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LETTER

Heat capacity and entropy of melanophlogite: Molecule-containing porosils in nature

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ABSTRACT

The heat capacities of two different molecule-containing melanophlogites of approximate composition $46SiO_2 \cdot 1.80CH_4 \cdot 3.54N_2 \cdot 1.02CO_2$ from Mt. Hamilton, California, and $46SiO_2 \cdot 3.59CH_4 \cdot 3.10N_2 \cdot 1.31CO_2$ from Racalmuto, Sicily, along with a heat-treated (molecule-free) sample of composition SiO_2, were studied between 5 and 300 K using heat-pulse microcalorimetry. The molecule-free sample was obtained by heating natural Racalmuto crystals at 1173 K for 24 h. The standard third-law entropy of the molecule-free sample is $S° = 2216.3 \pm 6.6$ J/(mol·K) for $46SiO_2$ and the natural Mt. Hamilton and Racalmuto samples give $S° = 2805.7 \pm 8.4$ J/(mol·K) and $S° = 2956.8 \pm 8.9$ J/(mol·K), respectively. The entropy and Gibbs free energy for molecule-free melanophlogite relative to quartz at 298 K are $\Delta S_{\text{trans}} = 6.7$ J/(mol·K) and $\Delta G_{\text{trans}} = 7.5$ kJ/mol, respectively and, thus, it does not have a thermodynamic field of stability in the SiO_2 system. The difference in C_P values between molecule-containing and molecule-free melanophlogite is characterized by an increase in C_P from 0 to ~70 K, and it then reaches a roughly constant value at $70 \text{ K} < T < 250$ K. The ΔS^{rxn} at 298 K for $46SiO_2\text{(melan.)} + xCH_4\text{(gas)} + yCO_2\text{(gas)} + zN_2\text{(gas)} = 46SiO_2 \cdot (xCH_4)^{12} \cdot (yCO_2, zN_2)^{14}$ is estimated to be about –642 and –802 J/(mol·K) for the Mt. Hamilton and Racalmuto samples, respectively. The thermodynamic data, as well as published results on the occurrence of natural molecule-containing samples suggest that melanophlogite crystallizes metastabily. The occurrence of melanophlogite and the lack of other porosils in nature are probably due to the essential role of molecular structure-directing agents. For melanophlogite they can be CO_2, N_2, and CH_4, whereas the crystallization of other porosils requires more chemically and structurally complex molecules that are not naturally abundant.

Keywords: Melanophlogite, heat capacity, entropy, clathrasils, microporous minerals, clathrate

INTRODUCTION

The SiO_2 group of phases shows great variation in crystal structure in both nature and in the laboratory. It includes several low-density SiO_2 porosils, which are further divided into the clathrasils and zeosils (Liebau 1988). The mineral melanophlogite is the only known natural molecule-containing porosil/clathrasil. It was first described by Lasaulx (1876) in Sicilian sulfur deposits, but has since been found in other localities worldwide in various low-temperature geologic environments (Zák 1972; Cooper and Dunning 1972; Grasselini Troysi and Orlandi 1972; Kropatsheva and Makarov 1975; Dunning and Cooper 2002; Tribaudino et al. 2008). Melanophlogite has the ideal formula $46SiO_2 \cdot 2M^{12} \cdot 6M^{14}$, where the superscripts are the coordination numbers of the guest molecules M.

Melanophlogite, whose high-temperature crystal-structure was refined by Gies (1983), Nakagawa et al. (2005), and Tribaudino et al. (2008) and low-temperature modification by Nakagawa et al. (2001, 2005), has a microporous framework built-up of corner-sharing SiO_4 tetrahedra. It is isostructural with gas hydrate I (Kamb 1965; Zák 1972). Both structures are classified as clathrates and they contain two different polyhedral cages (Fig. 1[1]), labeled by the notation $[5^{12}]$ and $[5^{12}6^2]$, where the superscripts give the number of pentagonal and hexagonal faces making up the cage polyhedron. The cages in melanophlogite can enclathrate simple molecular guest species such as CH_4, N_2, H_2S, and CO_2 but not H_2O (Gies et al. 1982; Kortus et al. 2000; Kolesov and Geiger 2003; Tribaudino et al. 2008) and is, thus, hydrophobic. Their exact role in the crystallization behavior and the geochemical conditions under which melanophlogite forms in nature have not been fully addressed.

