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Hydrothermal diamond-anvil cell study of melts: Eutectic melting of the assemblage $Ca(OH)_2 + CaCO_3$ with excess H_2O 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_2O were determined along six isochores of H_2O 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_2O 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_2O 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 meltings of the assemblage $Ca(OH)_2 + CaCO_3$ in the presence of excess H_2O 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_2O 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_2O in a sealed Au capsule at 2 kbar H_2O 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-

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TABLE 1. *P-T* conditions determined by the HDAC technique for the eutectic melting of the $Ca(OH)_2 + CaCO_3$ assemblage in the presence of excess H_2O

P_m* (bar)	T_m** (°C)	T_h† (°C)	ρ‡ (g/cm³)
1204	610	371.8	0.426
1745	609	357.3	0.542
3522	594	289.5	0.733
4972	590	238.9	0.815
5805	588	211.0	0.852
7203	583	164.3	0.903

* Melting pressure calculated from T_m and density using the equation of state of H_2O formulated by Saul and Wagner (1989).

** Measured melting temperature.

† Measured liquid-vapor homogenization (to liquid) temperature of H_2O.

‡ Density of H_2O at T_m and P_m calculated from T_h (Wagner and Pruss, 1993).

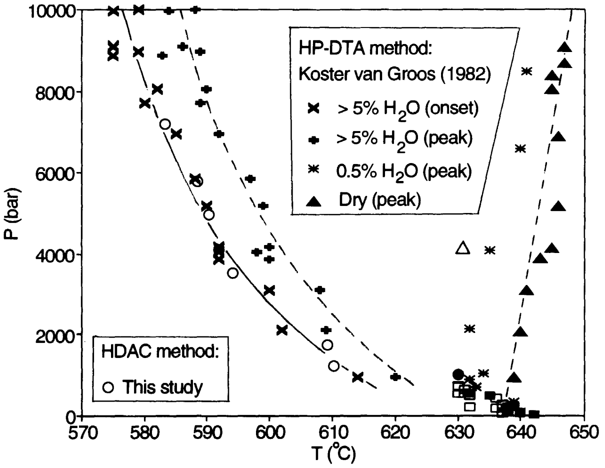

Fig. 1. Eutectic melting temperatures for the assemblage $Ca(OH)_2 + CaCO_3$. The solid curve and the two dashed lines are visually fit to the data. Note that almost all the extra DTA peaks obtained by Bai et al. (1994; open and solid rectangles for their open- and closed-capsule experiments, respectively) 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.

scope. A fragment of the material (170 × 250 × 30 μm) together with distilled, deionized H_2O and an air bubble were enclosed in the sample chamber, which is a 500 μm diameter hole in a 125 μm thick Re gasket sandwiched between two diamond-anvil faces. The sample was heated externally first along the liquid-vapor *P-T* curve of H_2O and then more or less along an isochore after the disappearance of the vapor bubble at the homogenization temperature (T_h). The sample chamber as seen through an optical microscope was displayed on a video monitor, and the images were recorded continuously by a video cassette recorder (VCR). Melting was indicated by the formation of beads; the movement and coalescence of these beads as well as convective motion observed in bigger beads confirmed that they were indeed melts. The heating rates were between 75 and 125 °C/min with an average of 100 °C/min. After the initial melting was detected at T_m, the sample was cooled isochorically until a vapor phase was nucleated, and a new T_h was obtained by slow heating of a few degrees. The densities of H_2O at T_m and at this new T_h are the same (<1% deviation; see discussions in Shen et al., 1993), and the value is obtained from Wagner and Pruss (1993). The pressure at T_m (P_m) is then calculated from the density of H_2O and T_m by using the equation of state of H_2O (Saul and Wagner, 1989). After obtaining one set of T_m-P_m data, the experiment was repeated along another isochore of H_2O simply by pressing the two diamond-anvil faces closer together to increase density or by releasing some of the H_2O to reduce density. The reported values of T_h and T_m are accurate to ±0.2 and ±2 °C, respectively. The reported values of P_m are accurate to ±3%. The effects of dissolved species on the calculated H_2O density and P_m are expected to be small because, under the investigated *P-T* conditions, the solubilities of both $Ca(OH)_2$ and $CaCO_3$ are small; the maximum molality of Ca is <0.01 (Walther, 1986).

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 meltings. 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.

THE PORTLANDITE II PHASE (?)

