

Experimental investigations and geological applications of orthopyroxene geobarometry¹

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Abstract

The effect of magnesium on the relative stabilities of ferrosilite-rich orthopyroxene and fayalitic olivine + quartz has been determined with reversed experiments in piston-cylinder apparatus. Reaction reversals to within 0.2 kbar indicate instability of $\text{Fs}_{95}\text{En}_5$, below 9.8, 11.0, and 12.4 kbar, $\text{Fs}_{90}\text{En}_{10}$ below 8.2, 9.5, and 10.8 kbar at 800°, 900°, and 1000°C, respectively; $\text{Fs}_{85}\text{En}_{15}$ below 7.8 and 9.1 kbar, and $\text{Fs}_{80}\text{En}_{20}$ below 6.1 and 7.3 kbar at 900° and 1000°C, respectively. $\text{Fa}_{95}\text{Fo}_5$ + quartz and $\text{Fa}_{90}\text{Fo}_{10}$ + quartz react to orthopyroxene + olivine + quartz above 7.4, 8.7, and 10.0 kbar and 5.4, 6.7, and 8.1 kbar at 800, 900 and 1000°C, respectively. Electron microprobe analyses of run products indicate $K_{\text{Mg-Fe}}^{\text{opx-oliv}} = 2.2 \pm 0.3$ at 900° and 1000°C and 2.2 ± 0.7 at 800°C. Each mole % MgSiO_3 extends orthopyroxene stability by ~0.34 kbar, relative to FeSiO_3 (Bohlen *et al.*, 1980a). These data combined with data for manganese (each mole % MnSiO_3 extends orthopyroxene stability by ~0.12 kbar, Bohlen *et al.*, 1980b) allow inference of equilibration pressures for Fe-rich orthopyroxene and orthopyroxene-quartz-olivine bearing assemblages in numerous localities throughout the world. Pressures determined from assemblages in the Adirondack Mountains, New York, southern Labrador Trough, Canada and Lofoten-Vesterålen, Norway indicate that thick (~70 km) continental crust was not uncommon mid-to-late Proterozoic.

Introduction

Since Bowen and Schairer published the results of their now classic studies on the systems FeO-SiO_2 and MgO-FeO-SiO_2 (Bowen and Schairer, 1932 and 1935, respectively), wherein they concluded that FeSiO_3 may not exist as a mineral, Fe-rich pyroxene has been of great interest to petrologists. FeSiO_3 was named ferrosilite by Washington (1932), but only in reference to a convenient, hypothetical end-member for CIPW norm calculations. Until 1935 the most iron-rich pyroxene known was from an iron-slag; Bowen (1933) estimated it to have the composition

$\text{Fs}_{82}\text{En}_{10}\text{Rh}_0\text{Wo}_8^2$, if significant amounts of Al, Zn, and Fe^{3+} were ignored. Soon after Bowen and Schairer concluded that FeSiO_3 probably did not exist, Bowen (1935) discovered a mineral in lithophysae of obsidian from Lake Naivasha, Kenya having optical characteristics of pure or nearly pure monoclinic ferrosilite. Subsequent microprobe analyses of the pyroxene (Bowen, 1965) indicate the pyroxene to be $\text{Fs}_{95}\text{En}_0\text{Rh}_3\text{Wo}_0$. Without the benefit of chemical analyses, Bowen could only conclude that the pyroxene needles were either clinoferrosilite formed at low

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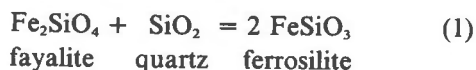
²Pyroxene compositions given by $\text{Fs}_w\text{En}_x\text{Rh}_y\text{Wo}_z$ refer to the molar proportions of ferrosilite, enstatite, rhodonite and wollastonite components respectively. Pyroxenes containing significant proportions of other components will be so noted.

temperatures, where experimental studies (Bowen *et al.*, 1933) suggested the mineral might be stable, or contained impurities such as Ti, Mn, and Fe³⁺, increasing the refractive indices to values near those inferred for ferrosilite. Bowen did point out that these pyroxenes are quite common in lithophysae of many obsidians.

Recently, nearly end-member orthorhombic ferrosilite has been reported from the southern Labrador Trough (Klein, 1978), Lofoten, Norway (Ormaasen, 1977) and a well-documented occurrence has been reported by Jaffe *et al.* (1978) from the Adirondack Mountains, New York. The significance of these and numerous other Fe-rich orthopyroxenes (see Table 9) can be interpreted in light of fifteen years of experimental investigation (see following section), the general results of which indicate that ferrosilite and other Fe-rich orthopyroxenes are stable only at high pressures relative to compositionally equivalent fayalitic olivine + quartz. Many investigators (*e.g.*, Wood and Strens, 1971; Smith, 1971) have emphasized the potential of this system as a geobarometer. Tightly constrained pressure estimates have been hampered by the lack of extensive calibration of the effects of additional components on the stability of ferrosilite. However, our experimental results on the effect of MgSiO₃ on the stability of FeSiO₃, combined with results from other studies (Smith, 1971; Bohlen *et al.*, 1980a, 1980b), are sufficient to calibrate the orthopyroxene-olivine-quartz geobarometer. Consequently, with the exception of the occurrence described by Bowen, pressure minima (*maxima*) can now be confidently determined for assemblages containing Fe-rich orthopyroxene (Fe-rich-olivine + quartz) and defined for coexisting orthopyroxene-olivine-quartz.

Previous studies

Nearly thirty years elapsed between Bowen's discovery of naturally occurring ferrosilite and the first experiments on its stability. Two groups of experimentalists (Akimoto *et al.*, 1964; Lindsley *et al.*, 1964) independently and nearly simultaneously demonstrated that ferrosilite could be synthesized at high pressures. Lindsley *et al.* (1964) were the first to define the stability at high pressures by reversing the reaction:



Lindsley *et al.* showed that fayalite + quartz react to ferrosilite above 18 kbar at 1150°C and that ferrosi-

lite breaks down to fayalite + quartz below 14 kbar at 1000°C. Shortly thereafter, Akimoto *et al.* (1965) demonstrated reversible equilibrium for the above reaction between 13.9 and 16 kbar at 960° and 950°C, respectively. Olsen and Mueller (1966) attempted to calculate the effect of MgSiO₃ on the stability of ferrosilite. This study showed qualitatively that Mg extends the stability of iron-rich orthopyroxenes to lower pressures. Nafziger and Muan (1967) showed that pyroxene compositions of up to Fs₅₇En₄₃ are stable at 1250°C and 1 atm, in agreement with the results of Bowen and Schairer (1935). Wood and Strens (1971) attempted to delineate the three-phase orthopyroxene-olivine-quartz field at 1250°C and 1100°C at 1 atm. Their results differ from those of Nafziger and Muan (1967) particularly in the *T-X* dependence of the three-phase field. Using the data of Lindsley *et al.* (1964), Akimoto *et al.* (1965), preliminary data of Smith (1970), and their own data at one atmosphere, Wood and Strens calculated the effect of up to 40 mole % MgSiO₃ on the stability of FeSiO₃, and proposed an orthopyroxene geobarometer. Despite the abundance of studies dealing directly or indirectly with ferrosilite prior to the early 1970's, the stability of this end-member pyroxene and the effect of additional components were unknown in detail. Smith (1971) experimentally reversed reaction 1 at 750°, 900°, and 1050°C and investigated the effect of MgSiO₃ component at 900°C. He showed that less than 35 mole % MgSiO₃ stabilizes the Fe-rich orthopyroxene at 900°C and atmospheric pressure. Additionally Smith showed how the compositions of coexisting orthopyroxene and olivine in the presence of quartz vary as a function of pressure at 900°C. These were the first experimental data which directly calibrated the effect of MgSiO₃ on ferrosilite stability.

