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

Electronic Supplementary Information

for

Insights on structural and dynamical features of water at halloysite interfaces probed by DFT and Classical Molecular Dynamics Simulations.

Davide Presti[1], Alfonso Pedone[1*], Giordano Mancini,[2*] Celia Duce,[3] Maria Rosaria Tinè[3] and Vincenzo Barone[2]

1) *Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio-Emilia, via G. Campi 103, I-41125 Modena, Italy.*
2) *Scuola Normale Superiore di Pisa, Piazza dei Cavalieri 7, I-56126 Pisa, Italy.*
3) *Dipartimento di Chimica e Chimica Industriale, Università di Pisa, via Moruzzi 13, 56124, Pisa, Italy.*

Table S1. Full potential parameters for the ClayFF,[1] employed for both MM and MD calculations. Clay-water interactions were modeled according to the SPC water model.[2]

Non-bond parameters				
Species	*Symbol*	*Charge (e)*	*D_0 (kcal/mol)*	*R_0 (Å)*
water hydrogen	h*	0.4100		
hydroxyl hydrogen	ho	0.4250		
water oxygen	o*	-0.8200	0.1554	3.5532
hydroxyl oxygen	oh	-0.9500	0.1554	3.5532
bridging oxygen	ob	-1.050	0.1554	3.5532
tetrahedral silicon	st	2.100	$1.8405*10^{-6}$	3.7064
octahedral aluminum	ao	1.5750	$1.3298*10^{-6}$	4.7943
Bond Parameters – Bond Stretch				
Species i	*Species j*		*k_1 (kcal/mol Å^2)*	*r_0 (Å)*
o*	h*		554.1349	1.0000
oh	ho		554.1349	1.0000
ohs	ho		554.1349	1.0000
Bond Parameters – Angle Bend				
Species i	*Species j*	*Species k*	*k_2 (kcal/mol rad^2)*	*θ_0 (deg)*
h*	o*	h*	45.7696	109.47
Metal	oh	ho	30.0	109.47
Metal	ohs	ho	30.0	109.47

TABLE S2. Full potential parameters for the PMMCS[3], employed for MM calculations. Clay-water interactions were modeled according to the SPC water model.[2]

Potential parameters – Bond Stretch					
Species/symbol	*Type*	*Charge (e)*	*Dij (eV)*	*Aij (Å^{-2})*	*R_0 (Å)*
Al-O	Morse	1.8/-1.2	0.361581	1.900442	2.164818
Si-O		2.4/-1.2	0.340554	2.006700	2.100000
O-O		-1.2/-1.2	0.042395	1.379316	3.618701
H-O		0.6/-1.2	0.4371659	3.06430	1.245132
Angle Bend					
	r_{12} (Å)	*r_{13} (Å)*	*r_{23} (Å)*	*k_1 (eV/ rad^2)*	*θ_0 (deg)*
Si-O-H	2.0	1.2	3.3	2.4	90.0
Non bond Parameters –Bond Stretch					
Species/symbol	*Type*	*A (kcal/mol)*	ρ (*Å*)	*C (kcal/mol Å^6)*	*R_{min} (Å)*
Si···Owater	Buckingham	1049.880	0.4	0.0	0.0
H···Ow		70.795	0.266200	0.0	0.0
O···Hw		70.795	0.245000	0.0	0.0
O···Ow		2840.780	0.318112	230.924	0.0
Non bond Parameters – H-Bond*					
		A (eV/Å^{12})	*B (eV/Å^{10})*	*r_{HO} Max. (Å)*	*r_{OO} Max.(Å)*
O/Ow-H/Hw···Ow/O		20000	0	3.0	4.0

*: The H-bond interaction is evaluated by using the following formula:

$$U_{Hbond} = \sum_{three-body}^{O-H\cdots O} \left(\frac{A}{r_{OO}^{12}} - \frac{B}{r_{OO}^{10}} \right) cos^4\theta_{O-H\cdots O}$$

where θ is the angle characterizing the H-bond atomic sequence O-H···O. When θ > 90° the energy angular term is that shown in the above equation, whereas it is set to zero when θ < 90°. The symbol is the distance between the two O atoms defining the O-H···O sequence.

Table S3. OH bonds and O(H)···O intermolecular distances, reported in Å. Absolute deviations in parentheses. Atoms labeling as given in Figure 1.

