outflows due to powerful AGN feedback are responsible for dispersing dense cool gas in the protocluster. However, the large cool gas mass $\sim 10^{11}\,M_{\odot}$ and high velocities ~1000 km s^{-1} imply an extremely large kinetic luminosity $L_{\rm wind} \sim 10^{44.6}$ for an AGN-powered wind, making the feedback scenario implausible (*25*). An even more compelling argument against a merger or feedback origin comes from the extremely small cloud sizes $r_{\rm cloud} \sim$ 40 pc implied by our measurements. Such small clouds moving supersonically ~1000 km s^{-1} through the hot $T \sim 10^7$ K shock-heated plasma predicted to permeate the protocluster will be disrupted by hydrodynamic instabilities in $\sim 5 \times 10^6$ years and can thus only be transported ~5 kpc (*47*). These short disruption time scales instead favor a scenario where cool dense clouds are formed in situ, perhaps via cooling and fragmentation instabilities, but are short-lived. The higher gas densities might naturally arise if hot plasma in the incipient intracluster medium pressure-confines the clouds, compressing them to high densities (*48*, *49*). Emission line nebulae from cool dense gas have also been observed at the centers of present-day cooling flow clusters (*50*, *51*), albeit on much smaller scales $\lesssim$50 kpc. The giant Lyα nebulae in $z \sim 2$ to 3 protoclusters might be manifestations of the same phenomenon, but with much larger sizes and luminosities, reflecting different physical conditions at high redshift.

The large reservoir of cool dense gas in the protocluster SDSSJ0841+3921, as well as those implied by the giant nebulae in other protoclusters, appear to be at odds with our current theoretical picture of how clusters form. This is likely to be symptomatic of the same problem of too much cool gas in massive halos already highlighted for the quasar CGM (*27*, *42*, *43*). Progress will require more cosmological simulations of massive halos $M \gtrsim 10^{13}\,M_{\odot}$ at $z \sim 2$, as well as idealized higher-resolution studies. In parallel, a survey for extended Lyα emission around ~100 quasars would uncover a sample of ~10 giant Lyα nebulae, likely coincident with protoclusters, possibly also hosting multiple AGNs, and enabling continued exploration of the relationship between AGNs, cool gas, and cluster progenitors.

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SUPPLEMENTARY MATERIALS

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PHOSPHORUS CYCLING

Major role of planktonic phosphate reduction in the marine phosphorus redox cycle

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Phosphorus in the +5 oxidation state (i.e., phosphate) is the most abundant form of phosphorus in the global ocean. An enigmatic pool of dissolved phosphonate molecules, with phosphorus in the +3 oxidation state, is also ubiquitous; however, cycling of phosphorus between oxidation states has remained poorly constrained. Using simple incubation and chromatography approaches, we measured the rate of the chemical reduction of phosphate to P(III) compounds in the western tropical North Atlantic Ocean. Colonial nitrogen-fixing cyanobacteria in surface waters played a critical role in phosphate reduction, but other classes of plankton, including potentially deep-water archaea, were also involved. These data are consistent with marine geochemical evidence and microbial genomic information, which together suggest the existence of a vast oceanic phosphorus redox cycle.

Phosphorus is an essential element for life, and in nature it is almost exclusively present at an oxidation state of +5. It is in this state that phosphorus forms phosphoester bonds in essential biochemicals such as phospholipids, nucleic acids, and nucleotides. In most of the oceans, variably protonated dissolved phosphate species of +5 oxidation state (primarily HPO_4^{2-}) are effectively the sole form of phosphorus (*1*). However, the notable exception to this is the surface water of the ocean's oligotrophic gyres, where dissolved organic phosphorus (DOP)

compounds may exceed phosphate by as much as a factor of 10 (*2*). About 5 to 10% of DOP is in the form of phosphonates (C–P bonds), which are organic molecules with phosphorus in an oxidation state of +3 (*3*). Thus, concentrations of dissolved phosphonates can potentially rival those of phosphate in the oligotrophic surface ocean.

