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Micro- and nano-environments of C sequestration in soil: A multi-elemental STXM–NEXAFS assessment of black C and organomineral associations

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HIGHLIGHTS

- STXM-NEXAFS identified terminal micro- and nano-organic C repository environments in undisturbed organomineral assemblage
- Produced multi-element images and fingerprint of physically entrapped particulate black C, non-black C and mineral matter
- Provided submicron-level multi-element insight about the most likely binding mechanisms in the organomineral interface
- Provided evidence for a "two-way" direct associative interaction between black C, non-black C and mineral matter
- Provided evidence for "three-way" indirect molecular-level linkage between black C, non-black C and mineral matter

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ABSTRACT

Black C is an essential component of the terrestrial C pool and its formation is often credited as a CO_2 sink by transferring the fast-cycling C from the atmosphere–biosphere system into slower cycling C in the geosphere. This study is the first multi-element K- (C, N, Ca, Fe, Al and Si) soft-X-ray STXM–NEXAFS investigation conducted at a submicron-scale spatial resolution specifically targeting black C and its interaction with the mineral and non-black C organic matter in the organomineral assemblage. The STXM–NEXAFS micrographs and spectra demonstrated that pyrogenic C was dominated by quinoide, aromatic, phenol, ketone, alcohol, carboxylic and hydroxylated- and ether-linked C species. There was also evidence for the presence of pyridinic, pyridonic, pyrrolic, amine and nitril N functionalities. The non-black C organic matter contained amino acids, amino sugars, nucleic acids and polysaccharides known to exhibit negatively charged carboxylic, phenolic, enolic, thiolate and phosphate functionalities highly reactive towards metal ions and black C. The metal-rich mineral matrix was composed of phyllosilicate clay minerals, Fe and Al hydroxypolycations, oxides, hydroxides and oxyhydroxide that can attract and bind organic biopolymers. STXM–NEXAFS provided evidence for interactive association between pyrogenic C, non-black C organic matter and the mineral oxide and oxyhydroxide communities in the organomineral interface. These intimate associations occurred through a "two-way" direct linkage between black C and the mineral or non-black C organic matter or via a "three-way" indirect association where non-black C organic matter could serve as a molecular cross-linking agent binding black C with the mineral matrix or vice versa where inorganic oxides, hydroxides and polycations could act as a bridge to bind black C with non-black C organic matter. The binding and sequestration of black C in the investigated micro- and nano-C repository environments seem to be the combined action of physical entrapment in seemingly terminal biotic exclusion zone through the action of metal oxides and organic matter induced microaggregation and through molecular-level association ranging from ligand exchange, polyvalent cation bridging to weak hydrophobic interactions including van der Waals and H-bonding.

1. Introduction

Soils, the complex biomaterials that promote growth of terrestrial organisms, are an integral compartment of the Earth's environment and the central organizer of ecosystem processes interacting constantly with the atmosphere, biosphere, and hydrosphere as a

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consequence of natural cycles and human activities (Huang, 2004). Global soils represent the largest reservoirs of terrestrial organic C pool (3300 Pg) in the biosphere, storing more C than is contained in all living plants (560 Pg) and the atmosphere (760 Pg) combined (Tarnocai et al., 2009). If this vast amount of C is destabilized through anthropogenic intervention and climate change, it can lead to accelerated emissions of greenhouse gases and could make a significant difference in the Earth's atmospheric composition. Despite its importance, however, the underlying biogeochemical mechanisms that control the long-term sequestration of soil C and the potential to further increase the current soil C storage capacity are not yet well understood and the full potential for C sequestration in the Earth's surface remains unknown (Trumbore, 2009).

The earliest investigations of soil C were documented in the 18th century (Achard, 1786) and the importance of the association between C and minerals in soil has been recognized more than one hundred years ago (Schloesing, 1902). It is, therefore, all the more astonishing that the precise geobiological mechanisms for the interaction between minerals and organic C in soils are still largely unknown.

