

Experimental determination of the brucite = periclase + water equilibrium with a new volumetric technique

JANET A. SCHRAMKE, DERRILL M. KERRICK AND JAMES G. BLENCOE

Department of Geosciences
The Pennsylvania State University
University Park, Pennsylvania 16802

Abstract

A new experimental method has been developed for the investigation of kinetically-rapid devolatilization reactions at pressures up to approximately 8 kbar. Using a volumeter system within an internally-heated pressure vessel, these reactions can be detected by monitoring volume changes of encapsulated samples. Thus, for example, devolatilization increases the volume of an experimental sample, and this increase can be measured electronically. An important advantage of our procedure is that reactions are monitored *during* experimentation, thereby avoiding quench problems that can occur with conventional hydrothermal techniques.

We have employed our volumetric method to obtain the following equilibrium brackets for the reaction brucite \rightleftharpoons periclase + water: 690–725°C at 4.0 kbar, 720–745°C at 5.1 kbar, 740–765°C at 6.1 kbar, and 785–806°C at 8.1 kbar. These results compare favorably with those of recent studies, and they are also in accord with an equilibrium pressure-temperature curve derived from thermochemical data.

Notation

- $f_{\text{H}_2\text{O}}$ = fugacity of H₂O
 ΔG_i = free energy of formation from the elements of phase *i*
 ΔG_R = free energy change of a reaction
 ΔG_R° = standard state free energy change of a reaction
 $G_{\text{H}_2\text{O}}$ = free energy of H₂O
 P = pressure
 R = gas constant
 ΔS_R = entropy change of a reaction
 ΔS_R° = standard state entropy change of a reaction
 ΔS_s° = standard state entropy change of the solids in a reaction
 σ = standard deviation
 T = temperature
 V = volume
 ΔV_s° = standard state volume change of the solids in a reaction
 X_{CO_2} = mole fraction of CO₂

Introduction

Experimental investigations of kinetically-rapid reactions are often plagued by the problem of back reaction during the quench. Quench problems are

usually countered by special quench techniques (*e.g.*, Barnes and Ernst, 1963; Wellman, 1970; Jacobs and Kerrick, 1980); however, for some reactions (*e.g.*, calcite + quartz \rightleftharpoons wollastonite + CO₂) such methods do not completely eliminate back reaction. To circumvent this difficulty, we have developed a new technique for the investigation of rapid devolatilization reactions. Employing a modified version of the internally-heated pressure vessel used for *P-V-T* studies of water by C. Wayne Burnham and co-workers (Burnham *et al.*, 1969a), forward and reverse devolatilization reactions can be monitored dynamically *during* a single experiment. Pressure, temperature, and volume are controlled and measured simultaneously, and reaction is detected from volume changes within sealed capsules. Using one set of starting materials, a series of equilibrium brackets can be obtained at pressures up to approximately 8 kbar.

The reaction brucite \rightleftharpoons periclase + water has been investigated with this volumetric technique. This reaction is important for establishing the *P-T-X*_{CO₂} conditions during metamorphism of ultramafics and siliceous dolomites. It was selected for this study because: (1) previous investigators have observed rapid reaction rates and consequent quench problems, and (2) experimental data have been

obtained for the reaction over a wide range of pressure by other methods (Barnes and Ernst, 1963; Weber and Roy, 1965; Yamaoka *et al.*, 1970; Irving *et al.*, 1977); hence, the validity of the volumetric technique can be evaluated. A review and comparison of these investigations appears in a later section of this paper.

Experimental methods

Apparatus

The main component of the volumeter system was a P - V - T cell connected by capillary tubing to a stainless steel bellows (Fig. 1). A calibrated screw press was used to load distilled, deionized water into this assembly which (after sealing) formed a closed system containing a fixed mass of water. As the volume inside the volumeter system increased or decreased, the bellows expanded or contracted, thus causing a "sleeve" attached to the top of the bellows to slide over a smooth stainless steel sheath which partially surrounded and supported the bellows. A slide wire attached to this sleeve moved along a potentiometer wire during contraction and expansion of the bellows. The potentiometer wire, which was mounted on a fired pyrophyllite post, was oriented parallel to the long dimension of the stainless steel sheath (Fig. 1). A millivolt potentiometer indicated the position of the sleeve in terms of a percentage of the full length of the supporting sheath. The practical working range of the bellows was 7–75 percent. The stroke of the bellows over this range was approximately 5 cm.

