

# The Role of Mineral Complexation and Metal Redox Coupling in Carbon Cycling and Stabilization

Donald L. Sparks and Chunmei Chen

**Abstract** The association of carbon with mineral phases has been increasingly recognized as a major stabilizing mechanism for protecting organic matter against microbial degradation in soils. However, direct investigation of organo-mineral interactions has been hampered by a lack of methods that can simultaneously characterize soil organic matter and soil minerals. To elucidate the specific mineral–OM binding mechanisms, scanning transmission X-ray microscopy–near-edge X-ray absorption fine structure spectroscopy (STXM–NEXAFS) was applied to map the major mineral elemental (Si, Al, Ca, Fe, K) composition and to determine the spatial distribution of carbon and carbon functional groups in soil clay fractions from a landscape topographic gradient at the Christina River Basin Critical Zone Observatory (CRB-CZO). Pyrolysis-field ionization mass spectrometry (Py-FIMS) was used to identify organic matter composition in soils. We also investigated Fe speciation to link iron-redox-coupling processes with soil C cycling. Selective chemical extractions, X-ray absorption spectroscopy (XAS), micro-XAS techniques, and Mossbauer spectroscopy were employed to characterize soil Fe speciation. Ferrihydrite, because of its ubiquitous occurrence in the environment and its high surface area, contributes significantly to the sorption of organic matter and protects it against microbial degradation in soils and sediments. In addition, ferrihydrite often forms in the presence of dissolved organic matter in the natural environment, which leads to coprecipitation of organic matter with ferrihydrite. To examine the mechanisms of organo-ferrihydrite complex formation associated with these two processes, C and N NEXAFS spectroscopic techniques were employed. Such studies on mineral complexation and metal redox cycling provide new insights on carbon cycling and stabilization in the Earth’s critical zone.

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## Introduction

The role of carbon (C)–mineral interactions in the long-term accumulation of soil organic matter (OM) is increasingly recognized as a key process in terrestrial C cycling (Baldock and Skjemstad 2000; Mikutta et al. 2006). However, the specific mineral phases or the mechanisms for the formations of the C–mineral complex are largely unknown. Redox changes, as a consequence of varying landscape topographic positions, will have important impacts on biogeochemical-C and mineral-cycling processes. Since both the organic matter and mineral phases of soils are involved in OM–mineral complex formation, differences in both mineralogy and organic matter composition could lead to differences in organo-mineral complexes. This study focused on pasture, forest, and agricultural hillslopes to investigate the nature of soil mineral–organic associations. Additionally, organic matter–ferrihydrite complexes, formed by coprecipitation and sorption, were synthesized in the laboratory. Our specific goals are (1) to identify distinctive binding mechanisms between OM and specific mineral components, (2) to determine the major mineral species important in OM–mineral complexation formation, and (3) to characterize solid-phase carbon and iron speciation along a redox gradient of different landscape positions and uses.

## Materials and Methods

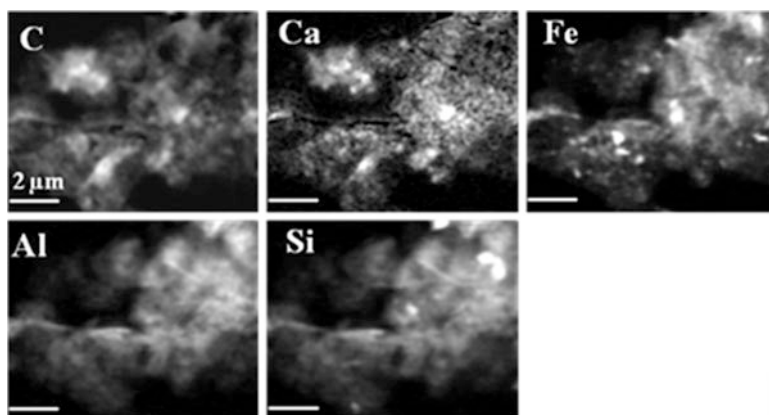
We collected soil samples under varying redox conditions from a wide range of landscape settings and uses, such as floodplain forest, upland forest, agriculture, and pasture sites within the Christina River Basin Critical Zone Observatory (CRB-CZO) located in the Piedmont region of southeastern Pennsylvania and northern Delaware. Synchrotron-based scanning transmission X-ray microscopy (STXM), coupled with near-edge X-ray absorption fine structure spectroscopy (NEXAFS) spectroscopy, provides an excellent approach for identifying and fingerprinting the molecular structure of organic C in soil organic matter (Lehmann et al. 2008). The wide STXM energy range (130–2,500 eV) of the SM beamline at the Canadian Light Source (CLS) is essential for understanding OM–mineral interactions in soils because it allows one to directly quantify the major mineral elemental (Si, Al, Ca, Fe) composition simultaneously with determinations of spatial distributions of carbon and carbon functional groups from the nm to the  $\mu\text{m}$  scale. The high spatial resolution of about 25 nm facilitates obtaining information on the spatial distribution of C, Si, Al, Ca, Fe, and K in the soils. Thin films of samples were prepared by

