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Iron oxides as Catalysts of Organic Phosphorus recycling: Benchmarking Kinetics and Environmental Relevance

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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 can serve as catalytic surfaces for the transformation of P_{org} biomolecules to generate P_i, the bioavailable P for plants and microbes. Therefore, there is special interest in determining both the relevance of this abiotic catalysis in environmental samples and the comparison of the abiotic rates to reported enzymatic rates (Fig. 1). In fact, current models of P cycling consider P_{org} mineralization only as an enzyme-mediated process. Here, we seek to investigate the effects of organic matter chemistry and mineral chemistry on the role of Fe oxides in P_{org} recycling in environmental matrices. We overcome the analytical challenge in this investigation 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 reacted ribonucleotides, phytate, and sugar-phosphate with Fe oxides as well as various other minerals (quartz, feldspars, micas, clays, Fe oxides) found in environmental samples. We uncover the high catalytic and adsorption reactivities of the Fe oxides relative to the other minerals. Importantly, we find the Fe oxide-mediated catalysis is manifested in soil samples. Our findings imply a missing role of Fe oxides as catalysts of P recycling in environmental matrices.

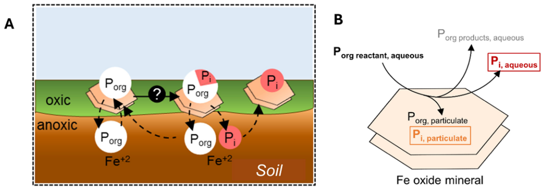

Figure 1. (A) Schematic illustration for the abiotic fate of P_{org} in a soil environment. (B) Schematic overview of the different P species monitored during dephosphorylation reaction of a P_{org} reactant with different Fe oxides and other minerals: P_{org} reactant in solution ($P_{org,\ reactant,\ aqueous}$), mineral-trapped P_{org} ($P_{org,\ particulate}$), P_{org} products in solution ($P_{org\ products,\ aqueous}$), produced P_i bound to the mineral ($P_{i,\ particulate}$), and produced P_i in solution ($P_{i,\ aqueous}$).