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Enthalpy of formation of wollastonite ($CaSiO_3$) and anorthite ($CaAl_2Si_2O_8$) by experimental phase equilibrium measurements and high-temperature solution calorimetry

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ABSTRACT

The Gibbs free energy of the reaction

$$\underset{\text{calcite}}{CaCO_3} + \underset{\text{quartz}}{SiO_2} = \underset{\text{wollastonite}}{CaSiO_3} + \underset{\text{vapor}}{CO_2}$$

was precisely determined at 700, 750, 800, and 850 °C by measuring the equilibrium pressures in an internally heated gas pressure apparatus. The mean $\Delta G^0_{R,298}$ is 41.78 ± 0.18 kJ. Using the accurately measured dissociation pressures of calcite in this temperature range and the available high-precision thermal data for calcite and wollastonite and their component oxides, a molar enthalpy of formation of wollastonite of $\Delta H^0_{f,298} = -89.61 \pm 0.21$ kJ from the oxides is derived. This value agrees very well with both acid and oxide melt solution calorimetry but is considerably more precise than the calorimetric determinations. It is 2–4 kJ more negative than the values of two widely used standard data sets.

The enthalpy of formation of anorthite was measured by $Pb_2B_2O_5$ melt solution calorimetry at 1000 K. A highly ordered natural metamorphic anorthite from Naxos and a well-crystallized sample prepared at 1650 K were measured. The reference assemblage was a homogenized equimolar mechanical mixture of pure natural wollastonite and quartz and synthetic corundum. The mean enthalpy of solution values $\Delta\overline{H}$, kJ/mol), twice the standard deviation on the mean (δ), and the number of solution experiments (N) are tabulated:

Material	N	$\Delta\overline{H}$	δ
anorthite (1650 K)	9	65.84	0.98
anorthite (Naxos)	11	67.17	1.11
wollastonite + corundum + quartz	10	53.69	1.04

With our phase equilibrium ΔH^0_f of wollastonite, the enthalpy of solution data yield $\Delta H^0_{f,298}$ (anorthite, natural) = -100.10 ± 1.56 kJ/mol and $\Delta H^0_{f,298}$ (anorthite, synthetic) = -98.77 ± 1.46 kJ/mol, both from the oxides. The small enthalpy difference between natural and synthetic anorthite would correspond to only about 2% Al-Si disorder in the 1650-K synthetic sample. The enthalpy of formation values are ~10 kJ/mol less negative than those given by older acid solution calorimetry, and 2–4 kJ/mol more negative than those given by more recent oxide melt calorimetry.

The present enthalpy of formation work on wollastonite and anorthite, together with the large number of hydrothermal reversals of the univariant P-T curve of the reaction

$$\underset{\text{grossular}}{Ca_3Al_2Si_3O_{12}} + \underset{\text{quartz}}{SiO_2} = \underset{\text{wollastonite}}{2CaSiO_3} + \underset{\text{anorthite}}{CaAl_2Si_2O_8}$$

leads to an accurate enthalpy of formation of grossular from the oxides of -329.44 ± 2.83 or -332.41 ± 2.83 kJ/mol, depending on which of two competing sets of thermal data for grossular are used.

Our enthalpy of formation data for wollastonite, anorthite, and grossular agree more closely with corresponding values of the data set of Holland and Powell (1990) than with that of Berman (1988).

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INTRODUCTION

Self-consistent data sets and calorimetry

The use of thermodynamic data sets for calculations of mineral equilibria is an increasingly important direction in geochemistry. These data sets incorporate the more precisely measured properties of minerals, mainly volumetric and thermophysical, and derive thermochemical properties, such as enthalpy of formation, mainly from the large body of experimental phase equilibrium data that now exists. Simultaneous regression of all experimental data generates an internally self-consistent set of the derived properties. Reliance on phase equilibrium derivations is necessary because of the small amount of solution calorimetric data available for minerals and because of the relatively low precision of many of the existing data. Entropy data of minerals are derived from phase equilibria for those substances that have not been investigated with thermophysical methods; entropy derivation often is necessary for minerals with configurational entropy of atomic disorder.

Solution calorimetry is important for the derived self-consistent data sets as a control on possible ranges of thermochemical properties. In the Berman (1988) method, solution calorimetry is actually an input quantity that serves to optimize the derived enthalpy of formation values for some minerals. The method of linear parametric analysis of experimental phase equilibrium data defines possible ranges of the enthalpy change, ΔH_R, and the entropy change, ΔS_R, of experimental reactions, and, if enough suitable reaction data are available, it is often possible to extract enthalpy of formation values, ΔH_f°, for individual minerals. By a method introduced by Day and Kumin (1980), ΔH_R and ΔS_R pairs are selected that show minimal deviations from calorimetrically measured values (solution calorimetric in the case of ΔH_R). Solution calorimetric data do not enter the Holland and Powell (1985, 1990) data sets as directly as in the Berman (1988) data set but are of considerable value for comparison with derived ΔH_f°.

Wollastonite, anorthite, and the calc-silicate minerals

Two of the best-characterized minerals of the data sets are wollastonite, $CaSiO_3$, and anorthite, $CaAl_2Si_2O_8$. Both minerals can occur as nearly pure end-member substances, and many measurements have been made of their thermophysical and thermochemical properties, using both natural materials and synthetic substances. There exists a large body of experimental phase equilibrium work on reactions involving the two minerals in the simple system $CaO\text{-}Al_2O_3\text{-}SiO_2\text{-}H_2O\text{-}CO_2$. Consequently, wollastonite and anorthite are among the most important minerals in the self-consistent data sets.

High-quality heat-capacity measurements are available for wollastonite, including precise high-temperature drop-calorimetry measurements by Richet et al. (1991). Several solution calorimetry studies have been carried out to define ΔH_f° (Table 1). As is typical for silicate minerals, however, the measurements of enthalpy of formation by high-temperature solution calorimetry are not of sufficient precision for many phase equilibrium calculations. The major data sets were created with derived values of ΔH_f° (Table 1).

