

Phase relations in the system MgO-NaCl-H₂O: The dehydroxylation of brucite in the presence of NaCl-H₂O fluids

T.B. BAI AND A.F. KOSTER VAN GROOS

Department of Earth and Environmental Sciences, University of Illinois at Chicago, 845 W. Taylor Street, Chicago, Illinois 60607-7059, U.S.A.

ABSTRACT

The dehydroxylation of brucite was determined in the presence of NaCl-H₂O fluids containing 0, 2, 6, 11, 14, 18, 30, and 38 mol% NaCl (0.0, 5.5, 17.0, 28.8, 34.5, 41.7, 58.2, and 66.6 wt% NaCl) to ~2500 bars and ~700 °C by high-pressure differential thermal analysis (HP-DTA). At pressures below 150 bars, brucite dehydrates in two separate reactions involving at least one intermediate phase. The dehydroxylation reaction of brucite at pressure to ~2 kbars follows $\ln P(\text{bars}) = 22.23 - 13620/T(\text{K})$. In the presence of NaCl-H₂O fluids, the dehydroxylation temperature is lowered because of the reduction of the activity of H₂O in these fluids. At 1 kbar pressure, mixing in the NaCl-H₂O fluids is virtually ideal, assuming a nearly complete association of NaCl, but at 2 kbars, the dissociation of NaCl is substantial. The phase relations in the system MgO-NaCl-H₂O show five univariant reactions emanating from an invariant assemblage, periclase + brucite + halite + liquid + vapor, located at 565 ± 5 °C and 440 ± 30 bars.

INTRODUCTION

Precise knowledge of the activity ($a_{\text{H}_2\text{O}}$) and the fugacity coefficient of H₂O ($\Gamma_{\text{H}_2\text{O}}$) at elevated temperatures and pressures is important for studies of reactions involving H₂O. However, experimental information is limited, especially for concentrated electrolyte solutions at high temperatures and high pressures (Helgeson 1969; Helgeson et al. 1981; Bowers and Helgeson 1983; Oelkers and Helgeson 1991). Consequently, the activity and fugacity coefficients are simplified to unity in most thermodynamic calculations. Although this approach may be satisfactory for dilute fluids, it is not valid for concentrated fluids (e.g., Helgeson et al. 1981; Bowers and Helgeson 1983; Franz 1982). Using a theoretical approach, the activity and fugacity coefficients for the more concentrated fluids may be derived if some data are available. For example, Anderko and Pitzer (1993), using existing experimental data, obtained an equation of state for the system NaCl-H₂O, from which internally consistent values of $a_{\text{H}_2\text{O}}$ and $\Gamma_{\text{H}_2\text{O}}$ can be obtained for concentrated solutions. However, recent experimental results for this system (Aranovich and Newton 1996) indicate that the activity-composition relations may be much simpler than considered in previous models. Because no experimental data are available for many systems, further development of experimental methods to obtain information on the temperature-pressure-compositional (*PTX*) relations of aqueous systems remains essential.

In aqueous fluids, $a_{\text{H}_2\text{O}}$ and $\Gamma_{\text{H}_2\text{O}}$ may be determined experimentally at various *P-T* conditions by studying a univariant reaction in which H₂O is a participating component, by comparing the *P-T* conditions of this reaction

in the presence of these fluids with the *P-T* conditions of the same reaction in the presence of pure H₂O. For example, Barnes and Ernst (1963), using the dehydroxylation reaction of brucite, determined the activity of H₂O in an H₂O-NaOH fluid. Likewise, Aranovich and Newton (1996) used the brucite dehydration reaction to determine $a_{\text{H}_2\text{O}}$ of relatively concentrated NaCl-H₂O fluids at high temperatures and pressures to 15 kbars. More recently, $\Gamma_{\text{H}_2\text{O}}$ in CaCl₂-H₂O fluids at elevated temperatures and pressures was obtained from a high-pressure differential thermal analysis (HP-DTA) of the dehydration of a Ca-exchanged montmorillonite in the presence of different CaCl₂-H₂O fluids (Wang et al. 1996). In the study presented here, we evaluate $a_{\text{H}_2\text{O}}$ and $\Gamma_{\text{H}_2\text{O}}$ in NaCl-H₂O fluids at pressures to 2500 bars using HP-DTA of the dehydroxylation reaction of brucite in the presence of these fluids. As in the work of Aranovich and Newton (1996), we selected the brucite dehydroxylation reaction because the solubility of MgO and Mg(OH)₂ in these fluids is very small (Walther 1986; Grabman and Popp 1991) and because the *P-T* conditions of this reaction are reasonably well established. Nevertheless, because we use this reaction as a baseline in this DTA study, it was necessary to assess the *P-T* relations of the brucite dehydroxylation at similar conditions.

