

# The $\text{Al}_2\text{O}_3$ Contents of Enstatite in Equilibrium with Garnet in the System $\text{MgO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ at 15–40 kbar and $900^\circ - 1,600^\circ \text{C}$

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**Abstract.** Forty-six reversed determinations of the  $\text{Al}_2\text{O}_3$  content of enstatite in equilibrium with garnet were made in the  $P/T$  range 15–40 kbar/900–1,600°C in the  $\text{MgO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$  system. Starting materials were mixtures of synthetic pyrope + Al-free enstatite and pyrope + enstatite (5–12%  $\text{Al}_2\text{O}_3$ ).  $\text{Al}_2\text{O}_3$  contents in reversal run pairs closely approached common values from both the high- and low-Al sides. Most experiments were done in a piston-cylinder device using a NaCl medium; some runs at very high temperatures were made in pyrex/NaCl or pyrex/talc assemblies.

The measured enstatite compositions, expressed as mole fractions of  $\text{Mg}_2(\text{MgAl})(\text{AlSi}_3)\text{O}_{12}(\text{X}_{\text{Opy}}^{\text{En}})$  were fitted by a Monte-Carlo method to the equilibrium condition:

$$\Delta H_{970}^0 - 970 \Delta S_{970}^0 + \int_1^P \Delta V_{970}^0 dP - \int_{970}^T \Delta S_T^0 dT + RT \ln X_{\text{Opy}}^{\text{En}} = 0$$

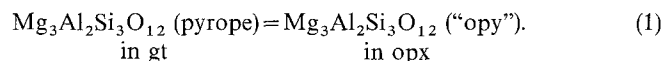
where the best fit parameters of  $\Delta H$ ,  $\Delta S$  and  $\Delta V$  (1 bar, 970 K) for the reaction pyrope = opy are 2,040 cal/mol, 2.12 eu and 9.55 cc/mol.

In addition to the determination of  $\text{Al}_2\text{O}_3$  contents of enstatite, the univariant reaction pyrope + forsterite = enstatite + spinel was reversibly located in the range 1,100–1,400°C. A “best-fit” line passes through 22, 22.5 and 25 kbar at 1,040, 1,255 and 1,415°C, respectively. Our results for the univariant reaction are in agreement with previous studies of MacGregor (1974) and Haselton (1979). However, comparison of the experimentally determined curve with thermochemical calculations suggests that there may be a small error in the tabulated  $\Delta H_{f(970,1)}^0$  value for enstatite. A value of –8.32 rather than –8.81 kcal/mole (Charlu et al. 1975) is consistent with the present data.

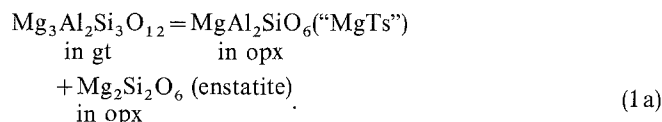
Application of garnet-enstatite-spinel-forsterite equilibria to natural materials is fraught with difficulties. The effects of non-ternary components are poorly understood, and the low solubilities of  $\text{Al}_2\text{O}_3$  in enstatite under most geologically reasonable conditions make barometric or thermometric calculations highly sensitive. More detailed studies, including reversed determinations in low-friction assemblies, are sorely needed before the effects of important diluents such as Fe, Ca and Cr can be fully understood.

## Introduction

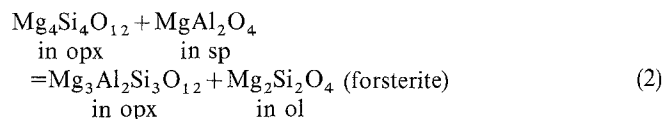
The solubility of  $\text{Al}_2\text{O}_3$  in orthopyroxene is of fundamental importance to petrologists. At high pressures, the saturation  $\text{Al}_2\text{O}_3$  content of orthopyroxene (opx) is buffered by coexisting garnet (gt) according to the reaction (Lane and Ganguly 1980):



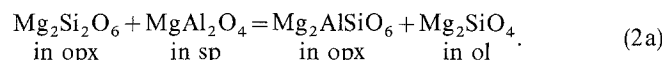
This reaction was expressed using different end members by Wood and Banno (1973):



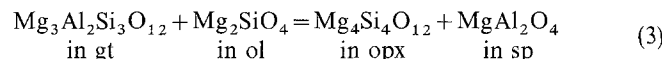
Reaction (1) is the basis of the most important geobarometer for garnet peridotites because of the large pressure dependence of the solubility of  $\text{Al}_2\text{O}_3$  in enstatite in the presence of garnet. At lower pressures in peridotite systems,  $\text{Al}_2\text{O}_3$  saturation is determined by the presence of olivine (ol) and spinel (sp) as described by the reaction:



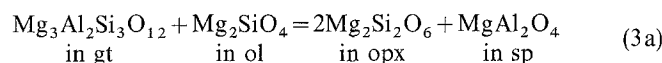
or its MgTs analogue:



These reactions have small volume change and are thus unsuitable as geobarometers, but may have considerable potential for geothermometry (Fujii 1977; Danckwerth and Newton 1978). Reactions (1) and (2) are related by a third which represents the transition of garnet peridotite to spinel peridotite:



or:



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All three of the reactions have been investigated experimentally in chemically simple systems approximating natural peridotites. The simplest and most-studied model system is  $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  in which reactions (1) and (2) are divariant. Reaction (1) was studied by Boyd and England (1964), MacGregor (1974), Howells and O'Hara (1978) and Lane and Ganguly (1980). Reaction (2) was studied by MacGregor (1974), Fujii (1977) and Danckwerth and Newton (1978), and additional experimental data were provided by Anastasiou and Seifert (1972) and Arima and Onuma (1977). Reaction (3) is univariant, and was studied by MacGregor (1974), Danckwerth and Newton (1978) and Haselton (1979), and Staudigel and Schreyer (1977) have provided additional data.

In spite of the numerous studies, inconsistencies and uncertainties remain, for two major reasons: difficulty of pressure calibration of the solid-medium piston-cylinder high pressure apparatus, and reliance on synthesis, rather than reversed equilibrium data in most of the studies. Only Danckwerth and Newton (1978) and Lane and Ganguly (1980), among previous investigators, experimentally demonstrated equilibrium enstatite compositions by reaction from  $\text{Al}_2\text{O}_3$ -undersaturated and -oversaturated directions at fixed  $P$  and  $T$  in runs with the low-strength NaCl solid pressure medium (Johannes 1973; Mirwald et al. 1975), for which pressure uncertainties are very small. Only three unambiguous reversals of reaction 2) by Danckwerth and Newton (1978) and two of reaction (1) by Lane and Ganguly (1980) have been achieved heretofore. Numerous determinations of reaction (3) were achieved by MacGregor (1974), but enstatites of high and low  $\text{Al}_2\text{O}_3$  content were not used as starting materials in the experiments, and it is possible that metastable pyroxene compositions can bias the  $P-T$  location of the univariant reaction.

Experimental data on reactions (1) and (2) in the three-component system serve as the starting point for geobarometry-geothermometry of natural peridotites. For this purpose, the experimental data may be reduced to simple thermodynamic expressions which relate  $P$ ,  $T$ , and the orthopyroxene  $\text{Al}_2\text{O}_3$  content. A simple but effective model of ideal solution of  $\text{Mg}_2\text{Si}_2\text{O}_6$  (En) and  $\text{MgAl}_2\text{SiO}_6$  (MgTs) components in enstatite was first used by Wood and Banno (1973) to smooth experimental data in the garnet field. This model has been used for garnet-field  $\text{Al}_2\text{O}_3$  isopleth calculations by Wood (1975) and Obata (1976) and by Wood (1975), Obata (1976), Stroh (1976), Fujii (1977), and Danckwerth and Newton (1978) for similar calculations in the spinel field. Depending on which set of experiments were used in the modeling, quite different  $\text{Al}_2\text{O}_3$  isopleth curves and standard reaction enthalpy and entropy changes,  $\Delta H^\circ$  and  $\Delta S^\circ$  for reactions (1a) and (2a) were derived. Lane and Ganguly (1980) advocated use of the aluminous orthopyroxene molecule  $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$  (Opy), recognizing that an aluminous end-member molecule closer to pure enstatite in composition is likely to mix more ideally with it.

