

Changes in the CEC of a soil smectite–kaolinite clay fraction as induced by structural iron reduction and iron coatings dissolution

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Abstract

Studies of the effects of changes in iron (Fe) redox status on cation exchange capacity (CEC) and other physical and chemical properties of clays have typically focused on purified clays or clay fractions, but little attention has been given to systems with mixed mineralogy, which is more typical of natural soils. The objective of this study was to measure and establish any correlation between changes in CEC and Fe mineralogy that occurs in a mixed-mineral clay system undergoing chemical reduction. The clay fraction (SE1089) of a soil containing a mixture of smectite, kaolinite, and Fe oxide was investigated using variable-temperature Mössbauer spectroscopy, chemical analyses, and reductive dissolution in CBD media. This study revealed that in the unreduced clay fraction half of the total Fe was structural iron (Fe_{Str}) in the smectite and half was in goethite. The goethite particles were estimated to be 9 nm in mean crystal diameter (MCD) and to contain 9% Al substituted isomorphously for Fe.

An evolution of the different Fe pools and changes in CEC of the mixture were observed. The CEC of SE1089 smectite fraction sharply increased upon reduction, similar to the SWa-1 reference clay, even though the Fe_{Str} content of SE1089 is much less. Results revealed a correlation of the increase in CEC with Fe_{Str} reduction and oxide dissolution, giving a direct connection between the total coating content and the rate of dissolution. For this reason, dissolution kinetics appears to be a key factor in understanding the control of CEC by iron coated material. In particular, in natural media governed by bacterial activity, different dissolution kinetics are expected. © 2006 Elsevier B.V. All rights reserved.

Keywords: CEC; Iron coatings; Structural iron; Reductive dissolution; Goethite; Oxidation-reduction

1. Introduction

Iron is an important electron acceptor for anaerobic respiration of microorganisms in the environment. The iron pool is thus an important controlling factor for the bio-geochemistry of natural solutions as well as for the weathering of minerals.

Charged clay minerals are ubiquitous in the natural environment. Among them, smectites are common in the

environment and well distributed in soils around the earth. The smectite layer charge controls many important characteristics, such as swelling, hydration, clay fabric, and surface reactivity (Stucki, 1988). These properties affect water transfer, nutrient retention, and pollutant degradation — major soil properties that control environmental quality. Virtually all smectites contain some ferric iron in the octahedral sheet (Fe_{Str}). Studies of reference smectite minerals in the laboratory revealed that chemical or bacterial reduction of Fe_{Str} sharply modifies the chemical and physical properties of the clay, including the layer charge and the cation exchange capacity (CEC) (Stucki and Roth,

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1977; Stucki et al., 1984a; Khaled and Stucki, 1991; Kostka et al., 1999).

These studies anticipated that many soil clay characteristics that control water transfer and surface chemistry also evolve under reducing environments in natural soils. Indeed, recent studies revealed that Fe_{Str} reduction occurs in soil clays in the field. Favre et al. (2002) measured a large increase in CEC upon structural Fe reduction in a rice paddy field.

In soils and natural environments, however, Fe oxides and Fe_{Str} coexist. The clay minerals and Fe oxides can be present as independent particles, but normally they are more intimately associated with the clay minerals either as stable organomineral particles or as Fe oxide coatings. Iron is highly susceptible to reductive dissolution if in the oxide form, but less susceptible if in the clay mineral form.

Numerous studies of dissolution rates of various Fe oxides have been conducted, with focus on both reductive and chelative factors which simulate soil conditions. The time dependence of reductive dissolution of goethite particles can be described by different mathematical expressions, as follows.

The first step of reaction can be linear. Departure from linearity is due to small initial curvature of either decreasing or increasing slope, which is typical of first order and S-shaped curves, respectively. In some cases, positive intercepts correspond to samples having significant amounts of amorphous Fe-oxide, which could indicate some preferential, rapid dissolution of poorly crystalline material (Torrent et al., 1987).

The crystal size and cation substitution are important controlling factors (Schwertmann, 1991). The isomorphous substitution of Al for Fe contributes to increased stability against dissolution in various media (Schwertmann, 1984; Torrent et al., 1987; Gonzalez et al., 2002). Even though Al substitution in goethites tends to decrease the crystal size and increase structural defects, the initial dissolution rate per unit of surface area is lower than in pure goethite (Gonzalez et al., 2002). Even in strong acids, the dissolution rate of Al-substituted goethite decreases with increasing Al content (Torrent et al., 1987).

The dissolution rate laws for oxides can also be used for Fe in coatings, as suggested by Roden (2004). These results show that the susceptibility of coating material, including natural oxides in coatings, to reductive dissolution is lower than in the oxide alone.

