

sion line and nonlinear dependence of the intensity are clearly observed up to a current of about 880 mA, where laser threshold is reached. Lasing takes place at ~ 4.4 THz, on the high-energy side of the luminescence line, probably owing to the reduced waveguide losses at shorter wavelengths. Single-mode emission is obtained, which is probably a consequence of the relatively narrow gain spectrum and the wide Fabry–Perot mode spacing. A high-resolution laser spectrum is shown in the inset; the measured linewidth is limited by the resolution of the spectrometer (3.75 GHz).

Figure 4 shows the light–current (L – I) and voltage–current (V – I) characteristics of a representative device. At a heat-sink temperature of 8 K, the output peak power is estimated to be more than 2 mW, with a threshold current density of 290 A cm^{-2} . The latter is a very small value for quantum-cascade lasers and allows operation at high duty cycles (up to 10%) even in this large device. We expect that narrower stripes and appropriate changes in sample processing would readily lead to continuous-wave operation. The initial high resistivity in the V – I characteristics stems from misalignment of the sub-bands at low field; at higher fields, the injector miniband lines up with the second miniband of the following stage and carrier injection into the upper laser level takes place. The electric field at threshold is 7.5 kV cm^{-1} . This is larger than the design value of 3.5 kV cm^{-1} , probably as a result of the non-negligible contact resistance. As expected, a negative differential resistance feature was observed at about 850 A cm^{-2} .

These experimental results match well the theoretical predictions of Fig. 1b. The V – I curve has all the distinctive qualitative features and the measured current densities are of the same order of the computed ones, showing that even at these small energies carrier relaxation and transport are dominated by electron–LO phonon and electron–electron scattering. The discrepancy is a factor of about 1.5, possibly related to acoustic phonon or impurity scattering or to a lower than specified free-carrier density in the sample. In fact, the simulation indicates that a reduction in the doping density of the injectors by 25% would lead to a reduction in current density of 35%. From the theoretical values of population inversion and confinement factor, we calculate a maximum modal gain of 23 cm^{-1} (ref. 18). This value compares well with the estimated cavity losses $\alpha_W + \alpha_M = (16 + 4) \text{ cm}^{-1} = 20 \text{ cm}^{-1}$, α_M being the mirror out-coupling of the 3.1-mm-long stripe. This consistency is confirmed by the experimental observation that laser stripes shorter than 1 mm, with corresponding larger mirror losses, do not reach laser threshold.

We believe that improved design of the active region of our device (in particular aiming at the reduction of thermal backfilling), together with optimized fabrication (junction-down mounting, facet coating, lateral overgrowth), would rapidly lead to continuous-wave emission and to operation at liquid-nitrogen temperatures. The present demonstration of a terahertz quantum-cascade laser, operating below the LO phonon band, represents a first step towards the development of widely usable terahertz photonics. □

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1. Miles, R. E., Harrison, P. & Lippens, D. (eds) *Terahertz Sources and Systems* Vol. 27 (NATO Science Series II, Kluwer, Dordrecht, 2001).
2. Han, P. Y., Cho, G. C. & Zhang, X.-C. Time-domain transillumination of biological tissue with terahertz pulses. *Opt. Lett.* **25**, 242–244 (2000).
3. Mittleman, D. M., Jacobsen, R. H. & Nuss, M. C. T-ray imaging. *IEEE J. Sel. Top. Quant. Electron.* **2**, 679–692 (1996).
4. Mittleman, D. M., Hunsche, S., Boivin, L. & Nuss, M. C. T-ray tomography. *Opt. Lett.* **22**, 904–906 (1997).
5. Pavlov, S. G. *et al.* Stimulated emission from donor transitions in silicon. *Phys. Rev. Lett.* **84**, 5220–5223 (2000).
6. Matsuura, S., Tani, M. & Sakai, K. Generation of coherent terahertz radiation by photomixing in dipole photoconductive antennas. *Appl. Phys. Lett.* **70**, 559–561 (1997).
7. Hu, B. B., Zhang, X.-C. & Auston, D. H. Terahertz radiation induced by subband-gap femtosecond optical excitation of GaAs. *Phys. Rev. Lett.* **67**, 2709–2712 (1991).
8. Kersting, R., Unterrainer, K., Strasser, G., Kauffmann, H. F. & Gornik, E. Few-cycle THz emission from cold plasma oscillations. *Phys. Rev. Lett.* **79**, 3038–3041 (1997).
9. Bründermann, E., Chamberlin, D. R. & Haller, E. E. High duty cycle and continuous terahertz emission from germanium. *Appl. Phys. Lett.* **76**, 2991–2993 (2000).

