

AN INCREASE IN PHOSPHORUS AVAILABILITY FROM REDOX-INDUCED CHANGES BY WATER-ROCK INTERACTIONS. M. A. Pasek, University of South Florida, 4202 E. Fowler Ave, NES 204, Tampa FL 33620. mpasek@usf.edu

The element phosphorus is a key nutrient in modern ecosystems, and given its prevalence in informational biomolecules (RNA and DNA), metabolism (ATP and other coenzymes), and cell structure (phospholipids), it has presumably been an important constituent since the onset of life. However, the liberation of phosphorus from rocks is confounded by the poor solubility of calcium phosphate minerals that are presumed to be the original phosphate source on a developing world. In addition, the poor reactivity of phosphate towards organic substrates suggests either unusual environmental conditions or reactive phosphorus phases were necessary to promote organophosphate formation for the prebiotic to biotic transition.

Here I argue an alternative route to making phosphorus available for the development of life that may have resulted from the natural geochemical cycle of phosphorus, if redox changes to phosphorus are considered (as opposed to immutable phosphate). First, the chemistry of phosphorus during water-rock interactions such as serpentinization (Fig. 1) is shown to change from phosphate to phosphite (P^{5+} to P^{3+}) due to the concomitant oxidation of iron (Fe^{2+} to Fe^{3+}). Second, due to the heightened solubility of P^{3+} , this phosphite can be extracted from rock as water flows through it, resulting in enrichment of total P. Third, the phosphite itself is stable to oxidation in the absence of free radicals, such as those formed by UV photolysis of water, or promoted by iron-catalyzed Fenton reactions. The result of this oxidation are high energy polyphosphates, which I then show to be capable phosphorylating organic substrates, able to make nucleotides from nucleosides, and possibly even nucleotide dimers through the excess energy stored from the oxidation of phosphite.

Altogether, this pathway may have been active on the early earth, and on water worlds where redox occurs at water-rock interfaces. The result is a potential solution to the problem of the low solubility and poor reactivity of phosphate. By considering the potential for redox changes of phosphorus, both issues may be addressed and provide a lead to the origin of phosphorylated biomolecules.

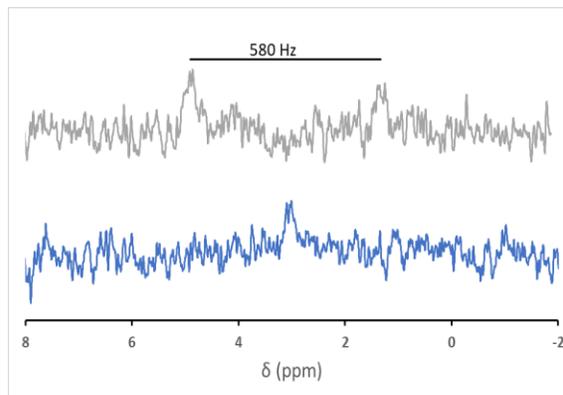


Fig. 1. ^{31}P NMR spectrum of phosphorus extracted from a serpentinite from Josephine county, OR, USA. The singlet at 3 ppm (bottom) splits into a wide doublet (top) with a J-coupling constant of about 580 Hz. The concentration of P measured using this method was about $\sim 10^{-5}$ M at this signal to noise for these scans.