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LETTER

Quasi-ice-like C_P behavior of molecular H_2O in hemimorphite $Zn_4Si_2O_7(OH)_2{\cdot}H_2O$: C_P and entropy of confined H_2O in microporous silicates

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ABSTRACT

Hemimorphite, $Zn_4Si_2O_7(OH)_2{\cdot}H_2O$, and its dehydrated analog $Zn_4Si_2O_7(OH)_2$ were studied by low-temperature relaxation microcalorimetry and their heat capacity determined to analyze the behavior of the confined H_2O between 5 and 300 K. An analysis of the data, which are corrected for the presence of a phase transition, shows that the C_P of H_2O in hemimorphite behaves more similar to the C_P of ice than to liquid water or steam. The H_2O molecule, with its four planar hydrogen bonds in hemimorphite, as well as its tetrahedral coordination in ice, is more rigidly hydrogen bonded in both than in liquid water. This is reflected in their respective C_P behavior. The heat capacity and entropy for the dehydration reaction at 298 K are $\Delta C_P^{rxn} = -2.1 \pm 3.6$ J/(mol·K) and $\Delta S^{rxn} = 134.7 \pm 4.0$ J/(mol·K). C_P behavior at $0 < T < 300$ K and entropy values at 298 K for confined H_2O in hemimorphite and hydrous Mg cordierite are compared to those in several zeolites. The entropy for confined H_2O in hemimorphite, analcime, and mordenite is around 54 J/(mol·K) at 298 K. The strength of the interactions (e.g., H bonding) between an H_2O molecule and its surroundings increases approximately from steam > cordierite > analcime > hemimorphite ≥ mordenite > heulandite > natrolite ≈ scolecite > liquid H_2O > ice and, in the case of microporous silicates, is inversely proportional to the S of the confined H_2O.

Keywords: Hemimorphite, heat capacity, entropy, microporous minerals, confined H_2O

INTRODUCTION

The H_2O molecule and hydrogen bonding play a key role in many geologic processes. Certain micro/nanoporous silicates offer the possibility for one to investigate the nature of confined H_2O and hydrogen bonding at a relatively simple, yet fundamental level. One such silicate, hemimorphite, $Zn_4Si_2O_7(OH)_2{\cdot}H_2O$, has been studied in terms of its crystal structure several times at different temperatures using both single-crystal X-ray and neutron diffraction (see Taylor 1962; Hill et al. 1977; Cooper et al. 1981; Libowitzky et al. 1998). Its structure has a single, confined H_2O molecule that is held in place only through hydrogen bonding. Complementary single-crystal IR absorption and Raman spectroscopic studies have provided vibrational properties of the H_2O molecule and information on the strength of the hydrogen bonding to the framework (Libowitzky and Rossman 1997; Kolesov 2006). Hemimorphite shares certain similarities with zeolites, because they also have H_2O molecules located in channel ways that are hydrogen bonded with their crystal frameworks and/or with each other, but differ in that their H_2O molecules are also bonded to extra-framework cations. In addition, the H_2O in hemimorphite can be removed without disruption of the framework structure, but it is not reversibly reabsorbed as in the zeolites.

To study confined H_2O and hydrogen bonding in hemimorphite, thermodynamic behavior, especially heat capacity at $0 < T < 300$ K, is of special interest. Because hydrogen bonding associated with confined H_2O is a relatively weak force in most silicates, it will express itself in C_P at low temperatures. Calorimetric work has been undertaken for several natural zeolites (e.g., Johnson et al. 1982, 1983, 1985, 1992; Paukov et al. 2002) and these studies show that the C_P contribution and the entropy, S, at 298 K of H_2O in zeolites are variable. In spite of this reported variability, thermodynamic studies (e.g., Helgeson et al. 1978; Robinson and Haas 1983; Van Hinsberg et al. 2005) have proposed "standard values" of S for confined H_2O in a variety of microporous silicates for use in calculations and databases.

Few heat capacity studies at low temperatures have been reported for non-zeolitic hydrous microporous silicates (see Paukov et al. 2007 for work on cordierite). More calorimetric work needs to be undertaken on a greater variety of phases to fully understand the thermodynamic properties of their confined H_2O. The new data reported here on hemimorphite, together with previously published calorimetric results on related phases, permit an analysis of C_P and S behavior of confined H_2O and their relationship to hydrogen bonding in microporous silicates.