The volumeter system was housed within an internally-heated pressure vessel (Holloway, 1971) in which argon served as the pressure medium. Pressure was generated by a two-stage Harwood pressure intensifying system, and monitored with a manganin cell calibrated against a bourdon-tube Heise gauge. Accuracy of the pressure measurements is considered to be better than $\pm 1\%$.

Experimental temperatures were achieved and maintained by a dual-zone cylindrical furnace and a solid-state temperature controller, and measured with inconel-sheathed, chromel-alumel thermocouples initially calibrated by the manufacturer. Based on extensive testing of other thermocouples of this type against reference thermocouples constructed of wire calibrated by the National Bureau of Standards, the accuracy of the sheathed thermocouples is estimated to be $\pm 5^\circ\text{C}$. Two such sheathed ther-

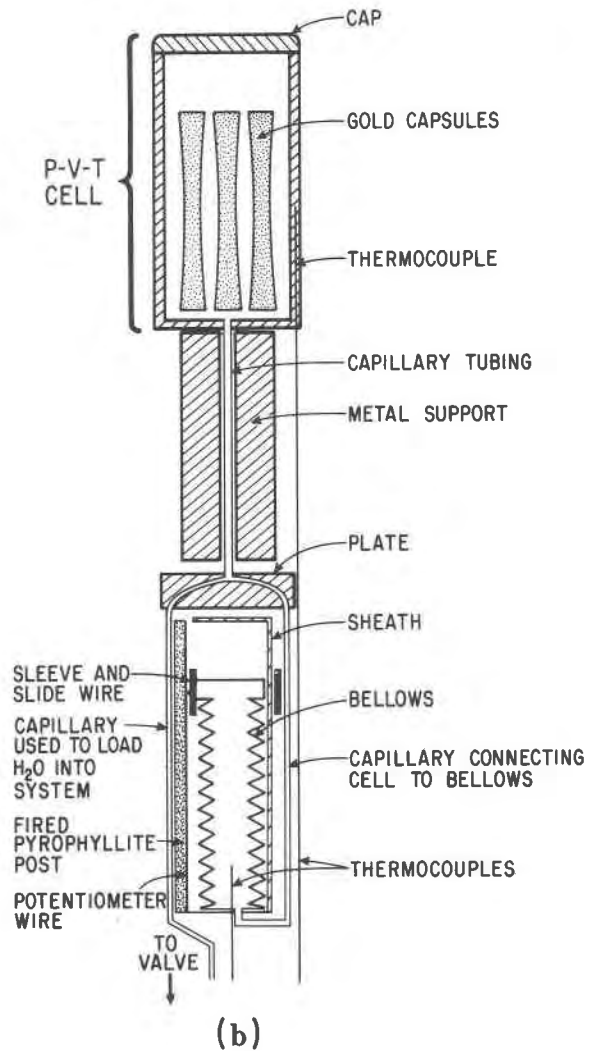


Fig. 1. Schematic diagram of the volumeter system. Only one of the two thermocouples that extended into the walls of the P - V - T cell is shown.

mocouples were placed in thermocouple wells drilled parallel to the axis of the P - V - T cell (Fig. 1). The tips of these "short" and "long" thermocouples extended 2.5 and 5.0 cm, respectively, from the base of the cell, and were separated by 120° around the circumference. The temperature gradient between these two thermocouples during experimentation was always 0.5°C or less. A third thermocouple extended approximately 1.25 cm into the bellows. This thermocouple was used to measure the water temperature inside the bellows, which was determined primarily by the temperature of tap water circulating through the copper cooling-coil jacket that surrounded the pressure vessel.

Experimental procedure

The solid starting material used in this investigation was Baker reagent grade MgO (lot #22490). This material was fired for four hours at 800°C, 1 atm to drive off adsorbed water. The X-ray diffraction pattern of the resultant fine-grained periclase is in excellent agreement with the pattern for synthetic periclase listed in ASTM file #4-829.

Six sealed, 5 mm O.D. gold capsules were used in the experiment. Each capsule had a length of 7 cm and a wall thickness of 0.015 cm, and was loaded with 0.330 ± 0.007 grams of periclase and 0.250 ± 0.005 grams of water. The capsules were placed inside the P - V - T cell (Fig. 1), and then the cap of the cell was welded into place. Next, the volumeter system was placed inside the pressure vessel, and distilled, deionized water was loaded into the system. During the experiment the temperature of the water inside the bellows slowly fluctuated between 11 and 16°C. This gradual temperature variation did not appreciably affect the volume of the water in the volumeter system, and hence had a negligible effect on the results of this study.

