

LAYER CHARGE INFLUENCES ON THE HYDRATION OF EXPANDABLE 2:1 PHYLLOSILICATES

DAVID A. LAIRD

USDA, ARS, National Soil Tilth Laboratory, 2150 Pammel Drive, Ames, Iowa 50011, USA

Abstract—The objective of this study was to investigate the influence of layer charge on the hydration of Mg-saturated expandable 2:1 phyllosilicates. Water retained by 12 Mg-saturated clays at 54% relative humidity was quantified gravimetrically. X-ray diffraction and total chemical analysis were used to determine the hydratable surface area ($447\text{--}759\text{ m}^2\text{ g}^{-1}$) and layer charge [$0.327\text{--}0.754$ electrons per formula unit (e f.u.⁻¹)] of each sample. Water retained by the clays increased with both hydratable surface area and layer charge of the clays. However, the increase in H₂O content with layer charge occurred only on external surfaces of the clays. This result suggests that the H₂O on external surfaces is localized around the cation/charge sites rather than forming multi-layers as was suggested previously. A model is proposed for the hydration of expandable 2:1 phyllosilicates. The model assumes that interlayer volume controls interlayer hydration and that the number of cation/charge sites on external surfaces controls hydration of external surfaces.

Key Words—External Surface, Hydration, Hydration Number, Layer Charge, SAZ-1, SHCa-1, Surface Area, SWa-1, Swelling, VTx-1.

INTRODUCTION

The hydration of expandable 2:1 phyllosilicates has been extensively studied for over 50 years. Early work (Mooney *et al.*, 1952) demonstrated that smectite hydration is strongly influenced by H₂O vapor pressure (p/p_0), the extent of crystalline swelling, and the nature of the exchangeable cations. Although, the work of Mooney *et al.* (1952) was criticized because the samples were H saturated prior to saturation with the desired cations, the essential features of their results were reproduced by Ormerod and Newman (1983), Newman (1987), Cases *et al.* (1997), and Chiou and Ruthenford (1997).

Crystalline swelling is a process whereby the basal spacings ($d(001)$ -values) of 2:1 phyllosilicates expand or collapse between 10–22 Å in a series of steps corresponding to the intercalation of 0, 1, 2, 3, or 4 discrete layers of H₂O molecules (Norrish, 1954). The extent of crystalline swelling is controlled by a balance between relatively strong swelling forces, due to the hydration potential of the interlayer cations and charge sites, and electrostatic forces of attraction between the negatively charged 2:1 phyllosilicate layers and the positively charged interlayer cations (Norrish, 1954; Kittrick, 1969; Laird, 1996). Isotherms relating $d(001)$ -values to p/p_0 , osmotic pressure, and temperature (Mooney *et al.*, 1952; Kittrick, 1969; Slade *et al.*, 1991; Laird *et al.*, 1995; Cases *et al.*, 1997) show broad regions where $d(001)$ -values are nearly constant, corresponding to discrete layer hydrates, and relatively narrow regions where abrupt changes in $d(001)$ -values occur. By contrast, isotherms relating the gravimetric H₂O content to p/p_0 typically show a nearly continuous increase in adsorbed H₂O with increasing p/p_0 . Only

small changes in slope of these isotherms are evident in regions where abrupt changes in $d(001)$ -values occur. The discrepancy between the shapes of isotherms showing the response of $d(001)$ -values to p/p_0 and isotherms showing variation in gravimetric H₂O content with p/p_0 is still not fully explained.

Ormerod and Newman (1983) investigated the relationship between $d(001)$ -values and gravimetric-H₂O sorption and desorption isotherms for Ca-montmorillonite (from Redhill, UK). They proposed a relatively simple model for the hydration of 2:1 phyllosilicates assuming that the volume of the interlayers determines the extent of interlayer hydration and that multi-layer adsorption occurs on external surfaces of smectite quasicrystals. Using this model, Newman (1983) argued that H₂O retained by smectites at $p/p_0 = 0.47$ closely approximates monolayer coverage, although he reported slightly greater H₂O retention on external surfaces than internal surfaces at this vapor pressure. Furthermore, Newman (1983) demonstrated that H₂O retained by 62 soil samples at $p/p_0 = 0.47$ was highly correlated with both the amount of ethylene glycol adsorbed by the soils and the cation exchange capacity (CEC) of the soils. Based on these analyses, Newman (1983) suggested that the specific surface area of soils and clays can be estimated from the H₂O content at $p/p_0 = 0.47$.

The primary interaction between H₂O and permanent charge surfaces is through hydration of the exchangeable metal cations (Russell and Farmer, 1964; Sposito and Prost, 1982; Güven, 1992; Johnston *et al.*, 1992). Early recognition of the importance of H₂O clustering around adsorbed metal cations led Quirk (1955) to speculate that, "At a given energy level, the number of H₂O molecules adsorbed on a clay would

Table 1. Names, sources, and symbols of various reference, soil, and reduced-charge clays used.

