

The behavior of H₂O and CO₂ in high-temperature lead borate solution calorimetry of volatile-bearing phases

ALEXANDRA NAVROTSKY, ROBERT P. RAPP, EUGENE SMELIK,
PAMELA BURNLEY, SUSAN CIRONE, LIANG CHAI, KUNAL BOSE

Department of Geological and Geophysical Sciences, Princeton University, Princeton, New Jersey 08544, U.S.A.

HENRY R. WESTRICH

Geochemistry Department, Sandia National Laboratories, Albuquerque, New Mexico 87185, U.S.A.

ABSTRACT

High-temperature oxide melt solution calorimetry with molten 2PbO·B₂O₃ as a solvent can be used for determining enthalpies of formation of carbonates and hydrous silicates. Under conditions of gas flow at 1–2 cm³/s, all H₂O and CO₂ is expelled from the solvent, leading to a reproducible final thermodynamic state. Both analytical data and a number of thermodynamic cycles show that, under these conditions, the volatiles neither dissolve in nor interact energetically with the melt.

INTRODUCTION

High-temperature oxide melt solution calorimetry has become a standard method in characterizing the thermodynamic properties of anhydrous silicate minerals of the mantle and crust. A comparison of oxide melt solution calorimetry and HF acid solution calorimetry as methods of obtaining enthalpies of formation was given by Navrotsky (1977). The former offers advantages of small sample mass, relatively rapid dissolution, and smaller heats of solution. Oxide melt calorimetry is particularly useful for refractory and Ca- and Mg-bearing phases, which tend to dissolve slowly or undergo secondary reactions, forming precipitates in HF. However, minerals of the crust and at the Earth's surface often contain volatile components, notably H₂O and CO₂. Thus, for the high-temperature technique to be applicable to the wide class of crustal minerals containing mainly Mg, Ca, Na, K, Al, Si, O, C, and H, the final state of H₂O and CO₂ after the sample has reacted with the molten oxide solvent must be both reproducible and well characterized.

Over the past eight years we have done many calorimetric experiments to understand the behavior of volatiles in molten lead borate. The purpose of this paper is to summarize these studies, show that reproducible and well-defined final states can be obtained, and to recommend a reliable procedure for calorimetry of phases with H₂O and CO₂, namely, solution or drop-solution calorimetry under a flowing gas atmosphere. We present a set of thermodynamic crosschecks to show that both accurate and precise data can be obtained. This study supports the methodology used in recent calorimetry of micas (Cirone and Navrotsky, 1992) and amphiboles (Pawley et al., 1993). It lays the groundwork for future studies of minerals that figure importantly in sedimentary and metamorphic environments and in subducting lithospheric slabs.

CALORIMETRIC PROCEDURES AND POSSIBLE PROBLEMS WITH VOLATILE-BEARING PHASES

The calorimeter, sample assembly, and data collection procedure have been described previously (Navrotsky, 1977). Three types of high-temperature calorimetric experiments are commonly performed. The first is direct solution calorimetry, used when the sample persists stably or metastably for several hours at calorimetric temperature. The persistence of volatile-bearing phases is checked by a dummy experiment, in which a sample is equilibrated above the solvent, then removed and checked for weight change and for changes in the X-ray pattern or optical properties. If these tests confirm that no decomposition has occurred, then solution calorimetry can be performed. In this type of experiment, 5–50 mg of sample are equilibrated in a small Pt sample holder positioned 3–4 mm above 30 g of 2PbO·B₂O₃ contained in a Pt crucible in the calorimeter. When thermal equilibrium is attained, typically in 3–12 h, the sample is stirred into the melt and dissolved. The reaction between the sample and lead borate is monitored, and the measured heat effect is the enthalpy of solution. When volatile-bearing phases react, the gases are released as the sample dissolves. The questions are whether they dissolve in the lead borate melt or evolve into the atmosphere above the melt, whether this is controlled by thermodynamic or kinetic factors, and whether a reproducible final state is attained.

The second type of experiment is transposed temperature drop calorimetry. The sample (with or without a capsule) is dropped into a hot calorimeter from room temperature, with no solvent present. If no phase transformations or decomposition occur, this experiment simply measures heat content, $H_T - H_{298}$. This is the case for volatile-bearing samples that do not decompose near 973 K, e.g., phlogopite and calcite. If the sample does