10. Faist, J. *et al.* Quantum cascade laser. *Science* **264**, 553–556 (1994).
11. Rochat, M., Faist, J., Beck, M., Oesterle, U. & Illegems, M. Far-infrared ($\lambda = 88 \mu\text{m}$) electroluminescence in a quantum cascade structure. *Appl. Phys. Lett.* **73**, 3724–3726 (1998).
12. Williams, B. S., Xu, B., Hu, Q. & Melloch, M. R. Narrow-linewidth terahertz intersubband emission from three-level systems. *Appl. Phys. Lett.* **75**, 2927–2929 (1999).
13. Ulrich, J., Zobl, R., Schrenk, W., Strasser, G. & Unterrainer, K. Terahertz quantum cascade structures: Intra- versus interwell transition. *Appl. Phys. Lett.* **76**, 1928–1930 (2000).
14. Helm, M., England, P., Colas, E., De Rosa, F. & Allen, S. J. Intersubband emission from semiconductor superlattices excited by sequential resonant tunnelling. *Phys. Rev. Lett.* **63**, 74–77 (1989).
15. Colombelli, R. *et al.* Far-infrared surface-plasmon quantum-cascade lasers at 21.5 μm and 24 μm wavelengths. *Appl. Phys. Lett.* **78**, 2620–2622 (2001).
16. Hofstetter, D., Beck, M., Aellen, T. & Faist, J. High-temperature operation of distributed feedback quantum-cascade lasers at 5.3 μm . *Appl. Phys. Lett.* **78**, 396–398 (2001).
17. Köhler, R., Iotti, R. C., Tredicucci, A. & Rossi, F. Design and simulation of terahertz quantum cascade lasers. *Appl. Phys. Lett.* **79**, 3920–3922 (2001).
18. Tredicucci, A. *et al.* High performance interminiband quantum cascade lasers with graded superlattices. *Appl. Phys. Lett.* **73**, 2101–2103 (1998).
19. Iotti, R. C. & Rossi, F. Nature of charge transport in quantum-cascade lasers. *Phys. Rev. Lett.* **87**, 146603–1–146603–4 (2001).
20. Iotti, R. C. & Rossi, F. Carrier thermalization versus phonon-assisted relaxation in quantum-cascade lasers: A Monte Carlo approach. *Appl. Phys. Lett.* **78**, 2902–2904 (2001).
21. Sirtori, C. *et al.* Long-wavelength ($\lambda \sim 8$ –11.5 μm) semiconductor lasers with waveguides based on surface plasmons. *Opt. Lett.* **23**, 1366–1368 (1998).
22. Rochat, M., Beck, M., Faist, J. & Oesterle, U. Measurement of far-infrared waveguide loss using a multisection single-pass technique. *Appl. Phys. Lett.* **78**, 1967–1969 (2001).
23. Köhler, R. *et al.* High-intensity interminiband terahertz emission from chirped superlattices. *Appl. Phys. Lett.* **80**, 1867 (2002).

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Ocean productivity before about 1.9 Gyr ago limited by phosphorus adsorption onto iron oxides

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After the evolution of oxygen-producing cyanobacteria at some time before 2.7 billion years ago¹, oxygen production on Earth is thought to have depended on the availability of nutrients in the oceans, such as phosphorus (in the form of orthophosphate). In the modern oceans, a significant removal pathway for phosphorus occurs by way of its adsorption onto iron oxide deposits^{2,3}. Such deposits were thought to be more abundant in the past when, under low sulphate conditions, the formation of large amounts of iron oxides resulted in the deposition of banded iron formations^{4,5}. Under these circumstances, phosphorus removal by iron oxide adsorption could have been enhanced. Here we analyse the phosphorus and iron content of banded iron formations to show that ocean orthophosphate concentrations from

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3.2 to 1.9 billion years ago (during the Archaean and early Proterozoic eras) were probably only ~10–25% of present-day concentrations. We suggest therefore that low phosphorus availability should have significantly reduced rates of photosynthesis and carbon burial, thereby reducing the long-term oxygen production on the early Earth—as previously speculated⁴—and contributing to the low concentrations of atmospheric oxygen during the late Archaean and early Proterozoic.

