In Situ Measurements of the Majorite-Akimotoite-Perovskite Phase Transition Boundaries in MgSiO$_3$

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Abstract. Here we report the phase boundaries between majorite, akimotoite (ilmenite), and perovskite in MgSiO$_3$ determined by in situ measurements in a multi-anvil apparatus. We used both gold and platinum as internal pressure standards at high pressure and temperature. Our results obtained at 1400-2000°C, together with previous results obtained at 1000-1200°C by *Ono et al.* [2001], precisely locate the akimotoite-perovskite transition boundary at P (GPa) = 25.09 - 0.0027 × T (°C), based on the P-V-T equation of state of gold [*Anderson et al.*, 1989]. Our new experimental data show the position of triple point to be 20.0 GPa and 1920°C. The present measurements reconfirm our earlier study [*Hirose et al.*, 2001] that Anderson's gold pressure scale gives slightly higher pressures than the platinum pressure scale proposed either by *Jamieson et al.* [1982] or *Holmes et al.* [1989].

1. Introduction

MgSiO$_3$-rich perovskite is the predominant mineral in the Earth's lower mantle. Attempts have been made repeatedly to determine its stability at high pressure and temperature, including recent in situ synchrotron X-ray diffraction measurements in a multianvil apparatus [*Kato et al.*, 1995; *Kuroda et al.*, 2000; *Ono et al.*, 2001]. The phase transition between akimotoite and perovskite was detected by observing the change in diffraction pattern during either a temperature or a pressure cycle in these previous studies. This method works well if the transition occurs relatively fast. However, a precise determination of the phase boundary was hindered in these studies by (1)the loss of diffraction peaks of akimotoite due to rapid grain growth at high temperature and (2)the slow phase transition between the high-pressure phases by a kinetic effect. In the present in situ measurement, therefore, the reaction kinetics is a concern.

We determined the majorite - akimotoite - perovskite phase transition boundaries in MgSiO$_3$ in a wide temperature range from 1400 up to 2000°C. To avoid kinetic effects, we collected only one data point per run at a P-T condition of interest, like a conventional quench experiment. Both gold and platinum were used as internal pressure standards,

and their consistency was examined by a simultaneous measurement. Our new experimental data also determine the position of the triple point.

2. Experimental

High-pressure experiments with in situ X-ray diffraction measurements were conducted at SPring-8 using the multi-anvil apparatus (SPEED-1500) [*Utsumi et al.*, 1998]. The same experimental techniques were applied as *Hirose et al.* [2001]. We used a high-pressure 8/3 assembly with a cylindrical Re-heater (25-μm thickness), similar to that described in *Bertka and Fei* [1997]. Temperatures were monitored by the W5%Re-W26%Re thermocouple. The anhydrous glass starting material with MgSiO$_3$ composition was loaded near the thermocouple. X-ray diffractions were collected from a 50×100 μm area of the pressure marker (mixture of Au or Pt and MgO) at high pressure and high temperature. Its position was precisely chosen using the CCD image looking through the anvil gap (Figure 1). The temperature difference over the entire region of the pressure marker was estimated to be less than 30°C at 2000°C assuming no pressure gradient. This temperature gradient could cause the uncertainty in pressure calculation less than 0.2 GPa using P-V-T equation of state. The primary pressure scales used here are the P-V-T equation of state of gold proposed by *Anderson et al.* [1989] and of platinum by *Jamieson et al.* [1982] (Table 1). The diffraction lines of Au (111, 200, 220,
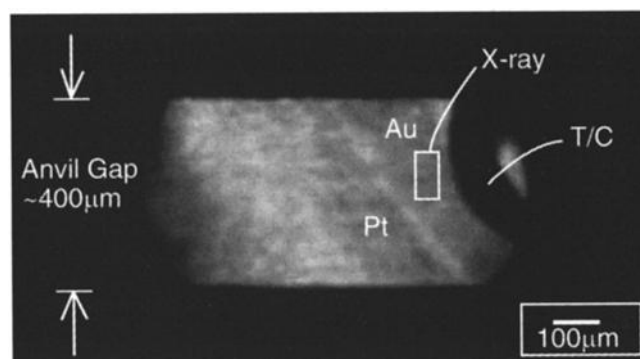
Figure 1. X-ray CCD image of the assembly at 21 GPa. The white square represents the area of 50×100-μm, from which X-ray diffraction was collected. Both gold and platinum were closely loaded but separated by a thin layer of MgO to avoid metal alloying.

