

# Calorimetric Study of $\text{MgSiO}_3$ Garnet and Pyroxene: Heat Capacities, Transition Enthalpies, and Equilibrium Phase Relations in $\text{MgSiO}_3$ at High Pressures and Temperatures

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Enthalpy of the  $\text{MgSiO}_3$  pyroxene-tetragonal garnet transition was measured by high-temperature solution calorimetry, giving  $\Delta H_{983}^0 = 30.80 \pm 3.11$  kJ/mol at 983 K. Heat capacities of  $\text{MgSiO}_3$  pyroxene and tetragonal garnet were also measured by differential scanning calorimetry from temperatures of 150 to 700 K. Using these calorimetric data and published thermodynamic data, equilibrium phase boundaries of high-pressure transitions in  $\text{MgSiO}_3$  were calculated at pressures up to 26 GPa and at temperatures up to 2600 K. In calculating the stability field of  $\text{MgSiO}_3$  tetragonal garnet, the effect of partial disorder of Mg and Si cations in the octahedral sites of garnet on the phase boundaries was examined. The calculated stability field of tetragonal garnet was generally consistent with the high-pressure experimental data. The calculated boundaries for the pyroxene-garnet and garnet-perovskite transitions have negative and positive slopes, respectively.

## INTRODUCTION

Thermodynamic properties of high-pressure phases in the system  $\text{MgO-SiO}_2$  are indispensable to calculating the equilibrium phase relations at high pressures and high temperatures as well as to estimating the thermal state of Earth's mantle. Experimental determination of phase relations for  $\text{MgSiO}_3$  in a wide pressure-temperature range has been carried out by several investigators [Akaogi and Akimoto, 1977; Ito and Yamada, 1982; Ito and Navrotsky, 1985; Kato and Kumazawa, 1985; Sawamoto, 1987; Ito and Takahashi, 1989; Presnall and Gasparik, 1990]. A stability field for  $\text{MgSiO}_3$  tetragonal garnet (majorite) was first found by Kato and Kumazawa [1985]. Subsequently, Sawamoto [1987] determined detailed phase relations in  $\text{MgSiO}_3$  involving majorite. Both studies, however, widely disagree, particularly in the stability field of the garnet phase, mainly because of uncertainties in determining pressures and temperatures. Presnall and Gasparik [1990] recently obtained a negative slope for the pyroxene-garnet transition boundary. This is in contrast to the positive slope reported by Kato and Kumazawa [1985] and Sawamoto [1987].

Several thermodynamic calculations of the phase relations at high pressures and high temperatures based on calorimetric measurements of high-pressure magnesian silicates have been

published [Akaogi and Navrotsky, 1984; Ito and Navrotsky, 1985; Akaogi *et al.*, 1987; Ashida *et al.*, 1988; Akaogi *et al.*, 1989; Ito *et al.*, 1990]. Akaogi *et al.* [1987] measured solution enthalpies of cubic garnet solid solutions in the compositional range from pyrope to 42% $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ -58% $\text{Mg}_4\text{Si}_4\text{O}_{12}$  in the system  $\text{Mg}_4\text{Si}_4\text{O}_{12}$ - $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$  and estimated the enthalpy of transition of  $\text{MgSiO}_3$  pyroxene to cubic garnet. However, direct measurements of the enthalpy of the pyroxene-tetragonal garnet transition in  $\text{MgSiO}_3$  are still unavailable. Fei *et al.* [1990] and Kuskov *et al.* [1989] calculated equilibrium phase relations in  $\text{MgSiO}_3$  in a wide pressure-temperature space from internally consistent thermodynamic data sets which were derived from the experimentally determined phase relations and the calorimetric measurements. Nevertheless, the stability field of the garnet phase has been poorly constrained, compared with those of the other phases, because the thermodynamic data are lacking.

In this study, the enthalpy of pyroxene-tetragonal garnet transition in  $\text{MgSiO}_3$  and heat capacities of pyroxene and tetragonal garnet phases were measured. Using these new data together with those of the other phases, all of the major transition boundaries in  $\text{MgSiO}_3$  are calculated up to 26 GPa and 2600 K. Effect of partial cation disorder observed in the tetragonal garnet [Angel *et al.*, 1989; Howell *et al.*, 1990] is taken into consideration.

## EXPERIMENTAL METHODS

### Sample Preparation

Single crystals of  $\text{MgSiO}_3$  orthopyroxene, synthesized by M. Ozima [Takei *et al.*, 1984], were pulverized and used for both calorimetry and as starting material for high pressure synthesis of

