Molecular mechanisms of H_2 gas adsorption in clays in the context of geological nuclear waste disposal: Insights from classical atomistic simulations

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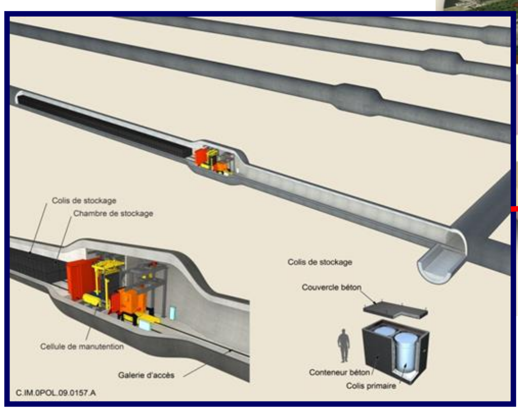

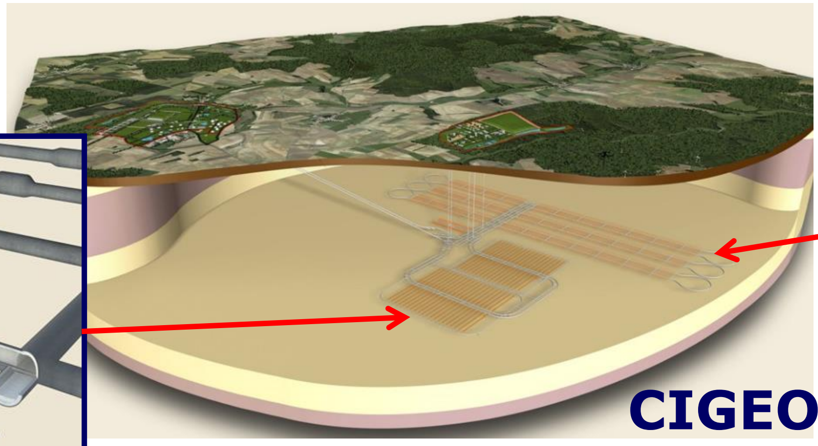

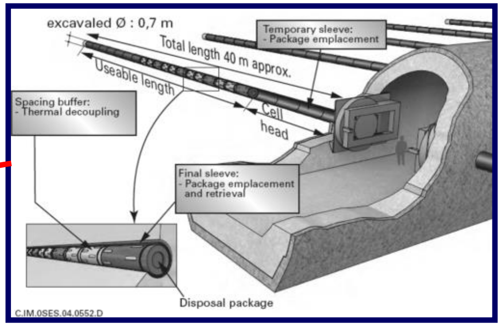

CIGEO

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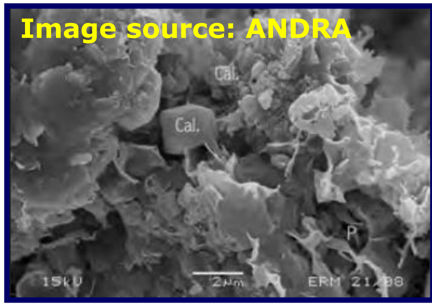
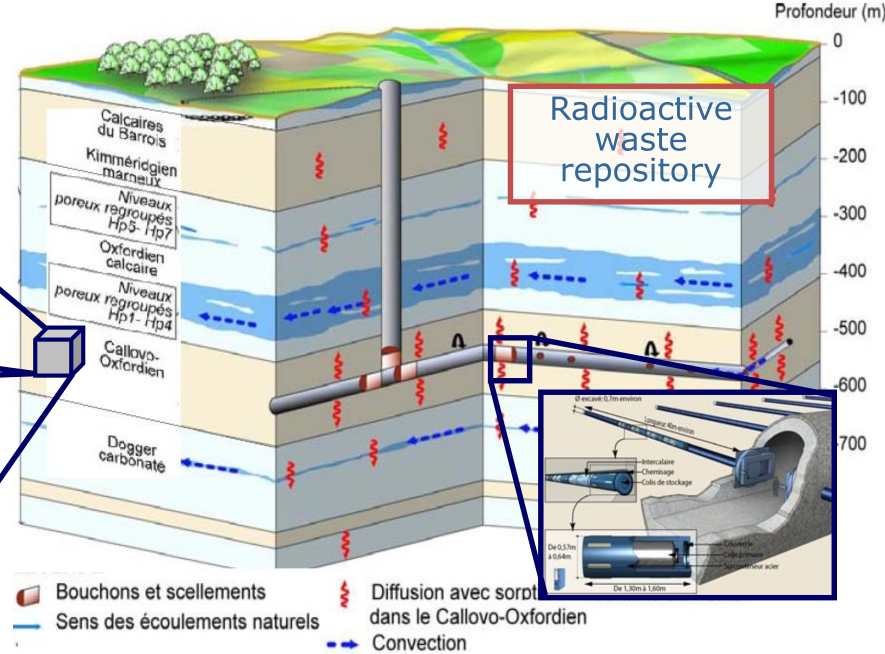
Molecular-Scale Understanding of the Adsorption and Transport of Radionuclides in Cox Clay Formations



- 41% clay (illite, smectite, and interstratified I/S)
- 31% calcite
- 25% quartz and feldspar
- 3% other minerals
- ~1% organic matter
- <1% gases

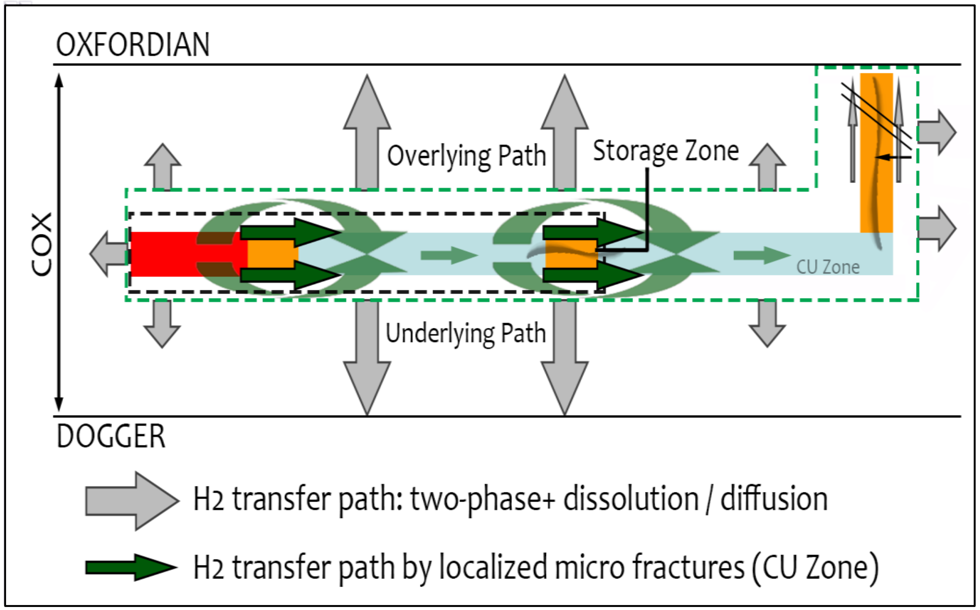


Primary objective:
improve molecular-scale understanding of the adsorption and transport properties of Callovo-Oxfordian clayey formations and cementitious materials in the context of radioactive waste disposal and storage

Gas Formation under Waste Storage Conditions

PhD thesis of Pinar CITLI (February 2024)

Anaerobic corrosion of metals	Degradation of organic matter	Radiolysis of water due to radioactive decay
H_2	CH_4	H_2
	CO_2	O_2
		CO_2
		CH_4



Gas accumulation → Gas pressure build-up → Over pressure → Fracture of surrounding clay rock

- ✓ Dissolution in water and diffusion
- ✓ Two-phase water flow
- ✓ Transfer along micro fractures
- ✓ Transfer along fractures

Computational Atomistic Modeling Tools

Molecular Dynamics (MD) - deterministic approach

Monte Carlo (MC) - stochastic approach

N ~ 10^3-10^6 atoms
t ~ 1-10 ns
t ~ 10^6-10^7 time steps
n ~ 10^6-10^7 config.

need significant computing power

In both approaches, MD or MC, the formalism of ***statistical mechanics*** is used to develop quantitative molecular-level understanding of the complex behavior of materials and their fluid interfaces:

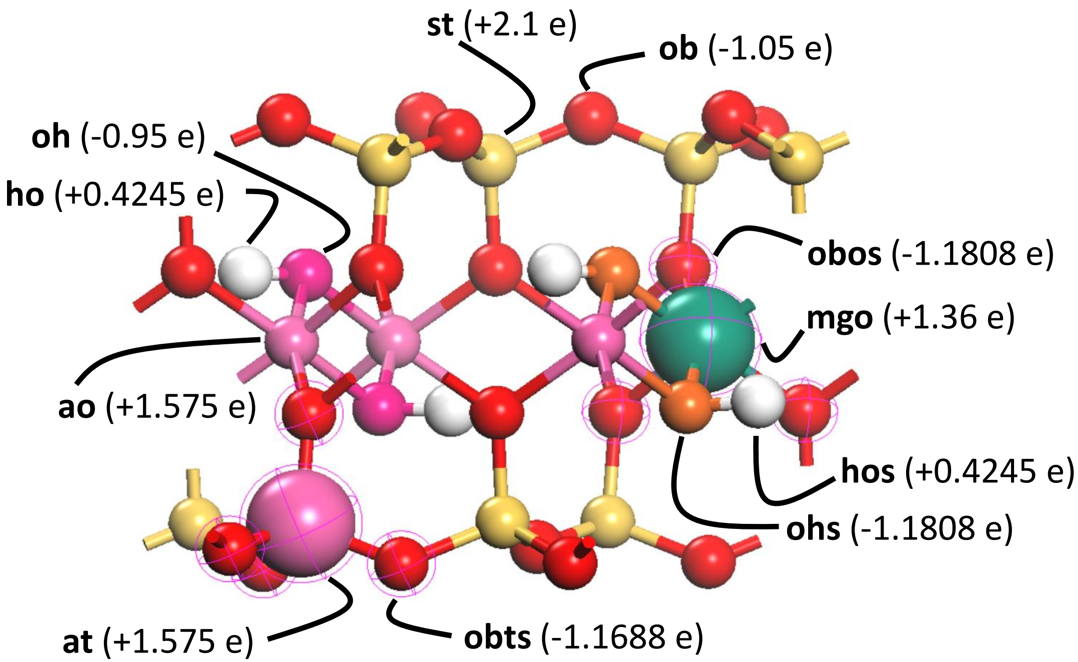
- ✓ Structure and dynamics of aqueous and interfacial species
- ✓ Hydration, adsorption, complexation, diffusion, intercalation, H-bonding
- ✓ Atomistic mechanisms of ionic sorption and transport

Atomistic computer simulations are used nowadays as any other tool of materials research, on par with any other physical and chemical experimental methods (IR, Raman, NMR, Brillouin spectroscopies, X-ray and neutron diffraction, etc.)

Models of Interatomic Interactions

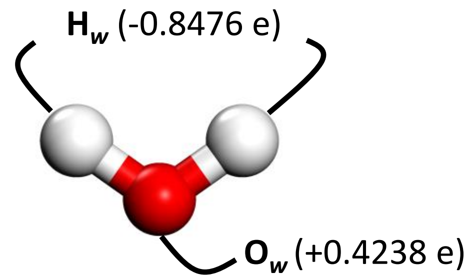
ClayFF

Cygan, Liang, Kalinichev, *J.Phys.Chem.B*, **108** 1255-1266 (2004)
Cygan, Greathouse, Kalinichev, *J.Phys.Chem.C*, **125** 17573-17589 (2021)



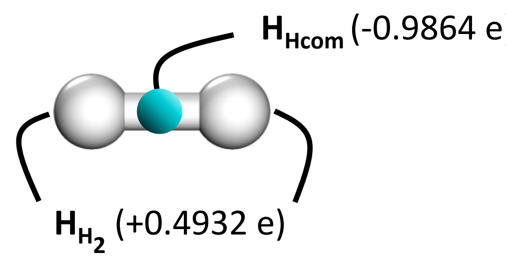
SPC/E H_2O model

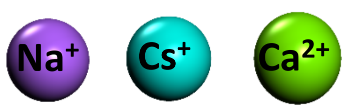
Berendsen et al. *J.Phys.Chem.*, **91**, 6269-6271 (1987)



3-site H_2 model

Alavi et al., *J.Chem.Phys.*, **123**, 024507 (2005)



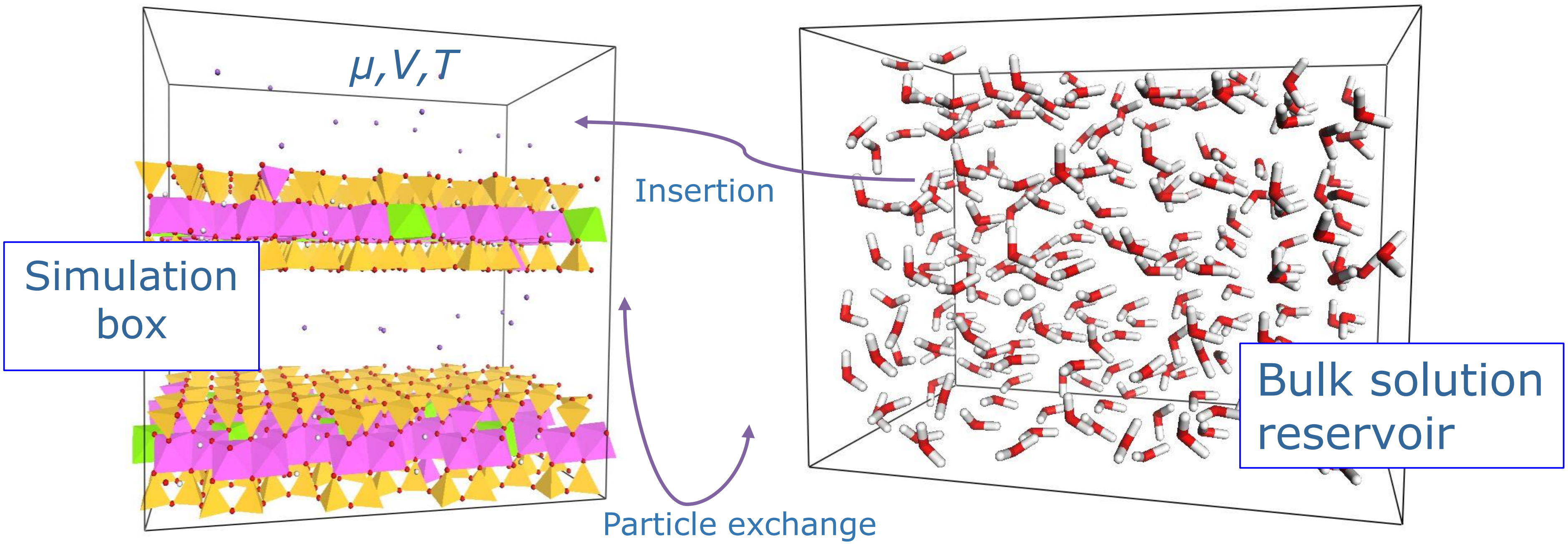


Li et al. *J. Chem. Theory Comput.*, **9**, 2733-2748 (2013); **11**, 1645-1657 (2015);

GCMC simulations of H_2 Adsorption in Clay

PhD thesis of Pinar CITLI (February 2024)

- ✓ Grand Canonical Monte Carlo (GCMC) simulations of H_2/H_2O binary mixtures
- ✓ T = 298, 323 and 363 K ; P = up to 120 bar, 1000 bar and 10,000 bar



- ✓ Solubility of H_2 in the clay interlayers
- ✓ Effect of pore size and hydration level
- ✓ Effect of interlayer cation

