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PROJECT SUMMARY REPORT

"Thermodynamics of Minerals Stable Near the Earth's Surface"

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Project Summary Report:

High temperature oxide melt calorimetry is a well established method for determining enthalpies of formation of anhydrous silicates. In this approach, a given phase or phase assemblage is dissolved in a molten oxide solvent, typically $2\text{PbO} \cdot \text{B}_2\text{O}_3$ at 700°C . The difference is heat of solution between reactants and products (e.g. stoichiometric mixture of 2MgO and SiO_2 versus Mg_2SiO_4) gives the enthalpy of formation. At the end of each dissolution experiment, the oxides are present in the solvent in a state essentially represented by Henry's Law dilute solution behavior.

To apply those methods to phases containing volatiles, the final state of H_2O and CO_2 on dissolution of the crystalline volatile-bearing phase must be determined. Our early work suggested that H_2O interacts exothermically with $2\text{PbO} \cdot \text{B}_2\text{O}_3$ melt under a static air atmosphere (Clemens et al., 1987; Circone, 1991). However weight change experiments and chemical analysis of the quenched solvent suggested that little H_2O remains dissolved. Because this final state was not as well constrained as we wished, and because the calorimetric runs had small but significant "baseline shifts", we have modified our experiments to be done under a flowing gas atmosphere (1-2 cc/sec Ar, air, or CO_2), which sweeps the evolved gas out of the hot calorimeter, returns the signal to the original baseline, and creates a well defined final state, namely completely evolved H_2O or CO_2 gas at 1 atm and calorimeter temperature. This is shown by the following thermodynamic cycle:

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Table 1. Enthalpy of Interaction of Water with Lead Borate

Reaction	ΔH (kJ/mol)	
	700 °C	800 °C
(a) $Mg(OH)_2$ (xl, 25 °C) = MgO (dissolved,T)+ H_2O (final state,T)	144.1 ± 3.6	156.0 ± 2.8
(b) MgO (dissolved, T) = MgO (xl, 25 °C)	-36.5 ± 1.0	-44.1 ± 0.7
(c) H_2O (gas, T) = H_2O (gas, 25 °C)	-2.50 ± 0.6	-29.2 ± 0.6
(d) MgO (xl, 25 °C) + H_2O (gas, 25 °C) = $Mg(OH)_2$ (xl, 25 °C)	-82.3 ± 0.8	-82.3 ± 0.78
(e) H_2O (gas, T) = H_2O (final state, T)	0.4 ± 3.8	0.5 ± 3.0

Reactions (a) and (b) represent our calorimetric measurements, and (c) and (d) are taken from the literature, and for the cycle $\Delta H(e) = \Delta H(a) + \Delta H(b) + \Delta H(c) + \Delta H(d)$. ΔH (reaction e) indicates that interaction between H_2O and the solvent and is zero within experimental error. For carbonates analogous cycles apply, and the measurement of the enthalpies of carbonate-silicate reactions such as $MgCO_3 + SiO_2 = MgSiO_3 + CO_2$ (Chai and Navrotsky, 1993) confirm the soundness of the method.

Another technical issue is to obtain, for oxide melt calorimetry, appropriate reference states for the alkali oxides, Na_2O and K_2O , which can not be measured directly because of their reactivity and corrosiveness. We are using three approaches to this (a) dissolving the carbonates, (b) using heat of solution data for ordered alkali feldspars for this reference, and (c) using the alkali aluminates, $NaAlO_2$ and $KAlO_2$. For MgO and CaO we have also refined values of heats of solution. These data will allow direct integration and comparison of thermochemical data obtained by high T oxide melt calorimetry and by other means such as HF solution calorimetry.

Now that we have a proven method for volatile-bearing phases, we are applying it to a number of important problems. This includes amphiboles, micas, and zeolites (see below) and carbonates in the (Mg, Fe, Ca) CO_3 system (see section 3.3).

