

Direct evidence for the availability of reactive, water soluble phosphorus on the early Earth. H-Phosphinic acid from the Nantan meteorite†

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Anoxic irradiation of a type III CD iron meteorite known to contain the phosphide mineral schreibersite ($\text{Fe}_3\text{Ni}_3\text{P}$) in the presence of ethanol/water affords the reactive oxyacid H-phosphinic acid (H_3PO_2) as the dominant phosphorus product.

The element phosphorus plays a central role in terrestrial biochemistry. The transmission of genetic information through self-replication (DNA and RNA), biochemical energy provision (ATP), cell bi-layer materials (lipids) and structural building blocks (hydroxyapatite) all exploit the orthophosphate group (PO_4^{3-}).¹ That phosphate should have become a key chemical entity for Nature is testament to its properties, elegantly summarised by Westheimer in 1987.² Nature has developed sophisticated mechanisms for the concentration, activation and functionalisation of orthophosphate [Fig. 1(a)]; however, there is still no reason to presume that phosphates were exploited exclusively in the earliest pre-biotic systems and indeed, several lines of evidence suggest that they might not! Gulick highlighted³ in his seminal 1955 paper the key problems with orthophosphate in pre-biotic chemistry: poor water solubility of metal salts (such as calcium)‡ and sluggish chemical reactivity in the absence of activating chemicals. Early seminal work suggested⁴ that life began on an Earth which was anoxic, reducing in chemical potential and bathed in UV radiation. Under such conditions, Gulick proposed³ that lower oxidation state compounds of phosphorus such as H-phosphonates and, even better in his view, H-phosphinates (Fig. 1b,c) would have been both more soluble in an early-Earth ocean and more reactive as pre-biotic precursor molecules than orthophosphate.⁵

The redox couples $\text{H}_3\text{PO}_4/\text{H}_3\text{PO}_3$ (-276 mV) and $\text{HPO}_4^{2-}/\text{HPO}_3^{2-}$ (-690 mV) suggest that *ca.* 13 and 32 kcal mol⁻¹ are required to reduce orthophosphate to H-phosphonate depending upon pH.^{6a} Whilst such energy input is accessible from electrical discharges associated with early-Earth volcanic activity,⁷ interest in exogenous delivery mechanisms of reduced oxidation state phosphorus as components of extraterrestrial ice-grains, meteorite

or cometary fragments is growing.⁸ In support of this hypothesis both methyl- and ethylphosphonic acids were detected at nmol g⁻¹ concentrations (Fig. 1d; X = Me, H) in addition to orthophosphate (at $\mu\text{mol g}^{-1}$ levels) in the Murchison meteorite.⁹ Enhanced isotopic D/H ratios (δD) of *ca.* 219 argued against terrestrial contamination.¹⁰ We have recently published an account of how such phosphonic acids might have been produced under interstellar conditions *via* the hydrolytic modification of condensed [P=C] species.¹¹ In addition, Pasek and Lauretta have recently reported the observation of H-phosphonic acid as a corrosion product of metal phosphide minerals.¹²

We have independently been exploring the hydrolytic modification of metal phosphides under different conditions to the Pasek–Lauretta study and demonstrate here that the water-soluble and chemically reactive H-phosphinic acid (Fig. 1c)³ is accessible from phosphide-containing iron meteorites. In addition, model studies suggest that organophosphorus compounds could have been readily prepared from H-phosphinic acid under pre-biotically accessible conditions.

Mixed iron–nickel phosphides such as $(\text{Fe},\text{Ni})_3\text{P}$, or schreibersite, are important minor constituents of meteorites.¹³ Such minerals are among the first phosphorus chemicals to condense from the solar nebula as part of a homogeneous accretion model and thus are among the most ancient of phosphorus chemicals within our solar system.¹⁴ Whilst schreibersites are principally associated with iron-rich meteorites, they are also found within the organic-rich carbonaceous chondrites. Chyba and Sagan have calculated the quantities of meteoritic and cometary material that accumulated during the early development of the Earth > 4 Gyrs ago through impact accretion.⁸ Depending upon the actual reducing potential of the early-Earth atmosphere, they estimate that between 10^8 – 10^{11} kg yr⁻¹ of pre-biotic organics should have accumulated as a result of exogenous delivery. Pasek and Lauretta refined this calculation for phosphorus¹² on the basis of known meteorite falls, suggesting a current in-fall *ca.* 10^3 kg yr⁻¹ of phosphide minerals. Presumably this is a lower limit to what may have been the case during the pre-biotic era. The question then is how might other, non-phosphate chemicals have been released from such meteoritic in-fall?

