



# Archean phosphorus recycling facilitated by ultraviolet radiation

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Of the six elements incorporated into the major polymers of life, phosphorus is the least abundant on a global scale [E. Anders, M. Ebihara, *Geochim. Cosmochim. Acta* 46, 2363–2380 (1982)] and has been described as the “ultimate limiting nutrient” [T. Tyrrell, *Nature* 400, 525–531 (1999)]. In the modern ocean, the supply of dissolved phosphorus is predominantly sustained by the oxidative remineralization/recycling of organic phosphorus in seawater. However, in the Archean Eon (4 to 2.5 Ga), surface waters were anoxic and reducing. Here, we conducted photochemical experiments to test whether photodegradation of ubiquitous dissolved organic phosphorus could facilitate phosphorus recycling under the simulated Archean conditions. Our results strongly suggest that organic phosphorus compounds, which were produced by marine biota (e.g., adenosine monophosphate and phosphatidylserine) or delivered by meteorites (e.g., methyl phosphonate) can undergo rapid photodegradation and release inorganic phosphate into solution under anoxic conditions. Our experimental results and theoretical calculations indicate that photodegradation of organic phosphorus could have been a significant source of bioavailable phosphorus in the early ocean and would have fueled primary production during the Archean eon.

Archean ocean | phosphorus cycle | recycling of organic phosphorus | UV radiation | photodegradation

Phosphorus (P) is an essential element in the synthesis of the biomolecules that form protein replication machinery (e.g., ribosomes and related molecules), membranes (e.g., phospholipids), and metabolic energy (e.g., ATP) across the tree of life. However, of the six major elements that comprise biological polymers (H, C, N, O, P, and S), phosphorus is the least abundant on Earth (1). The supply of P to the oceans is constrained by continental and seafloor weathering and the element, as phosphate, is poorly soluble in surface waters. Hence P has long been proposed to be the “ultimate” nutrient that limits marine biological productivity across geologic timescales (2–4). In contrast, many previous studies suggest that in the global ocean, nitrogen fixation limits primary production (5–8). The availability of fixed inorganic nitrogen depends on the biotic fixation of nitrogen gas to ammonia, and in the presence of molecular oxygen, the formation of nitrite and nitrate (9). All the reactions in the N cycle are biologically mediated by prokaryotes. Resolving this debate requires a better understanding of the evolution of these two biogeochemical cycles. Here, we focus on the evolution of the P cycle in the Archean ocean, before atmospheric oxygen became a major gas in Earth’s atmosphere.

In the modern ocean, the delivery of 10 to 15 × 10<sup>10</sup> mol P/y as orthophosphate via continental weathering and riverine transport provides the external P supply for biosynthesis (10, 11). Thus, nearly all (~99%) fixed P in the ocean is in the form of organic phosphorus, which is not available for direct uptake by microbes due to transport considerations (12, 13). However, there is some limited evidence suggesting the direct assemblage and uptake of small sugar phosphates, e.g., glucose-6-phosphate, by some eukaryotic microalgae under conditions when orthophosphate is nearly absent but there is relatively high dissolved organic P (13, 14). In natural settings, nearly all organic P would undergo rapid microbial and extracellular enzymatic degradation (i.e., remineralization) to preferentially hydrolyze the C-O-P bond (15, 16). These reactions release orthophosphate for marine primary productivity within the water column (11), with the remainder being sequestered as minerals in sediments (17). P recycling therefore plays a dominant role in sustaining the modern marine P cycle, supplying >99% (around 3.7 × 10<sup>13</sup> mol P/y) of total P for modern marine primary production (10).

