

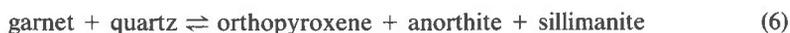
The stability of Mg-rich garnet in the system CaO–MgO–Al₂O₃–SiO₂ at 1000–1300°C and high pressure¹

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Abstract

Reactions limiting the stability of garnet + quartz in the CaO–MgO–Al₂O₃–SiO₂ (CMAS) and MgO–Al₂O₃–SiO₂ (MAS) systems have been experimentally reversed in a piston cylinder apparatus at 1000–1300°C and 10–25 kbar. At high temperatures, garnet composition is buffered successively by orthopyroxene + sillimanite, orthopyroxene + anorthite, clinopyroxene + anorthite and clinopyroxene + sillimanite/kyanite as garnet progresses from pure pyrope to more calcic compositions. The buffering assemblages are stable in separate divariant *P–T* fields, separated by three univariant reactions:



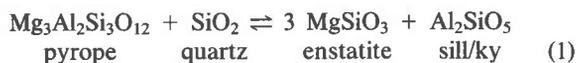
At 980°C, the reactions intersect at an invariant point near 14.5 kbar. At 1150°C and 1300°C they take place at 14.8, 15.9 and 19.8 kbar, and at 15.1, 17.4, and 21.8 kbar, respectively. At 1300°C the mole fractions of pyrope in garnet for the three reversed univariant reactions are 0.95, 0.90 and 0.85. The reaction pyrope + quartz = enstatite + sillimanite was reversed at 1000°C (15.4 kbar), 1150°C (17.0 kbar) and 1300°C (18.8 kbar).

The sequence of mineral assemblages determined in this study is consistent with natural parageneses. However, quantitative application of the present results to natural compositions is difficult due to lack of knowledge of exact pyroxene compositions taking place in Reactions (6), (7) and (8), and due to the unavailability of accurate activity-composition models for highly complex natural orthopyroxene, clinopyroxene and garnet.

Introduction

The stability of garnet in quartz-excess systems is of fundamental importance to petrologists because of the widespread occurrence of garnet–quartz assemblages in metamorphic terrains. Many previous studies have investigated the stability of garnet + quartz (Kushiro and Yoder, 1966; Kushiro, 1969; Emslie, 1971; Hensen and Essene, 1971; Hensen, 1976; Haselton and Newton, 1980; Hansen, 1981) but few have demonstrated equilibrium or adequately addressed the problem of solid solution in garnet and coexisting phases.

Although natural garnets are commonly solutions of several end members, most previous experimental studies have been conducted in the model systems MgO–Al₂O₃–SiO₂ (MAS) and CaO–MgO–Al₂O₃–SiO₂ (CMAS). Even within these systems, however, solid-solution in garnet and pyroxene has great importance. Hensen and Essene (1971) demonstrated that in the MAS system orthopyroxene may contain as much as 18 wt.% Al₂O₃ in the range 15–20 kbar and 1000–1400°C which causes significant curvature in the reaction:

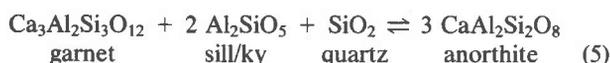
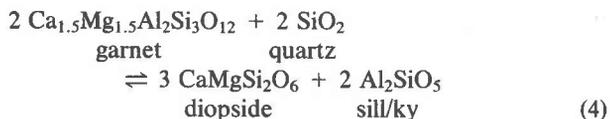
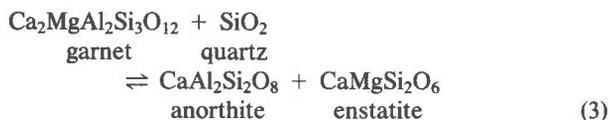
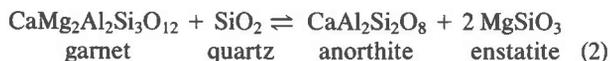


In modelling the CMAS system, Hensen (1976) noted that both orthopyroxene and clinopyroxene are solid solutions of Mg₂Si₂O₆, CaMgSi₂O₆ and Al₄O₆, and demonstrated the existence of additional important reactions

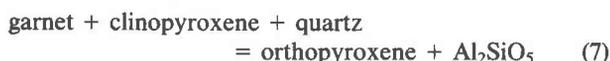
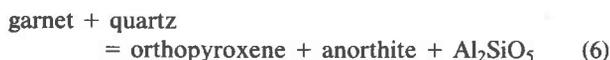
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that buffer garnet composition. For pyrope-rich garnet they are:



Reactions (1) through (5) are divariant in the CMAS system and occupy separate portions of pressure-temperature (P - T) space but become univariant if P or T is held constant. Thus, Hensen (1971) and Haselton and Newton (1980) were able to calculate pressure-composition (P - X) diagrams showing the variation in garnet composition as a function of pressure at 1200°C. In P - T space, Reactions (2) through (5) intersect at univariant reactions:



However, the compositions of garnet, orthopyroxene and clinopyroxene taking part in these reactions vary as functions of pressure and temperature. Experimental investigation of these reactions must not only demonstrate growth or loss of the phases present, but must also consider the compositions of the phases involved.

Perkins and Newton (1980) examined the compositions of coexisting garnet-clinopyroxene-orthopyroxene in the CMAS system at 15–30 kbar and 900–1100°C. Their results are directly applicable to Reaction (7) because the buffering of garnet and pyroxene compositions will not be affected by the presence of other minerals. In a recent study, Hansen (1981) examined Reaction (7) in detail. Using crystalline starting materials, he reversed the reaction at 900–1300°C and also determined the equilibrium compositions of orthopyroxene, clinopyroxene and garnet at several pressures and temperatures. The reversed pyroxene compositions of Hansen's "diffusion runs" are in excellent agreement with the (extrapolated) results of Perkins and Newton (1980). However, Hansen's reversed garnet compositions show slightly greater $\text{Ca}/(\text{Ca}+\text{Mg})$ values than those determined by Perkins and Newton. The discrepancy is only a few mole percent and may be

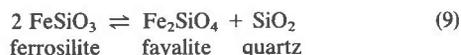
the result of the compositional "overlaps" (apparent overlap of $\text{Ca}/(\text{Ca}+\text{Mg})$ content when equilibrium is approached from two directions) noted by Perkins and Newton and by Hansen.