During the early stages of the experiment, the system remained in the brucite stability field for a period of 24 hours. It is assumed that periclase completely reacted to brucite during this time. This assumption was tested in an independent experiment by reacting relatively large (*ca.* 2 mm) cleavage fragments of periclase with water during a 5-hour run-up to 500 bars, 550°C. After quenching, it was observed that the cleavage fragments of periclase had been *completely* transformed into brucite. Therefore, at the beginning of the volumetric study where: (1) the periclase starting material was very fine-grained (\ll 400 mesh), and (2) the starting periclase + water assemblage was held in the brucite stability field for 24 hours, we believe that the periclase rapidly and completely reacted to brucite.

When the system reached P - T conditions within the periclase stability field, the dehydration of brucite liberated water; this expanded the capsules and increased the volume of the system. Upon cooling, when the system reentered the brucite stability field, periclase hydrated to form brucite, which caused contraction of the capsules and hence the bellows. During experimentation the temperature of the volumeter system was changed incrementally at time intervals of up to 42 hours, and for each

constant P - T stage the millivolt potentiometer reading was recorded at the beginning and end of the time period. Reaction was detected by noting a marked increase or decrease in the potentiometer reading during this time.

Results

During the experiment, the brucite-periclase equilibrium was bracketed at 8.1, 6.1, 5.1, and 4.0 kbar. Figure 2a illustrates the relationship between millivoltage and temperature for one up-temperature traverse and one down-temperature traverse at 6.1 kbar, and Figure 2b shows all of our results obtained at the four different pressures. The forward and reverse reactions are indicated by the sharp discontinuities in the curves. As the temperature of the system changed, both pressure and volume inside the volumeter system varied slightly in response to thermal expansion of the argon pressure medium and the water contained in the volumeter system. During time periods when temperature and pressure remained constant, and where hydration or dehydration did not occur, the volume of the contents of the volumeter system did not change.

At least two separate sets of reaction brackets were obtained at each pressure, and these near-replicate runs yielded very similar results. The zone within each bracket is the temperature range over which no observable reaction occurred during a 24 hour time period. Experimental brackets obtained in this study are listed in Table 1 and plotted in Figure 3.

Discussion

Analysis of the volumetric data

The end-points of the bracket obtained at 8.1 kbar have been extrapolated to other pressures up to 10 kbar using the interactive computer program of Slaughter *et al.* (1976). This program extrapolates an equilibrium curve from an experimentally-derived starting point P_1 - T_1 to the point P_2 - T_2 using the equation:

$$\Delta\Delta G_R = 0 = \int_{P_1}^{P_2} \Delta V_s^d dP - \int_{T_1}^{T_2} \Delta S_s^d dT + (G_{H_2O})_{T_2}^{P_2} - (G_{H_2O})_{T_1}^{P_1} \quad (1)$$

The standard state conditions in this calculation were unit activities of all phases at the pressure and