	ClayFF	PMMCS	B3LYP-D* [a]	B3LYP-D* [b]	B3LYP [c]	Exp.[d]
OH1	1.029 (0.054)	0.961 (-0.014)	0.967 (-0.008)	0.971 (-0.004)	0.970 (-0.005)	0.975
OH2	1.029 (0.047)	0.959 (-0.023)	0.961 (-0.021)	0.967 (-0.015)	0.967 (-0.015)	0.982
OH3	1.032 (0.056)	0.961 (-0.015)	0.963 (-0.013)	0.967 (-0.009)	0.968 (-0.008)	0.976
OH4	1.033 (0.058)	0.962 (-0.013)	0.962 (-0.013)	0.966 (-0.009)	0.967 (-0.008)	0.975
O2-O2'	2.908 (-0.180)	2.857 (-0.231)	2.951 (-0.137)	2.940 (-0.148)	3.126 (0.038)	3.088
O3-O3'	2.803 (-0.186)	2.886 (-0.103)	2.879 (-0.110)	2.946 (-0.043)	3.019 (0.030)	2.989
O4-O4'	2.760 (-0.193)	2.817 (-0.136)	2.837 (-0.116)	2.851 (-0.102)	2.964 (0.011)	2.953
Al1-OH1	2.045 (0.125)	2.059 (0.139)	1.942 (0.022)	-	1.926 (0.006)	1.920
Al1-OH2	1.909 (0.060)	1.899 (0.050)	1.863 (0.014)	-	1.862 0.013	1.849
Al1-OH3	1.898 (0.045)	1.907 (0.054)	1.861 (0.008)	-	1.860 0.007	1.853
Al1-OH4	1.878 (0.016)	1.970 (0.108)	1.859 (-0.003)	-	1.856 (-0.006)	1.862
Al2-OH1	2.079 (0.159)	2.072 (0.152)	1.945 (0.025)	-	1.925 0.005	1.920
Al2-OH2	1.890 (0.036)	1.896 (0.042)	1.862 (0.008)	-	1.864 0.010	1.854
Al2-OH3	1.890 (0.023)	1.879 (0.012)	1.853 (-0.014)	-	1.854 -0.013	1.867
Al2-OH4	1.869 (0.015)	1.861 (0.007)	1.853 (-0.001)	-	1.854 0.000	1.854
Si1-O1(oct.)[e]	1.556 (-0.049)	1.586 (-0.019)	1.620 (0.015)	-	1.622 0.017	1.605
Si1-O2'	1.585 (-0.037)	1.587 (-0.035)	1.633 (0.011)	-	1.641 0.019	1.622
Si1-O3'	1.589 (-0.027)	1.589 (-0.027)	1.636 (0.020)	-	1.643 0.027	1.616
Si1-O4'	1.593 (-0.022)	1.599 (-0.016)	1.640 (0.025)	-	1.646 0.031	1.615
Si2-O2(oct.)[e]	1.564 (-0.046)	1.568 (-0.042)	1.617 (0.007)	-	1.619 0.009	1.610
Si2-O2'	1.586 (-0.033)	1.586 (-0.033)	1.632 (0.013)	-	1.640 0.021	1.619
Si2-O3'	1.590 (-0.027)	1.599 (-0.018)	1.639 (0.022)	-	1.646 0.029	1.617
Si2-O4'	1.589 (-0.039)	1.592 (-0.036)	1.635 (0.007)	-	1.642 0.014	1.628

[a]: this work. ; [b]: from Ref.[4] ; [c]: from Ref.[5] ; [d]: from Ref.[6] ; [e]: oxygen shared with the Al octahedral site.

TABLE S4. Radial and angular parameters used in calculating hydrogen bond formation in the **Hal-10** system calculated from radial and angular OH distribution functions.

	r_e (Å)	r_{hw} (Å)	a_e (degrees)	a_{hw} (degrees)
O_{oct} - $H_{oct.}$ – OW [a,]	1.77	0.150	8.50	2.45
O_{oct} – $HW_{.}$ – OW [a]	1.80	0.175	8.50	2.60
O_{oct} - $H_{oct.}$ – OW [b,c]	1.75	0.140	9.50	2.80
O_{oct} – HW – OW[b,c]	1.78	0.160	9.50	2.80
O_{oct} – H_{oct} – OW[b,d]	1.79	0.150	9.50	2.80
O_{oct} – HW – OW[b,d]	1.81	0.155	9.50	2.80
SPC [e]	1.88	0.130	10.3	2.50

[a] upper slab

[b] lower slab

[c] excluding OH4

[d]OH4, lower slab

[e] water molecules between the two slabs

Section S1 Halloysite structure.