The goals of the present study are twofold: first, to determine by experimental reversal the garnet compositions buffered by Reactions (1) through (5); second, to determine the P - T locations of Reactions (6) through (8). Although no attempt has been made in this study to reverse the pyroxene compositions, estimates of their compositions may be made using the results of Wood (1976), Gasparik (1980), Perkins and Newton (1980), Hansen (1981) and Perkins *et al.* (1981).

Experimental methods

Pressure apparatus and calibration

Experiments were conducted in a 0.75-inch diameter piston-cylinder apparatus with a NaCl-soft glass pressure assembly surrounding a graphite sample capsule capable of holding 8–10 mg of reactants. In all experiments, a "piston-out" procedure was used; details are described elsewhere (Perkins *et al.*, 1981). Because of the strength of the glass (at low temperature) it was necessary to calibrate the pressure on the sample versus that being applied to the whole assembly. The reaction chosen for the calibration experiments was:



This reaction has been shown to have favorable kinetics (Bohlen *et al.*, 1980) and takes place at temperatures and pressures similar to those of Reactions (1) through (8).

All calibration runs were carried out using synthetic crystalline starting mixtures of ferrosilite, fayalite and quartz. Run times were typically five to eight hours; reaction direction was nearly always unambiguous. Two reversals (at 900 and 950°C) in a frictionless (no strength) NaCl pressure assembly yielded the same location of Reaction (9) as determined by Bohlen and Boettcher (1981). Reversals at 1000, 1050 and 1120°C in the salt/glass assembly showed that an 8% pressure correction is necessary at 1000°C, but that for temperatures above 1050°C no correction is needed. Similar results were found by Haselton (1979) in a study using a nearly identical pressure cell. Scale drawings of the pressure assembly and details of the calibration experiments are available from the author on request.

Temperature measurement and control

In most experiments temperatures were measured and controlled with a single W-3%Re vs W-25%Re (W-Re) thermocouple. The tip of the thermocouple was imbedded in the graphite capsule lid which protected it from contamination. Power being delivered to the run was carefully monitored and remained constant after initial equilibration. As a check for thermocouple drift, double thermocouples were used in nine of the 1000°C experiments. Temperature was simultaneously measured with W-Re and chromel-P-alumel (Cr-Al) thermocouples. The temperature readings of both thermocouples always agreed within $\pm 3^\circ\text{C}$ and no relative temperature drift was observed. The Cr-Al thermocouple usually read 1 to 3°C higher temperature. The remarkable stability of the thermocouples used in this study contrasts with results found in earlier studies (*cf.*

Table 1. Starting materials and synthesis conditions

No.	Composition	Pressure (kbar)	Temperature (°C)	Time (hours)	Remarks*
1	MgSiO ₃ (Opx)	20	1000	2	
2	Mg _{1.84} Al _{.32} Si _{1.84} O ₆ (Opx)	17	1050	3	For experiments on reaction (1)
3	Ca _{.033} Mg _{1.849} Al _{.237} Si _{1.881} O ₆ (Opx)	20	1000	4	Opx for experiments at 1000°C
4	Ca _{.053} Mg _{1.787} Al _{.321} Si _{1.838} O ₆ (Opx)	17	1050	2	Opx for experiments at 1150°C
5	Ca _{.072} Mg _{1.728} Al _{.4} Si _{1.8} O ₆ (Opx)	20	1050	2	Opx for experiments at 1300°C
6	CaMgSi ₂ O ₆ (Cpx)	20	1050	1	Diopside made from glass
7	Ca _{.881} Mg _{1.034} Al _{.169} Si _{1.916} (Cpx)	15	1200	1	Cpx for 1000°C experiments; dry synthesis from glass
8	Ca _{.820} Mg _{1.060} Al _{.231} Si _{1.889} O ₆ (Cpx)	22	1300	6	Cpx for 1150°C experiments; dry synthesis from glass
9	Ca _{.778} Mg _{1.081} Al _{.282} Si _{1.859} O ₆ (Cpx)	10	1300	1	Cpx for 1300°C experiments; dry synthesis from glass
10	Py ₁₀₀	20	1000	2	
11	Py ₉ ½Gr ₂ ½	20	1000	3	
12	Py ₉₅ Gr ₅	20	1000	1	
13	Py ₉₂ ½Gr ₇ ½	20	1000	2	
14	Py ₉₀ Gr ₁₀	25	1000	3	
15	Py ₈₇ ½Gr ₁₂ ½	25	1050	3	
16	Py ₈₂ ½Gr ₇ ½	30	1050	3	
17	Py ₇₇ ½Gr ₂₂ ½	30	1050	2	
18	CaAl ₂ Si ₂ O ₈ (anorthite)	20	1200	3	Dry synthesis from a glass

*All syntheses were performed in gold capsules with an H₂O flux unless indicated.

Abbreviations: Opx = orthopyroxene, Cpx = Clinopyroxene, Py = Pyrope, Gr = Grossular. Subscripts to Py and Gr indicate wt.%. .

Perkins *et al.* 1981) and is probably due to protecting the thermocouple junction by surrounding it with spectroscopically pure graphite.