Name	Source	Symbol
Bentonite, Wyoming	American Colloid Co.	B
Ferruginous smectite (SWa-1)	CMS Source Clay Repository	F
Vermiculite, South Carolina	Zonolite Co.	V
Zwingle soil smectite	Allamakee Co. IA	Z
Hectorite (SHCa-1)	CMS Source Clay Repository	H
Vermiculite, Llano Texas (VTx-1)	CMS Source Clay Repository	L
Smectite, Cheto Arizona (SAz-1)	CMS Source Clay Repository	C
Reduced-charge smectite (0% Li)	Prepared from C	0
Reduced-charge smectite (10% Li)	Prepared from C	1
Reduced-charge smectite (20% Li)	Prepared from C	2
Reduced-charge smectite (30% Li)	Prepared from C	3
Reduced-charge smectite (40% Li)	Prepared from C	4

increase in a general way as the surface density of charge increases." Experimental evidence of the influence of layer charge on hydration of smectites, however, was not presented until recently. Chiou and Rutherford (1997) observed greater H₂O retention by a high-charge smectite (SAz-1) relative to a low-charge smectite (SWy-1) over the full range of vapor pressures ($p/p_0 = 0-1$). They attributed this phenomenon to greater swelling by the high-charge smectite; however this explanation is contrary to the commonly accepted principal of decreased swelling with increasing layer charge. Furthermore, Chiou and Rutherford (1997) included only two clays in their study, hence it is not clear whether the differences they observed are due to effects of layer charge or other differences between the studied samples. The present study was designed to investigate the influence of layer charge on the hydration of Mg-saturated expandable 2:1 phyllosilicates.

MATERIALS AND METHODS

One soil smectite, four reference smectites, and two reference vermiculites were investigated. The soil smectite was separated from soil collected from the Bt horizon of a Zwingle pedon (Typic Albaqualfs) located in Allamakee County, Iowa. Organic matter was removed from the soil by wet oxidation with 30% H₂O₂, and free iron compounds were removed by treatment with sodium dithionate-sodium citrate-sodium bicarbonate (Lim and Jackson, 1982). Three of the reference clays also required processing prior to size fractionation. Clean macro flakes of both the Llano and South-Carolina vermiculites were dry ground in a water-cooled Waring[†] blender. The hectorite sample was treated with 0.1 M HCl to remove free carbonates. To obtain relatively pure specimens, all samples except the Zwingle smectite were saturated with Na, dis-

persed in distilled H₂O, and the <2- μ m fraction was separated by sedimentation. The Zwingle smectite was Na-saturated, dispersed in distilled H₂O, and fractionated by centrifugation to collect the <0.06- μ m fraction.

Five reduced-charge smectites were also used in the study. The reduced-charge smectites were prepared from the <2- μ m size fraction of the Cheto smectite (SAz-1) using a method similar to that described by Brindley and Ertem (1971). Briefly, homogenized, salt-free Li-smectite and Na-smectite suspensions (50 g L⁻¹) were volumetrically combined to form five mixed suspensions (Na-smectite:Li-smectite = 1:0, 9:1, 8:2, 7:3, 6:4). The mixed suspensions were shaken for 48 h, evaporated to dryness, and then the mixed ionic clays were heated at 220°C for 24 h. Under these conditions, Li ions penetrate the 2:1 layers and occupy vacant octahedral sites, where they partially neutralizes the layer charge. Names and symbols used for the reference clays, soil clay, and reduced-charge clays are listed in Table 1.

Magnesium saturated samples were prepared by washing the clays three times with 0.5 M MgCl₂, and then washing the clays with 95% ethanol to remove excess salt. The Mg-clays were oriented on glass slides by the paste method (Theissen and Harward, 1962) and immediately (while still wet) placed in a desiccator above a saturated solution of Mg(NO₃)₂ which yields a constant relative humidity (RH) of 54%. After >24 h the oriented samples were analyzed by X-ray diffraction (XRD) in a controlled atmosphere (54% RH) sample chamber to determine the $d(001)$ -values of the clays. After XRD analysis, the samples were returned to the desiccator containing saturated Mg(NO₃)₂ for an additional 1-5 wk before thermal gravimetric analysis (TGA). For the TGA, ~5 mg of Mg-saturated clay were transferred from the glass slide to the platinum sample pan of a Cahn Electrobalance. A hang-down-tube containing ~100 mL of saturated Mg(NO₃)₂ was connected to the housing of the electrobalance, such that the sample pan was ~1 cm above the Mg(NO₃)₂ solution. After 2 h, the sample weight

[†] Trade names and company names are included for the benefit of the reader and do not imply any endorsement or preferential treatment of the product listed by the United States Department of Agriculture.

