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THE STATE OF HYDRATION OF Ca-EXCHANGED MONTMORILLONITE AT A DEPTH OF 2–2.7 KILOMETERS

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Abstract

Monte Carlo simulations in $NP_{zz}T$ and μVT ensembles of the hydration of Ca-saturated Wyoming-type montmorillonite show that one-layer Ca-exchanged montmorillonite hydrate with a d_{001} of 12.11 Å is stable at 353 K, 300 bar, and –7.21 kcal/mol potential. Two- and three-layer hydrates do not appear stable. At 353 K and 625 bar, the one-layer hydrate is nearly stable. In the interlayer space, molecules of H_2O are clustered on the interlayer midplane, alternatively oriented with their protons toward the siloxane surfaces on both sides and on the midplane. The Ca^{2+} cations are solvated, in outer-sphere coordination, and located 2.77 Å from the H_2O molecules. In sedimentary basins under normal geotherms, one-layer Ca-exchanged montmorillonite is the single hydrate stable at 2 km depth. In overcompacted sediments at 2.7 km depth, the hydrate could be unstable.

Keywords: Ca-exchanged montmorillonite, relation with depth, simulated clay, stability relations.

Sommaire

Des simulations Monte Carlo de l'état d'hydratation de la montmorillonite de type Wyoming, utilisant les ensembles $NP_{zz}T$ and μVT, montrent que la montmorillonite hydratée à une couche, saturée en Ca et ayant une valeur d_{001} de 12.11 Å, est stable à 353 K, 300 bar, et à un potentiel de –7.21 kcal/mol. Les hydrates à deux ou trois couches ne semblent pas stables. A 353 K et 625 bar, la forme hydratée à une couche est presque stable. Dans l'espace interfoliaire, les molécules de H_2O sont agglomérées sur le plan mitoyen, orientées alternativement de sorte que leurs protons sont orientés vers les surfaces des groupes siloxane aux deux côtés et sur le plan mitoyen. Les cations Ca^{2+} sont solvés, en coordinence avec les sphères externes, et situés à 2.77 Å des molécules de H_2O. Dans les bassins sédimentaires ayant un gradient géothermique normal, la montmorillonite saturée en Ca à une couche serait le seul hydrate stable à une profondeur de 2 km. Dans les sédiments surcompactés à une profondeur de 2.7 km, cet hydrate pourrait s'avérer instable.

(Traduit par la Rédaction)

Mots-clés: montmorillonite saturée en Ca, relation avec la profondeur, argile simulée, relations de stabilité.

Introduction

The adsorption of water and chemical species by expandable clay minerals is important in diagenetic, metamorphic, petrological and geochemical processes (Huggett & Shaw 1993), in soil physics, pedology (Aylmore & Quirk 1967), in stability, retention and transport of contaminants (Cotter-Howells & Patterson 2000), waste management (Rutherford *et al.* 1980), in oil exploration and recovery, borehole stability (Hall 1993, Hall *et al.* 1986), adsorption of stabilizing additives and polymers, overpressure, and migration of hydrocarbons (Hall 1993). The hydration and dehydration of expandable clay minerals result in adsorption or separation of fluids and chemical species that affect contamination, rock strength, pore pressure, swelling,

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[§] *E-mail address*: liberto@servidor.unam.mx and the overall stability of the clay systems. Their interactions with fluids are of particular interest to soil stabilization and, in petroleum-rich basins, to the quality of the reservoir and the recovery of petroleum.

In this study, we have investigated the hydration of Ca-exchanged Wyoming-type montmorillonite by Monte Carlo simulations. This clay is a 2:1 expandable mineral that swells upon contact with water. This expansion is well known from experimental studies (Bray *et al.* 1998, Bray & Redfern 1999, 2000, and references therein) at ambient conditions of 300 K and 1 bar. These have shown that the hydration of the anhydrous phase having a d_{001} value of 9.55–9.96 Å swells the structure to a 11.19–12.45 Å one-layer hydrate, to a 15.00–15.50 Å two-layer hydrate, and to a 18.0–19.1 Å three-layer hydrate. Monte Carlo simulations (Chávez-Páez *et al.* 2001a) have shown that at those conditions, stable 9.82, 12.20, 14.70, and 18.4–19.0 Å anhydrous, one-, two-, and three-layer hydrates are formed. However, the characteristics and stability of Ca-exchanged montmorillonite at conditions other than atmospheric ones have been only rarely described (Khitarov & Pugin 1996, Koster von Groos & Guggenheim 1987, 1989, Siqueira *et al.* 1997, 1999, Stone & Rowland 1955, Wu *et al.* 1997).

The parent montmorillonite (Na-dominant) has been shown from simulation studies to form the stable monolayer hydrate at 353 K and 625 bar (de Pablo *et al.* 2004, Chávez *et al.* 2004). These conditions are particularly significant, as they are equivalent to a depth of 2.7 km in sedimentary basins, where sediments can be under normal compaction or overcompacted, fluids are adsorbed or desorbed from minerals, mineral transformations may occur, and low-depth gas and oil accumulations exist. The behavior of the clay sediments at these conditions will depend on their mineralogy, the adsorbed fluids and chemical species, and on the environment. Its characterization requires a knowledge of the properties of montmorillonite. Molecular simulations are particularly powerful, considering their applicability to *in situ* environments that otherwise are difficult to reproduce experimentally.

The characteristics and behavior of Ca-exchanged montmorillonite at low depths have not been described. In the present study, the stability and swelling of Wyoming-type Ca-exchanged montmorillonite are investigated by Monte Carlo simulations at constant stress in the isobaric–isothermal $NP_{zz}T$ ensemble and at constant chemical potential in the grand canonical μVT ensemble, for basin conditions of temperature 333–353 K and pressure in the range 300–625 bars.

METHODOLOGY

The hydration of Ca-saturated montmorillonite is studied by Monte Carlo simulation in the $NP_{zz}T$ and μVT ensembles (Allen & Tildesley 1987), at 333 K and 300 bar. Such conditions are equivalent to a depth of 2 km in a sedimentary basin (thermal gradient of 30°C/km, lithostatic gradient 150 bar/km) or to a depth of 2.7 km (353 K and 625 bar) where the sediments are overcompacted or overpressurized (*e.g.,* geotherms at the Gulf of Mexico, Hower *et al.* 1976).