Positively charged coatings on the clay surface may partly balance the negative layer charge of the clay (Roth et al., 1969; Zhuang and Yu, 2002). The presence of metal oxide coatings on minerals has a profound effect on the interaction of those surfaces with bacterial cells by increasing the sorption of bacteria from suspension

(Mills, 2003). The two Fe pools tend to accept electrons transferred during redox reactions. The reduction of positively charged coatings leads to the dissolution of the coatings that frees negative charges. The CEC is then susceptible to increase by this reductive dissolution process. Favre et al. (2002) explained the large increase in CEC observed in the field by both phenomena: a reduction of Fe_{Str} inducing new negative charges, and a dissolution of goethite coatings uncovering previously existing negative charges. The thermodynamics of an oxidation–reduction reaction of pure Fe oxides is well documented (Cornell and Schwertmann, 2003), but the thermodynamics of redox reactions in clays is documented by only a few authors (Xiang and Villemure, 1995; Amonette, 2003). The kinetics and thermodynamics of the complex system until now has been unknown, but are key to controlling the evolution of the clay CEC and associated soil characteristics upon reduction.

The aim of this study was to monitor the evolution of the clay layer charge upon reduction of the clay fraction of a rice-cropped vertisol containing Fe oxide sand and smectitic material; and to estimate the role of the two Fe pools in the charge evolution process. The Fe pools were characterized, then a model describing the evolution of the charge upon reduction of Fe_{Str} and Fe oxide coatings was proposed.

2. Materials and methods

2.1. Investigated clay fraction

This work was performed on a $<2\text{-}\mu\text{m}$ clay fraction, called SE1089, extracted from a previously characterized vertisol after removal of organic matter by H_2O_2 treatment and calcium carbonates by a cold acetate solution buffered at pH 5.5 (adapted from Robert and Tessier, 1974). TEM analyses performed on this vertisol sample revealed the presence of free iron oxides and coatings in its $<2\text{-}\mu\text{m}$ fraction (Favre et al., 2004). The clay fraction is composed of 32% kaolinite and 68% non-pure smectite (mainly a dioctahedral bediellite) containing octahedral Fe according to chemical analyses and Mössbauer spectroscopy. (Favre et al., 2002, 2004).

2.2. Clay reduction

Clay samples were reduced applying the method of Stucki et al. (1984b). The level of reduction was controlled by varying the amount of sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$) in the range of 0–150 mg per 40 mg of clay, or by altering the reaction time within a span of 0–240 min.

2.3. Iron analysis

The Fe content and speciation in oxidized and reduced clay samples were determined by combining Mössbauer

spectroscopy and chemical analysis. Mössbauer spectra were obtained at different temperatures, ranging from 4 K to 77 K, with a WEB Research/Janis® model SHI-850-5 closed-cycle cryostat system. The mathematical fitting of the Mössbauer spectra was achieved with the Recoil© V 1.05 program (Lagarec and Rancourt, 1997) assuming Lorentzian line shapes in the fitting procedure. Total and ferrous iron in the solid clay fraction before or after reaction were determined according to Komadel and Stucki (1988). The maximal variability of iron analysis using this photochemical method, based on five replicates, was estimated to be about 5% (Amonette et al., 1994, 1999).

2.4. Dissolved ions in solution

Ions dissolved upon reduction were analyzed in the reduction reaction solution (CBD buffer solution), as well as in the nine subsequent washing solutions, by ICP-AES. Reductive dissolution of Si in the CBD minerals was assessed based on the concentration of Si in the CBD solution. Using the structural formula of the clay established by Favre et al. (2004) a Si/Fe ratio per gram of clay can be calculated. Assuming a congruent dissolution during the treatment, Fe_{str} was calculated using this ratio and Si analyses. The extent of clay dissolution never exceeded 3% of the initial sample weight.