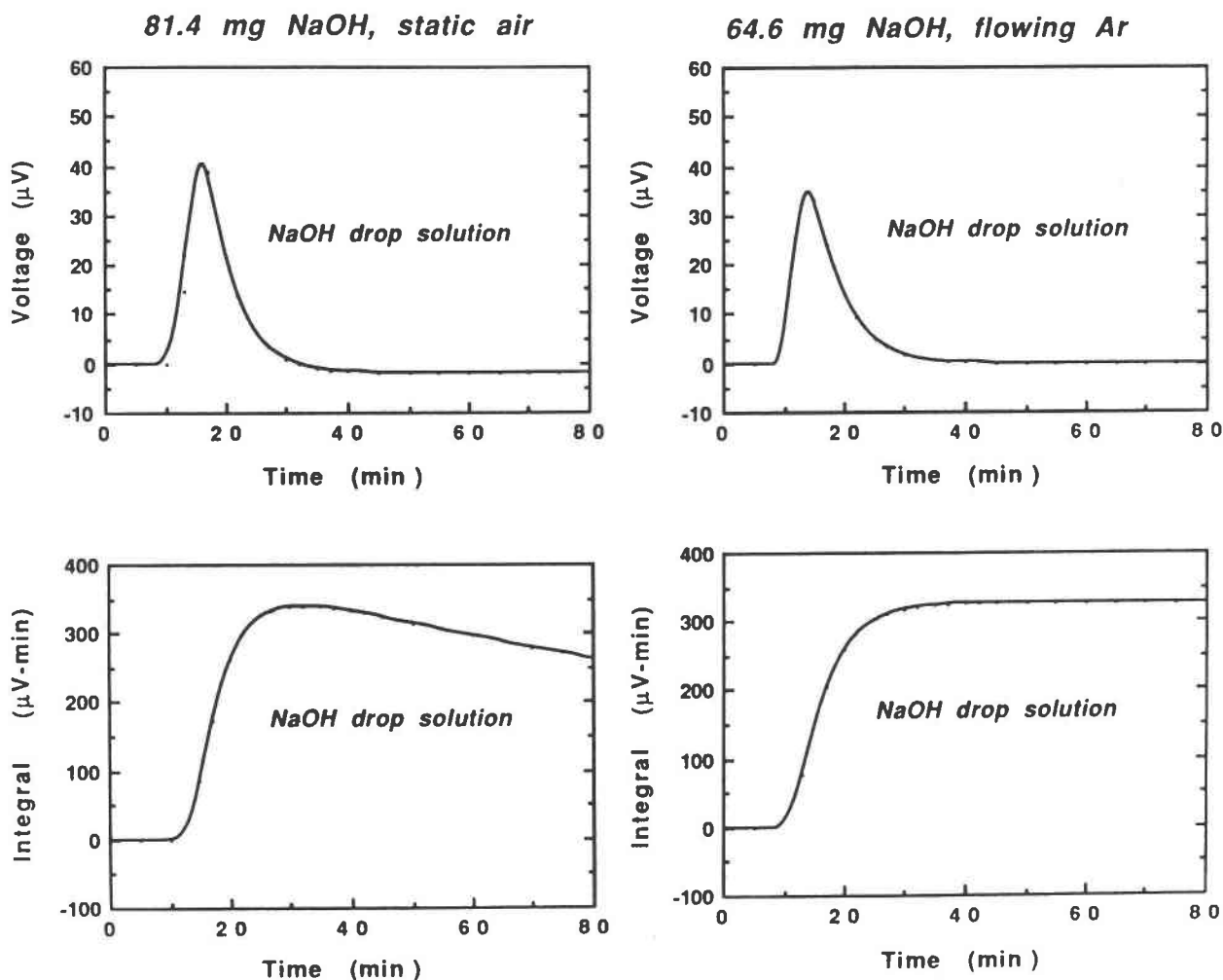


Fig. 1. Calorimetric curves showing: on left: base-line shift as encountered when volatiles are released to a static atmosphere; on right: normal reaction with good return to base line, when volatile-bearing sample is tested under flowing atmosphere. Top shows signal (microvolts) vs. time (min); bottom shows integral of signal (area under curve) that is proportional to the heat effect. For an experiment without a base-line shift, this area reaches a constant value; for one with a shift, it continues to change with time, introducing uncertainty.

devolatilize, the measured enthalpy is the heat content plus the enthalpy of decomposition. Several difficulties are possible in this measurement of decomposition enthalpy: decomposition could be slow or incomplete, the product could be poorly crystalline and not represent a well-defined final state, the evolved gas could perturb the calorimeter, and decomposition could conceivably be so rapid and violent that a part of the sample is lost during the drop or the sample begins to decompose before it reaches the calorimeter. These points are addressed in some detail below.

The third method is drop-solution calorimetry. It avoids the first two difficulties of transposed temperature drop calorimetry by putting the sample at room temperature into solvent in the hot calorimeter. The sample dissolves upon contact with the melt. Since the final state is a dilute solution in lead borate and enthalpy is a state function,

it does not matter whether the sample decomposes in the calorimeter before it dissolves, whether it dissolves before it transforms to another phase assemblage, or whether the rates of decomposition and dissolution are comparable. However, the final state of the volatiles must be known, just as for the case of direct solution calorimetry.

Several types of sample containment have been used for drop solution experiments. Early experiments generally used thin-walled Pt capsules, welded or crimped at the bottom and open at the top (Clemens et al., 1987). They were sometimes weighted with an additional piece of Pt to ensure that they sank directly into the melt and rapidly filled with solvent. Even so, poor contact between sample and melt could be troublesome for samples rich in MgO, which tend to dissolve slowly or locally saturate the solvent. To overcome this problem, three types of self-dissolving containers have been used, Pyrex glass

capsules (Ross et al., 1986), thin-walled silica glass globes (Burnley et al., 1992), and lead borate glass capsules identical in composition to the solvent (Ito et al., 1990). Bularzik et al. (1991) and Chai and Navrotsky (1993) have used pressed pellets of sample with no encapsulation. In general, the containment methodology needs to be optimized for each new sample.

To illustrate the features of a calorimetric experiment that affect its accuracy, Figure 1 shows reaction curves of thermopile voltage vs. time. A typical reaction curve for a normal calorimetric experiment with a proper return to base line is shown on the right side. The area under the reaction peak (thermopile voltage integrated over time) is proportional to the enthalpy of reaction. However, sometimes a base-line shift occurs (see left side of Fig. 1), in which the signal returns to a value significantly different from the original. In general, large base-line shifts render calorimetry inaccurate and raise doubts about the final state of the system, whereas a rapid return to the original base line indicates a well-controlled experiment. Calorimetric experiments with base-line shifts $>0.05 \mu\text{V}$ are generally considered problematic.

PREVIOUS CALORIMETRIC STUDIES OF VOLATILE-BEARING PHASES

Realizing the potential difficulties associated with volatile evolution during calorimetry, Westrich and Navrotsky (1981) and Graham and Navrotsky (1986) used F analogues of hydrous phases for thermochemical studies. The results appeared satisfactory, and base-line shifts were not considered a problem, although the overall calorimetric protocol was not as rigorously controlled as at present. Barton et al. (1982) also studied the enthalpy of formation of some F-containing minerals. They cautioned that one should determine a heat of formation as the difference in heats of solution between reactants, taken as a mechanical mixture rather than as separate components, and products, in order to incorporate the effects of possible F complexing reactions between various components in the lead borate. None of these early studies included analysis of the actual concentrations of F⁻ in the lead borate. Thus, although there is no evidence that F is evolved (e.g., as HF or SiF₄), there is no confirmation that it remains dissolved.

The first lead borate solution calorimetry done directly on hydrous phases was a study by Kiseleva and Ogorodova (1984). They determined the enthalpy of interaction between gaseous H₂O and molten 2PbO·B₂O₃ at 973 K to be $-31.0 \pm 2.1 \text{ kJ/mol}$ from drop solution experiments on brucite and $-24.7 \pm 4.2 \text{ kJ/mol}$ from solution experiments on talc. Their procedure was not described in detail, but no special problems were mentioned. Clemens et al. (1987) obtained values of $-23.8 \pm 2.9 \text{ kJ/mol}$ using drop solution calorimetry of Mg(OH)₂ at 986 K and $-24.7 \pm 3.3 \text{ kJ/mol}$ from corresponding experiments using Ca(OH)₂. These experiments in a static air atmosphere did not encounter any notable difficulties, though exothermic base-line shifts were noted. Clemens et al.

(1987) also determined the enthalpy of formation of phlogopite by solution calorimetry in a static air atmosphere.

Experiments involving SrCO₃ and BaCO₃ were done by Bularzik et al., 1991, and DiCarlo et al., 1992. Very large exothermic base-line shifts were seen in static air, which made interpreting the data impossible. Experiments in flowing gas (air, Ar, or CO₂ at 1–2 cm³/s) showed a normal return to base line, as did experiments in a static CO₂ atmosphere. The experiments in static CO₂, indicate that gas flow or its absence is not the crucial variable. Furthermore, the calibration factor of the calorimeter does not change with flow rate over the range 0–3 cm³/s. These observations suggest that changes in conditions within the calorimeter, rather than the enhanced loss of heat with gas that exits the top of the calorimeter, cause the shifts.

For drop solution calorimetry of Ca(OH)₂ and Mg(OH)₂ under static air, Circone and Navrotsky (1992) typically observed exothermic base-line shifts of 0.2–0.4 μV , whereas smaller shifts, (0.05–0.1 μV) were seen for amphiboles, micas, and hydrous glasses (Circone and Navrotsky, 1992; Circone, 1991). Though larger in magnitude than the random shifts (of -0.05 – $0.05 \mu\text{V}$) seen for volatile-free phases, these shifts were smaller than those seen for carbonates ($\geq 0.7 \mu\text{V}$). This could be related to two factors. First, a typical hydrous silicate contains a relatively small amount of H₂O ($<5 \text{ wt}\%$), whereas carbonates contain 20–50 wt% CO₂. Indeed, the magnitude of the base-line shift appears to increase with the amount of gas evolved (Circone, 1991), though the data scatter too much for a quantitative correlation. Second, since H₂O is less dense than air and CO₂ more dense, the former tends to rise out of the calorimeter chamber more readily than the latter.

Using a flowing Ar atmosphere (1–2 cm³/s), Pawley et al. (1993), in a study of tremolite-richterite amphiboles, generally obtained much smaller base-line shifts, (both exothermic and endothermic) than in static air. The present work pursues this direction, utilizing lead borate calorimetry at 975 or 1073 K under a flowing Ar atmosphere.