The existence 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) assumed to be a result of the solid-solid phase transition (rectangles) occur between the two dashed lines, one representing the eutectic temperatures of the anhydrous assemblage $56Ca(OH)_2$-$44CaCO_3$ (solid tri-

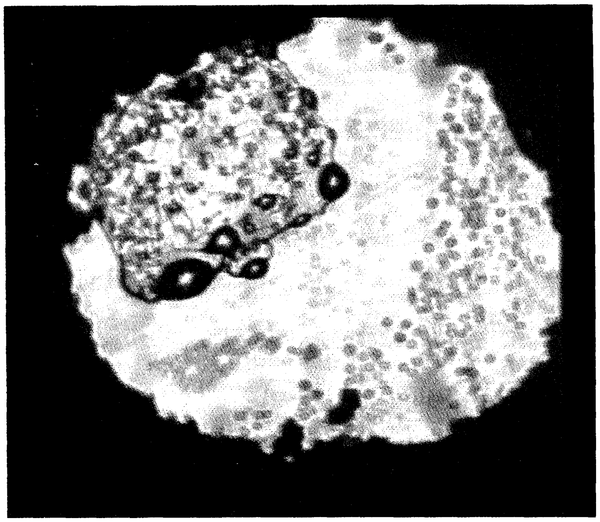

Fig. 2. Immiscible liquid (melt) formed on the rim and along the grain boundaries of a $Ca(OH)_2$ chip in the presence of $CaCO_3$ and excess H_2O in an HDAC at 4 kbar and 630 °C (open triangle in Fig. 1). The image is reproduced from the VCR tape. The sample chamber is about 500 μm in diameter. The small spheres appearing at the right side of the sample chamber are also melt but are slightly out of focus.

TABLE 2. Comparison of X-ray data of the portlandite II phase (Bai et al., 1994) and those of β-Ca_2SiO_4 and Pt

Portlandite II*			β-Ca_2SiO_4**		
No.	*d* (Å)	I/I_1†	*d* (Å)	I/I_1	*hkl*
1	3.907	<5	3.970	4	$\bar{1}11$
			3.827	8	012
2	3.392	15	3.377	12	020
3	3.086	10	3.046	14	112
4	2.949	15	2.876	35	120
5	2.806	100	2.795	100	$\bar{1}03$
			2.780‡	90	$\bar{1}21$
6	2.747	50	2.744	95	200
7	2.405§	5	2.407	20	211
8	2.304	50	2.304	6	$\bar{2}12$
9	2.230	10	2.282	35	023
			2.196	12	014
10	2.066	5	2.083	8	130
			2.048	20	221
11	1.993	20	2.019	20	131
12	1.993	10	1.983	35	$\bar{2}22$
			1.913	10	024
13	0.897	15	0.9000(Pt)	22	331
14	0.875	20	0.8773(Pt)	20	420
15	0.7985	50	0.8008(Pt)	29	422

* Data from Table 2 of Bai et al. (1994); other phases present were lime and Pt, and most of these lines were deleted from their list.

** Partial list; only those closely matching the listed portlandite II data are given, and the last three entries are for Pt. Data from Mineral Powder Diffraction File Databook (1993).

† Relative intensities for single phase (not mixture).

‡ May have been identified by Bai et al. (1994) as 111 peak for lime (*d* = 2.778 Å; I/I_1 = 34) and excluded from their list.

§ Should be deleted from the list because it coincides with the 200 peak of lime (I/I_1 = 100).

angles) and the other with excess H_2O (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 in portlandite cannot be excluded on the basis of current DTA data. However, the coincidence of these *P-T* conditions with the *P-T* conditions of the melting reaction 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). Second, the high-*T* X-ray data for the portlandite II phase reported by Bai et al. (1994, in their Table 2) match the X-ray reflections of β-Ca_2SiO_4 and Pt (see Table 2). Recent additional experiments confirm that their Table 2 is erroneous and that these reflections do represent β-Ca_2SiO_4 and Pt. The β-Ca_2SiO_4 was produced during their high-temperature (670 ± 10 °C) and high-pressure (20–30 bar) X-ray diffraction measurements by the reactions of their sample with the container (Na-poor silica glass capillary). Third, no solid-solid phase transition was detected either by visual or interferometric methods during isochoric heating or cooling of $Ca(OH)_2$ in the HDAC. The α-β phase transition in quartz is easily detected interferometrically in the HDAC (Shen et al., 1993), and it is expected that the solid-solid phase transition in portlandite, if present, could be detected in the same fashion because the volume change for this transition is estimated to be three times the volume change of the α-β quartz transition (Bai et al., 1994).

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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