PREVIOUS WORK

The reaction $\text{Mg}(\text{OH})_2 \leftrightarrow \text{MgO} + \text{H}_2\text{O}$ has been investigated extensively, using quench methods (Kennedy 1956; Roy and Roy, 1957; Fyfe 1958; Fyfe and Godwin 1962; Meyer and Yang 1962; Barnes and Ernst 1963; Aranovich and Newton 1996) and DTA techniques (We-

ber and Roy 1965; Kanzaki 1991; Johnson and Walker 1993). A summary of work at pressures below 2 kbars was given by Weber and Roy (1965) and for higher pressures by Schramke et al. (1982) and Johnson and Walker (1993).

The temperature found for the dehydroxylation of brucite by DTA may show significant variation depending on the nature and treatment of the sample and experimental method (Weber and Roy 1965). However, both the quench and DTA methods yielded comparable results. For example, at 2 kbars, the dehydroxylation temperature was found between about 660 °C (Barnes and Ernst 1963; Aranovich and Newton 1996) and 670 °C (Roy and Roy 1957; Franz 1982), whereas in the DTA study by Weber and Roy (1965) the onset temperature of the dehydroxylation peak, averaged for three different brucites and extrapolated to 2 kbars, was 655 °C. The onset temperature in the present study, as well as that of Weber and Roy, is defined as the temperature at which the DTA baseline intersects the extrapolated slope of the DTA peak. The agreement at lower pressures between the quench method (Barnes and Ernst 1963) and the DTA onset temperatures (Weber and Roy 1965) is equally good. It should be noted that the DTA peak temperatures were 20–100 °C higher than the onset temperatures.

Franz (1982) studied the brucite-periclase equilibrium experimentally at a total pressure of 2 kbars with different NaCl-H₂O fluids, using a quench technique. At 2 kbars and between 590 °C and 670 °C, $a_{\text{H}_2\text{O}}$ is between 0.611 and 1.00 for fluids ranging between 63 and 100 mol% H₂O. He concluded that mixing of H₂O and NaCl at these conditions is nearly ideal. Similarly, Joyce and Holloway (1993) determined $a_{\text{H}_2\text{O}}$ in NaCl-H₂O fluids using an H₂O fugacity buffer technique. It showed small positive deviations from ideality at 2 kbars and 850 °C. For dilute NaCl-H₂O fluids, Bowers and Helgeson (1983) showed that $\Gamma_{\text{H}_2\text{O}}$ increased with temperature, but decreased with increasing pressure. Aranovich and Newton (1996), using quench methods, concluded that the NaCl-H₂O solutions behave as nearly ideal mixtures of ions and molecules, with NaCl being undissociated at 2 kbars but nearly completely ionized at 10 kbars.

EXPERIMENTAL METHOD

The HP-DTA system (Koster van Groos 1979) consists of a copper cell, which accommodates three gold capsules that are made by extrusion. The capsules weigh ~130 mg and have a length of ~7 mm, a diameter of 3.2 mm, and a wall thickness of 0.07 mm. A Pt-Pt₉₀Rh₁₀ thermocouple makes thermal contact in a re-entry well at the bottom of each capsule. The DTA cell-thermocouple assemblage was made to fit in an internally heated pressure vessel similar to the one described by Holloway (1971). Argon was the pressure medium. Two of the capsules contain a sample and the third an Al₂O₃ reference with 20 wt% quartz added. The presence of quartz allows the use of the low-high quartz transition as an internal temperature standard (Koster van Groos and ter Heege 1973). The

experiments are conducted using either open or sealed sample capsules (closed vs. open experiments, respectively). The uniformity of the capsule and system geometry facilitates comparisons between the DTA signals from different experiments.

The DTA signals were recorded on the 50 μV range of a Kipp recorder, resolving temperature differences to 0.05 °C. Temperatures were determined by the reference capsule thermocouple and corrected using the differential temperature; they are believed accurate to within 1 °C. Pressures were measured using calibrated Bourdon-type Heise gauges with a 70 bars and a 3000 bars range, which are accurate to within 0.5%. The heating rate was maintained at 20 °C/min, using a Honeywell programmable controller.

The experiments were made with a natural, well-crystallized, and transparent brucite from Wakefield, Quebec, similar to the material used by Weber and Roy (1965) and Franz (1982), and with a synthetic brucite. The natural brucite was ground carefully to 200–300 mesh in an agate mortar. The synthetic brucite was obtained by reacting decarbonated MgCO₃ with H₂O steam at 60 °C after which it was dried at 110 °C. The purity of both brucites was confirmed by standard X-ray diffraction analysis and microscopy. In the experiments with NaCl, only synthetic brucite was used. It was mixed with 0.0, 5.5, 17.0, 28.8, 34.5, 41.7, 58.2, and 66.6 wt% dry NaCl powder. The compositions are accurate to within 0.02 wt%. All starting compositions were stored under vacuum.

In the experiments, the starting materials were either dry brucite or dry halite-brucite mixtures. Using dry starting mixtures instead of brucite-halite mixtures in the presence of NaCl-H₂O solutions ensures that the fluid composition is nearly uniform throughout the brucite dehydroxylation. Furthermore, the use of dry mixture ensured that compositional differences between the experiments are minimal. In addition, sealing the thin-walled capsules is greatly simplified in the absence of a substantial quantity of liquid. Assuming that all NaCl dissolves in the H₂O fluid generated by the complete dehydroxylation of brucite, the NaCl content of the fluid in these samples is 0, 2, 6, 11, 14, 18, 30, and 38 mol%. It should be noted that the dissolution rate of halite in the aqueous fluid is a continuous process and, therefore, it does not generate a DTA peak (Koster van Groos 1991).

