EFFECTS OF IRON OXIDATION STATE ON THE SPECIFIC SURFACE AREA OF NONTRONITE

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Abstract—The effect of Fe oxidation state on the specific surface area, S_m, of nontronite was studied using the <2-μm, Na^+-saturated fraction of the SWa-1 and Garfield nontronite reference clays. The reduction of structural Fe^{3+} in the octahedral sheet of the nontronite decreased S_m as measured by the adsorption of 2-ethoxyethanol (ethylene glycol-monoethyl ether, EGME). The swellability in water of the nontronite also decreased during reduction. The amount of nonexchangeable Na^+, on the other hand, increased with increasing Fe^{2+} content and was highly correlated with EGME adsorption ($r = -.985$). The relationship between S_m and Fe^{2+} was attributed to the collapse of partially or fully expanded layers to unexpanded layers.

Key Words—Ethylene glycol-monoethyl ether, Iron, Nontronite, Oxidation, Specific surface area.

INTRODUCTION

Several studies (Foster, 1953; Egashira and Ohtsubo, 1983; Stucki *et al.,* 1984b) have reported that the swelling of aqueous dispersions of aluminosilicate clay minerals is substantially altered by the oxidation state of octahedral Fe in the clay crystal structure. The underlying basis for this phenomenon, however, is still unknown. The present study was undertaken to provide greater understanding of the factors governing the effects of Fe oxidation state on clay-water interactions.

The swelling of clays in their natural oxidation state is commonly believed to be the result of electrical double-layer repulsion (van Olphen, 1963), but surface hydration is considered by many to be a more favorable concept (Low, 1987). According to the double-layer repulsion theory, the swelling pressure, Π, increases with increasing surface charge density, σ (van Olphen, 1963; Viani *et al.,* 1983), and, by definition, σ is the electrostatic charge per unit area of the clay surface, which is commonly obtained from the relation

$$\sigma = \omega/S_m, \tag{1a}$$

where ω is the cation-exchange capacity and S_m is the specific surface area, i.e., that portion of the total surface area that is available to water and exchangeable ions. Hence, Π must depend directly on the cation-exchange capacity (ω) and inversely on the specific surface area (S_m) of the clay, *viz.*

$$\Pi \propto \sigma = \frac{\omega}{S_m}. \tag{1b}$$

Low and coworkers (Odom and Low, 1978; Low and Margheim, 1979; Low, 1980), on the other hand, described clay swelling as a phenomenon deriving from the surface area of the clay with little dependence on ω, obeying the empirical equation

$$\ln(\Pi + 1) = \alpha/(m_w/m_c) + \ln B, \tag{2}$$

where m_w/m_c is the gravimetric water content of the clay in equilibrium with the corresponding applied swelling pressure, Π; B is a constant that depends on the clay; and α is a function that varies directly with S_m. The surface hydration model, therefore, requires Π to vary directly with S_m; whereas, according to double-layer theory, a direct relationship could exist between Π and S_m only if σ were to increase, i.e., ω would have to increase more than S_m. Knowledge of the variability of S_m with oxidation state is, consequently, fundamental to a complete understanding of the mechanism by which Fe oxidation state alters clay swelling, regardless of which model is applied.

The purpose of the present study was to determine the effect of Fe^{2+} on S_m, and thereby derive the relationship between Π and S_m in reduced clays. Further, because more than 95% of the specific surface area of swelling clays can be attributed to the planar surfaces of the clay plates, a change in S_m must be accompanied by a loss of planar surfaces; a secondary purpose was, therefore, to examine the implications of changes in S_m on the relative fractions of expanded and collapsed layers.

MATERIALS AND METHODS

The clays used in this study were the <2-μm fractions of ferruginous smectite SWa-1 (Source Clay Minerals Repository of The Clay Minerals Society) from Grant County, Washington; and Garfield, Washington, nontronite (API 33-a, Ward's Natural Science Establishment, Rochester, New York). The molecular compositions of these clays are respectively (Goodman *et al.,* 1976; Stucki *et al.,* 1984a)