mixing 1 mg of soil clay fractions with 1 ml water and depositing 1–2  $\mu\text{L}$  of the aqueous suspension on a  $\text{Si}_3\text{N}_4$  window. NEXAFS stack maps of C, K, Ca, Fe, Al, and Si were simultaneously collected at the SM beamline.

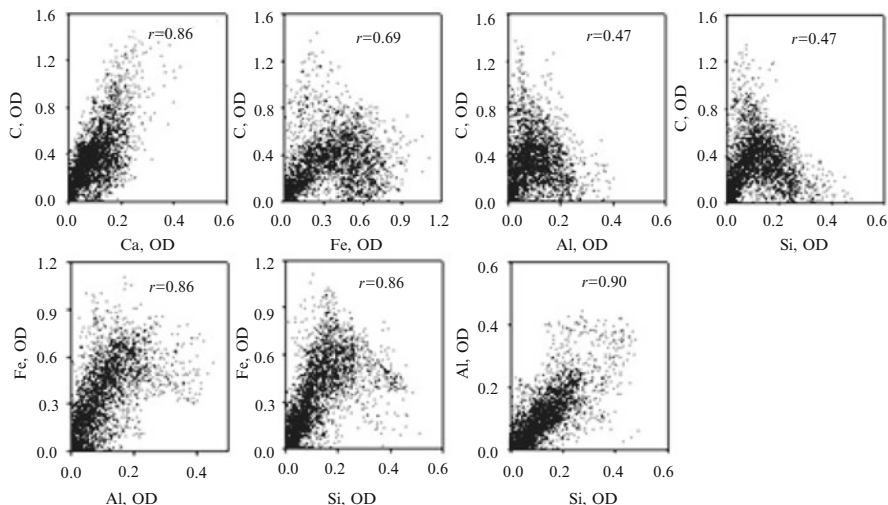
The challenge with STXM is that one can only image small regions of soil samples and consequently, this limits our ability to derive conclusions for whole soils, which are very heterogeneous, and to compare C speciation in whole soils influenced by landscape topography. The SGM beamline with a beam spot size  $1,000 \times 100 \mu\text{m}$  at the CLS allows one to perform C and N near-edge X-ray absorption fine structure (NEXAFS) analyses on bulk soil samples. Another great advantage of this technique is that it allows one to characterize in situ soil organic matter without extraction, given that soil organic matter extraction techniques can alter its composition. Thin films of samples were prepared by homogeneously mixing 1 mg of the finely ground sample material in 1 mL of DI water and by transferring 1  $\mu\text{L}$  of the aqueous samples on gold-coated silicon. C and N NEXAFS spectra of the samples were collected using a photodiode. Pyrolysis-field ionization mass spectroscopy was applied as a complementary technique to identify specific organic compounds in the soils. Additionally, X-ray absorption spectroscopy (XAS) and Mössbauer spectroscopy were applied to characterize soil Fe-mineral phases along the redox gradients.

## Results and Discussion

Figure 1 displays the relative elemental distributions at the particle scale. C was intimately associated with soil minerals in the soil clay fractions and was unevenly distributed, with distinct “hot spots” of C deposition within the mineral particles.



**Fig. 1** Relative elemental (C, Ca, Fe, Al, and Si) distribution of soil clay fractions from the upland footslope at a soil depth of 0–15 cm (*gray color scale, with black = low and brighter = high concentrations*)



