

Transport Mechanism of Guest Methane in Water-Filled Nano-Pores

Tai Bui¹, Anh Phan¹, David R. Cole², and Alberto Striolo^{1,*}

¹Department of Chemical Engineering, University College London, London, WC1E 7JE, UK

²School of Earth Sciences, The Ohio State University, Columbus, Ohio 43210, USA

Supplemental Material

* Address correspondence to: a.striolo@ucl.ac.uk

In **Figure S1** and **Figure S2** mean square displacements (MSD) data are shown for methane and water molecules, respectively, along the X, Y directions, and the X-Y plane in 5 hydrated slit-shaped pores. The density profiles calculated for water molecules along the direction perpendicular to the pore surfaces are shown in **Figure S3**. The oxygen atom of water was considered for these calculations, and the results are shown for water in the 5 hydrated pores considered. Similar results are shown for methane in **Figure S4**.

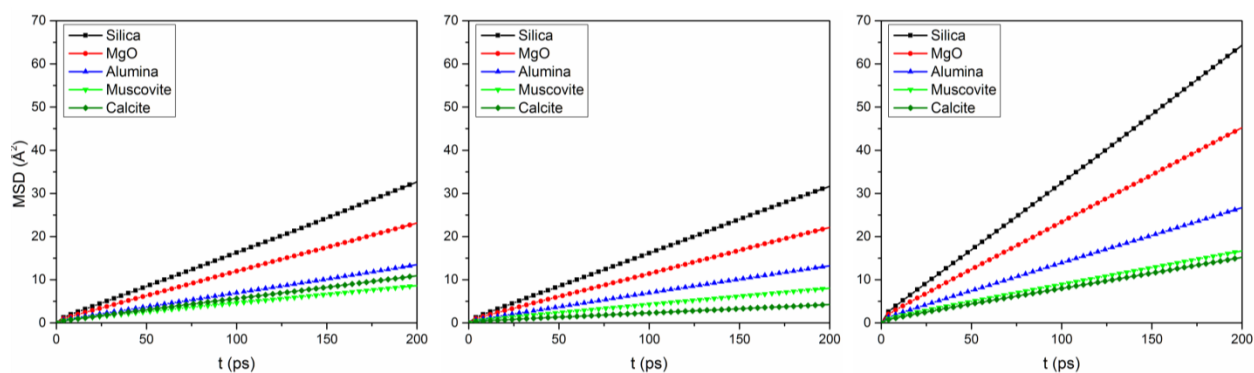


Figure S1. MSD of methane molecules in the X (left), Y (middle) direction, and X-Y plane (right) calculated for different hydrated pores.

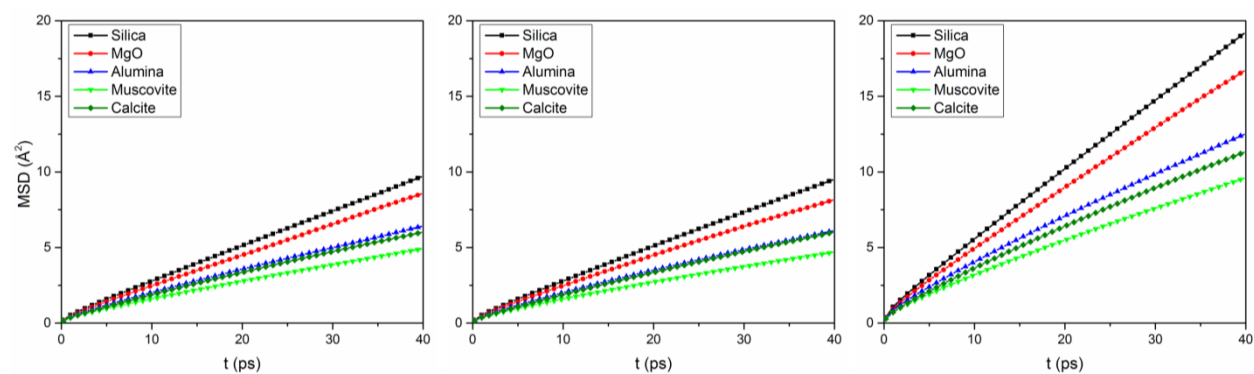


Figure S2. MSD of water molecules in the X (left), Y (middle) direction, and X-Y plane (right) calculated for different hydrated pores.

