

Supporting Information

Water–Hydrophobic Zeolite Systems.

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A simulation cell containing water and zeosil slabs is presented in Figure 1. Due to periodic boundary conditions these slabs form an unlimited system, which fills the space. The simulations were made in NVT canonical ensemble. Parameters of simulation cells are presented in the lower part of Table 1. Pressure in the cell is defined by the number of water molecules in the system

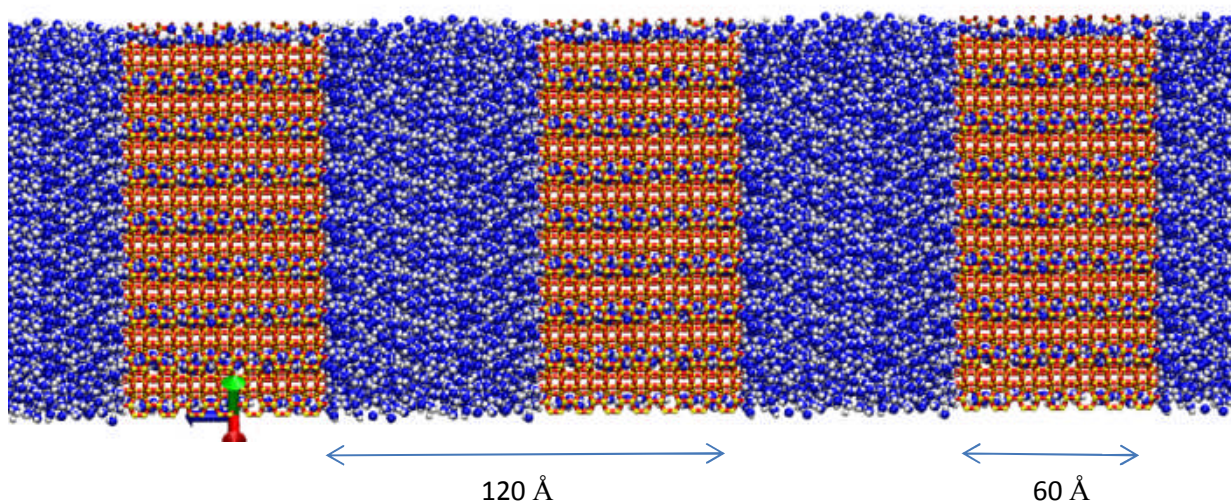


Figure S1. A water-zeolite simulation cell taken with periodic boundary conditions.

Files with configurations, force field, and parameters of simulations

GULP	DL_POLY
AFI_020_H2O_GULP	AFI_850_H2O_DLPOLY
IFR_017_H2O_GULP	IFR_625_H2O_DLPOLY
MTW_024_H2O_GULP	MTW_730_H2O_DLPOLY
TON_020_H2O_GULP	TON_610_H2O_DLPOLY

Force field parameters

Electrostatic charges, a.u.:

Si	O	O (OH)	H (OH)	O (water)	H (water)
2.1	-1.05	0.95	0.425	-0.82	0.41

Van der Waals interactions, $E=\epsilon[(\sigma/r)^{12}-2(\sigma/r)^6]$:

	Si-O	O -O	Si-Si
ϵ , eV	0.231913E-04	0.673883E-02	0.79812E-7
σ , Å	3.6298	3.5532	3.7064

Three body interactions,

$$E_{ijk}^{three-body} = \frac{1}{2} k_{ijk}^{tb} (\theta_{ijk} - \theta_{0,ijk})^2$$

<i>I-j-k</i>	k_{ijk}^{tb} (eVÅ ⁻²)	$\theta_{0,ijk}$ (deg)
O-Si-O	1.2614	109.47
Si-O-Si	1.4	142.0
Hw-Ow-Hw	3.9695	109.47

Intramolecular interactions

$$E_{ij}^{harmonic} = \frac{1}{2} k_{ij}^h (r_{ij} - r_{0,ij})^2$$

Ow-Hw	$k_{ij}^h = 48.0595 \text{ eVÅ}^{-2}; r_0 = 1 \text{ Å}$
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MTW zeosil was selected for testing the simulation method regarding framework rigid vs. flexible. It is expected that the framework flexibility may influence the adsorption isotherm. For this goal we performed additional simulations of the water – MTW system with a flexible framework, using the BS force field.