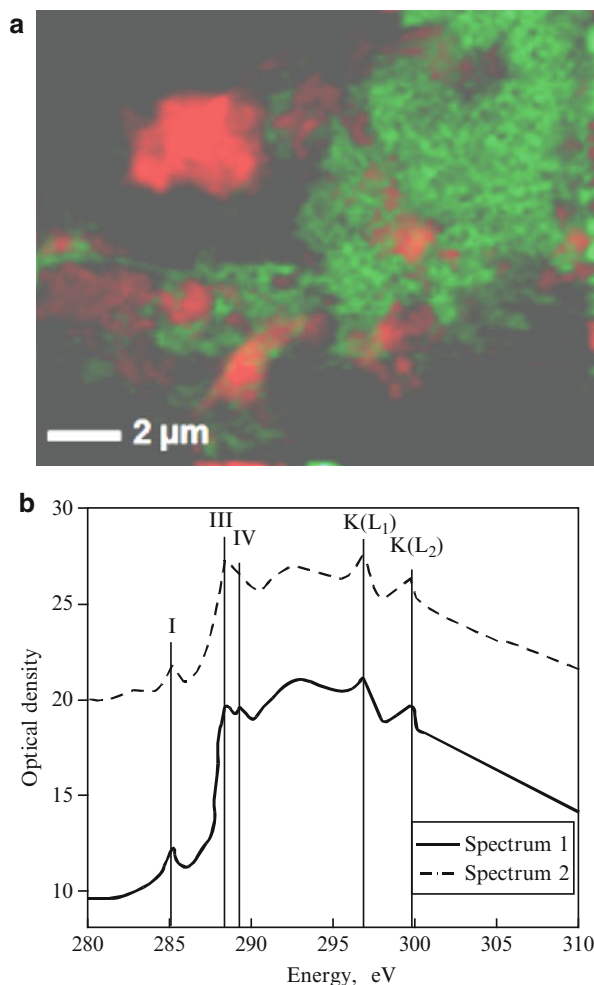
**Fig. 2** Correlation plots of optical density (OD) values obtained from STXM elemental maps of soil clay fractions from the upland footslope at a soil depth of 0–15 cm, as shown in Fig. 1. Linear correlation coefficients ( $r$ ) for these plots are also provided in the figure

Calcium was intimately associated with C. There is a prevalence of Fe, Al, and Si in the maps, consistent with the findings that the soil clay fractions are dominated by aluminosilicate minerals and Fe oxides. There are also nano-sized Fe oxide coatings on the clay minerals.

To show explicitly the spatial relationship between C and other elements, we aligned each elemental OD map to common reference features and then compared OD values on a pixel-by-pixel basis to determine the correlation coefficients among the different elements (Fig. 2). Carbon showed a good correlation with Ca. C NEXAFS spectra data from these samples do not have the diagnostic peak for carbonate at 290.3 eV, and therefore,  $\text{CaCO}_3$  cannot account for the C–Ca correlation in these samples (Fig. 3). We can infer that all of the carbon observed is organic. The good C–Ca correlations may suggest that Ca plays an important role in C-mineral complex formation probably via “cation bridging” mechanisms. STXM maps from the footslope displayed better correlations between C and Fe than with Al and Si suggesting that Fe oxides, which exhibit high surface area and reactivity, are more important for complexing C than aluminosilicates in the soil clay fractions.

Spatially distinct regions within soil clay particles showed highly variable carbon functional group composition on scales of nanometers to micrometers. Two regions within the clay particles exhibited different NEXAFS spectra (Fig. 3). The black regions represented background without detectable amounts of carbon. The green region corresponded to a thicker region in the particles and appeared to be denser than the regions shown in red. The green region showed a strong peak at 285.3 eV corresponding to aromatic C and at 288.6 eV corresponding to carboxylic C. The spectra patterns from the green region are similar to spectra

**Fig. 3** Carbon NEXAFS spectra (a) from color-coded composite maps (b) showing the heterogeneity of C forms, with distinct regions in soil clay fractions from the upland hillslope at a soil depth of 0–15 cm. Spectral features identified by the shaded gray bands correspond to C in (I) aromatic, (III) carboxylic, and (IV) O-alkyl-C functional groups. The peaks at the higher energies result from the  $L_1$  and  $L_2$  edges of potassium (K)



taken of proteins. Compared to the green region, the red region is richer in O-alkyl C, as indicated by a strong peak at 289.5 eV (O-alkyl C) and to prominent peaks at 285.3 eV (aromatic C) and at 288.6 eV (carboxyl C). The spectra from the red region resemble the spectra of polysaccharides. Polysaccharides are structural components of cell walls of bacteria, fungi, algae, and plants. These spectra suggest that the organic matter coating could consist mainly of microbial structural metabolites or organic debris. The ratio of O-alkyl C to aromatics or to carboxyl C increased from the red to the green region, suggesting a greater contribution of polysaccharides, compared to proteins, in C-mineral complexation. Furthermore, the red regions are less dense and thinner than the green regions. This suggests polysaccharides are preferentially attached on thin and small particles or on the outer region of clay particles, while proteins are likely located at the denser, inner region.

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