Goldschmidt 2026 Abstract
https://doi.org/10.46427/gold2026.36541

Dynamic Mineral–Organic Carbon Interactions: Influences of Mineralogy and Dissolved Metals

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Organic carbon (OC) dynamics is strongly influenced by minerals in soil and aquatic environments. Chemical sorption of OC by minerals can protect it from microbial respiration and influence C cycling. Laboratory and field studies have shown that the magnitude of OC sorption varies with mineral composition, surface area, and surface chemistry, and it can be modified by dissolved metals like Mg^{2+} and Ca^{2+}. However, the interplay between mineralogy and dissolved metals on OC preservation, particularly its composition, remains unclear.

We examined mineral–dissolved OC reactions for up to 180 days and characterized the samples using optical, FTIR, and C-XANES spectroscopies, and mass spectrometry (ESI-FT-ICR/Orbitrap). The minerals included quartz, calcite, 1:1 clay (kaolinite), 2:1 clay (smectite), Fe-oxide (goethite), Al-oxide (boehmite), Mn-oxide (δ-MnO_2), and a disordered Al-silicate (allophane), representing diverse soils and sediments. Mineral reactions were also examined in the presence of Mg^{2+} or Ca^{2+} at concentrations common in nature.

We found that mineralogy significantly influenced the magnitude and kinetics of OC sorption. Quartz and calcite retained the least OC, while Fe-/Al-oxides retained the most, with clays, Mn-oxide, and disordered Al-silicates in between. Dissolved metals enhanced the OC sorption by Mn-oxide and disordered Al-silicates, but weakly for other tested minerals. OC adsorption kinetics was also faster for Fe-/Al-oxides, with almost complete sorption in 24 h followed by slow kinetics. Clay minerals similarly began with quick OC uptake within the first 100–150 h, followed by slower sorption. Notably, Mg^{2+} or Ca^{2+} accelerated the sorption kinetics for affected minerals.

Spectroscopy and FT-ICR studies reveal that mineral adsorption induced strong OC fractionation, which was influenced by the mineral surface chemistry, reaction time, and dissolved metals. Major differences were observed for condensed aromatics, less-conjugated aromatics, and unsaturated, carboxyl-rich aliphatics at short time scales, exhibiting distinct two or three stages. Adsorption of aromatics continued over longer durations for all minerals.

We present a summary of how mineralogical and chemical variations impact mineral–OC interactions, and a comparison of these results with field observations of OC compositions from diverse soils, highlighting the importance of minerals on the abundance, composition, and cycling of OC in Earth surface environments.