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Interaction of methane hydrate complexes with smectites: Experimental results compared to molecular models

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Abstract

Molecular simulations were performed to determine the structure and behavior of methane hydrate complexes in the interlayer of Na-rich montmorillonite and beidellite smectite. Molecular dynamics (MD) simulations used NPT ensembles in a 4 × 4 × 1 supercell comprised of montmorillonite or beidellite with methane hydrate complexes in the interlayer. The simulations presented here are in agreement with experimental data that show a significantly expanded interlayer (Guggenheim and Koster van Groos 2003; Koster van Groos and Guggenheim 2009). The smectite 2:1 layer forms part of the coordination sphere enclosing methane molecules; the MD results show that water molecules close to the siloxane surface form mixed cages that enclose methane molecules between basal oxygen atoms of the silicate rings and water molecules from the hydrogen bonding network. However, the higher tetrahedral charge did not favor the formation of methane hydrate components in the interlayer. Thus, methane hydrate complexes can be formed in pure montmorillonite more easily than in beidellite.

Clay minerals obtained from marine localities with associated methane seeps and with variable Na, K, Ca, and Mg interlayer compositions were used to examine how swelling capacity affects the crystallization of smectite-methane-hydrate complexes. Results show that the formation of these complexes depends on the swelling capacity in the smectite. In samples with limited swelling properties, methane hydrate is formed in the pore spaces between particles and on the external surface of clays.

Keywords: Smectite, hydrate, methane, illite, clathrate