

Effects of Structural Fe Oxidation State on Physical-chemical Properties of Smectites : Evidence from Infrared Spectroscopy

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Abstract

Redox reactions involving structural Fe in smectite clay minerals contribute significantly to the chemistry of soils and sediments. Changes in oxidation state from Fe(III) to Fe(II) alters the clay structure, which in turn modifies the chemical nature of the smectite basal surfaces. These changes in structure are readily observed by infrared spectroscopy. Structural OH groups are progressively lost as the level of Fe(II) increases, and large shifts occur in the Si-O stretching and bending modes of the tetrahedral sheet. The communication between octahedral and tetrahedral sheets alters the configuration of basal oxygens, as well as changing the charge, pH, and reduction potential of the surface. Infrared spectra also provide evidence for the formation of trioctahedral domains as a result of extensive Fe(III) reduction.

Key words : pH, redox, charge, iron, clay.

1. Introduction

The physical-chemical properties of smectites have great importance in agriculture, industry, and the environment because of their high specific surface area and reactivity with plant nutrients, water, pesticides, organic pollutants, and other minerals. The smectite clay minerals are largely responsible for properties governing soil structure, porosity, and permeability. Every smectite contains some iron (Fe) in the octahedral sheet of its crystal structure (usually in the 3+ valence state), and some smectites also contain Fe(III) in the tetrahedral sheet. Octahedral Fe(III) is susceptible to reduction and reoxidation (redox) processes, which are common in nature due to bacterial activity and are often associated with wetting and drying events. The redox state of the clay can also be readily manipulated in the laboratory using chemical reductants such as sodium dithionite.

Redox reactions are significant because changes in the oxidation state of the Fe are

accompanied by changes in the chemical properties and physical behavior of the clay. Affected properties and behaviors include layer charge, cation exchange capacity, cation fixation (Stucki *et al.*, 1984 b ; Stucki and Roth, 1977 ; Lear and Stucki, 1985 ; Gates *et al.*, 1993 ; Kostka *et al.*, 1999), swelling (Kostka *et al.*, 1999 ; Gates *et al.*, 1993 ; Stucki *et al.*, 1984 a), surface area (Lear and Stucki, 1989 ; Kostka *et al.*, 1999), hydraulic conductivity (Shen *et al.*, 1992), magnetization (Lear and Stucki, 1987), surface pH (Cervini-Silva *et al.*, 2000 b), capacity to degrade organic compounds (Tor *et al.*, 2000 ; Xu *et al.*, 2001 ; Cervini-Silva *et al.*, 2000 a ; Yan and Bailey, 2001 ; Hofstetter *et al.*, 2003), and reactivity with redox-sensitive ions in solution (Taylor *et al.*, 2000 ; Gan *et al.*, 1996 ; Ernstsen *et al.*, 1998). The mechanism(s) by which a change in the valence state of Fe controls these properties is not well defined, but certain ancillary changes in structure during redox events and redox cycles reveal certain clues from which hypotheses can be formulated. Structural changes have been characterized by X-ray powder

diffraction (XRD) (Manceau *et al.*, 2000), Mössbauer spectroscopy (Lear and Stucki, 1987), infrared spectroscopy (FTIR) (Stucki and Roth, 1976; Fialips *et al.*, 2002 a, b), uv-visible spectroscopy (UV-VIS) (Anderson and Stucki, 1979; Komadel *et al.*, 1990), high-resolution electron microscopy (HRTEM) (Stucki and Tessier, 1991; Gates *et al.*, 1998; Kim *et al.*, 2003), polarized extended X-ray absorption fine structure spectroscopy (P-EXAFS) (Manceau *et al.*, 2000), and X-ray absorption near-edge spectroscopy (XANES) (Manceau *et al.*, 2000). Presented here is evidence obtained primarily from FTIR spectroscopy regarding changes in clay structure due to redox transformations.

2. Materials and Methods

The smectites studied included Garfield nontronite (sample API 33-a from Wards Natural Science Establishment, Rochester, New York, USA) and ferruginous smectite (sample SWa-1 from the Source Clays Repository of The Clay Minerals Society, USA). Structural Fe was reduced either chemically using the methods described by Stucki *et al.* (1984 c) or bacterially using the method described by Kostka *et al.* (1996). Structural Fe(II) and total Fe were determined quantitatively by the 1,10-phenanthroline method (Komadel and Stucki, 1988) and semi-quantitatively by Mössbauer spectroscopy.

