

## Experimental determination of the reaction: Magnesite + enstatite = forsterite + CO<sub>2</sub> in the ranges 6–25 kbar and 700–1100 °C

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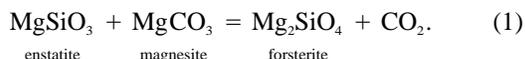
### ABSTRACT

The *P-T* equilibrium curve of the reaction of magnesite + enstatite = forsterite and CO<sub>2</sub> was determined in the ranges 6–25 kbar and 700–1100 °C by 53 reversed experiments carried out in 1.91 cm diameter piston-cylinder apparatus with NaCl pressure medium. Silver oxalate was used as a CO<sub>2</sub> source and charges were buffered at hematite-magnetite oxygen fugacity. Reaction progress was monitored by weight changes upon puncturing of CO<sub>2</sub>-inflated quenched charge capsules and was confirmed by comparing X-ray diffractograms of charges made before and after the experiments. The data satisfy the relation:  $P_{EQ} = -3.215 - 4.784 \times 10^{-3} T + 2.542 \times 10^{-5} T^2$  with *P* in kbar and *T* in °C. A *P-T* curve calculated with the 1994 version 2.3 THERMOCALC program agrees well with our results except in the highest pressure range. Our data, together with three existing tight experimental brackets on the decarbonation reaction of magnesite to periclase and CO<sub>2</sub>, give  $\Delta H_f^\circ$  (298 K) (forsterite) =  $-61.20 \pm 0.87$  kJ/mol from the oxides. This value is in agreement with the value adopted by Berman (1988). An analysis of various proposed equations of state for CO<sub>2</sub> shows that only those of Mäder and Berman (1991) and Frost and Wood (1997) meet the constraints imposed by this study near 1000 °C and 10–20 kbar. The modified Redlich-Kwong (MRK)-based equations of state overestimate CO<sub>2</sub> fugacity in this pressure range.

### INTRODUCTION

Carbonate minerals may be the major reservoir for C in the mantle and therefore may play an important role in the global carbon cycle. The system MgO-SiO<sub>2</sub>-CO<sub>2</sub> provides a simple chemical model for understanding the relationship between silicate, carbonate, and reduced carbon phases in the mantle. Mg-rich olivine and orthopyroxene are the major minerals of mantle peridotites, and magnesite is a stable carbonate at mantle pressures greater than about 3.5 GPa (Brey et al. 1983; Kushiro et al. 1975). Magnesite has been shown to be in equilibrium with (Mg,Fe)SiO<sub>3</sub> perovskite and magnesio-wüstite at 50 GPa and 1500–2500 K (Biellman et al. 1993), and it also has been noted, though rarely, as an inclusion in diamond (Wang et al. 1996).

The most important equilibrium governing the stability of magnesite in the Earth's mantle is



Normal upper mantle geothermal gradients lie well within the stability field of the left-hand assemblage; decarbonation may occur in mantle regions of abnormally high temperatures (Eggler et al. 1979; Newton and Sharp 1975). However, modeling the role of decarbonation reactions in the mantle requires an equation of state for CO<sub>2</sub> that is accurate at mantle pressure-temperature conditions.

This study presents the results of piston-cylinder experiments on reaction 1 conducted over a broad temperature-pressure range, 700 to 1100 °C and 6 to 25 kbar. This range bridges the gap between the previous high-pressure study of Newton and Sharp (1975) and the 2 kbar work of Johannes (1969). Analysis of our data along with results on the reaction magnesite = periclase + CO<sub>2</sub> (Johannes and Metz 1968; Koziol and Newton 1995) leads to an improved value for the enthalpy of formation of forsterite. In addition, because reaction 1 is tightly bracketed by our experiments from 6–25 kbar, we can place limitations on the fugacity of CO<sub>2</sub> in this pressure-temperature range and evaluate several published CO<sub>2</sub> equations of state.

### EXPERIMENTAL METHODS

Experiments on reaction 1 were made using procedures similar to those described in Koziol and Newton (1995). The experiments were carried out in two different piston-cylinder apparatus with slightly different designs and capabilities. All experiments were made under piston-out conditions. A press engineered for moderate pressures, referred to here as BG, was used for experiments at 6.5 to 15.5 kbar. Calibration experiments showed that no frictional pressure correction is required and that maximum pressure uncertainties are  $\pm 200$  bars. Another press, engineered for higher pressure conditions and referred to

