REDOX PROPERTIES OF STRUCTURAL Fe IN FERRUGINOUS SMECTITE. A DISCUSSION OF THE STANDARD POTENTIAL AND ITS ENVIRONMENTAL IMPLICATIONS

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Abstract—The aim of this study was to compare the redox properties of oxides and smectite structural Fe (Fe$_{Str}$). Structural Fe in smectite often accounts for about half of the Fe pool in soils and sediments, and is naturally reduced by indigenous bacteria. This reaction is, however, seldom taken into account in environmental studies. The equation for the oxidation-reduction of Fe$_{Str}$ and its application to the calculation of the standard electrode potential of Fe$_{Str}$, E_0, are discussed on the basis of literature review. The resulting redox properties were used in a new analysis of previously reported field monitoring data. This agreed well with experimental observations that remained unexplained, and showed that if equilibrium conditions prevail, the Fe$_{Str}$ pool in soils will reduce prior to the Fe in oxides. The Fe$_{Str}$ pool is, therefore, likely to play a major role in controlling the bio-geochemistry of temporarily water-logged soils, and this reaction should be taken into account in further studies.

Key Words—Goethite, Oxides, Reduction, Smectite, Standard Potential, Structural Fe.

INTRODUCTION

Iron is one of the most important electron acceptors for anaerobic respiration of micro-organisms in the environment. The Fe pool is thus an important controlling factor for the bio-geochemistry of natural solutions as well as for the weathering of minerals. The study of redox reactions in soils to date has involved mostly the Fe oxides; but, a large proportion of Fe in soils exists in the crystal structure of phyllosilicates (Fe$_{Str}$) (Stucki *et al.*, 1996). Studies of reference clay minerals in the laboratory revealed that chemical or bacterial reduction of this Fe pool sharply modifies the chemical and physical properties of the clays. Fe$_{Str}$ reduction decreases the specific surface area (Lear and Stucki, 1989; Kostka *et al.*, 1999), and increases the layer charge (Stucki and Roth, 1977; Stucki *et al.*, 1984b; Kostka *et al.*, 1999) and cation exchange capacity (CEC) (Stucki and Roth, 1977; Stucki *et al.*, 1984b; Khaled and Stucki, 1991; Kostka *et al.*, 1999). It decreases the swelling capacity (Foster, 1953; Egashira and Ohtsubo, 1983; Stucki *et al.*, 1984c; Gates *et al.*, 1991) and the permeability (Shen *et al.*, 1992) of the clay and increases the cation fixation capacity (Khaled and Stucki, 1991; Stucki *et al.*, 2000). Reduced smectite, moreover, induces dehydrochlorination of chlorinated organics,

reduces nitroaromatics, and degrades commonly used pesticides (Cervini-Silva *et al.*, 2000; Tor *et al.*, 2000; Xu *et al.*, 2001; Yan and Bailey, 2001; Cervini-Silva *et al.*, 2002; Cervini-Silva *et al.*, 2003; Hofstetter *et al.*, 2003). The degradation of pesticides by redox-modified smectite also has an important and complex impact on the cyto- and genotoxicity of pesticides toward mammalian cells (Sorensen *et al.*, 2004; Sorensen *et al.*, 2005). Stucki *et al.* (1996) anticipated that Fe$_{Str}$ reduction may be one of the most important factors governing the physical-chemical behavior of water-logged soils. Evidence from recent studies further revealed that Fe$_{Str}$ reduction occurs in soil clays in the field (Ernstsen, 1996; Favre *et al.*, 2002b). Soil reactivity, soil CEC, clay fabric (Favre *et al.*, 2004), and exchangeable cations (Favre *et al.*, 2002a) were observed to change sharply upon Fe$_{Str}$ reduction, as anticipated by Stucki and co-workers. The potential of redox-modified smectites for both industrial and environmental applications is, therefore, very large. Structural Fe in clay minerals often accounts for as much as 50% of the total Fe in water-logged soils. Therefore, if Fe in the clay structure is reduced before the Fe in the soil oxides, both microbial respiration and soil geochemistry in anaerobic conditions will be governed, at least initially, by the structural Fe pool.

