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Macro to Nanoscale Approaches to Study Mineral Transformations at the Liquid, Organic, Biological Interface.

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Rocks and mineral-based assemblages on Earth's surface are exposed to weathering processes, such as chemical mediated weathering influenced by percolation of meteoric waters and reactions with atmospheric CO_2, and biogenic driven weathering. These biogeochemical processes lead to mineral transformation, dissolution, and release of nutrients in the environment, which are vital for plant and microbial life cycle. Mineral transformations and dissolutions frequently occur at the grain-fluid and at the grain-microbe interfaces, via direct (chemical) and indirect (biological/chemical) weathering mechanisms. Investigating the mineral-fluid and mineral-microbe interface at submicron, nanoscale, and atomic scale can provide insights on the fundamental knowledge gaps about mechanisms of biotic and abiotic processes.

Here we present results attained with scanning electron microscopy equipped with Focused Ion Beam and energy dispersive X-ray Spectroscopy (SEM/FIB/EDX) in conjunction with transmission electron microscopy (TEM), aimed at assessing processes and reactions at the mineral-fluid-microbe interface. We present four electron microscopy approaches that address i) nucleation and transformation at the mineral-water interface; ii) interaction at mineral-organic matter interface; iii) contaminant sorption and fate in mineral soil and organic matter (OM); and iv) (bio)mineralization at mineral-microbe interface.

i. The transformation mechanisms of crystalline Fe(oxy)hydroxides, lepidocrocite and goethite, from the reductive dissolution of $Fe(OH)_3$ with Fe^{2+} has not been fully resolved. We studied transformation of $Fe(OH)_3$ at the mineral-liquid interface by applying a quasi in-situ SEM/TEM/cryoTEM method[1]. We observed incipient nucleation of crystalline Fe-(oxy)hydroxides at earlier induction time than previously thought (30 min.). In addition, we captured the nucleation and growth of lepidocrocite as 2D nano layer and the outward growth of goethite with irregular growth fronts. The results elucidate the mass transfer mechanism of $Fe(OH)_3$ transformation.

ii. Stability of OM in soil ecosystems depends on interaction between organic molecules and soil minerals and is directly correlated with the type of mineral and its specific surface area. To develop a fundamental understanding of OM stability and the mechanism of OM-mineral association we used the cryo-SEM system that examined mineral-OM interfacial region. This approach preserved the spatial orientation and association of organic molecules with mineral ($CaCO_3$) grains facilitating further interrogation of grain-OM boundaries with other methods, TEM and Atomic Probe Tomography.

iii. Nanosize particles of contaminants, released from mine tailings, pose increasing risks to humans and to biological life. Understanding the association of nanoparticulates (Ag, Co, As) with soil minerals and/or OM, is imperative for predicting contaminant fate and transport in soil environment. We used a traditional SEM/EDX/FIB/TEM method to investigate nanoparticles in the organic rich materials collected from the surface of contaminated soils. Interrogation of OM interfaces at high resolution with FIB/TEM revealed accumulation of nanoparticles within or attached to the layers of $Fe(OH)_3$, which had mineralized inside the OM matrix.

iv. Microorganisms interact with rocks and minerals in the soil, contributing to mineral (bio)weathering and secondary (bio)mineralization[2]. However, one remaining challenge is to separate biogenic from abiotic mineral weathering processes particularly in rocks and minerals collected from field experimental sites. We used FIB to expose and image the vertical cross-section of a pyroxene grain that was deployed for 1 year in natural environment. Characterization of fungi-mineral interfaces with TEM permitted not only identification of Fe-rich secondary precipitates found near fungal hyphae but the assessment of biogenic and abiotic controls of their formation.