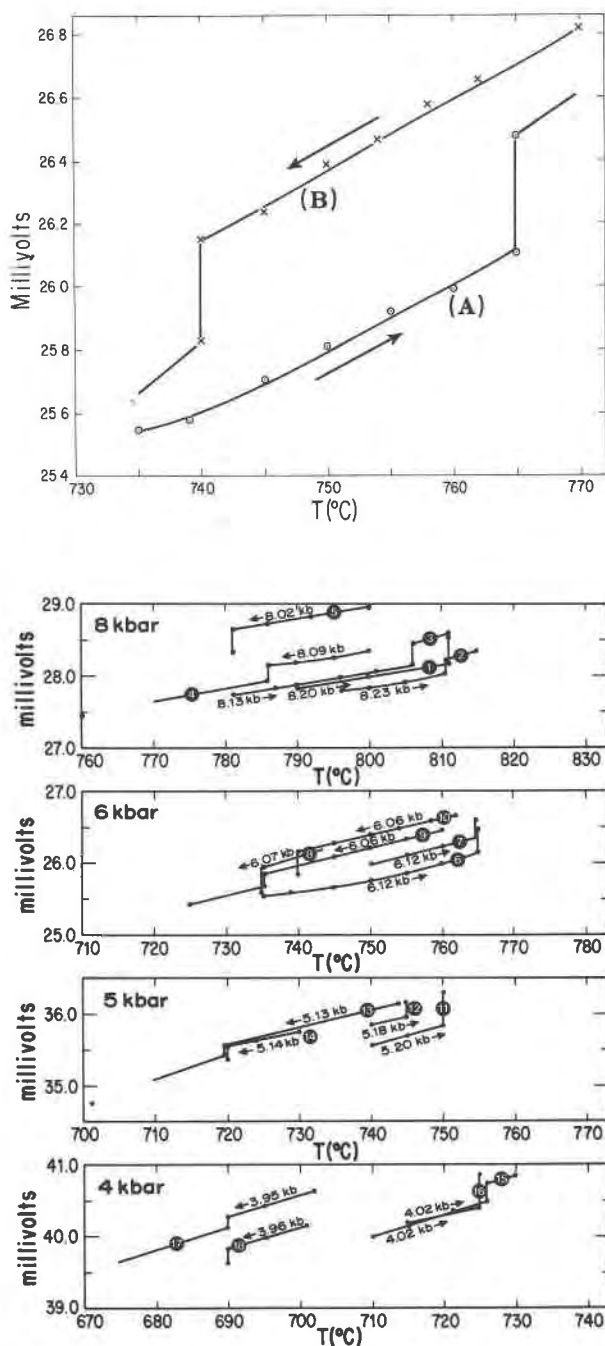


Fig. 2. (a) Illustration of the relationship between millivolt reading and temperature at 6.1 kbar for (A) an up-temperature traverse and (B) a down-temperature traverse. Crosses and circles represent temperatures at which readings were taken. (b) Experimental results of this study. Vertical axes illustrate millivolt potentiometer readings which are a function of the position of the bellows. Points on the lines indicate temperatures at which readings were taken. Numbers in circles correspond to the run numbers of Table 1.

temperature of interest. The entropies of brucite and periclase were obtained by fitting the high-temperature entropy data of Robie *et al.* (1978) to an integrated Maier-Kelley heat capacity equation. Thermodynamic properties for water were obtained from Burnham *et al.* (1969b) at pressures up to 10 kbar. Above 10 kbar the extrapolated curves were calculated by hand from equation (1), the aforementioned entropy data for brucite and periclase, and the thermodynamic properties for water from the modified Redlich-Kwong equation of Kerrick and Jacobs (1981). The extrapolation of the 8.1 kbar bracket appears as the shaded area in Figure 3, and this extrapolation shows that the brackets obtained at different pressures using the volumetric method are internally consistent. The solid line in Figure 3 represents an extrapolation from the point at 8.0 kbar and 800°C. This point was chosen because the curve so obtained provides the best agreement between our data and the results of Barnes and Ernst (1963).

The brucite-periclase equilibrium curve was also calculated from thermodynamic data (Burnham *et al.*, 1969b; Robie *et al.*, 1978; Kerrick and Jacobs, 1981) using the equation:

$$\Delta G_R = 0 = (\Delta G_R^{\circ})_{298.15} - \int_{298.15}^T \Delta S_R^{\circ} dT + \int_1^P \Delta V_s^{\circ} dP + RT \ln f_{H_2O} \quad (2)$$

Table 1. Experimental data for the reaction brucite \rightleftharpoons periclase + water

Run #	P (kbar)	T (°C)	Reaction direction	Δm_v^*	Run duration (hrs.)
1	8.23	811	Br \rightarrow P	0.201	27
2	8.20	811	Br \rightarrow P	0.376	5
3	8.13	806	Br \rightarrow P	0.309	16
4	8.09	785	Br \leftarrow P	-0.178	26
5	8.02	781	Br \rightarrow P	-0.316	16
6	6.12	765	Br \rightarrow P	0.365	20
7	6.12	765	Br \rightarrow P	0.256	26
8	6.07	735	Br \rightarrow P	-0.387	26
9	6.06	735	Br \leftarrow P	-0.219	22
10	6.06	740	Br \leftarrow P	-0.288	42
11	5.20	751	Br \rightarrow P	0.445	24
12	5.18	745	Br \rightarrow P	0.176	24
13	5.13	720	Br \rightarrow P	-0.140	18
14	5.14	720	Br \leftarrow P	-0.206	23
15	4.02	726	Br \rightarrow P	0.244	23
16	4.02	725	Br \rightarrow P	0.439	20
17	3.95	690	Br \leftarrow P	-0.170	25
18	3.96	690	Br \leftarrow P	-0.191	24

* Δm_v is the change in millivoltage that occurred during the time (right column) the run remained at constant temperature and pressure.

