



# The effects of microstructural changes on montmorillonite–microbial interactions



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## HIGHLIGHTS

- Effects of structural changes on montmorillonite–microbial interactions are studied.
- Infrared spectroscopy and allied analytical techniques are applied.
- Microbial interactions with acid-treated clay are confirmed.
- Pure clay display greater affinity for microbes than its acid-treated counterparts.
- Spatial co-variation of microbes with mineral cations is a primary adsorption mechanism.

## ARTICLE INFO

### Article history:

Received 29 August 2013  
 Received in revised form 11 October 2013  
 Accepted 14 October 2013  
 Available online 23 October 2013

### Keywords:

Acid-treated clay minerals  
 Adsorption  
 Montmorillonite  
 Octahedral cations  
 Organic matter  
 Soil microbial biomass

## ABSTRACT

Clay minerals are important natural adsorbents of soil organic matter (SOM) and therefore are natural modulators of soil-atmospheric carbon fluxes. Although such effects have been reported, little is known about the spatial distribution of organic matter (OM) on the surfaces of soil minerals and even less is known about the effects of microstructural changes on clay–organo interactions. Here we employ acid hydrolysis to induce varying degrees of microstructural changes to montmorillonite clay mineral as a function of time and combine IR spectroscopy, X-ray diffraction, and SEM-EDX as primary techniques to independently provide molecular-level information on the effects these changes on microbial interactions with the mineral. We observed that progressive dissolution of octahedral cations and the simultaneous enrichment of amorphous silica are prominent structural changes induced by hydrolysis, and that the adsorption of microbial-derived components (in particular lipids) on the surfaces of acid-treated clay decreases with increasing acid dissolution time. Although the precise mechanism(s) of interactions remains unclear, we speculate that this adsorption behavior is most likely due to spatial co-variation of microbial-derived OM with octahedral cations in the mineral, acid erosion of biochemically active binding sites, and/or a progressive increase in the hydrophilicity of the mineral surfaces by acid attack over time.

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## 1. Introduction

Clay minerals are important natural adsorbents of soil organic matter (SOM) and therefore are natural modulators of soil-atmospheric carbon fluxes. Although the effects of clay minerals on the adsorption and stabilization of SOM have been reported [1,2], little is known about the extent of the spatial distribution of organic matter (OM) on the surfaces of soil minerals or the factors controlling it. Moreover, our knowledge of the effects of microstructural changes on the interactions between clay minerals and OM may also be considered rudimentary. Recently, the microbial contribution to SOM has been shown to be much larger than previously thought, and therefore its role in the carbon and

nitrogen biogeochemical cycles may also be underestimated [3,4]. Considering the expected increase in global atmospheric CO<sub>2</sub> concentrations over the next decades [5], there is an express need for better empirical understanding of the interactions between pristine and structurally altered (degraded) soil minerals and microbial-derived OM. This knowledge may then be used to facilitate further advances in our understanding of the carbon and nitrogen biogeochemical cycles.

Ubiquitous and abundant in soil environment, the expandable (2:1) smectite group mineral montmorillonite has large reactive surface areas for ion exchange and provides a considerable sink for SOM. The crystal structure of the mineral comprises two tetrahedral sheets (SiO<sub>2</sub>) linked on either side of an octahedral sheet [Al(OH)<sub>3</sub>] via shared apical oxygen atoms. Within the crystal structure of montmorillonite, trivalent atoms occupy only two-thirds of the available octahedral coordinated sites. Isomorphous substitu-

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tions within the mineral lattice confer a permanent negative charge on the basal surfaces [hydroxyl (OH) and oxygen of siloxane surfaces]), which is balanced by hydrated exchangeable cations in the interlayers (primarily  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Na}^{+}$ ) and on the mineral particle edges [6]. The sum of the charges of the exchangeable cations is the cation exchange capacity (CEC) of the mineral [7]. Similarly, charges are generated on the edge surfaces as a result of deprotonation or protonation of surface groups. Given the physico-chemical properties of montmorillonite, it is capable of participating in organo-interactions through various chemical and physical mechanisms. A detailed conceptual model on the mechanisms of organo–mineral interactions can be found elsewhere [8].

In addition to the adsorption and stabilization of SOM, it has also been suggested that the degradation of siliceous minerals plays an important role in the dynamics of the global carbon biogeochemical cycle [9,10]. Specifically, the weathering of silicates in terrestrial biosystems has been linked with feedback control of  $\text{CO}_2$  levels in the atmosphere [11]. In soils, mineral degradation is a consequence of the combined effects of physical, chemical and biological processes. For instance, the degradation of minerals, particularly in the rhizosphere has been shown to be accelerated by localized root-induced acidification attributed to the exudation of  $\text{H}^{+}$  ions,  $\text{CO}_2$  and low molecular weight organic acids such as acetic, succinic, and oxalic acids [12]. The rhizosphere represents a unique microenvironment in which the physico-chemical properties and intensity of biogeochemical processes differ considerably from those of bulk soils due to plant root- and microbial-induced chemical changes [13,14]. Hydrolysis is an important component of soil formation, and is generally recognized as a dominant mechanism involved in the degradation of minerals. Furthermore, soil acidification (exogenous) could become an important factor in the decades ahead.

