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Contrasting Fe speciation in two humid forest soils: Insight into organomineral associations in redox-active environments

Elizabeth K. Coward [a,b,*], Aaron Thompson [c], Alain F. Plante [b]

[a] Delaware Environmental Institute, University of Delaware, Newark, DE 19716-7310, USA
[b] Department of Earth & Environmental Science, University of Pennsylvania, Philadelphia, PA 19104-6316, USA
[c] Department of Crop & Soil Science, University of Georgia, Athens, GA 30602-0000, USA

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Abstract

While the contribution of iron (Fe)-bearing minerals to organic carbon (C) stabilization in terrestrial systems is well-described, the influence of Fe solid-phase speciation on organomineral associations is unclear in highly dynamic, oxidation-reduction (redox)-active soils. In humid tropic forest soils, fluctuations in redox state accelerate weathering of Fe-bearing mineral phases, producing a spectrum of mineral sizes and bonding environments available for C stabilization, and confounding our understanding of C stability. Characterizing these Fe-bearing phases can improve predictions of the response of redox-active soil systems to climatic changes that may alter Fe mineral crystallinity and solubility, such as precipitation intensity, storm event frequency and temperature. Leveraging inorganic selective dissolution techniques, ^{57}Fe Mössbauer spectroscopy (MBS), specific surface area (SSA) analyses and X-ray diffraction (XRD), we investigated mineral speciation in surface soils of contrasting lithologies from the Luquillo Critical Zone Observatory (LCZO), Puerto Rico. The LCZO provides a model investigatory framework in which high C inputs to surface horizons by similar vegetation, topography and climatic forcings are intercepted by highly-weathered, volcaniclastic Oxisols or quartz diorite-derived Inceptisols, producing a gradient of Fe content and speciation. Strong correlations observed between Fe concentrations and extraction-induced changes in SSA indicated target Fe phases contribute substantially to SSA of the bulk mineral matrix. MBS analysis of untreated soils reveal both Oxisol and Inceptisol soils are largely composed of Fe^{III}-oxyhydroxides, accompanied by substantial Fe^{II} and silicate Fe^{III} contributions in Inceptisol soils. Fe^{III}-oxyhydroxides in the Oxisol soils were largely short-range-ordered (SRO), and notably, a fraction of particularly low-crystallinity Fe^{III}-oxyhydroxide mineral phases in these soils appear protected against harsh reductive dissolution, whereas the overall higher crystallinity Fe phases in the Inceptisol soils do not. These findings suggest that some high-SSA, SRO Fe^{III} phases, which likely also have high C sorption capacities, may be immobilized against reduction in these Oxisol soils. Consequently, C associated with these Fe^{III} phases may be preferentially stabilized in Oxisol soils, potentially driving disparate C mineralization and CO_2 production rates across contrasting lithologies.

Keywords: Fe oxides; Solid-phase speciation; C stabilization; Mössbauer spectroscopy

1. INTRODUCTION

Despite storing between one third and half of the global organic carbon (C) stock as soil organic matter (SOM) (Jobbágy and Jackson, 2000), humid tropical forest soils are dynamic systems, with high temporal and spatial variability in C stabilization. These soils support the fastest

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* Corresponding author at: Delaware Environmental Institute, University of Delaware, Newark, DE 19716-7310, USA.
E-mail address: ekc@udel.edu (E.K. Coward).

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rates of decomposition globally, have the highest soil CO_2 fluxes of any terrestrial biome (Raich and Schlesinger, 1992), and are often characterized by fluctuating oxidation-reduction (redox) dynamics that vary across the landscape. Copious precipitation, warm temperatures, finely-textured mineral matrices, and high soil respiration rates drive oxygen (O_2) availability over scales of hours to weeks (Silver et al., 1999; Schuur et al., 2001; Cleveland et al., 2010; Liptzin et al., 2010). Such frequent redox oscillations may partly explain the diversity in C residence times in these systems, as much of the C in surface soils may be complexed with the abundant iron (Fe)-bearing minerals present in humid tropical soils, which are themselves susceptible to O_2-driven changes in speciation and reactivity.

Under consistent oxic conditions, the accumulation of secondary short-range-ordered (SRO) minerals(e.g., ferrihydrite [$5Fe_2O_3{\cdot}9H_2O$; Fh] or nano-phase goethite [α-FeO (OH); n-Gt]) is followed by slow transformation to crystalline Fe-oxides such as hematite [α-Fe_2O_3] (Shoji et al., 1993); while under consistent anoxic conditions, reductive dissolution of all phases can ensue (Bonneville et al., 2004). Short-range crystal order and small particle sizes distinguish the most reactive, high-surface area Fe components from larger bulk Fe-oxides (Bonneville et al., 2004; Roden, 2006). These SRO minerals are thus the most reactive phases for a range of processes including chemical stabilization of SOM (Stumm, 1987; Deng and Stumm, 1994; Kögel-Knabner et al., 2008), particle adhesion, and reductive dissolution (Sulzberger et al., 1989; Lovley et al., 2004).