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garnet. The 1000-ton and 5000-ton uniaxial split-sphere apparatus [Ito and Takahashi, 1989] at Institute for Study of the Earth's Interior, Okayama University, were used for the synthesis. Eight tungsten carbide cubes, with truncated corners of 5 mm, were combined, with a sintered  $\text{MgO}$  octahedron of 10 mm edge length. The starting material was put into a rhenium or tantalum capsule, 1.7 mm in diameter and 8 mm in length, which also served as a heater. The capsule was surrounded by a  $\text{LaCrO}_3$  sleeve as a thermal insulator. The temperature at the center of the sample was measured by a  $\text{W3\%Re/W25\%Re}$  thermocouple for the tantalum furnace and a  $\text{Pt/Pt13\%Rh}$  thermocouple for the rhenium furnace. The synthesis condition was  $2300 \pm 50$  K and  $18 \pm 0.5$  GPa. The run duration was 5 ~ 10 min. The run products were examined using a microfocussed X ray diffractometer. This method allowed identification of the phases present in a very small area of about 100  $\mu\text{m}$  in diameter. In the central region of the sample, where the temperature was the highest, complete conversion to garnet was observed. At the colder margins of the sample, lower-temperature phases were present because of thermal gradient in the heater. These phases were  $\beta\text{-Mg}_2\text{SiO}_4$  (wadsleyite) + stishovite and  $\gamma\text{-Mg}_2\text{SiO}_4$  (ringwoodite) + stishovite, in addition to the unreacted orthopyroxene at the extreme end portions. In several runs, ilmenite was also observed. The temperature gradient of the sample was not measured but was estimated to be about 300–400 K/mm along the long axis of the sample. Complete removal of these phases by grinding using a diamond file under a polarizing microscope was confirmed by powder X ray diffractometry. The grain size of garnet was about 5 ~ 10  $\mu\text{m}$ . The quantity of garnet obtained from one run product was 1 ~ 4 mg. Total amount of garnet of 10 runs was about 19 mg.

In order to examine metastability of garnet at high temperature and atmospheric pressure, about 1 mg of the garnet sample was heated in a furnace at 1000 K in air for 3 hours. No changes in the heated sample were observed under the polarizing microscope or through powder X ray diffraction. However, further heating at 1070 K for 3 hours converted the sample to an optically isotropic powder with a lower refractive index than the original garnet. The recovered sample possessed no diffraction peaks, indicating retrograde transformation to glass.

#### Heat Capacity Measurements

Heat capacities of  $\text{MgSiO}_3$  orthopyroxene and tetragonal garnet were measured with a differential scanning calorimeter (DSC; Rigaku 8230B). Detailed procedures are given by Akaogi *et al.* [1990]. Each powdered sample (18.36 mg for garnet and 18.73 mg for orthopyroxene) was packed in a tightly crimped aluminum pan. Pure  $\alpha\text{-Al}_2\text{O}_3$  powder was used as the standard, along with published data by Dittmars and Douglas [1971]. The heat capacity measurements were made at a constant heating rate of 10 K/min with a sensitivity of 20 mJ/s. The sample and the standard were measured alternately. The heat capacity data were collected at the interval of 10 or 20 K. The temperature of the calorimeter was calibrated by melting points of indium, tin, lead, and zinc. Data were collected over two intervals (150–400 K and 350–700 K) because different containers were required at low and high temperature. For measurements below room temperature, the sample was first cooled by liquid nitrogen, and then heat capacities were measured in dry nitrogen gas flow at a rate of 5  $\text{cm}^3/\text{min}$  to avoid condensation of  $\text{H}_2\text{O}$ .

#### Enthalpy Measurements

The enthalpy measurements were performed using a twin Calvet-

type microcalorimeter (Setaram HT-1000) as described previously [Akaogi, 1990; Akaogi *et al.*, 1990]. Molten  $2\text{PbO} \cdot \text{B}_2\text{O}_3$  at 983 K was used as the solvent. The difference of enthalpies of solution between pyroxene and tetragonal garnet is the enthalpy of the pyroxene-tetragonal garnet transition. To check the metastability of tetragonal garnet under the same condition as the enthalpy measurement, garnet powder was put in a Pt sample holder about 5 mm above the surface of solvent and kept in the calorimeter at 983 K for 5 hours. No evidence of transition in the heated sample was found by X ray powder diffraction or by microscopic observations. In the measurements for garnet, equilibration time prior to solution runs was 5 hours. For garnet, four runs were carried out with about 3.8 ~ 4.4 mg sample in each run, while 10 runs were performed with about 4.2 ~ 6.3 mg sample for pyroxene. The dissolution of garnet in the solvent was initially exothermic but later became endothermic. For pyroxene, however, only an endothermic reaction was observed. The typical time required for complete dissolution was about 20 and 45 min for garnet and pyroxene, respectively.

Heat contents of  $\text{MgSiO}_3$  orthopyroxene were also measured by drop calorimetry. About 26 ~ 33 mg of powdered orthopyroxene were crimped in a platinum capsule weighing 65 to 77 mg and were dropped from room temperature into the calorimeter at 981 K. The heat content of orthopyroxene was calculated by subtracting the heat content of platinum from the total measured enthalpy.

#### RESULTS

The measured heat capacities of  $\text{MgSiO}_3$  orthopyroxene and tetragonal garnet are summarized in Table 1 and Figure 1. The data points are the averages of eight independent measurements in the temperature range 150–400 K and the averages of 14 measurements in the temperature range 350–700 K. The heat capacity of garnet above 160 K is smaller than that of pyroxene, and this difference expands gradually with increasing temperature. The heat capacity of  $\text{MgSiO}_3$  orthopyroxene was measured by Krupka *et al.* [1985a, b] below room temperature by adiabatic calorimetry and above room temperature by DSC. The average deviations between their and our values of about 1.5% above room temperature and about 0.5% below room temperature are within the experimental error of the DSC measurements. Berman and Brown's [1985] heat capacity equation,  $C_p = A + BT^{-0.5} + CT^{-2} + DT^{-3}$  ( $B, C \leq 0$ ,  $T \geq 250\text{K}$ ), was used to extrapolate the measured heat capacities of pyroxene and garnet to temperatures above the measurements. The coefficients in the equation were calculated by a least squares fit to the measured heat capacities (Table 2). The data for the heat contents of orthopyroxene are summarized in Table 3. The averaged heat content of orthopyroxene is  $75,323 \pm 2279$  J/mol, which is in good agreement with the value of 76,176 J/mol calculated from the heat capacity equation.

