

Probing Catalytic Recycling of Phosphorus from Mineral-Organic Associations: Establishing a Suitable Conceptual Framework

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The fraction of organophosphate (P_o) biomolecules can account for 30% to 65% of total phosphorus (P) in soils and sediments [1]. These P_o biomolecules include simple ribonucleotides, polymers of nucleic acids, phospholipids from cell membranes, phytic acid, and sugar phosphates. Beyond strong adsorption of inorganic phosphate (P_i) and P_o compounds, reactive mineral oxides including iron (Fe) (oxyhydr)oxides can serve as catalytic surfaces for the hydrolysis of P_o biomolecules [2-4]. However, a long-standing knowledge gap in the geochemical P cycling is a mechanistic elucidation of this catalytic recycling, which has important implications for critical associations between the P and carbon cycles, accurate evaluation of P_o as a sustained sourcing flux of P_i trapped on minerals, and accounting for abiotic means of P recycling. The current conceptual framework for probing the catalytic reactivity for P_o hydrolysis by mineral oxides relies primarily on tracking the appearance of P_i in solution. However, recent work from my group has reported that the absence of solution P_i does not necessarily translate to lack of catalytic reactivity for ribonucleotides reacted with ferrihydrite [5]. We revisited the conceptual framework to establish a suitable one, which must include the monitoring P_i and P_o , both free in solution and bound on the mineral surface. Different theorems were included within this framework will inform when mass balance from solution species would suffice or explicit quantification of surface speciation would be warranted, thus guiding the choice of experimental techniques to be applied. Finally, experimental validation is provided by liquid chromatography-mass spectrometry and synchrotron X-ray absorption analyses following reactions of ribonucleotides of different P stoichiometry with Fe-oxide minerals. We highlight previously missing insights into the catalytic reactivity of P recycling from mineral-organic associations.



[1] Jones and Oburger, 2011 in *Phosphorus in action* (pp. 169-198). Springer, Berlin, Heidelberg. [2] Herndon, et al. (2019), *J. Geophys. Res. Biogeosci.* 124, 227-246; [4] Olsson, R. et al. (2010), *Langmuir*, 26, 18760-18770 [5] Klein et al. (2019), *J. Colloid Interface Sci.* 547, 171-182.