The most important simple reaction that serves to define the properties of wollastonite from phase equilibrium derivations is

$$\underset{\text{calcite}}{CaCO_3} + \underset{\text{quartz}}{SiO_2} = \underset{\text{wollastonite}}{CaSiO_3} + \underset{\text{vapor}}{CO_2}. \quad (1)$$

This is an important reaction in the high-temperature contact metamorphism of impure limestones and is an isograd reaction of high-grade regional metamorphism. In spite of its importance to the data sets and to petrology, the available experimental determinations (Harker and Tuttle, 1955; Greenwood, 1967; Ziegenbein and Johannes, 1974) are fragmentary and inconsistent. A considerable improvement in the tabulated properties of the calc-silicate minerals could be realized by a superior experimental determination of Reaction 1.

Anorthite is one of the two major solid-solution components of plagioclase feldspar. It occurs as a nearly pure substance in many calc-silicate rocks and skarns derived from the high-temperature metamorphism of limestones, in some gabbros and peridotites, and in lunar rocks. Plagioclase is a participant in many reactions that form a basis for geothermometric and geobarometric analysis of crustal processes.

Anorthite is a highly ordered framework silicate principally because of its 1:1 ratio of $^{[4]}Al$ and $^{[4]}Si$. This ratio makes possible a three-dimensional linkage in which Al-bearing tetrahedra alternate with Si-bearing tetrahedra; the preference of framework silicates for Al-O-Si linkages rather than Al-O-Al linkages has been called Al avoidance (Goldsmith and Laves, 1955). In this regard, anorthite is more easily characterized crystallographically than albite, $NaAlSi_3O_8$, the other principal component of plagioclase, which exists both in synthetic and natural materials in the high (Al-Si disordered) and low (Al-Si ordered) structural states.

Small amounts of Al-Si disorder in anorthite nonetheless exercise an important influence on the thermodynamics of anorthite stability. Configurational enthalpy is a significant quantity, even for small amounts of cation disorder, as emphasized for the spinel minerals by Navrotsky and Kleppa (1968). For anorthite, only 4% of cation disorder would result in a configurational entropy increment of 3 J/(K·mol), an amount that would have a large effect on calculated phase equilibrium relations with other rock-forming minerals. Such a small amount of disorder would be difficult to observe by ordinary X-ray diffraction methods. The fact that some natural anorthite samples show X-ray diffraction criteria of disordering (Smith, 1974), as do synthetic high-temperature samples (Angel et al., 1990) indicates that possible enthalpy and entropy effects of anorthite disorder should be considered.

TABLE 1. Measured and derived values of enthalpy of formation from the oxides of wollastonite ($CaSiO_3$) and anorthite ($CaAl_2Si_2O_8$)

Wollastonite		Anorthite
	Calorimetrically measured values	
	Acid	
−89.43 ± 0.54	Hemingway and Robie (1977) (review)	−110.85 ± 3.43
(N) −88.91 ± 0.54	Torgesen and Sahama (1948)	
	Oxide melt	
(S) −87.52 ± 1.51	Charlu et al. (1978)	(S) −92.74 ± 1.88
(N) −87.98 ± 1.50		(N) −96.34 ± 1.42
(N) −87.91 ± 1.05	Kiseleva et al. (1979)	
	Newton et al. (1980)	(S) −96.80 ± 0.96
	Derived values	
−89.43 ± 0.54	Robie et al. (1979)	−96.9 ± 3.4
−87.91 ± 1.05	Halbach and Chatterjee (1984)	−103.41
−88.90	Saxena and Chatterjee (1986)	−98.52
−85.71	Berman (1988)	−96.54
−88.09 ± 1.29	Holland and Powell (1990)	−101.15 ± 1.98
	Present	
−89.61 ± 0.21	(Natural)	−100.10 ± 1.56
	(Synthetic)	−98.77 ± 1.46

Note: 298 K, kJ/mol; S = synthetic, N = natural.

Deductions from experimental phase equilibrium relations have suggested to several workers that synthetic anorthite characteristically shows 2–4 J/(K·mol) of disorder entropy (Wood and Holloway, 1984; Gasparik, 1984; Koziol and Newton, 1988). The systematic variation in enthalpy of solution at high-temperature synthetic anorthite with length of annealing time found by Carpenter (1991) in his extensive calorimetric study suggests that an equilibrium disordering state may be approached in several hours in samples annealed at 1400 °C. Two major mineral data sets (Berman, 1988; Holland and Powell, 1990), however, were created with anorthite as an essentially ordered phase: the tabulated 298 K entropy values are within 1 J/(K·mol) of the Third Law entropy determined by precise adiabatic calorimetry on synthetic samples (Krupka et al., 1979).

A problem with determination of ΔH°_f of lime-bearing minerals by solution calorimetry has been the difficulty of using CaO as a reference substance. Lime has a very large negative heat of solution in $Pb_2B_2O_5$ (Charlu et al., 1978) and $(Li,Na)_2B_2O_4$ (Brousse et al., 1984); small errors in the enthalpy of solution of CaO can cause large errors in the ΔH°_f of lime silicates. Moreover, CaO is hygroscopic; this causes weighing errors and, probably, uncontrolled heat effects in solution experiments. A more reliable reference substance for lime-bearing minerals is needed. $CaSiO_3$ is potentially a good reference substance for calorimetry; for this purpose its formation properties must be characterized independently by phase equilibrium derivations superior to those that currently exist.

Scope of the present work

In order to define more accurately the standard enthalpy of formation of anorthite by high-temperature solution calorimetry, it is important to investigate both a synthetic high-temperature anorthite and a natural metamorphic near end-member anorthite with a very high degree of ordering. The present study uses pure natural wollastonite as the reference for CaO. The enthalpy of solution values of well-characterized natural and synthetic anorthite samples are compared with the enthalpy of solution of a homogeneous equimolar mixture of wollastonite, corundum, and quartz, thus defining ΔH°_R for the reaction

$$\underset{\text{wollastonite}}{CaSiO_3} + \underset{\text{corundum}}{Al_2O_3} + \underset{\text{quartz}}{SiO_2} = \underset{\text{anorthite}}{CaAl_2Si_2O_8}. \qquad (2)$$

The enthalpy of formation of anorthite from the oxides can be retrieved with high accuracy, subject to an improved determination of the formation enthalpy of wollastonite. This quantity can be measured accurately by a precise phase equilibrium determination of the Reaction 1. It will be shown that the uncertainty in the derived ΔH°_f (wollastonite) contributes almost negligibly to the uncertainty in the calorimetric ΔH°_f of anorthite.

