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Catalytic Recycling of Ribonucleotide-Phosphorus by Different Iron Oxides: Mechanistic Insights from Time-Resolved Solution and Surface Speciation

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Field-scale data have long implicated iron (Fe) (oxyhydr)oxide minerals in controlling phosphorus bioavailability by mediating strong adsorption of inorganic phosphate (P_i) and organophosphate (P_o) compounds [1]. Beyond adsorption, these minerals can also mediate the catalytic hydrolysis of P_o biomolecules to release P_i and organic by-products [2-4]. A mechanistic understanding of this abiotic turnover, however, is lacking. Previous phosphorus speciation was achieved mainly by measuring P_i in solution colorimetrically and bulk total P analysis [2, 3]. However, the accounting of both solution and surface-bound P_i and P_o species is required [4]. Here we apply high-resolution liquid chromatography-mass spectrometry (LC-MS) and synchrotron X-ray absorption near edge structure (XANES) spectroscopy to investigate the dephosphorylation of ribonucleotide compounds reacted with ferrihydrite (estimated stoichiometry, $5Fe_2O_3 \cdot 9H_2O$), goethite (α-FeOOH), or hematite (α-Fe_2O_3). Using LC-MS, we obtained direct quantification of solution P_o species and, with mass balance with solution P_i, amounts of surface-bound P_o and P_i were determined. The relative abundance of the surface-bound species was also confirmed by XANES analysis. Time-resolved data, from 1 hour to 7 days, on the evolution of the P_o and P_i species provide new insights into the catalytic mechanisms of the different minerals (Fig 1).

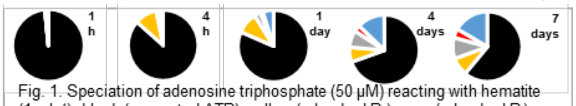

Fig. 1. Speciation of adenosine triphosphate (50 μM) reacting with hematite (1 g L^{-1}): black (unreacted ATP), yellow (adsorbed P_o), gray (adsorbed P_i), red(solution P_i) blue (solution P_o).

[1] Herndon, et al.. (2019), *J. Geophys. Res. Biogeosci.* 124, 227-246; [2] Baldwin et al. (1995), *Environ. Sci. Technol.* 29, 1706-1709. [3] Olsson, R. et al. (2010), *Langmuir*, 26, 18760-18770 [4] Klein *et al.* (2019), *J. Colloid Interface Sci.* 547, 171-182.