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REINVESTIGATION AND APPLICATION OF OLIVINE-QUARTZ-ORTHOPYROXENE BAROMETRY

STEVEN R. BOHLEN * and ERIC J. ESSENE

Department of Geology and Mineralogy, University of Michigan, Ann Arbor, MI 48104 (U.S.A.)

A.L. BOETTCHER

*Institute of Geophysics and Planetary Physics and Department of Earth and Space Sciences, University of
California at Los Angeles, Los Angeles, CA 90024 (U.S.A.)*

Experiments in a piston-cylinder apparatus have been carried out at 700–1050°C, 10–16 kbar to determine the
stability of ferrosilite (FeSiO$_3$) relative to fayalite + quartz. Reaction reversals within 0.1-kbar intervals locate the
equilibrium at 10.5, 11.0, 11.5, 12.0, 12.6, 13.3, 14.1 and 14.8 kbar at 700, 750, 800, 850, 900, 950, 1000, and
1050°C, respectively, reflecting the intercept with the α-β quartz transition at about 880°C. The tight reversals
severely constrain the reaction slope, providing a basis for limited extrapolation and calculations. However, the lack
of accurate activity and cation-distribution data for orthopyroxene and olivine generates substantial uncertainties
when considering the effects of large proportions of additional components such as MgO. Experiments and cal-
culations indicate that additional components dramatically extend the pyroxene stability field and that pressures
that have been inferred from ferrosilite-rich pyroxenes in natural assemblages are 1–3 kbar too high.

1. Introduction

In the pioneering experiments on the MgO-FeO-SiO$_2$ system, Bowen and Schairer [2] have shown
that fayalite-quartz is the stable assemblage relative
to the compositionally equivalent iron pyroxene,
FeSiO$_3$, at atmospheric pressure. Other workers [3–5] have shown that FeSiO$_3$ is a stable phase at high
pressures. More recently Smith [1] and Wood and
Strens [6] have attempted to experimentally calibrate
parts of the Fe$_2$SiO$_4$-SiO$_2$ and Fe$_2$SiO$_4$-Mg$_2$SiO$_4$-SiO$_2$ systems. Smith [1] has determined the pres-

sure-temperature dependence of the reaction:

$$2 \text{ FeSiO}_3 \rightleftharpoons \text{Fe}_2\text{SiO}_4 + \text{SiO}_2$$
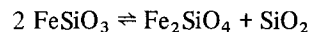
and has also experimentally evaluated the effect of
MgO on the orthopyroxene-olivine-quartz system at
900°C. Wood and Strens [6] experimentally investi-
gated the Fe$_2$SiO$_4$-Mg$_2$SiO$_4$-SiO$_2$ system with up to
40 mole % Mg$_2$SiO$_4$ at 1100°C and 1250°C and have
thermodynamically modeled the system for all
relevant *P-T*. These investigators have emphasized the
potential of the system for use as a geobarometer,
and within the past few years a number of workers
[7–9] have applied this barometer to natural Fe-rich
orthopyroxene and/or olivine-quartz assemblages.
However, because of uncertainties in pressure correc-
tions in piston-cylinder apparatus and a lack of tight
reversals constraining reaction slopes, there may be
significant error in estimation of metamorphic
pressures using this system. Additionally, the experi-

* Present address: Institute of Geophysics and Planetary
  Physics, University of California at Los Angeles, Los
  Angeles, CA 90024, U.S.A.

mental data and extrapolations of the data in the Fe_2SiO_4-Mg_2SiO_4-SiO_2 system have been applied to natural assemblages without proper regard for substantial amounts of additional components in orthopyroxene, typically up to 1.5 wt.% CaO, 4 wt.% MnO, and 1 wt.% Al_2O_3. Data from natural orthopyroxene-olivine-quartz assemblages indicate that Ca and Al are very strongly partitioned into the pyroxene while Mn shows slight preference for pyroxene. Qualitatively the effect of these impurities is to extend the stability of pyroxene. However, with the exception of MnO [11] (see following paper), the magnitude of the necessary pressure correction is uncertain. In applying the barometer, this effect has generally been ignored. Ferrosilite component in orthopyroxene has usually been calculated as $Fe^{2+}/(Fe^{2+} + Mg)$, and an equilibrium pressure inferred on that basis. However, both field data and thermodynamic calculations suggest that the magnitude of the shift in orthopyroxene-olivine-quartz equilibria, because of impurities such as Ca, Mn, Ti, Al^{VI}, Al^{IV}, Fe^{3+}, etc., is substantial and must be considered. In the Adirondack Highlands, for instance, Jaffe et al. [9] have inferred minimum pressures of 9–11 kbar based on the occurrence of ferrosilite (Fs_{95} *) for metamorphic $T = 780 \pm 50°C$ [12,13]. However, any pressure estimates greater than 9.7 kbar are inconsistent with nearby sillimanite localities, Pressure estimates of greater than 7 kbar are inconsistent with an akermanite occurrence at Cascade Slide [14,15] only a few kilometers from the ferrosilite$_{95}$ locality. Similar inconsistencies also noted from other field areas (Nain [7], Greenland [8], and Norway [10,45]) suggest that this barometer, as it has been applied thus far, apparently yields pressures that are about one to three kilobars too high. Consequently, we have undertaken an experimental and theoretical re-evaluation of this important barometer.

