Thermochemistry of guest-free melanophlogite

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ABSTRACT

Melanophlogite is a naturally occurring clathrasil possessing a framework of linked silicate tetrahedra surrounding small, isolated cages, which can host small molecules. The energetics of a guest-free natural sample was determined by oxide-melt solution calorimetry. Melanophlogite is energetically metastable with respect to α-quartz by 9.5 ± 0.5 kJ/mol, a value similar to that for amorphous silica and for synthetic small-pore zeolitic silicas (Petrovic et al. 1993, Piccione et al. 2001). Thus, its occurrence in nature, for example in environments where it can occlude volcanic gases, is reasonable on energetic grounds.

Molecular modeling of the internal pore volume of melanophlogite confirms that this enthalpy follows the trend previously established for a variety of silica zeolites, which defines an internal surface energy of 0.093 ± 0.010 J/m², similar to that of the external surface energy of amorphous silica. Thus melanophlogite, despite its unique topology and isolated cages, behaves energetically as predicted from the enthalpies of more-open zeolitic frameworks.

INTRODUCTION

Melanophlogite is one of a series of silica polymorphs known as clathrasils whose structures comprise a clathrate-type framework of corner-sharing [SiO$_4$] tetrahedra. Clathrasils are structurally related to zeolites. Both consist of interconnected networks of tetrahedra that define cages or pores, but clathrasils differ from zeolites in that their cages do not form channels accessible to large molecules because the cages are isolated by small openings. Clathrasils have higher framework densities than many more-open zeolites.

The structure of melanophlogite is composed of columns of tetrakaidecahedral ($5^{12}6^2$) cages running along the [100], [010], and [001] directions in which adjacent cages share hexagonal faces. The voids between these columns of cages are pentagonal dodecahedra (5^{12}) cages. There are six $5^{12}6^2$ and two 5^{12} cages in the unit cell. At 473 K (Gies 1983), the polyhedral volumes of these two cages are ~136 and ~97 Å^3, respectively.

Melanophlogite occurs as a mineral, contains up to 8 wt% volatile guest molecules (CH$_4$, CO$_2$, and N$_2$) (Liu et al. 1997; Nakagawa et al. 2001), and may be a host for greenhouse gases and radon. Many new members of the clathrasil series have been synthesized (Liebau 1983). By careful thermal treatment, the guest molecules can be removed.

This communication reports the first measured enthalpy of formation of a clathrasil, low- or α-melanophlogite. Its enthalpy is discussed in the context of the systematics developed for zeolitic silicas.
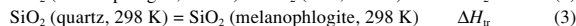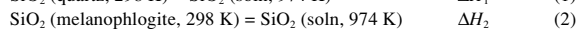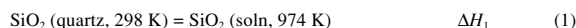
CALORIMETRIC STUDY

The sample of melanophlogite from Livorno, Italy (Natural History Museum, London, specimen no. BM1973-116), heat-treated for six hours at 1223

K to remove all guest molecules, is the same as that used by Liu et al. (1997) in their NMR study of phase transitions.

High-temperature calorimetric measurements were performed using a Tian-Calvet microcalorimeter operating at 974 K with molten lead borate (2PbO·B$_2$O$_3$) as solvent (Navrotsky 1997). A sample pellet weighing approximately 5 mg was dropped from room temperature into the solvent in the hot calorimeter. The measured heat effect includes the enthalpy associated with heating the sample from room temperature to 974 K (heat content) plus its enthalpy of solution. Eight sample pellets were dropped, and the heats of drop solution, ΔH_{ds}, are listed in Table 1. The average is 29.86 ± 0.44 kJ/mol.

We have remeasured ΔH_{ds} of quartz in lead borate at 974 K to be 39.35 ± 0.12 kJ/mol (12 experiments), in excellent agreement with our previous value of 39.1 ± 0.3 kJ/mol (Kiseleva et al. 1996) and numerous internal laboratory checks thereafter. The enthalpy of the hypothetical transition from quartz to melanophlogite, here called ΔH_{tr}, can be calculated based on the following thermochemical cycle:

$$SiO_2 \text{ (quartz, 298 K)} = SiO_2 \text{ (soln, 974 K)} \qquad \Delta H_1 \qquad (1)$$
$$SiO_2 \text{ (melanophlogite, 298 K)} = SiO_2 \text{ (soln, 974 K)} \qquad \Delta H_2 \qquad (2)$$
$$SiO_2 \text{ (quartz, 298 K)} = SiO_2 \text{ (melanophlogite, 298 K)} \qquad \Delta H_{tr} \qquad (3)$$

from which $\Delta H_{tr} = \Delta H_1 - \Delta H_2 = 9.5 \pm 0.5$ kJ/mol.