Since the discovery of phosphonates (*4*), much information on the biological origin and biogeochemical roles of these molecules has emerged. The nitrogen-fixing cyanobacterium *Trichodesmium*, a denizen of oligotrophic gyres, contains ~10% of its cellular phosphorus in the form of phosphonates (*5*). Several classes of planktonic cyanobacteria, heterotrophic bacteria, and archaea appear to carry genes for the synthesis, processing, and/or uptake of phosphonates, including the low–molecular weight (LMW) phosphonate molecules methylphosphonic acid (MPn) and 2-aminoethylphosphonic acid (2-AEP) (*6*–*12*). Direct synthesis of MPn by a representative deep-ocean archaeon has also been shown (*7*). *Trichodesmium* is able to grow with phosphonates as the sole source of phosphorus (*13*, *14*), and the degradation of MPn by these and other microorganisms is thought to fuel the aerobic production of methane in the ocean gyres (*10*, *12*, *15*). In addition to phosphonates, variably protonated phosphite species, which also contain phosphorus in the +3 oxidation state, might also play a role in the biogeochemistry of the oligotrophic gyres. Strains of cyanobacteria within the *Prochlorococcus* genus, which together compose the single most abundant group of phytoplankton in oligotrophic gyres, are capable of growing on phosphite as their sole phosphorus source (*11*). These organisms also carry the genes for phosphite uptake and oxidation to phosphate, as does *Trichodesmium* (*11*, *16*).

To provide direct quantitative information on the cycling rates of phosphorus between the +5 and +3 oxidation states, common experimental approaches and analytical techniques were combined and applied (fig. S1) in the oligotrophic surface waters of the western tropical North Atlantic (*17*). Natural samples of plankton, either samples of the whole planktonic community from raw seawater or *Trichodesmium* colonies concentrated from seawater, were incubated in the presence of ^{33}P-phosphate. Preparative ion chromatography (IC) was then employed to isolate fractions from intracellular extracts that corresponded with the elution times of LMW P(III) compounds, including phosphite, MPn, and 2-AEP (Fig. 1A and figs. S2 and S3). IC has been applied in a number of previous studies of reduced-P compounds in natural samples (*18*–*20*). Finally, these fractions were combined and their radioactivity was measured by liquid scintillation counting (Fig. 1B). We express the yield of ^{33}P-labeled P(III) compounds from the chemical reduction of ^{33}P-phosphate as a percentage of the total uptake of ^{33}P-phosphate into biomass, which was determined independently in parallel ^{33}P-phosphate incubations of identical design. Data were obtained on a cruise from Bermuda to Barbados (Fig. 2A), which spanned a range of surface-dissolved phosphate concentrations from below our limit of quantification (<2 nmol liter^{-1}) to 13 nmol liter^{-1}.

We observed that a substantial fraction of ^{33}P-phosphate uptake could be assigned to the production of intracellular P(III) compounds (Figs. 2B and 3). In surface waters, the production of P(III) compounds by the whole planktonic community was 3.4% (n = 1 individual incubation) of phosphate incorporation at station 5, whereas at station 9 values ranged from 0.7 to 1.7% (n = 3) (Fig. 3). If these percentages are representative of phosphate uptake by plankton throughout the ocean (*21*), then on the order of 10^{11} moles of phosphate per year are reduced by plankton in the surface ocean. This is probably a conservative estimate because our method does not capture the production of high–molecular weight P(III) compounds. For comparison, the preanthropogenic riverine input of phosphate to the ocean is on the order of 10^{10} moles P per year (*22*).

We also repeated our incubations with the whole community at depths of 40 and 150 m at station 5, yielding P(III) compound production of 1.5 to 2.8% (n = 3) and 15.3 to 16.5% (n = 3) of phosphate uptake, respectively. Thus, it appears that chemical phosphate reduction becomes an even more important component of phosphorus physiology within the planktonic community as depths increase and approach the mesopelagic zone, where archaea compose nearly 40% of the planktonic community (*23*). Estimating the role of deep-ocean archaea by ascribing all of the observed P(III) compound production at 150 m to archaea (*7*), applying an estimate of archaeal carbon fixation (*24*), and assuming a C:P stoichiometry of 100:1 yields an additional 10^{11} moles of chemical phosphate reduction per year in the deep ocean.

In *Trichodesmium* colonies, we found that 0.9 to 16.0% of the phosphate that was taken up was reduced to P(III) compounds intracellularly (Fig. 2B). The percentages at stations 5 and 9 were considerably greater than the concomitant percentage of the whole planktonic community in surface waters at these same locations (Fig. 3). Thus, *Trichodesmium* colonies appear to be sites of particularly intense intracellular chemical phosphate reduction, which is in agreement with previous work (*5*, *8*, *10*, *13*, *14*). The *Trichodesmium* data showed no meaningful correlations with phosphate concentrations, phosphate turnover times, or DOP concentrations. Thus, at the present time, the environmental factors that contribute to the regulation of phosphate reduction to P(III) compounds in surface waters remain unknown.