Given that the abiotic hydrolysis of phosphate esters is prohibitively slow, with an average half-life time > 10<sup>7</sup> y at 25 °C and neutral pH (18), alternative pathways of P recycling would have been required to sustain orthophosphate concentrations in the Archean ocean during the evolution of early marine microbial communities. In the modern ocean, oxidants (e.g., O<sub>2</sub>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>) promote efficient P recycling via the oxidative degradation of P-bearing organic compounds (19). In contrast, prior to the oxidation of

## Significance

Biological recycling of organic phosphorus is the largest source for marine phosphorus in the contemporary ocean. However, on the early Earth, this recycling pathway is thought to have been inefficient prior to the Great Oxidation Event 2.35 billion years ago, prompting the hypothesis that a “phosphorus famine” limited primary production in the Archean oceans. Here, we show that UV light can photochemically degrade organic phosphorus within simulated Archean waters over biologically relevant timescales. Our models suggest that UV light-mediated recycling of organic phosphorus at the surface of the Archean oceans would have provided more than enough phosphorus for early marine primary productivity to flourish, eliminating the limitation imposed by “phosphorus famine” on the development of the early biosphere.

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the atmosphere and surface seawater during the Paleoproterozoic around 2.4 billion years ago (Ga), few sources of oxidants are thought to have been available to drive P recycling (19). Furthermore, Archean seawater was likely rich in reductants (20) that would efficiently scavenge reactive oxygen species (ROS) such as  $\cdot\text{OH}$ , thereby limiting their role in the recycling of organic phosphorus.

Various models have attempted to constrain the recycling flux of P in the Archean ocean with estimates ranging between 0.01% and 10% of modern values (19). A diminished rate of P recycling might have limited early marine primary productivity, a condition referred to as phosphorus "famine" (19). Recently, Hao et al. (21) estimated the weathering flux of P, and together with a previously estimated recycling flux (22), proposed a total P flux of between  $18$  and  $154 \times 10^{10}$  moles P/y in late Archean ocean (21), corresponding to <5% of modern marine primary productivity. However, such estimates did not consider the role of photochemistry, a potentially viable pathway to degrade organic phosphorus in the early anoxic ocean.

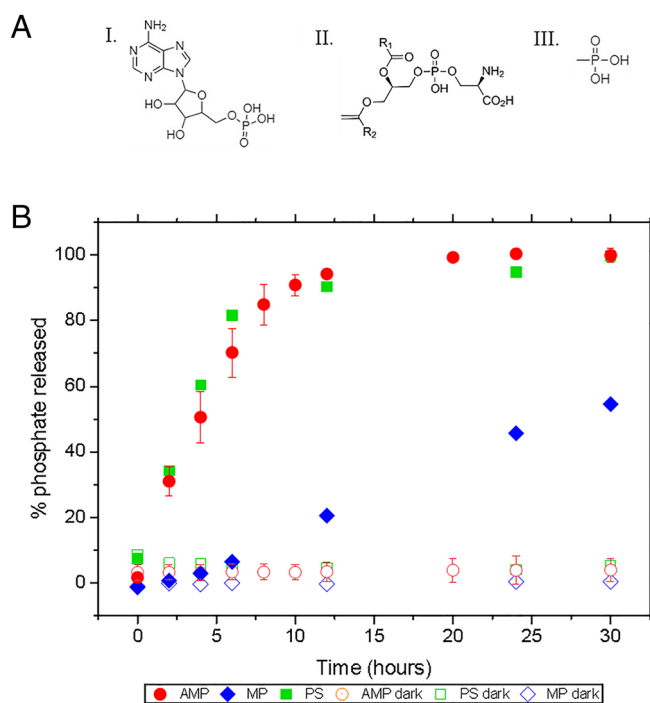
Prior to the appearance of the ozone layer in the Paleoproterozoic, ultraviolet (UV) radiation, ranging from 200 to 400 nm, could directly reach the Earth's surface (23) and interact with surface waters, likely reaching a depth of a few to 10 s of meters (24). These high energy photons have been shown to drive many endothermic chemical reactions in seawater (25, 26). It is also well known in the wastewater treatment industry that UV radiation can facilitate the degradation of various organic phosphorus compounds (27, 28), but this observation is based on experiments mainly conducted with synthetic organic phosphorus compounds and the addition of strong oxidants (e.g.,  $\text{H}_2\text{O}_2$ ,  $\text{O}_2$ , and  $\text{NO}_3^-$ ), which generate large amounts of ROS following UV radiation. Whether the photodegradation of natural organic phosphorus was possible and prominent under the anoxic/reducing conditions relevant to the Archean ocean remains poorly understood. Moreover, the quantum yield ( $\Phi_\lambda$ , defined as amount of product formed per spectrally absorbed photon) of organic phosphorus photodegradation, which is critical to quantifying light-driven organic phosphorus recycling in the Archean ocean, is poorly constrained.

