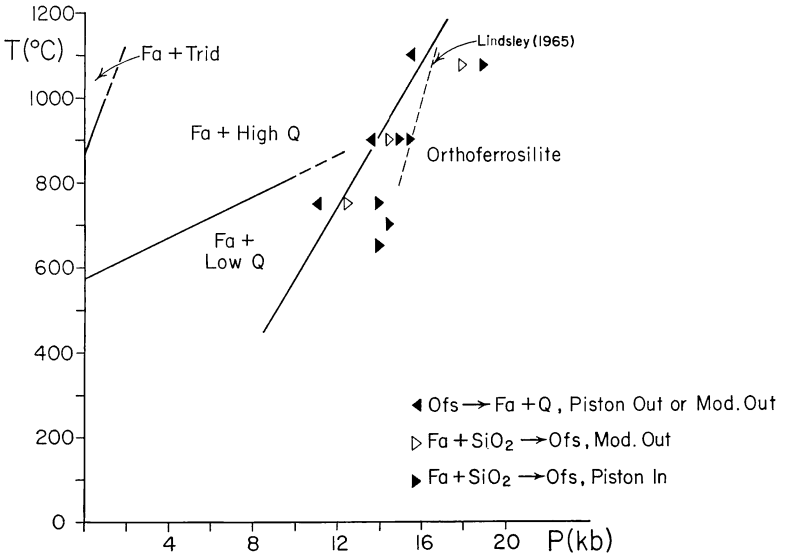

Fig. 2. Results of experiments in a solid-media, piston-cylinder apparatus on pure orthoferrosilite and fayalite plus silica. Piston-in, piston-out, and modified piston-out experiments were made by the techniques of Richardson, Bell, and Gilbert (1968). Piston-in and piston-out (or modified piston-out) experiments would bracket the actual pressure of reaction if piston friction were the only source of error. Actual reaction pressures may be somewhat lower than the values bracketed by piston-out and modified piston-out experiments (see text). The dashed line is the orthoferrosilite–fayalite–quartz boundary of Lindsley (1965). The tridymite-high quartz and high-low quartz boundaries are from Tuttle and Bowen (1958) and Yoder (1950), respectively. Experimental results are listed in table 4 (appendix).

Results of experiments starting with orthopyroxene and olivine plus quartz compositions in the system Mg_2SiO_4–Fe_2SiO_4–SiO_2[1] are reported in figures 3A and 3B. The composition of olivine in the three-phase assemblage has been bracketed between Fa_{85} and Fa_{80} at 800°C and 1 kb by the results shown in figure 3A. The data reported in figure 3A also establish maximum limits of iron enrichment in orthopyroxene stable at pressures of 1 kb or lower. The limiting compositions (molecular proportions) are $Fs_{80}En_{20}$ at 600° and 700°C, $Fs_{75}En_{25}$ at 800°C, and $Fs_{70}En_{30}$ at 900° and 1000°C. The results of Bowen and Schairer (1935) first indicated that compositions of orthopyroxene in the three-phase assemblage become less iron-rich with increasing temperature at low pressure. The composition at 1 atm pressure and 1200°C has been shown as about Fs_{60} by Bowen and Schairer (1935, fig. 8) and Nafziger and Muan (1967, fig. 5).

[1] Though compositions of starting materials were on the orthopyroxene join, excess silica was added to all hydrothermal experiments to saturate the fluid phase. All experiments except those in vacuum and in piston-cylinder apparatus were buffered with respect to oxygen fugacity (see appendix). Minor ferric iron was undoubtedly present, but it should have only a slight effect on the reactions studied here.

The actual compositions of orthopyroxene stable with olivine plus quartz in the 600° to 1000°C temperature range of figure 3A must be slightly less iron-rich than the limiting values listed above. These limiting results are significantly less iron-rich than the composition of about $Fs_{85}En_{15}$ suggested by Bowen and Schairer (1935, fig. 8) as the stability limit for iron-rich pyroxene at temperatures lower than 950°C at low pressures. The "forbidden zone" of the pyroxene quadrilateral was drawn by Lindsley and Munoz (1969) partly on the basis of the data of Bowen and Schairer. The results in figure 3A indicate that this area in which iron-rich pyroxenes are not stable at low pressure should extend about twice as far into the quadrilateral along the enstatite–ferrosilite join as previously drawn.

