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Methane Hydrate Formation on Clay Mineral Surfaces: Thermodynamic Stability and Heterogenous Nucleation Mechanisms

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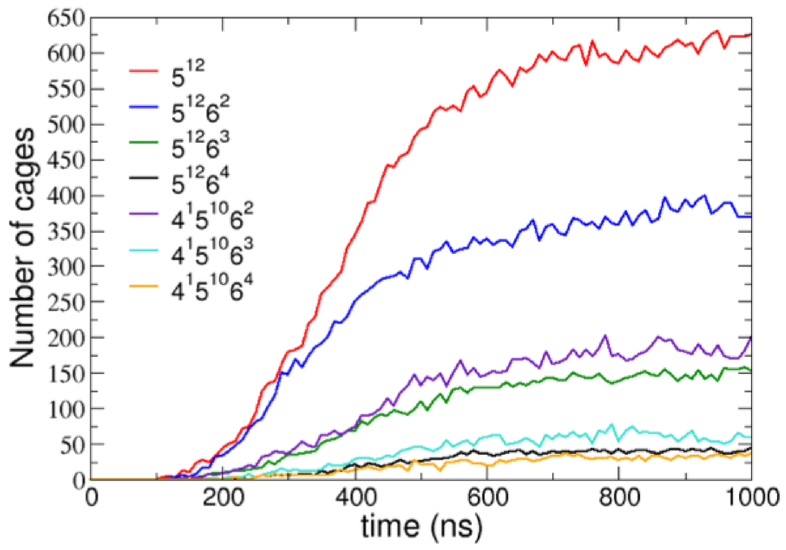
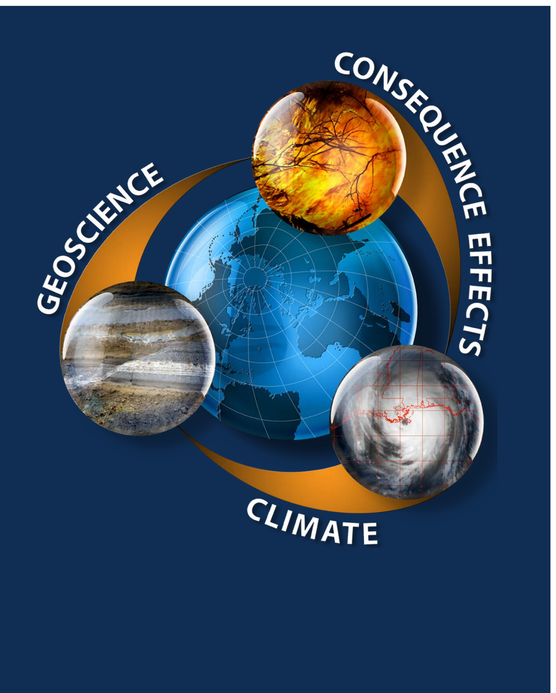
Objectives

Develop a comprehensive understanding of clay mineral surface effects on the heterogeneous nucleation of methane hydrates and their subsequent thermodynamic properties using both simulation and experiment.

