American Mineralogist, Volume 80, pages 1252–1260, 1995

Experimental determination of the reactions magnesite + quartz = enstatite + CO_2 and magnesite = periclase + CO_2, and enthalpies of formation of enstatite and magnesite

ANDREA M. KOZIOL,* ROBERT C. NEWTON
Department of the Geophysical Sciences, University of Chicago, Chicago, Illinois 60637, U.S.A.

ABSTRACT

The equilibrium *P-T* curve of the reaction

$$\underset{\text{magnesite}}{MgCO_3} + \underset{\text{quartz}}{SiO_2} = \underset{\text{enstatite}}{MgSiO_3} + CO_2 \qquad (1)$$

was determined by reversed reactions in well-calibrated, solid-pressure medium (NaCl) piston-cylinder apparatus. External hematite + magnetite + H_2O f_{O_2} buffers were used in all experiments. A reversed point at 715 °C of the reaction

$$\underset{\text{magnesite}}{MgCO_3} = \underset{\text{periclase}}{MgO} + CO_2 \qquad (2)$$

was obtained in an internally heated Ar pressure vessel, using a coarse-grained synthetic periclase to inhibit quenching back reaction, along with synthetic magnesite and silver oxalate. At 715 °C our pressure for Reaction 1 is 10.4 ± 0.2 kbar, and for Reaction 2 it is 590 ± 30 bars. From these two reactions we derive $\Delta H^0_{f,298} = 33.41 \pm 0.83$ kJ for enstatite from the oxides. Using an extrapolated heat-capacity equation for magnesite, we obtain $\Delta H^0_{f,298} = -116.68$ kJ (from the oxides) and −1111.68 kJ from the elements for magnesite, somewhat less negative than the values of either the Holland and Powell (1990) or the Berman (1988) data sets. A calculated 2 kbar temperature for the magnesite + quartz reaction is 492 °C, about 25 °C lower than the data set predictions but in agreement with a prediction based on natural occurrences of magnesite, quartz, and enstatite in metacarbonates from the Alps by Trommsdorff and Connolly (1990).

INTRODUCTION

Enstatite, $MgSiO_3$, is one of the most important of Earth materials. It is the dominant member of orthopyroxene solid solutions, which is the second most abundant mineral species in the upper mantle and a definitive phase of the major peridotite assemblages. The presence of orthopyroxene in quartzofeldspathic and mafic crustal rocks virtually defines the granulite facies of metamorphism. Enstatite is a component of the CO_2-metasomatic ultramafic rocks that have figured importantly in definition of the *P-T* history of alpine metamorphism (e.g., Evans and Trommsdorff, 1974). Orthopyroxene is a characteristic phase in felsic to mafic volcanic rocks and the large layered intrusions. Much of its importance to petrogenesis lies in its major role as a participant in mineral reactions that are the basis for geothermometry, geobarometry, and oxygen fugacity analysis. As the simplest and most easily characterized magnesian silicate, enstatite anchors the self-consistent thermodynamic data sets (Berman, 1988; Holland and Powell, 1990); uncertainties in its thermodynamic properties propagate throughout the data sets, with far-reaching effects on all the tabulated data.

Despite the chemical simplicity of enstatite, its thermodynamic properties have eluded exact definition, with adverse consequences for calculations of mineral equilibria. The relative insolubility of MgO in aqueous acids and salt melts has hindered measurement of the enthalpy of formation (Charlu et al., 1975; Torgeson and Sahama, 1948) and, hence, of the free energy of formation. Newton (1987) summarized the large spread of measured values of these properties and concluded that measured thermochemical data for enstatite were not sufficiently precise for practical utility.

Many workers (e.g., Helgeson et al., 1978) have realized that if suitable high-quality experimental reactions are available, thermodynamic properties of minerals can be derived from these data more accurately than from other physicochemical measurements. For enstatite, the experimental database is marginal for this purpose. The only stable formation reaction of enstatite that can be investigated in accessible pressure-temperature space is the decarbonation reaction of magnesite in the presence

---

* Present address: Department of Geology, University of Dayton, Dayton, Ohio 45469, U.S.A.

0003–004X/95/1112–1252$02.00

of quartz:

$$\underset{\text{magnesite}}{MgCO_3} + \underset{\text{quartz}}{SiO_2} = \underset{\text{enstatite}}{MgSiO_3} + CO_2. \qquad (1)$$

This reaction has not previously been reversed because of very slow reactions in silicate systems in which CO_2 is the only volatile substance. An equilibrium temperature of 521 °C at 2 kbar was estimated by Johannes (1969) by projection of other experimental reactions in mixed H_2O-CO_2 systems to pure CO_2. Using this point, the formation properties of enstatite may be derived in conjunction with the experimentally determined reaction

$$\underset{\text{magnesite}}{MgCO_3} = \underset{\text{periclase}}{MgO} + CO_2. \qquad (2)$$

The two determinations of the univariant *P-T* curve of Reaction 2 are somewhat discrepant. The broad reversed brackets of Harker and Tuttle (1955) place the reaction curve approximately 15 °C higher than the two tight reversed brackets of Johannes and Metz (1968). Additional uncertainty arises from the poorly known heat capacity of magnesite above 400 °C: the data sets use extrapolations of lower temperature data, and none of these extrapolations consider the possible onset of carbonate rotational disorder at higher temperatures. All these uncertainties compound the difficulty in extracting the enthalpy and free energy of formation of enstatite from phase equilibria.

Both the Berman (1988) and Holland and Powell (1990) data sets yield a 2 kbar equilibrium point near 520 °C for Reaction 1, in apparent agreement with Johannes's (1969) projection. However, Trommsdorff and Connolly (1990) have challenged the data set predictions. Their revision is based on analysis of natural parageneses in carbonate rocks from the Alps. According to their assessment, Reaction 1 should lie at significantly lower temperatures than the reaction of dolomite + quartz to diopside and CO_2. The latter reaction was experimentally determined by Slaughter et al. (1975) to be close to 520 °C at 2 kbar. Trommsdorff and Connolly's revision locates a 2 kbar equilibrium point of Reaction 1 near 490 °C. Their consequent revision of *PTX* topology in the system CaO-MgO-SiO_2-H_2O-CO_2 is in better agreement with the observed metamorphic zonation in metacarbonates in the central Alps than the topologies predicted by the widely used data sets. They suggest that the discrepancy with the Berman (1988) data set can be rectified by assuming a free energy of formation of magnesite 2 kJ more positive than that used by Berman (1988). This assumption is equivalent to relocating Reaction 2 to considerably higher pressures and lower temperatures than those predicted by Berman. The discrepancy in Reaction 1 could, however, be equally well accounted for by an adjustment of the free energy of formation of enstatite.

