A MODEL FOR THE MECHANISM OF Fe^{3+} TO Fe^{2+} REDUCTION IN DIOCTAHEDRAL SMECTITES

V.A. DRITS[1,2] AND A. MANCEAU[1]

[1] Environmental Geochemistry Group, LGIT-IRIGM, University Joseph Fourier and CNRS,
38041 Grenoble Cedex 9, France
[2] Geological Institute of the Russian Academy of Sciences, 7 Pyzhevsky Street, 109017 Moscow, Russia

Abstract—A model to compensate the 2:1 layer having excess negative charge owing to the reduction of Fe^{3+} to Fe^{2+} by sodium dithionite buffered with citrate-bicarbonate in nontronite, beidellite, and montmorillonite is proposed. This model is based on reassessing published experimental data for Fe-containing smectites and on a recently published structural model for reduced Garfield nontronite. In the reduced state, Fe^{2+} cations remain six-fold coordinated, and increases of negative charge in the 2:1 layer are compensated by the sorption of Na^+ and H^+ from solution. Some of the incorporated protons react with structural OH groups to cause dehydroxylation. Also, some protons bond with undersaturated oxygen atoms of the octahedral sheet. The amount of Na^+ (p) and H^+ (n_i) cations incorporated in the structure as a function of the amount of Fe reduction can be described quantitatively by two equations: $p = m/(1 + K_0 m_{rel})$ and $n_i = K_0 m m_{rel}/(1 + K_0 m_{rel})$; with $K_0 = CEC (9.32 - 1.06m_{tot} + 0.02m_{tot}^2)$, where m_{tot} is the total Fe content in the smectite, m is the Fe^{2+} content, m_{rel} is the reduction level (m/m_{tot}), CEC is the cation-exchange capacity, and K_0 is a constant specific to the smectite. The model can predict, from the chemical composition of a smectite, the modifications of its properties as a function of reduction level. Based on this model, the structural mechanism of Fe^{3+} reduction in montmorillonite differs from that determined in nontronite and beidellite owing to differences in the distribution of cations over *trans-* and *cis*-octahedral sites.

Key Words—CMS Source Clay SWa-1, Dioctahedral Smectite, Iron Reduction, Structural Formula.

INTRODUCTION

One of the most important factors governing the geochemical behavior of Fe in soils and sediments is the ability of Fe to change oxidation state. Therefore, oxido-reduction reactions of layer silicates often play an important role in environmental processes including weathering, microbial activity, and diagenetic transformations (Egashira and Ohtsubo, 1983; Stucki *et al.,* 1987, 1996). Redox reactions modify the chemical and physical properties of Fe-containing smectites, such as cation-exchange capacity (CEC), specific surface area, swelling behavior, and ability to fix interlayer cations (Khaled and Stucki, 1991; Lear and Stucki, 1985, 1989; Stucki *et al.,* 1984, 1996). Consequently, the texture (Gates *et al.,* 1998; Stucki and Tessier, 1991), permeability (Shen *et al.,* 1992), and fertility of formations in which Fe-containing smectites are present (Stucki, 1988) are affected. The potential for modification of smectite properties for industrial, engineering, and environmental applications by controlling the oxidation state of Fe is great (Chen *et al.,* 1987; Low *et al.,* 1983). The knowledge of the reduction mechanism of Fe^{3+} to Fe^{2+} is, therefore, essential for understanding a number of natural weathering processes as well as for purposely modifying specific properties of smectite (Ernstsen, 1998). This subject has been extensively studied in the past two decades, and also largely reviewed in the literature (Heller-Kallai, 1997; Rozenson and Heller-Kallai, 1976; Russell *et al.,*

1979; Stucki, 1988; Stucki *et al.,* 1976, 1996; Stucki and Roth, 1976, 1977).

Reliable results describing the reduction of Fe were obtained in dioctahedral smectites with $Na_2S_2O_4$ in a citrate-bicarbonate medium. Although parameters controlling Fe^{3+}–Fe^{2+} redox reactions in smectites were identified, an atomic-level understanding of these transformations is lacking, essentially because the crystal structure of reduced smectites was unknown until recently. An atomic-level understanding is crucial because revealing structural changes, which occur during the reduction of ferric iron, may provide insight, not only on the mechanism of the Fe^{3+} reduction, but also how structural Fe^{2+} modifies structural and surface properties of clays. Progress towards describing the structure of reduced smectites was achieved recently by Manceau *et al.* (2000), who investigated by polarized extended X-ray absorption fine structure (P-EXAFS) spectroscopy and powder X-ray diffraction (XRD) the modifications of the local structure of Fe atoms in reduced nontronite from Garfield, Washington. They proposed a model for the reduction mechanism of Fe^{3+} to Fe^{2+}.

Published models on redox reactions in Fe^{3+}-containing dioctahedral smectites are first examined here. It is shown that they fail to explain several important experimental results, specifically, the dependence of the layer charge on the Fe^{2+} content in reduced smectites. Stucki (1988) noted that "the source of this discrepancy is intriguing and may offer clues for the spe-
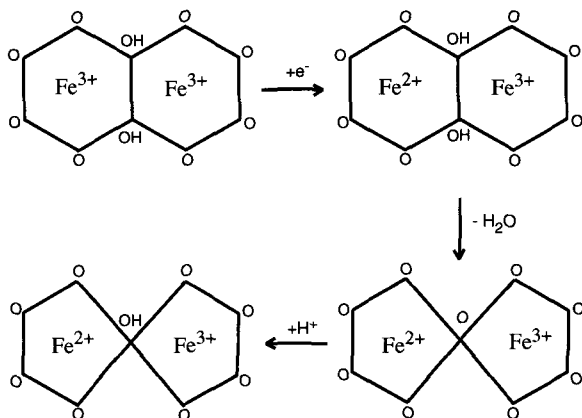
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Figure 1. Structural transformations corresponding to the Fe^{3+} to Fe^{2+} reduction mechanism proposed by Stucki and Roth (1977) in Equation (2).

cific reaction involved in the redox processes". A model describing the structural modifications of dioctahedral smectites as a function of Fe^{2+} content is proposed, and the capacity to explain experimental data is demonstrated. This model can be used to calculate, at least semi-quantitatively, the cationic and anionic composition of dioctahedral smectites for any amount of Fe^{3+} reduction.

MODELS FOR THE REDUCTION MECHANISM OF Fe^{3+} TO Fe^{2+}

Solution-chemistry experiments have shown that the reduction mechanism of iron-containing dioctahedral smectites depends partly on the reducing agent, and on the physico-chemical characteristics of the solution where the redox reaction takes place (Stucki, 1988). For this reason, the following descriptions of previously proposed mechanistic models for the reduction of Fe^{3+} to Fe^{2+} in dioctahedral ferruginous smectites is restricted to those involving sodium-dithionite reductant buffered with citrate-bicarbonate solution (CBD). This review shows those physico-chemical problems that have been solved and those that warrant further examination.