Natural orthopyroxenes in magmatic rocks with compositions more iron-rich than the low-pressure stability limits must either have crystallized metastably or have been stabilized by pressure. The pressures necessary to stabilize pure orthoferrosilite are shown in figure 2; the increase in orthopyroxene stability with pressure is shown by the 900°C data in figure 3B. Since the compositions of olivine and orthopyroxene in the three-phase assemblage are uniquely a function of pressure at a given temperature, the assemblage may be used as a geobarometer, if the temperature can be estimated. If only orthopyroxene is present, the results in figure 3B may still be used to obtain an approximate minimum pressure for the stable crystallization of sufficiently iron-rich, calcium-poor pyroxenes in magmatic rocks (for example, Smith, 1971).

The stability of the olivine–orthopyroxene–quartz assemblage is limited at low temperatures and sufficiently high water pressure by the formation of amphibole in the cummingtonite–grunerite series. Olivine (Fa_{85}) reacted with quartz to yield minor amphibole at 650°C, 1 kb H_2O. Orthopyroxene (Fs_{80}) partly broke down to olivine, quartz, and amphibole at 600°C, 1 kb H_2O. Amphibole compositions were not determined.

WIDTH OF THE THREE-PHASE FIELD

The boundaries of the three-phase orthopyroxene–olivine–silica fields in figures 3A and 3B could be determined more precisely if exact values of the field widths were known. The width of one of the fields at any point is the difference in iron enrichment between coexisting olivine and orthopyroxene. This width is defined here as ΔX, where

$$\Delta X = \left(\frac{Fe}{Fe + Mg}\right)_{olivine} - \left(\frac{Fe}{Fe + Mg}\right)_{orthopyroxene}$$

Since ΔX is a measure of the partition between the two phases, it is a function of pressure, temperature, and the composition of either phase. The pressure dependence of ΔX will be small, however, as shown by the calculations of Ramberg and DeVore (1951) and Medaris (1969). Likewise, the temperature dependence will be slight as shown by the experi-

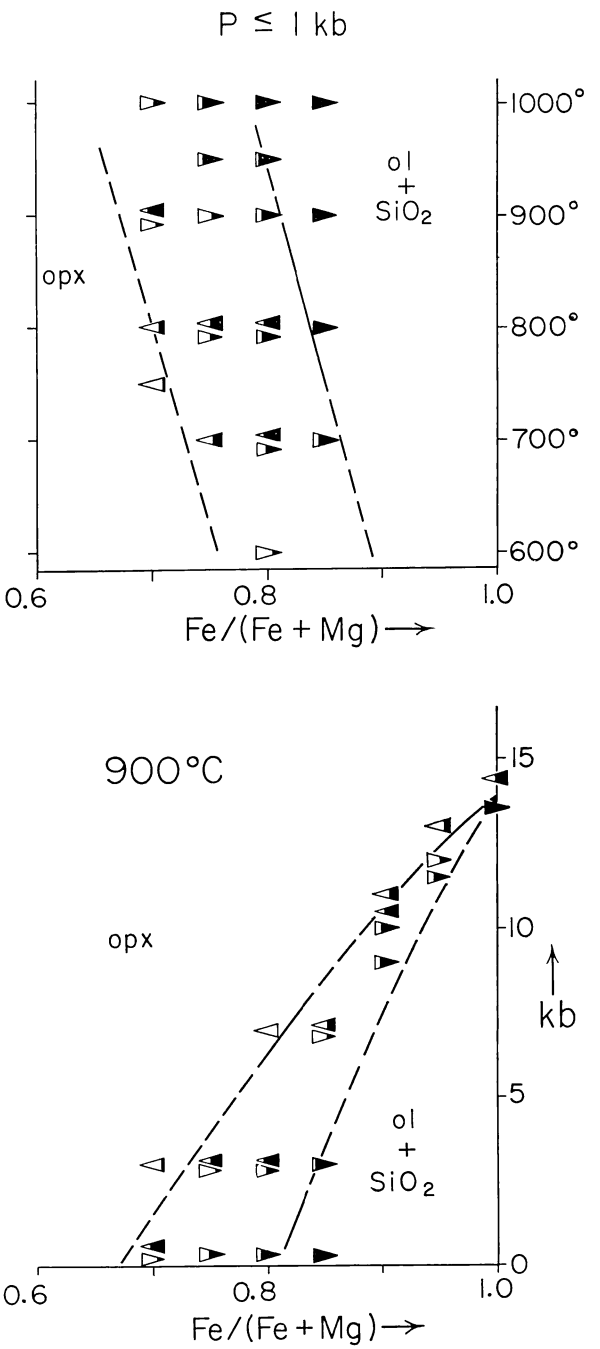
P ≤ 1 kb
1000°
900°
800°
700°
600°
ol
+
SiO2
opx
0.6
0.8
1.0
Fe/(Fe + Mg)→
900°C
15
10
5
0
kb
opx
ol
+
SiO2
0.6
0.8
1.0
Fe/(Fe + Mg)→