The phase relations for both guest-containing and guest-free melanophlogite are unknown. The enthalpy for guest-free melanophlogite relative to quartz at 298 K was determined (Navrotsky et al. 2003). They discussed the enthalpy systematics for melanophlogite, as well as for several low-density SiO_2 polymorphs such as the zeosils. All studied molecule-free porosils are enthalpically unstable compared to quartz (Navrotsky et al. 2003). However, there are no data on the heat capacity of

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[1] Deposit item AM-08-036, Figure 1, Tables 1a, 1b, 1c, and 1d (raw experimental C_P data and thermodynamic functions) and Table 2 (thermodynamic properties for various SiO_2 phases). Deposit items are available two ways: For a paper copy contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. For an electronic copy visit the MSA web site at http://www.minsocam.org, go to the American Mineralogist Contents, find the table of contents for the specific volume/issue wanted, and then click on the deposit link there.

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melanophlogite and its standard third-law entropy. This prohibits an assessment of its thermodynamic stability via its Gibbs free energy and, thus, a better analysis regarding its occurrence in nature. To do this, we have measured the heat capacity of two natural molecule-containing melanophlogites and a degassed sample containing no molecules. Finally, we discuss the occurrence of melanophlogite, as well as possible reasons for the absence of other clathrasils and zeosils in nature.

EXPERIMENTAL METHODS

Samples

The melanophlogite crystals that were investigated are from Mt. Hamilton, California, and Racalmuto, Sicily (Smithsonian Institute label NMNH C1279). The first occurrence is discussed in Cooper and Dunning (1972) and Dunning and Cooper (2002). Gies (1983) determined an average cage occupation of 90% CH_4 in the small [5^{12}] cage and 59% N_2 and 17% CO_2 in the large [$5^{12}6^2$] cage from an X-ray study of a crystal from Mt. Hamilton. Kolesov and Geiger (2003) argued from their Raman spectra that CH_4 and CO_2 molecules in these crystals are found in both cages and that they could be compositionally inhomogeneous and zoned with respect to the various guest species, as shown first by Gies et al. (1982) using mass spectrometry. The occurrence of the Racalmuto crystals is described in Lasaulx (1876) and Skinner and Appleman (1963). For it, Gies et al. (1982) presented a composition of $46SiO_2{\cdot}3.59CH_4{\cdot}3.10N_2{\cdot}1.31CO_2$ assuming full cage occupancies. H_2S may also occur in some Racalmuto crystals (Tribaudino et al. 2008).

For our C_P study, small melanophlogite crystals were handpicked and separated under a binocular microscope from their underlying matrix. X-ray diffraction, both powder and single crystal, showed that much of the Mt. Hamilton sample consists of quartz, even for crystals with a cubic morphology, as described by Dunning and Cooper (2002). For the C_P measurements "pure" melanophlogite samples, based on slow-scan powder X-ray patterns, were obtained and gently ground to a powder.

Following completion of the C_P measurements on both natural samples, the Mt. Hamilton sample was heated at 50 K/h to 1223 K and held for 10 h. The Racalmuto sample was heated at 50 K/h to 1173 K and held there for 24 h. This was done using a four-zone tube furnace with a temperature control of $T \approx 1$ K, which was further checked by use of an external Ni-NiCr thermocouple. Gies et al. (1982) and Navrotsky et al. (2003) note that these temperatures should allow for the degassing of melanophlogite, but should not cause recrystallization to another phase. Skinner and Appleman (1963) observed a breakdown to cristobalite at $T \geq 1173$ K, but not at 1073 K. Slow-scan powder X-ray measurements for 20 h between 10 and 60° 2θ were made on both heat-treated samples. Both heated samples were studied further by heat-pulse calorimetry.

Low-temperature calorimetry

Low-temperature heat capacities were measured with a commercially designed heat-pulse calorimeter [i.e., heat capacity option of the Physical Properties Measurement System (PPMS), produced by Quantum Design]. The measurements were performed at temperatures between 5 and 300 K on small milligram-sized samples (about 13 to 15 mg) sealed in an Al-container and covered by a lid. C_P values below 5 K were estimated by a linear extrapolation to 0 K in a plot of C_P/T vs. T^2. The C_P data were collected at 60 different temperatures on cooling with a logarithmic or linear spacing, with C_P determined three times at each temperature. Details behind the heat-pulse calorimetric method are given in Dachs and Bertoldi (2005) and Dachs and Geiger (2006).