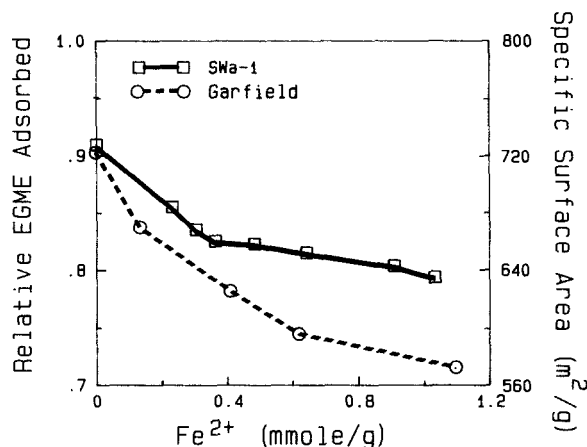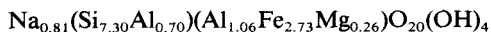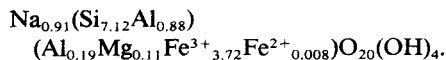[1] Current address: EPL Bio-Analytical Services, Inc., Decatur, Illinois 62525.

Figure 1. Relationship between ethylene glycol-monoethyl ether (EGME) adsorbed relative to Upton, Wyoming, montmorillonite (left ordinate) and corresponding specific surface area, S_m (right ordinate) vs. Fe^{2+} content of nontronite samples SWa-1 and Garfield, Washington.

$$Na_{0.81}(Si_{7.30}Al_{0.70})(Al_{1.06}Fe_{2.73}Mg_{0.26})O_{20}(OH)_4$$

and

$$Na_{0.91}(Si_{7.12}Al_{0.88})$$
$$(Al_{0.19}Mg_{0.11}Fe^{3+}_{3.72}Fe^{2+}_{0.008})O_{20}(OH)_4.$$

The clays were saturated with Na^+, dialyzed, and freeze-dried.

The reduction of clay suspensions in citrate-bicarbonate buffer solution with sodium dithionite $(Na_2S_2O_4)$ salt was accomplished as described by Lear and Stucki (1985) and the swellability in water, by the method of Stucki *et al.* (1984b). The specific surface area of clay gels was determined using the method described by Odom and Low (1978), which was patterned after the 2-ethoxyethanol (also known as ethylene glycol-monoethyl ether, EGME) method of Carter *et al.* (1965). Implicit to this method is the assumption that EGME wets the same surfaces as water. Freeze-dried samples were equilibrated for 20 days and weighed. Both operations were carried out inside a glove box (Vacuum/Atmospheres Model HE-43 Dri-Lab equipped with a Dri-train) in an atmosphere of <10 ppm O_2 to prevent reoxidation of reduced samples. The surface area of the sample was calculated from the ratio of EGME adsorbed relative to Upton, Wyoming, montmorillonite, which was assumed to have the ideal total surface area of 8×10^6 cm^2/g. EGME is assumed to form a monolayer on all surfaces available to water, thus producing two EGME layers between each pair of partially or fully expanded layers of the clay.

Nonexchangeable Na^+ was determined on a series of reduced SWa-1 samples following the procedure of Stucki *et al.* (1984a) for layer-charge determinations, except that the clay was first washed twice with 20 ml

Table 1. Effect of octahedal Fe^{2+} on the mass ratio of water to SWa-1 clay (m_w/m_c) at four swelling pressures, Π.[1]

Π (atm)	Fe^{2+} (mmole/g)	m_w/m_c (g/g)
1.0	0.0	2.4120
	0.414	2.3458
	0.713	2.2589
	0.859	2.1840
	1.000	2.0239
	1.605	2.1483
3.0	0.0	1.4789
	0.047	1.5996
	0.538	1.3156
	0.847	1.1614
	1.201	1.1617
	1.937	1.0754
5.0	0.0	1.1006
	0.323	0.9902
	0.708	0.9682
	0.872	0.9314
	1.275	0.8599
	1.727	0.8572
7.0	0.0	1.0130
	0.179	0.9404
	0.352	0.9100
	0.829	0.8431
	1.274	0.7781

[1] Total Fe = 3.549 mmole/g.

of degassed 1 M LiCl solution, then three times with 30 ml of degassed, distilled deionized H_2O. Fe^{2+} was measured as described by Stucki (1981), and total Fe was measured by atomic absorption.

RESULTS AND DISCUSSION

As shown in Figure 1, a significant inverse relationship exists between the amount of EGME adsorbed and the Fe^{2+} content of both the Garfield and SWa-1 nontronite samples, indicating that the oxidation state of Fe had a significant effect on surface properties of the clay. Fe^{2+} had a similar depressing effect on the water retention capacity of these clays (Table 1; Stucki *et al.*, 1984b).

