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Investigating the complexation of soil organic carbon by calcium using spectroscopy and thermodynamics.

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Organo-mineral association and complexation processes are important for the retention and accumulation of soil organic carbon (SOC). However, most of the research into these complexation processes has focused on the biogeochemical interactions between SOC and Fe or Al, largely overlooking a role of Ca. Recent studies have shown the Ca can be linked to increased organo-mineral association in soils with a circumneutral to alkaline pH (> 6), but these processes are largely thought to be non-existent in acidic soils (Rasmussen et al., 2018; Rowley et al., 2018, 2021). To evaluate this paradigm, we investigated the complexation of SOC by Ca in experimental and acidic soils using isothermal titration calorimetry (ITC) and synchrotron-based spectro-microscopy.

Standard organic compounds and soil extracts were complexed with Ca, measuring thermodynamic parameters of these processes with ITC at different pH levels. Shifts in their C K-edge and Ca L-edge spectra were also measured using scanning transmission X-ray microscopy (STXM). We then investigated the interaction between SOC and Ca in the acidic soils of Point Reyes National Seashore, CA, which were characterised using traditional techniques. Calcium K-edge X-ray absorption spectra were collected on standard compounds and bulk soil samples. Additionally, organo-metal associations in our samples were investigated using micro-probe coupled X-ray absorption spectroscopy (μ-XAS) and STXM.

The ITC managed to accurately produce thermodynamic parameters for different complexes, while STXM demonstrated a shift in the C k-edge spectra of standards during complexation by Ca. Though the Point Reyes soils were acidic in nature, STXM also confirmed that Ca presented a higher spatial correlation with C, relative to Fe-C. The C spectra associated with Ca differed from those associated with Fe or Fe-Ca-C, highlighting a link between Ca and C with a lignin-like signal, even at 70 cm depth. This work implies that there might be a preferential stabilisation of specific functional groups by Ca, even in acidic soils, where Ca complexation processes may still play a role in the accumulation of C. This work also highlights that the coupling of spectroscopic and thermodynamic techniques could be used to further investigate the bonding of metals and carbon in soils.