RESULTS

The heat-treated samples were dark in color as reported by Zák (1972). The X-ray pattern of the heat-treated Mt. Hamilton melanophlogite showed substantial amounts of cristobalite. That of the Racalmuto sample showed a small amount (less than a couple of percent) of what appears to be a synthetic SiO_2 zeosil phase or possibly cristobalite. No reflections could be indexed to graphite in either sample. Zák (1972) reports in his study of a heat-treated melanophlogite that no graphite could be observed at 1600× magnification under the microscope. The powder IR spectrum of the Mt. Hamilton sample showed no measurable amounts of CH_4 or CO_2.

The raw experimental C_P data for the two natural melanophlogites of approximate composition $46SiO_2{\cdot}1.80CH_4{\cdot}3.54N_2{\cdot}1.02CO_2$ and $46SiO_2{\cdot}3.59CH_4{\cdot}3.10N_2{\cdot}1.31CO_2$ and the degassed samples of composition $46SiO_2$ are given in Table 1a[1]. No correction for the presence of the minor SiO_2 phase in the heat-treated Racalmuto sample or for cristobalite in the Mt. Hamilton sample was made. The C_P data were fitted to polynomials of the general form $C_P = k_o + k_1T^{-0.5} + k_2T^{-2} + k_3T^{-3} + k_4T + k_5T^2 + k_6T^3$. For this purpose, a data set was divided into three temperature regions, whereby each was fit individually, but such that a certain overlap of data were present. From this, smoothed molar thermodynamic functions for all phases were obtained (Tables 1b, 1c, and 1d[1]). Their heat capacity behavior is shown in Figure 2. The Racalmuto sample probably shows the beginning of a phase transition at $T \approx 280$ K with increasing temperature, while the Mt. Hamilton sample and the heat-treated melanophlogites show no such behavior. The standard third-law entropy, $S°$, was determined by analytically solving the integral:

$$S^\circ = \int_0^{298.15} \frac{C_P}{T} dT \,. \qquad (1)$$

The uncertainty in $S°$ was calculated as described in Dachs and Geiger (2006) and the entropy at $T = 0$ K was assumed to be zero. We obtained third-law entropies values $S° = 2805.7 \pm 8.4$ J/(mol·K) and the $S° = 2956.8 \pm 8.9$ J/(mol·K) for the natural Mt. Hamilton and Racalmuto melanophlogites, respectively, and $S° = 2216.3 \pm 6.6$ J/(mol·K) for the guest-free Racalmuto sample (the $S°$ value for the heated Mt. Hamilton sample cannot be interpreted, due the presence of substantial cristobalite, and will not be considered further).

DISCUSSION

Crystal-chemical and thermodynamic properties

Melanophlogite is tetragonal with space group $P4_2/nbc$ at room temperature (Zák 1972) and it undergoes a phase transi-

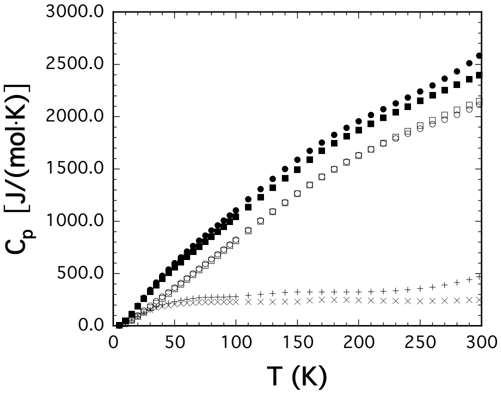

FIGURE 2. Heat capacity of natural guest-containing and heat-treated melanophlogite from Mt. Hamilton, California (filled and open squares) and Racalmuto, Sicily (filled and open circles) from 0 to 300 K using smoothed data. The cross and plus symbols show the difference in C_P between the natural Mt. Hamilton and Racalmuto samples and their heat-treated analogs, respectively.

tion around 338 K to a cubic phase of space group $Pm\overline{3}$. This depends on the composition of the enclathrated guest molecules in both natural and synthetic samples (Gies 1983). The molecules, which are partitioned between the two cages (Fig. 1[1]) in manner that is not precisely understood, are quasi free and show weak interactions with the neutral SiO_2 framework or with each other, as shown by single-crystal Raman spectroscopy (Kolesov and Geiger 2003). In addition to melanophlogite, other clathrasils have been synthesized in the laboratory (Liebau 1988; Higgins 1994; Gies et al. 1998). We are not aware of any C_P studies that have been made on any clathrasil and, thus, their P-T relations are not known.