For application of the simple system data to complex natural systems, it is necessary to evaluate the effects of  $\text{Fe}^{2+}$ , Ca, Na and Cr and, to a lesser extent,  $\text{Fe}^{3+}$  and Mn, on the activities of garnet, pyroxene and spinel components. This was done by Wood and Banno (1973) as ideal ion-site substitutions for Mg and Al in the minerals, an approximation which works best if the concentrations of the non-ternary cations are relatively low, as they generally are in garnet and spinel peridotites.

Important information results from comparison of the standard  $\Delta H^\circ$  and  $\Delta S^\circ$  of reaction derived from experimental isopleth sets with calorimetrically measured values. Danckwerth and Newton (1978) concluded that  $\Delta H^\circ$  for reaction (2a) based on

their three reversals of enstatite composition was in good agreement with high temperature solution calorimetry of Charlu et al. (1975) on synthetic  $\text{Mg}_2\text{Si}_2\text{O}_6$ ,  $\text{MgAl}_2\text{O}_4$ ,  $\text{Mg}_2\text{SiO}_4$ , and an aluminous pyroxene of composition  $\text{En}_{0.8}\text{MgTs}_{0.2}$ .  $\Delta H^\circ$  for reaction (1a) derived by Wood (1975) from the MacGregor (1974) isopleth set is 7.0 kcal, much higher than the  $3.1 \pm 1.9$  from solution calorimetry, but the Boyd and England (1964) garnet-field isopleths lead to  $\Delta H^\circ$  (1a) = 4.2 kcal (Wood and Banno 1973). Thus, the existing isopleth data do not allow definitive testing of the ideal solution theory against solution calorimetry. Low-temperature and high-temperature heat capacity measurements now exist for pyrope (Haselton and Westrum 1980) and enstatite (Krupka et al. 1979) which permit evaluation of  $\Delta S^\circ$  for the reactions and provide another test of the ideal aluminous pyroxene theories, if definitive experimental enstatite compositions are secured.

Forty-six reversed determinations of the  $\text{Al}_2\text{O}_3$  content of enstatite in equilibrium with garnet in the system  $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  were made in the present study. Fluxes were used in all experiments to produce enstatite crystals large enough for electron microprobe analysis. The objective was to define as accurately as possible the enstatite  $\text{Al}_2\text{O}_3$ -isopleth curves in the garnet field, for purposes of testing the ideal aluminous pyroxene theories and to provide a data base for theoretical extension to more complex chemical systems emulating natural peridotites.

## Experimental Techniques

*High Pressure Apparatus and Calibration.* Experiments were carried out in conventional piston-cylinder apparatus with 1/2"-diameter and 3/4"-diameter chambers. Four different pressure assemblies with internal graphite heater sleeves were used. Scale drawings of these assemblies may be obtained from the authors on request. Brief descriptions follow:

a) At pressures less than 32 kbar and temperatures below the melting point of NaCl, 3/4" NaCl cells (assembly A) identical to those of Holland (1980) were used. This assembly has been shown to require essentially zero pressure correction in the "piston-out" mode, even at 600° C, based on Holland's (1980) comparisons with the albite to jadeite + quartz equilibrium determined in a gas-pressure apparatus (Hays and Bell 1973).

b) At pressures less than 32 kbar and temperatures close to or above the melting point of NaCl, the pressure medium outside the heater sleeve was NaCl, but the inner parts were pyrex and boron nitride, similar to the assembly used by Newton (1972), except for the smaller (3/4") diameter. This assembly is termed B in the run tables. The inner diameter of the heater sleeve was 0.4". The pyrex assembly is not frictionless, but requires pressure calibration relative to equilibria determined in frictionless apparatus. Four calibrants were used. The reaction albite = jadeite + quartz was reversibly bracketed at 1,025°–1,050° C using the same starting materials as Holland (1980). The reaction ferrosilite = fayalite + quartz was bracketed hydrothermally with synthetic starting materials at 900° and 950° C with the NaCl assembly, giving results identical to those of Bohlen et al. (1980), and then bracketed with the NaCl-pyrex-BN setup, which showed substantial pressure loss (negative pressure correction). The reaction pyrope + forsterite = enstatite + spinel with 7 wt.%  $\text{Al}_2\text{O}_3$  in the enstatite was reversed hydrothermally at 1,085°–1,100° C in the NaCl assembly, giving results identical to those of Danckwerth and Newton (1978), and then bracketed with assembly B at 1,110°–1,145° C. Finally, the reaction anhy-

drous Mg-cordierite=sapphirine + quartz (Newton 1972) was reversed at 1,250° and 1,380° C with synthetic starting materials and compared to a bracketed at 1,250°–1,280° C of  $7.2 \pm 0.2$  kbar done in a gas apparatus (R.C.N. unpublished data). The  $dP/dT$  slope of the univariant equilibrium was computed accurately to be 0.4 bar/°C from heat of solution measurements (Charlu et al. 1974). The results of all of these calibration runs, given in Table 1 (available from the authors), was a negative pressure correction (pressure loss) of 6–11%, with the highest corrections below 1,000° C. As a reasonable overall compromise, we have used  $9 \pm 1\%$  correction for all runs with pressure medium B.

c) At pressures of 32 kbar and above and temperatures of 1,300° C or less, a 1/2" NaCl assembly was used. The albite=jadeite+quartz reaction was bracketed at 1,050° and 1,300° C with results exactly in agreement with Holland's (1980) calibration formula, thus indicating zero friction correction.

d) At temperatures of 1,500° C and above, a 1/2"-diameter assembly with talc and pyrex outer sleeves and pyrex inner parts was used. This assembly was calibrated at 1,200° C with the albite=jadeite+quartz reaction. The bracketing runs are given in Table 1. A plot of the ratio of the intensities of the  $27.8^\circ 2\theta$  (CuK $\alpha$ ) albite reflection to the  $30.6^\circ$  jadeite reflection versus pressure for runs of equal duration (3 h) gave –15% correction on the basis of the same ratio in the starting mix.

In all calibration runs and experimental runs with NaCl, the "piston-out" technique was used. A nominal pressure several kbar lower than the final run pressure was applied. Then the sample was heated to the final temperature. Thermal expansion of the NaCl increased the pressure by a precalibrated amount, which brought the sample very near to the final desired pressure. Sometimes a small amount of pressure bleeding was required to prevent overshoot. With the pyrex assemblies, the procedure was as follows. First a "locking" pressure of several kbar was applied. Then the sample was heated to 700°–800° C to soften the pyrex and prevent brittle fractures during loading. The assembly was taken to the final desired nominal pressure and heated to the final temperature. Continual pumping was necessary to maintain gauge pressure against relaxation of the glass. Thus, the final condition was advancing piston, or "piston-in". The pressures reported in the run tables are the ranges of gauge pressure observed during the runs.

**Temperature Measurement.** Temperature uncertainty has been a problem in previous experimental studies of subsolidus equilibria. Thermocouple emf drift can occur, especially with Pt-PtRh thermocouples, in the long run times often necessary for equilibration. The pressure effect on thermocouple calibration is not well known, and is highly dependent on the specific geometry of the pressure assembly used. These problems were addressed in the present study by using side-by-side chromel-P-alumel thermocouples and W-3% Re vs. W-25% Re thermocouples in many of the runs. Temperatures were controlled automatically on the W-Re thermocouple. Both thermocouples were monitored at intervals with a potentiometer. The readings, given in the run tables, were always within a few degrees of each other, indicating that the combined effects of poisoning and pressure effect are small, because it is highly unlikely that they would result in identical readings of thermocouples of greatly differing emf. After several hours in runs at temperatures above 1,000° C the thermocouples usually showed a tendency to diverge, with the Cr-Al indication falling below that of the W-Re thermocouple. The runs were always terminated at this point. Quenching by power cut-off brought temperatures below 100° C in about 10 seconds.