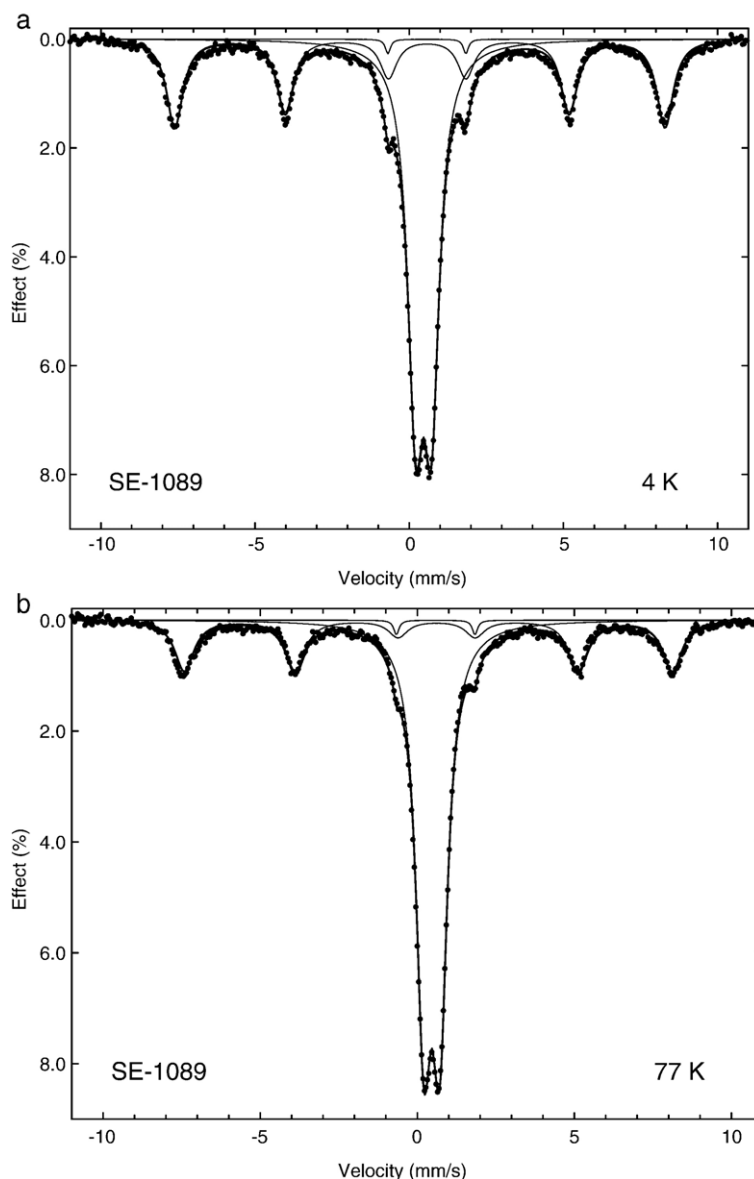


Fig. 1. a. Mössbauer spectrum of SE1089 at 4 K unaltered. Dots are experimental data, thin lines are doublet or sextet contribution curves, thick line is the fitting. b. Mössbauer spectrum of SE1089 at 77 K unaltered. Dots are experimental data, thin lines are doublet or sextet contribution curves, thick line is the fitting.

Table 1
Fitting parameters for Mössbauer spectra of unaltered SE1089 at 4 K, 77 K in a velocity range of ± 12 mm/s

Parameters [units]	SE1089 4 K 12 mm/s	SE1089 77 K 12 mm/s
QSD sites		
δ [mm/s]	0.46	0.46
Δ [mm/s]	0.51	0.51
Γ [mm/s]	0.31	0.29
Area [%]	61.2	71.5
Site 2		
δ [mm/s]	0.57	0.59
Δ [mm/s]	2.52	2.49
Γ [mm/s]	0.10	0.10
Area [%]	0.9	0.7
HFD sites		
Site 1		
δ [mm/s]	0.46	0.48
B_{hf} [T]	49.3	48.18
ε [mm/s]	-0.12	-0.13
Γ [mm/s]	0.32	0.35
Area [%]	37.9	28.7
Reduced χ^2	1.01	1.20

δ [mm/s] is the isomer shift, Δ [mm/s] is the quadrupole splitting, area is the relative percentage of each iron form, B_{hf} is the magnetic hyperfine field.

Dissolved Fe oxides were calculated as the sum of the soluble Fe concentration in all the washing solutions, while the Fe provided from clay mineral dissolution had to be subtracted.

2.5. CEC measurements

CEC was determined according to Khaled and Stucki (1991). Reoxidation of Fe_{Str} was avoided by continuously maintaining the samples under an inert N_2 atmosphere and using deoxygenated solutions prepared according to Stucki et al. (1984b). The CEC of clay samples was measured by

Na^+ and Fe concentrations in the $MgCl_2$ exchange solutions, determined by ICP-AES (Perkin Elmer® 2000) and expressed in cmol/kg of smectite according to the following transformation: as the original clay fraction contains 68% of smectite and 32% of kaolinite (Favre et al., 2004) and assuming an equivalent dissolution of smectite and kaolinite upon reduction, the smectite content of the reduced clay can be calculated as

Smectite content

$$= (\text{initial mass} - (\text{dissolved oxides upon reduction} + \text{dissolved clay upon reduction})) * 68 / 100.$$

