

# Sequestered carbon on clay mineral probed by electron paramagnetic resonance and X-ray photoelectron spectroscopy

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## Abstract

This paper describes the interaction among soil organic matter components with kaolinite, an important clay mineral present in tropical soils, especially in Brazil. XPS data show that the soil organic matter adsorbed on kaolinite has aromatic and aliphatic structures, with phenolic and/or alcoholic functions and carbonyl carbons (C=O) of amide and/or carboxylic groups. The N1s spectrum of the kaolinite shows an asymmetric peak that is assigned to amide and protonated amines probably from humin. The interaction between them is strong enough to resist chemical oxidative or reductive attack besides loose amide functionalities. EPR data show that reductive treatment reduces some Fe<sup>3+</sup> of the kaolinite structure, losing organic components. A schematic representation of the reduction of structural Fe<sup>3+</sup> in the concentrated domains and consequently increased concentration of Fe<sup>3+</sup> ions in diluted domains of the spectrum is presented. This reinforces the hypothesis that humin is a stable carbon sink in soils when adsorbed to clays.

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## 1. Introduction

Kaolinite, Al<sub>4</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>8</sub>, a clay mineral of a 1:1 type, is composed of tetrahedral silicate and octahedral gibbsite-like sheets, showing two distinct interlayer surfaces. One side of the layer has a gibbsite-like sheet with Al<sup>3+</sup> cations coordinated octahedrally to corner oxide ions and hydroxyl groups, some of the Al<sup>3+</sup> ions being replaced by Fe<sup>3+</sup> ions. A silica-like sheet constitutes the other side of the layer, where the silicon ions are coordinated tetrahedrally to oxide ions. The adjacent layers are linked by hydrogen bonding involving aluminol (Al–OH) and siloxane (Si–O) groups. It presents low cation-exchange capacity (CEC), common characteristic of tropical land, where kaolinite is widespread.

The potential of the kaolinite to interact with organic structures is relevant in the formation of aggregates, which are resistant to the degradation and consequent accumulation of recalcitrant organic substance in soils, favoring carbon sequestration. Kaolinites are claimed, also, to have a relevant role in the catalytic activity for the formation of humic substances in soils [1].

Previous characterization of the kaolinite denominated as PP-0559 from the Brazilian Amazon region, mined from the Brazilian state of Pará, was already reported [2]. The surface characterization of the PP-0559 sample by XPS showed that kaolinite presents impurities of natural organic substance inferred from asymmetric XPS spectra of C1s and N1s regions. The asymmetric peak of the C1s photoelectric line was fitted for components at energies of 284.6, 286.3, and 288.5 eV, and for N1s of 398.7 and 400.0 eV [3]. In the present work, the effect of reducing/chelating treatment, called DCB (aqueous solutions

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of sodium dithionite, sodium citrate, and sodium bicarbonate [4], or oxidative treatment with NaOCl (pH  $\sim$  9.5) on kaolinite PP-0559 is reported. DCB treatment is used to remove adsorbed iron oxides from clay mineral surfaces. The NaOCl aqueous solution treatment has been claimed to be highly useful in diminishing the amount of organic matter adsorbed on the surfaces of clays [5] as a consequence of the oxidation potential of  $\text{ClO}^-/\text{Cl}^-$  electrochemical couple ( $E^0 = 0.890$  V) [6]. Regardless of the decrease on bulk total organic matter as assessed by carbon and nitrogen analysis by bulk techniques, as Kjeldahl or combustion methods, there is no study on the effect on surface layers, which may play a fundamental role in soil properties as, for example, agrochemical–soil interaction, water adsorption, and ion-exchange properties. Studies of organic–inorganic interactions in soils are crucial in understanding the carbon sequestration power of the environment.

Coupled to agronomic issues, humus dynamics and carbon storage in soils are of global significance because of their contribution to the decrease of atmospheric  $\text{CO}_2$  and the greenhouse effect [7]. The protection of the ecological equilibrium of the atmosphere must be provided by a better knowledge of the processes that stabilize humus in soils. In particular, humic substances, the recalcitrant or passive fraction of soil organic matter (SOM), are expected to play a significant role as a carbon sink.

The ability of organic carbon to resist enzymatic attack by the soil decomposer community, with increasing resistance corresponding to increased stability, is defined as “biological stability.” This biological stability of SOM is controlled by the existence of various mechanisms of protection offered by the soil matrix and soil minerals and specific chemical structures of this SOM [8].