2. Experimental methods

2.1. Starting materials

Starting materials were prepared from electrolytically reduced Fe powder and natural quartz from

* Pyroxene and olivine compositions cited in this paper refer to the ratio $Fe^{2+}/(Fe^{2+} + Mg)$ unless otherwise specified.

Brazil. An equimolar mixture of Fe + quartz was reacted in a CO_2/H_2 gas mixing furnace at approximately 1100°C and $f_{O_2} \simeq 10^{-13}$ for 3 days with grinding to approximately −200 mesh every 12 hours. The fayalite was then analyzed by optical, X-ray and electron microprobe techniques to insure that it was homogeneous and stoichiometric and did not contain any inclusions of unreacted Fe metal. This mixture was then reacted in a piston-cylinder device using silver capsules with 1 wt.% H_2O at approximately 20 kbar and 900°C (~24 hours) to synthesize ferrosilite ($FeSiO_3$). The run product (pyroxene with traces of quartz) was also analyzed by optical, X-ray, and microprobe to insure that the pyroxene was homogeneous and stoichiometric. Small excesses of SiO_2 were used in the synthesis of orthopyroxene and olivine to ensure complete reactions and to saturate the vapor phase in runs where water was used to enhance reaction rate. These two starting materials as well as $FeSiO_3$ synthesized in a 48-hour run (at 20 kbar, 900°C and 2 wt.% H_2O) were analyzed with Mössbauer spectroscopy to check for Fe^{3+}. Spectra were collected for approximately 72 hours, and no Fe^{3+} was detectable in any of the starting materials (the limit of detection was <1% of the total Fe) (Dollase, written communication; see also following paper.)

2.2. Capsules and run procedure

Although the f_{O_2} in our furnace assemblies for the piston-cylinder apparatus is buffered at values near those of Ni-NiO (Hill and Boettcher, unpublished), which is somewhat above the stability of fayalite, no magnetite was found in any of the run products. Consequently, no external solid buffer was deemed necessary. For every run an equimolar amount of ferrosilite and fayalite-quartz was sealed in silver (Ag_{100}) capsules. For runs of ⩽900°C approximately 1 wt.% H_2O was also loaded in the capsules to help promote reaction rates. Experiments above 900°C were run dry.

All experiments were in a piston-cylinder apparatus similar to that described by Boyd and England [16]. For all runs we used a 25.4-mm-diameter furnace assembly and piston (Boettcher, in Johannes et al. [17]). Capsules were placed horizontally in the notched top surface of a cylinder of boron nitride

that overlay a cylinder of talc and disc of pyrophyllite. To avoid contamination of the thermocouple a strip of Pt foil was placed between the capsule and the thermocouple, which passed successively through cylinders of Solenhofen limestone, pyrophyllite and boron nitride in the upper part of the furnace assembly. These were surrounded by a cylindrical graphite furnace inside a cylinder of talc with a ring of fired pyrophyllite at the base of the talc cylinder. The entire assembly was surrounded by a sheet of lead foil and lubricated with a slurry of MoS_2 and perfluorkerosene. Temperatures were measured by $Pt-Pt_{90}Rh_{10}$ thermocouples. No correction for the effect of pressure on emf was applied.

For every experiment we used the piston-in method [17]. First, a pressure of roughly 10% below that to be maintained during the run was applied to the furnace assembly. The temperature was then increased to the appropriate value over a period of approximately 10 minutes. Finally, the pressure was increased to the desired value. A pressure correction of −6% was applied. This correction was determined by comparison with the LiCl melting curve [18] and the albite-quartz-jadeite boundary [17] as corroborated by the hydrostatic determinations of Hays and Bell [19].