The oxidation of dissolved ferrous iron produces insoluble iron oxyhydroxides, which strongly adsorb phosphates at pH values of less than 9 (ref. 6). The extent of phosphorus adsorption can be expressed as: $[P_{\text{ads}}] = K_{\text{ads}}[P_{\text{d}}][\text{Fe}^{3+}]$, where $[P_{\text{ads}}]$ is the concentration (μM) of phosphate adsorbed onto iron oxides, $[P_{\text{d}}]$ is the concentration (μM) of dissolved orthophosphate (PO_4^{3-}) in solution, $[\text{Fe}^{3+}]$ is the concentration (μM) of iron oxide particles, and K_{ads} (μM^{-1}) is the adsorption constant. Particles of iron oxide formed from Fe^{2+} oxidation in submarine hydrothermal systems adsorb phosphate with a K_{ads} value of $0.07 \pm 0.01 \mu\text{M}^{-1}$ (ref. 7). As phosphorus adsorbs predictably onto newly formed iron oxide surfaces, the phosphorus content of ancient sediments rich in iron oxide indicates, in principle, the phosphorus concentration of the water from which the oxides formed⁷.

Here we use the phosphorus and Fe^{3+} content of Archaean and early Proterozoic banded iron formations (BIFs), and the value for K_{ads} determined for modern hydrothermal systems⁷, to estimate the

$[P_{\text{d}}]$ of contemporaneous sea water:

$$[P_{\text{d}}] = (1/K_{\text{ads}})(P_{\text{ads}}/\text{Fe}^{3+}) \quad (1)$$

The ratio $P_{\text{ads}}/\text{Fe}^{3+}$ is directly available, in many instances, from BIF analyses (Fig. 1). An average Archaean and early Proterozoic phosphorus concentration of $0.15 \pm 0.15 \mu\text{M}$ is calculated (ranging from 0.03 to $0.29 \mu\text{M}$) for the waters where BIFs deposited (Fig. 1). Generally lower values of $[P_{\text{d}}]$ are indicated at 1.9–2.0 Gyr ago, compared to earlier BIFs.

We have avoided siderite-rich BIFs in the analysis as some contain unusual ^{13}C -depleted carbonates ($\delta^{13}\text{C} < -5\text{‰}$)^{8,9}, indicating the oxidation of sedimentary organic carbon, possibly by Fe reduction¹⁰, and the probable inclusion of original organic P into the total P pool. This would complicate our calculation. Furthermore, iron oxide (re)crystallization or iron reduction during early diagenesis could have induced a loss of P from the oxide-rich BIFs. In modern sediments preserving hydrothermally derived iron oxides, a loss of up to 50% of the originally adsorbed P is indicated¹¹. A 50% loss in P_{ads} would mean that our calculated $[P_{\text{d}}]$ could be too low by as much as a factor of two (ref. 11). However, this is probably a maximum correction, because hydrothermal sediments with higher iron content, approaching that of BIFs, have experienced ~25% P loss¹¹. Acknowledging that further tests of our approach are required, we conservatively estimate that BIFs deposited in sea water containing between, on average, 0.15 and $0.6 \mu\text{M}$ dissolved P.

We note that P retention in sediments under anoxic ocean conditions in the Archaean and early Proterozoic was probably different from today. This is indicated by the preservation of Fe oxides in BIFs, which deposited from anoxic ocean waters containing dissolved Fe^{2+} (ref. 4). Today, ocean anoxia results in a sulphidic water column which effectively reacts all of the available reactive Fe to form Fe sulphide minerals⁵. Thus, today, anoxia leads to some P loss from sediments^{12–15}, whereas anoxia during BIF deposition probably led to P retention on Fe oxides, and as ferrous phosphate minerals when there was Fe reduction in the sediment. The main difference between now and then was probably low sulphate concentrations in Archaean and early Proterozoic oceans, significantly reducing rates of sulphate reduction⁵. Even in the modern world, controlled sediment incubation experiments show that loss of adsorbed P is minimal under sediment diagenesis with low

