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EFFECTS OF IRON OXIDATION STATE AND ORGANIC CATIONS ON DIOCTAHEDRAL SMECTITE HYDRATION

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Abstract—Reduction of structural Fe in Na-exchanged dioctahedral smectites decreases swellability in water, but because clay interlayers also collapse in the process the concomitant effect on surface hydration energy is uncertain. This study examined the hydration behavior of oxidized and reduced dioctahedral smectite clays exchanged with polar (Na) and weakly-polar (organic) cations to determine the nature of the surface before and after Fe reduction, and to determine if clay surfaces are hydrophilic or hydrophobic. The H_2O content in various dioctahedral smectites decreased if Na was replaced by tetramethylammonium (TMA), trimethylphenylammonium (TMPA), or hexadecyltrimethylammonium (HDTMA). Among the organo-clays, H_2O adsorption decreased with increasing complexity of the cation. For oxidized smectites, those exchanged with TMPA retained less H_2O than those exchanged with Na at all pressures. The extent of this difference depended on the clay and decreased with increasing applied pressure. Reduction of Fe(III) to Fe(II) in the octahedral sheets decreased the swelling of Na-saturated smectites, apparently causing some previously swelling interlayers to collapse. If the Na interlayer cation was exchanged to alkylammonium after reduction, but prior to swelling-pressure measurements, the swelling increased or remained near constant, suggesting that the organo-cation disrupted the collapse process of the interlayers associated with the reduced smectite layers. Reduced TMPA-saturated smectite surfaces are more strongly hydrated if the octahedral sheet is reduced than if oxidized. Thus, reduction of structural Fe increases the hydration energy of smectite basal surfaces, but swellability could decrease or increase depending on the extent of interlayer collapse occurring with different exchangeable cations.

Key Words—Alkylammonium, Ferric Iron, Ferrous Iron, HDTMA, Hydrophilic Surface, Hydrophobic Surface, Interlayer Cation, Oxidation, Reduction, Surface Hydration, Swelling, TMA, TMPA.

INTRODUCTION

Clay minerals and humic substances substantially influence the sorption properties of soils. Among clay minerals, smectites have the greatest effect on the sorption of cations, owing to the negative charge derived from isomorphous substitution in the octahedral and/or tetrahedral sheets, and to water, because of surface hydration energy. The negative surface charge is balanced by exchangeable cations, which are mostly hydrated inorganic cations (*e.g.*, Na^+, K^+, Ca^{2+}, Mg^{2+}) in nature. Such clays may be ineffective as sorbents for poorly water-soluble (hydrophobic) organic contaminants (Sheng and Boyd, 1998), but replacement of the inorganic cation with an organic cation such as tetraalkylammonium causes considerable change in the hydration and swelling properties of the clay. Replacement of the inorganic cation with an organic cation decreases the affinity of the smectite surface for H_2O because the hydration energy of the organic cations is much lower than that of inorganic cations. Moreover, the substantial amount of organic carbon associated with the organo-clay causes these modified clays to become effective sorbents for removing organic contaminants from water (Boyd and Jaynes, 1994; Lawrence *et al.*, 1998; Xu *et al.*, 1997).

Exchange of inorganic cations by alkylammonium is also a well-known method for measuring the layer charge of smectites, vermiculites, and other clay minerals (Lagaly and Weiss, 1976; Laird, 1994). Charge heterogeneity is a common property of swelling 2:1 clay minerals which arises from charge density variations from layer to layer or within individual layers (Lagaly, 1994). Inhomogeneous charge-density distributions were reported for H-exchanged smectites which had auto-transformed to (H, Al, Fe, Mg)-exchanged forms with aging (Janek *et al.*, 1997). In that study, the fraction of highest-charge layers was decreased or completely removed during auto-transformation.

The Li-fixation method has been used to create reduced-charge montmorillonites to study the effects of layer charge on clay-organic interactions. The basis of this method is that the net negative charge of a silicate layer of a clay mineral, which is related to cation-exchange capacity (CEC), depends on the extent of isomorphous substitution of lesser-valent for greater-valent cations in the mineral structure. Such substitutions may occur either during or after clay-mineral formation, but the net negative charge of the 2:1 layer of montmorillonite can be decreased by heating a Li-sat-

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urated montmorillonite at 200–300°C for several hours, causing Li cations to enter the 2:1 layer and thereby decrease the negative charge on that layer. This treatment is known to decrease both the expandability and the CEC of the montmorillonite (Hofmann and Klemen, 1950), and has been widely used to distinguish between montmorillonite and other smectites. Jaynes and Boyd (1991) used a series of reduced-charge clays prepared by a Li-treatment method (Jaynes and Bigham, 1987) to study the organophilic character of clay surfaces. They exchanged the inorganic interlayer cations with the small, hydrophobic trimethylphenylammonium (TMPA) cation and found that subsequent sorption of several aromatic hydrocarbons was directly proportional to surface area and inversely related to layer charge and TMPA content, *i.e.,* more hydrocarbons were sorbed on clays with lower negative charge on the 2:1 layers. They suggested that the adsorbing surfaces were the siloxane oxygens at the layer surface and TMPA cations served as pillars to keep adjacent layers apart. Water and competitive water-arene sorption studies on tetramethylammonium (TMA)- and TMPA-exchanged montmorillonites showed that H_2O preferentially hydrates methyl groups of the exchangeable organo-cations, while in the presence of bulk water arene adsorption occurs primarily on the siloxane surface (Stevens and Anderson, 1996; Stevens *et al.,* 1996). These investigators assert that clay surfaces are, therefore, primarily hydrophobic.

Contradictory to these arguments that clay surfaces are inherently hydrophobic are numerous studies by Low and co-workers (*e.g.,* Low and Margheim, 1980; Viani *et al.,* 1983; Low, 1987) revealing that clay surfaces carry a direct hydration energy. Infrared spectroscopic evidence indicates that interlayer water is strongly coupled to the clay-mineral surface (Yan *et al.,* 1996a, 1996b, 1996c). The bond energy of Si-O in the tetrahedral sheet of the clay is modified by the interlayer H_2O content, and is independent of the inorganic univalent cation in the interlayer. The bond energy of interlayer H_2O is likewise modified, giving a linear relationship between the shifts of Si-O and H-O-H vibrational energies. This evidence is consistent with earlier reports of an epitaxial relationship between H_2O and clay surfaces (Ravina and Low, 1972, 1977), and that clay surfaces hydrate directly (Low and Margheim, 1980; Low, 1987). The oxidation state of structural Fe in the clay also influences the coupling between interlayer H_2O and structural Si-O bands (Yan and Stucki, 1999). This coupling would be inconceivable if H_2O is repelled by the clay surfaces or only hydrates the interlayer cation.