The simulations employ the model and approach described by Chávez-Páez *et al.* (2001b). The clay considered is the Ca-saturated Wyoming-type montmorillonite with composition $(Si_{7.75}Al_{0.25})(Al_{3.50}Mgrr_{0.50})O_{20}(OH)_4Ca_{0.375}\bullet nH_2O$ and charge of 0.75, 33% of which originates from the sheet of tetrahedra. Eight unit-cells form the 320-atom simulation cell, measuring 21.12 Å in the *x* dimension, 18.28 Å in the *y* dimension, and 6.56 Å in the *z* dimension. The positions and charges of the atoms in the unit cell are those of pyrophyllite (Skipper *et al.* 1995), with replacement in the simulation cell of octahedrally coordinated Al^{3+} at positions (–3.52, –3.05,0), (7.04,–3.05,0), (–3.52,6.09,0), and (7.04,6.09,0) by Mg^{2+}, and of Si^{4+} at positions (2.64,1.52,2.73) and (0.88,1.52,–2.73) by Al^{3+}.

The interaction energy between atoms is defined by Equation 1, which includes the Coulomb and Lennard–Jones contributions. Chávez-Páez *et al.* (2001a) simulated the interaction energy from Equation 2, which combines the model of Skipper *et al.* (1995a, 1995b), for the clay – water system and the TIP4P model of water of Jorgensen *et al.* (1983). In this equation, the first term of the summation represents the Coulomb contribution, whereas the remaining terms correspond to the Lennard–Jones contribution, m_i and m_j are the number of sites in molecules *i* and *j*, q_{ia} is the charge at site *a* of molecule *i*, q_{jb} is the charge at site *b* of molecule *j*, r_{iajb} is the distance between atom *a* in molecule *i* and atom *b* in molecule *j*. The parameters *A*, *B*, *C*, *D*, *E*, *F*, and *G* are site-specific and developed to describe the interaction between calcium and TIP4P water. In the present case, the parameters of Bounds (1985) (Table 1) are used.

$$U_{ij} = U_{ij}^{Coul} + U_{ij}^{LJ} \tag{1}$$

$$U_{ij} = \sum_{a=1}^{m_i}\sum_{b=1}^{m_j}\left|\begin{array}{l} \dfrac{q_{ia}\bullet q_{jb}}{r_{iajb}} - A_{isjb}\bullet e^{-B_{iajb}\bullet r_{iajb}} \\ + C_{iajb}\bullet e^{-D_{iajb}\bullet r_{iajb}} \ldots \\ + \dfrac{E_{iajb}}{\left(r_{iajb}\right)^{12}} - \dfrac{F_{iajb}}{\left(r_{iajb}\right)^{6}} - \dfrac{G_{iajb}}{\left(r_{iajb}\right)^{4}} \end{array}\right| \tag{2}$$

In a constant-stress simulation, $NP_{zz}T$, the stress P_{zz} normal to the clay surface, the temperature *T*, and the number of molecules *N* are kept constant. The system is allowed to sample the configuration space through molecular displacements and volume fluctuations. Volume fluctuations are allowed only in the direction normal to the clay surface. The acceptance probability of a new configuration *n* generated from a configuration *m* by displacing an atom or by changing the volume of the simulation box is given by Equation 3,

$$P_{acc} = \min\left(1, \exp\left(-\beta \cdot \left| \begin{array}{l} \Delta U_{nm} + P_{zz} \cdot \Delta V_{nm} \\ -\dfrac{N}{\beta} \cdot \ln\left(\dfrac{V_n}{V_m}\right) \end{array} \right| \right)\right) \tag{3}$$

where ΔU_{nm} is the energy gradient, ΔV_{nm} is the difference in volume, and V_n and V_m are the corresponding volumes, $\beta^{-1} = k_b T$ is the inverse temperature, k_b is Boltzmann's constant, and T is the absolute temperature.

In the grand canonical ensemble, μVT, the chemical potential μ, the volume V, and the temperature T are all kept constant. The system samples the configuration space through molecular displacements and fluctuations in concentration. However, owing to the high density that water can reach in the clay interlayer, sampling can be inefficient, and a biasing technique has to be implemented to improve the quality of sampling. This is achieved by implementing a rotational-bias method of insertion, where a molecule of H_2O is inserted randomly in the system and its orientation is biased. Trial insertions are accepted with probability

$$P_{acc} = \min\left(1, \exp\left(-\beta \cdot \left| \begin{array}{l} \delta U_{nm} + \ln\left(\dfrac{zV}{N+1}\right) \\ +\dfrac{1}{\beta} \cdot \ln\left(kP_j\right) \end{array} \right| \right)\right) \tag{4}$$

and deletion of water molecules is accepted with probability

$$P_{acc} = \min\left(1, \exp\left(-\beta \cdot \left| \begin{array}{l} \delta U_{nm} + \ln\left(\dfrac{N}{zV}\right) \\ +\dfrac{1}{\beta} \cdot \ln\left(kP_j\right) \end{array} \right| \right)\right) \tag{5}$$

In Equations 4 and 5, δU_{nm} is the energy difference between the two configurations, P_j is the probability of selecting the j^{th} orientation from k randomly generated orientations, $z = exp(\beta\mu)/\wedge^3$ is the activity, $\wedge$ is the thermal length of the molecule, and μ is the chemical potential of bulk water (Allen & Tildesley 1987, Chávez-Páez *et al.* 2001b).

TABLE 1. INTERACTION PARAMETERS FOR Ca-EXCHANGED MONTMORILLONITE, TIP4P WATER MODEL*

Site	C	D	E	F	G
O-O	0	0	592840.4	602.71152	0
O-Ca	37146	2.9902	0	-2185.3	1578.6
H-Ca	3.7234	3.7234	0	0	0

* Boek *et al.* (1995).