The Fe$_{Str}$ reduction mechanism is still a matter of controversy and quantitative treatment of the reduction potential is lacking. The model mechanism for Fe$_{Str}$ reduction proposed by Drits and Manceau (2000), which encompassed the models of Stucki and Roth (1977), Lear

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and Stucki (1985), Stucki and Lear (1989), and Gan *et al.* (1992), is assumed to be a reversible electron transfer reaction, which requires reducing agents of increasing reduction capacity as the percentage of the Fe_{Str} reduced increases. The resulting increase in layer charge is *pro parte* compensated by elimination of structural OH. Based on crystal stability considerations, the stoichiometry of dehydroxylation varies with increasing levels of Fe_{Str} reduction. Increasingly greater OH release is expected with increasing reduction levels. Hence, the relationship between Fe_{Str} reduction level and layer charge as estimated by fixed and exchangeable cation analysis; interlayer Na content (Stucki *et al.*, 1984a; Lear and Stucki, 1985; Khaled and Stucki, 1991) usually has a slope of <1 and is non linear (Stucki *et al.*, 1984b).

Hypotheses regarding reduction mechanisms have been based entirely on laboratory measurements with Na dithionite as the reducing agent, so the model of Drits and Manceau (2000), for example, may be restricted to the reaction of smectite with Na dithionite. Stucki (1988) hypothesized that the reduction mechanism may depend partly on the reducing agent. The reduction of Fe_{Str} in the environment is probably produced by bacteria rather than by strong inorganic agents such as dithionite (Kostka *et al.*, 1996, 2002a, 2002b).

In order to account fully for, and to be able to predict, Fe_{Str} reduction in the environment and in soil behavior models, the redox reaction and its standard electrode potential must be known. Of fundamental importance is knowing whether Fe_{Str} is reduced at a higher potential than the most common soil oxides. Such empirical information for soil or reference clay minerals is sparse, at best. From theoretical calculations, Amonette (2003) estimated the standard potential of nontronite, an Fe-rich smectite that is uncommon in soils, to be 0.7 V. Using clay-modified electrodes, Xiang and Villemure (1995) observed direct electron transfer from structural Fe sites of a synthetic Fe-rich smectite, and the corresponding cathodic wave was located at 0.6 V in a 0.05 M Na_2SO_4 solution of unknown pH, corresponding to a standard potential of 0.84 V. Favre *et al.* (2002b) observed that the *in situ* reduction of Fe_{Str} in soil smectite occurred simultaneously with the reductive dissolution of goethite at a pH close to neutral.

The objective of the current study was to discuss the possible environmental impact of Fe_{Str} reduction on the basis of: (1) the implications of the Fe_{Str} oxidation-reduction reaction model of Drits and Manceau (2000) for the Eh-pH stability diagrams of the forms of structural Fe; and (2) analysis of field monitoring data of Fe forms and soil solution geochemistry.
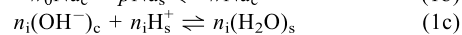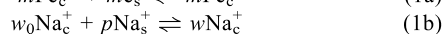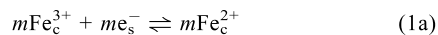
THEORY

Redox reaction with Fe_{Str}

Based on experimental observations and theoretical considerations, an Fe_{Str} reduction reaction model was

proposed by Drits and Manceau (2000) for a solution in which the only cation is Na^+, as follows.

Half-cell reactions of Fe_{Str} reduction:

$$mFe_c^{3+} + me_s^- \rightleftharpoons mFe_c^{2+} \qquad (1a)$$
$$w_0Na_c^+ + pNa_s^+ \rightleftharpoons wNa_c^+ \qquad (1b)$$
$$n_i(OH^-)_c + n_iH_s^+ \rightleftharpoons n_i(H_2O)_s \qquad (1c)$$
$$m = p + n_i \qquad (1d)$$

where m, n_i, and p are stoichiometric parameters, and w and w_0 correspond to interlayer Na^+ content in the reduced and unreduced Fe_{Str} state, respectively. Subscripts s and c denote solution or solid (or exchanged) phase, respectively.