SAMPLE PREPARATION AND CHARACTERIZATION

The starting materials and preparation conditions for hydroxide and carbonate samples are shown in Table 1. All products were examined by X-ray diffraction and optical microscopy and found to be single-phase materials, except for the first Ca(OH)₂ sample, which was corrected for 5 wt% CaCO₃ impurity.

ANALYTICAL STUDIES

The purpose of these studies was to determine, by direct weight change and by chemical analysis of the lead borate glass recovered after calorimetry, how much H₂O or CO₂ remains in the solvent after dissolving a volatile-bearing sample. Analyses were done on samples cooled to room temperature over a period of several minutes; a

TABLE 1. Synthesis conditions for hydroxides and carbonates used for calorimetry

Starting materials		T (K)	P (bars)	t (h)
Mg(OH) ₂	MgO	823	1000	20
Mg(OH) ₂	MgO	923	5400	43
Mg(OH) ₂	Mg(OH) ₂	*		
Mg(OH) ₂	MgO	873	1500	36
Ca(OH) ₂	CaO	1043	1000	0.5
Ca(OH) ₂	CaO	1023	1000	3
Ca(OH) ₂	CaO	883	1800	50
CaCO ₃	CaCO ₃	*		
MgCO ₃	basic carbonate**	673	†	24
MgCO ₃	basic carbonate**	673	†	72
MgCO ₃	MgO	973	†	24

* Commercial powders dried at 383 K.

** Starting composition 4MgCO₃·Mg(OH)₂·4H₂O.

† Pressure generated by dry ice, between 1 and 2 kbar.

true quench is impossible within the calorimetric assembly. Thus some uncertainty remains whether any gas is evolved during cooling. Because the lead borate becomes very viscous below about 873 K and remains a glass upon cooling, we believe it likely that any dissolved gas at 973 K (calorimetric temperature) remains in solution. Furthermore, gas solubility in a liquid should generally increase with decreasing temperature (because of the large negative entropy associated with the large negative volume change on dissolution), and so there should not be any thermodynamic driving force to exsolve H₂O or CO₂ on cooling. Thus it is reasonable, though not proven, that the experiments described below do indeed reflect the gas solubility under calorimetric conditions. Calorimetric evidence is also consistent with these interpretations (see below).

It would be desirable to monitor the exiting gas for H₂O or CO₂, but that is presently not feasible. We attempted to analyze for H₂O by infrared spectroscopy but did not pursue it in detail after we found that the H₂O peaks did not stand out clearly from the lead borate background. This may also be indirect evidence for very limited H₂O retention on sample dissolution (see below).

Weight change studies

Two sets of experiments on hydrous phases, separated in time by about 2 yr, were done. The first involved a static air atmosphere in conjunction with calorimetry of micas along the phlogopite-eastonite join (Circone, 1991; Circone and Navrotsky, 1992). Lead borate was heated in a Pt calorimeter crucible in a vertical tube furnace at 975 ± 6 K for several hours to drive off any residual H₂O and then cooled and weighed. The lead borate was then heated to 975 K and a sample of Mg(OH)₂ in a lead borate glass capsule was dropped into the melt. The crucible remained in the furnace for 1 h (the length of a typical drop solution experiment). Then it was removed, cooled, and weighed. The experimental procedure was checked using empty capsules and α-Al₂O₃. We observed weight gains corresponding to 100% of the capsule weight when

an empty capsule was dropped and weight gains corresponding to 100% of the sample plus capsule for four drops of α-Al₂O₃ weighing 5 and 15 mg. The accuracy of the weight changes was limited to ±0.1 mg because the total weight of the Pt crucible plus lead borate (~60 g) necessitated the use of a standard, rather than semimicro, analytical balance.

The observed weight gains in a static air atmosphere (see Fig. 2a) are mostly intermediate between those for complete H₂O retention and complete H₂O loss. A least-squares fit suggests that 22 ± 6% of the H₂O remains in the melt after calorimetry and cooling. However, the data show enough scatter that they could also be consistent with essentially zero H₂O retention. They definitely preclude complete H₂O retention and show no evidence for a solubility limit, below which H₂O is completely retained and above which H₂O is lost, in the concentration range of these experiments (5–15 mg brucite, corresponding to 1.5–5 mg H₂O in 30 g of lead borate).

We have direct evidence that some H₂O is lost during the drop solution experiment itself; 2–3 s after the sample is dropped into the furnace, condensation appears on the interior of the silica glass tube. That is not observed in the α-Al₂O₃ experiments. In actual calorimetry, the sample chamber cannot be seen, but condensation is occasionally observed in the silica glassware when it is removed after drop solution calorimetry on large samples (>20 mg of hydroxide).

A second set of weight change experiments was done in conjunction with later calorimetric studies under flowing Ar. Samples of Cu(OH)₂, Mg(OH)₂, and KOH were dropped as loosely pressed pellets rather than encapsulated. The data (see Fig. 2b) indicate that all the H₂O is evolved into the flowing atmosphere. The data for Mg(OH)₂ show more scatter than those for Ca(OH)₂ and KOH.

The results of weight change studies on carbonates are shown in Figure 2c. In all cases, complete (>99%) loss of CO₂ is seen. These experiments were done using smaller Pt crucibles in a furnace outside the calorimeter. The weighing accuracy is ±0.02 mg on a semimicro balance.

Analytical determination of H₂O content by Karl Fischer titration

A number of lead borate glasses were prepared for direct chemical analysis of H₂O content by Karl Fischer titration. A set of blank samples, in which no hydrous phase had been dissolved, were prepared at calorimeter temperature (973 K, 2 d). These samples served as a dry solvent blank. Seven other lead borate glasses were prepared with varying amounts of dissolved hydroxide; four of these were the products from a number of brucite drop solution experiments and the remaining three were the products of a series of NaOH drop solution experiments in flowing Ar. All the lead borate glasses were heated at 473 K to drive off adsorbed water, prior to the titration. Figure 3 summarizes the analytical results. In all cases, the analyzed H₂O content was <10% of that which would

result from complete retention; in most cases it was <2%. Two of the blank samples, prepared at calorimeter conditions in both static and flowing Ar, contained <25 ppm of dissolved H₂O. In contrast, two other blanks contained 40–60 ppm of H₂O, as did two brucite-containing samples. However, these four samples represent glasses that had been prepared at least a year before analysis and had been left open to ambient air for part of that time. The rather similar H₂O content of these glasses with and without added brucite suggests that the H₂O is a result of later hydration (presumably mainly of the surface) under ambient conditions, rather than of Mg(OH)₂ addition. All samples with added NaOH or Mg(OH)₂ contained <30 ppm of H₂O, even for hydroxide additions corresponding to as much as 4000 ppm of H₂O. These data suggest that, under flowing Ar, the lead borate does not retain significant H₂O.

The solubility of H₂O in lead borate glasses as a function of composition has been reported (Eagan and Bergeron, 1972). Solubility decreases with increasing PbO content, with glasses of 40–50 mol% PbO showing about 0.004 wt% H₂O, which would correspond to 1.2 mg of H₂O in 30 g of glass. The reported experiments did not attempt to assess the uncertainty in their infrared calibration, which Eagan and Bergeron suggested might be appreciable. In any case, the solubility in more PbO-rich glass may be even less. The above results are in qualitative agreement with our findings that in a static atmosphere a fraction of the H₂O released from the hydrous phase is retained, but that under flowing atmosphere essentially all H₂O is degassed.

