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Supply of phosphate to early Earth by photogeochemistry after meteoritic weathering

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During terrestrial differentiation, the relatively small amount of phosphorus that migrated to the lithosphere was incorporated into igneous rock, predominantly in the form of basic calcium orthophosphate ($Ca_{10}(PO_4)_6(OH,F,Cl)_2$, apatite). Yet the highly insoluble nature of calcium apatite presents a significant problem to those contemplating the origin of life given the foundational role of phosphate (PO_4^{3-}) in extant biology and the apparent requirement for PO_4^{3-} as a catalyst, buffer and reagent in prebiotic chemistry. Reduced meteorites such as enstatite chondrites are highly enriched in phosphide minerals, and upon reaction with water these minerals can release phosphorus species of various oxidation states. Here, we demonstrate how reduced phosphorus species can be fully oxidized to PO_4^{3-} simply by the action of ultraviolet light on H_2S/HS^-. We used low-pressure Hg lamps to simulate ultraviolet output from the young Sun and ^{31}P nuclear magnetic resonance spectroscopy to monitor the progress of reactions. Our experimental findings provide a cosmochemically and geochemically plausible means for supply of PO_4^{3-} that was widely available to prebiotic chemistry and nascent life on early Earth and potentially on other planets.

Over the past few years, reports have described advances in prebiotic chemistry regarding the terrestrial synthesis of sugars, amino acids, components of ribonucleic acid and vesicles, the bulk of the constituents of the citric acid cycle and potential means to activate nucleotides[1–4]. Furthermore, the chemistry described in these reactions adheres to a geochemical scenario that has developed in tandem with the chemical discoveries and runs in a progressive, logical sequence of events[2,3,5]. This scheme has been outlined several times before and will not be detailed again here[2,3,5], but the key requirements are cyanide, sulfurous reductants and reagents, and ferrous iron at a sunlit location on an emergent landmass that previously experienced meteor impact(s) and was then subjected to fluvial processes. Drainage rivulets are thought to be essential as they allow divergence and confluence of reaction streams, thus enabling separation of subtly different chemistries and remixing of the various products[2,3,5], an idea that has recently garnered support[6,7]. Prebiotic sources for all starting materials, reagents and catalysts have been accounted for within the geochemical scheme, with one exception—phosphate. One source of globally significant amounts of phosphorus would have been meteoritic delivery of the mineral schreibersite ($(Fe,Ni)_3P$). When it was demonstrated that PO_4^{3-} was one of the corrosion products of schreibersite, a plausible source of prebiotic PO_4^{3-} appeared to have been established[8,9]. Although encouraging, the mixture of products obtained from aqueous alteration of $(Fe,Ni)_3P$ is highly variable depending on the conditions employed and may result in hypophosphite ($H_2PO_2^-$), phosphite (HPO_3^{2-}) or PO_4^{3-} being the major product, although PO_4^{3-} is never formed as the sole product[8–12]. This means that any incorporation of phosphorus into prebiotic molecules would probably be indiscriminate and result in a heterogeneous mixture that would seem to frustrate prebiotic chemistry and its transition to biology.

Ultraviolet (UV) light is essential for the prebiotic chemistry that we have described; consequently, we wondered whether photochemical oxidation of $H_2PO_2^-$ and HPO_3^{2-} could provide PO_4^{3-}. We were initially intrigued by a report that identified PO_4^{3-} as a by-product of a reaction involving HPO_3^{2-} and formaldehyde (CH_2O) under UV irradiation[13], although this appeared incongruous with the results from another study involving irradiations of HPO_3^{2-} alone in H_2O where $P_2O_6^{4-}$ was identified as the major product[14]. After re-investigation, we concluded that there may have been a misassignment and that PO_4^{3-} not $P_2O_6^{4-}$ appears to be the product of photolysis of HPO_3^{2-} in H_2O (Supplementary Discussion 1 and Supplementary Figs. 1, 3 and 4). However, in these reports it was assumed that a UV component at 185 nm was responsible for the observed chemistry through photolysis of H_2O, although the direct photolysis of HPO_3^{2-} at 185 nm cannot be ruled out (Supplementary Discussion 1 and Supplementary Figs. 5–7)[13,14]. This mechanism of oxidation of HPO_3^{2-} to PO_4^{3-} cannot be considered plausible because an early Earth atmosphere containing H_2O and CO_2 would not be expected to permit light <200 nm to reach the planet's surface due to absorption and scattering[15], and even light <220 nm may have been limited[16]. Although an alternatative mechanism for the photochemical production of hydroxyl radicals, potentially capable of oxidizing $H_2PO_2^-$ and HPO_3^{2-} to PO_4^{3-}, may have been possible using light with wavelength >200 nm, we instead pursued a solution that would be consistent with our prebiotic scheme and operated at a wavelength fully compatible with models of Earth's early atmosphere[15,16].