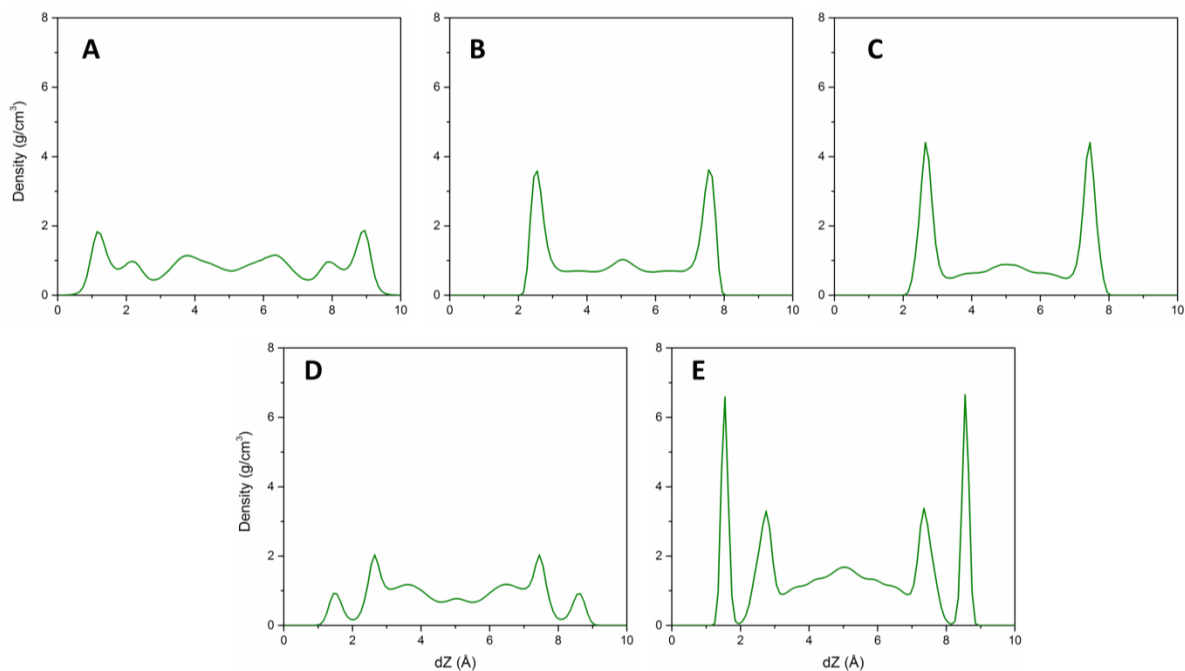


Figure S3. Density profiles of water along the Z direction of the simulation box in infinite pore systems: silica (A), MgO (B), alumina (C), muscovite (D), and calcite (E). The pore center is located at dZ=5.

