Modelling CEC variations versus structural iron reduction levels in dioctahedral smectites. Existing approaches, new data and model refinements

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ABSTRACT

A model was developed to describe how the 2:1 layer excess negative charge induced by the reduction of Fe(III) to Fe(II) by sodium dithionite buffered with citrate–bicarbonate is balanced and applied to nontronites. This model is based on new experimental data and extends structural interpretation introduced by a former model [36–38]. The 2:1 layer negative charge increase due to Fe(III) to Fe(II) reduction is balanced by an excess adsorption of cations in the clay interlayers and a specific sorption of H^+ from solution. Prevalence of one compensating mechanism over the other is related to the growing lattice distortion induced by structural Fe(III) reduction. At low reduction levels, cation adsorption dominates and some of the incorporated protons react with structural OH groups, leading to a dehydroxylation of the structure. Starting from a moderate reduction level, other structural changes occur, leading to a reorganisation of the octahedral and tetrahedral lattice: migration or release of cations, intense dehydroxylation and bonding of protons to undersaturated oxygen atoms. Experimental data highlight some particular properties of ferruginous smectites regarding chemical reduction. Contrary to previous assumptions, the negative layer charge of nontronites does not only increase towards a plateau value upon reduction. A peak is observed in the reduction domain. After this peak, the negative layer charge decreases upon extended reduction (>30%). The decrease is so dramatic that the layer charge of highly reduced nontronites can fall below that of its fully oxidised counterpart. Furthermore, the presence of a large amount of tetrahedral Fe seems to promote intense clay structural changes and Fe reducibility. Our newly acquired data clearly show that models currently available in the literature cannot be applied to the whole reduction range of clay structural Fe. Moreover, changes in the model normalising procedure clearly demonstrate that the investigated low tetrahedral bearing nontronites (SWa-1, GAN and NAu-1) all exhibit the same behaviour at low reduction levels. Consequently, we restricted our model to the case of moderate reduction (<30%) in low tetrahedral Fe-bearing nontronites. Our adapted model provides the relative amounts of Na^+ (p) and H^+ (n_i) cations incorporated in the structure as a function of the amount of Fe reduction. Two equations enable the investigated systems to be described: $p = m/(1 + K_r \cdot \omega \cdot m_{rel})$ and $n_i = K_r \cdot \omega \cdot m \cdot m_{rel}/(1 + K_r \cdot \omega \cdot m_{rel})$; where m is the Fe(II) content, m_{rel}, the reduction level (m/m_{tot}), ω, the cation exchange capacity (CEC, and K_r, an empirical constant specific to the system).

1. Introduction

Iron is one of the most common redox species in soils and sedimentary rocks [1]. Oxidation and reduction reactions involving the Fe(II)/Fe(III) redox couple are usually kinetically fast, especially when the reaction is catalysed by the presence of a mineral surface (e.g. [2–5]). For this reason, the redox properties of Fe are a key issue in understanding the redox dynamics of natural systems [6]. Among the different Fe(II)/Fe(III) couples present in soils and sediments, the reactivity of structural Fe (Fe_{str}) and adsorbed Fe (Fe_{ads}) in clay materials has been investigated in detail (e.g. [3,5,7–13]). Structural Fe and Fe ions adsorbed at clay edges are more reactive than aqueous iron (Fe_{aq}) and exchangeable iron (Fe_{exch}) at the basal surfaces of swelling clay particles [14,15].

From a kinetic point of view, the available studies demonstrate unambiguously that structural Fe^{3+}/Fe^{2+} is a versatile redox

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Abbreviations

Fe_{str}	Structural iron
CEC	Cation exchange capacity
ω_0, ω	CEC of oxidised and reduced clay, respectively (in $mmol_c\,g^{-1}$)
m	Amount of reduced iron (in $mmol\,g^{-1}$)
m_{tot}	Total Fe_{str} content (in $mmol\,g^{-1}$)
m_{rel}	Reduction level (i.e. m/m_{tot})

p, n_i	Amount of sorbed cations X^+ and H^+ upon reduction, respectively (in $mmol\,g^{-1}$)
K_r	An empirical constant specific to the system (in $g\,mmol^{-1}$)

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couple. Depending on the reducing agent, reduction of structural Fe can occur at the edge surfaces of the smectite layers or at the basal surfaces [16,17]. Clay structural Fe^{2+} oxidation, following initial reduction by sodium dithionite, exhibits biphasic pseudo first order kinetics that are dependent on the clay structure and the extent of preliminary reduction [5,12]. In clays with rather high Fe content, several structural Fe^{2+} sites react with organic compounds sensitive to oxidation processes [12]. Fe atoms are located in various structural sites in the clay lattice and thus could exhibit different redox properties as a function of their structural environment (for example, tetrahedral versus octahedral Fe or Fe in cis- and trans-OH sites [18]). For this reason, not only one but a variety of Fe^{3+}/Fe^{2+} redox couples may coexist in the same structure, thus exhibiting decreasing E_h values and/or kinetic reactivities as a function of reduction reaction progress (and vice versa for oxidation). It is thus necessary to understand the nature of the Fe sites in the structure as well as the mechanisms of conversion from one type of site to another in order to model the redox properties of structural iron as a function of reduction/oxidation changes.

