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The phase boundary between $CaSiO_3$ perovskite and Ca_2SiO_4 + $CaSi_2O_5$ determined by in situ X-ray observations

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[1] The phase transition between $CaSiO_3$ perovskite and Ca_2SiO_4 larnite + $CaSi_2O_5$ titanite has been investigated using a Kawai-type multianvil apparatus (KMA) combined with synchrotron radiation. This phase boundary is located by our experiments as P (GPa) = 9.8(4) + 0.0017(3) × T (°C), which is 2–4 GPa lower than the most recent results using laser heated diamond anvil cell and those based on thermodynamic calculations, but is consistent with earlier studies based on quench experiments using KMA. The present results suggest some diamond inclusions recently found in Kankan distinct, Guinea, may originate from depth of 240–360 km in the upper mantle. **Citation:** Sueda, Y., T. Irifune, A. Yamada, T. Inoue, X. Liu, and K.-I. Funakoshi (2006), The phase boundary between $CaSiO_3$ perovskite and Ca_2SiO_4 + $CaSi_2O_5$ determined by in situ X-ray observations, *Geophys. Res. Lett.*, *33*, L10307, doi:10.1029/2006GL025772.

1. Introduction

[2] $CaSiO_3$ perovskite (CaPv) is one of the major constituent minerals in the lower part of the mantle transition zone and the lower mantle [e.g., *Irifune and Ringwood*, 1993; *Ono et al.*, 2005]. It is also one of the major hosting phases for Ca, Al, Ti, rare earth elements, and so on in the Earth's mantle [*Walter et al.*, 2004; *Hirose et al.*, 2004]. Moreover, it was suggested that some Ca-rich inclusions in diamonds probably originated from CaPv in the Earth's mantle [e.g., *Joswing et al.*, 1999; *Brenker et al.*, 2005]. In order to understand the genesis of these Ca-rich inclusions, it is important to study the stability of CaPv where the phase transition between CaPv and these Ca-rich inclusions takes place.

[3] $CaSiO_3$ wollastonite transforms to $CaSiO_3$ walstromite at ~3 GPa, and the latter dissociates to Ca_2SiO_4 larnite + $CaSi_2O_5$ titanite at ~10 GPa and 1200°C [e.g., *Huang and Wyllie*, 1975; *Gasparik et al.*, 1994]. At still higher pressures Ca_2SiO_4 larnite and $CaSi_2O_5$ titanite combine to form CaPv. The phase boundary between Ca_2SiO_4 larnite + $CaSi_2O_5$ titanite and CaPv was initially located at ~11–12 GPa and 1500°C by *Wang and Weidner* [1994] and *Gasparik et al.* [1994], but recently relocated to ~17 GPa on the basis of laser heated diamond anvil cell (LHDAC) experiments [*Shim et al.*, 2000], whereas a thermodynamic estimation based on calorimetric measurements suggested intermediate transition pressures of ~14 GPa [*Akaogi et al.*, 2004].

[4] In order to solve this discrepancy, we conducted in situ X-ray diffraction measurements using Kawai-type multianvil apparatus (KMA).

2. Experimental Methods

[5] In situ X-ray observations were made using a KMA (SPEED-1500) installed at BL04B1, SPring-8. The incident white X-ray beam, 100 μm length and 50 μm width, was detected by a pure Ge solid-state detector at a fixed diffraction angle of $2\theta = 6°$. Diffraction data were acquired by a multichannel analyzer with 4096 channels, which was calibrated using characteristic X-rays of some metal standards (Cu, Mo, Ag, Au, Ta, Pt, Pb). The data acquisition duration for one X-ray diffraction observation was 600 seconds.

