Iron-mediated organic matter mineralization during redox fluctuations

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Iron (Fe) oxidation and reduction driven by biotic and abiotic processes, are closely linked to the biogeochemical cycling of carbon (C), phosphorus, nitrogen, and cations. Fe redox cycling plays an important role in organic matter (OM) preservation and mineralization. In this study, we sought to quantify how redox oscillations affect Fe speciation and reactivity, as well as OM mineralization. We hypothesized that shifts in redox conditions and Fe reduction and oxidation (and re-precipitation) will alter the mineralization of OM compounds and Fe (hydr)oxide mineral crystallinity. To test this hypothesis, we amended ¹³C-labeled DOM (dissolved organic matter) and ⁵⁷Fe-enriched Fe(II)_{ag} to soil slurries along with associated no-addition control soil slurries. We incubated these soil slurries under either static oxic (21 d) or fluctuating redox (5 d oxic followed by 11 d anoxic and then another 5 d oxic conditions) conditions. Throughout the experiment, we tracked Fe(II), 57Fe, CO2 and 13CO2 and documented Fe mineralogical changes using 57Fe Mössbauer spectroscopy. During the initial oxic period, Fe(II) oxidation resulted in the formation of ⁵⁷Fe-lepidocrocite and -goethite. In the no C-added control, the Fe(II) oxidation period stimulated soil OM mineralization (CO₂ production), likely due to the generation of reactive oxygen species via fenton reactions. In contrast, in the DOM-amended treatments, Fe(II) oxidation decreased DOM concentration and suppressed DOM-derived CO₂ production, likely because OM-Fe(III) oxide complexes were formed. After transitioning to anoxic conditions, both DOM and Fe additions stimulated Fe(III) reduction, the release of DOM and promoted mineralization of the added DOM over native soil OM. In fact, despite lower total CO₂ production in the anoxic period than in the oxic period, DOM-derived CO₂ production was greater under anoxic conditions than under oxic conditions for the DOM and Fe addition treatment, where Fe(III) reduction was most rapid. This suggest that rapid Fe(III) reduction may stimulate the anaerobic mineralization of the recently stabilized DOM and may therefore accelerate C losses. This study provides the mechnistic understanding of the linkage of soil redox conditions to Fe-mediated biogeochemcial mechanisms of C stablization and loss.