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Pore size effects on noble gas uptake in naturally occurring zeolites

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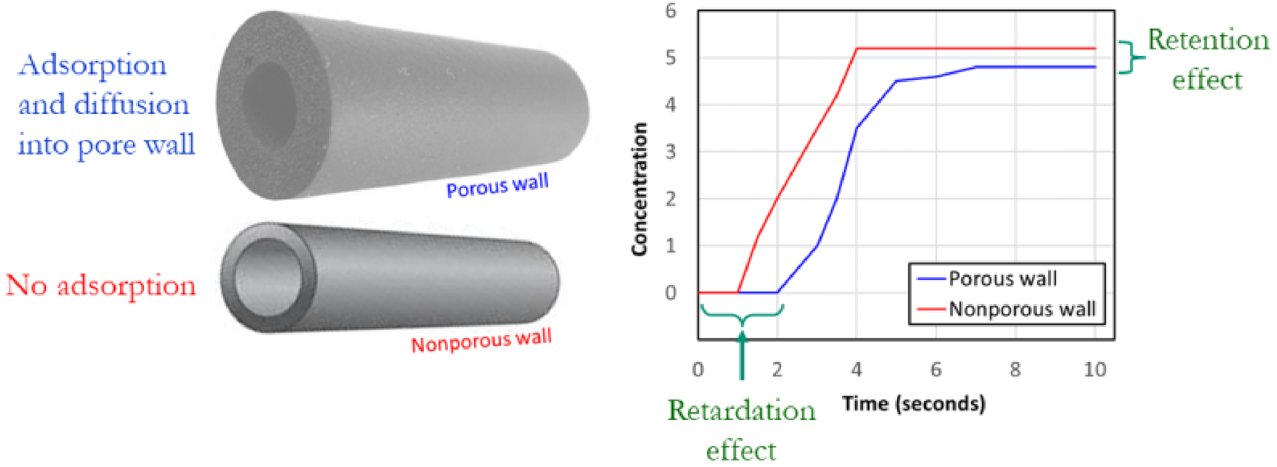
Gas transport in the subsurface

Problem

- Subsurface gas transport behavior can show significant deviations from conceptual models that do not include the chemical or physical properties of the host rock.
- Existing gas transport codes: input parameters derived from core samples, or assume homogeneous rock phases.
- Relevance: trace gas migration, extraction, sequestration



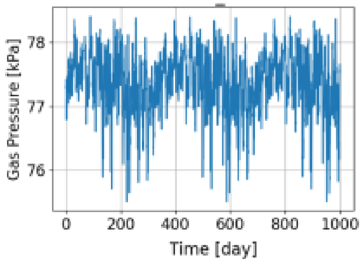
Strategy. Obtain a fundamental understanding of gas migration in porous media, particularly for which **adsorption** could affect the transport properties.

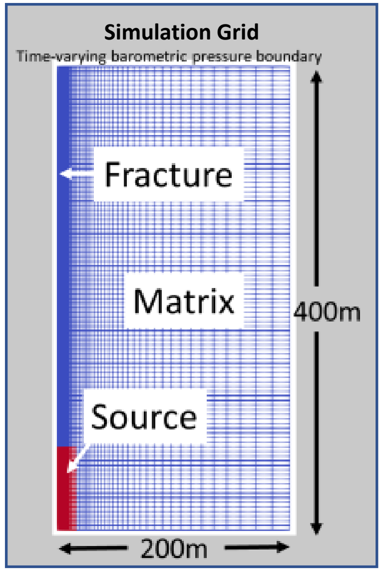
Gas properties in pure mineral phases → Predicted transport in different lithologies (shale, granite, tuff)

Transport Modeling: **Testing of 2D Field Scale Model in PFLOTRAN**

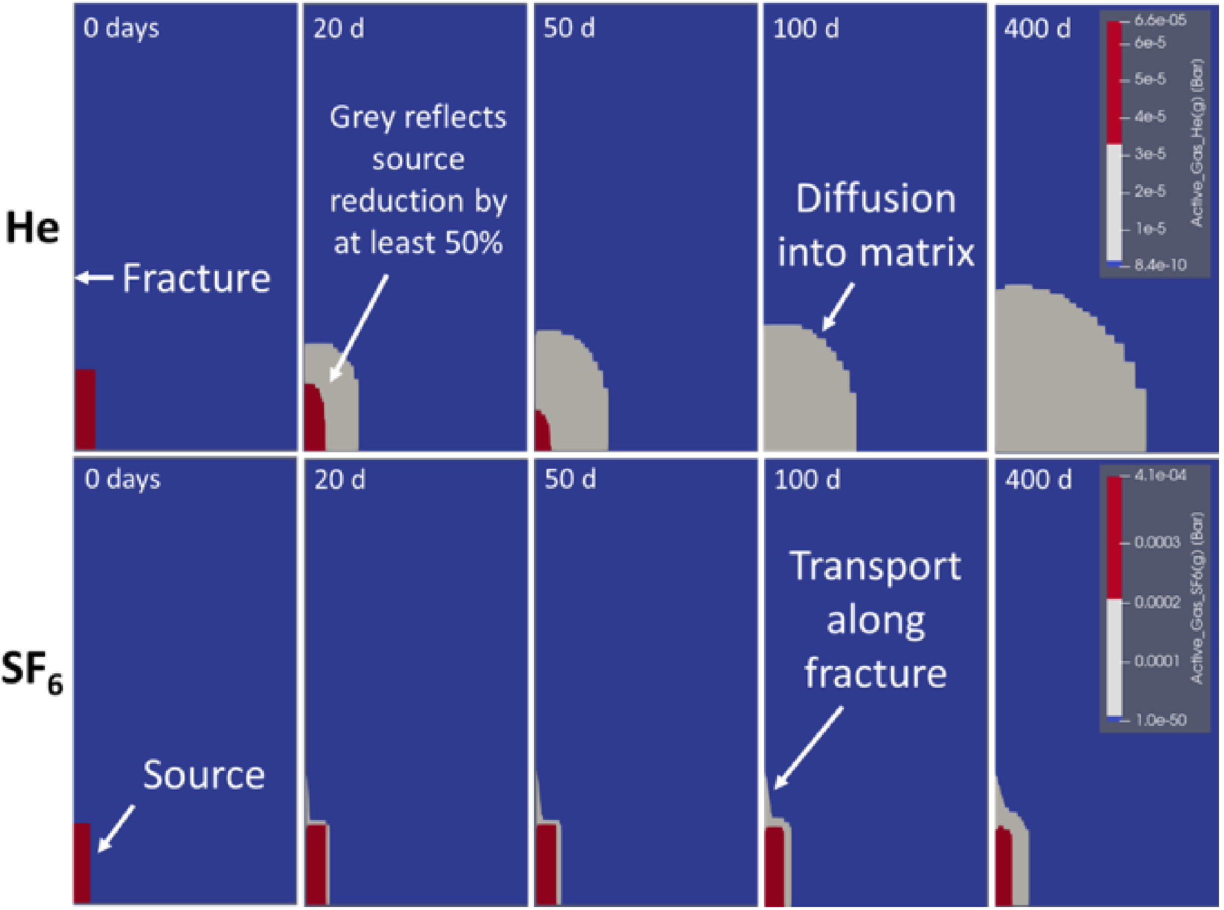
- Breakthrough modeling for He and SF_6 compared to exp. and previous model results
- Varying of input parameters is currently being modeled and finalized for publication
  - Henry's Constant (K_H)
  - Diffusion Coefficients (D)
  - Partition Coefficient (K_d)
  - Longitudinal dispersivity (LD)

Surface Barometric Pressure



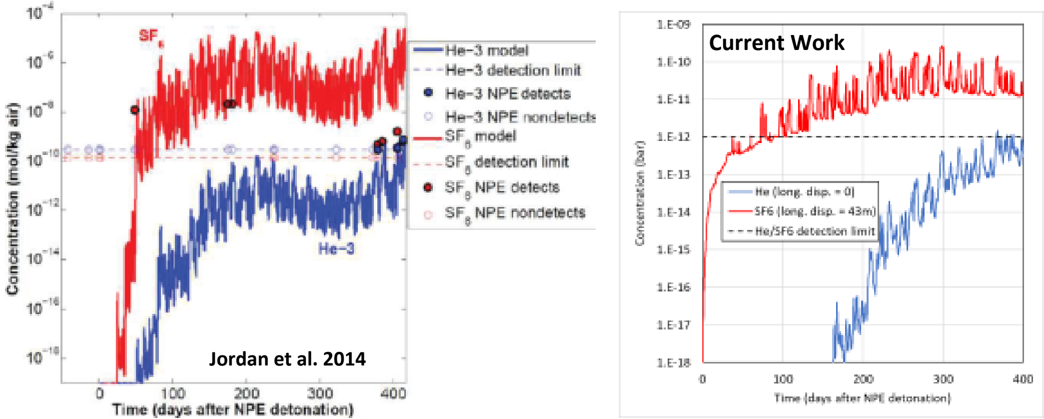


Gas Concentration Profile Evolution for He and SF_6

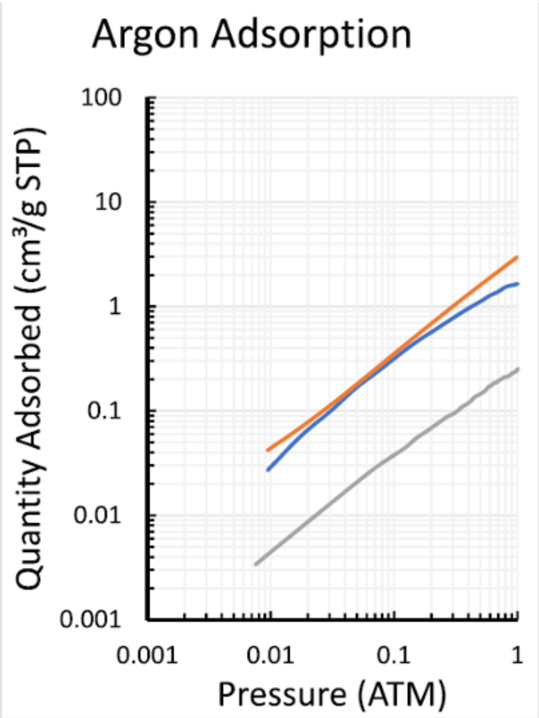


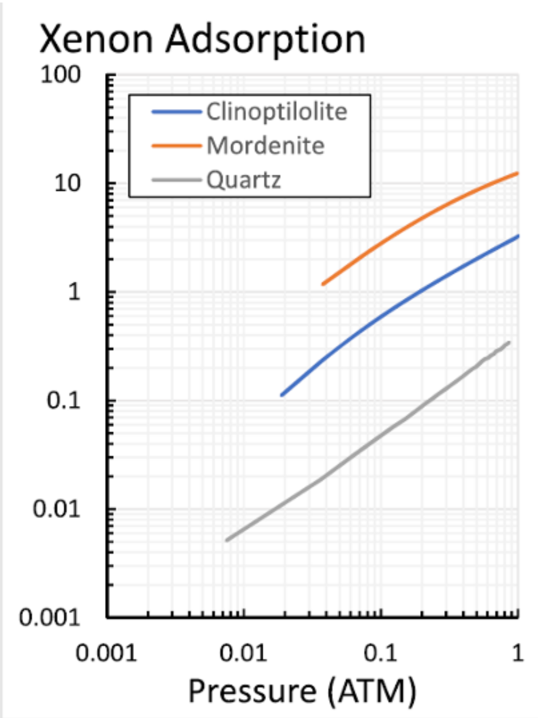
Time evolution of concentration profiles for He and SF_6, showing ***difference in gas transport behavior***; He shows more diffusion into matrix, while SF_6 shows more directed transport along fracture toward the surface.

Breakthrough Modeling



Gas adsorption in zeolites





Adsorption isotherms

- Enhanced adsorption in nanoporous zeolites vs. nonporous quartz.
- Reduced Xe adsorption in clinoptilolite due to size exclusion.