We begin our analysis of the C_P data of molecule-free melanophlogite with a comparison to the C_P behavior of various SiO_2 phases, especially the structurally related zeosils (Liebau 1988; Higgins 1994; Gies et al. 1998). The latter SiO_2 phases are, unlike clathrasils, more related to the zeolite group of phases, because they have infinite structural channels in which molecules can diffuse. In terms of C_P behavior, molecule-free melanophlogite has a slightly larger low-temperature heat capacity (Fig. 3) than other low-density SiO_2 phases (Table 2[1]). Indeed, its C_P between 0 and 240 K is the largest of all the SiO_2 phases plotted in Figure 3. Thus, clathrasil phases may behave in a similar and unusual fashion as zeosils (Boerio-Goates et al. 2002), because both have higher C_P values in the low-temperature region (excepting zeolite beta) compared to silica glass.

Melanophlogite's entropy relative to quartz at 298 K (i.e., $\Delta S_{trans} = S^{\circ}_{melan} - S^{\circ}_{qtz}$) is 6.7 J/(mol·K). This value is slightly larger than those reported for various zeosils, which lie between 3.2 and 4.2 J/(mol·K) at 298 K (Piccione et al. 2001, Table 2). These workers showed that the entropies of various zeosils are approximately constant as a function of their molar volumes. Melanophlogite has a slightly larger entropy value of $S^{\circ} = 48.2 \pm 0.2$ J/(mol·K) for 1 mol of SiO_2 compared to the entropies of various zeosils that fall within a range of 45.1 ± 0.7 J/(mol·K) (Piccione et al. 2001). Our S° determination, together with the enthalpy data of Navrotsky et al. (2003), show that guest-free melanophlogite has a larger Gibbs free energy than quartz at 298 K and 1 bar (i.e., ΔG_{trans} = 7.5 kJ/mol). Thus, it does not have a thermodynamic P-T field in the SiO_2 system. Moreover, its thermodynamic stability is not measurably different from that of the zeosils.

The C_P and S° values of guest-containing melanophlogites from Mt. Hamilton and Racalmuto are larger than its guest-free counterpart (Fig. 2), obviously reflecting the presence of the enclathrated CH_4, N_2, and CO_2 molecules. In terms of enclathration energetics, the thermodynamic properties for the reaction:

$$46SiO_2(\text{melan.}) + xCH_4(\text{gas}) + yCO_2(\text{gas}) + zN_2(\text{gas}) = 46SiO_2\cdot(xCH_4)^{12}\cdot(yCO_2, zN_2)^{14} \qquad (2)$$

need to be determined. The heat capacity and entropy of reaction, ΔC_P^{rxn} and ΔS^{rxn}, at 298 K can be calculated using results from this work. We stress, though, that a precise determination is difficult, because the concentrations and distributions of the various molecules in both natural melanophlogites are not known quantitatively (i.e., crystals are sometimes inhomogeneous in composition and partial cage occupancies can occur). With respect to cage occupancies, those for the Mt. Hamilton sample have been determined by Gies (1983), whereas for the Racalmuto sample full cage occupancies were assumed (Gies et al. 1982). With this caveat, using the heat capacity and entropy values for the natural samples and the degassed melanophlogite, along with thermodynamic properties for ideal gaseous CH_4, N_2, and CO_2 (Chase 1998), we obtain ΔC_P^{rxn} = 80.1 J/(mol·K) and ΔS^{rxn} = –642.2 J/(mol·K) for the Mt. Hamilton sample and ΔC_P^{rxn} = 202.2 J/(mol·K) and ΔS^{rxn} = –802.2 J/(mol·K) for the Racalmuto sample at 298 K and 1 bar. Measurements to determine ΔH^{rxn} are needed to obtain ΔG^{rxn}. In addition, any configurational entropy contribution needs to be determined and this will require further spectroscopic study of the enclathrated molecules.

Kolesov and Geiger (2003) showed that the internal vibrations of the enclathrated CO_2, N_2, and CH_4 molecules in melanophlogite are similar in wave number to those that these molecules posses in the free state. This implies that the molecules have only weak interactions with the SiO_2 framework. In terms of P-T stability of molecule-containing melanophlogite, the enthalpies of mixing will have to be negative to counteract the entropy decrease associated with enclathration energetics (Eq. 2). Figure 2 shows the difference in C_P values between molecule-containing and molecule-free melanophlogites. Here, the difference in C_P values rise from 0 to ~70 K and then reach a roughly constant value at $70 < T < 250$ K. C_P behavior at $T < 70$ K will be strongly controlled by the nature of the lowest energy external librational and translational modes of the CO_2, N_2, and CH_4 molecules. They have yet to be determined (cf. the case for quasi-free molecular H_2O in microporous Mg-cordierite, Paukov et al. 2007).