**Table 2.** Synthesis conditions of starting materials

#	Phase	P (Kb)	T (°C)	Comments
1	MgSiO <sub>3</sub> (Opx)	20	1,000	hydrothermal from clinoenstatite
2	MgSiO <sub>3.95</sub> Al <sub>2</sub> O <sub>3.5</sub> (Opx)	20	1,000	hydrothermal from oxides
3	MgSiO <sub>3.95</sub> Al <sub>2</sub> O <sub>3.7</sub> (Opx)	20	1,000	hydrothermal from oxides
4	MgSiO <sub>3.91.5</sub> Al <sub>2</sub> O <sub>3.8.5</sub> (Opx)	20	1,000	hydrothermal from oxides
5	MgSiO <sub>3.90</sub> Al <sub>2</sub> O <sub>3.10</sub> (Opx)	15	1,100	hydrothermal from oxides
6	MgSiO <sub>3.88</sub> Al <sub>2</sub> O <sub>3.12</sub> (Opx)	18	1,000	hydrothermal from oxides, reground and recycled at 1,600° and 40 Kb
7	Mg <sub>3</sub> Al <sub>2</sub> Si <sub>3</sub> O <sub>12</sub> (Gt)	30	1,100	hydrothermal from oxides
8	MgAl <sub>2</sub> O <sub>4</sub> (Sp)	1 atm.	1,425	dry from a sintered oxide pellet
9	Mg <sub>2</sub> SiO <sub>4</sub> (Fo)	1 atm.	1,425	dry from a sintered oxide pellet

**Starting Materials and Encapsulation.** The synthetic crystalline starting materials used in reversal experiments were made hydrothermally in sealed gold capsules from oxides, except as noted in Table 2. Homogeneous high-Al enstatites were difficult to synthesize. A nominal 12% Al<sub>2</sub>O<sub>3</sub> enstatite was prepared hydrothermally at 1,000° C and 18 kbar. It is possible to achieve very high metastable Al<sub>2</sub>O<sub>3</sub> contents in hydrothermal runs under these conditions (Fawcett and Yoder 1963). The charge was rerun at 1,600° C and 28 kbar for several hours. The X-ray pattern improved greatly, indicating 11.3 weight percent Al<sub>2</sub>O<sub>3</sub> by the reflection difference method of Boyd and England (1960), and a small amount of garnet. Details of synthesis of the other materials are given in Danckwerth and Newton (1978) and Perkins and Newton (1981).

In the 3/4" apparatus NaCl runs, reversal pairs of sealed Pt capsules were run side-by-side to determine the enstatite Al<sub>2</sub>O<sub>3</sub> contents. The thermocouple tip was lodged between the capsules, whose combined width was about 4 mm. One capsule contained pyrope+orthopyroxene oversaturated in Al<sub>2</sub>O<sub>3</sub> (5, 10, or 12 wt.%) in nearly equal amounts, and the other contained pyrope+orthopyroxene undersaturated in Al<sub>2</sub>O<sub>3</sub> (0 or 5 wt.%). Only one capsule at a time could be run in the 1/2" apparatus and the 3/4" NaCl-pyrex assemblies. Single sealed Pt capsules containing a mixture of pyrope+forsterite+enstatite+spinel in reacting proportions were used to locate reaction (3). The enstatite had 7 wt.% Al<sub>2</sub>O<sub>3</sub> for runs near 1,100° C, 8.5 wt.% Al<sub>2</sub>O<sub>3</sub> for runs near 1,250° C, and 10 wt.% Al<sub>2</sub>O<sub>3</sub> for runs near 1,400° C. These were previously-determined equilibrium Al<sub>2</sub>O<sub>3</sub> contents at the different run conditions, selected so as to minimize effects of metastable Al<sub>2</sub>O<sub>3</sub> content on the position of the univariant boundary.

In order to grow run products of sufficient size (and to avoid fine intergrowths of garnet and pyroxene) for accurate microprobe analysis it was necessary to use a flux. Starting mixes for runs below 1,500° C were sealed into 1/16" Pt tubes with fluxing materials. At temperatures below 1,150° C, 30 wt.% H<sub>2</sub>O

**Table 3.** Reversal runs defining the Al<sub>2</sub>O<sub>3</sub> content of enstatite in the presence of garnet

Run #	Pressure media	P (Kbar)	T <sub>W-Re</sub> (° C)	T <sub>Cr-Al</sub> (° C)	Run duration (h)	Initial wt% Al <sub>2</sub> O <sub>3</sub>	Final wt% Al <sub>2</sub> O <sub>3</sub>
G1	A	24.8–25.2	1,089–1,094	1,095–1,097	5	0	5.40
G1	A	24.8–25.2	1,089–1,094	1,095–1,097	5	10	4.60
G3	A	29.8–30.2	1,093–1,105	1,090–1,104	1	0	3.45
G3	A	29.8–30.2	1,093–1,105	1,090–1,104	1	10	3.05
G5	A	20.6–21.0	1,073–1,079	1,076–1,080	6	0	6.60
G5	A	20.6–21.0	1,073–1,079	1,076–1,080	6	10	6.00
G7	A	25.0–25.4	1,043–1,046	1,048–1,049	12	0	4.90
G7	A	25.0–25.4	1,043–1,046	1,048–1,049	12	10	4.30
G9	A	19.8–20.2	1,047–1,052	1,046–1,051	12	0	7.60
G9	A	19.8–20.2	1,047–1,052	1,046–1,051	12	10	6.20
G13	C	30.4–32.0	1,088–1,091	1,095–1,105	5	0	3.10
G14	C	31.2–32.0	1,093–1,100	1,090–1,100	5	10	2.45
G19	C	39.6–41.2	—	1,092–1,098	4	0	1.80
G20	C	39.6–41.2	1,096–1,105	1,097–1,101	5	10	1.40
G22	C	34.4–35.2	1,104–1,107	1,092–1,106	7	0	2.70
G23	C	34.8–35.2	1,099–1,105	1,104–1,106	11	10	1.50
P3	A	22.0–22.8	1,038–1,044	1,036–1,049	50	0	6.05
P3	A	22.0–22.8	1,038–1,044	1,036–1,049	50	10	5.65
P8	A	21.1–22.2	898– 918	901– 903	104	0	3.95
P8	A	21.1–22.2	898– 918	901– 903	104	5	3.10
P16	A	29.5–30.5	951– 966	943– 950	23	0	2.25
P16	A	29.5–30.5	951– 966	943– 950	23	5	1.45
P17	A	29.6–31.1	865– 873	872– 877	143	0	1.60
P17	A	29.6–31.1	865– 873	872– 877	143	5	1.20
P19	A	29.2–30.1	1,000–1,001	985–1,003	33	0	2.65
P19	A	29.2–30.1	1,000–1,001	985–1,003	33	10	2.05
P24	A	26.0–26.5	1,092–1,095	—	3	0	4.80
P24	A	26.0–26.5	1,092–1,095	—	3	10	4.00
P25	A	27.9–28.3	1,092–1,098	1,092–1,107	4	0	3.72
P25	A	27.9–28.3	1,092–1,098	1,092–1,107	4	10	2.77
P26	A	29.7–30.3	1,028–1,050	1,027–1,035	3	0	3.20
P26	A	29.7–30.3	1,028–1,050	1,027–1,035	3	10	2.40
P27	A	29.6–30.5	1,070–1,075	1,066–1,077	3	0	3.25
P27	A	29.6–30.5	1,070–1,075	1,066–1,077	3	10	2.45
P28	A	23.7–24.3	1,094–1,096	1,091–1,097	3	0	5.35
P28	A	23.7–24.3	1,094–1,096	1,091–1,097	3	10	4.65
P30	A	21.8–22.6	944– 951	942– 948	67	0	4.10
P30	A	21.8–22.6	944– 951	942– 948	67	10	3.20
P32	A	23.8–24.4	899– 901	890– 900	24	0	4.20
P32	A	23.8–24.4	899– 901	890– 900	24	10	2.70
P33	A	25.3–26.5	887– 901	887– 900	47	0	3.45
P33	A	25.3–26.5	887– 901	887– 900	47	10	2.55
P34	A	27.4–28.5	896– 902	892– 901	50	0	2.15
P34	A	27.4–28.5	896– 902	892– 901	50	10	1.65
P36	A	29.6–30.4	897– 902	892– 900	8	0	1.70
P36	A	29.6–30.4	897– 902	892– 900	8	10	1.35
P37	A	21.8–23.0	1,046–1,054	1,043–1,053	12	0	6.00
P37	A	21.8–23.0	1,046–1,054	1,043–1,053	12	10	5.85
P41	A	22.6–23.5	1,090–1,095	1,080–1,091	5	0	5.55
P41	A	22.6–23.5	1,090–1,095	1,080–1,091	5	10	4.95
P57	A	20.9–31.9	1,095–1,096	1,088–1,090	4	0	7.45
P63	A	21.2–22.1	1,094–1,096	1,086–1,091	4	10	6.50
p65	B	29.4–30.2 <sup>a</sup>	1,298–1,301	—	2	0	6.60
P66	B	29.6–30.1 <sup>a</sup>	1,296–1,300	—	2	10	6.20
P67	A	30.0–30.4	1,195–1,200	—	3	0	3.85
P67	A	30.0–30.4	1,195–1,200	—	3	10	3.55
P68	A	29.9–30.9	1,250–1,252	—	2	0	4.35
P68	A	29.9–30.9	1,250–1,252	—	2	10	4.25
P73	A	25.4–26.6	1,191–1,203	—	3	0	5.80
P73	A	25.4–26.6	1,191–1,203	—	3	10	5.20
P76	A	21.7–22.4	1,000–1,004	995–1,004	29	0	5.05
P76	A	21.7–22.4	1,000–1,004	995–1,004	29	10	4.85
P77	A	27.9–28.8	1,185–1,200	—	5	0	5.20
P77	A	27.9–28.8	1,185–1,200	—	5	10	4.70
P78	A	29.8–30.3	1,150–1,151	1,153–1,156	3	0	3.40