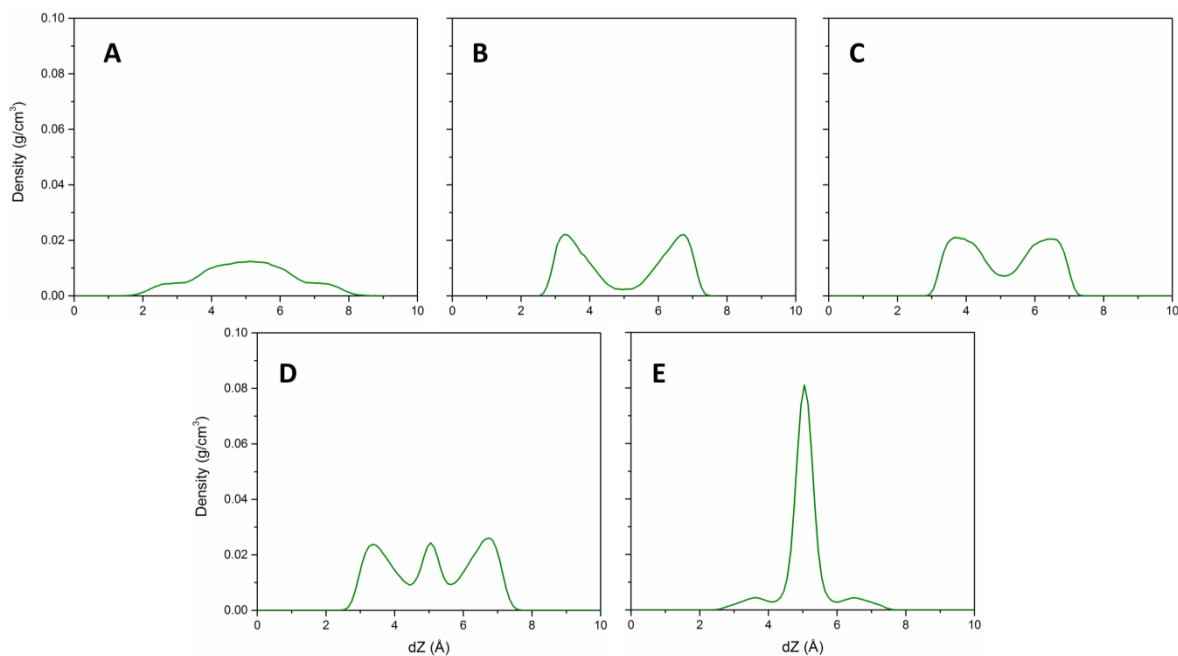


Figure S4. Density profiles of methane along the Z direction of the simulation box in infinite pore systems: silica (A), MgO (B), alumina (C), muscovite (D), and calcite (E). The pore center is located at dZ=5.

Figure S5 shows the potential of mean force profiles calculated using the umbrella sampling algorithm^{1,2} as one methane molecule is dragged following one straight line along the X direction of the simulation box, while maintained at the center of the pore along the Z direction. The general purpose of using umbrella sampling simulations is to determine the energy landscape of a system along a specific reaction coordinate (ξ) by introducing a bias potential to the system at many points (windows) along the reaction coordinate. From a collection of equilibrium simulations at each window, the biased probability of the configurations along the reaction coordinate is calculated. The unbiased probabilities of the configurations and free energy profile are calculated by using the weighted histogram analysis method (WHAM).^{3,4}

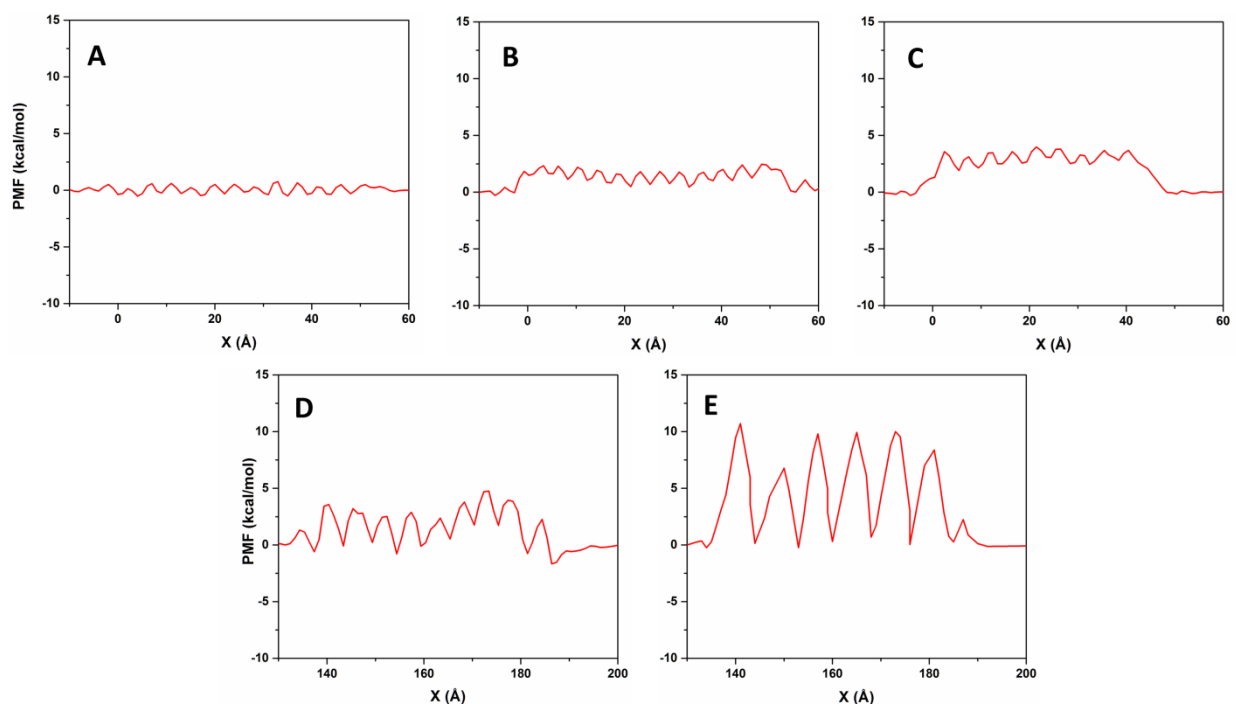


Figure S5. Potential of mean force profiles for the transport of methane along the X direction of the simulation box in finite pore systems: silica (A), MgO (B), alumina (C), muscovite (D), and calcite (E). The results were obtained from umbrella sampling simulations.

