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Electronic Supplementary Information

Uranyl Adsorption at Solvated Edge Surfaces of 2:1 Smecites. A Density Functional Study

Alena Kremleva,[a] Sven Krüger,[a] Notker Rösch[b,c,*]

[a] *Department Chemie, Technische Universität München, 85747 Garching, Germany*

[b] *Department Chemie and Catalysis Research Center, Technische Universität München, 85747 Garching, Germany*

[c] *Institute of High Performance Computing, Agency for Science, Technology and Research, 1 Fusionopolis Way, #16-16 Connexis, Singapore 138632, Singapore*

* Corresponding author. Email: roesch@mytum.de, Tel: +49 89 2891 3620, Fax: +49 89 2891 3468

The bulk structures of pyrophyllitic (pyro), beidellitic (beid), and montmorillonitic (montm) models used in the present study are shown in Fig. S1. The optimized lattice parameters are given in Table S1.

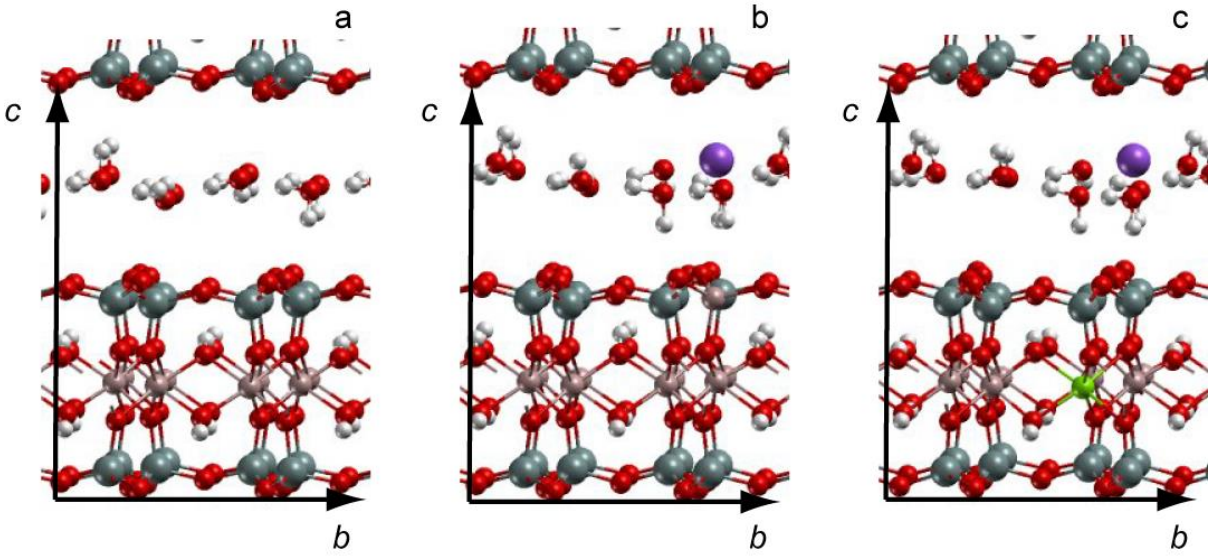

Figure S1. Optimized bulk structures of (a) the neutral pyrophyllitic model with a water interlayer, (b) the beidellitic smectite model with Na^+ counterion and interlayer water, (c) montmorillonitic smectite model with Na^+ counterion and interlayer water. Color coding: red – O, grey – Si, brown – Al, green – Mg, violet – Na, white – H.

Table S1. Optimized lattice parameters of the three models of 2:1 clay minerals used in the present study. The stoichiometric formula of all models is $Na_l(Si_{8-n}Al_n)(Al_{4-m}Mg_m)O_{20}(OH)_4$, lattice vectors are given in pm, angles in degree. The unit cells are monoclinic.

clay	*A*	*b*	*c*	*β*
pyro	1047.7	903.0	1309.2	99.2
beid	1047.6	903.7	1323.4	99.1
montm	1050.8	905.2	1330.6	97.2

The lattice parameters of all three models are very similar, except for the *c* vector that determines essentially the distance between the layers. The neutral pyrophyllitic model exhibits the shortest *c* vector, 1309 pm, as it accommodates only water between the layers. Due to the presence of Na^+ counter ions, the beidellitic and montmorillonitic models exhibit longer *c* vectors, 1323 pm and 1330 pm, respectively.