2.6. CEC evolution upon reduction modeling

In order to investigate the increase of CEC due to Fe_{Str} reduction, the mechanistic model of Drits and Manceau (2000) established for pure reference 2:1 dioctahedral clay minerals was modified and implemented. The model integrates the observed changes upon reduction in layer charge (Stucki and Roth, 1977; Lear and Stucki, 1985) and hydroxyl composition of the clay structure upon reduction. According to this model, the increase of negative charge of the layer resulting from the reduction of Fe_{Str} is compensated in two ways:

- (1) by an increase in the amount of positive interlayer charge through the adsorption of Na^+ provided by $Na_2S_2O_4$ and the buffer salts in solution (Stucki et al., 1984a).
- (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) and/or protonation of structural hydroxyl groups (Manceau et al., 2000).

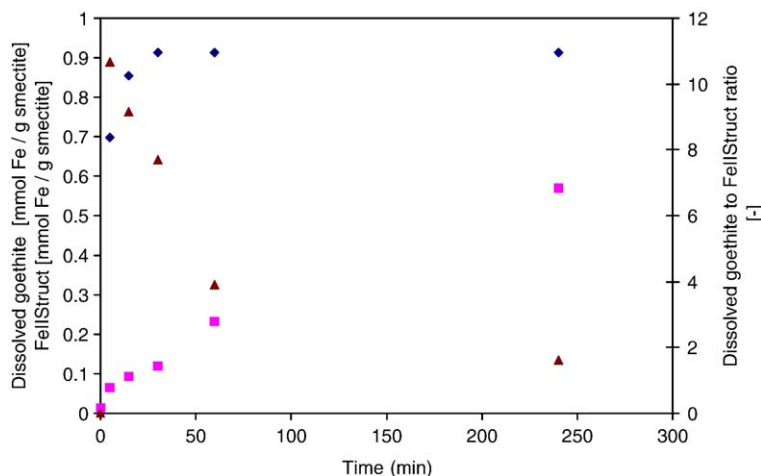


Fig. 2. Goethite dissolution [mmol/g of smectite] (diamonds) Fe_{Str}^{II} [mmol/g of smectite] (squares) and dissolved goethite to Fe_{Str}^{II} ratio (triangles) as a function of time.

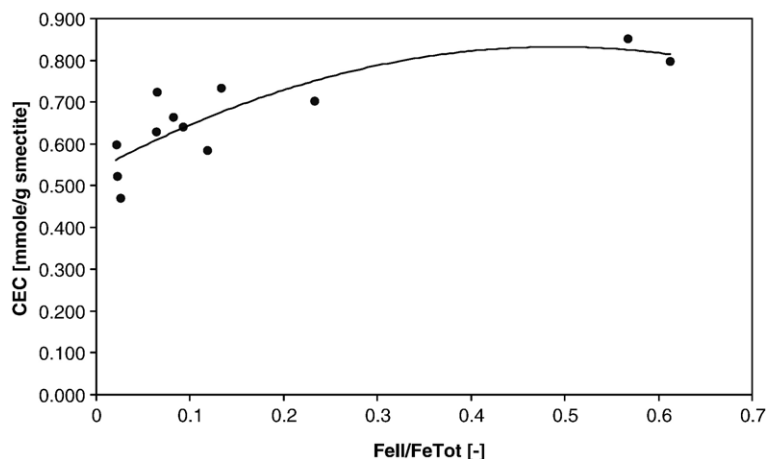


Fig. 3. CEC evolution upon reduction [mmol/g of smectite] as a function of structural Fe^{II}/Fe^{Tot} ratio [-] in CB buffer with 50 or 150 mg of dithionite. Experimental points are circles. A second degree polynomial adjustment of the experimental data is in full line.

Adsorption of Na⁺ reflects an increase in CEC, whereas dehydroxylation or protonation decreases the total layer charge. The final expression of the model is:

$$w = w_0 + \frac{m_{\text{rel}} \cdot m_{\text{tot}}}{1 + K_0 \cdot m_{\text{rel}}} \quad (1)$$

where w is the clay layer charge [meq/g] at a given Fe_{Str} reduction level, w_0 is the initial clay layer charge [meq/g], m_{rel} is the Fe_{Str}^{II} to Fe_{Str}^{Tot} ratio measured by chemical analyses (Komadel and Stucki, 1988), m_{tot} is the Fe_{Str}^{Tot} [mmol/g], and K_0 is a clay dependent parameter adjusted by the model to the experimental data.

