Supporting information (Shahsavari et al)

The ClayFF potential:

R.T. Cygan, J.-J. Liang and A. G. Kalinichev, J. Phys. Chem. B **108**, 1255 (2004)

1- Interaction potential functions

The total energy is the sum of Coulombic (electrostatic) interactions, short-range interactions (named as Van der Waals, VDW), and bonded (stretching/angular) interactions:

$$U_{total} = U_{Coul} + U_{VDW} + U_{bond} + U_{angle} \quad (1)$$

For bonded intramolecular interactions, the Coulombic and VDW interactions are excluded. The Coulombic energy is represented as:

$$U_{Coul} = \frac{e^2}{4\pi\varepsilon_0}\sum_{i<j}\frac{q_i q_j}{r_{ij}} \quad (2)$$

where q_i and q_j are partial charges, e is the charge of the electron while ε_0 is the dielectric permittivity of vacuum ($8.85419.10^{-12}$ F/m). Note that the Coulombic interaction is long range and requires techniques such as the Ewald sums (see below) to be properly calculated. The VDW interactions are represented with the conventional 12-6 Lennard-Jones function that includes the short-range repulsion and the attractive dispersion energy:

$$U_{VDW} = \sum_{i<j} D_{ij}\left[\left(\frac{R_{ij}}{r_{ij}}\right)^{12} - 2\left(\frac{R_{ij}}{r_{ij}}\right)^{6}\right] \quad (3)$$

D_{ij} and R_{ij} are empirical parameters derived from the fitting of the Clay-FF model to a number of observed structural property data for oxides, hydroxides and oxy-hydroxides. The interaction parameters between the unlike atoms are calculated according to the arithmetic mean rule for the distance parameter, R_{ij}, and the geometric mean rule for the energy parameter D_{ij}:

$$R_{ij} = \frac{1}{2}\left(R_i + R_j\right) \quad and \quad D_{ij} = \sqrt{D_i D_j} \quad (4)$$

Bond stretching energy is considered between *O* and *H* of either a hydroxyl or a water molecule and is described by a simple harmonic term as:

$$U_{bond} = k_1 \left(r_{ij} - r_0 \right)^2 \qquad (5)$$

where k_1 is a force constant and r_0 represents the equilibrium bond length, both values taken from the flexible version of the SPC water model. To improve the description of the vibrational (librational) motion of hydroxyl groups, a bending (three-body) term is introduced in form of a harmonic relationship:

$$U_{angle} = k_2 \left(\theta_{ijk} - \theta_0 \right)^2 \qquad (6)$$

where k_2 - similar to Eq. (5) - is a force constant, θ_{ijk} is the bond angle for the metal-oxygen-hydrogen, and θ_0 refers to the equilibrium bond angle. The species in the first column of table A3 are considered to be on the vortex of the angle bond (three-body) terms. Finally, in table A4, we have used Eq. (4) for unlike atomic interactions.

2-Parameters for the ClayFF potential

Species	**charge (ē)**	**D_o (Kcal/mole)**	**R_o (Å)**
Water hydrogen (Hw)	0.41	-	-
Hydroxyl hydrogen (Ho)	0.42	-	-
Water oxygen (Ow)	-0.82	0.1554	3.5532
Hydroxyl oxygen (Oh)	-0.95	0.1554	3.5532
Bridging oxygen (O)	-1.05	0.1554	3.5532
Silicon (Si)	2.1	1.84E-06	3.7064
Calcium (Ca)	1.05	5.03E-06	6.2428

Table A1: *nonbonded species potential parameters.*

		k_1 (eV Å^2)	R_o (Å)
Oh	**Ho**	48.0574	1
Ow	**Hw**	48.0574	1

Table A2: *bonded species potential parameters*

			k_2 (eV rad^2)	θ_o (degree)
Ow	**Hw**	**Hw**	3.9694	109.47

Table A3: *three-body potential parameters for harmonic terms.*

		R_{ij} (Å)	D_{ij} (eV)
Ca	**Oh**	4.898	3.83368e-05
Ca	**Ow**	4.898	3.83368e-05
Ca	**O**	4.898	3.83368e-05
Si	**Ow**	3.6298	2.31904e-05
Si	**Oh**	3.6298	2.31904e-05
Si	**O**	3.6298	2.31904e-05
Ca	**Ca**	6.2428	2.18105e-07
Ca	**Si**	3.7064	7.98088e-08
Si	**Si**	4.9746	1.31934e-07