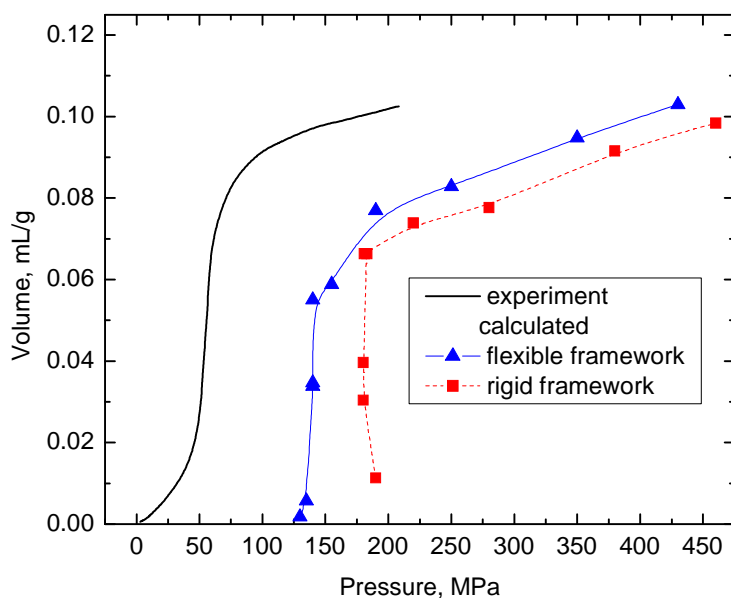


Figure S2. Experimental and calculated adsorption isotherms for MTW zeosil with flexible and rigid frameworks.

Flexibility affects the adsorption isotherm shifting the intrusion pressure by 35-40 MPa toward lower values. Adsorbed water volumes at high pressure are approximately the same.

A twofold strategy was used for the investigation of the influence of the water-zeosil interactions. We increased the electrostatic charges on Si and O atoms approximately by 10%. As expected, a higher polarity shifts the adsorption isotherm toward lower pressure. The shift of intrusion pressure is about 25 MPa with respect to the isotherm calculated for the original flexible BS force field. In the second case we increased the strength of the van der Waals water-zeolite O-O interactions usually calculated as $\epsilon_{ij}=(\epsilon_{ii}\epsilon_{jj})^{0.5}$. Two calculations were made with $\epsilon_{00}=1.5\epsilon_{00}$ and $\epsilon_{00}=2\epsilon_{00}$. Increasing of water-zeolite attraction corresponds to higher hydrophilicity of the material. The intrusion pressure is lower in both cases and when the strength of interactions increased twice, the zeolite channels were filled by water even at zero pressure. This behavior is usual for alumino-silicate natural zeolites, whose name means ‘boiling stones’, but this is never the case for pure silica zeolites (zeosils).

We may conclude that the amount of adsorbed water does not depend on the flexibility of the framework or the strength of water-zeolite interactions. It is defined by the free accessible volume of the zeolite. The intrusion pressure, the position of the adsorption isotherm on the V-p plot, depends on the flexibility of the framework and on the water - zeolite

attractive interactions. The BS force field was calibrated according to experimental and structural data. We have neglected zeolite framework flexibility in our calculations because we expected only a small systematic shift of the intrusion pressure. In the case of MTW the shift is about 40 MPa, whilst the estimated accuracy of the pressure determination is about 15 MPa. A large shift of intrusion pressure is observed only at large deviation from the original parameters of water-zeolite van der Waals interactions.

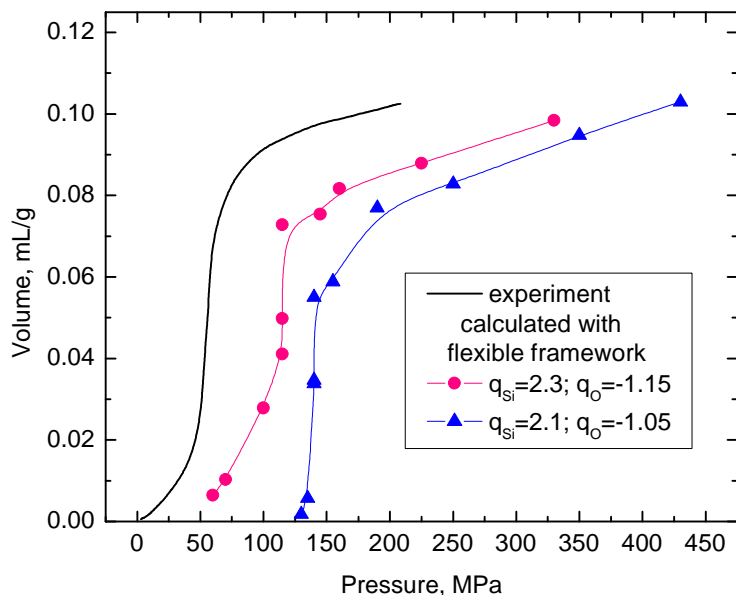


Figure S3. Experimental and calculated adsorption isotherms of MTW zeosil. Calculations were made with the original BS force field and with a modified force field with increased electrostatic charges on Si and O atoms. A flexible framework was used in both simulations.