Starting materials

The synthetic starting materials were hydrothermally synthesized from oxide mixes in gold capsules except as noted in Table 1. Details of syntheses have been given elsewhere (Perkins and Newton, 1980; Perkins *et al.*, 1981). All starting materials were analyzed by electron microprobe and, with the exception of the most calcic garnets, were homogeneous and agreed with the theoretical compositions to within ±2% of the amount present. The most calcic garnets showed slightly greater heterogeneity (±3%).

Estimates of equilibrium pyroxene compositions were made on the basis of previous studies. For Reaction (1), starting orthopyroxene compositions were chosen so as to be consistent with the results of Perkins *et al.* (1981). For all other reactions, starting pyroxene compositions were chosen so as to be consistent with the results of Perkins and Newton (1980) and Hansen (1981) for CMAS pyroxenes in equilibrium with garnet. Clinopyroxene compositions were similarly chosen. The starting pyroxenes may have varied slightly from the true equilibrium compositions for some of the reactions studied, but such small errors should not significantly effect the equilibria. As a check

for the effect of metastable pyroxene composition, Reactions (1) and (6) were reversed at 1300°C using pure enstatite and Reaction (8) was reversed at 1300°C using pure diopside. The results obtained using the end member pyroxenes were identical to those obtained using the intermediate compositions.

Quartz from Brazil and sillimanite from Custer, South Dakota were used in starting mixtures. Microprobe analyses revealed the only impurity in the sillimanite to be 0.1–0.2 wt.% Fe₂O₃. The sillimanite and quartz were fired briefly at 1300°C prior to combination in reaction mixtures. Although some of the experiments were conducted slightly into the kyanite field, sillimanite was used in order to simplify analysis of the results. Several experiments were conducted to confirm that the metastable sillimanite persisted (kyanite did not nucleate and grow). A mixture of finely ground sillimanite with 5 percent kyanite seeds was reacted at 1300°C, 22 kbar, for 14 hours and at 1000°C, 16 kbar, for 23 hours. Both experiments showed no detectable growth of kyanite. As a final check, Reaction (1) was reversed using kyanite instead of sillimanite at 1000°C and Reaction (8) was reversed using kyanite instead of sillimanite at 1300°C. Both reactions showed the expected small shift relative to the sillimanite experiments (the Al₂SiO₅ side of the reaction expanded).

Reversal mixtures were hand ground for 20 minutes in an agate mortar. In all experiments, bulk compositions were initially

Table 2. Experimental results

Run No.	Reaction No.	Reactants*	Pressure** (kbar)	Temperature (°C)	Time (Hours)	Results***
<u>P-X Section at 1300°C</u>						
30	1	Py ₉₇ ½-Q-Opx ₅ -Sill	17.14-17.42	1300	8	Moderate growth Opx
26	1	Py ₉₇ ½-Q-Opx ₅ -Sill	17.40-17.60	1300	7	No apparent reaction
29	1	Py ₉₇ ½-Q-Opx ₅ -Sill	17.41-17.83	1300	8	No apparent reaction
33	1	Py ₉₇ ½-Q-Opx ₅ -Sill	17.77-18.03	1300	6	Moderate growth Gt
25	1	Py ₉₅ -Q-Opx ₅ -Sill	15.60-15.89	1300	9	Moderate growth Opx
20	1	Py ₉₅ -Q-Opx ₅ -Sill	15.81-16.10	1300	7	Moderate growth Gt
57	2	Py ₉₂ ½-Q-Opx ₅ -An	15.77-15.91	1300	8	Moderate growth Opx, An
38	2	Py ₉₂ ½-Q-Opx ₅ -An	16.03-16.29	1300	6	No apparent reaction
37	2	Py ₉₂ ½-Q-Opx ₅ -An	16.29-16.55	1300	6	Strong growth Gt
36	2	Py ₉₀ -Q-Opx ₅ -An	16.59-16.75	1300	6	Minor growth Opx, An
32	2	Py ₉₀ -Q-Opx ₅ -An	16.79-16.99	1300	6	No apparent reaction
35	2	Py ₉₀ -Q-Opx ₅ -An	17.16-17.42	1300	7	Strong growth Gt
44	2	Py ₈₇ ½-Q-Opx ₅ -An	17.33-17.60	1300	8	Moderate growth Opx; minor growth Cpx
47	2	Py ₈₇ ½-Q-Opx ₅ -An	17.60-17.86	1300	7	No apparent reaction; minor growth Cpx
45	2	Py ₈₇ ½-Q-Opx ₅ -An	17.86-18.12	1300	6	Strong growth Gt; minor growth Cpx
147	3	Py ₉₅ -Q-An-Cpx ₉	18.47-18.73	1300	7	No apparent reaction; Gt shifted to Py ₉₀
146	3	Py ₉₅ -Q-An-Cpx ₉	19.25-19.43	1300	8	No apparent reaction; Gt shifted to Py ₉₀
148	3	Py ₉₅ -Q-An-Cpx ₉	20.00-20.30	1300	6	No apparent reaction; Gt shifted to Py ₈₇ ½
125	3	Py ₉₀ -Q-An-Cpx ₉	20.91-21.17	1300	25	No apparent reaction; Gt shifted to Py ₈₅
46	3	Py ₈₂ ½-Q-An-Cpx ₉	18.73-18.99	1300	7	No apparent reaction; Gt shifted to Py ₈₆
50	3	Py ₈₂ ½-Q-An-Cpx ₉	19.22-19.48	1300	9	No apparent reaction; Gt shifted to Py ₈₄ ½
51	3	Py ₈₂ ½-Q-An-Cpx ₉	19.74-20.00	1300	8	No apparent reaction; Gt shifted to Py ₈₅ ½
60	3	Py ₇₇ ½-Q-An-Cpx ₉	20.00-20.30	1300	6	Minor growth An, Cpx, Gt shifted to Py ₈₆
145	3	Py ₇₇ ½-Q-An-Cpx ₉	21.00-21.17	1300	10	No apparent reaction; Gt shifted to Py ₈₃ ½
52	4	Py ₇₇ ½-Q-Sill-Cpx ₉	22.09-22.35	1300	6	Minor growth Cpx, Gt shifted to Py ₈₃
149	4	Py ₉₀ -Q-Sill-Cpx ₉	22.09-22.35	1300	6	Minor growth Gt; shifted to Py ₈₅
<u>Univariant Reactions</u>						
127	1	Py-Q-Opx ₂ -Sill	16.19-16.36**	1000	20	Minor growth Opx
129	1	Py-Q-Opx ₂ -Sill	16.42-16.59**	1000	18	No apparent reaction
132	1	Py-Q-Opx ₂ -Sill	16.48-16.82**	1000	21	No apparent reaction
138	1	Py-Q-Opx ₂ -Sill	16.90-17.16**	1000	28	Moderate growth of Py
	2	Py-Q-Opx ₂ -Sill	16.80-17.01	1150	24	Moderate growth Opx
	3	Py-Q-Opx ₂ -Sill	17.11-17.23	1150	23	No apparent reaction
134	1	Py-Q-Opx ₂ -Sill	17.33-17.60	1150	20	No apparent reaction
135	1	Py-Q-Opx ₂ -Sill	17.86-18.12	1150	20	Moderate growth of Py
	5	Py-Q-Opx ₂ -Sill	18.30-18.60	1300	6	Moderate growth of Opx
	6	Py-Q-Opx ₂ -Sill	18.90-19.25	1300	6	Minor growth of Py
144	1	Py-Q-Opx ₂ -Sill	19.25-19.51	1300	20	No apparent reaction
150	1	Py-Q-Opx ₂ -Sill	19.51-19.77	1300	18	Moderate growth of Py
142	1	Py-Q-Opx ₂ -Sill	20.00-20.30	1300	21	Strong growth of Py
74	6	Py ₉₅ -Q-Opx ₃ -An-Sill	14.98-15.24**	1000	26	Moderate growth Opx, An
101	6	Py ₉₅ -Q-Opx ₃ -An-Sill	15.28-15.45**	1000	23	Moderate growth Opx, An
83	6	Py ₉₅ -Q-Opx ₃ -An-Sill	15.51-15.77**	1000	25	No apparent reaction
78	6	Py ₉₅ -Q-Opx ₃ -An-Sill	15.74-16.00**	1000	13	No apparent reaction
82	6	Py ₉₅ -Q-Opx ₃ -An-Sill	16.03-16.29**	1000	26	Moderate growth Gt