The apparent contradiction regarding the nature and properties of clay surfaces merits further investigation because the interaction mechanism between clay surfaces and H_2O or organic compounds is fundamental to many natural and industrial processes. The purpose of the present study was to examine the hydration behavior of smectite clays exchanged with polar (inorganic) and weakly-polar (organic) cations to understand the nature of the surface. This study utilizes changes in Fe oxidation state as the method for varying the layer charge in the 2:1 layer. This method is preferred over the Li-fixation method because more is known about the effects on clay hydration and structural changes.

BACKGROUND

The substitution of Fe(III) for Al(III) in smectites has no effect on layer charge, but reduction of structural Fe(III) to Fe(II) increases the negative charge of the layers and thus the number of interlayer cations needed for charge compensation. The oxidation state of structural Fe in smectite has a profound effect on the chemical and physical behavior of the smectite (Stucki, 1988), but relatively little is known about the underlying mechanisms for these effects. Results by Stucki and co-workers (Gates *et al.,* 1993; Lear and Stucki, 1989; Stucki *et al.,* 1984a) revealed that the reduction of structural Fe(III) to Fe(II) in the octahedral sheet of smectite greatly decreases swelling in water, whether reduced by sodium dithionite (Stucki *et al.,* 1984a) or by bacteria (Gates *et al.,* 1993; Kostka *et al.,* 1999). Stucki *et al.* (1984a) attributed differences in swellability of oxidized and reduced clays to the collapse of clay interlayers as a result of Fe reduction, which removed a portion of the structure from the swelling component of the system. This explanation is consistent with the swelling model proposed by Viani *et al.* (1983). This assertion was supported by direct X-ray diffraction evidence for at least partially collapsed interlayers in reduced smectites (Wu *et al.,* 1988); and indirectly by surface area (ethylene glycol monoethyl ether adsorption) measurements (Lear and Stucki, 1989; Kostka *et al.,* 1999). These results imply that the effect of Fe oxidation state on clay hydration is governed by multiple factors, including the interlayer cation, non-specific surface-hydration forces, and other forces that influence interlayer collapse.

The extent to which a clay surface will hydrate is determined by the difference in partial molar Gibbs free energy of H_2O in the clay compared to bulk water, denoted the relative partial molar Gibbs free energy or $\overline{G} - \overline{G}^o$, where the superscript ^{o} refers to pure bulk water, *i.e.,* the reference state. This is the macroscopic driving force that causes H_2O to move from one phase to another, and, assuming the water is virtually incompressible over the pressure range used and the water vapor behaves ideally, can be calculated from the equation (Low, 1951):

$$\overline{G} - \overline{G}^o = -\overline{V}\Pi = RT \ln p/p^o \quad (1)$$

where $\overline{V}$ is the partial molar volume of H_2O in the clay, which in most clay systems deviates from that of

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Table 1. Water content (m_w/m_c) of oxidized and reduced smectites exchanged with Na or TMPA and equilibrated at different swelling pressures, Π.

Smectite	Total Fe (mmol/g)	Π (MPa)	Na-saturated Smectite			TMPA-saturated Smectite		
			Fe(II) mmol/g	m_w/m_c (g H_2O/g clay) Mean	S.D.	Fe(II) mmol/g	m_w/m_c (g H_2O/g clay) Mean	S.D.
Upton Unaltered[1]	0.449	0.1	0.040	4.4590	0.0814	0.040	1.6846	0.0165
		0.3		2.2592	0.1340		1.1661	0.0157
		0.5		1.5192	0.0202		0.8295	0.0037
		0.7		1.2131	0.0246		0.6025	0.0082
		0.9		1.0567	0.0366		0.5231	0.0022
Upton Reduced		0.1	0.366	3.7022	0.0484	0.382	4.3052	0.0846
		0.3		2.0434	0.0437		2.2863	0.0047
		0.5		1.4154	0.0124		1.6047	0.0212
		0.7		1.1090	0.0244		1.3004	0.0290
		0.9		0.9530	0.0220		1.0837	0.0080
SWa-1 Unaltered	2.775	0.1	0.008	3.7890	0.0589	0.008	2.7430	0.0091
		0.3		1.9731	0.0359		1.6235	0.0042
		0.5		1.3756	0.0623		1.2617	0.0185
		0.7		1.0990	0.0269		1.0400	0.0199
		0.9		0.9214	0.0067		0.8749	0.0072
SWa-1 Reduced		0.1	2.506	2.6460	0.0718	2.725	4.4625	0.0561
		0.3	2.556	1.6065	0.0623		2.7431	0.1056
		0.5	2.676	1.1923	0.0300		1.9541	0.0678
		0.7	2.570	0.9632	0.0157		1.6250	0.0215
		0.9	2.651	0.8445	0.0062		1.2815	0.0242
JP Unaltered	0.477	0.3	0.010	1.9864	0.0802	0.011	1.0161	0.0502
JP Reduced			0.342	1.2778	0.0023	0.043	1.1324	0.0532
St Unaltered	2.193		0.007	1.7265	0.0727	0.009	1.0288	0.0253
St Reduced			1.318	1.2529	0.0415	0.851	1.0789	0.2608
Hr Unaltered	1.815		0.629	1.5401	0.0298	1.280	1.0623	0.0060
Hr Reduced			1.192	1.2306	0.0291	0.889	0.9499	0.2160

[1] For comparison, Li-saturated Upton at Π = 0.3 MPa has m_w/m_c = 2.2962 ± 0.0357 g/g.

bulk water by less than ~2% (Anderson and Low, 1958); Π, the swelling pressure; p/p^o, the relative vapor pressure of water in equilibrium with the clay-water system; *R*, the universal gas constant; and *T*, the absolute temperature. Values of $\overline{G} - \overline{G}^o$ for the Na-exchanged clays and organo-clays at various H_2O contents can thus be determined by measuring Π (drying curve) or p/p^o (wetting curve) as a function of gravimetric water content (m_w/m_c).