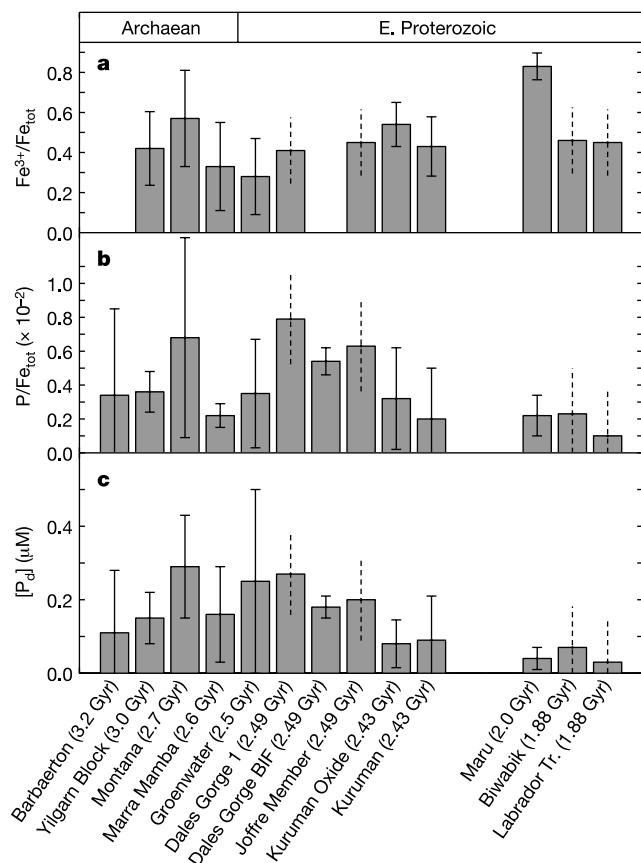


Figure 1 Element ratios in BIFs and calculated dissolved phosphate concentrations. Mole ratios of $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ (a) and $\text{P}/\text{Fe}_{\text{tot}}$ (b) are from the literature (see Supplementary Information). c, Dissolved phosphate concentrations are calculated from equation (1). Phosphate loss during early diagenesis can result in up to a factor of two error in P_{d} (see text and ref. 11). Standard deviation for each BIF unit is shown as solid error bars. Dashed error bars indicate that no standard deviation could be calculated from the literature. In cases where Fe^{3+} content is not available, we use the mean $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratio of 0.43.

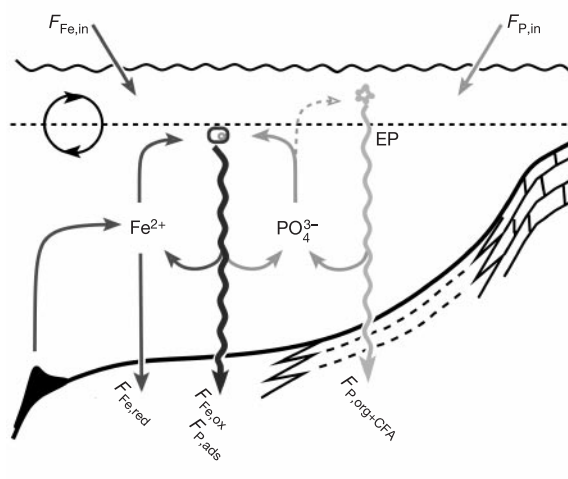


Figure 2 Simplified phosphate and iron cycle model of the Archaean and early Proterozoic. Dissolved ferrous iron (Fe^{2+}) is oxidized at the base of the oxic mixed layer, leading to iron oxide burial ($F_{\text{Fe,ox}} = \alpha F_{\text{Fe,in}}$) and BIFs with adsorbed P ($F_{\text{P,ads}}$). Organic matter export production (EP) is limited by upwelled P and leads to the burial of organically derived phosphate ($F_{\text{P,org+CFA}}$). For simplicity, ferrous iron is assumed to be buried ($F_{\text{Fe,red}}$) without associated phosphate. The total reactive iron input, $F_{\text{Fe,in}}$, is the sum of iron from land (dissolved+particulate) and hydrothermal iron.

sulphate concentrations¹⁶. The fact that BIFs are preserved, and contain phosphate, shows that the usual view of anoxia leading to P release is probably not valid during the periods in Earth's history when BIFs formed.

BIFs deposited in environments ranging from shelf and upper slope to the abyssal plain¹⁷. The Barberton BIF, associated with, and probably related to, local volcanism, was deposited at a water depth of approximately 900 m, the deepest water yet recognized for BIFs¹⁸. The other generally larger BIFs analysed here, lacking an obvious local volcanic source, deposited on the outer shelf or slope well below storm wave influence¹⁹. The Fe-oxide-rich facies of the Kuruman Iron Formation, a reasonable representative of the large 2.6-Gyr and younger BIFs in the data set, was deposited in deeper

water than the contemporaneous siderite-enriched BIF and shales¹⁹. Furthermore, the siderite-enriched BIF formed in water with dissolved inorganic carbon highly ¹³C-depleted compared to surface ocean water^{8,20}. Thus, the siderite-enriched BIF, and by extension the Fe-oxide-rich facies, deposited well below a pronounced chemocline where the accumulation of phosphate should have accompanied the steep gradients in isotopic composition of dissolved inorganic carbon. Therefore, our calculated phosphate concentrations characterize a region well below the chemocline and may represent the deep ocean. Phosphate concentrations of 0.15 to 0.6 μM are considerably less than the average modern ocean value of 2.3 μM .