CALORIMETRIC RESULTS AND THE ENTHALPY OF INTERACTION OF H₂O AND CO₂ WITH MOLTEN 2PbO·B₂O₃

Hydrous phases under static air atmosphere

Data from drop solution calorimetry are shown in Table 2. The calorimetric temperature is different for the several experiments because they were done over a period of 8 yr, using different calorimeters, initially at Arizona State University but mostly at Princeton University.

The apparent enthalpy of interaction of H₂O with the solvent can be calculated using the following thermodynamic cycle, where *T* = calorimetric temperature.

M(OH)₂ (crystal, 298 K)

= MO (solution, *T*) + H₂O (final, *T*)

$$\Delta H_1 = \Delta H_{\text{dropsol}} \quad (1)$$

MO (solution, *T*) = MO (crystal, *T*)

$$\Delta H_2 = -\Delta H_{\text{sol,MO}} \quad (2)$$

MO (crystal, 298 K) + H₂O (liquid, 298 K)

= M(OH)₂ (crystal, 298 K)

$$\Delta H_3 = \Delta H_{f,\text{M(OH)}_2} \quad (3)$$

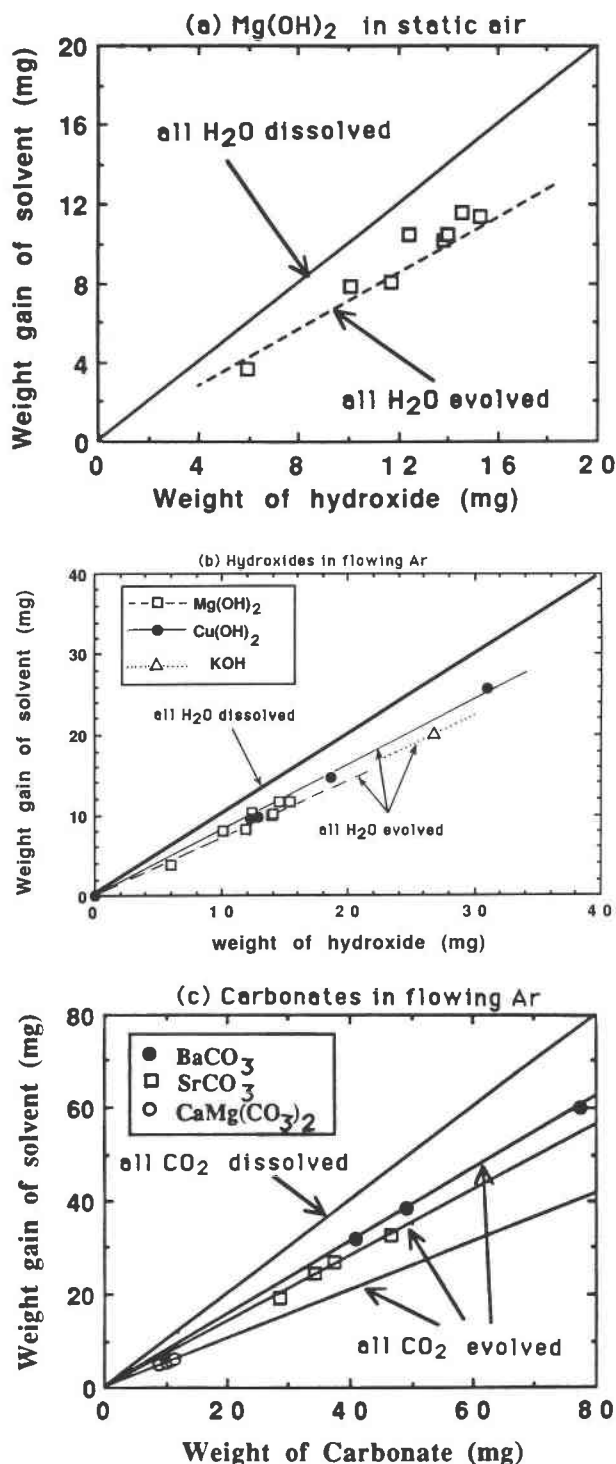


Fig. 2. Weight loss experiments in lead borate under conditions similar to those for drop solution calorimetry. (a) Mg(OH)₂ in static air, at 975 K, (b) Mg(OH)₂, Cu(OH)₂, and KOH in flowing Ar, (c) CaMg(CO₃)₂, BaCO₃, and SrCO₃ in flowing Ar.

TABLE 2. Results of drop solution calorimetry on hydroxides and carbonates under static and flowing atmosphere and calculated enthalpy of interaction of H₂O and CO₂ with molten lead borate

Sample	Calorimeter <i>T</i> (K)	Containment	Atmosphere	Enthalpy (kJ/mol)	
				Drop solution*	H ₂ O or CO ₂ interaction**
Mg(OH) ₂	987	Pt	static air	120.1 ± 2.2(10)	-23.8 ± 2.8
Mg(OH) ₂	977	lead borate	static air	117.8 ± 1.5(11)	-26.2 ± 2.3
Mg(OH) ₂	975	SiO ₂ glass globes	flowing Ar	144.1 ± 3.6(5)	+0.4 ± 3.8
Mg(OH) ₂	1075	SiO ₂ glass globes	flowing Ar	156.0 ± 2.8(5)	+0.5 ± 3.0
Ca(OH) ₂	987	Pt	static air	90.7 ± 5.3(6)†	-27.6 ± 5.9
Ca(OH) ₂	973	Pt	static air	90.5 ± 2.5(8)†	-26.5 ± 3.4
Ca(OH) ₂	975	pellet	flowing Ar	111.2 ± 0.6(9)	-0.5 ± 1.9
H ₂ O	975	Pt	flowing Ar	70.2 ± 2.7(8)	+1.1 ± 3.0
MgO	975		static air	36.5 ± 1.0(7)‡	
MgO	1075	SiO ₂ glass globes	static air	44.1 ± 0.7(6)	
CaCO ₃	977	pellet	flowing CO ₂	190.8 ± 0.8(6)	+0.3 ± 1.6
CaCO ₃	977	pellet	flowing Ar	189.6 ± 1.1(9)	-0.9 ± 1.7
CaCO ₃	977	pellet	all samples	189.9 ± 0.7(15)	-1.5 ± 1.5
MgCO ₃	977	pellet	flowing CO ₂	185.2 ± 0.4(12)	-1.9 ± 1.6
MgCO ₃	977	pellet	flowing Ar	186.9 ± 2.6(3)	-0.2 ± 3.0
MgCO ₃	977	pellet	all samples	185.6 ± 0.8(15)	-1.5 ± 1.6

* The uncertainties quoted are 2 sd of the mean. Values in parentheses are the number of experiments.

** Values in this column calculated using Eqs. 1–7, drop solution data, heat contents from Robie et al. (1978), enthalpies of solution of MgO (Davies and Navrotsky, 1981), and CaO (Navrotsky and Coons, 1976).

† Corrected for 5 wt% CaCO₃ impurity.

‡ Calculated as sum of heat content and heat of solution measured separately.

