Phase transition, dehydration, and melting relationships of portlandite

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Abstract

The dehydration and melting reactions of portlandite were studied at temperatures to 800 °C and pressures to 740 bars, using high-pressure differential thermal analysis. The dehydration of portlandite in P-T space increases from 510 °C at 1 atm to 640 ± 1 °C at 17.8 ± 1 bars, where portlandite transforms to the phase called portlandite II, and to 789 ± 2 °C at 105 ± 3 bars, where it meets a series of portlandite melting reactions at an invariant point. The P-T slope of the reaction portlandite $\rightleftharpoons$ portlandite II is slightly negative, indicating a lower molar volume ($\Delta V = 0.43$ cm³/mol) for portlandite II. The enthalpy of this reaction is estimated as 31.5 ± 8.2 kJ/mol. A high-temperature and high-pressure X-ray diffraction study of portlandite II provided provisional d values.

Introduction

Interest in hydrated phases, which may store H_2O in the mantle, has inspired the study of hydroxides, including brucite and portlandite. The phase relations of system CaO-H_2O at elevated P values were studied by Wyllie and Tuttle (1960), using a quench technique, and by Harker (1964) and Irving et al. (1977), using high-pressure differential thermal analysis (HP-DTA). In this paper we present new data on the portlandite system, using an HP-DTA technique. The invariant reaction involving portlandite, lime, liquid, and vapor was located at 810 °C and 100 bars by Wyllie and Tuttle (1960), on the basis of experiments at 83 and 140 bars. Subsequently, the T was revised downward by 30 °C (Wyllie and Raynor, 1965). Harker (1964) found an additional DTA peak at 630 °C and 1 kbar. He assumed this peak was the result of a small amount of melting, caused by $CaCO_3$ contamination of the sample. Wyllie and Boettcher (1969) noticed that at high P-T (>20 kbar, >600 °C) portlandite exhibits well-developed laminar twinning, which they attributed to a phase transition. In an HP-DTA study of the system $CaCO_3$-$Ca(OH)_2$-H_2O, Koster van Groos (1982) observed an extra peak at about 630 °C, which temperature was not greatly affected by P. He suggested this peak may represent the phase transition in portlandite, as suggested by Wyllie and Boettcher (1969). Recently, Parise et al. (1993), using neutron powder diffraction, found evidence for a phase change in portlandite at high P. Similarly, K. Leinenweber (personal communication) identified a portlandite phase transition at very high P (70 kbar) using in-situ X-ray diffraction (XRD).

Experimental methods

The HP-DTA method was described by Koster van Groos (1979). Fine-grained (<200 mesh) $Ca(OH)_2$ was prepared by decarbonizing $CaCO_3$ at 950 °C for 5 h and hydrating the resulting CaO in saturated water vapor at 57 °C for 5 h. The product is pure portlandite, verified by XRD and microscopic examination. To prevent reaction with CO_2, the material was stored under vacuum and routinely examined by XRD. In open and closed experiments, the sample weight was about 10 and 4 mg, respectively. Since the capsules burst at $P < 50$ bars because of the high molar volume of H_2O, open capsules were used at low P. Using only about 1 mg of the sample, several experiments were made at 45–86 bars. Distilled water in the amount of 0–25 wt% was added to open experiments in an attempt to maintain $P_{H_2O} = P_{tot}$.

We designed an apparatus for in-situ high-T studies at elevated P (20–30 bars) in a Debye-Scherrer X-ray powder camera to investigate the solid phase transition from portlandite to another portlandite phase, called portlandite II, associated with the DTA peak. A heating coil of Pt wire was placed around a glass capillary, with the X-ray beam aimed between the windings. Samples were sealed in a low-Na silica glass capillary (wall thickness of 0.2 mm) to withstand P to ≈ 30 bars. Experiments were made without the protective cover of the camera, with the film wrapped in paper to prevent exposure by light. Experiments were made within the portlandite II field at 670 ± 10 °C. P was controlled by the dehydration of portlandite at ≈ 20–30 bars and 670 ± 10 °C. The high background caused by the glass walls allowed only the stronger reflections to be observed. Exposure time was between 5 and 40 h, depending on the type of X-ray film used. Because the thermal mass of the furnace is small, the quench is very fast.