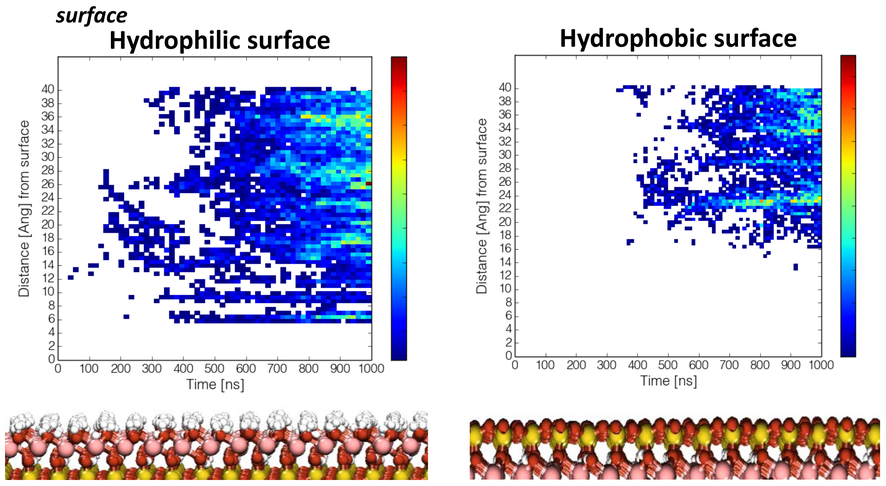
MD simulation

Developed large-scale MD simulation scheme and quantified nucleation process. Cage formation begins at 100 ns and the rate of formation increases at approximately 200 ns. Figure 3-10 presents the occurrence of 5^{12} cages during the evolution of the simulation as a function of distance from both the hydrophilic and hydrophobic surfaces. The water rings of the 5^{12} cage occur with a higher frequency closer to the hydrophilic gibbsite surface of kaolinite earlier in the simulation than they do at the hydrophobic siloxane surface. To investigate the how surface atoms participate in ring formation, we monitor the number of surface atoms participating in cage formation throughout the simulation. We observe that only half pentagonal rings (5^{12}) and half hexagonal rings ($5^{12}6^2$) contain surface atoms from the clay mineral.



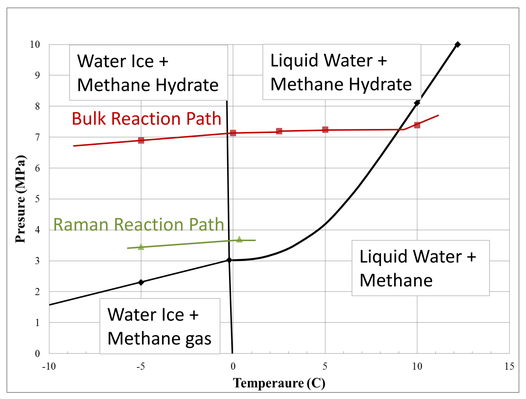


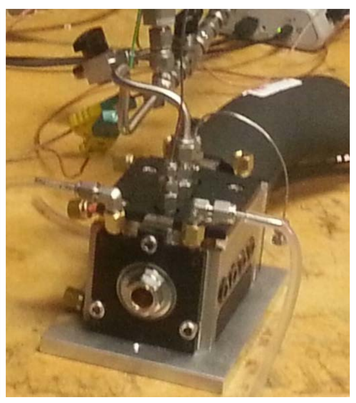
Frequency of 5^{12} cage formation as a function of time and distance away from surface

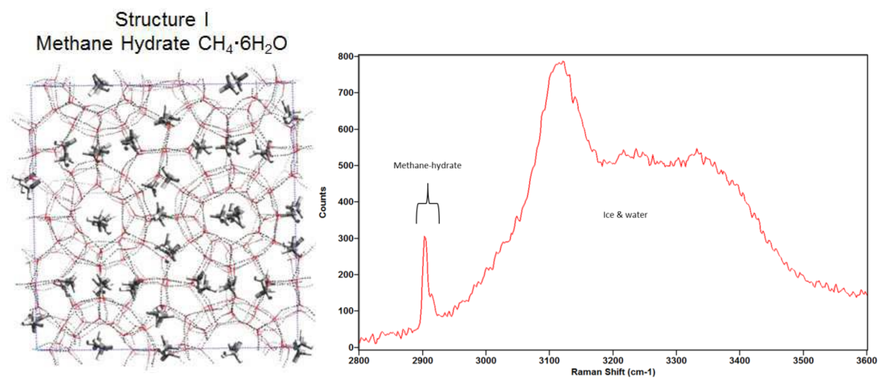


Methane Hydrate Synthesis in a specialized Raman Cell

Methane hydrates were synthesized in a Raman spectroscopic cell designed for this purpose. The specialized cell maintains the required pressure and temperature for methane hydrate stability throughout the synthesis and Raman spectroscopic analysis process. Raman spectra collected confirm the presence of methane hydrates. A time-series scan while warming the cell evaluated the melting of remnant ice in the cell followed by methane hydrate decomposition, demonstrating the sensitivity of the instrument and utility of this cell for *in situ* work.







Results

Heterogeneous nucleation of methane hydrates has been examined using molecular simulation, experimental bulk synthesis, and scanning probe microscopy. Theoretical nucleation rates were determined using molecular dynamics simulations as a function of clay surface represented by hydrophobic and hydrophilic systems. Methane hydrates were synthesized with and without Na-montmorillonite in a bulk reactor pressure assembly. X-ray diffraction and Raman spectroscopy confirm the nucleation and growth of the synthesized hydrates. Various kinetic pathways were explored to produce methane or isobutene clathrates in an ultra-high vacuum apparatus at very low temperatures but scanning probe microscopy only indicates the formation of ice.

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