H₂O (vapor, *T*) = H₂O (liquid, 298 K)

$$\Delta H_4 = - \left(\int_{298}^{373} C_{P,H_2O(l)} dT + \Delta H_{\text{vap}}^{373} + \int_{373}^T C_{P,H_2O(g)} dT \right) \quad (4)$$

MO (crystal, *T*) = MO (crystal, 298 K)

$$\Delta H_5 = - \int_{298}^T C_{P,MO} dT \quad (5)$$

H₂O (vapor, *T*) = H₂O (final, *T*)

$$\Delta H_{\text{interaction}} \quad (6)$$

$$\Delta H_{\text{interaction}} = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5. \quad (7)$$

The term ΔH_f refers to the formation of M(OH)₂ (crystal) from MO (crystal) and H₂O (liquid) at 298 K, and $\Delta H_{\text{interaction}}$ refers to the energetic difference between H₂O as it is found after the calorimetric experiment, and standard state gaseous H₂O at the calorimetric temperature. Were all the H₂O dissolved in the lead borate, $\Delta H_{\text{interaction}}$ would simply be a heat of solution of H₂O, analogous to the heat of solution of other oxides. Since the analytical results above suggest that much of the H₂O is evolved, we prefer to call this term an interaction enthalpy, with some ambiguity as to the final state.

Using this cycle and the data in Table 2, we obtain an interaction enthalpy of -24 to -28 kJ/mol of H₂O for experiments in static air. This is an agreement with previous studies (Clemens et al., 1987; Kiseleva and Ogorodova, 1984).

Up to three drop solution experiments were made in

each 30-g batch of lead borate. The measured enthalpies of drop solution of the hydroxides showed no systematic variation with the weight of the sample or with the weight of previously dissolved samples.

Figure 4a shows the enthalpy actually observed during a calorimetric experiment (J, not J/g or J/mol) plotted against the weight of the sample. The Mg(OH)₂ and Ca(OH)₂ data each fall on a straight line with zero intercept. The molar enthalpy of drop solution does not depend on the amount of sample reacting, which therefore implies that the final state of the H₂O is energetically the same for all experiments in each series. There is thus no calorimetric evidence for a solubility limit and change in dissolution or reaction mechanism. Rather, the data are consistent with a constant fraction of the H₂O entering the solvent. The analytical data and observation of degassing argue that this fraction is much less than 100%. The significant negative interaction energy suggests that some H₂O must be chemically reacting with the melt under conditions of static atmosphere. If the interaction enthalpy observed is attributed to only that part of the H₂O that appears to remain dissolved (<20%), the magnitude of the interaction enthalpy would be much more negative, i.e., approximately -100 kJ/mol of dissolved H₂O. Such negative interaction seems inconsistent with most of the H₂O being evolved from the melt. Thus the final state of H₂O in these experiments in static air, though seemingly reproducible, appears enigmatic.

Hydrous phases under flowing atmosphere

Drop solution calorimetric data for Mg(OH)₂ and Ca(OH)₂ under flowing atmosphere are shown in Table 2. The base-line shifts are essentially eliminated under flowing gas (air, Ar, CO₂, or N₂); any small base-line in-

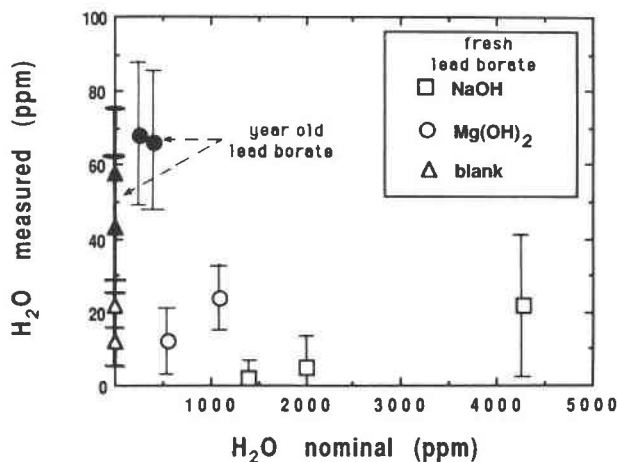


Fig. 3. H₂O content of lead borate excess after hydroxide dissolution in flowing Ar, as determined by Karl Fischer titration, plotted against maximum H₂O content attainable had all the H₂O remained dissolved. Error bars are 2 esd.

stabilities that do occur are randomly exothermic or endothermic and no larger than in experiments with anhydrous oxides in a static atmosphere (-0.05 – 0.05 μ V). In flowing gas, as in static air, there is a linear correlation (with essentially zero intercept) between reaction enthalpy (J), and sample weight (see Fig. 4b), implying a constant molar enthalpy of drop solution throughout the concentration range used.

The gas flow does not change calorimetric temperature (measured to ± 0.5 °C with a calibrated Pt-Pt10Rh thermocouple). The base line remains as stable as without gas flow as long as the flow does not cease. Small variations ($\pm 10\%$) in flow rates do not affect the base line. Thus the gas flow in itself does not perturb the calorimeter. We have made similar observations when using flowing Ar to prevent oxidation of anhydrous Fe²⁺-bearing samples (Akaogi et al., 1989; Brown and Navrotsky, 1994).

The results are consistent with an essentially zero enthalpy of interaction of H₂O with the solvent under flowing gas (see Table 2) for Mg(OH)₂ dissolved at both 975 and 1075 K and for Ca(OH)₂ dissolved at 975 K, using calculations analogous to those for static air (Eqs. 1–7).

Comparison of calorimetry of hydrous phases under static and flowing atmospheres

The enthalpy of interaction of H₂O with lead borate in static air also can be estimated directly from the difference in calorimetric heats of reaction in static and flowing atmosphere if one assumes, as argued above, that the energy of interaction in the latter is zero. Table 3 shows the heats of drop solution for Mg(OH)₂ and Ca(OH)₂ and the heat of solution for phlogopite, KMg₃AlSi₃O₁₀(OH)₂. The differences are all consistent with an enthalpy of interaction in static air near -20 kJ/mol, similar to values calculated above using Equations 1–7.