Calculating the absolute intracellular chemical phosphate reduction rates requires accurate data on phosphate concentrations, and phosphate concentrations were below our limit of quantification (< 2 nmol liter^{-1}) in the surface waters at stations 5 and 9. However, we were able to accurately quantify phosphate concentrations at 40 and 150 m at station 5, which enabled us to calculate absolute rates of 18.0 to 42.2 pmol liter^{-1} hour^{-1} and 1.6 to 5.9 pmol liter^{-1} hour^{-1}, respectively. Degradation rates of MPn in surface waters of the North Pacific subtropical gyre were previously reported to be ~0.01 pmol liter^{-1} hour^{-1} (*15*). The greater rates we report suggest that the redox cycle of phosphate is more extensive than prior methods were able to detect. Possible explanations are that LMW P(III) compounds other than MPn were produced in our incubations or that MPn could be residing only briefly in the LMW form before being incorporated into the reservoir of high–molecular weight phosphonates (*15*).

We conducted an additional set of experiments to quantify the amount of phosphate reduction that results in the release of extracellular P(III) compounds by *Trichodesmium*. To do this, we took an aliquot of the seawater from the incubations with ^{33}P-labeled phosphate and then isolated the LMW P(III) compounds by preparative IC, as mentioned above (*17*). We did this at station 7, a location where phosphate concentrations were fortuitously high (13 nmol liter^{-1}), and found extracellular production rates of P(III) compounds that ranged from 7.5 to 13.3 pmol colony^{-1} day^{-1}. The intracellular production rates

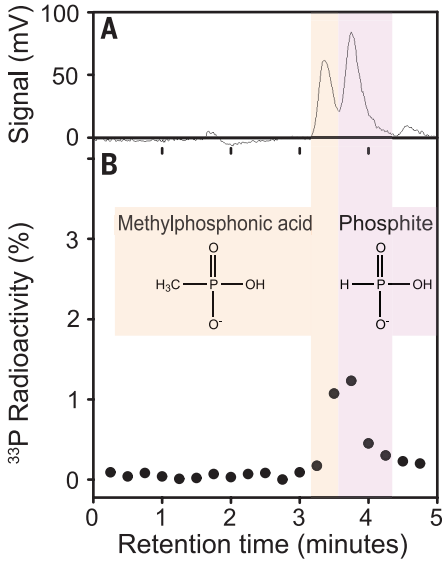

Fig. 1. ^{33}P radioactivity of P(III) compounds. (**A**) Conductivity IC chromatogram of an intracellular extract from *Trichodesmium* at station 19, which shows the elution of the methylphosphonic acid [P(III); highlighted in orange] and phosphite [P(III); highlighted in purple] internal recovery standards. (**B**) ^{33}P-radioactivity of fractions that eluted from the IC. The graph shows a peak in the P(III) fraction that is clearly indicative of the chemical reduction of ^{33}P-phosphate. Hydrolyzable phosphate-containing species and phosphate itself [P(V) compounds; figs. S2 and S4] eluted later than the P(III) compounds. Fractions were not collected at a time resolution that was fine enough to distinguish methylphosphonic acid and phosphite (fig. S3); thus, they were combined and are reported as "P(III) compounds."

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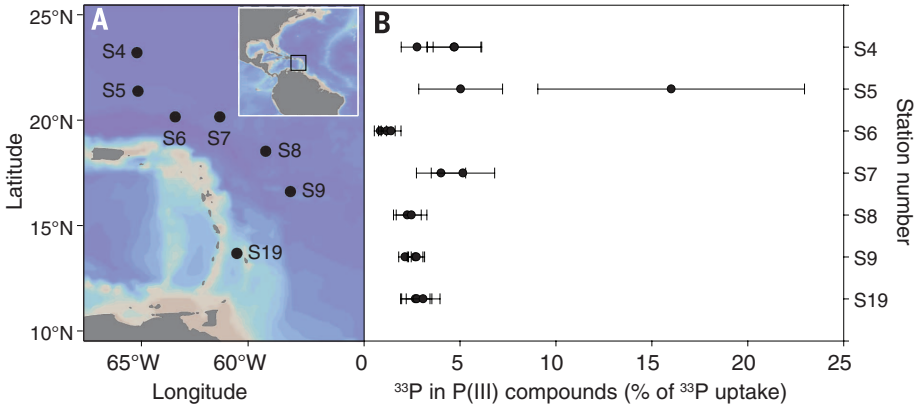

