

## Experimental determination of phase relations in the CaSiO<sub>3</sub> system from 8 to 15 GPa

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### ABSTRACT

Phase relations in the CaSiO<sub>3</sub> system were experimentally determined at 8–15.2 GPa and 850–2510 °C with a split-sphere anvil apparatus. Below the solidus, a field of Ca<sub>2</sub>SiO<sub>4</sub> + CaSi<sub>2</sub>O<sub>5</sub> is stable between that of CaSiO<sub>3</sub> walsstromite at lower pressures and CaSiO<sub>3</sub> perovskite at higher pressures, within the following limits:  $P$  (GPa) =  $7.9 + 0.0014T$  (°C) and  $P$  (GPa) =  $9.0 + 0.0021T$  (°C). These univariant boundaries intersect the solidus at two triple points: one at 10.4 GPa and 1800 °C, the other at 13.5 GPa and 2150 °C. Results of melting experiments indicate a moderate increase (200 °C) in the temperature of melting over a pressure interval of 8 GPa for walsstromite, followed by a sharp increase (700 °C) over 5 GPa after its breakdown, resulting in an unusually deep cusp in the melting curve. The observed major increase in the melting temperature of CaSiO<sub>3</sub> perovskite with pressure provides additional support for the high melting temperatures of MgSiO<sub>3</sub> perovskite in the Earth's lower mantle.

### INTRODUCTION

CaSiO<sub>3</sub> perovskite is the primary Ca-bearing phase in the Earth's lower mantle (Mao et al., 1977; Irifune et al., 1989; Tamai and Yagi, 1989). Hence, the experimental determination of its low-pressure stability limit is important for understanding the mineral composition of the mantle. Because the perovskite composition remains close to CaSiO<sub>3</sub> even in a chemically complex mantle (Gasparik, 1989, 1990), perovskite reaches its maximum stability in the pure CaSiO<sub>3</sub> system. Kanzaki et al. (1991) synthesized CaSiO<sub>3</sub> perovskite at 15 GPa and 1500 °C and CaSiO<sub>3</sub> walsstromite at 10 GPa and 1500 °C, whereas two experiments at 12 GPa and 1500 and 2000 °C produced two coexisting phases: Ca<sub>2</sub>SiO<sub>4</sub> + CaSi<sub>2</sub>O<sub>5</sub> (Fig. 1). Lopez and Gasparik (1991) investigated the melting of CaSiO<sub>3</sub> perovskite and located the low-pressure stability limit of CaSiO<sub>3</sub> perovskite at 2400 °C between 14 and 15.2 GPa. The study showed that the equilibration rates below the solidus were very slow, and thus an experimental investigation of the subsolidus phase relations would require the use of catalysts to increase the reaction rates. In the present study, the subsolidus phase relations were investigated using H<sub>2</sub>O and CO<sub>2</sub> as fluxes. Partial results were reported by Wolf and Gasparik (1992). Additional experimental constraints on the low-pressure stability limit of CaSiO<sub>3</sub> perovskite were determined by Wang and Weidner (1994).

### EXPERIMENTAL TECHNIQUES

Experiments were conducted with a split-sphere anvil apparatus (USSA-2000) using 10-mm sample assemblies (Gasparik, 1989). Starting materials were pure wollastonite, synthesized from high-purity CaCO<sub>3</sub> and amorphous SiO<sub>2</sub> held at 1200 °C for 3 d, and synthetic wollastonite mixed with Ca(OH)<sub>2</sub> or CaCO<sub>3</sub> (Table 1). The starting materials were loaded into Re capsules, compressed, and subsequently heated with a lanthanum chromite furnace. Temperature was measured with W<sub>3</sub>Re vs. W<sub>25</sub>Re thermocouples and controlled with a Eurotherm temperature controller. Because of the temperature gradients in the samples, each experiment provided information on phase relations in a temperature interval of 200 °C. The sample in the assembly was located slightly off center, so that the hot spot was near one end of the sample, referred to as the hot end. The temperatures measured by the thermocouple were approximately the same as those in the center of the samples; the temperature increase from the center to the hot spot was about 50 °C. Details of the temperature and pressure calibrations and experimental procedures were given by Gasparik (1989).