Fig. 3b

ments and calculations of Larimer (1968), Medaris (1969), and Williams and Eugster (1969).

The experimental data in figures 3A and 3B provide limiting values for the width of the three-phase field at low pressures. Results at 800°C indicate that ΔX must exceed 0.05. The complete and nearly complete reactions at 750°, 800°, and 900°C establish that ΔX cannot be substantially greater than 0.15 for these temperatures in this iron-rich composition range. Slow reaction rates prevented a more precise experimental determination. The reaction of olivine plus quartz to pyroxene was particularly slow at fluid pressures lower than 1 kb, even in hydrothermal, seeded experiments, and complete reaction of olivine plus quartz was achieved only above 6 kb. Measurement of the compositions of coexisting olivine and orthopyroxene in the products of these experiments would define exactly the positions of the boundaries and the width of the three-phase field only if equilibrium were achieved. Comparison of the proportions of phases in the products of various experiments (figs. 3A and 3B) indicates that equilibrium was not always attained. However, three independent lines of evidence can be examined to determine ΔX: (1) direct experimental studies of the Fe–Mg partition between olivine and orthopyroxene, (2) an examination of the partition in natural occurrences of the three-phase assemblage, and (3) thermodynamic calculations.

The most direct evidence for the field width over the temperature range studied here is based on the experimental studies of the partitioning of Fe and Mg between synthetic olivine and orthopyroxene by Medaris (1969). The best-fit equation he derived for his partition data at 900°C yields the following compositions for coexisting olivine and orthopyroxene: olivine, Fa_{80}, orthopyroxene, Fs_{71} ($\Delta X = 0.09$); olivine, Fa_{85}, orthopyroxene, Fs_{77} ($\Delta X = 0.08$); olivine, Fa_{90}, orthopyroxene, Fs_{84} ($\Delta X = 0.06$). However, these olivine and orthopyroxene compositions are more iron-rich than most of those used in his experiments.

← Fig. 3. Experiments with orthopyroxene and olivine plus silica starting materials. Triangles pointing right show that orthopyroxene of the indicated Fe/(Fe + Mg) ratio at least partly broke down to olivine plus silica. Triangles pointing left show that olivine of the indicated Fe/(Fe + Mg) ratio partly reacted with silica to yield orthopyroxene. The percentage of shading in each triangle is approximately proportional to the percentage of olivine plus silica in the reaction products; estimated percentages may be obtained from tables 2 and 3 (appendix). Compositions of olivine and orthopyroxene coexisting with silica should lie on the dashed lines, which are projections of the boundaries of the three-phase field.