**TABLE 1.** Reversed experiments on the reaction magnesite + enstatite = forsterite + CO<sub>2</sub> (reaction 1)

Expt. no.	Press used	T (°C)	P (kbar)	Time (h)	Expected CO <sub>2</sub> loss (mg)	Actual CO <sub>2</sub> loss (mg)	Reaction direction by XRD
5.154	BG	712	6.5	145	1.12	0.84	magn + en
5.135	BG	712	7.1	99	1.13	0.56	magn + en
MEF-11	BG	720	6.5	168	1.09	1.08	no reaction
5.148	BG	722	7.0	118	1.19	1.01	magn + en
MEF-13	BG	725	6.5	169	0.82	1.01	fo + CO <sub>2</sub>
5.143	BG	732	6.9	119	1.14	1.24	no reaction
5.151	BG	737	6.9	116	1.10	1.13	no reaction
MEF-12	BG	740	7.0	266	0.89	1.14	fo + CO <sub>2</sub>
5.121	BG	742	8.5	88	1.07	0.84	magn + en
5.122	BG	750	6.7	142	1.16	1.50	fo + CO <sub>2</sub>
5.146*	BG	750	8.1	118	—	—	magn + en
MEF-5	BG	755	8.0	148	0.84	0.64	magn + en
5.128	BG	757	8.1	120	0.97	1.12	no reaction
MEF-6	BG	760	8.0	144	1.15	1.04	magn + en
MEF-3	BG	765	8.0	150	1.59	1.83	fo + CO <sub>2</sub>
MEF-4	BG	774	8.0	124	1.22	1.61	fo + CO <sub>2</sub>
MEF-2	BG	780	8.0	146	0.86	1.09	fo + CO <sub>2</sub>
5.119	BG	782	8.0	96	1.09	1.44	fo + CO <sub>2</sub>
MEF-1	BG	800	8.0	165	1.31	1.71	fo + CO <sub>2</sub>
5.118	BG	801	10.0	70	1.12	0.82	magn + en
5.133	BG	812	10.2	73	1.10	0.77	magn + en
5.138	BG	815	10.0	119	1.16	0.75	magn + en
5.123	BG	822	10.2	120	1.10	0.97	magn + en
MEF-7	BG	825	10.0	73	1.07	1.21	fo + CO <sub>2</sub>
5.116	BG	832	10.1	73	0.976	1.17	fo + CO <sub>2</sub>
5.120	BG	842	10.0	93	1.17	1.41	fo + CO <sub>2</sub>
5.129	BG	842	10.2	17	1.07	1.08	no reaction
MEF-10	BG	850	12.0	71	0.81	0.41	magn + en
MEF-9	BG	870	12.0	72	1.17	1.43	fo + CO <sub>2</sub>
MEF-8	BG	880	12.0	69	1.2	1.46	fo + CO <sub>2</sub>
5.126	BG	914	14.1	16	1.13	1.02	magn + en
5.141	BG	923	14.0	68	1.07	0.78	magn + en
5.131	BG	928	14.1	24	1.17	1.02	magn + en
5.127	BG	951	14.2	20	1.19	2.03	fo + CO <sub>2</sub>
5.130	BG	955	15.5	14	1.10	0.54	magn + en
5.140	BB	963	16.2	7	1.15	0.75	magn + en
5.142	BB	983	16.3	6.5	1.17	0.70	magn + en
5.136	BB	984	18.3	18	1.14	0.57	magn + en
5.137	BB	993	16.4	25	1.10	1.95	fo + CO <sub>2</sub>
5.139	BB	1005	18.3	20	1.07	0.66	magn + en
5.152	BB	1006	15.9	46	1.18	2.02	fo + CO <sub>2</sub>
5.134	BB	1020	18.3	14	1.13	1.44	fo + CO <sub>2</sub>
5.145	BB	1022	18.6	24	1.14	0.85	magn + en
5.144	BB	1023	18.5	1	1.07	1.41	no reaction
5.132	BB	1044	18.5	22	1.11	1.99	fo + CO <sub>2</sub>
5.147	BB	1044	20.3	42	1.10	0.47	magn + en
5.150	BB	1063	20.0	49	1.19	1.91	fo + CO <sub>2</sub>
5.153	BB	1065	21.8	42	1.03	0.45	magn + en
5.149	BB	1082	20.1	44	1.13	1.73	fo + CO <sub>2</sub>
5.155	BB	1084	22.4	43	1.10	0.58	magn + en
5.158	BB	1100	22.3	43	1.14	1.78	fo + CO <sub>2</sub>
5.159	BB	1113	24.2	20	1.18	0.51	magn + en
5.160	BB	1131	24.3	22	1.07	0.38	magn + en

Note: The column "Reaction Direction by XRD" lists results of our analysis of the solid experimental product. Analysis of the CO<sub>2</sub> weight loss data is discussed in the text. In all cases reaction direction as judged by CO<sub>2</sub> loss is the same as that judged by XRD analysis.