Results

A total of 14 open- and 24 closed-capsule experiments were made between 1 and 740 bars (Table 1). The experimental products were examined by microscope and XRD. The open-capsule experiment products are composed of lime (CaO) and a small amount of portlandite;

TABLE 1. Experimental conditions and results of portlandite dehydration, phase transition, and melting reactions

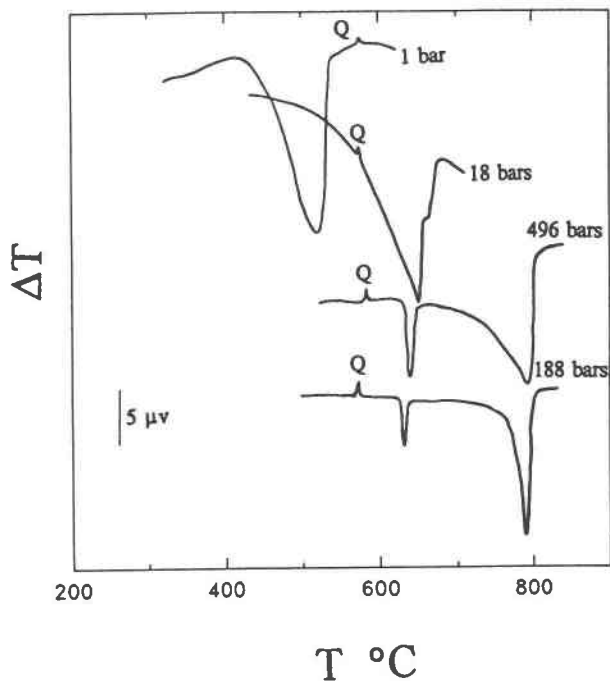| H_2O (wt%)	Peak		Peak	
	T (°C)	P (bar)	T (°C)	P (bar)
Open-capsule experiments				
10	—	—	512	1
0	—	—	509	1
25	—	—	608	8
10	—	—	627	16
25	642	18	655	18
20	640	57	683	58
8	640	57	678	58
15	640	77	670	78
0	638	95	720	98
10	638	173	742	179
14	638	202	794	210
8	638	214	787	222
15	635	475	795	496
20	632	531	787	571
Closed-capsule experiments				
0	637	47	741	45
0	638	70	752	69
0	638	86	781	86
0	637	96	783	96
0	637	96	782	96
0	638	103	788	102
0	638	108	790	108
0	638	120	798	120
0	638	188	798	188
0	638	188	799	188
0	637	275	799	275
0	637	275	795	275
0	636	400	797	390
0	636	400	800	390
0	631	640	792	648
0	630	685	799	688
10	636	170	787	170
5	636	172	792	172
10	632	214	780	221
20	632	473	779	496
13	631	530	778	555
18	630	530	778	555
20	630	711	776	740
10	630	710	776	740

Fig. 1. Representative HP-DTA curves of portlandite dehydration, phase transition, and melting reactions. Q indicates the transition between low quartz and high quartz. The DTA curve at 1 bar shows the dehydration peak and that at 18 bars shows the overlap of dehydration peak and phase transition peak. The DTA curves at 188 bars (closed experiment) and 496 bars (open experiment) show the melting peak at higher temperature and the sharp phase transition between portlandite and portlandite II at lower temperature.

the closed-capsule experiment products consist of platy portlandite crystals, similar to the ones described by Wyllie and Tuttle (1960). Peak temperature, defined as the T at the maximum deflection of the endotherm, was used to define the T of the reaction.

Open-capsule experiment results

Experiments in open capsules were made between 1 and 571 bars. At <18 bars, a strong ($\Delta T = 1-3$ °C), well-developed peak (Fig. 1) represents the portlandite dehydration reaction. The peak T increased rapidly from 510 °C at 1 bar to 655 °C at 18 bars. At these conditions, the molar volume of H_2O is large, and $P_{H_2O} = P_{tot}$ was maintained during dehydration (Koster van Groos and Guggenheim, 1987). The dehydration peak was present also in experiments between 58 and 179 bars. At these conditions, the molar volume of H_2O is smaller. Also, the Ar pressure medium dilutes the H_2O vapor, resulting in $P_{H_2O} < P_{tot}$. As a result, the observed dehydration temperatures are low compared with conditions for $P_{H_2O} = P_{tot}$. At 642 °C and >18 bars (Table 1), a smaller sharp

