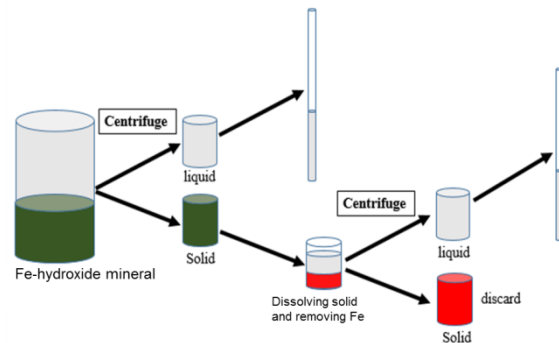


**PHOSPHORUS AND AMINO ACID ADSORPTION IN IRON OXYHYDROXIDES REPRESENTING EARLY EARTH SEAFLOOR OR HYDROTHERMAL CHIMNEY SYSTEMS.** Y. Abedian<sup>1,2,4</sup>, D. VanderVelde<sup>3,4</sup>, E. Flores<sup>1,4</sup>, L. M. Barge<sup>1,4</sup>, <sup>1</sup>NASA Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena CA 91109 ([laura.m.barge@jpl.nasa.gov](mailto:laura.m.barge@jpl.nasa.gov)). <sup>2</sup>NanoEngineering, University of California, San Diego, 9500 Gilman Dr, La Jolla, CA 92093; <sup>3</sup>Department of Chemistry, California Institute of Technology, 1200 E. California Blvd, Pasadena, CA, 91125, USA; <sup>4</sup>NASA Astrobiology Institute Icy Worlds team.

**Introduction:** Phosphorous 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 phosphorus in origin of life reactions is heavily debated; one issue is the very dilute concentration of phosphate ( $\text{HPO}_4^{2-}$ ) that would have been present in the early Earth's oceans [2]; the reduced form phosphite ( $\text{HPO}_3^{2-}$ ) has also been proposed as a likely prebiotic source [3]. One possible mechanism for concentrating phosphorus species for prebiotic chemistry is adsorption in minerals. In particular, iron oxyhydroxides including Green Rust (GR) are good phosphate adsorbers [4], are easily formed in natural environments, and would have been common in hydrothermal precipitates on the early Earth. GR also figures prominently in the alkaline hydrothermal model for the origin of life since it would have been a significant component of hydrothermal chimneys forming in the early iron-rich oceans [5]. The presence of amino acids with phosphorus species in the mineral chimneys 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 precipitates and measured their capability for absorbing phosphate and phosphite, as a function of whether amino acids were also present (and of the type of amino acid).

**Methods:** Iron hydroxides are formed from hydroxide ( $\text{OH}^-$ ) precipitating with different ratios of  $\text{Fe}^{2+}$  /  $\text{Fe}^{3+}$ . To simulate the early Earth conditions as closely as possible the experiment was done using Argon purged solutions and performed entirely in a glove box. Minerals were formed by combining a  $\text{FeCl}_2$  /  $\text{FeCl}_3$  and NaOH solution to produce a precipitate. After 24 hours, the supernatant liquid was removed and a dilute solution of  $\text{HPO}_4^{2-}$  or  $\text{HPO}_3^{2-}$  (sometimes with amino acid, ala or asp) (pH 6.5) was added instead, and the mineral was left to stir in the phosphate solution for 24h. pH was measured initially and when samples were taken. Liquid and solid phases were separated as shown in Fig. 1; solids were dissolved in HCl and iron was removed [7], and samples were analyzed with liquid  $^{31}\text{P}$  and  $^1\text{H}$  NMR.



**Figure 1:** Sample preparation and analysis procedure.

**Results and Discussion:** Phosphate and phosphite were adsorbed into the iron hydroxides after 24 hours. Over the course of the 24h experiment, we observed that phosphite adsorption resulted in a pH decrease in the bulk solution, whereas phosphate adsorption increased the pH to a value close to 10. However, the amount of P adsorbed in the iron hydroxides was affected by the simultaneous presence of amino acids. In the presence of alanine, phosphate absorption in the iron hydroxides was enhanced by a factor of 2-3 compared to when aspartic acid was present instead. This could be since aspartic acid has a negatively charged side chain unlike alanine, thus it has greater affinity to bind with the positively charged iron hydroxide surfaces and filled some of the empty spaces in the mineral surface thus causing less phosphorous absorption. Our 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. Interactions of phosphate/phosphite with amino acid or peptides inside these catalytic minerals are of interest; since the type of amino acid determines the degree of P adsorption, more work is needed to determine what chemistries are most likely to support organic-mineral-P feedbacks.

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