As H_2S/HS^- had been implicated in our previous work, often under photochemical conditions[1,2], we contemplated chemistry that may result from photolysis of H_2S/HS^- (a process that has been studied for decades and is known to occur under irradiation at 254 nm (refs.[17,18])). When HS^- is irradiated, an electron is detached from the anion, or excited state of the anion, which is then solvated by H_2O, resulting in a hydrated electron ($e^-_{(aq.)}$) and a hydrosulfidic radical ($HS^\bullet$, Fig. 1)[19]. Hydrated electrons possess a pK_b of ~9.6 (ref. [20]), and a general acid (GA-H) can protonate $e^-_{(aq.)}$ to form a hydrogen atom, $H^\bullet$ (ref. [21]). If this hydrogen atom then abstracted a second such atom from HPO_3^{2-}, radical recombination of the resulting phosphite

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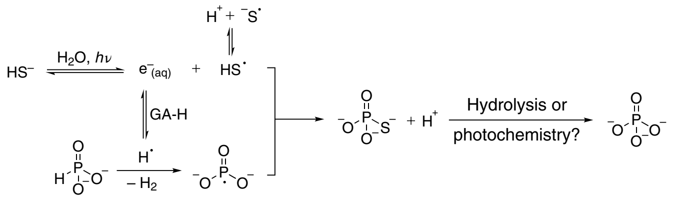

Fig. 1 | Proposed photochemical synthesis of orthophosphate (PO_4^{3-}). Recombination of a phosphite radical with $HS^•$ or $^-S^•$ would lead to thiophosphate (PSO_3^{3-}), a useful reagent for prebiotic chemistry[22].

radical with the remaining $HS^•$ would afford thiophosphate (PSO_3^{3-}) and thence PO_4^{3-} (Fig. 1). This pathway was especially attractive as we have found PSO_3^{3-} to be an extremely versatile prebiotic reagent, although a plausible prebiotic source had remained elusive[22].

Experimental oxidation of reduced phosphorus species

To investigate this proposal, a solution of NaSH (50 mM) and HPO_3^{2-} (30 mM) in 10% D_2O (pH 6.5) was irradiated under our standard conditions, and the sample was inspected using ^{31}P NMR spectroscopy. Clean formation of PO_4^{3-} resulted and a significant rate enhancement was observed when compared with the reaction without HS^- (Fig. 2 and Supplementary Fig. 8). After 8 h irradiation in the presence of HS^-, the reaction was near completion, with ~94% PO_4^{3-} present (Fig. 2). Furthermore, PSO_3^{3-}, as revealed by acidifying the sample before spectroscopy, was also present in the reactions (Supplementary Figs. 9 and 10). Interestingly, there was a lag phase of ~1 h when little PO_4^{3-} was produced. Production of H_2 was evident as gas evolution could be seen from the sample, which implied the concurrent formation of polysulfides ($HS(S)_nS^-$), and we therefore reconsidered the reaction mechanism (Supplementary Discussion 2 and Supplementary Fig. 11). Hence, the oxidation of HPO_3^{2-} to PO_4^{3-} appears to be prebiotically plausible and to rely mainly or solely on polysulfide species, which can be produced in situ by the action of UV light on a solution containing HS^-.

