

## Molecular dynamics simulations of the three-layer hydrate in smectites: A sensitivity analysis

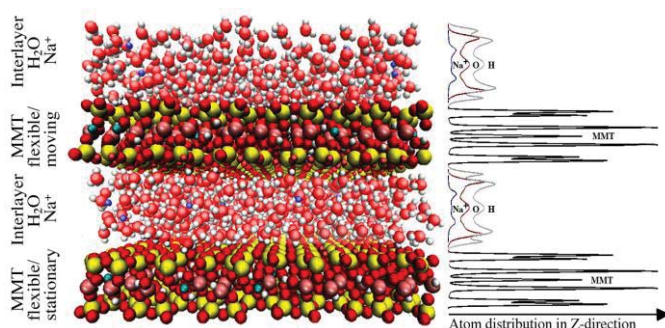
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### Abstract

Bentonite (smectite-rich) clays is under consideration as a buffer material for geological nuclear waste repositories in many countries. Molecular simulation techniques such as Monte Carlo (MC) and molecular dynamics (MD) simulations have played an important role in characterizing these materials by yielding detailed atomistic insights into the structural, dynamical and thermodynamic properties of water in smectite interlayer nanopores. Most of these studies used classical MD simulations of small smectite/water systems ( $< 10^4$  atoms) with fixed smectite clay layers, in order to save computational time, although size dependent effects using more realistic and flexible smectite layers were observed in large-scale MD simulations ( $> 10^5$  atoms) of flexible smectite layers [1]. In this work we compare the results of MD simulations with 6900, 7710 and 8520 atoms, carried out with either fixed or flexible smectite layers of a typical 2:1 sodium exchanged smectite (Wyoming montmorillonite), at different water contents and temperatures. The simulations were performed using the MD code LAMMPS with the SPC/E water model and the ClayFF force field, which are known to correctly reproduce structural and thermodynamical properties of smectite interlayer water and exchangeable cations [2]. We focus in particular on the diffusion coefficients and structural data for the three-layer hydration state, which is expected to be the predominant hydration state in different concepts for geological nuclear waste disposal, such as the Swedish KBS-3 method [3].



**Figure 1:** Typical “snapshot” from a MD simulation of two montmorillonite layers in the three-layer hydrate state. Right hand side shows the atom distribution in the vertical direction.

- [1] Suter et al. (2007) *J. Phys. Chem. C* **111**, 8248-8259.  
 [2] Bourg & Sposito. (2010) *Environ. Sci. Technol.* **44**, 2085-2091.  
 [3] Holmboe et al. (2012) *J. Contam. Hydrol.* **128**, 1-4, 19-32.

## Ca-isotope tracing of submarine groundwater discharge—Florida Bay

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Florida Bay is a seasonally hypersaline estuarine lagoon located on the southernmost tip of the submerged Florida shelf. It is roughly triangular in shape with barriers that limit circulation with open marine waters. To the east, the nearly continuous exposure of Pleistocene limestone, composing the Florida Keys, keeps surface Atlantic waters out of Florida Bay (with the exception of a few tidal passes). To the south, a series of shallow mudbanks limits circulation with the Gulf of Mexico. To the north, Florida Bay is bounded by mangrove wetlands of the Florida Everglades. Waters are typically  $< 3$  m deep, and it is common to find areas that have been scoured of sediment to reveal the underlying Pleistocene limestone bedrock. Outcrop exposures of Pleistocene limestone occur in the coastal region of northern Florida Bay extending into the wetlands of the southern Everglades.

The coastal region of northeastern Florida Bay has been identified in hydrogeological models as an area of submarine groundwater discharge (SGD) [1]. Other studies have shown seawater penetration beneath the southern Everglades extending for 25 km inland from the coastline [2], and that brackish groundwaters are not conservative with respect to Ca, showing an ‘excess Ca’ effect; i.e., more Ca than would be expected on the basis of seawater-freshwater mixing in the subterranean estuary [3]. The excess Ca originates from the dissolution of carbonate-aquifer minerals.

The tracer potential of Ca-isotopes ( $\delta^{44/40}\text{Ca}$  values) in this setting stems from the  $\sim 1.1\%$  difference between  $\delta^{44/40}\text{Ca}$  values of carbonate bedrock ( $-1.1\%$ ) and seawater ( $0\%$ ). Therefore, the excess Ca picked up during the circulation of seawater in the subsurface serves as a fingerprint of SGD inputs into coastal Florida Bay, where water circulation restriction enables the seepage flux of isotopically light Ca to be resolved before it is ‘mixed out’ by circulation with the ocean. A  $0.7\%$  gradient in  $\delta^{44/40}\text{Ca}$  values is found in both waters and sediment of northeastern Florida Bay, decreasing towards the Florida Everglades. Results of a quantitative Ca-isotope mixing model indicate that 20% of the water and 30% of the Ca in Joe Bay is from SGD. The estimates are even higher in the southern Mangrove fringe of the Florida Everglades [4].

More work is needed to determine the global-scale SGD Ca-flux to the oceans. Quantitative flux estimates would help to close the Ca isotope budget of the oceans, where the traditional input Ca-fluxes from rivers and hydrothermal fluids are too small to balance the output Ca-flux into carbonate sediments.

- [1] Langevin et al. (2004) USGS Open File Report 2004-1097, 30p. [2] Fitterman and Deszcz-Pan (1998) *Explor. Geophys.* **29**, 240-243.  
 [3] Price et al., (2006) *Hydrobiology* **569**, 23-36. [4] Holmden et al. (2012) *Geochim. Cosmochim. Acta*, IN PRESS.