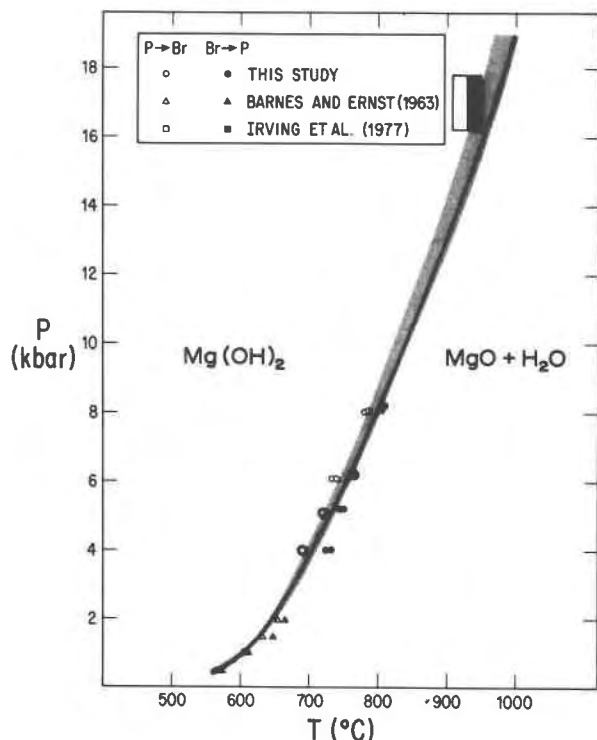


Fig. 3. A P - T diagram comparing the results obtained in this study with those of Barnes and Ernst (1963) and Irving *et al.* (1977). The shaded area represents the extrapolation from the end-points of the 8.1 kbar bracket of this study. The solid line is the extrapolated equilibrium curve from the starting-point at 8.0 kbar and 800°C.

In this calculation (unlike the calculations with equation (1)) the standard state was unit activity of all phases at T and 1 bar. Compressibility and thermal expansion of the solids were assumed to be negligible. The calculated equilibrium appears as the solid curve in Figure 4. Uncertainty in this calculation was determined according to the method outlined by Anderson (1978). At a given pressure, uncertainty in the calculated temperature is given by:

$$\sigma_T = \frac{\sigma_{\Delta G_R}}{\Delta S_R} \quad (3)$$

where:

$$\sigma_{\Delta G_R} = \sqrt{\sigma_{\Delta G_{MgO}}^2 + \sigma_{\Delta G_{Mg(OH)_2}}^2 + \sigma_{\Delta G_{H_2O}}^2} \quad (4)$$

The σ_T calculated for the brucite-periclase equilibrium curve is 5°C, which results in a $\pm 2\sigma_T$ band of 20°C. This uncertainty is indicated by the bars in

Figure 4. The equilibrium brackets obtained in our experiment (Fig. 3) overlap the $\pm 2\sigma_T$ band.

The effect of interfacial free energy on the position of an equilibrium curve can be significant for fine-grained reactants and/or products (Weber and Roy, 1965; Langmuir, 1971). Due to the complete conversion of periclase to brucite during quenching at the end of our experiment, it was impossible to directly measure the grain sizes of the brucite and periclase involved in the forward and reverse reactions. In order to obtain an estimate of these grain sizes, we performed an additional, independent experiment which proceeded as follows. First, three 2 mm O.D. Ag₅₀-Pd₅₀ capsules were loaded with the same reagent grade periclase used as starting material for the volumetric study. These capsules were left open at one end, and placed in a cold-seal hydrothermal pressure vessel wherein water served as the pressure medium. Next, the capsules were heated isobarically ($P = 3$ kbar) to 600°C, and held at these conditions for 14 hours to form brucite. The temperature was then raised to 700°C at 3 kbar in order to form periclase. The