RESULTS AND DISCUSSION

Measurement of the energetics of a large number of silica zeolites by high-temperature oxide-melt solution calorimetry shows them to be energetically metastable with respect to quartz by 9–15 kJ/mol and to amorphous silica by 0–5 kJ/mol (Petrovic et al. 1993; Piccione et al. 2000). This energy difference varies roughly linearly with both the molar volume and the framework density of the zeolite, the more open structures being higher in energy.

TABLE 1. Enthalpies of drop solution of guest-free melanophlogite in lead borate at 974 K

Sample Mass (mg)	4.66	5.16	5.34	5.69	4.71	5.23	4.46	5.15
ΔH_{ds} (kJ/mol)	29.14	29.88	28.94	30.72	29.81	30.31	29.64	30.44

Average: ΔH_{ds} = 29.86 ± 0.44 kJ/mol (8 experiments, error is two standard deviations of the mean).

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The value for melanophlogite obtained here is in good agreement with the trend of ΔH_{tr} as a function of molar volume, V_m, observed in other silica zeolites: $\Delta H_{tr} = -10.1$ (± 1.9) + 0.55 (± 0.06) V_m (Piccione et al. 2000). Specifically, the unit-cell volume of guest-free α-melanophlogite was reported to be 2398 Å^3 (Liu et al. 1997 and see modeling discussion below), and thus its molar volume is 31.76 cm^3/mol. The predicted ΔH_{tr} for guest-free melanophlogite from the above equation is 7.4 $\pm$ 2.7 kJ/mol, which agrees with the measured value (9.5 $\pm$ 0.5 kJ/mol) within the uncertainty.

Moloy et al. (2002) used molecular modeling of these structures to calculate their internal surface area and showed that the enthalpy varies linearly with the computed surface area, concluding that the slope of this line produces a physically realistic internal surface energy comparable to the surface energy of amorphous silica.

We explored the applicability to the clathrate structure of the correlation presented in Moloy et al. (2002) between energetics and internal surface area. The internal surface area (ISA) was calculated using the Free Volume utility ("Occupiable" mode) in the Visualizer module of the Cerius2 4.2 MS software package (Accelrys ref.) using an SGI O^2 similar. The calculation details have been presented previously (Moloy 2002), but will be discussed briefly. A spherical probe atom is moved algorithmically through the various structural models to generate both internal surfaces and internal void-volumes. The probe atom and the framework atoms are modeled as hardspheres, and the framework atoms are assigned ionic radii consistent with Shannon (Shannon 1976). When the probe atom comes in "contact" with framework atoms, after following a pre-established trajectory, the position of the probe atom *centroid* is recorded. By "contact", we mean the external surface of the hard-sphere probe atom coming in contact with the external surface of a hard-sphere framework atom. The position of the centroid then becomes one point in a grid that eventually defines the internal surface and, in turn, the internal void volume. For reasons discussed in Moloy et al. (2002), a probe atom radius of 0.96 Å was used to calculate the internal surfaces.

The first detailed structural analysis of guest-bearing α-melanophlogite was presented by Nakagawa et al. (2001). They described the structure as having a tetragonal supercell, $P4_2/nbc$ (no. 133), with $a = 26.818$ Å and $c = 13.365$ Å. Although that work provided accurate lattice parameters and fractional coordinates for the guest-bearing phase, the guest-free phase was not discussed. However, Liu et al. (1997), using powder X-ray diffraction data, discussed the thermal evolution of the unit-cell paramters for the guest-bearing and guest-free phases, and suggested that there is only a 0.22% difference in the unit cell parameters at 30 °C. Thus, the structural differences between the two phases are probably insignificant for the present study. Therefore, the structure proposed by Nakagawa et al. (2001) has been used to construct the molecular model to calculate the internal surface area, and the guest-molecules are simply omitted from the model.

The calculated internal surface area of melanophlogite is 1690 m^2/g or 101 000 m^2/mol. Figure 1 shows the variation of ΔH_{tr}, for dense silica polymorphs, silica zeolites, and melanophlogite. The slope of the best-fit line obtained gives a
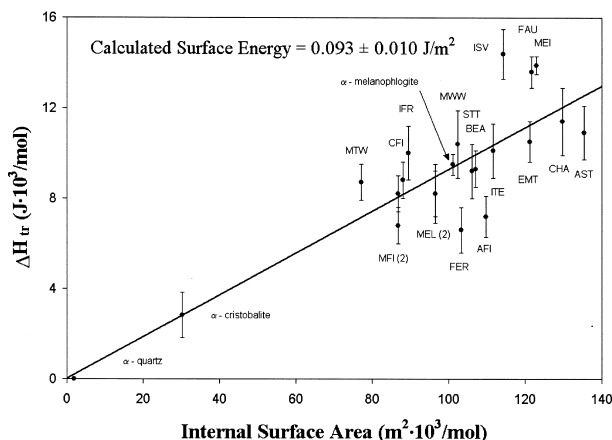