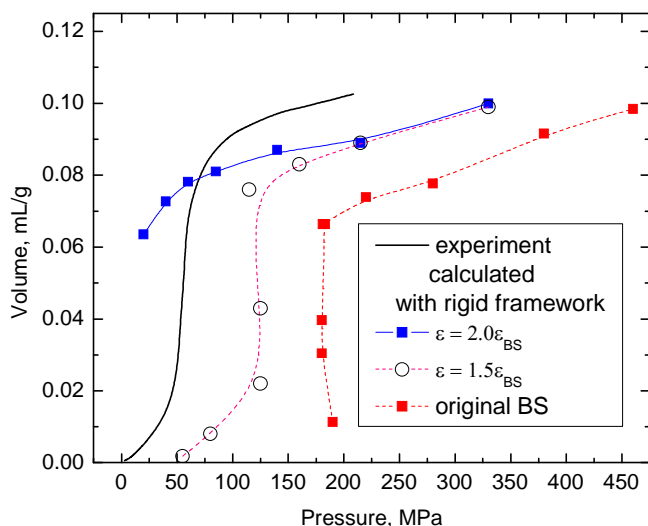


Figure S4. Experimental and calculated adsorption isotherms of MTW zeosil. The parameter for the strength of water-zeosil van der Waals interactions was increased by 1.5 and 2.0 times.

Supporting information to the section “Structure of water in zeolites”.

Here are presented Figures S5-S14, which show consecutive stages of water penetration in zeolites with increasing water pressure.

AFI ZEOSIL

AFI zeosil has the largest pore opening among discussed zeolites. On early stage of water penetration into straight channels small water columns growing up from bulk water into channels are observed. Tips of columns resemble convex menisci. Some compact water clusters, which move like ‘water drops’, are observed in channels (Figure S5).

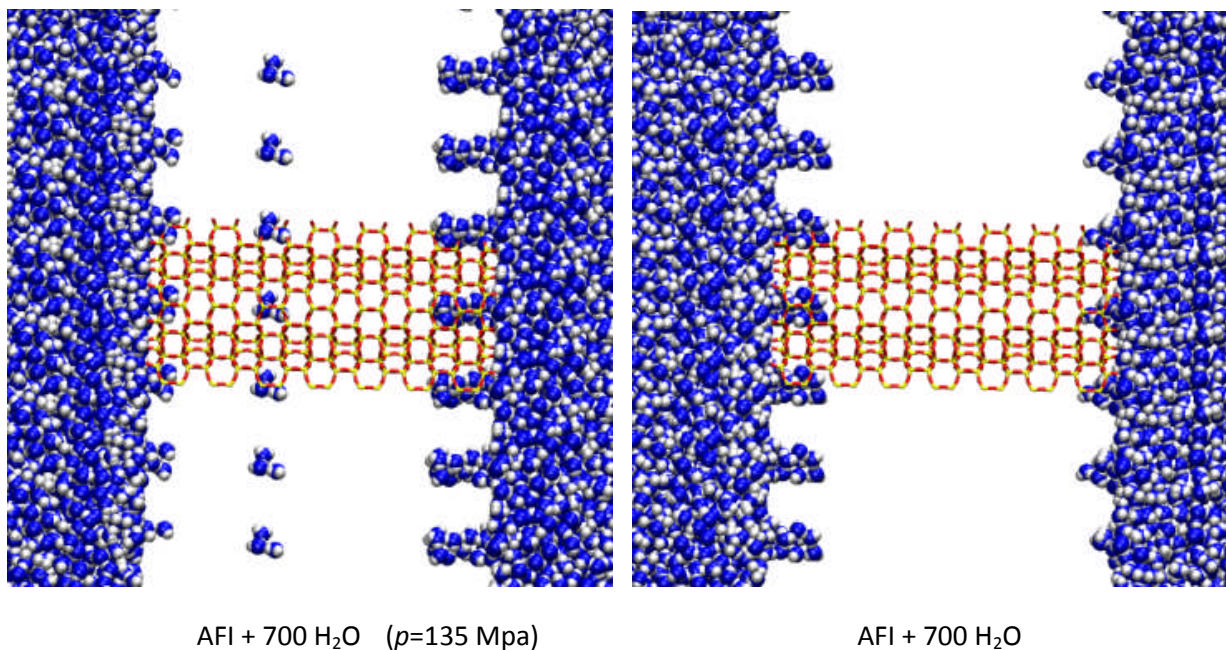


Figure S5. Water inside AFI zeosil on early stage of penetration.