The general half-cell reaction is therefore:

$$mFe_c^{3+} + me_s^- + w_0Na_c^+ + pNa_s^+ + n_i(OH^-)_c +$$
$$n_iH_s^+ \rightleftharpoons mFe_c^{2+} + wNa_c^+ + n_iH_2O_s \quad (1)$$
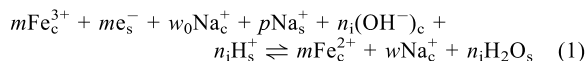
The reaction is assumed to be reversible and is pH dependent. The relative values of p and n_i are assumed to vary with the reduction level. Based on experimental observations (Drits and Manceau, 2000), the *pro parte* compensation of the layer charge as a function of the reduction level was written as:

$$n_i/p = K_0 \, m/m_{tot} = K_0 \, m_{rel} \qquad (2)$$

where m and m_{tot} are the amount of reduced Fe and the total amount of Fe per unit-cell, respectively, m_{rel} is the reduction level ($m_{rel} \leqslant 1$), and K_0 is a sample-dependent constant, which was fitted as $K_0 = 4.73$ for SWa-1. The physical meaning of this constant is unclear.

Equations 1 and 2 are written for a clay suspension where Na^+ is the only available cation. These equations have no meaning when n_i, p and $m \rightarrow 0$, and a clay suspension is not stable at low pH (clay dissolution) or lower if $[Na^+]$ is $< [H^+]$ (clay protonation and dissolution, McBride, 1994). We therefore assert that these equations apply only under conditions compatible with clay stability, *i.e.* the solution not limited in Na^+, $3 < pH < 10$ and $pNa < 4$.

In the environment, Ca^{2+} and Mg^{2+} are generally more abundant than Na^+. No theroretical reasons exist to preclude reactions 1−2 from applying to the case of a cation other than Na^+ in solution and on the exchange complex. In particular, the relations between m_{rel} and the clay CEC, that allowed calculation of K_0, should be unchanged if Na were to be replaced by Ca, but experimental verification of this assertion has yet to be carried out. For a general formulation of reaction 1, one must replace Na_c^+ and Na_s^+ by C_c^+ and C_s^+, respectively, where C^+ represents an equivalent monovalent cation, and in the equilibrium equations below, $[Na^+]$ should be replaced by $[C^+]$, the concentration of cations in solution in equivalents.

Standard electrode potential of Fe_{Str}

According to Clark (1972), the electromotive force of the half-cell reaction 1 at equilibrium and at 25ºC is:

$$E_h = E^0 + \frac{RT}{mF} \ln \frac{(Ox)}{(Rd)} \qquad (3)$$

with (Ox) and (Rd) representing the total activities of the oxidized and reduced forms. By assuming that concentration gives the total activity, this simplifies to:

$$E_h = E_0 + \frac{RT}{mF} \ln \frac{[Ox]}{[Rd]} \qquad (4)$$

[] being the concentrations, and therefore writing E_0 instead of E^0 following the conventions of Clark (1972). Applied to reaction 1, with conventional assumptions that solid phase activity is 1, reaction 4 becomes:

$$E_h = E_0 - \frac{0.059}{m} \log(K)$$

with:

$$K = \frac{1}{[Na_s^+]^p \times [H_s^+]^{n_i}} \qquad (5)$$

$$\log(K) = -p \log[Na_s^+] - n_i \log[H_s^+] \qquad (6)$$

Combining reactions 1d and 2 yields:

$$p = m/(1 + K_0(m/m_{tot})) = m/(1 + K_0 m_{rel}) \qquad (7)$$

and

$$n_i = K_0 m m_{rel}/(1 + K_0 m_{rel}) \qquad (8)$$

Replacing n_i and p in reaction 6 yields:

$$\log(K) = \frac{-m}{1 + K_0 m_{rel}} \log[Na_s^+] - \frac{m K_0 m_{rel}}{1 + K_0 m_{rel}} \log[H_s^+] \qquad (9)$$

With the conventions of Clark (1972), this yields:

$$E_h = E_0 + \frac{0.059}{1 + K_0 m_{rel}} \log[Na_s^+] - \frac{0.059 K_0 m_{rel}}{1 + K_0 m_{rel}} pH \qquad (10)$$

or

$$E_0 = E_h - \frac{0.059}{1 + K_0 m_{rel}} \log[Na_s^+] + \frac{0.059 K_0 m_{rel}}{1 + K_0 m_{rel}} pH \qquad (11)$$

where $[Na_s^+]$ is the concentration of Na in the solution in mole L^{-1} at 25°C.