A. Results at pressures of 1 kb or lower. Experiments at and below 800°C were hydrothermal and were at 1 kb. Those at 900° and 950°C were hydrothermal at pressures of 0.5 and 0.3 kb. All hydrothermal experiments were buffered by the fayalite-magnetite-quartz reaction. Experiments at 1000°C were in evacuated and sealed silica-glass tubing.

B. Experiments at 900°C over a range of pressures. Those below 1 kb are repeated from figure 3A. Hydrothermal experiments at 3 and 7 kb were carried out in an internally heated gas apparatus. Higher pressure experiments were made in silver capsules in a solid-media, piston-cylinder apparatus by piston-out and modified piston-out techniques.

Compositions of olivine and orthopyroxene occurring with quartz in two geologic settings are similar, and they yield values of ΔX distinctly larger than those in accord with the extrapolation of the 900°C partition experiments of Medaris to more iron-rich compositions. Electron probe data for three olivine–orthopyroxene pairs in one thin section of olivine quartz monzonite are presented in table 1. The rock is from one of a series of minor intrusions associated with the Nain, Labrador, anorthosite complex (Wheeler, 1968; Smith, 1971); the pressure and temperature of formation of the phases are unknown. Bonnichsen (1969) determined compositions of olivine–orthopyroxene pairs (table 1) from six rocks containing the three-phase assemblage; the maximum crystallization temperatures of these rocks, which are from an iron formation in the contact aureole of the Duluth gabbro, have been estimated to be in the range 700° to 750°C (Bonnichsen, 1969, p. 219). The ΔX for orthopyroxene coexisting with Fa_{91} olivine is about 0.14 in both cases, a value more than twice that of 0.06 derived from the best-fit equation of Medaris (1969). The difference between the natural and predicted values could reflect lack of equilibration in the natural samples or the effect of other elements in them. The geologic settings of the two occurrences are quite different, however, and the similarity of compositions suggests that the partitions represent an approach to equilibrium. It is possible that the olivine–orthopyroxene pairs may have equilibrated at similar temperatures and pressures, and the effect of these intensive variables on the partition might be greater than that predicted by Larimer (1968) and Medaris (1969). Alternatively, it may not be feasible to extend the results of Medaris to such iron-rich compositions.

A thermodynamic calculation suggests that the somewhat larger partition indicated by the natural assemblages is more nearly correct for these iron-rich compositions, even at 900°C. The stability field for the three-phase assemblage may be described by two equations, one requiring that olivine and orthopyroxene be in exchange equilibrium

TABLE 1

Fe/(Fe + Mg) ratios of olivine and orthopyroxene occurring with quartz in two different geologic settings

	Olivine quartz monzonite*			Metamorphosed iron formation**		
	Olivine	Ortho-pyroxene	ΔX	Olivine	Ortho-pyroxene	ΔX
	0.91	0.76	0.15	0.91	0.76	0.15
	0.92	0.76	0.16	0.90	0.74	0.16
	0.90	0.77	0.13	0.90	0.75	0.15
				0.91	0.79	0.12
				0.90	0.79	0.11
				0.91	0.77	0.14
Averages	0.91	0.767	0.15	0.905	0.767	0.14

* Electron probe analyses, three pairs of grains in rock W2-1568

**Analyses by Bonnichsen (1969); six different rocks

and the other that the orthopyroxene be in equilibrium with olivine plus silica. The latter requirements yields the following relationship:

$$\mu_{Fs,Px} - 1/2\mu_{Fa,Ol} - 1/2\mu^\circ_{SiO_2} = 0$$

This equation can be rewritten,[2]

$$\Delta\mu^\circ = \mu^\circ_{Fs} - 1/2\mu^\circ_{Fa} - 1/2\mu^\circ_{SiO_2} = RT \ln (a_{Fa,Ol}/a_{Fs,Px})$$