The present work seeks to resolve these uncertainties using improved experimental determinations of Reactions 1 and 2. A linear combination of these reactions yields the formation reaction of enstatite

$$\underset{\text{periclase}}{MgO} + \underset{\text{quartz}}{SiO_2} = \underset{\text{enstatite}}{MgSiO_3}. \qquad (3)$$

Because Reaction 3 does not involve magnesite, the unknown high-temperature thermal properties of magnesite are not an issue in deriving the free energy of formation of enstatite. The heat-capacity functions of enstatite, periclase, and quartz are very well-measured quantities.

EXPERIMENTAL METHODS

Piston-cylinder experiments

Experiments on the reaction of magnesite and quartz, Reaction 1, were made in a 0.75 in. diameter piston-cylinder apparatus with NaCl pressure medium and a graphite heater element. Calibrated matched pairs of W-25% Re vs. W-3% Re thermocouples measured the temperatures and served as automatic temperature control sensors. The manufacturer's stated precision is better than ±1 °C, and the temperature-controller variation was less than ±2 °C. However, the need for a double-capsule high-f_{O_2} buffer to insure purity of the CO_2 gas phase resulted in a separation of as much as 1 mm between the thermocouple tip and the sample charge. The samples were positioned in a level interval of the temperature gradient, on the basis of previous gradient measurements, but the temperature uncertainty required independent fixed-point calibrations as described below. Experiments were conducted under piston-out conditions, and maximum nominal pressure variation during an experiment was ±70 bars. There is almost no frictional correction for NaCl under these conditions; the pressures are believed accurate to ±200 bars at 10 kbar.

Samples consisted of homogenized powder mixes of synthetic enstatite, synthetic magnesite, and natural quartz sealed in 1 mm diameter platinum tube segments with weighed amounts of silver oxalate ($Ag_2C_2O_4$) as the CO_2 source. Magnesite was synthesized from Baker hydrous magnesium carbonate reagent by recrystallizing under CO_2 pressure at 400 °C and about 1 kbar in a Morey vessel for 2 d. The result was well-crystallized magnesite with average grain size of about 15 μm. The unit-cell constants were determined by powder X-ray diffractometry, scanning at ¼°/min with an internal quartz standard. Five major peaks in the range 30–55° 2θ (Cu$K\alpha_1$ radiation) were used to calculate the cell constants by a least-squares method: $a_0 = 4.636 \pm 0.001$ and $b_0 = 15.016 \pm 0.001$ Å. Enstatite was synthesized from this magnesite mixed intimately with finely ground natural quartz in sealed platinum containers at 1000 °C and 15 kbar for 6 h. The product was nicely crystallized enstatite averaging 30 μm in length with the following unit-cell constants, based on seven X-ray diffraction peaks in the range 26–40° 2θ: $a_0 = 18.226 \pm 0.003$, $b_0 = 8.811 \pm 0.002$, and $c_0 = 5.178 \pm 0.001$ Å. Another sample of synthetic enstatite used in some experiments was prepared by Eckert et al. (1992) from reagent MgO and SiO_2 by dry synthesis at 1400 °C and 17–20 kbar for 24 h.

TABLE 1. CO_2 yield tests of $Ag_2C_2O_4$ on the basis of weight (g) of capsule and contents

Expt.	1	2	3	4	5
Before decarbonation expt.					
Pt capsule	0.18777	0.18358	0.17454	0.18194	0.30180
+ $Ag_2C_2O_4$	0.19415	0.19039	0.18160	0.18966	0.31136
Sealed	0.19410	0.19034	0.18156	0.18963	0.31130
After decarbonation expt.					
Pt capsule	0.19408	0.19033	0.18157	0.18961	0.31130
Punctured	0.19228	0.18838	0.17956	0.18743	0.30859
Dried	0.19228	0.18839	0.17956	0.18744	0.30855
Actual CO_2 released (mg)	1.80	1.95	2.01	2.18	2.71
Expected CO_2 (mg)	1.84	1.97	2.04	2.23	2.76

All experiments were conducted with a hematite + magnetite buffer consisting of 35 mg of reagent hematite and 10 mg of H_2O sealed with the platinum sample capsule in a 3 mm diameter gold tube segment of 0.15 mm wall thickness. Experiments were considered well buffered if there was no weight loss of the gold capsule at the end of the experiment, and if the presence of both magnetite and hematite was verified optically after opening this outer capsule.

Characterization of vapor phase

Purity of the CO_2 gas phase is a critical issue because admixture of other volatile components would deflect the decarbonation equilibrium point to lower temperatures and higher pressures. To check the purity of the CO_2 yielded by our silver oxalate (ICN Pharmaceuticals), we performed five puncture weight-loss tests under liquid nitrogen on quenched platinum capsules that had been sealed with several milligrams of the silver oxalate and heated to 400 °C for 1–2 d in a Morey vessel under an external CO_2 pressure of several hundred bars. The results of the tests are given in Table 1. Within weighing error, the CO_2 yields were as expected from the formula $Ag_2C_2O_4$, except for a possible, marginally detectable (about 1%) mass deficiency. Subsequent drying showed that this deficiency did not result from H_2O in the silver oxalate. Nitrogen also is ruled out: If nitrogen were present in the form of ammonium oxalate, silver nitrate, or ammonium nitrate in the silver oxalate, the puncture mass loss would have been greater than expected. We suggest that the slight CO_2 deficiency resulted from photodecomposition of the silver oxalate.