EXPERIMENTAL METHODS

Preparation and characterization of material

Starting materials for solution calorimetry and phase equilibrium measurements consisted of both synthetic and pure natural materials. Synthetic anorthite was prepared by annealing a glass of $CaAl_2Si_2O_8$ composition at 1375 °C for 48 h in a Pt crucible in a DelTech MoSi furnace. The glass was prepared from a thorough mechanical mixture of fine-grained high-purity reagent $CaCO_3$ (calcite), SiO_2 (glass), and Al_2O_3 (γ), decarbonated by stages and finally melted at 1600 °C and quenched in air. The glass was finely ground in an agate mortar, rehomogenized, and remelted. A pure synthetic corundum sample was prepared by annealing the γ-Al_2O_3 for 3 d in a Pt crucible at 1400 °C.

Natural materials were a sample of wollastonite from Jefferson County, New York, a sample of anorthite (An

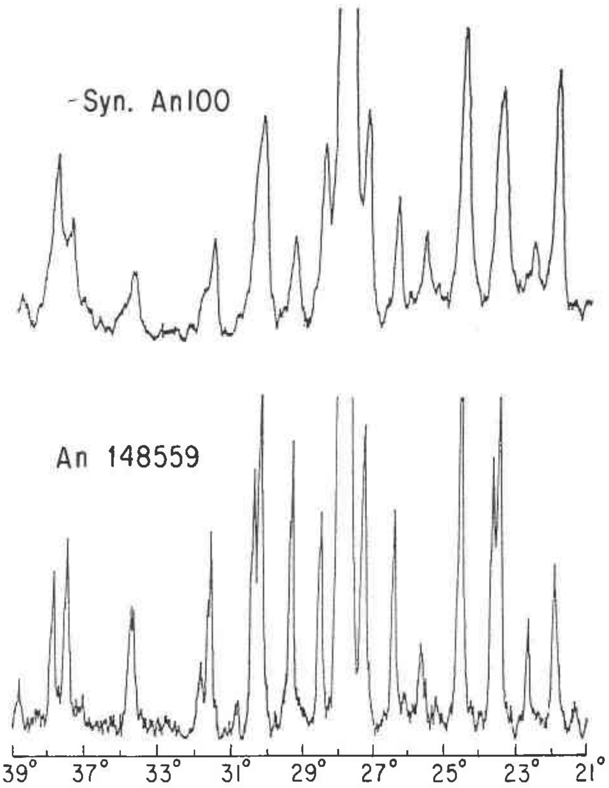

Fig. 1. X-ray powder diffraction scans at ½° 2θ/min on synthetic and natural anorthite samples. The markedly better resolution of the spectra of the natural sample is attributable to a higher degree of crystalline perfection, including more highly ordered Al and Si.

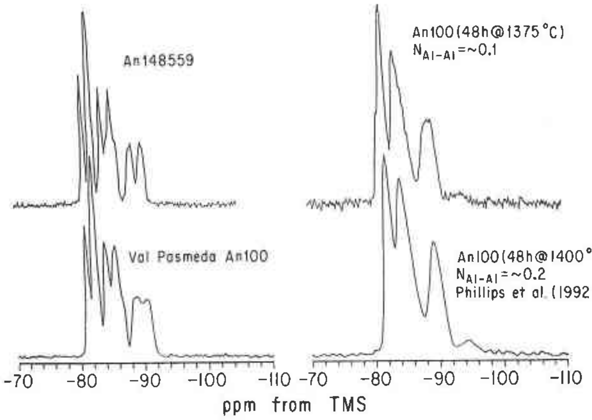

Fig. 2. The ^{29}Si magic-angle NMR spectra of synthetic and natural anorthite samples. Procedures were the same as those of Phillips et al. (1992). Broadening of the peaks and relative chemical shift compared with the natural samples (present Naxos no. 148559 and Val Pasmeda sample of Phillips et al., 1992) are attributed to a higher degree of Al-Si ordering of the natural samples. The number of moles of Al-O-Al linkages per four moles of (Al + Si) is estimated at 0.1 for the present synthetic sample, corresponding to 2.5% disorder.

99+) from Naxos, Greece, and a sample of quartz from Lisbon, Maryland. The wollastonite and quartz samples were the same as those used in the solution calorimetry of Charlu et al. (1978). Table 2 gives chemical data and unit-cell constants of the natural and synthetic anorthite and natural wollastonite, determined by powder X-ray diffractions scans at ⅛° 2θ/min using Cu*Kα* radiation and an annealed corundum internal standard. The comparison of powder diffraction scans at ½° 2θ/min of the two anorthite samples (Fig. 1) shows the superior crystallinity of the natural sample.

The ^{29}Si magic-angle NMR spectra of the natural and synthetic anorthite are compared in Figure 2. The perfection of crystallinity of the natural sample compared with the synthetic sample is evident in the fine resolution of the peaks. The chemical shift of the principal NMR peak of the synthetic sample corresponds to at most a few percent of Al-O-Al linkages (B. Phillips, 1991 personal communication).

A starting mix for the experiments on Reaction 1 was prepared from the natural wollastonite and quartz and the synthetic calcite used in the preparation of anorthite. The minerals were ground under acetone in an agate mortar numerous times until complete evaporation to homogenize the mix. Standard X-ray diffraction patterns of the starting mix were made at ½° 2θ/min.

The synthetic and natural materials for calorimetry were crushed in a agate mortar and sieved to a size fraction between −200 and −325 mesh. The materials were stored in a desiccator.

Experimental apparatus and techniques

About 6-mg portions of the Reaction 1 starting mix were sealed with weighed amounts of reagent silver oxalate ($AgC_2O_4H_2$), about 4 mg in each portion, in welded Pt tube segments of 1.6-mm diameter and 0.13-mm wall thickness. Experiments were made in an Ar-medium gas pressure vessel of the type described by Holloway (1971).