The present study is focused on the prediction of clay structural Fe site changes in dioctahedral smectites as a function of reduction. Experiments have shown that the mechanism of Fe(III) to Fe(II) conversion in iron containing dioctahedral smectites depends partly on the reducing agent, on the physicochemical parameters of the solution where the redox reaction takes place and on specific structural properties of the clay mineral (composition, localisation and amount of excess charge) [19]. As a consequence, the present study is restricted to Fe_{str} reduction involving sodium dithionite reducing agent ($Na_2S_2O_4$).

Reduction of Fe(III) in dioctahedral smectites by sodium dithionite is followed by an increase in the cation exchange capacity (CEC) due to the increase in the clay layer charge deficit when Fe^{3+} is transformed into Fe^{2+}. However, this increase in CEC (ΔCEC) is not directly proportional to the amount of Fe(III) that is reduced (ΔFe^{3+}), i.e. $\Delta CEC/\Delta Fe^{3+} < 1$ [20]. This experimental feature is direct evidence of a change in the nature of the Fe structural sites and/or proportions as a function of reduction progress. Moreover, the ratio $\Delta CEC/\Delta Fe^{3+}$ is not constant as a function of reaction progress, evidencing a link between the CEC, the iron content and the redox reactivity of the clay towards sodium dithionite. Thanks to the acquisition of new data (CEC vs. amount of reduced iron), the present work aims (i) at reviewing current empirical models linking CEC variations to a reduction level and (ii) at proposing a link between these empirical model parameters and structural properties of Fe.

2. Materials and methods

2.1. Chemicals

All solutions for the reduction procedure and CEC measurements were prepared with ultra-pure water (Milli-Q 18 MΩ),

boiled for 1 h and cooled under N_2 flux overnight prior to its introduction in a N_2 atmosphere glove-box (Jacomex GP, $[O_2] < 2$ ppm). Dissolution of analytical grade salts was carried out inside the glove-box at 25 °C. Only the solutions used in acidic digestion were prepared and used out of the glove-box. A complete list of the chemicals used in this study is given in Supporting information section.

2.2. Solid samples

2.2.1. Clay material preparation procedure

Australian (NAu-1 and NAu-2) and German (NG-1) nontronites were obtained from the Source Clay Repository (Columbia, Missouri). NAu-1 and NAu-2 samples were first roughly powdered in an agate mortar by hand and then mechanically in an agate bowl. NG-1 sample was supplied in the form of sand containing approximately 2.5% of clay. Each sample was fractionated to <2 μm and air-dried prior to use. Purification and fractionation have been carried out by elutriation technique [21]. For NG-1, a significant quantity of magnetic oxides was removed with a magnetic bar [22]. No other pre-treatment has been applied on the resulting fine fraction.

2.2.2. Initial material characterisation

Clay content and iron impurities of the initial NAu-1 and NAu-2 samples were assessed by X-ray diffraction (XRD) and Mössbauer spectrometry. For NG-1, only Mössbauer spectra were recorded. XRD diagrams were performed on a Siemens D5000 diffractometer with variable slits, a cobalt anticathod and equipped with a diffracted beam monochromator. Diagrams were acquired from 3° to 36° 2θ with a rotation speed of 0.05° 2θ per second. The Mössbauer spectra were recorded at 77 K using a constant acceleration spectrometer and a ^{57}Co source diffused into a Rh matrix. Velocity calibrations were carried out using α-Fe foil at room temperature (RT, 295 K). The values of the hyperfine parameters were refined using a least-squared fitting procedure using a discrete number of independent quadrupolar doublets of Lorentzian lines. All isomer shifts are reported relative to the α-Fe spectrum obtained at RT.

2.2.3. Clay reduction procedure

Reduced clay minerals were prepared by a modified citrate–bicarbonate–dithionite (CBD) method [23]. Reduction procedure was carried out under anoxic condition (N_2 atmosphere, $[O_2] < 2$ ppm), in a glove-box containing a centrifuge and an oven, hence simplifying the method described in [23]. Clay reductions were carried out at room temperature in 50 mL centrifuge tubes, by first suspending ~300 mg of clay in 40 mL citrate bicarbonate buffer (2:1 ratio of 1.2 M citrate and 1 M bicarbonate solution, the same proportion as in [24]). After 1 h mixing on a rotating disc, varying amounts of sodium dithionite were added (1–3 times the mass of clay) under continuous stirring. In order to obtain various reduction levels, the initial amounts of dithionite varied