\* Capsule in experiment 5.146 was inadvertently pierced before weighing and no weight-loss data could be collected.

here as BB, was used for experiments at 16 to 24.5 kbar. All operating parameters such as pressure medium, thermocouples, etc., were the same as for the low-pressure experiments. The BB press was calibrated against various fixed points in the range 800 to 900 °C, which indicated a pressure correction of -200 bars. Similar results were

obtained for the BB press by Jenkins et al. (1985) and Koziol and Newton (1988). Pressures reported in this paper are nominal pressures.

Samples consisted of homogenized powders of synthetic enstatite, synthetic magnesite, and synthetic forsterite, sealed in 1 mm diameter platinum tube segments with weighed amounts of silver oxalate (Ag<sub>2</sub>C<sub>2</sub>O<sub>4</sub>) as the CO<sub>2</sub> source. Synthetic forsterite was prepared from a thoroughly homogenized stoichiometric mix of ultrapure SiO<sub>2</sub> glass and synthetic magnesite. The mix was decarbonated in a platinum crucible at 800 °C and then sintered at about 1200 °C for 3 d. The material was finely ground, pelletized, and recycled at approximately 1400 °C for 2 d. The resulting material was 99% forsterite, with a very small amount of protoenstatite, as shown by optical examination and X-ray diffraction. Unit-cell dimensions of the forsterite determined by X-ray scans with an internal standard, are (in angstroms):  $a = 4.752(1)$ ,  $b = 10.200(2)$ , and  $c = 5.984(1)$ . Preparation of other materials is discussed in Koziol and Newton (1995).

All experiments were conducted with a hematite-magnetite buffer consisting of 35–50 mg sintered reagent hematite and 5–10 mg of H<sub>2</sub>O sealed with the platinum capsule in a 3 mm diameter gold tube segment of 0.15 mm wall thickness. Magnetite formed from this mixture very quickly at the temperatures and pressures of the experiments. Experiments were considered well-buffered if no weight loss of the gold capsule was detected and if the presence of both magnetite and hematite was confirmed in the buffer product.

Two methods were used to monitor reaction direction. Powder X-ray diffractometer scans of the same charges obtained before and after the experiments were compared. In addition, weight loss upon puncturing of the sample capsule was recorded. Details of the weighing technique used are in Koziol and Newton (1995). A CO<sub>2</sub> yield larger than expected from the Ag<sub>2</sub>C<sub>2</sub>O<sub>4</sub> decomposition indicated reaction to forsterite + CO<sub>2</sub> whereas a CO<sub>2</sub> yield smaller than expected signified magnesite growth. Final CO<sub>2</sub> amounts either 20% more or 20% less by weight were considered significant. X-ray diffraction scans were examined for relative increase or decrease in strength of forsterite reflections and corresponding decrease or increase in strength of enstatite and magnesite reflections.

## RESULTS OF EXPERIMENTS

### Character of reaction

Experiments on reaction 1 are listed in Table 1 and shown in Figure 1. These include all experiments in which the inner and outer capsules maintained constant mass. In most experiments a definite indication of reaction direction by volatile weight loss was confirmed by X-ray diffraction. A few experiments in which neither volatile nor change in X-ray reflection intensity was significant are tabulated as "no reaction."

No new phases other than silver from the decarbonation of Ag<sub>2</sub>C<sub>2</sub>O<sub>4</sub> were detected optically or with X-ray

analysis. A darker charge occasionally resulted when all of the  $\text{Ag}_2\text{C}_2\text{O}_4$  was loaded in one place in a capsule. This darkening might be due to small amounts of graphite. However, graphite was never identified on the X-ray diffraction scans, so we cannot confirm its presence. It was found that loading the  $\text{Ag}_2\text{C}_2\text{O}_4$  in increments interspersed with the reaction mix yielded snow-white charges. We were unable to detect any systematic perturbation of the experimental results coincident with darker color of the charges.

Purity of the  $\text{CO}_2$  fluid phase during the experiments is a critical issue. Calculations using the THERMOCALC version 2.3 program of Holland and Powell (1990) indicate that at our experimental conditions a 10% reduction in  $\text{CO}_2$  fugacity lowers the apparent position of reaction 1 by 10–15 °C. It is possible that amounts of  $\text{H}_2\text{O}$  too small to detect by our drying and weight-loss technique could have entered the experimental charges either by  $\text{H}_2$  infiltration during the experiments, by adsorbed  $\text{H}_2\text{O}$  in the starting mineral mix, or from the silver oxalate. The first two sources are unlikely because of the highly oxidizing buffer used and the stringent drying procedures before sealing of the capsules. Weight loss tests by Koziol and Newton (1995) indicated that the  $\text{Ag}_2\text{C}_2\text{O}_4$  used both in that study and the present study produced effectively pure  $\text{CO}_2$  upon decarbonation.