The purpose of conducting EGME adsorption experiments was to determine the specific surface area, S_m, of clays in their water-swollen state as a function of Fe^{2+} in the clay crystal. The amount of adsorbed EGME will correlate directly with relative values of S_m only if (1) the EGME wets the same surfaces as water, (2) the freeze-dried clay rewets to the same surface area as existed in the original swollen state, and (3) a full monolayer of EGME develops on every available planar surface.

EGME is commonly accepted as capable of wetting the same surfaces as water, so this was presumed in the present study. To determine the effect of freeze-drying on the ability of the clay to rewet, several freeze-dried samples were resuspended in deionized water and their equilibrium water contents determined at 3-atm

Table 2. Effect of octahedral Fe^{2+} on total layer charge (ν), Na^+ exchangeable by Li^+ (ω), and Na^+ non-exchangeable by Li^+ ($\nu - \omega$) in sample SWa-1.

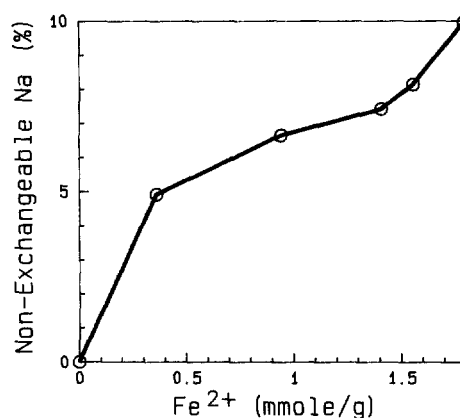| Fe^{2+} (mmole/g)	ν (meq/g)	ω (meq/g)	$\nu - \omega$ (meq/g)
0.0	0.806	0.806	0.0
0.356	0.996	0.947	0.049
0.930	1.147	1.072	0.076
1.389	1.335	1.236	0.099
1.535	1.410	1.295	0.115
1.769	1.357	1.222	0.135

Figure 2. Relationship between nonexchangeable Na^+, expressed as percentage of total layer charge ($100(\nu - \omega)/\nu$) and Fe^{2+} content of nontronite sample SWa-1.

applied pressure. The resulting water contents were comparable to values obtained during the first wetting-drying cycle. Condition (2) was, therefore, fulfilled.

Verification of condition (3) was somewhat more difficult, but was also considered fulfilled in this study based on the following observations. Any of the following phenomena should change the amount of EGME adsorbed: (1) a rearrangement of clay layers resulting in the complete collapse of some layers and a corresponding decrease in available surface area; (2) a sufficient partial collapse of some clay layers to prevent two full layers of EGME from entering the interlaminar spaces, such as reported by Nguyen et al. (1987) for Ca-montmorillonite; and (3) a change in the interaction energy between the surface and the adsorbate molecule, which could result in only a single layer or less of EGME within the interlayer region. Occurrence of either phenomenon (2) or (3) should prevent fulfillment of condition (3) above, and EGME adsorption should underestimate S_m.

With regard to phenomenon (1), several studies have reported the coexistence of collapsed, partially expanded, and fully expanded layers in clay-water systems (Foster et al., 1955; Rhoades et al., 1969; Viani et al., 1983, 1985). If during Fe reduction some layers collapse completely, a portion of the exchangeable cation should become non-exchangeable or fixed between the layers. The findings by Chen et al. (1987) that Fe reduction enhances K^+ fixation supports this postulate, but conventional X-ray powder diffraction analysis of reduced Na-nontronite gels by Wu et al. (1989) revealed only partially and fully expanded layers. To explain the difference in these results, Wu et al. (1989) suggested that either the number of collapsed layers was insufficient to create large diffracting domains, or the K^+ fixation reported by Chen et al. (1987), while dependent upon Fe oxidation state, occurred only after the sample had been dried, and rewetting failed to reexpand the K^+-collapsed layers. The samples studied by Wu et al. (1989) were never dried.

The question of whether collapsed layers existed in undried, reduced gels is clarified by results presented in Table 2 and Figure 2. As the amount of Fe^{2+} increased, both the amount of non-exchangeable Na^+ ($\nu - \omega$) and the fraction of total exchange capacity neu-

tralized by non-exchangeable Na^+ increased. The fact that some Na^+ was unavailable for exchange by Li^+ indicates that some layers were unexpanded even though drying had never occurred. This suggests that the correct explanation for the results of Wu et al. (1989), which showed no unexpanded layers in reduced nontronite gels, is that unexpanded layers were present but sufficiently randomly interstratified to avoid detection by conventional X-ray powder diffraction. In light of this interpretation the possible influence of layer collapse on EGME adsorption (phenomenon (1) above) can be evaluated.