The model of Roth and Tullock (1973)

According to the model of Roth and Tullock (1973), the reducing agent transfers an electron to structural Fe^{3+} to produce Fe^{2+}. This process occurs with dehydroxylation of the octahedral sheets, followed by protonation of oxygen atoms that are undersaturated. The sequence of these reactions is described as follows:

$$Fe_c^{3+} + e^- \rightarrow Fe^{2+}; \qquad 2(OH)_c^- \rightarrow O_c^{2-} + (H_2O)_c;$$

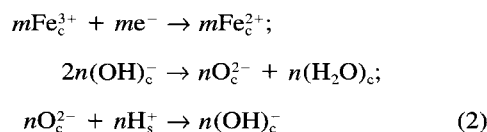$$O_c^{2-} + H_s^+ \rightarrow (OH)_c^- \qquad (1)$$
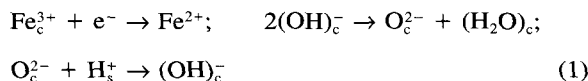
where subscripts c and s denote species from the crystal structure and from solution, respectively. Water molecules formed by dehydroxylation migrate from the clay framework, and the residual oxygen atoms incorporate protons from solution to form OH groups. This mechanism accounts for the decrease of structural OH groups observed experimentally during the reduction of Fe^{3+} and implies that ferrous atoms have five-fold coordination. Equation (1) indicates also that the layer charge should be invariant with the amount of iron reduction.

The model of Stucki and Roth (1977)

Measurements obtained for the first time under controlled atmospheric conditions showed that the layer charge of reduced smectites increased with Fe^{2+} content, in contrast to the prediction of the model of Roth and Tullock. To explain this result, Stucki and Roth (1977) proposed the following reaction mechanism:

$$mFe_c^{3+} + me^- \rightarrow mFe_c^{2+};$$

$$2n(OH)_c^- \rightarrow nO_c^{2-} + n(H_2O)_c;$$

$$nO_c^{2-} + nH_s^+ \rightarrow n(OH)_c^- \qquad (2)$$

where m and n are stoichiometric parameters. Equation (2) suggests that dehydroxylation occurs by a coalescence of edge-sharing OH groups during reduction to form H_2O molecules that diffuse from the structure, leaving behind oxygen ions. These oxygen ions are subsequently reprotonated by hydrogen ions from solution. The stoichiometry coefficient, n, refers to sorbed H^+ which remains in the clay structure after reduction. A schematic representation of the reaction mechanism corresponding to this model is shown in Figure 1. The main difference between Equations (1) and (2) is that the layer charge in the model of Stucki and Roth depends on the number, n, of OH groups that undergo dehydroxylation. By using tritium as a label element, Lear and Stucki (1985) showed that the initial loss of structural protons and subsequent sorption of protons from the solution to structural positions occurred near the ratio of 2:1. This result is in agreement with Equation (2) and with the structural model of Figure 1 because the loss of $2H^+$ from the structure is partly balanced by the sorption of one H^+ from the solution. The agreement between theory and experiment was considered by Stucki and Roth as strong support in favor of this mechanism. However, according to Equation (2) and Figure 1, Fe^{2+} ions are in five-fold coordination in reduced dioctahedral ferruginous smectites. This model was recently discounted by Manceau *et al.* (2000), who showed by P-EXAFS and XRD that Fe^{2+} cations remain in six-fold coordination in the reduced state.
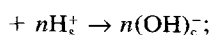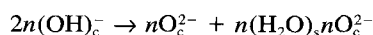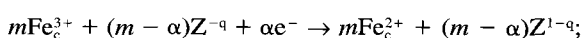
From titration experiments on nontronite (Clay Minerals Society Source Clay, SWa-1), Lear and Stucki (1985) determined that the n/m ratio of 0.32 was invariant over the range of Fe^{2+} content explored. Based on this result, the following relationship between the layer charge, w, and the Fe^{2+} content was calculated:

$$w = w_0 + Km(1 - n/m) = w_0 + 0.68Km \quad (3)$$

where w_0 is the layer charge of the oxidized sample, m is the Fe^{2+} content, and K is a constant, the value of which depends on the units used for the terms in Equation (3). If w and w_0 are expressed in meq/g, and m in mmole/g of clay, then K = 1 meq/mmole. Stucki et al. (1984) and Lear and Stucki (1985) measured the dependence of layer charge on the amount of reduced iron present. The layer charge was estimated from the total Na content in reduced samples. Figure 2 shows that the linear relationship between w and n based on titration results (dotted lines) differs substantially from experimental data (curvilinear solid lines). Since theory [Equations (2) and (3)] and experiment disagree, this model should be reconsidered.

The model of Gan et al. (1992)

Electron spin resonance (ESR) spectroscopy was used to determine the reductant species responsible for the transfer of electrons during reduction. In solution, sodium dithionite ($Na_2S_2O_4$) dissociates to Na^+ and $(S_2O_4)^{2-}$ ions. The disulfite anion also dissociates in water, partly according to $2(S_2O_4)^{2-} + H_2O \rightarrow (S_2O_3)^{2-} + 2(HSO_3)^- \rightarrow (S_2O_3)^{2-} + 2(SO_3)^{2-} + 2H^+$, and partly into the paramagnetic free radical species, $SO_2^-\bullet$, which contains unpaired electrons as indicated here by "$\bullet$" (Dunitz, 1956; Lynn et al., 1964; Rinker et al., 1958). Gan et al. (1992) showed that in $Na_2S_2O_4$ solutions, these free radicals are responsible for the reduction of structural Fe^{3+}. They observed a correlation between the concentration of $SO_2^-\bullet$ in solution and the reducing ability of the reagent. In particular, the reductive capacity of the $Na_2S_2O_4$ solution decreased with time as a result of the progressive diminution of the number of free radicals in the $Na_2S_2O_4$ solution. However, surprisingly, the addition of $Na_2S_2O_4$ to a nontronite suspension did not decrease the free-radical content, and the concentration of paramagnetic species was preserved or enhanced. To explain this result, Gan et al. (1992) assumed that, at a certain stage of Fe^{3+} reduction, unpaired electrons were produced within the nontronite structure, and that Al sites may serve as sources of these unpaired electrons. Gan et al. (1992) emphasized that the migration of the internal high-potential electrons to structural Fe^{3+} occurs only after sufficient Fe^{3+} is reduced owing to the incorporation of electrons from the $Na_2S_2O_4$ solution. Based on these results, Gan et al. (1992) and Stucki et al. (1996) adapted the reaction sequence in (2) to:

$$m Fe_c^{3+} + (m - \alpha)Z^{-q} + \alpha e^- \rightarrow m Fe_c^{2+} + (m - \alpha)Z^{1-q};$$

$$2n(OH)_c^- \rightarrow nO_c^{2-} + n(H_2O)_s nO_c^{2-}$$

$$+ nH_s^+ \rightarrow n(OH)_c^-;$$

$$n = 0.32m \quad (4)$$

where Z is an unidentified electron donor of electrical charge $-q$ located within the nontronite structure, which may be Al^{3+} substituted for Si^{4+} in tetrahedral sites; e^- represents the reducing agent $SO_2^-\bullet$ in the $Na_2S_2O_4$ solution; and $w, m, n,$ and α are stoichiometry coefficients. Equation (4) can not be used to simulate experimental observations because the value of α is unknown.

