



Neutron reflectometry reveals the internal structure of organic compounds deposited on aluminum oxide[☆]

Melanie Mayes^{a,*}, Sindhu Jagadamma^a, Haile Ambaye^b, Loukas Petridis^c, Valeria Lauter^b

^a Climate Change Science Institute and Environmental Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831, USA

^b Neutron Sciences Directorate, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831, USA

^c Biological Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831, USA

ARTICLE INFO

Article history:

Received 19 March 2012

Received in revised form 24 July 2012

Accepted 25 July 2012

Available online 17 November 2012

Keywords:

Organic carbon

Soil mineral

Neutron reflectivity

Reflectometry

Adsorption

Organo-mineral interface

ABSTRACT

Organic carbon (OC) stabilization in soils plays a significant role in the global C cycle, therefore understanding the structure and function of the OC–soil mineral interface is of high importance. To study the interface, films of simple OC compounds and natural organic matter (NOM) were deposited onto a soil mineral analogue (Al_2O_3) using spin coating and were exposed to humidity. The thickness, density and structure of the films were studied using a depth-sensitive, nano-scale technique of neutron reflectometry. A single homogenous layer was observed when NOM and glucose (GL) were adsorbed onto Al_2O_3 . However, when stearic acid (SA) was added to either NOM or GL, separate layers attributed to SA and either NOM or GL were detected. The formation of distinct, immiscible layers is due to insolubility of SA with NOM and GL. In contrast, GL and NOM are both water-soluble, and therefore soluble with each other, forming a homogenous layer on the mineral surface. Our results suggest that the extent of complex layering formed on the OC–mineral interface may depend on the relative solubility of the compounds.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Soil organic carbon (OC) is an important component of the global carbon (C) cycle, as soils contain twice the OC of the atmosphere and three times that of the biosphere. In mineral soil horizons, stabilization of dissolved OC occurs via physical and chemical adsorption. Some new soil C cycling modeling approaches rely upon microbial consumption of dissolved OC as the central mechanism of CO_2 release (Allison et al., 2010; Lawrence et al., 2009; Schimel and Weintraub, 2003). The structure and function of the OC–soil mineral interface is poorly understood, however, leading to uncertainty in the extent of bioavailability of sorbed OC to the microbial community and therefore, uncertainty in the release of mineralized C to the atmosphere. In order to accurately represent the rates and mechanisms of OC cycling in soil C models, we need to understand the structure and functional characteristics of the OC–soil mineral interface.

Several researchers have proposed models describing the OC–soil mineral interface as a layered sequence of OC compounds (Kleber et al., 2007; Wershaw, 1986, 1993). Both Wershaw and Kleber models

proposed self-organization of layered, membrane-like structures within humic materials, which is consistent with new understanding of soil organic matter as being composed of simple, recognizable molecules (Kelleher and Simpson, 2006; Sutton and Sposito, 2005). Hydrophobic functional groups are proposed to partition themselves to avoid contact with polar soil solutions, while hydrophilic functional groups do the opposite. The location of an OC compound within this theoretical structure may determine its bioavailability to the microbial community, i.e., compounds closer to the mineral may be more resistant to microbial degradation due to limited physical access by microbes and stronger binding to mineral surfaces. If so, layer formation may influence the residence time of different OC compounds in soils and therefore, soil C cycling (Kleber et al., 2007; Sutton and Sposito, 2005). However, experimental observations of the structure of the OC–mineral interface and its function with respect to C bioavailability to the microbial community are missing. New models representing soil C cycling, nutrient bioavailability, and contaminant interactions would benefit from improved understanding of the OC–mineral interface.

The current situation is due to a lack of appropriate techniques for interrogating the OC–mineral interface at the appropriate scale. The size of simple OC compounds is a few nanometers (nm), complex compounds may be tens of nm, and layers of compounds may be tens to hundreds of nm (Cárdenas et al., 2007). Extraction techniques that remove the intense signal of the mineral phase are not adequate to examine the intact organo-mineral interface (e.g., nuclear magnetic resonance and many infrared spectroscopic techniques), while surface techniques (e.g., atomic

Abbreviations: (OC), organic carbon; (NOM), natural organic matter; (NR), neutron reflectivity; (SA), stearic acid; (GL), glucose.

