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Non-reductive, ligand-promoted dissolution is responsible for enhanced weathering of ferric (oxy)hydroxides in the Pine (mycor)rhizosphere

RYAN VINCENT TAPPERO[1], HUI-LING (SUNNY) LIAO[2], JENNIFER BHATNAGAR[3], COLIN AVERILL[4], KO-HSUAN (KOKO) CHEN[5], KAILE ZHANG[2], ADESUWA ERHUNMWUNSE[2], PAUL NORTHRUP[6], TIFFANY VICTOR[1], SARAH L NICHOLAS[1], LIAM MCCARTHY[1] AND RYTAS VILGALYS[7]

[1]Brookhaven National Laboratory
[2]University of Florida
[3]Boston University
[4]ETH Zürich
[5]Academia Sinica
[6]Stony Brook University
[7]Duke University

Presenting Author: rtappero@bnl.gov

Iron (Fe) is an essential plant nutrient and cofactor of numerous plant enzymes but exists in soil as sparingly-soluble minerals and coatings (e.g., oxyhydroxides). We hypothesize that biogeochemical perturbations due to ectomycorrhizal symbiosis can cause enhanced weathering of soil minerals leading to a larger pool of bioavailable nutrients for plant uptake. We used the well-established ectomycorrhizal *Pinus-Suillus* model symbiont system to investigate Fe dynamics across the plant-mycorrhiza-soil interface. *P. contorta* seedlings were inoculated with *Suillus brevipes* (SB 120) and then grown for two months in a nutrient-poor sand culture supplemented with ferrihydrite-coated sand. Morphological changes to roots were visibly evident for the ectomycorrhizal fungi (EMF) treatments. *In-situ* X-ray fluorescence (XRF) imaging revealed spatial and chemical differences between the +EMF and -EMF treatments. The *Pinus-Suillus* system contained roots with a fungal sheath enriched with iron. Microcosms lacking EMF contained predominantly unaltered grains of iron-coated sand following the 2-month growth period while those with EMF contained grains with severely altered coatings that had 'disintegrated' near roots. Time-series XRF imaging of the mycor(rhizosphere) showed an expanding interaction zone around roots. Spatially-resolved Ca K-edge micro- X-ray absorption spectroscopy (µXAS) revealed the presence of tiny Ca-oxalate crystals in the (mycor)rhizosphere and Fe K-edge µXAS identified an Fe(III) organometallic complex associated with the fungal sheath surrounding +EMF roots. As a direct consequence, *P. contorta* root cortical cells are bathed continuously with Fe(III)-chelators similar to ones used in hydroponics solutions. Early indications from this work are that the plant uses its Fe-reductase system to acquire Fe(II) from the pool of Fe(III)-chelators at the plant-microbe interface. Future work planned at harvest includes OMICS, bulk tissue analyses, and *ex-situ* imaging of radial sections to interrogate Fe speciation in root cortical cells and the Hartig net. These findings support the hypothesis that ectomycorrhizal symbiosis enhances mineral weathering and can dissolve Fe coatings and transform them into plant-available forms without reduction, which in turn enhances plant biomass.

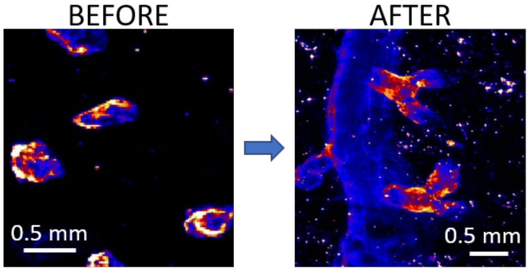
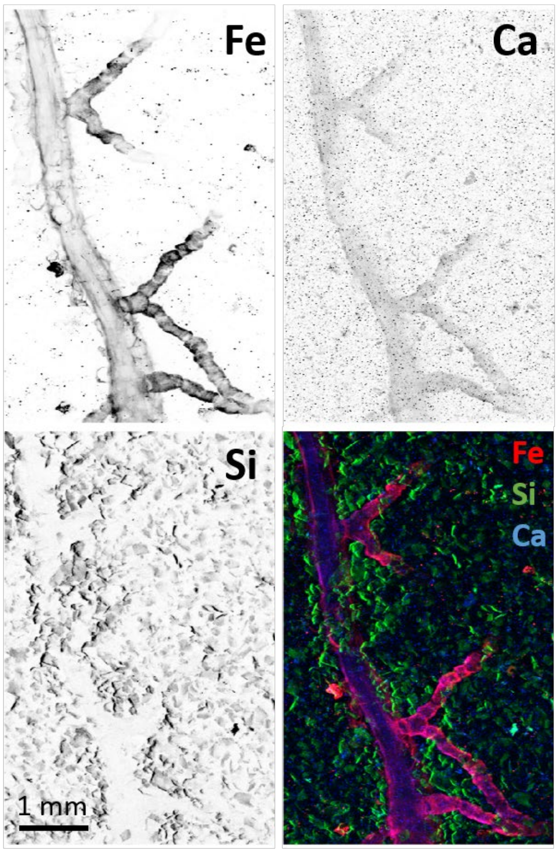


Image of iron (Fe) in model soil before and after 2 months mutualistic growth of *Pinus-Suillus*.



In-situ X-ray fluorescence (XRF) images of iron (Fe), silicon (Si), and calcium (Ca) in *Pinus-Suillus* rhizosphere after 2 months mutualistic growth. Images from the XFM Beamline at the NSLS-II.