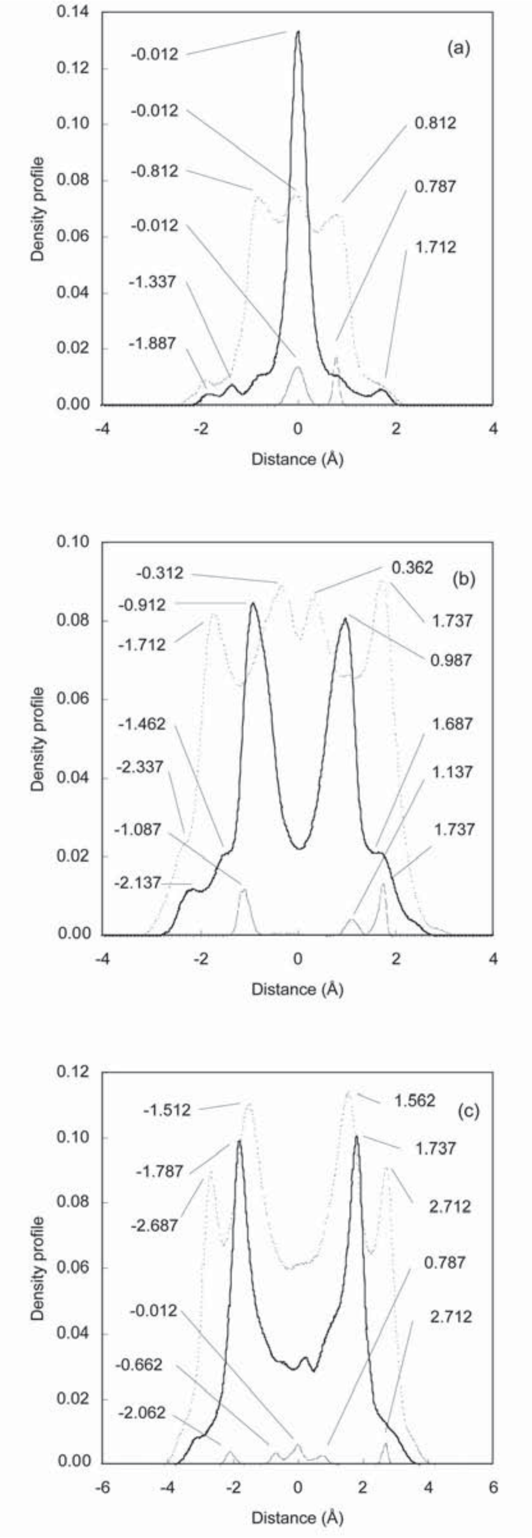
We simulate the water – calcium interaction by applying the TIP4P water model of Jorgensen *et al.* (1983), and the parameters of Bounds (1985) (Table 1). The TIP4P model is preferred at 300 K and 333 bar, and at 353 K and 625 bar, because its influence on the density or the energy does not appear significant, and also because our results can then be compared with known ones on the behavior and stability of Ca-saturated montmorillonite under ambient surface-environments (Boek *et al.* 1995, Chávez-Páez *et al.* 2001b). In the simulations, the water – clay and clay – calcium interactions are neglected.

RESULTS AND DISCUSSION

$NP_{zz}T$ *simulations*

Simulations in the $NP_{zz}T$ ensemble at constant mass, pressure, and temperature indicate that Ca-saturated montmorillonite, at basin conditions of 353 K and 625 bar, adsorbs water to form one- and two-layer hydrates. The adsorption of 32 molecules of water (98 mg/g of clay) results in the formation of the one-layer hydrate with a d_{001} value of 11.83 Å (Table 2). The water molecules are clustered on the interlayer midplane, tilted with their hydrogen atoms oriented toward the siloxane surfaces on both sides and to the midplane (Table 2, Fig. 1a). The Ca^{2+} ions are on the interlayer midplane solvated in outer-sphere complexes with the water molecules, but some are closer to the clay surface. A distance of 1.624 Å separates the outermost layers of protons. The configuration is illustrated in Figure 2a.

Increasing adsorption to 64 molecules of water (196 mg/g) develops the two-layer hydrate with a d_{001} value of 13.73 Å, which places the water molecules in two well-defined layers, one on each side of the interlayer midplane, 1.899 Å apart from each other (Table 2, Fig. 1b). The protons on the molecules of water are distributed over four layers, two outermost ones 3.449 Å apart, and two closer to the central plane. The Ca^{2+} ions are solvated in both layers of water, slightly aside from the plane formed by the oxygen atoms of the water; none are found between the two layers of water, closer to the clay surface or in inner-sphere coordination with the siloxane oxygen atoms (Fig. 2b). At higher water contents, namely at 96 molecules (294 mg/g), a full two-layer hydrate of 15.60 Å results, with the molecules of water separated by 3.524 Å from each other, the outmost protons 5.399 Å apart, and minor excess molecules of water located about the interlayer midplane (Table 2, Fig. 1c). The Ca^{2+} ions are on the interlayer midplane and in-between the two layers of water, with few atoms closer to the siloxane surface.



The results indicate that at 353 K and 625 bar, the adsorption of 32, 64, and 96 molecules of water places the molecules at 0.012, 0.912–0.987, and 1.787–1.737 Å, respectively, from the interlayer midplane. The interlayer configuration changes from one-layer when the amount of adsorbed water is between 32 and near 64 molecules to the two-layer when it increases to the interval 64–96 molecules. The Ca^{2+} ions are essentially in outer-sphere complexes in the water layers, symmetrical to the protons and slightly off the plane clustering the oxygen atoms.

At 333 K and 300 bar, corresponding to conditions prevailing at depths of 2 km, the adsorption of 50 molecules of water develops a one-layer hydrate having a d_{001} value of 12.11 Å, similar to that formed under higher temperature and pressure. The density profile shows that some molecules of water are off the interlayer midplane, closer to the clay surface (Table 2). Figure 2c illustrates a bulkier interlayer relative to the one at 353 K, where 32 molecules were adsorbed (Fig. 2a).

TABLE 2. MONTE CARLO SIMULATION OF HYDRATED Ca-EXCHANGED MONTMORILLONITE, $NP_{zz}T$ ENSEMBLE

	1	2	3	4
Temperature (K)	353	353	353	333
Pressure (bar)	625	625	625	300
Clay layers	2	2	2	2
Ca (atoms/cell)	3	3	3	3
H_2O content (molecules/cell)	32	64	96	50
H_2O content (mg/g clay)	98	196	294	153
d_{001} spacing (Å)	11.830	13.730	15.600	12.110
Density (g/mL)	0.210	0.360	0.470	0.320
Energy interaction (kcal/mol)	-24.245	-19.664	-17.714	-23.360
Lennard-Jones contrib. (kcal/mol)	-26.369	-13.167	-7.648	-18.600
Coulomb contrib. (kcal/mol)	1.415	-6.679	-10.137	-4.750
r_{CaO} 1st coordination shell (Å)	2.775	2.815	…	2.775
$g_{CaO}(r)$ coordination probability	10.026	7.441	…	7.906
r_{CaO} 2nd coordination shell (Å)	4.715	4.710	…	4.665
$g_{CaO}(r)$ coordination probability	1.804	1.710	…	1.432
H_2O (layers/cell)	1	2	2	1
O^{2-} distance to midplane (Å)	-0.012	-0.912	-1.787	0.012
"	…	0.987	1.737	-1.081
O^{2-} outermost distance (Å)	0	1.899	3.524	0.910
H^+ distance to midplane (Å)	-0.812	-1.712	-2.687	-0.963
"	-0.012	-0.312	-1.512	0.062
H^+ outermost distance (Å)	1.624	3.449	5.399	1.890
Ca^{2+} distance to midplane (Å)	-0.012	-1.087	-2.062	-0.086
"	0.787	1.137	-0.662	0.961
"	…	1.737	-0.012	…
"	…	…	0.787	…
"	…	…	2.712	…

FIG. 1. Density profiles of hydrated Ca-exchanged montmorillonite, $NP_{zz}T$ ensemble. Adsorbed molecules of H_2O per simulation cell at 353 K and 625 bar are: (a) 32, (b) 64, (c) 96. Oxygen of H_2O molecules: bold line; protons: dashed line; calcium: black line.