		R_{ij} (Å)	D_{ij} (eV)
Ow	**Ow**	3.5532	0.00673854
Ow	**Oh**	3.5532	0.00673854
Ow	**O**	3.5532	0.00673854
O	**O**	3.5532	0.1554
O	**Oh**	3.5532	0.1554
Oh	**Oh**	3.5532	0.1554

Table A4: *non-bonded Lennard Jones parameters for different interaction types.*

The core-shell potential:

J. D. Gale, J. Chem. Soc. Faraday Trans. **93**, 629 (1997)

1- Interaction potential functions

The core-shell model is based on Born model description for ionic and iono-covalent crystal structures. Point charges interact by means of electrostatic and short range semi-empirical potential functions. An essential ingredient for the transferability of the core-shell approach is the use of formal ionic charges for in-solid species. The electrostatic (Coulombic) interactions are evaluated using the Ewald sum technique expressed by two convergent series in the real and reciprocal space:

$$U_{coul}^{recip} = \frac{2\pi}{V}\sum_{G}\frac{\exp\left(-\frac{G^2}{4\eta}\right)}{G^2}\sum_{i}\sum_{j} q_i q_j \exp\left(-i\vec{G}\cdot\vec{r}_{ij}\right) \quad (7)$$

$$U_{coul}^{real} = \frac{1}{2}\sum_{i}\sum_{j}\frac{q_i q_j erfc\left(\eta^{1/2} r_{ij}\right)}{r_{ij}} \quad (8)$$

where *erfc* is the complementary error function, r_{ij} the distance between two atoms *i* and *j*, *G* a reciprocal space vector ($G \neq 0$), q_i the ionic charge of atom *i*. *V* is the volume of the unit cell and η a parameter that controls the division of work between real and reciprocal spaces. Note that *(i)* the total electrostatic energy now refers to the ionic self-energy given by $U_{self} = -\sum_{i=1}^{N} q_i^2 \left(\frac{\eta}{\pi}\right)^{1/2}$ that is constant in canonical conditions (fixed number *N* of ions); *(ii)* the choice of η controls the number of *G* vectors to be chosen for a given convergence accuracy; here set to 10^{-5} eV. In modeling oxygen in silicate materials, electronic polarizability effects are taken into account by splitting the anion into two entities: a core and a massless shell, the (formal) ionic charge (*qt*=*qs*+*qc*) being shared between these two species. The core and the shell interact *via* a harmonic oscillator with a spring constant K_{cs}. The shell polarizability is then expressed by:

$$Y = \frac{q_s^2}{\left(K_{cs} + F_s\right)} \quad (9)$$

where F_s is a force acting on the shell and due to the local environment. During energy minimization process, the shell is allowed to relax relatively to its core, creating a local instantaneous dipole mimicking ion polarizability. Thus far, the explicit inclusion of polarization in the core-shell approach is the main difference with core-only potential based-model such as ClayFF. The short range interactions are described by a Buckingham potential which gathers an exponential repulsive and an attractive dispersive term (analogous to U_{VDW} in ClayFF) :

$$U_{short} = \sum_{i<j} A_{ij} \exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6} \qquad (10)$$