($\mu_{A,B}$ is the chemical potential of A in solid solution B; μ°_A is the chemical potential of pure A; $a_{A,B}$ is the activity of A in solid solution B), or more simply, as:

$$a_{Fa,Ol}/_{Fs,Px} = e^{(\Delta\mu^\circ/RT)}$$

The free energy of the reaction of pure fayalite plus quartz to orthoferrosilite ($\Delta\mu^\circ$) can be obtained from the results in figure 2. Extrapolation of these data to obtain values for the reaction at low temperature is subject to considerable error because of the uncertainty in the slope of the phase boundary; however, values may be obtained at high temperature with considerably more certainty by correction with a simple pressure-volume term, if the assumption is made that errors due to differences in thermal expansion and compressibility are relatively negligible. Using a ΔV of 1.63 cm^3 (from Robie, Bethke and Beardsley, 1967; Skinner, 1969) and the bracketed pressure of 14 kb at 900°C, we obtain a value of 0.54 kcal for $\Delta\mu^\circ$ (900°C) for the reaction

$$1/2Fe_2SiO_4 + 1/2SiO_2 \text{ (high quartz)} \rightarrow FeSiO_3 \text{ (orthoferrosilite)}$$

The principal uncertainty in this value is determined by the uncertainty in pressure due to the strength of the solid media in the piston-cylinder apparatus. Richardson, Bell, and Gilbert (1968) showed that the nominal pressure of piston-out experiments may be several kilobars too high with the type of furnace-cell assembly used here. An error of 3 kb in pressure would affect the value of $\Delta\mu^\circ$ by about 20 percent. Assignment of errors due to the uncertainty in pressure suggests that the value of $\Delta\mu^\circ$ (900°C) may be in an interval of −20 percent to +10 percent about 0.54 kcal, that is, in the range of 0.43 to 0.59 kcal.

The ratio $a_{Fa,Ol}/a_{Fs,Px}$ is plotted in figure 4 as a function of the activities for the calculated and limiting values of $\Delta\mu^\circ$ at 900°C. Dashed lines representing constant values of $\Delta a = a_{Fa,Ol} - a_{Fs,Px}$ are also plotted. The 800° and 900°C experiments (figs. 3A and 3B) indicate that the composition of olivine in the three-phase assemblage at 900°C and low pressure is approximately Fa_{80}. If olivine and orthopyroxene behaved as ideal solid solutions, Δa would equal ΔX, and the range of values for ΔX corresponding to the range for $\Delta\mu^\circ$ could be read directly from figure 4 at $a_{Fa,Ol} = 0.8$. Δa is notably insensitive to variations in $\Delta\mu^\circ$; for

[2] An expression for the chemical potential of fayalite in the Fe_2SiO_4–Mg_2SiO_4 solid solution can be written $\mu_{Fa,Ol} = \mu^\circ_{Fa} + 2RT \ln a_{Fa,Ol}$, since there are two cation sites for Fe and Mg in the olivine formula used (Thompson, 1967, p. 342). With this model, $X_{Fa,Ol} = a_{Fa,Ol}$ for ideal solid solution behavior.