Table 2. (continued)

Run No.	Reaction No.	Reactants*	Pressure** (kbar)	Temperature (°C)	Time (Hours)	Results***
114	6	Py ₉₅ -Q-Opx ₄ -An-Sill	14.49-14.66	1150	21	Moderate growth Opx, An
122	6	Py ₉₅ -Q-Opx ₄ -An-Sill	14.66-14.94	1150	21	Minor growth Opx, An
120	6	Py ₉₅ -Q-Opx ₄ -An-Sill	14.83-15.00	1150	25	No apparent reaction
130	6	Py ₉₅ -Q-Opx ₄ -An-Sill	15.00-15.17	1150	21	Minor growth Gt
55	6	Py ₉₅ -Q-Opx ₅ -An-Sill	14.46-14.72	1300	6	Moderate growth Opx, An
58	6	Py ₉₅ -Q-Opx ₅ -An-Sill	14.91-15.01	1300	8	No apparent reaction
67	6	Py ₉₅ -Q-Opx ₅ -An-Sill	15.09-15.26	1300	10	No apparent reaction
56	6	Py ₉₅ -Q-Opx ₅ -An-Sill	15.24-15.51	1300	9	Moderate growth Gt
75	7	Py ₉₀ -Q-Cpx ₇ -Opx ₃ -An	15.77-16.03**	1000	25	Minor growth Opx, An
77	7	Py ₉₀ -Q-Cpx ₇ -Opx ₃ -An	16.03-16.29**	1000	26	No apparent reaction
81	7	Py ₉₀ -Q-Cpx ₇ -Opx ₃ -An	16.29-16.55**	1000	28	Minor growth Gt, Cpx
131	7	Py ₉₀ -Q-Cpx ₈ -Opx ₄ -An	15.48-15.68	1150	22	Moderate growth Opx, An
123	7	Py ₉₀ -Q-Cpx ₈ -Opx ₄ -An	16.03-16.29	1150	20	Moderate growth Cpx, Gt
116	7	Py ₉₀ -Q-Cpx ₈ -Opx ₄ -An	16.38-16.72	1150	24	Minor growth Gt, Cpx
139	7	Py ₉₀ -Q-Cpx ₉ -Opx ₅ -An	16.90-17.16	1300	26	Moderate growth Opx, An
68	7	Py ₉₀ -Q-Cpx ₉ -Opx ₅ -An	17.16-17.42	1300	9	Moderate growth Cpx
136	7	Py ₉₀ -Q-Cpx ₉ -Opx ₅ -An	17.42-17.68	1300	20	No apparent reaction
69	7	Py ₉₀ -Q-Cpx ₉ -Opx ₅ -An	17.68-17.94	1300	9	Moderate growth Cpx, Gt
73	7	Py ₉₀ -Q-Cpx ₉ -Opx ₅ -An	17.94-18.21	1300	9	Moderate growth Cpx, Gt
87	8	Py ₈₅ -Q-An-Cpx ₇ -Sill	16.03-16.29**	1000	22	Moderate growth An, Gt
91	8	Py ₈₅ -Q-An-Cpx ₇ -Sill	16.29-16.55**	1000	24	Minor growth Gt; moderate growth An
84	8	Py ₈₅ -Q-An-Cpx ₇ -Sill	16.55-16.81**	1000	24	Minor growth Cpx
103	8	Py ₈₅ -Q-An-Cpx ₇ -Sill	17.07-17.51**	1000	27	Moderate growth Cpx
126	8	Py ₈₅ -Q-An-Cpx ₇ -Sill	18.64-18.90	1150	24	Moderate growth Gt, An; minor Opx
133	8	Py ₈₅ -Q-An-Cpx ₈ -Sill	19.16-19.43	1150	22	No apparent reaction
137	8	Py ₈₅ -Q-An-Cpx ₈ -Sill	19.51-19.77	1150	28	Minor growth Gt, An
143	8	Py ₈₅ -Q-An-Cpx ₈ -Sill	20.03-20.30	1150	22	Minor growth Cpx
107	8	Py ₈₅ -Q-An-Cpx ₉ -Sill	21.34-21.60	1300	23	Very strong growth Gt, An
98	8	Py ₈₅ -Q-An-Cpx ₉ -Sill	21.86-22.13	1300	8	Strong growth Cpx; moderate growth An
141	8	Py ₈₅ -Q-An-Cpx ₉ -Sill	22.39-22.65	1300	20	Strong growth Cpx