We have explored the anoxic hydrolytic modification of the family of iron phosphides, Fe_nP ($n = 1$ –3) in both the absence and presence of UV radiation.¶ Samples of Fe_nP (0.5 g) were loaded separately into Schlenk tubes in a dinitrogen-filled glove-box, H_2SO_4 (25 cm³; 0.1 M) added and each system incubated under positive dinitrogen pressure at 298 K for 7 days. The phosphides were subsequently filtered and excess aqueous Na_2S (1 M) added to the solutions to precipitate the iron as FeS which was removed

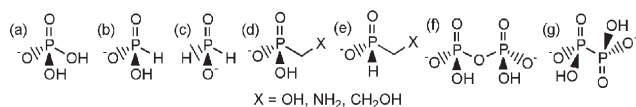


Fig. 1 (a) orthophosphate; (b) H-phosphonate; (c) H-phosphinate; (d) functionalised alkyl phosphonate; (e) functionalised alkyl phosphinate; (f) pyrophosphate; (g) hypophosphate.

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by centrifugation and filtration. The resultant solutions were reduced to dryness and taken up in D₂O (0.5 cm³) for study by ³¹P-NMR analysis. The solution derived from Fe₂P contained salts of H-phosphonic acid (Fig. 1b; 69% total soluble P), phosphoric acid (Fig. 1a; 30% total soluble P) and hypophosphate (Fig. 1g; 1% total soluble P). The solution derived from the identically managed Fe₃P system contained salts of H-phosphonic acid (59% total soluble P), orthophosphoric acid (31% total soluble P), pyrophosphate (Fig. 1f; 1% total soluble P), and hypophosphate (2% total soluble P). Identification was established readily by sequential addition of authentic samples to the NMR tubes. Acid is not a prerequisite for the hydrolysis reaction, however. Thus, Fe₃P (0.5 g) was suspended in degassed water (10 cm³) for 5 days after which time a good ³¹P-NMR signal for H-phosphonate was obtained. It was also established that hydrolysis of Ni₂P and FeP led to solutions containing H-phosphonate, phosphate and hypophosphate (FeP) or pyrophosphate (Ni₂P). These results parallel those of Pasek and Lauretta.¹² Furthermore, repeated cycling of incubation, drying, re-incubation and testing results in continuous leaching of these phosphorus chemicals.

Corrosion under terrestrial conditions is known to be dependent upon di-oxygen^{6b} whereas pre-biotic “corrosion” of meteoritic phosphides would most likely be anoxic. Consequently, we wished to determine if the oxygen in both H-phosphonate and orthophosphate is supplied solely from H₂O or a combination of H₂O and O₂. To address this point, a sample of Fe₃P (0.1 g) was vial-sealed within a glove-box with isotopically-enriched H₂¹⁸O (1 g; 98.5% : 1.0% : 0.5% ¹⁸O : ¹⁷O : ¹⁶O, Cambridge Isotope Laboratories) for eight weeks. Subsequent analysis *via* ³¹P{¹H}-NMR spectroscopy revealed both H-phosphonate and orthophosphate as pairs of resonances at δ4.03(¹⁶O) : 3.95(¹⁸O) in the ratio 1.1 : 1 and δ6.45(¹⁶O) : 6.37(¹⁸O) in the ratio 2.3 : 1 respectively. In each case the separation of the ¹⁶O : ¹⁸O isotopomer resonances was found to be 77 ppb compared to an expected isotopic shift for a single [P–¹⁸O] bond of *ca.* 20 ppb.¹⁵ We interpret these results as follows. The observation of significant ¹⁶O H-phosphonate and orthophosphate suggests the minerals to have already undergone aerobic hydrolysis prior to our experiments, a result which is supported further by XPS analyses (see ESI).[†] Our observation of only one resonance for each of the ¹⁸O-isotopomers for both H-phosphonate and orthophosphate with the same isotopomer shift difference (δΔ) of 77 ppb suggests that, in each case, three oxygen atoms in both H-phosphonate and orthophosphate are supplied solely by the water.¹⁵ Under these conditions there is: (i) no ¹⁶O : ¹⁸O exchange between phosphonate and phosphate which would lead to separate resonances for ¹⁶O_n¹⁸O_{3–n}-phosphonate and ¹⁶O_n¹⁸O_{3–n}-phosphate. (ii) ¹⁶O : ¹⁸O₃-phosphate is produced from ¹⁸O₃-phosphonate *via* reaction with trace di-oxygen rather than *via* the oxidative hydrolysis mechanism proposed by Pasek–Lauretta which would have resulted in ¹⁸O₄-phosphate.^{12||}