Table 1. Experimerntal conditions and results

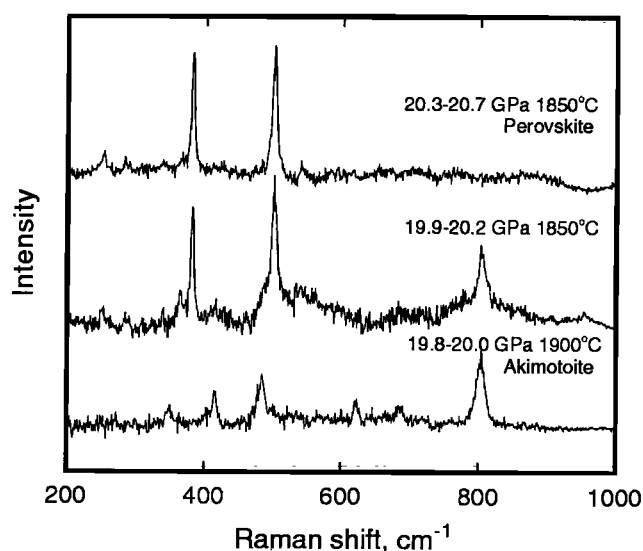| Run no.	Temperature (°C)	duration (min)	Pressure (GPa)				Run product
			Au*		Pt**		
			initial	final	initial	final	
1	1400	60	20.701	20.226	20.147	19.688	Ak
2	1400	60	21.350	20.994	20.646	20.290	Ak+Pv(trace)
3	1850	30	20.155	19.895			Ak+Pv
4	1850	30	20.659	20.254			Pv
5	1900	15	19.979	19.794			Ak
6	2000	4	20.02***		19.174	n.d.	Mj
7	2000	10	20.34***		19.248	19.057	Pv

*Au scale by *Anderson et al.* [1989].

**Pt scale by *Jamieson et al.* [1982].

***Pressure was estimated by load-pressure relationship (Figure 4).

Ak, akimotoite; Pv, perovskite; Mj, majorite.

311) or Pt (111, 200, 220, 311, 222) were used to calculate the unit cell volumes. The precision of the pressure determination was normally within 0.1-0.2 GPa. The sharpening of diffraction peaks and the consistency of unit-cell parameter calculated from each diffraction line of gold showed that the deviatoric stress approached zero at high temperature above 800-1000°C [*e.g.*, *Weidner et al.*, 1992 and 1998].

To avoid kinetic problems, we took the glass sample to a P-T condition of interest, and kept that condition (constant load force of the apparatus and temperature) for 4-60 mins while repeatedly taking diffraction patterns of the pressure maker. Pressure dropped by 0.18-0.48 GPa during heating (Table 1). Then, we quenched the sample to room temperature immediately by turning off the power, so that we could examine the quenched sample. The experimental procedure adopted here allowed us to obtain only one data point for each high P-T run, unlike other in situ measurements that can obtain multiple data points in a single run. Phase identification of the quenched sample was made by micro-Raman spectroscopy measurements (Figure 2). The microprobe analysis showed that the bulk of the sample showed

no evidence of chemical reaction with the surrounding MgO or Al_2O_3.