The measured solution enthalpies of  $\text{MgSiO}_3$  tetragonal garnet and orthopyroxene in  $2\text{PbO} \cdot \text{B}_2\text{O}_3$  at 983 K are shown in Table 4 and Figure 2. The enthalpy of the  $\text{MgSiO}_3$  pyroxene-tetragonal garnet transition is  $30.80 \pm 3.11$  kJ/mol at 983 K, calculated from the difference of the solution enthalpies in Table 4. Calorimetric study of garnet and pyroxene solid solutions in the system  $\text{Mg}_4\text{Si}_4\text{O}_{12}$ – $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$  was reported by Akaogi *et al.* [1987]. In their study, solution enthalpies of garnet solid solutions with  $\text{Mg}_4\text{Si}_4\text{O}_{12}$  component of 0 ~ 58 mol % were measured. They estimated that the solution enthalpy of  $\text{Mg}_4\text{Si}_4\text{O}_{12}$  cubic garnet is  $1 \pm 7$  kJ/mol by assuming an ideal solid solution model. The solution enthalpy of  $\text{Mg}_4\text{Si}_4\text{O}_{12}$  tetragonal garnet ( $20.4 \pm 5.0$  kJ/mol per 12 oxygen mol) is slightly higher than that of cubic garnet

TABLE 1. Measured Heat Capacities of MgSiO<sub>3</sub> Tetragonal Garnet and Orthopyroxene

T(K)	C <sub>p</sub> (J·mol <sup>-1</sup> ·K <sup>-1</sup> )	
	Gar	Opx
150	41.68	38.59
160	43.01	44.56
170	46.65	47.99
180	49.90	52.09
190	53.10	55.19
200	56.58	58.61
210	59.33	61.47
220	62.03	63.96
230	64.77	67.20
240	67.12	69.61
250	69.24	71.90
260	71.50	73.17
270	73.89	75.07
280	76.03	77.20
290	77.25	79.44
300	79.79	81.80
310	81.67	84.17
320	83.22	85.40
330	84.69	87.02
340	86.33	89.29
350	87.53	90.49
360	89.59	92.65
370	90.63	92.85
380	91.12	93.84
390	92.18	94.46
400	93.03	95.37
410	94.09	96.28
420	94.98	97.76
430	96.17	99.24
440	96.50	100.42
450	98.34	101.00
450	98.34	101.00
460	100.07	101.67
470	101.08	103.47
480	101.67	104.84
490	102.33	104.84
500	103.91	105.83
510	104.43	107.05
520	104.87	108.13
530	105.79	108.61
540	105.70	109.81
550	106.89	110.30
560	108.04	110.82
570	108.61	111.75
580	109.33	112.24
590	109.32	113.80
600	110.40	113.71
610	110.85	114.11
620	111.20	114.91
630	111.67	115.09
640	111.34	115.96
650	111.44	115.68
660	113.35	116.71
670	113.44	117.17
680	114.03	117.32
690	114.41	118.39
700	115.40	118.39

(Figure 2). This suggests that tetragonal garnet is more stable than cubic garnet. The solution enthalpy of MgSiO<sub>3</sub> orthopyroxene obtained in the present study is in good agreement with the value obtained by Ito and Navrotsky [1985].

THERMODYNAMIC CALCULATION OF PHASE DIAGRAMS OF MgSiO<sub>3</sub>

## Thermodynamic Data

The enthalpy of the pyroxene-tetragonal garnet transition and heat capacities of both phases measured in this study together with previous thermodynamic data (discussed below) allow calculation of all phase relations in MgSiO<sub>3</sub>. The heat capacities of relevant phases are summarized in Table 2. The heat capacity equations of  $\beta$ - and  $\gamma$ -Mg<sub>2</sub>SiO<sub>4</sub> were reported by Fei and Saxena [1986], who calculated the coefficients by fitting the Berman and

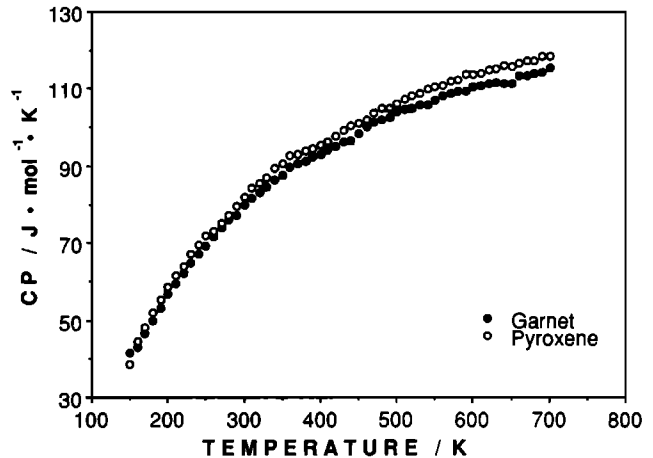


Fig. 1. Measured heat capacities of tetragonal garnet and orthopyroxene in MgSiO<sub>3</sub>. Solid and open circles show the heat capacities of tetragonal garnet and orthopyroxene, respectively.