Here, we investigate the photodegradation rates of several natural organic phosphorus compounds (adenosine monophosphate or AMP, methylphosphonic acid or MP, and phosphatidylserine or PS; see *SI Appendix, section S1*) by UV light under anoxic conditions simulating the Archean ocean. These organic phosphorus compounds represent abundant forms of organic phosphorus found in either meteorites (phosphonic acid, like MP; ref. 29) or modern seawater released from decaying biomass (nucleotides and phospholipids, like AMP and PS, respectively; ref. 12) as well as two major types of chemical bonds in natural organic phosphorus, i.e., C-P and C-O-P (12, 30). Meteoritic delivery likely served as the major source of organic phosphorus to prebiotic ocean in early Archean (31), and consequently, phosphonic acid, as the major organic phosphorus compound found in carbonaceous meteorites (29), may have been the major organic phosphorus compound in primitive seawater (31). Moreover, MP is a major constituent of phosphonic acid in carbonaceous meteorites (29). However, following the emergence of life and waning impact events (32), the biosynthesis of organic phosphorus compounds such as nucleotides and phospholipids, although phospholipids may have evolved later (33), should have dominated the supply of organic phosphorus in Archean seawater (30). We therefore measured quantum yields ( $\Phi_\lambda$ ) of the photodegradation of these organic phosphorus compounds in terms of orthophosphate release, and, using these values, estimated the overall UV-driven recycling flux of P in the Archean ocean.

## Results and Discussion

Our UV irradiation experiments revealed the rapid release of free phosphate from organic phosphorus photooxidation under anoxic conditions (Fig. 1). Among them, AMP, as a common nucleotide that forms DNA, RNAs and ATP, has a strong absorbance peak at 260 nm due to the optically active  $\pi$ -bonds in its nucleoside group (Fig. 1A; see also *SI Appendix, section S2 and Fig. S1*). The decrease in UV absorbance of AMP over the course of UV exposure (*SI Appendix, Fig. S1*), together with an increase in free inorganic phosphate at an initial rate  $9.50 \times 10^{-5}$  moles orthophosphate  $\text{d}^{-1}$ , demonstrates simultaneous photolysis of both the nucleoside group and C-O-P bond. In comparison, PS, a common component of cellular membranes, released phosphate at a slightly faster initial rate ( $1.48 \times 10^{-4}$  moles P  $\text{d}^{-1}$ ) than AMP (Fig. 1), probably reflecting the effect of carboxyl groups in PS's side chain via Norrish type reactions (34). In contrast, MP, a trace compound in biology (35) but a major organic-P constituent in carbonaceous meteorites (29), released phosphate during UV exposure with an initial rate of  $2.2 \times 10^{-5}$  moles P  $\text{d}^{-1}$ , more than four times slower than AMP and PS, likely due to the lower reactivity of C-P bond in MP toward hydrolysis than that of O-P bond in AMP and PS (36).