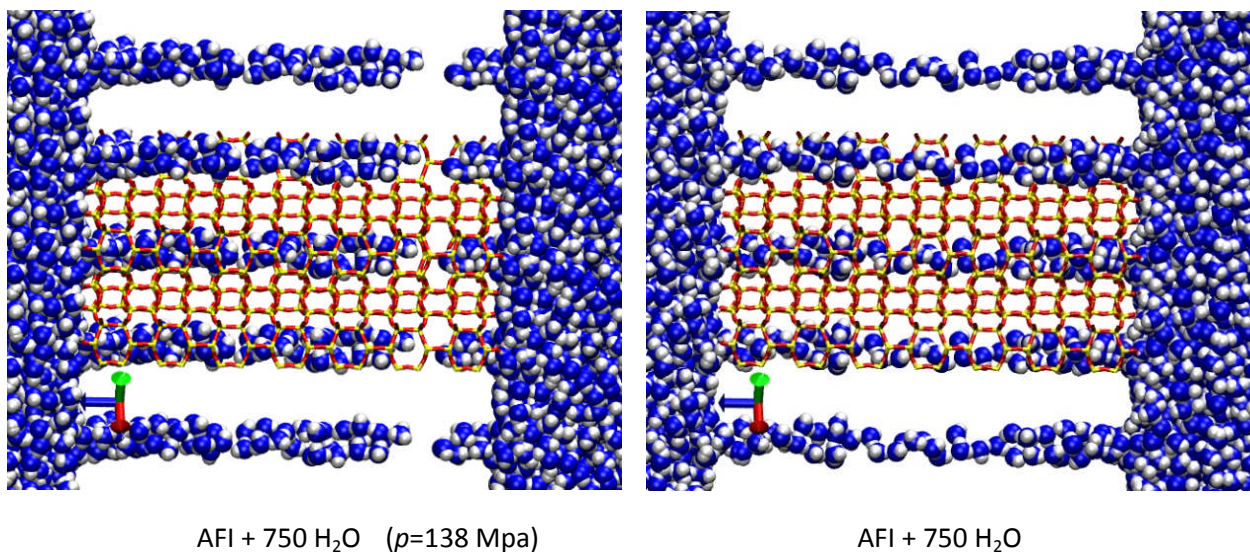
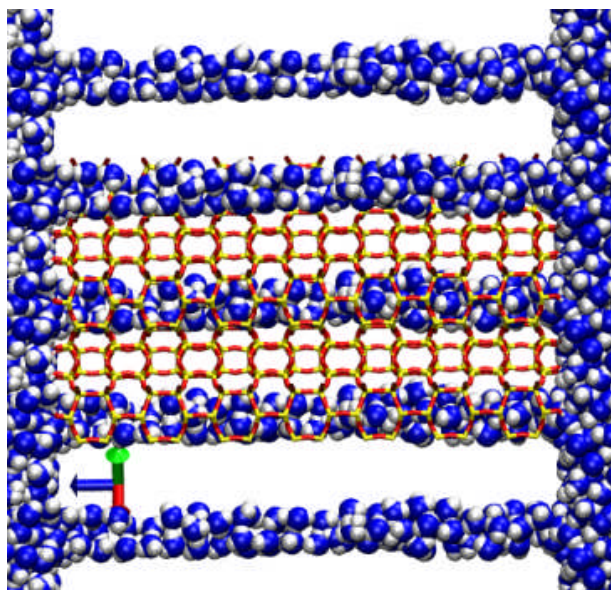
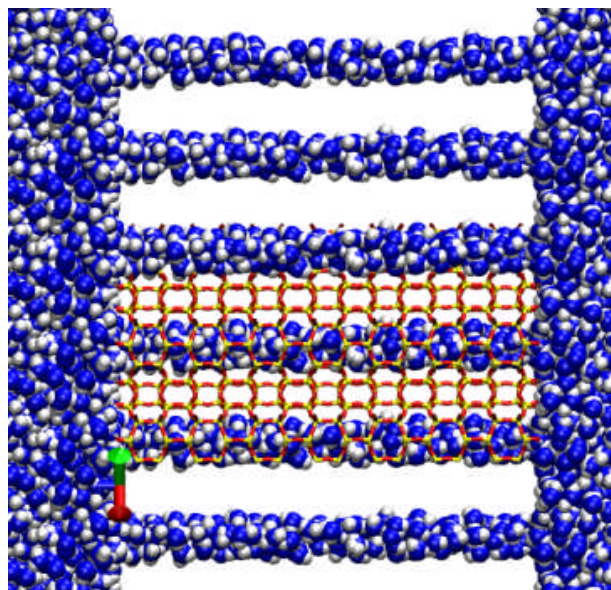


Figure S6. Water inside AFI zeosil near a percolation threshold.

Water columns, growing from both sides of a channel, coalesce and form a percolated cluster (Figure S6). Bulky water clusters are observed at the final stage of water loading (Figure S7)



AFI + 770 H₂O ($p=142$ Mpa)

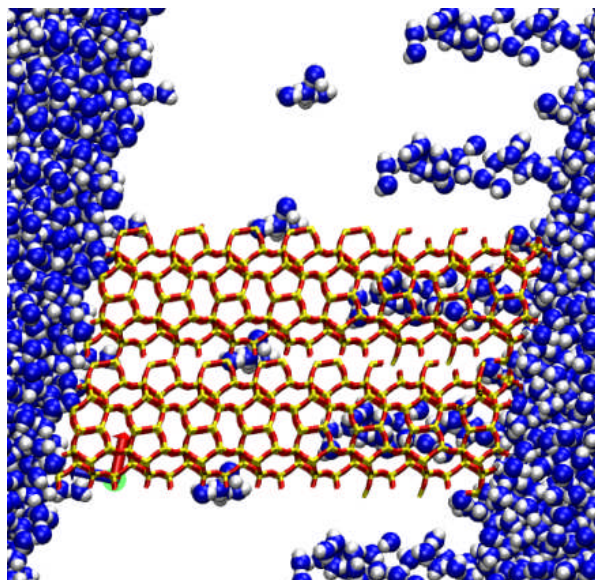


AFI + 850 H₂O ($p=255$ Mpa)