Using the plots in Figure 1, values of EGME adsorption were estimated for the levels of Fe^{2+} reported in Table 2 and were plotted against the corresponding amount of non-exchangeable Na^+ ($\nu - \omega$). The resulting linear regression coefficient (r) was $-.985$, indicating that the two properties probably derived from the same phenomenon, i.e., the collapse of fully and/or partly expanded layers to unexpanded layers. Hence, complete layer collapse accounts for most ($\sim 98\%$) of the change in EGME adsorption, suggesting that phenomena (2) and (3) were of little importance. In other words, the partially expanded layers which were present apparently permitted entry of two layers of EGME into their interlayer regions, and any variability that may have existed in the surface itself apparently gave rise to little or no attenuation of EGME adsorption. It follows, then, that condition (3) was fulfilled and that EGME adsorption is an acceptable method to calculate relative values of S_M. The data in Figure 1, therefore, may be transformed to represent the values of S_m (relative to Upton, Wyoming, montmorillonite, which was assumed to be 8×10^6 cm²/g) and are given on the right ordinate of Figure 1 and in Table 2.

These results show that the reduction of structural Fe in the crystal structure decreased S_m. Stucki et al. (1984a) and Lear and Stucki (1985) observed that the
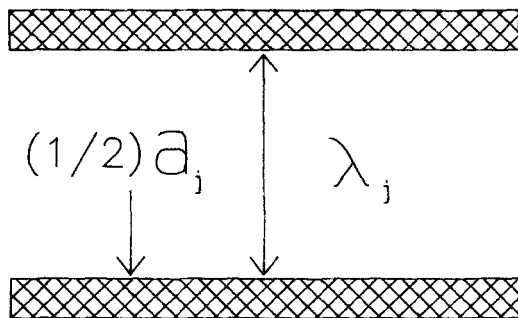
Figure 3. Diagram of two parallel clay layers. λ_j is the distance separating the plates and a_j is the basal surface area of a single planar surface.

Figure 4. Transformation of results from Figure 1, using Eq. (6), illustrating the effect of Fe^{2+} on fraction of completely collapsed (unexpanded) layers in nontronite samples SWa-1 and Garfield, Washington.

reduction of structural Fe caused ω to increase, so by Eq. (1), σ must also have increased. Further by Eq. (1), Π should have increased, but Table 2 and the results of Stucki *et al.* (1984b) demonstrate that Π decreases with increasing Fe^{2+} content. Eq. (1), therefore, fails to represent correctly the observed relationship among Π, ω, and S_m for reduced nontronite. Experimental results (Table 1; Stucki *et al.*, 1984b) are consistent, however, with Eq. (2), indicating that the hydration model is more satisfactory than the double-layer repulsion model in describing the swelling of reduced nontronite.

The current hypothesis concerning the method by which Fe^{2+} evokes a change in S_m is similar to that proposed by Stucki *et al.* (1984b) to explain the effect of Fe^{2+} on clay swelling, namely, that some clay layers completely collapse (i.e., unexpanded) and therefore are unavailable for the adsorption of water or EGME. The existence of partly expanded layers should have attenuated swelling in water, but apparently had little impact on S_m, as explained above. To understand the significance of these results with respect to the fractions of layers existing in various states of expansion or collapse, consider the physical model for the swelling of clay particles in water presented by Low (1980), which consists of n crystallographic layers (~ 10-Å thick) oriented parallel (Figure 3). For a clay-water system in which partially expanded and fully expanded layers coexist, Low (1987) derived the equation

$$\gamma(m_w/m_c) = \tfrac{1}{2}\rho_w S(f_p\lambda_p + f_e\lambda_e), \qquad (3)$$

where γ is the fraction of water present between the clay layers; ρ_w is the density of adsorbed water; S is the total area of interlaminar surfaces of the clay, regardless of their degree of expansion, neglecting only the contribution of crystal edges; f_p and f_e are the fractions of partially and fully expanded layers, respectively; and λ_p and λ_e are the corresponding interlayer distances. Eq. (3) also is valid for a clay-water system that contains unexpanded layers in addition to partly or fully expanded layers. Here, S can be expressed as the
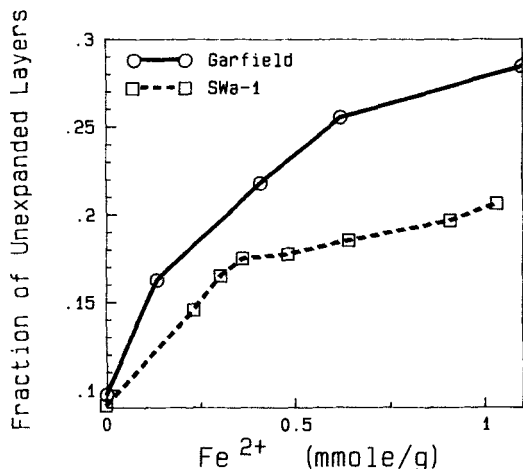
sum of contributions from the three corresponding fractions