Table 2. Mineralogical and surface properties of the studied clays.

Name	Layer charge (e f.u. ⁻¹)	CEC (mmol (+) g ⁻¹)	<i>d</i> (001) _z -value (Å)	Total surface area (m ² g ⁻¹)	Hydratable surface area (m ² g ⁻¹)	External ¹ surface area (m ² g ⁻¹)
B	0.327	0.883	14.85	759	759	34
F	0.474	1.167	14.85	703	702	73
V	0.654	0.971	14.24	738	447	40
Z	0.397	0.802	14.85	729	566	52
H	0.350	0.909	14.85	755	748	48
L	0.754	1.748	14.24	732	663	61
C	0.469	1.250	14.85	761	743	116
0	0.460	1.249	14.85	762	759	130
1	0.438	1.190	14.85	763	759	111
2	0.398	1.079	14.85	763	759	97
3	0.370	1.006	14.85	763	759	107
4	0.338	0.914	14.85	764	759	88

¹ Estimated using Equation (4) and assuming ϵ is equal to 7.18×10^{-22} g-H₂O e⁻¹.

at 54% RH was recorded, then the hang-down-tube containing the Mg(NO₃)₂ solution was replaced with a dry hang-down-tube, the sample chamber was evacuated (-75 KPa), and the samples were heated at 15°C per min to >200°C. The weight loss between 54% RH at room temperature and 200°C in a -75 KPa vacuum relative to the 200°C weight was used to quantify H₂O content of the clays at 54% RH. The results for the reference and soil clays are averages of three determinations of dehydration weight-loss. The first determination was conducted after the samples had been in a desiccator above the saturated Mg(NO₃)₂ solution for 1–5 wk, the second and third determinations were conducted after the samples had been in the desiccator ~3 and ~6 mo, respectively. The results for the reduced-charge clays are based on single determinations following 1–5 wk above saturated Mg(NO₃)₂.

Portions (~0.5 g) of each sample were washed three times with 0.5 M CaCl₂ and then washed free of excess salt with 95% ethanol. Chemical analyses of Ca-saturated, salt-free samples were performed by inductively coupled plasma-atomic emission spectroscopy using suspension nebulization (Laird *et al.*, 1991a). Structural formulae were calculated from results of the chemical analyses assuming a framework anionic charge of -22 per formula unit for all samples except the Llano vermiculite. For the Llano vermiculite, the octahedral occupancy was assumed to equal 3.00 and the framework anionic charge was treated as a variable. Layer charge was determined from the structural formulae (Laird, 1994).

The *d*(060)-values were measured by transmission XRD. Oriented clay specimens were prepared on Parafilm and attached to a plastic frame. The frames were mounted perpendicular to the focal plane of the goniometer. Samples were analyzed between 50–68 °2 θ using CuK α radiation. Total theoretical surface areas were calculated as the product of the *a* and *b* unit-cell

dimensions divided by the formula-unit weight. Surface area capable of being hydrated (hereafter referred to as “hydratable surface area”) were determined from the product of the total theoretical surface area and the ratio of the CEC to the sum of the exchangeable and nonexchangeable interlayer cations (expressed in equivalents).

RESULTS AND DISCUSSION

Mineralogical and surface properties of the studied reference, soil, and reduced-charge clays are listed in Table 2. The studied samples have a wide range in layer charge (0.327–0.754 e f.u.⁻¹) and a moderate range in hydratable surface area (447–759 m² g⁻¹). Eight samples are fully expandable smectites, with nearly equal hydratable surface areas (between 740–759 m² g⁻¹). The remaining four samples have hydratable surface areas ranging between 447–702 m² g⁻¹. Of these, Llano vermiculite, South-Carolina vermiculite, and Zwingle smectite have significant proportions of non-expandable layers as indicated by the presence of non-exchangeable K (0.182, 0.232, and 0.632 mmol K g⁻¹, respectively). The ferruginous smectite has only 702 m² g⁻¹ of hydratable surface area due to a high structural iron content and consequently a high formula-unit weight relative to the other samples.

The use of a correction based on levels of non-exchangeable K to estimate hydratable surface areas from total theoretical surface areas (see Materials and Methods) may be controversial because of the implicit assumption of equivalence of layer charge for the expandable and nonexpandable layers. The correction has a negligible influence on estimates of hydratable surface area for the fully expandable smectites but does influence estimates of hydratable surface area for Llano vermiculite, South-Carolina vermiculite, and Zwingle smectite. The implicit assumption of equivalence of layer charge for the expandable and nonexpandable layers is reasonable for the vermiculites because they have high values of layer charge. The assumption is supported for the Zwingle smectite by Laird *et al.* (1991b) and Laird and Nater (1993) who found a low-charge illitic phase in randomly interstratified smectite-illite in soil clays.