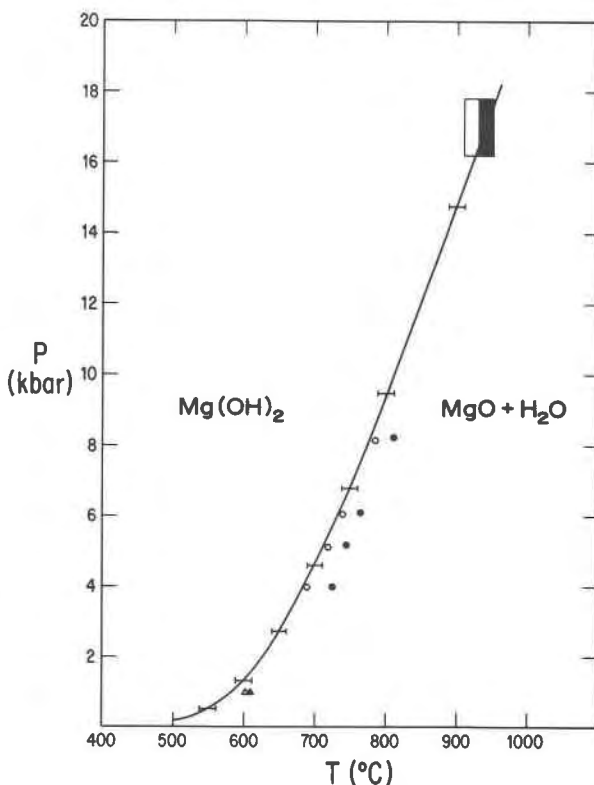


Fig. 4. A P - T curve for brucite-periclase equilibrium derived from thermodynamic data (see text). The bars indicate $\pm 2\sigma$. Symbols are the same as in Figure 3.

quenching procedure was similar to that of Barnes and Ernst (1963); *i.e.*, after 24 hours at 700°C and 3 kbar the run was terminated by first releasing pressure, and then quenching the vessel with compressed air. By quenching through the periclase field, back reaction of periclase to brucite was avoided. After quenching, the capsules contained a mixture of periclase and residual brucite. The run-up conditions in the cold-seal pressure vessel closely approximated the conditions of growth of brucite and periclase during the volumetric investigation. SEM examination of the run-products of the cold-seal investigation indicated that the periclase grains formed during this experiment averaged 3 μm in diameter. The residual brucite appeared as platelets up to 24 μm in diameter, with the majority of grains in the 5–10 μm range, each having a thickness of about 1.5 μm .

The effect of interfacial free energy on the position of the brucite–periclase equilibrium was calculated in a manner similar to that described by Berner (1980). For these calculations, brucite crystals were assumed to be cylinders with radius 3.5 μm and thickness 1.5 μm , whereas grains of periclase were modeled as spheres of radius 1.5 μm . Molar surface areas were then derived by: (1) calculating the total number of grains in one mole of brucite and one mole of periclase, respectively, according to the molar volume data of Robie *et al.* (1978); and (2) multiplying these numbers of grains by the “unit” (per grain) surface areas of brucite and periclase—109.96 and 28.27 μm^2 , respectively. Data on the interfacial free energies of brucite and periclase are not available, so the respective values for $\text{Ca}(\text{OH})_2$ and CaO (Brunauer, 1956) were substituted. The molar surface free energies of the two phases were then obtained by multiplying the molar surface areas by the interfacial free energies.

The effects of surface free energy on the P – T locations of brucite–periclase equilibria were found to be negligible, and this result is consistent with the observation of Berner (1980) that interfacial free energy effects are generally unimportant for grain sizes larger than approximately 2 μm . It can therefore be assumed that the interfacial free energies did not significantly affect brucite–periclase equilibrium in our experiment. However, it is likely that the grain sizes of the reactants and products changed progressively during the experiment. In particular, there was probably a continuous variation in average grain sizes (and, hence, a continuum of molar surface free energies) over the period of nucleation

and growth of a product phase. Because we were unable to document such a progressive change in grain size during our experiment, we could not account for this complicating factor in the analysis of surface free energy effects.

During experimentation it was observed that longer time intervals between temperature increments reduced overstepping in the direction of dehydration. Thus, it is to be expected that our equilibrium brackets could be narrowed slightly by increasing the length of time between each temperature increment. Furthermore, it is evident from Figure 3 that our equilibrium brackets are narrower at 8.1 kbar (20°C) than at 4.0 kbar (35°C). Increased pressure therefore appears to increase the rate of reaction near the equilibrium boundary.

Finally, we wish to point out that by calibrating the bellows in our volumeter system (Burnham *et al.*, 1969a), data could be obtained on the extent to which a devolatilization reaction has proceeded. This additional exercise, which we did not perform for our brucite–periclase experiment, would permit calculation of the mass of fluid liberated or consumed by reaction. This amount of fluid could then be converted into percent reaction.

Previous investigations

The purpose of this section is to compare our results with those from several other studies of the brucite–periclase equilibrium. (See also Weber and Roy (1965) for a discussion of data acquired in early studies.) The results of principal interest here are those obtained by Barnes and Ernst (1963), Weber and Roy (1965), Yamaoka *et al.* (1970), and Irving *et al.* (1977).