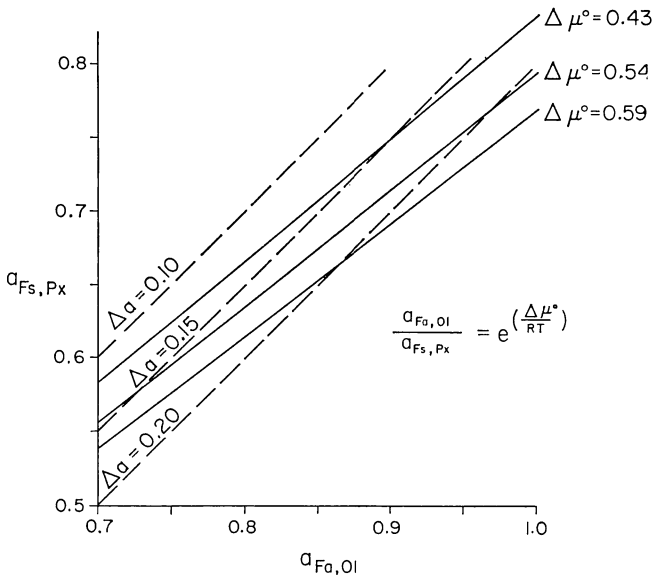

Fig. 4. Solid lines are plots of the function $a_{Fa,Ol}/a_{Fs,Px} = \exp(\Delta\mu^\circ/RT)$ for three values of $\Delta\mu^\circ$ at a temperature of 1173°K (900°C). The ratio of the activity of fayalite in olivine ($a_{Fa,Ol}$) to the activity of ferrosilite in pyroxene ($a_{Fs,Px}$) will fit this equation when the two phases are in equilibrium with high quartz. The dashed lines are plots of $\Delta a = a_{Fa,Ol} - a_{Fs,Px}$. Values of Δa are rather insensitive to the exact values chosen for $\Delta\mu^\circ$ and $a_{Fa,Ol}$.

the ideal approximation ($\Delta X = \Delta a$), ΔX lies in the range 0.13 to 0.18, values distinctly greater than the 0.09 figure derived from the partition data of Medaris (1969) for orthopyroxene in equilibrium with Fa_{80}. Both olivine and $FeSiO_3$–$MgSiO_3$ solid solutions show similar, positive deviations from ideality at 1200° (Kitayama and Katsura, 1968; Kitayama, 1970). ΔX will be less than ΔA only if $a_{Fa,Ol} - x_{Fa,Ol} > a_{Fs,Px} - X_{Fs,Px}$ for the compositions in the three-phase assemblage; this could occur only if the olivine solid solution had a significantly greater positive deviation from ideality than the orthopyroxene solution. The distribution of Fe and Mg between the M_1 and M_2 sites of orthopyroxene becomes increasingly ordered at lower temperatures, and the positive nonideality of the orthopyroxene solid solution increases (Virgo and Hafner, 1969); Saxena and Ghose, 1970). Olivines show much less pronounced lower temperature ordering (Finger, 1971), and it seems unlikely that olivine will be significantly less ideal than orthopyroxene at 900°C. The calculations thus suggest that ΔX will be greater than 0.13 for the three-phase assemblage at 900°C and low pressure.

Further partition experiments for iron-rich compositions are needed to define the width of the three-phase field more accurately. Such data, together with the results in figure 4, will be useful in checking the consistency of activity-composition relationships determined for the olivine

TABLE 2

Hydrothermal experiments in cold-seal bombs, Tuttle press, and internally heated gas apparatus*

Starting material	Temperature (±10°C)	Pressure (kb)	Duration (hours or days)	Products, with visually estimated percentage of orthopyroxene in parentheses	
$Fs_{75}En_{25}$	950	0.3	24 h	ol + SiO_2 + opx	(30)
$Fs_{80}En_{20}$	950	0.3	23 h	"	(10)
$Fs_{70}En_{30}$	900	0.3	70 h	"	(>90)
$Fs_{75}En_{25}$	900	0.3	66 h	"	(80)
$Fs_{80}En_{20}$	900	0.3	43 h	"	(30)
$Fs_{85}En_{15}$	900	0.3	53 h	"	(<1)
$Fs_{75}En_{25}$	900	3	16 h	"	(>90)
$Fs_{80}En_{20}$	900	3	6 h	"	(50)
$Fs_{85}En_{15}$	900	3	8 h	"	(<5)
$Fs_{85}En_{15}$	900	7	5 h	"	(80)
$Fa_{70}Fo_{30}$ + SiO_2	900	0.5	15 d	"	(10)
$Fa_{70}Fo_{30}$ + SiO_2	900	3	8 h	"	(90)**
$Fa_{75}Fo_{25}$ + SiO_2	900	3	6 h	"	(30)
$Fa_{80}Fo_{20}$ + SiO_2	900	3	6 h	"	(<5)†
$Fa_{80}Fo_{20}$ + SiO_2	900	7	6 h	"	(>99)
$Fa_{85}Fo_{15}$ + SiO_2	900	7	5 h	"	(50)
$Fs_{75}En_{25}$	800	1	52 d	"	(70)
$Fs_{80}En_{20}$	800	1	81 d	"	(30)
$Fs_{85}En_{15}$	800	1	98 d	ol + SiO_2	(0)
$Fa_{70}Fo_{30}$ + SiO_2	800	1	71 d	ol + SiO_2 + opx	(70)
$Fa_{75}Fo_{25}$ + SiO_2	800	1	52 d	"	(30)
$Fa_{80}Fo_{20}$ + SiO_2	800	1	81 d	"	(1)
$Fa_{70}Fo_{30}$ + SiO_2	750	1	100 d	"	(90)
$Fs_{80}En_{20}$	700	1	25 d	"	(50)
$Fs_{85}En_{15}$	700	1	56 d	"	(30)
$Fa_{75}Fo_{25}$ + SiO_2	700	1	56 d	"	(50)
$Fa_{80}Fo_{20}$ + SiO_2	700	1	25 d	"	(20)
$Fa_{85}Fo_{15}$ + SiO_2	650	1	39 d	ol + SiO_2 + amphibole	
$Fs_{80}En_{20}$	600	1	50 d	opx + ol + SiO_2 + amphibole	

