



Supporting Information

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# Production of Potentially Prebiotic Condensed Phosphates via Phosphorus Redox Chemistry\*\*

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## Supporting Information

### Experimental Section

*Fenton Chemistry:* A series of solutions were prepared with  $\text{Na}_2\text{HPO}_3$  or  $\text{NaH}_2\text{PO}_2$  in concentrations between 0.001 M to 0.1 M, iron (as  $\text{FeCl}_2 \times 4\text{H}_2\text{O}$  or as  $\text{FeSO}_4$ ) concentrations between 0.001 M to 0.1 M, and  $\text{H}_2\text{O}_2$  concentrations between 0.002 M to 0.5 M (Table S1), each with a starting pH of  $7 \pm 1$ , unless otherwise noted. Peroxide was added last to promote the reactions. One experiment was performed with a formaldehyde concentration of 1.2 M to act as a reductant. The solutions were stirred for 1-20 days, a 2 mL aliquot of each solution was extracted and placed in 2 mL of a 1:1 mixture of 10 M NaOH solution and  $\text{D}_2\text{O}$  to quench the reaction, precipitate  $\text{Fe}^{\text{III}}$  and prepare the sample for analysis by NMR. Decanted samples were analyzed using  $^{31}\text{P}$  NMR on a Varian 300 four-nucleus probe FT-NMR spectrometer at 121.43 MHz and 24.5 °C for 256 to 6000 scans following prior work<sup>[6a,c]</sup>, or on a Bruker Avance 500 four-nucleus FT-NMR system operating at 25°C and 202.46 MHz for phosphorus with 400-9000 scans. Spectra were acquired in both  $^1\text{H}$ -decoupled and coupled modes. The peaks were identified based on comparison to known standards and previous work, with abundances determined from peak areas.<sup>[6,15]</sup> From these data, we determine that approximately 34.5% of reduced P becomes oxidized to condensed P (Fig. S1, *vide infra*). Some solutions were prepared with a starting solution pH of 13. In these experiments, the  $\text{Fe}^{\text{II}}$  precipitated to green rust and did not promote any Fenton chemistry. These solutions also showed no oxidation of reduced compounds. From these experiments, we determined that the reactions were quenched by addition of base to the solution, hence the addition of NaOH does not promote further reaction of phosphorus species.