Our simulated d_{001} values of 11.83 and 12.11 Å for the one-layer hydrates at 353 K and 625 bar and at 333 K and 300 bar are within the range of 11.19–12.45 Å known from experimental studies (Bray & Redfern 1999, 2000, McEwan & Wilson 1980) and are shorter than the 12.20 Å simulated for Ca-saturated montmorillonite under surface conditions of 300 K and 1 bar (Laird 1996, Laird *et al.* 1995, Chávez-Páez *et al.* 2001b) (Table 3). The simulated 15.60 Å spacing limiting the two-layer hydrate, with 96 adsorbed molecules of water, compares with the experimental 15.0–15.8 Å spacing (Bray *et al.* 1998, Keren & Shainberg 1975, Posner & Quirk 1964, Sato *et al.* 1992), the 15.0 Å spacing measured at 260–300 K and 48–7075 bar (Wu *et al.* 1997), and the 14.7 Å spacing (Chávez-Páez *et al.* 2001b) known from simulations at 300 K

TABLE 3. EXPERIMENTAL AND SIMULATED d_{001} OF Ca-EXCHANGED MONTMORILLONITE AT 300 K AND 1 BAR

Posner & Quirk (1964)	...	...	15.50	18.50
Glaeser & Mering (1968)	...	...	15.0--15.50	...
Suquet *et al.* (1975)	...	...	...	19.10
Keren & Shainberg (1975)	...	12.00	15.00	18.00
Rutherford *et al.* (1980)	9.55-9.70	...	...	...
Anderson *et al.* (1999)	...	...	15.50	18.50
Bray *et al.* (1998)	10.30	11.70	15.00	...
Sato *et al.* (1992)	9.76-9.80	11.19-12.45	15.24-15.81	...
Wu *et al.* (1997) [1]	...	...	15.00	19.05
Wu *et al.* (1997) [2]	...	...	...	19.05
Chávez-Páez *et al.* (2001b) [3]	9.82	...	14.70	19.00
Chávez-Páez *et al.* (2001b) [3]	...	12.20	14.70	18.40

Experimental data: [1] at 260–300 K and 48–7075 bar; [2] at 310–350 K and 260–8265 bar. Simulation data: [3] $NP_{zz}T$ simulation; [4] µVT simulation.

TABLE 4. MONTE CARLO SIMULATION OF HYDRATED Ca-EXCHANGED MONTMORILLONITE, µVT ENSEMBLE, AT 353 K AND 625 BAR

	1	2	3	4	5	6	7	8	9
Temperature (K)	353	353	353	353	353	353	353	353	353
Pressure (bar)	625	625	625	625	625	625	625	625	625
Clay layers	2	2	2	2	2	2	2	2	2
Ca (atoms/layer)	3	3	3	3	3	3	3	3	3
H_2O adsorbed (molecules/layer)	39.27	51.70	55.21	61.36	80.02	93.03	108.52	124.31	140.40
H_2O adsorbed (mg/g)	120.36	158.46	169.22	188.07	245.26	285.14	332.61	381.01	430.33
Spacing (Å)	11.5	12.0	12.5	13.0	14.0	15.0	16.0	17.0	18.0
Density (g/mL)	0.264	0.207	0.342	0.365	0.442	0.480	0.525	0.566	0.604
Internal energy (kcal/mol)	-22.871	-21.805	-21.107	-20.288	-18.970	-18.370	-17.437	-16.948	-16.383
Lennard-Jones contribution (kcal/mol)	-22.116	-16.742	-15.737	-13.826	-9.544	-8.065	-6.878	-5.396	-3.970
Coulomb contribution (kcal/mol)	-0.601	-4.726	151	-6.324	-9.539	-10.613	-10.653	-11.660	-12.358
P_{zz} pressure tensor (bar)	24519.7	2001.9	1086.8	6322.2	7444.2	4080.6	4828.5	4347.7	5376.6
r_{CaO} first coordination shell (Å)	2.725	...	...	2.775	...	...	...	...	...
$g_{CaO}(r)$ coordination probability	7.504	...	...	7.774	...	...	...	...	...
r_{CaO} second coordination shell (Å)		...	...	4.795	...	...	...	...	...
$g_{CaO}(r)$ coordination probability	1.524	...	...	1.615	...	...	...	...	...
r_{CaO} third coordination shell (Å)	5.515	...	...	5.505	...	...	...	...	...
$g_{CaO}(r)$ coordination probability	1.543	...	...	1.461	...	...	...	...	...
O^{2-} distance to midplane (Å), H_2O mol.	0.012	...	-1.812	-1.612	...	...	...	...	...
"	...	0.012	-1.112	-0.537	...	...	...	...	...
"	...	...	0.087	0.587	...	...	...	...	...
"	...	...	1.262	1.687	...	...	...	...	...
"	...	...	1.562	1.124	...	...	...	...	...
O^{2-} outermost layers separation (Å)	0	0	0	1.124	...	...	...	...	...
H^+ distance to midplane (Å), H_2O mol.	-0.762	-0.862	-1.087	-1.087	...	-1.437	...	...	...
"	0.012	0.437	0.082	0.062	...	0.062	...	...	...
"	0.612	0.887	1.137	1.137	...	1.462	...	...	...
H^+ outermost layers separation (Å)	1.374	1.749	2.224	2.224	...	2.899	...	...	...
Ca^{2+} distance to midplane (Å)	0.012	-0.787	-1.012	-1.012	...	-0.887	...	...	...
"	0.562	-0.237	-0.512	-0.512	...	0.912	...	...	...
"	...	0.912	0.537	0.537	...	1.262	...	...	...
"	...	...	1.112	1.112	...	...	...	...	...

and 1 bar. The reported three-layer hydrates with a spacing of 18.50–19.10 Å spacing (Chávez-Páez *et al.* 2001b, Posner & Quirk 1964, Sato *et al.* 1992, Suquet *et al.* 1975, Wu *et al.* 1997) were not simulated in the present study.