TABLE 2. Coefficients of Heat Capacity Equations Used for Phase Boundary Calculations

Phase	C <sub>p</sub> = A + BT <sup>-0.5</sup> + CT <sup>-2</sup> + DT <sup>-3</sup> , J mol <sup>-1</sup> K <sup>-1</sup>			
	A×10 <sup>-2</sup>	B×10 <sup>-3</sup>	C×10 <sup>-6</sup>	D×10 <sup>-8</sup>
Pyroxene <sup>a</sup>	1.688	-1.272	-1.790	1.751
Garnet <sup>b</sup>	1.768	-1.603	-0.644	0.659
Ilmenite <sup>c</sup>	1.427	-0.516	-4.394	4.375
Perovskite <sup>d</sup>	1.564	-0.889	-2.394	0.827
β-phase <sup>e</sup>	2.164	-1.472	0.0	-5.579
γ-phase <sup>e</sup>	2.002	-1.037	-1.320	-4.916
Stishovite <sup>f</sup>	1.092	-1.100	0.0	-0.813

Hofmeister and Ito [1992] and Fei et al. [1990] are based on vibrational model calculations, while the others are from measured heat capacities.

<sup>a</sup>Average of C<sub>p</sub> of this study and Krupka et al. [1985b].

<sup>b</sup>This study.

<sup>c</sup>Hofmeister and Ito [1992].

<sup>d</sup>Fei et al. [1990].

<sup>e</sup>Fei and Saxena [1986].

<sup>f</sup>H. Yusa et al. (unpublished data, 1991).

TABLE 3. Measured Heat Contents of  $\text{MgSiO}_3$  Orthopyroxene

Sample Weight, mg	$H_{981}^{\circ} - H_{299}^{\circ}$ , J/mol
26.34	74,231
32.35	73,285
27.97	75,255
30.97	78,522
Average	75,323 $\pm$ 2279
Calculated <sup>a</sup>	76,176

<sup>a</sup>Calculated from heat capacity equation in Table 2.TABLE 4. Measured Solution Enthalpies of  $\text{MgSiO}_3$  Tetragonal Garnet and Orthopyroxene

Sample Weight, mg	$\Delta H_{983}^{\circ, \text{sol}}$ , J/mol
<i>Garnet</i>	
4.37	6,432
4.04	2,093
4.24	4,080
3.85	7,787
Average	5,098 $\pm$ 2522
<i>Orthopyroxene</i>	
4.67	35,827
5.76	38,452
4.54	36,363
5.26	36,890
4.25	33,281
4.72	35,914
5.83	32,635
6.27	36,013
5.75	35,563
5.88	38,037
Average	35,897 $\pm$ 1824

Brown's [1985] equation to Watanabe's [1982] data. The heat capacity of stishovite was measured by DSC (H.Yusa et al., unpublished data, 1991). For ilmenite, high-temperature heat capacity was estimated from Kieffer's model [Hofmeister and Ito, 1992]. The heat capacity of perovskite was also estimated from Kieffer's model [Fei et al., 1990]. Transition enthalpies measured by solution calorimetry are summarized in Table 5. The enthalpies of  $\alpha$ - $\beta$ - $\gamma$  transitions in  $\text{Mg}_2\text{SiO}_4$  were measured by Akaogi et al. [1984, 1989]. Transformation enthalpies concerning with stishovite and ilmenite were reported by Akaogi and Navrotsky [1984] and Ashida et al. [1988], respectively. Recently, Ito et al. [1990] measured the enthalpy of the ilmenite-perovskite transition. We used the above enthalpy and heat capacity data together with our data to calculate the phase boundaries up to 26 GPa and 2600 K.

Molar volume ( $V_{298}^{\circ}$ ), thermal expansion ( $\alpha$ ), bulk modulus ( $K_0$ ), and its pressure derivative ( $K'_0$ ) used in the calculations are listed in Table 6. Because the thermal expansivity of  $\text{MgSiO}_3$  tetragonal garnet has not yet been measured, it was assumed to be the same as that of natural pyrope [Suzuki and Anderson, 1983].

$\text{MgSiO}_3$  orthopyroxene transforms to clinopyroxene at about 8-10 GPa and 1200-1500 K [Akaogi and Akimoto, 1977; Yamamoto and Akimoto, 1977; Pacalo and Gasparik, 1990; Kanzaki, 1991]. Recently, Pacalo and Gasparik [1990] proposed that  $\text{MgSiO}_3$  clinopyroxene that is stable above about 8 GPa has a slightly

different pyroxene structure (space group  $C2/c$ ) from that previously believed ( $P2_1/c$ ) and has a considerably smaller volume than orthopyroxene. No experimental data have been reported for the thermodynamic properties of the  $C2/c$  clinopyroxene. Nor has

