Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for

Swelling of Different Clay Minerals: Dual Characteristics of K^+ ions and Exploration for Critical Influence Factor

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Table S1. Detailed information for clay systems per unit cell

System	Interlayer ion	Number of charges	Charge location	Chemical formula [a]	Molar mass [a]
1.00O(K^+)	K^+	-1.00	octahedral	$KSi_8Al_3MgO_{20}(OH)_4$	757.100
1.25O(K^+)	K^+	-1.25	octahedral	$K_{1.25}Si_8Al_{2.75}Mg_{1.25}O_{20}(OH)_4$	788.045
1.50O(K^+)	K^+	-1.50	octahedral	$K_{1.5}Si_8[Al_{2.5}Mg_{1.5}]O_{20}(OH)_4$	775.250
1.75O(K^+)	K^+	-1.75	octahedral	$K_{1.75}Si_8Al_{2.25}Mg_{1.75}O_{20}(OH)_4$	784.325
1.00T(K^+)	K^+	-1.00	tetrahedral	$K_1[Si_7Al_1]Al_4O_{20}(OH)_4$	758.700
1.25T(K^+)	K^+	-1.25	tetrahedral	$K_{1.25}[Si_{6.75}Al_{1.25}]Al_4O_{20}(OH)_4$	768.175
1.50T(K^+)	K^+	-1.50	tetrahedral	$K_{1.5}[Si_{6.5}Al_{1.5}]Al_4O_{20}(OH)_4$	777.650
1.75T(K^+)	K^+	-1.75	tetrahedral	$K_{1.75}[Si_{6.25}Al_{1.75}]Al_4O_{20}(OH)_4$	787.125
1.00O(Na^+)	Na^+	-1.00	octahedral	$NaSi_8Al_3MgO_{20}(OH)_4$	741.100
1.75O(Na^+)	Na^+	-1.75	octahedral	$Na_{1.75}Si_8Al_{2.25}Mg_{1.75}O_{20}(OH)_4$	739.075
1.00T(Na^+)	Na^+	-1.00	tetrahedral	$Na_1[Si_7Al_1]Al_4O_{20}(OH)_4$	742.700
1.75T(Na^+)	Na^+	-1.75	tetrahedral	$Na_{1.75}[Si_{6.25}Al_{1.75}]Al_4O_{20}(OH)_4$	741.250

[a] Before hydration.

Table S2. Parameters for the CLAYFF potential [a]

Symbol	Description	q (e)	ε (kcal/mol)	σ (Å)
ao	octahedral aluminum	+1.575	1.3298×10^{-6}	4.7949
st	tetrahedral silicon	+2.1	1.8405×10^{-6}	3.7064
ob	bridging oxygen	-1.05	0.1554	3.5532
oh	hydroxyl oxygen	-0.95	0.1554	3.5532
obos	bridging oxygen with octahedral substitution	-1.1808	0.1554	3.5532
obts	bridging oxygen with tetrahedral substitution	-1.1688	0.1554	3.5532
ohs	hydroxyl oxygen with substitution	-1.0808	0.1554	3.5532
ho	hydroxyl hydrogen	+0.425		
hw	water hydrogen	+0.4100		
ow	water oxygen	-0.8200	0.1554	3.5532
Na	aqueous Na^+ ion	+1.0	0.1301	2.6378
K	aqueous K^+ ion	+1.0	0.1000	3.7423

Bond stretch [b]	k_1 (kcal/mol Å^2)	r_0 (Å)
oh-ho	554.1349	1.0
ow-hw	554.1349	1.0
ohs-ho	554.1349	1.0

Angle bend [c]	k_2 (kcal/mol rad^2)	θ_0 (deg)
hw-ow-hw	45.7696	109.47

[a] q is partial charge, σ is the finite distance at which the inter-particle Lennard-Jones potential approaches zero, and ε is the well depth of Lennard-Jones potential;

[b] k_1 is the harmonic potential constant and r_0 is equilibrium bond length;

c k_2 is the harmonic angle potential and θ is the equilibrium angle.

Table S3. The *d*-spacings (Å) of zero-layer (0W), one-layer (1W) and two-layer (2W) hydration states for the **1.00O(K^+)** systems

Source	Hydration states		
	0W	1W	2W
This work	9.95	12.62	15.91
Ref. 7	9.95		
Ref. 14		12.49	15.61
Ref. 18		12.46	16.30
Ref. 38		12.25	14.75
Ref. 39		12.75	15.0
Ref. 60		12.5	15.3
Ref. 61		12.5	16.0