Equations 10 and 11 are derived from the process written by Drits and Manceau (2000), which is compatible with the previous model of Stucki *et al.* (1996), and represents our state of knowledge on the reduction process (Stucki, 2006). Inherent in equation 10 is a relationship between m_{rel}, pH, $[Na_s]$ and Eh. Exploring this relationship leads to certain constraints on and limitations to this reaction.

The Eh-pH relation for a given value of m_{rel} is linear, the slope of which decreases as m_{rel} increases. The rate of decrease in slope is greater for lower m_{rel} values. This is consistent with the findings that more OH is released from the structure as the reduction level increases, thereby decreasing the change in layer charge, which gives greater proton to electron stoichiometry for the lowest m_{rel} values. Considering a unique E_0 value for the whole m_{rel} range leads to inconsistencies, however, because in some pH ranges, Eh will be greater for the largest m_{rel} values than for the smallest. An example of this is illustrated in Figure 1, where the Eh-pH relations are reported for m_{rel} values ranging from 0.02 to 0.7, and pNa = 3, for a SWa-1 clay the E_0 of which was set to 0.7 V. The Eh-pH equilibrium lines intersect at pH = 3, which is nonsense.

The condition to preclude the intersection of the Eh-pH lines of different m_{rel} values is that E_0 must decrease as m_{rel} increases, consistent with the expectation that an increase in the energy of the reducing agent is needed to increase the reduction level of the clay (Stucki *et al.*, 1996; Drits and Manceau, 2000). The minimal condition on E_0 can be written from equation 10 as:

$$E_{0,m_{rel}} = E_{0Ref} + 0.059 \frac{K_0 m_{rel}}{1 + K_0 m_{rel}} \left(\log[Na_s] + pH \right) \qquad (12)$$

The larger decrease condition on E_0 is for pNa = 4 and pH = 3 and is represented in Figure 2 for SWa-1 (*i.e.* $K_0 = 4.73$), with an E_{0Ref} value of 0.7 V, and m_{rel}
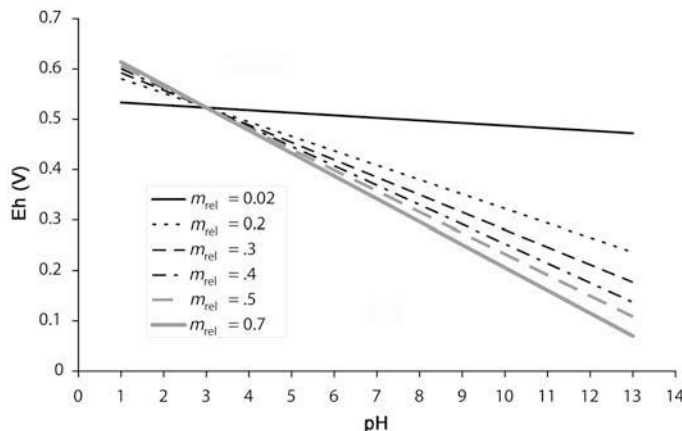

Figure 1. Example of Eh-pH relation obtained using equation 10, with arbitrary constant $E_0 = 0.7$ V, pNa = 3 and m_{rel} ranging from 0.02 to 0.7. Intersection of the lines occurs for pH = pNa.
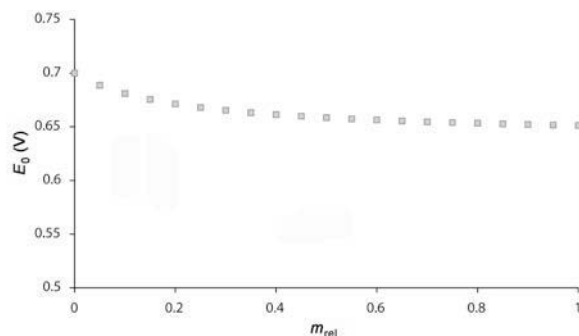
Figure 2. Minimum E_0 drop condition for m_{rel} values ranging from 0 to 1, pNa = 4, smectite Fe_{Str} with arbitrary E_0 of 0.7 V for m_{rel}=0, and conditions of intersection of Eh-pH lines at pH = 3.

ranging from 0 to 1. It shows a drop in the minimum condition of $E_{0,mrel}$ of 0.05 V from $m_{rel} = 0$ to $m_{rel} = 1$. The rapid drop of $E_{0,mrel}$ for low m_{rel} values, with asymptotic stabilization at the highest m_{rel} values, as presented in Figure 2, contradicts the model of Drits and Manceau (2000) in which E_0 is expected to be constant for low reduction levels, and to decrease later on. As seen from equations 10−12, this contradiction derives from the assumptions made regarding increasing loss of OH by the clay to partially compensate the increasing layer charge upon increasing Fe_{Str} reduction.