One of the key differences of our work to the Pasek–Lauretta study focuses on the role of photochemical irradiation in effecting chemical reactions of interstellar and/or pre-biotic significance, as illustrated in our recent contribution.¹¹ Thus, Fe₃P (0.5 g) was loaded into a purpose-built photochemical reactor *via* a dry, dinitrogen filled glove-box and the reactor evacuated and cooled to 77 K on a vacuum-inert atmosphere manifold. Under continuous evacuation, degassed water (10 cm³) was allowed to condense from vapour onto the surface of the phosphide and reactor walls. The

Table 1 Composition of soluble phosphorus derived from the hydrolysis of Fe₃P under thermal (System A: 0.5 g Fe₃P; 25 cm³, 0.1 M H₂SO₄; 7 d; 298 K) and photochemical (System B: 0.5 g Fe₃P, 10 cm³ H₂O; UV; 3 h; 77 K) conditions; (System C: 19.1 g Nantan, 20 cm³ EtOH : H₂O 1 : 1 v/v; UV; 15 h; 77 K). Determined by ³¹P-NMR spectroscopy (101 MHz, 300 K, D₂O). * Not detected below *ca.* 0.5%. ** 8% unidentified P. *** 2% unidentified P

Compound	[H ₂ PO ₂] [–]	[HPO ₃] ^{2–}	[HPO ₄] ^{2–}	[P ₂ O ₇] ^{4–}	[P ₂ O ₆] ^{4–}
System A (%)**	0*	59	31	1	2
System B (%)**	61	26	5	0*	0*
System C (%)***	87	11	0*	0*	0*

combined frozen ice–mineral composite was irradiated by a low pressure mercury vapour arc tube (emissions at 254 nm; *ca.* 500 mW and 185 nm; *ca.* 40 mW) for 3 h.^{**} The resulting solution was examined by ³¹P{¹H}-NMR spectroscopy in D₂O, following Na₂S treatment as outlined above revealing signals at δ4.3 and δ6.3 which have been identified as H-phosphonate and orthophosphate respectively by doping the NMR mixture with authentic samples and contribute 26% and 5% respectively of the total soluble phosphorus. These are as expected from our earlier experiments. However, also present are a set of resonances between δ9.5–6.3 which comprise a remarkable 61% of the total soluble phosphorus. These resonances have also been unambiguously identified, by doping with an authentic sample, as being associated with a single phosphorus species, H-phosphinate (Table 1). The multiple resonances in this region may be deconvoluted into a mixture of [H₂P(O)(O)][–] (singlet at δ8.1 ppm); [HDP(O)(O)][–] (1 : 1 : 1 triplet at δ7.7 ppm; ¹J_{PD} 79 Hz); and [D₂P(O)(O)][–] (1 : 2 : 3 : 2 : 1 pentet at δ7.3; ¹J_{PD} 79 Hz); whose identity we have subsequently confirmed by treating a D₂O solution of authentic Na[H₂P(O)(O)] with a catalytic quantity of acid (Fig. 2C) affording the same sequence of resonances. The complexity arises from rapid hydrogen–deuterium exchange in D₂O catalysed by acid or the presence of Fe²⁺ and the process appears to be much more rapid than for H-phosphonate, a