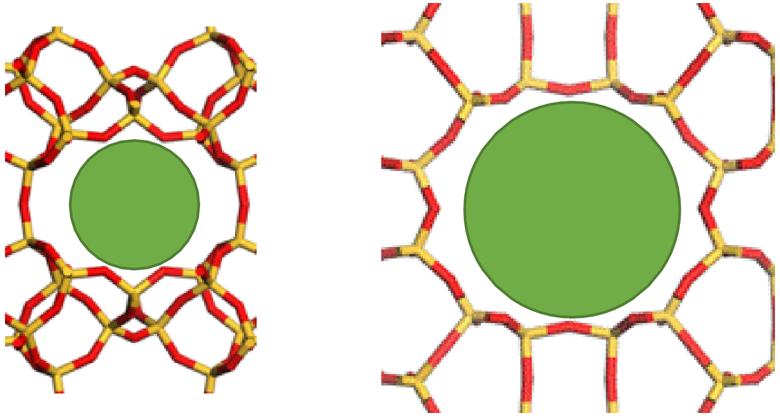
Feldman et al, *J. Env. Radioact.* ***2020***, *220-221*, 106279

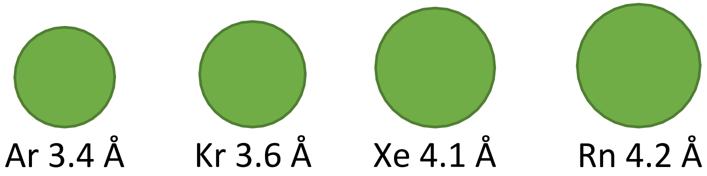
Zeolites are common mineral constituents in many geologic environments.

Nanopores are responsible for gas adsorption and separation properties.

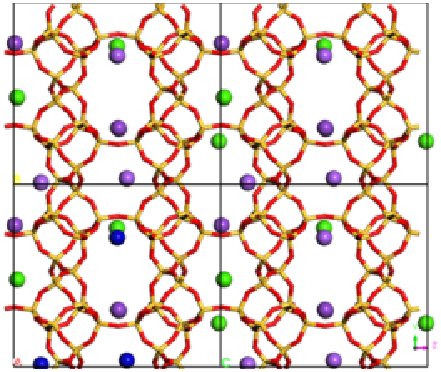
Noble gas uptake facilitates a systematic variation of size effects.

	Clinoptilolite	Mordenite
Pores	Small/inaccessible 3.3 Å – 5.5 Å	Large/accessible 4.4 Å – 7.2 Å



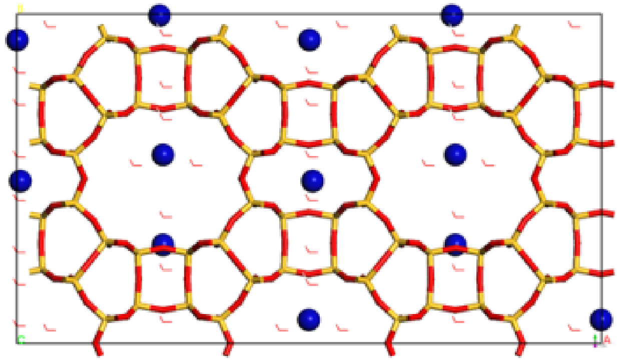


Simulation Methods



Clinoptilolite
“clino”
$(Na, K, Ca)_{2-3}Al_3(Al, Si)_2Si_{13}O_{36}\cdot 12H_2O$

Mordenite ($Na_2Al_2Si_{10}O_{24}\cdot 7H_2O$)



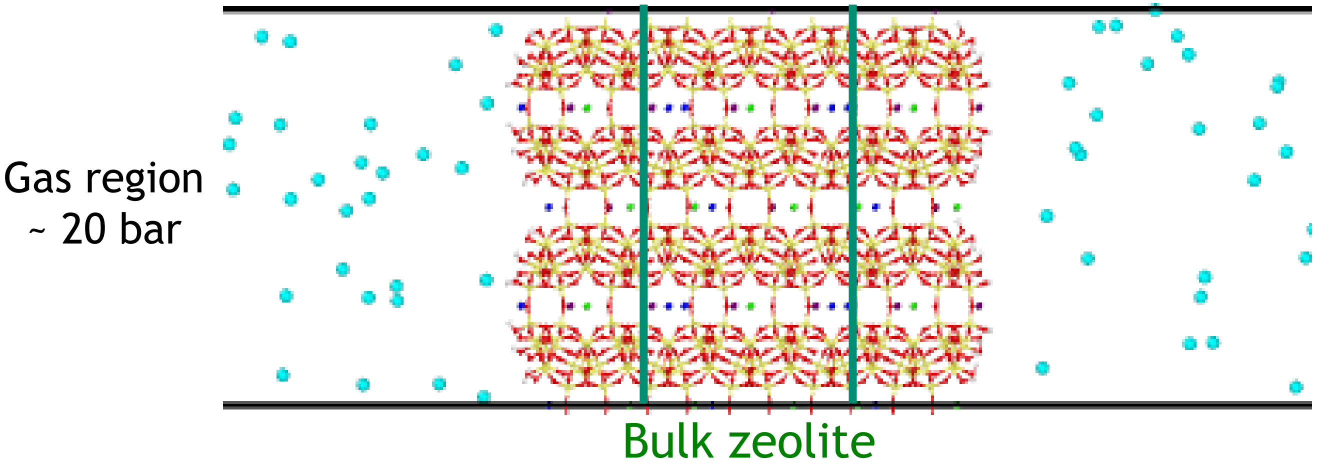
Gas adsorption and mobility (bulk zeolites)

- 3D periodic boundary conditions.
- LAMMPS code: Grand Canonical Monte Carlo (GCMC), molecular dynamics (MD), 300 K.
- Flexible zeolite, force field from Jeffroy et al[1,2].
- Fluid: flexible SPC water,[3] noble gases[4,5].
- Adsorption isotherms, dry and wet conditions (GCMC).
- Water and gas mobility (MD).

1. Jeffroy et al, *J. Phys. Chem B* **2011**, *115*, 15059
2. Jeffroy et al, *Mol. Sim.* **2014**, *40*, 6
3. Teleman et al, *Mol. Phys.* **1987**, *60*, 193
4. Pellenq and Levitz, *Mol. Phys.*, **2002**, *10*, 2059
5. van LOEF, *Physica B & C* **1981**, *103*, 362

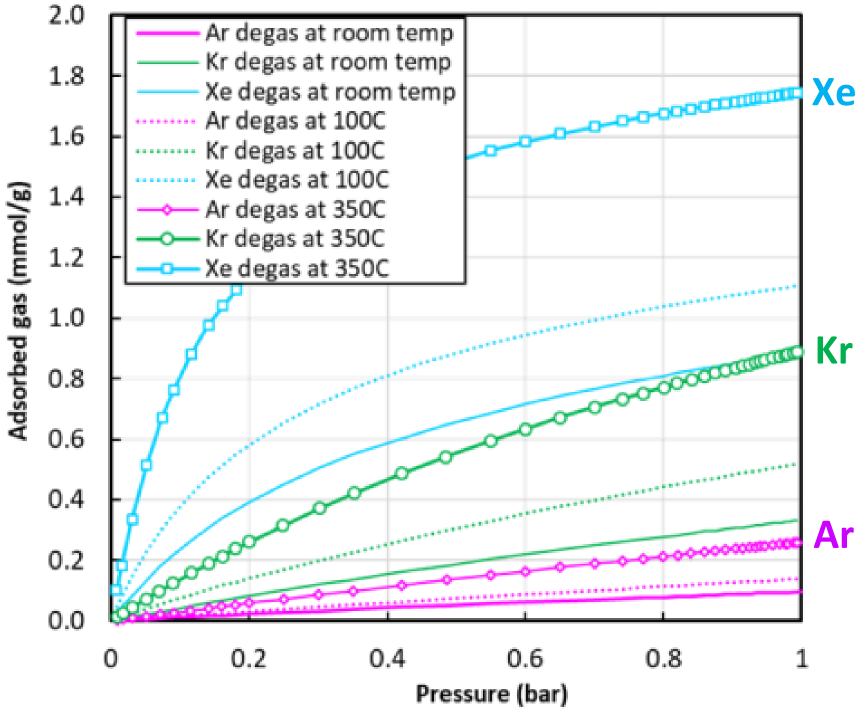
Kinetics of gas adsorption (slab models)

- MD simulations at 250-350 K.
- Flexible zeolite slabs with bulk gas regions.
- Separate models for each pore axis.
- Hydroxyl groups used to maintain Si and O coordination at the edges.

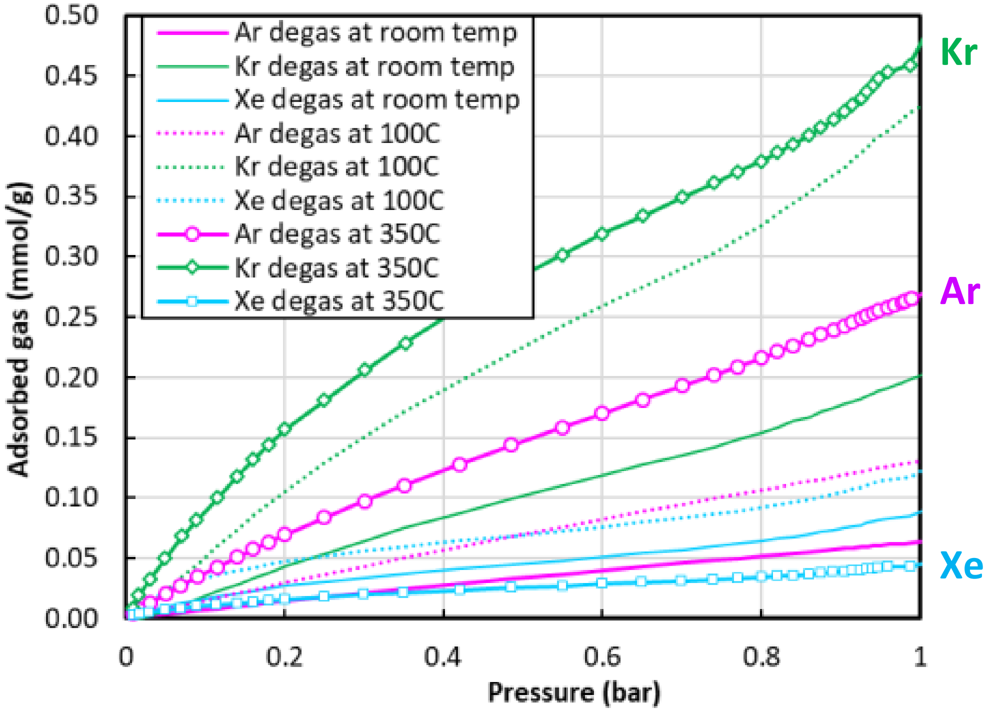


Experimental adsorption isotherms, 300 K

Mordenite



Clinoptilolite



Mordenite

Expected gas adsorption behavior under dry and wet conditions:

Xe > Kr > Ar

Clinoptilolite (dry)

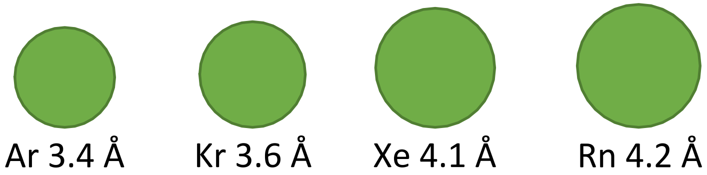
Increased Ar and Kr uptake compared to original (hydrated sample).