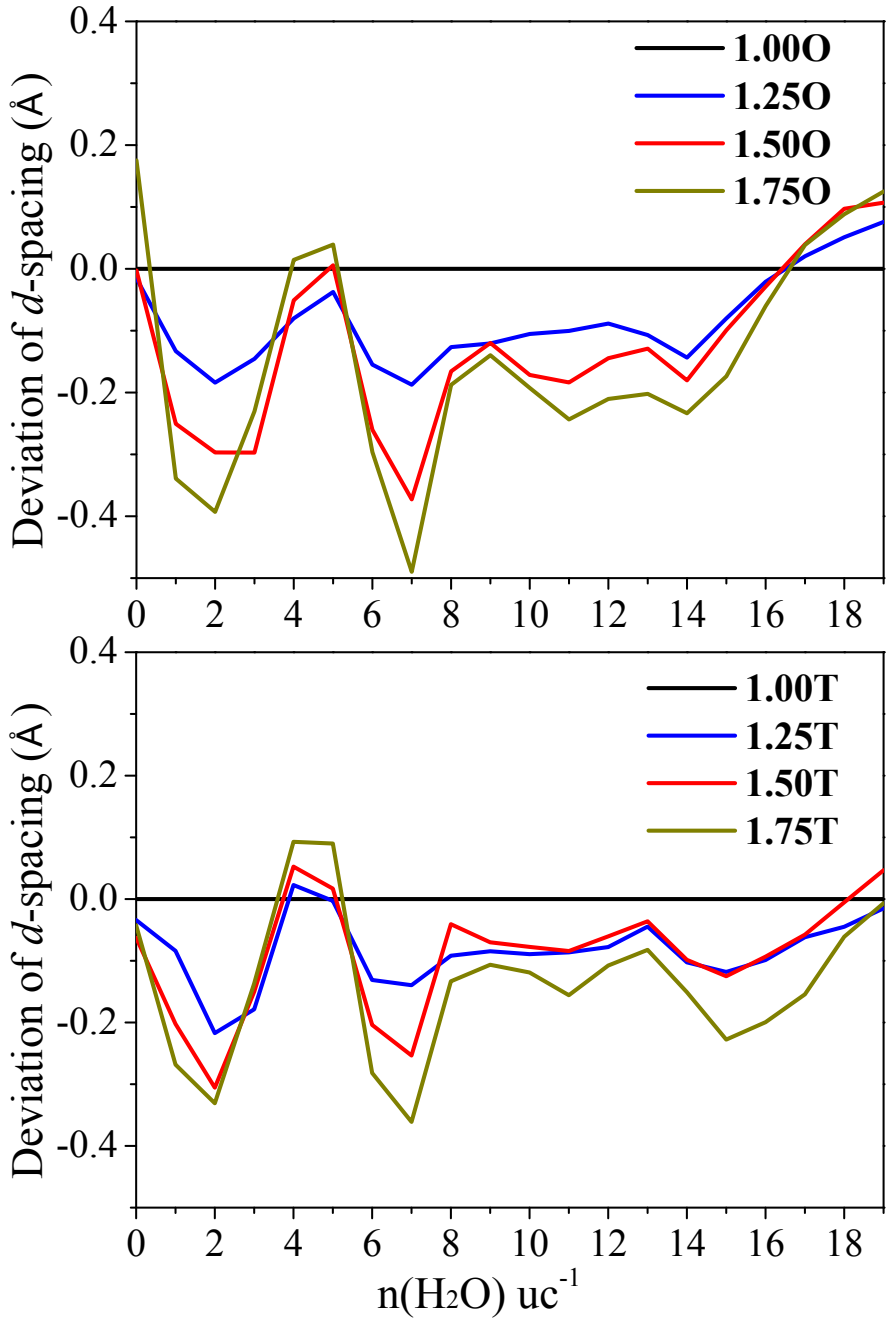

Figure S1. Deviations of the *d*-spacing values for K^+-bearing clay systems from those with 1.00 $e \cdot uc^{-1}$.

The *d*-spacings of 1.00 $e \cdot uc^{-1}$ were set to 0 and used benchmarks.