EXPERIMENTAL METHODS

Sample, characterization, and calorimetry

The hemimorphite investigated is from the Ojuela Mine, Mapimi, Durango, Mexico (University of Kiel mineral collection). Two euhedral, colorless and transparent, crystals 5–10 mm in size were separated from their underlying matrix. Electron microprobe analysis showed only the presence of Zn and Si. The crystals were ground in an agate mortar to obtain roughly 400 mg of sample. X-ray powder diffraction measurements using a Siemens D-5000 diffractometer with 0.1° step scans every 10 s between 10 and 60 °2θ showed only reflections that could be indexed to hemimorphite. A 100 mg fraction was used for heating experiments to expel the confined H_2O. It was placed in an open Au capsule, heated in air at 50 K/h to 748 K, and held for 6 h using a tube furnace with a temperature control of ±1 K, which was also checked by an external Cr-CrNi thermocouple. Following heating, the sample was removed from the furnace, cooled, and characterized by X-ray powder diffraction. The X-ray powder diffraction pattern of the dehydrated hemimorphite also matches well that calculated from the single-crystal data of

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Libowitzky et al. (1997). X-ray patterns for the natural and heat-treated samples are shown in Figure 1[1].

Low-temperature heat capacities were measured with a commercial relaxation calorimeter, i.e., the Physical Properties Measurement System (PPMS) made by Quantum Design. Measurements were made between 5 and 300 K on 20.2 mg of hemimorphite and 22.5 mg of dehydrated hemimorphite held in a covered Al-container. C_P data were collected at 60 temperatures on cooling with a logarithmic or linear spacing, with C_P determined three times at each temperature. Details behind the PPMS method, as well as description of the data acquisition and evaluation procedures and error analysis, are given in Dachs and Bertoldi (2005), Dachs and Geiger (2006), and Benisek and Dachs (2008).

Results

Raw C_P data for both natural and heat-treated hemimorphite are given in Tables 1a and 1b[1], and they each show evidence for a phase transition around 102 and 86 K, respectively. The phase transition in hemimorphite has been studied and will be discussed briefly below, whereas the phase transition in dehydrated hemimorphite is new. For this study, we excluded the C_P data between 54–120 K that encompasses these phase transitions to focus our analysis on the difference in C_P between the two samples that describes the behavior of the confined H_2O. Thus, the raw C_P data for the natural and the heated-treated sample below and above 54–120 K were fitted to the equation (Boerio-Goates et al. 2002):

$$C_P = 3R[n \cdot D(\theta_D) + m \cdot E(\theta_E) + n_s \cdot S(\theta_S)] , \quad (1)$$

where $D(\theta_D)$, $E(\theta_E)$, and $S(\theta_S)$ are Debye, Einstein, and Schottky functions, respectively, and n, m, n_s, θ_D, θ_E, and θ_S are adjustable parameters. The resulting fitted C_P values are given in Table 2[1]. Using Equation 1, the experimental heat capacities above and below the transitions could be reproduced within 0.35 ± 0.28% at $10 < T < 54$ K and within 0.25 ± 0.2% at temperatures above 120 K. The values between 54 and 120 K were interpolated. The third-law entropies for hemimorphite and dehydrated hemimorphite were obtained by appropriate integration of Equation 1.

Discussion

Hemimorphite structure, confined H_2O, and quasi-ice-like C_P behavior

The crystal structure of hemimorphite is a framework of corner-sharing Si_2O_7 dimers and ZnO_3OH tetrahedra. The room-temperature orthorhombic *Imm*2 structure is shown in Figure 2a. Cavities are connected via six-membered rings of tetrahedra to form infinite channel ways running parallel to the *c*-axis. A single H_2O molecule within each cavity has four coplanar hydrogen bonds, located in the (010) plane, to the surrounding crystal framework. The H-bonding arrangement is unusual for a silicate because the H_2O molecule acts as both a hydrogen-bond acceptor and donor. The structure of hemimorphite and the effect of elevated temperatures and dehydration were studied by Taylor (1962) and Cooper et al. (1981). The low-temperature structure was investigated by Libowitzky et al. (1998). At $T > 300$ K, the framework undergoes only minor adjustments with loss of the H_2O molecule and even retains the same symmetry when all the H_2O molecules are removed to become $Zn_4Si_2O_7(OH)_2$ (Cooper et al. 1981). Dehydroxylation of $Zn_4Si_2O_7(OH)_2$ to β-Zn_2SiO_4 begins around 933 K (Taylor 1962).