Reverse selectivity (Ar/Xe, Kr/Xe)

Clinoptilolite (5-8% water)

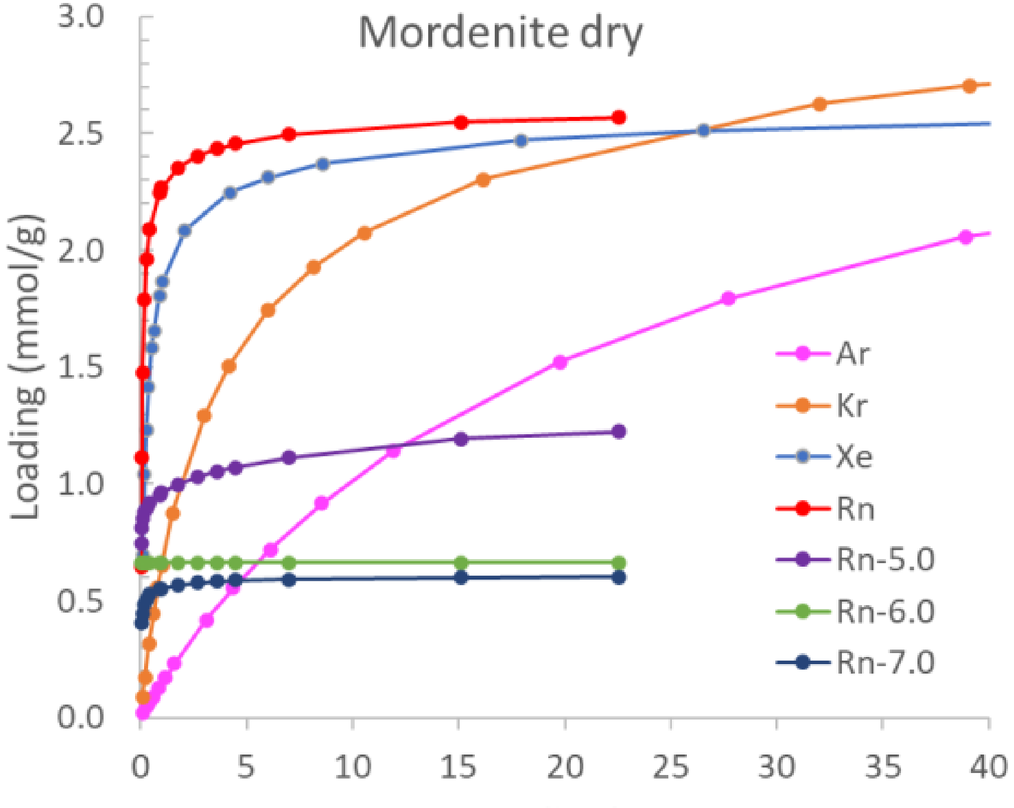
Reduced gas uptake due to presence of water in pores.

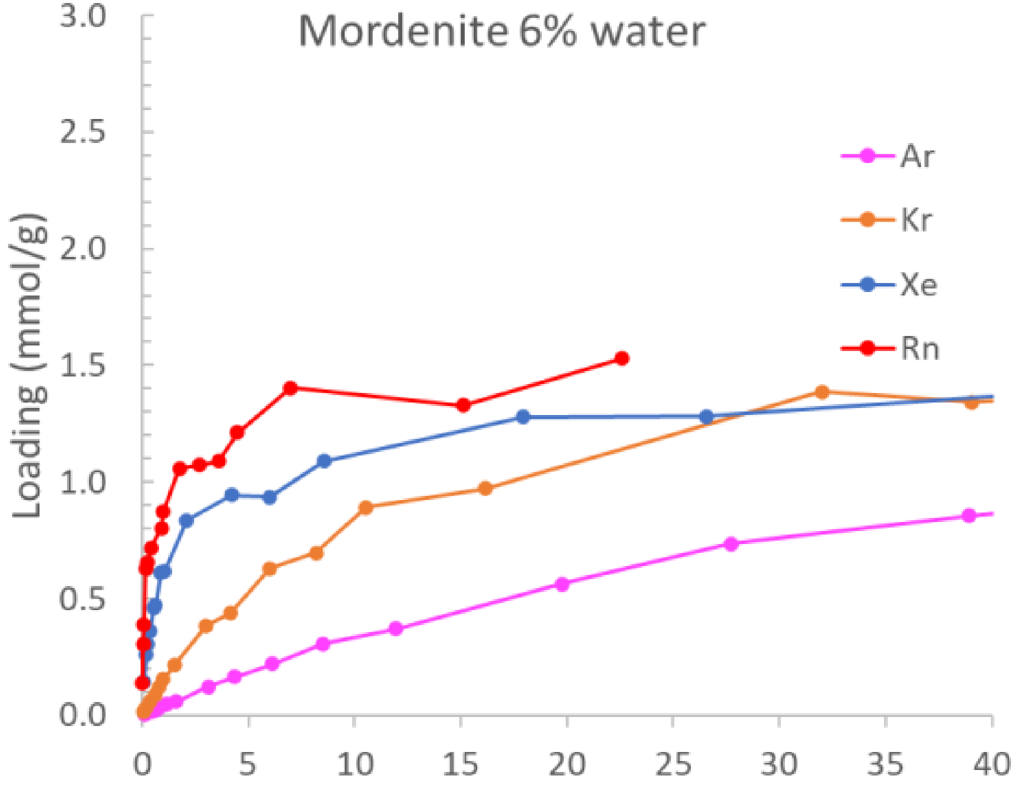
Reverse selectivity (Kr/Xe).

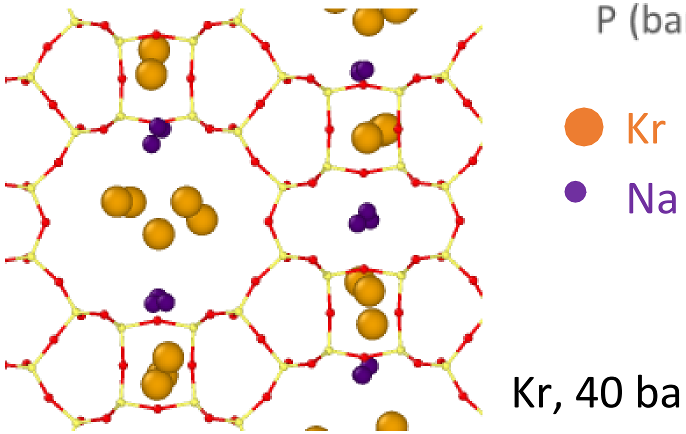


Xe atoms appear to be blocked from entering the clinoptilolite pores.

Simulated adsorption isotherms, mordenite 300 K

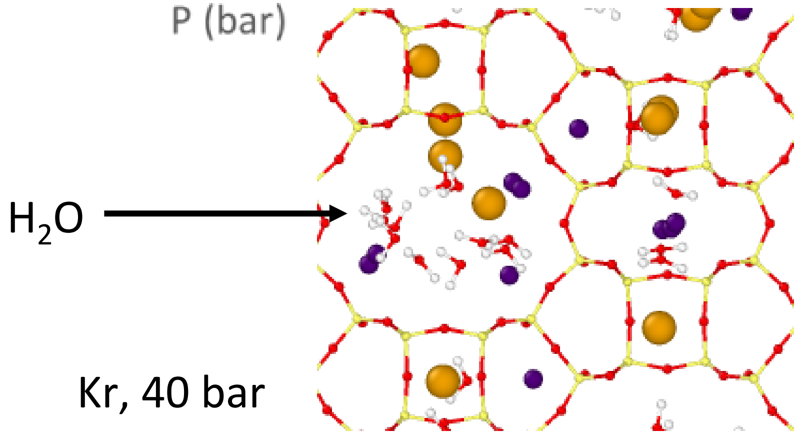






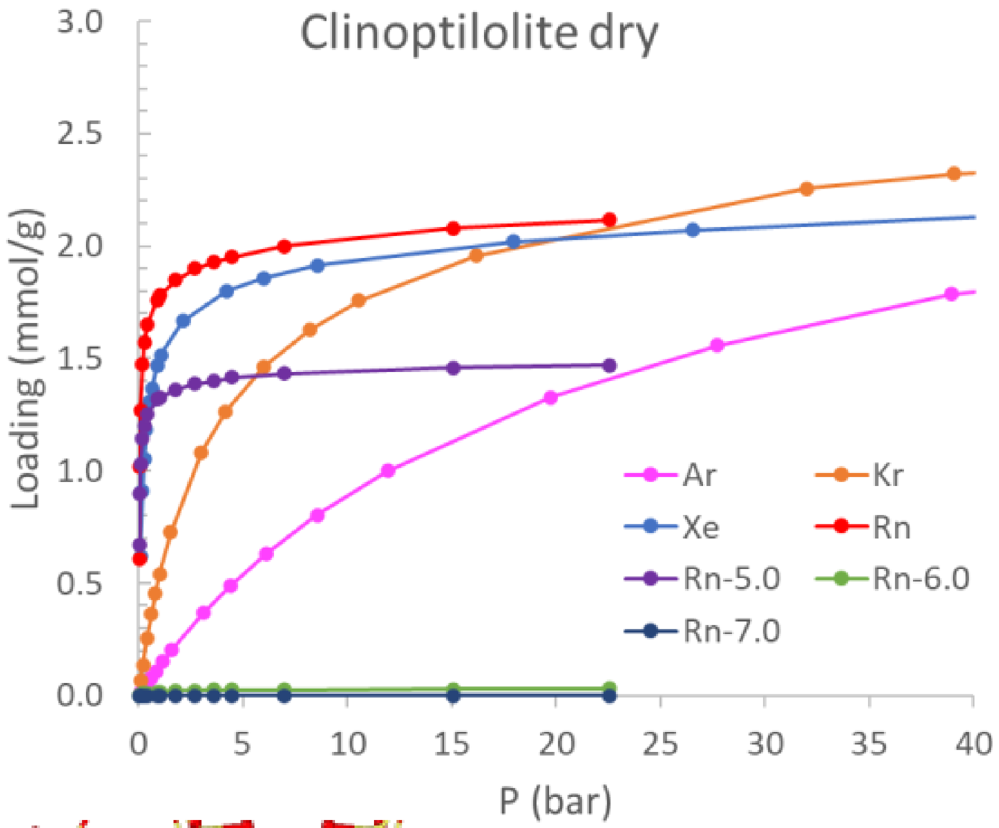
Kr, 40 bar

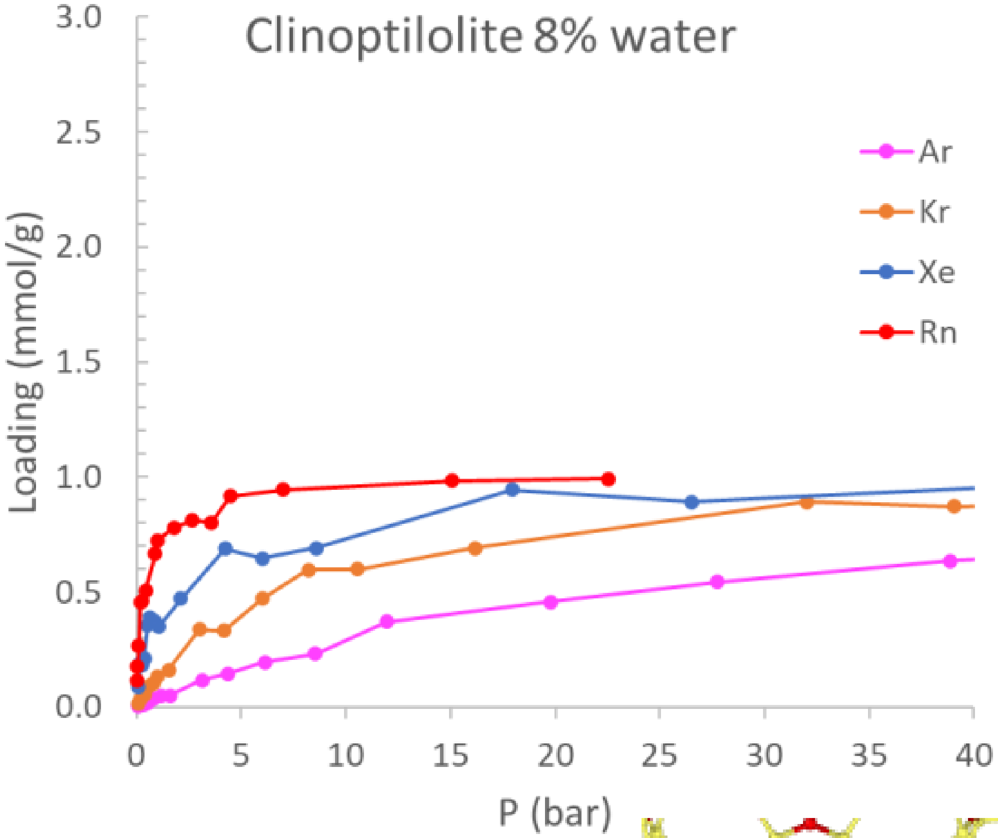
Mordenite ($Na_2Al_2Si_{10}O_{24}$)

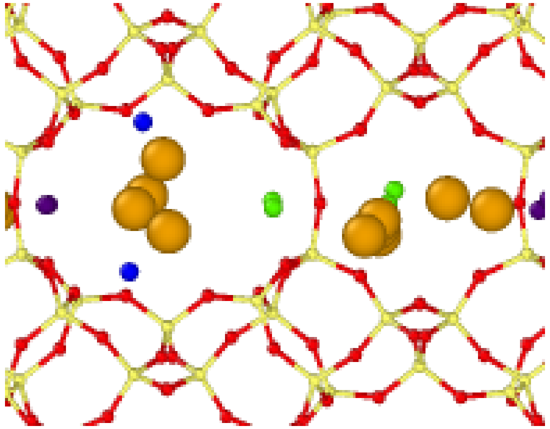


Kr, 40 bar

Simulation adsorption isotherms, clinoptilolite 300 K







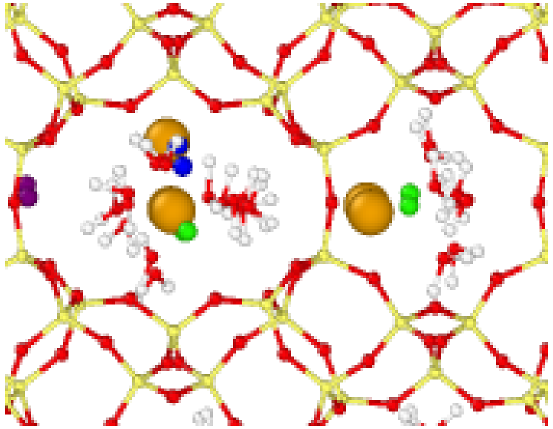
● Kr

Kr, 40 bar

Clinoptilolite cages are accessible to Kr and Xe.