The observed average RMSD of the heavy atoms in the Hal-single system reported in Figure S1 spans from a minimum of 0.32 ± 0.011 Å for Si atoms to a maximum of 0.38 ± 0.010 Å for hydroxyl groups located above in the octahedral layer (i.e. the OH2, OH3 and OH4 groups shown in Figure 1a of the main text). In all cases, the RMSD drift is very small (the maximum slope obtained by linear regression was $3.01 \cdot 10^{-6}$ Å/ns for the O-H group), meaning that the clay structure is highly stable in the studied time window, with small oscillations around equilibrium positions (the maximum skewness obtained is 0.6 for bridging oxygen atoms). No local alterations of the clay structure were observed during the simulation; note that only the hydroxyl O-H bond is present in ClayFF, all other interactions being Coulombic or van der Waals.

Comparable results were obtained studying the Hal-10 system, although smaller absolute deviations are present, partially due to the reduced size of the two clay slabs. The results are shown in Figure S2 and no relevant differences are discernible between the upper and lower clay layer. The minimum RMSD is obtained for Si atoms (0.19 Å) atoms and the maximum RMSD for octahedral hydroxyl groups (0.27 Å), i.e. the same relative order as for the Hal-single system. The drift and asymmetries observable in the distribution are negligible.

Figure S3 shows the results obtained for the Hal-10 system using the SPC/E water model. Results are in line with those obtained with SPC: RMSD ranges from 0.190 Å (Si atoms in both slabs atoms) to 0.42 Å (hydroxyl oxygen atoms in the lower slab) with no observable drifts. This small increase in the structural disorder of the lower layer was caused by the partial dislocation of an Al atom and a nearby OH1 group which were shifted upwards by 1.2 Å at the beginning of the simulation and then remained stable in those distorted positions. No other deformation or defects of the halloysite clays were observed during the simulation.

Figure S1. RMSD of Al and Si atoms (upper panel) and hydroxyl (octahedral), bridging or tetrahedral oxygen atoms (lower panel) atoms as a function of time calculated from the Hal-single system. Histograms showing the distribution of RMSD values are reported on the right. "Octahedral" denotes the OH1-OH4 groups, "bridging" denotes the atoms joining the Al and Si layers and "octahedral" denotes the O2', O3' and O4' atoms bound only to Si atoms (see Figure 1 of the main text). Note that in the left panels, the curves are drawn using a running average window five points wide (for clarity reasons) and that the actual width of distributions may be evaluated looking at the histograms on the right.