The influence of hydratable surface area on H₂O retained by soils and clays has long been recognized (Quirk, 1955; Newman, 1983; Cases *et al.*, 1997). Results of the present study are consistent with previous findings, as the gravimetric H₂O content of the clays was found to increase linearly with the hydratable surface area (Figure 1). Although the correlation between H₂O content and hydratable surface area is relatively strong (*r*² = 0.828), the relationship is clearly driven by the four samples with <740 m² g⁻¹ of hydratable surface area. The gravimetric H₂O content at 54% RH for the eight fully expandable clays ranges from 0.21

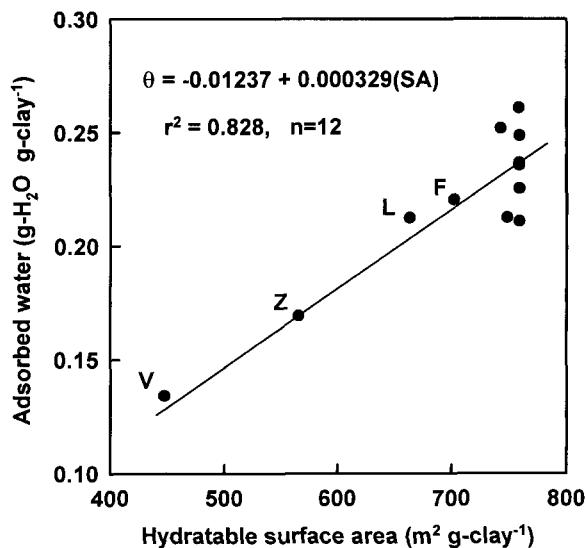


Figure 1. Relationship between hydratable surface area and gravimetric H₂O content of various expandable 2:1 phyllosilicates equilibrated at 54% RH. Clays with <740 m² g⁻¹ hydratable surface area are identified with symbols.

to 0.26 g-H₂O g-clay⁻¹ and this variation is unrelated to minor differences in hydratable surface area among these samples.

The influence of layer charge on the retention of H₂O by expandable 2:1 phyllosilicates is illustrated in Figure 2. The eight fully expandable smectites exhibit a strong positive correlation ($r^2 = 0.878$) between gravimetric H₂O content and layer charge. By contrast, the four samples with <740 m² g-clay⁻¹ hydratable surface area are randomly scattered in Figure 2. The data in Figures 1 and 2 demonstrate that both hydratable surface area and layer charge influence H₂O retained by expandable 2:1 phyllosilicates.

An increase in gravimetric H₂O content with increasing layer charge (Figure 2) for the eight fully expandable smectites is consistent with the results of Chiou and Rutherford (1997) who attributed this phenomenon to greater swelling by high-charge smectites. In the present study, however, $d(001)$ -values of the studied clays were determined by XRD while the samples were in an atmosphere controlled at 54% RH. The XRD data (Table 2) indicate that the $d(001)$ -values are nearly equal for the smectites (14.8 Å), whereas the vermiculites have slightly lower $d(001)$ -values (14.2 Å). Thus the extent of swelling can not explain the increase in H₂O content with increasing layer charge observed for the eight fully expandable clays.

The relationship between effective hydration numbers and layer charge provides additional insight into mechanisms controlling hydration of expandable 2:1 phyllosilicates (Figure 3). Effective hydration numbers are herein defined as the average number of H₂O molecules per charge site retained at 54% RH on the hy-

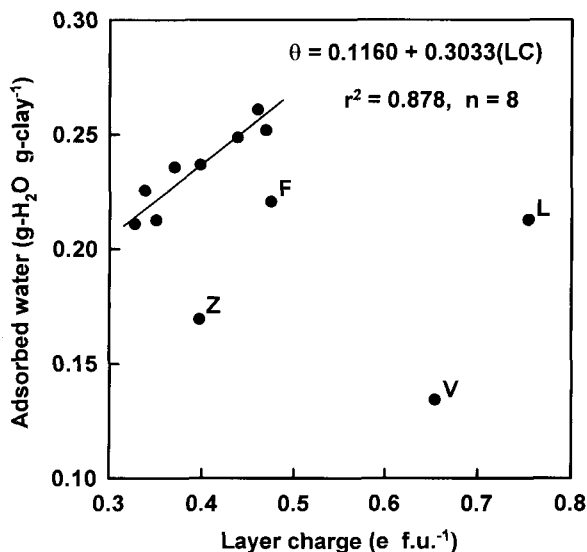


Figure 2. Relationship between layer charge and gravimetric H₂O content of various expandable 2:1 phyllosilicates equilibrated at 54% RH. Clays with <740 m² g⁻¹ hydratable surface area are identified with symbols.