MATERIALS AND METHODS

Smectites

The smectite minerals used in this study were ferruginous smectite (sample SWa-1, Source Clays Repository of The Clay Minerals Society, Columbia, Missouri), Upton montmorillonite (from American Colloid Company, Arlington Heights, Illinois, USA), Jelšový Potok (JP) montmorillonite (from Jelšový Potok, Slovak Republic), Stebno (St) beidellite (from Stebno, Czech Republic), and Fe(II)-rich Hroznětín (Hr) montmorillonite (from Hroznětín, Czech Republic). The latter three were described in more detail by Čičel *et al.* (1992a, 1992b). Each clay sample was prepared by mixing a portion of the untreated clay thoroughly with highly purified H_2O (18 MOhm-cm) overnight, then separating the <2-μm size fraction by centrifugation and decantation. Samples were then homoionically saturated with Na^+ by adding NaCl salt to bring the suspension to 1 M, mixing thoroughly for several hours, centrifuging to a clear supernatant (~35,000 × *g* for 30 min), and discarding the supernatant. This procedure was repeated three times. The NaCl concentration in the clay suspension was then decreased to 0.1 mM by first washing with a 0.5 mM NaCl solution four times and then diluting 1:5 with H_2O after the final wash. The purpose of maintaining the concentration at this level was to avoid hydrolysis of exchanged Na^+ at the clay surface. The suspension was then freeze-dried and a portion analyzed for total Fe by the method of Komadel and Stucki (1988) (see Table 1). The unaltered Upton montmorillonite was also prepared in the Li-saturated state by the same method.

Reduction of Fe(III) to Fe(II) and organo-ion exchange

Structural Fe in the clays was reduced by resuspending a 30-mg portion of the freeze-dried stock material in 20 mL of highly purified H_2O in a septum-sealable, polycarbonate Oak Ridge-type centrifuge tube, then bringing the suspension to 30-mL volume with concentrated citrate-bicarbonate buffer solution

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(prepared as 1 part by volume of 3 M $NaHCO_3$ and 8 parts of 0.9 M $Na_3C_6H_5O_7$). The resulting suspension was washed once with a more dilute buffer solution (prepared as 1 part by volume of 1 M $NaHCO_3$ and 8 parts of 0.3 M $Na_3C_6H_5O_7$), heated to 75°C, and reduced by adding $Na_2S_2O_4$ and purging the suspension with N_2 using the method of Komadel *et al.* (1990). The Fe(II) in the sample was adjusted by altering the amount of $Na_2S_2O_4$ added, ranging from 0 to 200 mg. The reduced suspension was cooled and washed free of excess salts using deoxygenated H_2O. In some samples the counter ion was then changed, by repeated centrifuge washings, from Na^+ to one of the following monovalent organic cations: TMA, TMPA, or HDTMA (hexadecyltrimethylammonium), prepared as deoxygenated aqueous solutions of their respective chloride salts. All solutions were exchanged under inert-atmosphere conditions using a version of the apparatus described by Stucki *et al.* (1984b).

Clay hydration at p/p^o = 1.00 (wetting curve)

One preparation of each Na-clay and organo-clay was freeze-dried, then duplicate 30-mg portions of the resulting powder were placed in pre-weighed weighing bottles and rehydrated by exposure to and equilibration with pure water in an atmosphere of 100% relative humidity (p/p^o = 1.00) in a desiccator at room temperature. Following equilibration (determined as the point after which no change in water content occurred), m_w/m_c of the sample was determined by weighing the sample before and after oven drying at 105°C.

Clay dehydration at varying swelling pressure, Π (drying curve)

Another preparation of each Na-clay or organo-clay suspension was submitted to swelling-pressure measurements without freeze-drying. For the organo-clay preparation of samples Upton and SWa-1, reduction, washing, and organo-ion exchange were performed on 25 identical samples in 50-mL Oak Ridge tubes as described above, with the suspension volume being adjusted to slightly less than 10 mL after the final wash. Then, all samples were placed inside an inert-atmosphere glove box (Vacuum Atmospheres Model HE-493 with a <1 ppm O_2 atmosphere) and combined into a single 250-mL bottle. An aliquot was removed and analyzed for Fe(II)/total Fe by the 1,10-phenanthroline method of Komadel and Stucki (1988), using the absorptivity-corrected absorbance ratio. This method enabled the direct analysis of the suspension by avoiding the necessity of analyzing a known quantity of smectite.

Approximately 12.5 mL of the combined suspension was then transferred, inside the glove box, to a 50-mL Oak Ridge tube, septum sealed, and removed from the glove box. This suspension was divided equally among five cells of a miniature swelling-pressure apparatus (Stucki *et al.*, 1984a; Gates *et al.*, 1993) by inserting two septum-penetration needles into the suspension. Through one needle, O_2-free N_2 gas was applied to pressurize the tube, forcing the suspension out through the other needle into the swelling-pressure cell via an open ball valve at its top. During the transfer, the cell was continuously purged from within with O_2-free N_2 gas, as described by Stucki *et al.* (1984a). The ball valve was then closed and the gas pressure above the clay suspension in the cell rapidly reached the value previously established in the pressure apparatus, and the water was expressed through the Millipore filter (0.025-μm pore size) at the bottom. Once equilibrium was established, the filter cake in each of the five cells was quickly removed, its water content determined gravimetrically, and the mean value calculated. This process was repeated for each of the applied gas pressures (Π) of 0.1, 0.3, 0.5, 0.7, and 0.9 MPa by transferring another 12.5-mL aliquot from the glove box. A separate, subsequent preparation was made for samples submitted to 0.01 MPa applied pressure.

Only one swelling pressure (0.3 MPa) was used with clay samples JP, St, and Hr, so tubes containing reduced samples of these clays were not combined inside the glove box, but were taken directly to the swelling-pressure apparatus after washing. Iron(II)/total Fe contents were measured in samples prepared in parallel.