Table 2. Unit-cell constants, molar volume, and chemical data of calorimetric and experimental material

	a (Å)	*b* (Å)	*c* (Å)	*α* (°)	*β* (°)	*γ* (°)	*V* (Å³)	V_m (cm³)
Anorthite (synthetic, 1375 °C, 1 bar)	8.179(2)	12.871(2)	14.171(3)	93.14(2)	115.78(1)	91.25(1)	1139.7(7)	100.85(5)
Anorthite (natural, Naxos, Greece)	8.175(1)	12.873(1)	14.169(3)	93.13(1)	115.90(1)	91.25(1)	1337.5(6)	100.69(5)
Wollastonite (natural, Jefferson Co., NY)	7.917(2)	7.227(4)	7.069(2)	89.55(7)	95.38(3)	102.99(3)	395.1(3)	39.66(3)

Note: detectable chemical impurities: anorthite (Naxos): Na_2O = 0.06 wt%; FeO = 0.04 wt%; SrO = 0.07 wt% (An 99.0). Wollastonite (New York): MgO = 0.11 wt%; MnO = 0.03 wt%. Uncertainties in unit-cell constants (last decimal places) in parentheses.

Table 3. Experiments on the reaction of calcite + quartz to wollastonite + CO_2

Expt.	*T* (°C)	*P* (kbar)	*t* (h)	CO_2 weight loss (mg)		X-ray results
				Ex- pected	Actual	
CQW-26	700	1.86	91.0	1.14	1.56	Wo only
CQW-27	700	2.17	45.0	1.14	1.03	Cc + Qz growth
CQW-28	700	2.06	96.0	1.11	1.34	Wo growth
CQW-30 -31	700	2.12	88.0	1.06 1.06	1.10 1.11	No apparent reaction
CQW-2	750	2.74	13.5	0.98	1.45	Wo only
CQW-3	750	3.82	5.0	0.98	0.57	Cc + Qz only
CQW-16 -17	750	2.85	46.0	1.01 1.18	1.45 1.44	Wo growth
CQW-18 -19	750	3.00	45.5	1.18 0.94	1.09 0.91	Cc + Qz growth
CQW-20	800	4.03	19.0	1.12	0.94	Cc + Qz growth
CQW-21	800	3.89	17.5	1.12	1.58	Wo growth
CQW-25	800	3.94	21.0	1.10	1.06	No apparent reaction
CQW-15	850	4.90	23.5	0.98		Wo only
CQW-23 -24	850	5.00	20.0	1.20 1.19	1.60 1.61	Wo growth
CQW-32	850	5.22	9.0	1.05	0.38	Cc + Qz growth
CQW-33	850	5.12	9.5	1.08	1.22	Cc + Qz growth

Note: Wo = wollastonite; Cc = calcite, and Qz = quartz.

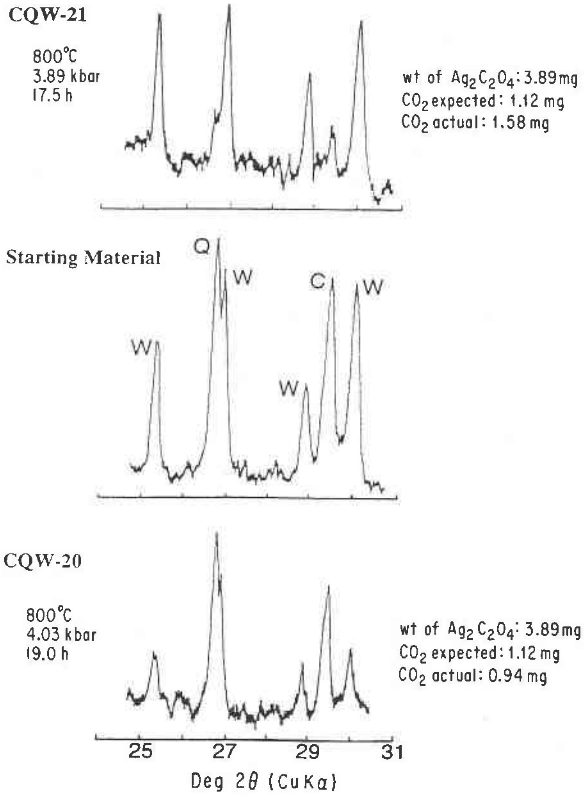

Fig. 3. X-ray diffraction scans at ½° θ/min of homogenized starting material used to investigate the reaction of calcite (C) + quartz (Q) to wollastonite (W) + CO_2. Relative increase or decrease of peak heights of reactant or product assemblage after an experiment compared with those of the starting material was a principal criterion of the direction of equilibrium, as was the apparent generation or absorption of CO_2, as determined by puncture-and-weigh tests of quenched capsules.

Capsules were held in a thick Cu holder stuffed with hematite to absorb H_2 from the pressure medium. Cr-Al thermocouples at either end of the 7-mm-long capsules always read <2 °C apart; one of these was used as an automatic control sensor. An experiment was brought to the final temperature through the *P-T* stability field of calcite + quartz, so as to avoid premature decarbonation.

Pressures were read from a Wheatstone bridge balancing a manganin cell, which in turn was calibrated from a high-precision Heise bourdon tube gauge. The precision of pressure measurement was ±15 bars or ±0.3% at 5000 bars.

The purity of the CO_2 vapor phase during the experiments was shown by puncturing the gas-inflated quenched capsules and measuring weight loss. The instantaneous weight loss was always very near the value expected from the initial weight of the silver oxalate. The punctured capsules were then dried at 120 °C for ½ h and reweighed. There was never any detectable additional weight loss. As a further check, a quenched capsule initially containing only silver oxalate was tested at typical experimental conditions. The quenched capsule was punctured into the gas line of a mass spectrometer, and the gas was analyzed by J. R. Rosenbaum. The CO_2 yield was exactly that expected, and H species and CO were below detection limits.

The direction of reaction was determined in two ways. If the weight of CO_2 released from a punctured capsule was greater than the amount expected from the initial weight of silver oxalate, it was concluded that calcite broke down during the experiment, i.e., that Reaction 1 went to the right. If the CO_2 yield was less than expected, it was presumed to have been absorbed in calcite formation. Second, X-ray scans of the quenched charges were made in the same way as the starting material scans, and the heights of the diffraction maxima of the charges were compared with those of the starting material. It was generally obvious at a glance at the diffractogram which way a reaction proceeded. One apparent contradiction of the criteria occurred in reaction CQW-33, Table 3, for unknown reasons. Figure 3 shows the reaction criteria of a typical bracketing pair of experiments.

Calorimetric methods

Enthalpy of solution measurements were performed in a Calvet-type twin Ni-block microcalorimeter, of the type described in Kleppa (1972). The calorimeter solvent was $Pb_2B_2O_5$, prepared as a glass from Mathey-Johnson ultrapure PbO and anhydrous B_2O_3. Methods of preparing the lead borate are described in Eckert et al. (1991). The calorimeter temperature was maintained at 1000 ± 1 K throughout the course of the measurements.