If CO were present in our quenched experimental charges, it would not be detected by our weight loss technique. Rosenbaum and Slagel (1995) noted that pure  $\text{CO}_2$  was produced from silver oxalate using a double capsule method similar to ours. However, in one piston-cylinder experiment carried out at 800 °C and 8 kbar, they observed that the mole fractions of  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and CO in the fluid were 0.90, 0.08, and 0.02, respectively.

To investigate the integrity of our procedure, two definitive experiments at 10 kbar, 830 and 825 °C, were repeated without any silver oxalate added to the sample capsule. Both experiments resulted in complete reaction to forsterite +  $\text{CO}_2$  after 4 d. The quenched platinum capsules were inflated with  $\text{CO}_2$ . There was no drying loss of the punctured capsules after heating at 320 °C for 20 min. If our earlier experiments had been displaced by significant quantities of  $\text{H}_2\text{O}$  or CO, then these experiments should have indicated the stability of magnesite and enstatite. It is concluded that any  $\text{H}_2\text{O}$  introduced in the silver oxalate had no significant effect on our decarbonation experiments.

Newton and Sharp (1975) found a slight increase of the unit-cell parameters of magnesite quenched from an experiment conducted at 1450 °C and 41.5 kbar. We examined the strong (104) peak of magnesite from our highest temperature experiments with X-ray diffraction at  $\frac{1}{8}^\circ/\text{min}$  using the nearby (610) peak of enstatite as an internal standard. No change of the position of the magnesite peak was evident, indicating that no quenchable changes occur in magnesite over the present experimental conditions.

The data plotted in Figure 1 were fitted by hand. Several fitting trials yielded virtually identical curves, as did

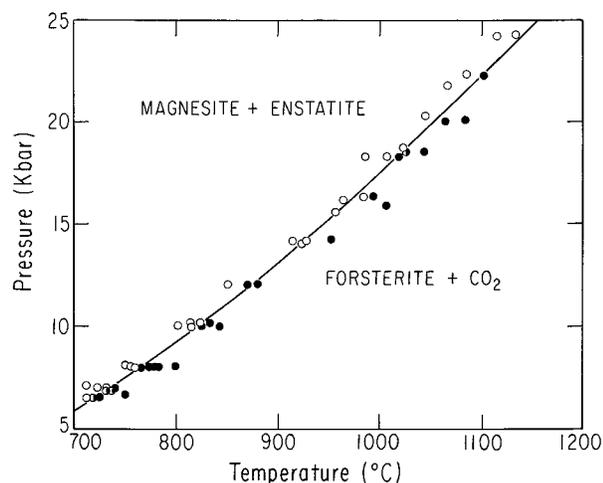


FIGURE 1. All reversal experiments of the present study on the reaction magnesite + enstatite = forsterite +  $\text{CO}_2$  (reaction 1). Open symbols = growth of magnesite and enstatite. Filled symbols = growth of forsterite and  $\text{CO}_2$ . Half-filled symbols = no reaction. Experimental uncertainties are the size of the symbols. Also plotted is a hand-fitted curve to the equilibrium that obeys the equation  $P_{\text{EQ}} = -3.215 - 4.784 \times 10^{-3} T + 2.542 \times 10^{-5} T^2$ , with  $T$  in °C and  $P$  in kbar.

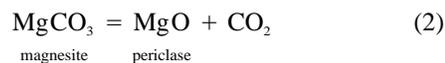
a mathematical fit to the midpoints of the experimental brackets. The hand-drawn curve was modeled with a polynomial expression:

$$P_{\text{EQ}} = -3.215 - 4.784 \times 10^{-3} T + 2.542 \times 10^{-5} T^2$$

with  $P$  in kbar and  $T$  in °C. This function is valid in the pressure range 6–25 kbar and satisfies all of the experimental brackets with the exception of one datum at 983 °C and 16.3 kbar (experiment no. 5.142, Table 1).