*Subscript for Py indicates wt% Mg₃Al₂Si₃O₁₂; subscripts for Opx and Cpx refer to starting material numbers given in Table 1.

**Reported pressures are nominal gauge pressures. No correction made for rigidity of pressure media at 1000°C

***The adverbs strong, moderate and weak refer to > 100%, 50 - 100% and 25 - 50% increase in ratios of x-ray peak heights for products/reactants.

chosen such that complete reaction in either direction was possible. For the *P-X* experiments, garnets of varying compositions were used in the starting mixtures in order to obtain pressure reversals at constant temperature. For experiments on Reactions (6), (7) and (8) garnet composition was estimated from the *P-X* results. Compositions of all starting mixes are given in Table 2. Five wt.% excess quartz (in addition to the amount needed for the reaction) and 2 wt.% PbO were added to provide a Pb-silicate melt as a flux. The compositions of garnets and pyroxenes used in each run are given in Table 2.

Analysis of run-products

After quenching, the graphite sample capsules were split open with a razor blade; the finely sintered pellets usually separated

entirely from the capsule. A portion of the charge was preserved for microprobe analysis while the bulk was ground for X-ray diffraction.

X-ray scans from 15 to 40° 2θ were conducted at a scan speed of 0.5°/min and compared with similar scans of the initial mixtures. Growth or depletion of garnet, clinopyroxene and orthopyroxene were easily detected and served to identify reaction direction. However, the X-ray results for anorthite, sillimanite, kyanite and quartz were often difficult to interpret as a result of interferences and preferred orientation. In experiments involving sillimanite, there was an apparent decrease in the amount of sillimanite present in all experiments (in either the kyanite or the sillimanite field), including those that were clearly (on the basis of garnet or pyroxene growth) on the

Table 3. Microprobe analyses of product pyroxenes

Run No.	Reaction No.	P (kbar)*	T (°C)	Phase	No. of Analyses**	Ca	Mg	Al	Si
6	1	19.1	1300	Opx	4	—	1.77	0.49	1.74
3	1	19.5	1300	Opx	3	—	1.77	0.40	1.83
57	2	15.8	1300	Opx	4	0.07	1.75	0.41	1.77
131	7	15.6	1150	Opx	2	0.07	1.73	0.37	1.83
50	3	19.3	1300	Cpx	3	0.78	1.07	0.30	1.85
52	4	22.2	1300	Cpx	3	0.74	1.03	0.47	1.76
60	3	20.1	1300	Cpx	5	0.76	1.06	0.34	1.84
146	3	19.2	1300	Cpx	4	0.76	1.04	0.42	1.78
149	4	22.2	1300	Cpx	4	0.76	1.07	0.35	1.82

*Pressure is average pressure recorded during experiment

**Mean analyses reported; totals were always 100±2%. Results are normalized to 4 cations

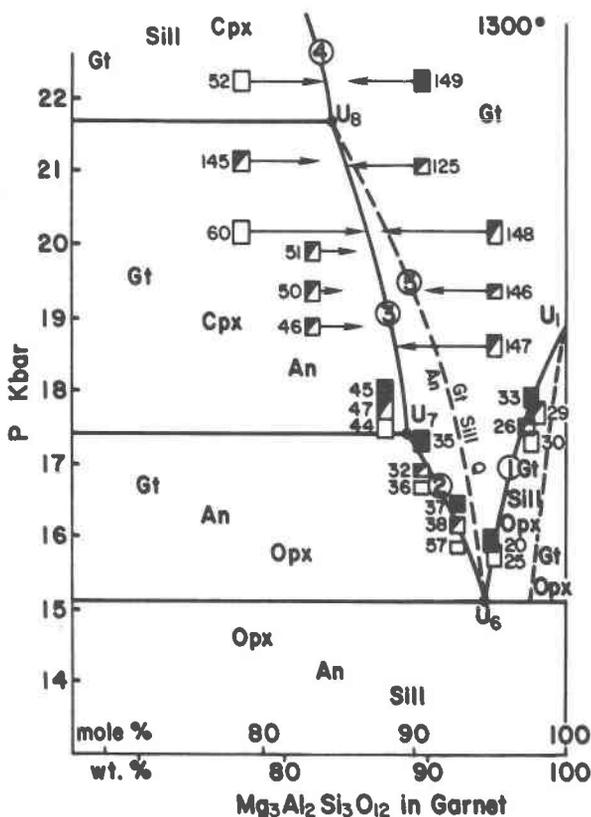


Fig. 1. *P*-*X* section at 1300°C showing experimental results. Open, half-shaded and shaded symbols represent growth of low-pressure assemblage, no reaction and growth of high-pressure assemblage, respectively. Dashed lines represent inferred or approximately located reactions. Some symbols have been shifted slightly right or left for clarity. Numbers next to symbols are the experimental run numbers. In the abscissa, the top and bottom numbers are mole% and wt.% respectively.

sillimanite side of the reaction. This effect could have been due to the formation of highly aluminous (metastable) pyroxenes but microprobe analysis did not reveal them.