Soil organic C is composed of a complex mixture of organic compounds released from living plant and microbial cells to complex plant, animal and microbial residues ranging in size and complexity from simple monomers to complex biopolymers (Baldock and Skjemstad, 2000). Its composition is also strongly influenced by fire, which can thermally modify the structural chemistry of the incoming biomass and detrital C resulting in the formation of a suite of refractory carbonaceous substances ranging from partially charred biomass to highly graphitized soot; collectively referred to as black C (Preston and Schmidt, 2006). Black C is one of the most ubiquitous materials in the environment, and it is often regarded as a chemically and biologically stable C pool that can persist in nature for a very long time. The formation of black C is credited as a CO_2 sink by transferring fast-cycling C from the atmosphere–biosphere system into much slower cycling C in the geosphere (Lehmann et al., 2005). Further impetus for black C research arises from the fact that it plays a key role in a wide range of chemical processes due to its amphipathic nature, and may serve as an effective sorbent for potentially hazardous organic compounds and other pollutants in soils (Loganathan et al., 2009). Literature evidence suggests that the mechanisms for stabilization of black C in soils appear to be the result of physicochemical processes involving (i) selective preservation of recalcitrant C molecules and extracellular neoformations, (ii) spatial inaccessibility of C due to localized "biotic exclusion" zones and (iii) inter-molecular interactions between C and minerals (Sollins et al., 1996; Lützow et al., 2006; Solomon et al., 2007). One of the major limiting factors to past investigations is that these processes operate at the micro-, nano- and atomistic-levels, well below the scale that most studies were able to observe C. Most of the information gathered so far about organomineral associations and interfacial chemical processes was obtained indirectly from approaches that involve batch experiments, gas-sorption analysis and oxidative or other wet-chemical techniques often performed under adverse experimental conditions that may not preserve natural conditions (Haumaier and Zech, 1995). Therefore, direct multi-element evidence for the precise mechanisms operating at micro-, nano- and atomistic scales will constitute a major breakthrough in soil science and could generate unparalleled opportunities to sequester C for climate change mitigation. With the advent of non-invasive synchrotron-based scanning transmission X-ray microscopy (STXM) and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy techniques, it is now possible to circumvent the limitations of wet-chemical techniques and investigate not only the fine structures of C but also directly image organic C forms in nanometer spatial resolution (Kinyangi et al., 2006; Yoon et al., 2006; Lehmann et al., 2008). However, most of these investigations were conducted using beamlines optimized for C, but lacking energy fluxes to quantify the most abundant soil minerals restricting the information generated from these investigations mostly to C. STXM–NEXAFS has potential to access the K or L-edge of Ca, N, Fe, Al, Si and may lead to acquisition of spatially defined high-resolution geobiological information about submicron-C repository environments (Wan et al., 2007) and the molecular-level associations between organic C moieties, minerals and polyvalent metal ions, as well as other surficial and interactive features.

The objectives of the present investigation were (i) to identify, image and fingerprint the fine structures of black C present in intimate association with non-black C organic C and mineral matter in the micro- and nano-C repository environments of organomineral assemblage of a mineral soil and (ii) to conduct a submicron-level investigation of the compositional chemistry and interactive features of the various elements (N, Al, Si K-edge, and Ca and Fe $L_{2,3}$-edge) present in association with black C using novel non-destructive high-resolution STXM–NEXAFS spectromicroscopy.

2. Materials and methods

2.1. Study site description and sample background information

This study was conducted using soil samples collected from the Kakamega forest of western Kenya. The Kakamega forest is located at 00°14′19″N and 34°57′13″E. The natural vegetation is composed of tropical (*Aningeria altissima* A. Chev. and *Chrysophyllum albidum* G. Don) and montane (*Olea capensis* L. and *Croton megalocarpus* Hutchinson) forest tree species. The altitude of the area ranges from 1700 to 1800 m above sea level, with mean annual temperature of 19 °C and precipitation of 2080 mm. The soils of the area are well-drained, deep red to yellowish red, friable sandy clay loam to clay loam texture developed from undifferentiated basement system rocks and classified as Ferralo-Chromic Acrisols (FAO-UNESCO, 1997). The organic C content was 119 g kg^{-1} soil, total N was 11 g kg^{-1} soil, total S was 2.9 g kg^{-1} soil, with pH-KCl of 5.3. Detailed chemical properties can be found in Kinyangi et al. (2006).

2.2. Ultrathin section preparation

One gram of undisturbed soil was sieved to pass through a 250 μm sieve but trapped on a 150 μm sieve, and the free stable microaggregates were isolated. The microaggregates were sprinkled on a glass fiber filter (Whatman GF/A, 90 mm diameter), mounted onto a 1000 μm sieve surface, and fixed to a chimney funnel that transferred mist from a humidifier chamber filled with double deionized water. After 18 h of misting the microaggregates were considered to be water saturated. Excess droplets were drained off before shock-freezing the microaggregates. Lehmann et al. (2008) demonstrated that this procedure enables to observe the spatial arrangement of organic matter in organomineral assemblages without compromising the sample's spatial integrity. Approximately 150 μm diameter microaggregate subsample was selected and ultrathin section (400 nm) was produced at −55 °C using cryomicrotome. Glass knife attached to an ultramicrotome (Ultracut UTC, Leica Microsystems Inc., USA) was used for initial trimming and a diamond knife (Ultra 45 °C, Diatome Ltd., Switzerland) was employed for final cutting at 1.2 mm s^{-1}. The thin section was transferred to a silicon monoxide (SiO) impregnated copper grid (200 meshes, Ladd Research, USA) and stored in trays placed in wide mouth airtight Mason jar under argon environment. The Cu grid was mounted onto stainless steel sample stage plate for STXM–NEXAFS measurements. Details about the thin sectioning procedure are described by Kinyangi et al. (2006) and Lehmann et al. (2008).