### Comparison with previous results

In the  $\text{MgO-SiO}_2\text{-CO}_2$  system, equilibrium 1 and the carbonation-decarbonation reactions:

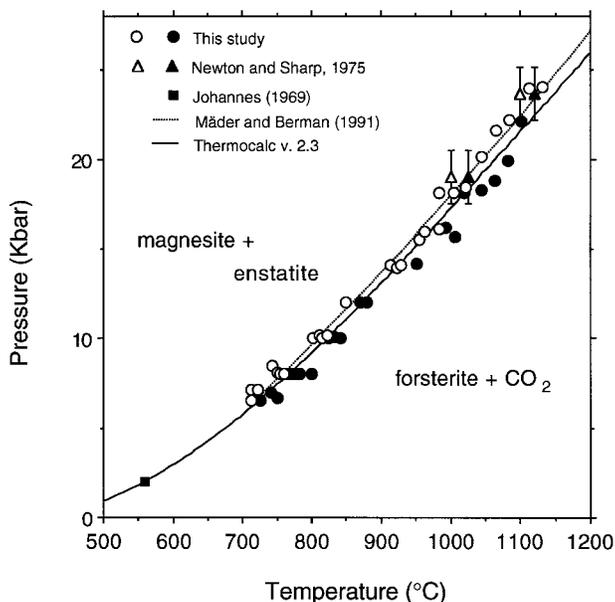


and



have been determined by several experimental studies. For reaction 2, the two brackets of Johannes and Metz (1968),  $705 \pm 5$  °C at 500 bars, and  $765 \pm 5$  °C at 1000 bars, appear to be definitive. Koziol and Newton (1995) produced an additional bracket at 715 °C,  $590 \pm 30$  bars. The brackets of Harker and Tuttle (1955) are too broad for our analysis and the experiments of Irving and Wyllie (1975) were performed at conditions outside our study. Recent experimental work by Koziol and Newton (1995) determined reaction 3 from 640 to 900 °C in the pressure range 7.5 to 18 kbar.

Johannes (1969) was able to place constraints on re-



**FIGURE 2.** Present reversals of reaction 1 compared with unreversed experimental data of Newton and Sharp (1975) and Johannes (1969 = Half-bracket in forsterite + CO<sub>2</sub> field). Open symbols = growth of magnesite and enstatite. Filled symbols = growth of forsterite and CO<sub>2</sub>. Solid curve = position of reaction 1 calculated from the Holland and Powell THERMOCALC (version 2.3) computer program. Dashed curve = position of reaction 1 as calculated by Mäder and Berman (1991).

action 1 with several experiments in the MgO-SiO<sub>2</sub>-H<sub>2</sub>O-CO<sub>2</sub> system. In hydrothermal experiments conducted at 2 kbar and 560–565 °C, a mixture of crystalline enstatite, magnesite, and a small amount of H<sub>2</sub>O reacted to form forsterite and a fluid containing 95–98 mol% CO<sub>2</sub>. A short projection to pure CO<sub>2</sub> placed reaction 1 at 558 °C at 2 kbar.

Numerous experimental brackets on reaction 1 at pressures above 19 kbar have been determined in solid pressure media apparatus (Eggler et al. 1979; Haselton et al. 1978; Newton and Sharp 1975). The latter two studies used starting mixtures of enstatite and magnesite in un-

sealed platinum capsules that allowed escape of CO<sub>2</sub> when decarbonation occurred. Eggler et al. (1979) used sealed platinum capsules that held either forsterite and Ag<sub>2</sub>C<sub>2</sub>O<sub>4</sub> or a mixture of magnesite, MgO, and SiO<sub>2</sub>. None of these studies were done with oxygen fugacity buffers to eliminate the possibility of H<sub>2</sub> infiltration during the experiments. No study has demonstrated whether, when the same starting mineral mixture was used, the direction of reaction 1 was reversed by changing the experimental pressure or temperature.

Only two previous experimental brackets, those of Newton and Sharp (1975) at 19 kbar and 23.7 kbar, lie within the pressure range of the present study (Fig. 2). Their brackets agree quite well with the present determinations, considering the large pressure uncertainties ( $\pm 1.5$  kbar) associated with the use of talc-glass pressure media in these earlier experiments.

A *P-T* equilibrium curve of reaction 1 was calculated with version 2.3 of THERMOCALC based on the data set of Holland and Powell (1990), with an equation of state for CO<sub>2</sub> similar in form to that of Holland and Powell (1991). For comparison, the position of this equilibrium calculated by Mäder and Berman (1991) is also plotted. The curves, shown in Figure 2, agree quite well with our experimental brackets, except for slight divergence by the Holland and Powell (1990) curve to lower pressures in the highest temperature range. Both curves provide a consistent extrapolation to lower temperatures and pressures and pass very close to the projected point at 2 kbar and 558 °C of Johannes (1969).