MATERIAL AND METHODS

We used equation 11, the E^o value of 0.7 V from Amonette (2003), and the field monitoring data from

Boivin *et al.* (2002) to discuss the impact of Fe_{Str} reduction at field scale. Eh, pH and composition of the soil solution were monitored during three successive cropping seasons and fallow periods, in a rice-cropped Vertisol from Senegal River Valley. On the same site, Favre *et al.* (2002b) simultaneously monitored Fe forms. Those authors reported changes in smectite Fe_{Str} reduction level upon flooding, and showed that the Fe oxide was goethite. Boivin *et al.* (2002) presented the soil-solution monitoring data on a Pourbaix diagram, which is reproduced in Figure 3. The intersection between fallow period and irrigation stands at Eh = 0.5 V and pH = 5.5. Upon flooding, the pH remains constant while the Eh drops, and a cluster of points fall on the goethite equilibrium line calculated with goethite equilibrium constant taken from Cornell and Schwertmann (1996) and for pFe^{2+} = 3, which is the observed concentration of the soil solution in Fe^{2+} during cropping season. The pH of flooded soil is usually assumed to become neutral upon flooding (Ponnamperuma, 1972). The drop in Eh at constant pH = 5.5 was interpreted as a result of increasing pCO$_2$, thus balancing the alkalinity released by oxide reductive dissolution. The dots above the goethite equilibrium line and corresponding to irrigation period were not interpreted. Favre *et al.* (2002b) observed a reduction of structural Fe(III) to Fe(II) in the soil smectite, from m_{rel} = 0.02 to m_{rel} = 0.1 upon flooding, with simultaneous reductive dissolution of goethite. The smectite was shown to be a beidellite with ~4% of total Fe content (Favre *et al.*, 2004).
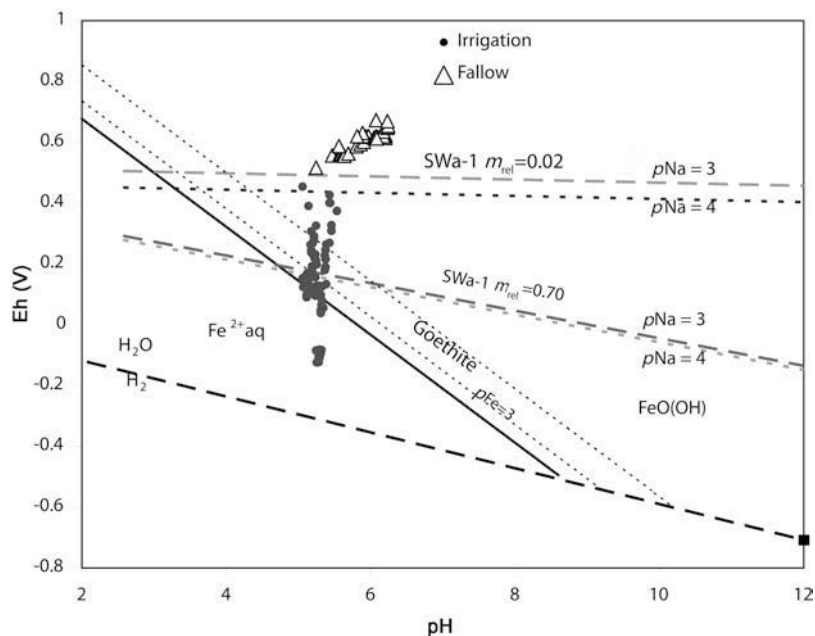

Figure 3. Pourbaix diagram comparing goethite and smectite Fe_{Str} redox properties. The goethite lines were drawn for pFe^{2+} = 3, 4 and 6, respectively, with the equilibrium constant of goethite taken from Cornell and Schwertmann (1996). The Fe_{Str} lines are drawn for m_{rel} values of 0.02 and 0.77 (E_0 = 0.7 and 0.45 V, respectively) and pNa = 3 and 4. Black circles and open triangles are field observations during flooding and fallow periods, respectively, taken from Boivin *et al.* (2002).