Infrared spectra were obtained from dried films or from powders mixed with KBr using a Midac Model 2000 FTIR spectrometer, and Mössbauer spectra were obtained with a constant acceleration spectrometer operating with a triangle wave form over 512 data channels using a ^{57}Co (10% in Rh matrix) as the (-ray) source. Mössbauer spectra were deconvoluted using a least-squares fitting procedure, usually constraining the component peaks to be of Lorentzian line shape.

All sample preparations, manipulations, and analyses were performed using inert-atmosphere techniques. These included a controlled-atmosphere liquid exchanger for replacing

and/or removing entrained salt solutions in reduced suspensions, septum-sealed screw caps on reaction vessels, and a glove box in which the clay was dried either as a film on a filter membrane or as a freeze-dried powder.

3. Results

The FTIR spectrum of smectite from 400 to $4,000\text{ cm}^{-1}$ encompasses four principal spectral regions in which significant changes occur during redox reactions. These regions are: Region I. $3,400$ to $3,600\text{ cm}^{-1}$, associated with the O-H stretching vibrations of structural hydroxyls and adsorbed water; Region II. $1,000$ to $1,150\text{ cm}^{-1}$, associated with the Si-O vibrations; Region III. 750 to 950 cm^{-1} , associated with the M-O-H bending modes (M=Fe, Al, or Mg); and, Region IV. 400 – 700 cm^{-1} , associated with various other modes involving Fe and Si. Structural changes due to the reduction of octahedral Fe are readily monitored by changes in all four of these regions of the spectrum.

Region I

The O-H stretching band in oxidized Fe(III)-rich, dioctahedral smectite is found at $3,570\text{ cm}^{-1}$ (Fig. 1), characteristic of an $[\text{Fe(III)}]_2\text{OH}$ environment, and systematically shifts to lower wavelength to about $3,535\text{ cm}^{-1}$ as Fe(III) ions all become completely reduced to Fe(II). The O-H stretching band also diminishes in intensity and two other features increase; one being a very broad band centered at about $3,400\text{ cm}^{-1}$ and the other being a sharp, small band at $3,622\text{ cm}^{-1}$. The latter small band is likely due to a portion of the Fe migrating to adjacent vacant sites within the octahedral sheet to form some trioctahedral $[\text{Fe(II)}]_3\text{OH}$ arrangements (Manceau *et al.*, 2000). The position of this band is similar to the O-H stretching band in biotite, a trioctahedral mica where the Fe(II) is clearly coordinated to OH from all three octahedral sites. The relative intensity of this band is expected to be low because the symmetrical electric field due to uniform distribution of Fe(II) causes the OH dipole moment to be oriented normal to the plane of the clay

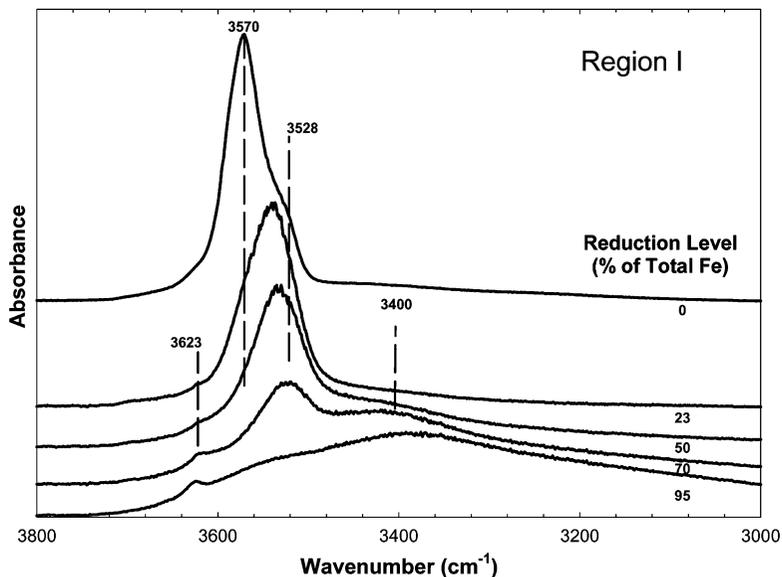


Fig. 1 FTIR spectra of O-H stretching region (Region I, see text) of Garfield nontronite reduced to various levels by citrate-bicarbonate buffered dithionite suspension.

layer. This leads to a small interaction with the electric field vector of the incident infrared radiation impinging on the oriented clay film (Barshad and Kishk, 1968). If the dipole orientation is normal to the clay layer, the band intensity should be pleiochroic, i.e., it should depend on the orientation of the clay film. Confirmation that this is indeed the case is given in Fig. 2.

