MOLECULAR DYNAMICS SIMULATION STUDY OF PORE SIZE EFFECTS ON GAS ADSORPTION KINETICS IN ZEOLITES

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SUPPLEMENTARY INFORMATION

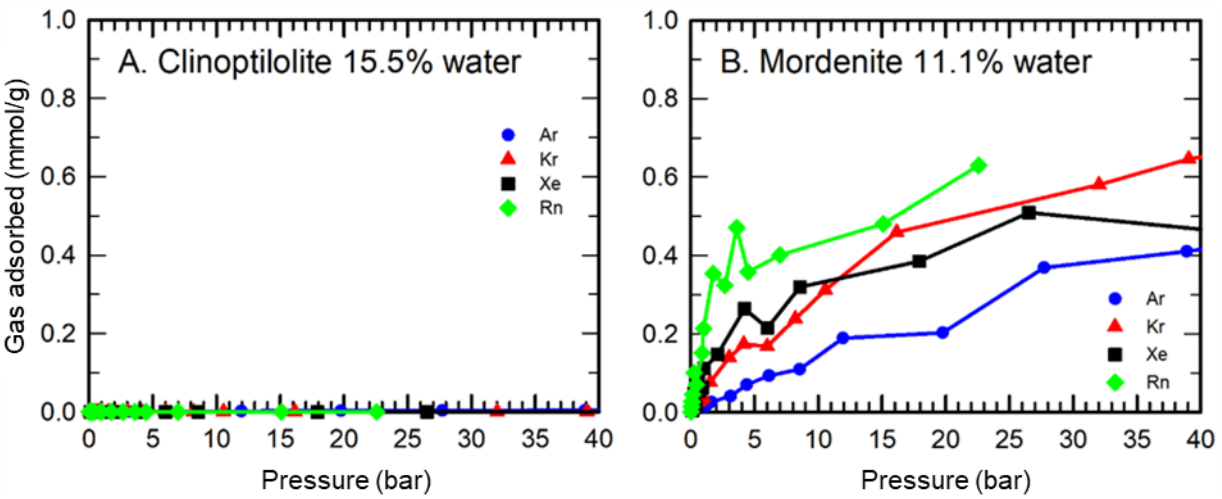

Figure S1. Adsorption isotherms at 300 K from GCMC simulations for (A) clinoptilolite and (B) mordenite in fully hydrated conditions.

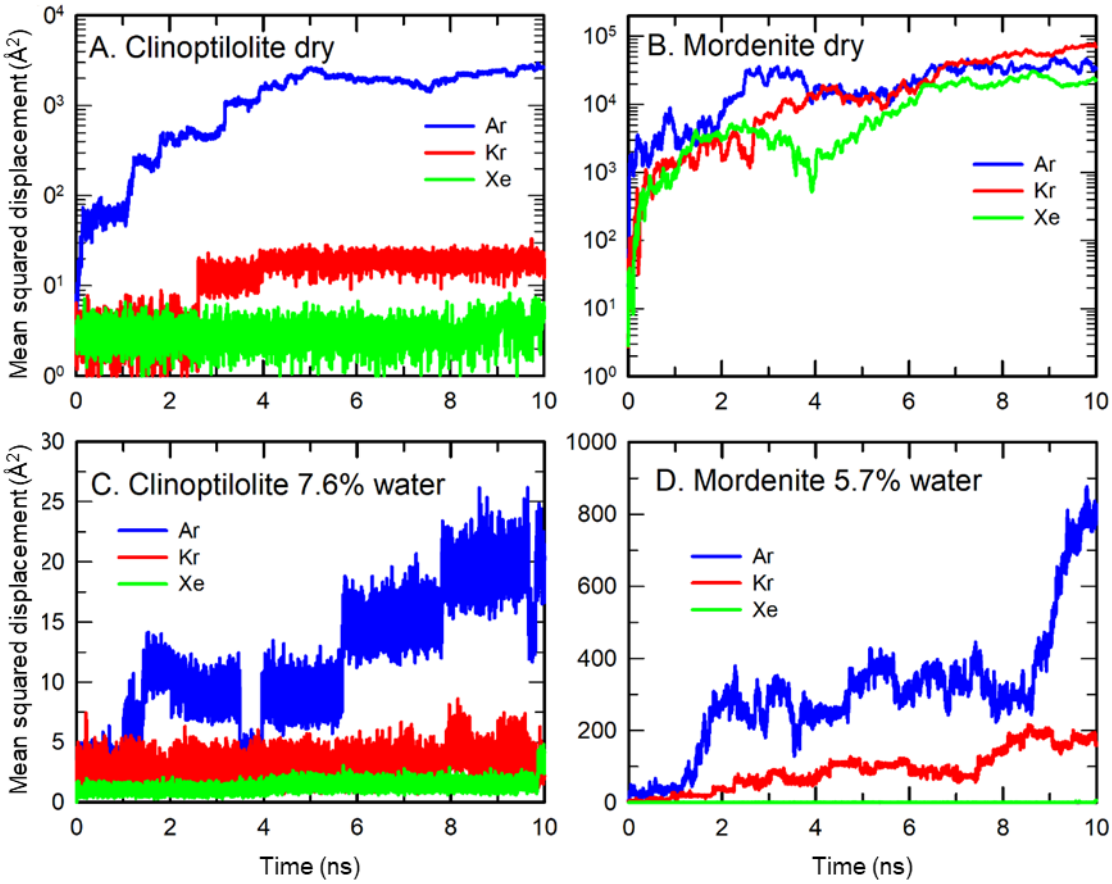

Figure S2. Time evolution of gas mean square displacement during 10 ns MD simulations at 300 K in bulk zeolites in (A, B) dry and (C, D) partially hydrated states.

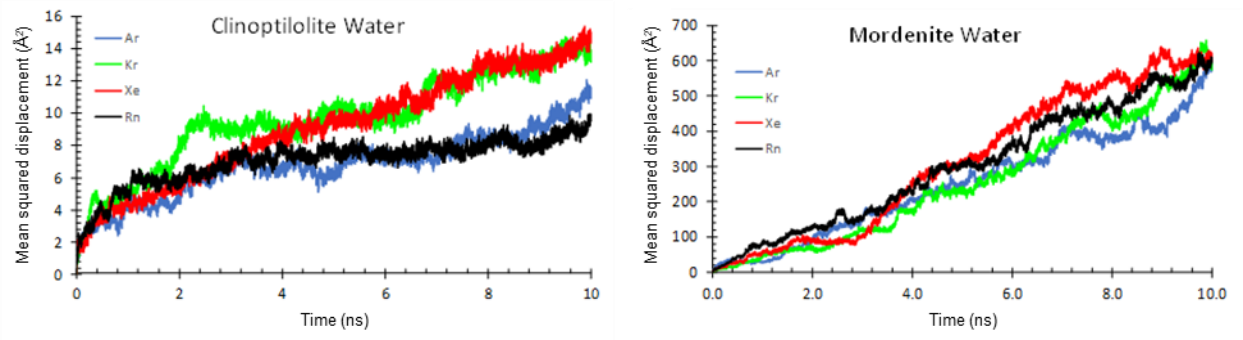

Figure S3. Time evolution of water mean squared displacement from 10-ns simulations in partially hydrated bulk zeolites with different gases. Slopes over the range 6 – 10 ns correspond to water diffusion coefficients of 0.005×10^{-9} $m^2 \cdot s^{-1}$ and 0.25×10^{-9} $m^2 \cdot s^{-1}$ for clinoptilolite and mordenite, respectively.