H_2 infiltration into the platinum sample capsules occurred during the experiments, reacting to H_2O and carbon monoxide or graphite, until the H_2 pressure, calculated to be 0.25 bar at the hematite + magnetite buffer at 1000 K and 10 kbar, was equilibrated in the charge. The absence of graphite in the samples places an upper fugacity limit of 48 bars of H_2O inside the CO_2-filled platinum capsules, on the basis of calculations using data for hematite, magnetite, CO_2, and H_2O from Robie et al. (1978), Shmulovich and Shmonov (1978), and Burnham et al. (1969). Using the Lewis and Randall rule, this fugacity is equivalent to an H_2O mole fraction of 0.003, which is negligible in terms of displacement of decarbonation equilibria. It is possible that graphite is metastably overstepped under our experimental conditions, and that CO and H_2O contents of the vapor phase may not be negligible. However, Rosenbaum and Slagel (1995) showed by mass spectrometry that quenched charges initially consisting of silver oxalate in platinum capsules, buffered externally by hematite + magnetite + H_2O, contained no detectable CO after being held at 800 °C and 8 kbar for 24 h. Failure to detect significant weight loss in drying of our punctured capsules confirms the virtual absence of H_2O in the gas phase of the platinum capsules. We conclude that the gas phase inside the platinum capsules was effectively pure CO_2.

Determination of reaction direction

Each experimental charge contained approximately 4 mg of $Ag_2C_2O_4$ to provide approximately 1 mg of CO_2 fluid at experimental conditions. The exact amount of $Ag_2C_2O_4$ as weighed on a Mettler AE240 microbalance was noted for each experiment. Reaction direction was monitored by careful measurement of the amount of vapor present at the end of an experiment.

Upon removing and cleaning of the platinum sample capsule, our procedure was as follows. The capsule was initially weighed. Any leaks during the experiment were discovered at this time. The capsule was partially immersed in liquid N_2, punctured, then removed from the liquid N_2. In warming from liquid N_2 temperature, the CO_2 boiled away from the punctured capsule while H_2O (if present) was still frozen. The capsule was immediately reweighed, then heated at 120 °C for at least 20 min and weighed again. There was no further weight loss, indicating no detectable H_2O in the samples.

Direction of Reaction 1 could be monitored by the weight loss upon puncturing of the sample capsule and by comparing powder X-ray diffractometer scans of the same charges before and after the experiments. Release upon puncture of an amount of CO_2 that was less than the amount initially present as $Ag_2C_2O_4$ indicated growth of magnesite and quartz and consumption of enstatite and CO_2. Release of an amount of CO_2 that was greater than the amount initially present indicated consumption of magnesite and quartz and growth of enstatite and CO_2.

In every case this was supported by the relative growth or reduction of X-ray peak heights in the X-ray diffraction scans.

Calibration of pressure and temperature readings

A test of the pressure and temperature calibration of our experimental assemblies was provided by determining the reaction of anorthite + H_2O to zoisite + kyanite + quartz. This reaction is readily reversible at conditions almost the same as those of our most definitive reversals of Reaction 1 (near 10 kbar and 700 °C) in experiments of the same duration (a few to several days). The anorthite-H_2O reaction was determined in internally heated gas-pressure apparatus by Jenkins et al. (1985) and Chatterjee et al. (1984) and is one of the reactions best constrained by the standard data sets in that thermodynamic data are available for all the phases.

Synthetic anorthite was prepared hydrothermally from reagent silica glass, γ-Al_2O_3, and calcite mixtures at 8 kbar and 730 °C for 48 h. The high-pressure zoisite-bearing assemblage was prepared from the same mixture, with 30 mg of H_2O added, at 15 kbar and 700 °C for 48 h. The mix was seeded with a small amount of kyanite, and kyanite was the only Al_2SiO_5 polymorph produced along with well-crystallized zoisite and quartz. Subequal portions of the 8 and 15 kbar samples were thoroughly mixed under acetone to make a reversal mix. X-ray diffraction peak heights of the starting mix were compared with those of the quenched samples to assess the reaction progress. The calibration samples were sealed in 1 mm platinum tubes with 20% excess H_2O, and these in turn were placed in 3 mm gold tubes with 10 mg of H_2O and 30 mg of calcite (rather than hematite). The geometry of these double capsules exactly emulated the geometry of the buffered experiments on Reaction 1. Calcite was used instead of hematite to avoid the possibility of diffusion of Fe through the platinum capsule, which might influence zoisite stability. These experiments were performed in the same smooth carbide pressure chamber as the Reaction 1 experiments and using the same apparatus and thermocouple. Results of these calibration experiments are shown in Figure 1. The Holland and Powell (1990) data set predicts a pressure of 9.7 kbar at 700 °C, in agreement with the present experiments, and Berman (1988) gives 9.6 kbar. The present Reaction 1 experiments near 10 kbar and 700 °C are therefore not subject to substantial uncertainty of apparatus calibration.

Internally heated gas-vessel experiments

A tight reversal on Reaction 2, the magnesite decomposition equilibrium, was determined at 715 °C in an internally heated gas-pressure vessel with argon medium. The starting material consisted of a homogeneous mix of nearly equal masses of ground synthetic magnesite and periclase. The sample powders were heated at 350 °C immediately before sealing with silver oxalate in platinum tube segments. The original periclase was in the form of large limpid crystals made by an arc-fusion process by Muscle Shoals Electrochemical Company and had a maximum impurity of 0.1 wt% CaO. Use of coarsely crystalline periclase eliminated the problem of back reaction during quenching to magnesite, a problem encountered by all previous investigators of this equilibrium. Hematite + magnetite buffered double capsules of the same geometry as that used for Reaction 1 were positioned in the gas-pressure vessel so that the two thermocouples were at the extreme ends of the platinum capsule (about 0.8 cm apart). Sintered hematite powder as an H getter was packed around the gold capsule inside a thick copper holder, which greatly reduced the temperature gradient in the sample vicinity. Temperature readings of the two sheathed chromel-alumel thermocouples were always within 5 °C of each other and usually within 2 °C. Pressures were read from a Heise bourdon-tube gauge with a precision of ±4 bars. Constancy of pressure was monitored by the output of a manganin-resistance pressure