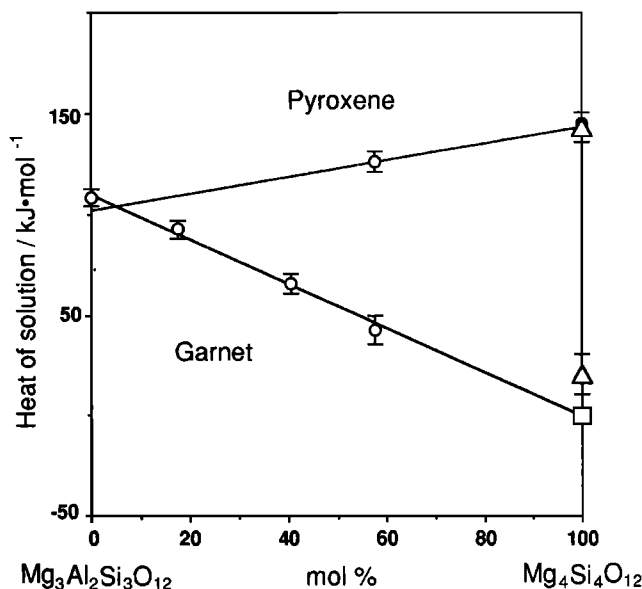


Fig. 2. Solution enthalpies of garnets and pyroxenes in the system  $\text{Mg}_4\text{Si}_4\text{O}_{12}$ - $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ . Open triangles show the data of  $\text{Mg}_4\text{Si}_4\text{O}_{12}$  orthopyroxene and tetragonal garnet measured at 983 K in this study. Open circles show the data for orthopyroxenes and cubic garnets measured at 987 K by Akaogi et al. [1987] and Ito and Navrotsky [1985]. Square represents enthalpy of solution of  $\text{Mg}_4\text{Si}_4\text{O}_{12}$  cubic garnet estimated by Akaogi et al. [1987].

TABLE 5. Enthalpy, Entropy and Volume Changes for Phase Transitions in  $\text{MgSiO}_3$ 

Transition	$\Delta H_{983}^{\circ}$ , kJ mol <sup>-1</sup>	$\Delta S_{983}^{\circ, a}$ , J mol <sup>-1</sup> K <sup>-1</sup>	$\Delta V_{298}^{\circ, b}$ , cm <sup>3</sup> mol <sup>-1</sup>
Px→Gar	30.80 $\pm$ 3.11 <sup>a</sup>	-4.2 $\pm$ 1.7	-2.74
Px→ $\beta$ +St	44.98 $\pm$ 2.12 <sup>a, c, d</sup>	-4.7 $\pm$ 1.5	-4.06
Gar→ $\beta$ +St	14.18 $\pm$ 3.76 <sup>a, c, d</sup>	-0.4 $\pm$ 2.3	-1.32
Gar→Il	25.00 $\pm$ 5.27 <sup>a, e</sup>	-6.8 $\pm$ 2.3	-2.23
Gar→Pv	79.68 $\pm$ 5.15 <sup>a, f</sup>	6.0 $\pm$ 2.2	-4.14
Il→Pv	54.68 $\pm$ 6.60 <sup>e, f</sup>	12.8 $\pm$ 2.8	-1.91
$\beta$ +St→Il	10.82 $\pm$ 5.01 <sup>c, d, e</sup>	-6.4 $\pm$ 2.4	-0.91
$\gamma$ +St→Il	6.28 $\pm$ 4.76 <sup>d, e, g</sup>	-2.8 $\pm$ 2.5	-0.42
$\beta$ +St→ $\gamma$ +St	4.54 $\pm$ 1.06 <sup>g</sup>	-3.5 $\pm$ 0.6	-0.49

<sup>a</sup>This study.<sup>b</sup>See Table 6.<sup>c</sup>Akaogi et al. (1984).<sup>d</sup>Akaogi and Navrotsky (1984).<sup>e</sup>Ashida et al. (1988).<sup>f</sup>Ito et al. (1990).<sup>g</sup>Akaogi et al. (1989).

TABLE 6. Parameters Used for Phase Boundary Calculation in MgSiO<sub>3</sub>

Phase	$V_{298}^{\circ}$ cm <sup>3</sup> mol <sup>-1</sup>	$K_0$ GPa	$K'_0$	$\alpha=a+bT+cT^{-2}$ , K <sup>-1</sup>		
				$a \times 10^5$	$b \times 10^9$	$c \times 10$
Pyroxene	31.32 <sup>a</sup>	108 <sup>b</sup>	5.0 <sup>c</sup>	2.95	2.69	-5.59 <sup>d</sup>
Garnet	28.58 <sup>e</sup>	160 <sup>f</sup>	4.5 <sup>f</sup>	2.87	2.89	-5.44 <sup>g</sup>
Ilmenite	26.35 <sup>h</sup>	210 <sup>i</sup>	4.0 <sup>j</sup>	2.44	0.0	0.0 <sup>k</sup>
Perovskite	24.44 <sup>h</sup>	261 <sup>l</sup>	4.0 <sup>j</sup>	1.73	15.7	0.0 <sup>m</sup>
β-phase	40.51 <sup>n</sup>	173 <sup>o</sup>	4.3 <sup>p</sup>	2.71	6.89	-5.77 <sup>d</sup>
γ-phase	39.53 <sup>q</sup>	183 <sup>r</sup>	4.1 <sup>s</sup>	2.37	5.30	-5.70 <sup>d</sup>
Stishovite	14.01 <sup>t</sup>	314 <sup>u</sup>	2.8 <sup>v</sup>	1.02	13.5	0.0 <sup>d</sup>