* Orthopyroxene or the compositionally equivalent mixture of olivine plus silica were used as starting materials. Experiments were buffered with fayalite–magnetite–quartz unless otherwise indicated. Only runs in which reaction occurred are listed.

** Wüstite-magnetite buffer used.

† Approximately half the pyroxene present had inclined extinction.

TABLE 3

Experiments at 1000°C on orthopyroxene in evacuated, sealed silica-glass tubing

Starting material	Duration (days)	Products, with visually estimated percentages in parentheses
$Fs_{70}En_{30}$	44	opx (70), ol (13,) SiO_2 (13), cpx (3)
$Fs_{75}En_{25}$	44	opx (10), ol (45), SiO_2 (45)
$Fs_{80}En_{20}$	52	ol + SiO_2
$Fs_{85}En_{15}$	52	ol + SiO_2

and orthopyroxene solid solutions. Likewise, a knowledge of the activity-composition relationships together with the data of figure 4 will permit calculation of ΔX. The better the partition is known for these iron-rich compositions, the more accurately it will be possible to apply the experimental results as a geobarometer. All experimental results obtained here are consistent with the partition data of Medaris (1969). Nevertheless, the widths of the olivine–orthopyroxene–silica fields in figures 3A and 3B have been drawn slightly greater than would be consistent with an extrapolation of his results because of the larger values suggested by both calculations and natural assemblages. Virgo and Hafner (1970) noted that a relationship describing the intracrystalline distribution of Fe and Mg over the M positions in magnesian orthopyroxenes could not be extended to describe the distribution in iron-rich orthopyroxenes. Similarly, the results obtained here suggest that relationships describing the intercrystalline partition of Fe and Mg between magnesian orthopyroxene and other phases may not describe the partition correctly for extremely iron-rich compositions.

ACKNOWLEDGMENTS

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Appendix

Oxide mixes of orthopyroxene composition were made from Fe Sponge (Johnson and Matthey), Fe_2O_3 (Fisher's "Certified," lot 76442), SiO_2 glass (Corning 7940), and MgO (prepared by D. H. Lindsley from 0.99995 Mg metal) according to the techniques of Lindsley and Munoz (1969). These initial mixtures were wrapped in $Ag_{80}Pd_{20}$ foil and reacted in evacuated, sealed silica-glass tubes or in H_2–CO_2 gas mixtures at oxygen fugacities lower than those of the wüstite–magnetite buffer and at temperatures from 900° to 1025°C. Generally several reaction periods separated by grinding in an agate mortar were required. The reaction products—olivine plus tridymite plus SiO_2 glass—served as one set of starting materials. The olivine plus SiO_2 mixtures were reacted with 10 mg H_2O and sufficient excess SiO_2 to saturate the fluid phase in mechanically sealed Ag capsules in a large volume piston-cylinder apparatus to produce orthopyroxene at temperatures of 900° to 925°C and pressures of 20 to 22 kb. Reaction products were greater than 95 percent orthopyroxene with less than 1 percent magnetite (visual estimate) and minor olivine plus quartz. These orthopyroxenes served as the other set of starting materials.