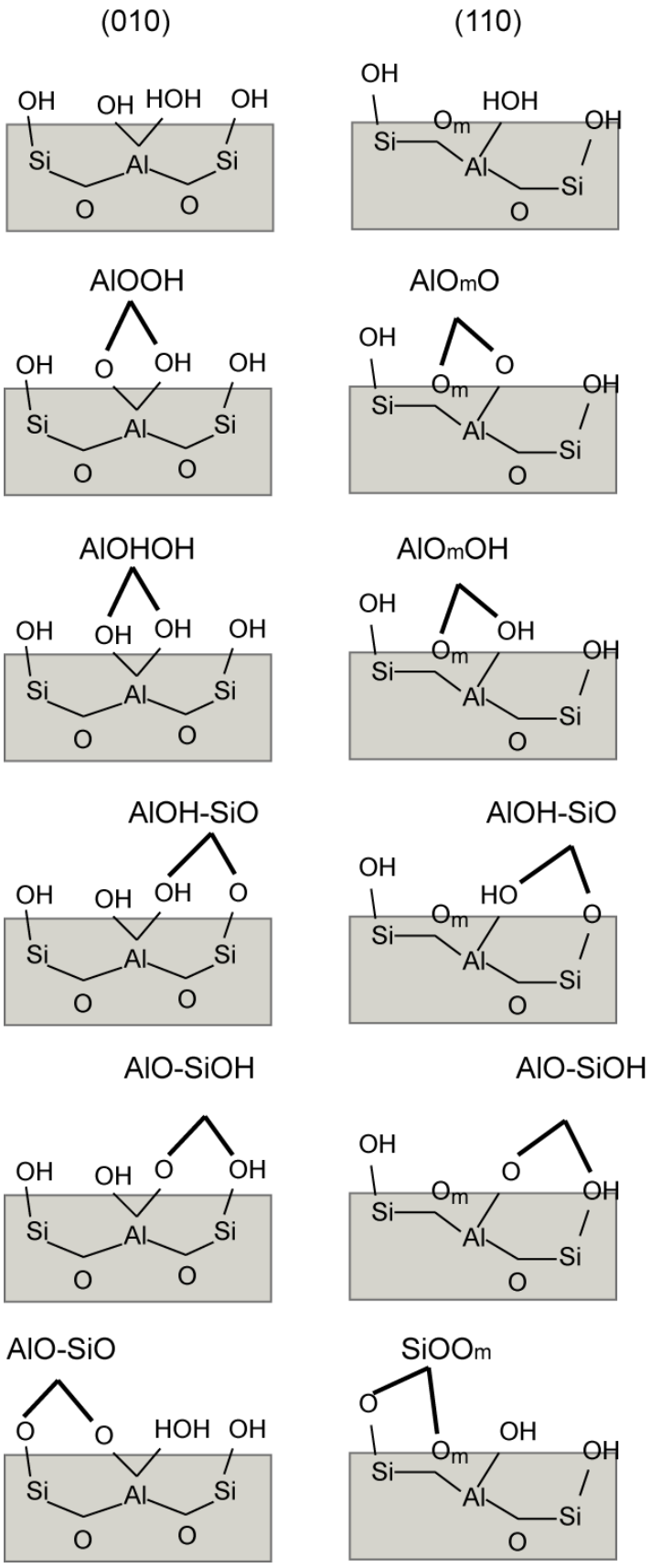

Figure S2. Schematic representations of adsorption sites on the (010) and (110) surfaces of 2:1 clay mineral models.

Table S2. Structural parameters (pm) of uranyl adsorption complexes on various sites of (010) edge surfaces of 2:1 smectites. Average terminal uranyl bond length U-O_t, bond lengths U-O_s to surface oxygen centers, U-OH distance to OH ligands arising from deprotonated aqua ligands, bond lengths U-O_w to aqua ligands, average equatorial U-O bond length U-O_{eq}, U-Al and U-Si distances to the nearest surface Al and Si centers. Formations energies (kJ mol^{-1}) are calculated according to Eq. 1 of the main text.