Table 3 (continued)

Run #	Pressure media	<i>P</i> (Kbar)	<i>T</i> <sub>W-Re</sub> (°C)	<i>T</i> <sub>Cr-Al</sub> (°C)	Run duration (h)	Initial wt% Al <sub>2</sub> O <sub>3</sub>	Final wt% Al <sub>2</sub> O <sub>3</sub>
P78	A	29.8–30.3	1,150–1,151	1,153–1,156	3	10	3.20
P79	B	24.8–25.3 <sup>a</sup>	1,293–1,298	—	1	0	9.60
P81	B	24.8–25.2 <sup>a</sup>	1,298–1,301	—	2	12	9.50
P82	B	25.0–25.3 <sup>a</sup>	1,195–1,200	—	5	0	8.00
P83	B	24.8–25.3 <sup>a</sup>	1,199–1,201	—	5	10	7.30
P84	B	27.6–28.1 <sup>a</sup>	1,398–1,403	—	3	0	9.60
P85	B	27.4–27.8 <sup>a</sup>	1,299–1,302	—	3	12	7.80
P91	B	29.9–30.3 <sup>a</sup>	1,400–1,401	—	1	12	7.85
P96	B	29.9–30.4 <sup>a</sup>	1,395–1,405	—	3	5	8.28
P92	B	27.6–28.1 <sup>a</sup>	1,393–1,407	—	2	12	9.55
P94	B	27.3–27.7 <sup>a</sup>	1,290–1,298	—	2	5	8.25
P95	A	20.3–21.1	1,088–1,093	1,085–1,088	2	0	7.45
P95	A	20.3–21.1	1,088–1,093	1,085–1,088	2	10	7.00
P97	C	39.6–41.0	1,283–1,308	—	1	5	2.86
P100	C	39.6–40.4	1,296–1,305	—	3	0	3.29
P98	C	36.4–36.9	1,297–1,309	—	2	5	3.68
P101	C	36.6–37.0	1,298–1,305	—	2	0	4.11
P99	C	32.6–33.4	1,295–1,306	—	3	5	4.50
P102	C	32.8–33.4	1,297–1,304	—	1	0	4.95
E4	D	33.0–33.8 <sup>a</sup>	1,495–1,505	—	5	0	8.85
E5	D	32.8–33.6 <sup>a</sup>	1,495–1,505	—	8	12	9.65
E6	D	32.8–33.6 <sup>a</sup>	1,595–1,605	—	2	0	10.80
E7	D	32.8–33.6 <sup>a</sup>	1,595–1,605	—	3	12	? <sup>b</sup>
E8	D	41.2–42.0 <sup>a</sup>	1,495–1,505	—	3	12	6.05
E9	D	41.2–42.0 <sup>a</sup>	1,495–1,505	—	3	0	5.75
E10	D	41.6–42.4 <sup>a</sup>	1,595–1,605	—	2	12	8.32
E11	D	41.6–42.4 <sup>a</sup>	1,595–1,605	—	3	0	7.78

<sup>a</sup> The reported pressures are nominal (gauge) pressures. See text for details of friction corrections

<sup>b</sup> No apparent change

was added. At temperatures of 1,150°C and above, hydrous melting occurred, and 10 wt.% oxalic acid was added instead, to lower H<sub>2</sub>O activity. At 1,500°C and above, extensive melting occurred with oxalic acid, and 3–5 wt.% PbO, intimately mixed with the charge, was used, in graphite rather than Pt containers.

**Analysis of the Run Products.** For runs to determine Al<sub>2</sub>O<sub>3</sub> content of enstatite, the quenched charges were examined optically and by X-ray diffraction. Charges run with H<sub>2</sub>O were white and sugary, with crystals of garnet and pyroxene up to 50 μm in longest dimension. Charges run with oxalic acid were gray and coarsely crystalline (30 μm) mixes of garnet and pyroxene, and, occasionally, a small amount of glass. Charges with PbO were dark hard pellets consisting of 10–15 μm pyroxene and garnet crystals separated by thin coatings of PbO-rich glass.

Several hydrothermal samples were examined by 1/8°2θ per min X-ray diffractometer scans with an annealed corundum internal standard. The degree of equilibration of some of the highest pressure hydrothermal runs was sufficient to give an indication of the enstatite composition from the Boyd and England (1960) 2θ-difference method (62–63° peaks). The agreement with the microprobe analyses was usually good. In all runs, the presence of garnet and enstatite was verified by fast-scan X-ray diffraction. The reversal runs for reaction (3) were scanned at 1/2°2θ per minute in the range 20°–50°2θ, and the X-ray peak heights of the phases were compared with those in the diffractogram of the starting mix. Clear indication of the direction of reaction was usually possible by this method.