The samples still inside the capsule were mounted in epoxy. Polished mounts contained a lengthwise section of the sample, allowing inspection of phase relations along the full interval of 200 °C. The experimental products were inspected visually under a microscope. When nec-

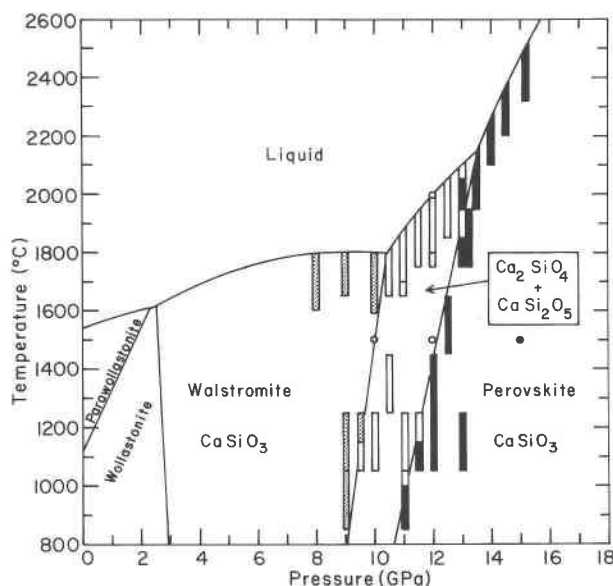


Fig. 1. Temperature-pressure phase diagram for  $\text{CaSiO}_3$ . Bars indicate the  $P$ - $T$  location of the present experiments and the observed experimental products in the temperature interval corresponding to the subsolidus portion of the samples. Circles show the experiments reported by Kanzaki et al. (1991). Phase relations below 3 GPa are from Osborn and Schairer (1941), Kushiro (1964), and Essene (1974). Solid symbols are perovskite; open symbols are  $\text{Ca}_2\text{SiO}_4$  and  $\text{CaSi}_2\text{O}_5$ ; dotted symbols are walstromite.

essary for identification, the products were also analyzed for Ca, Si, and O with a Cameca electron microprobe.

### EXPERIMENTAL RESULTS

The experimental conditions and results for 32 significant experiments are listed in Table 1, and the obtained phase relations are shown in Figure 1. Melting under anhydrous conditions was determined in 14 experiments in the pressure range 8–15.2 GPa. Melting of  $\text{CaSiO}_3$  walstromite was observed at 1800 °C in three experiments at 8, 9, and 10 GPa. The melting became incongruent between 8 and 9 GPa: a thin layer of  $\text{Ca}_2\text{SiO}_4$  was present between  $\text{CaSiO}_3$  walstromite and melt at 9 and 10 GPa, and the adjacent melt was slightly enriched in  $\text{SiO}_2$  with respect to a stoichiometric  $\text{CaSiO}_3$  composition. Comparison with the data of Kushiro (1964) and Essene (1974) shows a moderate increase in the melting temperature of  $\text{CaSiO}_3$  walstromite from 1620 °C at 2.5 GPa to 1800 °C at 8–10 GPa.

Melting of the two-phase assemblage  $\text{Ca}_2\text{SiO}_4 + \text{CaSi}_2\text{O}_5$  was observed in six experiments at 10.5–13 GPa. The melting temperature increased substantially with pressure, from 1800 to 2150 °C. The two-phase assemblage was fine-grained and easily plucked during polishing, which resulted in a partial loss of this part of the samples. The plucking was not observed at 13 GPa, and the two-phase assemblage was present only in a narrow