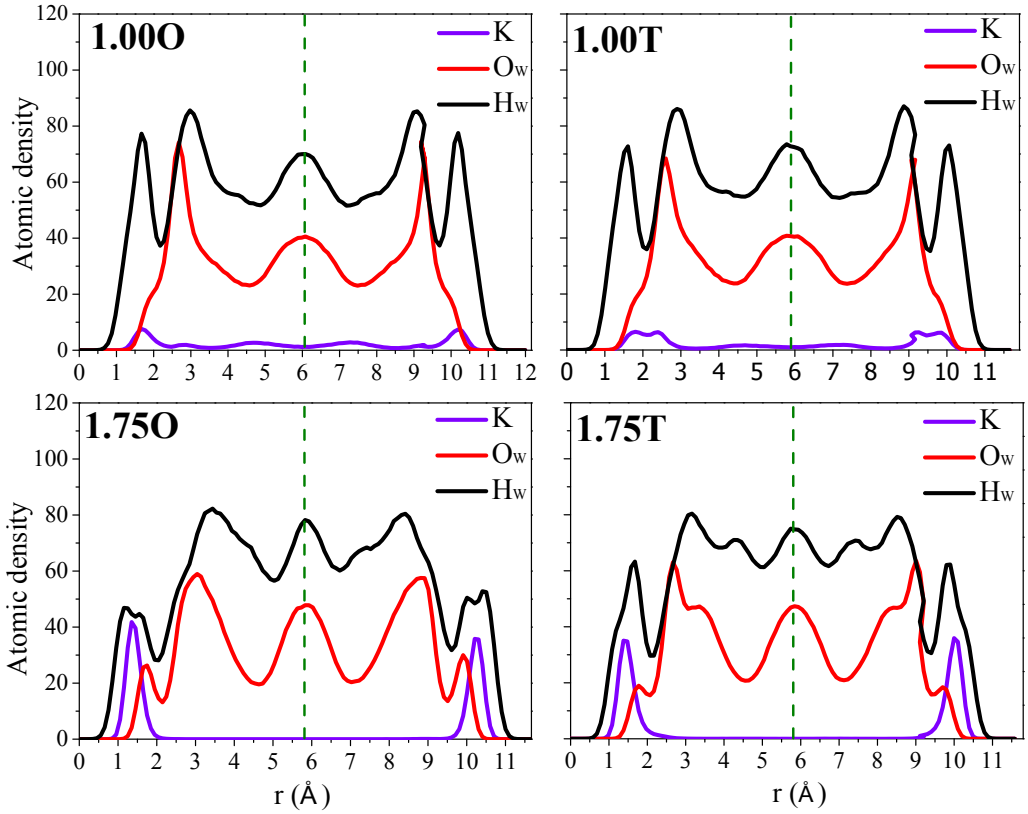

Figure S2. Atomic density profiles of K^+, O_W and H_W for the three-layer hydrated (3W) states of K^+-bearing clay systems.

The central plane of interlayer space is marked in the green dashed line.

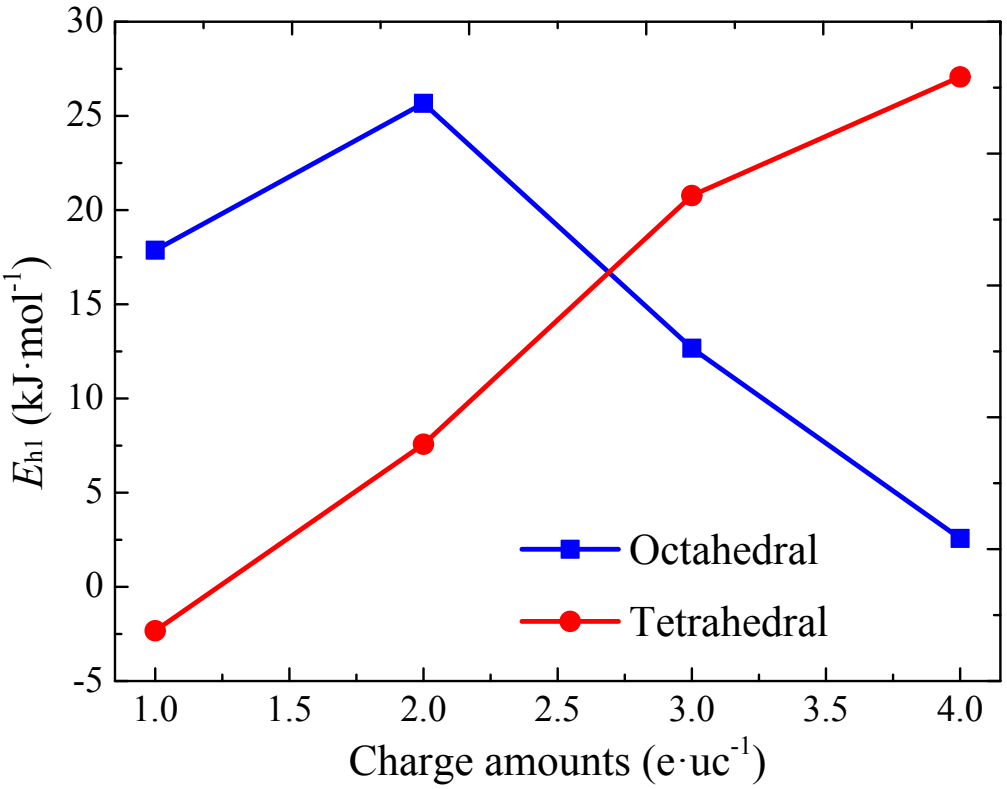

Figure S3. Hydration energies for the first water molecules per unit cell (E_{h1}) for K^+-bearing clay systems, where the charges can be distributed in the octahedral (blue line) and tetrahedral (red line) sheets.