The energy contribution of this term is summed up within a predetermined cutoff R_{max} set to 12 Å throughout this work. A_{ij}, ρ_{ij} and C_{ij} are adjustable parameters. When using formal ionic charges in the case of iono-covalent systems such as silicates, a three body harmonic term has to be considered in order to mimic the correct angle O-Si-O distribution (see Eq. (6)). As tobermorite is a hydrous calcium-silicate, the O-H covalent interaction is simulated by a so-called Morse analytical form (analogous to U_{bond} in ClayFF, see Eq. (5)):

$$U_{Morse} = \sum_{i<j} D\left[\left[1 - \exp\left(-\alpha\left(R - R_0\right)\right)\right]^2 - 1\right] \qquad (11)$$

where R_0 is the equilibrium position, D the potential well depth and α its width. All potential parameters used in this work are taken from the literature and are reported in Tables A5-A10. These parameters are optimized to describe simple crystalline mineral oxides and their surface and water adsorption properties. No further fitting to tobermorite properties was attempted in this work. Thus the results presented here are predictions for the used potential models and related parameters. Note that in tables A5 to A10 in supporting information, Cw is the interlayer calcium species, Ow and Hw are components of water, Oh corresponds to layer oxygen linked to a H. « Buck », « Lennard », and « Morse » stands for Buckingham, Lennard-Jones and Morse potential functions as given above. « Three » means three-body interaction on the form of a harmonic bending term. “Inter/intra” marks the difference between inter and intra atomic potentials: when a pair of atoms is defined as chemically bonded, the electrostatic

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Coulombic interaction is not calculated between them unless otherwise specified (this is the case of H_2O).

2-parameters for the core-shell model

	Charge (ē)		
species	**Core**	**Shell**	**core-shell (eV Å^2) coupling constant**
Ca	+2		
Si	+4		
H	+0.426		
$Oh^{-0.8}$	+0.869020	-2.29502	74.92
O^{-2}	+0.869020	-2.86902	74.92
$Ow^{-0.8}$	+1.25	-2.05000	209.45
Hw	+0.4		
Cw	+2		

Table A5: *Coulombic interaction parameters.*

Analytic form	**Inter / intra**	**Species 1**	**species 2**	**A (eV)**	**ρ (Å)**	**C_6 (eV Å^6)**	**R_{min} (Å)**	**R_{max} (Å)**
Buck	inter	Cw core	Ow shell	777.27	0.34370	0.00000	0.0	12.0

Table A6: *short range interaction parameters for water-interlayer Ca.*

Analytic form	**Inter / intra**	**species 1**	**species 2**	**A (eV)**	**ρ (Å)**	**C_6 (eV Å^6)**	**R_{min} (Å)**	**R_{max} (Å)**
Buck	inter	Cw core	O shell	1090.4	0.34370	0.00000	0.0	12.0
Buck	inter	Cw core	Oh shell	1090.4	0.34370	0.00000	0.0	12.0

Table A7: *short range interaction parameters for O_h-interlayer Ca.*

Analytic form	**Inter / intra**	**species 1**	**species 2**	**A (eV)**	**ρ (Å)**	**C_6 (eV Å^6)**	**R_{min} (Å)**	**R_{max} (Å)**
Buck	inter	Ca core	O shell	1090.4	0.34370	0.00000	0.0	12.0
Buck	inter	Ca core	Oh shell	777.27	0.34370	0.00000	0.0	12.0
Buck	inter	Si core	O shell	1283.9	0.32052	10.66158	0.0	12.0
Buck	inter	Si core	Oh shell	983.50	0.32052	10.66158	0.0	12.0
Buck	inter	O shell	O shell	22764.	0.14900	27.87900	0.0	12.0
Buck	inter	O shell	Oh shell	22764.	0.14900	13.94000	0.0	12.0
Buck	inter	Oh shell	Oh shell	22764.	0.14900	6.97000	0.0	12.0
Buck	inter	H core	O shell	311.97	0.25000	0.00000	0.0	12.0
Analytic form	**Inter / intra**	**species 1**	**species 2**	**D (eV)**	**α (Å-1)**	**R_0 (Å)**	**R_{min} (Å)**	**R_{max} (Å)**
Morse	inter	H core	Oh shell	7.0525	3.1749	0.9428	1.0	1.4

