Goldschmidt 2025 Abstract
https://doi.org/10.7185/gold2025.30495

Spectroscopic and computational investigations of organic phosphorus recycling catalyzed at iron oxide interfaces

LUDMILLA ARISTILDE

Northwestern university

Iron (Fe) oxides are well known to play an important role in phosphorus (P) cycling in aquatic and terrestrial environments by trapping orthophosphate (P_i) and phosphorylated organic compounds (P_{org}). Beyond adsorption, Fe oxides provide catalytic surfaces fto transform P_{org} biomolecules to generate P_i, but current models of P cycling consider P_{org} mineralization only as an enzyme-mediated process do not include the role of minerals as catalysts. Here, we demonstrate the role of Fe oxides in P_{org} recycling in environmentally relevant matrices by reacting ribonucleotides as representative P_{org} with a forest soil sample and different types of Fe oxides (Fig. 1). We overcome previous analytical challenges by applying high-resolution mass spectrometry to analyze P_{org} reactants and products in solution and synchrotron-based P K-edge X-ray absorption spectroscopy to determine the speciation of P adsorbed on the mineral. We found that ribonucleotide-derived P_i was associated primarily with Fe-oxides in the soil matrix. We combined infrared spectroscopy with molecular modeling simulations to reveal the conformations of mineral-ribonucleotide complexes that may explain reactivity of different Fe oxide minerals. Our findings highlight the exceptional catalytic and adsorption reactivities of the Fe oxides relative to the other minerals that dictate their role in the geochemical fate of P_{org}.

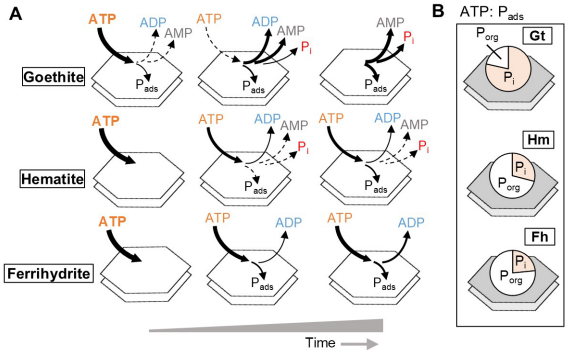

Figure 1. Evolution of ribonucleotide dephosphorylation templated on Fe oxide surfaces. (A) Schematic illustration of time-dependent transformation during 7-d reaction of ATP with (top) goethite (Gt), (middle) hematite (Hm), and (bottom) ferrihydrite (Fh) based on high-resolution liquid chromatography-mass spectrometry for P_{org} reactant and products. **(B)** Fractions of P_i and P_{org} of total adsorbed P after 7-d reactions of ATP reactions with (top) Gt, (middle) Hm, and (bottom) Fh based on particulate species analysis by P K-edge XANES spectroscopy.