Charges for reaction (1) were mounted in epoxy resin, generally as loose grains or aggregates, for microprobe analysis. The PbO runs were mounted as cylindrical slugs. The surfaces of

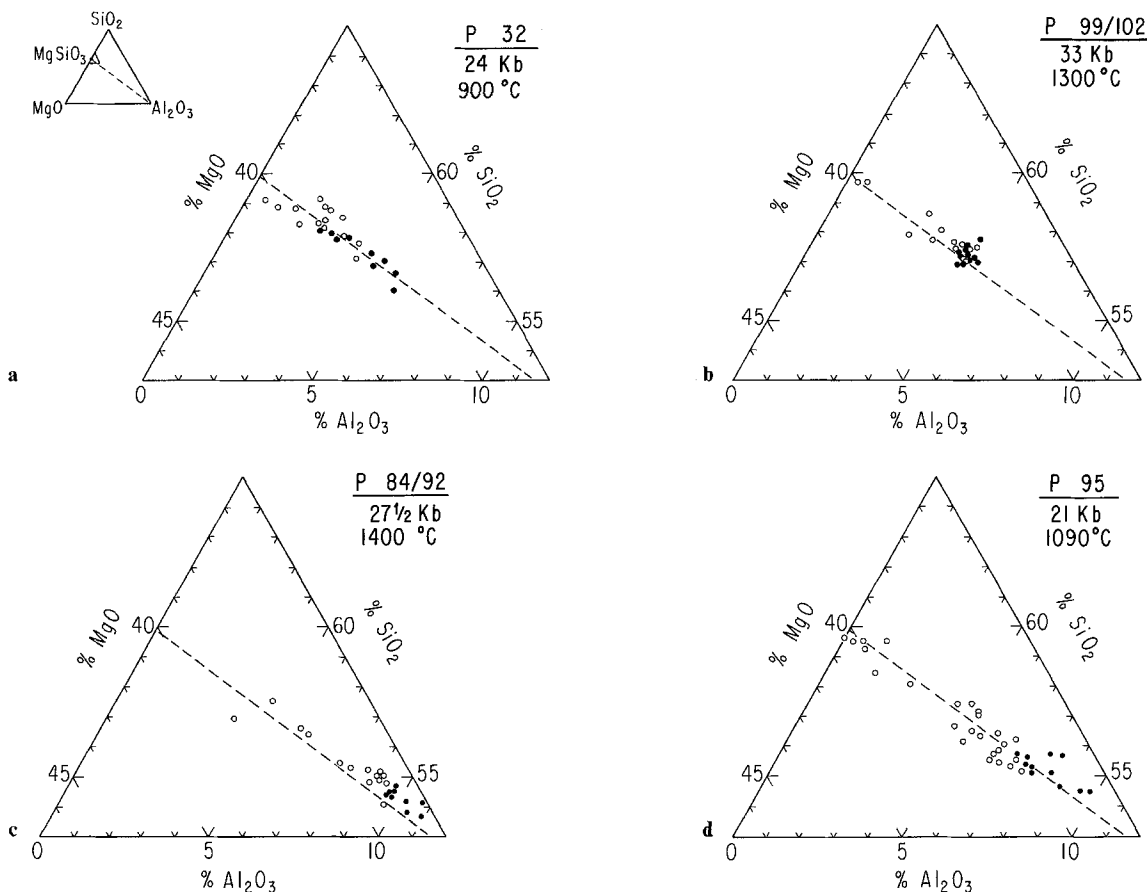
the probe mounts were carefully polished to avoid excessive erosion of the grains. The polished PbO-run slugs were etched for 30 min in 60% fluoroboric acid to define the crystal shapes by preferential dissolution of the surrounding glass.

Energy dispersive microprobe analyses were obtained with an ARL-EMX electron microprobe. All analyses were made at 15 kv and 0.1 μamp beam current with a beam diameter of about 1 μm. The standards used, synthetic pyrope glass and several MgSiO<sub>3</sub>–Al<sub>2</sub>O<sub>3</sub> glasses, were chemically very close to the unknowns, so that fluorescence and absorption corrections were negligible. At least 20 grains of orthopyroxene were analyzed in each sample, and several analyses were made on each grain. An analysis was rejected if it did not total 100 ± 2%.

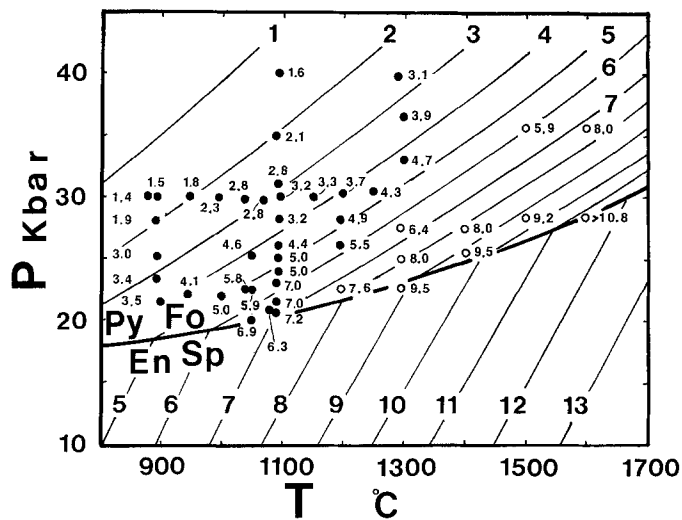
## Results of Experiments

**Enstatite Al<sub>2</sub>O<sub>3</sub> Contents.** All charges contained enstatite plus garnet, assuring continuous Al<sub>2</sub>O<sub>3</sub> buffering throughout the runs, except for one charge, that of run E6 (Table 3). In this run the pyrope was entirely consumed to make the high-Al<sub>2</sub>O<sub>3</sub> pyroxene from pure MgSiO<sub>3</sub>. Therefore, a true reversal bracket was not obtained with this run, but only a lower limit for Al<sub>2</sub>O<sub>3</sub> content.

Most grains of orthopyroxene in the run charges were zoned. The cores sometimes retained the original starting compositions, with interiors grading in Al<sub>2</sub>O<sub>3</sub> content, sometimes to broad, nearly equilibrated rims. In nearly all hydrothermal and oxalic acid runs, there was a small overlap of extreme Al<sub>2</sub>O<sub>3</sub> analyses coming from opposite directions. Some of this overlap results from analytic scatter and pressure and temperature variations



**Fig. 1.** **a** Analytical results for experiment P32 projected on the MgO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> ternary. In this and the following three figures the open circles represent pyroxenes which started on MgSiO<sub>3</sub> composition and the closed circles represent pyroxenes originally oversaturated in Al<sub>2</sub>O<sub>3</sub>. No apparent crossover of Al<sub>2</sub>O<sub>3</sub> contents as equilibrium was approached from two directions. **b** Analytical results for experiments P99 and P102. Note the tight cluster and minor crossover of analyses. **c** Analytical results for experiments P84 and P92. Note apparent excess SiO<sub>2</sub> in pyroxene. **d** Analytical results for experiment P95 showing well equilibrated compositions



**Fig. 2.** Experimental results and “best-fit” curves for reaction (1). Solid circles represent experiments conducted in NaCl pressure media; open circles represent experiments with an associated friction correction. Points are plotted at mean pressures and temperatures. Mean % Al<sub>2</sub>O<sub>3</sub> determinations are shown. See Table 3 for ranges. The solid line for the reaction Py + Fo = En + Sp and the isopleth in the spinel field are calculated from the thermochemical value discussed in text

during the runs, but some is undoubtedly because of “path looping”; that is, overstepping of the equilibrium composition and reapproach from the opposite direction. In general, crossovers were more pronounced at lower temperatures and pressures (Fig. 1a) than at higher temperatures and pressures, where tight clusters of analyses with only slight overlap indicated nearly complete reequilibration of the charges (Fig. 1b). The region of overlap was usually small, and the equilibrium compositions were taken at the centers of crossover bands. The problem of overlap due to path looping arose in the hydrothermal runs on aluminous pyroxenes of Lane and Ganguly (1980) and Perkins and Newton (1981). The present runs with PbO did not show crossover; therefore it is presumably a capricious effect of hydrothermal nucleation and growth. In some runs, especially at higher temperatures and pressures, departures from the MgSiO<sub>3</sub>–Al<sub>2</sub>O<sub>3</sub> join in the direction of excess SiO<sub>2</sub> were observed (Fig. 1c), compared to runs of similar Al<sub>2</sub>O<sub>3</sub> content at lower temperatures and pressures (Fig. 1d). Boyd and England (1960) also detected a probable excess of Si/Mg ratio over the ideal value of unity by the X-ray diffraction characteristics of some of their aluminous enstatites synthesized at very high temperatures and pressures.