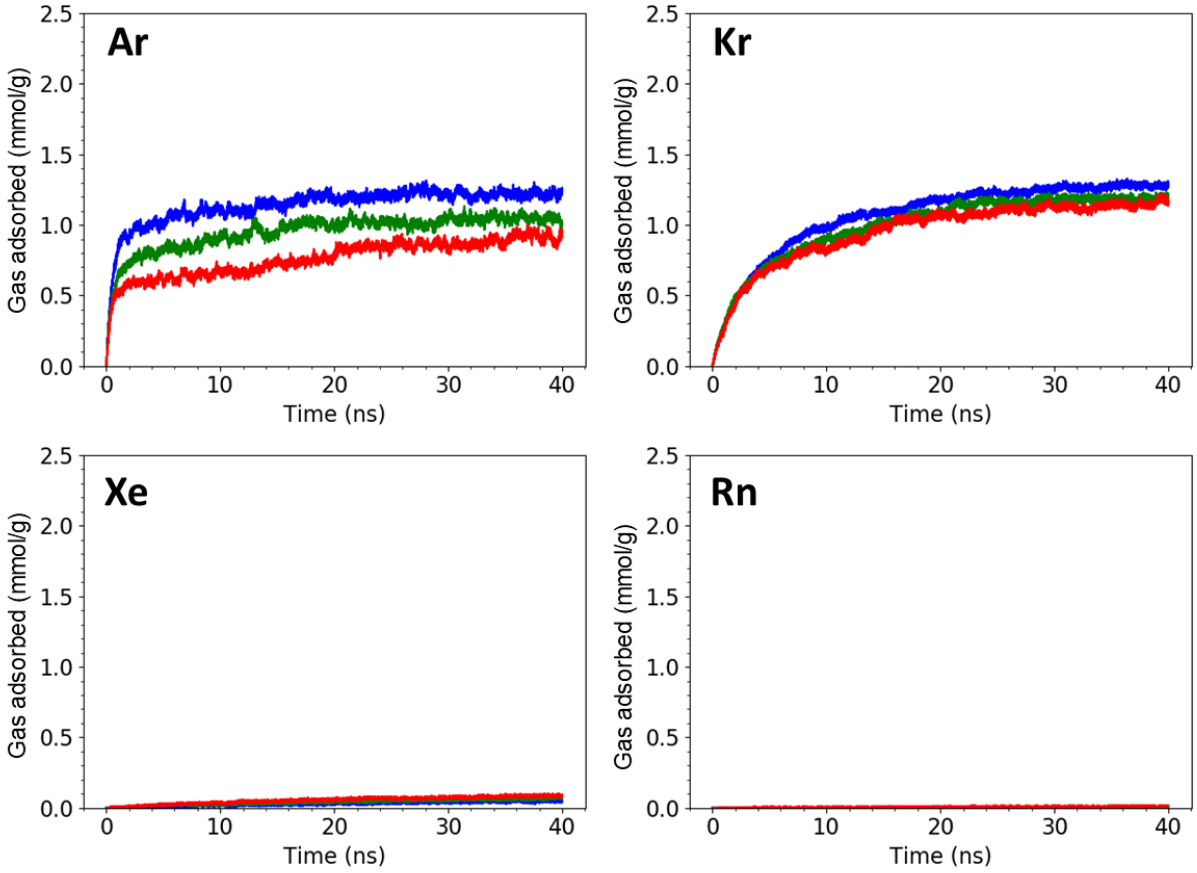

Figure S4. Results from MD simulations showing gas loading profiles in the bulk region of dry clinoptilolite slabs at low gas concentration (50 atoms on each side).