The broad band centered at about $3,400\text{ cm}^{-1}$ is assigned to H_2O in the smectite structure. At least two scenarios can be considered to explain the formation of this H_2O band, namely, that the hydration energy of reduced smectite is greater than oxidized smectite or that structural OH groups are converted to structural H_2O groups during reduction. Attention is drawn to the fact that all samples were submitted to the same dehydration process involving desiccation in vacuum and over P_2O_5 (Huo, 1997), which was effective in removing all adsorbed H_2O from the oxidized sample, as evidenced by the absence of any significant absorbance in the $3,200\text{--}3,400\text{ cm}^{-1}$ region for that sample, but not from the reduced sample (Fig. 1). The H_2O molecules responsible for the large band at

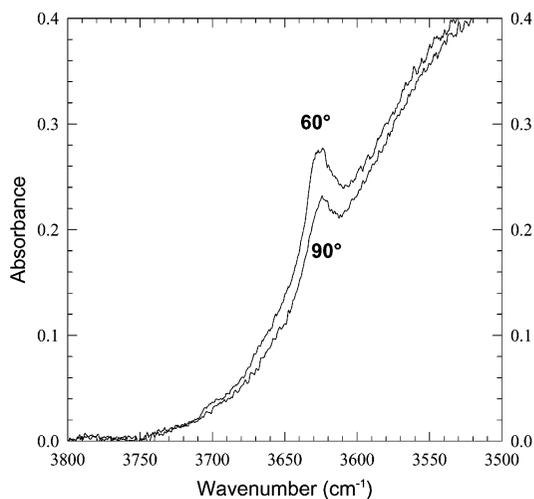


Fig. 2 FTIR spectra of a 95% reduced Garfield nontronite film oriented at 60° and 90° relative to the incident beam, showing pleochroic behavior of this band.

$3,400\text{ cm}^{-1}$ in the reduced samples could, therefore, be adsorbed to the basal surfaces of the smectite, but held to the surface with greater energy than in the oxidized samples. Other evidence for this scenario is found in the studies of Yan and Stucki (1999, 2000), who

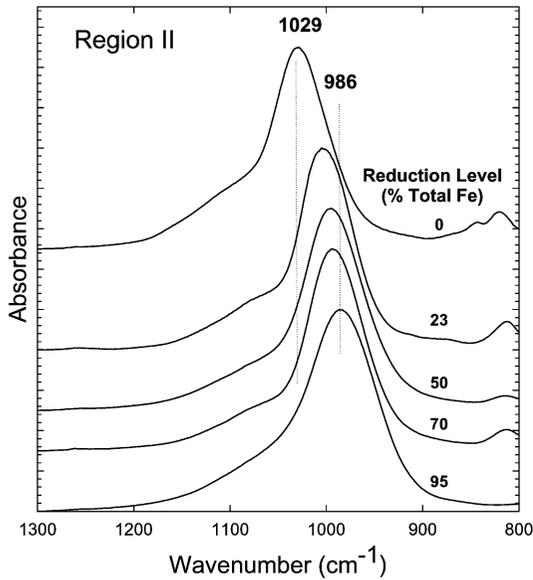


Fig. 3 FTIR spectra of the Si-O vibrations (Region II) of oxidized and reduced Garfield nontronite.

observed an increase in the interaction between basal Si-O groups and adsorbed H₂O as the extent of Fe reduction increased, and of Stucki *et al.* (2000) who concluded that the surface hydration energy of reduced smectite is greater than oxidized smectite.

A second scenario to explain the 3,400 cm⁻¹ band is that the H₂O molecules are actually located inside the clay layer as protonated OH groups. Drits and Manceau (2000) proposed a reduction reaction mechanism by which electron transfer to structural Fe(III) from reducing agents in solution is accompanied by protonation of structural OH groups. While they further suggested that these internal H₂O molecules then diffuse back into solution, perhaps, in reality, at least some of them remain in the octahedral sheet in order to stabilize it with respect to increased charge due to structural Fe(II).

