

Characterizing the localization of organic C on mineral surfaces: a correlative microscopy/spectroscopy approach

Odetta Qafoku¹, Brian O'Callahan¹, Qian Zhao², Mark Bowden³, Ravi Kukkadapu², John Loring² and Amity Andersen²

¹Environmental Molecular Sciences Laboratory, Richland, Washington, United States, ²Environmental Molecular Sciences Laboratory, United States, ³Pacific Northwest National Laboratory, United States

It is estimated that the quantity of organic carbon (OC) in soils exceeds the amount of OC in the atmosphere and vegetation pools combined.¹ Given the current changes in climate, the fraction of OC sequestered in soils and sediments is more sensitive to decomposition and release as CO₂ in the atmosphere. Evidence implies that sorption and association of dissolved OC with inorganic soil components, i.e., soil minerals, is a key mechanism that contributes to stabilization and retention of OC in soils². Studies have shown a direct correlation between sorption of dissolved OC and soil mineral surface properties and their surface area. In addition, properties of organic compounds such as their chemical structure and functional groups play a significant role in the interaction of dissolved organic species with mineral surfaces. Association of OC with minerals via ligand exchange reactions, polyvalent tertiary bonding, or complexation with metal ions, is found to be preferential and dependent on the organic compounds' functional groups.³

Here, we present a macroscopic and spectroscopic correlative method that includes nano to macroscale measurements and gives insights into OC interaction with common soil minerals. The data are attained with scanning electron microscopy equipped with energy dispersive X-ray Spectroscopy (SEM/EDX), Infrared Scanning Near-field Optical Microscopy (IR-SNOM), and X-ray Photoelectron Spectroscopy (XPS). We investigated interaction of Fe, Al, and Ca - soil minerals with four organic compounds that represent major classes of soil organic matter, namely lipid, protein, carbohydrate, and lignin. The experiments included reaction of organic compounds with mineral powders for investigating sorption specificity in connection with organic chemical structure, and for probing changes in organic species following the reaction. In addition, experiments with mineral single crystals were performed to investigate the interaction and possible accumulation of organic species at specific surface sites.

IR-SNOM (Fig. 1) was used for collecting chemical IR maps of mineral powders and single crystals after they were reacted with individual and with the mixture of four organic compounds and compared with attenuated total reflection infrared spectroscopy. The SEM/EDX and chemical IR correlative maps of mineral powders gave insights into the composition of organic species after reaction, demonstrating that lignin and amino acid were the main components that took part in the organic compounds' arrangement. Meanwhile XPS and chemical IR maps of mineral single crystals gave insights on localization and spatial distribution of organic compounds at mineral surface sites. The results from this correlative approach combined with theoretical molecular dynamics (MD), suggest that the interaction of organic compounds with mineral surfaces occurred at step and etch voids and consequently at higher energy surface sites.

Our results give mechanistic insights onto OC sorption on mineral surfaces. Understanding the pathways of how mineral-organic driven interactions stabilize the organic matter in soil and sediments will contribute in predicting OC residence time and its persistence in environment.

Acknowledgement

A portion of the research was performed using EMSL (grid.436923.9), a DOE Office of Science User Facility sponsored by the Office of Biological and Environmental Research.

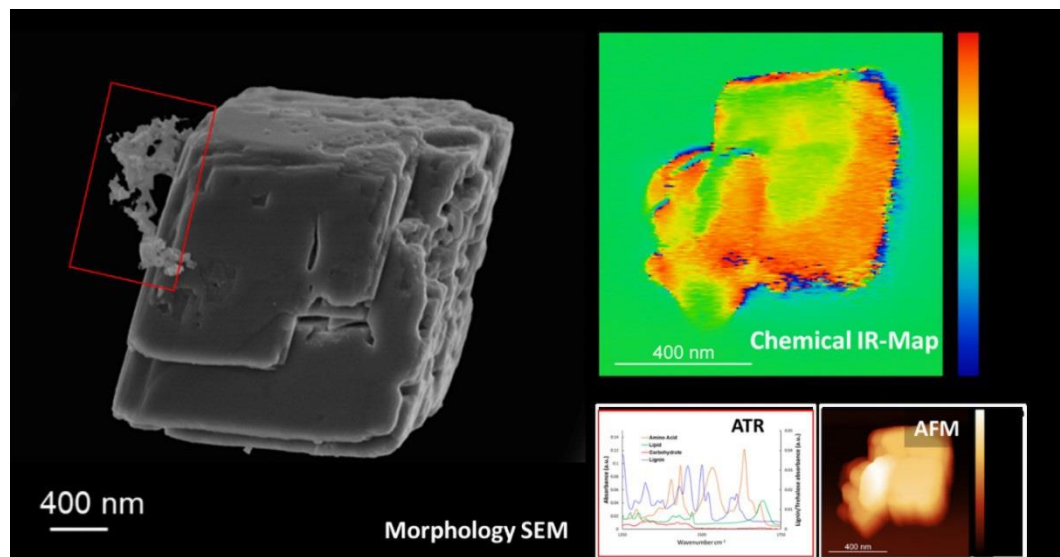


Figure 1. Left, SEM image shows calcite morphology and the presence/accumulation of organic compounds (area in red) nearby calcite particle. Right, map of Infrared absorption at 1500 cm⁻¹ of calcite nanocrystal reacted with the mixture of 4 organic compounds for 7 days. Corresponding ATR spectra of organic compounds and AFM nanocalcite topography is also shown.

References

- [1] Schmidt, M. W. I.; Torn, M. S.; Abiven, S.; Dittmar, T.; Guggenberger, G.; Janssens, I. A.; Kleber, M.; Kögel-Knabner, I.; Lehmann, J.; Manning, D. A. C.; Nannipieri, P.; Rasse, D. P.; Weiner, S.; Trumbore, S. E. Persistence of soil organic matter as an ecosystem property. *Nature*, 2011, 478 (7367), 49-56.
- [2] Hemingway, J. D.; Rothman, D. H.; Grant, K. E.; Rosengard, S. Z.; Eglinton, T. I.; Derry, L. A.; Galy, V. V. Mineral protection regulates long-term global preservation of natural organic carbon. *Nature*, 2019, 570, 228–23.
- [3] Kleber, M.; Sollins, P.; Sutton, R. A conceptual model of organo-mineral interactions in soils: self-assembly of organic molecular fragments into zonal structures on mineral surfaces. *Biogeochem.*, 2007, 85, 9–24