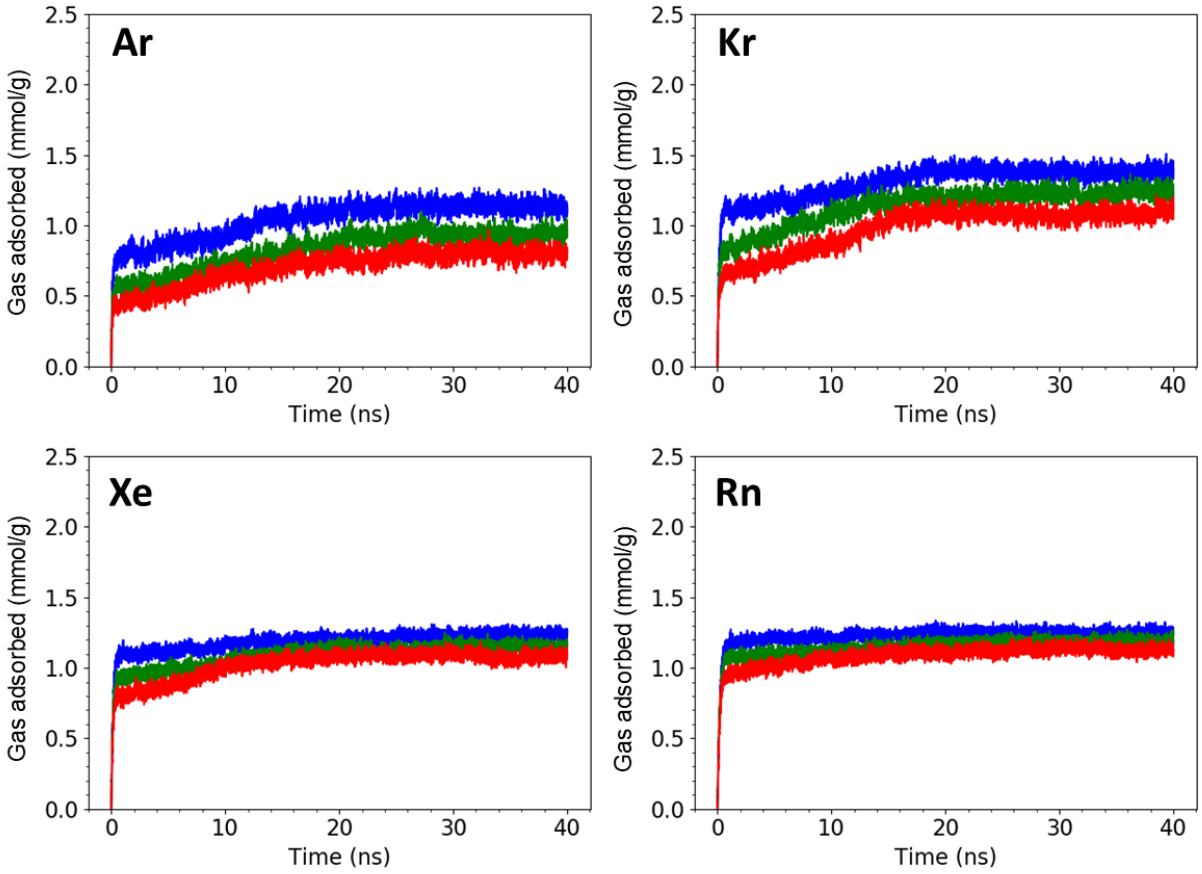

Figure S5. Results from MD simulations showing gas loading profiles in the bulk region of dry mordenite slabs at low gas concentration (50 atoms on each side).

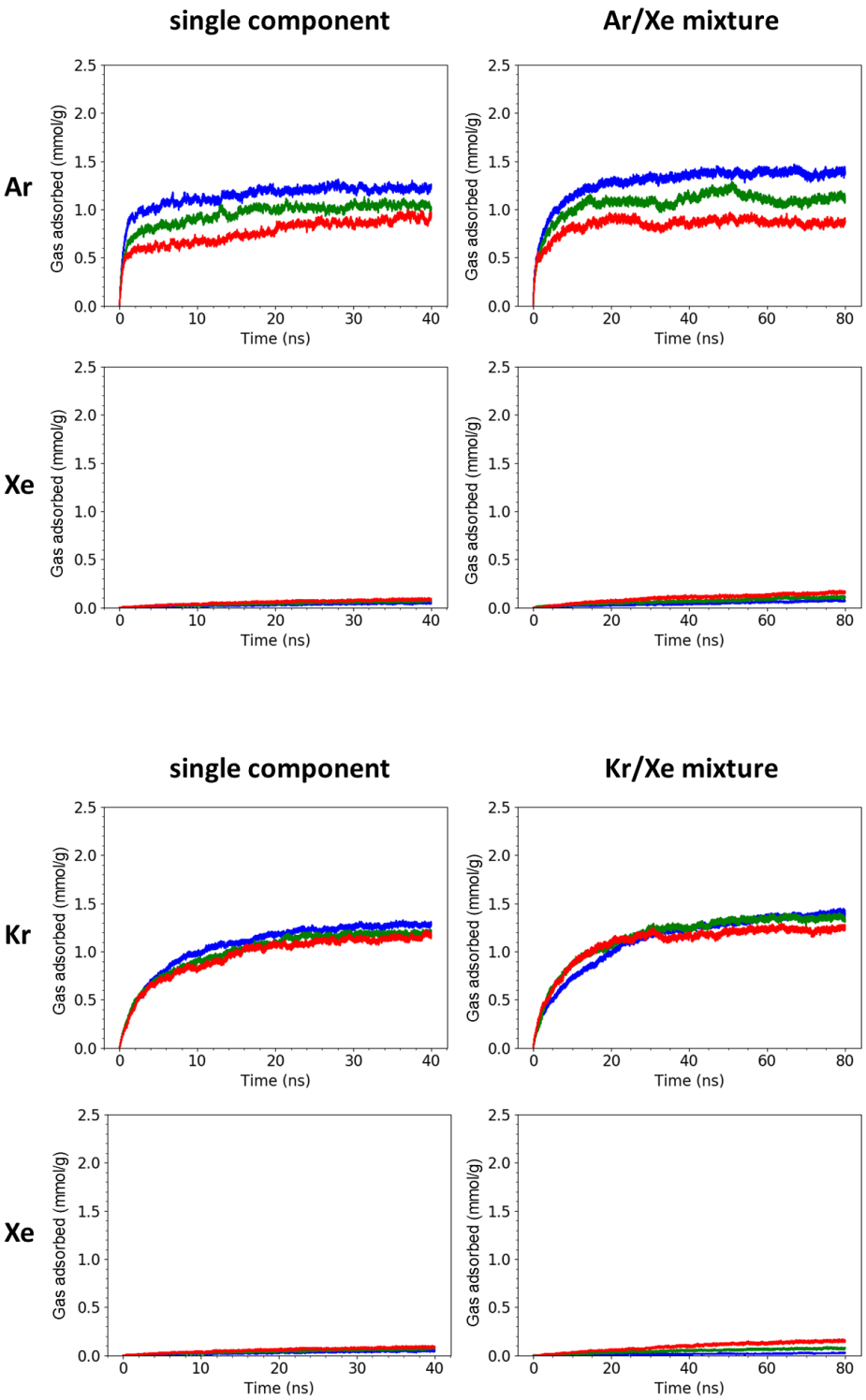

Figure S6. Results from MD simulations of Ar/Xe and Kr/Xe mixtures showing gas loading profiles in the "bulk zeolite" region of 4.4 nm clinoptilolite slabs for (dry models). Gas concentrations are 50 atoms of each gas on each side (low concentrations). Results in the left column show gas loading profiles from single gas simulations (Figure S4). Simulation temperatures are 250 K (blue), 300 K (green), and 350 K (red).