We also tested the effect of Fe(II) on the photodegradation of organic phosphorus by introducing 1 mM of dissolved Fe(II) as  $\text{FeCl}_2$ , which is relevant to Archean seawater (37). We observed the change of the solution color indicating Fe(II) photooxidation and possible Fe(III) precipitation under anoxic conditions, consistent with a previous report (25), but found no significant effect on the rate of phosphate release (*SI Appendix, Fig. S2*). Our results are in contrast to a previous study showing that the presence of Fe(III) could promote the generation of ROS and thus organic phosphorus degradation (38), probably reflecting the less efficient generation of ROS under anoxic conditions and/or the faster



**Fig. 1.** Organic phosphorus (OP) photodegradation by UV light. (A) Chemical structures of model OP, i.e., I. AMP, II. PS, and III. MP, investigated in this study. (B) Phosphate released by OP photodegradation. Open symbols display the results of dark controls.

photodegradation of organic phosphorus than  $\text{Fe}^{2+}$  photooxidation. Moreover,  $\text{HCO}_3^-$  was proposed to scavenge  $\bullet\text{OH}$  radical and slow organic phosphorus photolysis (39) (see also *SI Appendix, section S3*), but no significant effect was observed here (*SI Appendix, Fig. S2*). This suggests there was limited  $\bullet\text{OH}$  radical formation in the experimental solutions. Finally, we performed a positive test by adding  $\text{H}_2\text{O}_2$  to our experiments and observed very rapid photolysis of organic phosphorus (*SI Appendix, Fig. S3*), confirming that oxic, radical-rich conditions would favor the photolysis of organic phosphorus, consistent with previous studies (27, 40).

### Implications for Archean Phosphorus Cycle and Habitability of the Early Ocean.

Organic phosphorus compounds are essential in the assembly of cellular life as we know it. However, the abiotic formation of C-O-P and C-P bonds is usually endothermic and thus thermodynamically unfavorable in aqueous solutions relevant to primitive seawater chemistry (41, 42). Thus, the availability and accumulation of organic phosphorus could have been chemically challenging for the origin of life (41, 42). Previous studies have suggested a sunlight-driven, wet-dry cycling mechanism in lacustrine or coastal marine settings as an essential process for prebiotic synthesis (43–45). Several studies have also proposed meteoritic impacts as either a direct (e.g., supplying phosphonic acid) or an indirect (via providing reactive inorganic phosphorus that could readily form organic phosphorus in the presence of organic precursors) route to supply organic phosphorus to the Archean ocean (29, 31, 46). However, our experimental results strongly suggest that UV radiation would have greatly facilitated the breaking of both C-P and C-O-P bonds under anoxic conditions, thereby reducing the stability and accumulation of organic phosphorus in shallow waters or on land. Moreover, another recent study observed that UV radiation could drive the hydrolytic oxidation of reactive inorganic phosphorus, including phosphite ( $\text{HPO}_3^{2-}$ ) and hypophosphite ( $\text{H}_2\text{PO}^-$ ) (47), possibly reducing their accumulation for further organic phosphorylation in surface waters on the primitive Earth. Therefore, UV radiation would potentially inhibit the synthesis and accumulation of the organic phosphorus compounds (as well as their formation bases, including reactive inorganic phosphorus) necessary for life's

emergence, unless protected by natural shielding mechanisms, e.g. through UV absorbers in the primitive atmosphere (48) or seawater (49) or by mineral adsorption (50, 51).