Individual solution samples were 30 mg of anorthite or the reference assemblage. The sized material was inspected under the microscope for impurities. The components of the reference assemblage were weighed individually into the Pt sample holder. The order of weighing was varied in many loadings, which had no effect on the heat of solution measurements. Eckert et al. (1991) showed that the largest errors in weighing could not have contributed an error as great as ±1% in the heat of solution measurements.

A reference assemblage containing the oxides CaO, Al_2O_3, and SiO_2 was initially investigated. The CaO was calcined from $CaCO_3$, pelletized, and fired at 1500 °C for 2 d to render it as inert as possible. CaO prepared in this way was used successfully for a reference material by Charlu et al. (1978). However, mixtures of the oxides gave very erratic results in the present investigation. Some experiments yielded both exothermic and endothermic portions of the heat signal, and consistent results could not be obtained. The difference in the behavior of CaO from that used in the Charlu et al. (1978) study may be caused by our use of anhydrous $Pb_2B_2O_5$. In contrast, the reference assemblage containing $CaSiO_3$ behaved as expected: the precision of measurements with this assemblage was comparable with that of the experiments on anorthite.

RESULTS OF EXPERIMENTS AND DISCUSSION

Reaction 1

Four tight brackets were secured from the equilibrium curve of the quartz-calcite reaction (Table 3 and Fig. 4). The average uncertainty from all sources of the equilibrium pressure at the four temperatures is ±65 bars. The data agree fairly closely with the abstract of Ziegenbein and Johannes (1974). No data are given in their abstract, which describes the stability of calcite + quartz in CO_2-H_2O fluids, and the equilibrium temperatures of Reaction 1 at various pressures can only be read approximately from their figure.

A test for consistency of the present experimental brackets can be made by calculating the standard free energy of the reaction at 298 K, which should be a constant. According to Redfern et al. (1989), calcite is partially disordered at the highest temperatures of our study; therefore a modification to the heat-capacity data for calcite of Jacobs et al. (1981) must be made. For this purpose, a five-parameter equation was fitted by least squares to the 17 drop-calorimetry data of Redfern et al. (1989) in the range of 973–1261 K and to the 19 tabulated heat contents at 25 K intervals in the range 325–775 K of Jacobs et al. (1981). The resulting parameters, given in Table 4, reproduce the entropy and enthalpy data of both studies very well in the range 300–1260 K. They are not valid outside that range. With interpolated f_{CO_2} values from the tables of Shmulovich and Shmonov (1978) and the other thermodynamic data of Table 4, the ΔG_1° values are 41.61 kJ from our 700 °C bracket, 42.00 kJ from the 750 °C bracket, 41.85 kJ from the 800 °C bracket, and 41.67 kJ from the 850 °C bracket. The standard deviation of the four determinations is only ±0.18 kJ, which demonstrates the high degree of consistency of the determinations.

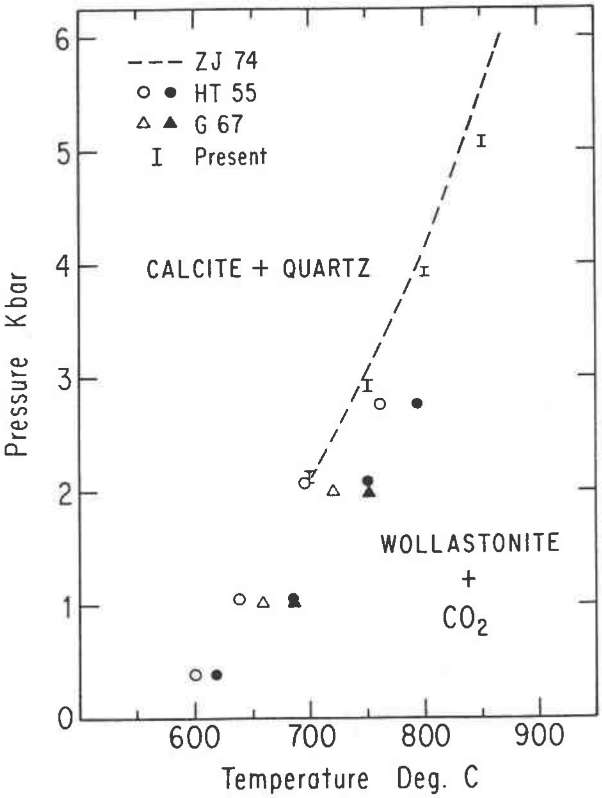

Fig. 4. Present tight brackets of the calcite + quartz = wollastonite + CO_2 equilibrium, compared with reversal experiments of previous workers (ZJ 74 = Ziegenbein and Johannes, 1974; HT 55 = Harker and Tuttle, 1955; G 67 = Greenwood, 1967). The Ziegenbein and Johannes (1974) curve is based on our visual estimates of the CO_2 intercepts of their T-X_{CO_2} curves at 2, 4, and 6 kbar.

The free energy and enthalpy of formation of wollastonite from the oxides can be gotten from the present brackets of Reaction 1 combined with the precise experimental determination of Smyth and Adams (1923) on the decarbonation of calcite:

$$\underset{\text{calcite}}{CaCO_3} = \underset{\text{lime}}{CaO} + \underset{\text{vapor}}{CO_2}. \qquad (3)$$

Calcite may be eliminated between Reactions 1 and 3 to yield the formation reaction of wollastonite. In so doing, the complex problem of temperature-dependent carbonate rotational disordering in calcite is bypassed. The only assumption necessary is that calcite achieved an equilibrium state of order in the various experiments and in the heat-capacity measurements. This assumption is justified because the higher order transition in calcite is rapid and nonquenchable.

