Hydrothermal diamond-anvil cell study of melts: Eutectic melting of the assemblage Ca(OH)$_2$ + CaCO$_3$ with excess H$_2$O and lack of evidence for “portlandite II” phase

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ABSTRACT
Eutectic melting temperatures for the assemblage Ca(OH)$_2$ + CaCO$_3$ in the presence of excess H$_2$O were determined along six isochores of H$_2$O in a hydrothermal diamond-anvil cell. These temperatures range from 610 °C at 1204 bar to 583 °C at 7203 bar; they agree very well (within 3 °C) with data obtained from high-pressure differential thermal analysis (HP-DTA) and are about 20 °C lower than those obtained from quench experiments. The additional DTA peaks near 630 °C for the melting experiments of pure portlandite reported by Harker (1964) and Bai et al. (1994) may be the result of a small amount of melting, caused by CaCO$_3$ contamination, and not the result of a solid phase transition between portlandite and “portlandite II.”

INTRODUCTION
The newly developed hydrothermal diamond-anvil cell (HDAC; Bassett et al., 1993a, 1993b) is a versatile device for hydrothermal experimentation. In this study, the utility of the HDAC has been extended to the investigation of melts.

The univariant melting pressure-temperature (P-T) relations for the assemblage Ca(OH)$_2$ + CaCO$_3$ in the dry system and also in the presence of excess H$_2$O were determined by Wyllie and Tuttle (1960) to 40 kbar and Wyllie and Raynor (1965) to 4 kbar using quench methods, and by Koster van Groos (1982) to 10 kbar using high-pressure differential thermal analysis (HP-DTA). At a given pressure, the melting temperature determined by the quench method is about 20 °C higher than that obtained from HP-DTA. In his DTA study of the melting of pure portlandite, Harker (1964) found an additional peak at 630 °C and 1 kbar during heating. He concluded that CaCO$_3$ and H$_2$O were present as impurities in the portlandite, and that this peak was the result of a small amount of melting. Similarly, in their HP-DTA study of the melting of portlandite, Bai et al. (1994) observed this additional peak during heating at 640 °C and 17.8 bar, and they observed that the peak temperature drops about 1.4 °C for every 100 bar increase in pressure (up to 711 bar). In these experiments, microscopic examination of the starting material and the experimental products showed no evidence for calcite contamination. They assumed that these additional DTA peaks were caused by a phase transition from portlandite to an unknown phase called “portlandite II.” X-ray data obtained in situ at high temperature were presented to support their assumption. Searching actively for suitable pressure calibrants in the HDAC (Chou and Haselton, 1994), we were excited by the prospect of using this highly pressure-sensitive phase transition as a pressure indicator in the HDAC. Therefore, experiments were designed originally for calibrating the P-T relationship of this phase transition in the HDAC, but, instead, the eutectic melting of the assemblage Ca(OH)$_2$ + CaCO$_3$ in the presence of excess H$_2$O were observed as a result of unexpected contamination of the Ca(OH)$_2$ sample by atmospheric CO$_2$. We present results of these meltings along six isochores of H$_2$O and raise the question about the existence of the portlandite II phase.

EXPERIMENTAL METHOD
The HDAC method was described by Shen et al. (1993) and Bassett et al. (1993a, 1993b). Ca(OH)$_2$ was synthesized from CaO and H$_2$O in a sealed Au capsule at 2 kbar H$_2$O pressure in a cold-seal pressure vessel. The sample was first melted and held at 810 °C for 30 min, cooled to 555 °C in an hour, and then kept at this temperature for 16 h before quenching. To minimize reaction with CO$_2$, the material was stored in an evacuated bottle after being extracted from the capsule. The reaction with CO$_2$, however, is unavoidable once the sample is exposed to the atmosphere. As a result, the sample contained a small amount of CaCO$_3$, the presence of which was verified by examination under a petrographic microscope and by the generation of gas bubbles (presumably CO$_2$) when it reacted with a drop of 1 N HCl solution under the micro-
The existence of the portlandite II phase reported by Bai et al. (1994) is questionable for three reasons. First, such low crystallization temperatures may have resulted from the fast cooling rate; they have not been reported in Figure 2, which was reproduced from an image observed at 4 kbar and 630 °C (open triangle in Fig. 1) and recorded on the VCR tape. On cooling (~50 °C/min) along an isochore, the last drop of melt was observed to crystallize at a temperature normally about 100 °C below T_m. Such low crystallization temperatures may have resulted from the fast cooling rate; they have not been reported because all previous experimental methods do not have the comparable sensitivity.