[6] The starting material used in this study was wollastonite, previously synthesized from a $CaSiO_3$ gel at 1000°C and 1 atm for 12 hours. In the run S791 and S939, the starting material was mixed with the pressure marker of pure gold powder (10 wt%); in S1422 and S1423, however, the starting material was separated from the pressure marker of a palletized MgO + Au mixture in a weight ratio 10: 1. The hot junction of the thermocouple ($W_{97}Re_3 - W_{75}Re_{25}$) was put in the experimental material in the former case, while it was placed between the starting material and the pressure marker in the latter case. A pair of TiC sheets were used as the leads for electric power supply to the TiC + diamond sheet heaters, by which the sample was sandwiched. The details of the cell configuration are reported by *Irifune et al.* [2002]. X-ray diffraction data were collected from the sample near the hot junction of the thermocouple. During an experiment, the nominal temperatures were kept within ±10°C to the target values. Pressure was calculated from the unit cell volume changes of Au using the equation of state by *Anderson et al.* [1989]. Although some debates have been made on the validity of the pressure scales [e.g., *Hirose et al.*, 2001; *Matsui and Nishiyama*, 2002], the difference in pressures with various equations of state is insignificant for the relatively low pressure and temperature range of this study. We actually compared the pressures determined using two different scales [*Anderson et al.*, 1989; *Shim et al.*, 2002] and found the difference is generally within 0.5 GPa, as shown in Table 1.

[7] For in situ X-ray diffraction measurements, we first increased the press load to reach a pressure target under room temperature, then increased the temperature to an aimed value while keeping the press load constant. We conducted in situ X-ray observation during this process and also after having reached the target temperature. We changed temperature or pressure later if it is desirable in

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Table 1. Experimental Conditions and Results

	Au				
Run No.	V, Å^3	$P_{Anderson}$, GPa	P_{shim}, GPa	Temp., °C	Phase Results
S1422	65.54(2)	11.56(07)	11.84(07)	800	CaPv[a]
	65.83(3)	11.40(09)	11.68(09)	900	CaPv
	66.01(3)	11.59(07)	11.88(07)	1000	CaPv
	66.50(5)	11.63(13)	11.90(13)	1200	lar + tit + CaPv
S1423	65.23(5)	12.48(14)	12.78(14)	800	CaPv
	65.71(3)	12.41(09)	12.75(09)	1000	CaPv
	65.89(3)	12.58(08)	12.92(08)	1100	CaPv
	66.19(2)	12.44(06)	12.77(06)	1200	CaPv
	66.46(5)	12.44(14)	12.75(14)	1300	CaPv (+tr. lar + tit)
	66.91(3)	12.00(08)	12.24(08)	1400	lar + tit
	66.98(5)	11.82(12)	12.03(12)	1400	lar + tit
	66.78(3)	12.31(07)	12.57(07)	1400	CaPv
	66.98(2)	12.52(06)	12.76(06)	1500	CaPv
S939	66.69(1)	8.38(04)	8.54(04)	800	lar + tit
	67.49(25)	7.79(60)	7.87(60)	1000	lar + tit
	68.70(15)	6.55(73)	6.39(73)	1200[c]	wal[d]
S791	65.49(5)	11.70(16)	11.98(16)	800	CaPv
	64.82(2)	13.73(07)	14.07(07)	800	CaPv
	64.09(4)	16.11(12)	16.50(12)	800	CaPv
	63.62(5)	17.74(17)	18.15(17)	800	CaPv
	65.04(3)	14.38(09)	14.80(09)	1000	CaPv
	64.34(4)	16.58(12)	17.08(12)	1000	CaPv
	63.94(6)	17.91(21)	18.44(21)	1000	CaPv
	65.93(5)	13.16(15)	13.53(15)	1200	CaPv
	65.28(3)	15.00(09)	15.48(09)	1200	CaPv
	64.63(5)	16.97(15)	17.55(15)	1200	CaPv

[a] CaPv represents $CaSiO_3$ perovskite.
[b] lar + tit represents Ca_2SiO_4 larnite + $CaSi_2O_5$ titanite.
[c] Temperature was estimated based on the supplied power.
[d] wal represents $CaSiO_3$ walstromite.

constraining the phase boundary. Some of the recovered samples were inspected by electron microprobe after quenching, while others were used for *P-V-T* measurements under further high pressures [Y. Sueda, manuscript in preparation, 2006].