Circone and Navrotsky (1992) considered the reaction

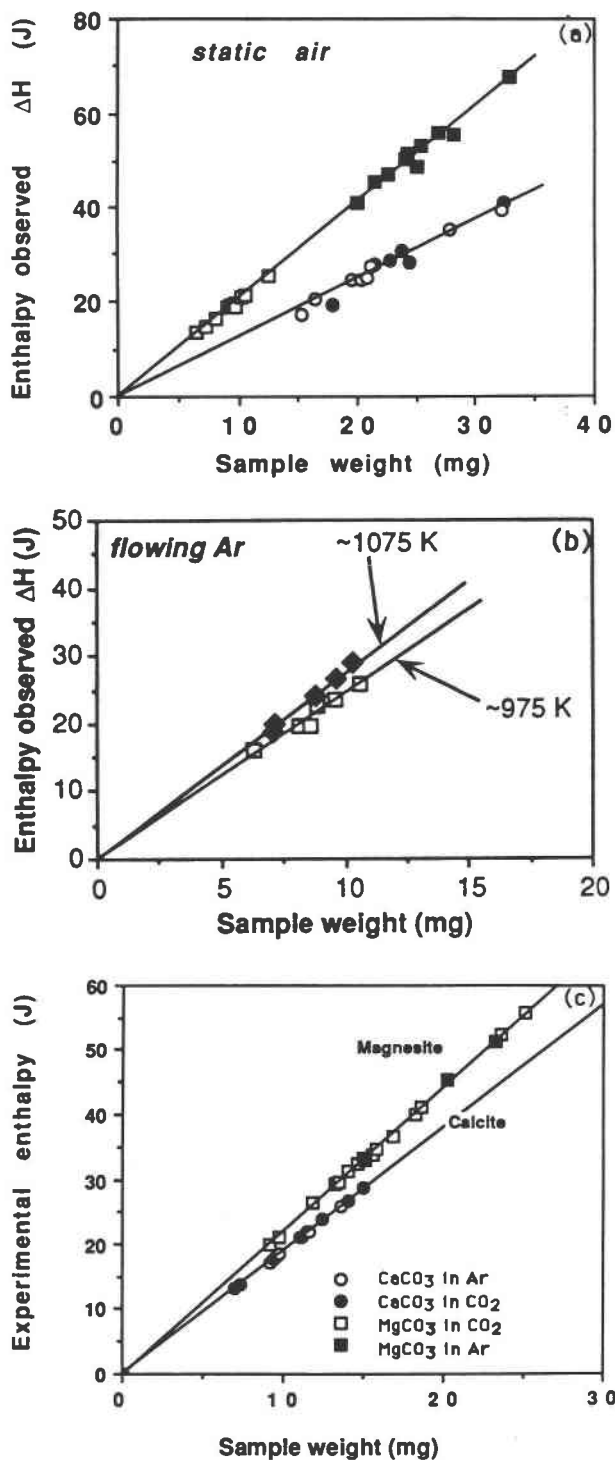


Fig. 4. Enthalpy observed in a drop solution calorimetric experiment (J) vs. weight of sample (mg). (a) Mg(OH)₂ (squares) and Ca(OH)₂ (circles) in static air at 975 K (solid and open symbols represent two different samples). (b) Mg(OH)₂ in flowing Ar at 975 and 1075 K. (c) CaCO₃ and MgCO₃ in flowing Ar and flowing CO₂ at 975 K.

TABLE 3. Comparison of enthalpies of calorimetric reaction in static and flowing atmospheres

Sample	Enthalpy of calorimetric reaction (kJ/mol) near 975 K		Enthalpy of interaction of H ₂ O (kJ/mol)
	Static air	Flowing Ar	
Mg(OH) ₂	117.8 ± 1.5 ^{* **}	144.1 ± 3.6 [*]	-26.3 ± 3.9 [†]
Ca(OH) ₂	90.7 ± 5.3 ^{* **}	111.2 ± 0.6 [*]	-20.5 ± 5.3 ^{**}
KMgAlSi ₃ O ₁₀ (OH) ₂	280.2 ± 2.2 ^{‡ §}	302.1 ± 1.8 [‡]	-21.9 ± 3.6 [†]

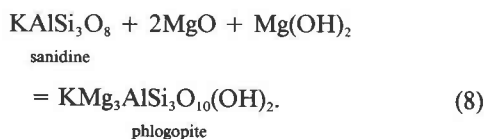
^{*} Drop solution calorimetry.

^{**} Circone (1991) and Circone and Navrotsky (1992).

[†] Calculated as $\Delta H(\text{static air}) - \Delta H(\text{flowing Ar})$.

[‡] Solution calorimetry.

[§] Clemens et al. (1987).



When static and flowing atmospheres are compared, the difference in the enthalpy of solution of phlogopite is almost completely compensated for by the difference in the brucite data. Thus the enthalpy of Reaction 8 is the same within experimental error whether the measurements are done in flowing or static atmosphere. This suggests that the enthalpy of interaction of H₂O with the melt is the same whether the water comes from brucite or phlogopite. Therefore any other formation reaction calculated from these data, i.e., formation of phlogopite from binary oxides or elements, also has the same value, within a propagated experimental error of about ±5 kJ/mol. We conclude that the work of Circone and Navrotsky (1992) on heats of formation and mixing along the phlogopite-eastonite join remains valid.

Although drop solution calorimetry in static air on Ca(OH)₂, Mg(OH)₂, and phlogopite results in consistent results for the enthalpy of interaction of H₂O with lead borate, the data must be used with caution in thermodynamic cycles for heats of formation of hydrous phases for several reasons. The large base-line shifts add uncertainty. The final state of H₂O (i.e., how much remains dissolved) remains ambiguous. It is quite possible that the state is kinetically controlled and may vary for different materials. Some experiments using a hydrous multicomponent silicate glass (Circone, 1991), in which part of the water is present as OH and part as H₂O, suggest a less exothermic enthalpy of interaction of the water with the calorimetric solvent, (approximately -10 kJ/mol) compared with the -24 to -28 kJ/mol derived from the hydroxides.

Thus, the interpretation of data under flowing atmosphere, with essentially zero enthalpy of interaction of H₂O with the solvent, is much more straightforward than that of data under static atmosphere. We recommend flowing atmosphere for all future experiments using hydrous phases and carbonates.

One assumes for the thermochemical cycles that the evolved gas is at the temperature of the calorimeter by

the time it exits the calorimeter proper, i.e., the volume over which the thermopiles sense heat flow. One might envision a scenario in which a sample dropped into the calorimeter devolatilizes so quickly that this would not be the case, and that a significant systematic error would then arise. The following arguments and observations render this complication very improbable for the carbonates and hydrous silicates we might wish to study, even when their thermodynamic stability field at 1 atm lies well below calorimetric temperature. A 10–30 mg sample dropped into the calorimeter from room temperature is near 300 K when it hits the melt or bottom of the calorimetric crucible; this is known from numerous earlier experiments on heat pickup for samples of different mass and diameter dropped as calibration pieces. Thus devolatilization during drop is not a problem. Once the sample is in the calorimeter, it heats to calorimeter temperature (973 K) in 2 min or less and to 800 K in 1 min or less, on the basis of simple thermal conduction calculations. Consideration of the measured rates of dehydration of talc (Bose and Ganguly, 1994), kaolinite (Brindley et al., 1967), and brucite (Gordon and Kingery, 1967) suggests that even for very fine-grained samples under very low H₂O pressures (or in vacuum), dehydration does not occur significantly on the minute time scale till about 1073, 773, and 673 K, respectively. Phyllosilicates appear to dehydrate with larger activation energies than simple hydroxides. Taking brucite as a worst case, we can ask whether gas released at 673 K will heat to 973 K ($\Delta T = 300$ K) as it rises through the calorimeter. At a flow rate of 1.5 cm³/s, a diameter of 1.5 cm, and a thermopile height of 12.5 cm, the residence time is about 15 s. During that time, a point source of gas spreads to a plume of several centimeters by diffusion, and so dilution alone is enough to equilibrate the gas thermally. In reality, the sample is not degassed instantaneously. The gas may first be released into the lead borate melt, in which bubbles must nucleate, and there may be a layer of gas of lower vertical velocity directly above the melt surface. Thus the gas leaving the top of the thermopile is almost certainly thermally equilibrated.