[☆] The submitted manuscript has been authored by a contractor of the U.S. Government under contract DE-AC05-00OR22725. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes.

* Corresponding author. Tel.: +1 865 574 7336; fax: +1 865 576 8646.

E-mail address: mayesma@ornl.gov (M. Mayes).

force microscopy) are inadequate to resolve depth or chemical composition. The resolution of synchrotron spectroscopy is much smaller than the nm scale, enabling determination of nearest neighbor atoms and the speciation of target elements. Two dimensional spectroscopic imaging techniques, which have a larger spatial resolution, have been used to investigate the chemistry and arrangement of OC in microaggregates in soils (Kinyangi et al., 2006; Lehmann et al., 2008). Results from this technique suggest that OC in soils is composed of regular arrangements of simple compounds in a variety of soils, but two dimensional imaging is insufficient to determine the depth signatures of the arrangements.

For this study, thermal neutron scattering was chosen because of its high and non-destructive penetration through the layers of an organic–mineral interface, and its high sensitivity to light elements. Lipid membrane bi-layers adsorbed to mineral surfaces are readily detected using neutron reflectometry (NR) (Generosi et al., 2004; Johs et al., 2009; Lu et al., 2003). The sorption of human saliva on alumina was observed to produce self-arrangement of two layers consisting of an inner dense layer that sorbs rapidly to alumina and an outer region that extends outward toward the bulk solution (Cárdenas et al., 2007). This model has similarity to the models of Kleber et al. (2007) and Wershaw (1986, 1993). Exposure of the samples to water vapor or humidity resulted in different degrees of swelling depending on the functional groups of the surfactants (Generosi et al., 2004; Wang et al., 2009). In addition, differences in temperature, ionic strength and cation concentration influenced layer thickness (Dodoo et al., 2011; Hellsing et al., 2011; Tucker et al., 2011). The culmination of previous NR research suggests that layer formation of OC compounds on soil mineral surfaces is likely, that various solution and chemical characteristics influence layer formation, and that NR is a promising analytical technique to understand the principles of layer formation. The objective of this research was to determine how simple OC compounds (e.g., sugar, fatty acid) become incorporated into a model OC–mineral interface.

2. Materials and methods

2.1. Sample preparation

Silicon (Si) wafer substrates (El-Cat Inc.) of 2.54 cm diameter and 1 mm thickness were cleaned by ultra-violet/ozone (UVO) method for 15 min. Aluminum oxide (Al_2O_3) was deposited on the wafers at a rate of 0.4 nm s^{-1} in 2×10^{-5} Torr vacuum using the electron beam at the Center for Nano-phase Materials Sciences (CNMS), Oak Ridge National Laboratory (ORNL), TN, USA.

A complex natural organic matter (NOM) sample was deposited to the alumina-coated Si substrate to represent soil OC, and stearic acid (SA) (Sigma Aldrich) and deuterated glucose (GL) (CDN Isotopes) were deposited to represent simple compounds found in soil solutions. Dissolved NOM was obtained and concentrated from a wetlands pond near a peat deposit at Clemson University's Baruch Forest Science Institute in Georgetown, SC (Chen et al., 2002; Gu et al., 1994; McCarthy et al., 1993). Fourier transformed infrared and nuclear magnetic resonance spectroscopies show that the NOM resembles humic substances in aquatic systems and fulvic acids in soil. More details on the chemistry of the NOM are available in Chen et al. (2002). Separate solutions (1000 mg CL^{-1}) of each OC compound were prepared immediately before deposition onto the alumina-coated Si wafer by dissolving GL and NOM in Milli-Q water, and SA in toluene. Solutions were filtered through a $0.20 \text{ }\mu\text{m}$ filter. The filtered solutions were coated on the alumina mineral surface using spin coating at CNMS. Spin coating offers the opportunity to deposit dissolved compounds on solid substrates uniformly, quickly and by using a minimal amount of sorbate (Generosi et al., 2004; Wang et al., 2009). The Al_2O_3 coated Si substrates were placed on the spin coater head and $60 \text{ }\mu\text{L cm}^{-2}$ of solution was dispensed on the substrate surface as very small droplets using a Pasteur pipet. The substrate was rotated immediately at an initial speed of 1000 rpm for 15 s for uniform deposition of organic compounds. Subsequently the