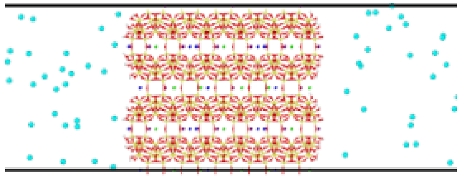
Reverse selectivity seen in experiments must be due to kinetics or blocked pores (adsorbed water or gas).

$(Na, K, Ca)_{2-3}Al_3(Al, Si)_2Si_{13}O_{36}$

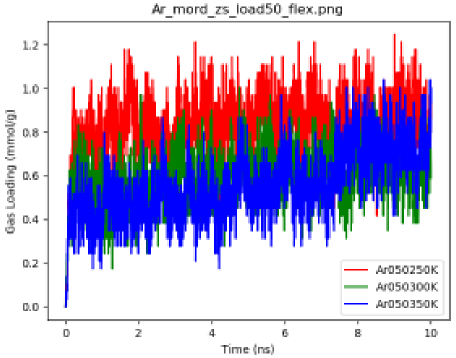


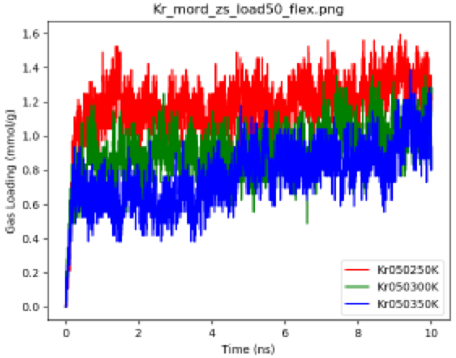
Kr, 40 bar

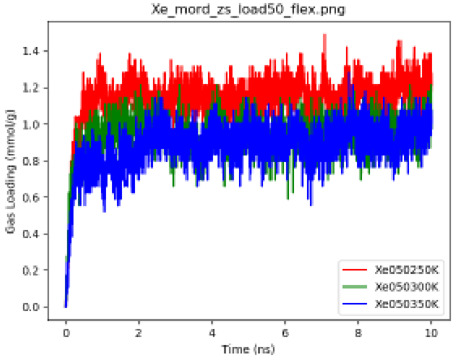
MD: large pores in mordenite are accessible to all gases

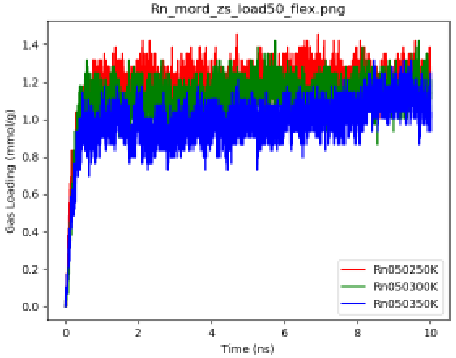


Ar Kr Xe Rn

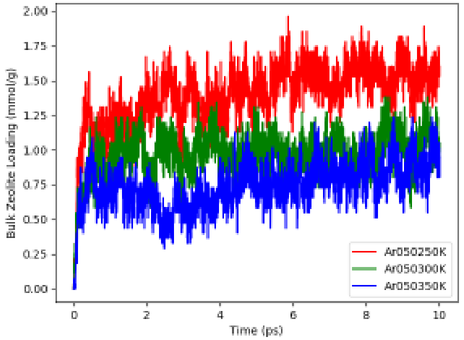


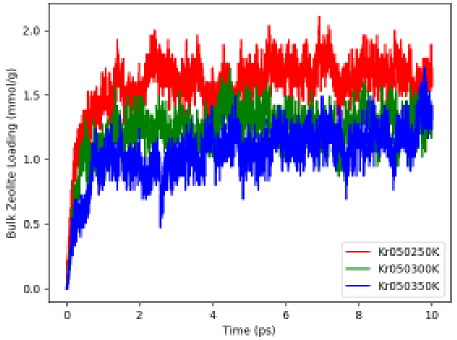


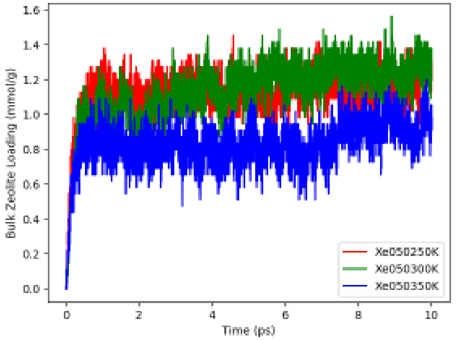


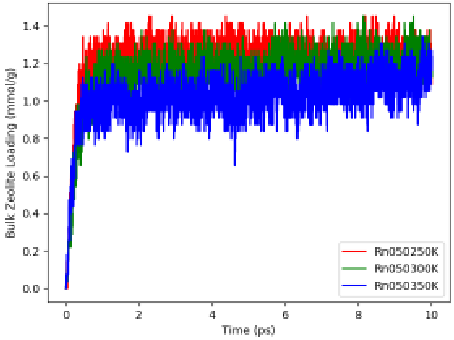


dry
with cations

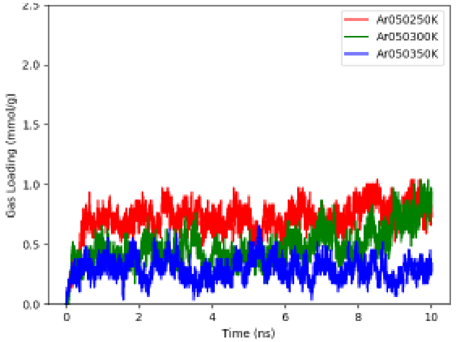


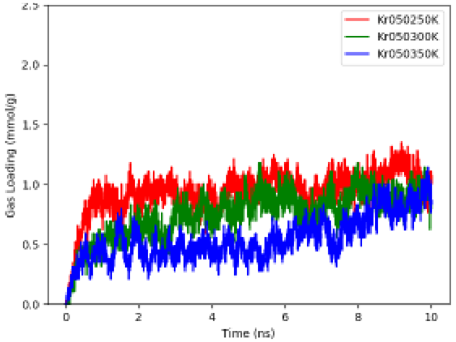


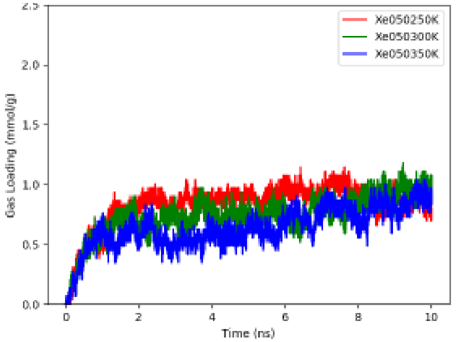


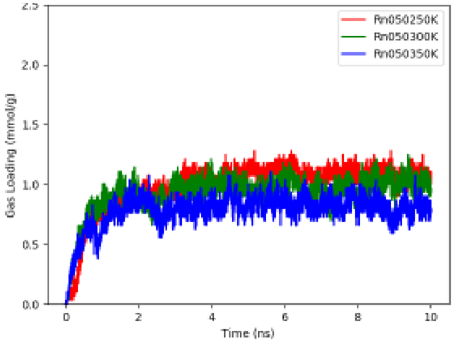


dry
empty pores
(no cations)



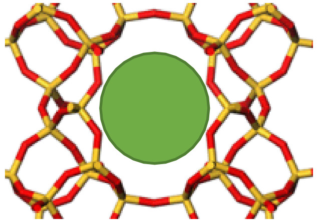


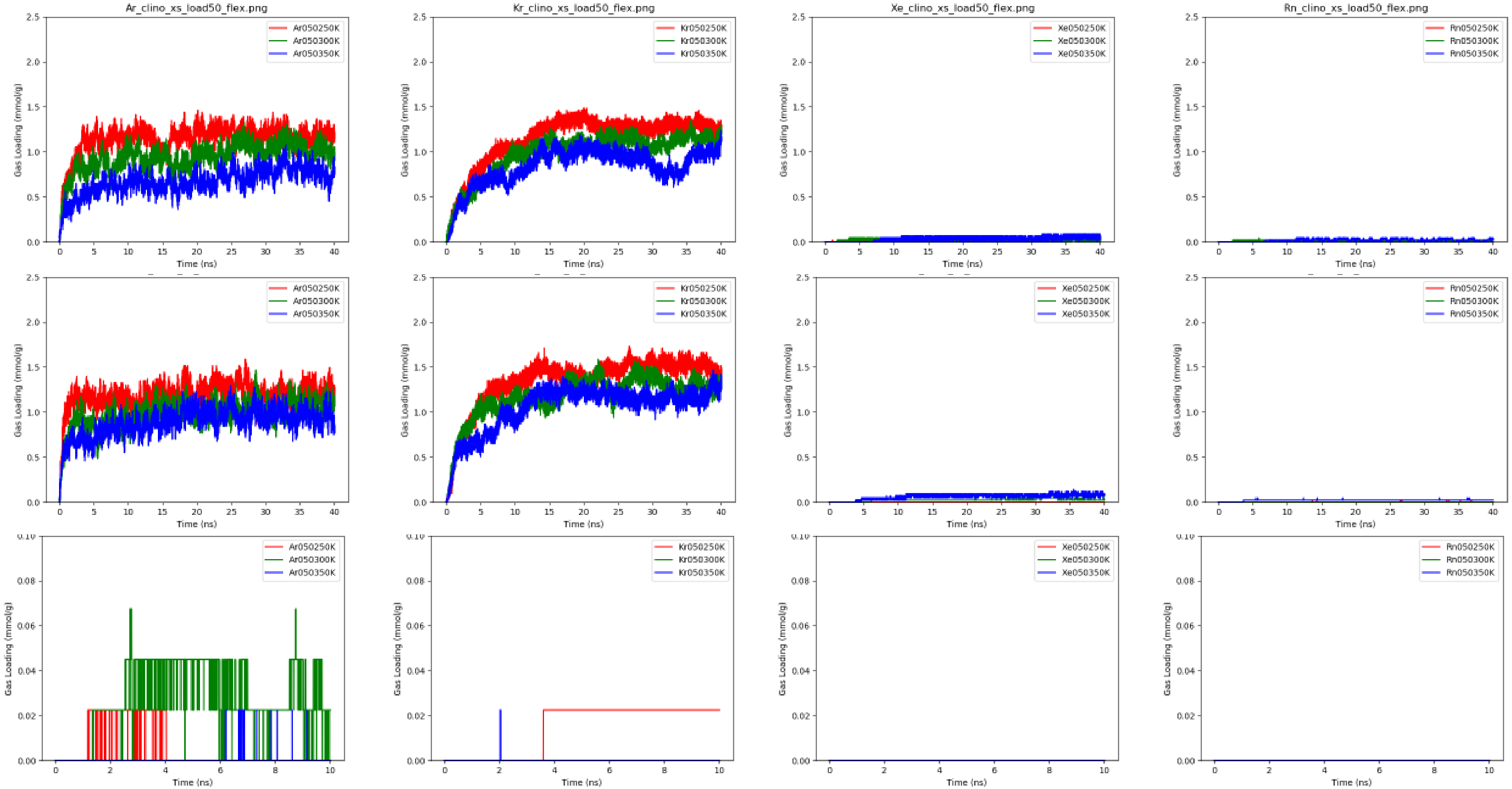




wet (50% RH)