Region II

Changes are also observed in the Si-O stretching region (Fig. 3), including a large (up to 43 cm⁻¹) downward shift of the main Si-O stretching band of the reduced samples (Stucki

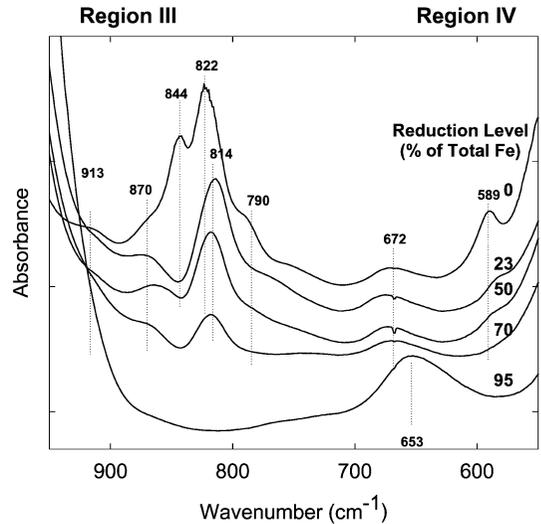


Fig. 4 FTIR spectra of the M-O-H bending modes (Regions III and IV) of oxidized and reduced Garfield nontronite.

and Roth, 1976 ; Fialips *et al.*, 2002 a, b ; Yan and Stucki, 1999, 2000). Such a large shift indicates that the change in Fe oxidation state in the octahedral sheet strongly affects the structural properties of the tetrahedral sheet, which is also reflected in the alternate clock-wise, counter-clock-wise rotations of the Si tetrahedra as measured by an increase in the crystallographic b-dimension 9.13 Å to 9.21 Å (Manceau *et al.*, 2000).

These changes in the tetrahedral sheet affect physical and chemical properties at the mineral surface, such as those that are configurationally dependent. A good example of this is found in the results of Yan and Stucki (1999, 2000) who linked these changes in Si-O vibrations to the coupling of H₂O molecules with the basal oxygen surfaces. Other examples are found in the change in pH (Cervini-Silva *et al.*, 2000 b) and reduction potential (Cervini-Silva *et al.*, 2000 a).

Region III

In the M-O-H deformation region (Fig. 4), the primary band is due to Fe(III)-O-H at 821 cm⁻¹, which shifts downward by about 5 cm⁻¹ with increasing Fe reduction, then disappears alto-

gether, along with all other features in this Region, with complete Fe reduction. A lesser band at 843 cm^{-1} , which appears as a shoulder on the principal peak, is assigned to an Fe-OH bending mode, where the OH is taken as a single unit. This assignment was originally given by Stucki and Roth (1976), but has not been widely accepted. Nevertheless, no better assignment has been found. These major modifications clearly indicate that changes occurred within the clay crystal far beyond merely a change in Fe oxidation state. Partial dehydroxylation and redistribution of Fe, and perhaps Al, cations occurred upon reduction, changing the structural properties of the tetrahedral and octahedral sheets.

The loss of structural O-H stretching and bending vibrations is direct evidence that the OH groups are intimately involved in the reduction mechanism of the smectites. In nontronite, the ratio of Fe to OH in the clay structure is about 1 : 1. If electron transfer is accompanied by protonation of the structural OH (Drits and Manceau, 2000), one would expect complete reduction to eliminate all structural O-H vibrational modes and replace them with either H-O-H modes or nothing, depending on the extent to which the newly formed H-O-H diffuses out of the smectite structure. This appears in fact to be the case (Figs. 1 and 4).

Region IV

The bands in Region IV (Fig. 4) seem to have some correlations with the bands in Region III, but these relationships are only poorly established at this point. The attribution of the 589 cm^{-1} band is uncertain but it may be due to a combined Si-O-Fe(III) bending mode (Stubican and Roy, 1961 a, b). Upon reduction, this band completely disappears and a new band emerges at 653 cm^{-1} . No apparent connection is observed between this new band and any of the disappearing ones in Region III, but a band located in the same region is generally observed for $[\text{Fe}(\text{II})_3\text{OH}]$ deformation modes in talcs (Wilkins and Ito, 1976). The band at 653 cm^{-1} in the fully reduced sample could, there-