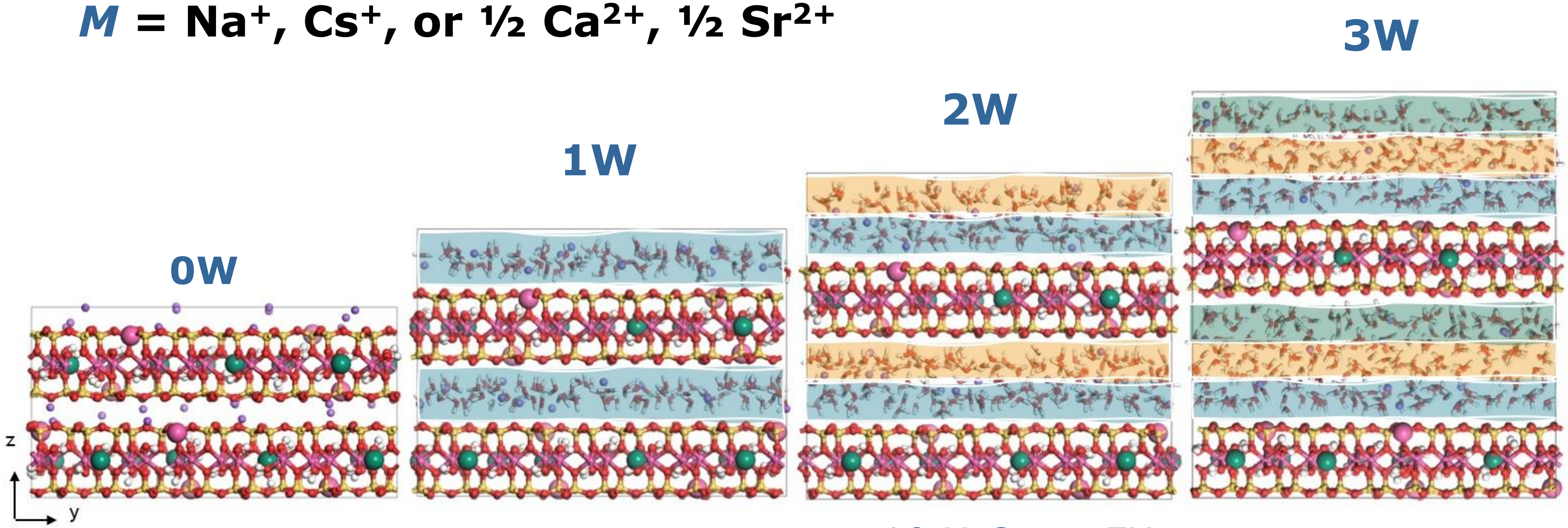
- ✓ Effect of temperature
- ✓ Effect of pressure
- ✓ Comparison of simulations results with experimental data

Smectite Clay Models

- Dry, monolayer (1W), bilayer (2W) and trilayer (3W) hydrated interlayers of Na-, Ca- and Cs-montmorillonite (MMT)

$$[M_{24}]\,(Si_{248}Al_8)(Al_{112}Mg_{16})O_{640}(OH)_{128}.nH_2O$$

M = Na^+, Cs^+, or ½ Ca^{2+}, ½ Sr^{2+}

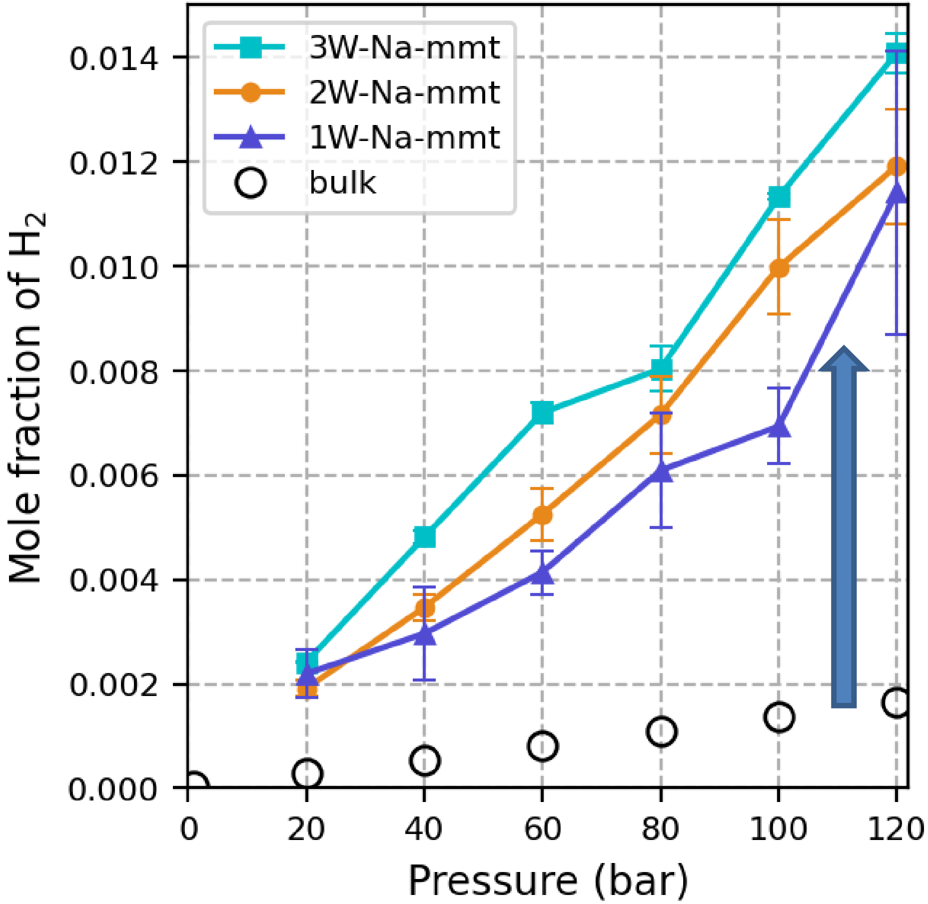


n = 5 H_2O per FU n = 10 H_2O per FU n = 15 H_2O per FU

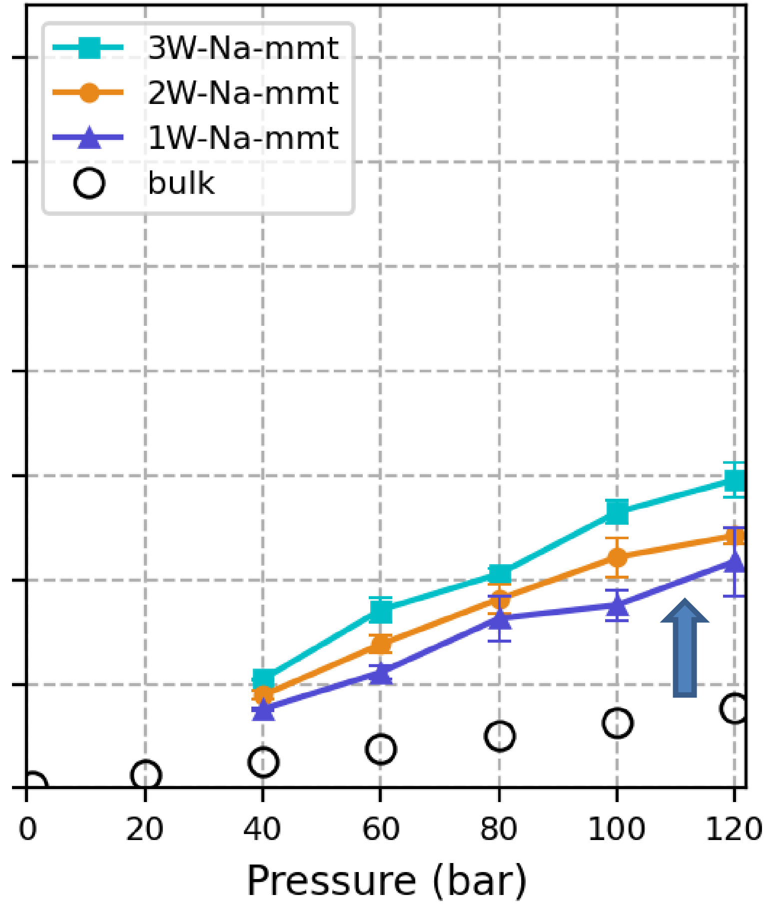
per each $O_{20}(OH)_4$ crystallographic for mono-, bi-, tri-layer hydrated MMT