All run products were analyzed optically and by X-ray diffraction. For most runs (see Table 1) reaction direction was immediately obvious by optical examination. For those runs where ferrosilite, fayalite and quartz were all present in significant amounts, a change in X-ray peak intensities was used to infer reaction direction. A change of X-ray peak intensities of less than 20% was taken as "no reaction". Many (approximately 15) of the run products were analyzed by electron microprobe. The fayalite and ferrosilite were analyzed on the automated ARL-EMX electron microprobe analyzer at UCLA using wavelength dispersive ADP and LiF crystals, with synthetic fayalite, magnetite, and a natural spessartine-rich garnet (to check SiO_2 against fayalite) as standards. Spectrometer data were reduced using the correction procedures of Bence and Albee [20]. We checked for the presence of any other elements besides Si and Fe by analyzing run products using EDA with counting times up to 1000 seconds under conditions that would have easily allowed detection of elements $Z \geqslant$ Na at levels of 0.1 wt.%, were any present. These

results indicate that within the capabilities of the analytical techniques, the ferrosilite and fayalite are homogeneous and stoichiometric.

Microprobe analyses of Adirondack iron-rich orthopyroxenes (Table 2) were obtained using an ARL-EMX microprobe analyzer at the University of Michigan with wavelength dispersive LiF, PET, and TAP crystal spectrometers. Microprobe procedures identical to those used in this study are described in detail in Bohlen and Essene [21].

3. Experimental results and discussion

Results from the piston-cylinder experiments are listed in Table 1 and plotted in Fig. 1. The reversals locate the equilibrium boundary between ferrosilite

TABLE 1

Run data

Run No.	T (°C)	P (kbar)	Duration (hours)	Products
46	700	10.5	48	fayalite + qtz + fs
47	700	10.6	48	fs + fayalite + qtz
93	750	11.0	22	fs + (fayalite + qtz)
94	750	10.8	23	fayalite + qtz + (fs)
30	800	11.0	18.5	fayalite + qtz
31	800	11.2	15	fayalite + qtz + (fs)
36	800	11.4	22	fayalite + qtz + (fs)
38	800	11.5	12	fayalite + qtz + fs
42	800	11.6	22	fs + fayalite + qtz
39	850	11.8	19	fayalite + qtz
41	850	12.0	23.5	fs + (fayalite + qtz)
11	900	13.5	23.5	fs
12	900	12.0	19	fayalite + qtz
13	900	12.5	21	fayalite + qtz + (fs)
14	900	13.0	23	fs + (fayalite + qtz)
15	900	12.7	23	fs + (fayalite + qtz)
16	900	12.6	24	fs + (fayalite + qtz)
92	950	13.3	19	fayalite + qtz (fs)
89	950	13.4	23	fs + (fayalite + qtz)
20	1000	14.5	23	fs
22	1000	14.0	26	fayalite + qtz
24	1000	14.3	22.5	fs + fayalite + qtz
26	1000	14.2	24.5	fs + (fayalite + qtz)
28	1000	14.1	20	fs + (fayalite + qtz)
27	1050	15.3	21	fs
29	1050	15.0	9	fs + (fayalite + qtz)
33	1050	14.8	16	fayalite + qtz (fs)

Italics indicate dominant phase(s).
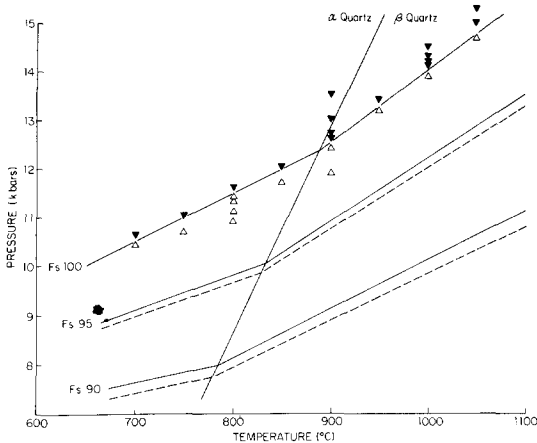Parentheses indicate very minor to trace amounts.

Fig. 1. Pressure-temperature projection for ferrosilite $\leftrightarrows$ fayalite + quartz. ▼ indicates that ferrosilite grew from fayalite-quartz; △ indicates that ferrosilite broke down to fayalite-quartz. The calculated effect of 5 and 10 mole % $MgSiO_3$ on pyroxene stability is shown for K_D defined by Fig. 3. The solid line indicates the effect using the activity data of Saxena and Ghose [33]; the dashed line indicates the effect assuming $a_{FeSiO_3} = (X_{Fe})^2$.

and fayalite-quartz reproducibly to within 0.1 kbar. The boundary changes slope from $dP/dT = 10$ bar/°C to $dP/dT = 15$ bar/°C where it intersects the α-β quartz transition [22]. This change agrees precisely with that calculated from entropy and volume data [49] (assuming the change in the ΔS reaction = ΔS α-β quartz at T, P of intersection of ferrosilite breakdown with α-β quartz), but only if the volumes of the solid phases are corrected for thermal expansion and compressibility. The reversals agree well with those of Smith [1] if a −8% pressure correction is applied to his uncorrected, nominal pressures. Our uncorrected data pass through two of three of Smith's reversals. Only at 900°C do our uncorrected data fail to pass through his reversal, but even there the two data sets disagree by less than 0.2 kbar. In short, there is excellent agreement between the two studies considering that Smith used 12.7-mm furnace assemblies with a modified piston-out technique and we used piston-in with 25.4-mm furnace assemblies.