Carbon dioxide pressures in equilibrium with calcite and lime were taken from the empirical equation of Smyth and Adams (1923), given in Table 4, which also takes

TABLE 4. Molar volume, thermal expansion, compressibility, standard entropy, thermal parameters, and related data of phases

	S_{298}	a	$b \times 10^3$	$c \times 10^{-4}$	$d \times 10^5$	e	V_{298}	$\alpha V \times 10^5$	$\beta V = 10^6$
Anorthite	199.29	516.83	−92.492	−140.850	4.1883	−4588.5	10.079	14.3	13.0
Wollastonite	81.69	198.762	−15.291	10.220	0	−1884.49	3.993	9.6	3.6
Grossular$_1$	260.12	516.347	32.184	−994.202	0	−1403.1	12.535	30.0	
Grossular$_2$	254.72	1633.30	−759.90	911.300	26.690	−20783.0	12.535	30.0	
Calcite	91.70	−134.412	131.294	−762.136	0.9289	4483.6	3.689		5.3
Corundum	50.92	157.36	0.719	−189.690	0	−988.04	2.558	6.4	0.9
α Quartz	41.46	81.145	18.283	−18.099	0.5406	−698.46	2.269	8.0	5.9
β Quartz		57.959	9.330	183.471	0	0	2.367	0	2.6
Lime	38.21	52.422	3.6734	−75.068	0	−50.988			
CO$_2$	213.79	87.82	−2.644	70.641	0	−998.86			

Note: $C_P = a + bT + cT^{-2} + dT^2 + eT^{-1/2}$. $V = V_{298} + (T - 298)(\alpha V) - P(\beta V)$. Only relevant data are tabulated.

Sources: volumes, thermal expansions, and compressibilities: Holland and Powell (1990). Calcite molar volumes, respectively, at 973, 1023, 1073, 1123 K: 3.751, 3.760, 3.769, 3.779 (Dove and Powell, 1989). Thermal parameters: anorthite: Krupka et al. (1979); wollastonite: Richet et al. (1991); grossular$_1$: Haselton (1979); grossular$_2$: Krupka et al. (1979); calcite: Jacobs et al. (1981), Redfern et al. (1989), and present derivation; corundum, lime, and CO$_2$: Robie et al. (1979); quartz: Hemingway (1987) [gives $\Delta H(\alpha \rightarrow \beta) = 625$ at 844 K]. CO$_2$ free energy: $RT \ln f_{CO_2} = 66979$ (973, 2.12); 75439 (1023, 2.91); 84766 (1073, 3.93); 94330 (1123, 5.06), interpreted from Shmulovich and Shmonov (1978). CO$_2$ vapor pressure of calcite: $\log_{10}P$ (mm Hg) $= -11355T - 5.388 \log_{10}T + 29.119$ (Smyth and Adams, 1923).

account of the earlier work of Johnston (1910) at temperatures below 1000 K. Since the vapor pressure of calcite to 1123 K is a fraction of a bar, no fugacity correction is necessary. Other input data are given in Table 4. The molar enthalpy of formation values from the oxides at 298 K yielded by the present four experimental brackets are, from the 700, 750, 800, and 850 °C brackets, respectively, −90.24, −89.67, −89.39, and −89.76 kJ. The largest source of error in these derivations stems from the ±0.18-kJ uncertainty in the brackets for Reaction 1. The resultant uncertainty in the mean enthalpy of formation is only ±0.28 kJ. This uncertainty is smaller by a factor of at least five than what is achievable by oxide melt solution calorimetry.

The molar enthalpy of formation value of −90.24 kJ at 700 °C differs from the mean value by more than twice the standard deviation and may be less satisfactory than the other three determinations. Smyth and Adams (1923) noted a tendency for superheating of calcite in their lowest temperature experiments. Moreover, their empirical equations begins to diverge from the experimental data of Johnston (1910) below 1000 K (723 °C). For this reason it may be preferable to exclude the determination at 700 °C. The mean of the ΔH_f^0 determinations from the other three temperatures is −89.61 kJ, with a standard deviation of ±0.21 kJ. This value is in marginal agreement with the enthalpy of formation of wollastonite determined by the solution calorimetry of Charlu et al. (1978). Their measured value of ΔH_f^0 is −89.87 ± 1.51 kJ at 970 K and is −87.75 ± 1.51 kJ at 298 K.

The enthalpy of formation of wollastonite from the elements may be derived from the tabulated enthalpies of formation of CaO and SiO$_2$, which are virtually identical in all the major data sets. The oxide ΔH_f^0 data of Robie et al. (1979) yield −1635.40 kJ/mol. This value is identical to the calorimetrically based value of −1635.40 kJ/mol given by Robie et al. (1979) but is not in good agreement with the values of −1631.50 and −1633.15 kJ/mol tabulated by Berman (1988) and Holland and Powell (1990), respectively. Their values were derived from consideration of many experimental equilibria in multicomponent systems and are compromised heavily by simultaneous derivation of properties of substances less well characterized than wollastonite.

The results of the solution calorimetry are presented in Table 5. The few results enclosed in parentheses had abnormalities in the base line or in the shapes of the temperature-time curves and were rejected. The uncertainties listed for the two calorimetry assemblages (anorthite and wollastonite + corundum + quartz) are twice the standard deviations on the means, in conformity with the accepted procedure for solution calorimetry. The precision obtained, ±1.5%, is near the best precision standard currently obtainable from molten salt solution calorimetry. No systematic bias was evident that could be traced to concentration of the solutes, as illustrated in Figure 5.

A somewhat surprising result is that the ΔH of solution of the synthetic anorthite is only slightly lower than that of the superbly crystalline natural sample. The enthalpy effect of 1 mol% of NaAlSi$_3$O$_8$ in the natural sample would be too small to be detected by solution calorimetry (Newton et al., 1980). The decrement of 1.34 kJ is in the expected direction but is considerably smaller than would be expected for Al-Si disordering of as much as 5%. This can be shown by a simple Bragg-Williams disordering model applied to the calorimetric data. If ΔH^{ex} is the enthalpy of interchange of $^{[4]}$Al and $^{[4]}$Si in perfectly ordered anorthite, the mole fraction X of Al or Si on the wrong sites is given, according to Navrotsky et al. (1973), by simultaneous solution of the two equations:

$$\left.\begin{aligned} -\frac{\Delta H^{ex}}{RT} &= \ln \frac{X^2}{(1 - X)^2} \\ 2X\Delta H^{ex} &= 1.34 \end{aligned}\right\}.$$

These equations yield $\Delta H^{ex} = 76.14$ kJ and $X = 0.0088$. According to this calculation, which assumes that the natural anorthite is perfectly ordered, the 1650 K synthetic anorthite is only 2% disordered. This calculation gives the critical temperature of anorthite disorder of $T_c = \Delta H^{ex}/$