The radial-distribution function $g(r)$ shows that at 353 K and 625 bar, in the one-layer hydrate, there is a coordination probability of 10.026 molecules of water per cation at a Ca–O separation of 2.775 Å (Table 2, Figs. 3a, b). Increasing the adsorption to the two-layer hydrate raises the Ca–O distance to 2.81 Å and reduces the coordination probability to 7.441 molecules of water. When the temperature and pressure are decreased to 333 K and 300 bar, the probability is limited to 7.906 molecules of water and the r_{CaO} distance decreases to 2.775 Å. Integration of $g(r)$ as per Equation 6 (Allen & Tildesley 1986) indicates solvation of the cation by 10 water molecules, which lies within the 9–10 range known for the system Ca – H_2O (Bounds 1985).

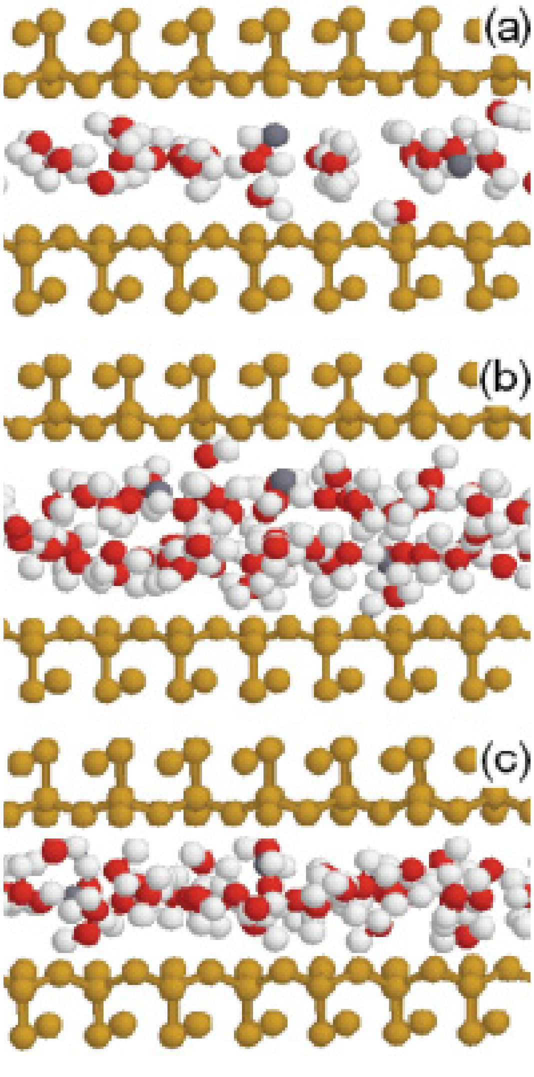


FIG. 2. Snapshots of Ca-exchanged montmorillonite: (a) one-layer hydrate, 32 adsorbed molecules of H_2O at 353 K and 625 bar; (b) two-layer hydrate, 64 molecules of H_2O; (c) one-layer hydrate, 50 molecules of H2O at 333 K and 300 bar.

$$\mathrm{N}_{\mathrm{CaO}} = 4 \cdot \pi \cdot \frac{\mathrm{N_O}}{\mathrm{V}} \cdot \int_0^r g_{\mathrm{CaO}} \cdot (r) \cdot r^2 \, \mathrm{d}r \qquad (6)$$

The progressive hydration of Ca-saturated montmorillonite increases the d_{001} value and the separation of the water layers from the interlayer midplane (Table 2, Fig. 4a). The internal energy increases in the order –24.245, –19.664, and –17.714 kcal/mol as the amount of adsorbed H_2O changes from 32 to 96 molecules (Table 2, Fig. 4b). The Coulomb contribution to the energy decreases from 1.415, to –6.679, to –10.137 kcal/mol, inverse of the Lennard–Jones contribution, which increases to –26.369, –13.167, and –7.648 kcal/mol. Lower energies are simulated where the montmorillonite is in the 333 K, 300 bar environment.

Grand canonical μVT simulations

To evaluate the thermodynamic stability of hydrated clay complexes under basin conditions, simulations were conducted in the grand canonical ensemble. The simulations started by calculating the chemical potentials of bulk water for a system of 216 molecules (Chávez-Páez *et al.* 2001b) at 353 K and 625 bar and at 333 K and 300 bar. For the former, the simulated chemical potential was –5.58 kcal/mol, and for the latter, –7.21 kcal/mol.

Simulations in the grand canonical ensemble define the stability of the clay mineral when the chemical potentials of the fluid in the mineral interlayer and of the bulk supernatant fluid are identical. The thermodynamic stability of the Ca-saturated montmorillonite hydrates are determined from the minima in the swelling free energy as a function of the interlayer separation (Chávez-Páez *et al.* 2001b). The free energy is calculated from Equation 7, where P_{zz} is the interlayer pressure tensor and $(P_{zz})^{npp}$ is the normal external bulk pressure. The derivative of this expression indicates that the stable hydrates are defined by the intercepts of the curve depicting the variation of the pressure tensor P_{zz} with the d_{001} value or the adsorbed water, with the line representing the external bulk pressure on the system.

$$\Delta \mathrm{E}_{s(z)} = -\mathrm{L_x} \cdot \mathrm{L_y} \cdot \int_{z0}^{z} \left| P_{zz} \cdot (\mathrm{s}) - (P_{zz})^{npp} \right| \mathrm{ds} \qquad (7)$$

The simulations performed using the TIP4P water model (Jorgensen *et al.* 1983) show that for values of

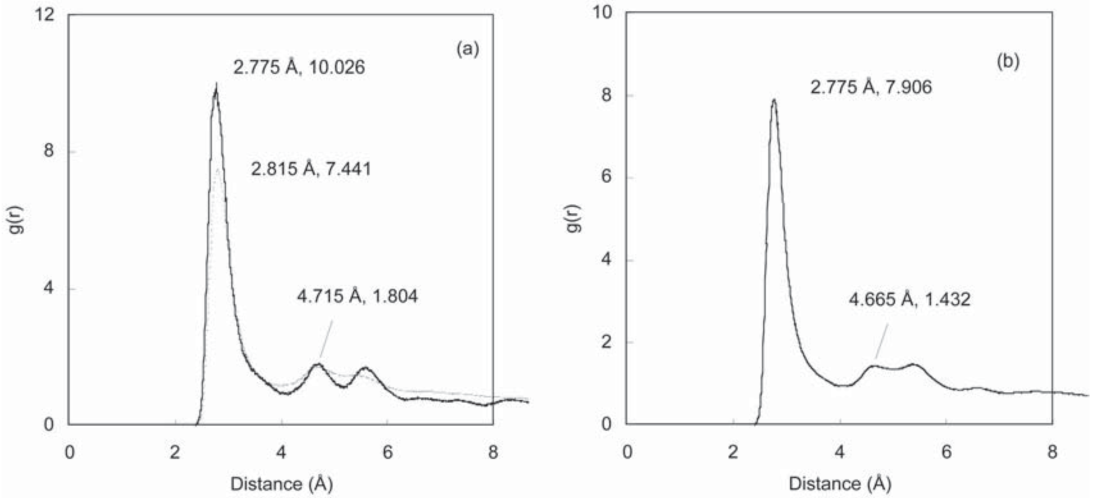


FIG. 3. Radial distribution function $g_{CaO}(r)$ of hydrated Ca-exchanged montmorillonite at (a) 353 K and 625 bar, 32 (solid line) and 64 adsorbed molecules of H_2O; (b) 333 K and 300 bar, 50 adsorbed molecules of H_2O.