<sup>a</sup>Ohashi [1984].<sup>b</sup>Weidner et al. [1978].<sup>c</sup>Duffy and Anderson [1989].<sup>d</sup>Fei et al. [1990].<sup>e</sup>Angel et al. [1989].<sup>f</sup>Yagi et al. [1992].<sup>g</sup>Same as pyrope, Suzuki and Anderson [1983].<sup>h</sup>Ito and Yamada [1982].<sup>i</sup>Weidner and Ito [1985].<sup>j</sup>Assumed.<sup>k</sup>Ashida et al. [1988].<sup>l</sup>Mao et al. [1991].<sup>m</sup>Ross and Hazen [1989] and

Chopelas and Boehler [1989].

<sup>n</sup>Horiuchi and Sawamoto [1981].<sup>o</sup>Sawamoto et al. [1984].<sup>p</sup>Tanaka et al. [1987].<sup>q</sup>Akaogi et al. [1989].<sup>r</sup>Weidner et al. [1984].<sup>s</sup>Sawamoto et al. [1986].<sup>t</sup>Robie et al. [1978].<sup>u</sup>Weidner et al. [1982].<sup>v</sup>Ross et al. [1990].

the direct transformation of C2/c clinopyroxene to garnet or β + stishovite at high pressures and high temperatures been confirmed. For the present, we assume that no significant difference exists between the thermodynamic properties of MgSiO<sub>3</sub> orthopyroxene and clinopyroxene.

#### Calculation Method

Phase equilibria in MgSiO<sub>3</sub> were calculated by using the same method as did Akaogi et al. [1989] and Fei et al. [1990]. The phase boundary is defined by

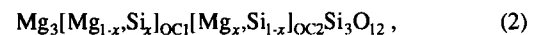
$$\Delta G(P, T) = \Delta H_T^{\circ} - T\Delta S_T^{\circ} + \int_{1 \text{ atm}}^P \Delta V(P, T) dP = 0, \quad (1)$$

where  $\Delta G(P, T)$  and  $\Delta V(P, T)$  are Gibbs free energy and volume changes, respectively, between high- and low-pressure phases at  $P$  and  $T$ .  $\Delta H_T^{\circ}$  and  $\Delta S_T^{\circ}$  are enthalpy and entropy changes, respectively, at  $T$  and 1 atm. In equation (1), effects of temperature on the enthalpy and entropy of transition, and pressure and temperature dependence of volume of each phase are corrected using the methods of Akaogi et al. [1989]. In this calculation, temperature dependence of bulk modulus or pressure dependence of thermal expansion was not included, because these experimental data are not available for most of these high-pressure phases. However, these effects should roughly cancel in the calculation of  $\Delta V$ . Because entropies are generally unavailable or poorly constrained,  $\Delta S_T^{\circ}$  is calculated from the measured  $\Delta H_T^{\circ}$  and one  $P$ ,  $T$  point on the phase boundary (triple point) using equation (1) as

discussed later. The calculated transition entropies are shown in Table 5. The errors in  $\Delta S_T^{\circ}$  shown in Table 5 are calculated from the uncertainties in the measured  $\Delta H_T^{\circ}$  and in location of the triple points in  $P$ - $T$  space, as described below. These entropies of transition in Table 5 are better constrained than those by Fei et al. [1990]. The  $\Delta S_T^{\circ}$  for the ilmenite-perovskite transition is larger than that estimated by Hofmeister and Ito [1992].

#### Effect of Partial Disorder in Garnet

Interchange enthalpy  $\Delta H_{int}$  and configurational entropy  $S_{conf}$  derived from the partial disorder of cations among the octahedral sites of MgSiO<sub>3</sub> tetragonal garnet must be added to  $H$  and  $S$  of fully ordered majorite. These quantities were calculated by a method similar to that of Navrotsky [1977]. For MgSiO<sub>3</sub> tetragonal garnet with two octahedral sites, the cation distribution is expressed as



where OC1 and OC2 represent octahedral sites 1 and 2, respectively, and  $x$  represents degree of disorder. In the garnet structure, the interchange reaction is



We assume that effect of pressure on the Mg-Si disorder in garnet is negligible, because of the very small volume difference between tetragonal and cubic garnets [Akaogi and Akimoto, 1977; Kanzaki, 1987; Angel et al., 1989]. If the non configurational entropy change associated with the partial cation disorder is negligibly small, and  $\Delta H_{int}$  is independent of temperature, then the equilibrium constant  $K$  is given as

$$K = x^2/(1-x)^2 = \exp(-\Delta H_{int}/RT), \quad (4)$$

where  $R$  is the gas constant.  $\Delta H_{int}$  is calculated from the measured degree of disorder using equation (4). In this calculation, configurational entropy is calculated from

$$S_{conf} = -2R[(1-x)\ln(1-x) + x\ln x]. \quad (5)$$

Two different values of  $x$  for MgSiO<sub>3</sub> tetragonal garnet have been reported. Angel et al. [1989] determined  $x$  to be 0.20 for a sample quenched at 2073 K and 17 GPa by X ray structural analysis, whereas Howell et al. [1990] determined  $x$  as 0.08 for a sample quenched at 2273 K and 17 GPa through nuclear magnetic resonance. Because the measured degrees of disorder are uncertain and could depend on the conditions of synthesis, we choose  $x = 0.15$  as a representative degree of disorder at 2073 K. This gives  $\Delta H_{int}$  as 59.8 kJ/mol.