FIGURE 1. Enthalpy of silica polymorphs relative to quartz, ΔH_{tr}, vs. calculated internal surface area. Points represent data for dense and microporous silicas, reported by Moloy et al. (2002). The point for quartz has a zero ΔH_{tr} by definition but is offset from the y-axis because it does have a small calculated internal surface area. The new datum for melanophlogite falls on the line, whose slope gives the surface enthalpy. Two ΔH_{tr} values are presented for MFI and MEL [Piccione et al. (2000) and Petrovic et al. (1993)].

surface enthalpy of 0.093 $\pm$ 0.010 J/m^2 (95% confidence level). The melanophlogite datum falls right on the line. Thus, the small isolated cages in melanophlogite do not change its energetics from those predicted from the behavior of more open zeolitic structures with larger windows that form interconnected cages.

The geologic occurrence of melanophlogite can be rationalized on energetic grounds: it is similar in energy to amorphous silica and, thus, is readily accessible under conditions where amorphous silica may form. The volcanic sample from Livorno may be templated by its guest gas molecules, but the important conclusion is that such templating or structure direction is not necessary to stabilize the structure and may act primarily in a kinetic rather than thermodynamic sense, to nucleate and enhance its growth. Presumably, other clathrasils, such as dodecasil, may be similar in energy to melanophlogite and could exist in natural environments where the proper small-molecule, structure-directing agents are present.

Several phase transitions, both above and below room temperature, may occur in melanophlogite, both with and without guest molecules. The calorimetric data here refer to the tetragonal structure existing at room temperature. The energetic effect of these distortional transitions is expected to be small. Preliminary differential scanning calorimetry shows no peaks associated with transitions reported previously (Liu et al. 1997) at 333 K (tetragonal to cubic) and 423 K (cubic to cubic), implying enthalpy changes of a few tenths of a kJ/mol or less. Thus, the systematics reported here apply to the cubic β-phase(s) as well.

We conclude that melanophlogite has an enthalpy similar to that of amorphous silica and follows the energetic trends established for silica zeolites. Future work includes the study of the energetics of incorporation of guest molecules and of phase transitions as a function of guest content.

REFERENCES CITED

Accelrys (2001). San Diego, CA: Online Documentation Library: http://www.msi.com/doc/cerius40/modenv/7_GeomAnal.html#973179.

Gies, H. (1983) Studies on clathrasils. III. Crystal structure of melanophlogite, a naturalclathrate compound of silica. Zeitschrift für Kristallographie, 164, 247–257.

Kiseleva, I., Navrotsky, A., Belitsky, I.A., and Fursenko, B.A. (1996) Thermochemistry of natural potassium sodium calcium leonhardite and its cation-exchanged forms. American Mineralogist, 81, 668–675.

Liebau, F. (1983) Zeolites and clathrasils—two distinct classes of framework silicates. Zeolites, 3, 191–193.

Liu, S., Welch, M.D. and Klinowski, J. (1997) NMR study of phase transitions in guest-free silica clathrate melanophlogite. Journal of Physical Chemistry B, 101, 2811–2814.

Moloy, E.C., Davila, L.P., Shackelford, J.F., and Navrotsky, A. (2002) High-silica zeolites: a relationship between energetics and internal surface areas. Microporous and Mesoporous Materials, 54, 1–13.

Nakagawa, T., Kihara, K. and Harada, K. (2001) The crystal structure of low melanophlogite. American Mineralogist, 86, 1506–1512.

Navrotsky, A. (1997) Progress and new directions in high temperature calorimetry revisited. Physics and Chemistry of Minerals, 24, 222–241.

Petrovic, I., Navrotsky, A., Davis, M. E., and Zones, S. I. (1993) Thermochemical study of the stability of frameworks in high silica zeolites. Chemistry of Materials, 5, 1805–1813.

Piccione, P.M., Laberty, C., Yang, S., Camblor, M.A., Navrotsky, A. and Davis, M.E. (2000) Thermochemistry of pure-silica zeolites. Journal of Physical Chemistry B, 104, 10001–10011.

Shannon, R.D. (1976) Revised effective ionic radii and systematic studies on interatomic distances in halides and chalcogenides. Acta Crystallographica, A32, 751–767.