MD: access to small pores in clinoptilolite depends on gas size



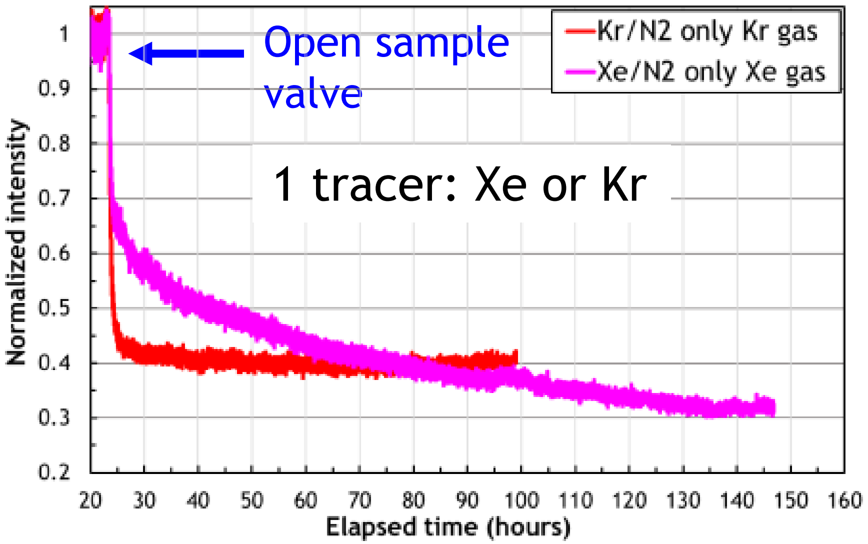


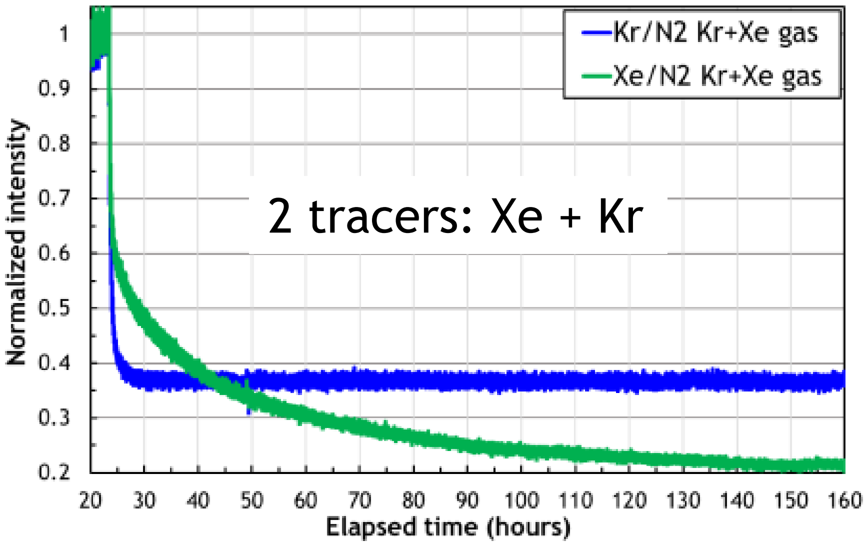
dry
with cations

dry
empty pores
(no cations)

wet (50% RH)

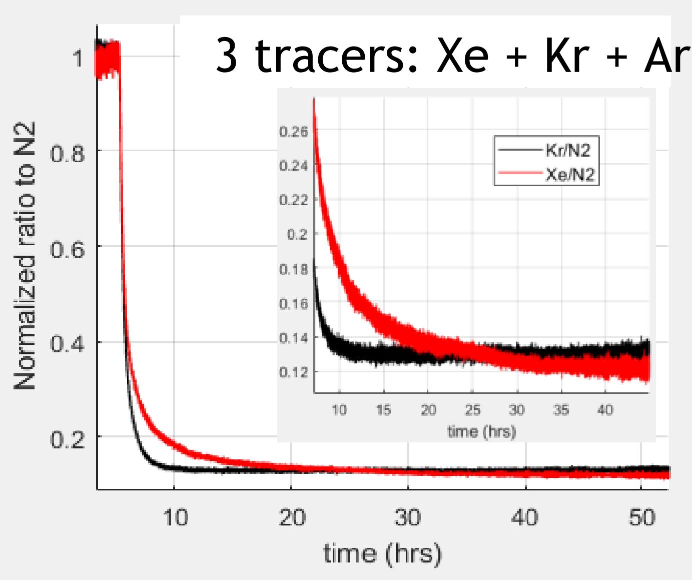
Experimental results for gas loading in clinoptilolite





Results for zeolite core plug with ambient air (N_2)

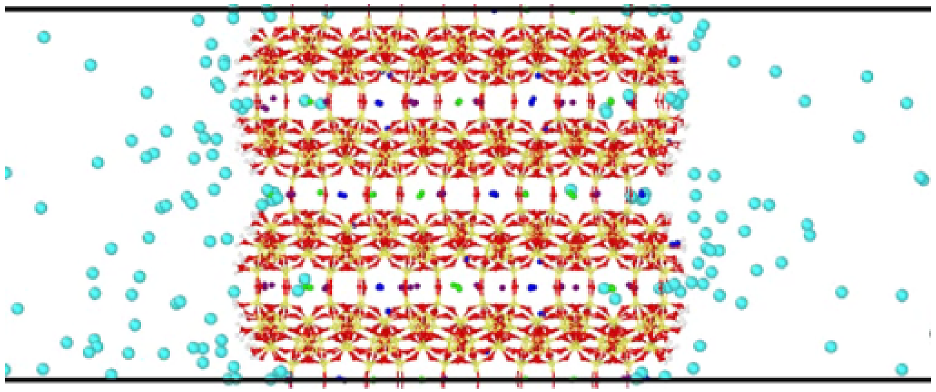
- ❑ Kr quickly penetrated the core plug within a few hours.
- ❑ Xe is taken up slowly but steadily, surpassing Kr in loading.
- ❑ Presence of N_2 and O_2 may affect the diffusion rate, but does not prohibit Kr or Xe adsorption.



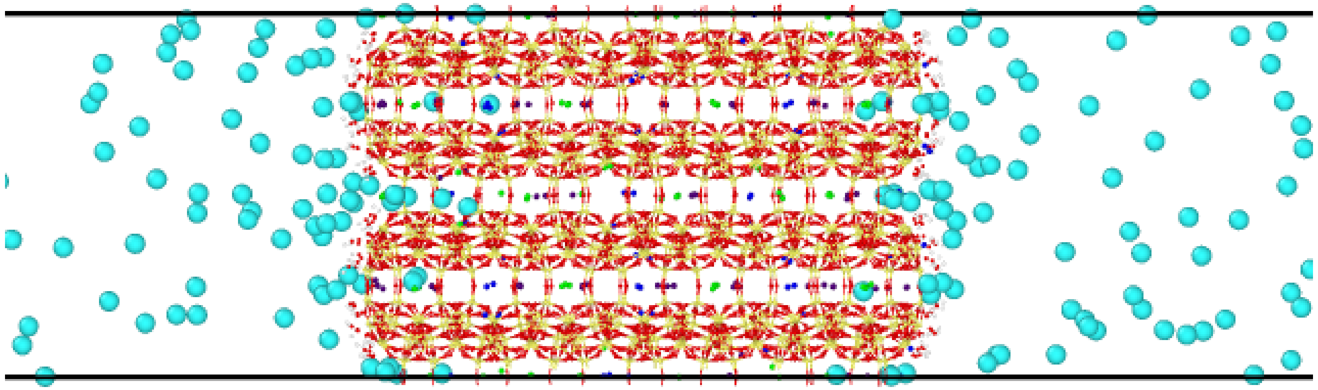
Gas loading in small pores: A closer look

Longer simulation times (100s of ns)