dratable surfaces of 2:1 phyllosilicates. Effective hydration numbers are readily calculated as the gravimetric H₂O content (g-H₂O g-clay⁻¹) divided by both the molecular weight of H₂O and the CEC (mol(+) g-clay⁻¹; determined from the structural formula) of the clay. The convention of expressing effective hydration numbers relative to monovalent charge sites was cho-

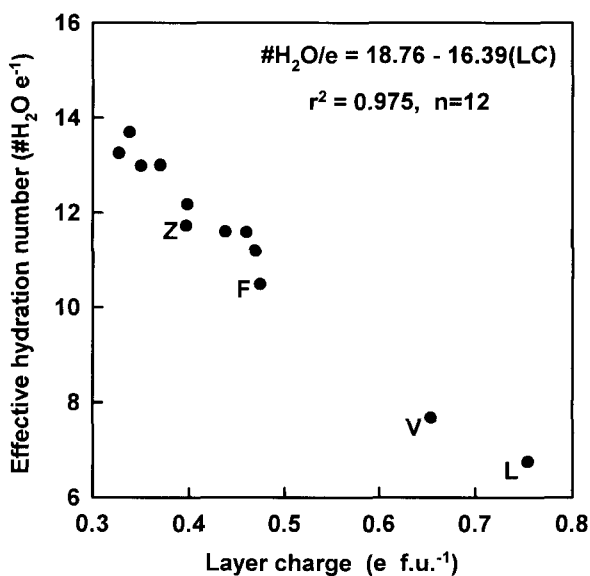


Figure 3. Relationship between layer charge and effective hydration numbers for surface charge sites on various expandable 2:1 phyllosilicates equilibrated at 54% RH. Clays with <740 m² g⁻¹ hydratable surface area are identified with symbols.

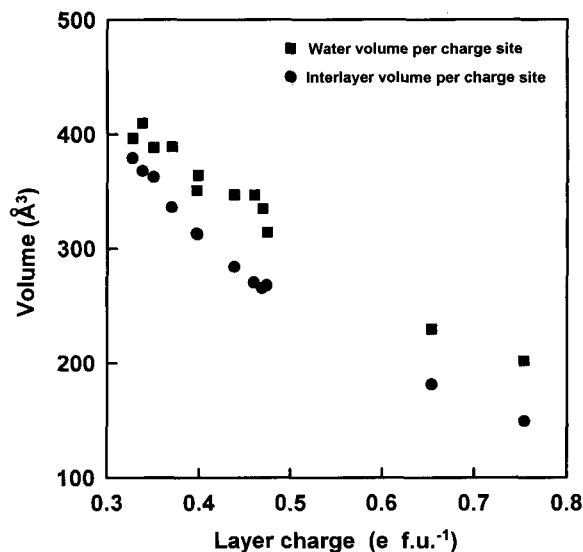


Figure 4. Relationship between layer charge and both the average interlayer volume per charge site (circles) and the average volume occupied by H₂O per charge site (squares) for the various expandable 2:1 phyllosilicates equilibrated at 54%.

sen for convenience, however, note that the primary interaction between H₂O and permanent charge surfaces is through the exchangeable cations (Quirk, 1955; Sposito and Prost, 1982).

The correlation ($r^2 = 0.975$) between effective hydration number and layer charge is striking (Figure 3). Significantly, each of the studied clays conforms to the same inverse relationship, regardless of hydratable surface area. The observed decrease in effective hydration number with increasing layer charge suggests that the hydration of expandable 2:1 phyllosilicates is influenced by the volume available for hydration in the interlayers.

The role of interlayer volume on limiting hydration of 2:1 phyllosilicates can be further evaluated by comparing the average interlayer volume per charge site (V_e) with the average volume occupied by H₂O per charge site (V_w). V_e is readily estimated using:

$$V_e = 0.5S_h(d - D)/CEC \quad (1)$$

where S_h is the hydratable surface area ($m^2 \text{ g-clay}^{-1}$), d is the $d(001)$ -value (m), D is the unit layer thickness (9.5×10^{-10} m), and CEC is the cation exchange capacity expressed in mol(+) g-clay^{-1} . V_w is estimated from:

$$V_w = \theta_w/(\rho_w CEC) \quad (2)$$

where θ_w is the gravimetric H₂O content ($\text{g-H}_2\text{O g-clay}^{-1}$), and ρ_w is the density of the interlayer H₂O ($\text{g-H}_2\text{O m}^{-3}$). Assuming that ρ_w is approximately $1 \times 10^6 \text{ g-H}_2\text{O m}^{-3}$ then V_w is readily obtained. Both V_e and V_w decrease nearly linearly with increasing layer