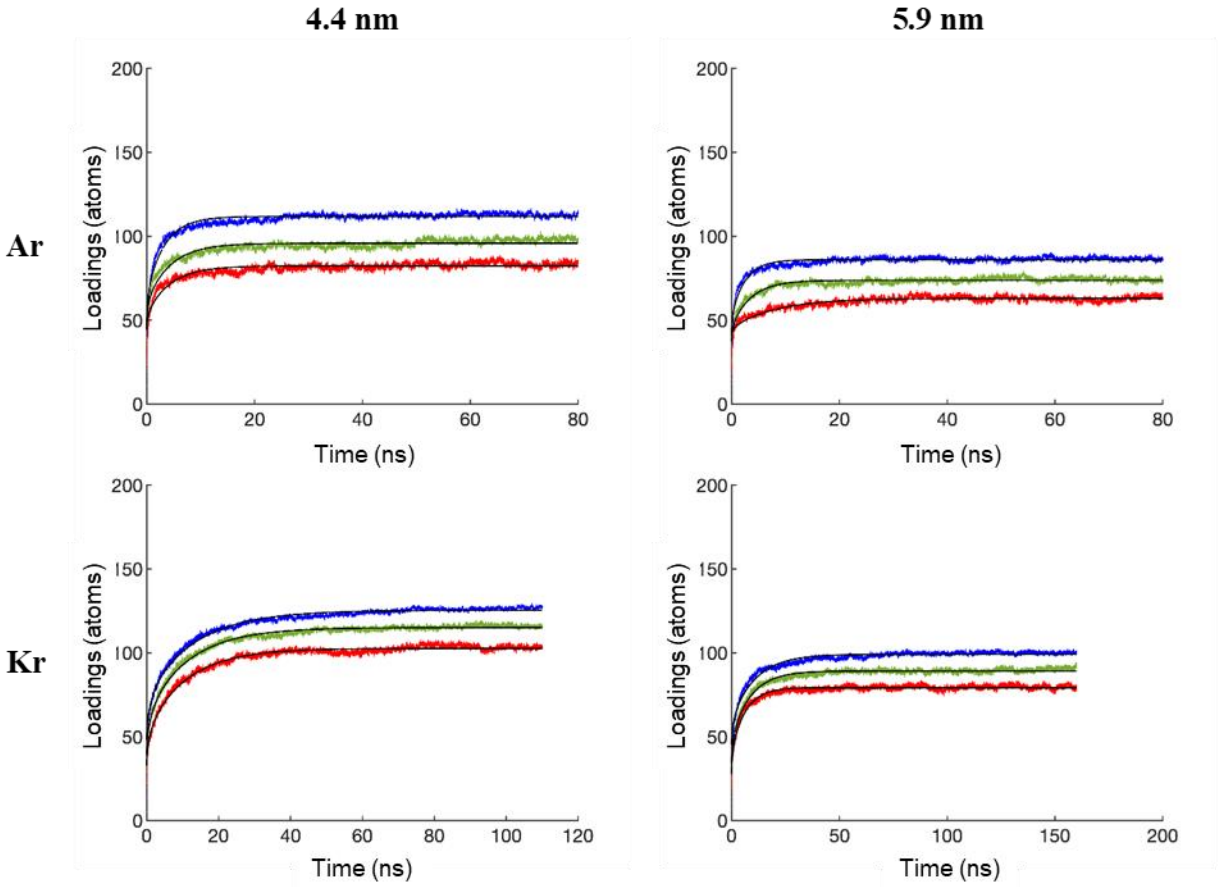

Figure S7. Kinetic model fits (black lines) of MD simulation results at 250 K (blue), 300 K (green), and 350 K (red) of total gas loading profiles ("interface" and "bulk" regions) for Ar and Kr in the 4.4 nm and 5.9 nm clinoptilolite slabs at high gas concentration (100 atoms on each side).

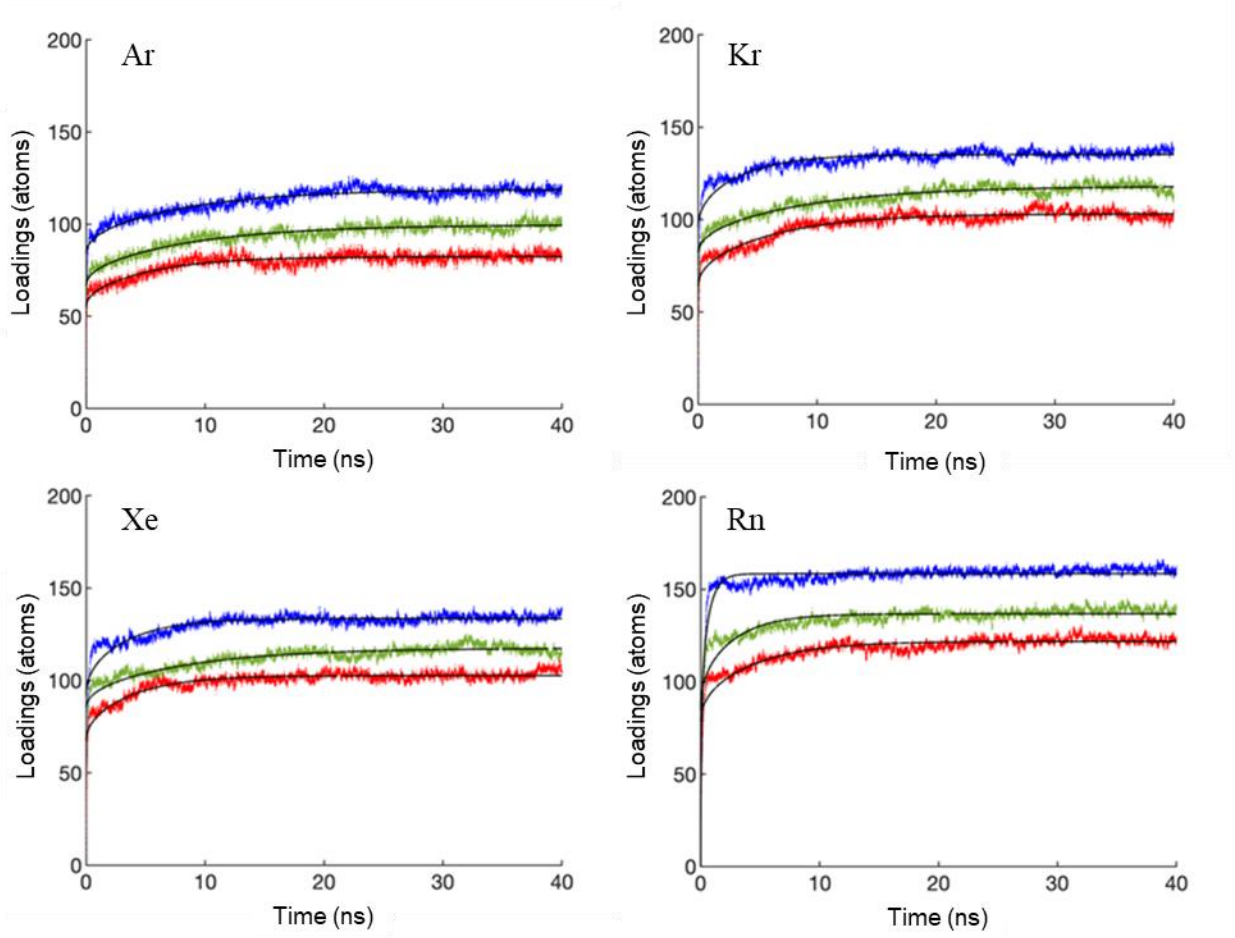

Figure S8. Kinetic model fits (black lines) of MD simulation results at 250 K (blue), 300 K (green), and 350 K (red) of total gas loading profiles ("interface" and "bulk" regions) for single component noble gases in the 3.9 nm mordenite slab at high gas concentration (100 atoms on each side).