**The portlandite II phase (?)**

The results of the portlandite II phase reported by Bai et al. (1994) is questionable for three reasons. First, as shown in Figure 1, almost all the DTA signals that Bai et al. (1994) obtained by Koster van Groos (1982) in his heating experiments for samples containing 56Ca(OH)_2-44CaCO_3 with more than 5 wt% H_2O (shown as Xs, which were defined by the onset temperatures of his DTA signals). The agreement is excellent (within 3 °C), indicating that the DTA technique is a very reliable method for studying P-T relationships for at least the eutectic melting. However, it should be noted that the HDAC method is much more efficient, and that the significant difference in heating rates (10 vs. 100 °C/min) does not seem to spoil the agreement. The solid line in Figure 1 represents a visual fit to both sets of data. A typical appearance of the immiscible liquid (melt) is shown in Figure 2, which was reproduced from an image observed at 4 kbar and 630 °C (open triangle in Fig. 1) and recorded on the VCR tape. On cooling (~50 °C/min) along an isochore, the last drop of melt was observed to crystallize at a temperature normally about 100 °C below T_m. Such low crystallization temperatures may have resulted from the fast cooling rate; they have not been reported because all previous experimental methods do not have the comparable sensitivity.

**RESULTS**

Experiments were performed along six isochores of H_2O. The results are listed in Table 1 and plotted as open circles in Figure 1. Also shown in Figure 1 for comparison are the HP-DTA data obtained by Koster van Groos (1982) in his heating experiments for samples containing 56Ca(OH)_2-44CaCO_3 with more than 5 wt% H_2O (shown as Xs, which were defined by the onset temperatures of his DTA signals). The agreement is excellent (within 3 °C), indicating that the DTA technique is a very reliable method for studying P-T relationships for at least the eutectic melting. However, it should be noted that the HDAC method is much more efficient, and that the significant difference in heating rates (10 vs. 100 °C/min) does not seem to spoil the agreement. The solid line in Figure 1 represents a visual fit to both sets of data. A typical appearance of the immiscible liquid (melt) is shown in Figure 2, which was reproduced from an image observed at 4 kbar and 630 °C (open triangle in Fig. 1) and recorded on the VCR tape. On cooling (~50 °C/min) along an isochore, the last drop of melt was observed to crystallize at a temperature normally about 100 °C below T_m. Such low crystallization temperatures may have resulted from the fast cooling rate; they have not been reported because all previous experimental methods do not have the comparable sensitivity.

**Fig. 1. Eutectic melting temperatures for the assemblage Ca(OH)_2 + CaCO_3.** The solid curve and the two dashed lines are visually fit to the data. Note that almost all the extra DTA peaks obtained by Bai et al. (1994; open and solid rectangles for their open- and closed-capsule experiments, respectively) and Harker (1964; solid circle) for their melting DTA experiments of pure portlandite are located between the two dashed lines. The open triangle indicates the P-T condition for the sample shown in Fig. 2.
that all the P-T points shown here were for the DTA peak angles) and the other with excess H$_2$O (plus signs). Note that all the P-T points shown here were for the DTA peak signals obtained in heating experiments using the same HP-DTA apparatus. For comparison, the P-T point for the extra DTA signal reported by Harker (1964) is shown by the solid circle. The possibility of a solid phase transition caused by calcite contamination (Harker, 1964) suggests that a very small amount of calcite may have been present in the DTA experiments but was not detected by Bai et al. (1994). The grain boundaries of a Ca(OH)$_2$ chip in the presence of CaCO$_3$ are also melt but are slightly out of focus.

The conflicting evidence from DTA and X-ray data (Bai et al., 1994) and from the visual or interferometric methods seen in the present study remains unresolved. Because of the sensitivity of direct visual methods for the determination of phase transitions or melting reactions, we consider that the formation of portlandite II, as proposed by Bai et al. (1994) is questionable. We hope a definite answer can be provided by in situ determination of lattice parameters of portlandite at high P-T conditions in an HDAC using synchrotron radiation, the approach that has been applied successfully for the study of calcite (Wu et al., 1995). If portlandite II phase does exist, its relation with other potential ultrahigh-pressure polymorphs, detected by the use of neutron powder diffraction and in situ X-ray diffraction methods (Bai et al., 1994, and references therein), will then become an interesting question.

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