The portion of the charge served for microanalysis was mounted in epoxy resin and polished. Ten to thirty minutes etching in fluoro-boric acid prior to carbon coating served to highlight the garnets and pyroxenes and simplified microprobe identification. A few examples were examined using a scanning electron microscope. Back-scattered electron imaging easily distinguished garnet, quartz, anorthite and small blebs of a PbO-rich melt. The garnet and quartz were typically 10–30 μm equant grains. Pyroxenes, anorthite and sillimanite, were considerably smaller—usually laths no more than 3–5 μm in width.

Microprobe analyses of pyroxenes

Details of microprobe analyses and standards have been reported elsewhere (Perkins and Newton, 1980; Perkins *et al.*, 1981). Microprobe analyses totalling to 100±2% and showing good pyroxene stoichiometry were only obtained in a few runs (Table 3). None of the pyroxene grains analyzed were large enough to permit detailed examination of compositional zoning. With the exception of Reaction (4), the average pyroxene compositions in the run products were similar to those in the starting mixture. However, the limited number of analyses and the lack of ability to examine zonation in the grains precludes definite conclusions being drawn.

The clinopyroxene analyses for Reaction (4) may represent a shift towards equilibrium CaTs contents. Wood (1976) in an examination of compositions on the diopside-anorthite join found as much as 15 wt.% Al₂O₃ in clinopyroxene at pressures and temperatures near 20 kbar and 1300°C. Further investigation of Reaction (4) involving reversal of the clinopyroxene composition is needed.

Microprobe analyses of garnet were rejected if they did not total 100±2 wt.% or if the stoichiometry varied by more than two percent from ideal garnet. Garnets were invariably zoned, with rims closer to the final inferred equilibrium compositions. The change in garnet composition was used to locate Reactions (3) and (4); the other reactions were located on the basis of growth or depletion of phases.

Experimental results

P-X Section at 1300°C

Experimental results are tabulated in Table 2. The results of the 1300°C experiments have been combined to create a pressure-composition diagram (Fig. 1) which is qualitatively similar to the diagram of Hensen (1976) and of Haselton and Newton (1980). Reactions (1) and (2) were located on the basis of the growth of garnet versus that of orthopyroxene (and anorthite for Reaction 2). Even small displacement of garnet from its equilibrium composition could be detected for Reactions (1) and (2) since small changes in garnet composition require large changes in the relative abundances of phases. However, for Reactions (3) and (4), the stoichiometric garnet compositions (Py₃₃ and Py₅₀, respectively) are far enough away from the buffered compositions so that growth or depletion of phases was not a precise way to locate the reactions. For these two reactions, garnets in the run-products were analyzed; the changes in compositions, plotted in Figure 1, served to locate the reactions. Several tight compositional reversals were obtained for Reaction (3) and one for Reaction (4). No significant compositional overlap (*cf.* Lane and Ganguly, 1980; Perkins and Newton, 1980; Perkins *et al.*, 1981) of garnet composition was observed, perhaps due to the absence of an H₂O-rich flux in the sample capsules.

At 1300°C the composition of garnet is buffered successively by orthopyroxene + sillimanite, orthopyroxene + anorthite, clinopyroxene + anorthite and clinopyroxene + sillimanite/kyanite (Reactions 1 through 4, respectively) as garnet composition progresses from pure pyrope to pyrope₈₈-grossular₁₂. Calculations by Hensen (1976) and unreversed experiments by Green (1969) suggest that Reaction (4) (the buffering of garnet composition by clinopyroxene + Al₂SiO₃) will continue to buffer garnet composition for even more calcic garnets.

Univariant reactions

The univariant Reactions (1), (6), (7) and (8) were reversed at 1000, 1150 and 1300°C. Garnet compositions consistent with the *P-X* results were used in the reversal mixtures (see Table 2) so that metastable garnet compositions would not affect the location of the reactions.

Experimental results for Reaction (1) are shown in Figure 2. The results plotted are for experiments in which Al-bearing enstatite and sillimanite were used in the starting mixture. The experimentally determined location for Reaction (1) is about 1 kbar greater in pressure than the earlier determinations of Hensen and Essene (1971). Hensen and Essene conducted most of their experiments using a seeded oxide mix which may have resulted in metastable growth of pyrope + quartz. Their one reversal using entirely crystalline reactants (1000°C, 14.4–15.3 kbar) does overlap the 1000°C reversal of this study. Part of the discrepancy between the present results and those

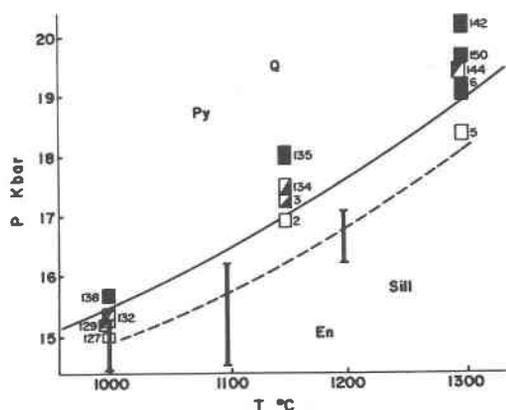


Fig. 2. Experimental results relevant to Reaction (1). The results of Hensen and Essene (1971) are shown for comparison (I-beams and dashed line).

of Hensen and Essene may also have resulted from the high (and presumably metastable) Al-contents of enstatite reported by Hensen and Essene. When compared with the results of Lane and Ganguly (1980) and of Perkins *et al.* (1981), it appears that the Al isopleths of Hensen and Essene are several percent too high.

