

Goethite-Catalyzed Dephosphorylation of Ribonucleotides Modulated by Other Minerals: Experimental and Molecular Modeling Investigations

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Iron (Fe) oxides are well known adsorbents of phosphorus (P)-containing compounds. Beyond adsorption, recent reports have implicated Fe oxides in catalyzing the hydrolytic cleavage of organic P (P_{org}) to generate inorganic P (P_i). It is not yet known, however, how other mineral components may influence this catalytic reactivity by Fe oxides. For instance, the heterogeneous soil matrix is often enriched in quartz and clay minerals and contains a relatively small fraction (less than 20%) of Fe oxide content. Here, we probed the effects of quartz or kaolinite (4 g L^{-1}) on the reactivity of goethite (1 g L^{-1}) towards the ribonucleotide adenosine triphosphate (ATP, 50 $\mu\text{mol } L^{-1}$). To monitor both aqueous and surface-bound products, we employed high-resolution liquid chromatography-mass spectrometry and P K-edge X-ray absorption near-edge structure spectroscopy, respectively. With goethite alone, over 60% of ATP was hydrolyzed to yield 31% of the total ATP-derived P as aqueous P_i and 35% as surface-bound P_i (**Fig. 1a**). By contrast, we obtained minimal P recycling (<9%) after ATP reactions with quartz alone or kaolinite alone. Remarkably, even when goethite accounted for one-fifth of a mineral mixture with either quartz or kaolinite, goethite maintained its high catalytic reactivity (up to 50%) for the ribonucleotide dephosphorylation. The decreased reactivity of goethite in the presence of the other minerals was characterized by the near-complete loss of mineral-bound P_i and the accumulation of adsorbed P_{org} . We performed molecular modelling simulations to identify the functional groups and binding structures involved in the adsorption of ribonucleotide reactants onto the different minerals (**Fig. 1b**). Our findings provide new insights on how goethite and related Fe oxides may remain catalytically active for recycling ribonucleotide-sourced P_i in the heterogeneous soil matrix.

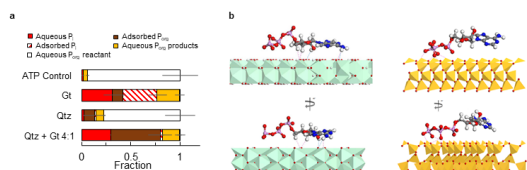


Figure 1. Catalytic and adsorption reactivities in ATP-mineral reaction mixtures. (a) Aqueous and mineral-bound species after ATP reactions with goethite (Gt), quartz (Qtz), and Gt:Qtz mixtures. (b) Optimized model conformations of ATP adsorbed onto Gt (left) and Qtz (right). Atom color legend in b: Hydrogen (white), oxygen (red), nitrogen (blue), phosphorus (pink), carbon (gray), Fe (green), and silicon (yellow).