In **Figure S6** we present the density profile of hydrogen bonds as a function of position along the Z direction of the calcite pore. Densities are expressed in $1/\text{\AA}^3$. In **Figure S7** we show in-plane density distributions of water-water hydrogen bonds (left panel), methane (middle) and their overlaps (right) within a $12 \times 12 \text{\AA}^2$ section along the X-Y plane at the center of the calcite pore.

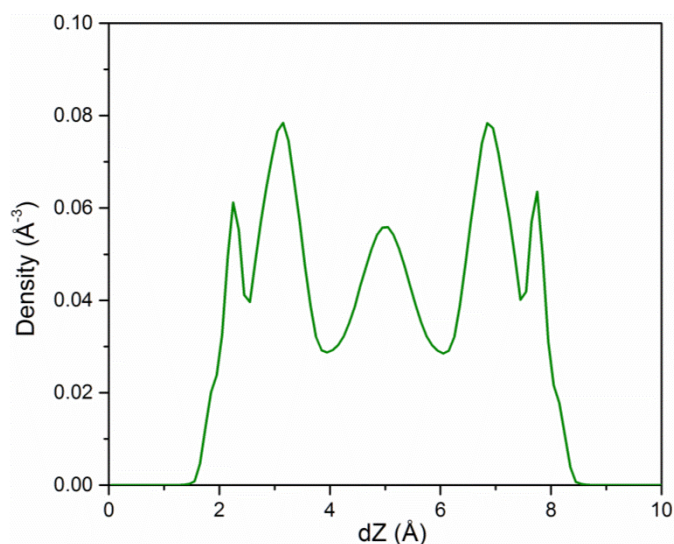


Figure S6. Density profile of hydrogen bonds along the Z direction of the simulation box in infinite hydrated calcite pore. The pore center is located at $dZ=5$.

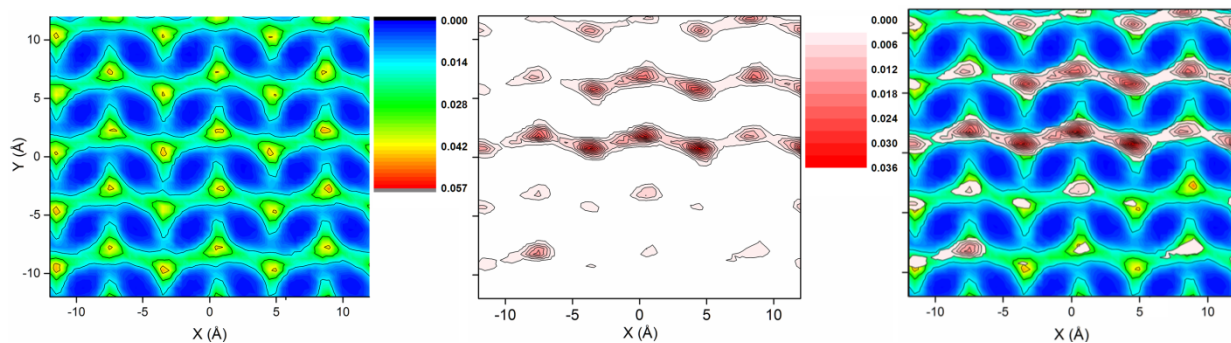


Figure S7. In-plane density distributions of water-water hydrogen bonds (left panel) and methane (middle panel) within a $12 \times 12 \text{\AA}^2$ section along the X-Y plane at the center of the hydrated calcite pore. The right panel represents the overlap of the left and middle panels. Densities are expressed in $1/\text{\AA}^3$.

Figure S8 shows the in-plane density distributions of water oxygen atoms in the second hydration layer respect to the pore surface (left panel), methane in the middle region of the pore (middle panel) and their overlaps (right panel) within a $12 \times 12 \text{ \AA}^2$ section along the X-Y plane at the center of the calcite pore. **Figure S9** shows the methane-water oxygen radial distribution function as a function of the methane-oxygen distance in hydrated calcite pore.