H_2 Oversolubility in Clay Interlayers

298 K



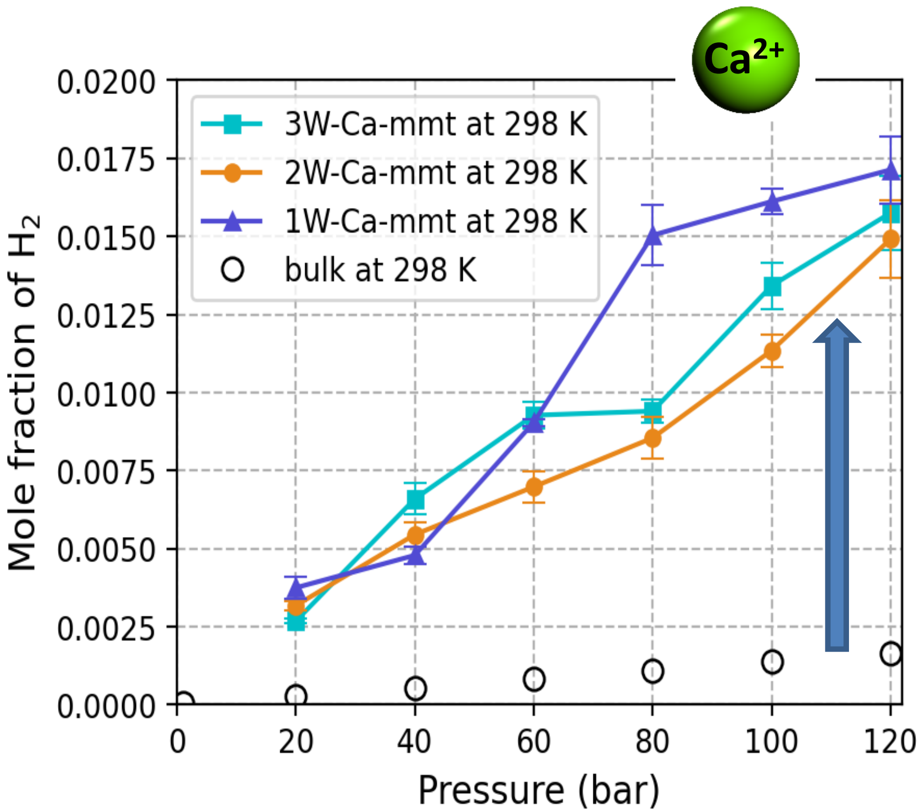
323 K

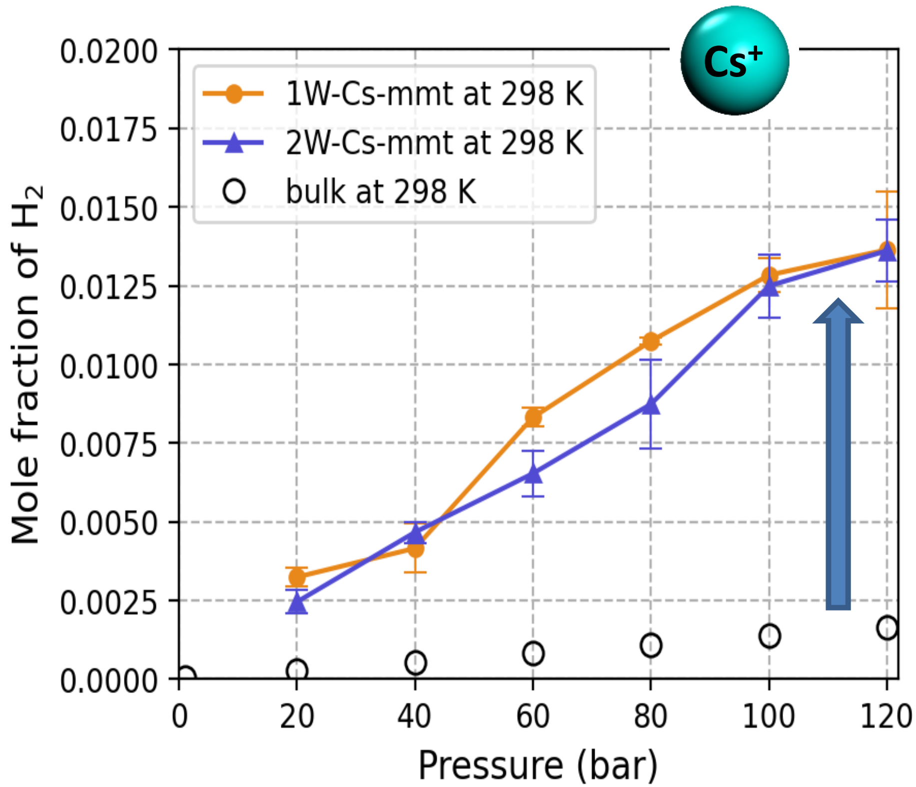


7 to 8 times greater solubility than in bulk

2 to 4 times greater solubility than in bulk

H_2 Oversolubility in Clay Interlayers



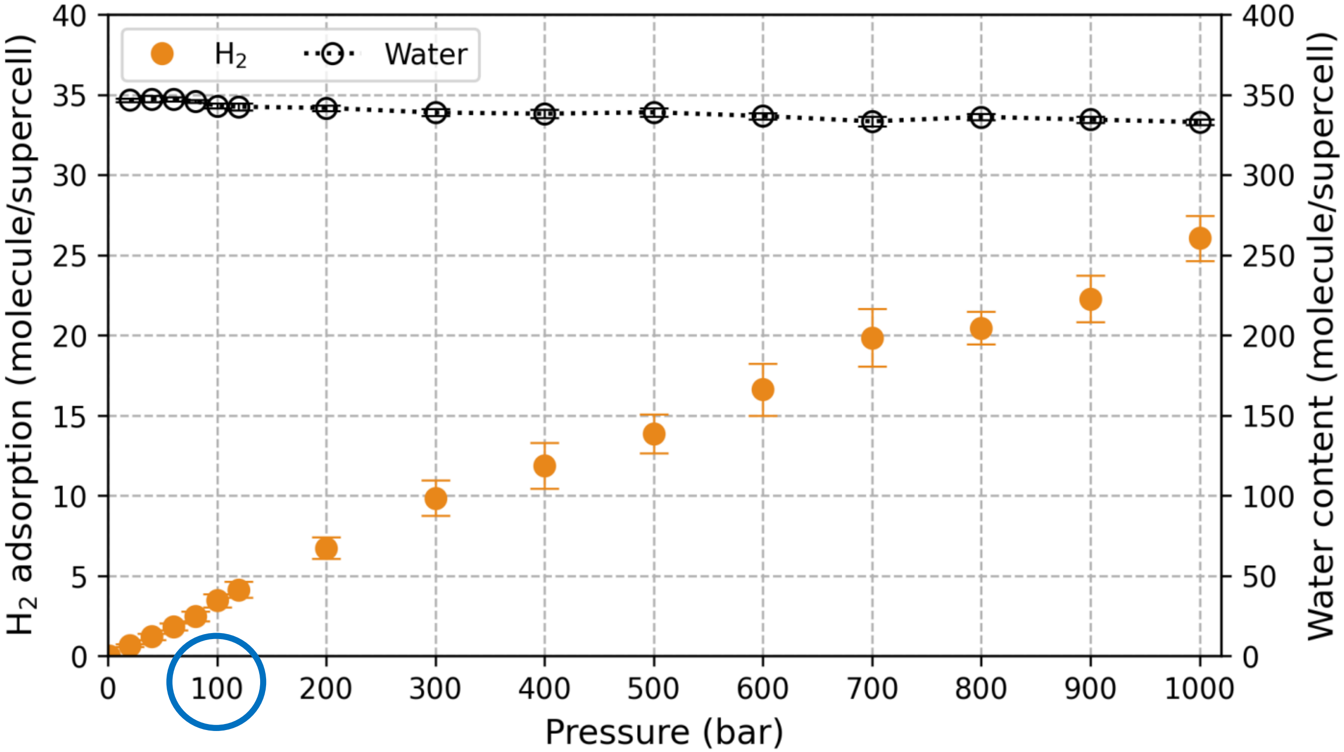


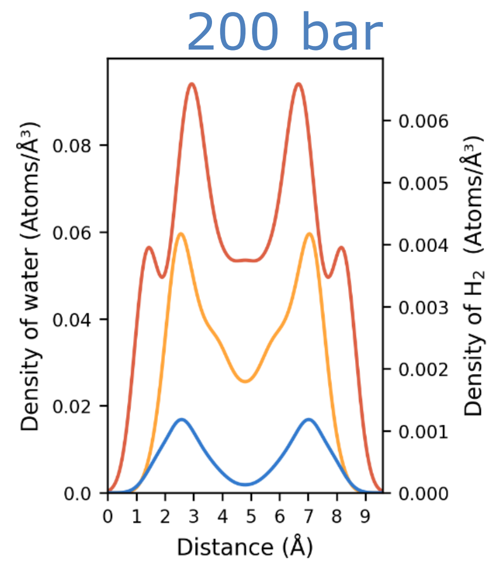
Up to 9 times greater solubility than in the bulk