Barnes and Ernst (1963) investigated the brucite–periclase equilibrium at pressures up to 2 kbar using cold-seal hydrothermal pressure vessels with water as the pressure medium. In their study, they developed two procedures to avoid back reaction during the quench:

- (1) Sealed capsules containing brucite + water were run up and quenched through the brucite stability field. Consequently, the occurrence of periclase in the run products indicated that experimental P – T conditions were within the periclase stability field.
- (2) Open capsules containing periclase were run up and quenched through the periclase stability field. The appearance of brucite in the products of these runs demonstrated that the experimental P – T conditions were within the brucite stability field.

Barnes and Ernst employed these quenching

techniques for experiments at 1.0 kbar, and they noted that the brucite-periclase equilibrium temperatures so obtained were nearly identical to those determined from quenching procedure (1) alone. Therefore, to expedite their experimentation, all subsequent runs were performed using procedure (1) exclusively. It should be noted, however, that employment of *both* procedures is required to unequivocally demonstrate reaction reversal.

The experimental data acquired by Barnes and Ernst are shown in Figure 3. Extrapolations of the end-points of our 8.1 kbar bracket are in excellent agreement with their results at 0.5 and 1.0 kbar, but their 1.5 and 2.0 kbar data are at slightly higher temperatures than our extrapolations. Investigations in our cold-seal laboratory indicate that the quench problems associated with the brucite-periclase equilibrium are magnified by higher temperatures and pressures. Therefore, Barnes and Ernst's results at 1.5 and 2.0 kbar *could* be slightly in error due to undetected quench reaction; that is, a small amount of periclase formed at 1.5 or 2.0 kbar near the equilibrium boundary may have reacted to form brucite during the quench, thereby yielding results higher in temperature than the equilibrium value.

Weber and Roy (1965) conducted a differential thermal analysis study of brucite dehydration. The results of their study at 1.0 kbar are 30°C higher than the extrapolation of the results of the present investigation. The heating rate in their study was 10°C/minute. In the present study it was observed that, at 4.0 kbar, the dehydration temperature of brucite was elevated 20°C by increasing the heating rate from 5°C/24 hours to 5°C/30 minutes. Therefore, it is likely that brucite persisted above the 1.0 kbar brucite-periclase equilibrium temperature in Weber and Roy's experiments.

Yamaoka *et al.* (1970) and Irving *et al.* (1977) independently investigated the brucite-periclase equilibrium using piston-cylinder devices. Yamaoka *et al.* obtained brackets between 5 and 40 kbar; the brackets of Irving *et al.* are at 17 kbar and 33 kbar. The equilibrium curves obtained in these two studies diverge at pressures greater than 20 kbar. On a $\ln f_{\text{H}_2\text{O}}$ vs. $1/T$ plot showing the 1.0 kbar results of Barnes and Ernst, along with the data obtained by Yamaoka *et al.*, Irving *et al.*, and the present investigators (Fig. 5), it can be seen that our $\ln f_{\text{H}_2\text{O}}$ vs. $1/T$ curve is consistent with the experimental data up to 20 kbar. At higher pressures, our curve extrapolates between the results of Yamaoka *et al.* and Irving *et al.* The slight curvature of our

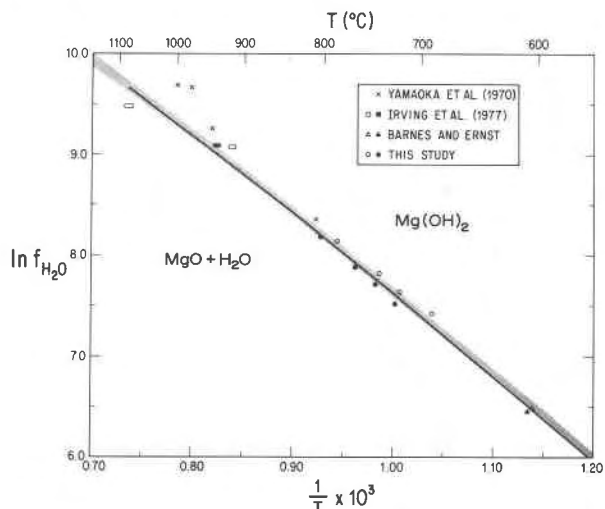


Fig. 5. Isobaric (1.0 kbar) $\ln f_{\text{H}_2\text{O}}$ vs. $1/T$ diagram. The shaded area and solid line are the same as in Figure 3.

equilibrium curve in Figure 5 reflects the variation of ΔH_R with temperature.