Gan et al. (1992) and Stucki et al. (1996) proposed a conceptual model where they assumed the existence of a relationship between the energy of reducing electrons, the structural Fe^{2+} content, and the progression of the reduction process. Three steps were distinguished. At first, reducing agents with modest reductive capability (RC) act on a small number of Fe^{3+}, and the charge deficit in the reduced structure provokes a concomitant increase of layer charge. Then, the reduction of Fe^{3+} by $SO_2^-\bullet$ free radicals with higher RC results in the partial dehydroxylation of the nontronite structure. Finally, corresponding to the highest reducing electron energy of free radicals, internal electrons of the nontronite structure become delocalized, thereby increasing further the rate of reduction.

Thus, according to this model, the reduction mechanism of Fe^{3+} in dioctahedral ferruginous smectites includes two predominant processes. The first is the reduction of Fe^{3+} by electrons produced by free radicals. The second process is the initial elimination of structural OH and eventual incorporation of protons from solution to compensate, *pro parte,* the negative layer charge resulting from further reduction of iron. This model requires also a five-fold coordination for reduced Fe and an internal source of electrons with a high reducing energy. In addition, this model does not account for the measured variation of the layer charge with Fe reduction (Figure 2).

PROPOSED MODEL

Let us consider a nontronite model with the ideal structural formula:

$$Na_1(Si_7Al_1)Fe^{3+}_4O_{20}(OH)_4. \quad (5)$$
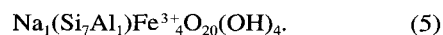
The increase of negative charge of the layer resulting from the reduction of Fe^{3+} is compensated two ways: (1) by an increase in the amount of positive interlayer charge through the adsorption of Na from $Na_2S_2O_4$ in solution (Stucki et al., 1984), and (2) by a decrease in total negative charge of the anionic framework of the 2:1 layer through a loss of structural hydroxyl groups (Roth and Tullock, 1973). Both processes may occur simultaneously. Based on these observations, the reduction of Fe^{3+} proceeds as:

$$m Fe_c^{3+} + m e_s^- \rightarrow m Fe_c^{2+} \quad (6a)$$
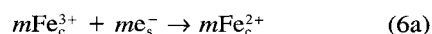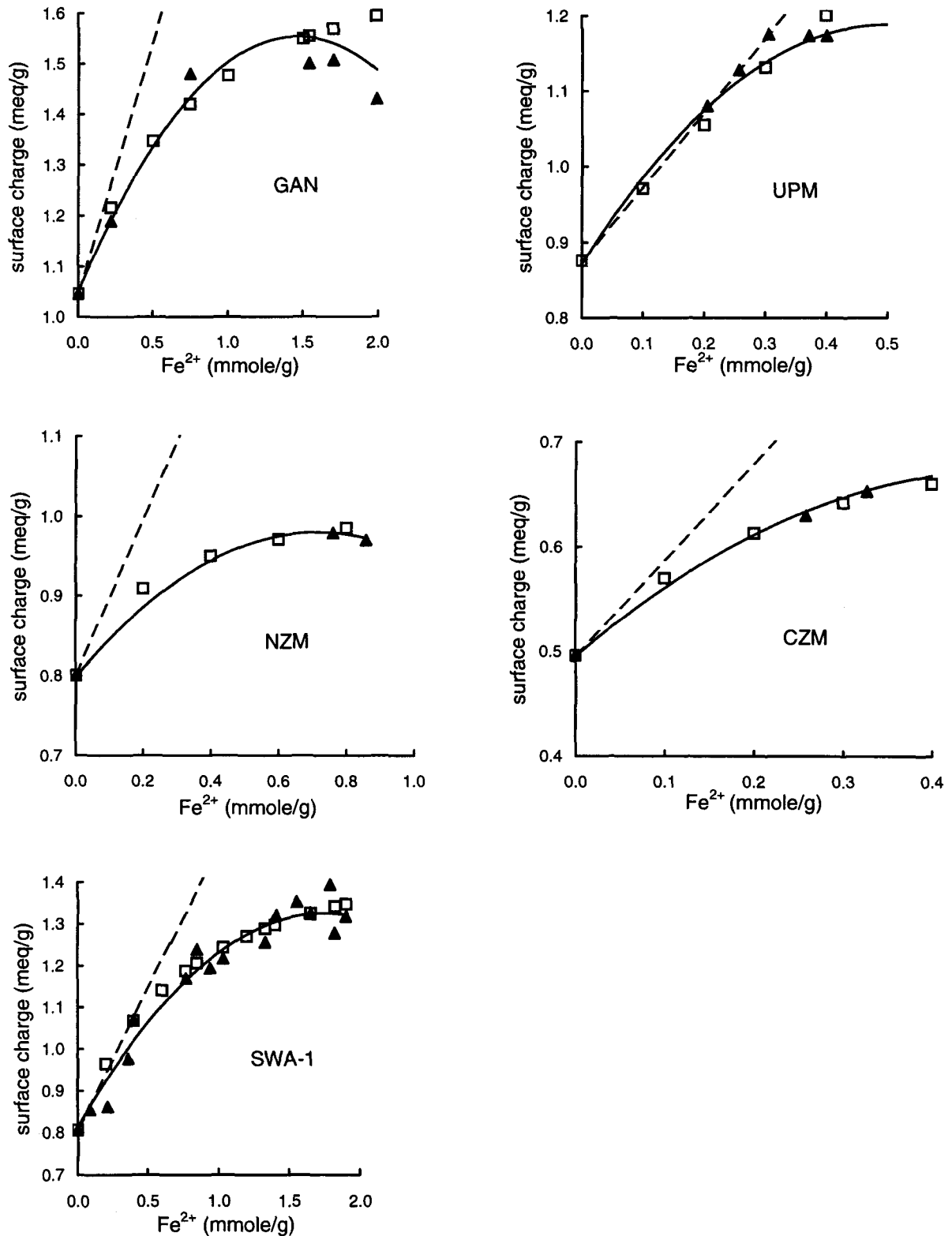
and is accompanied by:

Figure 2. Relationships between the experimental and theoretical surface charge and the fraction of reduced Fe^{3+} in various dioctahedral smectite samples. Observed data are from Stucki *et al.* (1984) and Lear and Stucki (1985), calculated data are from Equation (9). Dotted lines correspond to Equation (3) and curvelinear solid lines to Equation (10).