The Na form of each of the JP, St, and Hr clays was prepared by the same procedure as described above for the organo-clay, except a new preparation of five samples was made for each swelling pressure rather than beginning with 25 samples simultaneously. Unaltered (oxidized) samples of Na- and organo-clay were treated identically to the reduced samples, except no reducing agent was added.

RESULTS AND DISCUSSION

Oxidized (unaltered) smectites

The water content (Figure 1) of SWa-1 saturated with various cations, which was achieved by wetting the freeze-dried clay from the vapor phase at 100% relative humidity (p/p^o = 1.00), decreased if Na was replaced by any of the selected organic cations. Among the organo-clays, the amount of water adsorbed decreased with increasing complexity of the cation (chain length, functional groups, and non-polar segments), revealing that the wetting-curve water contents decreased in the order Na > TMA > TMPA > HDTMA.

Drying-curve water contents, obtained at increasing swelling pressures, of unaltered Na- and TMPA-saturated Upton and SWa-1 smectites (Table 1; Figure 2) were greater for Na-saturated Upton than for Na-sat-

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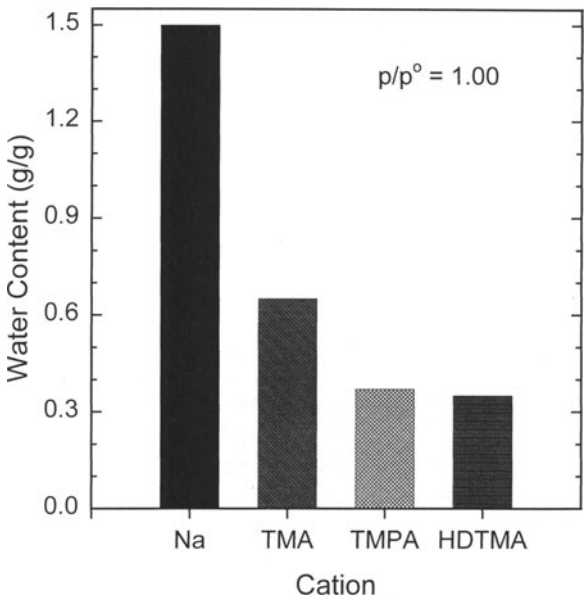


Figure 1. Equilibrium water content (m_w/m_c) at 100% relative humidity (p/p^o = 1.00) of SWa-1 saturated with Na or with one of three organo-cations.

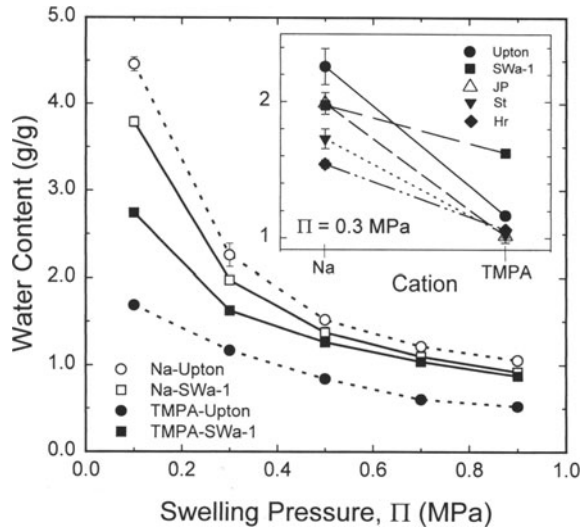


Figure 2. Effect of swelling pressure (Π) on equilibrium water content (m_w/m_c) of unaltered (oxidized) SWa-1 and Upton saturated with Na or TMPA. Insert compares water contents of Na- and TMPA-saturated smectites JP, St, or Hr with SWa-1 and Upton at Π = 0.3 MPa.

urated SWa-1 at all pressures. This result was expected because Upton is one of the highest-swelling clays known (Low, 1981), and it is considered to be fully dispersed in its Li-exchanged form (Banin and Lahav, 1968). As shown in Table 1 (see footnote to Table 1 also), the swellability of the Upton sample was nearly identical in either the Li- or Na-saturated forms, indicating that the oxidized Na-saturated Upton was fully dispersed.

The TMPA form of both Upton and SWa-1 retained less water than the Na forms at all pressures, and this difference decreased with increasing pressure. Although Na-saturated Upton contained substantially more H_2O than TMPA-saturated Upton at all pressures, the difference between Na-saturated SWa-1 and TMPA-saturated SWa-1 systematically decreased with increasing pressure until no significant difference was evident (at 0.7 MPa and above). The relatively low H_2O content of TMPA-saturated Upton confirms that replacing Na with an organo-cation substantially decreased the ability of this clay to retain H_2O. This behavior is related to limited intracrystalline swelling of TMPA-saturated Upton, in contrast to the high values for Na-saturated Upton (Zhang *et al.,* 1993), and may be attributed to the differences in size as well as hydration energy of the respective cations. The substitution of TMPA for Na also decreased the drying-curve H_2O contents of smectites JP, St, and Hr at 0.3 MPa (Table 1; Figure 2 inset), with the difference between Na- and TMPA-forms decreasing in the above order. Except for SWa-1, the H_2O contents of all TMPA-saturated smectites at Π = 0.3 MPa were similar, within the range of 1.02–1.17 g/g. The value for SWa-1 was 1.62 g/g.

The changes in interlayer H_2O content of the smectites owing to the various cations indicate [Equation (1)] that the partial molar Gibbs free energy of H_2O next to the clay interlayer surfaces increases, or becomes more like pure bulk water, in the order Na ≪ TMA < TMPA ≤ HDTMA. This is also the order of decreasing perturbation on H_2O molecules by the clay-cation system, consistent with decreasing hydration energy of these cations. If the clay system is assumed to be fully swellable in all of these ionic forms, meaning that little or no variation is expected in the specific surface area exposed to H_2O and in the number of layers participating in the swelling or surface-hydration process (Low, 1980), then these observed differences in swelling of oxidized smectites are best explained by differences in cation polarity. This could decrease the affinity of the interlayer region for H_2O based either on entropy or on the hydration energy of the cation (Chen *et al.,* 1987).