The photochemical reaction of $H_2PO_2^-$ with HS^- was markedly more rapid than the corresponding reaction of HPO_3^{2-}, and after only 1 h, a signal corresponding to PSO_3^{3-} was visible that integrated for ~56% of total phosphorus-containing species (Supplementary Figs. 12 and 13). Oxidation of all species to phosphate was essentially complete in 5.5 h (~96% yield, Supplementary Figs. 12 and 13). Clearly, the mechanism of oxidation of $H_2PO_2^-$ is different from that of HPO_3^{2-} (Supplementary Discussion 2), and considering the immediate reaction of $H_2PO_2^-$ under the conditions, it appears likely that $H^•$ is able to abstract a hydrogen atom from $H_2PO_2^-$ (Fig. 3). Radical recombination of $H\dot{P}O_2^-$ with $HS^•$ or $^-S^•$ leads to $HPSO_2^{2-}$. The subsequent rapid formation and accumulation of PSO_3^{3-} indicates $HPSO_2^{2-}$ is converted to PSO_3^{3-} and does not proceed via HPO_3^{2-} (vide supra and Supplementary Discussion 2). How $HPSO_2^{2-}$ is converted to PSO_3^{3-} is unclear, but we note that another intermediate could not be observed by ^{31}P NMR spectroscopy.

Global abundances of HS^-/H_2S on early Earth are thought to have been low; thus, we repeated the reaction using 400 µM $H_2PO_2^-$ and 800 µM HS^-/H_2S and found all $H_2PO_2^-$ was consumed in 10 min, producing PSO_3^{3-} in ~33% yield. After 4 h, PO_4^{3-} was the only phosphorus-containing species present (Supplementary Fig. 14). Even on present-day oxic Earth, low millimolar concentrations of H_2S/HS^- (<4.1 mM) have been found in the waters emanating from geothermal fields[23]. As noted previously, radical reactions involving $e^-_{(aq.)}$ and/or $H^•$ seem to be little perturbed by dilution in water, making them excellent candidates to perform reactions at geologically relevant concentrations[5]. Alternatively, H_2S could have accumulated as HS^-/S^{2-} in small bodies of alkaline water. Re-running the experiment at pH 9.0 (Supplementary Fig. 15) or pH 10.3 (Supplementary Fig. 16) had little effect on the reaction. As high pH did not perturb the reaction, we wondered whether diamidophosphate (DAP ($(H_2N)_2PO_2^-$), a suggested reagent for prebiotic phosphorylations[24]) could be formed if the reaction were run in the presence of ammonia. After several experiments, we were unable to find a prebiotically plausible synthesis of DAP using our oxidative conditions (Supplementary Figs. 17 and 18). However, a recent report has described the synthesis of DAP by reacting the schreibersite surrogate Fe_3P with concentrated (>1 M) ammonia solutions[25]. The same study also showed that UV irradiation of HPO_3^{2-} in ammonia solution provides access to amidophosphate ($(H_2N)PO_3^{2-}$) (ref. [25]).

Correlation of experimental results with early Earth environments

The low-pressure mercury lamps used during our experiments emit the majority of their output over a narrow range of light centred at 254 nm (~252–256 nm), which has been considered a suitable proxy for the emission of light from the young Sun at these wavelengths but does not represent its expected broadband emission[15]. A comparison of the UV flux from the equipment used in our experiments with that from the young Sun at Earth's surface has been made before and was estimated as being roughly five orders of magnitude more powerful[16]. However, the photochemical oxidation of HS^- ($\lambda_{max} = 230$ nm (ref. [26])) presumably takes place over a much broader range of wavelengths than the output of the Hg lamps used in these experiments, and we thus consider a 100,000-fold reduction in rate of photochemical oxidation of HS^- on Hadaean Earth, under analogous conditions to those used here, to be a lower limit (this equates to the reaction taking place on the scale of tens of years rather than hours). While the direct photolysis of HO^- may have produced $HO^•$, this would presumably require light <220 nm (and optimally <200 nm, λ_{max} ~195 nm (ref. [26])). Although the young Sun's UV output would have provided light of these wavelengths, the viability of such a process would have depended heavily on the shielding properties of Earth's atmosphere to shorter wavelength light[15,16]. It is also possible that Fenton chemistry (Fe^{2+}/H_2O_2) oxidized reduced phosphorus species to phosphate, a process that may have been operational in the mid-Archaean but was unlikely in the Hadaean, particularly in a highly reduced environment[27].