$$w_0Na_c + pNa_s \rightarrow wNa_c \qquad (6b)$$

$$n_i(OH^-)_c + n_iH_s^+ \rightarrow n_i(H_2O)_s \qquad (6c)$$
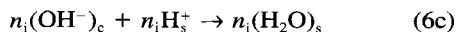
$$m = p + n_i \qquad (6d)$$

where m, n_i, and p are stoichiometric parameters, and w and w_0 correspond to interlayer Na content in the reduced and unreduced state, respectively. Equation (6a) corresponds to the reduction step by electrons produced by free radicals. Equations (6b) and (6c) represent changes in composition of the interlayer and anionic framework. Equation (6d) indicates that the charge deficit created by the Fe^{3+} to Fe^{2+} reduction is balanced by the sorption of Na^+ and H^+. Note that Equations (6a)–(6d) are based on the structural model proposed by Manceau et al. (2000) for reduced nontronite. According to this model, each pair of edge-forming OH groups coordinated to reduced Fe^{2+} ions receives two protons, thus forming two H_2O molecules, which diffuse from the structure to the solution. This reaction is accompanied by the migration of Fe^{2+} ions from cis-sites to nearest trans-sites along the [010] direction. In accordance with this model, the stoichiometric coefficient n_i refers to the amount of sorbed H^+ and of structural OH groups, which both leave the structure after protonation. Unfortunately, the concentration of structural OH groups in reduced smectites is unknown, and the bonding mechanism of the incorporated H^+ cannot be easily derived (discussed in more detailed below). Initially, we assume that all incorporated H^+ ions are consumed in the process of dehydroxylation of the 2:1 layer (6c). Based on this model, the structural formula (5) is rewritten as a function of the amount of iron reduction ("reduction level"):

$$Na_{1+p}(Si_7Al_1)(Fe^{3+}_{4-m}Fe^{2+}_m)O_{20}(OH)_{4-n_i}. \qquad (7)$$
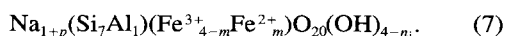
To evaluate if this model can account for the observed variation of the layer charge of Figure 2, the relationship between m, n_i, and p must be obtained.

Based on crystal chemical considerations, the relative values of p and n_i are assumed to vary with the reduction level. The reduction of small amounts of ferric iron will not appreciably disturb the crystal-lattice stabilization energy because dioctahedral smectites can accommodate a limited amount of divalent octahedral species in their structure (Güven, 1991). Therefore, when the content of Fe^{2+} is relatively low, the layer charge is compensated predominantly by the sorption of Na. In this case, $p > n_i$. When the reduction level increases, the proportion of Na sorbed from solution will decrease progressively, and the crystal-lattice energy will stabilize by the hydration of structural OH groups. Thus, at a certain stage of the reduction process, $n_i > p$. The compensation of the layer charge as a function of the reduction level can thus be written:

$$n_i/p = K_0m/m_{tot} = K_0m_{rel} \qquad (8)$$

where m and m_{tot} are the amount of reduced Fe^{3+}, and the total amount of Fe per unit cell, respectively, m_{rel} equals the reduction level ($m_{rel} \leq 1$), K_0 is a sample-dependent constant ($K_0 > 0$). The physical meaning of K_0 is discussed below. Equation (8) shows that when $K_0m_{rel} < 1$, then $p > n_i$, and vice versa. Combining of Equations (6d) and (8) leads to:

$$p = m/(1 + K_0m_{rel}) \qquad (9a)$$

$$n_i = K_0mm_{rel}/(1 + K_0m_{rel}). \qquad (9b)$$

Because p and n_i depend only on m and m_{tot}, Equations (9a) and (9b) can be applied to any Fe^{3+}-containing dioctahedral smectite. Indeed, a structural formula of a partially reduced dioctahedral smectite can be written: $Na_{x+z+p}(Si_{8-x}Al_x)(Al_{4-m_{tot}-z}Fe^{3+}_{m_{tot}-m}Fe^{2+}_mMg_z)-O_{20}(OH)_{4-n_i}.$

In contrast to Equation (3), Equations (9a) and (9b) show that the relationships between n_i and m, and between p and m, are not constant, but they depend on the reduction level and on the value of K_0. For a given reduction level, p and n_i depend on the amount of Fe^{2+}, and thus on the total Fe content in the smectite: The higher the m_{tot}, the higher the m and, consequently, the higher p and n_i. However, the ratio of p/n_i is independent of m_{tot}. It is convenient to exclude the amount of Fe^{2+} from Equations (9a) and (9b):

$$p = m_{rel}m_{tot}/(1 + K_0m_{rel}) \qquad (9c)$$

$$n_i = K_0m_{rel}^2m_{tot}/(1 + K_0m_{rel}). \qquad (9d)$$

Thus, p and n_i may now be calculated as a function of m_{rel} and m_{tot} if K_0 is known. If this model is valid, we can provide a rationale to explain quantitatively the change of surface-charge properties of smectites as a function of the reduction level. Thus, then Equations (6) and (9) may predict from the initial chemical composition, the evolution of the structural and chemical modifications of the layer and interlayer during Fe^{3+} reduction.

RESULTS AND DISCUSSION

Comparison between the observed and predicted layer charge as a function of reduction level

Stucki et al. (1984) and Lear and Stucki (1985) studied the influence of Fe^{2+} concentration on the layer charge for five dioctahedral smectites of different chemical compositions: Nontronite from Garfield, Washington (GAN) and Grant County, Washington (SWa-1), beidellite from Czechoslovakia #650 (CZM) and New Zealand (NZM), and montmorillonite from Upton, Wyoming (UPM). CEC and total Fe contents measured by Stucki et al. (1984) and Lear and Stucki (1985) are listed in Table 1. The layer charge of reduced samples (w_{exp}) as a function of Fe^{2+} (m_{exp}) was determined by Stucki et al. (1984) on the basis of the

Table 1. CEC (w_0), Fe concentration, and K_0, and K_r values for the smectite specimens studied by Stucki *et al.* (1984) and Lear and Stucki (1985).

Sample	w_0 (meq/g)	Total Fe^{3+} (mmole/g clay)	K_0	K_r (g/meq)
GAN	1.046	4.201	5.50	5.26
SWa-1	0.806	3.545	4.73	5.83
NZB	0.799	1.502	6.25	7.81
CZB	0.496	1.257	3.93	8.00
UPM	0.876	0.539	0.32	0.37

Figure 3.   Loss of H^+ by dehydroxylation as determined by tritium experiments (^3H) (after Lear and Stucki, 1985) and calculated by Equation (9) (n_i). The solid line was obtained by *least-squares* fit of observed data.

total Na concentration, and their results are shown in Figure 2. The trend of layer charge with Fe^{2+}, as predicted by Equation (3), is represented by straight lines. As noted above, experimental results deviate from straight lines, and Stucki *et al.* (1984) found that the empirical relationship between w_{exp} and m_{exp} is described by:

$$w_{exp} = C_0 + C_1 m_{exp} + C_2 m_{exp}^2 \qquad (10)$$

where C_0, C_1, and C_2 are empirical coefficients of unknown physical meaning. These values were determined by the best fit of experimental data (Stucki *et al.,* 1984). According to our model, w is expressed as a function of m by:

$$w = w_0 + p = w_0 + m/(1 + K_0 m_{rel}) \qquad (11)$$

where w_0 and m are expressed in mmoles of Na and of Fe^{2+} per gram of clay. The layer charge, w, for each sample was calculated as a function of Fe^{2+} by optimizing K_0 values to superpose w functions and w_{exp} (Table 1). Note that Figure 2 shows that satisfactory fits of w values to experimental data were obtained, which provides good support of the validity of our model. As shown below, K_0 values can be determined by an additional and independent method. Thus, Equation (11) may be used to predict layer charge of an iron-containing smectite as a function of its reduction level, provided that w_0, K_0, and m_{tot} are known.