The CEC evolution upon reduction of the complex clay fraction containing iron coatings might be controlled by an additional process. As Fe coatings may be positively charged, they can balance a part of the clay charge. The reductive dissolution of this coating fraction might liberate exchangeable sites on the clay surface and thereby increase the CEC. The model is then modified as follows to take this process into account:

$$w = w_0 + \frac{m_{\text{rel}} \cdot m_{\text{tot}}}{1 + K_0 \cdot m_{\text{rel}}} + \lambda(Q_0 - Q) \quad (2)$$

where Q_0 = initial Fe in oxide content in the clay fraction in [mmol/g] and Q is Fe from the dissolved oxide content upon reduction in [mmol/g]. $\lambda = \lambda_1 \cdot \lambda_2$, where λ_1 is the fraction of dissolved oxides that was in coatings and λ_2 is the charge balanced by this fraction expressed in mmol/g of Fe in coatings, or the opposite of the charge of this coating.

3. Results

3.1. Iron pool characterization:

Total Fe content, measured after acid digestion according to Komadel and Stucki (1988), was 6.8%, with a standard deviation (SD) of 0.137; and, Fe(II) content in the oxidized sample was 1.3% of total Fe, with a SD of 0.056.

Mössbauer spectra of the unaltered clay fractions obtained at 4 K (a) and 77 K (b) over the velocity range of $\pm 12 \text{ mm s}^{-1}$ (Fig. 1) revealed both sextets and doublets from which the hyperfine parameters and relative percentages of the different Fe forms were calculated (Table 1). The two spectra were fitted with one sextet and two doublets, even though the second doublet contribution was negligible (<1% of total absorption). The change in temperature from 77 to 4 K shifted the hyperfine parameters slightly and altered the relative intensities of the sextet and doublet contributions. The hyperfine field, B_{hf} was 49.3 T at 4 K and 48.4 at 77 K. The similarity of the sextet between these two temperatures indicates that it represents a single mineral phase rather than a mixture of different Fe(III) (hydr)oxides and the values of B_{hf} and other parameters give strong evidence for goethite (Vandenberghe et al., 1990). Previous studies undertaken on the geochemistry of the soil from which the clay was extracted also revealed a soil solution at equilibrium with goethite (Boivin et al., 2002).

The nature of the goethite particles was determined by recalling the relationships among B_{hf} (in Tesla), MCD (in nm), surface area (S , in m^2/g), and Al substitution for Fe in the goethite structure (Al, in mole fraction relative to Fe + Al) (Golden et al., 1979; Murad and Schwertmann, 1983; Murad, 1988), viz.,

$$B_{\text{hf}}^{(77 \text{ K})} = 49.8 - 13.6 \text{ Al} - 0.001S$$

$$B_{\text{hf}}^{(4.2 \text{ K})} = 50.65 - 4.2 \text{ Al} - 0.00624S$$

where

$$\text{MCD} = \frac{6 \cdot 10^3}{\rho \cdot S}$$

Table 2

Adjustment parameters for the model of [Drits and Manceau \(2000\)](#) and the modified model. K_0 is a clay dependent parameter, w_0 is the initial clay charge, $\lambda = \lambda_1 \cdot \lambda_2$, with λ_1 as the fraction of total Fe in coating, λ_2 the coating's surface charge

Fitting parameters	K_0 [–]	w_0 [mmol/g smectite]	λ [mmol/mmol goethite coating]	R^2
Modified model	1.952	0.565	–0.079	0.651
*D&M model	1.792	0.554	–	0.647
*D&M model, K_0, w_0, λ fixed	1.952	0.565	0	0.642

*D&M means Drits and Manceau.

The observed values for B_{hf} at 4 and 77 K ([Table 1](#)) were substituted into these expressions, assuming ρ (the density of goethite) to be 4.3 g/cm³, and the average Al substitution was calculated as 0.0916 and the MCD as 9 nm. The specific surface area was 155 m²/g. These are reasonable values for a typical soil goethite ([Fabris et al., 1985](#)) and the hyperfine parameter values fully support this assignment ([Golden et al., 1979](#); [Murad and Schwertmann, 1983](#); [Murad, 1988](#); [Vandenberghe et al., 1990](#)).

With 50 mg of dithionite, the increase in $\text{Fe}_{\text{Str}}^{\text{II}}$ is regular with an average reduction rate of about 0.0022 mmol/g smectite/min ([Fig. 2](#)). Fitting the data with a linear model gives a small positive intercept. During the first 5 min of reaction, the reduction rate is 0.01 mmol/g smectite/min.