Fig. 2. Sampling locations and synthesis of P(III) compounds by *Trichodesmium* colonies. (**A**) Map of the tropical western North Atlantic Ocean showing station locations. The inset shows the broader western Atlantic. (**B**) Yield of ^{33}P-labeled P(III) compounds from the chemical reduction of ^{33}P-phosphate as a percentage of the total uptake of ^{33}P-phosphate into biomass in *Trichodesmium* colonies. Error bars represent the propagated errors of the IC blank subtraction and the total ^{33}P-phosphate uptake rate. The exceptionally high data point (16.0%) at station 5 (S5) underscores the potential heterogeneity in the rates of phosphate reduction in *Trichodesmium* colonies.

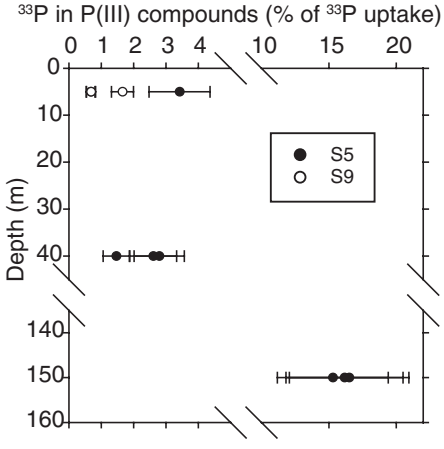

Fig. 3. Synthesis of P(III) compounds in the water column. The relative amount (percentage) of ^{33}P-phosphate incorporated into intracellular P(III) compounds by the whole planktonic community at station 5 (S5) and station 9 (S9). Error bars are as in Fig. 2. Note that two of the data points from S9 at 5 m are directly on top of one another: 0.67 ± 0.13% and 0.68 ± 0.14%.

by *Trichodesmium* at the same location were only 0.5 to 1.1 pmol colony^{-1} day^{-1}, which suggests that the vast majority of phosphate reduced by *Trichodesmium* colonies was released into the environment. Phosphorus has been implicated as a limiting nutrient for *Trichodesmium* in the tropical North Atlantic (*25*, *26*), and thus this result is unexpected. Because colonies contain both *Trichodesmium* and epibiotic bacteria that appear to cooperate in the cycling of phosphorus (*27*, *28*), we suggest that P(III) compounds could act as a phosphorus currency that is rapidly cycled between *Trichodesmium* and other microorganisms that live in association with the colony. With dissolved phosphonate concentrations in the range of 500 pmol liter^{-1} (*5*) and *Trichodesmium* abundances approaching 10 colonies liter^{-1} in our study area (*29*, *30*), *Trichodesmium* alone could drive the turnover of the entire dissolved P(III) reservoir in critical P-stressed regions of upper ocean on the time scale of a few days.

We also measured phosphite uptake by *Trichodesmium* at station 9. Phosphite was recently detected in rivers and estuaries using IC (*20*) but was below our detection limits in the oligotrophic waters of the western tropical North Atlantic. We synthesized ^{33}P-labeled phosphite (*17*, *31*) and measured phosphite uptake in incubation experiments of the same design as those used to measure ^{33}P-phosphate uptake. However, unlike the ^{33}P-phosphate incubations, in which the radiotracer amendment represented a vanishingly small addition of phosphate (6 pmol liter^{-1}) (*7*), the specific radioactivity of the ^{33}P-phosphite was fairly low (0.1 Ci mol^{-1}). Thus, an amendment of ~1.5 μmol liter^{-1} was necessary to achieve a sufficient signal of uptake. Phosphite uptake rates ranged from to 307 to 925 pmol colony^{-1} hour^{-1} (n = 3) in *Trichodesmium*, probably representing maximum uptake rates indicative of saturated transmembrane phosphite transport or surface adsorption.

Overall, our study suggests that the production of phosphonates and/or phosphite contributes to a globally vast phosphorus redox cycle that exceeds the magnitude of phosphate inputs to the ocean. Phosphorus atoms are therefore likely to pass between +5 and +3 oxidation states on numerous occasions over the course of their ~20,000- to 100,000-year residence time in the ocean (*22*). The attendant changes in the chemical properties of phosphorus are likely to have major effects on the biogeochemical cycling of this critical bioactive element.

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SUPPLEMENTARY MATERIALS

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