The consistency of the thermochemical data from cycles involving Ca(OH)₂, Mg(OH)₂, CaCO₃, and MgCO₃ and from thermochemical cycles involving carbonate-sil-

TABLE 4. Enthalpies of solution near 975 K of binary oxides

Oxide	Method	ΔH_{sol} at 973–977 K (kJ/mol)
MgO	Mg(OH) ₂ drop solution	5.1 ± 3.7 (this study)
	MgCO ₃ drop solution	3.3 ± 1.5 (this study)
	MgO solution	4.8 ± 1.0 (this study)
	MgO solution	4.9 ± 0.6 (Davies and Navrotsky, 1981)
	MgO solution	4.8 ± 0.6 (Navrotsky and Coons, 1976)
	MgO solution	4.9 ± 0.3 (Charlu et al., 1975)
CaO	CaCO ₃ drop solution	−55.0 ± 1.2 (this study)
	CaO solution	−56.6 ± 0.8 (this study)
	CaO solution	−54.5 ± 0.9 (Navrotsky and Coons, 1976)
	CaO solution	−56.4 ± 0.7 (Newton et al., 1980)
	Ca(OH) ₂ drop solution	−57.1 ± 1.8 (this study)

Note: enthalpies measured directly and calculated using thermochemical cycles involving hydroxides and carbonates in flowing gas atmosphere, assuming the enthalpy of interaction of H₂O and CO₂ with molten lead borate is zero.

icate equilibria (Chai and Navrotsky, 1993) suggest the absence of systematic errors involving gas release.

We note that the geometry of our calorimeter, in which a thermopile surrounds a cylindrical sample chamber, in which every flowing gas resides for a significant time, is very different from that of a conventional DSC-DTA, in which heat is sensed through the bottom of the small sample pan, and gas rising vertically loses thermal contact with the detector essentially instantaneously.

Finally, in our study of carbonates, CaCO₃ is stable at calorimeter temperature, MgCO₃ is not. The calorimetric behavior of both in drop solution experiments is similar, and both give consistent results in carbonate-hydroxide exchange reactions (this work) and in carbonate-silicate equilibria (Chai and Navrotsky, 1993). This provides additional evidence that whether or not the sample is stable at calorimeter temperature does not bias the outcome of a drop solution calorimetric experiment.

Carbonates under flowing atmosphere

Drop solution calorimetric data are shown in Table 2. The following thermodynamic cycles are used to determine the enthalpy of interaction of CO₂ with the calorimetric solvent.

MCO₃ (crystal, 298)

= MO (solution, T) + CO₂ (final, T)

$$\Delta H_{\text{dropsol}} \quad (9)$$

MO (crystal, 298) + CO₂ (gas, 298)

= MCO₃ (crystal, 298)

$$\Delta H_{f,298} \quad (10)$$

CO₂ (gas, T) = CO₂ (gas, 298)

$$- \int_{298}^T C_{P,\text{CO}_2} dT \quad (11)$$

MO (crystal, T) = MO (crystal, 298)

$$- \int_{298}^T C_{P,\text{MO}} dT \quad (12)$$

MO (solution, T) = MO (crystal, T)

$$\Delta H_{\text{sol,MO}} \quad (13)$$

CO₂ (gas, T) = CO₂ (final, T)

$$\Delta H_{\text{interaction}} \quad (14)$$

$$\Delta H_{\text{interaction}} = \Delta H_{\text{dropsol}} + \Delta H_{f,298} - \int_{298}^T C_{P,\text{CO}_2} dT - \int_{298}^T C_{P,\text{MO}} dT - \Delta H_{\text{sol,MO}} \quad (15)$$

In the above, CO₂ (final, T) represents the final state of CO₂ after the sample reacts with molten lead borate at calorimeter temperature.

For MgCO₃ and CaCO₃ where the heats of solution of MgO and CaO are known independently, this cycle gives -0.6 ± 1.5 and -1.5 ± 1.6 kJ/mol, respectively, for the enthalpy of interaction of CO₂. This essentially zero value confirms the weight change experiments, which show that no CO₂ remains in the melt.

OTHER CHECKS OF CONSISTENCY AND VALIDITY OF CALORIMETRIC METHODOLOGY

Calculation of enthalpies of solution of oxides from hydroxide and carbonate data

One can use the thermochemical cycles given above to calculate the enthalpy of solution of anhydrous oxides under the assumption that the enthalpy of interaction of H₂O and CO₂ with the solvent is zero. Results are shown in Table 4. The agreement of the ΔH_{sol} data obtained, when the same value (zero) of interaction enthalpy of H₂O and of CO₂ with the solvent is used throughout, is another indication of internal consistency. The values of ΔH_{sol} calculated from hydroxides and carbonates agree within experimental error with those measured directly.

Carbonate-hydroxide exchange reaction

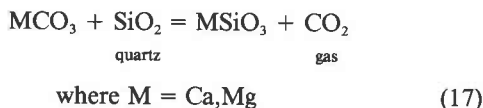
The enthalpy of the reaction



can be calculated directly from the drop solution data under flowing atmosphere in Table 2 as $\Delta H_{298} = -37.6 \pm 3.8$ kJ/mol. Using tabulated enthalpies of formation from the elements (Robie et al., 1978; Woods and Garsels, 1987), one gets -33.5 ± 4 kJ/mol, where the error reflects the spread of heat of formation values in different studies. Our enthalpy of exchange calculated from calorimetric data does not depend on values of heats of solution of the anhydrous oxides in molten lead borate. This method therefore provides a completely independent check of our calorimetric methodology.

The reactions of carbonates with quartz

The reaction



is an important metamorphic reaction occurring in siliceous carbonates, whose thermodynamics are generally well known. By comparing the enthalpies of drop solution of magnesite + quartz, calcite + quartz, or dolomite + quartz with those of enstatite, wollastonite, or diopside, respectively, the enthalpies of reaction can be calculated under the assumption that the energy of interaction of CO₂ with molten lead borate is zero. Chai and Navrotsky (1993) found good agreement with the values in the literature for these reactions. The measured enthalpies of these reactions do not require knowledge of the heats of solution of MgO and CaO. This concordance further confirms our calorimetric approach for carbonates.

Heat content of H₂O

Open weighted Pt capsules containing water were dropped into molten lead borate in the calorimeter at 975 K, under flowing Ar atmosphere. Base-line shifts were less than 0.05 μ V in magnitude. The results (see Table 2) show that the heat content of H₂O is indeed obtained in drop solution experiments under conditions where the gas flow is expected to sweep all evolved water vapor out of the calorimeter. These results confirm that no water is lost before the sample is within the thermopile of the calorimeter, that heat pickup of the sample during drop is negligible, and that there is no enthalpy of interaction between water and lead borate. Since pure H₂O is an extreme case both in terms of rate of volatilization and in terms of the mass of H₂O introduced during the calorimetric experiment, these experiments can be taken to mean that, when hydrous phases are dropped into the melt, all the enthalpy associated with volatile release at calorimetric temperature is sensed by the calorimeter. They also imply that the sample is still essentially at room temperature when it enters the thermopile.

The constant temperature zone of the calorimeter extends about 10 cm above the top of the thermopiles. Thus, as flowing gas rises out of the calorimeter, it only begins

to cool in a region well above the calorimetric detector, where the thermopiles do not sense its enthalpy. Thus the final state of evolved gas sensed by the calorimeter is indeed at calorimeter temperature, as indicated by the experiments above.

CONCLUSIONS AND RECOMMENDATIONS FOR CALORIMETRIC PROCEDURES FOR VOLATILE-BEARING PHASES

These studies have shown that a flowing atmosphere of 1–2 cm³/s produces a reproducible final state for solution calorimetry of samples containing H₂O and CO₂, a state in which all the volatiles are evolved from the calorimeter and have no enthalpy of interaction with the molten lead borate solvent. This procedure eliminates problems of base-line shifts, probably caused by changes in the atmosphere within the calorimeter, which are encountered when volatile-bearing phases are dissolved under a static air atmosphere. In this case, there appears to be some exothermic interaction of H₂O with the solvent, but this does not involve the dissolution of all the water in the molten lead borate. Thus we recommend flowing atmosphere conditions (air, N₂, CO₂, or Ar, at 1–2 cm³/s) for all future solution and drop solution experiments on volatile-bearing phases.