Occurrence of melanophlogite in nature

Melanophlogite is the only porosil that has been identified on Earth, although others can be synthesized in the laboratory (Liebau 1988; Higgins 1994; Gies et al. 1998). Little mineralogical and geochemical research has been undertaken in this area. Gies et al. (1998) discuss the crystallization behavior of

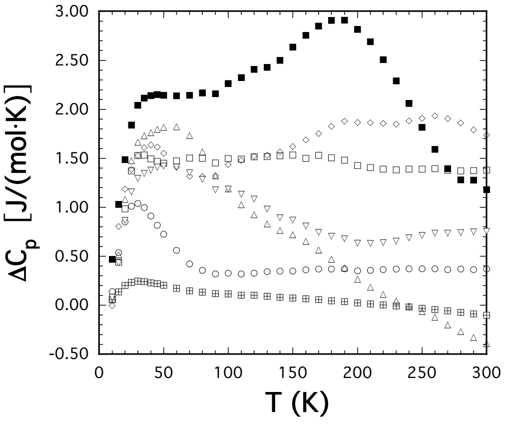

FIGURE 3. Heat capacities for various SiO_2 phases (all are guest free) relative to quartz from 0 to 300 K, i.e., $\Delta C_P = C_P[SiO_2\text{ (phase)}] - C_P\text{ (quartz)}]$. The data for quartz, cristobalite (open circles) and silica glass (squares with crosses) are from Westrum (1954), for the zeosil ZSM-23 (open squares), silica faujasite (inverted triangle) and zeolite beta (normal triangle) from Boerio-Goates et al. (2002), silicalite (ZSM-5 = diamonds) from Johnson et al. (1987) and melanophlogite (solid squares) from this study.

various porosils in the laboratory and their analysis is useful in understanding possible natural processes. Of central importance is the role of molecular structure-directing agents (SDAs) in porosil formation.

Melanophlogite often occurs with cristobalite and chalcedony or opal in low-temperature geologic environments (Zák 1972; Cooper and Dunning 1972; Tribaudino et al. 2008). Cooper and Dunning (1972, p. 1496) state that at Mt. Hamilton there were "interchanging and overlapping periods of crystallization of cristobalite and melanophlogite." This is consistent with the observation that cristobalite crystallizes from aqueous solution before melanophlogite in synthesis experiments (Gies et al. 1982). At Racalmuto, melanophlogite occurs with opal and quartz and is often nucleated around these phases (Skinner and Appleman 1963). A thermodynamic analysis and the field observations are consistent and suggest a metastable crystallization process. However, melanophlogite may crystallize in nature more often than realized, because it remains unrecognized or is later pseudomorphed by other SiO_2 phases.

Except for melanophlogite, no other clathrasils or zeosils have been found in nature. It appears, at least for molecular-free species, that their thermodynamic stabilities are similar. Gies et al. (1998) note that the formation of synthetic porosils is a kinetically controlled process and write, "spherical molecules favor cage-like voids, whereas chain-like molecules lead to 1-D channels." Thus, the simplest explanation for the occurrence of guest-containing melanophlogite and the absence of other porosils in nature is related to bulk composition, i.e., the presence or absence of SDAs. Gies et al. (1982, 1998) showed that the presence of various molecules other than CH_4, N_2, and CO_2, such as aliphatic and cyclic amines, is a prerequisite for the crystallization of most clathrasils. Many of these molecules are either not found in nature or only occur in small concentrations. Melanophlogite seems to be different and perhaps unique as a natural clathrasil (if another clathrasil will be found in nature, it would probably be dodecasil 3C), because it can crystallize in the presence of common naturally occurring molecular SDAs such as CO_2. As with most clathrasils, the case for synthetic zeosils is similar. Their formation requires even larger and naturally uncommon SDAs (see Gies et al. 1998). The zeolite, mutinaite, of composition $(Na_{2.76}K_{0.11}Mg_{0.21}Ca_{3.78})_{6.86}(Al_{11.20}Si_{84.91})_{96.11}O_{192}\cdot 60H_2O$, is a natural counterpart of the zeosil ZSM-5 and it has been found at one locality (Galli et al. 1997). In its case, H_2O molecules and extra framework cations are present and they may act as SDAs and allow crystallization as described by Breck (1974).

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