4. Effect of additional components

Perhaps the most significant of all diluents in the Fe_2SiO_4-SiO_2 system is Mg_2SiO_4. Previous workers

have expended much effort to model or experimentally calibrate the effect of Mg^{2+} on orthopyroxene-olivine-quartz stability. Smith [1] experimentally investigated the effect of Mg_2SiO_4 on the system at 900°C and showed how small amounts of $MgSiO_3$ in $FeSiO_3$ dramatically extend pyroxene stability. Unfortunately Smith did not reverse the position of the three-phase olivine-quartz-pyroxene field and did not analyze his run products by microprobe. As a result, the position of the three-phase loop is not tightly constrained, and the experiments cannot be used as a solid basis from which to extrapolate the effect of $MgSiO_3$ solution on pyroxene stability to other P-T-X conditions. Accurate location of the three-phase loop is equivalent to experimentally reversing the K_D *, which is important in modeling the effect of additional components.

Successful thermodynamic modeling of Fe_2SiO_4-Mg_2SiO_4 depends on several factors, perhaps the most important of which is the need for accurate activity data. Other factors such as the change in $\Delta V_{reaction}$ with P and T and the change in $K_{D\,Mg\text{-}Fe}^{opx\text{-}oliv}$ with composition can further complicate matters. Fig. 2 shows the volume change of the reaction as a function of P-T. It can be seen that the $\Delta V_{reaction}$ is quite small and that changes of molar volumes as a function of P-T result in changes of up to 20% in the $\Delta V_{reaction}$ in the P-T range of interest. We have assumed that $\Delta V_T^P = \Delta V_T^0 + \Delta V_{298}^P° - \Delta V_{298}^0°$ (high-temperature volume data from Skinner [26], Smyth [27], Sueno et al. [28], using compressibility data from Birch [50], orthopyroxene compressibility estimated from other pyroxenes), and small errors could remain in the calculated ΔV_T^P.

Fig. 3 shows Mg-Fe distribution data for coexisting Fe-rich olivine and orthopyroxene from several field areas where the assemblages equilibrated at approximately the same temperature (800 ± 50°C) [7,8,29, 30]. The diagram shows the effect of composition on K_D, an effect that was originally noted by Ramberg and DeVore [51]. Other parameters such as P and T apparently have little effect on K_D within the conditions of interest [31,32]. The effect of composition

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* K_D, the distribution coefficient is defined as the ratio of cations in coexisting minerals. For example $K_{D\,Mg\text{-}Fe}^{opx\text{-}oliv}$ is calculated: $K_{D\,Mg\text{-}Fe}^{opx\text{-}oliv} = [Mg^{opx}/Fe^{opx}]\,[Fe^{oliv}/Mg^{oliv}]$.
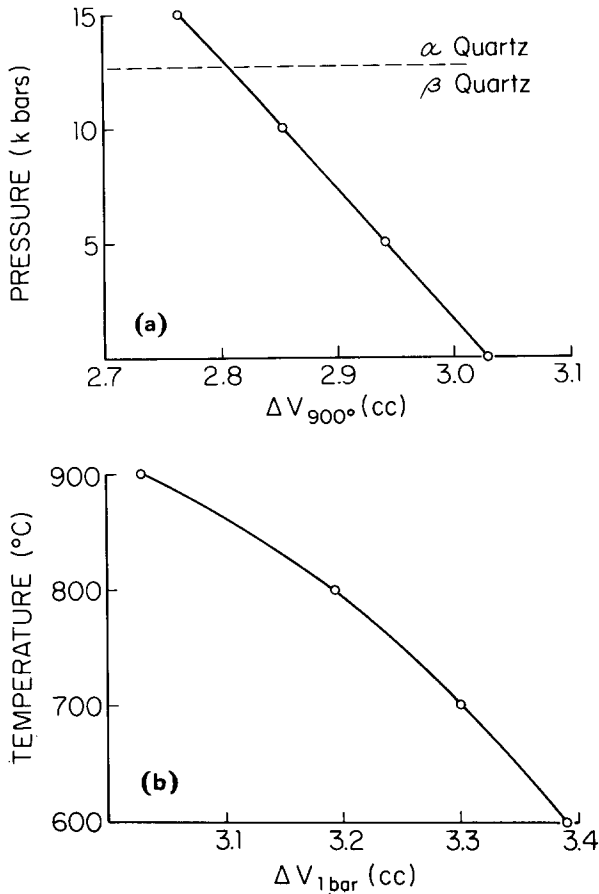
Fig. 2. (a) Plot of volume change of the reaction $2\,FeSiO_3 \rightleftharpoons Fe_2SiO_4 + SiO_2$ as a function of pressure at 900°C. Data for the α-β quartz transition from Cohen and Klement [22]. (b) Plot of volume change of the reaction as a function of temperature at 1 bar.