On Figure 3 we have drawn the goethite equilibrium lines $p\mathrm{Fe}^{2+}$ values of 6, 4 and 3, which represent the common range of $p\mathrm{Fe}^{2+}$ in temporarily waterlogged soils. We also constructed in Figure 3 the equilibrium lines of SWa-1 for $m_{\mathrm{rel}} = 0.02$ and $m_{\mathrm{rel}} = 0.7$ from equation 11, with E_0 equal to 0.7 V and 0.45 V, respectively. Each line represents two $p\mathrm{Na}$ values, namely, 3 and 4, which are values relevant to those observed under field conditions, such as by Favre *et al.* (2002b) and Boivin *et al.* (2002).

RESULTS AND DISCUSSION

The use of equations 1−11 assumed that reaction 1 is a reversible equilibrium reaction. The reversibility of $\mathrm{Fe}_{\mathrm{Str}}$ reduction is generally assumed, and was observed, for example, by Stucki *et al.* (1984b) with three montmorillonites (from the Czech Republic, New Zealand and Wyoming) and one nontronite (from Garfield, Washington) which were reduced to a limited extent only. Using ^{3}H-labeled H_2O, Lear and Stucki (1985) described a reoxidation process implying reversible changes occurring during reduction and reoxidation of SWa-1. In a more recent study, Fialips *et al.* (2002) found that the structural changes in the octahedral sheet of Garfield nontronite increased significantly as complete reduction of Fe(III) to Fe(II) was approached. Reoxidation of their completely reduced clays failed to restore the FTIR spectrum to that of the unaltered sample, even though the amount of Fe(III) was largely restored in most instances. They reported nothing regarding the possible consequences of such structural changes on the clay surface and redox properties. Xiang and Villemure (1995) suggested an irreversible process when working with a clay-modified electrode coated with a synthetic Fe-rich smectite, as they observed a partial disappearance of the cathodic wave. In this case, the experimental conditions and the synthetic clay properties were too different from the experiments presented here to allow further comparisons.

The 0.7 V E° value was calculated by Amonette (2003) for nontronite. The Fe(III) reduction potential calculated is on a single Fe atom basis and thus should be independent of the structural formula, as the calculation is based solely on the inner-sphere coordination shell (bond-length and deviation from perfect octahedral character). Smectites should, therefore, all have approximately the same potential, although the severe distortion and rearrangement in a reduced nontronite might yield a smaller potential for some Fe sites than for a typical smectite containing only a few percent Fe (J. Amonette, pers. comm.).

As illustrated in Figure 3, according to equation 11 and $E_0 = 0.7$ V, in the soil pH range of 5 to 8.5, the smectite structural Fe is likely to be reduced before the Fe in goethite at equilibrium. At pH 7, we calculated that >50% of the $\mathrm{Fe}_{\mathrm{Str}}$ would be reduced prior to goethite

reductive dissolution. Even with the small unlikely E_0 value of 0.45 V, 70% of the $\mathrm{Fe}_{\mathrm{Str}}$ would reduce prior to significant goethite reductive dissolution. In waterlogged soils, lepidocrocite is a more common Fe oxide than goethite (Ponnamperuma, 1972). Because most soil Fe oxides have equilibrium lines that lie close to that of goethite, the same conclusion could be drawn for other Fe oxides such as lepidocrocite that may be present. The $\mathrm{Fe}_{\mathrm{Str}}$ equilibrium line for the $m_{\mathrm{rel}} = 0.02$ observed at the beginning of the cropping season (Favre *et al.*, 2002b), stands at the intersection of fallow and irrigation measurements, which is also the beginning of anaerobic conditions in the soil. At these observed pH and Eh values, goethite cannot be dissolved reductively, but $\mathrm{Fe}_{\mathrm{Str}}$ will start to reduce according to equation 11, in accordance with the observed drop in Eh. The measured Eh values drop perpendicularly to the $\mathrm{Fe}_{\mathrm{Str}}$ equilibrium line, *i.e.* towards increasing $\mathrm{Fe}_{\mathrm{Str}}$ reduction levels, prior to reaching the reductive dissolution of the goethite domain. The corresponding recorded data would have no meaning if $\mathrm{Fe}_{\mathrm{Str}}$ reduction were not considered, and the field observations reported in Boivin *et al.* (2002) and Favre *et al.* (2002b) are in good agreement with the $E^\circ = 0.7$ V and the redox reactions 1−11.