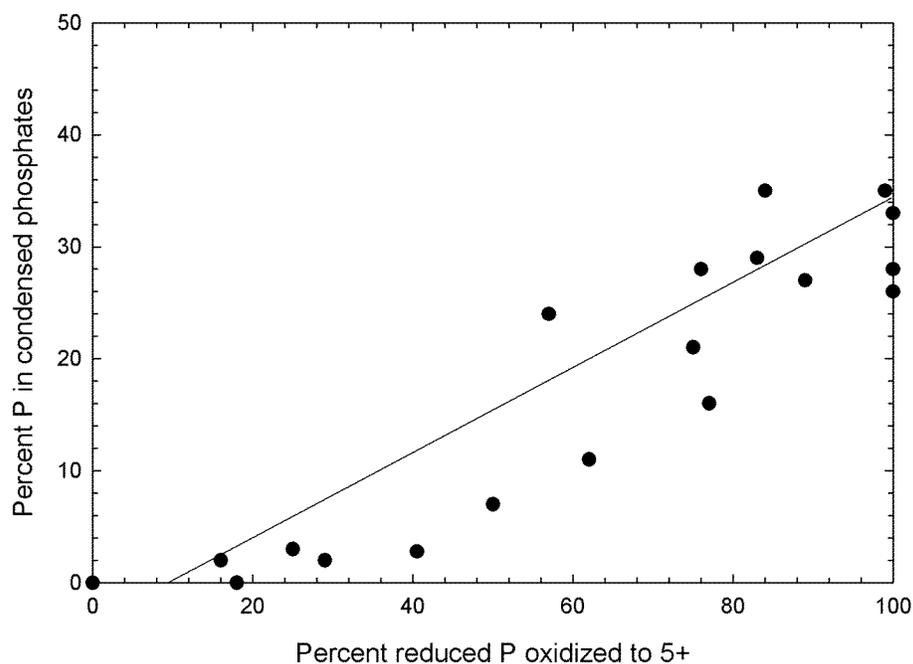


**Table S1.** Fenton-initiated reaction conditions and products<sup>a</sup>.

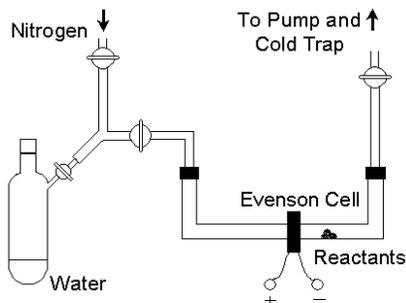
Starting Materials (M)			Yields (%)			Notes*
P comp	Fe <sup>II</sup>	H <sub>2</sub> O <sub>2</sub>	Pi	PPi	PPPi	
0.0010	0.0020	0.1	72	28	BDL	As HPO <sub>3</sub> <sup>2-</sup>
0.085	0.085	0.3	62	24	3	As HPO <sub>3</sub> <sup>2-</sup> , reacted over 2 hrs
0.10	0.1	0.5	67	23	10	As HPO <sub>3</sub> <sup>2-</sup>
0.002	0.002	0.008	64	34	1	
0.0066	0.0067	0.027	61	13	3	
0.010	0.10	0.4	74	26	BDL	
0.10	0.010	0.4	27	2	BDL	
0.050	0.10	0.4	54	18	3	Added 0.05 M PO <sub>4</sub> <sup>3-</sup>
0.010	0.10	0.4	SM	2	BDL	Added 0.1 M PO <sub>4</sub> <sup>3-</sup>
0.10	0.10	0.4	48	27	1	pH 3
0.10	0.10	0.4	54	26	3	pH 7
0.10	0.10	0.4	49	28	7	pH 10.5
0.10	0.10	0.4	43	7	BDL	Used FeSO <sub>4</sub>
0.10	0.10	0.2	25	SM	4	Added 0.1 M PPI
0.10	0.10	0.5	38	3	BDL	Added 1.2 M CH <sub>2</sub> O
0.11	0.11	0.5	48	18	3	Added 0.7 g Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> F
0.10	0.11	0.5	20	21	2	Added 0.14 M CaCl <sub>2</sub>
0.10	0.10	0.4	33	21	3	2 hrs

<sup>a</sup> P compound oxidized was H<sub>2</sub>PO<sub>2</sub><sup>-</sup> unless denoted otherwise. SM is starting material, PPI is pyrophosphate, PPPi includes both triphosphate and cyclic trimetaphosphate. BDL is below detection limit.

**Figure S1. Condensed phosphate yields versus total reduced P oxidized.** Line shown is a linear regression line with Condensed P% = Reduced P oxidized% × 0.3469 – 3.769%, and R<sup>2</sup> = 0.8562. Note that experiments with condensed P as a starting material have been excluded from this graph.



*Microwave Plasma Experiments:* Reactants were loaded into a glass tube of diameter 1 cm. The tube had two 90° bends and was used with the open ends pointing vertically upwards and with the reactants located within the main horizontal section. Reactants were added as solid powders and maintained under a nitrogen stream prior to initiation of the experiment (*below*).