Since H₂O and CO₂ are completely evolved, they do not interact with either the solvent or other dissolved species in it. Thus the methodology developed for anhydrous phases should apply as well to volatile-bearing phases, in which the heat of solution of an oxide is independent of the concentration of that oxide and of other oxides dissolved in the lead borate in the concentration range used in this study. This is indeed supported by the composition-independent molar enthalpies of solution of hydroxides and carbonates in the present study. Nevertheless, for the highest precision in enthalpy of reactions, the product and reactant assemblages should each be dissolved and their enthalpies of solution or drop solution compared directly, rather than by adding together individual oxide data with their accumulated uncertainties.

Using the procedures described here, high-temperature oxide melt calorimetry can become increasingly useful, especially with drop solution techniques, for hydrous minerals such as amphiboles, micas, clays, and zeolites, for carbonate minerals, and for volatile-bearing high-pressure phases.

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REFERENCES CITED

- Akaogi, M., Ito, E., and Navrotsky, A. (1989) Olivine-modified spinel-spinel transitions in the system Mg₂SiO₄-Fe₂SiO₄; Calorimetric measurements, thermochemical calculations, and geophysical application. *Journal of Geophysical Research*, 94, 15671–15685.

- Barton, M.D., Haselton, H.T., Jr., Hemingway, B.S., Kleppa, O.J., and Robie, R.A. (1982) The thermodynamic properties of fluor-topaz. *American Mineralogist*, 67, 350–355.
- Bose, K., and Ganguly, J. (1994) Thermogravimetric study of the dehydration kinetics of talc. *American Mineralogist*, 79, 692–699.
- Brindley, G.W., Sharp, J.H., Patterson, J.H., and Narahari, B.N. (1967) Kinetics and mechanism of dehydroxylation processes: I. Temperature and vapor pressure dependence of dehydroxylation of kaolinite. *American Mineralogist*, 52, 201–211.
- Brown, N.E., and Navrotsky, A. (1994) Hematite-ilmenite (Fe₂O₃-FeTiO₃) solid solutions: The effects of cation ordering on the thermodynamics of mixing. *American Mineralogist*, 79, 485–496.
- Bularzik, J., Navrotsky, A., DeCarlo, J., Bringley, J., Scott, B., and Trail, S. (1991) Energetics of La_{2-x}Sr_xCuO_{4-y} solid solutions (0.0 ≤ x ≤ 1.0). *Journal of Solid State Chemistry*, 93, 418–429.
- Burnley, P., Navrotsky, A., and Bose, K. (1992) Heat of formation of synthetic and natural talc by drop solution calorimetry: A test of a new technique (abs.). *Eos*, 73, 43.
- Chai, L., and Navrotsky, A. (1993) Thermochemistry of carbonate-pyroxene equilibria. *Contributions to Mineralogy and Petrology*, 114, 139–149.
- Charlu, T.V., Newton, R.C., and Kleppa, O.J. (1975) Enthalpies of formation at 970 K of compounds in the system MgO-Al₂O₃-SiO₂ from high temperature solution calorimetry. *Geochimica et Cosmochimica Acta*, 39, 1487–1497.
- Circone, S. (1991) ^{IV,VI}Al substitution in phlogopite: Compositional, structural, and thermochemical properties of trioctahedral micas in the phlogopite-castonite solid solution, Ph.D. thesis, Princeton University, Princeton, New Jersey.
- Circone, S., and Navrotsky, A. (1992) Substitution of ^{IV,VI}Al in phlogopite: High-temperature solution calorimetry, heat capacities, and thermodynamic properties of the phlogopite-castonite join. *American Mineralogist*, 77, 1191–1205.
- Clemens, J.D., Circone, S., Navrotsky, A., McMillan, P.F., Smith, B.K., and Wall, J.V. (1987) Phlogopite: High temperature solution calorimetry, thermodynamic properties, Al-Si and stacking disorder, and phase equilibria. *Geochimica et Cosmochimica Acta*, 51, 2569–2579.
- Davies, P.K., and Navrotsky, A. (1981) Thermodynamics of solid solution formation in the systems NiO-MgO and NiO-ZnO. *Journal of Solid State Chemistry*, 38, 264–276.
- DiCarlo, J., Bularzik, J., and Navrotsky, A. (1992) A thermochemical study of La_{2-x}A_xCuO_{4-y} (A = Ba, Sr, Ca, Pb). *Journal of Solid State Chemistry*, 96, 381–389.
- Eagan R., and Bergeron, J. (1972) Determination of water in lead borate glasses. *Journal of the American Ceramic Society*, 55, 53–54.
- Gordon, R.S., and Kingery, W.D. (1967) Thermal decomposition of brucite: II. Kinetics of decomposition in vacuum. *Journal of the American Ceramic Society*, 50, 8–14.
- Graham, C.M., and Navrotsky, A. (1986) Thermochemistry of the tremolite-cedenite amphiboles using fluorine analogues, and applications to amphibole-plagioclase-quartz equilibria. *Contributions to Mineralogy and Petrology*, 93, 18–32.
- Ito, E., Akaogi, M., Topor, L., and Navrotsky, A. (1990) Negative *P-T* slopes for reactions forming MgSiO₃, perovskite confirmed by calorimetry. *Science*, 249, 1275–1278.
- Kiseleva, I.A., and Ogorodova, L.P. (1984) High temperature solution calorimetry for determining the enthalpies of formation for hydroxyl containing minerals such as talc and tremolite. *Geochemistry International*, 2, 36–46.
- Navrotsky, A. (1977) Recent progress and new directions in high temperature calorimetry. *Physics and Chemistry of Minerals*, 2, 89–104.
- Navrotsky, A., and Coons, W.E. (1976) Thermochemistry of some pyroxenes and related compounds. *Geochimica et Cosmochimica Acta*, 40, 1281–1288.
- Newton, R.C., Charlu, T.V., and Kleppa, O.J. (1980) Thermochemistry of the high structural state plagioclases. *Geochimica et Cosmochimica Acta*, 44, 933–941.
- Pawley, A.R., Graham, C.M., and Navrotsky, A. (1993) Tremolite-richterite amphiboles: Synthesis, compositional and structural characterization, and thermochemistry. *American Mineralogist*, 78, 23–35.
- 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 (10⁵ pascals) pressure and at higher temperatures. *U.S. Geological Survey Bulletin*, 1452, 456 p.
- Ross, N.L., Akaogi, A., Navrotsky, A., Susaki, J., and McMillan, P. (1986) Phase transitions among the CaGeO₃ polymorphs (wollastonite, garnet, and perovskite structures): Studies by high pressure synthesis, high temperature calorimetry, and vibrational spectroscopy and calculation. *Journal of Geophysical Research*, 91, 4685–4698.
- Westrich, H.R., and Navrotsky, A. (1981) Some thermodynamic properties of fluorapatite, fluorpargasite, and fluorphlogopite. *American Journal of Science*, 281, 1091–1103.
- Woods, T.L., and Garrels, R.M. (1987) Thermodynamic values at low temperature for natural inorganic materials: An uncritical summary, 242 p. Oxford University Press, New York.

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