## DISCUSSION

### Enthalpy of formation of forsterite

A value of the enthalpy of formation ( $\Delta H_f^\circ$ ) of forsterite was derived from the present data, the experimental results for reaction 3 of Koziol and Newton (1995), and the three existing tight brackets for reaction 2. Supporting data, given in Table 2, include measured low-temperature and high-temperature heat capacities. Heat capacities of all the phases except magnesite were determined calorimetrically in the temperature range of the calculations; magnesite heat capacity has been measured only up to

**TABLE 2.** Thermodynamic data and sources relevant to derivations in the text

Phase	$\Delta H_f^\circ/298$	$S_{298}^\circ$	a	$b \times 10^3$	$c \times 10^{-4}$	$d \times 10^5$	e	$V_{298}$	$\alpha V \times 10^5$	$\beta V \times 10^6$	Ref.
Forsterite	-61.20	94.11	87.36	87.17	-369.9	-2.237	843.6	4.366	16.0	3.2	1, 2, 3
Mg <sub>2</sub> SiO <sub>4</sub>	$\pm 0.87$										
Enstatite	-33.41	66.27	350.7	-147.3	167.9	5.826	-4296.0	3.131	9.0	2.3	3, 4, 5
MgSiO <sub>3</sub>	$\pm 0.83$										
Magnesite	-116.83	65.09	81.12	52.25	-183.20	0	0	2.803	12.7	2.6	3, 4, 6*
MgCO <sub>3</sub>	$\pm 0.47$										
Periclase	0	26.94	65.211	-1.270	-46.185	0	-387.24	1.125	4.6	0.7	6, 3
CO <sub>2</sub>	0	213.79	87.82	-2.644	70.641	0	-998.86				6

Note: Values for enthalpy (*H*), entropy (*S*), heat capacity coefficients (a–e), volume, expansivity ( $\alpha V$ ), and compressibility ( $\beta V$ ) are in J, K, bar. Heat capacity:  $C_p = a + bT + cT^{-2} + dT^2 + eT^{-1/2}$ . Specific volume:  $V(T, P) = V_{298} + (T - 298)(\alpha V) - P(\beta V)$ .

References: 1 = Present study; 2 = Robie et al. (1982); 3 = Holland and Powell (1990); 4 = Koziol and Newton (1995); 5 = Krupka et al. (1985a, 1985b); 6 = Robie et al. (1978). The  $\alpha V$  and  $\beta V$  values for magnesite agree with Zhang et al. (1997).

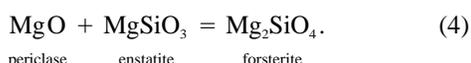
\* Magnesite heat capacity coefficients are the extrapolation of ref. 6.

**TABLE 3.** Enthalpy of formation of forsterite derived from experimental data

$T$ (°C)	$P_1$ (kbar)	$f_{\text{CO}_2}$ (reaction 1)	$P_2$ (kbar)	$f_{\text{CO}_2}$ (reaction 2)	$\Delta H_4$	$\Delta H_f^\circ$ Fo (oxides)	$\Delta H_f^\circ$ Fo (elements)
705	6.05	47.88	0.50	0.55	-27.79	-61.20	-2174.82
715	6.36	55.50	0.59	0.67	-27.54	-60.95	-2174.57
765	8.00	112.17	1.00	1.28	-28.04	-61.45	-2175.07
Average						-61.20(87)	-2174.82(99)

Note: Fugacity and enthalpy values are in kJ/mol. Enthalpy values are at 1 bar, 298 K.  $\text{CO}_2$  fugacity from Shmulovich and Schmonov (1978).  $P_1$  is the pressure of reaction 1 (enstatite + magnesite = forsterite +  $\text{CO}_2$ ) at the given  $T$ .  $P_2$  is the pressure of reaction 2 (magnesite + quartz = enstatite +  $\text{CO}_2$ ) at the given  $T$ . Equilibrium pressures for reaction 1 from present work; for reaction 2 from Johannes and Metz (1968) and Koziol and Newton (1995). The  $\Delta H_4$  value is the enthalpy change of reaction 4 (enstatite + periclase = forsterite).