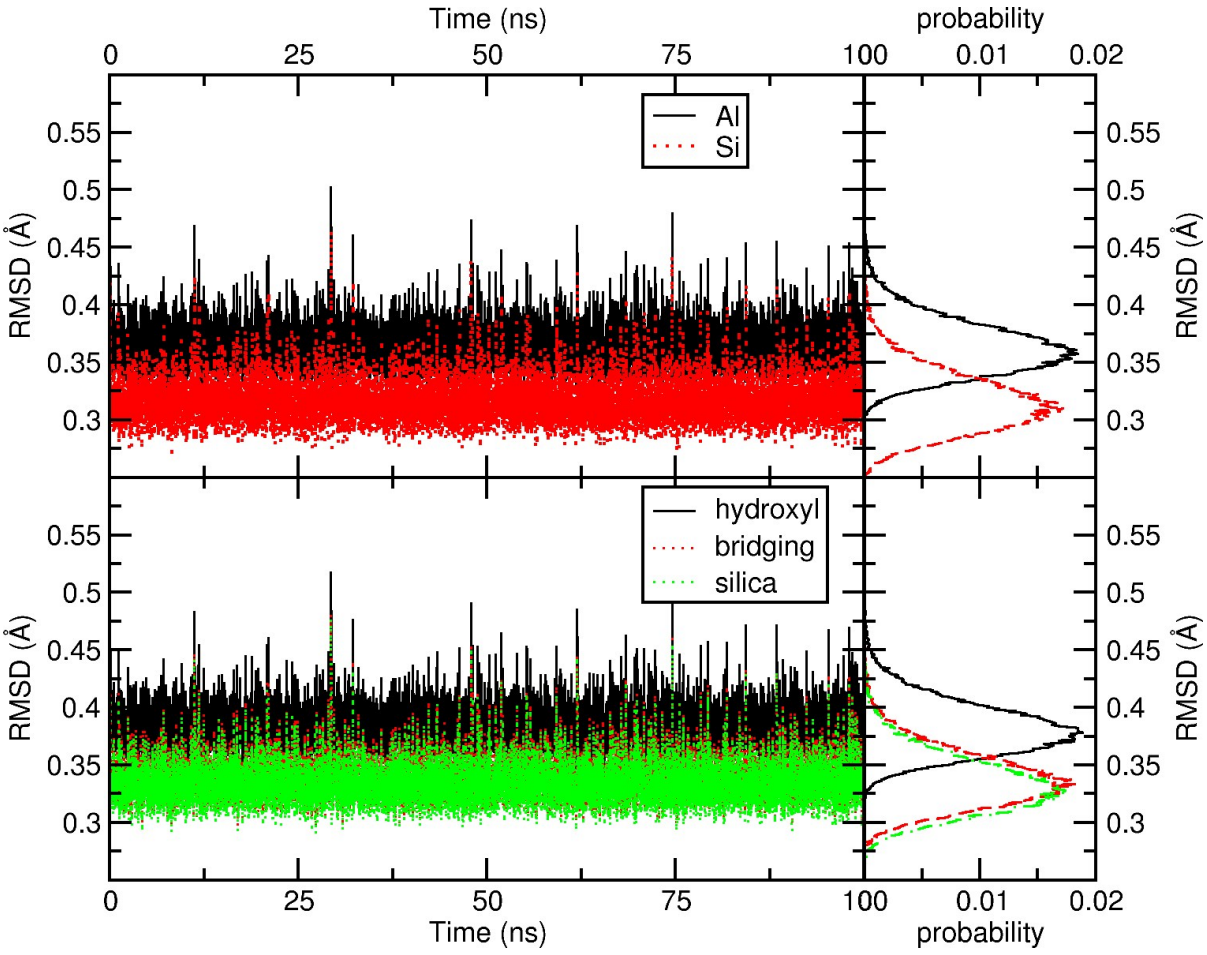

Figure S2. RMSD of Al and Si atoms (upper panel), tetrahedral and bridging (middle panel) and hydroxyl oxygen atoms (lower panel) atoms as a function of time calculated from the Hal-10 system. Note that only the results obtained from the upper panel trajectory are actually shown, while the results for the lower panel are summarized by a green (Al, octahedral and bridging oxygen atoms) or cyan (Si and tetrahedral oxygen atoms) dot-dashed line representing the average value. Histograms showing the distribution of RMSD values are displayed on the corresponding panels on the right, using the same colors.