The goethite dissolution curve as a function of time ([Fig. 2](#)) follows the typical shape described by several authors ([Rueda et al., 1992](#); [Komadel et al., 1998](#); [Gonzalez et al., 2002](#)). The reductive dissolution rate of goethite is divided into three steps: a very fast reductive dissolution process for 5 min reaction time with a rate of 0.15 mmol/min, a slower reduction rate of 0.06 mmol/min for 15 min of reaction time, and for 30 min reaction time the rate is 0.03 mmol/min. After 30 min reaction time, all the Fe oxides seem to be dissolved and a plateau is reached.

As expected from previous studies ([Stucki et al., 1984b](#)), CEC drastically increased upon Fe_{Str} reduction from 60 cmol/kg smectite to 90 cmol/kg smectite for a $\text{Fe}_{\text{Str}}^{\text{II}}:\text{Fe}_{\text{Str}}^{\text{Tot}}$ ratio increasing from 0.02 to 0.60 ([Fig. 3](#)). The clay fraction used in this study initially contains Fe coatings, which probably occlude part of the layer charge or CEC. The measured CEC of the untreated clay fraction should not, therefore, be used as the value for w_0 , the initial clay layer charge in Eq. (1). This value, as well as the values for K_0 and λ , must be obtained using the corrected model (Eq. (2)). The calculated parameters K_0 , w_0 , λ , and the mean square error calculated with the

adapted model are reported in [Table 2](#). The K_0 parameter for the smectite fraction is 1.952, its initial layer charge is 0.565 meq/g smectite, and λ equals –0.079. R^2 is 0.651. While this value for R^2 indicates some scatter in the data, the corrected model is able to satisfactorily fit the experimental data obtained with SE1089 samples to a first approximation. K_0 and w_0 represent the pure smectite fraction, assuming that the total influence of the oxides is included in the corrected model. The results of the implementation of the model without correction (Eq. (1)) for the Fe coatings are also reported in [Table 2](#) and are $K_0=1.792$, the initial layer charge is 0.554 meq/g smectite, and R^2 is equal to 0.647.

The initial model was then implemented with the parameters calculated with the corrected model, but to emphasize the role of Fe coatings, λ was fixed to 0. The value of R^2 was 0.642.

4. Discussion

The clay fraction of sample SE1089 contains Fe in the clay mineral structure and in a finely divided (9 nm MCD), Al-substituted (0.0916 mole fraction relative to Fe) goethite, as determined by variable-temperature Mössbauer spectroscopy. Hyperfine parameters were analyzed by well established methods ([Murad, 1988](#)) for extracting MCD and Al substitution in goethite. This analysis also eliminated possible assignments to other Fe minerals such as ferrihydrite.

According to [Favre et al. \(2004\)](#) the smectite component in the SE1089 clay fraction is a beidellite with 69% of the charge in the tetrahedral sheet. According to its structural formula, the total layer charge is 0.734 meq/g of smectite. Its Fe content and calculated layer charge are close to those of Upton montmorillonite (UPM) ([Stucki et al., 1984a](#)) but the two clays differ in charge distribution. SE1089 smectite is more closely related to nontronite or beidellite-type smectite. The predicted clay layer charge from the corrected model in the current study of 0.565 meq/g is much lower than estimated by [Favre et al. \(2004\)](#).

Concomitant reduction of Fe_{Str} and goethite reductive dissolution are revealed by the chemical analyses ([Fig. 2](#)). During the 5-minute reduction treatment with sodium dithionite, the dissolution of goethite was about 75% ([Fig. 2](#)) of the original goethite content. This short treatment evidently yielded a small reduction of Fe_{Str} (less than 10%) confirming that goethitic forms of Fe are more easily reduced than Fe_{Str} . The average reductive dissolution rate of goethite is one order of magnitude higher than the average Fe_{Str} reduction rate. Trends with 100 or 150 mg dithionite (in CBD) are similar (not

shown). The shape of the goethite dissolution curve is similar to results reported by Rueda et al. (1992) for reductive dissolution in similar media. Dissolution rates calculated from these observations, as the fraction of dissolved goethite per unit time, range from 0.05 [min^{-1}] for 5 min of reaction to 0.04 [min^{-1}] for 15 min of reaction, and 0.03 [min^{-1}] for 30 min of reaction. In SE1089 clay fraction, dissolution rates expressed in [min^{-1}] range from 0.15 for 5 min of reaction, 0.06 for 15 min of reaction, and 0.03 for 30 min of reaction. Dissolution rate in SE1089 clay fraction is one order of magnitude higher for the 5 min reaction time than for the longer reaction time and constant for longer reaction time. This suggests some preferential, rapid dissolution in the SE1089 sample (Torrent et al., 1987). Total dissolution of goethite is achieved faster in the SE1089 sample than in experiments presented by Rueda et al. (1992) but the initial goethite loading is much smaller than in Rueda et al. (1992).