Where H-phosphonate was one of the reactants this was heated *in situ* to its melting point of 70°C to remove moisture and increase its surface area. The outlet of the glass tube was connected *via* Swagelok fittings and rubber tubing to a vacuum line. The inlet was connected *via* Swagelok fittings to a “Y” connector, one branch of which was connected to a nitrogen line and the other to a Schlenk tube containing deionised, de-oxygenated water. The tube was then exposed to vacuum and the water in the Schlenk tube evaporated leading to, after a few minutes, a stable low pressure in the tube of between 0.4 and 1.0 mbar water vapour. The microwave plasma generator was switched on and adjusted to 50W output and a plasma in the tube struck with the aid of a Tesla coil. The Evenson microwave cavity was positioned 2-3 cm upstream from the reactants. At the end of the experiment the tube was allowed to fill with nitrogen gas and was washed out with 30 mL NaOH (0.33 M) into a round bottomed flask. The pH, which was typically  $10.3 \pm 0.2$ , was adjusted to  $8.5 \pm 0.2$  using 1.0M HCl solution. The solution was reduced in volume on a rotary evaporator, D<sub>2</sub>O added and the pH readjusted if necessary. The product solution was analysed using <sup>31</sup>P NMR on a Bruker Avance 500 four-nucleus FT-NMR system operating at 25°C and 202.46 MHz for phosphorus with 400-9000 scans and the peak integrals used to estimate the amounts of various products. Products were identified by addition of authentic samples to the NMR tubes. Results of the experiments and controls are tabulated as Table 2 showing the integrals of condensed phosphates as percentage of the total phosphorus signal (the remainder being unreacted starting material and phosphate). Earlier qualitative experiments had also shown that H-phosphonate alone will produce significant amounts of pyrophosphate and traces of linear triphosphate. Pyrophosphate is also produced, along with other oxyacids when the reactant is elemental white phosphorus (P<sub>4</sub>) alone. It is well established that H<sub>3</sub>PO<sub>3</sub> can lose a H atom to form a radical and subsequently dimerize to hypophosphate H<sub>4</sub>P<sub>2</sub>O<sub>6</sub>.<sup>[16]</sup> This can in turn disproportionate to give H<sub>2</sub>P<sub>2</sub>O<sub>5</sub> and H<sub>4</sub>P<sub>2</sub>O<sub>7</sub>. We performed an experiment using H<sub>3</sub>PO<sub>3</sub> under a N<sub>2</sub> vapour plasma which yielded no polyphosphates. This serves to show dimerization is not happening under these experimental conditions in the absence of OH radicals from water. Condensed phosphates can also be obtained thermally under suitable drying conditions requiring temperatures in excess of 160°C. We used KH<sub>2</sub>PO<sub>4</sub> under a N<sub>2</sub> vapour plasma, which yielded no condensed phosphates. This experiment shows that condensation products are not forming thermally under these reaction conditions.

**Table S2.** Microwave plasma experimental conditions and products. (2450 MHz; 50W; 0.4 and 1.0 mbar water-He vapor pressure)<sup>a</sup>

<b>Starting Conditions</b>		<b>Yields (%)</b>		
<b>Materials</b>	<b>Time (hrs)</b>	<b>PPi</b>	<b>PPPi</b>	<b>Cyclic Pi</b>
<b>+ H<sub>3</sub>PO<sub>3</sub> (4.3 mM)</b>				
NaH <sub>2</sub> PO <sub>2</sub> (2.8 mM)	4	28.2	4.1	0.28
Na <sub>4</sub> P <sub>2</sub> O <sub>7</sub> (0.4 mM)	9	SM	4.0	0.2
Na <sub>4</sub> P <sub>2</sub> O <sub>7</sub> (0.4 mM)	5.5	SM	4.6	0
H <sub>3</sub> PO <sub>3</sub> (0.30g)*	2	0	0	0
KH <sub>2</sub> PO <sub>4</sub> *	3	0	0	0

<sup>a</sup>SM is starting material, PPi is pyrophosphate, PPPi is triphosphate.

\*Experiments used N<sub>2</sub> as plasma, as opposed to H<sub>2</sub>O.