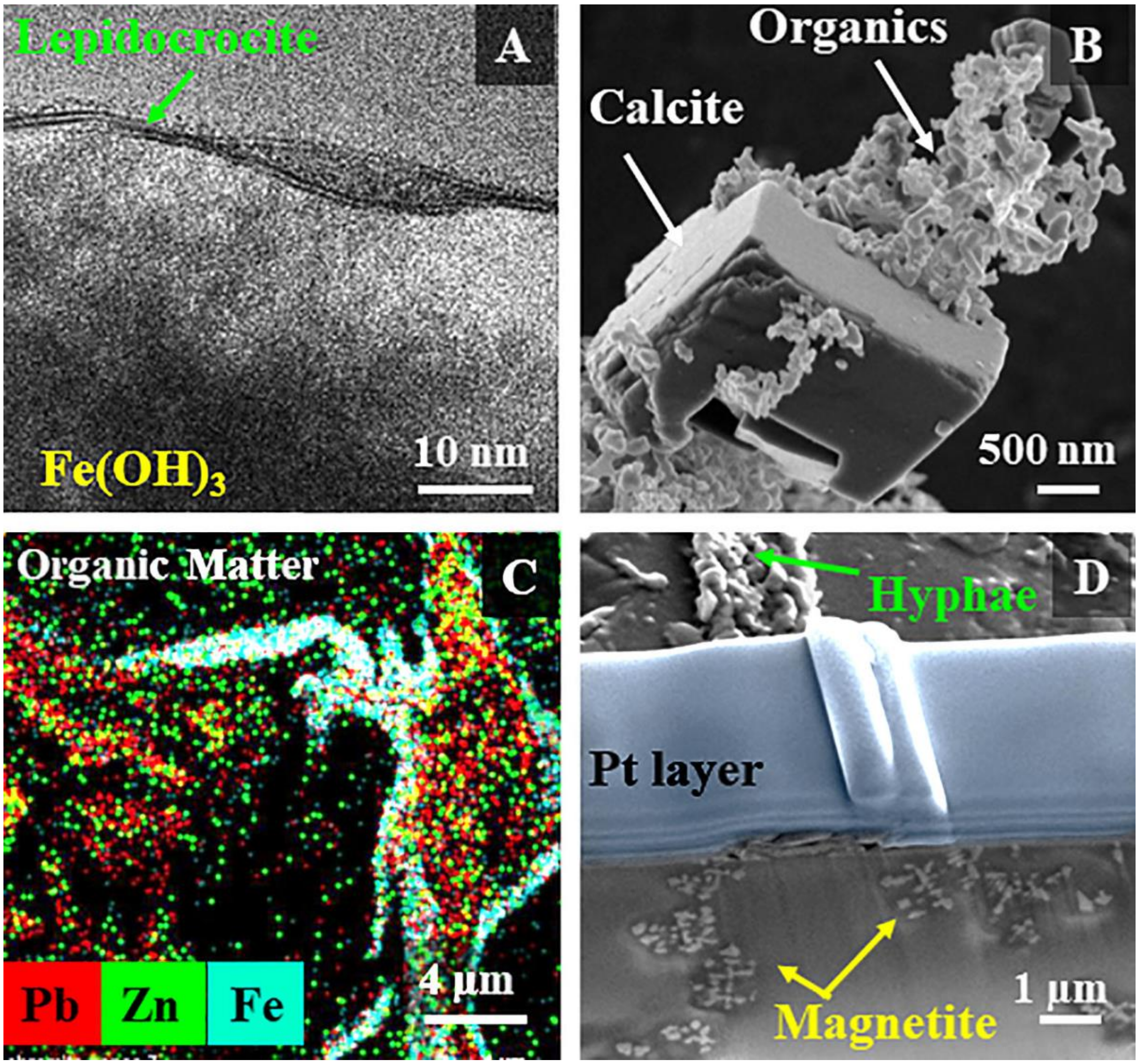

Figure 1. Collection of images demonstrate four electron microscopy approaches that investigate fluid - mineral - microbe interfaces, A) two dimensional lepidocrocite nanolayer nucleation on Fe(OH)3; B) interaction of calcite crystal with OM; C) distribution of nanocontaminants within the OM and Fe(OH)3 D) vertical cross section of mineral-fungi interface showing Fe-rich (mangetite) nanoparticles next to fungi hyphae, which is adhered to a pyroxene grain.

References

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[2] Lybrand et al., *Sci. Rep,* 2019, 9:5377, https://doi.org/10.1038/s41598-019-41357-0

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