Reduced smectites

Previous studies (Lear and Stucki, 1989; Stucki *et al.,* 1984a; Wu *et al.,* 1988; Gates *et al.,* 1993) found that reduction of structural Fe(III) to Fe(II) in the structure of Na-exchanged smectite dramatically decreases swellability. Results here confirm the earlier observations and expand the number of Na-saturated smectites that follow the same trend (Figure 3; Table 1), indicating that the effect of structural Fe(II) on the loss of swellability of Na-exchanged smectites is probably a general phenomenon. The magnitude of the ef-

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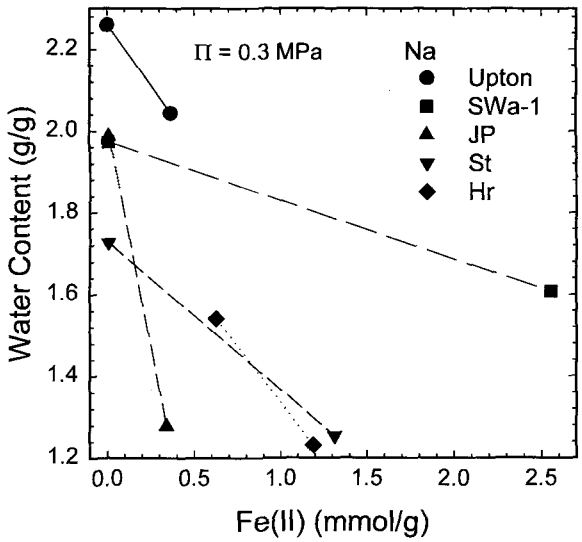


Figure 3. Effect of Fe oxidation state on equilibrium water content of five Na-saturated smectites equilibrated at Π = 0.3 MPa.

fect of Fe(II) on m_w/m_c at a given value of Π, however, varies depending on the smectite. For example, at 0.3 MPa, the slope of the plot of m_w/m_c *vs.* Fe(II) content increases in the order SWa-1 < Upton < Hr < St < JP (Figure 3).

Two models to explain the effect of Fe(II) on Na-saturated smectite swelling are considered here. The first relato the Langmuir equation from Gouy-Chapman theory (van Olphen, 1963), which is based on the assumption that an osmotic pressure develops within the clay interlayer because of exchangeable cations, *viz.*,

$$P = 2n^{o}kT\sqrt{\text{Cosh}(U - 1)} \qquad (2)$$

where P is the repulsive pressure between clay plates; n^{o}, the cation concentration in the outer solution of the clay-water system; k, Boltzmann's constant; T, the absolute temperature; and U, a function >1 that depends directly on the surface-charge density. Reduction of structural Fe increases the surface-charge density (Lear and Stucki, 1987, 1989; Kostka *et al.*, 1999), which by Equation (2) should also increase P. However, results shown in Figure 3a reveal that the opposite occurs. Thus, this model for explaining the effect of Fe(II) on Na-exchanged smectite swelling is inadequate.

The second model is consistent with experimental evidence, and is based on observations (Odom and Low, 1978; Viani *et al.*, 1983; Mulla *et al.*, 1985; Low, 1987) that the swelling of a given Na-saturated smectite depends primarily on specific surface area and the number of interlayers that expand fully. Previous studies (Stucki *et al.*, 1984a; Lear and Stucki, 1989; Wu *et al.*, 1988) attributed the effect of Fe oxidation state on swelling to its influence on the number of partially or fully collapsed interlayers. Whereas the fraction of expandable interlayers was not measured in the current study, the changes in m_w/m_c of Na-saturated smectites followed the same trends as in the previous studies.

Organo-clays offer insight as to whether structural Fe reduction actually alters the hydration force or partial molar Gibbs free energy of water at the clay surface. If Na counterions are replaced by TMA, TMPA, or HDTMA after reduction, but prior to swelling-pressure measurements, the swelling of the reduced clay increases rather than decreases relative to a more oxidized counterpart (Figure 4). For example, after reaching equilibrium at 0.01 MPa (0.1 atm), reduced TMA-, TMPA-, and HDTMA-saturated SWa-1 retained 2.2, 4.0, and 3.7 times more water, respectively, than the unaltered counterparts (Figure 4a). Organo-exchanged Upton exhibited a similar trend, and Hr, JP, and St retained nearly the same amount of H_2O as in the oxidized state (Figure 4b). In no case did the H_2O content decrease as observed for the Na form.

Samples Upton and SWa-1 were further studied at additional swelling pressures, and the same trends were observed (Figure 5). The increases in swellability of reduced TMPA-saturated Upton and TMPA-saturated SWa-1 over their oxidized counterparts were most dramatic. For TMPA-saturated Upton, the H_2O content of the reduced sample was equal to or slightly greater than that of the oxidized Na-saturated Upton (Figure 5a); but in the reduced TMPA-saturated SWa-1, the H_2O content greatly exceeded that of the oxidized Na-saturated Upton (Figure 5b). Because TMPA has such a large effect on decreasing the swellability of the oxidized smectites (Figures 1, 2, and 5), this observation is of great significance and indicates that the reduction of structural Fe in the 2:1 layer has a much greater and more complex effect on surface hydration forces than originally believed.

One possibility is that the decrease in H_2O content of Na-saturated smectite upon Fe reduction may be related solely to a decrease in the number of fully expanded interlayers, requiring no change in the hydration energy of the participating surfaces. Indeed, Wu *et al.* (1988) observed that the number of fully expanded interlayers in Na-saturated nontronite decreases with Fe reduction, and Lear and Stucki (1989) and Kostka *et al.* (1999) noted that the specific surface area declines. However, reduced smectite surfaces at the clay-water interface are more strongly hydrated than oxidized surfaces. This conclusion is based on: (1) The H_2O content of organo-exchanged smectites increases upon Fe reduction (Figure 4), thus reversing the trend observed with Na-saturated smectites (Figure 3). These differences cannot be explained by the hydration energy of the interlayer cation because the effect of the organic cation alone causes the system to retain less H_2O than if Na is the cation (Figures 1 and 2).