TABLE 1. Experimental conditions and results

Expt.	Mix*	$t$ (min)	$P_g^{**}$ (bar)	$P_s^\dagger$ (GPa)	$T_r^\ddagger$ (°C)	$T_e^\S$ (°C)	Result
<b>Anhydrous melting</b>							
2130	A	6	114	8.0	1750	1800	W = L
2127	A	6	136	9.0	1800	1800	W = L
2140	A	6	160	10.0	1740		W
2125	A	6	160	10.0	1850	1800	W = L
2134	A	6	176	10.5	1800	1800	2P = L
2128	A	6	190	11.0	1850	1900	2P = L
2160	A	6	208	11.5	1900	1950	2P = L
2146	A	6	226	12.0	1950	2000	2P = L
2121	A	6	246	12.5	2000	2050	2P = L
2108	A	6	270	13.0	2050	2100	2P = L
2115	A	6	294	13.5	2100	2150	CaPv = L
2141	A	5	320	14.0	2250	2260	CaPv = L
2153	A	5	350	14.5	2350	2390	CaPv = L
1371	A	2	400	15.2	2470	2510	CaPv = L
<b>Melting with carbonate flux</b>							
1904	B	20	190	11.0	1800	1700	2P = L
1911	B	15	226	12.0	1900	1920	2P = L
1920	B	30	246	12.5	2000	1920	2P = L
1898	B	25	270	13.0	2000	1950	2P = L
1927	B	4	270	13.0	1900		CaPv
1917	B	10	280	13.2	1900		CaPv
<b>Hydrous experiments</b>							
1589	C	300	136	9.0	1000		W
1566	C	60	136	9.0	1200		W
1582	C	60	148	9.5	1200	1150	W = 2P
1571	C	60	160	10.0	1200		2P
1586	C	60	174	10.5	1400		2P, hP
1590	C	300	190	11.0	1000	1000	2P = CaPv
1550	C	20	190	11.0	1200		2P, hP
1583	C	60	208	11.5	1200	1150	2P = CaPv
1567	C	60	226	12.0	1200		CaPv
1578	C	60	226	12.0	1400		CaPv, L
1587	C	4	246	12.5	1600		CaPv
1558	C	60	270	13.0	1200		CaPv, hP

\* Starting materials (in moles): A = synthetic wollastonite ( $\text{CaSiO}_3$ ); B = 9  $\text{CaSiO}_3$ , 1  $\text{CaCO}_3$ ; C = 9  $\text{CaSiO}_3$ , 1  $\text{Ca(OH)}_2$ .

\*\* Gauge pressure ( $P_g \times 1.096 = \text{load in metric tons}$ ).

† Sample pressure.

‡ Temperature recorded by the thermocouple.

§ Estimated temperature at the reaction boundary.

|| Observed reactions and phases: CaPv =  $\text{CaSiO}_3$  perovskite; hP =  $\text{CaSi}_2\text{O}_5$ ; L = liquid; 2P =  $\text{Ca}_2\text{SiO}_4 + \text{CaSi}_2\text{O}_5$ ; W =  $\text{CaSiO}_3$  walstromite.

region at the solidus. Presumably metastable  $\text{CaSiO}_3$  perovskite was located in the rest of the sample.

Melting of  $\text{CaSiO}_3$  perovskite was observed in four experiments at 13.5–15.2 GPa, and the melting temperature increased by 360 °C in this pressure interval. The melting was congruent and produced a sharp, clearly visible boundary between the melt, preserved in the product as quenched crystals, and  $\text{CaSiO}_3$  perovskite, which transformed to an amorphous substance on decompression. This caused an expansion of the part of the sample containing  $\text{CaSiO}_3$  perovskite and fragmentation of the Re capsule.

Experiments with the carbonate flux as a catalyst were designed to eliminate the metastable  $\text{CaSiO}_3$  perovskite from the subsolidus part of the samples, which was often present in the flux-free melting experiments. The two-phase assemblage was present in the subsolidus part of four samples from 11 to 13 GPa. The  $\text{CaSiO}_3$  perovskite

was observed in two experiments at 13 and 13.2 GPa. The presence of CO<sub>2</sub> produced an unusual brown transparent glass, which melted under the electron beam of the microprobe. Such glass was not observed in the carbonate-free experiments. An example of an experimental product from melting with the carbonate flux is shown in Figure 2.