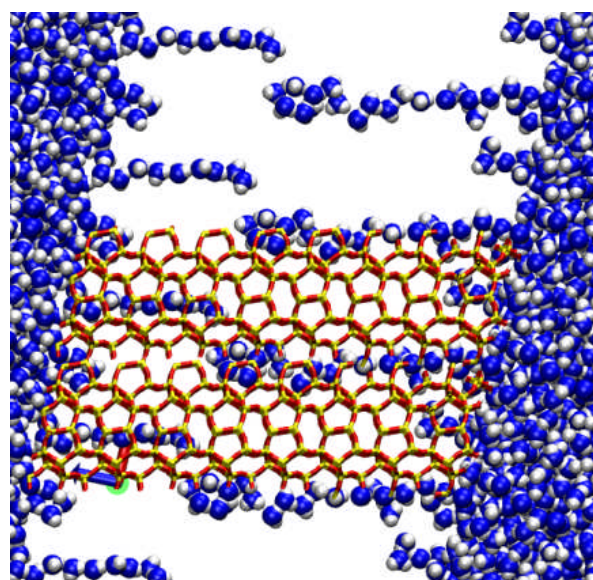
Figure S7. Water inside AFI zeosil at saturation.

IFR ZEOSIL

IFR has smaller channel opening than AFI, but due to the sinusoidal shape of channels IFR zeosil has the largest free volume. These channels promote the formation of chain-like water clusters and a combination of bulky and chain motives are visible in Figures S8-S10. Water clusters formed are commensurate with the channel shape and length.

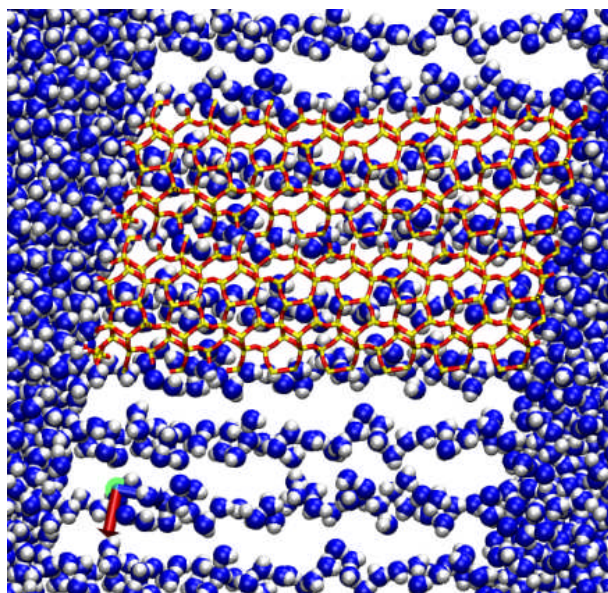


IFR + 535 H₂O ($p=105$ Mpa)

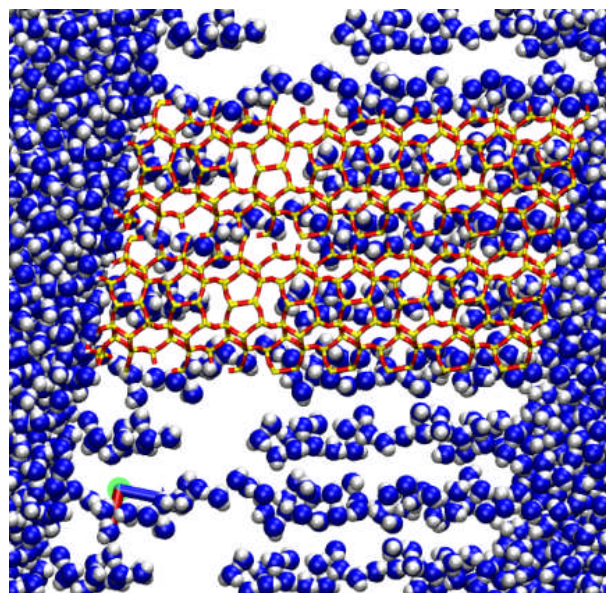


IFR + 535 H₂O

Figure S8. Water inside IFR zeosil on early stage of penetration.