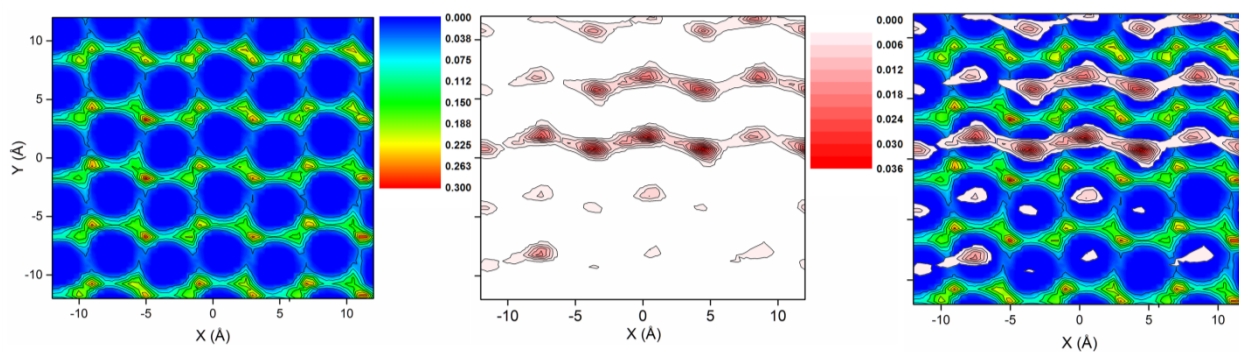


Figure S8. In-plane density distributions of water oxygen atoms in the second hydration layer (left panel) and methane (middle panel) within a $12 \times 12 \text{ \AA}^2$ section along the X-Y plane at the center of the hydrated calcite pore. The right panel represents the overlap of the left and middle panels. Densities are expressed in $1/\text{\AA}^3$.

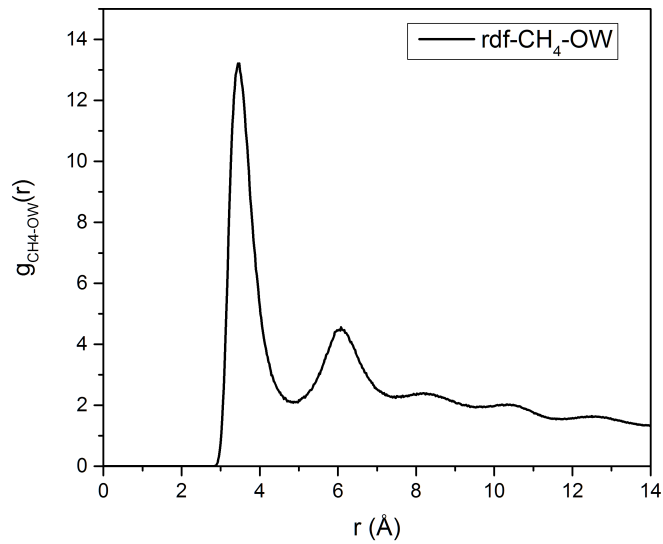


Figure S9. The radial distribution function of water oxygen atoms around methane molecules in hydrated calcite pore.

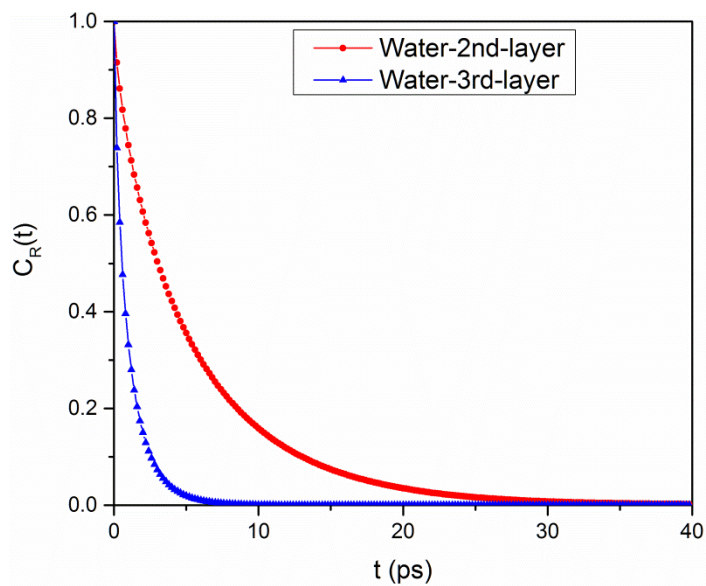


Figure S10. Residence correlation functions for oxygen atoms in the second and the third (middle pore) hydration layer of the hydrated calcite pore.