The amount of sample depended upon whether open or closed capsules were used. At pressures <150 bars, the experiments must be made in open capsules because the molar volume of H₂O released during heating is sufficiently large to cause failure of sealed capsules. In these capsules, the dehydroxylation reaction produced broad peaks, and a 10–20 mg sample was required. In closed experiments, at pressures >150 bars, the dehydroxylation peak was much sharper, and a 5 mg sample was sufficient (Fig. 1). In our study, both the onset and the peak temperatures were reproducible to within 5 °C. In the experiments with the brucite-NaCl mixtures, the DTA peak is

TABLE 1. HP-DTA for pure brucite

| Onset | | First peak | | Second/single peak | |
|----------|--------|------------|--------|--------------------|--------|
| P (bars) | T (°C) | P (bars) | T (°C) | P (bars) | T (°C) |
| 1 | 400 | 1 | 430 | 1 | 480 |
| 1 | 395 | 1 | 429 | 1 | 488 |
| 1 | 390 | 1 | 431 | 1 | 495 |
| 1 | 383 | 1 | 422 | 1 | 489 |
| 1 | 386 | 1 | 423 | 1 | 479 |
| 15 | 442 | 15 | 481 | 15 | 521 |
| 29 | 466 | 29 | 493 | 29 | 530 |
| 32 | 455 | — | — | 33 | 538 |
| 241* | 546 | 241 | 556 | 248 | 602 |
| 255 | 546 | — | — | 261 | 580 |
| 261 | 540 | — | — | 270 | 600 |
| 407* | 569 | 409 | 591 | 412 | 627 |
| 415 | 580 | — | — | 421 | 608 |
| 452 | 597 | — | — | 455 | 611 |
| 452 | 594 | — | — | 455 | 608 |
| 710 | 595 | — | — | 715 | 631 |
| 724 | 605 | — | — | 730 | 635 |
| 875* | 602 | 880 | 628 | 883 | 666 |
| 1301* | 632 | — | — | 1310 | 652 |
| 1712* | 646 | — | — | 1717 | 684 |
| 1984* | 661 | — | — | 1993 | 691 |
| 2163* | 660 | — | — | 2172 | 700 |
| 2445* | 674 | — | — | 2455 | 708 |

* Rehydrated brucite.

TABLE 2. HP-DTA for brucite-NaCl mixtures

| NaCl (mol%) | First peak | | Second/single peak | |
|-------------|------------|--------|--------------------|--------|
| | P (bars) | T (°C) | P (bars) | T (°C) |
| 2.0 | 363 | 569 | 366 | 616 |
| 2.0 | 417 | 590 | 419 | 611 |
| 2.0 | 491 | 597 | 494 | 619 |
| 2.0 | 588 | 608 | 590 | 632 |
| 2.0 | 697 | 616 | 703 | 642 |
| 6.0 | 341 | 576 | 348 | 617 |
| 6.0 | — | — | 483 | 603 |
| 6.0 | — | — | 571 | 615 |
| 6.0 | — | — | 630 | 620 |
| 6.0 | — | — | 697 | 623 |
| 6.0 | — | — | 809 | 631 |
| 6.0 | — | — | 910 | 635 |
| 6.0 | — | — | 1017 | 640 |
| 6.0 | — | — | 1155 | 643 |
| 6.0 | — | — | 1331 | 646 |
| 6.0 | — | — | 1514 | 651 |
| 6.0 | — | — | 2190 | 644 |
| 6.0 | — | — | 2326 | 661 |
| 11.0 | 341 | 575 | 348 | 615 |
| 11.0 | — | — | 483 | 601 |
| 11.0 | — | — | 571 | 609 |
| 11.0 | — | — | 630 | 615 |
| 11.0 | — | — | 697 | 620 |
| 11.0 | — | — | 809 | 627 |
| 11.0 | — | — | 910 | 633 |
| 11.0 | — | — | 1017 | 637 |
| 11.0 | — | — | 1155 | 641 |
| 11.0 | — | — | 1331 | 644 |
| 11.0 | — | — | 1614 | 650 |
| 11.0 | — | — | 2420 | 660 |
| 14.0 | — | — | 394 | 588 |
| 14.0 | — | — | 454 | 596 |
| 14.0 | — | — | 526 | 599 |
| 14.0 | — | — | 627 | 612 |
| 14.0 | — | — | 758 | 621 |
| 18.0 | 345 | 576 | 352 | 613 |
| 18.0 | — | — | 395 | 599 |
| 18.0 | — | — | 448 | 597 |
| 18.0 | — | — | 454 | 599 |
| 18.0 | — | — | 527 | 604 |
| 18.0 | — | — | 619 | 615 |
| 18.0 | — | — | 628 | 615 |
| 18.0 | — | — | 760 | 627 |
| 18.0 | — | — | 788 | 624 |
| 18.0 | — | — | 1194 | 632 |
| 18.0 | — | — | 1779 | 641 |
| 18.0 | — | — | 2290 | 648 |
| 18.0 | — | — | 2455 | 650 |
| 30.0 | 283 | 568 | 288 | 604 |
| 30.0 | 328 | 574 | 332 | 615 |
| 30.0 | — | — | 462 | 597 |
| 30.0 | — | — | 523 | 599 |
| 30.0 | — | — | 628 | 603 |
| 30.0 | — | — | 834 | 612 |
| 30.0 | — | — | 1703 | 618 |
| 30.0 | — | — | 1834 | 628 |
| 38.0 | 345 | 580 | 352 | 614 |
| 38.0 | — | — | 446 | 587 |
| 38.0 | — | — | 611 | 587 |
| 38.0 | — | — | 779 | 588 |
| 38.0 | — | — | 1179 | 594 |
| 38.0 | — | — | 1745 | 604 |
| 38.0 | — | — | 2248 | 610 |
| 38.0 | — | — | 2428 | 613 |