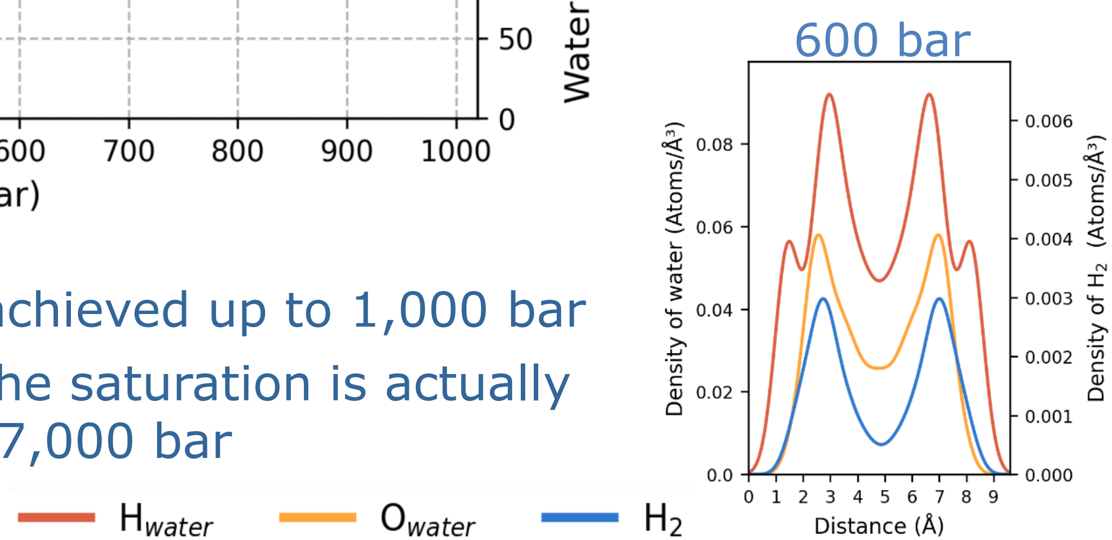
8 times greater solubility than in the bulk

Citli, Kalinichev (2024) Grand Canonical Monte Carlo simulations of hydrogen adsorption in the interlayers of hydrated montmorillonite. *Applied Clay Science*, (in preparation).

Pressure Dependence of H_2 Adsorption on 2W-Na-MMT

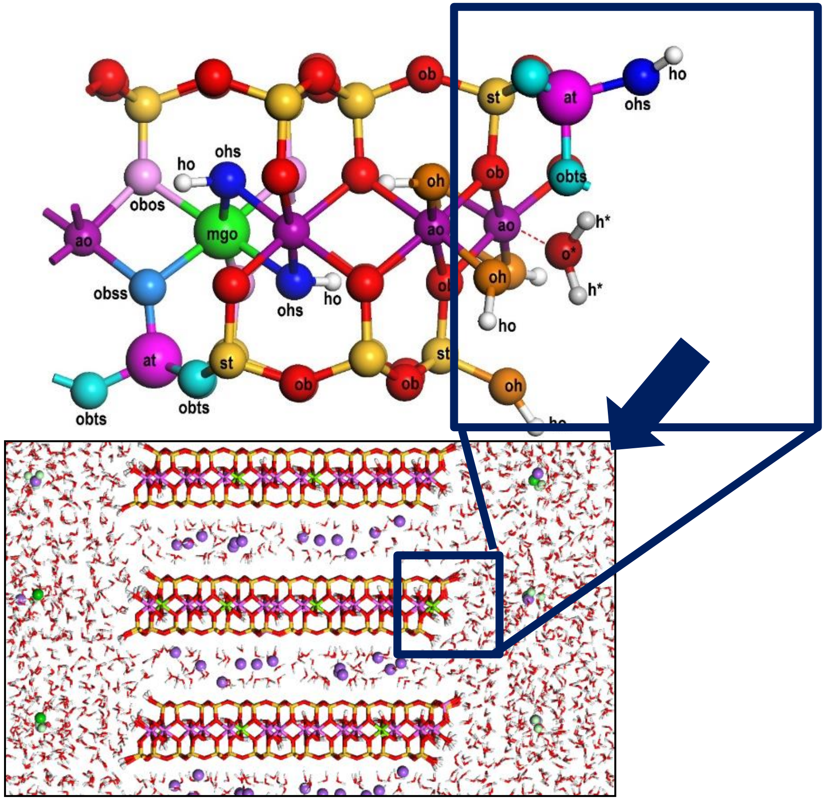


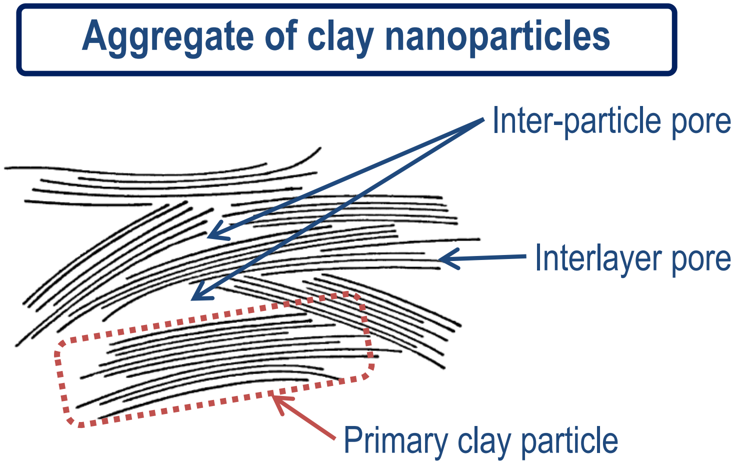




- No H_2 saturation has been achieved up to 1,000 bar
- In dry Cs-MMT at room *T*, the saturation is actually reached somewhere above 7,000 bar

ClayFF - Modeling of Clay Nanoparticle Edges

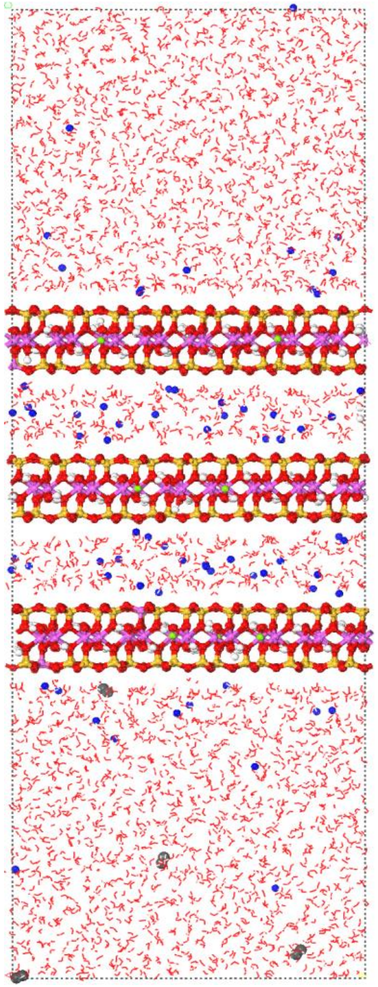




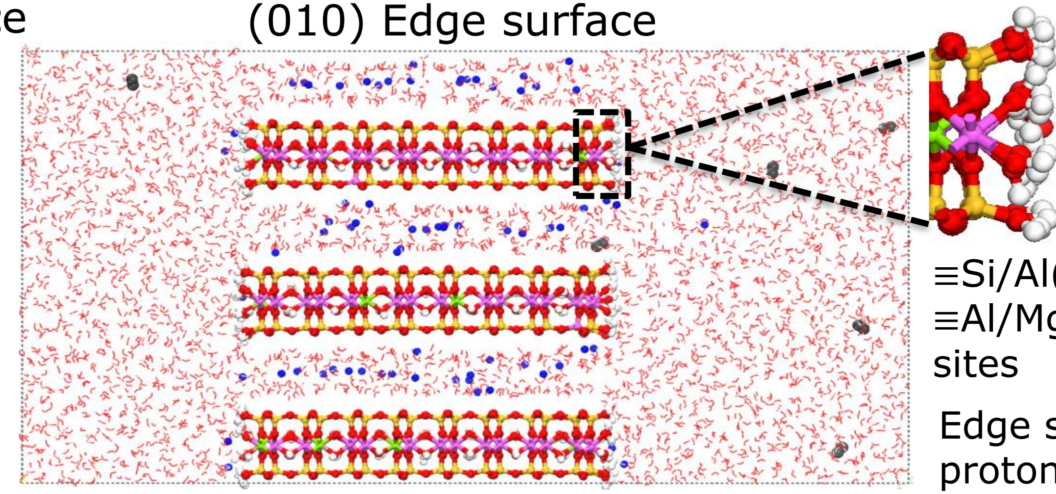
Pouvreau, Greathouse, Cygan, Kalinichev (2017) *J.Phys.Chem.C*, **121**, 14757-71
Pouvreau, Greathouse, Cygan, Kalinichev (2019) *J.Phys.Chem.C*, **123**, 11628–38
Cygan, Greathouse, Kalinichev (2021) *J.Phys.Chem.C*, **125** 17573-17589