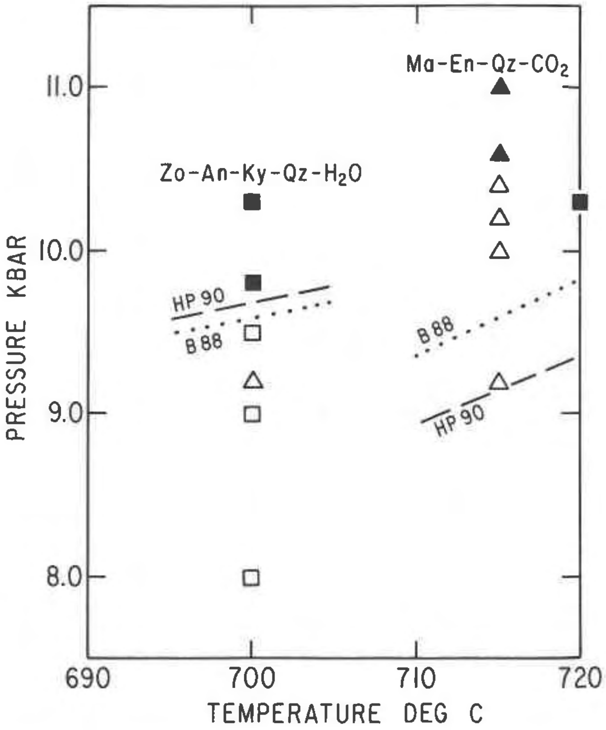

Fig. 1. Reversal experiments of the calibration reaction 2 zoisite (Zo) + kyanite (Ky) + quartz (Qz) = 4 anorthite (An) + H_2O at 700 °C (squares: solid = zoisite-kyanite-quartz stable, open = anorthite-H_2O stable) and the reaction magnesite (Ma) + quartz = enstatite (En) + CO_2 at 715 °C (triangles: solid = magnesite-quartz stable, open = enstatite-CO_2 stable). The calibration experiments agree closely with the predictions of the Holland and Powell (1990) (HP 90, dashed line) and Berman (1988) (B 88, dotted line) data sets, but the magnesite-quartz reaction was reversed about 1 kbar higher than the data set predictions. This comparison shows that our results on the latter reaction are not the product of temperature or pressure miscalibration, but rather that there is some internal inconsistency in both data sets.

Table 2. Reversed experiments on the reaction magnesite + quartz = enstatite + CO_2 (Reaction 1)

Expt.	*T* (°C)	*P* (kbar)	*t* (h)	Expected CO_2 loss (mg)	Actual CO_2 loss (mg)	Results by XRD
5.105	638	7.5	353	1.12	0.29	magn + qtz
5.56	640	7.9	166	1.02	0.68	magn + qtz
5.86	660	8.1	211	1.07	1.11	no reaction
5.104	663	7.5	291	1.24	1.51	en + CO_2
5.95	670	8.0	238	1.21	1.36	en + CO_2
5.54	680	8.0	136	0.85	1.31	en + CO_2
5.22	700	8.5	211	0.82	1.49	en + CO_2
5.21	700	9.0	141	1.24	1.23	no reaction
5.32	700	9.2	138	0.91	1.26	en + CO_2
ME-1	700	9.2	214	1.65	1.41	no reaction
5.24	700	9.4	119	0.88	0.79	no reaction
5.33	700	9.9	120	0.90	0.86	no reaction
ME-2	715	9.2	190	3.71	4.01	en + CO_2
ME-4	715	10.0	172	1.23	1.53	en + CO_2
ME-5	715	10.0	172	1.23	1.53	en + CO_2
ME-9	715	10.0	216	0.32	0.47	en + CO_2
ME-8	715	10.2	271	1.47	1.75	en + CO_2
ME-3	715	10.4	261	1.27	1.57	no reaction
ME-7	715	10.6	240	0.95	0.75	magn + qtz
ME-6	715	11.0	245	1.55	0.90	magn + qtz
5.34	720	10.1	113	1.00	1.47	en + CO_2
5.103	721	10.2	143	1.13	1.07	no reaction
5.53	730	12.0	143	1.10	0.64	magn + qtz
5.75	750	12.0	141	1.14	0.97	no reaction
5.23	750	13.5	139	0.83	0.23	magn + qtz
5.111	762	12.5	134	1.07	0.56	magn + qtz
5.46	770	12.0	67	1.09	1.15	no reaction
5.65	770	14.1	73	0.65	0.22	magn + qtz
5.106	781	12.5	95	1.14	1.25	no reaction
5.55	782	11.9	166	0.97	1.90	en + CO_2
5.67	800	15.7	43	1.03	0.36	magn + qtz
5.102	801	14.0	110	1.13	0.44	magn + qtz
5.101	816	15.5	91	1.03	0.82	magn + qtz
5.96	820	13.9	89	1.14	1.76	en + CO_2
5.69	840	15.9	70	0.94	0.79	no reaction
5.71	850	16.0	67	0.89	0.29	magn + qtz
5.99	851	15.4	73	0.94	1.43	en + CO_2
5.93	870	15.9	62	1.19	1.52	en + CO_2
5.97	870	17.5	30	1.12	0.82	magn + qtz
5.94	870	17.8	44	1.06	1.33	en + CO_2
5.100	890	17.6	25	1.13	1.59	en + CO_2
5.70	890	17.8	45	1.06	1.60	en + CO_2

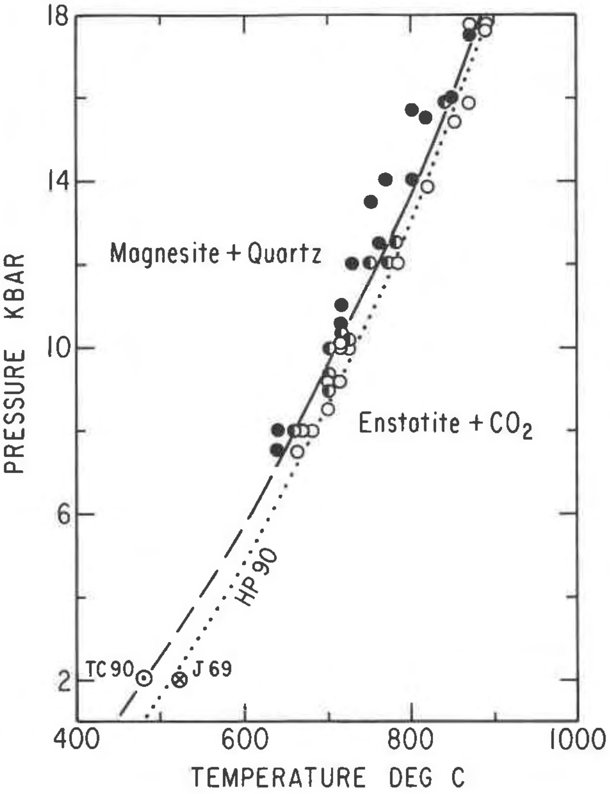

Fig. 2. Reversals of the equilibrium magnesite + quartz = enstatite + CO_2. The dashed portion of the equilibrium curve is an extrapolation based on the measured thermodynamic data of Table 5. Our curve comes close to the 2 kbar equilibrium temperature of 490 °C suggested by Trommsdorff and Connolly (1990) (TC 90) on the basis of interpretation of natural parageneses. Shown for comparison is the predicted equilibrium curve of Holland and Powell (1990) (HP 90). At 2 kbar their prediction is close to the projected temperature estimate of 520 °C of Johannes (1969) (J 69). The predicted curve of Berman (1988) is very similar to the Holland-Powell curve.

sensor throughout an experiment. Reaction progress in the quenched samples was determined both by mass loss upon puncturing the sample capsules and by comparing X-ray diffraction peak heights for a sample before and after an experiment.