Low phosphate concentrations in the Archaean and early Proterozoic oceans could have arisen from changes in the weathering flux of dissolved and reactive phosphate ($F_{\text{P,in}}$) to the ocean and/or significant changes in the ocean phosphate sinks (Fig. 2). We have no evidence supporting significantly reduced weathering fluxes of reactive phosphate. Continents may have reached their present size early in Earth's history and the intensity of chemical weathering, controlled by temperature and soil pH, might have been high in the Archaean and early Proterozoic. Alternatively, and more probably, low P concentrations originated from a strong P sink owing to significant adsorption onto, and removal by, iron oxide particles.

We use a simple ocean model to explore the possible influence of BIF deposition on ocean P concentrations (Fig. 2). P is delivered to the oceans from rivers ($F_{\text{P,in}}$) and is removed by adsorption onto iron oxides (P_{ads}) and as organically derived reactive P ($P_{\text{org+CFA}}$), which includes organic-bound P and P liberated from organic matter and mainly reprecipitated into carbonate fluorapatite (CFA) (refs 12, 13). Of the total reactive iron flux ($F_{\text{Fe,in}}$) to the ocean⁵, only a fraction (α) is buried as Fe oxides with adsorbed P; the rest is assumed to be buried as ferrous iron phases to which P does not adsorb (that is, sulphides and siderite). The burial flux of adsorbed P is then:

$$F_{\text{P,ads}} = (K_{\text{ads}}[P_{\text{d}}])(\alpha F_{\text{Fe,in}}) \quad (2)$$

The burial flux of $P_{\text{org+CFA}}$ (designated as $F_{\text{P,org+CFA}}$) depends on $[P_{\text{d}}]$, the upwelling velocity, u , of deep water supplying P_{d} to the euphotic zone, γ , and the relationship, η , between the export of organic P from the surface ocean and its burial^{4,21}:

$$F_{\text{P,org+CFA}} = \gamma(u[P_{\text{d}}]) \quad (3)$$

At steady state $F_{\text{P,in}} - (F_{\text{P,org+CFA}} + F_{\text{P,ads}}) = 0$, allowing a solution for $[P_{\text{d}}]$:

$$[P_{\text{d}}] = \frac{F_{\text{P,in}}}{\gamma u + \alpha K_{\text{ads}} F_{\text{Fe,in}}} \quad (4)$$

Figure 3 shows $[P_{\text{d}}]$ contoured as a function of the fraction, α , of total reactive iron buried with adsorbed P, versus reactive phosphate input ($F_{\text{P,in}}$). $[P_{\text{d}}]$ increases as $F_{\text{P,in}}$ increases, and decreases with increasing α . With today's range in $F_{\text{P,in}}$ (ref. 12) and $F_{\text{Fe,in}}$ (ref. 5) we find a $[P_{\text{d}}]$ similar to that obtained in the above BIF analysis if approximately half of the reactive iron flux is buried with adsorbed P ($0.4 < \alpha < 0.6$). Thus, low values of ocean P_{d} can be maintained if about half of $F_{\text{Fe,in}}$ is removed as freshly precipitated iron oxides. Such a high $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratio is indicated for BIFs^{8,19} (Fig. 1a), and if this ratio represents the removal of $F_{\text{Fe,in}}$ in general, then the initial adsorption of P into BIF explains the low $[P_{\text{d}}]$ inferred for Archaean and early Proterozoic sea water.

Low values of ocean $[P_{\text{d}}]$ would have probably limited rates of primary production, and by extension, organic carbon burial, and the input of oxygen to the atmosphere^{4,20,22}. The relationship between $[P_{\text{d}}]$ and the burial rate of organic carbon ($F_{\text{C,org}}$) is given as the product of equation (4) and the ratio of organic carbon to organically derived P ($\eta_{\text{cp}} = C_{\text{org}}/P_{\text{org+CFA}}$):