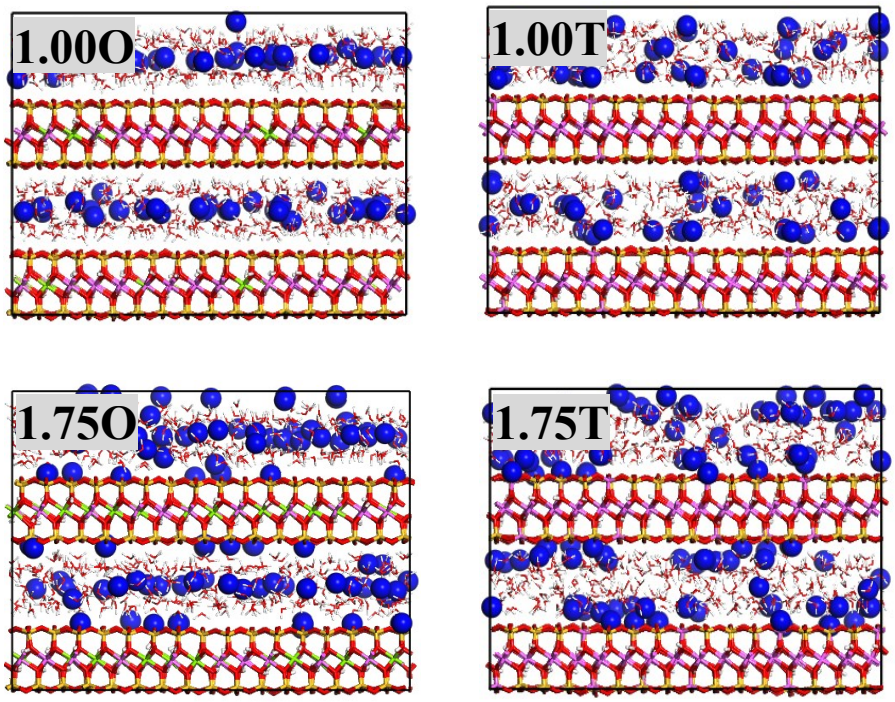

Figure S4. Equilibrium snapshots for the two-layer hydrated (2W) states of Na^+-bearing clay systems, which differ in the number and location of charges as indicated in the legends.

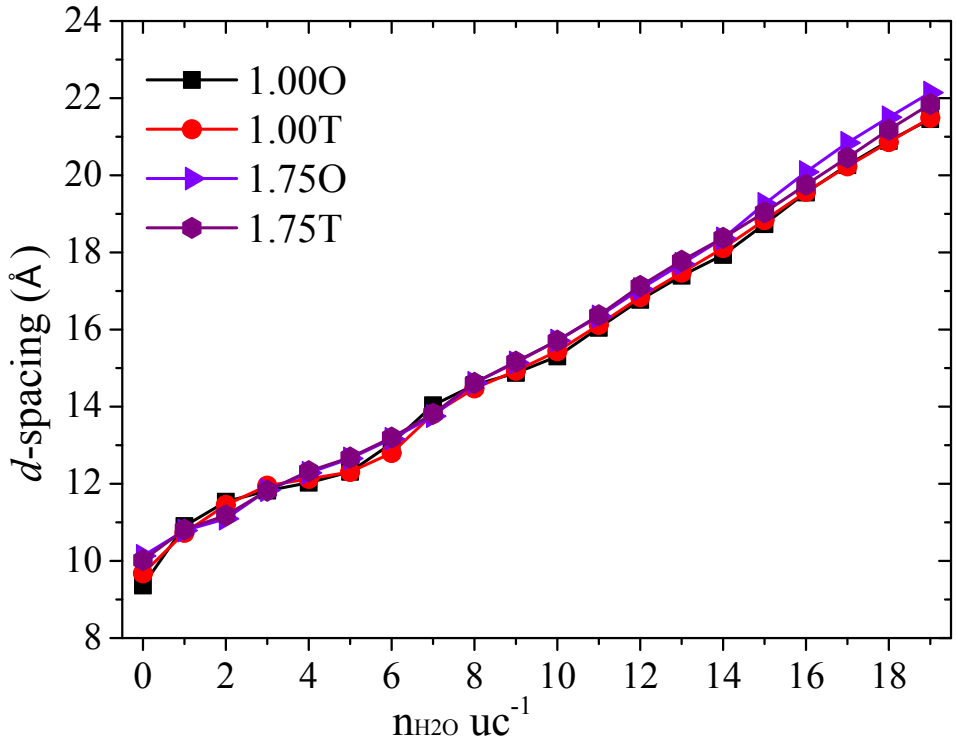

Figure S5. The *d*-spacing curves of Na^+-bearing clay systems as a function of water contents (n_{H2O} uc^{-1}).

The error bars are less than the size of symbols.