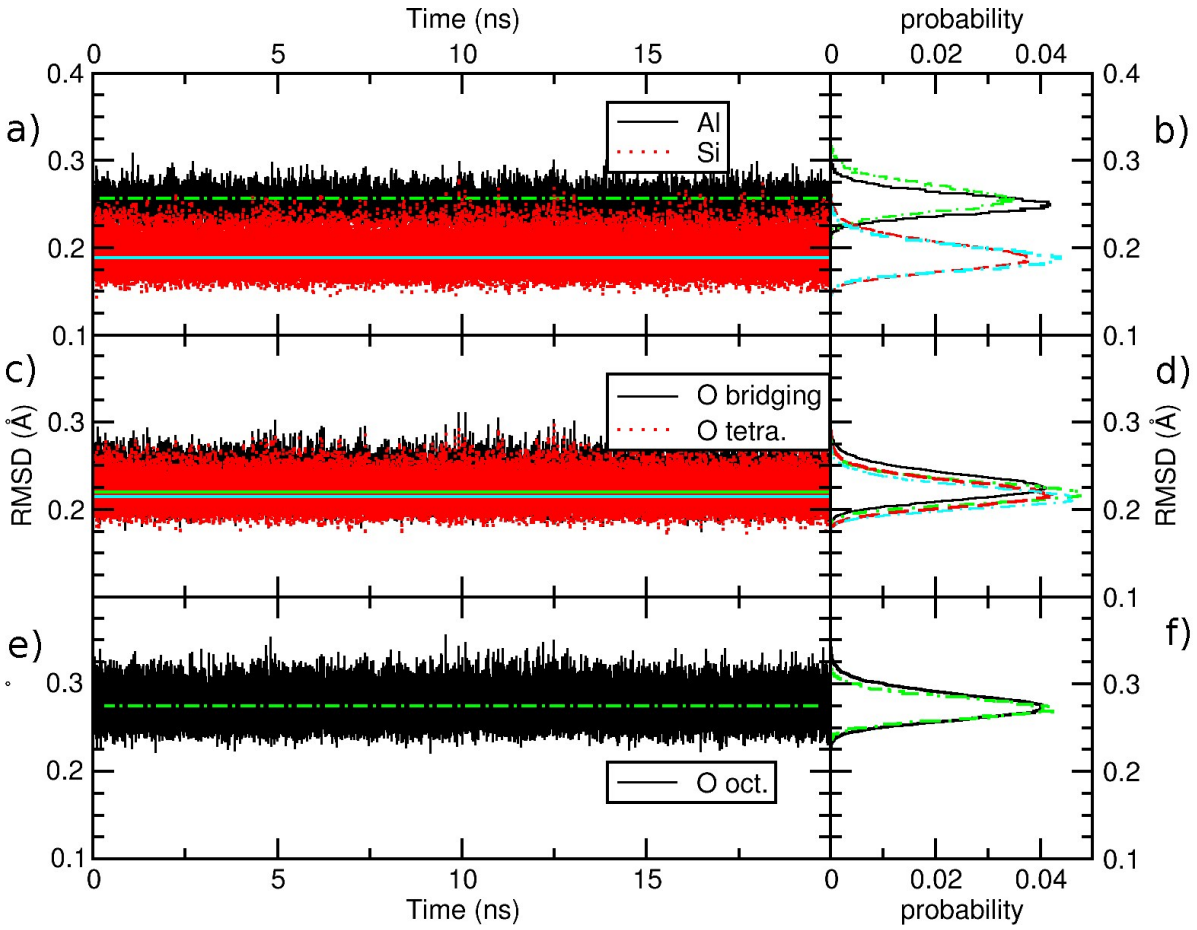

Figure S3. RMSD of Al and Si atoms (upper panel), tetrahedral and bridging (middle panel) and hydroxyl oxygen atoms (lower panel) atoms as a function of time calculated from the Hal-10 system using the SPC/E water model. Note that only the results obtained from the lower panel trajectory are actually shown, while the results for the upper panel are summarized by a green (Al, octahedral and bridging oxygen atoms) or cyan (Si and tetrahedral oxygen atoms) dot-dashed line representing the average value, with the exception of hydroxyl groups in the last panel. Histograms showing the distribution of RMSD values are displayed on the corresponding panels on the right, using the same colours.