$$F_{\text{C,org}} = \gamma(u[P_{\text{d}}])\eta_{\text{cp}} \quad (5)$$

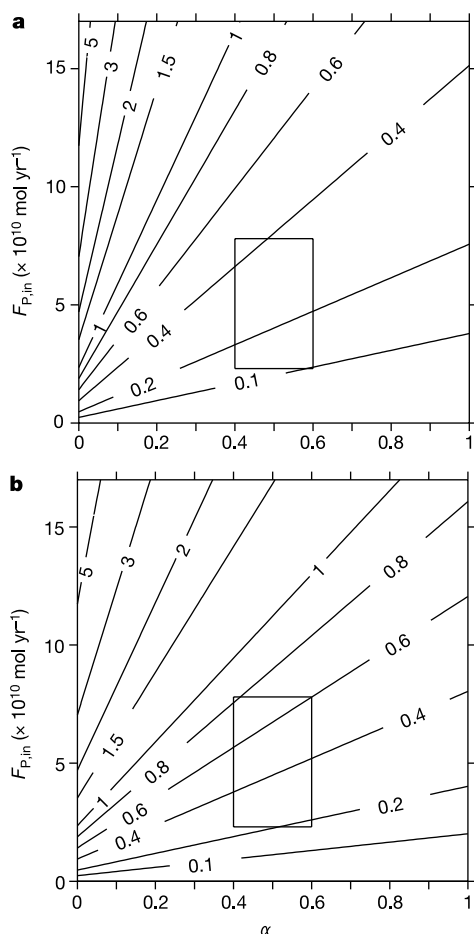


Figure 3 Modelled mean ocean phosphate concentration $[P_{\text{d}}]$ from equation (4). **a**, The standard case with $K_{\text{ads}} = 0.07 \mu\text{M}^{-1}$; **b**, The possible case of a 50% P_{ads} loss during early diagenesis with $K_{\text{ads}} \approx 0.035 \mu\text{M}^{-1}$. The $[P_{\text{d}}]$ values (in μM) are shown on the contours as a function of the fraction (α) of total iron buried with adsorbed P, and reactive phosphate input ($F_{\text{P,in}}$). Very low ocean phosphate concentrations occur if a large fraction of reactive iron input is buried with adsorbed P. Boxed regions correspond to the diagnosed Archaean conditions with the pre-industrial range of $F_{\text{P,in}}$ (refs 12, 30) and present $F_{\text{Fe,in}}$ (ref. 5). At present P, burial fluxes after early diagenesis are partitioned into: $F_{\text{P,org}} = 3.6 \times 10^{10} \text{ mol P yr}^{-1}$, $F_{\text{P,CFA}} = 3.6 \times 10^{10} \text{ mol P yr}^{-1}$ and $F_{\text{P,ads}} = 0.7 \times 10^{10} \text{ mol P yr}^{-1}$ (refs 12, 30). Part of the $F_{\text{P,CFA}}$ is originally reprecipitated from P liberated from decaying organic matter as well as P from reduction of iron oxides. Assuming, conservatively, that ~50% of the CFA burial flux originates from decay of organic matter, then $F_{\text{P,org+CFA}} = 5.4 \times 10^{10} \text{ mol P yr}^{-1}$. With a burial efficiency $\gamma = 1.9 \times 10^{-2}$, the above $F_{\text{P,org+CFA}}$ is reproduced for the present mean ocean P concentration (2.3 μM) and mixing $u = 1.26 \times 10^{18} \text{ l yr}^{-1}$. At present $F_{\text{P,org+CFA}}$ is associated with an organic carbon burial of $\sim 1 \times 10^{13} \text{ mol P yr}^{-1}$ (ref. 23), which gives a $C_{\text{org}}/P_{\text{org+CFA}}$ ratio of 185.

With values of γ , u and η_{CIP} comparable to today, a reduction in $[P_d]$ to 10–25% of present-day concentration (as we infer for the late Archaean and early Proterozoic) implies a 75–90% reduction in the rate of organic carbon burial. By contrast, if much less $P_{\text{org+CFA}}$ was buried with organic carbon, as has been argued for modern euxinic sediments¹⁴ (see also in ref. 15), then low $[P_d]$ would support substantial organic carbon burial, and oxygen production⁴. Thus, with $\eta_{\text{CIP}} \approx 1,000$, carbon burial would approach modern values²³. However, we believe that such high η_{CIP} ratios are probably inappropriate for an anoxic Fe-containing Precambrian ocean for two reasons. First, the high η_{CIP} ratios in modern euxinic sediments are partly a result of P loss^{13–15} under high sulphate conditions that were not present during BIF deposition²⁴. Second, even in modern settings, η_{CIP} may be much lower than previously thought¹⁵, with ratios of 150–200 recently reported from the euxinic, and rapidly depositing, Saanich Inlet sediments¹³. Thus, low $[P_d]$ in late Archaean and early Proterozoic oceans should have resulted in reduced rates of carbon burial. Higher heat flow and tectonic activity could have accelerated rates of geochemical cycling including rates of all of the processes discussed here, although the quantitative influence of heat flow on geochemical cycling rates is poorly known^{25,26}.