Comparison between the observed and predicted losses of structural OH groups as a function of reduction rate

The loss of structural OH groups as a function of the reduction level is difficult to measure. Lear and Stucki (1985) used tritium (^3H) as a label element where 26% of structural H^+ in SWa-1 was replaced by $^3H^+$ by suspending the nontronite sample in a ^3H solution heated at 125°C for 24 h. Then, the labeled sample was reduced by $Na_2S_2O_4$, and ^3H was measured against Fe^{2+}. Lear and Stucki (1985) assumed that the loss of ^3H is proportional to the loss of structural OH groups in reduced samples and, based on this assumption, they determined the amount of structural protons lost as a function of the reduction level (Figure 3). The experimental relationship was fitted by the empirical linear equation: $n_i = 0.77m$.
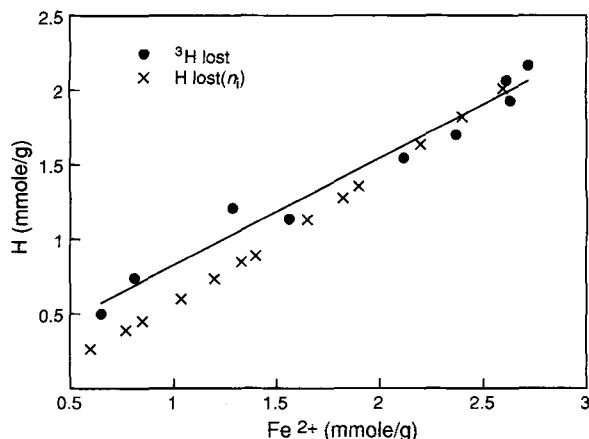
The loss of structural OH groups in SWa-1 (n_i) can be calculated from Equation (9b), which supposes that the increase of the negative charge of the layer resulting from Fe^{3+} reduction is entirely compensated by the sorption of Na and H^+, and that all H^+ ions in the structure are consumed for the dehydroxylation of OH groups. The calculated n_i values are compared to the observed data in Figure 3. The match between the predicted and observed values is good, which supports our theoretical approach. However, the loss of structural H determined from the ^3H experiment is higher than that calculated in an amount equal to 0.2 mmole H^+/g of clay where the Fe^{2+} content is equal to 0.6–1.3 mmole/g; the differences between calculated and observed values gradually decreases to zero at greater reduction levels. The reason for this small discrepancy is unclear.

Determination of K_0

It follows from Equation (8) that the value of K_0 determines the n_i/p ratio during the reduction process. The value of K_0 of a smectite may be assumed to depend on the initial Fe^{3+} content. This assumption is substantiated by the fact that the structural modification of *trans*-vacant (tv) Fe^{3+}-containing dioctahedral 2:1 layer silicates during dehydroxylation depends on the amount of Al and Fe in the octahedral sheet. Indeed, the dehydroxylation of tv 2:1 layer silicates by heating results in the migration of 50% of the octahedral cations from *cis*- to *trans*-sites where $Fe^{3+} > Al$. In contrast, octahedral cations preserve the original *cis*-site occupancy where Al is higher than Fe^{3+} (Drits *et al.,* 1993; Muller *et al.,* 2000; Tsipursky *et al.,* 1985). Although these results were obtained for thermally treated samples, cation migration does not depend on the way the dehydroxylation is achieved (*i.e.,* either thermally or by reduction). Instead, it is deter-
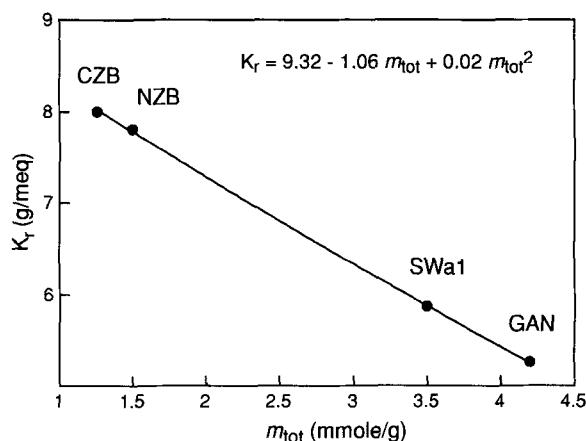
Figure 4. Relationship between K_r and total content of Fe^{3+} (m_{tot}) for different beidellite and nontronite samples.

mined by the crystal chemistry because Manceau *et al.* (2000) showed that in the fully reduced Garfield nontronite, Fe^{2+} cations occupy *trans-* and *cis*-sites to form trioctahedral domains. Cation migration and dehydroxylation of the octahedral sheet probably destabilize the crystal-lattice energy of reduced smectites, in an amount dependent on the total Fe content. To minimize this effect, Fe-rich smectites will tend to maximize the number of Na^+ ions in the interlayer and to minimize the loss of structural OH groups. Thus, the incorporation of Na^+ ions in the interlayer *vs.* cation migration and loss of structural OH groups are stabilizing and destabilizing factors, respectively.

Let us write Equation (9c) in the form: $p/m_{rel} = m_{tot}/(1 + K_0 m_{rel})$. This equation establishes that Fe-rich nontronites have a small K_0 value to maximize the amount of sorbed Na (p) at a given reduction rate. Conversely, the lower the Fe^{3+} concentration, the lower the destabilization of the crystal-lattice energy is upon reduction and, accordingly, K_0 is higher. However, Table 1 shows that there is no significant dependence between K_0 and m_{tot}. In contrast to Equation (9c), both m_{tot} and K_0 decrease in the order GAN, SWa-1, CZB, and UPM. Moreover, samples NZB and CZB have a similar m_{tot} but different values of K_0. However, the amount of Na sorbed from solution is controlled by the CEC of the oxidized smectite. Therefore, smectites with the same m_{tot}, but a different CEC value, have a different capacity to sorb Na in the interlayer for a given reduction rate. Based on electrostatic reasons, the higher the CEC, the lower the number of Na^+ ions can be assumed to be sorbed in the structure upon reduction because the interlayer has initially much Na.

To test this hypothesis, we normalize K_0 values to the CEC by

$$K_r = K_0/CEC. \tag{12}$$

Note in Figure 4 that K_r and m_{tot} values are almost proportional for beidellite and nontronite samples. This relationship is expressed by:

$$K_r = 9.32 - 1.06 m_{tot} + 0.02 m_{tot}^2. \tag{13}$$

The dependence between K_r and m_{tot} of Equation (13) is in full agreement with the theoretical prediction: as the value of m_{tot} increases, the value of K_r decreases. Thus, the structural formula of a smectite sample is sufficient to determine K_r and K_0 from Equations (12) and (13). However, Equations (12) and (13) are not universal and do not apply to montmorillonite. The K_r value for the UPM montmorillonite predicted from Equation (13) is equal to 8.75 g/meq and not 0.37 g/meq (Table 1). This large difference between predicted and experimental K_r values for UPM probably occurs because of a difference in the Fe^{3+} reduction mechanism between montmorillonite and beidellite-nontronite. This is addressed below.

Relationship between p and n_i as a function of m_{tot}, m_{rel}, K_0, and CEC

From the relationships between m_{tot}, K_0, and CEC [Equations (12) and (13)], Equation (9) may be used to predict the amount of sorbed Na (p) and H^+ (n_i) from solution during the reduction of Fe^{3+}. The $p = f(m_{rel})$ and $n_i = f(m_{rel})$ functions for three hypothetical smectites containing 4.0, 2.5, and 1.0 Fe^{3+} atoms per unit cell, and having the same CEC of 1 meq/g, are plotted in Figure 5a. K_0 values are calculated from Equations (12) and (13), and are equal to 5.4, 6.8, and 8.28, respectively.