Montmorillonite Clay Nanoparticle Edge Surfaces

(001) Basal surface



(010) Edge surface

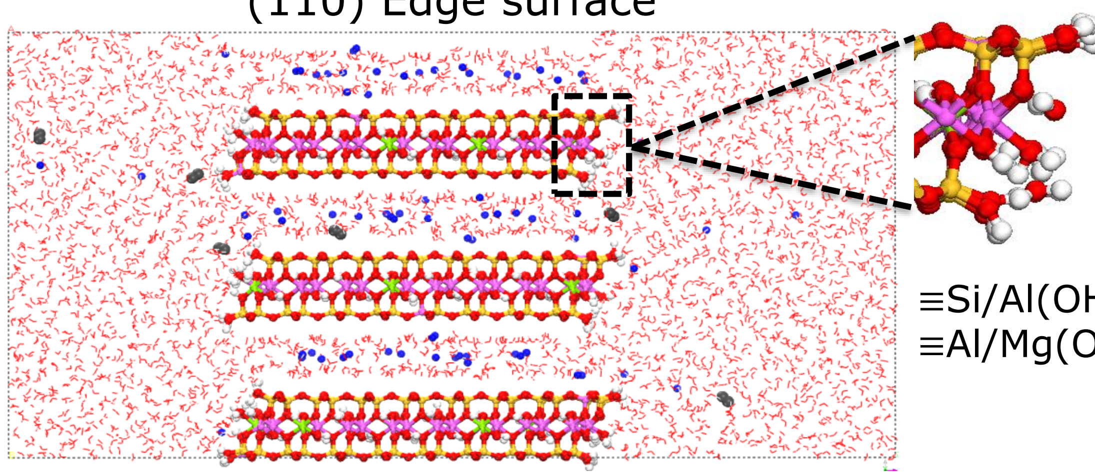


B chains

≡Si/Al(OH) and
≡Al/Mg(OH_2)(OH)
sites

Edge surface
protonation at
near-neutral pH

(110) Edge surface

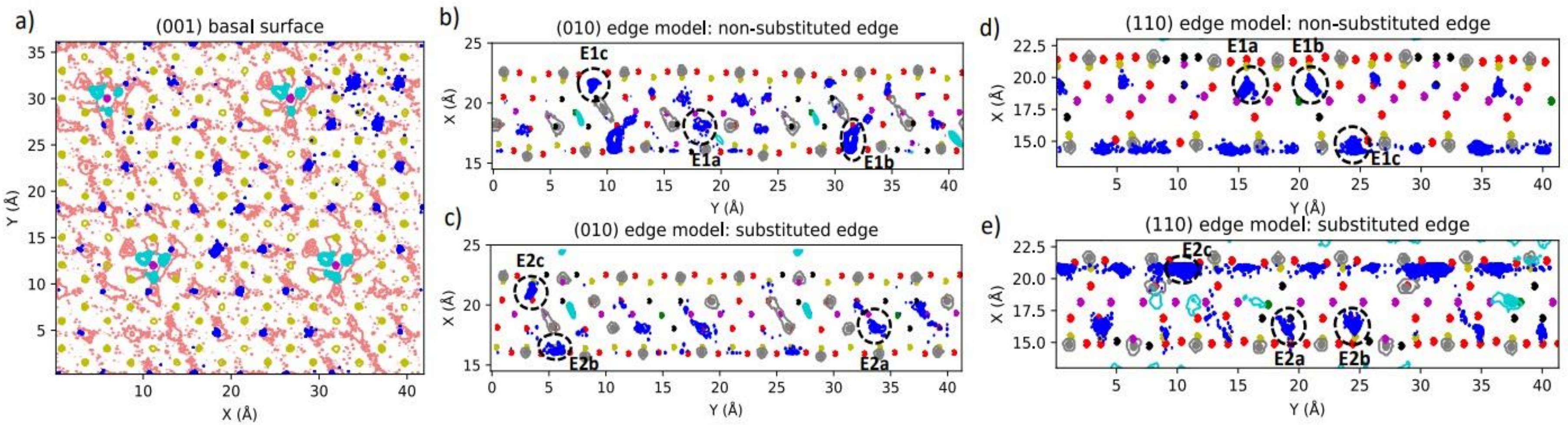


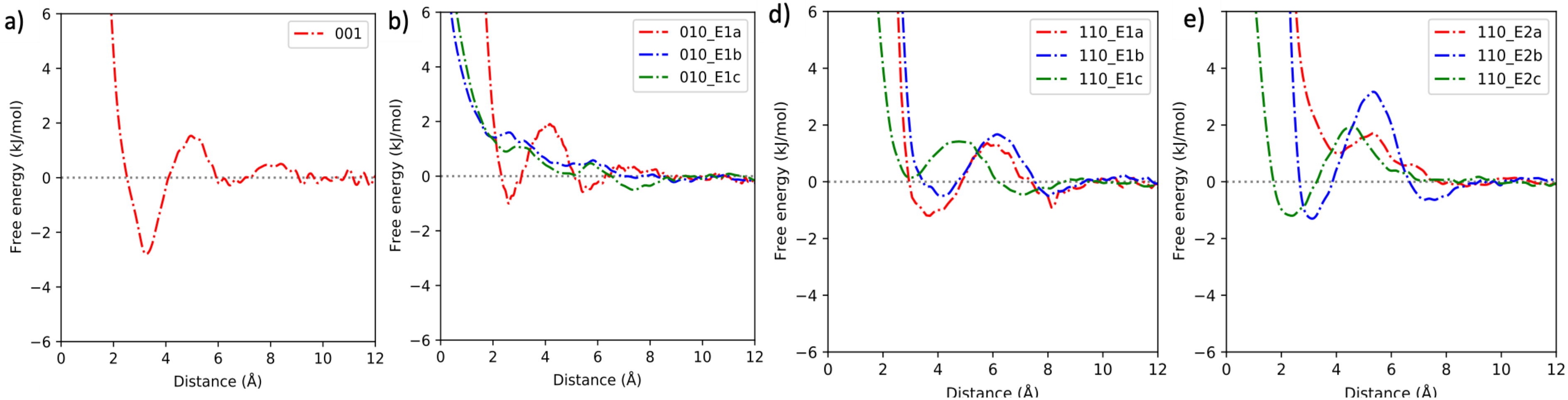
AC
chains

≡Si/Al(OH) and
≡Al/Mg(OH_2) sites

Ngouana-Wakou et al. (2024) *J.Phys.Chem.C*, (in preparation)