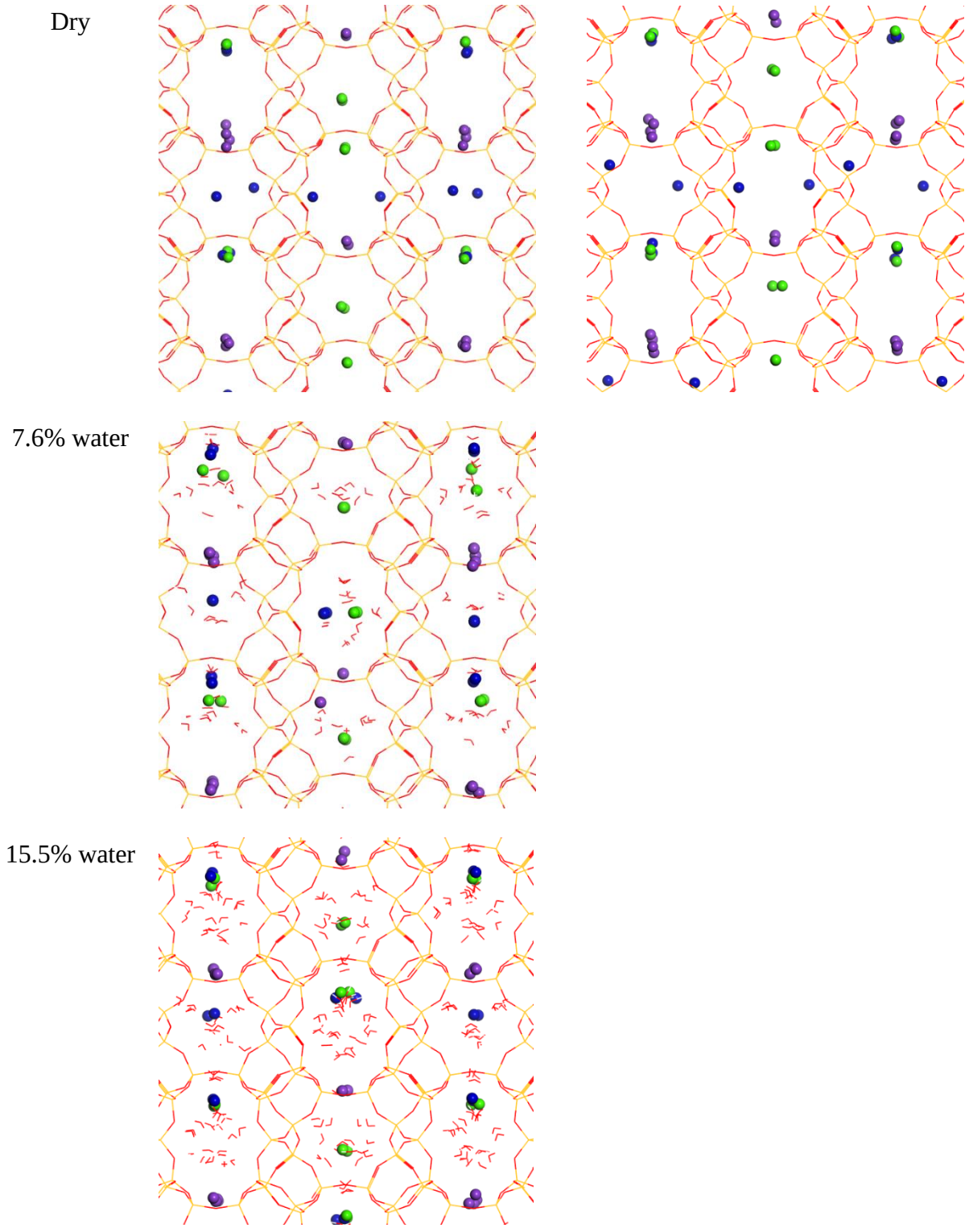

Figure S9. Snapshots from 1-ns MD simulations of clinoptilolite in dry, 7.6% water, and 15.5% water. Cations are shown as spheres (K = purple, Na = blue, Ca = green). For the dry state, snapshots are shown after simulation at 300 K (left) and after simulation at 623 K (350 °C) followed by cooling to 300 K (right).