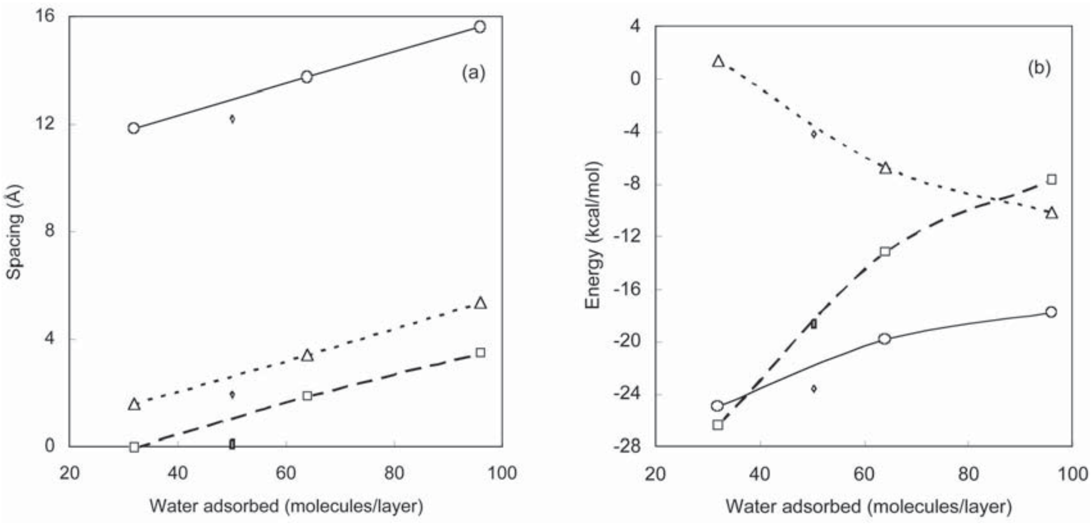


FIG. 4. Solvation of Ca-exchanged montmorillonite, $NP_{zz}T$ ensemble, at 353 K and 625 bar. (a) Variation of the d_{001} value (o), outermost separation of H^+ atoms (Δ), O^{2-} separation of H_2O molecules (□). (b) Variation of the internal energy (o), Coulomb contribution (Δ), and Lennard–Jones contribution (□). Small circles represent the same variables at 333 K and 300 bar.

d_{001} between 11.5 and 18 , the adsorbed water increases from 39.27 to 140.40 molecules per layer or 120.36 to 430.33 mg/g (Table 4, Fig. 5a), the total energy changes from –22.871 kcal/mol to –16.383 kcal/mol, the Lennard–Jones contribution varies from –22.116 to –3.970 kcal/mol, and the Coulomb contribution, from –0.601 to –12.538 kcal/mol (Fig. 5b). Simulations at 333 K and 300 bar (Table 5, Fig. 5c) indicate adsorption of 150.86–316.53 mg water/g, a value of d_{001} of 12.0–16.0 Å, an internal energy in the range –23.549 to –19.110 kcal/mol, a Lennard–Jones contribution in the range –18.118 to –11.396, a Coulomb contribution in the range –5.647 to –7.564 kcal/mol, and a pressure tensor from 10654.69 to 2532.54 bar.

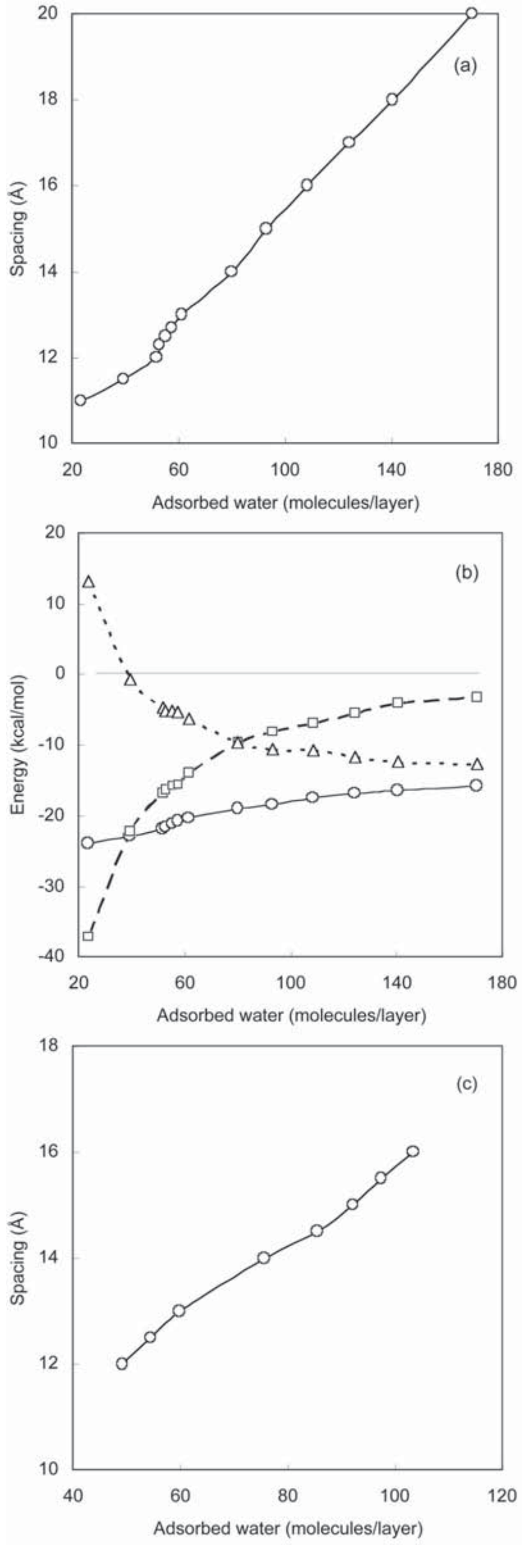


FIG. 5. Effect of adsorbed H_2O on the d_{001} value and the energy of Ca-saturated montmorillonite, grand canonical μVT ensemble, (a) and (b) at 353 K and 625 bar, (c) at 333 K and 300 bar. Internal energy (o), Lennard–Jones contribution (□), and Coulomb contribution (Δ).