Fig. 3. Plot of $K_{D\,Mg\text{-}Fe}^{opx\text{-}oliv}$ as a function of mole fraction of Fe in olivine for metamorphic olivine-pyroxene pairs. The symbols o, •, □, ■ indicate data from Nain [7], Minnesota [29], Greenland [8], and Norway [30], respectively.

on K_D and P-T on ΔV are both significant and must be considered in calculations on Fe-Mg pyroxene stability.

Taking into account the dependence of ΔV on P and T and the dependence of K_D on $Fe^{2+}/(Fe^{2+} + Mg)$, we have calculated the effect of 5 and 10 mole % $Mg_2Si_2O_6$ on orthopyroxene stability (Fig. 1). We have assumed an ideal ionic model ($a = X_{Fe}^2$) for olivine and have chosen two models for orthopyroxene activities, one based upon calculated activities, assuming a simple mixing model for pyroxene sites [33], the other an ideal ionic model ($a = X_{Fe}^2$). We have calculated the pressure shift using the following
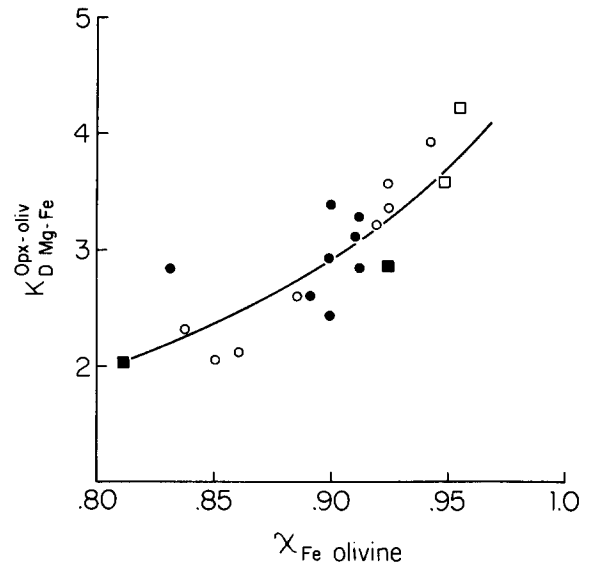
equation:

$$\Delta P = \frac{-RT(41.84)}{\Delta V} \ln \frac{a_{fayalite\ in\ olivine}}{a_{ferrosilite\ in\ opx}} \qquad (1)$$

For these diluents, the two models are very similar, and consideration of still other models, such as an ideal-molecular model yields a similar ΔP for $X_{Fe} \geqslant 0.9$ in orthopyroxene. However, the two models shown in Fig. 1 become increasingly dissimilar with larger amounts of $Mg_2Si_2O_6$ solid solution. Using the Saxena and Ghose activity data [33], the slopes of the isopleths become negative for $X_{Fe\ opx} \leqslant 0.8$ and linear extrapolation of their activity coefficients from 800 to 900°C yields a slight disagreement (1−2 mole % $FeSiO_3$) between the calculated isopleths and Smith's half-reversals. The ideal ionic model also yields similar disagreements between the calculated isopleths and experimental brackets, even though the slopes of the isopleths remain positive through $X_{Fe\ opx} = 0.7$. Very slight changes in the pyroxene activity data change the topology significantly; therefore, these models need to be tested against reversed experiments at 800−1000°C to allow modeling of pyroxene and olivine activities. It is important to

note that for less than 10 mole % $Mg_2Si_2O_6$ several models yield quite similar ΔP, suggesting that the calculated ispleths are approximately correct, perhaps to within ±0.5 kbar.

Berg [7] and Jaffe et al. [9] have used a phase diagram showing isopleths with constant slope, parallel to the end-member equilibrium boundary. This requires a constant ΔP (from equation 1) or a ln K that decreases with increasing temperature. The diagram does not take into account the effect of the α-β quartz transition, the effect of P and T on ΔV and the compositional dependence of $K_{D\,Mg-Fe}^{opx-oliv}$ (which *reduces*, not increases, ΔP unless pyroxene activity coefficients are sufficiently large to counterbalance the K_D shift), and apparently neglects uncertainties concerning pyroxene and olivine activity data. Unless there is some fortuitous counterbalancing of errors in these variables, their phase diagram cannot be correct in detail.