Figure 5a shows the following: (1) For each sample, there is a value of $m_{rel} = 1/K_0$ (or m_{rel}^{eq} where eq equals equilibrium) for which $p = n_i$. Below m_{rel}^{eq}, $p > n_i$, which means that the increase in the negative charge of the layer is compensated predominantly by the sorption of Na^+ from solution. In contrast, above m_{rel}^{eq}, the increase in the negative charge of the layer is compensated by the sorption of H^+. (2) The n_i function is nearly linear whereas p has a logarithm-like shape. Consequently, over most of the range of Fe reduction, H^+ is regularly sorbed, whereas most Na^+ is sorbed below m_{rel}^{eq}. For instance, for nontronite ($m_{tot} = 4.0$), an increase of m_{rel} from 0.2 to 0.35 corresponds to an increase of sorbed Na^+ from 0.38 to 0.48 atoms per unit cell, whereas the H^+ content more than doubles from 0.42 to 0.92 atoms per unit cell. The variations of p and n_i functions with the total Fe concentration (m_{tot}) for a given m_{rel} above the m_{rel}^{eq} value indicates a proton-exchange reaction. For example, at $m_{rel} = 0.5$, p values for smectite samples with $m_{tot} = 4.0$, 2.5, and 1.0 are equal to 0.54, 0.28, and 0.09 Na, whereas n_i values for the same samples are equal to 1.46, 0.96, and 0.40 H^+ per unit cell. Therefore, a change of m_{tot} from 4.0 to 1.0 decreases p by only 0.45 Na, whereas n decreases by 1.06 H^+.

Figure 6.   Different lengths of OH-OH edges in tv (a) and cv (b) octahedral sheets.

$= 0.15$, $m_{tot} = 4.0$, $K_0 = 6.5$, CEC $= 1.20$; point 2: $m_{rel}^{eq} = 0.28$, $m_{tot} = 4.0$, $K_0 = 3.5$, CEC $= 0.65$; point 3: $m_{rel}^{eq} = 0.15$, $m_{tot} = 2.0$, $K_0 = 6.5$, CEC $= 0.89$; and point 4: $m_{rel}^{eq} = 0.28$, $m_{tot} = 2.0$, $K_0 = 3.5$, CEC $= 0.48$. Points 1 and 3, and 2 and 4 are aligned vertically because they have equal m_{rel}^{eq} values. Samples belonging to a vertical line have different m_{tot} and CEC values but equal K_0 values. Points 1 and 2, and 3 and 4 are linear with the origin. Each line indicates an equal Fe content (m_{tot}), but a different CEC. CEC increases towards the origin, and this trend is indicated on Figure 5b by the location of point 2 above point 1, and point 4 above point 3. This variation at constant m_{tot} value indicates that the layer charge is preferably compensated by the sorption of H^+ rather than Na when CEC increases. This interesting finding is illustrated in Figure 5b by the line at $m_{rel} = 0.24$. At this reduction level, for a smectite with a total Fe content of 2.0, an increase in the CEC from 0.48 (point 4) to 0.89 meq/g (point 3) leads to a decrease in the amount of sorbed Na from 0.26 to 0.19 atoms per unit cell ($\Delta p = 0.07$), and a concomitant increase of H^+ from 0.22 to 0.29 ($\Delta n_i = 0.07$).

Structural changes in reduced trans- and cis-vacant 2:1 layers

As shown above, Equations (12) and (13) successfully apply to Fe-rich beidellite and nontronite samples, but not to the UPM montmorillonite, and this is now discussed. According to Tsipursky and Drits (1984), montmorillonite has *cis*-vacant (cv) 2:1 layers, whereas beidellites and nontronites possess tv 2:1 layers. The octahedral edge formed by the two adjacent OH groups is short in tv sheets (2.40–2.45 Å), and longer in cv sheets (2.85–2.90 Å) because of the different electrostatic interactions owing to the configurations of octahedral cations in the two structures (Drits *et al.*, 1984, 1995) (Figure 6). This structural
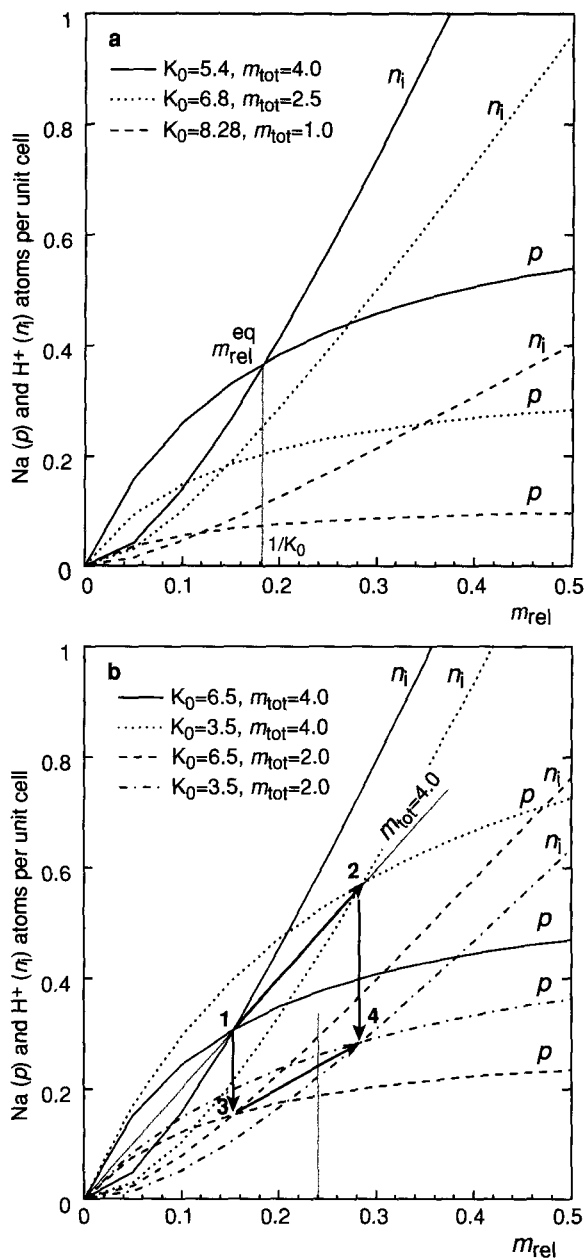

Figure 5.   a) Variations in the predicted amount of sorbed Na (p) and loss of structural OH groups (n_i) as a function of the Fe^{3+} reduction level (m_{rel}) for three hypothetical smectites having a total Fe content (m_{tot}) of 4.0, 2.5, and 1.0 atoms per unit cell, and an identical CEC of 1 meq/g ($5.4 \le K_0 \le 8.28$). b) Same representation as a) for $m_{tot} = 4.0$ and 2.0 and $K_0 = 3.5$ and 6.5 ($0.48 \le$ CEC ≤ 1.20 meq/g).