3. Results and Discussion

[8] We conducted four runs at pressures from 8 to 18 GPa and temperatures up to 1500°C (Table 1). In S1422, $CaSiO_3$ wollastonite was first pressurized to 15.1 GPa at room temperature, where we found significant broadening of diffraction peaks, suggesting a possibility of partial amorphization of wollastonite at shown in Figure 1a. When the temperature was increased to 800°C, CaPv starts to grow from wollastonite at 11.6 GPa (Figure 1b). With further heating up to 1000°C, almost pure CaPv was formed, and we didn't observe any new phase except for some minor diffractions from larnite and titanite, which are supposed to be present due to the thermal gradient in the sample (Figure 1c). Upon further increasing temperature, CaPv started to transform to Ca_2SiO_4 larnite + $CaSi_2O_5$ titanite at 11.6 GPa and 1200°C (Figure 1d). The coexistence of CaPv and Ca_2SiO_4 larnite + $CaSi_2O_5$ titanite suggests this *P-T* condition is very close to the phase boundary.

[9] In S1423, CaPv formed from the wollastonite starting material upon increasing temperature up to 1200°C at pressures 12.4–12.6 GPa (Table 1), while it partially transformed to Ca_2SiO_4 larnite + $CaSi_2O_5$ titanite when temperature was increased to 1300°C (Figure 2a). CaPv transformed to the assemblage of Ca_2SiO_4 larnite + $CaSi_2O_5$ titanite almost with increasing temperature to 1400°C

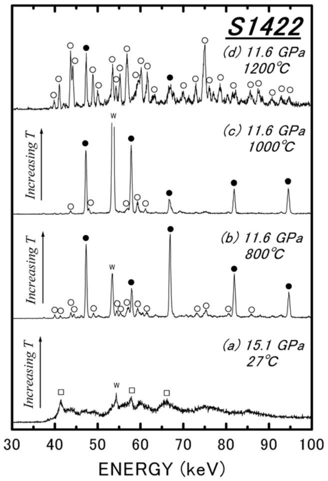

Figure 1. X-ray diffraction profiles of $CaSiO_3$ at different temperatures and pressures in S1422. (a) Wollastonite was pressurized up to 15.1 GPa under room temperature, (b) where we increased temperature and found CaPv started to form at 11.6 GPa and 800°C. (c) With further increasing temperature, pure CaPv was found at 11.6 GPa and 1000°C. (d) Ca_2SiO_4 + $CaSi_2O_5$ started to form at a temperature of 1200°C at 11.6 GPa, suggesting that this *P-T* condition is close to the phase boundary between Ca_2SiO_4 + $CaSi_2O_5$ and CaPv. Squares represent wollastonite, solid circles represent CaPv, open circles represent Ca_2SiO_4 + $CaSi_2O_5$, and W represents tungsten (thermocouple).

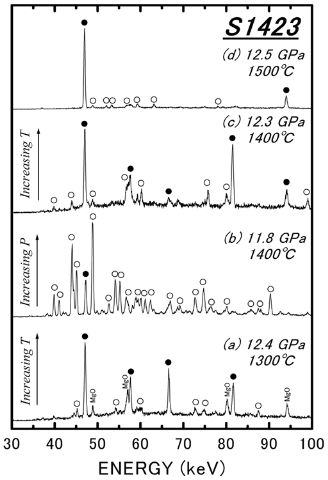

Figure 2. X-ray diffraction profiles of $CaSiO_3$ at different temperatures and pressures in S1423. (a) CaPv was observed with increasing temperature to 1300°C at a pressure of ~12.4 GPa. (b) An assemblage of Ca_2SiO_4 + $CaSi_2O_5$ started to form from CaPv at 1400°C at 11.8 GPa. (c) With increasing pressure at a constant temperature of 1400°C, the phase transition from Ca_2SiO_4 + $CaSi_2O_5$ to CaPv was observed at 12.3 GPa. (d) No further phase transition was observed at 12.5 GPa and 1500°C for a period of 50 minutes, except for the significant crystal growth of CaPv, which yields spotty Debye ring and hence only very few peaks in one-dimensional diffraction profile. MgO represents diffractions from the surrounding pressure medium.