In **Figure S10** we report the residence correlation functions for oxygen atoms (used to identify water molecules) in specific hydration layers of interest in calcite pore. The algorithm is described elsewhere.⁵ Calculations were applied on water molecules confined in a slab of thickness 1 Å corresponding to the peaks that appear in the density profile of water along the Z direction (see **Figure S3 E**). The faster the correlation function decays from 1 to 0, the lower residence time the water molecules stay in specific hydration layers. **Figure S11** shows in-plane density distributions of water as a function of position within a 40×40 Å² section within the X-Y plane in 5 different hydrated pores. Water molecules belonging to the first and second hydration layers identified from the density profiles along the Z direction (see **Figure S3**) were considered.

Figure S12 reports in-plane density distributions of methane as a function of position within a 40×40 Å² section within the X-Y plane of 5 hydrated pores. Methane molecules belonging to the highest density regions along the Z direction (e.g. in the middle of the pore for silica and calcite pores, or between the middle of the pore and the pore surfaces for MgO, alumina and muscovite pores) were used for the calculations.

Figure S13 shows the free energy landscape projected onto X-Y plane overlaid with the density distribution of methane molecules in the same X-Y plane section for calcite pore system.

In **Figure S14** we show the crystal structure of the calcite substrate used in this study in 3 and 2-Dimensional graphs.

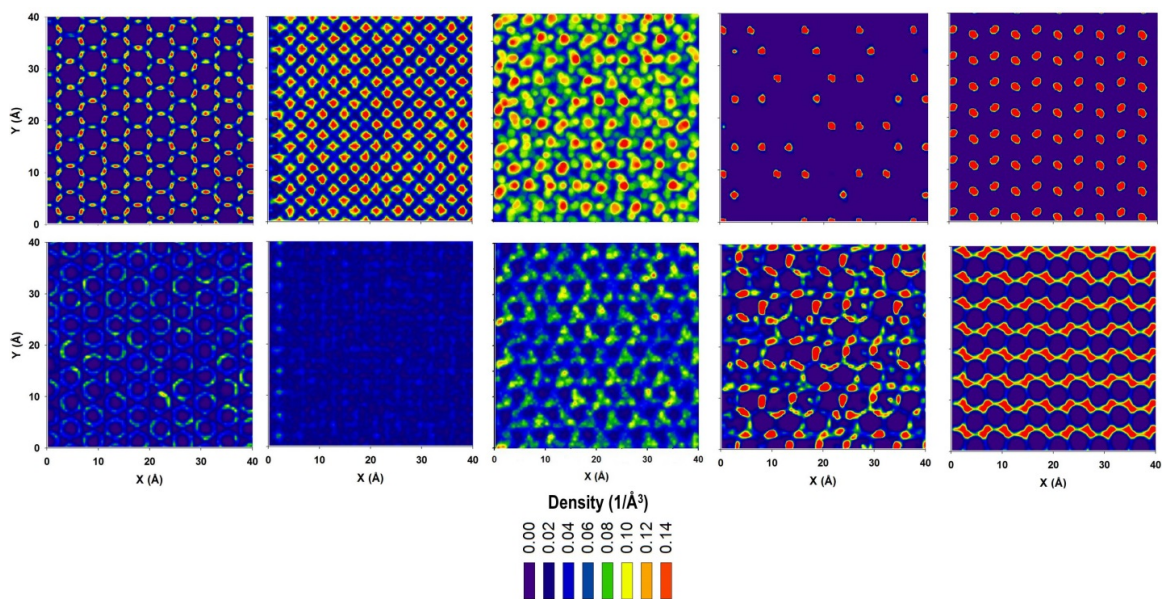


Figure S11. From left to right: density distributions of water in the first (top panels) and second (bottom panels) hydration layers next to the pore surfaces of silica, MgO, alumina, muscovite, and calcite.