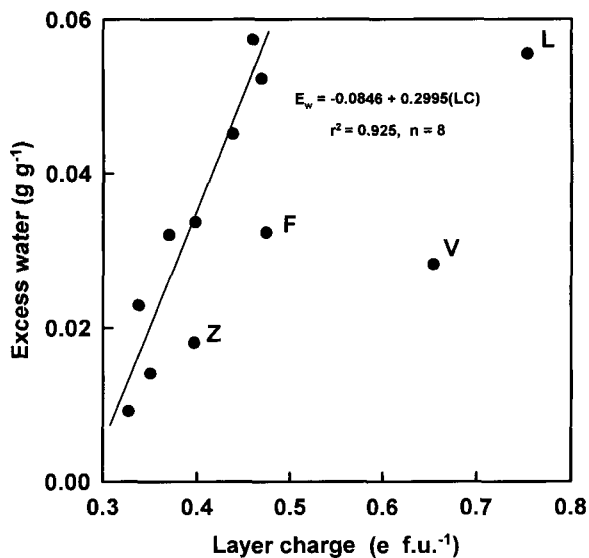


Figure 5. Relationship between layer charge and excess external surface H₂O for the various expandable 2:1 phyllosilicates equilibrated at 54% RH. Clays with $<740 \text{ m}^2 \text{ g}^{-1}$ hydratable surface area are identified with symbols.

charge (Figure 4); however, V_w ranges between 4–26% larger than V_e for all samples.

V_w is probably greater than V_e because charge sites on external surfaces have substantially larger effective hydration numbers than charge sites on internal surfaces. This explanation is consistent with the fact that the hydration of cations (and the associated charge sites) on external surfaces is unconstrained, whereas the hydration of cations/charge sites on internal surfaces is limited by the available interlayer volume per charge site. Another possible explanation for $V_w > V_e$ is if the density of the interlayer H₂O is greater than $1 \times 10^6 \text{ g-H}_2\text{O m}^{-3}$. Although the density of interlayer H₂O is not known with great certainty it is probably less than $1 \times 10^6 \text{ g-H}_2\text{O m}^{-3}$ rather than greater.

Assuming the density of the interlayer H₂O in expandable 2:1 phyllosilicates is $1 \times 10^6 \text{ g-H}_2\text{O m}^{-3}$, then the amount of excess H₂O on external surfaces (E_w) is estimated by:

$$E_w = (V_e - V_w)\rho_w \quad (3)$$

Note that E_w is not the total H₂O on external surfaces. Rather, E_w is the H₂O retained on external surfaces in excess of that which would be retained by an equal area of internal surfaces.

The relationship between layer charge and E_w is presented in Figure 5. In Figure 5, the four samples with $<740 \text{ m}^2 \text{ g-clay}^{-1}$ of hydratable surface area are again distinguished from the eight fully hydratable smectites. The excess H₂O retained on the external surfaces of the eight fully hydratable samples increases linearly with layer charge ($r^2 = 0.925$), and the slope of this relationship (0.299) is nearly equal to the slope (0.303)

of the relationship between total hydration H_2O and layer charge (Figure 2). These results indicate that the observed increase in hydration H_2O with layer charge (Figure 2) is due to an increase in excess H_2O held on external surfaces. The results also indicate that the amount of H_2O retained on external surfaces is directly proportional to the number of charge sites on the external surfaces rather than the external surface area.

Based on the above analysis, a new model is proposed for the hydration of Ca and Mg-saturated expandable 2:1 phyllosilicates:

$$\theta_w = 0.5\rho_w(d - D)(S_h - S_x) + \epsilon S_x \sigma, \quad (4)$$

where S_x is the external-surface area ($m^2 \text{ g-clay}^{-1}$), ϵ is the total amount of H_2O per charge site on external surfaces ($\text{g-H}_2\text{O e}^{-1}$), σ is the surface-charge density (e m^{-2}), and other symbols are defined above. The first term in Equation (4) estimates the quantity of interlayer H_2O as the product of interlayer volume and the density of the interlayer H_2O . This approach is identical to that used by Ormerod and Newman (1983) for estimating interlayer H_2O . The second term estimates the H_2O retained on external surfaces as the product of the number of charge sites located on external surfaces ($S_x \sigma$) and the H_2O retained by each charge site (ϵ). By contrast, other researchers (Ormerod and Newman, 1983; Cases *et al.*, 1997) assumed unrestricted multi-layer adsorption of H_2O on external surfaces, which is dependent on the external surface area rather than the number of charge sites on the external surfaces.