Mean values of Al<sub>2</sub>O<sub>3</sub> contents in weight percent are shown in Fig. 2. The isopleth lines in Fig. 2 were derived from a statisti-

**Table 4.** Experimental runs defining the reaction anstatite + spineel = pyrope + forsterite

Run #	Pressure media	P (Kbar)	T ( $\pm 5^\circ$ C)	Run duration (h)	Starting opx (wt% $\text{Al}_2\text{O}_3$ )	Results
PF1	B	23.9–24.0 <sup>a</sup>	1,315	7	10	moderate reaction to En + Sp
PF2	B	21.8–22.1 <sup>a</sup>	1,260	7	10	complete reaction to En + Sp
PF3	B	28.8–29.3 <sup>a</sup>	1,465	2	10	complete reaction to Py + Fo
PF4	B	28.0–28.3 <sup>a</sup>	1,435	2	10	complete reaction to Py + Fo
PF5	B	26.0–26.1 <sup>a</sup>	1,375	8	10	moderate reaction to En + Sp
PF6	B	26.8–27.2 <sup>a</sup>	1,405	8	10	strong reaction to En + Sp
PF7	B	24.2–24.6 <sup>a</sup>	1,250	4	8 <sup>1/2</sup>	no apparent reaction
PF8	B	24.8–25.1 <sup>a</sup>	1,270	6	8 <sup>1/2</sup>	weak reaction to Py + Fo
PF9	B	23.8–24.2 <sup>a</sup>	1,240	5	8 <sup>1/2</sup>	strong reaction to En + Sp
PF10	B	21.4–21.6 <sup>a</sup>	1,100	4	7	complete reaction to En + Sp
PF11	B	21.8–22.2 <sup>a</sup>	1,100	5	7	complete reaction to En + Sp
PF12	B	25.0–25.3 <sup>a</sup>	1,260	4	8 <sup>1/2</sup>	complete reaction to Py + Fo
PF13	B	22.3–22.5 <sup>a</sup>	1,110	4	7	strong reaction to En + Sp
PF14	B	22.7–22.9 <sup>a</sup>	1,120	3	7	no apparent reaction
PF15	B	23.0–23.3 <sup>a</sup>	1,135	3	7	no apparent reaction
PF16	A	20.3–20.7	1,100	7	7	complete reaction to Py + Fo
PF17	B	27.4–27.9 <sup>a</sup>	1,425	2	10	strong reaction to Py + Fo
PF18	A	20.0–20.0	1,085	5	7	strong reaction to En + Sp
PF19	B	23.6–23.6 <sup>a</sup>	1,145	3	7	strong reaction to Py + Fo

<sup>a</sup> The reported pressures are nominal (gauge) pressures for pressure media B. See text for details

cal and thermodynamic treatment of all of the experimental points, as explained in the next section. Complete analytic data are given in Table 3.

**Univariant Reaction.** Table 4 presents the experimental observations bearing on reaction (3) and Fig. 3 shows the reversal runs and the earlier brackets of Danckwerth and Newton (1978). Their 1,100° C bracket in the NaCl medium was repeated in the present study with identical results. The NaCl-pyrex-BN medium runs just above 1,100° C show that the pressure correction of –8% to –10% is appropriate, at least in this pressure-temperature range. The solid curve of Fig. 3 is a statistical and thermodynamic fit to the nine reversal brackets, as explained in the following section.

### Thermodynamic Treatment of Results

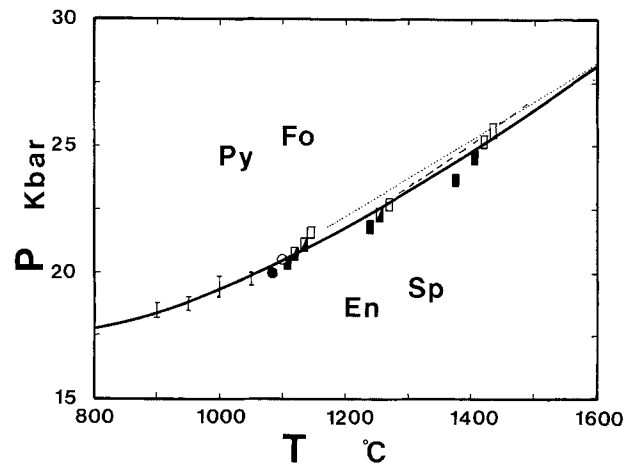
**Garnet-Field  $\text{Al}_2\text{O}_3$  Isopleths of Enstatite.** Thermodynamic analysis of the data proceeds from the equilibrium relation:

$$-\Delta G^0(T, P) = RT \ln K \quad (4)$$

where  $\Delta G^0$  is the Gibbs energy change for reaction (1) or (1a) at a fixed temperature and pressure.  $K$ , a constant at fixed  $T$  and  $P$ , is evaluated as  $X_{\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}}^{\text{opx}}$  for the ideal opy theory or  $X_{\text{MgAl}_2\text{SiO}_6}^{\text{opx}} \cdot X_{\text{Mg}_2\text{Si}_2\text{O}_6}^{\text{opx}}$  for the ideal MgTs theory, where  $X$  denotes mole fraction.  $\Delta G^0(T, P)$  is evaluated as:

$$\Delta G^0(T, P) = \Delta H^0(970, 1) - 970 \Delta S^0(970, 1) - \int_{970}^T \Delta S^0(T, 1) dT + (P - 1) \Delta V^0 \quad (5)$$

A reference temperature of 970 K was chosen because the enthalpy of solution measurements on pyrope and enstatite to evaluate  $\Delta H^0$ , the standard enthalpy change, were made at that temperature (Charlu et al. 1975). The approximation of constant  $\Delta V^0$  and variable-pressure standard state (Lane and Ganguly 1980) are chosen for simplicity. Low-temperature and high-temperature heat capacity data are available for pyrope and enstatite



**Fig. 3.** Experimental results and “best-fit” curve for reaction (3). I-beam brackets are from Danckwerth and Newton (1978); circles are the present results using NaCl pressure media and rectangles are the present results using pyrex pressure media. Solid symbols, half filled symbols and open symbols represent growth of low-pressure assemblage, no reaction, and growth of high pressure assemblage, respectively. The fine dotted line is the curve of MacGregor (1974); dashed line is from Haselton (1979)

(Haselton and Westrum 1980; Krupka et al. 1979; Haselton 1979) to evaluate the standard entropy change,  $\Delta S^0(T)$ . The heat capacity of opy was estimated as the sum of the heat capacities of  $3\text{MgSiO}_3 + \text{Al}_2\text{O}_3$  (corundum), the latter heat capacity taken from Robie et al. (1978), and the heat capacity of MgTs was similarly evaluated. The heat capacity difference,  $\Delta C_p$ , is nearly constant in the range 1,000–1,500 K, and was assumed constant for extrapolation above 1,500 K to get  $\Delta S^0(T)$  from the formula:

$$\Delta S^0(T) = \Delta S^0(970) + \int_{970}^T \frac{\Delta C_p}{T} dT \quad (6)$$