highly asymmetric, with a poorly defined onset, a broad slope toward the peak, and a sharp return to the baseline. This shape is consistent with the assumption that the initial high concentration of NaCl in the fluid decreases continuously during the dehydroxylation. As the reaction progresses, the rate of change in the NaCl concentration in the fluid decreases and, therefore, the rate of change in the dehydroxylation temperature decreases as well, resulting in a DTA peak. It is likely, however, that at the peak temperature the brucite is not yet fully dehydrated, and that the NaCl concentration of the fluid is higher than the nominal NaCl concentration based on the NaCl and H₂O content of the experiment.

Capsules were weighed before and after each experiment to check for leaks. If an experiment lost weight, it was considered an open experiment. After the experiments, the experimental material was inspected routinely by optical microscopy and X-ray diffraction. In the experiments with natural brucite, several capsules could be used again, because the periclase produced during the heating cycle reacted with the fluid during the quench, forming brucite. However, after a few cycles, these capsules began to fail.

RESULTS AND DISCUSSION

In total, 23 experiments were made with natural brucite, 8 of which were with rehydrated material (Table 1), and 64 experiments were made with synthetic brucite-NaCl mixtures (Table 2). For the experiments with natural brucite, both the onset and the peak temperatures are listed. For the experiments with the brucite-NaCl mixtures only the peak temperatures are given, because the onset temperatures in these experiments are neither well defined nor relevant, as discussed above.

Intermediate phase(s)

At pressures below 30 bars, a small peak or a slight break in slope is present on the low-temperature shoulder of the dehydroxylation peak of the natural brucite (first peak, Tables 1 and 2; Fig. 1), similar to a peak found by

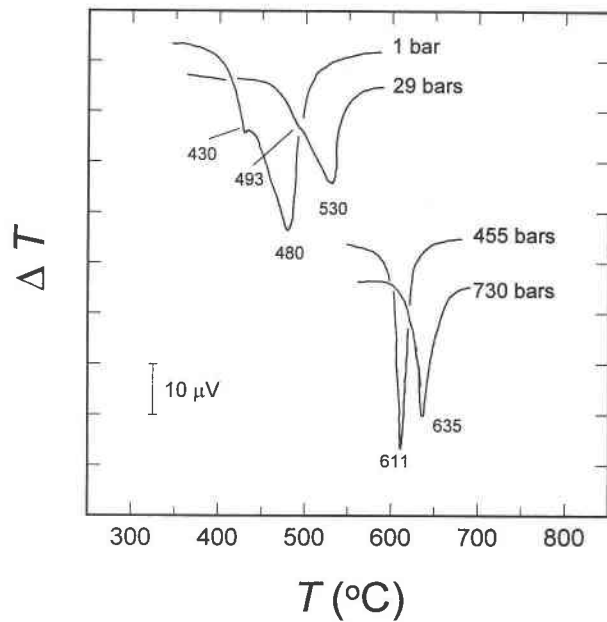


FIGURE 1. Selected HP-DTA patterns with brucite in open experiments (top two) and in closed experiments (bottom two).

Weber and Roy (1965). Both peaks are also present in several experiments with rehydrated natural brucite and brucite-NaCl mixtures at pressures to 900 bars (Tables 1 and 2). They are shown in Figure 2 by the symbols connected with a thin horizontal dashed line. The P - T slope of both the first and the second peak are nearly parallel to each other (Fig. 2), suggesting that both reactions involve release of H_2O .

Ball and Taylor (1961), in an X-ray diffraction study, suggested that the dehydroxylation of brucite involves two additional phases, $Mg_3O_4H_2$ with a spinel-like structure and a periclase-like material with a larger unit cell. They proposed that the spinel-like intermediate phase resulted from cation migration during the dehydroxylation process. Martens et al. (1976), studied the dehydroxylation of brucite under vacuum conditions and found that the release of H_2O involves two events, at 325 and 450 °C, respectively. They suggested that the initial loss of H_2O generates numerous defects, such as residual $(OH)^-$ groups and cation vacancies, and gives rise to weak "superstructure" lines in the X-ray data. They found that this intermediate phase can persist in experiments with up to 90% dehydroxylation of the sample before it recrystallizes to cubic MgO . These additional phases are not related to a recently observed phase transition in brucite at very high pressures (Duffy et al. 1995). Although we do not have any information on the stability, structure, or composition of the intermediate phase(s), it is likely that these phases are products of metastable reactions. Because we are interested in the stable brucite-periclase reaction in the presence of NaCl brines, we did not consider these phases or their dehydroxylation reactions any further.