Interestingly, Favre *et al.* (2002b) reported the reductive dissolution of goethite simultaneously with $\mathrm{Fe}_{\mathrm{Str}}$ reduction in the field, and observed a maximum m_{rel} of 0.1. While appearing to contradict the results in Figure 3, it may not be a contradiction for three reasons. First, Favre *et al.* (2004) showed that the smectite in this soil is coated with goethite, which may limit the accessibility of bacteria to $\mathrm{Fe}_{\mathrm{Str}}$. Second, a partial reoxidation of the $\mathrm{Fe}_{\mathrm{Str}}$ prior to Mössbauer analysis cannot be excluded. Third, the Eh-pH monitoring shows a rapid drop in Eh due to intense bacterial activity under the high temperature of the tropical climate. No $\mathrm{Fe}_{\mathrm{Str}}$ analysis was done during this short time period (first five days after flooding) corresponding to the upper part of the cluster of data recorded during the irrigation period. Hence, this apparent discrepancy between the field monitoring and the thermodynamic properties of $\mathrm{Fe}_{\mathrm{Str}}$ reduction merely stresses the problems of kinetics and micro fabric of the solid phase at the field scale. Field measurements should be taken at more frequent intervals, especially during the first days of flooding, or the experiments should be performed in a reactor with controlled bacterial growth.

According to this discussion, soil smectites are likely to be largely reduced prior to Fe oxides under field conditions. One could argue that this may not be the case, however, because the redox properties of soil smectites may differ from those estimated by Amonette (2003) or Xiang and Villemure (1995). To evaluate this hypothesis, consider the following deductions and arguments. If goethite were to be reduced before $\mathrm{Fe}_{\mathrm{Str}}$ (Figure 3), then at pH 5 the E° of the clay $\mathrm{Fe}_{\mathrm{Str}}$ must be <0.35 V when $p\mathrm{Fe} = 6$ and $m_{\mathrm{rel}} = 0.02$, and <0.2 at pH 7

with the same pFe and m_{rel} values. As far as we know, no theoretical reason exists for the E^o values of common soil smectites being significantly smaller than the E^o value calculated by Amonette (2003). Hence, if this range for the value of E^o and empirical equation 1 applies to Fe$_{Str}$ in soil smectite, this Fe$_{Str}$ pool will be largely reduced prior to soil oxides, and must, therefore, play a predominant role in ruling the biogeochemistry of water-logged soils.

CONCLUSIONS

In this study, we showed how the E_0 of structural Fe (Fe$_{Str}$) in clay can be calculated from redox reaction experiments, using the results of Stucki et al. (1996) and Drits and Manceau (2000). If the presented relations 1–11 hold, then the Eh must be a function of m_{rel}, which is the ratio of reduced structural Fe to total Fe$_{Str}$ in the clay. Moreover, we showed that reaction 1 implies that E_0 decreases with m_{rel}, and that boundary conditions must be defined with respect to pH and pNa for this equation to be used.

This allowed us to compare Fe$_{Str}$ redox properties with goethite reductive dissolution properties. Apparently, a large proportion of the clay Fe$_{Str}$ is likely to reduce prior to the dissolution of free Fe oxides in soils. These calculations closely follow results obtained in the field by monitoring the Eh and pH of a paddy-soil. A much lower E_0 value (0.2–0.35 V) would be needed to reverse this anticipated reduction sequence between free Fe oxides and Fe$_{Str}$ in smectite, which seems unacceptable from the theoretical point of view. We therefore prefer to propose that the clay Fe$_{Str}$ pool is an important factor governing microbial anaerobic respiration and the geochemistry of water-logged soils having significant 2:1 clay content. Owing to the strong impact of Fe$_{Str}$ reduction on soil properties, accounting carefully for such reactions in the environment is of vital importance if a full understanding of the soil behavior is to be obtained.

ACKNOWLEDGMENTS

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