Analytic form	**Inter / intra**	**species 1**	**species 2**	**species 3**	**κ_2 (eV rad-2)**	**θ_0 (°)**	**R_{max}^{1-2} (Å)**	**R_{max}^{1-3} (Å)**	**R_{max}^{2-3} (Å)**
Three	inter	Si core	O shell	O shell	2.0972	109.47	1.8	1.8	3.2
Three	inter	Si core	O shell	Oh shell	2.0972	109.47	1.8	1.8	3.2

Table A8: *short range interaction parameters for tobermorite.*

Analytic form	**Inter / intra**	**species 1**	**species 2**	**A ($eV Å^{12}$)**	**B ($eV Å^{6}$)**	**R_{min} (Å)**	**R_{max} (Å)**
Lennard	inter	Ow shell	Ow shell	39344.98	42.1500	0.0	12.0

Analytic form	**Inter / intra**	**species 1**	**species 2**	**A (eV)**	**ρ (Å)**	**C_6 (eV $Å^6$)**	**R_{min} (Å)**	**R_{max} (Å)**
Buck	inter	Hw core	Ow shell	396.27	0.25000	0.00000	0.0	12.0

Analytic form	**Inter / intra**	**species 1**	**species 2**	**D (eV)**	**α ($Å^{-1}$)**	**R_0 (Å)**	**R_{min} (Å)**	**R_{max} (Å)**
Morse	intra	Hw core	Ow shell	6.203713	2.22003	0.92376	1.0	1.4

Analytic form	**Inter / intra**	**species 1**	**species 2**	**species 3**	**κ_2 ($eV rad^{-2}$)**	**θ_0 (°)**	**R_{max}^{1-2} (Å)**	**R_{max}^{1-3} (Å)**	**R_{max}^{2-3} (Å)**
Three	intra	Ow shell	Hw core	Hw core	4.19978	108.69	1.2	1.2	1.8

Table A9: *short range interaction parameters for water molecule.*

Analytic form	**Inter / intra**	**species 1**	**species 2**	**A (eV)**	**ρ (Å)**	**C_6 (eV $Å^6$)**	**R_{min} (Å)**	**R_{max} (Å)**
Buck	inter	Ca core	Ow shell	777.27	0.34370	0.00000	0.0	12.0
Buck	inter	Si core	Ow shell	983.556	0.32052	10.66158	0.0	12.0
Buck	inter	H core	Ow shell	311.97	0.25000	0.00000	0.0	12.0
Buck	inter	O shell	Ow shell	22764.0	0.14900	13.94000	0.0	12.0
Buck	inter	Oh shell	Ow shell	22764.0	0.14900	6.97000	0.0	12.0
Buck	inter	O shell	Hw core	311.97	0.25000	0.00000	0.0	12.0
Buck	inter	Oh shell	Hw core	311.97	0.25000	0.00000	0.0	12.0

Table A10: *short range interaction parameters for water molecule and tobermorite.*

The CSH-FF parameters (a re-parametrized version of ClayFF for calcio silicate):

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Species	charge (ē)
Water hydrogen (Hw)	0.41
Water oxygen (Ow)	-0.82
Oxygen (formally carrying a H atom) (Oh)	-1.00
Bridging oxygen (O)	-1.14
Silicon (Si)	1.72
Calcium (Ca)	1.43
Calcium (Cw)	1.70
Hydrogen (H)	0.29

Table A11: *Partial charges for the CSH-FF force field.*

		D_{ij} (eV)	R_{ij} (Å)
Ca	O	0.3773E-04	4.8980
Ca	Oh	0.3055E-04	6.1250
Cw	O	0.6331E-04	4.8980
Cw	Oh	0.4510E-04	4.9866
Si	O	0.2433E-04	3.6716
Si	Oh	0.2579E-04	3.6627
O	O	0.5392E-01	3.0687
Oh	Oh	0.2684E-02	3.8652
O	Oh	0.1975E-02	4.0654
Si	Ow	0.2299E-04	3.6298
Ca	Ow	0.3802E-04	4.8980
Cw	Ow	0.2617E-04	5.0168
O	Ow	0.2278E-03	4.7557
Oh	Ow	0.3775E-01	3.2513

Table A12: *Non-bonded Lennard-Jones parameters for different interaction (CSH-FF).*