Even though $Mg_2Si_2O_6$ may be the most important diluent in Fe-rich orthopyroxenes, other components including Ca, Na, Al, Fe^{3+}, Ti and Mn typically make up between 2–10 mole %. To date, only the effect of Mn has been experimentally calibrated ([11], see following paper). Mn shows a slight preference for orthopyroxene relative to olivine and extends the stability of opx by about 0.6 kbar for 0.05 X_{MnSiO_3}. Data from natural orthopyroxene-olivine-quartz assemblages indicate that Ca, Na, Al, Ti, and Fe^{3+} are all strongly partitioned into orthopyroxene, suggesting that these impurities would also extend the stability of pyroxene and that their effects may be larger than those for equivalent amounts of Mn. Unfortunately, the magnitude of the extension cannot be accurately determined because of the lack of pertinent activity data. However, an ideal model should permit calculation of an approximate extension to within ±20–40% of the actual value. To emphasize the potential significance of additional components, one can take, for example, an Fe-rich orthopyroxene from the Adirondacks (Po-17, Table 2) and calculate the ΔP (from eq. 1) using different models for pyroxene activity. If we choose a simple model such as $a_{Fe_2Si_2O_6} = Fe^{2+}/(Fe^{2+} + Mg)$, the activity of the ferrosilite component in Po-17 is 0.95. However, this model completely neglects the effect of other components and will yield unrealistically high pressures. Another simple model such as

TABLE 2

Microprobe analyses of Fe-rich orthopyroxenes from the Adirondacks

	XY-6	IL-8	SR-29	SL-26	Po-17 *
SiO_2	46.7	46.2	45.4	45.7	45.2
TiO_2	0.1	0.1	0.1	0.1	0.1
Al_2O_3	0.3	0.4	0.2	0.3	0.5
Cr_2O_3	<0.1	<0.1	<0.1	<0.1	0.1
MgO	4.3	2.9	4.5	1.8	1.4
ZnO	<0.1	<0.1	<0.1	<0.1	0.6
FeO **	46.3	49.8	47.9	49.4	50.1
MnO	1.1	0.5	0.7	0.8	1.3
CaO	0.7	0.5	0.8	0.9	0.8
Na_2O	<0.1	<0.1	<0.1	<0.1	0.1
K_2O	<0.1	<0.1	<0.1	<0.1	<0.1
Total	99.5	100.4	99.6	99.0	100.2
Si	1.99	1.98	1.93	1.99	1.97
Al^{IV}	0.01	0.02	0.01	0.01	0.02
Al^{VI}	0.01	0.00	0.00	0.01	0.00
Ti	0.00	0.00	0.00	0.00	0.00
Cr	0.00	0.00	0.00	0.00	0.00
Fe^{3+}	0.00	0.02	0.01	0.01	0.02
Mg	0.27	0.18	0.29	0.12	0.09
Zn	0.00	0.00	0.00	0.00	0.02
Fe^{2+}	1.65	1.77	1.70	1.79	1.80
Mn	0.04	0.01	0.03	0.03	0.05
Ca	0.03	0.02	0.03	0.04	0.04
Na	0.00	0.00	0.00	0.01	0.01
K	0.00	0.00	0.00	0.00	0.00

* Taken from Jaffe et al. [46].

** Total iron as FeO; Fe^{3+} calculated from stoichiometry:
$Fe^{3+} = Al^{IV} - Al^{VI} + Na + K - 2\,Ti - Cr$.

$a_{Fe_2Si_2O_6} = Fe^{2+}/2$ treats additonal components as inert diluents and neglects activity coefficients that might be as large as 1.1 [33]. Taking a somewhat more complicated model, a two-site ionic model of the sort $a_{Fe_2Si_2O_6} = [1 - (Na + K + Mn + Ca + 1/2\, Mg)] \cdot [1 - (Ti + Al^{VI} + Cr + Zn + 1/2\, Mg)]$, one can calculate $a_{Fe_2Si_2O_6} = 0.79$. This model treats Mg-Fe as an ideal solution, but it accounts for reduction in Fs activity by considering the blocking effect of cations ordered into the M2 and M1 sites. For Al^{IV} one can assume a molecular model as discussed by Wood [34]; hence the activity of $Fe_2Si_2O_6$ is already reduced by the dilution effect of Al on the M1 site. To calculate a ΔP from equation (1) one must