fore, be due to $[\text{Fe}(\text{II})_3\text{OH}]$ deformation, which supports the hypothesis of trioctahedral domain formation upon reduction. The high intensity of this band, however, seems to be out of proportion to the possible number of trioctahedral groupings, so an additional contribution to this band may exist. A possible candidate is the band located at 672 cm^{-1} in the unaltered nontronite, which is attributed to Fe-O out-of-plane vibrations (Farmer, 1974). This band is expected to shift to lower wavenumber upon Fe(III) reduction, but no evidence of such a shift was observed (Fialips *et al.*, 2002 b). Perhaps it does not change significantly upon reduction and could still be present in the spectrum of the fully reduced sample, in which case the 653 cm^{-1} band observed for this sample could be generated by the overlap of one band at 672 cm^{-1} and one band due to $[\text{Fe}(\text{II})_3\text{OH}]$ deformation at lower wavenumber.

4. Conclusions

Infrared spectra reveal significant differences in structural vibrational modes in Fe-rich smectites when structural Fe(III) is reduced to Fe(II). These differences clearly indicate that structural OH groups are being eliminated as a part of the reduction process, either directly by dehydroxylation or by protonation. The latter appears to be the better explanation. A portion of the protonated hydroxyl groups evidently remain in the smectite structure after complete reduction. Those sites from which structural OH groups are lost evoke a migration of the structural Fe from the original site to an adjacent vacant site, thereby creating a trioctahedral domain and a defect in the octahedral sheet. The relative number of such domains has yet to be determined.

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構造 Fe の酸化状態がスメクタイトの物理的および化学的特性に及ぼす影響 : 赤外分光分析による立証

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要 旨

スメクタイト鉱物の構造 Fe に関わる還元反応は土壌および堆積物の化学性に大きく寄与する。Fe(III) から Fe(II) への酸化状態の変化は粘土の構造を変え、ひいてはスメクタイトの底面構造の化学的性質を改質する。構造におけるこれらの変化は、赤外分光学によって容易に観察することができる。構造 OH 群は Fe(II) レベルの増大とともにだんだんと失われ、4 面体シートの Si-O 伸張と屈曲様式に大きなシフトを生じる。8 面体シートと 4 面体シートの連携は底面酸素の配列ばかりでなく、表面の荷電、pH および酸化還元ポテンシャルを変化させる。赤外分光スペクトルから、Fe(III) 還元の結果、3-八面体ドメイン形成されることが立証される。

キーワード : pH, 酸化還元, 荷電, 鉄, 粘土

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STUCKI 氏講演に関する質疑応答

赤江剛夫 (岡山大学環境理工学部) :

バクテリアの活動で結晶構造内 Fe 全体の 65% が Fe (II) に還元されるとのお話でしたが, 自然環境のバクテリア活動では何%まで Fe (II) が生じ得るでしょうか。

Stucki :

このことは最近になって Favri (2002 a, b) らが研究しています。彼らは, 湛水した水田土壌サンプルにおいて重量比で 15% の Fe (II) 含量を報告しています。こうした土壌での Fe の還元は, 湛水における青みがかった灰色への度食の変化として明瞭に現れます。このレベルの還元はバクテリア活動によるものと考えられます。私たちはこうした土壌からバクテリアを隔離し, バクテリアが粘土鉱物中の鉄の効果的な還元者であることを見だしています (Xu *et al.* 2001 ; Kostka *et al.* 2002 ; Cervini-Silva *et al.*, 2003)。

赤江 :

Fe 還元率は, FTIR (フーリエ変換赤外吸収スペクト

ル) やメスバウアー (Mössbauer) 法でうまく測定できるとのことでした。しかしながら, 我々は, 還元状態の尺度として, 酸化還元ポテンシャル (ORP) の測定を行うのが通常です。ORP と還元 Fe 率とは, どのような関係がありますか。

Stucki :

疑いもなくそのような関係が存在します。しかし, その関係はまだ定量化されていません。我々は, 野外条件での ORP と, 化学的分析 (Komadel and Stucki, 1988), およびあるいはメスバウアー分光法により明らかにした Fe (II) 含量との経験的な相関関係を作成する研究の途上にいます。また, いろいろな還元段階にある標準粘土の標準的な還元電位を確立しようとする試みも行っています。試料をフィールドから実験室へ輸送する間, 還元状態を保つことについていくつかの問題に遭遇します。こうした場合には, Fe (II) の現地測定法があれば, 現地 ORP 測定との相関において特に有用であると思います。

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