Experiments in piston-cylinder apparatus (table 4) at and below 900°C were made in Ag capsules together with 1 mg H_2O and approximately 0.5 mg excess silica. For compositions containing Mg, reaction products with more than a trace of opaque oxides were discarded. Experiments at 1075° and 1100°C were made in Fe capsules. Ferrosilite was broken down under dry conditions at 1100°C, whereas olivine plus silica was reacted wet with excess silica at 1075°C; no melting was observed. Furnace-cell assemblies and operational techniques were those of Richardson, Bell, and Gilbert (1968). Nominal pressures are reported, and no correction was made for the effects of pressure on the Pt–$Pt_{90}Rh_{10}$ thermocouples.

Reactants for hydrothermal experiments were sealed together with water and approximately 0.5 mg excess silica in capsules made from $Ag_{80}Pd_{20}$ tubing (table 2). All experiments were buffered by the fayalite–magnetite–quartz reaction except one, for which the iron–wüstite buffer was used. Experiments at pressures of 0.3 to 1 kb

were made in standard cold-seal and Tuttle press apparatus (Tuttle, 1948, 1949). Experiments at 3 and 7 kb were carried out by H. S. Yoder in an internally heated gas apparatus (Yoder, 1950).

Products of all reactions were studied optically in appropriate index oils; many were also X-rayed. Orthopyroxene was the only pyroxene polymorph observed in most experiments and the predominant one in all. Minor twinned pyroxene laths with inclined extinction were formed in experiments in evacuated tubes at 1000°C, in piston-cylinder apparatus at temperatures from 650° to 1100°C, and in several of the hydrothermal experiments at low pressures.

TABLE 4

Experiments in solid-media, piston-cylinder apparatus*

Starting material	Temperature (±15°C)	Pressure** (kb)	Duration (hours)	Products, with visually estimated percentage of orthopyroxene in parentheses†	
$Fs_{90.5}En_{9.5}$	900	9 mpo	22	ol + SiO_2 + opx	(30)
$Fs_{90.5}En_{9.5}$	900	10 mpo	24	"	(40)
$Fa_{90.5}Fo_{9.5}$ + SiO_2	905	10.5 mpo	48	"	(20)
$Fa_{90.5}Fo_{9.5}$ + SiO_2	900	11 mpo	23	"	(40)
$Fs_{95}En_5$	905	11.5 mpo	23	"	(30)
$Fs_{95}En_5$	900	12 mpo	23	"	(70)
$Fa_{95}Fo_5$ + SiO_2	900	13 mpo	22	"	(70)
Fa_{100} + SiO_2	650	14 pi	150	"	
Fa_{100} + SiO_2	700	14.5 pi	88	"	
Fa_{100} + SiO_2	750	14 pi	64	"	
Fa_{100} + SiO_2	750	12.5 mpo	27	"	
Fs_{100}	750	11 mpo	25	"	
Fa_{100} + SiO_2	900	15.5 pi	16	"	
Fa_{100} + SiO_2	900	15 pi	16	"	
Fa_{100} + SiO_2	905	14.5 mpo	9	"	
Fs_{100}	900	13.5 mpo	23	ol + SiO_2	
Fa_{100} + SiO_2	1075	19 pi	4	opx + ol + SiO_2	‡
Fa_{100} + SiO_2	1075	18 mpo	3	"	‡
Fs_{100}	1100	15.5 po	24	"	§

* Starting materials were either orthopyroxene or the compositionally equivalent assemblage of olivine plus quartz. All experiments were hydrothermal in Ag capsules unless noted otherwise.

** Experiments made by piston-in (pi), piston-out (po), and modified piston-out (mpo) techniques described by Richardson and others (1968). Nominal pressures are reported.

† Percentages are not reported for experiments with pure orthoferrosilite or fayalite plus silica, as only the direction of reaction is important in this system of reduced variance.

‡ Hydrothermal experiments in Fe capsules.

§ Dry experiment in Fe capsule.

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