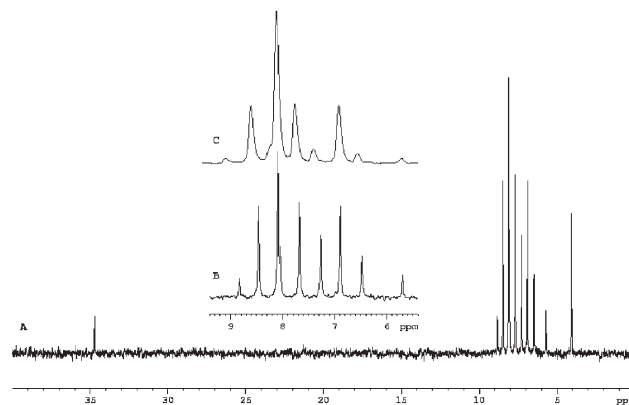


Fig. 2 ³¹P{¹H}-NMR spectrum (101 MHz, 300 K) of the D₂O-soluble phosphorus components following UV irradiation of an anoxic Nantan : H₂O mixture at 77 K. (A) full range, (B) expansion of H-phosphinate region, (C) signals from authentic Na[H₂P(O)(O)] (D₂O; H⁺).

testament to the greater reactivity of the [P–H] linkage in H-phosphinic over H-phosphonic acid. Moreover, H-phosphinates are thermodynamically highly disposed towards oxidation; E° for the $[\text{H}_2\text{PO}_2]^-/[\text{HPO}_3]^{2-}$ couple of -1570 mV represents a driving force of > 300 kJ mol $^{-1}$ towards oxidation of H-phosphinate to H-phosphonate under basic conditions.^{6a}

Having satisfied ourselves that photolytic hydrolysis of iron phosphides could lead to reactive forms of reduced oxidation state phosphorus, we turned our attention to an actual meteorite sample. The Nantan meteorite is an example of a type III CD iron meteorite whose Earth-impact was observed and documented in Guangxi, China in 1516.^{††} Its composition is $> 99\%$ Fe : Ni with a range of other elements present at trace levels. Of these trace elements, phosphorus is known to be present as schreibersite.¹⁶ A sample of Nantan meteorite (19.1 g) was incubated with de-gassed water (100 cm 3) under anoxic conditions for a period of two months. After this time, the aqueous solution was filtered, treated with excess aqueous Na $_2$ S (1 M), filtered again and the water evaporated. The residue was dissolved in D $_2$ O (0.5 cm 3) and analysed by ^{31}P -NMR spectroscopy which revealed only two P-containing products, H-phosphonate and orthophosphate in ca. 6 : 1 molar ratio. Subsequently, the same sample, after washing with de-oxygenated water and drying, was loaded into our photochemical reactor, evacuated and cooled in liquid nitrogen to 77 K on a vacuum-inert atmosphere manifold. Under continuous evacuation, a mixture of ethanol : water (20 cm 3 ; 1 : 1 v/v) was allowed to condense from vapour onto the surface of the phosphide and reactor walls. Irradiation by a low pressure mercury vapour arc tube for a period of 15 h followed. $^{31}\text{P}\{^1\text{H}\}$ -NMR spectroscopic examination of the water-soluble phosphorus products following filtration, Na $_2$ S treatment, evaporation and dissolution of the residue in D $_2$ O (0.5 cm 3) as outlined above revealed a remarkably clean spectrum with signals again for H-phosphonate (11% of soluble P) but essentially no orthophosphate. However, the signals for H-phosphinic acid indicated this to be by far the dominant product (87% of soluble P; Fig. 2A,B). Assignment of each species was again confirmed by doping with an authentic sample (see ESI). In addition, the same unidentified P-containing species as observed in the photochemical ethanol : water experiment on Fe $_3$ P (2% of soluble P) was observed at $\delta 34.7$.