TABLE 5. Results of solution calorimetric measurements at 1000 K in $Pb_2B_2O_5$

Synthetic anorthite*			Natural anorthite**			Wollastonite + corundum + quartz†		
No.	Wt (mg)	ΔH_{sol} (kJ/mol)	No.	Wt (mg)	ΔH_{sol} (kJ/mol)	No.	Wt (mg)	ΔH_{sol} (kJ/mol)
	Batch 1			Batch 1			Batch 1	
1	29.85	64.711	1	30.27	67.630	1	30.00	52.439
2	30.53	67.845	2	32.56	69.376	2	30.00	54.412
3	29.99	65.641	3	30.91	65.460	3	30.00	55.453
4	29.89	61.761	4	29.69	69.923	4	30.00	53.956
5	30.01	66.166	5	30.01	65.923	5	30.00	50.329
	Batch 2			Batch 2		6	30.00	52.193
6	30.35	68.227	6	30.37	65.415	(7)	30.00	44.952
7	29.74	64.405	7	30.87	65.082		Batch 2	
8	30.21	65.448	(8)	30.91	75.144	8	30.00	55.049
9	30.52	63.869	9	30.35	69.651	9	30.00	53.190
10	30.80	66.202	10	30.96	67.493	10	30.00	54.427
			11	29.48	65.409	11	30.00	55.454
			12	30.49	67.579			

Note: experiments in the same 30-g batch of $Pb_2B_2O_5$ grouped together. Numbers of obviously deviant experiments in parentheses.
* The $\Delta \bar{H}_{sol}$ = 65.835 ± 0.982.
** The $\Delta \bar{H}_{sol}$ = 67.176 ± 1.114.
† The $\Delta \bar{H}_{sol}$ = 53.690 ± 1.044.

$4R$ = 2289 K. This T_c is very close to Carpenter's (1991) suggested T_c of 2283 ± 80 K, deduced from his solution calorimetric study of the rate of ordering of synthetic anorthite, and the ΔH^{cx} is close to that predicted for Al-Si disordering in sillimanite by Navrotsky et al. (1973) (66.9 kJ).

Although the equilibrium degree of disorder is smaller than that predicted by some evaluations of experimental anorthite reactions, the enthalpy of disorder is not negligible. Two percent of disorder gives an entropy supplement to anorthite of 1.68 J/(K·mol), which could have a substantial effect on some of the calculated phase relations. It is possible that experiments carried out at temperatures much lower than 1375 °C might have involved an even more disordered anorthite, which was metastable for kinetic reasons.

The enthalpy of formation of anorthite from the oxides is readily retrievable from the calorimetry data and the present experimental enthalpy of formation of wollastonite. The values are $\Delta H^0_{f,298}$ (natural) = -100.10 ± 1.56 kJ/mol and $\Delta H^0_{f,298}$ (synthetic) = -98.77 ± 1.46 kJ/mol. The uncertainties include the small uncertainties arising from the experimental determination of ΔH^0_f (wollastonite). The values are substantially more negative than those from the solution calorimetry of Charlu et al. (1978) for natural samples and correspond rather closely to the value tabulated by Holland and Powell (1990) (Table 1). The less negative value adopted by Berman (1988) is probably influenced by optimization of the experimental data with respect to the solution calorimetry of Charlu et al. (1978).

PHASE EQUILIBRIUM DERIVATIONS

A critical comprehensive discussion of important phase equilibria involving anorthite and wollastonite would not be warranted by the present limited data. However, a few comments may be made on an important equilibrium

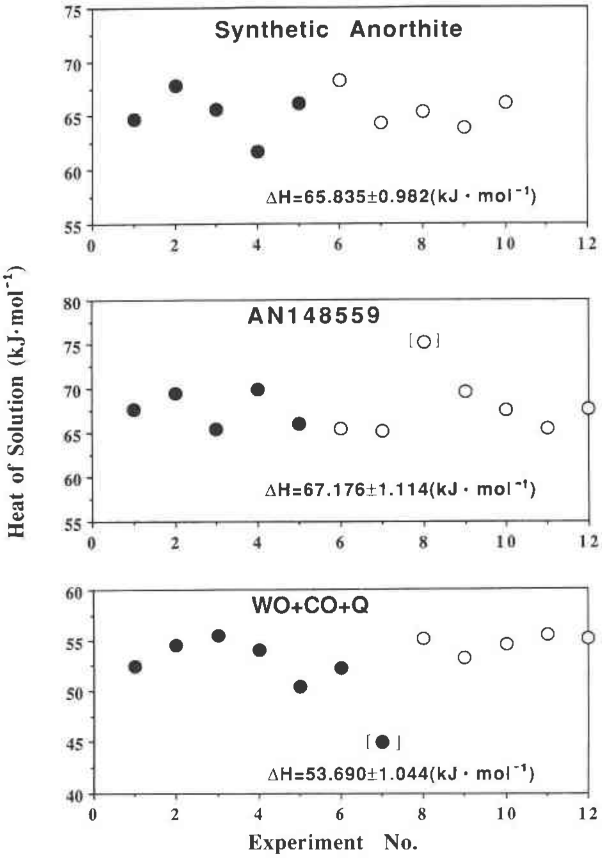

Fig. 5. Enthalpy of solution values on two anorthite samples (**top**, **middle**) and a homogeneous reference mixture of wollastonite (WO), corundum (CO), and quartz (Q) (**bottom**), plotted in the order in which the dissolution experiments were made. On each plot, the solid and open circles represent measurements made in different batches of $Pb_2B_2O_5$ melt. The plots show that there is no discernible effect of increasing concentration of the solute on the heat signals. The data points in brackets were rejected because of abnormalities in the temperature-time curves.