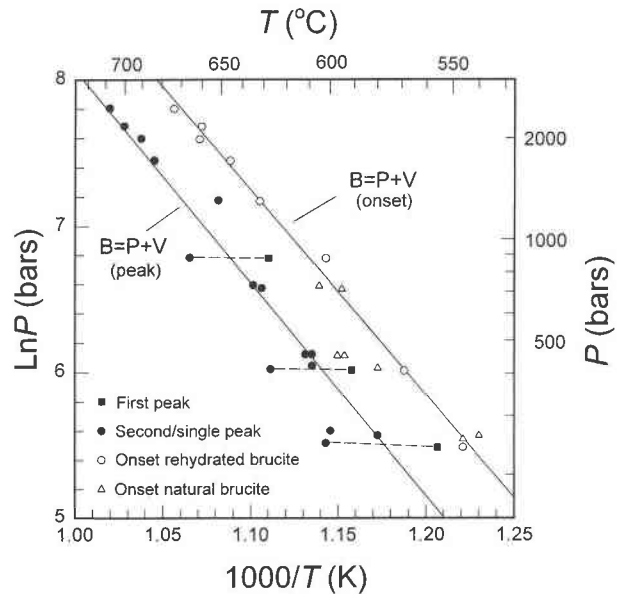


FIGURE 2. $\ln P$ vs. $1000/T$ projection of the dehydroxylation of brucite. The symbols connected by a dashed line indicates the first and second peak from the same experiment.

Dehydroxylation of brucite

The onset and peak temperatures of the DTA peak for the dehydroxylation of natural brucite and rehydrated brucite at pressures to 2500 bars are listed in Table 1. The onset temperature of the natural brucite at 1 atmosphere ($383\text{--}400$ °C), is somewhat higher than the temperature of 375 ± 5 °C given by Weber and Roy (1965) for the same brucite. The peak temperature is ~ 486 °C, which is significantly higher than the peak temperature of 440 ± 5 °C found by Weber and Roy (1965). Similar temperature differences were attributed by Weber and Roy (1965) to differences in grain size and degree of strain in the sample. Because the dehydroxylation temperatures depends directly on the fugacity of H_2O (f_{H_2O}) at the dehydroxylation site within the crystal (e.g., Koster van Groos and Guggenheim 1987), we attribute these discrepancies to a substantial increase of the internal f_{H_2O} of the natural brucite during heating because of the low diffusivity of H_2O in these crystals. Differences in grain size, therefore, may result in different peak temperatures.

The P - T relations of the onset and peak temperatures at 150–2500 bars are shown on a $\ln P - 1000/T(K)$ diagram in Figure 2. Open capsule data ($P < 150$ bars) were not used because of the uncertainty in f_{H_2O} . The P - T relation of the onset temperature of the dehydroxylation of unstrained, rehydrated brucite follows $\ln P = 22.66 - 14015/T(K)$. This relation agrees well with previous work. For example, at 240 bars, the onset of the dehydroxylation reaction is at 543 ± 5 °C, compared to 549 ± 5 °C in the quench study of Barnes and Ernst (1963) and ~ 541 °C in the DTA study of Weber and Roy (1965). Similarly, at 2 kbars the onset of the dehydroxylation is at 658 ± 5 °C, which is in excellent agreement with the

onset temperature of 657 °C in the HP-DTA study of Weber and Roy (1965) and the reaction temperatures of 660 ± 5 °C, 669 ± 5 °C, and 663 ± 5 °C in the quench studies of Barnes and Ernst (1963), Franz (1982), and Aranovich and Newton (1996), respectively. These results show that in HP-DTA, the dehydroxylation temperature of brucite is represented by the onset of the DTA peak. We conclude that the dehydroxylation temperature of brucite between ~ 0.25 and 15 kbars, as determined both by equilibrium and dynamic methods, is now known with sufficient precision to allow its use in the experimental investigation of aqueous salt systems.