Fitting the proposed model to the hydration data for the 12 studied clays is problematic as there are two unknowns, ϵ and S_x , in Equation (4). The amount of external surface area, S_x , varies depending on properties of the mineral (*e.g.*, composition, structure, morphology of fundamental particles) and history of the sample (*e.g.*, grinding, sonication, *etc.*). In contrast, Figure 5 indicates that the H_2O retained per charge site on external surfaces, ϵ , is independent of layer charge. Relative humidity and the type of exchangeable cations are anticipated to have a large influence on ϵ , but these were constant in the present study. Thus by assuming that $\epsilon = 7.18 \times 10^{-22} \text{ g-H}_2\text{O e}^{-1}$ (equivalent to 24 H_2O molecules per charge site or 48 H_2O molecules per Mg^{2+}), Equation (4) can be solved and an estimate for external surface area can be obtained (Table 2). External surface areas determined using Equation (4) for Wyoming bentonite, Cheto montmorillonite, and California hectorite (34, 116, and 48 $m^2 \text{ g}^{-1}$, respectively) are comparable to measured external surface areas (31, 94, and 64 $m^2 \text{ g}^{-1}$, respectively) based on N_2 adsorption isotherms (van Olphen and Fripiat, 1979).

The effect of vapor pressure on the hydration of expandable 2:1 phyllosilicates was not quantified in the present study. However, numerous published ad-

sorption and desorption isotherms (Mooney *et al.*, 1952; Ormerod and Newman, 1983; Chiou and Ruth-erford, 1997; Cases *et al.*, 1997) may be reevaluated in light of the findings of this study. Three general hydration regions may be defined for Ca and Mg-saturated, fully-expandable 2:1 phyllosilicates: In Region I, the H_2O content ranges from 0 to 0.20 $\text{g-H}_2\text{O g-clay}^{-1}$ and p/p_0 ranges from 0 to ~ 0.4 ; in Region II, the H_2O content ranges from 0.20 to 0.27 $\text{g-H}_2\text{O g-clay}^{-1}$ and p/p_0 ranges from ~ 0.4 to ~ 0.8 ; and in Region III, the H_2O content is $>0.27 \text{ g-H}_2\text{O g-clay}^{-1}$ and p/p_0 ranges from ~ 0.8 to 1.

In Region I, Ca and Mg-2:1 phyllosilicates are interstratified with layers having 0, 1, and 2 discrete layers of interlayer H_2O molecules. As p/p_0 increases the proportion of layers with two layers of interlayer H_2O molecules increases and therefore both the interlayer volume and the amount of interlayer H_2O increase. The amount of H_2O retained on external surfaces also increases with p/p_0 in Region I. Hydration numbers for cations/charge sites located on external surfaces are about the same as average hydration numbers for cation/charge sites located on internal surfaces.

In Region II, nearly all of the layers in Ca and Mg-2:1 phyllosilicates have two layers of interlayer H_2O molecules. Both the interlayer volume and the amount of interlayer H_2O are constant throughout Region II. As p/p_0 increases the increase in H_2O content for a sample is due to an increase in the hydration of cation/charge sites located on the external surfaces. Hydration numbers for cations/charge sites located on external surfaces are larger than hydration numbers for cation/charge sites located on internal surfaces.

In Region III, 2:1 phyllosilicates are dominated by 2-layer hydrates although some interstratification of 3-layer hydrates may occur, particularly as p/p_0 approaches 1. Some of the increase in H_2O content observed with increasing p/p_0 in Region III is due to increasing interlayer volume; however, most of the increase in H_2O content observed in Region III is due to capillary condensation.

The proposed model, Equation (4), is only valid for describing the hydration of fully expandable Ca and Mg-rich 2:1 phyllosilicates in Region II. Clays saturated with cations other than Ca or Mg have different hydration ranges and are often interstratified, which complicates estimation of the interlayer volume.

CONCLUSIONS

The amount of H_2O retained by Mg-saturated 2:1 phyllosilicates equilibrated at 54% RH increases with both the hydratable surface area and the layer charge of the clay. The increase in H_2O with layer charge, however, occurs entirely on external surfaces of the clay. This result indicates that at 54% RH, H_2O on external surfaces is localized around the cation/charge sites rather than forming multi-layers as was suggested

previously. Cations/charge sites located on external surface have substantially larger hydration numbers than cation/charge sites located on internal surfaces.

ACKNOWLEDGMENTS

The author thanks J.P. Quirk and S.D. Logsdon for many valuable comments, suggestions, and criticisms regarding this work.