AlOOH	**UO_2^{2+}**	**Defect**	**U=O**	**U-O_{AlO}**	**U-O_{AlOH}**	**U-OH**	**U-O_w**	**U-O_{eq}**	**U-Mg**	**U-Al**	**U-Si**	**E_{form}**
pyro	5		185	204	239		260, 261, 270	247		325		212
beid	5	Deep	186	203	243		252, 258, 269	245		323		166
	5	surf1	186	203	243		255, 260, 267	246		322		162
	5	surf2	186	203	240		252, 258, 272	245		322		153
montm	5	Deep	188	202	238		246, 258, 261	241		325		133
MgOOH	5	Surf	190	198	232		249, 261, 267	241	326			208
AlOHOH	**UO_2^{2+}**			**U-O_{AlOH}**	**U-O_{AlOH}**							
pyro	5		181	229	236		249, 252, 255	244		344		199
beid	5	deep	182	227	237		247, 252, 257	244		345		189
	5	surf1	183	223	239		247, 249, 261	244		342		142
	5	surf2	182	227	235		246, 252, 261	244		342		264
montm	5	deep	182	227	239		238, 250, 253	241		346		128
MgOHOH	5	surf	183	222	230		241, 257, 260	242	344			182
AlOHOH	**UO_2OH^+**			**U-O_{AlOH}**	**U-O_{AlOH}**							
pyro	5		183	238	239	224	253, 263	243		346		102
beid	5	deep	184	240	240	217	258, 263	244		348		182
	5	surf1	184	239	240	219	256, 261	243		348		152
	5	surf2	184	241	241	216	260, 262	244		349		182
montm	5	deep	185	234	242	217	253, 254	240		349		101
MgOHOH	5	surf	186	230	234	219	258, 258	240	347			175

AlO-SiO	**UO_2^{2+}**	**Defect**	**U=O**	**U-O_{AlO}**	**U-O_{SiO}**	**U-OH**	**U-O_w**	**U-O_{eq}**	**U-Mg**	**U-Al**	**U-Si**	**E_{form}**
pyro	4		189	202	222		246, 256	232		360	339	157
beid	4	deep	187	205	225		240, 247	229		367	332	176
AlO-AlO	4	surf1	189	209	213		242, 249	228		332, 364		206
	4	surf2	187	207	225		239, 244	229		367	336	137
montm	4	deep	187	205	225		244, 254	232		385	340	135
MgO-SiO	4	surf	189	198	228		244, 255	231	391		344	162
AlOH-SiO	**UO_2OH^+**			**U-O_{AlOH}**	**U-O_{SiO}**							
pyro	5		184	246	234	221	239, 268	242		408	349	142
beid	5	deep	185	242	226	218	259, 264	242		387	348	152
	5	surf1	185	242	226	216	259, 264	241		387	349	143
AlOH-AlO	5	surf2	186	244	211	224	261, 274	243		382, 345		204
montm	5	deep	182	251	227	227	250, 273	246		435	364	167
MgOH-SiO	5	surf	183	239	234	226	254, 270	245	435		369	180
AlOH-SiO	**UO_2OH^+**			**U-O_{AlOH}**	**U-O_{SiO}**							
pyro	4		186	235	223	214	248	230		386	340	146
beid	4	deep	184	243	221	217	251	233		396	343	197
	4	surf1	184	244	220	217	251	233		399	344	191
AlOH-AlO	4	surf2	185	250	211	220	256	234		391, 338		180
montm	4	deep	186	235	217	224	243	230		420	351	139
MgOH-SiO	4	surf	186	226	220	224	244	229	422		357	165
AlO-SiOH	**UO_2^{2+}**			**U-O_{AlO}**	**U-O_{SiOH}**							
pyro	4		186	199	254		242, 244	235		385	365	108
beid	4	deep	186	200	244		241, 254	235		368	356	189
	4	surf1	186	199	244		240, 253	234		370	358	175
AlO-AlOH	4	surf2	187	201	231		245, 255	233		368, 353		199
montm	4	deep	186	199	254		242, 244	235		385	365	183
MgO-SiOH	4	surf	187	195	261		241, 246	236	390		373	241

Table S3. Structural parameters (pm) of uranyl adsorption complexes on various sites of (110) edge surfaces of 2:1 smectites. Average terminal uranyl bond length U-O_t, bond lengths U-O_s to surface oxygen centers, U-OH distance to OH ligands arising from deprotonated aqua ligands, bond lengths U-O_w to aqua ligands, average equatorial U-O bond length U-O_{eq}, U-Al and U-Si distances to the nearest surface Al and Si centers. Formations energies (kJ mol^{-1}) are calculated according to Eq. 1 of the main text.