Results of experiments

All experiments on Reaction 1 are listed in Table 2 and shown in Figure 2. The data include all experiments during which both inner and outer capsules maintained constant mass. In every experiment the indications of the puncture mass loss and the X-ray diffraction peak-height criteria were in agreement. In a few experiments, the X-ray pattern had peak heights within statistical uncertainty of standardization of the starting material. These are tabulated as "no reaction." Usually the puncture mass loss was <10% different from the expected value in these experiments. In general, the experiments are, within experimental error, consistent with a univariant *P-T* curve that converges with the Holland and Powell (1990) data set prediction at high temperatures but diverges to higher pressures at lower temperatures. One of the present experiments, no. 5.94 (Table 2) at 870 °C and 17.8 kbar is in slight disagreement with the other experiments for unknown reasons.

Experiment no. ME-8 (Table 2) is a critical experiment for comparison with the data set predictions. Complete data for this experiment are given in Table 3. The buffer was completely effective: No H_2O was produced in the inner capsule by H_2 infiltration, and no reduction of CO_2 occurred. The sample inverted completely to enstatite + CO_2 in 11 d. The experiment shows that Equilibrium 1 lies above 10 kbar at 715 °C, in contrast to the 9.2 kbar predicted by Holland and Powell (1990) and 9.6 kbar of Berman (1988).

Newton and Sharp (1975) noted a slight expansion of the lattice constants of magnesite quenched from 1400 °C and 40 kbar, perhaps because of thermal disordering. We made an X-ray diffraction scan of the quenched sam-

Table 3. Data for experiment ME-8

	Weight (g)
Before expt.	
Pt capsule	0.14805
+ Ag oxalate	0.15311
+ Starting mix	0.15585
Welded	0.15576
After expt.*	
Pt capsule	0.15580
After puncture**	0.15405
Dried at 120 °C, 1 h	0.15405
Dried at 350 °C, 0.5 h	0.15404

Note: ME-8 experimental conditions were 715 °C, 10.2 kbar, for 271 h. The starting mix was enstatite, magnesite, and quartz, about equal masses of each, finely powdered. Expected CO_2 loss was 1.47 mg. Actual CO_2 loss was 1.75 mg.

* X-ray diffraction analysis showed nearly complete reaction to enstatite, with no detectable magnesite and a small amount of quartz present.

** Capsule was punctured as it was partially submerged in liquid N_2.

ple of experiment no. 5.97, Table 2, with an internal quartz standard. No angular departures from the peak positions of the starting material were detected in this 870 °C experiment.

Table 4 lists our experiments on Reaction 2, and these and all other reversed experiments on magnesite decomposition up to 1000 bars are shown in Figure 3. Our experiments are consistent with the two carefully determined brackets of Johannes and Metz (1968) but slightly violate one of the reversed experiments of Harker and Tuttle (1955). The discrepancy with the latter authors could result from fast back reaction in slow-quenching cold-seal apparatus, which could give a falsely high-temperature impression of magnesite stability, as emphasized by Johannes and Metz (1968). Our data constrain the equilibrium within the pressure interval of 560–620 bars at 715 °C. This is consistent with the prediction of the Holland-Powell data set but is considerably higher than the 430 bars predicted by Berman (1988).

DISCUSSION

Our results support the prediction of Trommsdorff and Connolly (1990), made on the basis of analysis of natural parageneses, that the reaction of magnesite and quartz to produce enstatite and CO_2 indeed lies higher in pressure and lower in temperature than predicted by the data set of Berman (1988). The discrepancy in pressure at 700 °C is about 1 kbar, and there is a slightly larger discrepancy with the prediction of Holland and Powell (1990). If this discrepancy persists down to 2 kbar, as is likely, the equilibrium temperature of Reaction 1 would be about 495 °C, close to the value shown by Trommsdorff and Connolly (1990). Their revision of the topology of mineral equilibria in the system $CaO\text{-}MgO\text{-}SiO_2\text{-}CO_2\text{-}H_2O$ is supported. The value of field testing thermodynamically calculated mineral equilibria receives an additional recommendation, in support of those who have advocated this method (Berg and Dokka, 1983; Johnson, 1963; Pattison, 1992; Schuiling, 1957).

Table 4. Reversed experiments on the reaction magnesite = periclase + CO_2 (Reaction 2)

Expt.	*T* (°C)	*P* (bar)	*t* (h)	Expected CO_2 loss (mg)	Actual CO_2 loss (mg)	Results by XRD
MP-16	717	560	188	1.03	2.06	periclase
MP-15	715	579	101	0.81	0.84	no reaction
MP-17	715	602	114	1.28	1.38	no reaction
MP-14	715	621	102	1.26	0.63	magnesite
MP-12	715	900	138	1.18	0.66	magnesite

Note: All experiments were performed in an internally heated gas-vessel apparatus (see text). Uncertainty in temperature measurement is ±2 °C. Uncertainty in pressure measurements is ±4 bars.