Conclusions

A volumetric investigation of the reaction brucite \rightleftharpoons periclase + water has yielded reproducible results which are in good agreement with data obtained by conventional hydrothermal methods. Our volumetric method is particularly suitable for kinetically-rapid devolatilization reactions because it eliminates quench problems, and because "fast" reactions require only short time periods for the observation of reaction direction. "Slow" reactions could also be investigated with our volumetric method, but they could probably be investigated as effectively using conventional hydrothermal techniques.

Acknowledgments

This paper reports some of the research conducted by J. A. Schramke for her Ph.D. dissertation. The research was supported by several grants from the Earth Sciences section of the National Science Foundation—NSF Grant EAR 80-26078 to D. M. Kerrick and A. C. Lasaga, NSF grant EAR 78-22443 to J. G. Blencoe, and NSF Grant EAR 78-12957 to C. Wayne Burnham—and also by an Owens-Corning Fiberglass Fellowship to J. A. Schramke. We thank J. W. Bradbury, D. E. Voigt, and M. W. Wilson for their assistance in the laboratory, and A. C. Lasaga for his helpful suggestions. Thanks are also extended to C. M. Graham and A. Navrotsky for suggesting ways to improve the original manuscript.

References

- Anderson, G. M. (1978) Uncertainties in calculations involving thermodynamic data. In H. J. Greenwood, Ed. Short Course

- in Application of Thermodynamics to Petrology and Ore Deposits, p. 199–215. Mineralogical Association of Canada, Toronto.
- Barnes, H. L. and Ernst, W. G. (1974) Ideality and ionization in hydrothermal fluids: the system $\text{MgO-H}_2\text{O-NaOH}$. *American Journal of Science*, 261, 129–150.
- Berner, R. A. (1980) *Early Diagenesis*. Princeton Press, Princeton, New Jersey.
- Brunauer, S., Kantro, D. L. and Weise, C. H. (1956) The surface energies of calcium oxide and calcium hydroxide. *Canadian Journal of Chemistry*, 34, 729–742.
- Burnham, C. Wayne, Holloway, J. R., and Davis, N. F. (1969a) The specific volume of water in the range 1000 to 8900 bars, 20°C to 900°C. *American Journal of Science*, 267-A, 70–95.
- Burnham, C. Wayne, Holloway, J. R., and Davis, N. F. (1969b) Thermodynamic properties of water to 1000°C and 10,000 bars. The Geological Society of America, Special Paper Number 132.
- Holloway, J. R. (1971) Internally heated pressure vessels. In G. C. Ulmer, Ed., *Research Techniques for High Pressure and High Temperature*, p. 217–258. Springer-Verlag, New York.
- Irving, A. J., Huang, W. L., and Wyllie, P. J. (1977) Phase relations of portlandite Ca(OH)_2 and brucite Mg(OH)_2 to 33 kilobars. *American Journal of Science*, 277, 313–321.
- Jacobs, G. K. and Kerrick, D. M. (1980) A simple rapid-quench design for cold-seal pressure vessels. *American Mineralogist*, 65, 1053–1056.
- Kerrick, D. M. and Jacobs, G. K. (1981) A modified Redlich-Kwong equation for H_2O , CO_2 and $\text{H}_2\text{O-CO}_2$ mixtures at elevated pressures and temperatures. *American Journal of Science*, 281, 735–767.
- Langmuir, D. (1971) Particle size effect on the reaction goethite \rightleftharpoons hematite + water. *American Journal of Science*, 271, 147–156.
- Robie, R. A., Hemingway, B. S. and Fisher, J. R. (1978) Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10^5 pascals) pressure and at higher temperatures. United States Geological Survey Bulletin 1425, 456 p.
- Slaughter, J., Wall, V. J. and Kerrick, D. M. (1976) APL computer programs for thermodynamic calculations in P - T - X_{CO_2} space. *Contributions to Mineralogy and Petrology*, 54, 157–171.
- Weber, J. N. and Roy, R. (1965) Complex stable \rightleftharpoons metastable solid reactions illustrated with the $\text{Mg(OH)}_2 \rightleftharpoons \text{MgO}$ reaction. *American Journal of Science*, 263, 668–677.
- Wellman, J. R. (1970) The stability of sodalite in a synthetic syenite plus aqueous chloride fluid system. *Journal of Petrology*, 11, 49–71.
- Yamaoka, S., Fukunaga, O. and Saito, S. (1970) Phase equilibrium in the system $\text{MgO-H}_2\text{O}$ at high temperatures and very high pressures. *Journal of the American Ceramic Society*, 53, 179–181.

*Manuscript received, June 4, 1981;
accepted for publication, October 21, 1981.*