More recently, Bohlen *et al.* (1980a) located the stability of ferrosilite and fayalite + quartz to within 0.1 kbar from 700–1050°C and showed that the α - β quartz transition causes an increase in slope from ~10 bars/°C to ~15 bars/°C in the β quartz field, a somewhat larger effect than that calculated previously by Olsen and Mueller (1966). Results of Bohlen *et al.* (1980a) are in good agreement with those of Smith (1971) and in reasonable agreement with the original work of Lindsley *et al.* (1964) and Akimoto *et al.* (1965), considering the different experimental techniques used in the various studies. Bohlen *et al.* (1980b) calibrated the effect of 5 and 10 mole % MnSiO₃ component, and they concluded that each mole % MnSiO₃ in FeSiO₃ extends the stability of the

pyroxene 0.12 kbar. Lindsley and Munoz (1969) investigated subsolidus phenomena on the join hedenbergite-ferrosilite and delineated the miscibility gap for Ca-rich and Ca-poor pyroxenes. Similar relations were determined by Smith (1972) on part of the join Wo_{100} - $Fs_{85}En_{15}$. Both studies indicate that Fe-rich orthopyroxene in equilibrium with Ca- and Fe-rich clinopyroxenes contain less than 3 mole % wollastonite component for temperatures of less than 850°C, in agreement with observed $CaSiO_3$ contents in natural orthopyroxenes coexisting with Ca-rich clinopyroxenes. Hence, wollastonite solid solution in orthopyroxene probably plays only a minor role in extending Fe-rich orthopyroxene stability to lower pressures.

Experimental methods

Starting materials

Starting materials were prepared from electrolytically reduced Fe powder (Mallinckrodt Lot BBA), spectroscopically pure MgO (Puratronic Batch S.85439) and natural Brazilian quartz leached in HNO_3 . Appropriate mixtures of Fe + quartz and Fe + MgO + quartz were reacted in a CO_2/H_2 gas-mixing furnace at 1100°C and $f_{O_2} \approx 10^{-13}$ for 3 days with grinding to approximately -300 mesh every 12 hours to produce olivines of compositions Fa_{100} , $Fa_{95}Fo_5$, $Fa_{90}Fo_{10}$, $Fa_{85}Fo_{15}$, and $Fa_{80}Fo_{20}$. The olivines were analyzed by optical, X-ray, and electron microprobe techniques (Table 1) to ensure that they were homogeneous and stoichiometric. Mixtures of olivine and quartz with traces of H_2O were reacted using Ag capsules in a piston-cylinder device at 25 kbar and 900°C for approximately 30 hours to synthesize ferrosilite (Fs_{100}), $Fs_{95}En_5$, $Fs_{90}En_{10}$, $Fs_{85}En_{15}$, and $Fs_{80}En_{20}$. The products (pyroxene with traces of quartz) were also analyzed by optical, X-ray and electron microprobe techniques (Table 1). The pyroxenes were homogeneous and stoichiometric. Small excesses of quartz over stoichiometry were used in the syntheses of orthopyroxenes and olivines to promote complete reaction and to saturate the vapor phase with SiO_2 in runs where water was used to enhance reaction rate. Metallic iron powder was packed around the capsules in the furnace assembly to help maintain a low ambient f_{O_2} . Some of the starting materials were analyzed with Mössbauer spectroscopy to check for Fe^{3+} . Spectra were collected for approximately 72 hours at room temperature. The limit of detectability of Fe^{3+} under the conditions

Table 1. Electron microprobe analyses of starting materials

	$Fs_{95}En_5$	$Fs_{90}En_{10}$	$Fs_{85}En_{15}$	$Fs_{80}En_{20}$	Fs_{100}
SiO ₂	45.9(.3)	46.6(.4)	47.5(.4)	47.1(.4)	46.0(.2)
FeO	52.6(.4)	50.9(.6)	47.8(.5)	46.4(.6)	54.7(.2)
MgO	1.5(.1)	3.0(.3)	4.9(.2)	6.5(.3)	0.0(.0)
Total	100.0	100.5	100.2	100.0	100.7
Si	1.99	1.99	2.00	1.98	2.00
Fe	1.91	1.81	1.69	1.61	2.00
Mg	0.10	0.19	0.31	0.41	0.00
# Points	12	12	14	16	12

	$Fa_{95}Fo_5$	$Fa_{90}Fo_{10}$	$Fa_{85}Fo_{15}$	$Fa_{80}Fo_{20}$
SiO ₂	30.1(.3)	30.8(.4)	31.1(.4)	31.1(.3)
FeO	68.0(.5)	66.4(.7)	63.3(.7)	59.9(.4)
MgO	2.2(.3)	4.3(.3)	6.2(.3)	8.8(.3)
Total	100.3	101.5	100.6	99.8
Si	1.00	1.00	1.00	0.99
Fe	1.89	1.79	1.70	1.60
Mg	0.11	0.21	0.30	0.41
# Points	6	10	6	11

employed is estimated as less than 1% of the iron present, and no Fe^{3+} was detected in any sample.

Capsules

In our previous studies on the stability of ferrosilite (Bohlen *et al.*, 1980a, 1980b) the experimental charge was loaded in silver capsules and run without an external buffer in talc furnace assemblies, since no magnetite was observed in the run products and Mössbauer results showed no detectable ferric iron in the orthopyroxenes. However, we are now using an anhydrous furnace assembly with no hydrous parts. Consequently the intrinsic f_{O_2} of the furnace assembly is higher (there is no H_2O to react with the graphite heater to produce H_2) and in our initial runs minute amounts of magnetite were observed. Therefore, to maintain f_{O_2} below the value defined by QFM a double capsule (Eugster, 1957) was used. For every run an equimolar amount of olivine + quartz and orthopyroxene was sealed in 2.5 mm $Ag_{80}Pd_{20}$ capsules. For runs of $\leq 900^\circ C$, less than one weight percent H_2O was added to promote reaction rates. The reactants in the inner capsule of experiments above 900°C were run dry. The inner capsule was loaded into a 5 mm Ag_{100} outer capsule containing Fe buffer and sufficient H_2O to react with roughly half of the Fe.

Apparatus and run procedure

All experiments were carried out in a piston-cylinder apparatus (Boyd and England, 1960) with 25.4 mm diameter furnace assemblies and pistons. The furnace assemblies differ from those used previously (Boettcher in Johannes *et al.*, 1971) in that the talc

bushing that surrounds a thin cylinder of pyrex which in turn surrounds the graphite furnace is replaced by KBr (Boettcher *et al.*, in preparation). Inside the graphite cylinder the capsule was placed horizontally in the notched top surface of a cylinder of BN, the remainder of the furnace was then filled with crushable alumina. Temperature was measured with Pt₁₀₀-Pt₉₀Rh₁₀ thermocouples with no correction for the effect of pressure on emf. We used the piston-in technique by bringing the pressure to 10% below that of the final run pressure, increasing the temperature to the final value and increasing the pressure to the final value. During the period over which the temperature was increased there was a concomitant increase in pressure due to the thermal expansion of the KBr. Typically the pressure increase did not exceed the final pressure. When this did occur, the pressure was reduced to roughly 5% below the desired value and then increased to the final pressure.

The assembly has been calibrated against the reaction fayalite + quartz = ferrosilite, Bohlen *et al.* (1980a) and quartz = coesite, Boettcher and Wyllie (1968). The results relative to those obtained in a talc assembly with a -6% pressure correction (Boettcher in Johannes *et al.*, 1971) indicate that the KBr assem-

Table 3. Experimental results for Ferrosilite₉₀Enstatite₁₀ bulk composition

Run#	T(°C)	P(Kbar)	Duration (hrs)	Reactants	Products
197	800	7.8	44.5	A	<u>opx</u> + <u>(oliv+qtz)</u>
198	800	6.6	39.5	A	<u>opx</u> + <u>oliv+qtz</u>
215	800	6.2	47	A	<u>opx</u> + <u>oliv+qtz</u>
275	800	5.8	62	B	<u>oliv+qtz</u> + <u>(opx)</u>
294	800	6.4	66	B	<u>opx</u> + <u>oliv+qtz</u>
282	800	8.2	69	A	<u>opx</u> + <u>(oliv+qtz)</u>
288	800	5.0	69	A	<u>oliv+qtz</u>
295	800	8.0	65	C	<u>opx</u> + <u>(oliv+qtz)</u>
296	800	5.4	54	D	<u>oliv+qtz</u> + <u>(opx)</u>
165	900	9.4	31	A	<u>opx</u> + <u>(oliv+qtz)</u>
180	900	8.6	23.2	A	<u>opx</u> + <u>oliv+qtz</u>
181	900	8.2	26.5	A	<u>opx</u> + <u>oliv+qtz</u>
200	900	7.8	30	A	<u>oliv+qtz</u> + <u>opx</u>
247	900	9.4	24	B	<u>opx</u> + <u>(oliv+qtz)</u>
264	900	7.8	28	B	<u>oliv+qtz</u> + <u>opx</u>
293	900	8.0	29.3	B	<u>opx</u> + <u>oliv+qtz</u>
280	900	7.0	27	A	<u>oliv+qtz</u> + <u>(opx)</u>
281	900	6.4	38	A	<u>oliv+qtz</u>
290	900	9.2	26.2	C	<u>opx</u> + <u>(oliv+qtz)</u>
291	900	6.7	26.2	D	<u>oliv+qtz</u> + <u>(opx)</u>
148	1000	10.0	24	A	<u>opx</u> + <u>oliv+qtz</u>
154	1000	10.4	24.5	A	<u>opx</u> + <u>oliv+qtz</u>
156	1000	9.6	23	A	<u>opx</u> + <u>oliv+qtz</u>
161	1000	9.2	24	A	<u>opx</u> + <u>oliv+qtz</u>
239	1000	10.4	28.5	B	<u>opx</u>
257	1000	9.2	25.5	B	<u>opx</u> + <u>oliv+qtz</u>
283	1000	8.6	17	A	<u>oliv+qtz</u> + <u>(opx)</u>
286	1000	11.0	23	A	<u>opx</u>
287	1000	8.1	25	A	<u>oliv+qtz</u>
289	1000	10.8	24.2	C	<u>opx</u> + <u>(oliv+qtz)</u>
292	1000	8.3	30.5	D	<u>oliv+qtz</u> + <u>(opx)</u>

