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Iron oxides as important abiotic catalysts for organic phosphorus recycling in soil and sediment samples

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Iron (Fe) oxides play an important role in phosphorus (P) cycling. In particular, the strong adsorption of orthophosphate (P_i) and phosphorylated organic compounds (P_{org}) on Fe oxides is well documented. In addition, recent studies highlight these minerals as possible abiotic catalysts in the hydrolytic cleavage of P_{org} to contribute to P_i in environmental matrices. However, this P_{org} mineralization is widely assumed to be solely a biological or enzyme-mediated process. Importantly, recent evidence of mineral-mediated catalysis has relied largely on solution analysis of P_i, which does not account for the role of Fe oxides as both adsorbents and catalysts. Here, we present our collaborative efforts to overcome this analytical challenge by employing high-resolution mass spectrometry to analyze organic reactants and products of P_{org} in solution, and synchrotron-based P K-edge X-ray absorption spectroscopy to determine the speciation of P adsorbed on the mineral. After reactions with ribonucleotides, which represent an important and ubiquitous class of P_{org}, we quantified the evolution of mineral surface-localized P_i associated specifically with Fe oxides in natural soils and sediments, even when these minerals represented a very small fraction (less than 20%) of the heterogeneous mineral matrix. Subsequent experiments with various minerals (quartz, feldspars, micas, clays, Fe oxides) found in the natural samples revealed the high catalytic and adsorption reactivities of the Fe oxides relative to the other minerals. Our new findings highlight an underexplored role of Fe oxides as abiotic players in the natural P recycling from soil and sediment P_{org}. This abiotic P_{org} mineralization is not yet accounted for in the P cycle models.