Any phosphate that was produced, either directly from the corrosion of schreibersite or via the oxidation chemistry we report herein, would have been susceptible to precipitation by Ca^{2+} ions at moderately high pH or by ferrous ions. For example, plagioclase alteration (albitization) by hot brine yields effluent fluids enriched in $CaCl_2$ and $Ca(OH)_2$ (ref. [28]). Springs, streams or lakes arising from these fluids may have been devoid of PO_4^{3-} following precipitation of calcium phosphates but could have contained high concentrations of $H_2PO_2^-$ and/or HPO_3^{2-}, which are far more soluble in the presence of calcium ions[29]. However, as albitization proceeded, the concentration of calcium ions in the exiting fluid waters would drop until eventually all calcium ions had been released or the concentration became negligible, a phenomenon indicated previously by the depletion of calcium in source rocks[30]. After this point, any oxidation of $H_2PO_2^-$ and HPO_3^{2-} would provide PO_4^{3-} in an environment devoid of Ca^{2+} ions. In the presence of Fe^{2+} ions, PO_4^{3-} forms the insoluble complex vivianite ($Fe[Fe_2(PO_4)_2]$). It was pointed out previously, however, that vivianite can be solubilized by cyanide, generating ferrocyanide ($Fe(CN)_6^{4-}$) and PO_4^{3-} in the process[2,3], an idea recently adopted by others[31]. As hydrogen cyanide is generated by a variety of mechanisms during meteoritic impacts[32–34], this method of 'rescuing' PO_4^{3-} from Fe^{2+} is consistent with the proposed source of PO_4^{3-} and our previously proposed geochemical and prebiotic scheme[2,3,5].

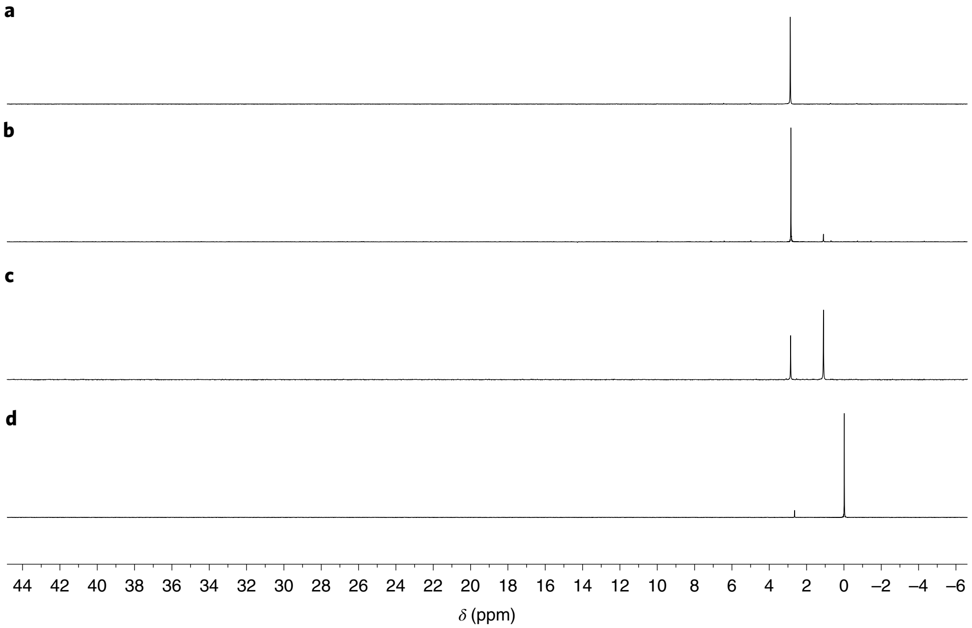

Fig. 2 | Photochemical oxidation of phosphite. a, The ^{31}P NMR spectrum of a commercial sample of phosphite at pH 6.5. **b**, The ^{31}P NMR spectrum of the irradiation of phosphite (30 mM) in 10% D_2O after 4 h. **c**, The ^{31}P NMR spectrum of the irradiation of phosphite (30 mM) in the presence of NaSH (50 mM) after 4 h according to procedure 1 (Methods). **d**, As spectrum **c** after 8 h irradiation. Differences in chemical shift (δ) are due to slight variations in pH.