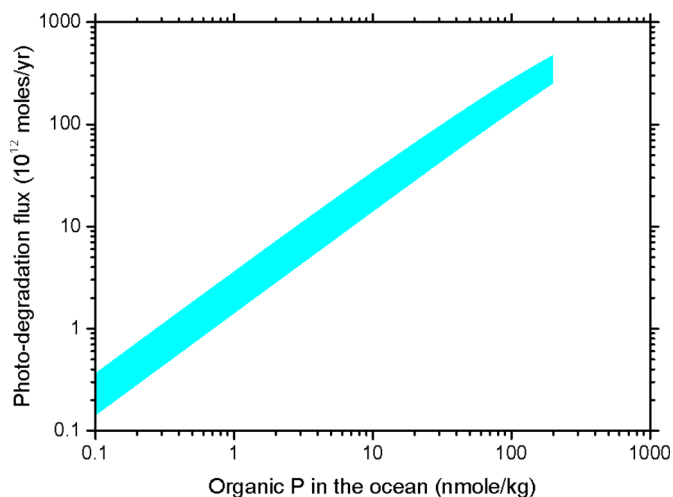
After life's emergence in the late Hadean or early Archean (52–54), the decomposition of biomass would soon become the predominant source of organic phosphorus in the ocean by the middle to late Archean. As prokaryotes evolved, dissolved organic phosphorus in the ocean would have been mainly composed of simple organic phosphorus species, e.g. nucleotides and possibly phospholipids. Even in the modern ocean, dissolved organic phosphorus is primarily composed of low-molecular-weight nucleotides and phospholipids (12, 30) (see also *SI Appendix, section S1*). Phosphate esters (C-O-P bond) are the predominant fraction in modern seawater and among them, AMP is one major species (12). PS represents another major type of phosphate ester in modern seawater (12, 30), but probably not in the Archean (33). Thus, we used AMP as the model organic phosphorus compound to calculate phosphorus recycling fluxes via photodegradation in the photic zone of the middle to late Archean ocean. Considering the faster photodegradation rate of PS over AMP (Table 1), our calculation represents a conservative estimate of photodegradation flux if phospholipids were a major type of organic phosphorus in the Archean seawater.

Our model suggests that phosphorus recycling *via* organic phosphorus photodegradation relies heavily on the concentration of organic phosphorus in the photic zone (Fig. 2). Even assuming that Archean surface seawater contained 1 nM organic phosphorus [50 to 200 times less than the levels in both the coastal and open ocean seawater (30)], photodegradation could still have released  $1.7$  to  $4.4 \times 10^{12}$  moles/y of free orthophosphate (Fig. 2). This is 4 to 10 times higher than previous calculations (19), which assume that phosphorus recycling relies on the availability of oxidants. Our estimates are also much higher than the reported continental input of phosphorus in the Archean, even assuming rapid growth of land in late Archean ( $0.04$  to  $0.34 \times 10^{12}$  moles/y bioavailable phosphorus) (21). Thus, the photolytic degradation of organic phosphorus could have greatly enhanced phosphorus recycling in anoxic Archean oceans and provided surplus bioavailable phosphorus for biological production, presumably easing the “phosphorus famine” (3, 21).

**Table 1. Initial release rates of phosphate under all tested conditions**

Organic P	Optical Filter (nm)*	Experiment Additive	Initial release rate (moles phosphate/day)	Quantum Yield (moles phosphate/photon)
AMP	No	No	$9.50 \times 10^{-5}$	No data
AMP	LP (>225)	No	$1.10 \times 10^{-5}$	No data
AMP	No	50 mM $\text{Fe}^{2+}$	$7.28 \times 10^{-5}$	No data
AMP	No	50 mM $\text{HCO}_3^-$	$9.90 \times 10^{-5}$	No data
AMP	No	50 mM $\text{H}_2\text{O}_2$	$4.81 \times 10^{-4}$	No data
AMP	No	50 mM $\text{C}_3\text{H}_8\text{O}$	$7.10 \times 10^{-5}$	No data
AMP	BP (200)	No	$4.16 \times 10^{-6}$	$1.75 \times 10^{-3}$
AMP	BP (230)	No	$5.30 \times 10^{-6}$	$1.41 \times 10^{-2}$
AMP	BP (260)	No	$6.00 \times 10^{-7}$	$4.86 \times 10^{-4}$
PS	No	No	$1.48 \times 10^{-4}$	No data
PS	BP (200)	No	$2.36 \times 10^{-5}$	$2.58 \times 10^{-1}$
PS	BP (230)	No	$1.06 \times 10^{-5}$	$2.81 \times 10^{-2}$
MP	No	No	$2.20 \times 10^{-5}$	No data
MP	BP (200)	No	$4.16 \times 10^{-6}$	$1.75 \times 10^{-3}$
MP	BP (230)	No	$2.96 \times 10^{-6}$	$7.85 \times 10^{-3}$

\*Filter type (LP represents long-pass filter; BP represents band pass filter) and transmission wavelength (center wavelength for BP).