Brucite dehydroxylation in the presence of NaCl-H₂O fluids

The P - T relations for the dehydroxylation of brucite in the presence of NaCl are shown in a $\ln P$ -1000/ T diagram in Figure 3. As was mentioned above, the temperatures represent DTA peak temperatures. The results define four specific sets of P - T conditions for the dehydroxylation reaction. At low pressures (<400 bars), all experiments have a multiple dehydroxylation peak. At these conditions, no dependency on the NaCl content was seen. At higher pressures, the P - T relations are complex. Above ~ 400 bars and over a limited P - T range depending on the NaCl contents, the P - T conditions of the dehydroxylation reactions are very similar and define line 1. The slope of this line is nearly parallel to the slope of the dehydroxylation reaction of brucite in the absence of NaCl. This indicates that $a_{\text{H}_2\text{O}}$ at these conditions is nearly constant and that the system is univariant. Therefore, in addition to brucite, periclase, and the fluid, either halite or a second fluid must be present. Note that in the experiments with $X_{\text{NaCl}} = 0.02$, the first and second peak straddle line 1, with the first peak lying very near this line. With increasing P - T and at a pressure and temperature that is specific for each composition studies, the P - T slope of the dehydroxylation reaction changes abruptly and becomes significantly steeper. For example, at ~ 850 bars and 642 °C, the slope of the dehydroxylation reaction of brucite with $X_{\text{NaCl}} = 0.11$ changes abruptly. The P - T relations of these reactions define region A. In this region, the P - T slope of the dehydroxylation reaction decreases monotonically with increasing NaCl content. This indicates that the dehydroxylation reaction in region (A) occurs under divariant conditions, with brucite, periclase, and a fluid with variable NaCl content present. In the experiments with the highest NaCl content ($X_{\text{NaCl}} = 0.38$), the slope of the reaction becomes nearly pressure independent between about 1000 and 400 bars. These conditions define line 2. As is evident from Figure 3, the slope of the dehydroxylation reaction for compositions with slightly higher or lower NaCl contents must intersect this line as well, requiring that the system along line 2 be univariant. The nearly constant dehydroxylation temperature indicates that here $f_{\text{H}_2\text{O}}$ is virtually independent of pressure, suggesting that no vapor phase is present and

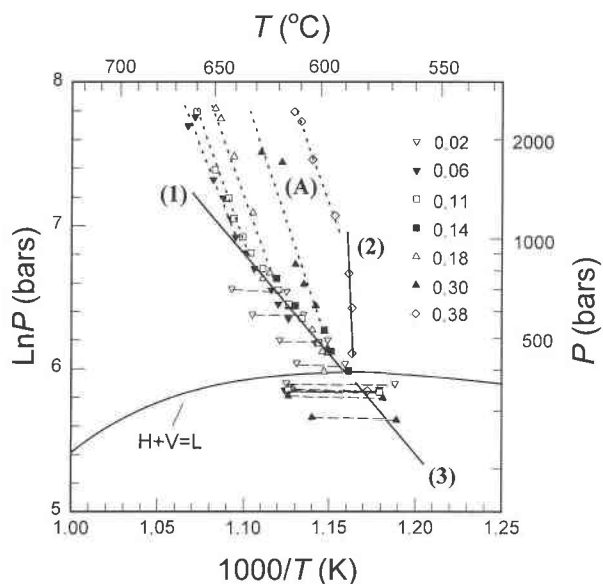


FIGURE 3. $\ln P$ vs. $1000/T$ projection of the dehydroxylation of brucite in the presence of NaCl-H₂O brines (see text for explanation). The symbols connected by a horizontal dashed line indicate the first and second peak from the same experiment.

that the phases along line 2 are brucite, periclase, a liquid phase, and halite.

The different P - T regimes in this part of the system MgO-NaCl-H₂O are related to the phase relations in the system NaCl-H₂O. The stable phases are: brucite (B), periclase (P), halite (H), liquid (L), and aqueous fluid (V). At the onset of the experiment, brucite and halite are present in the capsule. During heating, at some temperature, brucite begins to dehydroxylate. The extent of dehydroxylation is determined by the pore volume in the capsule. If this volume is negligible, the degree of dehydroxylation would be negligible, but if the pore volume is appreciable, as is likely in our experiments, significant dehydroxylation occurs, with halite continuously dissolving in the evolving fluid until the pore pressure reaches P_{vessel} .

At P - T conditions below the solubility curve $H + V = L$ (Fig. 3) in the system NaCl-H₂O (Sourirajan and Kennedy 1962), the assemblage $H + V$ is stable and the dehydroxylation of brucite must follow the univariant reaction $B + H = P + V$. Because the NaCl content of the vapor phase is low, all our experiments with NaCl contained these four phases. Therefore, all experiments at pressures <400 bars must show this reaction. Furthermore, $a_{\text{H}_2\text{O}}$ must be nearly constant along this univariant reaction, and the slope of the reaction should be subparallel to the dehydroxylation reaction of brucite in the presence of pure H₂O. Since $a_{\text{H}_2\text{O}}$ is slightly reduced in these experiments because of the NaCl content of the aqueous vapor, the dehydroxylation temperatures should be slightly reduced as well. Based on these considerations and on the DTA peak temperatures of the low-pressure experiments, this reaction is shown as line 3. It is located