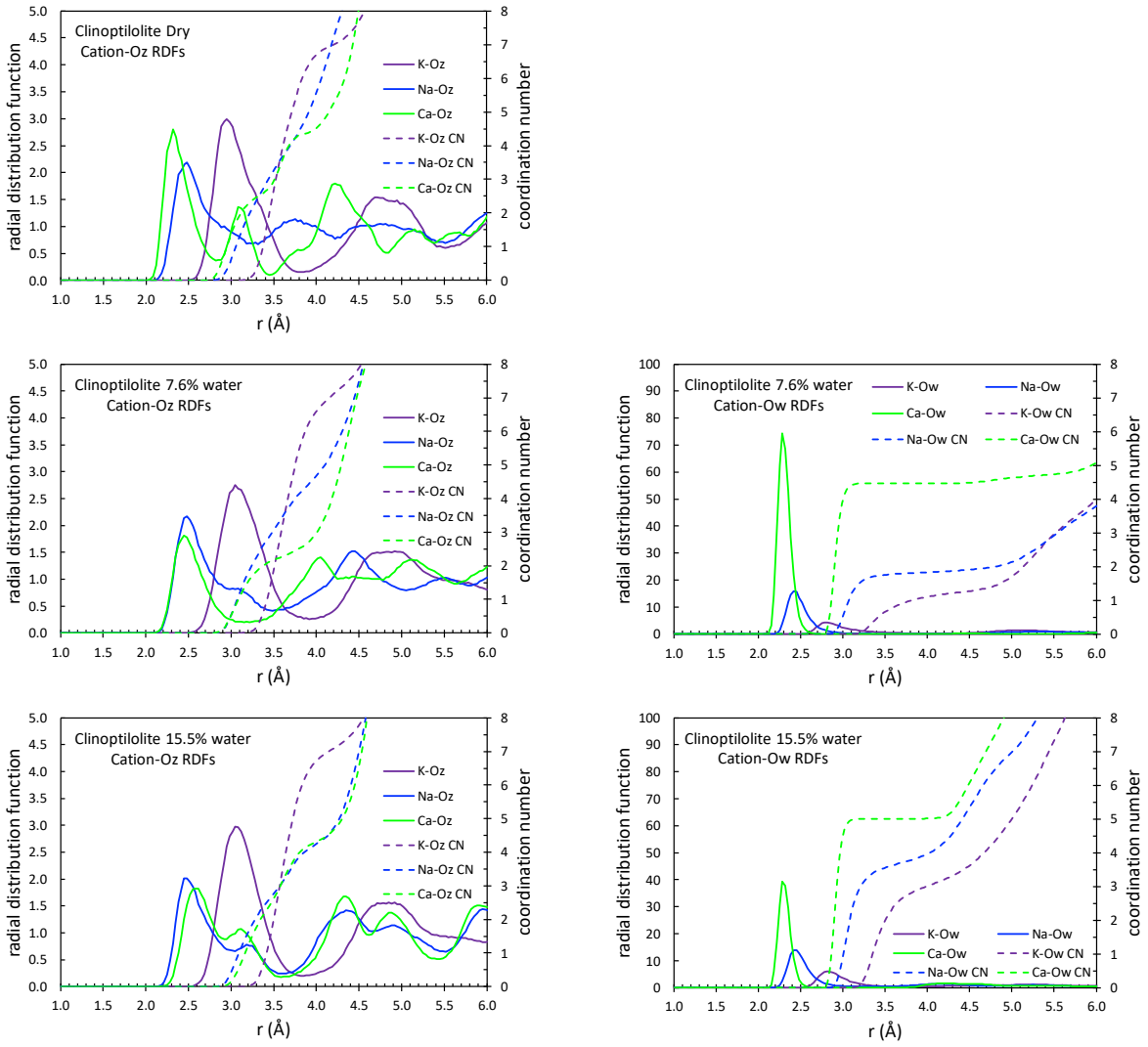

Figure S10. Cation-oxygen radial distribution functions (RDFs) and running coordination numbers (CN) from 1-ns MD simulations of clinoptilolite in dry, 7.6% water, and 15.5% water. Oz and Ow refer to zeolite oxygen and water oxygen, respectively.

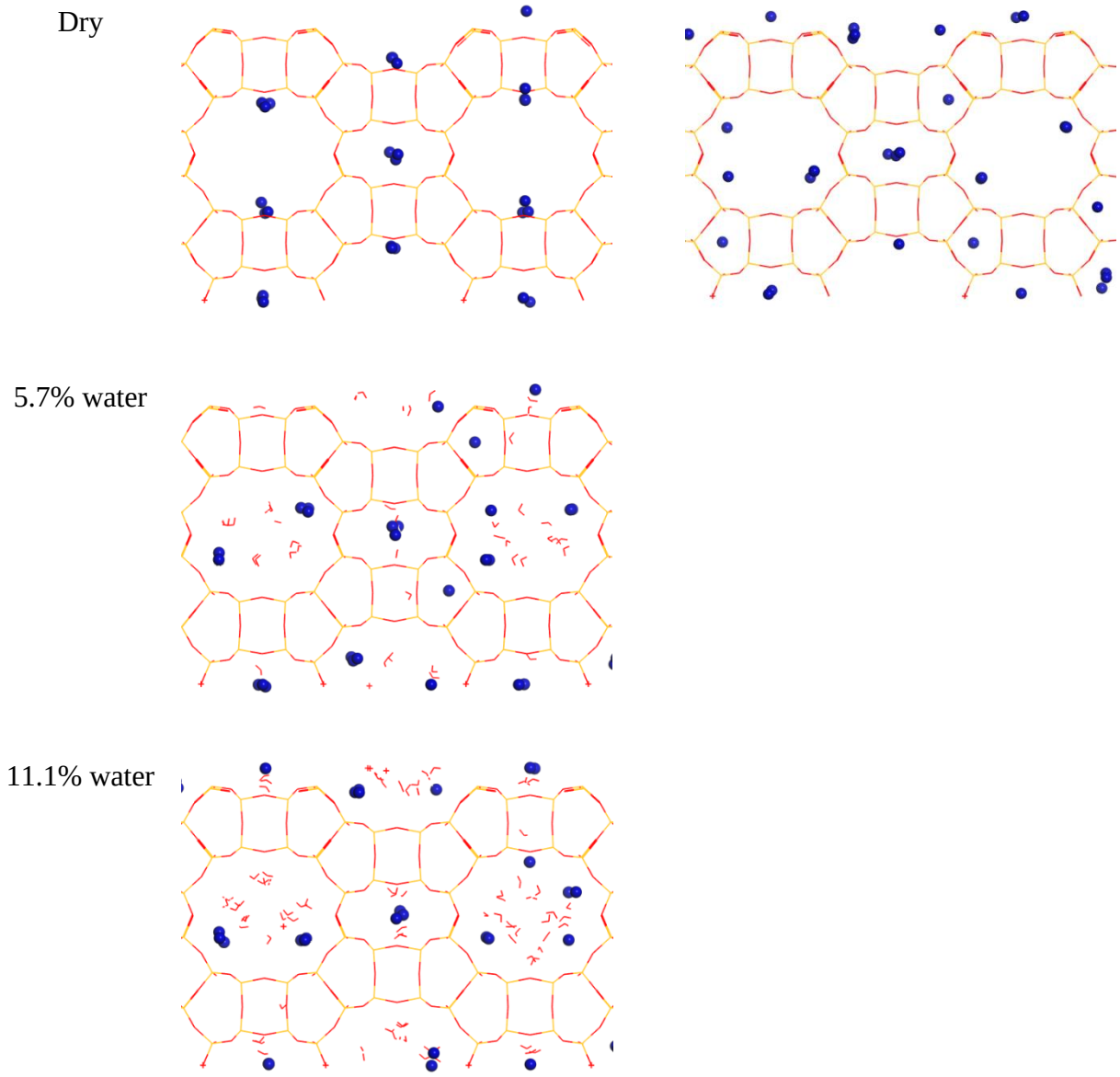

Figure S11. Snapshots from 1-ns MD simulations of mordenite in dry, 5.7% water, and 11.1% water. Cations are shown as spheres (K = purple, Na = blue, Ca = green). For the dry state, snapshots are shown after simulation at 300 K (left) and after simulation at 623 K (350 °C) followed by cooling to 300 K (right).