A = $Fs_{90}En_{10}+Fa_{90}Fo_{10}+quartz$; B = $Fs_{80}En_{20}+Fa_{100}+quartz$; C = $Fs_{90}En_{10}$; D = $Fa_{90}Fo_{10}+quartz$. Underlining indicates dominant phase(s). Parentheses indicate trace amounts.

Table 2. Experimental results for Ferrosilite₉₅Enstatite₅ bulk composition

Run #	T(°C)	P(Kbar)	Duration (hrs)	Reactants	Products
189	800	9.4	42	A	<u>opx</u> + <u>oliv+qtz</u>
190	800	8.2	40	A	<u>opx</u> + <u>oliv+qtz</u>
214	800	7.8	40	A	<u>oliv+qtz</u> + <u>opx</u>
244	800	9.4	47.5	B	<u>opx</u> + <u>oliv+qtz</u>
252	800	9.4	21	B	<u>opx</u> + <u>oliv+qtz</u>
255	800	9.4	43	B	<u>opx</u> + <u>oliv+qtz</u>
262	800	7.8	43	B	<u>opx</u> + <u>oliv+qtz</u>
263	800	8.6	43	B	<u>oliv+qtz</u> + <u>(opx)</u>
271	800	7.2	62	A	<u>opx</u> + <u>oliv+qtz</u>
272	800	10.0	48	A	<u>oliv+qtz</u>
273	800	9.8	64	C	<u>opx</u>
274	800	7.4	49	D	<u>opx</u> + <u>(oliv+qtz)</u>
164	900	11.0	30.5	A	<u>opx</u> + <u>(oliv+qtz)</u>
179	900	9.8	24	A	<u>opx</u> + <u>oliv+qtz</u>
199	900	9.4	30	A	<u>oliv+qtz</u> + <u>opx</u>
230	900	11.0	25	B	<u>opx</u> + <u>(oliv+qtz)</u>
231	900	9.4	38.3	B	<u>oliv+qtz</u> + <u>(opx)</u>
254	900	11.0	22	B	<u>opx</u> + <u>(oliv+qtz)</u>
258	900	9.4	24	B	<u>oliv+qtz</u> + <u>(opx)</u>
261	900	10.2	24	B	<u>opx</u> + <u>oliv+qtz</u>
276	900	8.6	23.5	A	<u>oliv+qtz</u>
277	900	10.8	23	C	<u>opx</u> + <u>(oliv+qtz)</u>
278	900	8.8	24.5	D	<u>oliv+qtz</u> + <u>(opx)</u>
143	1000	12.0	25.5	A	<u>opx</u> + <u>oliv+qtz</u>
144	1000	12.4	25	A	<u>opx</u> + <u>(oliv+qtz)</u>
155	1000	11.2	23	A	<u>oliv+qtz</u> + <u>opx</u>
160	1000	10.8	25.5	A	<u>oliv+qtz</u> + <u>(opx)</u>
172	1000	11.6	48	A	<u>opx</u> + <u>oliv+qtz</u>
228	1000	12.4	27	B	<u>opx</u>
229	1000	10.8	24.5	B	<u>oliv+qtz</u> + <u>(opx)</u>
237	1000	11.6	29	B	<u>oliv+qtz</u> + <u>opx</u>
268	1000	10.0	21.5	A	<u>oliv+qtz</u>
269	1000	10.3	24	D	<u>oliv+qtz</u> + <u>(opx)</u>
270	1000	12.2	24	C	<u>opx</u> + <u>(oliv+qtz)</u>

A = $Fs_{95}En_5+Fa_{95}Fo_5+quartz$; B = $Fs_{80}En_{20}+3Fa_{100}+3quartz$; C = $Fs_{95}En_5$; D = $Fa_{95}Fo_5+quartz$. Underlining indicates dominant phase(s). Parentheses indicate trace amounts.

bly requires no pressure correction at temperatures above the solidus of KBr, whereas, at temperatures greater than 50°C below the solidus of KBr a -2% pressure correction is required. Using different salts, other workers (Johannes, 1978; Holland, 1980) have also noted that salt assemblies require little or no pressure correction. Pressures given in Tables 2 and 3 for runs at 800°C are corrected assuming a -2% pressure correction. Nominal pressure values are listed for experiments at 900 and 1000°C.

Run products

All run products were analyzed optically and by X-ray diffraction. Many were analyzed by electron microprobe. Reversal of the olivine-out boundaries (the low pressure limit of stability of $Fs_{95}En_5$ and $Fs_{90}En_{10}$) and the orthopyroxene-out boundary (the high pressure limit of stability of $Fo_{95}Fo_5$ + quartz and $Fa_{90}Fo_{10}$ + quartz) requires detecting trace amounts of orthopyroxene or olivine by careful examination. Olivine occurs as green, birefringent, equant crystals; orthopyroxene typically occurs as bladed, subhedral crystals with very faint pleochroism (X = pale yellow-pink, Y = pale pink-yellow, Z = pale green). Microprobe analyses (Ta-

Table 4. Experimental results for Ferrosilite₈₅Enstatite₁₅ and Ferrosilite₈₀Enstatite₂₀ bulk compositions

Run #	T(°C)	P(Kbar)	Duration (hrs)	Reactants	Products
297	1000	9.0	42	C	opx+oliv+qtz
298	1000	9.4	45.5	A	opx
299	900	8.0	48	A	opx+(oliv+qtz)
300	900	7.7	63.5	C	opx+oliv+qtz

$A = \text{Fs}_{85}\text{En}_{15} + \text{Fa}_{85}\text{Fo}_{15} + \text{quartz}$; $C = \text{Fs}_{85}\text{En}_{15}$

Run #	T(°C)	P(Kbar)	Duration (hrs)	Reactants	Products
301	990	7.5	64	A	opx
302	990	7.2	42.5	C	opx+oliv+qtz
303	900	6.2	42.5	A	opx+(oliv+qtz)
304	900	5.9	46	C	opx+oliv+qtz

$A = \text{Fs}_{80}\text{En}_{20} + \text{Fa}_{80}\text{Fo}_{20} + \text{quartz}$; $C = \text{Fs}_{80}\text{En}_{20}$. Underlining indicates dominant phase(s). Parentheses indicate trace amounts.

bles 5 and 6) of orthopyroxene and olivine were obtained to check the phases for stoichiometry, homogeneity and to determine the relative proportions of Fe²⁺ and Mg between the coexisting phases. Analyses were obtained using an ARL-EMX electron microprobe analyzer with wavelength dispersive ADP, LiF, and TAP crystal spectrometers. Synthetic olivines (Fa₆₀Fo₄₀ and Fa₁₀₀) and natural orthopyroxene (Fs₁₀En₈₆Rh₃Wo₁) were used as standards. Spectrometer data were reduced using the correction procedures of Bence and Albee (1968). In general the phases were homogeneous, although an occasional,

somewhat inhomogeneous phase was encountered (analysis 180 opx, for example).