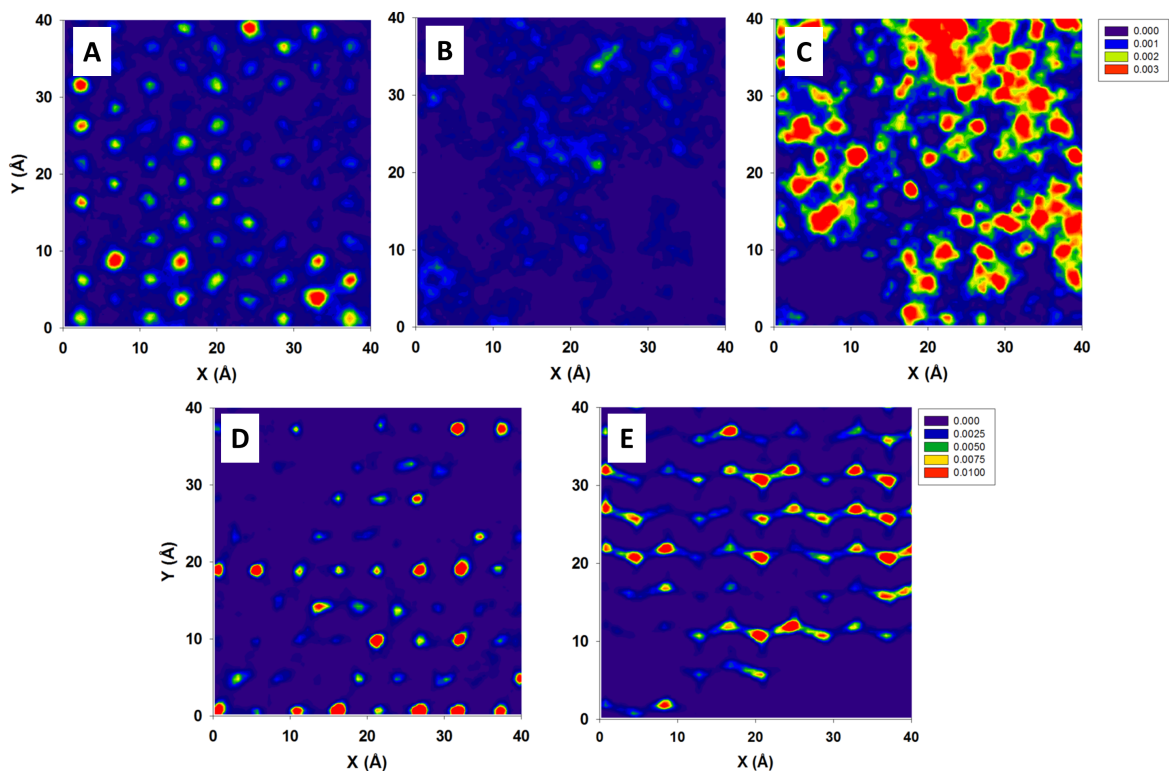


Figure S12. Density distributions of methane in silica (A), MgO (B), alumina (C), muscovite (D), and calcite (E) pores. Methane molecules belonging to the highest accumulation region along the Z direction were used to calculate (see Figure S2).

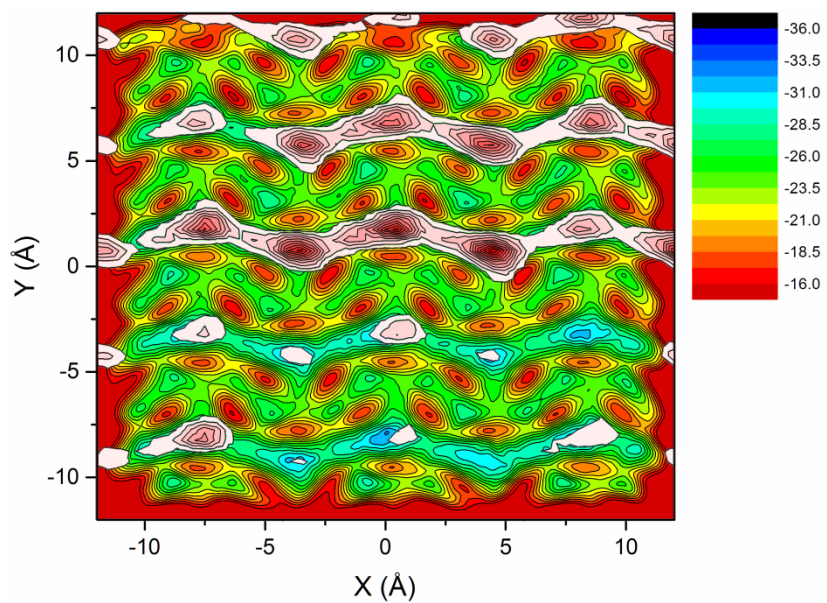


Figure S13. Free energy landscape projected onto X-Y plane for calcite pore obtained from well-tempered metadynamics simulations. Pink (read and white) areas represent in-plane density distribution of methane in the same section along the X-Y plane.