The variation of the pressure tensor P_{zz} with adsorbed water is shown in Figure 6. At 353 K and 625 bar, the data in Figure 6a show that within the statistical uncertainty associated with the simulation, the one-layer hydrate Ca-saturated montmorillonite approaches stability. In the less deep environment at 333 K and 300 bar, the one-layer hydrate is stable (Fig. 6b), characterized by a d_{001} value of 12.11 Å. Two- and three-layer hydrates do not appear to be stable under such conditions.

At 353 K and 625 bar, the nearly stable one-layer Ca-saturated montmorillonite hydrate has a d_{001} value of 12.50 Å. It develops by adsorption of 55.21 molecules of water (169.22 mg H_2O/g clay), a pressure tensor P_{zz} of 1086.8 bar, an internal energy –21.107 kcal/mol, and an interlayer density 0.342 g/mL. At 333 K and 300 bar, the stable one-layer hydrate has a d_{001} value of 12.11 Å, 54.50 molecules of water, an internal energy of –22.803 kcal/mol, a Lennard–Jones contribution of –6.345 kcal/mol, a Coulomb contribution of –16.449 kcal/mol, and a density 0.337 g/mL. The density profiles (Fig. 7) show that at 353 K and 625 bar, the water molecules cluster in a broad band 0.087 Å away from the interlayer midplane, with protons on the midplane and 1.087 Å and 1.137 Å to each side, and the calcium cations off the midplane, solvated in outer-sphere complexes within the layer of molecules of water. At 333 K and 300 bar, the density profiles indicate that the water molecules are on the interlayer midplane, oriented to both siloxane surfaces, with the protons 1.112 and 1.137 Å to both sides, slightly farther apart than at 353 K and 625 bar; the calcium atoms are solvated away from the interlayer midplane. Illustrations of both hydrates (Figs. 8a, b) show a broad layer of water molecules with the cations coordinated in the water layer, away from the siloxane surface.

The stable one-layer hydrate of 12.11 Å and the nearly stable one of 12.50 Å predicted from our simulations at 333 K and 300 bar and at 353 K and 625 bar are within range of those of 11.19–12.45 Å that are determined experimentally (Bray *et al.* 1998, Sato *et al.* 1992, Keren & Shainberg 1975) and that of 12.20 Å from simulation studies (Chavez-Paez *et al.* 2001b). At normal ambient environments, Ca-saturated montmorillonite exists as one- and two-layer hydrates, whereas at the higher simulated temperatures and pressures, only the one-layer hydrate seems to be stable. The data support the stability of the one-layer hydrate at basinal

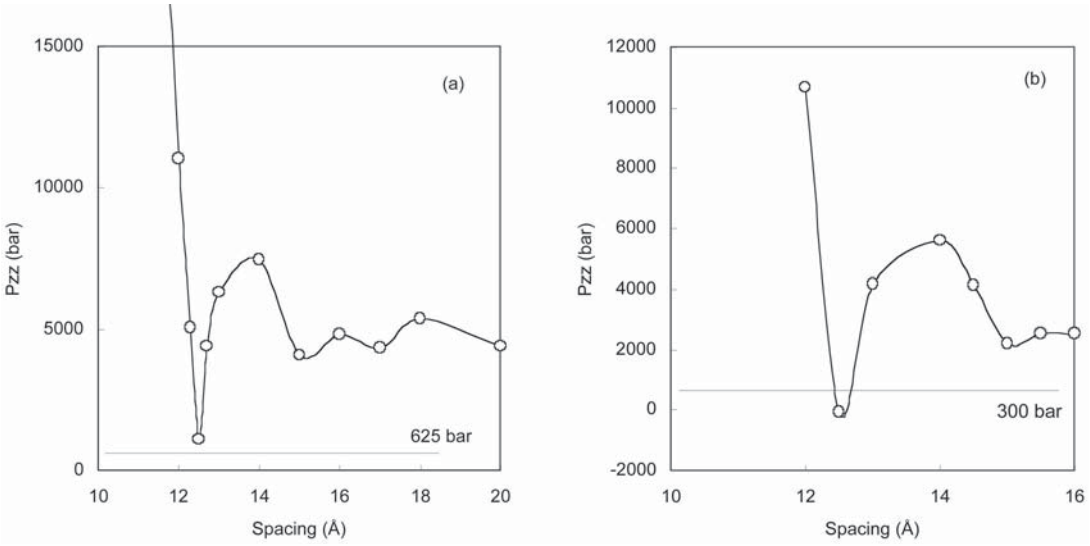


FIG. 6. Variation of the pressure tensor P_{zz} with the d_{001} value, grand canonical μVT ensemble, at (a) 353 K, 625 bar, –5.88 kcal/mol (b) 333 K, 300 bar, –7.21 kcal/mol. The horizontal bars correspond with the 625 and 300 bar pressures.

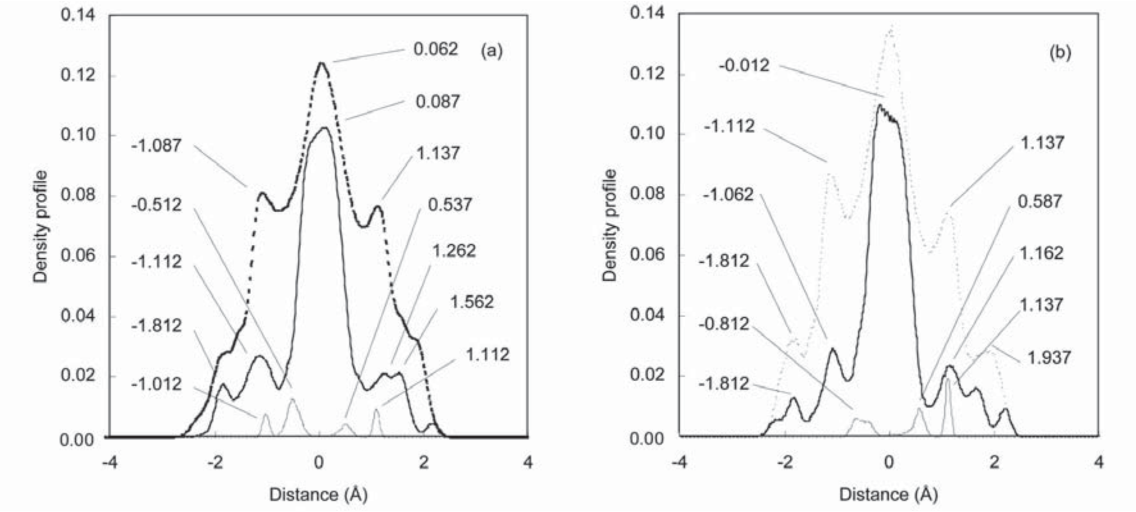


FIG. 7. Density profile of one-layer Ca-exchanged montmorillonite hydrate at (a) 353 K and 625 bar, (b) 333 K and 300 bar, μVT ensemble.

conditions and the absence or poor swelling that could result from any water adsorption to two- and three-layer hydrates and subsequent dehydration.