Meteoritic flux of phosphorus to Earth

There is growing understanding that a 'late heavy bombardment' spike in impact flux to Earth ~3.9 billion years ago (Ga)[35] did not occur and instead there was a gradual, monotonic decline of impactor frequency[36–38]. According to the latest models reconciled with cosmochemical tracers, subsequent to the Moon-forming impact there was one other colossal impact with Earth by a differentiated body (dubbed Moneta) that re-equilibrated Earth's silicate reservoirs for the final time (~4.48 Ga) and in turn explains both the over-abundance and relative chondritic proportions of highly siderophile elements in Earth's mantle[37,39]. Others have argued that a larger number of smaller impactors could account for the discrepancy between observed highly siderophile element abundances and those calculated or obtained from experimental models[40]. Assuming enstatite chondrite-type composition (Supplementary Discussion 3), we calculated the quantity of reduced phosphorus contained in Moneta's core to have been ~1.69×10^{20} kg (around six orders of magnitude higher than the combined phosphorus inventory of present-day Earth's oceans, soils and biomass[41], Supplementary Note 1). If a differentiated body of this size travelling at 16 km s^{-1} struck Earth at 45° (statistically the most likely angle[42]), the majority of the core would have experienced shock-induced melting followed by fragmentation. Upon re-accretion, this material would have fragmented further into ~1 mm sized metallic hail that would have rained onto the surface of early Hadaean Earth[37]. The reaction of $(Fe,Ni)_3P$ contained in this molten hail with H_2O under intensely reducing conditions at such extremes of temperature should have produced substantial amounts of phosphine (PH_3), especially considering the propensity of hypophosphorous and phosphorous acid, and oxy anions thereof, towards disproportionation[43,44]. If temperatures were high enough, direct evaporation of P_2 from $(Fe,Ni)_3P$ would have been possible, and under the high pressure of H_2, a portion of this would have been converted to PH_3. Atmospheric oxidation of PH_3, for example, by hydroxyl radicals, leads to the rapid rainout of much less volatile and more hydrophilic phosphorus oxy acids, for example, hypophosphorous acid. If PH_3 was not formed on impact, the overwhelming majority of $(Fe,Ni)_3P$ and other metallic materials from Moneta's core would have been subsumed in the ensuing magma ocean. Delivery of reduced phosphorus would then depend on late accretion of enstatite planetesimals and meteorites.

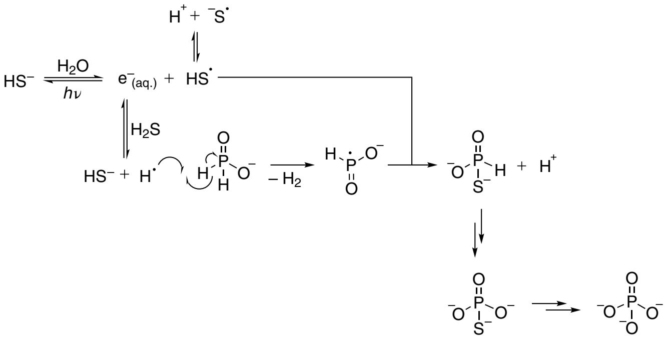

Fig. 3 | Proposed mechanism for the formation of PSO_3^{3-} and thence PO_4^{3-} from the irradiation of $H_2PO_2^-$ and HS^-. Apparently a weaker P–H bond of $H_2PO_2^-$ relative to HPO_3^{2-} allows immediate hydrogen atom abstraction by H•.

If we assume PH_3 production did not occur upon impact or re-accretion of these smaller objects, metallic spherules (and the small amount of fragmented metallic rock around the impact site) would have been subjected to weathering by rainfall and/or groundwater, producing $H_2PO_2^-$ and HPO_3^{2-} as previously described[8–12]. Therefore, on the basis of the late accretion production model developed by Mojzsis et al.[38], we calculated the amount of reduced phosphorus that could have been delivered to Earth during late accretion and subsequent to the Moneta impact, that is, excluding material delivered by Moneta, from 4.50 Ga to 3.50 Ga in million-year increments (Fig. 4, Supplementary Discussion 3 and Supplementary Table 1). At 4.40 Ga (the point at which Earth is thought to have been habitable[38]), 2.96×10^7 kg yr^{-1} of reduced phosphorus could have been

