Title: **Association Between Soil Organic Carbon and Calcium in Acidic Grassland Soils from Point Reyes National Seashore, CA**

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Project Abstract: Organo-mineral association and complexation processes are important for the retention and accumulation of soil organic carbon (SOC). Most of the research into these processes has focused on the biogeochemical interactions between SOC and Fe or Al, largely overlooking a role of Ca. Recent studies have demonstrated a strong link between calcium (Ca) and soil organic carbon (SOC) in a range of soil types (Rasmussen et al., 2018; Rowley et al., 2021; Yang et al., 2020), but a current paradigm suggests that Ca-mediated accumulation of SOC is predominantly constrained to soils with carbonates (pH > 6; Rowley et al., 2018).

To investigate the role of Ca in SOC accumulation of acidic soils, we combined classical characterisation and synchrotron-based spectro-microscopic methods to analyse three soil cores taken from grasslands with a pH gradient (soil pH 3.8 - 5.3) at the Point Reyes National Seashore, California. Bulk soil samples were characterised in detail, measuring classical soil physical (texture), mineralogical (X-ray diffraction), and chemical properties (pH, SOC, exchangeable and total elements). Subsequently, bulk Ca K-edge spectra were obtained for the core samples at three depths. We also used microprobe-coupled μ-X-ray absorption spectroscopy (μ-XANES; Ca K-edge) and STXM (Ca L-edge and C K-edge) to investigate the bonding environment of Ca and C in our samples, and their association with other elements (Al, Fe, K, Mg, Na, P, S, and Si).

Both the Ca and SOC content were high in our samples and were correlated in multivariate analyses of our standard characterisation dataset. Linear combination fitting of the bulk Ca K-edge XANES data revealed that Ca was predominantly associated with organic matter at our site. Additionally, STXM analysis showed that Ca had a strong spatial correlation with C, presenting a

higher spatial correlation than C with Fe. In characterising the SOC, we demonstrated that C associated with Ca had higher peaks in the alkyl and aromatic regions of the C K-edge spectra, relative to C associated with Fe or Fe-Ca-C. These spectral features are consistent with published spectra of C with a lignin-like nature and were observed in samples obtained from up to 70 cm depths. It therefore seems that Ca-C association is linked to the preservation of more plant-like products, even at depth in acidic grassland soils with no carbonate, potentially challenging existing paradigms (Rowley et al., 2018) that these Ca-mediated processes are only found in soils with a pH > 6.5.

References.

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