assume a K_D, because the Fs_{95} reported by Jaffe et al. [9] does not coexist with olivine + quartz. This will yield minimum pressures necessary to stabilize the pyroxene. Based on data in Fig. 3 the K_D will be near 3.5 ± 0.5. Calculations using the two activity models $[(1)\ a_{Fs} = Fe^{2+}/2; (2)\ a_{Fs} = (X_{Fe}^{M2})(X_{Fe}^{M1})]$ yield minimum pressures of 8 and 5 kbar, respectively. These probably establish upper and lower limits to the minimum pressure because of the manner in which each model treats the diluting components. Because the ΔV of this reaction is small, even minor amounts of additional components yield estimates which err to the side of high pressures. Therefore, it is important to check results obtained from ortho-pyroxene-olivine-quartz barometry against pressures obtained from other methods.

4. Application of orthopyroxene-olivine-quartz barometry — Adirondacks

Metamorphic pressures in the Adirondacks can be characterized by pyrite-pyrrhotite-sphalerite, Al_2SiO_5 minerals, plagioclase-garnet-Al_2SiO_5-quartz, ferrosilite-rich pyroxenes, fayalite-quartz and by the assemblage monticellite-wollastonite-akermanite. Because several of these barometers are temperature-dependent, equilibration temperatures must be known to within $50-75°C$ before pressures can be inferred.

Metamorphic temperatures have been determined across the Adirondacks [12,13]. These data were obtained using two independent thermometers, coexisting feldspars [47] and coexisting iron-titanium oxides [48], and both are in good agreement (Fig. 4). Using these temperature data, metamorphic pressures can be restricted to less than 9.8, 7.8, and 5.8 kbar for metamorphic temperatures of less than 800, 700, and 600°C. These were determined from sillimanite-bearing paragneisses found sporadically throughout the Adirondacks, using the kyanite-sillimanite boundary of Richardson et al. [35]. With the exception of one locality, sillimanite is the only Al_2SiO_5 polymorph found in the Adirondacks. The single kyanite locality in the Blue Mountain Lake Quadrangle (Geraghty, personal communication, and Boone [36]) is itself surrounded by sillimanite localities. Assuming that the Bohlen and Essene [12,13] thermometry is correct, metamorphic pressures in the Blue Moun-
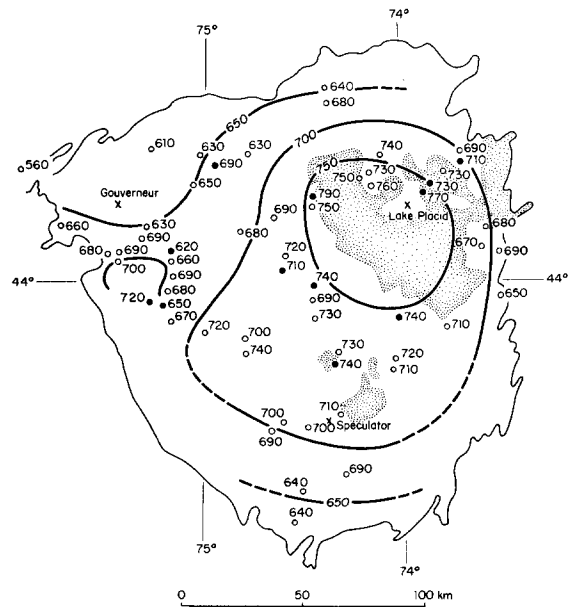

Fig. 4. Adirondack temperature data obtained by Fe-Ti oxides (●) and by two feldspars (○) (from Bohlen and Essene [13]).

tain Lake area can be restricted to 8 ± 0.5 kbar based on kyanite-sillimanite equilibria of Richardson et al. [35] for $T = 730 \pm 30°C$. In the Tupper Lake Quadrangle (just north of the Blue Mountain Lake Quadrangle) plagioclase-garnet-sillimanite-quartz assemblages yield pressures of 7.5 ± 1 kbar for metamorphic temperatures of $730 \pm 30°C$, again consistent with sillimanite in the area [37]. In the western Adirondacks near Balmat-Edwards, metamorphic pressures of 6 ± 1 kbar are inferred from sphalerite barometry [38,39]. These pressures are confirmed by numerous plagioclase-garnet-sillimanite-quartz localities within 20 km of Balmat yielding 6 ± 1 kbar for metamorphic temperatures of $630 \pm 30°C$ [37]. In the Mount Marcy Quadrangle, metamorphic P-T can be restricted to 7 ± 1 kbar and $765 \pm 30°C$ by the assemblage monticellite-wollastonite-akermanite [14,15]. This assemblage is extremely important as it fixes an upper pressure limit in an area where metapelitic rocks containing Al_2SiO_5 polymorphs are lacking. Based on several independent barometers and thermometers, the P-T path of metamorphism can best be described as a line roughly parallel to the kyanite-sillimanite