Figure 5b represents $p = f(m_{rel})$ and $n_i = f(m_{rel})$ functions for two hypothetical smectites with identical K_0 values (alternatively, either 3.5 or 6.5), but different total Fe contents (m_{tot} equals either 4.0 or 2.0). Thus, four m_{rel}^{eq} points shown in Figure 5b correspond to the following physico-chemical parameters: point 1: m_{rel}^{eq}
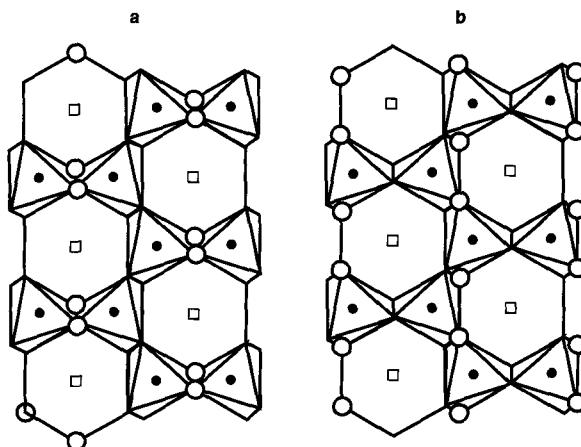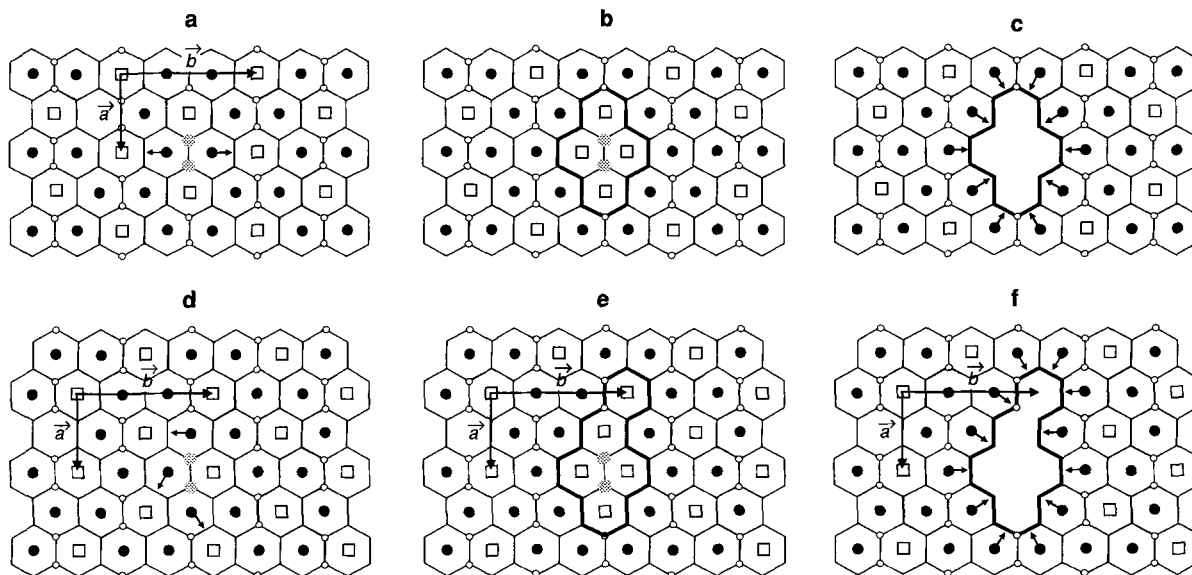
Figure 7. Proposed structural mechanisms for the reduction of Fe^{3+} to Fe^{2+} in tv (a,b,c) and cv (d,e,f) octahedral sheets. OH, Fe, and vacant sites are represented by empty circles, filled circles, and squares, respectively. In a, b, d, and e, H_2O molecules are in grey. See also Manceau et al. (2000).

difference is of key importance and it probably determines the behavior of tv and cv layers during the reduction of Fe^{3+}.

Now consider the successive structural changes in the octahedral sheet of reduced tv and cv 2:1 layers. Structural studies of nontronite by P-EXAFS and XRD (Manceau et al., 2000) and by Mössbauer spectroscopy (Russell et al., 1979) showed that Fe atoms preserve their octahedral coordination in the reduced state. To maintain six-fold coordination of iron and to allow dehydroxylation, Fe^{2+} must migrate to nearest vacant octahedral sites, otherwise Fe^{2+} will be coordinated to five, or even four, oxygens (Manceau et al., 2000). As seen in Figure 7, the most preferable local structural environment for the migration of Fe^{2+} is an adjacent empty trans-site. Manceau et al. (2000) showed that in the Garfield nontronite, Fe^{2+} migrates along the [010] direction to adjacent empty trans-sites to form trioctahedral-like Fe^{2+} clusters. H_2O molecules are formed owing to the protonation of edge-forming OH groups. A structural study of reduced SWa-1 (Manceau et al., unpublished) showed that the migration of Fe^{2+} cations also occurs despite the presence of Al and Mg in the octahedral sheet. Thus, Fe^{2+} atoms migrate in tv 2:1 layers of nontronite and Fe-rich beidellite.

In comparison with tv layers, structural changes in reduced cv 2:1 layers are probably more complex. In cv octahedral sheets, OH pairs are bridged to three octahedral cations, and only two octahedral cations in tv sheets (Figure 7). Therefore, dehydroxylation in a cv framework, and the creation of local trioctahedral clusters as in a tv framework, require the simultaneous

migration of three neighboring Fe^{2+} cations in [010], [$\overline{3}$10], and [310] directions. Such a significant structural modification requires high energy. This energy expenditure is probably even greater for low Fe^{3+}-containing montmorillonite because the reduction of Fe^{3+} requires that two Al, Mg cations migrate. Thus, in comparison with beidellites and nontronites, the greater activation energy of cv layers of montmorillonites will limit Fe^{2+} migration. Therefore, it is unlikely that layers dehydroxylate in montmorillonites, and the deficit of positive charge created by the Fe^{3+} to Fe^{2+} reduction is probably compensated entirely by sorption of Na. This interpretation explains the low value of K_0 for UPM (0.32, Table 1). Thus, for this sample, $p/n_i > 1$ [Equation (9)]. Further investigations are clearly needed to refine the local structure around Fe^{2+} atoms in Fe-poor montmorillonite and beidellite.