Previous analysis of the marine isotope record of organic and inorganic carbon suggests that for the Archaean (>2.5 Gyr ago) around 11% of the total carbon buried in ocean sediments was removed as organic carbon²⁷. By comparison, today, organic carbon represents 20% of the total carbon removal²⁷, or a burial percentage about twice that in the Archaean. Our results are generally consistent with this, and suggest reduced rates of organic carbon burial in the late Archaean and early Proterozoic. Further modelling studies, and a better resolution of the carbon isotope record, would better help to establish the concordance between our reconstruction of late Archaean and early Proterozoic nutrient chemistry and the carbon burial history as revealed from carbon isotope studies.

In addition to indicating relatively reduced rates of organic carbon burial in the Archaean, the isotope record of marine carbonates demonstrates at least one, and perhaps several, very large positive isotope excursions between 2.4 and 2.0 Gyr ago (refs 20, 27). These excursions indicate large increases in the relative proportions of organic carbon burial in ocean sediments, and possibly also indicate increases in the rate of organic carbon deposition²⁷. Recent compilations of the timing of BIF deposition indicate a curious lack of BIFs during this same time from 2.4 to around 2.0 Gyr ago (ref. 28). Furthermore, the isotope record of sedimentary sulphides²⁴ shows the first occurrence of highly ³⁴S-depleted marine sulphides around 2.4 Gyr ago. The sulphur isotope record indicates an increase in seawater sulphate concentrations to ~1 mM at around 2.4 Gyr ago, and a consequent increase in rates of sulphate reduction due to more sulphate availability²⁴. We propose that the burial pulse of organic carbon between 2.4 and 2.0 Gyr ago could have been driven, at least in part, by the P made available by increasing rates of sulphate reduction. Therefore, the rise in atmospheric oxygen concentrations^{4,20} that apparently accompanied the burial pulse of organic carbon²⁷ could also, in part, have resulted from a reduction in the Fe oxide sink and a consequently larger availability of P.

The decline of BIFs between 2.4 and 2.0 Gyr ago (ref. 28) could have been a logical consequence of the titration of deep-ocean Fe with sulphide owing to increasing rates of sulphate reduction⁵. For some reason not yet clear, BIF deposition, decreased organic carbon burial, and low P concentrations were reinitiated around 2.0 Gyr ago, persisting until around 1.8 Gyr ago (Fig. 1). Thereafter, consistent with an earlier proposal⁵, sulphidic conditions reoccurred. There is no indication of high burial fluxes of organic carbon after 1.8 Gyr ago, even though the iron oxide sink for phosphorus would have been substantially reduced under sulphidic ocean conditions.