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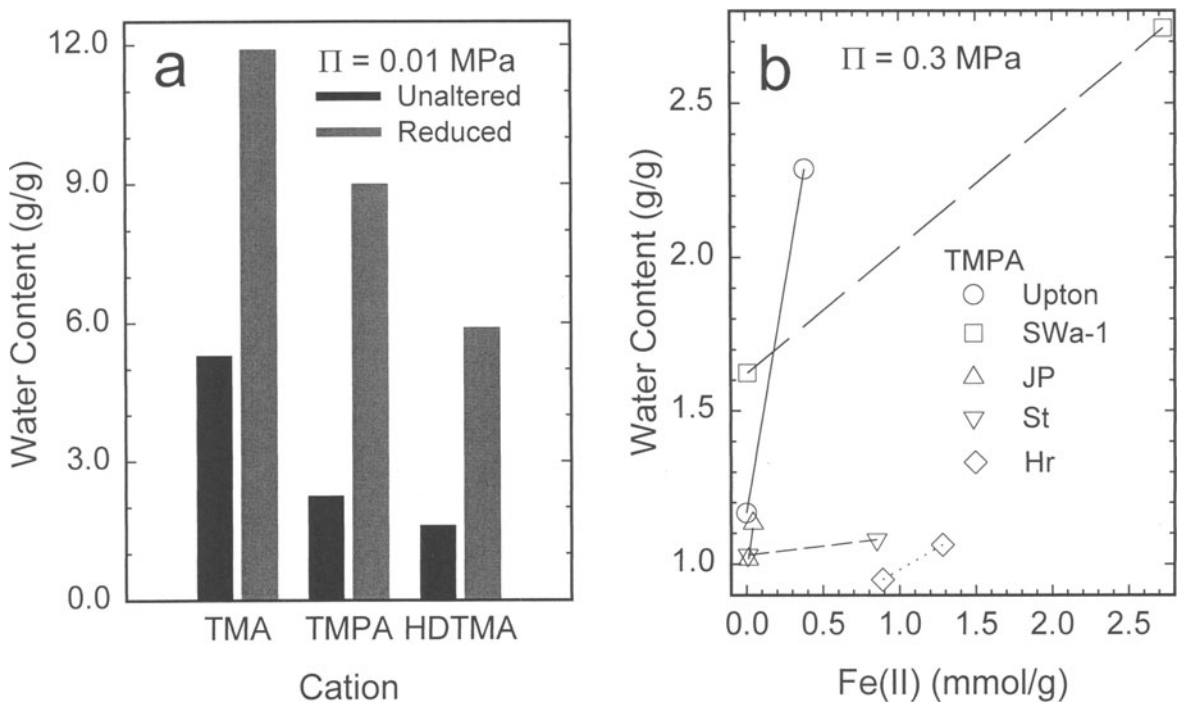


Figure 4. Effect of Fe oxidation state and saturating organic cation on equilibrium water content (m_w/m_c) of (a) oxidized and reduced [Fe(II) = 2.7 mmol/g] SWa-1 at Π = 0.01 MPa saturated with TMA, TMPA, or HDTMA; and (b) of five TMPA-saturated smectites equilibrated at Π = 0.3 MPa.

(2) The reduced organo-smectite must contain more expanded interlayers than the reduced Na-saturated smectite, otherwise a H_2O content greater than or equal to the Na-saturated reduced form is precluded unless (1) is violated. The organic cations evidently disrupt the mechanism that causes clay interlayers to collapse and become non-swelling. They keep more interlayers accessible for swelling and hydration than inorganic cations, such as Na^+. (3) The increased H_2O content of the reduced organo-smectite cannot be explained only by an increase in the number of expandable interlayers, however, because this requires the organo-clay to be more expanded than the unaltered Na form of Upton or SWa-1 (Figure 5). The Na or Li forms of Upton are the most dispersed or expanded forms of smectite, and both cations yielded similar H_2O contents here (Table 1). (4) For (1), (2), and (3) to be correct, the reduced smectite surface must be more strongly hydrated than the oxidized surface, enabling the reduced organo-smectite to contain more H_2O than the fully expanded Na-saturated smectite.

The net swellability of reduced smectites is, therefore, determined by the balance achieved between the opposing forces of increased hydration energy of reduced surfaces and the increased tendency for reduced layers to collapse. Under some conditions (*e.g.,* where organic cations inhibit interlayer collapse) the hydration energy dominates, whereas for other conditions (*e.g.,* Na-exchanged form) the tendency for interlayers to collapse is dominant. These results also provide further evidence that the clay surface hydrates directly and strongly, even in the presence of a hydrophobic organic cation (TMPA).

SUMMARY AND CONCLUSIONS

The H_2O content in various dioctahedral smectites decreased if Na was replaced by any of the organic cations TMA, TMPA, or HDTMA. Among these organic cations, the observed trend was that the amount of H_2O adsorbed decreased further with increasing complexity of the cation. TMPA-smectites retained less H_2O than Na-saturated forms at all pressures. This difference depended on the clay, and decreased with increasing pressure. Reduction of Fe(III) to Fe(II) in the octahedral sheet increased the layer charge and decreased the swelling of Na-saturated smectites by causing fewer interlayers to participate in the swelling process. The surfaces of reduced layers associated with uncollapsed interlayers hydrated more strongly than in the oxidized state. If the interlayer cation was changed from Na to an organo-cation after reduction, but prior to swelling-pressure measurements, the swelling of the reduced clays increased. For reduced TMPA-saturated Upton, the swelling was about the same or slightly greater than that of oxidized Na-saturated Upton, and for reduced TMPA-saturated SWa-

