



## Confined H<sub>2</sub>O in Micro/Mesoporous Silicates: Bonding, Vibrational and Thermodynamic Behavior

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Many micro/mesoporous silicates are hydrophilic. However, a physicochemical description for their mineral-H<sub>2</sub>O-molecule interactions is not at hand. We are studying the behavior of confined H<sub>2</sub>O in various micro/nanoporous silicates to better understand the nature of the local interactions and the macroscopic thermodynamic properties. Calorimetric heat capacity ( $C_p$ ) and DTA/TG determinations and powder IR and polarized single-crystal Raman spectroscopy are being used to investigate thermodynamic, bonding and vibrational behavior.

The first group of studied microporous silicates, namely cordierite, Mg<sub>2</sub>Al<sub>4</sub>Si<sub>5</sub>O<sub>18</sub>xH<sub>2</sub>O and beryl, Be<sub>2</sub>Al<sub>3</sub>Si<sub>6</sub>O<sub>18</sub>xH<sub>2</sub>O, can hold single H<sub>2</sub>O molecules in small microcavities. The molecules can exchange with the environment with no change in molar volume of either phase. The  $C_p$  behavior of the confined H<sub>2</sub>O, which interacts via weak van-der-Waals forces to the aluminosilicate framework, is greater than that for ice at  $T < 100$  K, but roughly similar to that of steam at  $T > 100$  K. Raman, IR and inelastic neutron scattering measurements show that the H<sub>2</sub>O molecule is quasi free in both phases. In cordierite, external translational, T(H<sub>2</sub>O), modes occur at 80 and 48 cm<sup>-1</sup> and a librational mode, L(H<sub>2</sub>O), at 218 cm<sup>-1</sup>, as based on inelastic neutron scattering spectroscopy (Winkler and Hennion, 1994). For beryl, Raman spectra indicate an external T(H<sub>2</sub>O) mode at about 10 cm<sup>-1</sup> and L(H<sub>2</sub>O) modes at 190 and 205 cm<sup>-1</sup>.

Micro/mesoporous zeolites (e.g., natrolite-Na<sub>16</sub>[Al<sub>16</sub>Si<sub>24</sub>O<sub>80</sub>]·16H<sub>2</sub>O, scolecite-Ca<sub>8</sub>[Al<sub>16</sub>Si<sub>24</sub>O<sub>80</sub>]·24H<sub>2</sub>O, and gmelinite-(Na<sub>2</sub>,Ca)[Al<sub>2</sub>Si<sub>4</sub>O<sub>12</sub>]·6H<sub>2</sub>O) constitute a

second, large group of hydrophilic silicates. Here, the H<sub>2</sub>O molecule shows various degrees of hydrogen bonding with different C<sub>p</sub> behavior. In general, zeolites show, unlike beryl and cordierite, measurable changes in their volumes with loss or gain of H<sub>2</sub>O. In small-pore zeolites, such as parnatrolite, C<sub>p</sub> behavior for H<sub>2</sub>O behaves roughly similar to that for ice at T < 100 K. At T > 100 K, C<sub>p</sub> increases and is greater than the C<sub>p</sub> of ice and also for H<sub>2</sub>O in cordierite at T > 250 K. In natrolite and scolecite, T(H<sub>2</sub>O) modes occur between 45 and 180 cm<sup>-1</sup> and L(H<sub>2</sub>O) modes at roughly 430-440 cm<sup>-1</sup>. In the case of gmelinite, which is characterized by large as well as small pores, the total C<sub>p</sub> behavior is “normal” at 0 K < T < 200 K. However, it then increases anomalously at T > 200 K as compared the C<sub>p</sub> behavior for many zeolites. The vibrational properties for the H<sub>2</sub>O molecules are not known, but the large increase in C<sub>p</sub> could be due to a weakening in H-bonding.

Several conclusions are: 1) At T < 200 K, C<sub>p</sub> behavior of confined H<sub>2</sub>O in micro/mesoporous silicates is controlled by the nature of low-energy external L(H<sub>2</sub>O) and T(H<sub>2</sub>O) modes. 2) The energies of L/T(H<sub>2</sub>O) modes reflect weak van-der-Waals and weak to moderately strong hydrogen-bond forces. The nature of H-bonding plays a central role in affecting confined H<sub>2</sub>O behavior in hydrophilic micro/mesoporous silicates. 3) The marked increase in C<sub>p</sub> in some zeolites with increasing T may indicate a change in hydrogen bonding behavior from more “ice-like” to increasing “liquid-water-like”. 4) Macroscopic C<sub>p</sub> and entropy values for confined H<sub>2</sub>O in silicates cannot be considered similar, as is done in crystal-chemical-based schemes that are used for modeling thermodynamic properties of H<sub>2</sub>O-bearing silicates.