The discrepancy of our results on Reaction 1 with the data sets indicates the need to revise the thermodynamic data for either enstatite or magnesite because the data of quartz and CO_2 are very well known in the temperature and pressure range around 700 °C and 10 kbar. By using our data for Reactions 1 and 2 simultaneously, magnesite may be eliminated and the Gibbs free energy of the resultant Reaction 3, the formation reaction of enstatite, may be obtained directly. The only quantities that need be considered, apart from the equilibrium pressures of Reactions 1 and 2, are the heat-capacity functions of enstatite and its component oxides, the molar volumes, the compressibilities and thermal expansions of the solid phases, and the f_{CO_2} at 10.4 and 0.6 kbar. The former fugacity requires a slight and straightforward extrapolation from the tables of Shmulovich and Shmonov (1978)

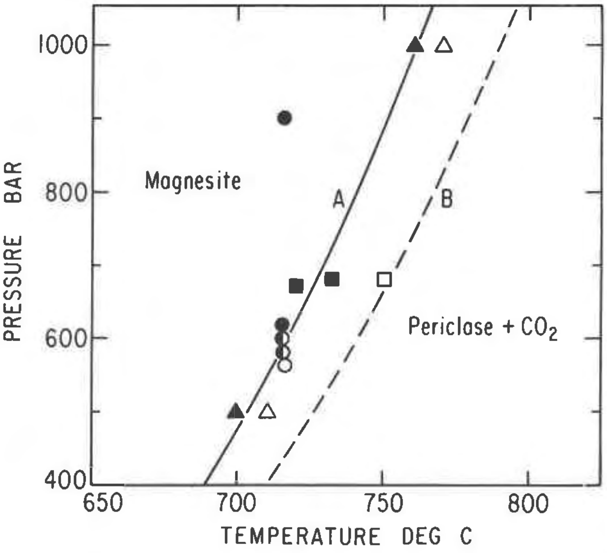

Fig. 3. Experimental reversals of the equilibrium magnesite = periclase + CO_2 in the range 400–1000 bars. Circles = present experiments. Half-solid circles indicate no observable reaction. Squares = Harker and Tuttle (1955). Triangles = Johannes and Metz (1968). Curve A is calculated from the data of Table 5. Curve B is the prediction of Berman (1988). The predicted curve of Holland and Powell (1990) is similar to the present experimental curve.

TABLE 5. Thermodynamic data and sources relevant to derivations in the text

	S_{298}	a	$b \times 10^3$	$c \times 10^{-4}$	$d \times 10^5$	e	V_{298}	$aV \times 10^5$	$bV \times 10^6$	Ref.*
Enstatite	66.27	350.7	−147.3	167.9	5.826	−4296.0	3.131	9.0	2.3	1, 2
Magnesite	65.09	81.119	52.254	−183.20	0	0	2.803	10.6	3.0	2, 3**
α quartz	41.46	81.145	18.283	−18.099	0.5406	−698.46	2.269	8.0	5.9	2, 4
β quartz		57.959	9.330	183.471	0	0	2.367	0	2.6	2, 4
Periclase	26.94	65.211	−1.2699	−46.185	0	−387.24	1.125	4.6	0.7	2, 3
CO_2	213.79	87.82	−2.644	70.641	0	−998.86				3
Corundum	50.92	157.36	0.719	−189.69	0	−998.04	2.558	6.4	0.9	3
Pyrope	266.27	544.95	20.68	−833.12	0	−2283.0	11.318	29.8	6.3	2, 5

Note: Heat capacity: $C_P = a + bT + cT^{-2} + dT^2 + eT^{-1/2}$. Specific volume: $V(T,P) = V_{298} + (T - 298)(\alpha V) - P(\beta V)$. Units for entropy ($S$), heat-capacity coefficients (a–e), volume (V), expansivity (αV), and compressibility (βV) are in joules, kelvin, and bars.

* References: 1 = Krupka et al. (1979), 2 = Holland and Powell (1990), 3 = Robie et al. (1978), 4 = Hemingway (1987), 5 = Haselton (1979). Ref. 4 gives ΔH (α-quartz to β-quartz) = 625 J at 844 K. Ref. 5 gives $H_{973} - H_{298}$ = 295 330 ± 1180 J and 74290 ± 300 J for pyrope and enstatite, respectively. Cohen and Klement (1967) give $\alpha - \beta$ quartz equilibrium at 5990 bar and 988 K. Shmulovich and Shmonov (1978) give interpolated and extrapolated f_{CO_2} at 988 K: 682 J at 600 bar; 349 261 J at 10400 bar.

** Magnesite heat-capacity coefficients are the extrapolation of Ref. 3.

to 10 kbar. Quantities necessary for the calculations are contained in Table 5. The resulting Gibbs free energy and enthalpy of formation of enstatite from the oxides are, respectively, −32.78 ± 0.73 kJ and −33.41 ± 0.83 kJ at 298 K. These quantities are compared in Table 6 with others resulting from solution calorimetry and those tabulated in several data set compilations.

There is good agreement between our direct experimental determination of ΔH^0_f of enstatite and the several experimentally derived data set predictions, except for the value of Holland and Powell (1990), which is 1 kJ less negative. Our value of the enthalpy of formation of enstatite is close to that of the most recent solution calorimetric determination, that of Brousse et al. (1984). These workers made use of a eutectic $(Li,Na)_2B_2O_4$ solvent operating at 800 °C, which is more reactive to MgO than the calorimetric solvents formerly used. The Brousse et al. (1984) study simultaneously dissolved mixtures of MgO and SiO_2 on the composition $MgSiO_3$ to maintain the stoichiometry of Reaction 3. This procedure appears to minimize solvent interactions with the basic (MgO) and acid (SiO_2) oxides that arise when they are dissolved separately, as was formerly the procedure in high-temperature solution calorimetry. Chai and Navrotsky (1993) also obtained a value for ΔH^0_f close to that of Brousse et al. (1984). Their value of −33.9 ± 2.8 kJ/mol was calculated from their calorimetry experiments on magnesite and quartz and the work of Ito et al. (1990). The present phase equilibrium value of ΔH^0_f (enstatite) is more precise by a factor of two than the Brousse et al. (1984) and the Chai and Navrotsky (1993) calorimetric values.