Experimental results and discussion

Experimental results for Fs₉₅En₅, Fs₉₀En₁₀, Fs₈₅En₁₅, and Fs₈₀En₂₀ bulk compositions are listed in Tables 2, 3, and 4 and shown graphically in Figures 1, 2, and 3. The boundaries of the orthopyroxene + olivine + quartz field were reversed by reacting equimolar mixtures of orthopyroxene and olivine + quartz completely to orthopyroxene or olivine + quartz and by reacting orthopyroxene or reacting olivine + quartz to the three-phase assemblage. In a few instances, the boundary was inferred when 100% reaction was not achieved. In such cases the microprobe analyses of run products (Tables 5 and 6) demonstrate that the overwhelmingly abundant Mg-Fe phase was identical to the bulk composition within analytical uncertainty (runs 164 and 254, for example), and therefore, they properly constrain the phase boundary. The results indicate that each mole % MgSiO₃ in FeSiO₃ extends the stability of pyroxene by approximately 0.34 kbar in comparison with the stability of ferrosilite as determined by Bohlen *et al.* (1980a). The upper-pressure limit of olivine + quartz in the absence of orthopyroxene is greatly reduced. Each mole % Mg₂SiO₄ in Fe₂SiO₄ reduces the stability field of olivine + quartz by an average of 0.8 kbar up to 5 mole %, and 0.6 kbar up to 10 mole %

Table 5. Electron microprobe analyses of experimental products for Ferrosilite₉₅Enstatite₅ bulk composition

Run #	189 Opx	190 Opx	190 Oliv	255 Opx	255 Oliv	272 Opx	164 Opx	179 Opx	179 Oliv
SiO ₂	46.1(.3)	46.0(.4)	29.8(.3)	46.7(.3)	30.3(.5)	45.4(.5)	46.3(.8)	46.4(.4)	30.6(.4)
FeO	52.6(.5)	51.9(.5)	68.8(.4)	49.2(.4)	69.5(.3)	52.0(.6)	52.2(.9)	51.0(.5)	67.6(1.1)
MgO	1.6(.1)	2.0(.2)	1.4(.1)	4.4(.3)	0.8(.1)	1.7(.2)	1.6(.2)	1.8(.2)	1.3(.0)
Total	100.3	99.9	100.0	100.3	100.6	99.1	100.1	99.2	99.5
Si	2.00	1.99	1.00	1.98	1.01	1.98	2.01	2.02	1.02
Fe	1.90	1.88	1.93	1.74	1.95	1.91	1.89	1.86	1.91
Mg	0.10	0.13	0.07	0.28	0.04	0.11	0.10	0.12	0.06
# Points	14	9	12	7	13	4	7	8	6
Run #	262 Opx	262 Oliv	263 Opx	263 Oliv	271 Oliv	254 Opx	254 Oliv	258 Oliv	261 Opx
SiO ₂	46.5(.4)	30.4(.8)	46.8(.5)	29.8(.2)	29.7(.3)	46.9(1.2)	30.2(.4)	30.0(.6)	45.8(.6)
FeO	50.0(.6)	70.1(.7)	50.1(.5)	70.1(.7)	68.2(.6)	52.1(.7)	68.3(1.2)	69.3(.7)	51.8(.5)
MgO	3.4(.2)	1.0(.2)	3.5(.2)	0.8(.1)	2.2(.2)	1.9(.1)	1.0(.0)	1.4(.0)	2.2(.1)
Total	99.9	101.5	100.4	100.7	100.1	100.0	99.5	100.7	99.8
Si	1.99	1.01	1.98	1.00	0.99	2.01	1.02	1.00	1.98
Fe	1.79	1.94	1.80	1.96	1.90	1.88	1.93	1.93	1.87
Mg	0.22	0.05	0.22	0.04	0.11	0.13	0.05	0.07	0.14
# Points	8	14	11	4	5	6	5	4	9

Table 5. (continued)

Run #	199 Opx	199 Oliv	143 Oliv	155 Opx	155 Oliv	160 Opx	160 Oliv	228 Opx
SiO ₂	46.7(.6)	30.3(.6)	31.6(.7)	46.7(.5)	31.2(.5)	45.6(1.2)	31.0(.7)	46.2(.4)
FeO	49.3(.7)	68.3(.4)	67.4(.9)	51.2(.9)	67.4(.6)	52.1(1.1)	67.0(.7)	52.6(.9)
MgO	2.1(.1)	1.4(.1)	1.3(.1)	2.0(.1)	1.4(.0)	2.2(.2)	1.5(.1)	1.6(.1)
Total	98.1	100.0	100.3	99.9	100.0	99.9	99.5	100.4
Si	2.02	1.01	1.05	2.02	1.04	1.98	1.04	2.00
Fe	1.83	1.92	1.88	1.85	1.89	1.88	1.88	1.90
Mg	0.14	0.70	0.06	0.13	0.07	0.14	0.08	0.10
# Points	5	8	5	6	5	8	7	5

Run #	261 Oliv	143 Opx	237 Opx	237 Oliv	229 Oliv
SiO ₂	30.2(.6)	46.1(1.1)	46.9(.5)	30.5(.4)	31.0(.7)
FeO	70.6(.6)	52.0(1.0)	51.0(.4)	68.5(.5)	67.5(.7)
MgO	1.4(.0)	1.8(.1)	2.3(.2)	1.3(.0)	1.6(.1)
Total	102.2	99.9	100.2	100.3	100.1
Si	0.99	2.00	2.02	1.02	1.03
Fe	1.94	1.88	1.84	1.92	1.88
Mg	0.07	0.12	0.15	0.06	0.08
# Points	8	8	6	7	4

Mg₂SiO₄. The transition from α to β quartz requires an increase in the dP/dT of the olivine-quartz-orthopyroxene reactions, but the amount of increase is not constrained by the data.

The results of our study agree quite well with the 900°C data of Smith (1971) if a small (~ 7%) nega-

tive pressure correction is applied to his data. Our data require a wider three-phase, orthopyroxene-olivine-quartz, field than is inferred by Smith. However, our data are consistent with Smith's experiments. Smith (1971) reports data obtained using an internally heated, gas apparatus where $Fa_{80}Fo_{20} +$

Table 6. Electron microprobe analyses of experimental products for Ferrosilite₉₀Enstatite₁₀ bulk composition

Run #	197 Opx	198 Opx	198 Oliv	215 Opx	215 Oliv	294 Opx	154 Opx	156 Opx	156 Oliv
SiO ₂	46.2(.5)	46.2(.7)	30.1(.5)	46.3(.8)	30.4(.2)	47.1(.4)	46.6(.8)	46.3(.9)	30.5(.3)
FeO	50.7(.9)	50.8(.9)	67.1(.6)	50.5(.5)	67.1(.6)	48.1(.6)	48.5(.8)	48.9(1.3)	68.0(1.1)
MgO	3.0(.2)	3.2(.1)	3.0(.2)	3.3(.1)	3.0(.1)	4.6(.1)	3.2(.1)	3.3(.1)	2.7(.1)
Total	99.9	100.2	100.2	100.1	100.5	99.8	98.3	98.4	101.2
Si	1.99	1.98	1.00	1.98	1.00	2.00	2.02	2.01	1.00
Fe	1.81	1.82	1.85	1.81	1.85	1.71	1.77	1.78	1.87
Mg	0.20	0.21	0.15	0.21	0.15	0.29	0.21	0.21	0.13
# Points	7	12	4	6	7	8	7	7	5

Run #	294 Oliv	165 Opx	180 Opx	180 Oliv	181 Opx	181 Oliv	239 Oliv	257 Opx	257 Oliv
SiO ₂	30.8(.8)	46.5(.6)	45.9(1.4)	30.9(.5)	46.2(.6)	30.3(.5)	30.2(.7)	47.6	30.2(.6)
FeO	67.0(.8)	51.4(.8)	50.0(1.5)	67.8(.9)	50.0(.8)	67.3(.8)	67.2(.5)	48.6	66.7(1.3)
MgO	2.5(.3)	3.0(.1)	3.3(.3)	2.5(.1)	3.6(.1)	2.6(.1)	3.4(.1)	4.6	3.3(.1)
Total	100.3	100.9	99.2	101.2	99.8	100.2	101.0	100.8	100.2
Si	1.02	1.98	1.98	1.01	1.98	1.00	0.99	2.00	1.00
Fe	1.86	1.83	1.80	1.86	1.79	1.87	1.84	1.71	1.84
Mg	0.12	0.19	0.22	0.12	0.23	0.13	0.17	0.29	0.16
# Points	5	8	4	8	8	7	5	9	3

Table 6. (continued)