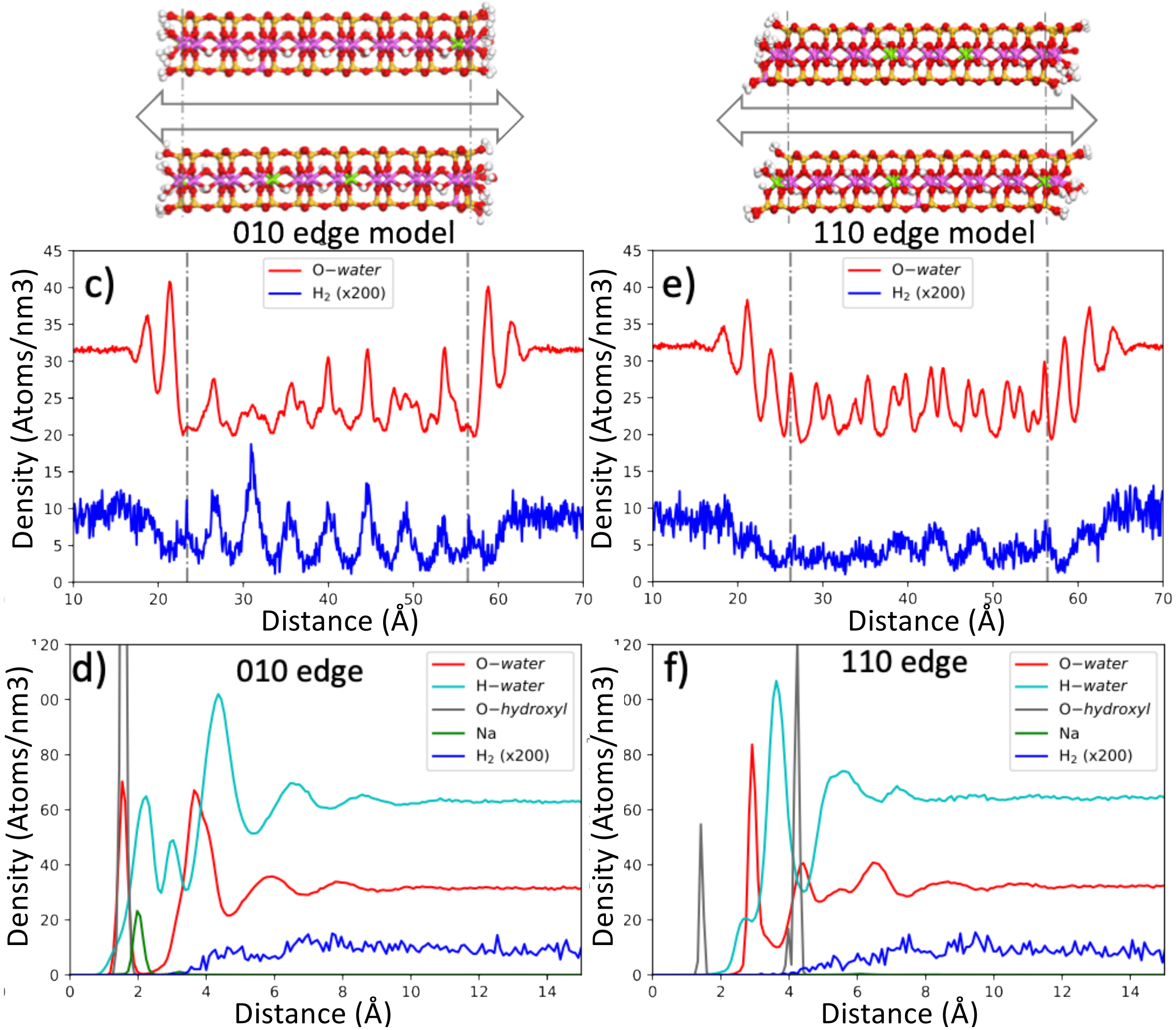
H_2 Gas Adsoption on Different Clay Surfaces