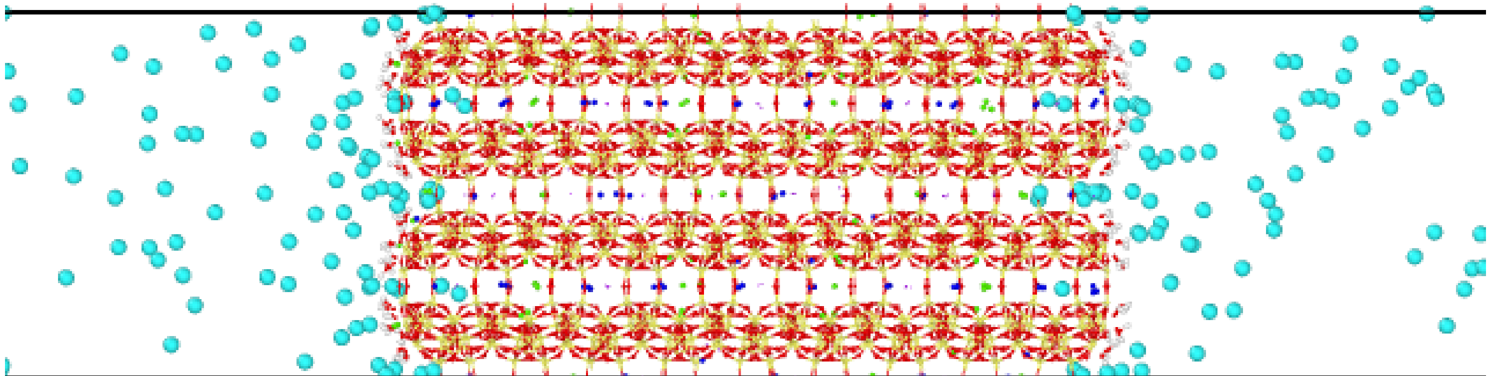
Average over 10 separate simulations



Original (thin) slab
4.4 nm

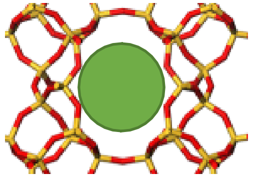


Medium slab (+1 unit cell)
5.9 nm



Thick slab (+2 unit cells)
7.4 nm

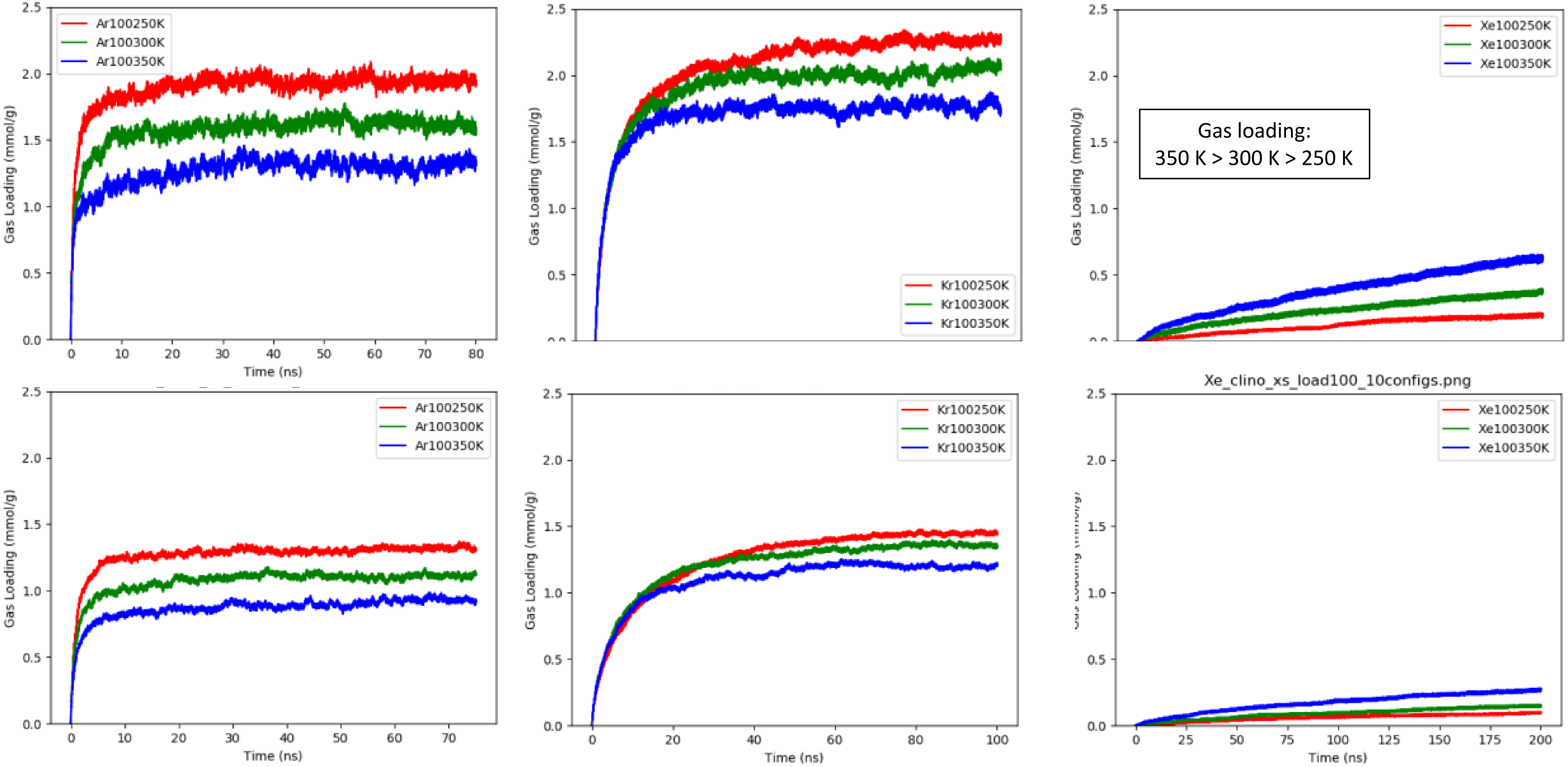
Effect of slab thickness on gas loading in small pores



Ar

Kr

Xe



Gas loading:
350 K > 300 K > 250 K

thin slab
4.4 nm

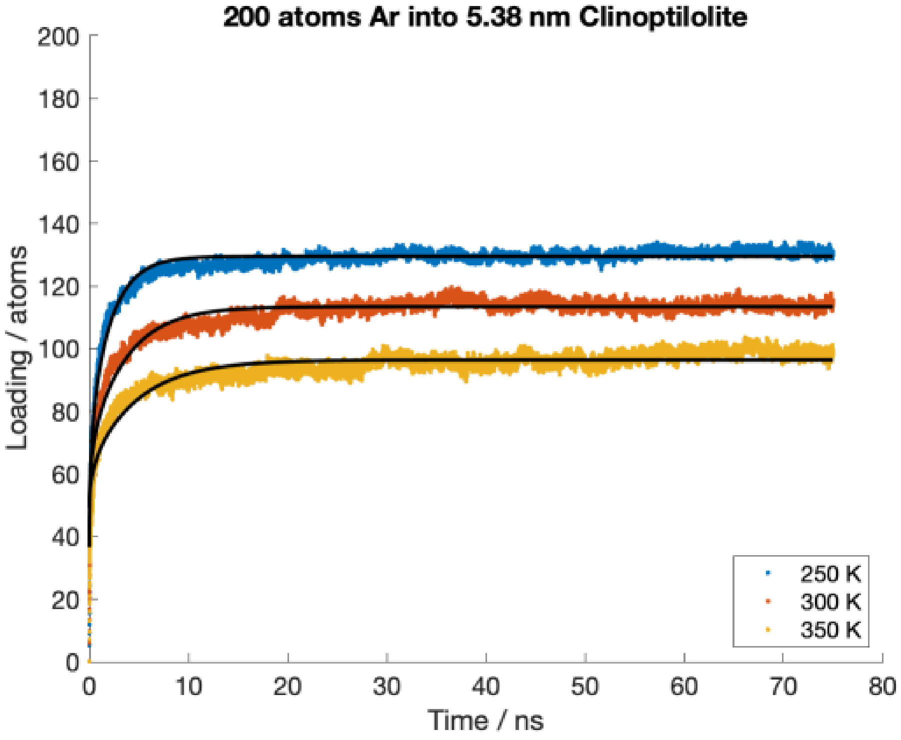
thick slab
7.4 nm

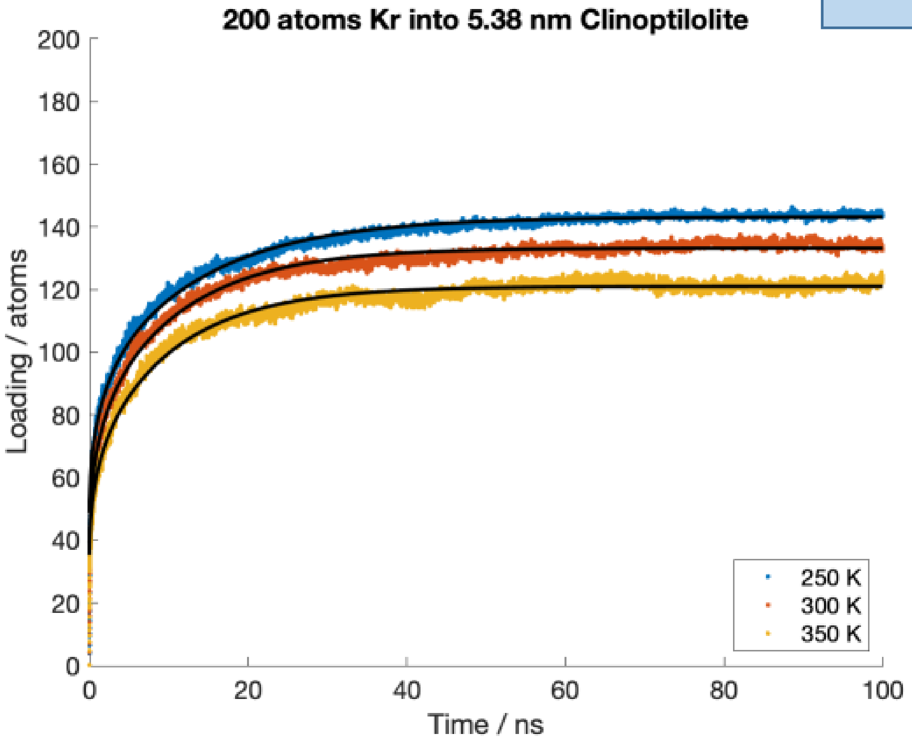
Kinetic models for gas loading in clinoptilolite

3 fitted parameters estimate diffusivity, external, and internal loading

$$M(t) = \frac{M_{tot} - M_{ext}}{1+\alpha}\left(1 - \sum_{n=1}^{\infty} \frac{2\alpha(\alpha+1)}{1+\alpha+\alpha^2 q_n^2} e^{-\beta q_n^2 t}\right) + M_{ext}$$

Diffusivity / Thickness^2	$\beta = \frac{D^*}{a^2}$
External Surface Loading	M_{ext}
Void / Matrix Loading	$\alpha = \frac{l}{ra}$





D^* (Å^2/ns)

T (K)	Ar	Kr
250	73.8	10.7
300	51.5	14.0
350	45.6	16.2

- Diffusivity corrected for non-ideal chemical potential
- Kr increases with temperature due to Arrhenius barrier
- Ar drops due to decreasing chemical potential

Barrer, *Trans. Faraday Soc.* **1949**, *45*, 358
Wilson, *Lond. Edinb. Dublin philos.* **1948,** 39:288, 48
Kärger and Ruthven, *New J. Chem.* **2016,** 40, 4027

Kinetic models for gas loading in clinoptilolite

At simulations far from equilibrium, α and β are interdependent

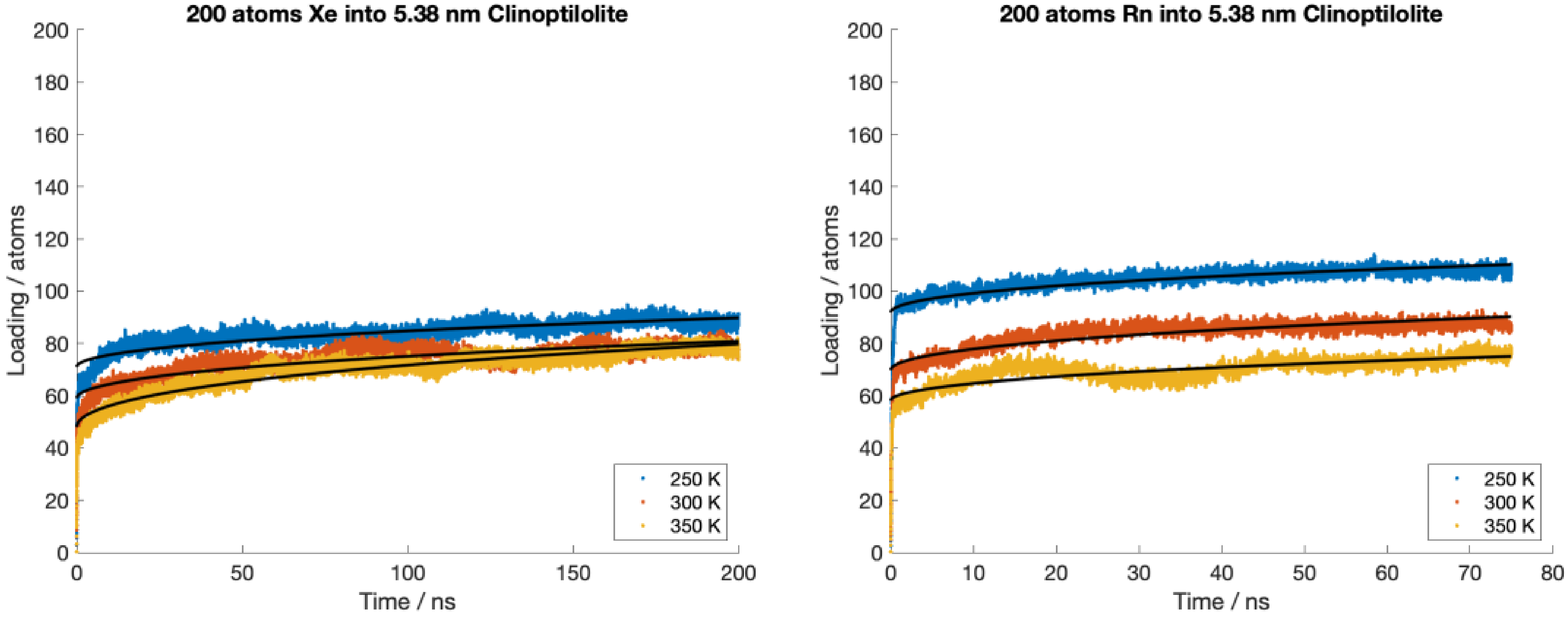
$$M(t) = M_{ext} + (M_{tot} - M_{ext})\left(1 - e^{\gamma t}\,\mathrm{erfc}\sqrt{\gamma t}\right)$$

As $\gamma t \rightarrow 0$, this approaches the $\sqrt{t}$-"law"

$$\gamma = \frac{\beta}{\alpha^2} = \frac{D^* r^2 \varepsilon^2}{l^2}$$

γ (1/μs)

T (K)	Ar	Kr	Xe	Rn
250	177.0	41.1	.108	.403
300	39.3	38.5	.123	.341
350	13.0	26.5	.249	.182

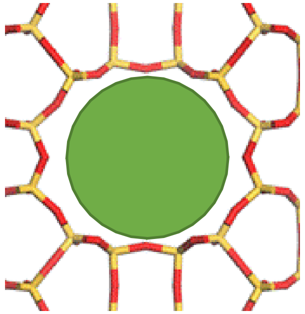


- Molecular sieving: Xe/Rn occlusion is very slow relative to Ar/Kr. I.e., molecular sieving
- Xe penetration increases with temperature (diffusivity increases)
- Rn penetration decreases with temperature (capacity decreases)

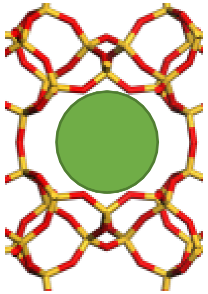
Crank, *Lond. Edinb. Dublin philos.* **1948,** 39:292, 362

Conclusions

- Molecular simulations and experiments were performed to investigate gas adsorption and mobility in zeolites with pores ***much larger than*** and ***similar in size*** *to* the gas species.



mordenite



clinoptilolite

- Similarity in size between gas species and zeolite pores results in hindered gas mobility. This is seen in adsorption experiments (reverse selectivity) and MD simulations.
- Simulations over 100-ns time scales revealed trends in gas uptake as functions of size and temperature.
- Fitting with a kinetic model allows the effective gas diffusion coefficient to be calculated.