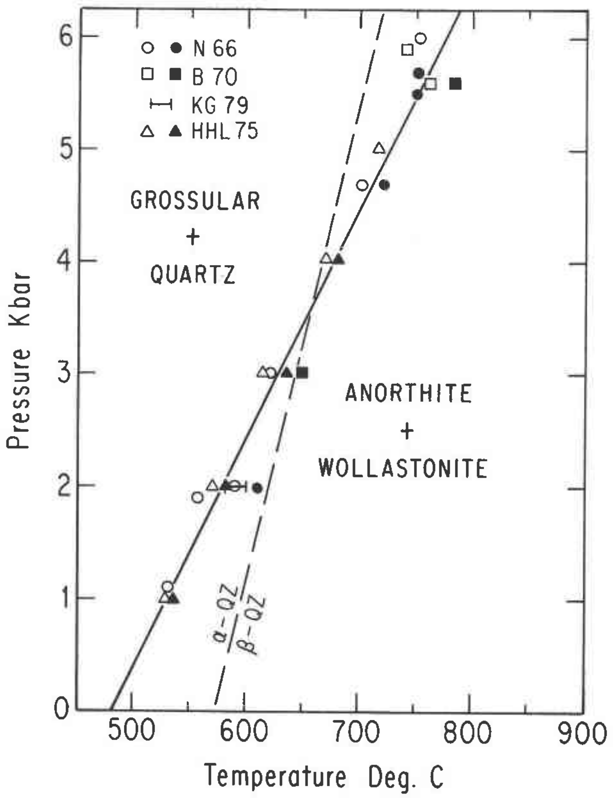

Fig. 6. Existing hydrothermal reversal data of the reaction of grossular + quartz to anorthite + wollastonite. N 66 refers to Newton (1966), B 70 to Boettcher (1970), and HHL 75 to Huckenholz et al. (1975). The experimental bracket of Kerrick and Ghent (1979: KG 83), determined by the method of crystal weight loss and weight gain and corrected by them for a small Fe content of their grossular, is shown.

involving these two minerals:

$$\underset{\text{grossular}}{Ca_3Al_2Si_3O_{12}} + \underset{\text{quartz}}{SiO_2} = \underset{\text{wollastonite}}{2CaSiO_3} + \underset{\text{anorthite}}{CaAl_2Si_2O_8}. \quad (4)$$

Grossular and quartz are a common assemblage of calc-silicate rocks and are replaced by anorthite and wollastonite in a few very high-temperature parageneses, as at Nanga Parbat, northern India (Misch, 1964).

Several experimental reversals of Reaction 4 exist that are in relatively good agreement. The data shown in Figure 6 are hydrothermal reversals under well-controlled experimental conditions. The thermodynamic properties of all of the reacting minerals except those of grossular are known well enough for an analysis of the equilibrium. Although grossular is a substance that is especially well defined crystallographically, there remain serious ambiguities in its thermodynamic parameters. Two competing sets of measurements of the low-temperature heat capacities and standard entropy are those of Haselton and Westrum (1980) on a synthetic pure grossular and of Westrum et al. (1979) on a natural sample of mole fraction of grossular about 0.90, with assumed corrections for Fe and OH contents. The high-temperature heat capacities of synthetic and natural grossular, investigated by Krupka et al. (1979) with differential scanning calorimetry, are also somewhat discrepant, as can be verified from the data of Table 4. The apparently higher heat capacity and standard entropy of the synthetic grossular yield an entropy at 873 K, which is higher by 9.1 J/(K·mol) than that of the natural sample.

Koziol and Newton (1988) showed that their experimental dP/dT slope of the high-pressure anorthite breakdown to grossular + kyanite + quartz could be matched equally well with the thermal data for the natural grossular, together with the Third Law entropy of anorthite, or with the thermal data for the synthetic grossular and an anorthite entropy that is augmented by a disordering entropy of 2–4 J/(K·mol). Both of the major self-consistent data sets have been created with the data for the natural grossular and an anorthite entropy close to the Third Law value (without significant disordering entropy). Berman (1988) considered that the thermal data for synthetic grossular are not compatible with most of the phase equilibrium data involving that mineral. The experimental data of Figure 6, together with the thermal data of Table 4, indicate that Reaction 4 can be modeled better with the Westrum-Krupka thermal functions for grossular than with the Haselton-Westrum functions. The latter would be consistent with the experimental data of Reaction 4 if disordering entropy of nearly 10 J/(K·mol) is present in the anorthite used in the experiments; that much disordering is not in keeping with the small difference in enthalpy of solution between the natural and synthetic samples found in the present study.

An assessment of the enthalpy of formation of grossular may be made from the present calorimetric and phase equilibrium determinations of ΔH_f° of anorthite and wollastonite. The line of Reaction 4 in Figure 6 gives a 1-bar equilibrium point at 484 °C (757 K). With the thermodynamic data of Table 4 and a dP/dT slope of 20.94 ± 1 bar/K from Figure 6 and with the data for the synthetic grossular of Haselton (1979), the enthalpy of formation of grossular from the oxides comes out to be -332.41 ± 2.83 kJ/mol. If the high-temperature C_P for the natural grossular of Krupka et al. (1979) are used, the ΔH_f° for grossular comes out to be -329.44 kJ/mol, with the same uncertainty.

The Holland and Powell (1990) data-set value of $\Delta H_{f,298}^\circ$ for grossular of -327.39 ± 3.91 kJ/mol is in reasonable agreement with the present derived values. The value of -319.79 kJ/mol given by Berman (1988) is considerably different and probably reflects the optimization of the phase equilibrium derivations with respect to the solution calorimetry of Charlu et al. (1978). Incorporation of the present solution calorimetry and phase equilibrium work into the Berman (1988) mathematical programming would shift the ΔH_f° value for grossular, as well as those for anorthite and wollastonite, in the direction of the values used by Holland and Powell (1990).

It is not clear why the calorimetric ΔH_f° of wollastonite of Charlu et al. (1978) is vindicated by the present study, whereas the ΔH_f^0 values for anorthite and grossular yielded by the present study are substantially more negative than those found by Charlu et al. (1978). The comparisons suggest that CaO dissolution was not the primary source of discrepancy, but rather that the assumption of infinite dilution of the component oxides in the $Pb_2B_2O_5$ melt invoked in that study might not be valid. Failure of this assumption would be minimal for a substance of smaller molecular weight (wollastonite) and greater for grossular. Also, solute interaction between CaO and Al_2O_3, as in the dissolution of anorthite and grossular, could be a perturbing factor that would not influence the results for wollastonite.

It is also unclear why the higher standard entropy and heat capacity of well-crystallized synthetic grossular by Krupka et al. (1979) and Haselton (1979) should be less consistent with the experimental phase equilibria than the thermal data for natural grossular of Westrum et al. (1979). Further calorimetric and spectroscopic studies are needed to characterize the difference between the synthetic and natural materials.

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