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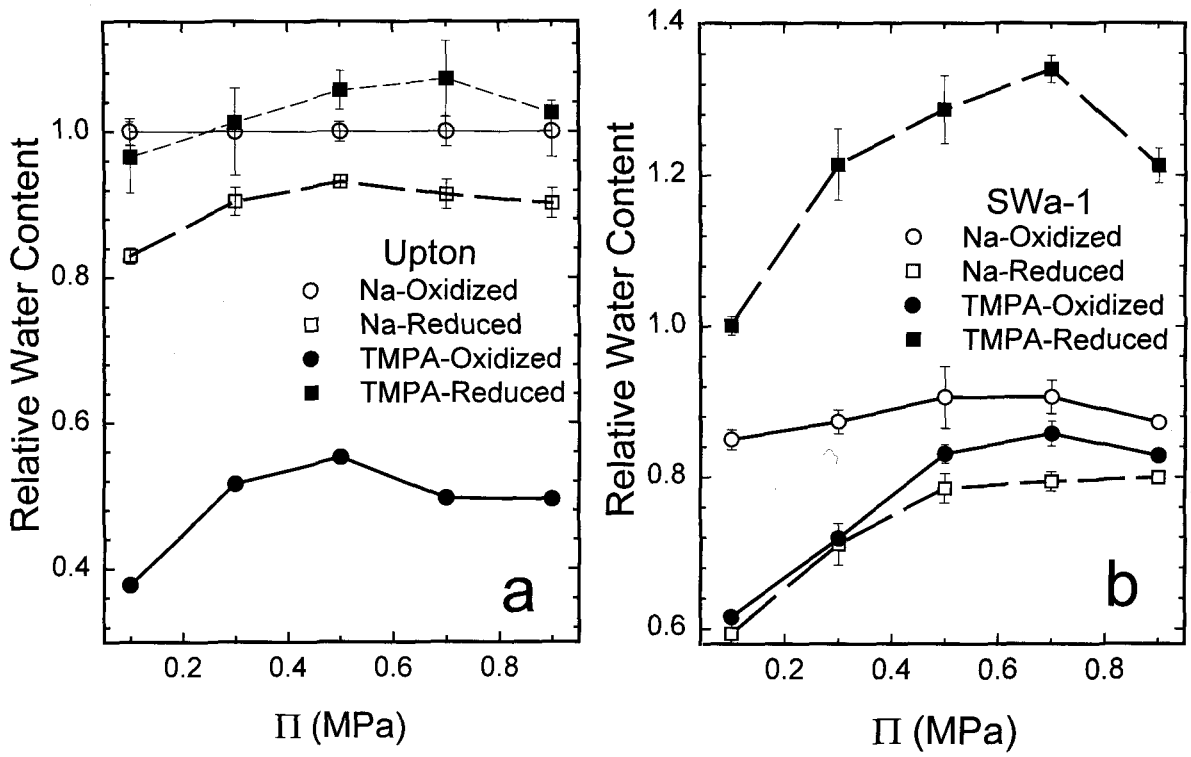


Figure 5. Comparisons of the effects of interlayer cation (Na or TMPA) and Fe oxidation state on the relation between equilibrium water content (m_w/m_c) and swelling pressure (Π) for (a) Upton, and (b) SWa-1. All H_2O-content values are relative to oxidized Na-saturated Upton at the corresponding value of Π.

1 the swelling was even greater. This dramatic increase in the swelling of reduced organo-clays is attributed to a large increase in the direct hydration energy of the clay surface. Both a greater surface hydration energy and the ability of organo-cations to prevent interlayers from collapsing and becoming non-swelling contributed to a higher H_2O content in reduced as compared to oxidized organo-clays. Smectite interlayer surfaces are, therefore, hydrophilic, and not hydrophobic.

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REFERENCES

Anderson, D.M. and Low, P.F. (1958) The density of water adsorbed by lithium-, sodium-, and potassium-bentonite. *Soil Science Society of America Proceedings,* **37,** 99–103.

Banin, A. and Lahav, N. (1968) An optical study of particle size of montmorillonite with various adsorbed ions. *Nature,* **217,** 1146–1147.

Boyd, S.A. and Jaynes, W.F. (1994) Role of layer charge in organic contaminant sorption by organo-clays. In *Layer Charge Characteristics of 2:1 Silicate Clay Minerals, CMS Workshop Lectures, Volume 6,* A.R. Mermut, ed., The Clay Minerals Society, Boulder, Colorado, 47–77.

Chen, S., Low, P.F., Cushman, J.H., and Roth, C.B. (1987) Organic compound effects on swelling and flocculation of Upton. *Soil Science Society of America Journal,* **51,** 1444–1450.

Čičel, B., Komadel, P., Bednáriková, E., and Madejová, J. (1992a) Mineralogical composition and distribution of Si, Al, Fe, Mg and Ca in the fine fractions of some Czech and Slovak bentonites. *Geologica Carpathica, Series Clays,* **43,** 3–7.

Čičel, B., Komadel, P., Lego, S., Madejová, J., and Vlèková, L. (1992b) Iron-rich beidellite in the fine fraction of Stebno bentonite. *Geologica Carpathica, Series Clays,* **43,** 121–124.

Gates, W.P., Wilkinson, H.T., and Stucki, J.W. (1993) Swelling properties of microbially reduced ferruginous smectite. *Clays and Clay Minerals,* **41,** 360–364.

Hofmann, U. and Klemen, R. (1950) Verlust der Austauschfahigkeit von Lithiumionen an Bentonit durch Erhitzung. *Zeitschrift für Anorganische Allgemeine Chemie,* **262,** 95–99.

Janek, M., Komadel, P., and Lagaly, G. (1997) Effect of autotransformation on the layer charge of smectites determined by alkylammonium method. *Clay Minerals,* **32,** 623–632.

Jaynes, W.F. and Bigham, J.M. (1987) Charge reduction, octahedral charge, and lithium retention in heated, Li-saturated smectites. *Clays and Clay Minerals,* **35,** 440–448.

Jaynes, W.F. and Boyd, S.A. (1991) Hydrophobicity of siloxane surfaces in smectites as revealed by aromatic hydrocarbon adsorption from water. *Clays and Clay Minerals,* **39,** 428–436.

https://doi.org/10.1346/CCMN.2000.0480216 Published online by Cambridge University Press

Komadel, P. and Stucki, J.W. (1988) Quantitative assay of minerals for Fe^{2+} and Fe^{3+} using 1, 10-phenanthroline: III. A rapid photochemical method. *Clays and Clay Minerals,* **36,** 379–381.

Komadel, P., Lear, P.R., and Stucki, J.W. (1990) Reduction and reoxidation of nontronite: Extent of reduction and reaction rates. *Clays and Clay Minerals,* **38,** 203–208.