The structure and stability of Fe-OM associations are important to a suite of ancillary ecosystem processes. Covering soil mineral surfaces with OM can inhibit sorption of ionic compounds (Lang and Kaupenjohann, 2003), enhance sorption of non-ionic compounds such as organic contaminants (Murphy et al., 1990), inhibit mineral dissolution (Welch and Vandevivere, 1994; Welch et al., 1999), and critically alter charge characteristics of soil surfaces (Chorover et al., 2004). In addition, the manner in which OM associates with mineral surfaces (e.g., surface bonding through covalent or ionic bonds vs. co-precipitation in mineral structures vs. aggregation-based association) may influence OM stabilization in soils and sediments (Mayer, 1994; Kaiser and Guggenberger, 2003; Mayer et al., 2004). As such, understanding the influence of Fe solid-phase speciation on organomineral associations may prove critical to predicting the response of these soils to changes in global climate and land use (Post and Kwon, 2000).

While stabilization of SOM by Fe-bearing phases via adsorption, co-precipitation, and outer-sphere mechanisms is well-documented across terrestrial ecosystems (e.g., Eusterhues et al., 2005; Wagai and Mayer, 2007; Kögel-Knabner et al., 2008), our understanding of the role of Fe solid-phase speciation in organomineral association is continuously developing. This is in part because quantifying Fe-OM association processes is an analytically challenging enterprise. Fe mineral composition is not fixed, but rather evolves dynamically in response to environmental conditions that drive precipitation and reductive dissolution of Fe phases. Fe-bearing mineral phases are typically assessed by selective chemical extractions, infrared spectroscopy and electron microscopy because they are difficult to detect using standard powder X-ray diffraction (XRD) techniques (Chorover et al., 1999; Mikutta et al., 2009).

This work leverages a previously described set of inorganic selective dissolution techniques (Coward et al., 2017), and new ^{57}Fe Mössbauer spectroscopy (MBS) experiments at 295, 77 and 5 K to distinguish between crystalline and short-range-ordered ferrous and ferric Fe species. MBS is capable of precise physical measurements of Fe nuclear energy levels, which facilitates detection of Fe phase composition and crystalinity. This work aims to quantify and characterize the contribution of Fe-bearing phases to OM associations in surface soils of contrasting lithologies from the Luquillo Critical Zone Observatory (LCZO). To do so, three physicochemical features of Fe-bearing phases were assessed pre- and post-selective dissolution: mineral composition, specific surface area, and Fe solid-phase speciation, which together allow for a thorough evaluation of often-unresolvable minerals. The LCZO provides a model field system for investigating Fe-OM associations as similar vegetation provides a consistent, substantial input of C to all surface horizons, which are underlain by either highly-weathered, volcaniclastic Oxisols or quartz diorite-derived Inceptisols. These conditions produced OM-rich mineral soils across a similar climatic setting, yet with large differences in soil Fe content and mineral composition, allowing for direct comparisons in Fe speciation and speciation-driven OM stabilization capacity.

2. MATERIALS AND METHODS

2.1. Notation

A list of abbreviations used in this text and their operational definitions is provided in Table 1.

2.2. Study site and sampling

Soil samples originated from an extensive sampling campaign completed in 2010 (Johnson et al., 2015). Across the humid tropical montane forests of the LCZO, 216 quantitative soil pits were dug, transecting gradients in rainfall, temperature, topography (ridges, slopes, and valleys), and two primary parent materials (quartz diorite and sedimentary rocks of volcanic origin) in a complete factorial design. The two parent materials differ substantially in their mineral composition (Stallard, 2011; White et al., 1998; Porder et al., 2015) and chemistry (Mage and Porder, 2013; Porder et al., 2015). The volcaniclastic rocks comprise the Fajardo, Tabonuco and Hato Puerco formations and contain volcanic sands, breccias, tuff, conglomerates, and calcareous limestone that accumulated on the sea floor and underwent greenschist-grade metamorphism in the Eocene (Porder et al., 2015). The primary mineral matrix is dominated by plagioclase, clinopyroxene, and hornblende, chlorite and hydrothermally-generated quartz (Murphy et al., 1998; Murphy et al., 2012). Volcaniclastic rocks range between 47% and 55% SiO_2, 5–10% CaO,