Run #	161 Opx	161 Oliv	239 Opx	200 Opx	200 Oliv	264 Opx	264 Oliv	280 Opx	280 Oliv
SiO ₂	46.6(1.1)	30.2(.4)	48.5(.4)	46.0(.6)	30.6(.6)	46.9(.5)	29.7(.6)	47.1(.5)	30.8(.9)
FeO	48.7(1.2)	67.0(1.1)	48.9(.6)	49.8(.7)	65.8(.9)	47.4(.8)	67.0(.9)	48.4(.7)	66.7(1.1)
MgO	4.0(.1)	2.7(.0)	4.7(.1)	3.3(.2)	2.9(.1)	4.8(.3)	3.2(.1)	3.6(.1)	3.0(.1)
Total	99.3	99.9	102.1	99.1	99.3	99.1	99.9	99.1	100.5
Si	2.00	1.00	2.01	1.99	1.02	2.00	0.98	2.02	1.01
Fe	1.75	1.86	1.70	1.80	1.84	1.69	1.86	1.74	1.84
Mg	0.25	0.13	0.29	0.22	0.14	0.31	0.16	0.23	0.15
# Points	6	4	9	8	9	7	6	6	6

Run #	283 Opx	283 Oliv	289 Opx	290 Opx	291 Oliv	293 Opx	293 Oliv	148 Opx	148 Oliv
SiO ₂	45.3(.9)	31.0(.7)	46.2(.6)	46.2(.7)	30.2(.6)	46.6(.8)	30.1(.6)	46.3(.9)	30.8(.3)
FeO	49.2(.9)	66.4(.6)	50.8(.8)	51.5(.9)	66.1(.7)	48.5(1.1)	66.7(1.5)	49.1(.9)	66.8(1.0)
MgO	3.7(.1)	3.2(.0)	3.0(.3)	3.0(.1)	3.8(.1)	4.8(.3)	2.9(.1)	3.9(.1)	3.0(.1)
Total	98.2	100.6	100.0	100.7	100.1	99.9	99.7	99.3	100.6
Si	1.97	1.02	1.98	1.98	1.00	1.98	1.00	1.99	1.01
Fe	1.79	1.83	1.82	1.84	1.82	1.71	1.86	1.76	1.84
Mg	0.24	0.15	0.19	0.19	0.18	0.31	0.14	0.25	0.15
# Points	5	6	6	6	4	4	5	6	6

quartz reacted almost completely to $Fs_{80}En_{20}$ at 7 kbar and 900°C in 6 hours, requiring that the lower pressure limit of $Fs_{80}En_{20}$ stability lie below seven kilobars. Our experimental runs locate the equilibrium between 5.9 and 6.2 kbar at 900°C.

The distribution coefficient K_D ³ was reversed by starting with low- K_D reactants ($Fs_{95}En_5$ + $Fo_{95}Fo_5$ + quartz; $Fs_{90}En_{10}$ + $Fa_{90}Fo_{10}$ + quartz) and high- K_D reactants ($Fs_{80}En_{20}$ + 3 Fa_{100} + quartz; $Fs_{80}En_{20}$ + Fa_{100} + quartz). Microprobe analyses of coexisting olivine and orthopyroxene (Tables 5 and 6) permitted us to determine the partitioning of Fe and Mg. Because Mg-Fe exchange and changes in modal ratios of olivine and orthopyroxene occur during the experiments, the final compositions of the phases appear to overlap in Figures 4a and 4b. Nevertheless the data constrain K_D . Limiting K_D values are 2.0–2.8, 2.0–2.4, 2.0–4.8 for $Fs_{95}En_5$ bulk composition and 1.9–2.3, 1.7–2.6, 1.5–3.0 for $Fs_{90}En_{10}$ bulk composition at 1000°, 900°, and 800°C, respectively. Despite several experimental studies on the partitioning of Fe and Mg between olivine and orthopyroxene (Larimer, 1968; Matsui and Nishizawa, 1974; Medaris, 1969; Nafziger and Muan, 1967; Williams, 1971) there are few data on Fe-rich compositions, and they

do not tightly constrain K_D . It is clear from natural opx–olivine pairs (Ramberg and DeVore, 1951; Bohlen *et al.*, 1980a) and experimental data that K_D is dependent on composition and temperature. Sack

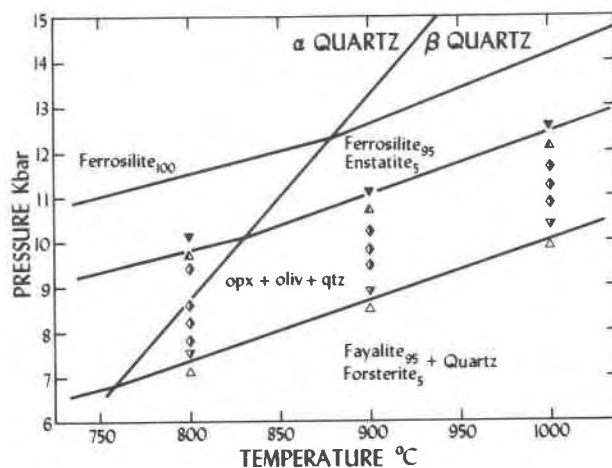


Fig. 1. Pressure-temperature projection showing the effect of 5 mole % $MgSiO_3$ on the stability of ferrosilite. ▼ indicates orthopyroxene + olivine + quartz reacted completely to opx ($Fs_{95}En_5$). ▲ indicates that orthopyroxene ($Fs_{95}En_5$) broke down to opx + oliv + qtz. ◆ indicates that reactants of opx + oliv + qtz showed little change in their relative proportions. Δ indicates that opx + oliv + qtz reacted completely to oliv ($Fa_{95}Fo_5$) + qtz. ▼ indicates that oliv ($Fa_{95}Fo_5$ + qtz) reacted to opx + oliv + qtz. Boundary for ferrosilite \rightleftharpoons fayalite + quartz from Bohlen *et al.* (1980a); α - β quartz transition from Cohen and Klement (1967).

³ The distribution coefficient K_D is the ratio of cations in coexisting minerals. $K_D^{opx-oliv}$ is calculated $(Mg^{opx}/Fe^{opx}) / (Mg^{oliv}/Fe^{oliv})$.

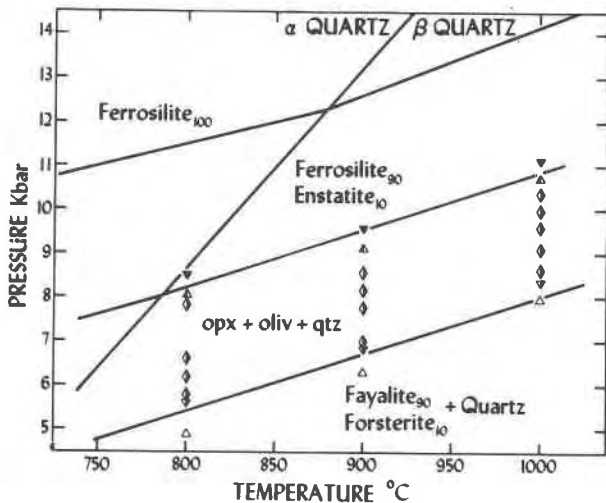


Fig. 2. Pressure-temperature projection showing the effect of 10 mole % MgSiO_3 on the stability of ferrosilite. Symbols the same as in Figure 1. Fs_{100} , Bohlen *et al.* (1980a), $\text{Fs}_{90}\text{En}_{10}$ from Figure 1, α - β quartz, Cohen and Klement (1967).

(1980) has reviewed the existing data and proposed a provisional calibration of the temperature-composition dependence of K_D . Our data indicate that $K_{D}^{\text{opx-oliv}}_{\text{Mg-Fe}}$ is significantly larger at 1000° and 900°C and may not be as sensitive to temperature (at constant bulk composition) as proposed by Sack. Still, our partitioning data do not unambiguously fix $K_{D}^{\text{opx-oliv}}_{\text{Mg-Fe}}$ and tighter reversals are necessary.

Accurate determination of $K_{D}^{\text{opx-oliv}}_{\text{Mg-Fe}}$ is necessary when formulating mixing models for these phases.