AlO_mO	**UO_2^{2+}**	**Defect**	**U=O**	**U-O_{AlO}**	**U-O_{AlOm}**	**U-OH**	**U-O_w**	**U-O_{eq}**	**U-Mg**	**U-Al**	**U-Si**	**E_{form}**
pyro	5		184	203	266		250, 250, 255	245		328		183
beid	5	deep	185	202	249		258, 258, 264	246		326		185
	5	surf1	185	202	257		255, 256, 262	246		329		227
$AlO_{Al}O$	5	surf2	186	205	232		253, 264, 270	245		314		147
montm	5	deep	187	199	251		247, 257, 277	246		330		233
	4	deep	185	202	235			240		329		212
MgO_mO	4	surf	186	197	238		250, 260	236	332			253
AlO_mOH	**UO_2OH^+**			**U-O_{AlOH}**	**U-O_{AlOm}**							
pyro	5		182	237	268	224	240, 248	243		353		123
beid	5	deep	183	233	259	226	238, 253	242		349		157
	5	surf1	183	230	262	226	239, 256	243		351		200
$AlO_{Al}OH$	5	surf2	184	239	237	229	242, 253	240		336		134
montm	5	deep	181	232	247	226	263, 265	247		352		213
MgO_mOH	5	surf	181	229	238	230	266, 270	247	348			199
SiO_mO	**UO_2OH^+**			**U-O_{SiO}**	**U-O_{SiOm}**							
pyro	5		181	234	261	226	253, 256	246			313	131
beid	5	deep	182	229	251	225	262, 266	247			308	182
	5	surf1	182	232	255	221	261, 265	247			308	182
AlOO	5	surf2	183	220	242	231	270, 270	247		305		167
montm	5	deep	182	225	261	229	246, 277	248			311	221
$SiO_{Mg}O$	5	surf	183	230	241	228	247, 295	248			303	207

AlOH-SiO	**UO_2^{2+}**	**Defect**	**U=O**	**U-O_{AlOH}**	**U-O_{SiO}**	**U-O_w**	**U-O_{eq}**	**U-Mg**	**U-Al**	**U-Si**	**E_{form}**
pyro	5		183	233	216	246, 249, 268	242		392	363	105
beid	5	deep	182	227	218	253, 265, 271	247		393	363	122
AlOH-AlO	5	surf1	184	234	205	257, 267, 273	247		389, 363		159
	5	surf2	181	229	219	251, 256, 268	245		384	362	97
montm	5	deep	183	225	219	247, 261, 273	245		398	359	160
MgOH-SiO	5	surf	184	225	223	244, 256, 267	243	399		369	167
AlOH-SiO	**UO_2^{2+}**			**U-O_{AlOH}**	**U-O_{SiO}**						
pyro	4		183	231	213	241, 242	232		392	359	116
beid	4	deep	183	224	216	241, 263	236		394	360	150
AlOH-AlO	4	surf1	185	230	205	245, 262	236		389, 362		178
	4	surf2	182	226	217	241, 252	234		383	359	68
montm	4	deep	183	226	221	235, 246	232		393	356	175
MgOH-SiO	4	surf	184	223	216	238, 247	231	399		362	173
AlO-SiOH	**UO_2^{2+}**			**U-O_{AlO}**	**U-O_{SiOH}**						
pyro	5		185	200	253	250, 251, 268	244		381	370	142
beid	5	deep	187	198	251	247, 254, 260	242		380	379	139
AlO-AlOH	5	surf1	188	199	237	249, 253, 264	240		380, 374		152
	5	surf2	185	201	259	247, 251, 254	242		380	387	87
montm	5	deep	185	199	258	253, 253, 274	247		382	387	213
MgO-SiOH	5	surf	186	197	263	256, 259, 261	247	391		393	225
AlO-SiOH	**UO_2^{2+}**			**U-O_{AlO}**	**U-O_{SiOH}**						
pyro	4		185	199	245	239, 250	233		387	366	173
beid	4	deep	186	198	245	246, 248	234		380	369	105
AlO-AlOH	4	surf1	187	199	234	250, 250	233		377, 363		158
	4	surf2	186	199	245	246, 247	234		378	367	116
montm	4	deep	185	198	249	251, 251	237		380	379	181
MgO-SiOH	4	surf	186	194	252	251, 255	238		387	384	207