At $T < 300$ K, the hemimorphite structure undergoes a phase transition at about 102 K, changing to the symmetry A*bm*2. The low-temperature structure has an ordered arrangement of non-equivalent hydroxyl groups and rotated water molecules, which doubles the *b*-axis (Libowitzky et al. 1998). In contrast, the low-temperature structure of dehydrated hemimorphite retains the *Imm*2 structure (Libowitzky et al. 1997). In that study, the crystal structure was refined at 110 and 293 K, single-crystal polarized FTIR spectra measured between 82 and 373 K, and optical birefringence measured between 83 and 373 K, but no phase transitions were observed. Our calorimetry work on dehydrated hemimorphite does indicate a phase transition at about 86 K, but this will be discussed elsewhere. For this study, the heat capacity contribution due to these phase transitions has been effectively removed by interpolating a smooth temperature dependence of C_P through that temperature region.

The C_P and the third-law entropy, $S°$, at 298 K for hemimorphite and the dehydrated phase are given in Table 3. Raw C_P data and the fitted values using Equation 1 are shown in Figure 3. To obtain C_P for the confined H_2O in hemimorphite, we subtracted the fitted C_P values of the heat-treated sample from the fitted C_P values of untreated hemimorphite (Fig. 3). Also plotted are the C_P values for ice and super-cooled liquid water and steam. Of the three different H_2O phases, the C_P behavior of H_2O in hemimorphite is most similar to that of ice at $0 < T < 270$ K. The

[1] Deposit item AM-09-021, Figure 1, Tables 1a, 1b, and 2. 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.

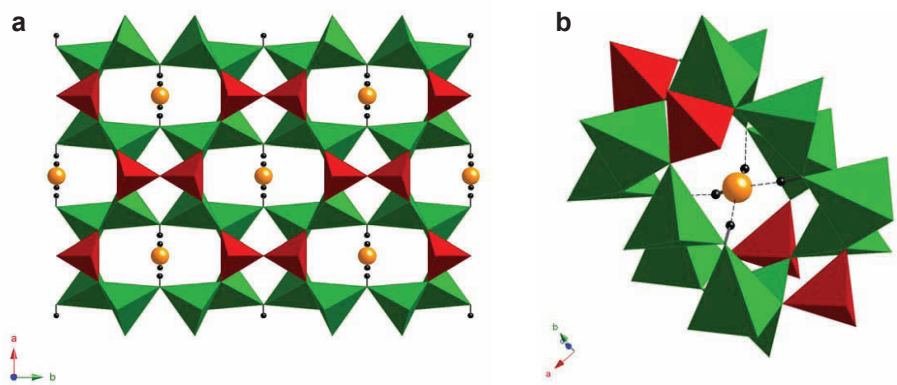

Figure 2. (**a**) Hemimorphite structure at 300 K. The green tetrahedra represent the $ZnO_3(OH)$ groups and the red, SiO_4 groups. The orange spheres are the O atoms of the H_2O molecules and the small black spheres are H atoms. (**b**) Cavity around the H_2O molecule showing the hydrogen bonds as dashed lines.

TABLE 3. Heat capacity and standard third-law entropy, $S°$, at 298.15 K of hemimorphite and dehydrated hemimorphite

Sample	C_P [J/(mol·K)]	$S°$ [J/(mol·K)]
hemimorphite	324 ± 2	368 ± 3
dehydrated hemimorphite	288 ± 2	314 ± 2

H_2O molecule in hemimorphite as well as in ice, but not as in liquid H_2O, is characterized by a relatively strong arrangement of hydrogen bonds. The confined H_2O in hemimorphite behaves like "quasi-two-dimensional ice," in contrast to the tetrahedrally coordinated H_2O molecules in hexagonal ice.

The heat capacity and entropy for the dehydration reaction, ΔC_P^{rxn} and ΔS^{rxn}, at 298 K:

