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Molecular simulations of CO_2 and mixed CH_4-CO_2 hydrates intercalated on smectites.

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Natural gas hydrates (NGH) are crystalline compounds consisting of methane molecules encaged in cavities of a hydrogen-bonded network of water molecules. Gas hydrates have a general formula X·nH2O, where X is the guest molecule within a water cage, and n is the hydration number per guest molecule. The crystal structure sI consists of 46 water molecules per unit cell, forming two dodecahedron (small 5^{12}) and six tetradecahedron (large $5^{12}6^{2}$) cages and is formed when small guest molecules such as methane or carbon dioxide are trapped. Considerable amounts of methane hydrates can be found in permafrost regions and sediments of the ocean floor in outer continental margin regions where medium pressures, low temperatures and high methane gas concentration in water can be reached. Gas hydrates are important because hydrate decomposition would cause the methane release into atmosphere causing great impact on Earth´s climate. On the other hand, these NGH are seen as a potential major energy resource.

The recent increase in anthropogenic CO_2 gas released to the atmosphere and its contribution to global warming, makes necessary to investigate new ways of CO_2 storage. The possibility of replacing natural gas by CO_2 from NGH has been investigated. There are thermodynamic evidences that support the replacement in hydrate at appropriate conditions. The comparison of their hydrate phase equilibrium conditions suggests the occurrence of a transition zone between both hydrate equilibrium curves where CO_2 hydrates can exist while CH_4 hydrates dissociate into methane gas and water. Any further investigation of the mixed CH_4–CO_2 gas hydrate properties could lead to major breakthroughs in the fields of unconventional resource production and carbon sequestration.

Clay minerals are major constituents of ocean sediments, the study of interactions between these minerals with hydrates on the seafloor can be useful to determine variations on hydrate stability field, and to know the properties and behavior of hydrate-smectite complex. Characterization and better understanding of those deposits are necessary to develop CO_2 storage as hydrates by methane replacement. Swelling clays usually contains multiple planes of weakly bonded H_2O in the interlayer between the 2:1 (silicate) layers. Koster van Groos et al. (2009) synthesized a smectite–methane hydrate intercalate with $d(001)=2.2$ nm indicating the presence of one unit cell of methane hydrate crystal intercalated between the 2:1 layers of smectite.

Due to the complexity of experimental studies with hydrates, Computational Mineralogy can be very helpful. In this study we compare the behavior of CO_2 and mixed CH_4-CO_2 hydrates intercalated in montmorillonite and beidellite. Our results are in agreement with the $d(001)=2.2$ nm in both hydrates intercalated as crystal lattice. However, comparing mean square displacement (MSD) profiles from molecular dynamics simulations of H_2O molecules in the hydrates, we found that hydrate crystal MSD show a typical solid profile without diffusion, while in the intercalates there is more diffusion of water molecules, hence CO_2 and mixed CH_4-CO_2 hydrate structure is more flexible and stable in the smectite-hydrate complex.

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