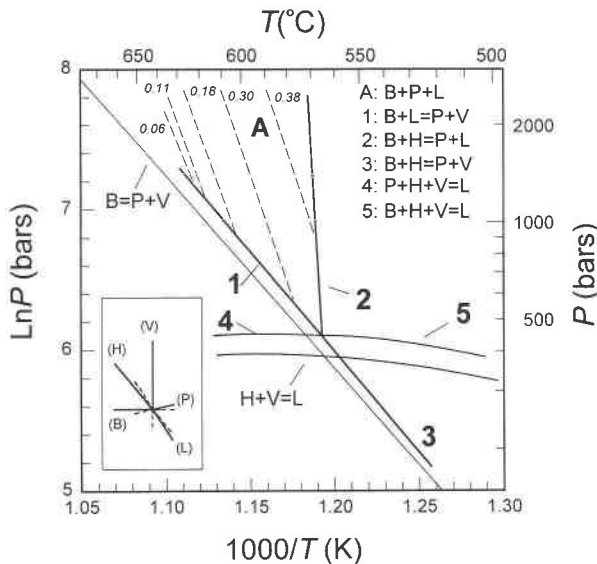


FIGURE 4. The four regimes of brucite dehydroxylation (see text for explanation). The insert shows the phase relations around the invariant point.

~10 °C below the peak temperatures of the dehydroxylation reaction of brucite in the presence of pure H₂O.

At P - T conditions above the solubility curve $H + V = L$, the reactions depend on the NaCl content. At high NaCl contents, the assemblage $H + L$ is stable and dehydroxylation proceeds according to the univariant reaction $B + H = P + L$. This reaction is encountered in the experiments with $X_{\text{NaCl}} = 0.38$ over a range of pressures (see line 2). With increasing temperature, further dehydroxylation produces more H₂O, which enters the liquid phase, and halite continues to dissolve. If all halite is consumed, the phase assemblage contains only $B + P + L$, and further dehydroxylation occurs under divariant conditions in field A. With $X_{\text{NaCl}} = 0.38$, all halite was consumed at ~950 bars and 590 ± 5 °C. In the system NaCl-H₂O at the same pressure, a liquid with this composition is in equilibrium with halite at 570 ± 5 °C (Koster van Groos 1991). This suggests that the peak temperatures of the brucite dehydroxylation in the presence of NaCl are ~20 °C too high. This is consistent with the difference between the onset and peak temperatures in the dehydroxylation of pure brucite. At moderately low NaCl contents and at pressures above the solubility curve, the assemblage $L + V$ is present in the system NaCl-H₂O. Brucite dehydroxylation under these conditions must follow the univariant reaction, $B + L = P + V$, represented by line 1. In this reaction, the NaCl content of the vapor is low (e.g., Sourirajan and Kennedy 1962; Bodnar et al. 1985), similar to the vapor phase in the $H + V$ field. The compositions of the coexisting liquids and vapors in this system are likely to be similar to the compositions of liquid and vapor phase in the system NaCl-H₂O at the same P - T conditions, because of the low solubility of the Mg-compounds. The intersections of the

TABLE 3. P - T relationship of brucite dehydroxylation in the presence of NaCl-H₂O liquid

| mol% NaCl | P - T relationship | Equation |
|-----------|---------------------------|----------|
| 0.0 | $\ln P = 22.23 - 13620/T$ | (1) |
| 6.0 | $\ln P = 40.02 - 29400/T$ | (2) |
| 11.0 | $\ln P = 43.92 - 32790/T$ | (3) |
| 18.0 | $\ln P = 45.05 - 33480/T$ | (4) |
| 30.0 | $\ln P = 47.70 - 35170/T$ | (5) |
| 38.0 | $\ln P = 50.16 - 36470/T$ | (6) |

Note: Pressures are in bars, temperatures are in degrees K.

univariant reaction $B + L = P + V$ (line 1) with the divariant curves ($B + P + L$) in field A for the fluids with $X_{\text{NaCl}} = 0.06, 0.11, 0.18,$ and 0.30 are ~975, 900, 720, and 450 bars, and ~640, 633, 622, and 597 °C, respectively. These temperatures are estimated to be ~25 °C too high, as was seen above. When these points are corrected for this temperature difference, they are very close to the liquid field boundary of the $L + V$ field in the system NaCl-H₂O (Bowers and Helgeson 1983).

These three univariant reactions as well as the divariant reactions and the halite solubility curve are shown in Figure 4. They define an invariant point, $B + P + H + L + V$, located at a corrected temperature of 565 ± 5 °C and at 440 ± 30 bars. Two additional univariant reactions, (5) $B + H + V = L$ and (4) $P + H + V = L$, are required to complete a Schreinemaker's bundle of univariant reactions (Fig. 4).

The relations between $\ln P$ and $1000/T$ for the dehydroxylation of brucite in the presence of these NaCl-H₂O fluids (dashed lines in Figure 3) are listed in Table 3. The dehydroxylation of brucite depends on $f_{\text{H}_2\text{O}}$ in these NaCl-H₂O fluids. Assuming that $f_{\text{H}_2\text{O}}$ in these fluids is the same as $f_{\text{H}_2\text{O}}$ during dehydroxylation of brucite in the presence of pure H₂O at the same temperature, $f_{\text{H}_2\text{O}}$ in these NaCl-H₂O fluids can be evaluated from the relations shown in Table 3. Thus, the activity ($a_{\text{H}_2\text{O}} = f_{\text{H}_2\text{O}}/f^{\circ}_{\text{H}_2\text{O}}$, in which $f^{\circ}_{\text{H}_2\text{O}}$ is the fugacity of pure H₂O at a fixed temperature and pressure, Burnham et al. 1969) and the fugacity coefficient of H₂O ($\Gamma_{\text{H}_2\text{O}} = f_{\text{H}_2\text{O}}/P_{\text{fluid}} \cdot X_{\text{H}_2\text{O}}$) in the NaCl fluids were calculated and presented in Table 4. For example, at 1 kbar,

