Joining STXM-NEXAFS and NanoSIMS technologies to map soil mineral-organic microstructures isolated from a decadal 15N litter experiment

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Mineral-organic associations are increasingly recognized as playing a key role in the retention of carbon (C) and nitrogen (N), but little is known on how organic compounds interact with mineral surfaces. To make inferences on mechanisms that govern the association, we imaged several soil microstructures at a scale relevant to mineral-organic interactions combining Scanning Transmission X-ray Microscopy coupled with Near Edge X-ray Absorption Fine Structure Spectroscopy (STXM-NEXAFS) and Nanoscale Secondary Ion Mass Spectroscopy (NanoSIMS). We took advantage of a 12 years-old litter 15N experiment conducted in a German forest and expected the combination of the two technologies to localize the 15N tracer at the surface of soil microstructures (NanoSIMS) and to characterize the chemistry of the surrounding organic matter (STXM-NEXAFS).

Few mineral-organic particules isolated from the 0-2.5 cm depth soil horizon were deposited as dry powder on individual Si3N4 windows. No pressure was applied to preserve the spatial distribution of C, N relative to oxygen, which is used to locate the inorganic material in the association. Samples were successively investigated using STXM-NEXAFS and NanoSIMS. We disregarded particles with optical density greater than 2.0 at any energy between 278 eV and 330 eV, i.e. the energy range of our carbon K-edge spectra. This limited selection to those smaller than approximately five microns. We collected stacks in the region of 278 eV to 330 eV for carbon NEXAFS. The NanoSIMS mapped C and N at the surface of soil structures, along with the 15N/14N ratio with a spatial resolution of 80 nm. The estimated sputtered thickness roughly corresponds to 150-250 nm. Even though organic matter covered very small areas, the analytical precision on the isotopic ratio was good enough to identify spatially resolved domains with the 15N label.

STXM and NanoSIMS images consistently indicated that C and N found in soil microstructures are heterogeneously distributed, which lead to spatially highly variable C/N ratios. The close comparison of images revealed some differences that likely result from acquisition methods. Indeed, when STXM sums contribution from the entire line of sight, the NanoSIMS only acquires data from the surface of the sample. NanoSIMS images revealed that N-rich areas are often found at the edge of the structures, likely indicating a thin microbial coating spread at the surface of soil microstructures. Even though the soil was exposed to a low 15N labelling, we succeeded in localizing sub microns 15N hotspots. NEXAFS spectra were extracted on these regions of interest to determine whether the label is included in organic matter processed by microorganisms.

This study shows that the combination of STXM and NanoSIMS techniques is promising to study mineral-organic interactions in natural complex structures at a relevant scale to understand molecular processes ruling the stabilization of organic components in soil. While both techniques have technical limitations, future methodological improvements will lead to applications interesting a broader community of biogeochemists.