Reaction (6) representing the lower pressure limit for garnet + quartz, has recently been studied by Hansen (1976). The present results are in nearly exact agreement with Hansen's (Fig. 3). X-ray, optical and microprobe examination of the run products failed to reveal any sapphirine in the run products despite the fact that the 1300°C reversal is several kbar into the sapphirine + quartz field (*cf.* Chatterjee and Schreyer, 1972; Newton 1972).

Reaction (7), the breakdown of orthopyroxene + anorthite to garnet + clinopyroxene + quartz, has recently been studied by Hensen (1976) and Hansen (1981). Hansen's results are in complete agreement with those of the present study (Fig. 4), while Hensen's unreversed curve is 1–2 kbar lower in pressure.

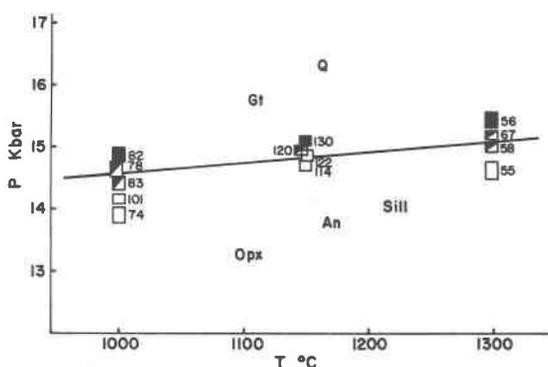


Fig. 3. Experimental results relevant to Reaction (6). TL study of Hensen (1976) gave an identical result.

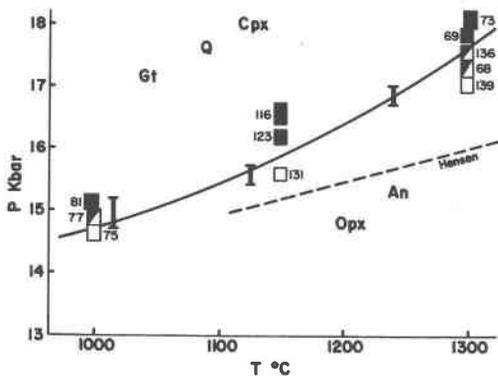


Fig. 4. Experimental results relevant to Reaction (7). For comparison the curve of Hensen (1976) (dashed line) and the reversal brackets of Hensen (1981) (I-beam) are shown.

Experimental results for Reaction (8) are shown in Figure 5, along with Hensen's (1976) unreversed curve. The present results show poor agreement with Hensen's, especially at lower temperatures. However, the results for Reaction (8) are consistent with those for Reactions (6) and (7) (they all intersect at an invariant point near 15 kbar and 1000°C). In order to satisfy the three experimental reversals, Reaction (8) must have significant curvature. Such curvature may arise because of increasing Ca-Tschermak (CaTs) component in clinopyroxene as pressure and temperature increase (*cf.* Wood, 1976; Gasparik, 1980). Microprobe analyses of product pyroxenes suggest that our starting pyroxene composition may have been too low in Al_2O_3 for reaction (8), especially at 1300°C. The composition of clinopyroxene was not, however, reversed. Thus, the curvature depicted in Figure 5 may in fact be an artifact of metastable pyroxene composition.

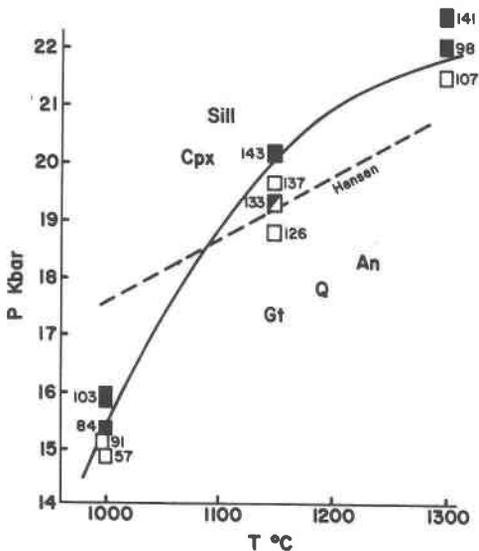
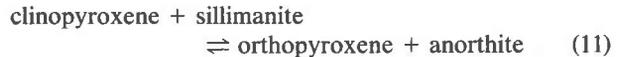
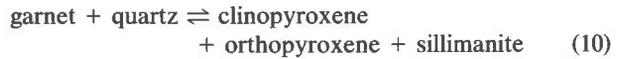


Fig. 5. Experimental results relevant to Reaction (8). For comparison the curve of Hensen (1976) is shown.

Discussion

Phase diagram

Figure 6 shows our experimentally determined locations for Reactions (6), (7) and (8) as well as qualitative locations for two other reactions emanating from an invariant point near 14.5 kbar and 1000°C:



Some of the reversals of Reactions (6) and (7) (in which sillimanite was used) are metastable because they are in the kyanite field. The volume changes for divariant Reactions (1) through (5) are as much as an order of magnitude greater than that for the sillimanite = kyanite equilibrium and thus, since the univariant reactions are intersections of the divariant fields, the difference in pressure between the kyanite and sillimanite equivalent reactions should be small.