LDRD
LABORATORY DIRECTED RESEARCH & DEVELOPMENT

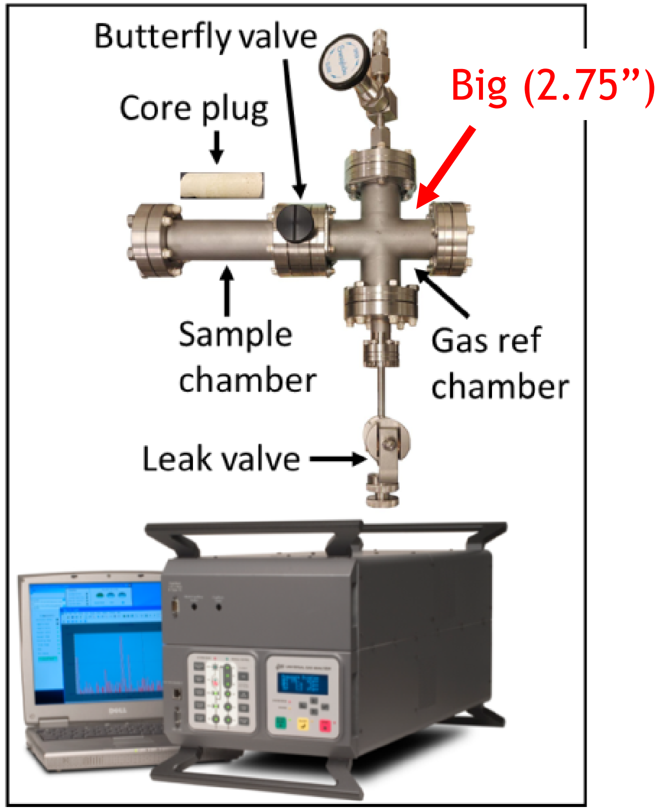
Acknowledgements
Joshua Feldman, PNNL

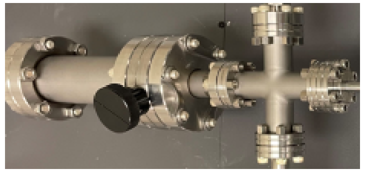
EXTRA SLIDES

Experimental Methods

Characterization and gas adsorption

- BET surface area (N_2, 77 K)
- Pore size distribution (CO_2, 273 K)
- Adsorption isotherms
- X-ray diffraction
- Total Gravimetric Analysis





Small (1.33")

Dynamic gas adsorption analyzer

- Both sample and reference chambers are in equilibrium with ambient air before injection of tracers (Kr/Xe/Ar).
- Quadrupole mass spectrometer continuously records gas concentrations in the reference chamber.
- Samples can be a core plug, rock chips or powders (natural rock or pure mineral

Reference chamber	Sample chamber	Tracer gas concentrations in air
Big (250 mL)	125 mL	~10% Kr
		~ 10% Xe
		~10% Kr + 10% Xe
Small (65 mL)	125 mL	5.9% Kr + 5.9% Xe + 6.6% Ar

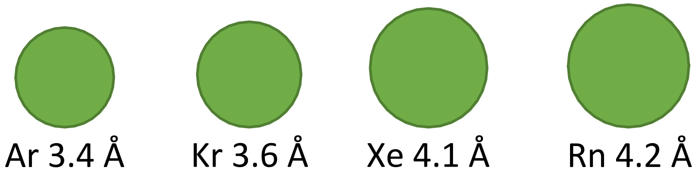
Zeolite characterization

Water Content (wt %)

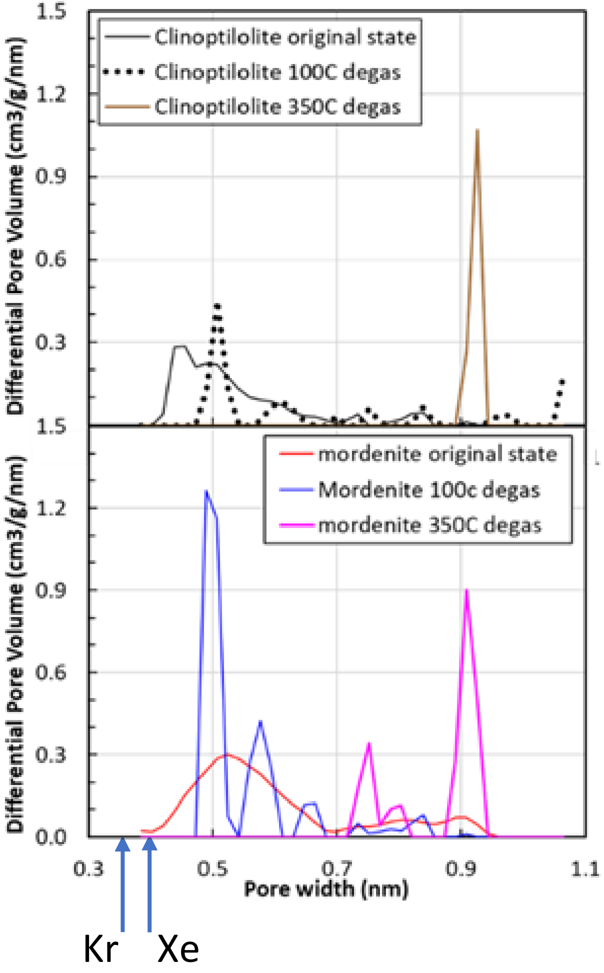
	Mordenite	Clinoptilolite
Original state	13.2%	13.5%
100 °C, 6 hrs	5-8%	5-8%
350 °C, 6 hrs	<1%	<1%

Pore water can be removed with heating.

Significant pore volume with pore size less than 4 Å which can not be accessed by Xe.



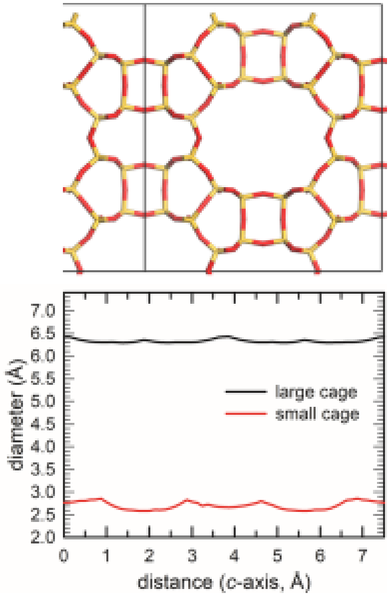
Pore Size Distribution (CO_2 adsorption, 273 K)



Pore Size Profile (crystal structures)

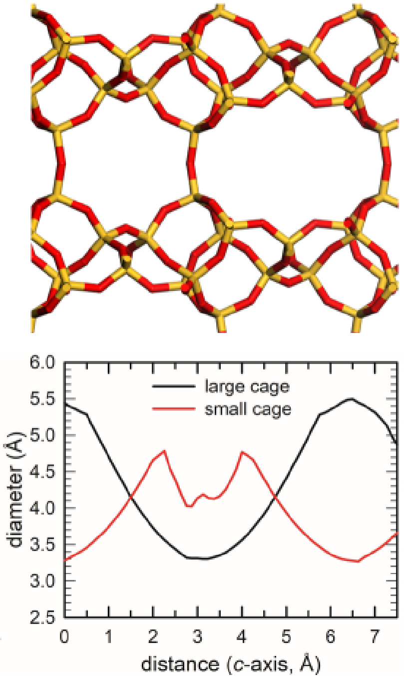
Mordenite

c-axis
12-member ring
(6.5 × 7.0 Å)
8-member ring
(2.6 × 5.7 Å)

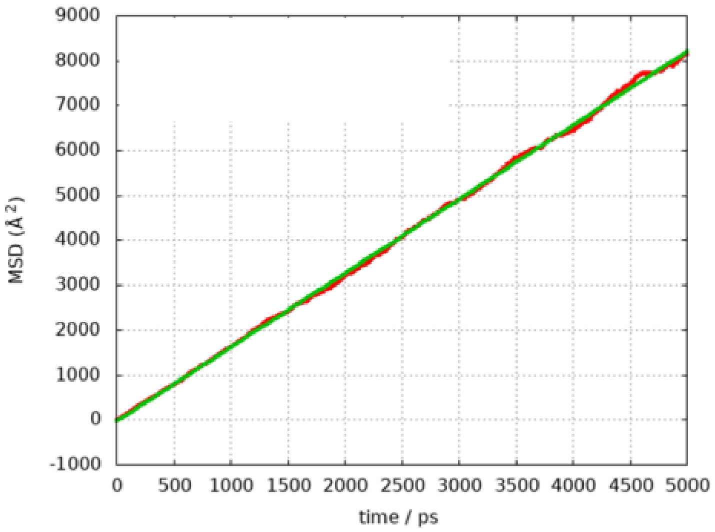


Clinoptilolite

c-axis
10-member ring
(4.4 × 7.2 Å)
8-member ring
(4.1 × 4.7 Å)



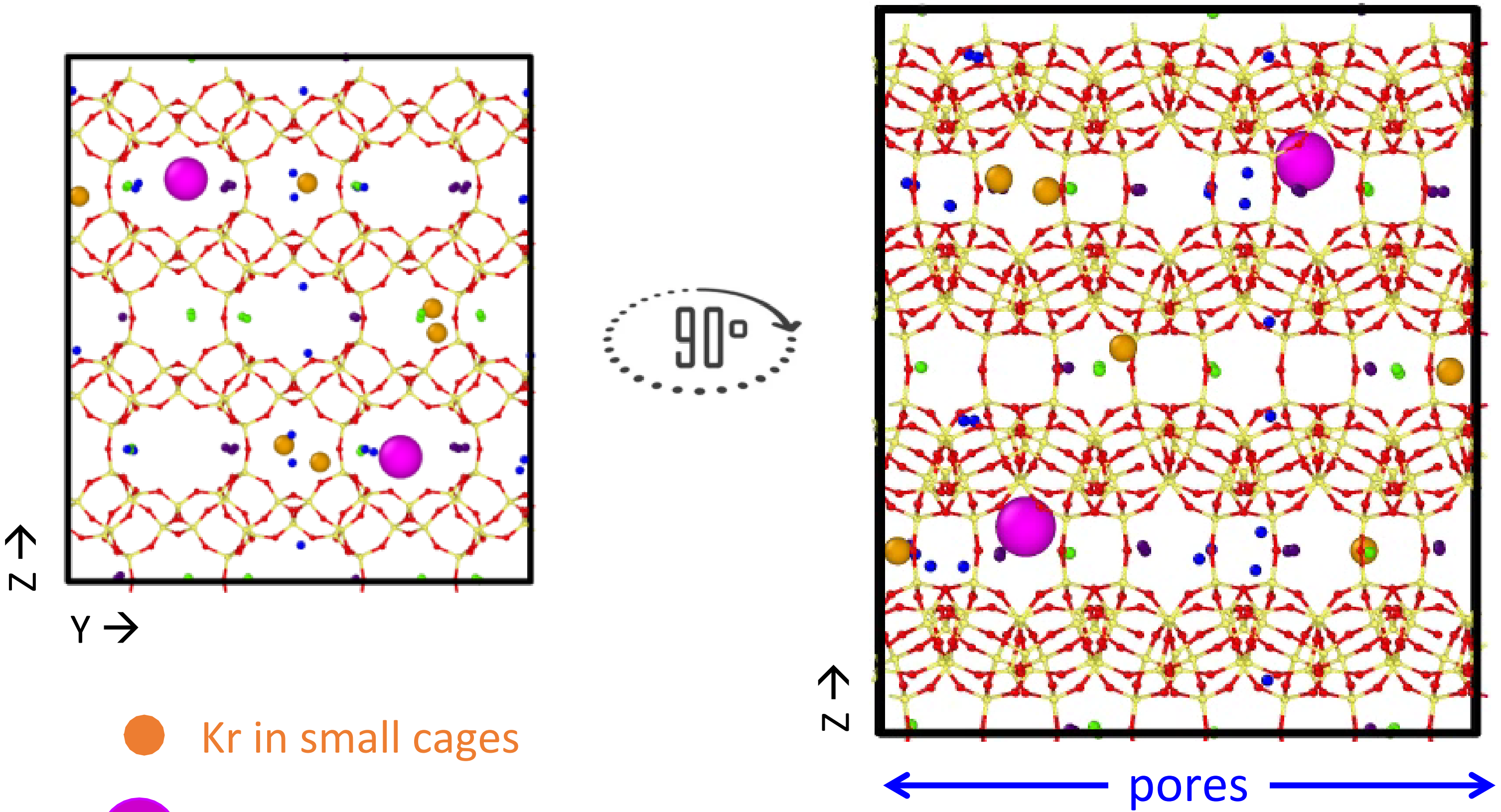
MD simulation of gas mobility (bulk zeolites)



