

Molecule-Mineral Inner-Surface Interactions in Nanoporous Silicates

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We have carried out single-crystal and powder Raman and studies of zeolites, SiO₂-clathrates and other silicate structure types with small nanopores (beryl, cordierite) to investigate the nature of inner-surface molecule-crystal interactions and the role of hydrogen bonding.

Bikitaite has a H-bonded H₂O chain along [010] termed 'one-dimensional ice'. The molecules are ordered, whereby one H atom per molecule is unbonded and the other is H-bonded. With increasing temperature, the H-bonding weakens continuously until the chain 'breaks' and isolated H₂O molecules are present.

Melanophlogite has quasi-free N₂, CO₂ and CH₄ molecules, but no H₂O, which partition between the [5¹²] and [5¹²6²] cages. The molecules are orientationally disordered in the cavities and they have only weak dispersion interactions with the SiO₂-crystal framework. However, the incorporation of molecules is necessary to allow the SiO₂ framework to condense.

Cordierite and beryl contain quasi-free CO₂ molecules, as well as H₂O, in small cavities. The CO₂ molecules are orientated parallel to the crystallographic *x*-axis. The H₂O molecules have their H-H vector parallel to the *z*-axis in alkali-free crystals and are dynamically disordered about the *z*-axis. They show weak H-bonding with their frameworks.

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