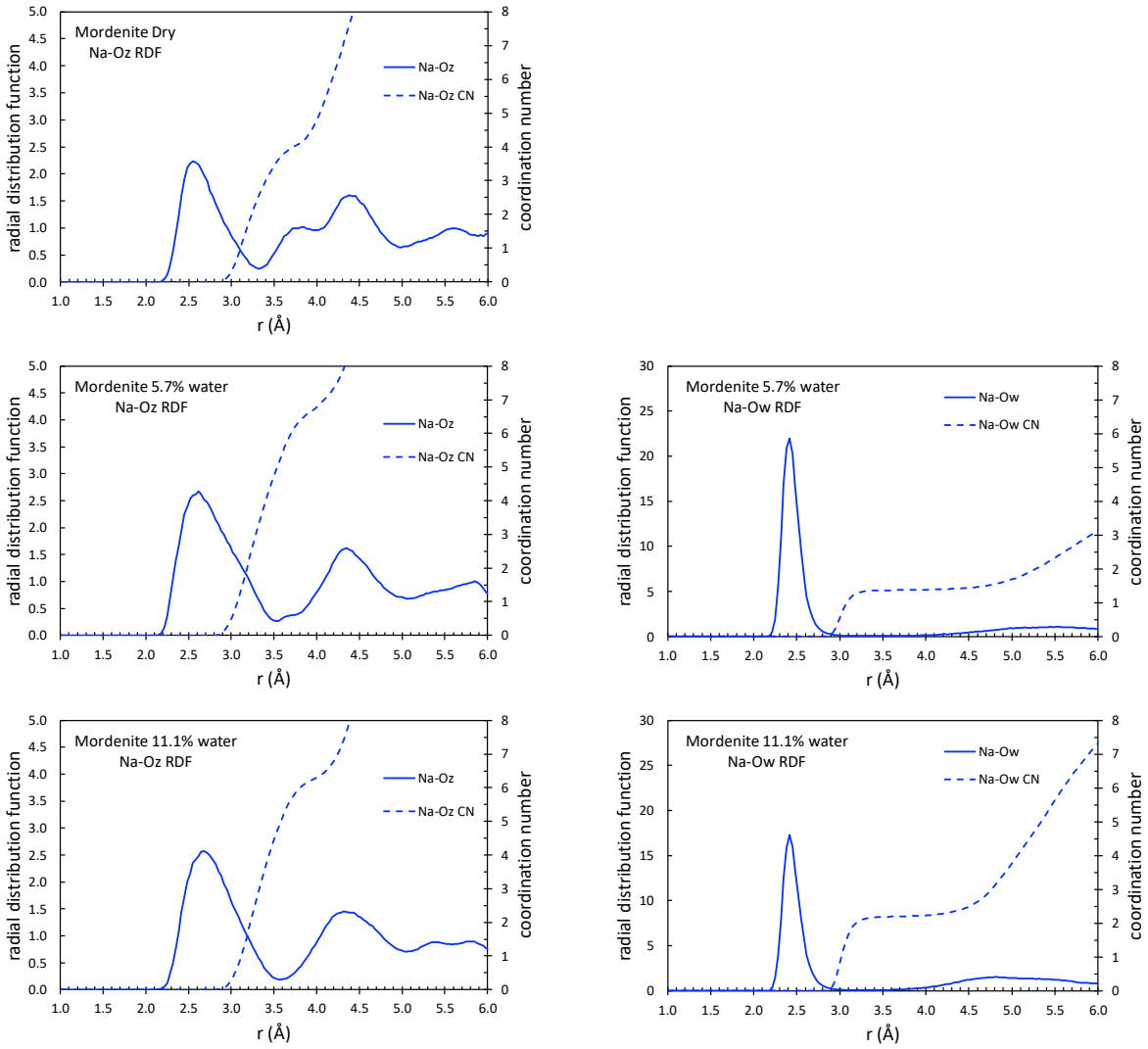

Figure S12. Sodium-oxygen radial distribution functions (RDFs) and running coordination numbers (CN) from 1-ns MD simulations of mordenite in dry, 5.7% water, and 11.1% water. Oz and Ow refer to zeolite oxygen and water oxygen, respectively.

Table S1. Gas Loadings (N_{gas} / unit cell) and Corresponding Pressures (bar) for MD Simulations of Gas Mobility in Bulk Clinoptilolite.

	Dry		7.6 % H_2O	
Gas	**N_{gas} / unit cell**	**P (bar)**	**N_{gas} / unit cell**	**P (bar)**
Ar	0.5	1.6	0.5	6.0
Kr	0.5	0.4	0.4	1.2
Xe	0.5	< 0.1	0.6	0.4
Rn	0.5	< 0.02	0.4	0.05

Table S2. Gas Loadings and Corresponding Pressures for MD Simulations of Gas Mobility in Bulk Mordenite.

	Dry		5.7 % H_2O	
Gas	**N_{gas} / unit cell**	**P (bar)**	**N_{gas} / unit cell**	**P (bar)**
Ar	0.8	2.0	1.2	12.0
Kr	1.5	3.0	1.2	1.2
Xe	2.3	0.1	1.8	0.8
Rn	1.0	< 0.02	1.3	0.1

Table S3. Fitted parameters and 95% confidence intervals (parentheses) from Ar kinetic models in clinoptilolite slabs (high gas concentration).

T(K)	***Slab Thickness 2w(Å)***	$\boldsymbol{\alpha}$	$\boldsymbol{\beta}$ **(ns^{-1})**	$\boldsymbol{M_{film}}$ **(atoms)**	$\boldsymbol{n_{\infty}}$ **(atoms/ Å)**	$\boldsymbol{D}$ **(Å^2/ns)**
250	43.7	2.587 (2.572, 2.602)	0.1192 (0.1183, 0.1201)	42.01 (41.75, 42.26)	1.008	56.91
250	58.6	1.339 (1.333, 1.345)	0.07827 (0.07784, 0.07871)	45.94 (45.63, 46.24)	1.124	67.19
250	73.8	0.7585 (0.7552, 0.7618)	0.102 (0.1015, 0.1025)	36.53 (36.13, 36.94)	1.260	138.88
300	43.7	3.491 (3.472, 3.51)	0.0901 (0.08944, 0.09076)	37.6 (37.4, 37.8)	0.827	43.02
300	58.6	2.221 (2.207, 2.234)	0.06771 (0.06716, 0.06826)	48.83 (48.54, 49.12)	0.801	58.13
300	73.8	1.345 (1.338, 1.352)	0.07113 (0.07069, 0.07158)	49.16 (48.83, 49.49)	0.872	96.85
350	43.7	6.171 (6.135, 6.207)	0.04297 (0.04257, 0.04336)	40.79 (40.66, 40.92)	0.508	20.51
350	58.6	3.115 (3.094, 3.135)	0.0732 (0.07254, 0.07386)	44.52 (44.27, 44.77)	0.645	62.84
350	73.8	2.205 (2.191, 2.219)	0.06302 (0.06247, 0.06356)	49.4 (49.09, 49.71)	0.637	85.81

Table S4. Fitted parameters and 95% confidence intervals (parentheses) from Kr kinetic models used to fit simulated gas loadings in clinoptilolite slabs (high gas concentration).