Table 5

Reaction	$\Delta H_{970}^0$ (cal/mol)		$\Delta S_{970}^0$ (cal/mol-deg)		$\Delta V^0$ (cc/mol)	
	experimental	thermochemical	experimental	thermochemical	experimental	volumetric
(1) $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ (Gt) = $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ (Opx)	$2,040 \pm 170$	$3,070 \pm 1,900$	$2.12 \pm 0.08$	—	$9.55 \pm 0.24$	9.42
(1a) $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ (Gt) = $\text{MgAl}_2\text{SiO}_6$ (Opx) + $\text{Mg}_2\text{Si}_2\text{O}_6$ (Opx)	$1,640 \pm 150$	$3,070 \pm 1,900$	$-0.15 \pm 0.14$	—	$8.65 \pm 0.29$	—
(3) $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ (Gt) + $\text{Mg}_2\text{SiO}_4$ (Fo) = $\text{Mg}_4\text{Si}_4\text{O}_{12}$ (Opx) + $\text{MgAl}_2\text{O}_4$ (Sp)	$-3,200 \pm 250$	$-5,510 \pm 460$	$-0.5 \pm 0.5$	-0.55	$7.10 \pm 2$	7.73
(3a) $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ (Gt) + $\text{Mg}_2\text{SiO}_4$ (Fo) = 2 $\text{Mg}_2\text{Si}_2\text{O}_6$ (Opx) + $\text{MgAl}_2\text{O}_4$ (Sp)	$-3,300 \pm 400$	$-5,510 \pm 460$	$-0.5 \pm 1.5$	-0.55	$10 \pm 5$	7.73

Equations (4), (5) and (6) were combined to derive best-fit values of  $\Delta H_{970}^0$ ,  $\Delta S_{970}^0$  and  $\Delta V^0$  (Table 5) for both the ideal opy and MgTs theories. A Monte Carlo method was used, wherein many combinations of  $\Delta H_{970}^0$ ,  $\Delta S_{970}^0$ , and  $\Delta V^0$ , each varying independently by closely-spaced increments, were tried. Each combination resulted in an isopleth set. The sum of the squared deviations of the experimental  $\text{Al}_2\text{O}_3$  values from the corresponding isopleths were tallied for each combination. The best fit was the combination with the smallest residual. The opy and MgTs theories gave equally good fits to the experimental data. With the exception of 8 experimental points the "best fit" models are completely consistent with the experimental determinations. For both models, the maximum deviation of the experimental determinations from the smoothed isopleths was about 150 cal/mole (experiments # P98/101 and P67). The standard deviation of the points from the best-fit isopleths, expressed as a Gibbs energy difference, is 50 cal for the opy theory and 42 cal for the MgTs theory. Table 5 gives the best fit parameters  $\Delta H^0$ ,  $\Delta S^0$  and  $\Delta V^0$  for both models, compared to the results of calorimetric and volume measurements. Note that the errors given for these values (Table 5) are two standard deviations from the mean and are not independent.

The thermochemical  $\Delta H_{970}^0$  for reaction (1) of Table 5 depends on a linear extrapolation of the enthalpy of solution of a  $(\text{MgSiO}_3)_{0.9}(\text{Al}_2\text{O}_3)_{0.1}$  enstatite (Charlu et al. 1975) and has large uncertainty. The experimental best-fit  $\Delta H_f^0$  is much more precise, and defines the standard enthalpy of formation at 970 K from the oxides of the  $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$  pyroxene (opy) as  $-18.17 \pm 0.42$  kcal, using the value for pyrope of  $-20.21 \pm 0.38$  kcal (Charlu et al. 1975). Using the entropy of pyrope at 970 K of 182.20 cal/K (Haselton, 1979) the standard entropy of opy at the same temperature is 184.32 cal/K. This is 4.59 cal/K greater than  $3S_{\text{MgSiO}_3} + S_{\text{Al}_2\text{O}_3}$  and is presumably due to disordering of Al on the octahedral and tetrahedral sites. The statistical mechanical calculations of Ganguly and Ghose (1979) lead to a maximum disorder entropy of 7.0 cal/K, and to a minimum disorder entropy of 4.3 cal/K corresponding to the "Al-avoidance" possibility, in which adjacent corner-linked tetrahedra do not both contain Al. The present findings support the Al-avoidance model. The standard Gibbs energy of formation from the oxides of opy at 970 K is thus  $-20.54$  kcal.

The experimental volume change of reaction (1) may be compared with X-ray diffraction measurements on aluminous enstatite. A molar volume versus composition curve was constructed

from volume data of three synthetic aluminous enstatites of Danckwerth and Newton (1978) and of five aluminous enstatites synthesized by Chatterjee and Schreyer (1972). These authors estimated the compositions of their pyroxenes from the *b*-axis plot of Skinner and Boyd (1964). The resulting molar volume relation is:

$$V(\text{cm}^3) = 125.26 - 4.130X_{\text{opy}} + 1.418X_{\text{opy}}^2 \quad (7)$$

The molar volume of opy is  $122.55 \text{ cm}^3$ , and  $\Delta V^0$  of reaction (1) is  $9.42 \text{ cm}^3$ , which is in good agreement with the best-fit volume parameter of  $9.55 \pm 0.24 \text{ cm}^3$ .

The MgTs theory gives as good a fit to the isopleth data as the opy theory in most respects, except that the molar volume of MgTs cannot be estimated accurately by extrapolation of the aluminous enstatite volume data. The best-fit volume is  $8.65 \text{ cm}^3$ , and there is no independent way to tell if this is a physically meaningful value or simply a data-fitting parameter.

**Univariant Curve.** A Monte Carlo fit for  $\Delta H_{970}^0$ ,  $\Delta S_{970}^0$  and  $\Delta V^0$  was made to the five experimental brackets of Danckwerth and Newton (1978) and the four of the present study. The resulting parameters from the opy and MgTs theories are given in Table 5. The uncertainties given in Table 5 are the total range of *H*, *S* and *V* values consistent with the experiments and are highly correlated.

The best fit value of  $\Delta H_{970}^0$  for reaction (3) is not in agreement with the enthalpy of solution data of Charlu et al. (1975). Moreover, the solution data are not consistent with the location of the univariant curve of reaction (3). Using the accurately measured entropy data, giving  $\Delta S^0 = -0.55 \text{ cal/K}$ , the enthalpy change from calorimetry of  $-5,510 \pm 460 \text{ cal}$ , and the volume change of  $7.73 \text{ cm}^3$ , one gets a pressure of  $27.0 \pm 2.5 \text{ kbar}$  at 1,000 K, compared to the 17.5 kbar of Fig. 3. Therefore, it is certain that some of the heat of solution values are incorrect. Since the  $\text{MgSiO}_3$  heat of solution is multiplied four times in the calculation, an error of 500 calories in this quantity is sufficient to account for the discrepancy. An enthalpy of formation of  $\text{MgSiO}_3$  of  $-8.32 \text{ kcal}$ , rather than the  $-8.81$  measured by Charlu et al. (1975) would give a  $\Delta H^0$  (3) in agreement with the experimental value and a pressure for the univariant equilibrium with Al-free pyroxene of 15.5 kbar at 970 K. The additional opy-theory stabilization of enstatite by 3.9 wt.%  $\text{Al}_2\text{O}_3$  brings the pressure to 17.5 kbar, in agreement with the experimental curve. The value of  $-8.32 \text{ kcal}$  compares well with that of



−8.39 kcal which results from the  $\Delta G_f^\circ$  of Zen and Chernosky (1976) deduced from phase equilibria and the  $\Delta S_f^\circ$  from the recent heat capacity work.

A large range of  $\Delta V$  allows agreement with the experimental brackets in both theories. This parameter is much more loosely constrained than for reaction (1).

**Spinel-Field  $\text{Al}_2\text{O}_3$  Isopleths of Enstatite.** Elimination of garnet between Eq. (1) and (3) yields Eq. (2), which governs the spinel-field isopleths, and the opy-theory parameters of  $\Delta H_{970}^\circ = 5,240$  cal,  $\Delta S_{970}^\circ = 2.67$  cal/K, and  $\Delta V^\circ = 1.69$  cm<sup>3</sup>. The slope of an isopleth  $X_{\text{opy}} = \text{constant}$  is given by:

$$\left. \frac{\partial P}{\partial T} \right)_{X_{\text{opy}}} = \frac{\Delta S^\circ(2) - R \ln \frac{X_{\text{opy}}}{X_{\text{en}}}}{\Delta V^\circ(2)} \quad (8)$$

The isopleths are shown in Fig. 2. It is to be emphasized that they are determined by the very oblique intersections of the garnet-field isopleths with the univariant curve. Slight shifts in the positions of either could cause large shifts in the spinel-field isopleths. Also, the volume change is only loosely constrained by the best-fit volumes for reactions (1) and (3). Therefore, the spinel-field isopleths of Fig. 2 have greater uncertainties than those of the garnet field.