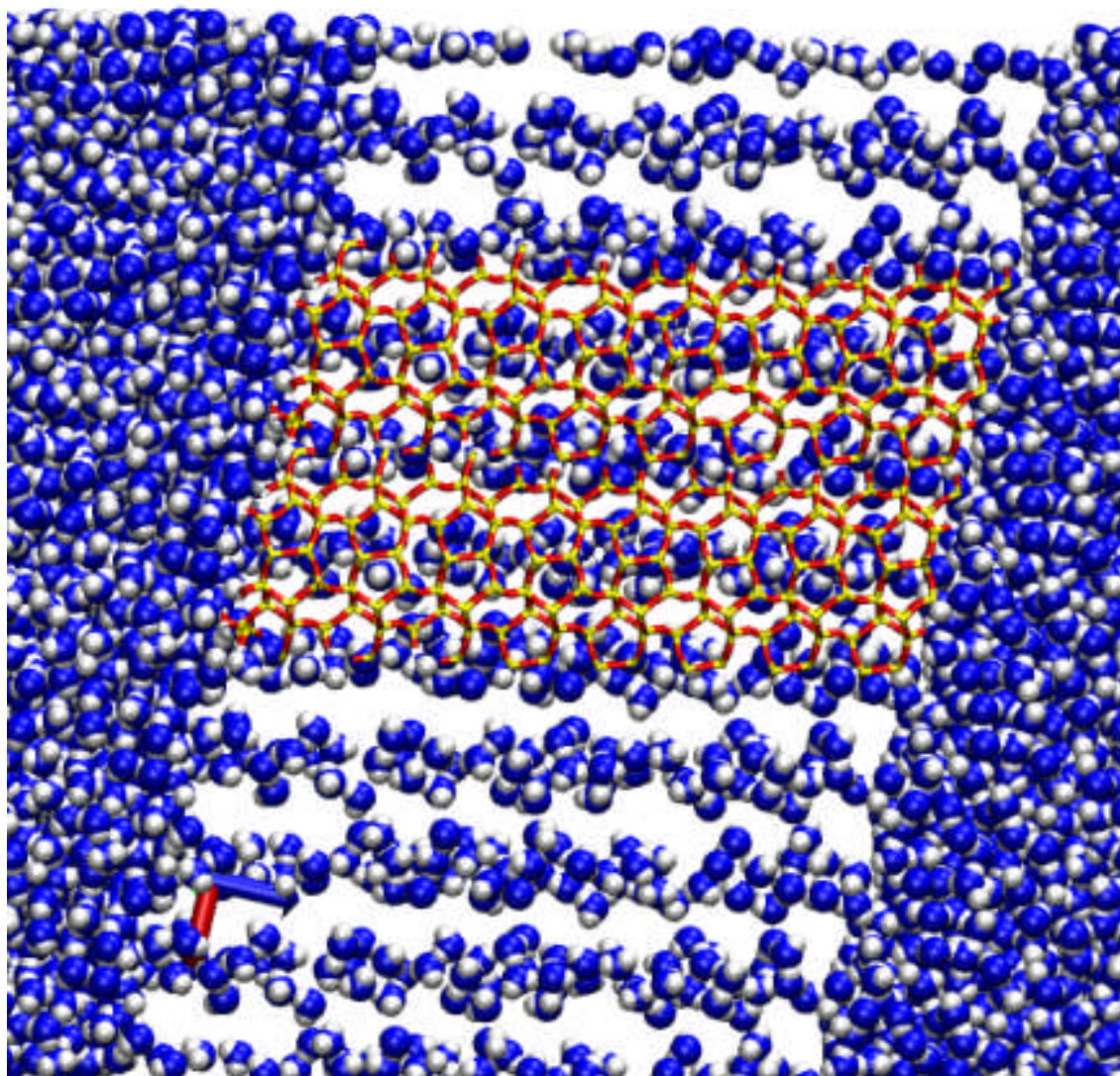


IFR + 590 H₂O ($p=118$ Mpa)



IFR + 590 H₂O

Figure S9. Water inside IFR zeosil near the percolation threshold.



IFR + 635 H₂O ($p=185$ Mpa)

Figure S10. Water inside IFR zeosil at saturation.

MTW ZEOSIL

The shape and position of MTW framework oxygens promote to formation of water linear chain-like clusters. A single file chain and double chain water drops are shown in the left part of Figure S11. At larger loading a double chain percolated cluster is formed only in one channel (Fig. S11). After the percolation threshold all channels are filled by water (Figure S12)