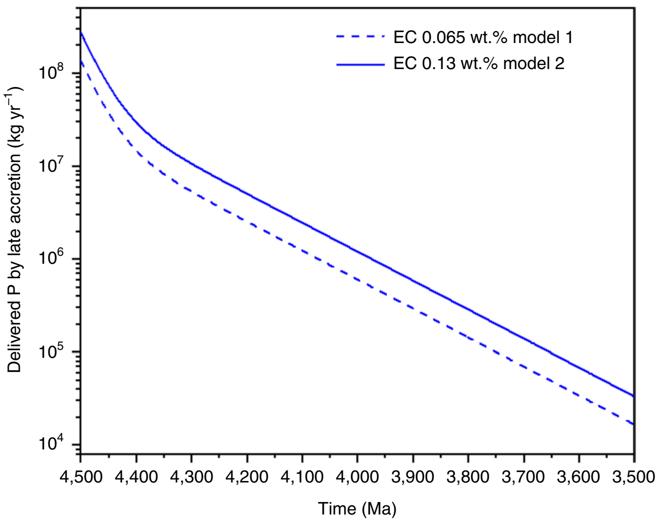

Fig. 4 | Delivery of reduced phosphorus to Earth by late accretion. Declining flux of reduced phosphorus delivered to Earth by Enstatite Chondrite (EC)-type planetesimals (≥1 km in diameter) throughout the Hadaean and early Archaean eons and subsequent to the proposed Moneta impact at ca. 4,500 Ma (based on the model developed by Mojzsis et al.[38]).

expected to be delivered to Earth; by 4.00 Ga this quantity would have dropped to 1.20×10^6 kg yr^{-1} and by 3.50 Ga to 3.30×10^4 kg yr−1 (using 0.13 wt.% as baseline model, see Supplementary Discussion 3 and Supplementary Table 1). The total mass of reduced phosphorus that late accretion could have delivered to Earth from 4.50 Ga to 3.50 Ga is 1.32×10^{19} kg (Supplementary Note 1 and Supplementary Table 1). Previous calculations of the meteoritic delivery of phosphorus to Earth during late accretion gave similar values to those we report here[45,46]. Until very recently[38,47], however, there existed no quantitative estimate for late accretion that used cratering data and highly siderophile element abundances combined with dynamics to show enstatite chondrites were a principle source of late accretion to Hadaean Earth. Clearly, it cannot be expected that the deposition of phosphorus resulting from late accretion occurred evenly over the surface of Earth; hence, we provide the flux in kg yr^{-1}. For the phosphorus content of a meteorite to be useful in the prebiotic chemistry we invoke, its payload must settle on dry land. Although impacts striking the ocean may have been capable of delivering material to dry land (depending on the size, velocity and impact angle of the impactor and depth of the water column), presumably maximal dispersion of a meteorite's content over a land mass would be by a (near) direct hit. The concentrated deposition of the contents of metal-rich meteorites on dry land has already been described[45]. The smallest objects considered in our calculations, and therefore the most abundant and likely to hit a subaerial landmass, were 1 km in diameter and could have individually delivered 3.2×10^9 kg of reduced phosphorus (Supplementary Note 1). Objects smaller than 1 km were not considered in the model as the mass augmentation to Earth from these objects relative to the rest of late accretion is considered negligible. However, this does not discount their potential significance for the origin of life given the inversely proportional relationship of impactor size and their impact frequency.

As reduced phosphorus was delivered throughout the Hadaean eon, the weathering of $(Fe,Ni)_3P$ and oxidation by UV/HS$^-$ could have provided a constant supply of thiophosphate and phosphate for prebiotic chemistry and early life. Furthermore, atmospheric photolysis of H_2S resulted in the deposition of polysulfides on Earth's surface and oceans[48], thus providing the apparent requisite species for phosphite oxidation. In addition, due to the decreased pK_a and volatility of polysulfides relative to H_2S[49], the accumulation of these species, particularly in oceans, may have been significant considering the potential for diagenetically produced phosphite[50]. Thus, the photochemical oxidation of phosphite by polysulfides could have provided a persistent low level of oceanic phosphate throughout the mid- to late Hadaean and early Archaean.

Online content

Any methods, additional references, Nature Research reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at https://doi.org/10.1038/s41561-020-0556-7.