Kostka, J.E., Wu, J., Nealson, K.H., and Stucki, J.W. (1999) The impact of structural Fe(III) reduction by bacteria on the surface chemistry of clay minerals. *Geochemica et Cosmochimica Acta,* **63,** 3705–3713.

Lagaly, G. (1994) Layer charge determination by alkylammonium ions. In *Layer Charge Characteristics of 2:1 Silicate Clay Minerals, CMS Workshop Lectures, Volume 6,* A.R. Mermut, ed., The Clay Minerals Society, Boulder, Colorado, 1–46.

Lagaly, G. and Weiss, A. (1976) The layer charge of smectitic layer silicates. In *Proceedings, International Clay Conference, Mexico City, Mexico, 1975,* S.W. Bailey, ed., Academic Publishers, Wilmette, Illinois, 157–172.

Laird, D.A. (1994) Evaluation of the structural formula and alkylammonium methods of determining layer charge. In *Layer Charge Characteristics of 2:1 Silicate Clay Minerals, CMS Workshop Lectures, Volume 6,* A.R. Mermut, ed., The Clay Minerals Society, Boulder, Colorado, 79–103.

Lawrence, M.A.M., Kukkadapu, R.K., and Boyd, S.A. (1998) Adsorption of phenol and chlorinated phenols from aqueous solution by tetrametylammonium- and tetramethylphosphonium-exchanged montmorillonite. *Applied Clay Science,* **13,** 13–20.

Lear, P.R. and Stucki, J.W. (1987) Intervalence electron transfer and magnetic exchange in reduced nontronite. *Clays and Clay Minerals,* **35,** 373–378.

Lear, P.R. and Stucki, J.W. (1989) Effects of iron oxidation state on the specific surface area of nontronite. *Clays and Clay Minerals,* **37,** 547–552.

Low, P.F. (1951) Force fields and chemical equilibrium in hetero-geneous systems with special reference to soils. *Soil Science,* **71,** 409–418.

Low, P.F. (1980) The swelling of clay. II. Montmorillonites. *Soil Science Society of America Journal,* **44,** 667–676.

Low, P.F. (1981) The swelling of clay: III. Dissociation of exchangeable cations. *Soil Science Society of America Journal,* **45,** 1074–1078.

Low, P.F. (1987) Structural component of the swelling pressure of clays. *Langmuir,* **3,** 18–25.

Low, P.F. and Margheim, J.F. (1980) The swelling of clay. I. Basic concepts and empirical equations. *Soil Science Society of America Journal,* **43,** 473–481.

Mulla, D.J., Low, P.F., and Roth, C.B. (1985) Measurement of specific surface area of clays by internal reflectance spectroscopy. *Clays and Clay Minerals,* **33,** 391–396.

Odom, J.W. and Low, P.F. (1978) Relation between swelling, surface area and *b* dimension of Na-montmorillonites. *Clays and Clay Minerals,* **26,** 345–351.

Ravina, I. and Low, P.F. (1972) Relation between swelling, water properties and *b*-dimension in montmorillonite-water systems. *Clays and Clay Minerals,* **20,** 109–123.

Ravina, I. and Low, P.F. (1977) Change of *b*-dimension with swelling of montmorillonite. *Clays and Clay Minerals,* **25,** 201–204.

Stevens, J.J. and Anderson, S.J. (1996) An FTIR study of water-sorption on TMA- and TMPA-montmorillonites. *Clays and Clay Minerals,* **44,** 142–150.

Stevens, J.J., Anderson, S.J., and Boyd, S.A. (1996) FTIR study of competitive water-arene sorption on tetramethylammonium- and trimethylphenylammonium-montmorillonites. *Clays and Clay Minerals,* **44,** 88–95.

Stucki, J.W. (1988) Structural iron in smectites. In *Iron in Soils and Clay Minerals,* J.W. Stucki, B.A. Goodman, and U. Schwertmann, eds., D. Reidel, Dordrecht, The Netherlands, 625–675.

Stucki, J.W., Low, P.F., Roth, C.B., and Golden, D.C. (1984a) Effects of oxidation state of octahedral iron on clay swelling. *Clays and Clay Minerals,* **32,** 357–362.

Stucki, J.W., Golden, D.C., and Roth, C.B. (1984b) The preparation and handling of dithionite-reduced smectite suspensions. *Clays and Clay Minerals,* **32,** 191–197.

van Olphen, H. (1963) *Introduction to Clay Colloid Chemistry.* Wiley-Interscience, New York, 301 pp.

Viani, B.E., Low, P.F., and Roth, C.B. (1983) Direct measurement of the relation between interlayer force and interlayer distance in the swelling of montmorillonites. *Journal of Colloid and Interface Science,* **96,** 229–244.

Wu, J., Low, P.F., and Roth, C.B. (1988) Effects of octahedral iron reduction and swelling pressure on interlayer distances in Na-nontronite. *Clays and Clay Minerals,* **37,** 211–218.

Xu, S., Sheng, G., and Boyd, S.A. (1997) Use of organoclays in pollution abatement. *Advances in Agronomy,* **59,** 25–62.

Yan, L. and Stucki, J.W. (1999) Effects of structural Fe oxidation state on the coupling of interlayer water and structural Si-O stretching vibrations in montmorillonite. *Langmuir,* **15,** 4648–4657.

Yan, L., Low, P.F., and Roth, C.B. (1996a) Swelling pressure of montmorillonite layers versus H-O-H bending frequency of the interlayer water. *Clays and Clay Minerals,* **44,** 749–765.

Yan, L., Roth, C.B., and Low, P.F. (1996b) Changes in the Si-O vibrations of smectite layers accompanying the sorption of interlayer water. *Langmuir,* **12,** 4421–4429.

Yan, L., Roth, C.B., and Low, P.F. (1996c) Effects of monovalent, exchangeable cations and electrolytes on the infrared vibrations of smectite layers and interlayer water. *Journal of Colloid and Interface Science,* **184,** 663–670.

Zhang, F., Zhang, Z.Z., Low, P.F., and Roth, C.B. (1993) The effect of temperature on the swelling of montmorillonite. *Clay Minerals,* **28,** 25–32.

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