#### Calculated Phase Diagrams in MgSiO<sub>3</sub>

The calculated phase relations in MgSiO<sub>3</sub> are shown in Figure 3. To construct this diagram, one triple point is initially selected, and the entropies of transitions are calculated using  $\Delta H^{\circ}$  and  $\Delta V^{\circ}$  in Table 5 and the parameters in Table 6. Next, the three boundaries emerging from the triple point are calculated and compared with the experimental data points. If the calculated boundaries are inconsistent with experimental data, the triple point is moved and the calculation is iterated until the three boundaries, as a whole, are most consistent with the experimental data. All four triple

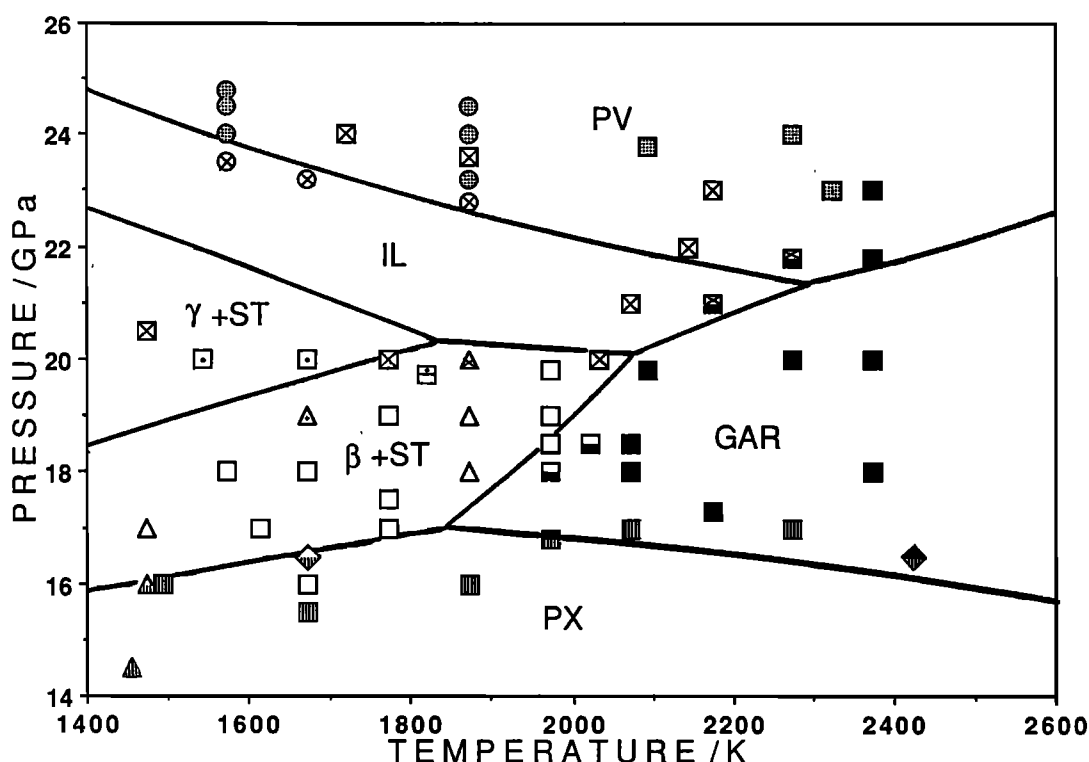


Fig. 3. Phase relations of  $\text{MgSiO}_3$ . All of the phase boundaries are calculated from thermodynamic data. Symbols are experimental data points: squares, Sawamoto [1987]; circles, Ito and Takahashi [1989]; triangles, Ito and Navrotsky [1985]; diamonds, Presnall and Gasparik [1990]. The phases are shown by a pattern filling the symbols: vertical bars, pyroxene; solid, garnet; open,  $\beta$  phase plus stishovite; dot,  $\gamma$  phase plus stishovite; cross, ilmenite; small dots, perovskite. The boundaries of garnet field are calculated assuming 15% cation disorder in garnet, see text.

points in Figure 3 are determined in this manner. It should be noted, however, that positions of all the triple points are mutually related and cannot be fixed independently, because all the boundaries are calculated using the internally consistent thermodynamic data set in Table 5. Estimated uncertainties for  $P$  and  $T$  of the four triple points are  $\pm 0.5$  GPa and  $\pm 50$  K, respectively. The errors of the transition entropies due to the uncertainties of the triple points are  $\pm 0.2$  to  $\pm 1.0$  J/mol K, depending on the transitions. These errors in  $\Delta S^\circ$  are included in Table 5. The boundaries of the garnet stability field are calculated including partial disorder in garnet ( $x = 0.15$  at 2073 K). As shown in Figure 3, the calculated boundaries are generally in good agreement with the experimental data points [Ito and Navrotsky, 1985; Sawamoto, 1987; Ito and Takahashi, 1989; Presnall and Gasparik, 1990]. Using the measured enthalpy, heat capacity, and bulk modulus of  $\text{MgSiO}_3$  tetragonal garnet, the garnet stability field is well constrained in our work in comparison with the previous thermodynamic calculation [Fei *et al.*, 1990]. The calculated negative slope for the pyroxene-garnet transition is consistent with the results by Presnall and Gasparik [1990], who determined the boundary as having a small negative gradient. The calculated ilmenite-perovskite transition boundary has a negative slope in accord with the experiments of Ito and Takahashi [1989].

