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Geological and experimental evidence of bioavailable phosphite during the Great Oxidation Event

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Phosphorus (P) is a key component for the origin and early evolution of life on the Earth as it is a major constituent of cell walls, ATP, DNA, and RNA. Therefore, its availability throughout geologic time has likely affected the co-evolution of life and environments on the Earth. Modern microbial life is heavily dependent on phosphate (P^{5+}), however, reduced P species such as phosphonate and possibly phosphite (P^{3+}) may become important P sources in phosphate-limiting environments[1,2]. Phylogenetic data suggest that phosphate was the main P source for microbial life in the Archean while phosphite became crucial in the Neoarchean-Paleoproterozoic, i.e., during the Great Oxygenation Event (GOE)[2]. However, phosphite concentrations in the Archean-Proterozoic seawater and underlying processes that might have triggered life's dependency on it are unknown. We performed laboratory experiments simulating the precipitation of banded iron formations (BIFs) as hydrous ferric oxyhydroxides (HFO) in various phosphate/phosphite-bearing solutions namely, deionized water, 10-times diluted seawater, and seawater (artificially made and containing 0.56 M NaCl, 0.055 M Ca, 0.045 M Mg with an ionic strength of 0.86 mol/L) with or without dissolved Si. These experiments suggest that phosphate removal by HFO in deionized water is weaker compared to seawater, suggesting that phosphate might have been more available in freshwater settings compared to the ocean in the Archean and Paleoproterozoic. More importantly, these experiments suggest very limited removal of phosphite by HFO unlike phosphate irrespective of solution chemistry. We also measured phosphite concentrations in samples from the Paleoproterozoic (2.45 Ga) Joffre BIFs, Australia, and found up to 4.3 ppb phosphite (0.43% of total P). Assuming phosphite to be primary, i.e., precipitated along with HFO, we use our experimental data to estimate phosphite concentrations in the Paleoproterozoic ocean for the first time. We suggest that phosphite concentration in the ocean during the GOE was significant and speculate that the preferential removal of phosphate by HFO and microbial assimilation might have created phosphate-depleted environments at some locales, in turn, this might have prompted life to utilise alternative phosphorus sources, particularly phosphite.

[1]*Martinez et al. (2012) Environ. Microbio. 14:1363-1377.*
[2]*Boden et al. (2024) Nature Comm., in press.*