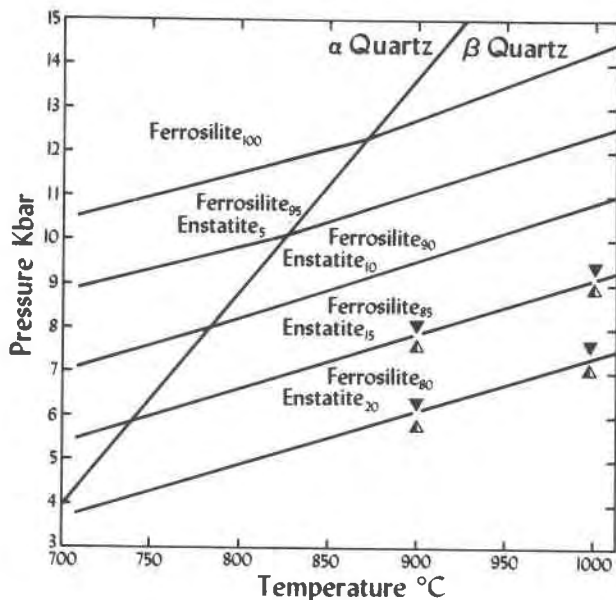


Fig. 3. Pressure-temperature projection showing relative effects of 5, 10, 15, and 20 mole % MgSiO_3 on the stability of ferrosilite. See previous figures for symbols.

For example, one can calculate a ratio of activity coefficients for fayalite in olivine ($\gamma_{\text{Fe}_2\text{SiO}_4}^{\text{oliv}}$) and ferrosilite in orthopyroxene ($\gamma_{\text{FeSiO}_3}^{\text{opx}}$), assuming that the $K_{D}^{\text{opx-oliv}}_{\text{Mg-Fe}}$ is known, using the following relation:

$$\Delta P \approx \frac{-RT(41.84)}{\Delta V_{P,T}} \ln \left(\frac{\gamma_{\text{FeSiO}_3}^{\text{opx}} X_{\text{FeSiO}_3}^{\text{opx}}}{\gamma_{\text{Fe}_2\text{SiO}_4}^{\text{oliv}} X_{\text{Fe}_2\text{SiO}_4}^{\text{oliv}}} \right)^2$$

where ΔP is the pressure shift of the reaction boundary resulting from non-endmember compositions of constituent phases as compared to the boundary for endmembers, $\Delta V_{P,T}$ is the volume change of the reaction at P and T and $X_{\text{FeSiO}_3}^{\text{opx}}$ and $X_{\text{Fe}_2\text{SiO}_4}^{\text{oliv}}$ are the mole fractions of FeSiO_3 and Fe_2SiO_4 in the orthopyroxene and olivine, respectively. Knowing the activity ratio will allow inference of Mg-Fe mixing parameters for one phase if they are known for the other. Because of the uncertainties, we hesitate to propose a mixing model and prefer to summarize the constraints placed on any mixing model by our data. Table 7 shows the calculated activity coefficient ratio for an assumed $K_{D}^{\text{opx-oliv}}_{\text{Fe-Mg}}$ constrained by our experiments (including uncertainties in phase compositions as determined by microprobe). If activity coefficients are between 1 and 1.01 as deduced from the data of Saxena and Ghose (1971) for Fe-rich orthopyroxene compositions between 800° and 1000°C, then it can be seen from Table 7 that the data require olivine solutions to be nearly ideal, in accord with the results of Engi (1980). However, if orthopyroxene solutions are nearly ideal (for these temperatures and compositions), as suggested provisionally by Sack (1980), then our data require that olivine solutions show slight negative deviations from ideality. In either case, the activity coefficient ratio is very sensitive to the assumed K_D .

Free energy and heat of formation (from the elements) have been calculated for ferrosilite from the experiments of Bohlen *et al.* (1980a), see Table 8. These data were calculated using ΔG_T° and S_T° for fayalite and quartz from Robie *et al.* (1978), but using $S_{298}^\circ = 152.13 \text{ J/mol K}$ for fayalite as determined by Essene *et al.* (1980), and assuming that $\Delta V_{\text{reaction}}^{\text{PT}} = \Delta V_T^\circ + \Delta V_{298}^{\text{PT}} - \Delta V_{298}^\circ$. Thermal expansion and compressibility are from published values.⁴ Entropy of ferrosilite was estimated assuming $S_T^\circ \approx S_{T}^{\circ} \text{MgSiO}_3 + 1/$

⁴ Volume data and thermal expansion data for fayalite and ferrosilite are from Smyth (1975) and Sueno *et al.* (1976), respectively; quartz from Robie *et al.* (1967) and Skinner (1966). Compressibility data for fayalite and quartz are from Yagi *et al.* (1975) and Birch (1966), respectively. Ferrosilite is assumed to be slightly less compressible than enstatite; enstatite compressibility is from Olinger (1977).

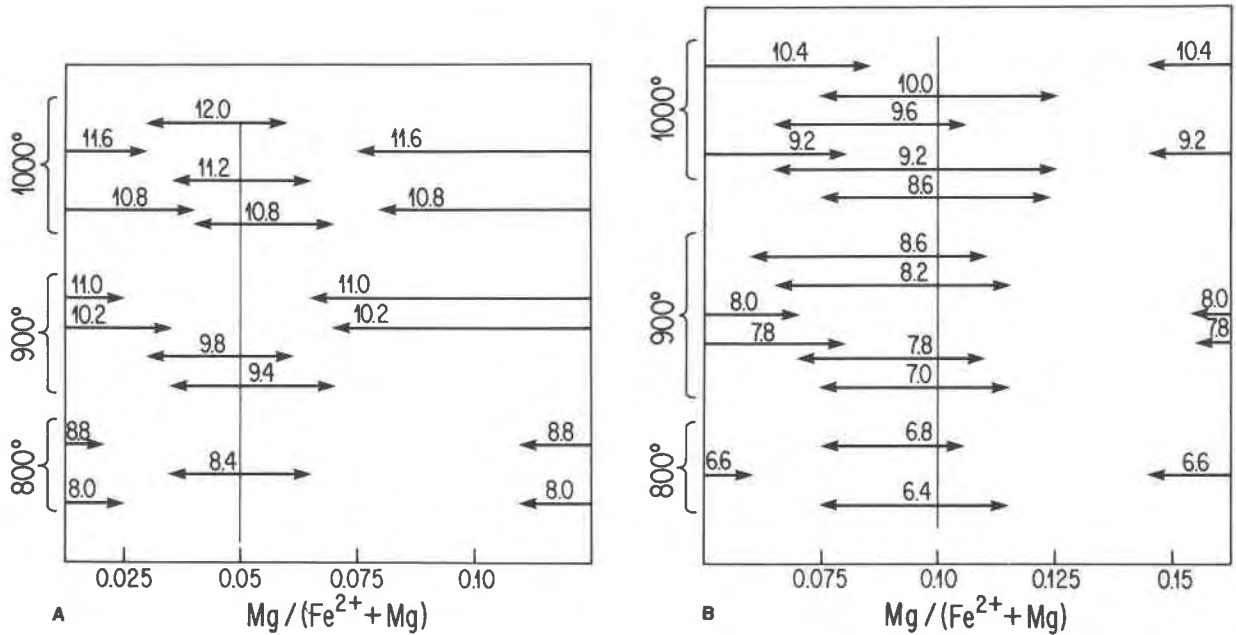


Fig. 4. (a) Compositions of coexisting olivine and orthopyroxene determined by electron microprobe analyses of run products. \longleftrightarrow indicate composition of coexisting phases whose reactants were $Fs_{95}En_5 + Fa_{95}Fo_5 + Qtz$. $\rightarrow\leftarrow$ indicate compositions of coexisting phases whose reactants were $Fs_{80}En_{20} + 3Fa_{100} + Qtz$. (b) Coexisting phases for $Fs_{90}En_{10}$ bulk composition. Symbols are the same as in 4a, reactants were $Fs_{90}En_{10} + Fa_{90}Fo_{10} + Qtz$ and $Fs_{80}En_{20} + Fa_{100} + Qtz$. Pressure indicated above arrows are in kbar.

$2 S_{TFe_2SiO_4}^\circ - 1/2 S_{TMg_2SiO_4}^\circ$ ($S_{MgSiO_3}^\circ$ from Krupka *et al.*, 1979; $S_{Mg_2SiO_4}^\circ$ from Robie *et al.*, 1978). The estimated entropy agrees with those calculated from the dP/dT of the experimentally determined reaction. Data below 1000 K were calculated by extrapolating the experimental results to lower temperatures. An error of up to ± 6 kbar in the extrapolated location of the reaction produces less than ± 2 kJ in the calculated free energy data because the $\Delta V_{\text{reaction}}$ is extremely small. The total estimated uncertainty in ΔG_T° for ferrosilite is ± 7 kJ/mol. Errors in ΔH_T° are difficult to evaluate as they depend on the estimated S_T° . The estimated entropy might be accurate to within 3–5% resulting in errors of ± 10 –15 kJ/mol in ΔH_T° .