In terms of reduction rate, expressed as dissolved goethite fraction, SE1089 goethite is similar to synthetic Al-substituted goethite G7 described by Gonzalez et al. (2002) that shows dissolution rates of 0.12, 0.09, and 0.06 for 5, 15, and 30 min of reaction time, respectively. These results agree with the Mössbauer data, which suggests the presence of Al-goethite. Of particular interest is the possibility that goethite particles in coatings, can be distinguished from free goethite particles by careful interpretation of the time dependence of goethite dissolution rates. Roden (2004) observed that Fe oxide coatings have lower susceptibility to reductive dissolution than free Fe oxides. As free iron oxides have been also observed in SE1089 sample <2 μm fraction (Favre et al., 2004), these observations could suggest that the fast dissolution occurring in the SE1089 goethite may be due to dissolution of free oxides and that the subsequent dissolution step is due to goethite coatings. Repetitions of the reductive dissolution measurement would be necessary to confirm this interpretation as well as the calculated dissolution rates.

The parallel reduction of both iron phases, structural and oxide, is surprising in light of thermodynamic analyses. Redox potential calculated for reference clays (Amonette, 2003) indicates that chemical Fe_{Str} reduction is thermodynamically more favorable than goethite reduction, emphasizing the necessity of a coupled kinetic and thermodynamic approach to the reduction process and the necessity to study the physical limitations that coatings may impose on access to structural Fe by electron donors. Further investigations by Mössbauer spectroscopy of the beginning of the reduction reaction in clay–oxide mixture could furnish a wider understanding of the process.

The CEC of the clay fraction increases by 70% upon reduction of 60% of total Fe, which also yields a total

dissolution of Fe oxides. Comparing the CEC evolution with reduction of the SE1089 smectite fraction with reference clays having either a similar Fe_{Str} content (UPM) or a similar charge distribution (ferruginous smectite Washington, SWa-1) found that a reduction level of 60% in UPM led to a CEC increase of about 30% only (Stucki et al., 1984b) and a reduction level of about 60% in SWa-1 produced a CEC increase of about 60%. The origin of these distinctly different behaviors may arise from the difference in charge distribution and because of the presence of Fe coatings. The CEC of reduced SWa-1 is the greatest such increase recorded until now and is very similar to the CEC changes observed after reduction of SE1089 smectite. The underlying mechanisms are probably different, however, due to the presence of surface coatings in SE1089.

The w_0 value of 56.5 (cmol/kg) calculated by the model corrected for coatings contribution is in the lower part of the range of reference smectite w_0 values. It is lower than the value of 73.4 (cmol/kg) calculated by Favre et al. (2004) using Quantarg2 code that uses a data base of analytical composition and characteristics of reference clays. The recorded CEC values of the data base ranged from 70 to 150 cmol/kg, which may be imposing 70 (cmol/kg) as a minimum value. As the particles of SE1089 clay fraction extracted from a soil were poorly crystallized, as shown by Favre et al. (2004) with TEM images, the CEC is expected to be lower than in reference clays. The K_0 fitting parameter is clay dependent, even though its mechanistic significance may be in doubt (Stucki, 2005). The values of K_0 for SE1089, as UPM, fails to follow the mechanistic relationship proposed for nontronite and beidellite reference clays by Drits and Manceau (2000).

The accuracy of either Eq. (1) or (2) in predicting the experimental CEC is similar, and neither model discriminates the role of total oxide fraction in the increased CEC upon Fe reduction. The relationship between CEC and m_{rel} described by Drits and Manceau (2000) has a similar curve shape as the relationship between goethite dissolution and m_{rel} . As long as no mechanistic significance is attributed to K_0 , this fitting parameter may account for several processes occurring simultaneously. Indeed, the K_0 of 1.792 calculated with the model of Drits and Manceau (2000) differs from the K_0 of 1.952 calculated with the model that corrects for oxide coatings, so empirical adjustment in this parameter causes the models to make similar predictions and masks their potential to discriminate the relative effects of coating removal and structural Fe reduction on the CEC. One should not, therefore, conclude, based on comparison of these models, that oxide coatings play no role in controlling the effective CEC of reduced smectites.

Exposure of SE1089 clay fraction for 60 min, with 50 mg of dithionite, the lowest quantity used, completely removed the Fe oxide fraction. The effect of Fe coatings on the CEC is then characterized primarily by reaction times less than 60 min or m_{rel} lower than 0.23. This part of the goethite dissolution curve can be approached by a linear model, as proposed in the corrected model.