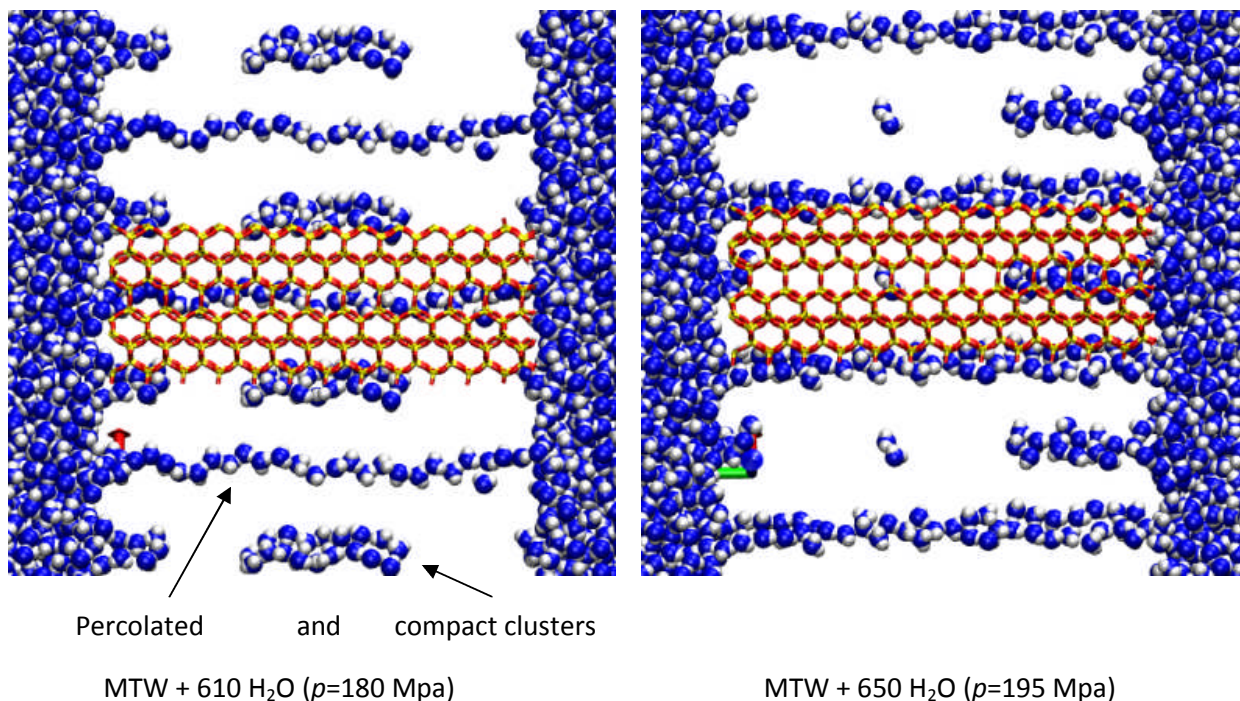


Figure S11. Water inside MTW zeosil near the percolation threshold. A percolated cluster is formed only in one channel.

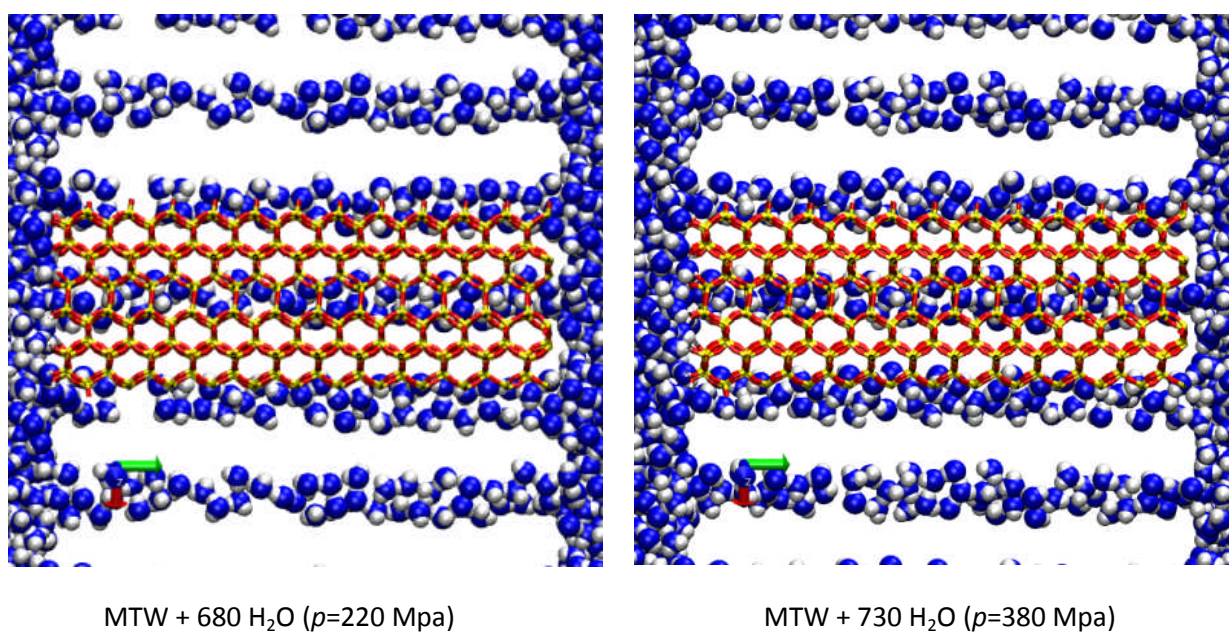


Figure S12. Water inside MTW zeosil after the percolation threshold.

TON ZEOSIL

This is a system with the strongest confinement effect among discussed. Single-file chain is a structural attractor for water in TON zeosil. On the early stage, at low water pressure, water chains start to penetrate into channels and may form percolated cluster in some channels meanwhile other channels are empty (Figure S13). At high hydrostatic pressure all zeosil channels are fully loaded and water structures are determined by channel sizes and shapes (Figure S14).