Our results confirm previous findings that hydrated Ca-saturated montmorillonite is enthalpically stable at burial depths up to 1.5 km and, that at greater depths, its conversion to other like minerals may occur (Siqueira *et al.* 1997).

SUMMARY

Monte Carlo simulations on the hydration of Ca-saturated montmorillonite under basin-like conditions

TABLE 5. MONTE CARLO SIMULATION OF HYDRATED Ca-EXCHANGED MONTMORILLONITE, μVT ENSEMBLE, AT 333 K AND 300 BAR

	1	2	3	4	5	6	7	8
Temperature (K)	333	333	333	333	333	333	333	333
Pressure (bar)	300	300	300	300	300	300	300	300
Clay layers	2	2	2	2	2	2	2	2
Ca (atoms/layer)	3	3	3	3	3	3	3	3
H_2O adsorbed (molecules/layer)	49.30	54.49	59.92	75.65	85.55	92.20	97.46	103.44
H_2O adsorbed (mg/g)	150.86	166.55	183.35	231.49	261.78	282.13	298.23	316.53
Spacing (Å)	12.0	12.1	13.0	14.0	14.5	15.0	15.5	16.0
Density (g/mL)	0.318	0.337	0.356	0.418	0.457	0.476	0.487	0.500
Internal energy (kcal/mol)	-23.549	-22.803	-21.867	-20.795	-20.014	-19.673	-19.529	-19.110
Lennard-Jones contribution (kcal/mol)	-18.118	-6.345	-6.704	-9.073	...	-10.636	...	-11.396
Coulomb contribution (kcal/mol)	-5.647	-16.449	-14.937	-11.819	...	-8.884	...	-7.564
P_{zz} pressure tensor (bar)	10654.690	-67.184	4179.982	5598.457	4137.781	2203.390	2539.388	2532.541
r_{CaO} first coordination shell (Å)	...	2.804	...	...	...	...	...	...
$g_{CaO}(r)$ coordination probability	...	6.349	...	...	...	...	...	...
r_{CaO} second coordination shell (Å)	...	4.725	...	...	...	...	...	...
$g_{CaO}(r)$ coordination probability	...	1.558	...	...	...	...	...	...
O distance to midplane (Å), H_2O molecule	...	-1.812	...	...	...	...	...	...
"	...	-1.062	...	...	...	...	...	...
"	...	-0.012	...	...	...	...	...	...
"	...	1.192	...	...	...	...	...	...
H^+ distance to midplane (Å), H_2O molecule	...	-1.812	...	...	...	...	...	...
"	...	-1.112	...	...	...	...	...	...
"	...	0	...	...	...	...	...	...
"	...	1.137	...	...	...	...	...	...
"	...	1.937	...	...	...	...	...	...
Ca^{2+} distance to midplane (Å)	...	-0.812	...	...	...	...	...	...
"	...	0.587	...	...	...	...	...	...
"	...	1.137	...	...	...	...	...	...

of 353 K and 625 bar and of 333 K and 300 bar reveal interlayer configurations similar to those known at surface conditions of 300 K and 1 bar. At low states of hydration, the molecules of water cluster on the interlayer midplane, with their protons alternatively oriented toward the siloxane surfaces and toward the interlayer midplane. At higher states of adsorption, the molecules of water are distributed in two separate layers close to the clay surfaces, with the molecules tilted so that their protons point toward the siloxane surfaces and the interlayer midplane. The calcium ions form outer-sphere complexes with the adsorbed molecules of water, invarially positioned off the interlayer midplane.

For the force field considered in this work, Ca-saturated montmorillonite forms a 12.11 Å one-layer hydrate stable at 333 K and 300 bar, which is equivalent to a depth of 2 km for sediments at normal geotherms. Two- and three-layer hydrates do not form. Under conditions of 353 K and 625 bar, equivalent to those prevailing at 2.7 km depth under overcompacted sediments, the one-layer hydrate approaches stability. Under equal conditions of temperature, pressure, and chemical potential, our previous simulations indicate that montmorillonite (Na > Ca) is clearly stable (de Pablo *et al.* 2004), whereas K-saturated montmorillonite is not (Chavez *et al.* 2004). A difference is established with clays under the ambient surface setting of 300 K and 1 bar, where two- and three-layer hydrates are formed. The results imply that Na-, K-, and Ca-saturated montmorillonite dehydrate to their one-layer hydrates at depth.

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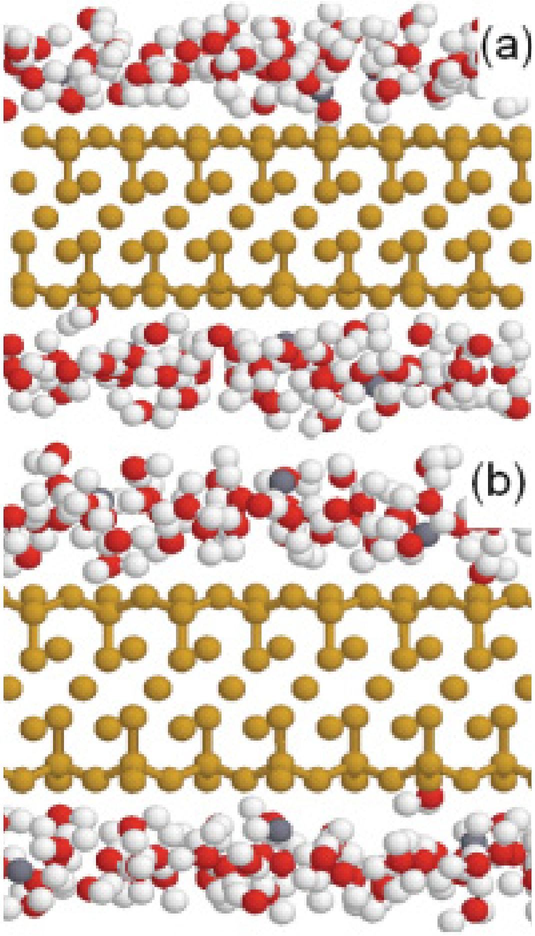

FIG. 8. Snapshot of one-layer Ca-exchanged montmorillonite at (a) 353 K and 625 bar, (b) 333 K and 300 bar, grand canonical ensemble.

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