Garnet + Quartz in natural systems

If the reactions studied here are to be applied to natural assemblages, the effect of additional components, notably Fe and Na, must be considered. With the addition of Fe, the univariant reactions examined here will become two-

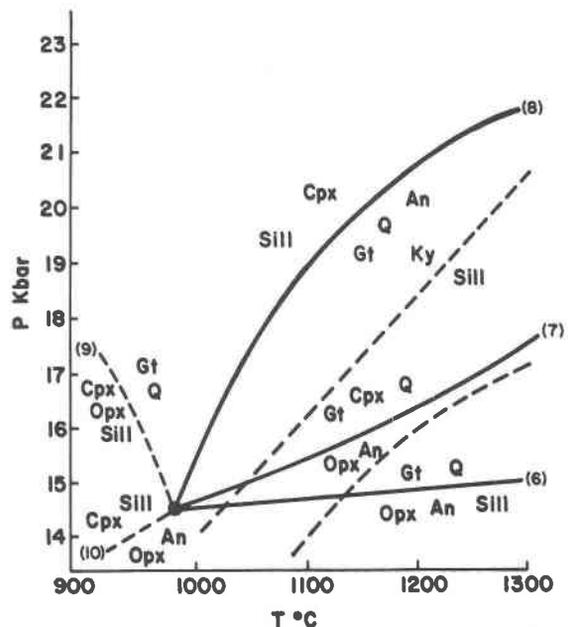


Fig. 6. Phase diagram summarizing the experimental results for Reactions (6), (7) and (8). Also shown are the inferred locations of Reactions (9) and (10), the kyanite = sillimanite boundary (after Holdaway, 1971) and the reaction sillimanite + enstatite = sapphirine + quartz (dashed line not labeled, after Chatterjee and Schreyer, 1972, and Newton, 1972).

phase fields. Fe partitions more strongly into garnet than into pyroxene, and thus the garnet bearing sides of the reactions will expand. Na will remain primarily in plagioclase at lower pressures, but becomes an important component of pyroxene at high pressures. In general, the effect of additional components is to shift Reactions (6) and (7) to significantly lower pressures. Indeed, unreversed experiments by Hensen (1976) demonstrated the formation of garnet at *cf.* 10 kbar and 1000°C for an Fe-bearing system. Almandine-rich garnet + quartz are stable at very low pressure as evidenced by natural occurrences in areas such as the Nain Province (Berg, 1977) and several locations in Scotland (Ashworth and Chinner, 1978) where andalusite is the common aluminum silicate.

The high pressure assemblage garnet-clinopyroxene (omphacite-kyanite-quartz (equivalent to the regions above Reactions (8) and (9) in Fig. 6) typifies kyanite eclogites such as those of the Tauern Window, Austria (Holland, 1979). Garnets are usually almandine-rich and the pyroxenes contain as much as a 60 percent jadeite component. Holland estimates the Tauern eclogites to have equilibrated at *cf.* 600°C and 20 kbar, significantly outside of the *P-T* range shown in Figure 6. The extended stability is presumably due to the presence of additional components.

The assemblages garnet-quartz-plagioclase-orthopyroxene and garnet-quartz-plagioclase-clinopyroxene, occupying a lower pressure region in Figure 6, are ubiquitous in granulite terrains. Perkins and Newton (1981) and Newton and Perkins (1982) have used these two assemblages to calculate metamorphic pressures for charnockites and mafic granulites. Their calculations indicate metamorphic pressures of 7–10 kbar for temperatures of 700–900°C for a variety of granulite terrains.

The univariant U_7 (Fig. 1) contains both of the barometric assemblages used by Perkins and Newton (1981) and by Newton and Perkins (1981). Application of their barometers based on Reactions (2) and (3) to the experimentally determined garnet compositions (Py_{89}) and estimated pyroxene compositions of this study yields pressures of 13.7 and 8.3 kbar, respectively, significantly lower than the 17.3 kbar depicted in Figure 1. The source of this disagreement is not certain. It may indicate that the estimated pyroxene compositions are not representative of equilibrium, that the barometric calibrations are in error or that some of the assumed activity models are not accurate. As pointed out by Newton and Perkins (1981), the garnet-quartz-pyroxene-plagioclase barometers are consistent with many independent thermometers/barometers. Thus, part of the discrepancy may be an effect of the highly mafic bulk compositions examined in this study versus the natural systems examined by Newton and Perkins. Reliable determination of equilibrium pyroxene compositions are needed to pin down the source of the inconsistency.

The lowest pressure assemblage depicted in Figure 6,

orthopyroxene-sillimanite-anorthite, has been reported in high-temperature granulites (Grew, 1980; Dougan, 1974; Ellis, 1980). Grew estimates metamorphic conditions of around 7 kbar and 900°C for orthopyroxene-plagioclase-sillimanite rocks from Enderby Land, Antarctica. Plagioclase and sillimanite are only present in minor amounts; sapphirine, cordierite and ossumilite are also present. Dougan (1974) estimated slightly lower pressures and temperatures for cordierite bearing rocks from the Guayana shield.

Conclusion

The qualitative aspects of Figure 6 are consistent with natural paragenesis. The kyanite-eclogite assemblage (garnet-kyanite-clinopyroxene) reacts to garnet-anorthite-pyroxene, characteristic of the granulite facies, at lower pressure. Finally, at the lowest pressure, orthopyroxene-sillimanite-anorthite are stable.

Quantitative application of the results of this study to natural parageneses requires detailed knowledge of the thermodynamics of the reactions as well as reliable activity models for the phases involved. No attempt has been made in this study to derive thermodynamic values for any of the reactions studied because of uncertainty surrounding pyroxene compositions. Future experimental studies should be directed toward the determination of equilibrium pyroxene stoichiometries. The role of additional components also requires more investigation. Studies in this regard will require not only the reversal of univariant equilibria but also reversal of phase compositions. Until such detailed experimental studies have been completed, application of reactions such as (1) through (8) to natural assemblages must rely heavily on thermodynamic modelling.

Note Added in Proof

Calculations by the author and by B. J. Wood suggest that the experimentally determined slope for Reaction (6) is too shallow. The discrepancy could be explained if the 1000° reversals of this study were metastable with respect to equilibrium phase compositions. If so, the invariant point depicted on Figure 6 would occur at lower temperature.

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