boundary very near but slightly below the kyanite stability field. Therefore, our data indicate that nowhere in the Adirondacks do the metamorphic pressures exceed 9 kbar, which has been assumed to be a maximum pressure by DeWaard [40], Essene and Valley [14], Bohlen and Essene [41,42,43], and Essene et al. [44]. However, application of the previously available experimental data on Fe-rich orthopyroxenes [1,6] to ferrosilite-rich pyroxenes in the Adirondacks (Fig. 5) has yielded significantly higher pressures. Based on the occurrences of Fs_{95} in the Mount Marcy Quadrangle (less than 5 km from the akermanite locality [14,15], Jaffe et al. have estimated *minimum* metamorphic pressures to be 9–11 kbar for metamorphic temperatures of 760–790°C. These data imply that metamorphism in the Mount Marcy area took place in the kyanite field. However, in light of the more recent experimental data presented here and the calculated effect of additional components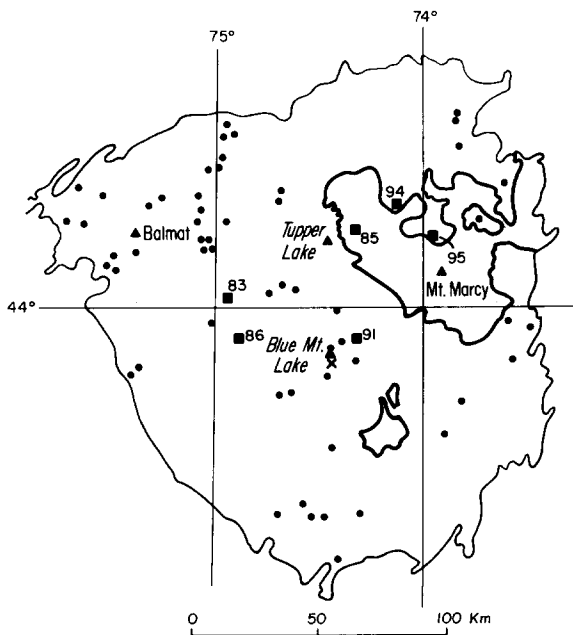, the pressure estimates of Jaffe et al. can be revised downward by approximately 2 kbar, placing Adirondack metamorphic pressures in the Mount Marcy area and the Adirondack Highlands in general at 7–9 kbar. Pressures of 7–9 (8 ± 1) kilobars are consonant with the widespread occurrences of sillimanite, occurrences of fayalite + quartz (Fa_{97}, Fa_{96}) in the central and eastern Adirondacks near Wanakena and Au Sable Forks, respectively, and the occurrence of akermanite at Cascade Slide [14,15], hence resolving inconsistencies that existed previously.

Reductions in estimates of metamorphic pressure for other field areas are also indicated by our data. The magnitudes of the reductions are similar to that for the Adirondacks, ranging generally between 1 and 3 kbar. In the Nain contact aureole, Berg [7] reports orthopyroxenes (Fs_{69-81}) that coexist with fayalitic olivine (Fa_{84-94}) and quartz. Berg's pressure estimates of 4–5 kbar should be reduced by 1–2 kbar based on our data. From occurrences of Fe-rich orthopyroxenes ($Fs_{77-78}En_{14-15}Rh_6Wo_2$) coexisting with olivine ($Fa_{89-90}Te_{5-6}Fo_{4-5}$) and quartz, Frisch and Bridgwater [8] inferred metamorphic pressures of 4–5.4 kbar for metamorphic temperatures of 750–900°C in iron-rich intrusions near Julianehaab, Greenland. They noted that their pressures might be high because of the effects of additional components and attempted to calculate the magnitude of these effects. We suggest a 1–2 kbar reduction of the pressures. However, it must be noted that because of the difficulty in modeling additional components, pressures inferred from orthopyroxene-olivine-quartz assemblages containing large amounts of impurities (as noted above) will be significantly less certain than those inferred from mineral compositions requiring minimal extrapolations of the present data. Hence, until the necessary experimental work and/or more highly refined pyroxene activity data are available, the orthopyroxene-olivine-quartz geobarometer should be applied with great caution and checked against other barometers where possible.

Fig. 5. Location of sillimanite (o), kyanite (×), and Fe-rich orthopyroxenes ($Fe^{2+}/(Fe^{2+} + Mg)$ ratio given) (■) in the Adirondacks. The map outlines the Precambrian terrane of upper New York State. Anorthosites are shown in heavy outline.

Acknowledgements

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