Hydrothermal experiments were carried out at 12 different *P-T* conditions at 9–13 GPa and 850–1650 °C. In combination with the melting experiments, the results place narrow constraints on the positions of two univariant boundaries that limit the stability field of the two-phase assemblage. The breakdown of CaSiO<sub>3</sub> walsstromite to Ca<sub>2</sub>SiO<sub>4</sub> and CaSi<sub>2</sub>O<sub>5</sub> is best described by the equation  $P$  (GPa) = 7.9 + 0.0014*T* (°C). The formation of CaSiO<sub>3</sub> perovskite from the two-phase assemblage is best approximated by  $P$  (GPa) = 9.0 + 0.0021*T* (°C). The resulting univariant boundaries intersect the solidus in triple points located at 10.4 GPa, 1800 °C, and 13.5 GPa, 2150 °C.

Several hydrothermal experiments produced a hydrous phase with the Ca/Si atomic ratio close to 3. O analyses indicated that the most likely formula was Ca<sub>3</sub>SiO<sub>2</sub>(OH)<sub>6</sub>. The hydrous phase was always present in the cold end of the samples. An experiment at 12 GPa and 1400 °C produced a hydrous melt located in the hot spot. Its Ca/Si ratio varied between 1.37 and 1.47.

## DISCUSSION

The phase relations for CaSiO<sub>3</sub> obtained in this study are in complete agreement with the results of four experiments by Kanzaki et al. (1991). Recently, Wang and Weidner (1994) presented new experimental data on the low-pressure stability limit of CaSiO<sub>3</sub> perovskite by in-situ observations of its breakdown in a DIA-type apparatus. Although, these results are in close agreement with the present study, Wang and Weidner placed the low-pressure stability limit of CaSiO<sub>3</sub> perovskite 0.4 GPa lower than the boundary of Wolf and Gasparik (1992), which is identical to our boundary. In the most significant experiment at 1317 °C, Wang and Weidner crossed the low-pressure stability limit of CaSiO<sub>3</sub> perovskite from higher pressures and observed no change at 11.6 GPa, but a rapid breakdown of CaSiO<sub>3</sub> perovskite at 11.0 GPa. Given that CaSiO<sub>3</sub> perovskite was observed in this study to persist metastably within the two-phase field in the absence of a flux even at the high temperatures close to the solidus, the observation of no change at 11.6 GPa and 1317 °C, only 0.17 GPa below our presumed equilibrium boundary, is not inconsistent with this boundary. Recent calibration of the coesite-stishovite boundary with the same DIA-type apparatus by Zhang et al. (1994) is fully consistent with our calibration, limiting the potential difference in the calibrations to <0.2 GPa. Hence, we believe that the experimental observations of Wang and Weidner (1994) do not justify the proposed modification of the Wolf and Gasparik (1992) boundary.

The observed large pressure dependence of the melting



Fig. 2. Backscattered electron image of an experimental product from melting experiments with carbonate flux (expt. 1898, 13 GPa, 1950 °C). Shown in the sequence with decreasing temperature from the top is the melt, preserved as brown transparent glass, a layer of Ca<sub>2</sub>SiO<sub>4</sub>, produced by incongruent melting and segregated from the melt, and the subsolidus assemblage of Ca<sub>2</sub>SiO<sub>4</sub> + CaSi<sub>2</sub>O<sub>5</sub> at the bottom. The scale is 100 μm long.

curve of CaSiO<sub>3</sub> perovskite reflects a large density difference between the melt and the perovskite at its low-pressure stability limit and can be expected in the melting of most perovskites, including MgSiO<sub>3</sub>. The triple point marking the first appearance of CaSiO<sub>3</sub> perovskite on the solidus is analogous to the triple point for coexisting majorite + perovskite + liquid in MgSiO<sub>3</sub>, located by Gasparik (1990) at 22.5 GPa and 2600 °C. The expected large pressure dependence of the melting curve of MgSiO<sub>3</sub> perovskite at the triple point of its formation would be inconsistent with the data of Heinz and Jeanloz (1987), but in agreement with the melting curve of Zerr and Bohler (1993).

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