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Phosphorous and Amino Acid Adsorption in Early Earth Seafloor Minerals

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Phosphorous (P) has always played a crucial role in living organisms and nature: it can be observed in the structure of DNA and RNA, exists in ATP which has an essential role in energy storage, and is present in many metabolic intermediates [1]. The precise role, form, and geological source of P in origin of life reactions is heavily debated. One issue is the very dilute concentration of phosphate that would have been present in the early Earth's oceans [2]; the reduced form, phosphite, has also been proposed as a likely prebiotic source [3]. A possible mechanism for concentrating P species for prebiotic chemistry is adsorption in minerals. In particular, iron oxyhydroxides including green rust are good phosphate adsorbers [4], are formed in natural environments, and would have been a common component in hydrothermal chimneys and sediments forming in the early iron-rich oceans [5]. The presence of amino acids with P species in the mineral precipitates is also significant as this system may have eventually led to peptide-phosphorus feedbacks and nests [6]. In this work, we simulated early Earth iron hydroxide seafloor precipitates and measured their ability to absorb phosphate and phosphite; we also tested how P adsorption was affected by the presence of amino acids (alanine or aspartate). By monitoring reactions with ^{31}P and ^{1}H NMR spectroscopy, both phosphate and phosphite were clearly adsorbed and concentrated into the iron hydroxides after 24 hours (phosphate more strongly than phosphite). The amount of P adsorbed in the iron hydroxides was also affected by the simultaneous presence of amino acids, with alanine presence demonstrating greater phosphate absorption than when aspartic acid was present. However, it appears that after several days to one week the additional adsorbed phosphate was released back into solution, and the P content of the solid phases began to equilibrate. These preliminary results suggest that iron hydroxides in early Earth hydrothermal/seafloor systems could have concentrated P species present in dilute concentration in the ocean and retained them in the mineral reaction system for prebiotic chemistry, but the degree to which phosphate or phosphite is adsorbed into minerals would also depend strongly on the amino acids (and presumably other organic species) that are present. More work is needed to determine which mineral / ocean / hydrothermal chemistries are most likely to support the emergence of organic-mineral-phosphorus feedbacks.

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