**Fig. 2.** Modeled flux of photochemically degraded phosphate as a function of OP concentration in Archean oceans. Variation in the recycled flux at a given OP concentration is largely due to optical depth of UV in seawater.

The recycling flux of P via photodegradation of organic phosphorus together with that for continental supply would support a biological productivity up to  $5.4 \times 10^{14}$  moles C  $y^{-1}$  in the late Archean ocean, assuming a C:P ratio of 114:1 (55). This accounts for 14% of modern marine primary production, but is higher than previous estimates (21, 56, 57). Particularly, our estimate is much higher than those reported by Ward et al. (57) (~0.1 % of modern marine primary production in late Archean), which concluded that Archean marine primary production was limited by the supply of electron donors before the advent of oxygenic photosynthesis. Our results confirm that the supply of P was likely not bio-limiting and that instead other parameters such as electron donors (57), nitrogen, or transition metals (7), imposed stronger constraints until the appearance of oxygenic photosynthesis. By then, rapid P recycling associated with photodegradation of organic phosphorus could have kept pace with expanding populations and the productivity of oxygenic photoautotrophs, and supported a rapid oxidation of the atmosphere (58). In short, there is no evidence that phosphate was ever a significant limiting nutrient for primary productivity in the Archean oceans.

## Materials and Methods

**Reaction Setup.** Solutions were prepared in a 5%  $H_2$  + 95%  $N_2$  purged anaerobic chamber (Coy Laboratory Products; <0.01 ppm  $O_2$ ) by dissolving 50  $\mu$ mol of AMP, PS, or MP in 0.5 molal solutions of NaCl. Additional experiments were also performed by separately testing effects of other major sea salts, i.e.,  $CaCl_2 \cdot 2H_2O$  (50 mmolal),  $MgCl_2 \cdot 6H_2O$  (50 mmolal),  $FeCl_2 \cdot 4H_2O$  (1 mmolal), and  $NaHCO_3$  (10 mmolal). Moreover,  $H_2O_2$  (1 mmolal; positive control) and isopropanol (1 mmolal; negative control) were introduced in another two runs to test the role of ROSs in OP photodegradation. Solutions were transferred to several quartz-bottomed reaction cells and sealed with butyl stoppers and aluminum crimp caps to prevent gas exchange with the open atmosphere. They were then purged with  $N_2$  (99.999% purity; Airgas INC.) to remove  $H_2$  in the headspace (inherited from the anaerobic chamber). Gas chromatography with a thermal conductivity detector (Model 310, SRI Instruments) was used to monitor the levels of  $O_2$ ,  $H_2$ , and  $CH_4$  throughout experiments.

**UV Irradiation Experiments.** A 450-W Hg vapor lamp (Hanovia PC451.050) in a photochemical quartz immersion well was used to irradiate the parallel samples (SI Appendix, Fig. S4). The suspensions were irradiated over 24 to 250 h. The dark controls were placed in  $N_2$ -purged serum bottles wrapped in

aluminum foil. Various 25-mm UV band-pass (Semrock FF01-260, Andover 228FS25, 200FS10-25), and long-pass (Schott WG-225) filters were introduced to determine the photodegradation rate of organic phosphorus at specific wavelength or range. One experiment was replicated in triplicate to ensure reproducibility (Fig. 1).

**Analyses of Reaction Products.** Samples were collected at various times from 1 to 400 h for analyses of  $H_2$  and dissolved phosphate and iron. Aliquots were removed from the reactors via syringe and stored at 8 °C prior to analysis using the molybdenum blue method for phosphate determination and the ferrozine method for dissolved iron (59).

A Thermo Scientific Orion 9863BN Micro pH Electrode was used to measure pH. The solutions maintained a pH of ~7 before and after photoirradiation apart from those containing Fe which decreased to ~3.6 following irradiation.