$$S = (f_u + f_p + f_e)S, \qquad (4)$$

where f_u is the fraction of unexpanded layers. The sum of all fractions, i.e., the term in parentheses, must equal unity. In a clay-water system, S_m represents only that surface area which is available to water, thus precluding those surfaces which are unexpanded. Hence,

$$S_m = (f_p + f_e)S. \qquad (5)$$

Substituting Eq. (5) into Eq. (4), and solving for S gives

$$S = \frac{S_m}{1 - f_u}. \qquad (6)$$

Substitution of Eq. (6) for S in Eq. (3) allows the latter to be rewritten as

$$\gamma(m_w/m_c) = \frac{\rho_w S_m(f_p\lambda_p + f_e\lambda_e)}{2(1 - f_u)}. \qquad (7)$$

Using the values of S_m report in Figure 1, the corresponding fractions of unexpanded layers, f_u, in reduced samples were calculated from Eq. (6), assuming $S = 8 \times 10^6$ cm^2/g, and plotted in Figure 4 for the SWa-1 and Garfield sample. Note from Figure 4 that the calculated fraction of unexpanded layers increased from about 10% to about 28% for the two clays over the range of Fe^{2+} contents studied. Verification of the presence of even this number of unexpanded, randomly interstratified layers by conventional X-ray powder diffraction is unlikely (Reynolds, 1980), suggesting that a more specialized small-angle X-ray scattering method, such as that described by Pons *et al.* (1981, 1982), is necessary.
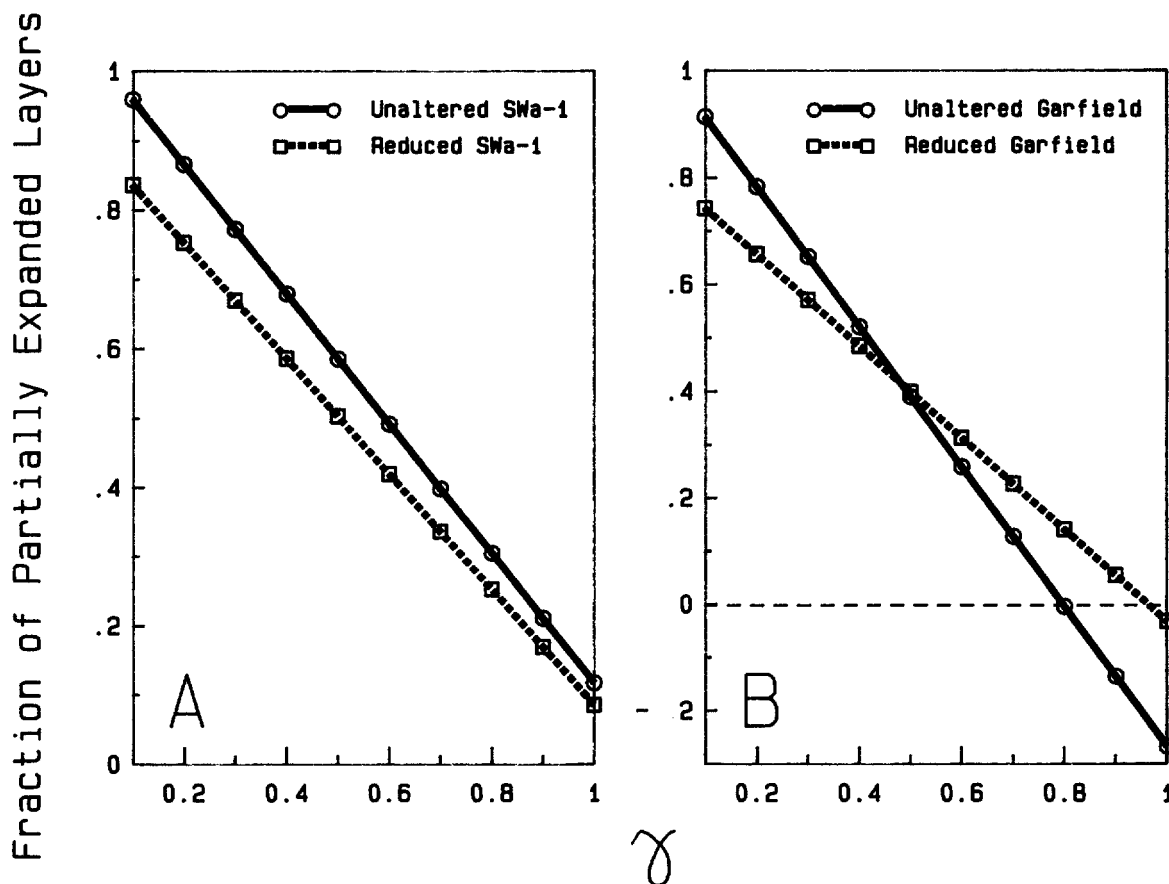
Figure 5.   Possible relationships between fraction of partially expanded layers (f_p) and fraction of water in interlayer regions (γ), according to Eq. (8), for nontronite samples SWa-1 (A) and Garfield, Washington (B) in oxidized (unaltered) and reduced (Fe^{2+} = 1.032 and 1.096 mmole/g, respectively) states. Values used for m_w/m_c were based on Table 1 and Stucki et al. (1984b) for Π = 1 atm; for S_m, Figure 1.