TABLE 6. Determinations of enthalpy of formation from the oxides ($\Delta H^0_{f,298}$) of enstatite, $MgSiO_3$ in kilojoules per mole

$\Delta H^0_{f,298}$ (kJ/mol)	Reference	Solvent, T(K)
	Calorimetric determination	
−35.73 ± 0.63	Torgeson and Sahama (1948)	HF, 346
−35.73 ± 0.83	Shearer and Kleppa (1973)	$Pb_2B_2O_5$, 970
−36.90 ± 0.71	Charlu et al. (1975)	$Pb_2B_2O_5$, 970
−34.18 ± 1.92	Kiseleva et al. (1979)	$Pb_2B_2O_5$, 1170
−35.98 ± 0.88	Chatillon-Colinet et al. (1983)	$(Na,Li)BO_2$, 1170
−33.93 ± 1.76	Brousse et al. (1984)	$(Na,Li)BO_2$, 1073
−33.9 ± 2.8	Chai and Navrotsky (1993)*	
	Phase-equilibrium determination	
−33.46	Day et al. (1985)	
−33.65	Berman et al. (1986)	
−34.15**	Saxena and Chatterjee (1986)	
−33.35	Berman (1988)	
−32.48 ± 1.04	Holland and Powell (1990)	
−33.41 ± 0.83	present study	

* Calculated as described in the text.

** Uses C_P data of Table 5 to correct from 970 K.

An enthalpy of formation of magnesite from the oxides at 298 K can be derived from the present determination of Reaction 2. The data of Table 5 are used in these calculations. These calculations use the Robie et al. (1978) extrapolation of the heat-capacity functions of magnesite. Our calculations give −116.68 ± 0.47 kJ, or −1111.68 kJ from the elements, compared with −1112.48 ± 0.81 kJ of Holland and Powell (1990) and −1113.64 kJ of Berman (1988). A recent revision by Chernosky and Berman (1989) based on experimental phase-equilibrium relations of magnesite, spinel, and clinochlore yields $\Delta H^0_{f,298}$ (magnesite) of −1114.51 kJ, in worse agreement with our phase-equilibrium value. It appears that the source of the discrepancy in Reaction 1 of the Berman (1988) data set lies primarily in ΔH^0_f of magnesite, which is about 2 kJ too negative. The source of error in the Holland and Powell (1990) data set exists in the ΔH^0_f of both magnesite and enstatite. Because of the lack of measured heat capacities of magnesite in this temperature range, it cannot be stated at present how much the uncertainty in high-temperature entropy of disordering of magnesite contributes to the discrepancy. The stability curve of magnesite calculated from the data of Table 5 is shown in Figure 3. The calculated curve (curve A) barely satisfies the 1000 bar bracket of Johannes and Metz (1968); the marginal agreement may be the result of the onset of significant temperature-dependent disorder of magnesite, not considered in the heat-capacity expression of Table 5. This disorder might stabilize magnesite to higher temperatures than predicted by Table 5.

The present improved enthalpy of formation value for enstatite may be used in conjunction with the heat of solution work of Eckert et al. (1992) to yield a calorimetric ΔH^0_f for pyrope garnet, $Mg_3Al_2Si_3O_{12}$. They measured the solution enthalpy of synthetic pyrope and of a chemically equivalent homogenous mixture of synthetic enstatite and corundum in molten $Pb_2B_2O_5$ at 973 K. Their value of ΔH^0 at that temperature for the reaction of pyrope to 3 enstatite + corundum is -27.73 ± 4.33 kJ. The heat contents of synthetic pyrope and enstatite at 973 K were determined precisely by Haselton (1979) using drop calorimetry, as was that of corundum much earlier by numerous workers, summarized in Robie et al. (1978). Relevant data are given in Table 5. These data unambiguously yield a calorimetric $\Delta H^0_{f,298}$ of pyrope of -70.39 ± 4.71 kJ from the oxides, or -6282.42 kJ from the elements. This value is in very good agreement with the value of -6283.32 ± 3.23 kJ of Holland and Powell (1990) derived from experimental phase-equilibrium data; the discrepancy between solution-calorimetry and phase-equilibrium determinations of ΔH^0_f of pyrope cited by Holland and Powell (1985) is resolved by the present work. The Berman (1988) value of -6286.55 kJ is marginally in agreement with our own value.

ACKNOWLEDGMENTS

This research was supported by National Science Foundation grant EAR-9310264 to R.C.N. Careful reviews by Alan Woodland and an anonymous reviewer led to significant improvement of this paper.

REFERENCES CITED

Berg, J.H., and Dokka, J.A. (1983) Geothermometry in the Kiglapait contact aureole, Labrador. American Journal of Science, 283, 414–434.

Berman, R.G. (1988) Internally-consistent thermodynamic data for minerals in the system Na_2O-K_2O-CaO-MgO-FeO-Fe_2O_3-Al_2O_3-SiO_2-TiO_2-H_2O-CO_2. Journal of Petrology, 29, 445–522.

Berman, R.G., Engi, M., Greenwood, H.J., and Brown, T.H. (1986) Derivation of internally-consistent thermodynamic data by the technique of mathematical programming: A review with application to the system MgO-SiO_2-H_2O. Journal of Petrology, 27, 1331–1364.

Brousse, C., Newton, R.C., and Kleppa, O.J. (1984) Enthalpy of formation of forsterite, enstatite, akermanite, monticellite and merwinite at 1073 K determined by alkali borate solution calorimetry. Geochimica et Cosmochimica Acta, 39, 1487–1497.

Burnham, C.W., Holloway, J.R., and Davis, N.F. (1969) Thermodynamic properties of water to 1,000°C and 10,000 bars. Geological Society of America Special Paper, 132, 1–96.

Chai, L., and Navrotsky, A. (1993) Thermochemistry of carbonate-pyroxene equilibria. Contributions to Mineralogy and Petrology, 114, 139–147.

Charlu, T.V., Newton, R.C., and Kleppa, O.J. (1975) Enthalpies of formation at 970 K of compounds in the system MgO-Al_2O_3-SiO_2 from high temperature solution calorimetry. Geochimica et Cosmochimica Acta, 39, 1487–1497.

Chatillon-Colinet, C., Kleppa, O.J., Newton, R.C., and Perkins, D. (1983) Enthalpy of formation of $Fe_3Al_2Si_3O_{12}$ (almandine) by high temperature alkali borate solution calorimetry. Geochimica et Cosmochimica Acta, 47, 439–444.

Chatterjee, N.D., Johannes, W., and Leistner, H. (1984) The system CaO-Al_2O_3-SiO_2-H_2O: New phase equilibrium data, some calculated phase relations, and their petrological applications. Contributions to Mineralogy and Petrology, 88, 1–13.

Chernosky, J.V., and Berman, R.G. (1989) Experimental reversal of the equilibrium: Clinochlore + 2 magnesite = 3 forsterite + spinel + 2 CO_2 + 4 H_2O and revised thermodynamic properties for magnesite. American Journal of Science, 289, 249–266.