### Calculation of structural formulae

From the chemical composition of nontronite or Fe-rich beidellite samples, Equation (13) permits the determination of K_r and, thereafter, K_0 is obtained from Equation (12). Then, the value of K_0 can estimate the amount of Na and H^+ sorbed from solution using Equation (9). If all the incorporated H^+ ions are consumed in dehydroxylation, then the structural formula of the reduced sample containing m_{tot} Fe^{2+} ions per unit cell can be written in the form given by Equation (7). For example, let us consider the Garfield nontronite sample GO studied by Manceau et al. (2000) with a structural formula:

$$Na_{0.81}(Si_{7.22}Al_{0.78})(Fe^{3+}_{3.64}Al_{0.32}Mg_{0.04})O_{20}(OH)_4 \quad (14)$$

in which 50% of structural Fe^{3+} was reduced. From Equations (9), (12), and (13), $K_0 = 4.92$, $p = 0.53$, $n_i = 1.29$, and $w = w_0 + p = 0.81 + 0.54 = 1.35$ atoms of Na per unit cell. Then, the structural formula of this reduced sample is:

$$Na_{1.34}(Si_{7.22}Al_{0.78})(Fe^{3+}_{1.82}Fe^{2+}_{1.82}Al_{0.32}Mg_{0.04})O_{20}(OH)_{2.71}. \quad (15)$$
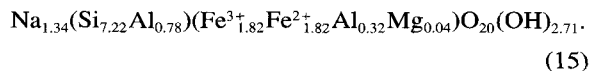
However, to preserve the octahedral coordination of reduced Fe^{2+}, limited dehydroxylation occurs (see also Manceau *et al.,* 2000). To illustrate, let us calculate a structural formula for a 100% reduction level, assuming that all initially sorbed H^+ participates in subsequent dehydroxylation. In this case $p = 0.63$, $n_i = 3.02$, and the resulting structural formula is:

$$Na_{1.44}(Si_{7.22}Al_{0.78})(Fe^{2+}_{3.64}Al_{0.32}Mg_{0.04})O_{20}(OH)_{0.98}. \quad (16)$$
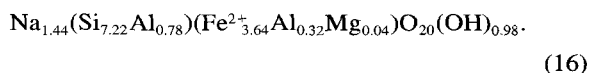
With such a low amount of OH groups, Fe^{2+} cannot be six-fold coordinated. If all H^+ ions in the structure are consumed by dehydroxylation, then Fe^{2+} will be five-fold, or even four-fold coordinated. This conclusion contradicts the structural results obtained by Russell *et al.* (1979) and Manceau *et al.* (2000), who showed that Fe^{2+} remains coordinated to six oxygens in reduced nontronite. Thus, the total OH of reduced nontronite will be much higher than that calculated in Equation (15). The structural model proposed by Manceau *et al.* (2000) for reduced Garfield contains 2.93 OH per unit cell. Based on this structural model, and on the reduction mechanism proposed here, the predicted structural formula is:
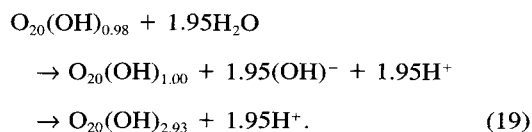
$$H_{1.95}Na_{1.44}(Si_{7.22}Al_{0.78})(Fe^{2+}_{3.64}Al_{0.32}Mg_{0.04})O_{20}(OH)_{2.93}. \quad (17)$$
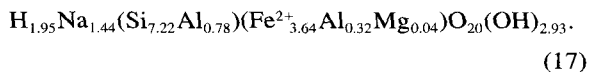
In this formula, the layer charge is compensated by the sorption of 1.44 Na and 1.95 H^+. This interlayer Na (1.44) is close to that determined by Manceau *et al.* (2000) for reduced Garfield (1.3 ± 0.1) by chemical analysis and P-EXAFS:

$$H_{2.07}Na_{1.30}(Si_{7.22}Al_{0.78})(Fe^{2+}_{3.64}Al_{0.32}Mg_{0.04})O_{20}(OH)_{2.93}. \quad (18)$$
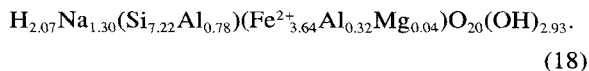
The agreement between these two structural formulae provides additional support to the validity of our proposed reduction mechanism of Fe^{3+} to Fe^{2+} in dioctahedral smectites.

Equation (17) indicates that a limited number of OH groups dehydroxylate, and that the negative layer charge is partly compensated by H^+ sorbed from solution. This conclusion contrasts with tritium measurements, which showed that in SWa-1, the loss of structural OH occurs to ≤80% of Fe^{3+} reduction. Figure 3 also shows that the measured loss of hydroxyls is in quantitative agreement with the prediction of Equa-

tions (6) and (9). The high number of hydroxyl groups in reduced nontronite [Equation (18)] despite the massive loss of hydroxyl groups observed in tritium measurements can be explained by considering that the reduction process occurs as two distinct steps. In the first step, reactions occur according to Equations (6), and all sorbed H^+ ions are used in dehydroxylation. This reaction produces an unstable environment around Fe^{2+} owing to the lower-coordination number, and also reduces the charge compensation of oxygen atoms, so they become strongly undersaturated (Manceau *et al.,* 2000). The stability of the local structure around Fe^{2+} atoms are then reestablished by the sorption of two H_2O molecules, which dissociate ($H_2O \rightarrow OH^- + H^+$). Newly formed hydroxyl groups then serve to rebuild the six-fold coordination of Fe^{2+} atoms, and H^+ protons balance the local charge. These reactions probably occur simultaneously with, or immediately after, the migration of Fe^{2+} from *cis* to *trans* sites. In this case, the reaction of the anionic framework to produce the transformation of (16) to (17) can be written:

$$O_{20}(OH)_{0.98} + 1.95H_2O$$
$$\rightarrow O_{20}(OH)_{1.00} + 1.95(OH)^- + 1.95H^+$$
$$\rightarrow O_{20}(OH)_{2.93} + 1.95H^+. \quad (19)$$

This two-step reduction mechanism accounts for the continuous loss of structural OH with increasing Fe^{2+} content as determined experimentally. This mechanism also accounts for the incorporation in the structure of aqueous H^+ ions measured by titration experiments for SWa-1 nontronite. As for reduced Garfield nontronite, this increase in H^+ may result from the partial or complete dissociation of sorbed H_2O molecules during the second stage of the reduction process. To determine this quantitatively, the content of structural OH groups per unit cell must be known at a given reduction level. Unfortunately, at present this value is known only for 100%-reduced Garfield nontronite (Manceau *et al.,* 2000). However, the structural formula for SWa-1 involving the Fe^{2+} content can be predicted from the initial composition $(Si_{7.30}Al_{0.70})(Al_{1.06}Fe^{3+}_{2.73}Mg_{0.26})O_{20}$-$(OH)_4$, Equation (9), and titration data (Figure 2; Lear and Stucki, 1985). For example, for $m = 2.32$, $m_{tot} = 2.73$, and $m_{rel} = 0.85$, the expected structural formula is:

$$H_{0.40}Na_{1.28}(Si_{7.30}Al_{0.70})(Al_{1.06}Fe^{3+}_{0.41}Fe^{2+}_{2.32}Mg_{0.26})O_{20}(OH)_{2.60} \quad (20)$$
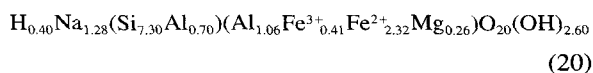
assuming that 0.40 H_2O was incorporated into the structure.

In conclusion, the proposed reduction mechanism of Fe^{3+} to Fe^{2+} in dioctahedral smectites satisfactorily accounts for the modifications of the physico-chemical properties of 2:1 layers as measured by solution chem-

istry by various investigators. However, the absence of experimental data for OH content in smectites as a function of the reduction level prevents the establishment of a structural formula for dioctahedral beidellite-nontronite samples containing a variable amount of Fe^{2+}.

ACKNOWLEDGMENTS

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E-mail of corresponding author: manceau@ujf-grenoble.fr