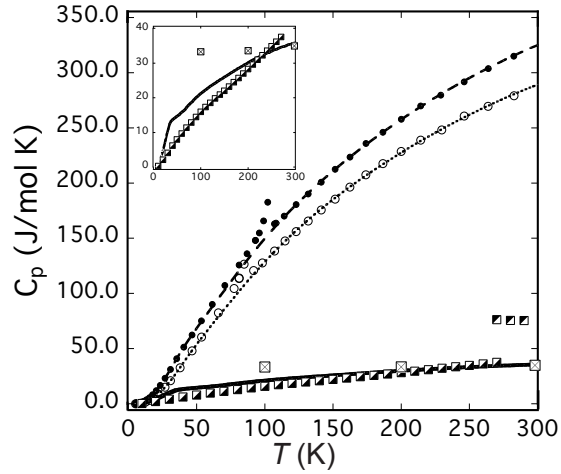

FIGURE 3. Heat capacity of natural and heat-treated hemimorphite (using selected raw data from Table 1), filled and open circles, respectively. The symbols are larger than the experimental uncertainty. C_P values for both phases from Equation 1 are shown as long and short dashed lines, and the lower solid line is the difference between them (i.e., C_P of H_2O in hemimorphite). The squares with the filled lower half are ice (Giauque and Stout 1936), the squares with the filled upper half are super-cooled liquid water (Angell et al. 1982) and the squares with crosses are super-cooled steam (from Paukov et al. 2007). The inset shows C_P of confined H_2O in hemimorphite (line) compared to ice and steam.

$$Zn_4Si_2O_7(OH)_2{\cdot}H_2O \rightarrow Zn_4Si_2O_7(OH)_2 + H_2O\ (gas) \qquad (2)$$

were calculated using the values in Table 3, along with thermodynamic properties for ideal gaseous H_2O. We obtain $\Delta C_P^{rxn} = -2.1 \pm 3.6$ J/(mol·K) and $\Delta S^{rxn} = 134.7 \pm 4.0$ J/(mol·K). The entropies of ice sublimation and water vaporization at 298 K are $\Delta S^{sub.} = 146.95$ J/(mol·K) and $\Delta S^{vap.} = 118.89$ J/(mol·K), respectively (Table 4). The entropy of dehydration of hemimorphite lies between the entropy of water vaporization and ice sublimation.

The system H_2O and confined H_2O in selected micro/nanoporous silicates: Thermodynamic, hydrogen-bonding, and vibrational behavior

To analyze the thermodynamic, bonding, and vibrational behavior of confined molecular H_2O in silicates, the pure H_2O system can be used as a reference state. Eisenberg and Kauzmann (1969) discuss the structures, vibrational states and thermodynamic properties of gaseous, liquid, and solid H_2O. An important difference between liquid and solid H_2O and gaseous H_2O (steam) is the presence of hydrogen bonding (Jeffrey 1997) in the first two phases.

Comprehensive understanding of the thermodynamic behavior of confined H_2O in micro/nanoporous minerals is lacking, whereas data exist for specific zeolites (e.g., Johnson et al. 1982, 1983, 1985, 1992; Paukov et al. 2002). Several attempts have been made to estimate or calculate S values for H_2O in microporous silicates. In some treatments, "standard transferable" S values have been proposed. Helgeson et al. (1978) estimated, based on older calorimetric data for analcime and dehydrated analcime, an entropy value of "zeolitic" H_2O for silicates to be 59 J/(mol·K) at 298 K. Robinson and Haas (1983) proposed a value of 54.0 J/(mol·K) for a "fictive hydrate component" (i.e., H_2O) in their empirical procedure for calculating the entropy of various minerals. More recently, Van Hinsberg et al. (2005) obtained a lower value of S = 44.1 J/(mol·K) for "free interstitial" H_2O at 298 K in their thermodynamic analysis of silicate phases. For various H_2O-containing inorganic salts, experimental entropy values of their confined H_2O are roughly around 42 J/(mol·K) (see Dunitz 1994).

Table 4 lists C_P and S values at 298 K for the three most common H_2O phases and for confined H_2O in various micro/nanoporous silicates. For the latter, C_P varies considerably, as does S with values between 32 and 80 J/(mol·K). There is no "standard value" for either function. For confined H_2O in silicates, hemimorphite, analcime, and mordenite have similar entropy values around 54 J/(mol·K), which lies between that of ice and liquid H_2O. The entropy for H_2O in heulandite and paranatrolite are less, namely 50.1 and 45.8 J/(mol·K), respectively. Each H_2O molecule in the two small-pore zeolites natrolite and scolecite has an entropy of approximately 32 J/(mol·K), which is the lowest entropy value reported for confined molecular H_2O in silicates. Hydrous Mg-cordierite is at the other extreme; its S value of 80.5 J/(mol·K) for H_2O is greater even than that of liquid H_2O.