Cohen, L.H., and Klement, W.J. (1967) High-low quartz inversion: Determination to 35 kilobars. Journal of Geophysical Research, 72, 4245–4251.

Day, H.W., Chernosky, J.V., and Kumin, H.J. (1985) Equililbria in the system MgO-SiO_2-H_2O: A thermodynamic analysis. American Mineralogist, 70, 237–248.

Eckert, J.O., Newton, R.C., and Kleppa, O.J. (1992) Enthalpy change of the reaction 3/2 enstatite + corundum = pyrope. Geochimica et Cosmochimica Acta, 56, 3971–3978.

Evans, B.W., and Trommsdorff, V. (1974) Stability of enstatite + talc, and CO_2-metasomatism of metaperidotite, Val d'Efra, Lepontine Alps. American Journal of Science, 283A, 274–296.

Harker, R.I., and Tuttle, O.F. (1955) Studies in the system CaO-MgO-CO_2: I. The thermal dissociation of calcite, dolomite and magnesite. American Journal of Science, 253, 209–224.

Haselton, H.T. (1979) Calorimetry of synthetic pyrope-grossular garnets and calculated stability relations. Ph.D. thesis, University of Chicago, Chicago, Illinois.

Helgeson, H.C., Delany, J.M., Nesbitt, H.W., and Bird, D.K. (1978) Summary and critique of the thermodynamic properties of rock-forming minerals. American Journal of Science, 278A, 1–204.

Hemingway, B.S. (1987) Quartz: Heat capacities from 340 to 1000 K and revised values for the thermodynamic properties. American Mineralogist, 72, 273–279.

Holland, T.J.B., and Powell, R. (1985) An internally consistent thermodynamic dataset with uncertainties and correlations: II. Data and results. Journal of Metamorphic Petrology, 3, 343–353.

——— (1990) An enlarged and updated internally consistent thermodynamic dataset with uncertainties and correlations: The system K_2O-Na_2O-CaO-MgO-MnO-FeO-Fe_2O_3-Al_2O_3-TiO_2-SiO_2-C-H_2-O_2. Journal of Metamorphic Petrology, 8, 89–124.

Ito, E., Akaogi, M., Topor, L., and Navrotsky, A. (1990) Negative pressure-temperature slopes for reaction forming $MgSiO_3$ perovskite from calorimetry. Science, 249, 1275–1278.

Jenkins, D.M., Newton, R.C., and Goldsmith, J.R. (1985) Relative stability of Fe-free zoisite and clinozoisite. Journal of Geology, 93, 663–672.

Johannes, W. (1969) An experimental investigation of the system MgO-SiO_2-H_2O-CO_2. American Journal of Science, 267, 1083–1104.

Johannes, W., and Metz, P. (1968) Experimentelle Bestimmungen von Gleichgewichtsbeziehungen im System MgO-CO_2-H_2O. Neues Jahrbuch für Mineralogie Monatshefte, 15–26.

Johnson, M.R.W. (1963) Some time relations of movement and metamorphism in the Scottish Highlands. Geologie en Mijnbouw, 42, 121–142.

Kiseleva, I.A., Ogorodova, L.P., Topor, N.D., and Chigareva, O.G. (1979) A thermochemical study of the CaO-MgO-SiO_2 system. Geochemistry International, 16, 122–134.

Krupka, K.M., Robie, R.A., and Hemingway, B.S. (1979) High-temperature heat capacities of corundum, periclase, anorthite, $CaAl_2Si_2O_8$ glass, muscovite, pyrophyllite, $KAlSi_3O_8$ glass, grossular, and $NaAlSi_3O_8$ glass. American Mineralogist, 64, 86–101.

Newton, R.C. (1987) Thermodynamic analysis of phase equilibria in simple mineral systems. In Mineralogical Society of America Reviews in Mineralogy, 17, 1–33.

Newton, R.C., and Sharp, W.E. (1975) Stability of forsterite + CO_2 and its bearing on the role of CO_2 in the mantle. Earth and Planetary Science Letters, 26, 239–244.

Pattison, D.R.M. (1992) Stability of andalusite and sillimanite and the Al_2SiO_5 triple point: Constraints from the Ballachulish Aureole, Scotland. Journal of Geology, 100, 423–446.

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. U.S. Geological Survey Bulletin, 1452, 1–456.

Rosenbaum, J.M., and Slagel, M.M. (1995) C-O-H speciation in piston-cylinder experiments. American Mineralogist, 80, 109–114.

Saxena, K., and Chatterjee, N. (1986) Thermochemical data on mineral phases: The system CaO-MgO-Al_2O_3-SiO_2. Journal of Petrology, 27, 827–842.

Schuiling, R.D. (1957) A geo-experimental phase diagram of Al_2SiO_5. Proceedings of the Netherlands Academy of Sciences, B series, 60, 220–226.

Shearer, J.A., and Kleppa, O.J. (1973) The enthalpies of formation of $MgAl_2O_4$, $MgSiO_3$, Mg_2SiO_4, and Al_2SiO_5 by oxidemelt calorimetry. Journal of Inorganic Nuclear Chemistry, 35, 1073–1078.

Shmulovich, K.I., and Shmonov, V.M. (1978) Tables of thermodynamic properties of gases and liquids (carbon dioxide), 165 p. USSR Academy of Sciences, Moscow Bureau of Standards, Moscow.

Slaughter, J., Kerrick, D.M., and Wall, V.J. (1975) Experimental and thermodynamic study of equilibria in the system CaO-MgO-SiO_2-H_2O-CO_2. American Journal of Science, 275, 143–162.

Torgeson, D.R., and Sahama, T.G. (1948) A hydrofluoric acid solution calorimeter and the determination of the heats of formation of Mg_2SiO_4, $MgSiO_3$, and $CaSiO_3$. Journal of the American Chemical Society, 70, 2156–2160.

Trommsdorff, V., and Connolly, J.A.D. (1990) Constraints on phase diagram topology for the system CaO-MgO-SiO_2-CO_2-H_2O. Contributions to Mineralogy and Petrology, 104, 1–7.

MANUSCRIPT RECEIVED DECEMBER 8, 1994
MANUSCRIPT ACCEPTED JULY 24, 1995