and symmetric peak is present on the shoulder of the dehydration peak (Fig. 1). In contrast with the dehydration peak, the T of this peak decreased slightly with increasing P, indicating a small volume decrease during the reaction. This peak represents a solid phase transition, which was confirmed by in-situ XRD experiments (see below). Above 210 bars, a third type of peak, which is smaller, wider, and less symmetric than the dehydration peak, is present (Fig. 1). The T of this peak is also nearly independent of P, indicating a small volume change. Because part of the portlandite must have been dehydrated to produce CaO during heating, we assume that this peak represents the reaction $Ca(OH)_2 + CaO = L$.

Closed-capsule experiment results

Closed-capsule experiments were made between 45 and 740 bars. A peak similar to the dehydration peak, observed in the open-capsule experiments, is present from 741 °C at 45 bars to 788 °C at 102 bars (Table 1). Above 102 bars, the peak becomes sharper, but it remains asymmetric and well developed. The peak is probably produced by the melting of portlandite. Cooling experiments show a strong DTA peak at a temperature 30 °C lower. It probably represents crystallization of portlandite. In

the presence of excess H_2O, the peak T is 10–15 °C lower than that in open experiments. However, in the absence of excess H_2O, the peak T is 5–8 °C higher than that in open experiments. The lower T reaction probably represents the reaction $Ca(OH)_2 + V = L$, whereas the other reaction may represent the reaction $Ca(OH)_2 = L$.

The sharp shoulder peak, observed in open experiments at ≥ 18 bars, was found in all closed experiments. No difference was seen between the peak in closed and open experiments. During cooling, a similar but exothermic peak is present, with peak $T \sim 3$–10 °C lower than that encountered during the heating cycle.

Discussion

Phase relations in the system CaO-H₂O

The DTA results indicate 11 univariant and invariant reactions involving five phases: portlandite (CH), portlandite II (CH_{II}), lime (C), liquid (L), and vapor (V). They are listed below:

$$CH = C + V \tag{1}$$

$$CH = CH_{II} \tag{2}$$

$$CH = CH_{II} (C, V) \tag{3}$$

$$CH_{II} = C + V \tag{4}$$

$$CH_{II} + C = L + V \tag{5}$$

$$C + V = L \tag{6}$$

$$C + CH_{II} = L \tag{7}$$

$$CH_{II} = L + V \tag{8}$$

$$CH_{II} = L (V) \tag{9}$$

$$CH_{II} + V = L \tag{10}$$

$$CH_{II} = L. \tag{11}$$

The schematic P-T relations are shown in Figure 2. They are very similar to the results of Wyllie and Tuttle (1960). All reactions, with the exception of Reaction 6, were observed by this study. Reaction 1, involving the dehydration of CH producing C and V, is defined by open-capsule experiments at ≤ 16 bars. Reaction 2, in which CH reacts to form CH_{II}, is defined by the sharp peak present in all experiments at >17 bars. The transition T decreases slightly with P, following T (°C) = 639.7 − 0.014P (bars). Reactions 1 and 2 intersect at 640 ± 1 °C near 18 bars, defining the invariant point I_1 (see Reaction 3) at 640 ± 1 °C and 17.8 ± 1 bars. With an increase in T, CH_{II} dehydrates to form C and V following Reaction 4. This reaction is defined by the closed experiments at 45–102 bars and the open experiment at 18 bars. Reaction 4 intersects Reaction 7, representing the eutectic melting of C + CH_{II}, at the invariant point I_2 (Reaction 5). Because Reaction 7 is nearly T independent, it defines the T of I_2. The resulting P-T conditions of I_2 are 789 ± 3 °C at 105 ± 3 bars. This is slightly above the P-T
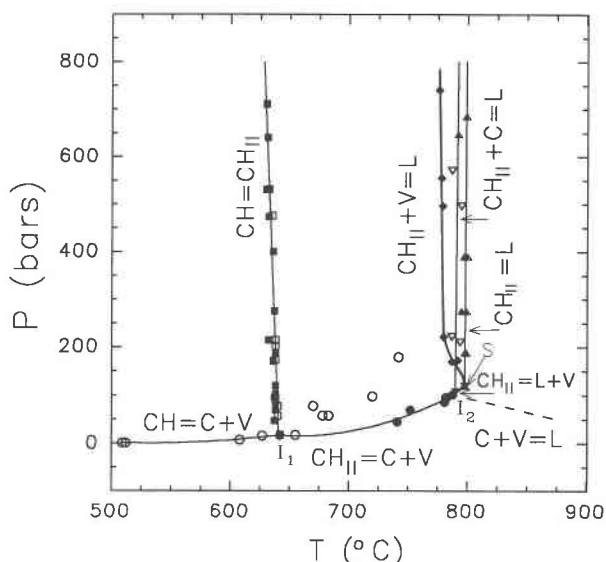