The mechanism for stabilizing SOM against biological attack can be improved by the presence of  $\text{Al}^{3+}$  cations and Al-hydroxy cations available in clay minerals. The presence of  $\text{Fe}^{3+}$  cations can also offer similar effects, since these cations are both classified by Pearson as hard acids.

Normally soil scientists analyze the carbon sequestration capacity of soils, and the organic–inorganic interactions, extracting and analyzing humic substances (HS), the most abundant and recalcitrant fraction of SOM. As HS maintain some inorganic constituents as impurities, they are used in the study of organic–inorganic interactions in the environment from which they are extracted. In the present work, a different strategy was adopted, studying stabilized organic structure impurities in the kaolinite structure, one of the most abundant inorganic constituents of tropical soils. Those organic impurities exemplify the best-fixed carbon structures in soils.

## 2. Experimental

The kaolinite sample employed in this work (PP-0559) was supplied by the Petrobrás Research Center (CENPES, Rio de Janeiro). It was received as a finely divided white-yellowish powder of high purity and low structural disorder, mined in the Brazilian State of Pará in the Amazon Basin, and was used without further purification.

In the reducing/chelating treatment, raw kaolinite was subjected to DCB treatment (dithionite–citrate–bicarbonate) [9], to remove the nonstructural iron impurities and to simulate environmental reduction reactions in the soil. This method is based on the addition of solid sodium dithionite to clay dispersions in a citrate–bicarbonate buffer aqueous solution. Citrate anion is used to complex the iron as well as aluminum, preventing the precipitation of those cations as oxides.

In the oxidation treatment, 2 g of raw kaolinite, was suspended in 4 mL of 4% NaOCl aqueous solution, at 373 K for 15 min. Afterward, the treated kaolinite was washed successively with  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  ( $0.05 \text{ mol L}^{-1}$ ) aqueous solutions and with deionized water, followed by centrifuging [10].

After natural drying, the samples were analyzed by EPR spectroscopy in a Bruker ESP 300E spectrometer, using X band ( $\sim 9.7$  GHz) at room temperature. For registration of the spectra the microwave power of 2 mW was used, with frequency modulation of 100 kHz and field modulation amplitude of 5 G. The EPR spectra of the impurity of  $\text{Fe}^{3+}$  ions from kaolinite, in the diluted domain region ( $g \sim 4.3$ ), were integrated and normalized, and the area under the curve, after base line correction, was calculated by integration [9].

XPS spectra were recorded in a VG Microtech ESCA 3000 equipment, under vacuum of  $3 \times 10^{-10}$  mbar, using  $\text{MgK}\alpha$  radiation and 0.8 eV resolution. The kinetic energy was corrected using  $\text{Au}4f$ . The binding energies were corrected for charging effects using the  $\text{Si}2p_{3/2}$  peak of the kaolinite structure (102.7 eV) [11]. The samples for XPS were sonicated in distilled and deionized water, casted on silicon plates ( $1 \text{ cm}^2$ ), and dried at room temperature (298 K).

All XPS peaks of insulating samples were fitted according to Leclercq and Pireaux’s method [12], using Gaussian–Lorentzian peaks. The atomic ratios of the samples were calculated using the instrumental sensitivity factor [13] based on Scofield’s cross sections [14].

## 3. Results and discussion

Fig. 1 shows the EPR spectra of the studied samples at a magnetic field of 5000 G. The EPR spectra for all samples

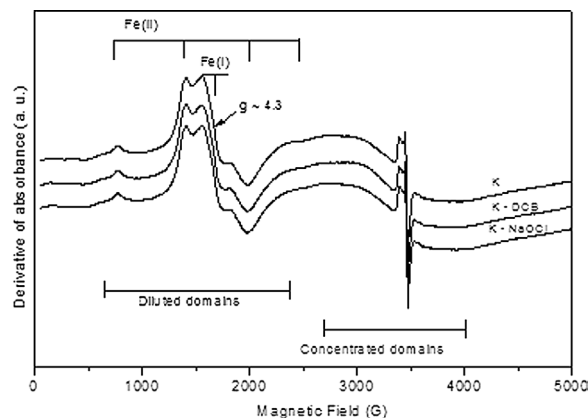


Fig. 1. EPR spectra at 5000 G of raw kaolinite (K), kaolinite after DCB treatment (K-DCB), and kaolinite after NaOCl treatment (K-NaOCl).

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