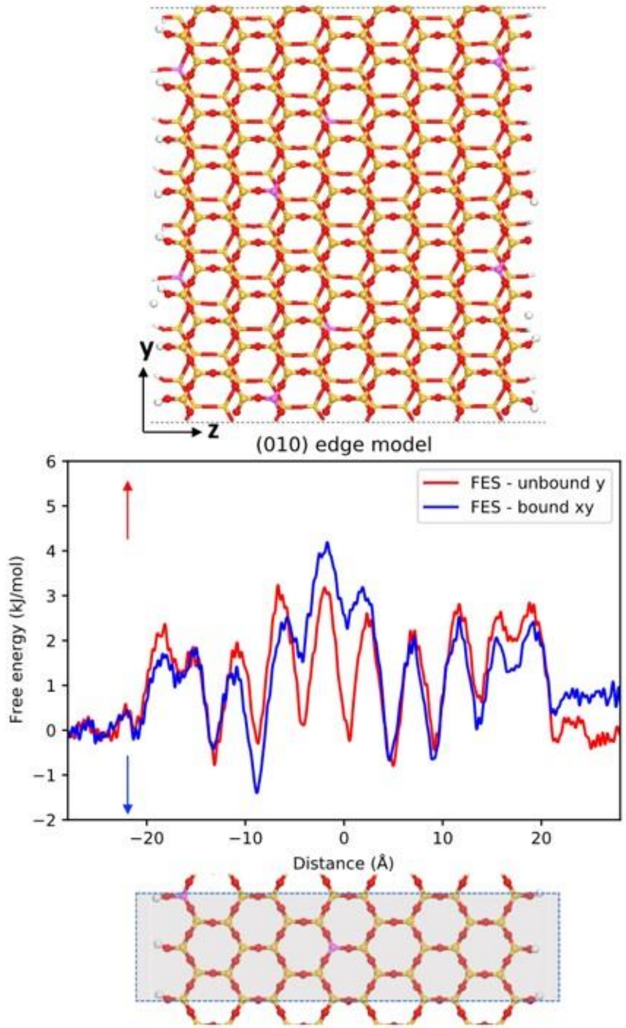


Mutisya, Kalinichev (2024) *J. Phys. Chem. C*, in preparation

H_2 Gas Adsoption on Different Clay Surfaces

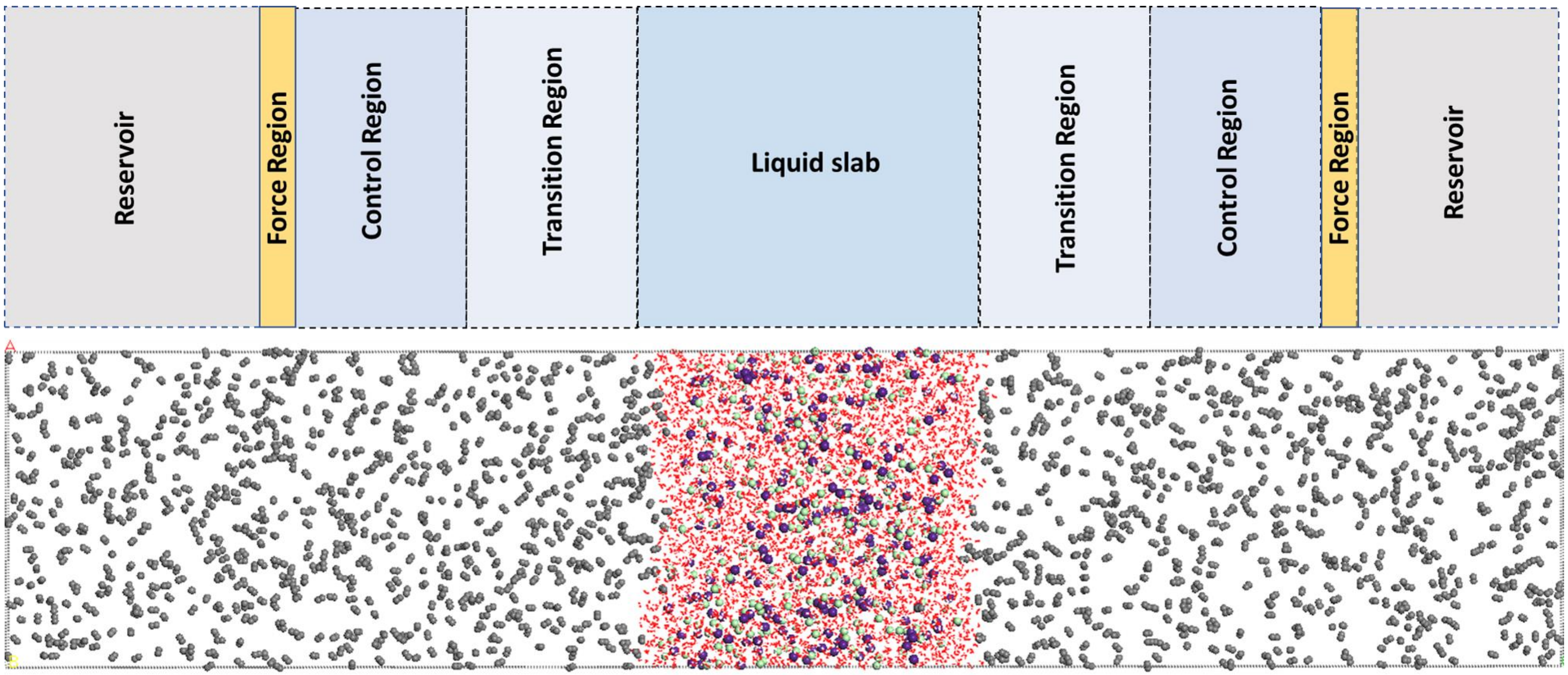


(010) Edge model



Mutisya, Kalinichev (2024) *J. Phys. Chem. C*, in preparation

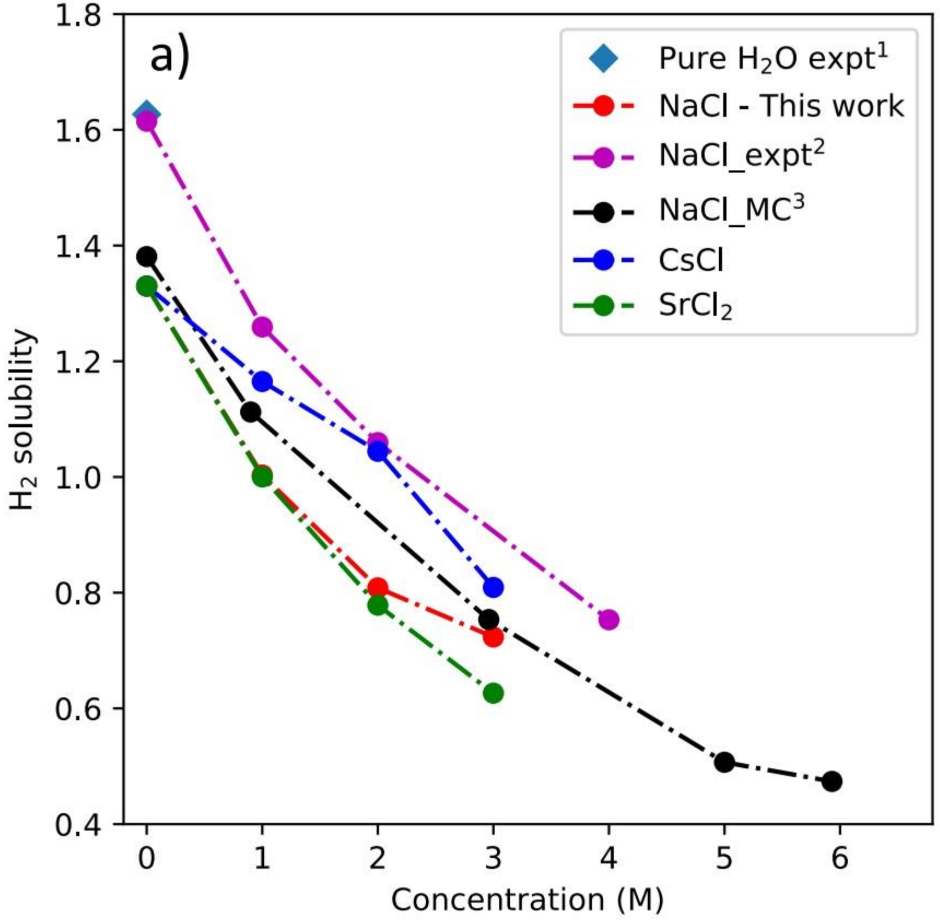
Constant Chemical Potential MD Simulations



Perego, Salvalaglio, Parrinello (2015) *J. Chem. Phys.*, **142**, 144113

Ozcan, Perego, Salvalaglio, Parrinello, Yazaydin (2017) *Chemical Science*, **8**, 3858-3865

H_2 Solubility in Salt Solutions



[1] Wiebe, Gaddy (1934) *JACS*, **56**, 76-79

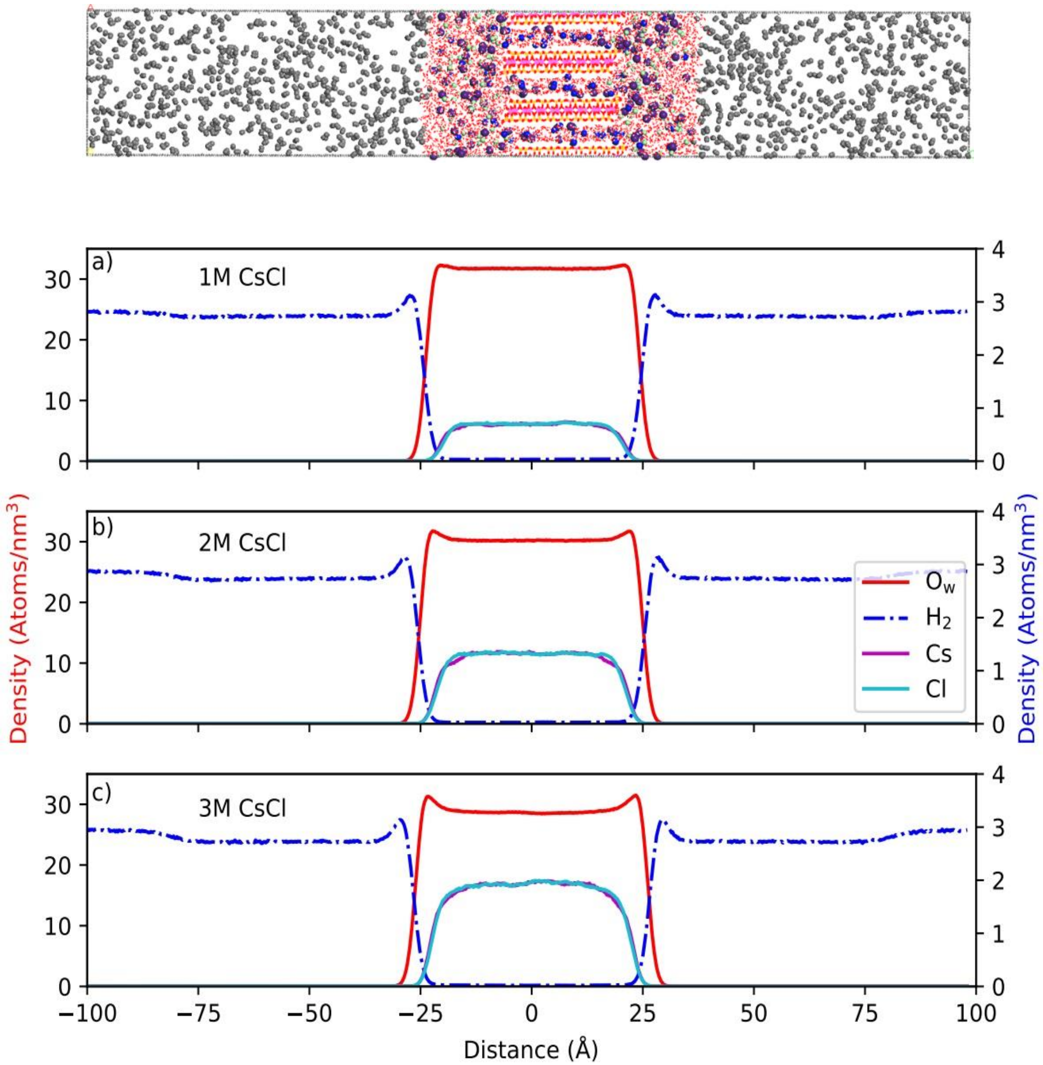
[2] Chabab et al. (2024) *Int. J. Hydr. Energy*, **50**, 648-658

[3] Van Rooijen et al. (2023) *J. Chem. Eng. Data*, **69**, 307-319

- Computed H_2 gas solubility in pure H_2O and bulk aqueous solutions is consistent with experimental data and other simulations
- "Salting out" effect is well reproduced

Mutisya, Kalinichev (2024) *J. Phys. Chem. C*, in preparation

H_2 Solubility in Clay Interlayers *vs* Solution Concentration



Computed solubility ($\times 10^{-3}$) of H_2 gas in clay interlayers

Region	Pure H_2O	3 M CsCl
Interlayer	2.39 ± 0.387	3.014 ± 0.8
Bulk	1.25 ± 0.133	0.812 ± 0.16
Over–solubility factor	2.03	3.71

- H_2 solubility in the bulk region is consistent with those obtained in bulk simulations
- However, H_2 shows a much higher solubility within the clay interlayers, consistent with other studies
- Presence of Cs^+ in clay nearly doubles the oversolubility factor of H_2 in the interlayers compared to the pure water system

Conclusions

- ✓ H_2 gas adsorption increases with, increasing *P*, decreasing *T*, increasing interlayer pore size / clay hydration level
- ✓ H_2 solubility in clay interlayers is up to 8 times higher than in the bulk
- ✓ In monolayer hydrated clays Ca-MMT accepts larger amounts of H_2
- ✓ In bilayer hydrated clays there is no significant effect of the interlayer cation type
- ✓ No H_2 saturation is observed in clay interlayers up to 1000 bar
- ✓ Under the anticipated *P-T* range of the deep geological nuclear waste repository, the saturation of H_2 is not achievable
- ✓ Presence of Cs^+ in the waste enhances H_2 gas adsorption within the clay interlayers, potentially further mitigating the risk of over-pressurization in the repository

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