Fig. 2. Phase relations in the system CaO-H₂O. Abbreviations: CH = portlandite, CH_{II} = portlandite II, C = lime, V = vapor, and L = liquid. The symbols represent the following reactions: circles: CH = C + V and CH_{II} = C + V; squares: CH = CH_{II}; diamonds: CH_{II} + V = L; triangles: CH_{II} = L; inverse solid triangles: CH_{II} = L + V; inverse open triangles: CH_{II} + C = L. I_1 and I_2 are invariant points, and S is a singular point. The open and solid symbols represent open- and closed-capsule experiments, respectively.

conditions of 780 °C and 100 bars, as found by Wyllie and Raynor (1965). Two additional reactions, 6 and 8, emanate from I_2. Reaction 6, representing the melting of C in the presence of V, was not observed. Reaction 8 is defined by closed-capsule experiments at 108 and 120 bars. At slightly higher P and T than I_2, the presence of a singular point S, represented by Reaction 9, in which CH_{II} melts in the presence of V, is inferred (e.g., Wyllie and Tuttle, 1960). From S, two closely related reactions (10 and 11) emanate. The melting reaction of CH_{II} + V (11), in which an increasing amount of V is dissolving into the liquid with increasing P and which occurs at decreasing T with increasing P, is encountered in a series of closed-capsule experiments. The melting reaction (11) of dry CH_{II} is seen in a series of closed-capsule experiments at >188 bars without additional H_2O. Whereas it is very difficult to distinguish Reactions 7 and 11 in quench experiments (Wyllie and Tuttle, 1960), it was relatively simple in our DTA with the open and closed experiments. However, the difference in peak T between the two reactions is very small.

Using the P-T relationship, the enthalpy of dehydration was calculated (e.g., Anderson, 1977; Koster van Groos and Guggenheim, 1987). The enthalpies calculated for Reactions 1 and 4 are 128.7 ± 4.7 and 97.2 ± 3.5 kJ/mol, respectively. These data are close to the 99.1 kJ/mol of portlandite dehydration calculated from Robie et al. (1978). From these values the enthalpy of Reaction 2,

TABLE 2. X-ray data of portlandite II phase

No.	d (Å)	Relative intensity
1	3.907	<5
2	3.392	15
3	3.086	10
4	2.949	15
5	2.806	100
6	2.747	50
7	2.405	5
8	2.304	50
9	2.230	10
10	2.066	5
11	1.993	20
12	1.933	10
13	0.897	15
14	0.875	20
15	0.7985	50

31.5 ± 8.2 kJ/mol, is derived. Using the Clausius-Clapeyron equation, a volume change of 0.47 cm³/mol was estimated for Reaction 2, which is about three times the volume change of the high-low quartz transition (Robie et al., 1978).

X-ray study of portlandite II

Three successful experiments were made, each consisting of three XRD exposures: one of the starting material at room T before heating, one at high T, and one after the quench. Both lime and Pt diffraction lines were observed with the long-duration high-temperature experiments. Lime is produced from the dehydration of portlandite, and Pt is the result of deposition of Pt onto the glass capillary, following partial evaporation of the heating coil. The values of d, which are believed to represent portlandite II, are listed in Table 2. At low 2θ angles, the background of the film is very high, and reflections, if present, could not be observed. Although we were not able to quench portlandite II in our DTA experiments, we were able to observe this phase in our experiments in the Debye-Scherrer camera because of the very fast quench. However, not enough material was available for conventional XRD analysis. In experiments in which the temperature was lowered more slowly, portlandite II was not observed.

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