3. Phase boundaries in $MgSiO_3$

Seven runs were conducted to determine the phase transition boundaries. The results are shown in Figure 3 based on Anderson's gold pressure scale. In the two 2000°C-runs, only platinum was loaded as a pressure standard, because we had lost the diffraction peaks of gold during the temper-

Figure 2. Examples of Raman spectra of the recovered samples.
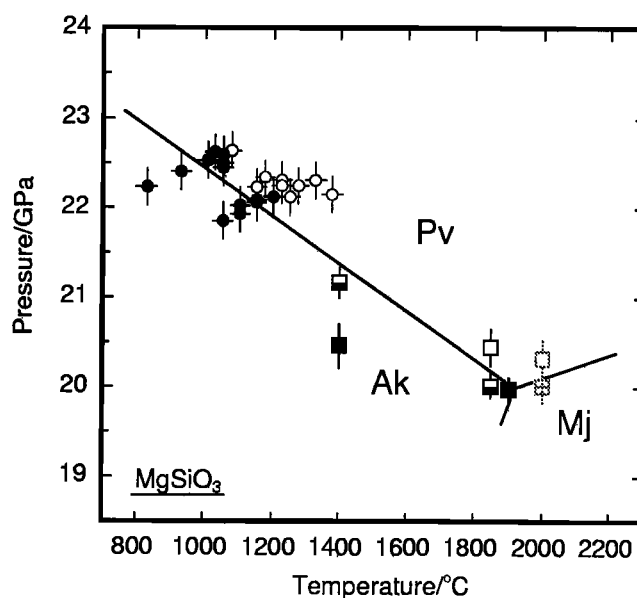
Figure 3. Phase transition boundaries in $MgSiO_3$ based on Anderson's gold scale [*Anderson et al.*, 1989]. Open symbols, perovskite (Pv); solid symbols, akimotoite (Ak); open symbol with cross, majorite (Mj). The half-filled squares show the coexistence of akimotoite and perovskite. The squares represent the data points obtained in this study. Bars represent initial pressure after reaching a temperature of interest and final pressure before quenching (Table 1). The circles are from [*Ono et al.*, 2001]. Pressures in the runs at 2000°C (gray symbols) were estimated from the calibration curve (Figure 4). Errors in these two runs are from the reproducibility of pressure at a given load force of the apparatus.

ature increase to 2000°C due to grain coarsening near the melting temperature. For these two runs conducted at 650 and 680-ton, pressures in Anderson's gold scale were best estimated from the pressure calibration curve at each temperature (pressure as a function of load force and temperature) (Figure 4). They were established by the total of eight runs we have made at 1750-2000°C using the same high-pressure assembly with the multi-anvil apparatus at SPring-8 [Hirose et al., 2001].

The precise phase boundary was not defined in the previous in situ X-ray observations by Kato et al. [1985] and Kuroda et al. [2000]. And the Clapeyron slope was not well determined by Ono et al. [2001], because the phase transition was observed only in the limited temperature range at 1000-1200°C. Our new experimental data obtained at 1400-2000°C, and together with those by Ono et al. [2001], tightly constrain the akimotoite-perovskite transition boundary. The boundary shown in Figure 3 is represented by a linear equation P (GPa) = 25.09 - 0.0027 × T (°C) based on Anderson's gold pressure scale.
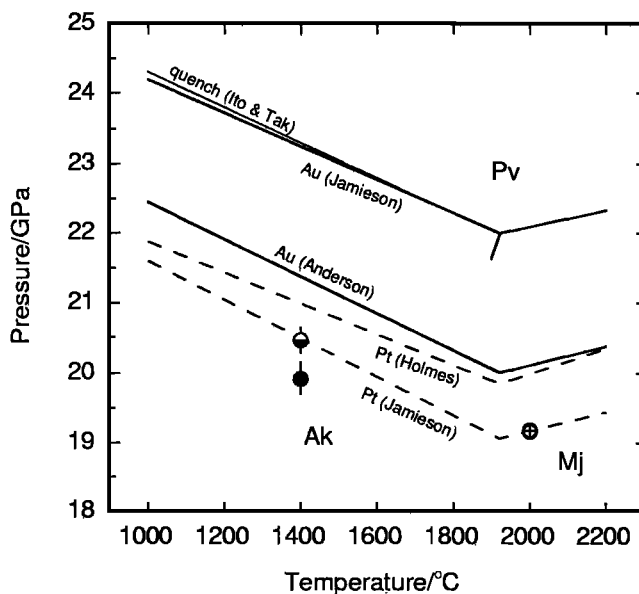
The Clapeyron slope of the majorite (tetragonal garnet) - perovskite transition boundary was not precisely determined in the present experiments. A thermodynamical calculation using the physical parameters shown by Akaogi and Ito [1999] gives the slope of 0.0013 GPa/°C for this boundary. If we take this value in Figure 3, the position of the triple point should be at 20.0 GPa and 1920°C.