The compositional complexity of amphiboles, micas, clays, and zeolites arises from extensive substitutional solid solutions. We are concentrating on the energetics of calcic amphiboles with edenitic and tschermakitic substitutions. This is the postdoctoral project of E. Smelik, who has a background in amphibole crystal chemistry and electron microscopy from D. Veblen's group at Johns Hopkins. D. Jenkins, professor at SUNY Binghamton, with expertise in amphibole phase equilibria and high pressure synthesis, is also a collaborator. Together we are synthesizing and doing calorimetry on edenitic and tschermakitic substitutions (see Fig. 1). Realizing that end members are other hard to come by, either as natural or synthetic samples, our approach is to obtain, characterize, and measure enough samples in which the two substitutions shown occur simultaneously (and other substitutions are minimal) to be able to fit end-member heats of solution and mixing properties. This will probably require about a dozen samples. Proper crystallographic, microprobe, and TEM characterization are essential. Our new Cameca SX-50 microprobe and a new Phillips CM-20 HRTEM, both housed in the new Princeton Materials Institute, will be used extensively.

The energetics of solid solution formation in F-tremolite-F-edenite, in tremolite-richterite, (Graham and Navrotsky, 1986; Pawley, et al., 1993) and in phlogopite-eastonite (Circone and Navrotsky, 1992) are shown in Fig. 2. The similarity between ΔH_{mix} of tremolite-richterite and fluor-tremolite-fluor-edenite amphiboles suggests that the A site controls the mixing energetics of both solid solutions, with A-site positional ordering and interactions with other cations playing an important role. Because the richterite and edenite exchanges are the two most important A-site substitutions that occur in calcic amphiboles, the same factors will influence the stability of

all amphiboles with Na in the A site. Therefore, metamorphic calcic amphiboles with small A-site occupancies should be stabilized relative to compositions with zero or high A-site occupancies, and any natural amphiboles with high A-site occupancies must have crystallized at a high temperature and presumably cooled relatively fast, thereby preventing exsolution.

In the micas studied, the $Mg + Si = 2Al$ substitution is also associated with a positive heat of mixing asymmetric toward the edenite end. This is consistent with destabilization due to layer mismatch, with a solvus in that system, and with limited extent of Al-substitution in natural systems. The X-ray and NMR data are consistent with significant Al, Si short range order and have been used to formulate configurational entropy models. (Circone et al., 1991; Circone and Navrotsky, 1992).

The energetics of high silica zeolites poses an intriguing question. In comparing quartz and an open framework such as faujasite, the molar volume increases by a factor of two, but this increase reflects the creation of zeolitic pores rather than major changes in the local bonding within the SiO_4 tetrahedra. Figure 3 shows enthalpy as a function of volume. The enthalpy of the zeolitic silicas relative to quartz is not very destabilizing and about the same as that of silica glass. (Petrovic et al., 1993).

A recent project, the senior thesis of Susan Ellsworth, has opened a new area - that of the energetics of radiation damage in minerals. The enthalpy of annealing of natural zircons as a function of radiation dose is shown in Fig. 4. The plateau at metamictization is pronounced, and the large value of the enthalpy, more than twice the heat of formation from the oxides, is consistent with pervasive damage on the nearest and next-nearest neighbor scale, rather than microcrystallinity. The increase in enthalpy of about 60 kJ/mol could cause a factor of three increase in the equilibrium solubility of ZrO_2 in an aqueous fluid in contact with zircon. Thus damaged zircons are thermodynamically as well as kinetically more reactive. This has ramifications for both radioactive waste disposal and isotope geochronology. We plan to expand this area in future research.

The work on crystalline silicas has been complemented by a set of studies on amorphous sol-gel silicas (Maniar and Navrotsky, 1990; Maniar et al., 1990; Ying et al., 1993).

Amphibole Compositions - Ferromagnesian Orthoamphiboles

an	: $Mg_2Mg_5Si_8O_{22}(OH)_2$
an-gd	: $Mg_2Mg_4AlSi_7AlO_{22}(OH)_2$
gd	: $Mg_2Mg_3Al_2Si_6Al_2O_{22}(OH)_2$
"ideal" gd	: $Na_{0.5}Mg_2Mg_{3.5}Al_{1.5}Si_6Al_2O_{22}(OH)_2$ (Robinson et al., 1971)

Fig. 1 Amphibole substitutions for thermochemical study.

Fig. 2 Enthalpies of mixing along amphibole and mica substitutional solid solutions.

Fig. 3 Enthalpy relative to quartz of SiO_2 polymorphs, open circles represent zeolite structures.

Fig. 4 The enthalpy of annealing of zircon as a function of radiation dose. An incubation stage is seen for samples with low radiation doses. ΔH_{anneal} saturates at a value of -59 kJ/mol for radiation doses greater than 5×10^{15} α -events/mg.

Publications from Grant

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