750 K, but magnesite is eliminated between reactions 1 and 2 in the derivation given below. The three definitive brackets of reaction 2 were performed in gas-pressure vessels under closely controlled  $P$ - $T$  conditions, with reversal of the equilibrium. This allows for three precise calculations of  $\Delta H_f^\circ$  of forsterite.  $\text{CO}_2$  is also eliminated between reactions 1 and 2 at each temperature to yield reaction 4:



The three values of  $\Delta H_f^\circ$  of forsterite from the oxides at 298 K, together with the  $\text{CO}_2$  fugacity data necessary for the calculation, are given in Table 3. Our average value is  $-61.20 \pm 0.87$  kJ from the oxides ( $-2174.72$  kJ from the elements). The calculation relies on the value of  $\Delta H_f^\circ$  of enstatite of  $-33.41 \pm 0.83$  kJ at 298 K of Koziol and Newton (1995). Using the heat capacity coefficients for forsterite of Gillet et al. (1991) makes no significant difference in the calculation. Our value of  $\Delta H_f^\circ$  agrees closely with that adopted by Berman (1988:  $-2174.42$  kJ from the elements) but less well with that used by Holland and Powell (1990:  $-2171.87 \pm 1.62$  kJ). Our value for  $\Delta H_f^\circ$  of forsterite and the data in Table 2 lead to an equilibrium temperature of reaction 1 of 547 °C at 2 kbar, slightly lower than the projection of Johannes (1969).

### $\text{CO}_2$ fugacity at mantle conditions

Previous experimental determinations of reaction 1 (Eggler et al. 1979; Haselton et al. 1978; Newton and Sharp 1975) have been used by various workers to evaluate their  $\text{CO}_2$  equation of state (Frost and Wood 1997; Holland and Powell 1991; Mäder and Berman 1991). These different equations of state are not compared easily because each study used different tabulated thermodynamic properties of forsterite, enstatite, and magnesite, in addition to different formulations of  $\text{CO}_2$  volume and fugacity data. Each study also incorporated different important assumptions, for example, the form of the extrapolation of the heat capacity of magnesite to temperatures above 750 K.

Our determination of the equilibrium magnesite + enstatite = forsterite +  $\text{CO}_2$  (reaction 1) provides a further test of literature models of the equation of state of  $\text{CO}_2$ . Our experimental results are in a critical pressure-tem-

perature range between the direct  $PVT$  measurements of  $\text{CO}_2$  volumes at low pressures and the previous studies on reaction 1 at high pressures. The position of this reaction in terms of pressure and temperature is constrained more stringently by reversed experiments than in previous studies.

Calculation of  $\Delta G^\circ$  of reaction 1 can be used to derive the fugacity of  $\text{CO}_2$  and evaluate the various equations of state. We use the expression

$$\Delta G^\circ = -P\Delta V^* - RT \ln f_{\text{CO}_2} \quad (5)$$

where  $\Delta G^\circ$  is the free energy change of reaction 1 at 1 bar and the temperature of interest,  $P$  is the equilibrium pressure of reaction 1 at that temperature, and  $\Delta V^*$  is the characteristic solid volume change evaluated at  $T$  and  $P/2$ . Volume and thermal expansion and isothermal compressibility coefficients are generally well-known and uncertainties due to less reliable thermodynamic data are eliminated, in particular the uncertain heat capacity of magnesite at elevated temperatures. Our tight experimental brackets allow us to evaluate  $\Delta G^\circ$  at 700, 750, 800, and 850 °C using volume data from Table 2 and the tabulated  $\text{CO}_2$  fugacities of Shmulovich and Shmonov (1978) (see Table 4). The data of Zhang et al. (1997) were used to derive values for the thermal expansion and isothermal compressibility of magnesite. The  $\Delta G^\circ$  is a regularly varying function of temperature that can be extrapolated with small uncertainty to 1000 °C. At this temperature reaction 1 is in equilibrium at 17.4 kbar. Our conservative estimate of the uncertainty in  $\Delta G^\circ$  is based in part upon a 2% uncertainty in  $\Delta V^*$ , which includes the range in calculated volumes from various data sets. In addition, we estimate the uncertainty in  $RT \ln f_{\text{CO}_2}$  at 10 kbar and 1000 °C from Shmulovich and Shmonov (1978) to be  $\pm 1300$  J. This value embraces all of the estimates of  $RT \ln f_{\text{CO}_2}$  from various published equations of state. Calculations using the  $\Delta H_f^\circ$  and heat capacity data in Table 2 also predict a reasonable value of  $\Delta G^\circ$  at 1000 °C (see Table 4), as do calculations using THERMOCALC version 2.3 (Holland and Powell 1990) and the Berman (1988) data set with updates and  $\text{CO}_2$  fugacities as described in Mäder and Berman (1991), even though values of  $\Delta H_f^\circ$  for the solids in the Holland and Powell and Mäder and Berman data sets are different.