REFERENCES

- Brindley, G.W. and Ertem, G. (1971) Preparation and solvation properties of some variable charge montmorillonites. *Clays and Clay Minerals*, **19**, 399–404.
- Cases, J.M., Berend, I., Francois, M., Michot, J.P., and Thomas, F. (1997) Mechanism of adsorption and desorption of water vapor by homoionic montmorillonite: 3. The Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+} exchanged forms. *Clays and Clay Minerals*, **45**, 8–22.
- Chiou, C.T. and Rutherford, D.W. (1997) Effects of exchanged cation and layer charge on the sorption of water and EGME vapors on montmorillonite clays. *Clays and Clay Minerals*, **45**, 867–880.
- Güven, N. (1992) Molecular aspects of aqueous smectite suspensions. In *Clay-Water Interface and its Rheological Implications*, N. Güven and R.M. Pollastro, eds., Clay Minerals Society Workshop Lectures, Volume 4, Clay Minerals Society, Boulder, Colorado, 2–79.
- Johnston, C.T., Sposito, G., and Erickson, G. (1992) Vibrational probe studies of water interactions with montmorillonite. *Clays and Clay Minerals*, **40**, 722–730.
- Kittrick, J.A. (1969) Interlayer forces in montmorillonite and vermiculite. *Soil Science Society of America Proceedings*, **33**, 217–222.
- 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*, A.R. Mermut, ed., Clay Minerals Society Workshop Lectures, Volume 6, Clay Minerals Society, Boulder, Colorado, 80–103.
- Laird, D.A. (1996) Model for crystalline swelling of 2:1 phyllosilicates. *Clays and Clay Minerals*, **44**, 553–559.
- Laird, D.A. and Nater, E.A. (1993) Nature of the illitic phase associated with randomly interstratified smectite/illite in soils. *Clays and Clay Minerals*, **41**, 280–287.
- Laird, D.A., Dowdy, R.H., and Munter, R.C. (1991a) Suspension nebulization analysis of clays by inductively coupled plasma-atomic emission spectroscopy. *Soil Science Society of America Journal*, **55**, 274–278.
- Laird, D.A., Barak, P., Nater, E.A., and Dowdy, R.H. (1991b) Chemistry of smectitic and illitic phases in interstratified soil smectite. *Soil Science Society of America Journal*, **55**, 1499–1504.
- Laird, D.A., Shang, C., and Thompson, M.L. (1995) Hysteresis in crystalline swelling of smectites. *Journal of Colloid and Interface Science*, **171**, 240–245.
- Lim, C.H. and Jackson, M.L. (1982) Dissolution for total elemental analyses. In *Methods of Soil Analysis, Part 2, 2nd edition*, A. Page, ed., Monograph 9, American Society of Agronomy, 1–11.
- Mooney, R.W., Keenan, A.G., and Wood, L.A. (1952) Adsorption of water vapor by montmorillonite. II. Effect of exchangeable ions and lattice swelling as measured by x-ray diffraction. *Journal of the American Chemical Society*, **74**, 1371–1374.
- Newman, A.C.D. (1983) The specific surface of soils determined by water sorption. *Journal of Soil Science*, **34**, 23–32.
- Newman, A.C.D. (1987) The interaction of water with clay mineral surfaces. In *Chemistry of Clays and Clay Minerals*, A.C.D. Newman, ed., Mineralogical Society Monograph No. 6., John Wiley and Sons, New York, 237–274.
- Norrish, K. (1954) The swelling of montmorillonite. *Discussions of the Faraday Society*, **18**, 120–133.
- Ormerod, E.C. and Newman, A.D.C. (1983) water sorption on Ca-saturated clays: II. Internal and external surfaces of montmorillonite. *Clay Minerals*, **18**, 289–299.
- Quirk, J.P. (1955) Significance of surface areas calculated from water vapor sorption isotherms by the B.E.T. equation. *Soil Science*, **80**, 423–430.
- Russell, J.D. and Farmer, V.C. (1964) Infrared spectroscopic study of the dehydration of montmorillonite and saponite. *Clay Minerals Bulletin*, **5**, 443–464.
- Slade, P.G., Quirk, J.P., and Norrish, K. (1991) Crystalline swelling of smectite samples in concentrated NaCl solutions in relation to layer charge. *Clays and Clay Minerals*, **39**, 234–238.
- Sposito, G. and Prost, R. (1982) Structure of water adsorbed on smectites. *Chemical Reviews*, **82**, 553–573.
- Theissen, A.A. and Harward, M.E. (1962) A paste method for preparation of slides for clay mineral identification by x-ray diffraction. *Soil Science Society of America Proceedings*, **26**, 90–91.
- van Olphen, H. and Fripiat, J.J. (1979) *Data Handbook for Clay Materials and Other Non-Metallic Minerals*. Pergamon Press Inc., New York, 208.

(Received 18 November 1998; accepted 5 April 1999; Ms. 301)