As an example of what might have been available and possible to pre-biotic chemistry, anoxic photolysis of a 1 mM solution of Na[H $_2$ PO $_2$] in ethanol : water (1 : 1 v/v) for 16 h affords a mixture of species which may be classified into two groups: group P $_o$ comprising species in which new [P–O] bonds have been produced and group P $_c$ comprising species in which [P–C] bonds have been formed. The P $_o$ group consists of just three species: un-reacted $[\text{H}_2\text{PO}_2]^-$ (14% of total P), $[\text{HPO}_3]^-$ (37% of total) and the H-phosphonate ester $[\text{HPO}_2(\text{OEt})]^-$ (16% of total). $\ddagger\ddagger$ The P $_c$ group together comprises 33% of the total soluble phosphorus and is a composite of at least three significant components ($> 90\%$ of P $_c$) each of which possesses the characteristics of an alkyl-H-phosphinate of the form $[\text{HPO}_2(\text{R})]^-$. Exactly the same scenario is played out when Na[H $_2$ PO $_2$] is irradiated in the presence of methanol : water (1 : 1 v/v) for 16 h, affording the H-phosphonate ester $[\text{HPO}_2(\text{OMe})]^-$ (38%) and alkyl-H-phosphinates (28%), principally hydroxymethylphosphinate.

In conclusion. (i) H-phosphonic acid is a key product of the anoxic hydrolysis of the iron phosphides and

schreibersite-containing meteorites. (ii) ^{18}O -Isotope experiments confirm that all oxygen in H-phosphonic acid derive exclusively from water. (iii) Subsequent photochemically induced reactions between H-phosphinate and aqueous alcohol efficiently produce organophosphorus compounds. Together we believe these results offer a significant contribution to pre-biotic chemistry and may open a new door to the role of reactive, water-soluble phosphorus as a route to organophosphorus biomolecules. Indeed, our attention is now focused on exploring such links.

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Notes and references

\ddagger Current oceanic water is a rather complex solution of at least 72 different elements. On average the concentration of calcium ions is ca. 0.4 ppt and sodium 11 ppt. Hydroxyapatite, one of the commonest forms of orthophosphate mineral, Ca $_{10}(\text{PO}_4)_6(\text{OH})$ has a solubility product in water K_{sp} of ca. 5×10^{-59} at room temperature.

\S Within phosphate-containing meteorites phosphides contribute 0.2–0.4 wt% of iron-rich meteorite mass. Two of the most well-known such iron meteorites, Canyon Diablo and Sikhote Alin, possess 0.26% and 0.46% phosphorus by weight respectively. See ref. 14b.

\P Our samples of Fe $_n$ P ($n=1-3$) were purchased from Alfa Aesar and used as received. Fe $_2$ P and Fe $_3$ P were stored and handled in a glove-box. Powder X-ray diffraction patterns were in agreement with those on the Cambridge Inorganic Structural database. SEM and EDX analyses are available as ESI.

\parallel In water, H-phosphonate can undergo oxidative hydrolysis to orthophosphate under photochemical irradiation due to the formation of phosphite radicals ($^{\cdot}\text{PO}_3^{2-}$). Thus, photolysis of a 3 mM aqueous solution of disodium H-phosphonate in 50 : 25 : 25 H $_2$ ^{18}O : H $_2$ ^{16}O : D $_2$ ^{16}O (v/v) in a sealed NMR tube under nitrogen over a period of four separate 16 h exposures to UV light (low pressure mercury arc tube) followed by $^{31}\text{P}\{^1\text{H}\}$ -NMR analysis revealed that the resonance for orthophosphate grows steadily with each exposure and finally could be resolved into ^{16}O : ^{18}O isotopomers with a $\delta\Delta$ of 19 ppb, consistent with incorporation of a single ^{18}O -atom per unit.¹⁵

$**$ The sun produces 6.5×10^{-20} of its total radiation in the 180–225 nm range and this energy would have been available in circumsolar space including on the early Earth prior to an oxygenated atmosphere.

$\dagger\dagger$ Our sample of Nantan meteorite (28 g) was purchased from British Jurassic Fossils and elemental compositional data collected *via* ICP shows it to be comparable to known compositional data for this particular meteorite (see ESI).

$\ddagger\ddagger$ Unambiguously identified by comparison against an authentic sample.

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