At pressures above 15 kbar the various  $\text{CO}_2$  equations

**TABLE 4.** Thermodynamic parameters of the reaction magnesite + enstatite = forsterite + CO<sub>2</sub> derived from the present experimental data

T (°C)	P (kbar)	RT ln f <sub>CO<sub>2</sub></sub> (kJ)	-ΔV* (J/bar)	-ΔG° (kJ)		Mäder & Berman 91	Holland & Powell
				Experimental	Table 2		
700	5.89	86.58	1.602	77.14	77.35		
750	7.5	97.17	1.603	85.15	85.27		
800	9.23	107.83	1.604	93.03	93.12		
850	11.09	118.57†	1.606	100.76	100.89		
1000	17.42	151.14 ±1.42	1.609	(123.11)	123.67 ±1.34	123.19	124.13

Note: RT ln f<sub>CO<sub>2</sub></sub> values from Shmulovich and Shmonov (1978). The -ΔG° experimental is derived from the relationship ΔG° = -PΔV\* - RT ln f<sub>CO<sub>2</sub></sub> (see text). The value in parentheses is an extrapolation which allows for the apparent decrease of |ΔG°| with T. The -ΔG° of Table 2 is calculated using data in Table 2. RT ln f<sub>CO<sub>2</sub></sub> at 1000 °C and 17.42 kbar of 151.14 kJ is consistent with our experimental ΔG°. Holland & Powell value calculated using version 2.3 (1994) of THERMOCALC.

\*ΔV\* (solid volume change evaluated at T and P/2) calculated from data in Table 2.

† Denotes short extrapolation.

of state (Bottinga and Richet 1981; Frost and Wood 1997; Holland and Powell 1991; Kerrick and Jacobs 1981; Mäder and Berman 1991; Saxena and Fei 1987; Sterner and Pitzer 1994) start to diverge in their estimates of volume and fugacity, and our data may be used to discriminate among them. This is shown in Figure 3, which is an isothermal plot of ln γ<sub>CO<sub>2</sub></sub> vs. pressure at 1000 °C. The bracket at 17.4 kbar is derived from the calculations described above and based on data in Table 4. Uncertainty in our calculated value of ln γ<sub>CO<sub>2</sub></sub> due to uncertainty in the

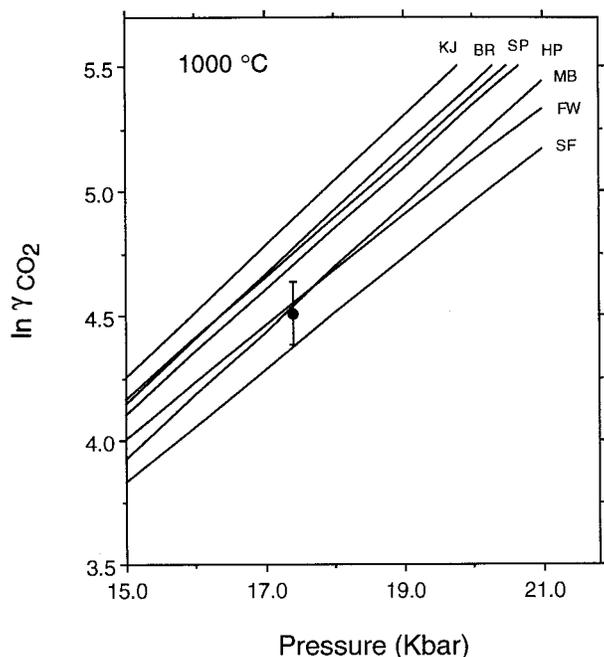
experimentally determined position of reaction 1 is negligible. The equations of state of Mäder and Berman (1991) and Frost and Wood (1997) fit the constraint calculated from our experimental data but the other models either over- or under-estimate ln γ<sub>CO<sub>2</sub></sub> with the MRK models in particular tending toward over-estimation. Kerrick and Jacobs (1981) note that their formulation may not be reliably extrapolated to pressure approaching 20 kbar. Further work on the enstatite-magnesite-forsterite-CO<sub>2</sub> equilibria or related equilibria will aid in the analysis of published equations of state for CO<sub>2</sub>.

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**FIGURE 3.** Isothermal plot of ln γ<sub>CO<sub>2</sub></sub> as calculated by various equations of state against pressure. The bracket at 17.4 kbar is calculated from our data as described in the text. KJ = Kerrick and Jacobs (1981); BR = Bottinga and Richet (1981); SP = Sterner and Pitzer (1994); HP = Holland and Powell (1991); MB = Mäder and Berman (1991); FW = Frost and Wood (1997); SF = Saxena and Fei (1987).

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