Eq. (2) implemented with the observed results shows that λ is negative: when the remaining Fe oxide fraction diminishes, the CEC increases, which is consistent with the hypothesis that positively charged Fe coatings balance a portion of the clay layer charge. To further test this hypothesis, the following example is given which compares the calculated charge of 1 mol of goethite in coating with goethite charge values expected from the literature.

Based on goethite dissolution rate analyses, the Fe oxide fraction in sample SE1089 is assumed to be present as a coating on the clay surface and, consequently, balances a part of the charge. With this assumption, λ_1 is 1 and λ_2 , calculated from the corrected model, is -0.079 [mmol/mmol of goethite]. The average charge balanced by goethite coatings can be calculated as follows:

Coatings content [mmol goethite/g smectite]

$$\times \lambda [\text{mmol/mmol goethite}]$$

According to the corrected model, before the reduction reaction begins, assuming conservatively that only half of the Fe oxide is present as a goethite coating, the coating controls 6% of the initial clay charge. This value rapidly decreases to zero upon reduction (Table 3). Expressed as mmol of charge per g of goethite, λ_2 equals -0.89 . The charge of 1 g of goethite is, then, 0.89 mmol.

Cornell and Schwertmann (2003) reported charge values for goethite ranging from 1.5 to 1 $\mu\text{eq}/\text{m}^2$ in neutral media and a specific surface area (SSA) ranging from 20 to 200 m^2/g . These values determine a minimal charge value of 0.02 mmol/g of goethite and a maximal value of 3 mmol/g of goethite, which values bracket the goethite charge calculated by the proposed model.

Table 3
Charge compensation by Fe coatings

Remaining Iron coatings [mmol Fe/ g smectite]	Balanced charge [mmol/g smectite]	Percentage of the total charge [%]
0.91	-0.036*	6.4*
0.31	-0.024	5.2
0.22	-0.017	2.4
0.06	-0.005	0.7
0.06	0.005	0.6
0	0	0

*Half of the total Fe content is assumed to be in coatings.

Generally, this value is low compared to typical values for pure goethites, but is probably attributable to the low SSA of the coating. Cornell and Schwertmann (2003) reported specific surface areas ranging from 45 to 110 m^2/g for oxides extracted from oxisols, but Roden (2004) found that the SSA of natural goethite coatings ranges from 6 to 20 m^2/g . A low charge value obtained in the SE1089 coatings fraction, close to the lower limit for reference goethite, seems not surprising.

Knowledge of the particle shape, size, and charge density of Fe oxide coatings on smectites would be necessary to improve the estimation of the role of such coatings in determining the evolution of smectite CEC upon reduction. Moreover, one should pay regard on reductive dissolution processes occurring in the environment, often controlled by biological processes, because chemical or bacterial reduction can produce different dissolution behaviors in Fe oxides according to Roden (2004).

5. Conclusions

SE1089 clay fraction is a complex mixture of goethite and smectite-kaolinite. Mössbauer analyses and reductive dissolution studies identified a finely divided, Al-substituted goethite, as determined by variable-temperature Mössbauer spectroscopy. Dissolution rate analyses show goethite particles coating the clay surface and free goethite particles.

Fe-goethite and Fe_{Stt} (Fe in the smectite octahedral sheet) are simultaneously used as electron acceptors during the reduction process of the SE1089 clay fraction. The reductive dissolution rate of goethite, however, is faster than the reduction rate of Fe_{Stt} . As Fe_{Stt} reduction is thermodynamically more favorable than goethite reduction, other factors must be involved, such as the coating providing protection to the Fe_{Stt} from electron transfer.

Reduction of Fe_{Stt} in the smectite of the SE1089 clay fraction extracted from a soil sharply increases its CEC to a value similar to that observed after reduction of SWa-1 reference clay. This behavior can be explained by two phenomena: Fe_{Stt} reduction and removal of the positively charged Fe coatings which frees exchangeable sites on the clay surface. An adaptation of the model of Drits and Manceau (2000) is proposed, which describes the relationship of CEC increase with $\text{Fe}^{\text{II}}_{\text{Stt}}$ and oxide coating dissolution. Using this adapted model, an average surface charge of 0.89 mmol/g of goethite was calculated. This value is congruent with other values inventoried in soils. In chemically reduced media, the contribution of oxide coatings to balance clay CEC is observed immediately as reduction begins and continues up to the point of total

dissolution of the oxide coatings. This contribution depends on the extent of the coatings and their dissolution rate. In the case of sample SE1089, the contribution of surface coatings to CEC was minor and never exceeded 6% of the initial total charge. In natural environments, reduction processes are under microbial control and may, therefore, follow different laws for dissolution kinetics than those observed here using chemical reduction methods. In that case, the contribution of oxide coatings to the CEC of natural smectites in soils could be different.

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