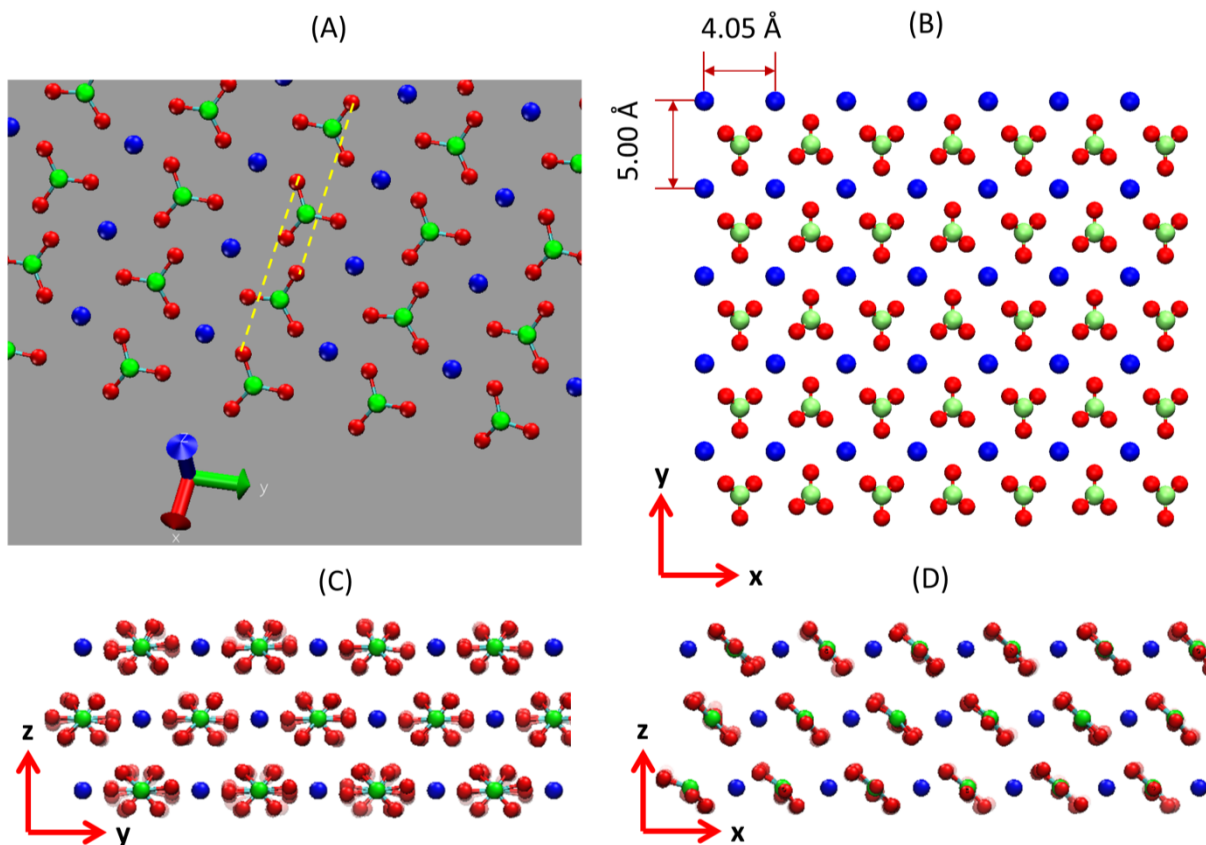


Figure S14. Crystallized structure of calcite substrate illustrated in 3D (panel A), 2D by projected on X-Y plane (panel B) for the surface layer, 2D by projected on Y-Z plane (panel C), and 2D by projected on X-Z plane (panel D). C=green; Ca=blue; O=red

References

- (1) Torrie, G. M.; Valleau, J. P. Nonphysical Sampling Distributions in Monte Carlo Free-Energy Estimation: Umbrella Sampling. *J. Comput. Phys.* **1977**, *23*, 187–199.
- (2) Kästner, J. Umbrella Sampling. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2011**, *1*, 932–942.
- (3) Kumar, S.; Rosenberg, J. M.; Bouzida, D.; Swendsen, R. H.; Kollman, P. A. The Weighted Histogram Analysis Method for Free-Energy Calculations on Biomolecules. I. The Method. *J. Comput. Chem.* **1992**, *13*, 1011–1021.
- (4) Souaille, M.; Roux, B. Extension to the Weighted Histogram Analysis Method: Combining Umbrella Sampling with Free Energy Calculations. *Comp. Phys. Comm.* **2001**, *135*, 40–57.
- (5) Phan, A.; Ho, T. a.; Cole, D. R.; Striolo, a. Molecular Structure and Dynamics in Thin Water Films at Metal Oxide Surfaces: Magnesium, Aluminum, and Silicon Oxide Surfaces. *J. Phys. Chem. C* **2012**, *116*, 15962–15973.