

**REDOX CONTROLS ON PHOSPHORUS AVAILABILITY IN THE ARCHEAN**<sup>1</sup>Barry Herschy\*, <sup>1</sup>Jacqueline Sampson, <sup>1</sup>Zachary Atlas, <sup>2</sup>Heather Abbot-Lyon, <sup>3</sup>Terence Kee and <sup>1</sup>Matthew Pasek<sup>1</sup>School of Geosciences, University of South Florida, 4202 E. Fowler Ave, Tampa, FL 33620, USA.\*[bherschy@usf.edu](mailto:bherschy@usf.edu), [mpasek@usf.edu](mailto:mpasek@usf.edu) <sup>2</sup>Department of Chemistry and Biochemistry, Kennesaw State University, 1000 Chastain Road, Kennesaw, GA 30144, USA. [habbot@kennesaw.edu](mailto:habbot@kennesaw.edu) <sup>3</sup>School of Chemistry, University of Leeds, Woodhouse Lane, Leeds, LS2 9JT, UK. [t.p.kee@leeds.ac.uk](mailto:t.p.kee@leeds.ac.uk)

The inclusion of phosphorus (P) in biochemistry is still one of the biggest unanswered questions in origins of life studies. The issues of low reactivity and low water solubility of phosphate minerals, particularly hydroxyapatite, leads to limited availability and inability for phosphate to react with organic materials. The availability and species of P in the early Earth oceans therefore needs to be properly established to fully understand how inclusion into biochemistry occurred.

It has been proposed that the Archaean ocean may have been strongly phosphorus-limited due to the selective binding of phosphate to iron (III) oxyhydroxide (IOH)[1-3] though the extent of removal by IOH has been a matter of question due to competition by silica [4,5] and arsenic [6,7]. A phosphorus depleted ocean would have affected the origin, development and diversification of life on Earth.

Several ways have been proposed to counter the “phosphate” problem including the use of alternative solvents [8] and sources of reduced P like meteoritic schreibersite [9,10] which increase both solubility and reactivity of phosphorus in biochemical reactions.

The issues with these proposed methods, in particular, the limited locations and environments available for reactions to take place. Pasek tried to address the issue of limited availability of schreibersite by proposing a terrestrial model for its formation [11] but again, the availability of reduced P is still limited to specific geographical locations and is reliant on very specific conditions for its formation.

Here we propose an alternative route to soluble, reactive P in the early oceans: reduction of phosphate to phosphite by iron (II) at low (< 200°C) diagenetic temperatures. Phosphite has a higher solubility compared to phosphate - a factor of 1000 or more which would result in large scale liberation of phosphorus from iron sediments and would greatly increase the amount of available reduced and relatively stable P available for inclusion in origin of life reactions.

Phosphite can be used to phosphorylate organics via an oxidative phosphorylation process such as the Fenton reaction. This process would allow oxidative phosphate coupling to polyphosphates which are known to phosphorylate organics such as nucleosides. This process would also account for the presence of phosphite detected in hydrothermal waters [12] and

also 3.5 Gya Archaean sedimentary carbonate rock deposits from the Pilbara [13] and Greenland (in prep).

**References:**

- [1] Berner, R.A., 1973. *Earth and Planetary Science Letters*, 18(1), pp.77-86. [2] Bjerrum, C.J. and Canfield, D.E., 2002. *Nature*, 417(6885), pp.159-162. [3] Jones, C., Nomosatryo, S., Crowe, S.A., Bjerrum, C.J. and Canfield, D.E., 2015. *Geology*, 43(2), pp.135-138. [4] Konhauser, K.O., Lalonde, S.V., Amskold, L. and Holland, H.D., 2007. *Science*, 315(5816), pp.1234-1234. [5] Planavsky, N.J., Rouxel, O.J., Bekker, A., Lalonde, S.V., Konhauser, K.O., Reinhard, C.T. and Lyons, T.W., 2010. *Nature*, 467(7319), pp.1088-1090. [6] Feely, R.A., Trefry, J.H., Lebon, G.T. and German, C.R., 1998. *Geophysical Research Letters*, 25(13), pp.2253-2256. [7] Fru, E.C., Hemmingson, C., Holm, M., Chiu, B. and Iniguez, E. *Earth and Planetary Science Letters*, 434, pp.52-63. [8] Burcar, B., Pasek, M., Gull, M., Cafferty, B.J., Velasco, F., Hud, N.V. and Menor-Salván, C., 2016. *Angewandte Chemie International Edition*. [9] Pasek, M.A. and Lauretta, D.S., 2005. *Astrobiology*, 5(4), pp.515-535. [10] Bryant, D.E. and Kee, T.P., 2006. *Chemical communications*, (22), pp.2344-2346. [11] Pasek, M.A., 2016. *Geoscience Frontiers*. [12] Pech, H., Henry, A., Khachikian, C.S., Salmassi, T.M., Hanrahan, G. and Foster, K.L., 2009. *Environmental science & technology*, 43(20), pp.7671-7675. [13] Pasek, M.A., Harnmeijer, J.P., Buick, R., Gull, M. and Atlas, Z., 2013. *Proceedings of the National Academy of Sciences*, 110(25), pp.10089-10094.