In the above calculations of the phase boundaries, effects of the uncertainties in the bulk moduli, their pressure derivatives, thermal expansivities, and heat capacities are generally small. For example, the ilmenite-perovskite transition pressure was recalculated by changing one parameter, keeping the other parameters and the triple point unchanged; changes in  $K_0$  by  $\pm 10$  GPa, in  $K'_0$  by  $\pm 1$ , and in  $\alpha$  by  $\pm 10\%$  move the ilmenite-perovskite transition pressure at 1573 K within small range of  $\pm 0.5$  GPa, whereas a  $\pm 3\%$  change

in the heat capacity alters the transition pressure by  $\pm 1$  GPa.

We also considered the effect of cation disorder in garnet on the garnet stability field. The boundaries involving garnet were recalculated, assuming complete order in garnet at any temperature ( $x = 0.0$ ), though it is inconsistent with the structural studies described earlier. In Figure 4, the calculated boundaries of the garnet field for complete order are compared with those calculated using  $x = 0.15$  at 2073 K. The garnet -  $\beta$  + stishovite boundary for  $x = 0.0$  has a shallower slope than that for  $x = 0.15$ . The pyroxene-garnet boundary for the completely ordered garnet has a positive slope. These features do not change even if the triple points are moved by  $\pm 1.5$  GPa and  $\pm 300$  K. The calculated results for garnet with a completely ordered cation distribution are inconsistent with the experimental data by Sawamoto [1987] and Presnall and Gasparik [1990]. Figure 4 shows that the pressure range of the garnet stability field at a given temperature is expanded by the partial disorder in garnet. The calculated boundaries in Figure 3 for  $x = 0.15$  at 2073 K are most consistent with the experimental data.

The garnet-perovskite transition boundary has not yet been determined precisely by high-pressure experiments. Our thermodynamic calculation shows that the boundary has a definitely positive slope, as shown in Figure 3. Ito and Takahashi [1987] and Irifune and Ringwood [1987] concluded that in the pyrolytic mantle, the transition from complex garnet solid solution to perovskite solid solution would occur near the top of the lower mantle, in addition to dissociation of spinel to perovskite plus magnesio-wüstite. Our results for the  $\text{MgSiO}_3$  garnet-perovskite transition suggest that this transition would have a positive slope in the mantle. The positive slope and large density increase (16.9% for  $\text{MgSiO}_3$ ) associated with the garnet-perovskite transition

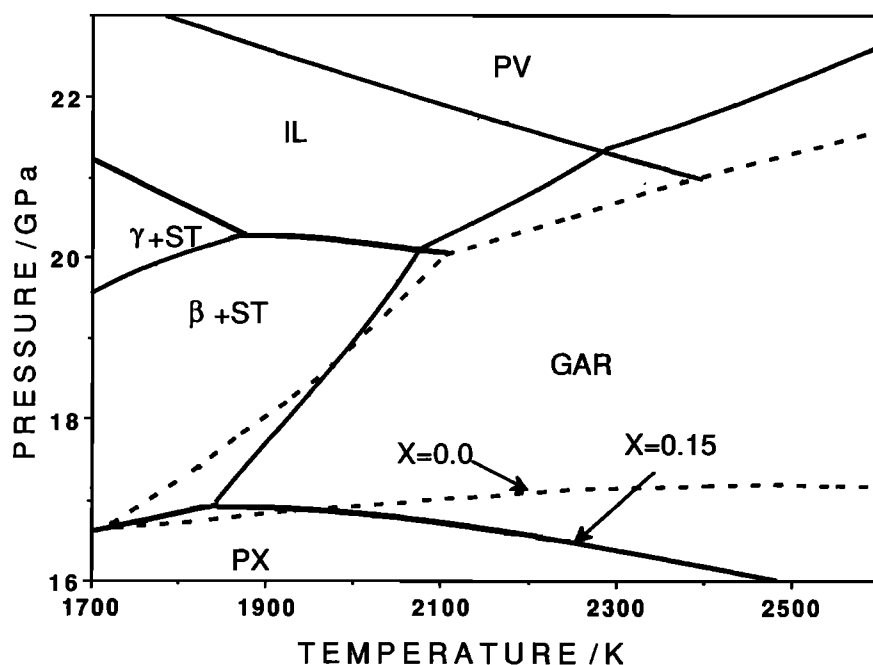


Fig. 4. Calculated boundaries of the stability field of  $\text{MgSiO}_3$  tetragonal garnet for the different degrees of cation disorder in garnet. Dashed lines show perfectly ordered state  $x = 0.0$ , and solid lines are the same boundaries as those in Figure 3, which are calculated for  $x = 0.15$ , see text.

suggest that the transition in the descending slab would play an important role in enhancing the slab subduction, in contrast to the spinel dissociation reaction which has a negative slope.

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