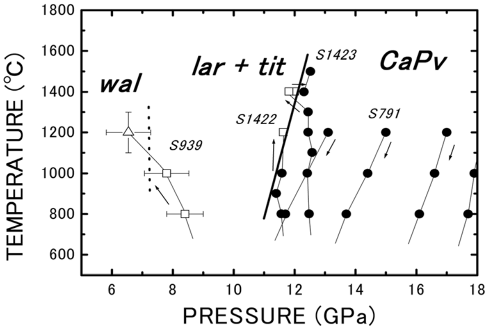

Figure 3. *P*-*T* conditions of the present in situ X-ray diffraction measurements. Solid line shows the phase boundary between CaPv and Ca_2SiO_4 larnite + $CaSi_2O_5$ titanite determined in the present study, which was well constrained by the forward and reverse phase transitions between CaPv and Ca_2SiO_4 + $CaSi_2O_5$, as indicated by arrows. Dashed line shows the phase boundary between $CaSiO_3$ walstoromite and Ca_2SiO_4 larnite + $CaSi_2O_5$ titanite, which was only poorly constrained in the present study. Vertical and horizontal bars indicate the uncertainties in temperature and pressure measurements in S939, where the temperature was estimated by the power-temperature relation due to failure of the thermocouple. Solid circles represent CaPv, squares represent Ca_2SiO_4 + $CaSi_2O_5$, and triangles represent walstrominte.

(Figure 2b). Keeping the temperature constant at 1400°C, where we observed that CaPv was mostly converted to this phase assemblage. We then started to increase the pressure and conducted in situ X-ray observations to observe the forward reaction from Ca_2SiO_4 larnite + $CaSi_2O_5$ titanite to CaPv. When the pressure reached 12.3 GPa, the phase transition from Ca_2SiO_4 larnite + $CaSi_2O_5$ titanite to CaPv took place (Figure 2c). This phase transition was so rapid that the effect of kinetics in defining the phase boundary was fairly small. Finally the temperature was increased to 1500°C and the experiment maintained for 50 min, but no phase transition from CaPv to other phases was observed, although significant crystal growth of this phase was noted as evident from the X-ray diffraction profile (Figure 2d).

[10] In S939, we observed the phase transition from Ca_2SiO_4 larnite + $CaSi_2O_5$ titanite to $CaSiO_3$ walstromite. We firstly pressurized the $CaSiO_3$ wollastonite starting material to 11.5 GPa under room temperature, and then conducted in situ X-ray observation during the process of heating the sample at constant press load. At 8.4 GPa and 800°C, Ca_2SiO_4 larnite + $CaSi_2O_5$ titanite started to form from the $CaSiO_3$ wollastonite. The stability of Ca_2SiO_4 larnite + $CaSi_2O_5$ titanite was confirmed at 7.8 GPa and 1000°C. When we further increased the experimental temperature, however, the thermocouple broke so that thereafter we could only determine temperature by the relation of power supply and temperature. Then the phase transition from Ca_2SiO_4 larnite + $CaSi_2O_5$ titanite to $CaSiO_3$ walstromite was observed to be complete at 6.6 GPa and 1200°C (Table 1). The experimental pressures in S939 could not be accurately determined also because most X-ray diffraction peaks of gold overlapped with those of Ca_2SiO_4 larnite + $CaSi_2O_5$ titanite. Thus, although our experiment did not define this phase boundary between $CaSiO_3$ walstromite and Ca_2SiO_4 larnite + $CaSi_2O_5$ titanite, precisely, it is suggested that this phase boundary should be close to 7 GPa at 1200°C (Table 1).

[11] In S791, we first synthesized CaPv at 13.2 GPa and 1200°C for 1 hour, and then changed temperature, or pressure, or both to collect some *P*-*V*-*T* data. No phase transition was observed in this experiment, encompassing the pressures between 12–18 GPa and temperatures 800–1200°C (Table 1).