Geobarometry

Experimental results from this and previous studies provide a precise calibration of the effects of Mg and Mn on the stability of Fe-rich orthopyroxenes, which, in turn, yields a widely applicable geobarometer. The geobarometer is imprecise to the extent that the effect of minor proportions of other components, notably Ca, Fe^{3+} , and Al, must be estimated, but these elements typically comprise less than five mole % of most Fe-rich orthopyroxenes, hence, any errors in the estimated effects of uncalibrated additional components will not affect the inferred pressures sig-

nificantly. Additionally, the barometer is temperature dependent, but an uncertainty of 50° yields a pressure uncertainty of only 0.7 kbar. With these problems in mind, we have applied this geobarometer to terranes throughout the world for which data on Fe-rich orthopyroxenes are available (Table 9). We have estimated the effects of small amounts of uncalibrated components using an ideal ionic model (see Bohlen *et al.*, 1980a). For several localities, equilibration temperatures were estimated from mineral assemblages coexisting with the orthopyroxene and on general petrologic descriptions. For pyroxene compositions outside of the limits of experimental investigation, pressure estimates are based on linear extrapolations of the experimental data. However, extrapolations are generally less than a few mole % and are probably not significantly in error. Many of the pyroxenes do not coexist with olivine and quartz, consequently only minimum pressure can be inferred. Nevertheless, note that pressure data can be inferred from assemblages spanning a broad range of composition and temperature. We have omitted localities where maximum pressures are constrained by olivine + quartz. Fayalite granites are common, but in most cases the olivine is nearly pure Fe_2SiO_4 ; the pressure limits are not very restrictive. A few localities contain numerous Fe-rich orthopyroxene and/

Table 7. Experimentally constrained activities for orthopyroxene and olivine

T (°C)	ΔP (kbar)	K_D Mg-Fe opx-oliv	$\gamma_{\text{opx}}/\gamma_{\text{oliv}}$ FeSiO ₃ /Fe ₂ SiO ₄
1000	1.9±0.2	1.9	1±0.005
		2.4	1.006
		2.8	1.01
900	1.7±0.2	1.9	1±0.005
		2.2	1.004
		2.4	1.007
800	1.7±0.2	2.2	1±0.005
		3.0	1.006
		4.0	1.009
1000	3.2±0.2	1.7	1±0.005
		1.9	1.007
		2.3	1.007
900	3.2±0.2	1.8	1±0.005
		2.1	1.007
		2.6	1.016
800	3.3±0.2	2.1	1±0.005
		2.6	1.005
		3.0	1.011

or (olivine + quartz)-bearing assemblages that constrain metamorphic pressures. These are discussed below.

Adirondack Mountains, New York

Numerous assemblages containing orthopyroxenes with $\text{Fe}^{2+}/(\text{Fe}^{2+}+\text{Mg}) \geq 0.75$ have been reported from the Adirondacks of upper New York State (see footnote to Table 9). Of these several place important barometric constraints on metamorphic conditions: $\text{Fs}_{91}\text{En}_5\text{Rh}_2\text{Wo}_2$ reported by Jaffe *et al.* (1978) and $\text{Fs}_{90}\text{En}_6\text{Rh}_2\text{Wo}_2$ reported by Bohlen *et al.* (1980a) require $P \geq 7.8$ kbar for temperatures of 750–770°C (Bohlen *et al.*, 1980c) in the Mount Marcy area (central Adirondack Highlands). Occurrences of coexisting akermanite + monticellite + wollastonite in the same area requires $P \geq 7 \pm 1$ kbar at 750°C (Valley and Essene, 1980), suggesting that the minimum pressures required by ferrosilite-rich orthopyroxenes are very close to the peak metamorphic pressures. Approximately 25 km NNE of the Mount Marcy area near Au Sable Forks, Bohlen and Essene (1979) report olivine ($\text{Fa}_{95}\text{Fo}_3\text{Te}_2$) + quartz. This assemblage restricts pressures to < 7.5 kbar at 700°C (Bohlen *et al.*, 1980c). In the central Adirondacks near Benson Mines, Jaffe *et al.* (1978) report olivine ($\text{Fa}_{96}\text{Fo}_1\text{Te}_3$) + quartz which restricts $P < 9.0$ kbar for 690°C. A few kilometers away $\text{Fs}_{89}\text{En}_9\text{Rh}_1\text{Wo}_1$ (Bohlen, unpublished data) requires $P \geq 7.0$ kbar at

700°C. Sillimanite in this area reduces the uncertainty to $7.8 \geq P \geq 7.0$ at 700°C (Richardson *et al.*, 1968). Finally, in the south-central Adirondacks near Blue Mountain Lake, Bohlen *et al.* (1980a) report $\text{Fs}_{89}\text{En}_8\text{Rh}_2\text{Wo}_1$ which requires $P \geq 7.5$ kbar for 740°C. This minimum pressure is in agreement with nearby occurrences of sillimanite and a single occurrence of kyanite (Boone, 1978) for which a pressure of 8 kbar is inferred. Pressures inferred from these Fe-silicate bearing assemblages are also in good agreement with other barometers (Bohlen *et al.*, 1980a; Valley and Essene, 1980).

Lofoten-Vesterålen, Norway

The Lofoten-Vesterålen province is a granulite-garnet granulite facies terrane along the northern coast of Norway (Griffin and Heier, 1969, 1973; Griffin *et al.*, 1974; Krogh, 1977; Ormaasen, 1977). Table 9 lists a few of the Fe-rich orthopyroxenes reported from the area. In the northeastern part of the terrane in the Raftsund mangerite, Griffin and Heier (1973) and Griffin *et al.* (1974) report $\text{Fs}_{81}\text{En}_{15}\text{Rh}_3\text{Wo}_1$ and $\text{Fs}_{79}\text{En}_{14}\text{Rh}_5\text{Wo}_2$, respectively, both of which require minimum pressures of ~6.7 kbar for their estimated temperature of 900°C. The latter occurs with olivine but quartz is only present in trace amounts. If the olivine-quartz-orthopyroxene were in equilibrium during metamorphism, then the inferred minimum pressure might be close to the peak metamorphic pressure. Near the western margin of the Raftsund mangerite Krogh (1977) reports $\text{Fs}_{75}\text{En}_3\text{Rh}_{22}\text{Wo}_0$ that coexists with a manganese pyroxferroite and indicates a pressure of ≥ 8 kbar at 800°C. Fifty kilometers to the southwest in the Hopen massif, Ormaasen reports $\text{Fs}_{92}\text{En}_2\text{Rh}_5\text{Wo}_1$ that occurs as coronas

Table 8 Entropy, heat of formation, and free energy data for FeSiO₃

TK	$S_T^{\circ 1}$ (J/mol K)	$S_T^{\circ 2}$ (J/mol K)	$\Delta H_T^{\circ 3}$ (kJ/mol)	ΔG_T° (kJ/mol)
			Formation from the elements	
298	94.5	(95.4) ⁴	-1194.9	-1117.3
uncertainty	?		?	±6.0
400	122.5	(123.7)	-1194.4	-1090.8
500	145.9	(147.5)	-1193.4	-1065.0
600	166.1	(168.3)	-1192.2	-1039.5
700	183.9	(186.6)	-1191.0	-1014.1
800	199.9	(203.2)	-1189.8	-989.0
900	214.5	218.2	-1188.7	-963.8
1000	227.7	231.5	-1188.9	-938.8
1100	240.0	243.9	-1189.5	-913.8
1200	250.9	255.5	-1189.1	-888.8
1300	262.3	265.8	-1187.8	-863.9
1400	272.5	276.3	-1185.5	-839.2

1 Estimated: $S_T^{\circ} \text{FeSiO}_3 = S_T^{\circ} \text{MgSiO}_3 + \frac{1}{2} S_T^{\circ} \text{Fe}_2\text{SiO}_4 - \frac{1}{2} S_T^{\circ} \text{Mg}_2\text{SiO}_4$

2 Calculated from dP/dT of experimental determination of the reaction $\text{Fe}_2\text{SiO}_4 + \text{SiO}_2 = 2\text{FeSiO}_3$