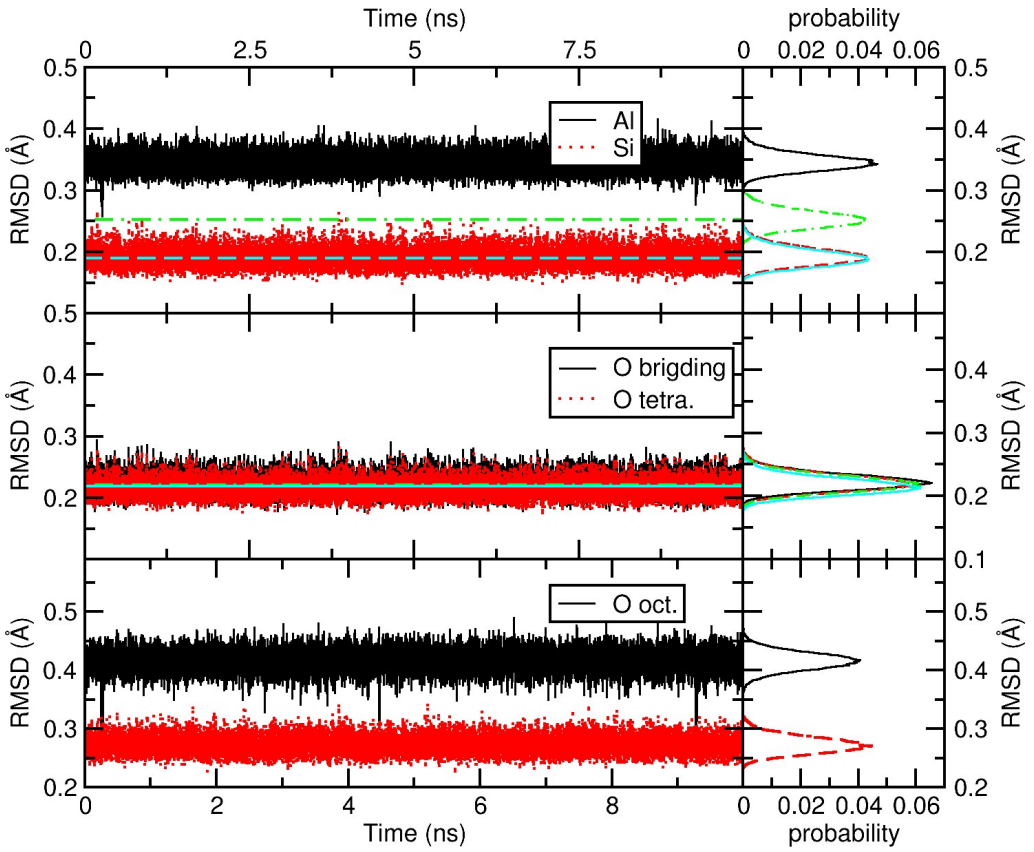

Figure S4. Upper panel: solvent density along the z axis in the Hal-10-SPC/E system. The dashed red line represents the density of SPC/E water (996 g/l), while the dashed green lines show the limits of the upper and lower clay slab. Lower panel: orientation of water molecules in the box. The average cosine of the z axis/ water dipole moment angle is shown.

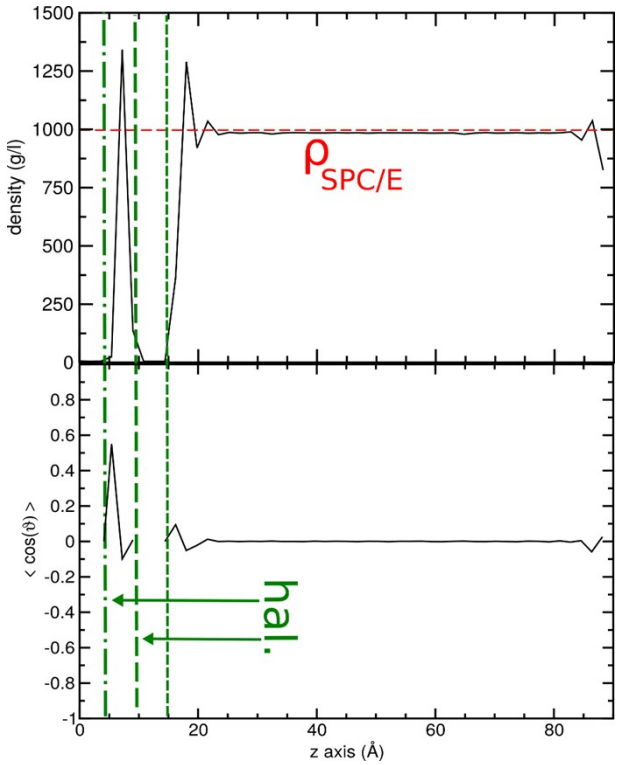

Table S5. Oxygen atom (water) residence times (in ps) for Hal-10 system.

		SPC	**SPC/E**
Lower Slab	Lower Tetrahedral surface	2.68	3.57
	Lower Octahedral surface	18.15	23.48
Upper slab	Upper Tetrahedral surface	17.22	23.14
	Upper Octahedral surface	11.56	16.29
	Water [a]	17.26	21.53
	Water [b]	2.04	2.88
	Water [c]	1.81	2.32

[a] between clay layers

[b] bulk

[c] between water molecules, in the first shell of hydroxyl clay atoms

References

1 R. T. Cygan, J.-J. Liang and A. G. Kalinichev, *J. Phys. Chem. B*, 2004, **108**, 1255–1266.

2 H. J. C. Berendsen, J. P. M. Postma, W. F. van Gunsteren and J. Hermans, in *Intermolecular Forces*, ed. B. Pullman, Springer Netherlands, 1981, pp. 331–342.

3 A. Pedone, G. Malavasi, M. C. Menziani, A. N. Cormack and U. Segre, *J. Phys. Chem. B*, 2006, **110**, 11780–11795.

4 P. Ugliengo, C. M. Zicovich-Wilson, S. Tosoni and B. Civalleri, *J. Mater. Chem.*, 2009, **19**, 2564–2572.

5 S. Tosoni, K. Doll and P. Ugliengo, *Chem. Mater.*, 2006, **18**, 2135–2143.

6 R. B. Neder, M. Burghammer, T. Grasl, H. Schulz, A. Bram and S. Fiedler, *Clays Clay Miner.*, 1999, **47**, 487–494.