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Methods

General experimental. Reagents and solvents were bought from Sigma-Aldrich, Alfa Aesar and Santa Cruz Biotechnology and were used without further purification. Photochemical reactions were carried out using a Rayonet RPR-200 photochemical reactor chamber, with cooling fans switched on and fitted with low-pressure RPR-2537A Hg lamps purchased from Rayonet (principle emission 254 nm). The UV reactions were run in Hellman QS Spectrosil 10.0 mm quartz cuvettes with four UV-transparent windows. The UV-visible (UV-Vis) spectra were acquired using a Varian 6000i UV-Vis-NIR spectrophotometer and Cary winUV software (Agilent Technologies) in Hellman QS Spectrosil quartz cuvettes. A Mettler Toledo SevenMulti pH/mv module fitted with a Thermo Scientific Orion 8103BN pH probe was used to measure pH, and deoxygenation of solvents was achieved by sparging with Ar for 20–30 min before use. The ^{1}H and ^{31}P NMR spectra were acquired using a Bruker Ultrashield 400 Plus (at 400.1 and 162.0 MHz, respectively) or Bruker Ascend 400 (at 400.2 and 162.0 MHz, respectively) using H_2O suppression to collect ^{1}H NMR data (reactions were run in 10% D_2O–H_2O solutions). Yields were calculated by relative integration of NMR signals. Chemical shifts (δ) are given in ppm.

Experimental. *Procedure 1.* For the oxidation of phosphite, sodium phosphite pentahydrate (0.060 mmol, 13 mg) and $NaSH{\cdot}xH_2O$ (>60%, 0.100 mmol, 9 mg) were dissolved in degassed 10% D_2O (1 ml) in an Eppendorf tube, and the pH was adjusted to 6.5 with degassed HCl. The volume was increased to 2 ml with degassed 10% D_2O; then the solution was transferred to a quartz cuvette and irradiated for the desired amount of time, after which the reaction was analysed by ^{31}P NMR spectroscopy.

Procedure 2. For the oxidation of hypophosphate, hypophosphorous acid (50% wt., 0.060 mmol, 6.2 µl) was dissolved in degassed 10% D_2O (1 ml) in an Eppendorf tube, and the pH was adjusted to near neutrality with degassed NaOH. $NaSH{\cdot}xH_2O$ (>60%, 0.100 mmol, 9 mg) was added, and the pH was adjusted to 6.5; then the volume was increased to 2 ml with degassed 10% D_2O. The solution was transferred to a quartz cuvette and irradiated for the desired amount of time, after which its contents were analysed by ^{31}P NMR spectroscopy.

Procedure 3. For the oxidation of hypophosphate at low concentration, hypophosphorous acid (50% wt., 1 µl) was dissolved in degassed 10% D_2O (1 ml, 9.1 mM solution), and 83 µl of this solution was added to degassed 10% D_2O (1 ml) in an Eppendorf tube. The pH was adjusted to near neutrality with degassed NaOH. $NaSH{\cdot}xH_2O$ (>60%, 1.9 mg) was dissolved in degassed 10% D_2O (1 ml, 20.3 mM solution), and 80 µl was added to the reaction; then the pH was adjusted to 6.5. The volume was increased to 2 ml with degassed 10% D_2O, and the solution was transferred to a quartz cuvette and irradiated for the desired amount of time, after which the reaction was analysed by ^{31}P NMR spectroscopy.

Procedure 4. For the oxidation of hypophosphate at high pH, hypophosphorous acid (50% wt., 0.060 mmol, 6.2 µl) was dissolved in degassed 10% D_2O (1 ml) in an Eppendorf tube, and the pH was adjusted to near neutrality with degassed NaOH. $NaSH{\cdot}xH_2O$ (>60%, 0.100 mmol, 9 mg) was added, and the pH was adjusted to 9.0; then the volume was increased to 2 ml with degassed 10% D_2O. The solution was transferred to a quartz cuvette and irradiated for the desired amount of time, after which its contents were analysed by ^{31}P NMR spectroscopy.

Data availability

The authors declare that all data associated and supporting this study are available in the published article and Supplementary information. We have chosen not to make the data available in a publicly accessible repository at this time.

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Author contributions

D.J.R. and J.D.S. designed the chemical experiments, D.J.R. carried out the chemical experiments, and D.J.R. and J.D.S. analysed the data. S.J.M. calculated the quantities of reduced phosphorus delivered to Earth from dynamical models. D.J.R. wrote the manuscript with input from J.D.S. and S.J.M. All authors read and approved the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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