3 Calculated using entropies inferred from experimental data

4 Values in parenthesis are estimated assuming $dP/dT = 10\text{b}/^\circ\text{C}$

Table 9. Pressures inferred from orthopyroxene + olivine + quartz barometry

Reference	Locality	Composition	T(°C)	Pressure (Kbar) ¹
Jaffe <i>et al.</i> (1978)	Adirondacks, N.Y. ²	Fs ₉₁ En ₅ Rh ₂ Wo ₂	750	≥7.8
Bohlen <i>et al.</i> (1980)	Adirondacks, N.Y. ²	Fs ₉₀ En ₆ Rh ₂ Wo ₂	760	≥7.8
Howie (Deer <i>et al.</i> , 1963)	Baffin Is.	Fs ₇₆ En ₂₁ Rh ₁ Wo ₂	(750) ³	≥3.0
Bonnichsen (1969)	Duluth Gabbro, Minn. ⁴	Fs ₇₄ En ₂₃ Rh ₀ Wo ₃	725	~2.0
Howie (1963, in Howie & Smith, 1966)	Gabon	Fs ₇₇ En ₂₀ Rh ₁ Wo ₂	(700)	≥3.0
Frisch and Bridgwater (1976)	Greenland, southern	Fs ₇₇ En ₁₅ Rh ₆ Wo ₂	800	~4.5
Ramberg and DeVore (1951)	Greenland	Fs ₈₄ En ₁₄ Rh ₁ Wo ₂	(750)	≥5.0
Zhang <i>et al.</i> (pers. comm.)	Hobie Province, China	Fs ₈₆ En ₁₂ Rh ₀ Wo ₂	750	~6.0
Klein (1978)	Labrador Trough ⁵	Fs ₉₄ En ₅ Rh ₁ Wo ₁	700	≥8.8
Bown (1965) (Bowen, 1935)	Lake Naivasha, Kenya	Fs ₉₅ En ₀ Rh ₅ Wo ₀	?	?
Ormaasen (1977)	Lofoten, Norway	Fs ₉₂ En ₂ Rh ₅ Wo ₁	800	~9.5 ⁶
Griffen and Heier (1969)	Lofoten-Vesterålen, Norway	Fs ₉₀ En ₆ Rh ₀ Wo ₂	(800)	≥7.8 ⁷
Griffen <i>et al.</i> (1974)	Lofoten-Vesterålen, Norway	Fs ₇₉ En ₁₄ Rh ₅ Wo ₂	900	~6.7
Krogh (1977)	Lofoten-Vesterålen, Norway	Fs ₇₅ En ₃ Rh ₂ Wo ₀	800	≥8.0 ⁸
Tsuru and Henry (1937)	Manchuria (Yu hsi kou)	Fs ₇₇ En ₁₁ Rh ₉ Wo ₃	(700)	≥4.5
Kuno (1954)	Manchuria (Je-ho-shen)	Fs ₈₆ En ₁₂ Rh ₀ Wo ₂	(700)	≥6.0
Henry (1935)	Mansjö Mtn. Sweden	Fs ₇₉ En ₁₆ Rh ₂ Wo ₃	(700)	≥4.0
Smith (1974)	Nain, Labrador	Fs ₈₀ En ₁₆ Rh ₁ Wo ₃	900? ⁹	~6.0
Berg (1977)	Nain, Labrador	Fs ₇₈ En ₁₈ Rh ₂ Wo ₂	750	~3.8
Howie (1958, in Howie & Smith, 1966)	Natal, Rep. of South Africa	Fs ₈₀ En ₁₆ Rh ₂ Wo ₂	(750)	≥4.6
Larsen and Draisin (1950)	Riverside, CA	Fs ₇₃ En ₂₄ Rh ₃ Wo ₂	(850)	≥2.0
Sundius (1932)	Tunaberg, Sweden	Fs ₇₅ En ₁₆ Rh ₇ Wo ₂	(750)	≥3.5
Schreyer <i>et al.</i> (1978)	Vreddefort, Rep. of South Africa	Fs ₇₅ En ₁₉ Rh ₄ Wo ₂	700? ⁹	≥3.0

1 Pressure estimates are based on the pyroxene compositions listed in this table with adjustments for minor (<5 mole %) additional components involving Fe³⁺, Al, Ti, Na, etc.

2 These analyses represent the most iron-rich orthopyroxenes found to date in the Adirondacks and are of the greatest significance for barometry. Numerous analyses of orthopyroxenes with Fe²⁺/(Fe²⁺+Mg)>0.75 have been reported by Buddington and Leonard (1962), deWaard (1970), Davis (1971), Jaffe *et al.* (1978), and Bohlen *et al.* (1980). Orthopyroxenes with Fe²⁺/(Fe²⁺+Mg)=0.75-0.90 are quite common in charnockites and quartz mangerites in the Adirondack Highlands.

3 Temperatures in parentheses are estimated.

4 A somewhat less iron-rich pyroxene (Fs₇₁En₂₆Rh₁Wo₄) has been reported by Simmons *et al.* (1974) in similar rocks from the contact aureole of the Duluth Gabbro.

5 In the same area, Kranck (1961) reports an orthopyroxene of composition Fs₇₁En₁₂Rh₁₃Wo₄. This pyroxene is of lesser significance for barometry than that reported by Klein.

6 The pressure given is probably a minimum pressure. Even though the orthopyroxene coexists with olivine and quartz, textures indicate that opx is growing at the expense of olivine+quartz. If the orthopyroxene grew as the terrane cooled isobarically, the inferred pressure may be near or slightly above peak metamorphic pressure.

7 The orthopyroxene coexists with olivine but primary quartz is present only in trace amounts. No data for manganese were included in the analysis.

8 The orthopyroxene coexists with a manganoan-pyroxferroite.

9 The equilibrium temperature is uncertain since the pyroxene composition given is the host composition of a pyroxene containing augite exsolution lamellae. The temperatures are probably lower than those given requiring a reduction in the inferred pressure.

around olivine, indicating that orthopyroxene is growing at the expense of olivine + quartz and suggesting a minimum pressure of 9.5 kbar at 800°C. However, if the orthopyroxene grew as the terrane cooled nearly isobarically, as Ormaasen proposes, the inferred pressure might be near or slightly above the peak metamorphic pressure. In the southwestern portion of the terrane, approximately 60 km southwest of the Hopen massif, Griffin and Heier (1969) report Fs₉₀En₈Rh₀Wo₂ for which a minimum pressure of 8 kbar at 800°C is required. These Fe-rich orthopyroxenes in the Lofoten-Vesterålen terrane indicate high metamorphic pressures of 7-10 kbar over a

broad area. A case might be made for higher pressure rocks toward the center and somewhat lower pressure rocks toward the margins of the exposed terrane. However, metamorphic temperatures are not unambiguously defined because of the intrusion of igneous bodies into the metamorphic terrane and constraints on maximum pressures are lacking in some areas.

Nain Complex, Labrador

Berg (1977) reports five orthopyroxene + olivine + quartz assemblages in the contact aureoles of the Nain anorthosite complex which define pressures in

the terrane. The compositions of the pyroxenes lie outside the investigated range, but only a short extrapolation of the experimental data is required to infer pressures. These data indicate that metamorphic pressures were quite similar (3.2 ± 0.2 kbar) in three widely separate localities suggesting that the regional pressure gradient proposed by Berg (1977) may not exist. If one assumes that the assemblages are isobaric, the data require the substantial differences in equilibration temperatures, inferred by Berg using various thermometers. This demonstrates that coexisting orthopyroxene + olivine + quartz in some cases might be used for thermometry.

Conclusion

Experimental data on the effect of Mn and Mg on the stability of orthopyroxene can be used to infer metamorphic pressures in numerous terranes, assuming metamorphic temperatures are reasonably well known. Occurrences of ferrosilite described by Bowen (1935) and Bown (1965) are not explained by the data. Based on the experimental data, we conclude, as Smith (1971) did, that these occurrences result from metastable crystallization. Pressures inferred from near end-member ferrosilites found in the Adirondacks, Labrador Trough, and Lofoten-Vesterålen indicate that the terranes were buried in excess of 25 km. These terranes are presently underlain by crustal thickness of 25–40 km, which suggests that thick (50–75 km) continental crust was not uncommon by mid-to-late Proterozoic. Alternatively, the observed crustal thickness might have resulted from tectonic underplating (O'Hara, 1977) after equilibration of Fe-rich-orthopyroxene assemblages at the base of the Proterozoic crust. Convincing arguments for such a model have yet to be presented.

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