spin speed was increased to 4000 rpm for 45 s in order to spin off the excess solution from the wafer surface and dry the samples. From multiple preliminary tests, we inferred that the selected speed and time of spin coating was optimized to obtain a uniform coating of the compounds on the mineral surface. We do not anticipate the presence of toluene residue in the spin coated samples because toluene evaporates quickly (vapor pressure 2933 Pa). Generosi et al. (2004) observed that organic solvents evaporate very quickly from spin coated samples.

A total of four OC-coated samples were prepared. Sample 1 is a monolayer of NOM; sample 2 is a bilayer with GL as the first layer on substrate surface and NOM as the second layer on top of GL; sample 3 is a bilayer with NOM on substrate surface and SA on top of NOM; and sample 4 is a bilayer in which SA was deposited on substrate surface followed by GL. After coating the first layers, samples were stored in the glove box under N_2 and 24 h later, samples were removed from the glove box for depositing the second layers. All samples were then stored in a glove box until NR measurements. Double-layer samples were removed from the glove box and exposed to humidity immediately before NR measurements to facilitate equilibration of the compounds that might occur in natural soil samples (e.g., Generosi et al., 2004; Wang et al., 2009). The samples were humidified by placing them with an open vial of H_2O inside a container under vacuum for 24 h.

2.2. Neutron reflectivity measurements and modeling

2.2.1. Background

The thickness and the structure of OC layering on alumina mineral were studied by the method of NR which is advantageous in several ways. Neutrons probe nuclear contrast rather than electron density and are therefore more sensitive for measuring lighter elements typical for organic matter: hydrogen, carbon, nitrogen, oxygen, etc. The sensitivity of neutrons allows contrast to be selectively enhanced using isotopic substitution (e.g., neutron scattering from hydrogen differs significantly from deuterium). Neutrons are highly penetrating and typically non-perturbing, which allows for great flexibility in sample environments like humidity cells, and the use of delicate sample materials (e.g., biological or organic specimens). In contrast X-rays may damage some materials and the laser light can modify some materials. Due to these evident advantages, we used this unique technique in our study.

2.2.2. Modeling theory and experimental application

Experiments were performed on MAGICS, the neutron reflectometer at the Spallation Neutron Source at Oak Ridge National Laboratory (Lauter et al., 2009). It is a time-of-flight instrument with incoming neutron wavelengths (λ) of 0.2 to 0.5 nm. One of the strengths of this technique is its ability to measure thicknesses of layers with a very high precision of around 0.5 nm. In grazing incidence geometry as shown in Fig. 1, a collimated beam of neutrons impinges the sample at an incident angle θ_i and the intensity reflected at angle θ_f is measured using a position-sensitive detector. For a specular reflection $\theta_i = \theta_f$. The reflectivity is measured as a function of the momentum transfer (Q_z) perpendicular to the sample plane, where $Q_z = \frac{4\pi}{\lambda} \sin\theta$ (Fig. 1). The neutrons probe the scattering length density (ρ) of the film depth profile, which depends on the property of the material to scatter neutrons and is a characteristic of its elemental and isotopic composition. The ρ is determined by the distribution of atoms per unit volume in each layer and is equivalent to $\rho = \sum_i^n N_i b_i$, where ρ (e.g., nm^{-2}), N_i is the number density of the i th component, and b_i is the coherent scattering length of the i th component, in the system. The scattering length b is a constant tabulated for most nuclei, and isotopes of the same element can have different b . Further, b can be positive or negative, e.g., b is $-3.742e-4 \text{ nm}$ for hydrogen (H) and b is $6.74e-4 \text{ nm}$ for deuterium (D), because neutrons deflected from H are out of phase relative to those deflected by most other

Download English Version:

<https://daneshyari.com/en/article/4573766>

Download Persian Version:

<https://daneshyari.com/article/4573766>

[Daneshyari.com](https://daneshyari.com)