**Quantum Yield Measurements.** To quantitatively link the lab-measured photoreaction rate to photon flux, three narrow band-pass filters (transmitting 200, 230, and 260-nm light) were used to determine  $\Phi_\lambda$  of photodegradation of organic phosphorus:

$$\Phi_\lambda = \frac{\nu_p}{I_\lambda \times (1 - 10^{-\epsilon_\lambda})}, \quad [1]$$

where  $\nu_p$  and  $I_\lambda$  are the moles of  $PO_4^{3-}$  produced and incident photons per unit time, respectively, and  $\epsilon_\lambda$  is the molar absorption coefficient of organic phosphorus ( $M^{-1} cm^{-1}$ ; reported in SI Appendix, Table S1).  $I_\lambda$  was measured using ferrioxalate actinometry (60). Initial rates (0 to 5 h) were used to calculate  $\nu_p$  value.

The denominator of Eq. 1 represents the number of absorbed photons per unit time, and thus  $\Phi_\lambda$  is independent on the concentration of organic phosphorus.

**Modeling Phosphate Production by the Photolysis of Organic Phosphorus in the Photic Zone of the Archean Ocean.** The rate of phosphate production by the photolysis of organic phosphorus ( $\theta_{OP}$  in mole/ $cm^2$ /y) was calculated using (61):

$$\theta_{OP} = 3.15 \times 10^7 s \cdot y^{-1} \times \frac{0.5 [OP]}{6.02 \times 10^{23}} \int_0^z \int_{200 nm}^{400 nm} \phi^{OP} \epsilon^{OP} F(\lambda, z) d\lambda dz, \quad [2]$$

where,  $3.15 \times 10^7$  converts years to seconds, 0.5 corrects diurnal variations in the incident flux of solar radiation, [OP] represents molal concentration of dissolved organic phosphorus,  $6.02 \times 10^{23}$  is the Avogadro number,  $z$  is the penetration depth of the UV light (in meters).  $F(\lambda, z)$  is the photon flux:

$$F(\lambda, z) = F_0 10^{-k_\lambda z / \cos \omega}, \quad [3]$$

where  $F_0$  is the photon flux at Earth's surface (23);  $k_\lambda$  accounts for the absorptivity of seawater ( $k_\lambda = \sum_i \epsilon_\lambda^X [X_i]$ ;  $X_i$  is light-absorbing species);  $\omega$  is the incident angle of the radiation ( $= 35^\circ$ ) (62). The shielding effect of dissolved  $Fe(II)$  was considered here using 0.1 mM  $Fe^{2+}$  (20) and  $\epsilon^{Fe^{2+}}$  from ref. 61.

Here, the wavelength of UV light ( $\lambda$ ) was set to between 200 and 400 nm, considering shielding of light <200 nm by the  $CO_2$ -rich Archean atmosphere (63). As a major variant, [OP] was modeled across a wide range (0.1 to 200 nM) that includes modern concentrations (50 to 200 nM) (11) and likely levels in Archean ocean (1 to 10 nM).  $z$  was set to be similar to the modern range, i.e. 1 to 50 m (24). The  $\epsilon^{OP}$  was calculated from our measurements or taken from published values (SI Appendix, Table S1).  $\phi^P$  was estimated using the measured quantum yield values at known wavelengths (Table 1) assuming a Gaussian distribution (26):

$$\Phi_\lambda^P = e^{-\frac{(\lambda - \lambda_{max})^2}{\sigma^2}}, \quad [4]$$

where  $\lambda_{max}$  is the wavelength at maximal effective adsorption cross-section and  $\sigma$  is a fitting variance. The coarse-grained parameter fitting method was applied to get the optimal fit.

To extrapolate our calculations to the global marine photic zone, we used the land exposure reconstruction results by Korenaga et al. (64) to estimate the total flux of P released during photodegradation of organic phosphorus in middle

to late Archean. However, Flament et al. (65) proposed slower continental land growth and therefore a larger area of ocean. If the latter scenario was adopted, the predicted flux of P would be larger than the presented estimates.

**Data, Materials, and Software Availability.** All study data are included in the article and/or *SI Appendix*.

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