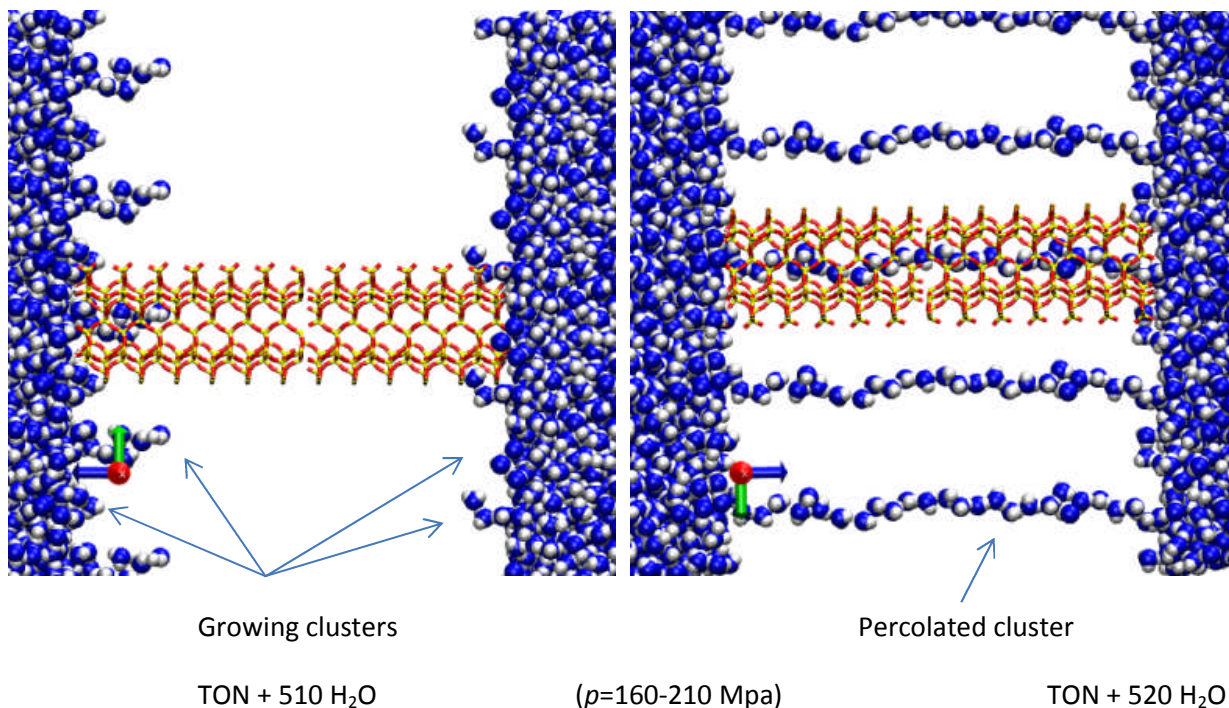


Figure S13. Water inside TON zeosil on the early stage of penetration and near the percolation threshold. A percolated cluster is formed only in one channel.

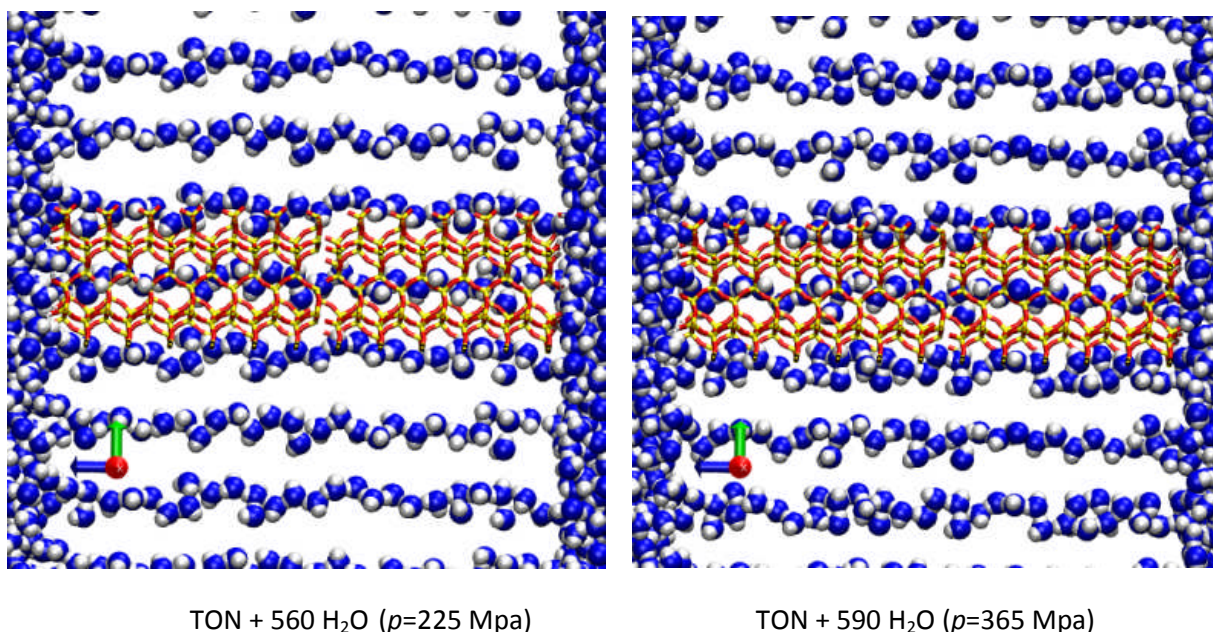


Figure S14. Water inside TON zeosil after the percolation threshold.