[12] All our experimental results are summarized in Figure 3. The phase boundary between CaPv and Ca_2SiO_4 larnite + $CaSi_2O_5$ titanite has been precisely determined as P (GPa) = 9.8(4) + 0.0017(3) × T (°C) based on the forward and reverse phase transition. Along a typical mantle geotherm [e.g., *Brown and Shankland*, 1981; *Ito and Katsura*, 1989], the stability field of Ca_2SiO_4 larnite + $CaSi_2O_5$ titanite spans a pressure interval of ~4 GPa between 7 and 11 GPa, much wider than previous result (~2 GPa between 9 and 11 GPa) [*Gasparik et al.*, 1994].

[13] As shown in Figure 4, the Clapeyron slope of the phase boundary between CaPv and Ca_2SiO_4 larnite + $CaSi_2O_5$ titanite defined here is in excellent agreement with the results determined by *Akaogi et al.* [2004] based on calorimetric measurements. On the other hand, the position of our phase boundary also generally agrees with *Kanzaki et al.* [1991], *Wang and Weidner* [1994], *Gasparik et al.* [1994] and *Kubo et al.* [1997], but contradicts with *Akaogi et al.* [2004] and the results of LHDAC experiments by *Shim et al.* [2000]. There are several factors which might contribute to the big difference between the results of *Shim et al.* [2000] and the present study. Firstly, the results of *Shim et al.* [2000] using LHDAC were probably affected by a large thermal gradient caused by the high thermal conductivity of diamond and an uneven temperature distribution caused by laser heating [*Irifune et al.*, 2005]. Secondly, *Shim et al.* [2000] just loosely bracketed the phase transition by experiments at the high pressure side and those at the low pressure side, with a pressure gap of ~4 GPa, and then drawn the phase transition through the *P*-*T* points in the middle. It is thus possible that the actual phase transition might take place at much lower pressures. In contrast, the smaller discrepancy of the transition pressure between this study and the result of *Akaogi et al.* [2004] is probably due

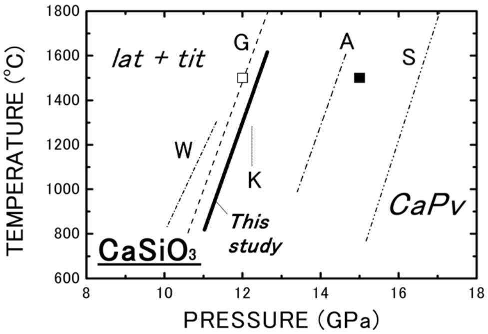

Figure 4. Phase boundaries between Ca_2SiO_4 larnite + $CaSi_2O_5$ titanite and CaPv. W represents *Wang and Weidner* [1994], G represents *Gasparik et al.* [1994], K represents *Kubo et al.* [1997], S represents *Shim et al.* [2000], and A represents *Akaogi et al.* [2004]. Open and solid square represent Ca_2SiO_4 + $CaSi_2O_5$ and CaPv reported by *Kanzaki et al.* [1991], respectively.

to the uncertainties in the pressure calibration of such quench experiments.

[14] Calcium silicate inclusions ($CaSi_2O_5$ titanite, Ca_2SiO_4 larnite and $CaSiO_3$ walstromite) in diamonds from the Kankan distinct in Guinea have been reported by *Joswing et al.* [1999] and *Brenker et al.* [2005]. In one diamond $CaSi_2O_5$ titanite touches Ca_2SiO_4 larnite, while in another $CaSiO_3$ walstromite stands alone. Our results here suggest that the former phase assemblage of $CaSi_2O_5$ titanite and Ca_2SiO_4 larnite should originate at least at depths of 240–360 km in the upper mantle, whereas the latter $CaSiO_3$ walstromite might have formed at shallower region of the mantle. Alternatively, the latter walstromite could have been formed from $CaSiO_3$ perovskite as a retrogressively transformed product on release of pressure in the course of the transportation of diamonds from the deeper regions in the mantle.

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