Nano-scale investigation of organic C sequestration and distribution on Fe oxides during ferrihydrite transformation: Effect of Al substitution

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Soil organic matter (SOM) is an essential component for global carbon (C) cycling and affects the mobility of nutrients and metals in soils. Iron (Fe) oxides are known to strongly interact with SOM and play a vital role in soil organic C stabilization. Poorly crystalline Fe oxides, such as ferrihydrite, can sequestrate a large amount of C via sorption or coprecipitation. Meanwhile, ferrihydrite can undergo a transformation process into more crystalline minerals, which is often accompanied by the presence of foreign elements, e.g., aluminum (Al), in natural environments. However, it is still unclear how the presence of Al affects the retention and the spatial distribution of organic C on Fe oxides during the Fe oxide transformation process.

In this study,^[1] the sorption capacity of Al-substituted Fe oxides for organic C was quantified and the spatial distribution of organic C species was visualized at different aging times of Fe oxides. Spherical aberration corrected scanning transmission electron microscopy (Cs-STEM) and X-ray diffraction (XRD) results indicated that the Al-substitution slowed down the ferrihydrite transformation rate and changed the transformation products from rhombus-shape hematite into shuttle- and diskshape. Wet chemistry experiments showed that Al-substitution in ferrihydrite increased the sorption capacity of organic C during the transformation process. Electron energy loss spectroscopy (EELS) results demonstrated that the carboxyl C was preferentially sorbed onto the surfaces of Fe oxides, forming the inner layer of the organo-mineral interfaces, while the aromatic C was dominantly bound to the outer layer of the organo-mineral interfaces, which supported the layer-by-layer "onion" model of organic C accumulation on minerals. In addition, Al-substitution promoted the sorption of aromatic C at the outer layer of the organo-mineral interfaces. Overall, our results help to elucidate the mechanisms of organic C sequestration during the Fe oxide transformation process in the presence of Al, which would be helpful for understanding the persistence and dynamics of SOM at the nano-scale.

[1] Fu Liu, et al. (2022) Environ. Sci.: Nano, 9, 4007-4017.