TABLE 4. Activities and fugacity coefficients of H₂O in the NaCl-H₂O fluids at 1000 and 2000 bars

| P_{fluid} | $X_{\text{H}_2\text{O}}$ | T (°C) | $f^{\circ}_{\text{H}_2\text{O}}$ | $f_{\text{H}_2\text{O}}$ | $a_{\text{H}_2\text{O}}$ | $\Gamma_{\text{H}_2\text{O}}^*$ |
|--------------------|--------------------------|----------|----------------------------------|--------------------------|--------------------------|---------------------------------|
| 1000 | 0.62 | 570 | 583 | 358 | 0.61 | 0.58 (0.58) |
| 1000 | 0.70 | 589 | 613 | 450 | 0.73 | 0.64 (0.61) |
| 1000 | 0.82 | 605 | 638 | 564 | 0.88 | 0.69 (0.64) |
| 1000 | 0.89 | 613 | 649 | 629 | 0.97 | 0.71 (0.65) |
| 1000 | 0.94 | 615 | 653 | 648 | 0.99 | 0.69 (0.65) |
| 2000 | 0.62 | 584 | 996 | 420 | 0.42 | 0.34 (0.59) |
| 2000 | 0.70 | 604 | 1059 | 559 | 0.53 | 0.40 (0.53) |
| 2000 | 0.82 | 621 | 1112 | 702 | 0.63 | 0.43 (0.56) |
| 2000 | 0.89 | 630 | 1139 | 799 | 0.70 | 0.45 (0.57) |
| 2000 | 0.94 | 634 | 1152 | 848 | 0.73 | 0.45 (0.58) |

Note: Fugacities are bars.

* The numbers in the parentheses are the fugacity coefficients of pure H₂O at the P - T conditions of the experiments.

brucite in the presence of a fluid with $X_{\text{NaCl}} = 0.3$ dehydroxylates at 589 °C (Eq. 5), with $P_{\text{H}_2\text{O}} = 478$ bars (Eq. 1). At 589 °C and 1 kbar, $f_{\text{H}_2\text{O}}^\circ = 613$ bars, while at 478 bars, $f_{\text{H}_2\text{O}}^\circ = 450$ bars (Burnham et al. 1969), producing $a_{\text{H}_2\text{O}} = 0.73$ and $\Gamma_{\text{H}_2\text{O}} = 0.64$.

At 1 kbar, $a_{\text{H}_2\text{O}}$ of the NaCl-H₂O fluids is slightly higher than $X_{\text{H}_2\text{O}}$ at the same P - T conditions (Table 4). Because this difference is within the experimental uncertainty, it suggests that mixing in these fluids, assuming NaCl is completely associated, is nearly ideal. At 2 kbars, however, $a_{\text{H}_2\text{O}}$ of the fluids drops substantially below $X_{\text{H}_2\text{O}}$. Experimentally, this decrease reflects the difference between the slope of the divariant dehydroxylation reactions and the slope of the brucite dehydroxylation reaction $B = P + V$ (Fig. 2) because, with a constant $a_{\text{H}_2\text{O}}$, the dehydroxylation reaction with constant X_{NaCl} should be nearly parallel to $B = P + V$. Aranovich and Newton (1996) report that up to 2 kbars NaCl is undissociated but that between 2 and 10 kbars it becomes fully dissociated. Franz (1982) and Joyce and Holloway (1993) reached a similar conclusion. Oelkers and Helgeson (1988) calculated the dissociation constant for NaCl in aqueous fluids from conductivity measurements of dilute NaCl solutions. Their results indicate that at the P - T range of our study, the dissociation of NaCl is <1%. However, in a follow-up study (Oelkers and Helgeson 1991), they found that in concentrated solutions at supercritical temperatures and pressures NaCl is strongly dissociated. Our data, which represent a relatively direct method of measurement, are in substantial agreement with the more recent study by Oelkers and Helgeson, but disagree with the results of Franz (1982), Joyce and Holloway (1993), and Aranovich and Newton (1996). Considering the geologic importance of obtaining a clear understanding of the properties of NaCl-rich brines, it is evident that further experimental work is necessary.

ACKNOWLEDGMENTS

This research was supported by the National Science Foundation (grant EAR-8816898) and the Petroleum Research Fund of the American Chemical Society (grant 20016-AC2). We thank Leonya Aranovich and David Jenkins for their reviews. Comments on an earlier version of the manuscript by David Joyce and Kenneth Pitzer greatly improved this paper.

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MANUSCRIPT RECEIVED JULY 5, 1996

MANUSCRIPT ACCEPTED NOVEMBER 14, 1997