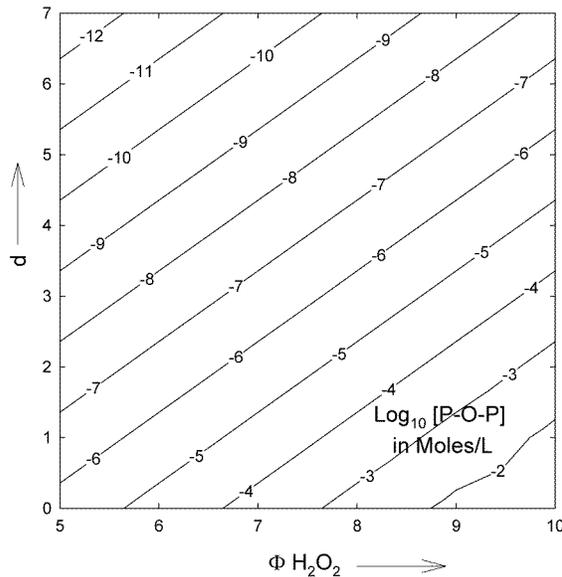
*Modelling:* The production of pyrophosphate and condensed phosphates from reduced phosphorus species depends on several factors; the amount of reduced phosphorus at the beginning of oxidation, the depth of the body of water in which phosphorus is being oxidized, the flux of H<sub>2</sub>O<sub>2</sub> to the water, the hydrolytic half-life, and the percent yield of condensed phosphorus from reduced phosphorus. We estimate the percent yield ( $\alpha$ ) as 30% in the calculations that follow. We estimate the global production of condensed phosphates from several model H<sub>2</sub>O<sub>2</sub> rain out fluxes. We assume that each H<sub>2</sub>O<sub>2</sub> molecule will oxidize one HPO<sub>3</sub><sup>2-</sup> in the presence of phosphate to form pyrophosphate or higher-order condensed phosphate. HPO<sub>3</sub><sup>2-</sup> and H<sub>2</sub>PO<sub>2</sub><sup>-</sup> are among the most reduced compounds likely present on the Earth based on thermodynamic data<sup>[4c]</sup> and hence these species will scavenge oxidants. Additionally, the presence of reductants does not inhibit the oxidation of reduced P species, hence production of condensed P species was most dependent on the flux of H<sub>2</sub>O<sub>2</sub>. The estimated H<sub>2</sub>O<sub>2</sub> flux is calculated using prebiotic atmosphere models.<sup>[17]</sup> Under prebiotic conditions, methane abundance should be assumed at a low value. The H<sub>2</sub>O<sub>2</sub> rainout flux was  $\sim 5 \times 10^7$  molecules/cm<sup>2</sup>s for an atmosphere consisting of pCO<sub>2</sub> = 0.2 bar, pN<sub>2</sub> = 0.77 bar, with no oxygen, and a hydrogen volcanic flux was fixed at 10<sup>10</sup> molecules/cm<sup>2</sup>s (today's value). The UV flux at Lyman Alpha was assumed 2.5 times larger than today's. Hydrogen is assumed to escape from the atmosphere at the diffusion limited escape. The steady-state abundance of hydrogen in this system was about 10<sup>-4</sup> (100 ppm). The corresponding rainout of H<sub>2</sub>CO would be  $2.76 \times 10^8$  molecules/cm<sup>2</sup>s. If hydrogen escaped at a lower rate then the H<sub>2</sub>O<sub>2</sub> flux would be lower because hydrogen would accumulate in the atmosphere and would react with H<sub>2</sub>O<sub>2</sub>. In contrast, if UV fluxes were higher then assumed more H<sub>2</sub>O<sub>2</sub> would be expected. Our estimates for the production of H<sub>2</sub>O<sub>2</sub> by UV photolysis range from 10<sup>4</sup> molecules/cm<sup>2</sup>s (reducing atmosphere) to  $7.5 \times 10^7$  molecules/cm<sup>2</sup>s (neutral atmosphere). Higher fluxes (10<sup>8</sup>-10<sup>10</sup> molecules/cm<sup>2</sup>s) may be expected under slightly oxidizing atmospheres. Additionally, radiolysis is estimated to form  $\sim 1.2 \times 10^6$  molecules/cm<sup>2</sup>s of H<sub>2</sub>O<sub>2</sub>.<sup>[18]</sup> With these assumed fluxes, the global production of condensed phosphates was calculated and is shown as Figure 2 assuming a total reduced P concentration of 10<sup>-2</sup> M. The concentration of condensed phosphates reaches steady state when counterbalanced by their hydrolysis. The hydrolysis of pyrophosphate is a pseudo-first order reaction, and is dependent on the concentration of pyrophosphate.<sup>[19]</sup> Although the rates of hydrolysis of pyrophosphate and larger condensed phosphates are highly solution-chemistry dependent, at room temperature chemical rate law kinetics suggest half lives on the order of 3 years to 30 years at pH 7 to 1000 years.<sup>[19]</sup> These half-lives are increased by the introduction of orthophosphate (increasing the stability of pyrophosphate to hydrolysis), increasing the pH, and by formation of complexes with divalent salts. The half-lives are decreased by decreasing the pH or removing phosphate from the system. Not all systems reach steady state. Systems in which the oxidation of reduced P is fast relative to the rate of hydrolysis of the products give yields close to the yields for complete, rapid oxidation of the reduced P (essentially  $\alpha$  times the starting concentration). For those systems that reach steady state, the abundance of pyrophosphate can be calculated from the generation rate and hydrolysis rate of pyrophosphate:

$$[\text{P}_2\text{O}_7^{4-}] = \alpha \Phi / \lambda \kappa$$

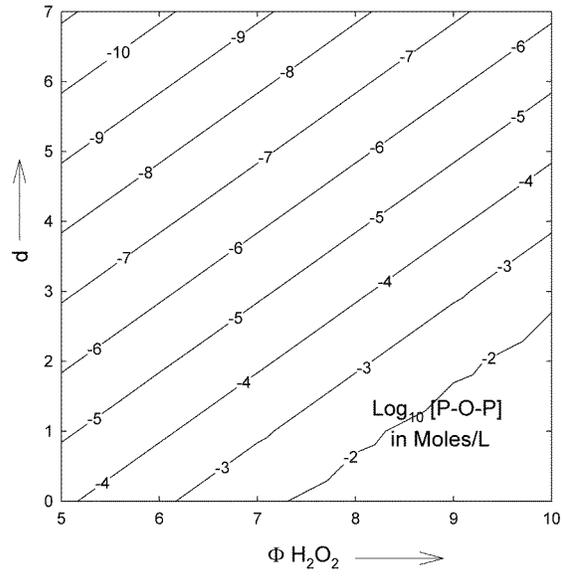
where  $\kappa$  is the rate constant for the hydrolysis of pyrophosphate,  $\alpha$  is the percent of  $\text{H}_2\text{O}_2$  that is used to form pyrophosphate,  $\lambda$  is the depth of the water column, and  $\Phi$  is the flux of peroxide rained down to the surface of the Earth. Systems that have not reached steady state (e.g.; those in which the rate of oxidation of reduced P is much higher than the hydrolytic rate of condensed P) are solved by modeling. We model the concentration of condensed phosphates for a range of hydrolytic half-lives, water depths and  $\text{H}_2\text{O}_2$  fluxes (Figure S2). The starting abundance of reduced P in solution only affects the maximum condensed phosphate production (lower right corner for Figure S3), thus all calculations were done with an assumed 0.1 M total concentration.

**Figure S2. Estimated condensed P concentrations.** Estimated concentrations are shown with respect to water body depths (denoted  $d$ , as exponent of the depth of the water body in cm) and  $\text{H}_2\text{O}_2$  flux (as  $\Phi \text{H}_2\text{O}_2$ ) for condensed P hydrolytic half-lives corresponding to A) 1 year, B) 30 years, C) 1000 years, and D) 30,000 years.

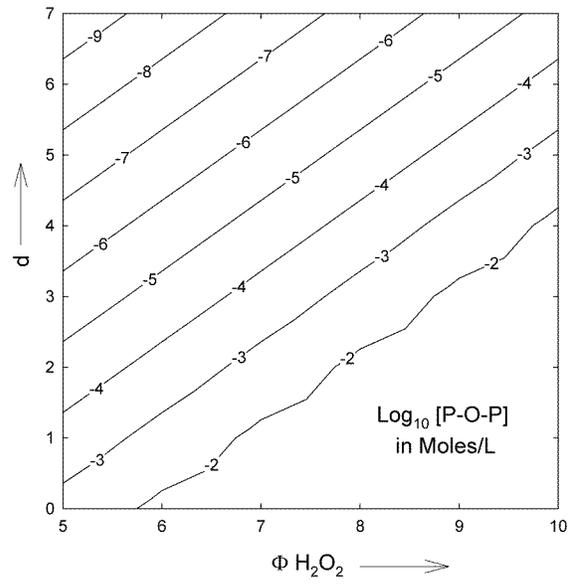
A)



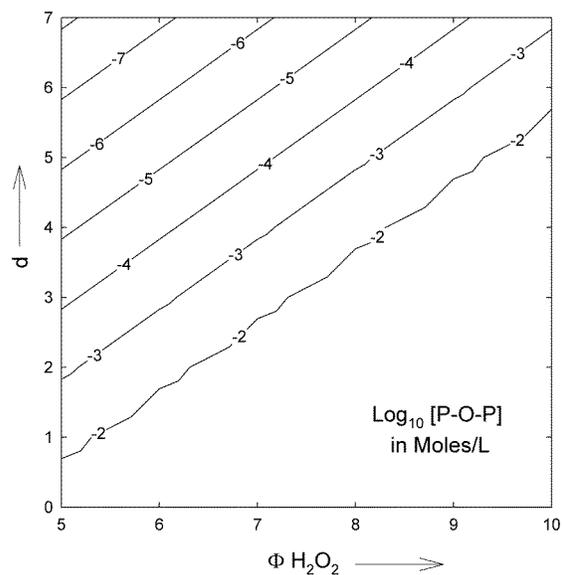
B)



C)



D)



### Additional References

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