The phase transition pressures were determined also by the platinum pressure standard (Figure 5). The simultaneous measurement of both the metal pressure standards in a single run at 1400°C showed that Jamieson's platinum scale gives 0.55-0.70 GPa lower pressures than Anderson's gold scale (Table 1) [Hirose et al., 2001].

The choice of equation of state, as well as the choice of pressure standard, could lead to a significant difference in the determination of phase transition pressures by the in situ X-ray diffraction measurements (Figure 5). The phase
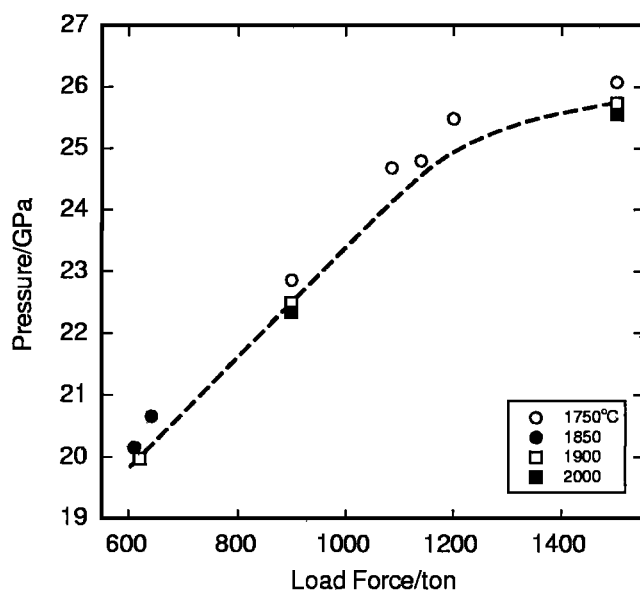
Figure 5. Phase transition boundaries in MgSiO₃ based on the different pressure standards and the equations of state. The circles represent the data points obtained in this study, using platinum as a pressure standard. The symbols as in Figure 3. The boundary determined by quench experiments [Ito and Takahashi, 1989] is also shown.

transition pressures in MgSiO₃ were recalculated using a different equation of state of gold [Jamieson et al., 1982] and platinum [Holmes et al., 1989], respectively, from the same unit cell volume data. The akimotoite-perovskite transition pressure based on Jamieson's gold equation of state is 2 GPa higher than that from Anderson's at 1600°C, and is consistent with that determined by conventional quench experiments [Ito and Takahashi, 1989]. It was, however, demonstrated that Jamieson's gold pressure scale deviates widely from other pressure scales such as NaCl, Pt, W, and Mo [Hirose et al., 2001]. On the other hand, pressures calculated from both the platinum equations of state are relatively similar. Holmes's equation gives 0.6 GPa higher pressure at 1600°C. Shim et al. [2001] suggested from laser-heated diamond cell experiments that Holmes's platinum scale gives 2 GPa higher pressures than Anderson's gold scale in a similar pressure range, which may explain their different results for the post-spinel phase transition pressure from those by Irifune et al. [1998]. The present simultaneous measurements of both the pressure standards by the multianvil apparatus, however, showed that the platinum scale either by Holmes et al. [1989] or Jamieson et al. [1982] predicts even lower pressures than Anderson's gold scale.

Figure 4. Pressure calibration curve for the SPEED-1500 at SPring-8 at high temperatures, based on Anderson's gold pressure scale. Only initial pressures were used for calibration.

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