The allowable fractions of partially expanded layers in reduced nontronites may also be deduced from Eq. (7), based on results reported in Figures 1 and 4 and in Wu et al. (1989). Solving Eq. (7) for f_p gives

$$f_p = \frac{(m_w/m_c)(2\gamma) - \rho_w S_m \lambda_e}{(\lambda_p - \lambda_e)\rho_w S} . \qquad (8)$$

Wu et al. (1989) reported that λ_p and λ_e in reduced Garfield nontronite gel in equilibrium with 1 atm applied pressure are about 9.5 and 75 Å, respectively. They also found these values to be independent Fe^{2+} content, but λ_e varied with Π. Using these values and the corresponding measured values of m_w/m_c and S_m for unaltered and reduced samples and by assuming a constant value of 1.0 g/cm³ for ρ_w, f_p was calculated from Eq. (8) for different values of γ, giving the relationships plotted in Figure 5. By substituting the appropriate value of λ_e, plots at other swelling pressures can also be constructed.

Although the utility of the plots presented in Figure 5 may be limited because of the uncertainty in the true

value for γ and its possible dependence on Fe^{2+} content, they do provide insight into the lower limit of external water content that may exist in these clays. For example, because f_p < 0 is impossible, only those values of γ which produce $f_p \geq 0$ are allowed. Consequently, at least about 20% ($\gamma \leq 0.8$) of the water in the oxidized Garfield sample must have been external to the interlayer spaces when at equilibrium with an applied pressure of 1 atm. Only at higher levels of reduction could the external water content have been much lower than 20%. In the SWa-1 sample, on the other hand, all of the water may have been present in the interlaminar region ($\gamma = 1.0$).

Figure 5 also reveals that the effect of Fe^{2+} on f_p clearly depends on γ. A reasonable assumption is that γ > .5, in which case the effect of Fe^{2+} on f_p in the Garfield sample is opposite to and greater than the effect in sample SWa-1. The difference may be due, at least partly, to the fact that values for λ_e and λ_p for the Garfield nontronite were used in Eq. (8) for both samples; whereas, in fact, their behavior may be different

with respect to these varaiables. Nevertheless, knowledge of the true relationship between Fe^{2+} and either f_p or γ is necessary for further conclusions to be drawn.

In summary, the above discussion reveals that the specific surface area of swelling nontronites decreased with increasing Fe^{2+} in the octahedral sheet, and that as many as 20% and 28% of the layers completely collapsed in the SWa-1 and Garfield samples, respectively. Although experiments were not devised to determine directly which relative fractions of remaining layers were either partially or fully expanded, the results suggest that the relative fraction of such layers may change markedly, depending on the clay and the extent to which the external water content varies with Fe^{2+} content. The specific forces by which structural Fe^{2+} causes layer collapse are still unidentified, but are manifest by a decrease in the specific surface area and swellability of reduced nontronite in water, and by a concomitant increase in counterion occlusion.

ACKNOWLEDGMENTS

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