Another nutrient may then have limited ocean primary productivity²⁹. □

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- Brocks, J. J., Logan, G. A., Buick, R. & Summons, R. E. Archaean molecular fossils and the early rise of eukaryotes. *Science* **285**, 1033–1036 (1999).
- Berner, R. A. Phosphate removal from sea water by adsorption on volcanogenic ferric oxides. *Earth Planet. Sci. Lett.* **18**, 77–86 (1973).
- Wheat, C. G., Feely, R. A. & Mottl, M. J. Phosphate removal by oceanic hydrothermal processes: An update of the phosphorus budget in the oceans. *Geochim. Cosmochim. Acta* **19**, 3593–3608 (1996).
- Holland, H. D. *The Chemical Evolution of the Atmosphere and Oceans* (Princeton Univ. Press, New York, 1984).
- Canfield, D. E. A new model for Proterozoic ocean chemistry. *Nature* **396**, 450–453 (1998).
- Stumm, W. & Morgan, J. J. *Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters* (Wiley & Sons, New York, 1981).
- Feely, R. A., Trefry, J. H., Lebon, G. T. & German, C. R. The relationship between P/Fe and V/Fe ratios in hydrothermal precipitates and dissolved phosphate in seawater. *Geophys. Res. Lett.* **25**, 2253–2256 (1998).
- Beukes, N. J., Klein, C., Kaufman, A. J. & Hayes, J. M. Carbonate petrography, kerogen distribution, and carbon and oxygen isotope variations in an early Proterozoic transition from limestone to iron-formation deposition, Transvaal Supergroup, South Africa. *Econ. Geol.* **85**, 663–690 (1990).
- Kaufman, A. J., Hayes, J. M. & Klein, C. Primary and diagenetic controls of isotopic compositions of iron-formation carbonates. *Geochim. Cosmochim. Acta* **54**, 3461–3473 (1990).
- Walker, J. C. G. Suboxic diagenesis in banded iron formations. *Nature* **309**, 340–342 (1984).
- Schaller, T., Morford, J., Emerson, S. R. & Feely, R. A. Oxyanions in metalliferous sediments: Tracers for paleoseawater metal concentrations. *Geochim. Cosmochim. Acta* **63**, 2243–2254 (2000).
- Compton, J. et al. in *Marine Authigenesis: From Global to Microbial* (eds Glenn, C. R., Prevot, L. L. & Lucas, J.) 21–33 (Society for Sedimentary Geology, Tulsa, 2000).
- Filippelli, G. M. Carbon and phosphorus cycling in anoxic sediments of the Saanich Inlet, British Columbia. *Mar. Geol.* **174**, 307–321 (2001).
- Van Cappellen, P. & Ingall, E. D. Redox stabilization of the atmosphere and oceans by phosphorus-limited marine productivity. *Science* **271**, 493–496 (1996).
- Anderson, L. D., Delaney, M. L. & Faul, K. L. Carbon to phosphorus ratios in sediments: Implications for nutrient cycling. *Glob. Biogeochem. Cycles* **15**, 65–79 (2001).
- Roden, E. E. & Edmonds, J. W. Phosphate mobilization in iron-rich anaerobic sediments: Microbial Fe(III) oxide reduction versus iron-sulfide formation. *Archiv. Hydrobiol.* **139**, 347–378 (1997).
- Fralick, P. & Barrett, T. J. in *Sedimentary Facies Analysis: A Tribute to the Research and Teaching of Harold G. Reading* (ed. Plint, A. G.) 137–156 (Special Publication of the International Association of Sedimentologists, Oxford, 1995).
- de Ronde, C. E. J., Channer, D. M., De, R., Faure, K., Bray, C. J. & Spooner, E. T. C. Fluid chemistry of Archaean seafloor hydrothermal vents: Implication for the composition of circa 3.2 Ga seawater. *Geochim. Cosmochim. Acta* **61**, 4025–4042 (1997).
- Klein, C. & Beukes, N. J. Geochemistry and sedimentology of a facies transition from limestone to iron-formation deposition in the early Proterozoic Transvaal Supergroup, South Africa. *Econ. Geol.* **84**, 1733–1774 (1989).
- Karhu, J. A. & Holland, H. D. Carbon isotopes and the rise of atmospheric oxygen. *Geology* **24**, 867–870 (1996).
- Shaffer, G. A model of biogeochemical cycling of phosphorous, nitrogen, oxygen, and sulphur in the ocean: One step toward a global climate model. *J. Geophys. Res.* **94**, 1979–2004 (1989).
- Lenton, T. M. & Watson, A. J. Redfield revisited 2. What regulates the oxygen content of the atmosphere? *Glob. Biogeochem. Cycles* **14**, 249–268 (2000).
- Holland, H. D. *The Chemistry of the Atmosphere and Oceans* (Wiley, New York, 1978).
- Canfield, D. E., Habicht, K. S. & Thamdrup, B. The archaean sulfur cycle and the early history of atmospheric oxygen. *Science* **288**, 658–661 (2000).
- Des Marais, D. J. Isotopic evolution of the biogeochemical carbon cycle during the Proterozoic eon. *Org. Geochem.* **27**, 185–193 (1997).
- Sleep, N. H. & Zahnle, K. Carbon dioxide cycling and implications for climate on ancient Earth. *J. Geophys. Res.* **106**, 1373–1399 (2001).
- Des Marais, D. J., Strauss, H., Summons, R. E. & Hayes, J. M. Carbon isotope evidence from the stepwise oxidation of the Proterozoic environment. *Nature* **359**, 605–609 (1992).
- Isley, A. E. & Abbott, D. H. Plume-related mafic volcanism and the deposition of banded iron formation. *J. Geophys. Res.* **104**, 15461–15477 (1999).
- Anbar, A. D. & Knoll, A. H. Trace metal limitation of primary production 1.85–1.25 Ga. (American Geophysical Union Fall Meeting, 1999); available at <http://www.agu.org/meetings/fm99top.html>.
- Berner, E. K. & Berner, R. A. *The Global Water Cycle, Geochemistry and Environment* (Prentice Hall, New Jersey, 1994).

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Competing interests statement

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