Here we employ IR spectroscopy, X-ray diffraction, and SEM-EDX as primary analytical techniques to independently verify and provide molecular-level information on the effects of acid-induced microstructural changes on the interactions between montmorillonite and soil microbial biomass. Of special interest was elucidation of the spatial organization and adsorption behavior of microbial-derived OM on the surfaces of the acid-treated mineral. Infrared spectroscopy is a useful technique to probe the chemical environment of clay–organo interactions, but has been seldom used. Published reports include analysis of kaolinite–microbial interactions [15] and the speciation of Cd on montmorillonite in the presence of soil microbial biomass [16]. The advantage of X-ray diffraction is that it can be used to confirm external surface and interlayer interactions of microbial-derived OM with clay minerals, and is therefore suitable to provide an overview of microbial interactions with changes in the crystalline structure of the mineral. The hyphenated SEM-EDX approach provides a direct measure of the topography and composition of the sample and may also be used as a semi-quantitative descriptor to follow the depletion and/or enrichment of specific mineral and/or microbial components.

## 2. Materials and methods

### 2.1. Bacterial growth and conditions

A mixed heterotrophic soil biome was prepared in trypticase soy broth (TSB) supplemented with 0.5% (w/v) yeast extract, according to a modified version of the protocol described by Borrok et al. [17]. The origin, physico-chemical properties and agricultural management history of the field site from which the inoculum was obtained can be found elsewhere [16]. Initially, 1 g of previously homogenized soil was added to 100 mL aliquots of sterile distilled

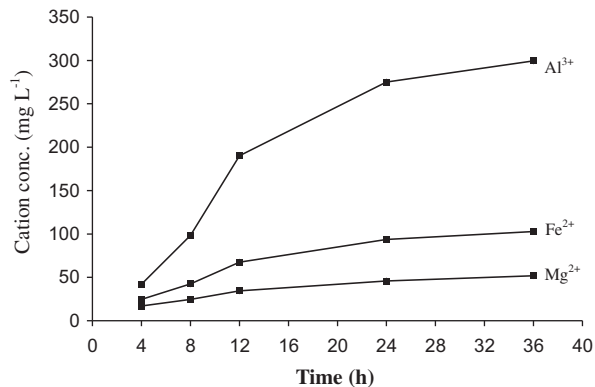
water and dispersed using a magnetic stirrer. Aliquots (1 mL) of the initial soil suspension were added to 9 mL diluted growth solution (TSB–yeast extract: sterile distilled water, 1:9), and mixed by gentle vortexing at  $\sim 120$  rpm for 15 s. The initial diluted suspension was used to prepare serial dilutions containing  $10^{-2}$  to  $10^{-4}$  g soil suspension. Finally, 1 mL aliquots from the  $10^{-4}$  dilution were used to inoculate 100 mL of the undiluted growth solution and the cultures incubated at room temperature for 72 h with shaking at 150 rpm. Note, dilutions were done to prevent any possible carry-over of soil particles from the initial soil suspension. After incubation, the cultures were spun down at 3500 rpm for 10 min, the supernatant discarded and the cell pellets washed five times in a large excess of ultrapure (18.2 M $\Omega$  cm) water. This was carried out to eliminate traces of undefined organic constituents carried over from the growth solution that may result in an overestimation of clay–organo interactions [18]. The washing protocol did not appear to produce a significant adverse effect on the integrity of the cells. Bacterial stock suspensions ( $1.0 \text{ g L}^{-1}$ ; wet mass) were prepared from the cleaned cell pellets in ultrapure water. All solutions and laboratory glassware and growth solutions used were sterilized by autoclaving for 20 min at 15 psi/121 °C. Identical controls were prepared without the addition of soil. In these controls, no microbial growth was observed; suggesting that the microbial biomass we produced was derived exclusively from the soil inoculum.

### 2.2. Acid digestion

Approximately 1.25 g of pure (untreated) montmorillonite (SWy-2; Source Clays Repository; The Clay Minerals Society), hereafter referred to as M, was hydrolyzed under reflux with 125 mL of  $6 \text{ mol L}^{-1}$  HCl at 105 °C for 0, 4, 8, 12, 24 and 36 h with stirring every hour. After acid treatment, the samples were allowed to cool, vacuum filtered through glass fiber filters (Whatman GF/C), and the residues washed with ultrapure water until free of chlorides (as determined by  $\text{AgNO}_3$  solution), centrifuged, dried and homogenized. The cleaned residues were placed in fresh glass vials, oven dried at 80 °C over night and then cooled over a desiccant ( $\text{P}_2\text{O}_5$ ) at room temperature for 2 h. The filtrate and wash supernatant solutions were combined and analyzed for Al, Mg and Fe (central octahedral atoms) and Si (central tetrahedral atom) by inductively coupled plasma–optical emission spectroscopy (ICP-OES; [19]).

### 2.3. Adsorption experiment

Duplicate adsorption experiments were conducted using pure and acid-treated M. In each experiment, 10 mg of dried mineral was added to 10 mL aliquots of previously prepared bacterial stock



**Fig. 1.** Concentrations of major octahedral cations leached from the structure of montmorillonite clay mineral using fixed ionic strength of a mineral acid ( $6 \text{ mol L}^{-1}$  HCl) over time (4, 8, 12, 24 and 36 h).

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