We now consider C_P behavior at $0 < T < 300$ K. In the case of cordierite, its C_P for H_2O at $100 < T < 300$ K is most similar to that of steam (see Fig. 8 in Paukov et al. 2007). As described above, H_2O in hemimorphite is more ice-like. For analcime and mordenite C_P is most similar to that of ice below 50 K, but above 50 K their C_P values for H_2O show larger and increased

TABLE 4. Heat capacity, entropy, and H_2O-stretching wavenumber values for H_2O phases and for confined H_2O in various microporous silicates at 298 K

Phase	Heat capacity [J/(mol·K)]	Entropy [J/(mol·K)]	H_2O/OH-stretching wavenumber (cm^{-1})	Reference for C_P and S
steam (ideal gas)	33.59	188.84	3657 (ν_1) and 3756 (ν_3)	Robie and Hemingway (1995)
liquid water	75.35	69.95	3280 (ν_1) and 3490 (ν_3)	Chase (1998)
ice (hexagonal)	40.96	41.89	~3200 ($\nu_{1/3}$)	extrapolated using Giauque and Stout (1936) data
cordierite	42.2	80.5	3595 (ν_1) and 3689 (ν_3)	Paukov et al. (2007)
analcime	47.9	55.0 ± 0.3	~3560 to 3675	Johnson et al. (1982)
mordenite	54.4	54.1 ± 0.3	~3285 to 3614	Johnson et al. (1992)
hemimorphite	36 ± 3	53 ± 4	~3340 to 3650	this study
heulandite	–	50.5	~3200 to 3620	Johnson et al. (1985)
paranatrolite	55.8	45.8	–	calculated from data in Paukov et al. (2007)
natrolite	–	32	~3320 and 3540	Johnson et al. (1983), from calorimetry and model calculations
scolecite	–	32	~3230 to 3590	"

deviation from ice-like behavior (see Fig. 8 in Paukov et al. 2007). Paranatrolite's C_P behavior for H_2O is the most different. It shows lower C_P values than ice at $T < 80$ K, but they increase at $T > 80$ K such that at 298 K it has the largest C_P value listed in Table 4. Clearly, values for C_P and S of H_2O in microporous silicates are variable. The macroscopic thermodynamic behavior of the various confined H_2O molecules at $0 < T < 300$ K is a function of the energies of their external (i.e., librational and translation) modes. Vibrational spectroscopic investigations have been made on most of these phases and they can be compared and analyzed in terms of their hydrogen-bonding behavior.

Consider hydrogen-bond strength described by the wavenumber of the internal stretching vibrations of the H_2O molecule and its relationship to the entropy of confined H_2O in the various phases in Table 4. It is known that the higher the wavenumber of the internal stretching vibrations (symmetric stretch = ν_1 and asymmetric stretch = ν_3), the weaker the hydrogen bonding (Jeffrey 1997). For a free H_2O molecule as in steam, the internal modes lie at 3657 (ν_1) and 3756 cm^{-1} (ν_3), while in liquid water they are about 3280 (ν_1) and 3490 (ν_3), and for ice they are around 3200 cm^{-1} (Eisenberg and Kauzmann 1969). Thus, H bonding is strongest in ice and, of course, absent in ideal gaseous H_2O. For Mg-cordierite the H_2O stretching modes are at high wavenumbers, 3595 (ν_1) and 3689 (ν_3) cm^{-1} (Paukov et al. 2007). In hemimorphite the H_2O/OH stretching modes lie between 3350 and 3600 cm^{-1} at ambient conditions (Libowitzky and Rossman 1997; Kolesov 2006). In the small-pore zeolites natrolite and scolecite stretching vibrations occur between 3200 and 3600 cm^{-1} (Kolesov and Geiger 2006). The stretching vibrations of confined H_2O in other natural zeolites are at higher wavenumbers as in analcime and mordenite (Breck 1974). Analcime, for example, shows modes between 3560 and 3675 cm^{-1} (Velde and Besson 1981). This indicates slightly weaker H bonding than in hemimorphite and considerably weaker than in natrolite and scolecite. Thus, the strength of H bonding with its surroundings increases approximately as:

$$\text{steam} > \text{cordierite} > \text{analcime} > \text{mordenite} \geq \text{hemimorphite} > \text{heulandite} > \text{natrolite} \approx \text{scolecite} > \text{liquid } H_2O > \text{ice}. \quad (3)$$

The H_2O molecules in natural zeolites are also bonded to cations in their channels. Thus, quantitative comparisons with hemimorphite and the H_2O phases, where H bonding is the exclusive interaction, are difficult to make. Nevertheless, the strength of the interaction between an H_2O molecule and its surroundings is approximately inversely correlated to its S (Table 4). The relationship is, however, not perfect, because the external translational and librational modes largely determine C_P at low temperatures and, thus S, at 298 K. Their energies are not known, but they are affected by the H-bond interaction acting on the H_2O molecules.

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