T(K)	***Slab Thickness 2w(Å)***	$\boldsymbol{\alpha}$	$\boldsymbol{\beta}$ **(ns^{-1})**	$\boldsymbol{M_{film}}$ **(atoms)**	$\boldsymbol{n_{\infty}}$ **(atoms/Å)**	$\boldsymbol{D}$ **(Å^2/ns)**
250	4.4	1.869 (1.864, 1.873)	0.0259 (0.02582, 0.02598)	45.24 (45.12, 45.37)	1.234	12.37
250	5.9	0.9649 (0.9633, 0.9665)	0.01726 (0.01722, 0.01731)	48.09 (47.96, 48.23)	1.319	14.82
250	7.4	0.6007 (0.5998, 0.6016)	0.01483 (0.0148, 0.01486)	48.68 (48.54, 48.81)	1.281	20.19
300	4.4	2.011 (2.007, 2.015)	0.03285 (0.03276, 0.03293)	34.09 (33.98, 34.2)	1.261	15.68
300	5.9	1.12 (1.118, 1.121)	0.02082 (0.02078, 0.02087)	39.18 (39.06, 39.3)	1.295	17.87
300	7.4	0.7084 (0.7072, 0.7096)	0.01934 (0.0193, 0.01939)	39.07 (38.9, 39.23)	1.276	26.33
350	4.4	2.347 (2.341, 2.353)	0.04688 (0.04673, 0.04703)	27.82 (27.69, 27.94)	1.177	22.38
350	5.9	1.39 (1.387, 1.392)	0.02347 (0.02341, 0.02353)	32.58 (32.45, 32.71)	1.195	20.15
350	7.4	0.9198 (0.918, 0.9215)	0.02242 (0.02236, 0.02247)	35.24 (35.08, 35.41)	1.163	30.53

Table S5. Characteristic timescales γ (μs^{-1}) from kinetic models used to fit simulated gas loadings in clinoptilolite slabs (high gas concentration).

Gas	***T* (K)**	**4.4 nm**	**5.9 nm**	**7.4 nm**
Ar	250	17.8	43.7	177.3
	300	7.39	13.73	39.32
	350	1.13	7.54	12.96
Kr	250	7.41	18.54	41.10
	300	8.12	16.60	38.60
	350	8.51	12.15	26.50
Xe	250	0.006	0.039	0.108
	300	0.016	0.054	0.123
	350	0.039	0.123	0.249
Rn	250	0.338	0.098	0.403
	300	0.236	0.089	0.341
	350	0.232	0.079	0.182

Atom types, masses, and charges for clinoptilolite in LAMMPS data file format

units real

Masses

1 28.086 # sz zeolite Si
2 15.9994 # oz zeolite O
3 15.9994 # o* SPC water O
4 39.102 # K
5 1.00797 # h* SPC water H
6 22.99 # Na
7 40.0798 # Ca
8 39.95 # Ar
9 83.80 # Kr
10 131.293 # Xe
11 222.0 # Rn
12 15.999400 # oh zeolite silanol O
13 1.007970 # ho zeolite silanol H

Atoms # full

1	1	1	1.299800	6.703092071	2.825806651	3.058940500	0	0	0 # sz
2	1	2	-0.733300	7.186179122	1.281011288	2.895677400	0	0	0 # oz
3	1	3	-0.820000	0.443236726	14.534976412	7.517279000	0	0	0 # o*
4	1	4	1.000000	5.749371076	3.702454326	8.970500000	0	0	0 # K
5	1	5	0.410000	14.487733424	14.256207043	8.100986293	-1	0	0 # h*
6	1	6	1.000000	1.286945185	0.638136326	8.970500000	0	0	0 # Na
7	1	7	2.000000	2.194336622	7.259788262	0.019999000	0	0	0 # Ca
8	1	8	0.000000	28.56	1.06	8.43	0	0	0 # Ar
9	1	9	0.000000	21.453	16.185	8.507	0	0	0 # Kr
10	1	10	0.000000	12.383	7.145	0.054	0	0	0 # Xe
11	1	11	0.000000	25.509	0.217	0.422	0	0	0 # Rn
12	1	12	-0.777200	51.823	12.912	15.102	0	0	0 # oh
13	1	13	0.410000	52.280	13.126	15.942	0	0	0 # ho

Atom types, masses, and charges for mordenite in LAMMPS data file format

```
units           real

Masses

1  28.086 # sz  zeolite Si
2  15.9994 # oz  zeolite O
3  15.9994 # o*  SPC water O
4  22.99 # Na
5   1.00797 # h*  SPC water H
6 15.999400 # oh zeolite silanol O
7   1.007970 # ho zeolite silanol H

Atoms # full

1     1   1  1.300000     3.553676000     8.756489000     4.031845600   0   0   0 # sz
2     1   2 -0.712500     2.248244000     8.571926000     3.129193600   0   0   0 # oz
3     1   3 -0.820000    18.111000000    14.826561000     2.271674200   0   0   0 # o*
4     1   4  1.000000    36.475945800    10.103798900     3.839279840  -1   0   0 # Na
5     1   5  0.410000     1.497493374    -0.080279899     3.402823501   0   1   0 # h*
6     1   3 -0.767600    15.808864525     8.422441465    50.642987944   0   0   0 # oh
7     1   4  0.410000    15.918548187     9.393552874    50.779020654   0   0   0 # ho
```

van der Waals parameters in LAMMPS format

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pair_coeff      2 4 buck/coul/long 121418 0.2833 3577   # oz K
pair_coeff      2 6 buck/coul/long 121418 0.2469 1501   # oz Na
pair_coeff      2 7 buck/coul/long 121418 0.2469 1501  # oz Ca
pair_coeff      3 3     lj/cut/coul/long        0.1553  3.1690  #       o* o*
pair_coeff      4 4     lj/cut/coul/long        0.1232  3.3320  #       K K
pair_coeff      6 6     lj/cut/coul/long        0.0999  2.5840  #       Na Na
pair_coeff      7 7     lj/cut/coul/long        0.0999  2.5840  #       Ca Ca
pair_coeff      8 8     lj/cut/coul/long        0.2385  3.4050  #       Ar Ar
pair_coeff      9 9     lj/cut/coul/long        0.3378   3.6900  #      Kr Kr
pair_coeff     10 10   lj/cut/coul/long        0.4193   4.1000  #      Xe Xe
pair_coeff     11 11   lj/cut/coul/long        0.5962   4.1700  #      Rn Rn
```

bond stretch and angle bend parameters in LAMMPS format

```
units             real
bond_style      harmonic
angle_style     harmonic
bond_coeff   1     1383.1   1.65 # sz-oz
bond_coeff   2     1383.1   1.65 # sz-oh
bond_coeff   3     553.935  1.0  # oh-ho
bond_coeff   4     553.935  1.0  # o*-h*
angle_coeff  1     298.1    110    # oz-sz-oz
angle_coeff  2     59.6     145    # sz-oz-sz
angle_coeff  3     298.1    110    # oz-sz-oh
angle_coeff  4     24.5     118.5  # sz-oh-ho
angle_coeff  5     45.77    109.47 # h*-o*-h*
```