Self-diffusion coefficient *(D)* is calculated by analyzing mean square displacement (MSD).

Slope $\propto D$

Kr mobility in clinoptilolite, 300 K
0.4 bar (0.25 mmol/g)



● Kr in small cages

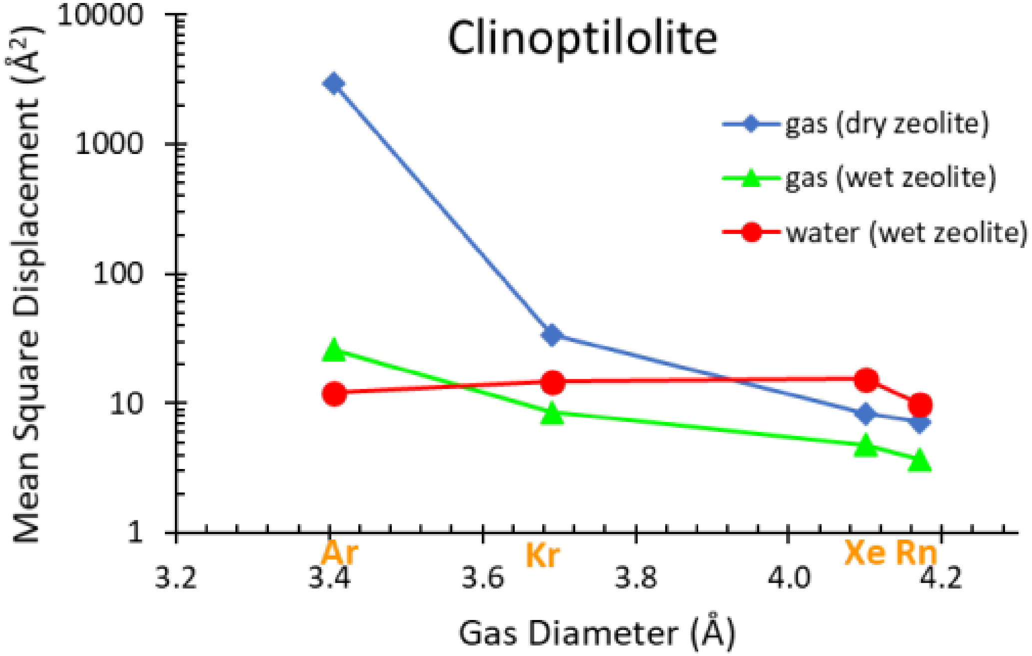
● Kr in large cages

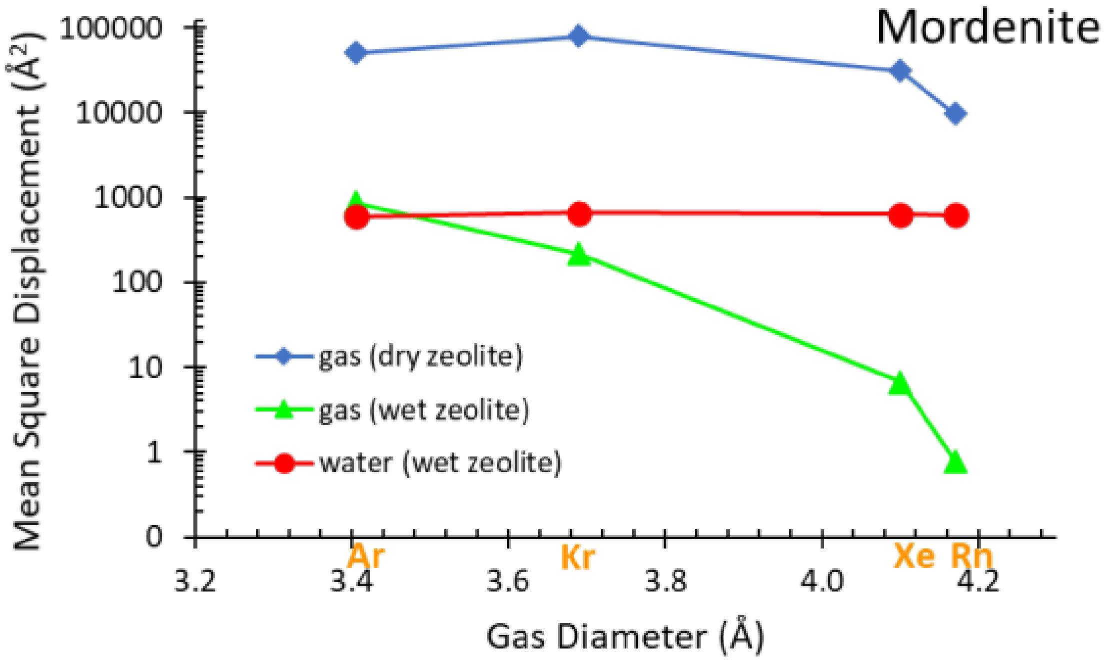
Limited gas mobility due to diffusion barriers at windows.

Trends in gas and water mobility (bulk zeolites)

10-ns simulations, similar gas loadings, 300 K

Dry and wet systems



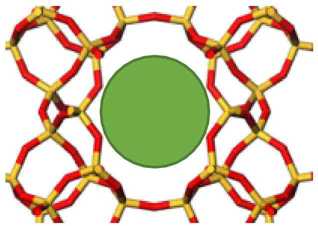


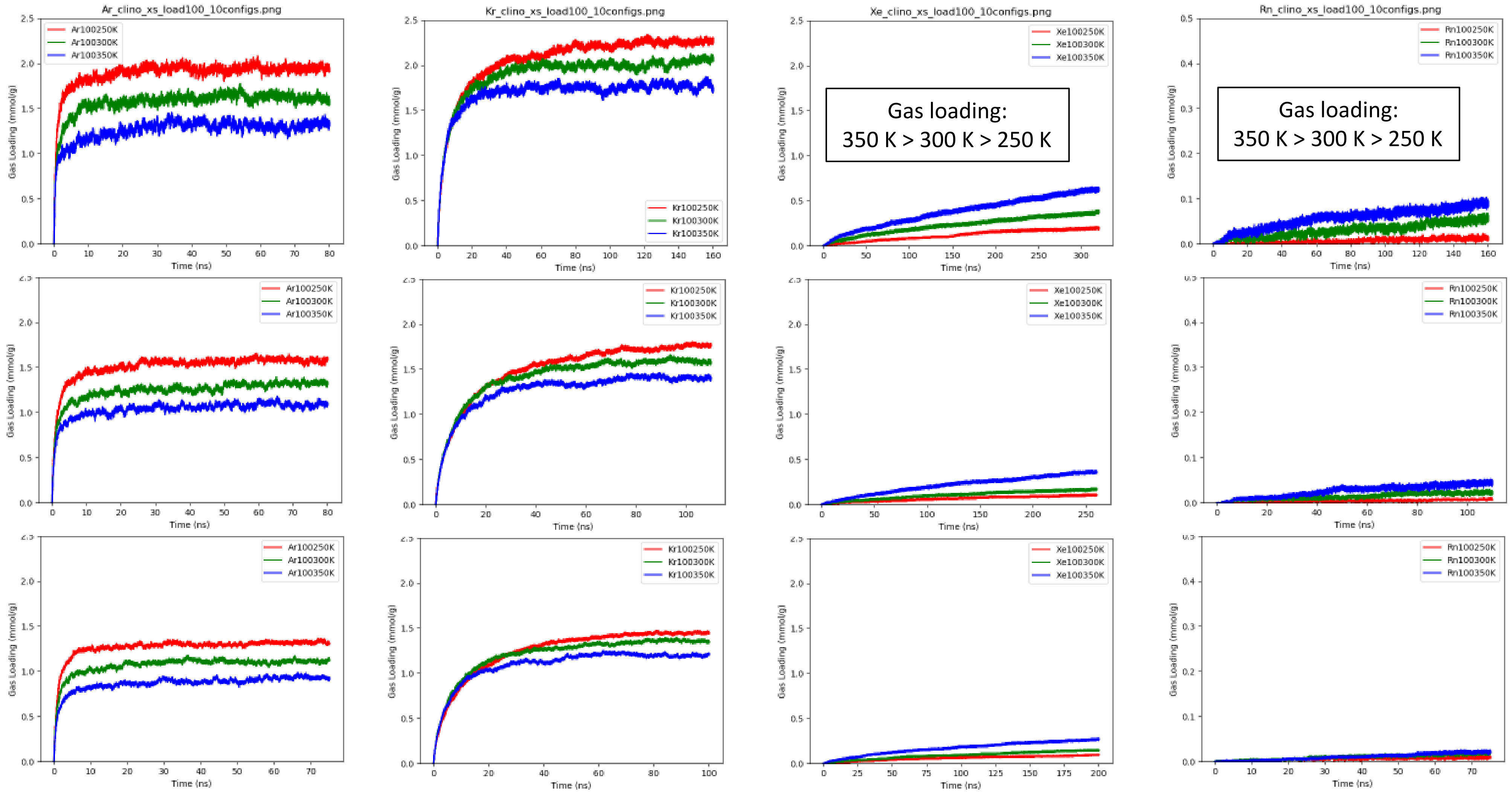
Significantly greater mobility in 1) mordenite vs clinoptilolite and 2) dry vs wet conditions.

Clinoptilolite: trend of reduced gas mobility with increasing size is consistent with experiment.

Similar water mobility for all gas sizes.

Effect of slab thickness on gas loading in small pores





Gas loading:
350 K > 300 K > 250 K

Gas loading:
350 K > 300 K > 250 K

thin slab
4.4nm

medium slab
5.9 nm

thick slab
7.4 nm

Kinetic models for gas loading in clinoptilolite

initial gas concentration

Amount adsorbed on external surface

diffusion coefficient

$$\square\square_{\square}(\square) = \frac{(\square\square_0 - \square\square_{\square\square\square\square})}{1 + \square}\left(1 - \sum_{\square=1}^{\infty} \frac{2\square(\square+1)}{1 + \square + \square\square^2\,\square\square^2_{\square}}\,\square\square^{-\square\square\square^2_{\square}\square}\right) + \square\square_{\square\square\square\square}$$

porosity/retardation factor

Barrer and Brook, *Trans. Faraday Soc.* **1953**, *49*, 1049

D^* (Å^2/ns)

T (K)	Ar	Kr
250	5.5	1.1
300	3.8	1.4
350	3.4	1.6