

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  $\geq$  mordenite > heulandite > natrolite  $\approx$  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  $H_2O$