### Comparison with Previous Work

**Garnet-Field Isopleths.** Figure 4 shows the present smoothed isopleth set and some of the experimental data of previous workers. All points claiming to be reversals are shown except that of Howells and O'Hara (1978) at 30 kbar and 1,500° C. Also shown are the unreversed data of MacGregor (1974).

The three reversals of Boyd and England (1964) show much more  $\text{Al}_2\text{O}_3$  than indicated by our isopleths. This may be due to the fact that they depended on the exsolution of pyrope from  $\text{Al}_2\text{O}_3$  saturated pyroxene, which may be hindered by the difficult nucleation of garnet. The two hydrothermal reversals of Lane and Ganguly (1980) in the range 1,000°–1,100° C and 25–30 kbar are in excellent agreement with our isopleths. This is to be expected inasmuch as their runs were carried out with procedures identical to ours (hydrothermal reversals in the NaCl medium). Agreement with their highest temperature runs is not as good. These runs were unfluxed and, in view of the difficulties encountered in this study of attaining equilibrium, it is suggested that equilibrium may not have been attained in these three runs or that the finely sintered nature of the run products led to inadvertent inclusion of garnet in the spots analyzed. The one hydrothermal reversal of Wood (1978) agrees quite well with our curves. The greatest discrepancy is with Howells and O'Hara (1978), who found a value of about 6 wt.%  $\text{Al}_2\text{O}_3$  at 30 kbar and 1,500° C. The present data indicate about 9% at the same conditions. The MacGregor data points are not in bad agreement with the present ones but diverge to higher  $\text{Al}_2\text{O}_3$  values at the higher temperatures.

The Wood (1975) and Obata (1976) isopleths were generated by modelling the MacGregor (1974) data with the ideal MgTs theory. These sets show somewhat greater  $\text{Al}_2\text{O}_3$  at fixed  $T$  and  $P$  over most of the field than do the present set.

**Univariant Reaction.** Figure 3 shows the experimental curve of MacGregor, to which a −10% pressure correction has been applied, and the experimental curve of Haselton (1979). The latter reversed study was done by much the same methods as

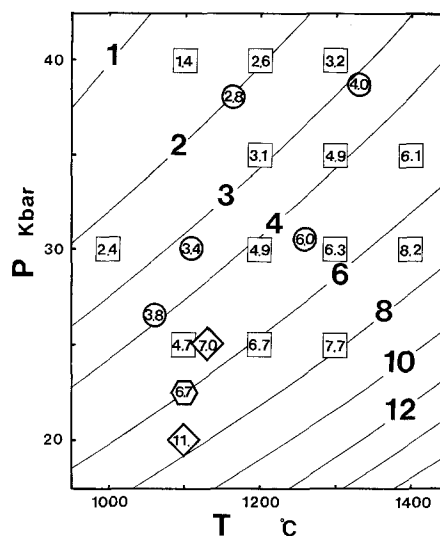


Fig. 4. Comparison of the present  $\text{Al}_2\text{O}_3$  isopleths for enstatite in the garnet field with other data. Bold symbols represent reversed determinations. Squares, circles, triangles and hexagons are the results of MacGregor (1974), Lane and Ganguly (1980), Wood (1974) and Boyd and England (1964)

the present. There is good agreement of the three studies. A single reversal bracket of Staudigel and Schreyer (1977) is two kbar higher than our curve at ~950° C. The calculated curve of Obata (1976) is generally in good agreement with the experimental ones.

**Spinel-Field Isopleths.** The calculated isopleths agree very well with the 20 kbar reversed points of Danckwerth and Newton: 7.2 wt.%  $\text{Al}_2\text{O}_3$  at 1,080° C, 6.2 wt.% at 1,000° C, and 5.6 wt.% at 950° C. The latter two points were metastable reversals a short distance into the garnet field, which was possible because of the difficulty of spontaneous nucleation of garnet near its stability limit (Boyd and England 1960). These points may be compared to the present spinel-field isopleths by short extrapolations past the univariant curve in Fig. 2. At 1,200° C the unreversed syntheses of Fujii agree well with our deduced isopleths. At 1,300° C the Fujii  $\text{Al}_2\text{O}_3$  contents are slightly greater, and at 1,400° C the discrepancy is about 1 wt.%.

Among calculated spinel-field isopleth sets, the Wood (1975), Obata (1976), and Danckwerth and Newton (1978) sets are all similar to the present ones. The latter set diverges to slightly higher  $\text{Al}_2\text{O}_3$  contents in the high temperature range. All of these show steep positive  $dP/dT$  slopes, which agree with the present study. The calculated curves of Stroh (1976), which modeled MacGregor's (1974) spinel-field data, have flatter  $dP/dT$  slopes and do not seem to be in accord with the measured small volume change of the isopleth reaction (reaction 2).

### Potential for Geobarometry-Geothermometry

The three-component garnet-field isopleths of MacGregor (1974) have been the basis of most recent geobarometers for garnet peridotites, following the demonstration of Boyd (1973) of the power of this method. The  $\text{Al}_2\text{O}_3$  contents of peridotite pyroxenes are usually very low, so that small analytical error and differences among model isopleth sets make large differences in calculated pressures. An additional serious problem is the combined effect of other garnet and pyroxene components, main-

ly Ca and Fe. Akella (1976) and Perkins and Newton (1981) showed that Ca in the garnet lowers the  $\text{Al}_2\text{O}_3$  content of coexisting orthopyroxene over that at a given  $T$  and  $P$  in the three-component system. Wood (1974) studied garnet-pyroxene equilibria in the  $\text{FeO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  system and concluded that Fe lowers the Al content of orthopyroxene over the three-component system. No reversals of the  $\text{Al}_2\text{O}_3$  contents were made. Quantitative garnet-pyroxene geobarometry awaits accurate reversal experimental evaluation of the effects of Ca and Fe.

Several authors (e.g. Ferguson et al. 1977) have concluded from the coexistence of garnet and spinel in exotic peridotite nodules in certain volcanic pipes that the assemblage equilibrated near the garnet-spinel peridotite boundary, assumed to be near-univariant. However, Jenkins and Newton (1979) showed that the combined effect of Ca and Fe on this transition amount to a pressure lowering of at least 6 kbar for the coexistence of garnet and olivine at 1,000° C. It is probable that spinel can coexist with garnet in peridotites over many kbar, especially when stabilized by high Cr content.

Most workers now agree that the spinel-field  $\text{Al}_2\text{O}_3$  isopleths of enstatite in peridotite have little potential as a geobarometer but may be useful as a geothermometer for spinel lherzolites. Obata (1980) used this thermometer for the Ronda, Spain, peridotite body, basing temperatures on his own (1976) spinel-field isopleth set. The present isopleths, those of Wood (1975) and Obata (1976) all give uncorrected temperatures within about 80° C of each other. The role of non-ternary ions is crucial however, especially the large and probably non-ideal effect of Cr in spinel (Evans and Frost 1975), which results in higher temperature indications for spinel lherzolites than given by the uncorrected ternary isopleths. The experimental finding that addition of Ca results in relatively flat  $dP/dT$  slopes of the orthopyroxene Al isopleths in the spinel peridotite field (Dixon and Presnall 1980), which isopleths may therefore be useful for geobarometry, has no obvious explanation in terms of simple volume and entropy considerations and needs additional experimental verification.

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