

plateau and the marine records from the Indian Ocean, interpreted with the aid of climate-model simulations that take into account both uplift and lateral extension of the Tibetan plateau, support and extend earlier conclusions^{11,17} concerning the nature and probable causes of the multi-stage evolution of Asian climates. □

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Phosphorus limitation of nitrogen fixation by *Trichodesmium* in the central Atlantic Ocean

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 Marine fixation of atmospheric nitrogen is believed to be an important source of biologically useful nitrogen to ocean surface waters¹, stimulating productivity of phytoplankton and so influencing the global carbon cycle². The majority of nitrogen fixation in tropical waters is carried out by the marine cyanobacterium *Trichodesmium*³, which supplies more than half of the new nitrogen used for primary production⁴. Although the factors controlling marine nitrogen fixation remain poorly understood, it has been thought that nitrogen fixation is limited by iron availability in the ocean^{2,5}. This was inferred from the high iron requirement estimated for growth of nitrogen fixing organisms⁶ and the higher apparent densities of *Trichodesmium* where aeolian iron inputs are plentiful⁷. Here we report that nitrogen fixation rates in the central Atlantic appear to be independent of both dissolved iron levels in sea water and iron content in *Trichodesmium* colonies. Nitrogen fixation was, instead, highly correlated to the phosphorus content of *Trichodesmium* and was enhanced at higher irradiance. Furthermore, our calculations suggest that the structural iron requirement for the growth of nitrogen-fixing organisms is much lower than previously calculated⁶. Although iron deficiency could still potentially limit growth of nitrogen-fixing organisms in regions of low iron availability—for example, in the subtropical North Pacific Ocean—our observations suggest that marine nitrogen fixation is not solely regulated by iron supply.

We collected surface water samples and colonies of *Trichodesmium* spp. using trace-metal clean methods along two transects in the tropical (0–6° N latitude; 50–28° W longitude) and subtropical (10–16° N; 30–55° W) Atlantic Ocean in April 1996, and analysed them for C, N, P and Fe content. We also measured N₂ fixation rates of colonies (Methods).

Strong spatial gradients in the N₂-fixing diazotrophic activity were observed along the tropical and subtropical transects. Cell C specific N₂ fixation in the subtropical northern transect (median was 152 μmol N per mol C per h) was four times higher than in the tropical transect (median was 38 μmol N per mol C per h) (Fig. 1a). *Trichodesmium* biomass (Fig. 1b) was also seven times higher in the northern subtropical transect (subtropical median was 1.44 per mg chl *a* per m²; tropical median was 0.20 per mg chl *a* per m²).

In contrast to N₂ fixation, dissolved Fe concentrations in surface waters of the sub-tropical (median was 0.77 nM) and tropical (median was 0.95 nM) Atlantic were relatively constant (Fig. 1c). Similarly, levels of Fe in field-collected *Trichodesmium* colonies

ranged from 3 to 13 pmol per colony (median was 6 pmol per colony), and were not significantly different in the two transects (Fig. 1d). These Fe levels in the colonies were an order of magnitude lower than those previously reported⁵, owing to our implementation of trace-metal-clean techniques for collection and analysis. Moreover, *Trichodesmium* N₂ fixation and biomass were independent of the dissolved Fe concentrations and the Fe content of the colonies (Fig. 2a, b).

High N₂ fixation rates in the Atlantic were measured at relatively low Fe concentrations in the colonies (median was 36 μmol Fe per mol C; range 22–72 μmol Fe per mol C; Fig. 1d). Although the Fe requirements of *Trichodesmium* and other oceanic algae are not yet well known, the Fe:C ratios of the *Trichodesmium* colonies we measured in the central Atlantic Ocean were similar to the published Fe:C values for prokaryotic cyanobacteria (~20 μmol Fe per mol C; ref. 8) growing on N (from nitrate) in cultures. Furthermore, the *Trichodesmium* Fe:C ratios we measured were nearly identical to the Fe:C uptake ratios of coastal diatoms (34–88 μmol Fe per mol C, ref. 9), despite the fact that coastal species might be expected to have higher Fe requirements than open-ocean organisms⁸, owing to their adaptation to higher ambient Fe levels in coastal waters¹⁰. These observations suggest that the Fe requirements for diazotrophic marine cyanobacteria such as *Trichodesmium* may not be 100-fold higher than for NH₄⁺-assimilating phytoplankton, as previously calculated⁶.

We recalculated the theoretical iron use efficiency (IUE) for growth supported by N₂ fixation (Table 1) previously reported by

Raven⁶. We found that the mol Fe required (specific to the nitrogenase complex only and assuming comparable structural and bioenergetic requirements between autotrophic and heterotrophic diazotrophs) to fix 1 mol C per second via N₂ fixation ranged from 1.0 to 3.2 mol Fe, rather than 78.7 mol Fe (ref. 6). Considering this new structural estimate (Table 1) and the previously reported estimate for bioenergetic Fe demands⁶, N₂-fixing phytoplankton may have Fe requirements only 2.5–5.2 times greater than NH₄⁺-assimilating phytoplankton⁶. This range of Fe requirements is still rather higher than values calculated for phytoplankton growing on N from nitrate¹¹. However, we cannot discount any additional Fe requirement due to physiological phenomena not directly related to the structural and bioenergetic Fe demand of nitrogenase, such as variations in Fe catalyst stoichiometry¹².

Our results suggest that N₂ fixation in the subtropical Atlantic Ocean may not be an iron-limited process at this time of the year, when Fe inputs are relatively high. The apparent absence of Fe control over these biological processes is consistent with the relatively high background levels of dissolved Fe found in surface waters of the central Atlantic ocean (~1 nM; Fig. 1c). Those levels are between 2 and 5 times higher than the levels reported in the subtropical north Pacific (0.2–0.5 nM; ref. 13), probably owing to the high Saharan aeolian fluxes¹⁴ and tropical river inputs to the Atlantic¹⁵.

In contrast to the relatively invariant levels of dissolved Fe and Fe content in the colonies measured along the two Atlantic transects

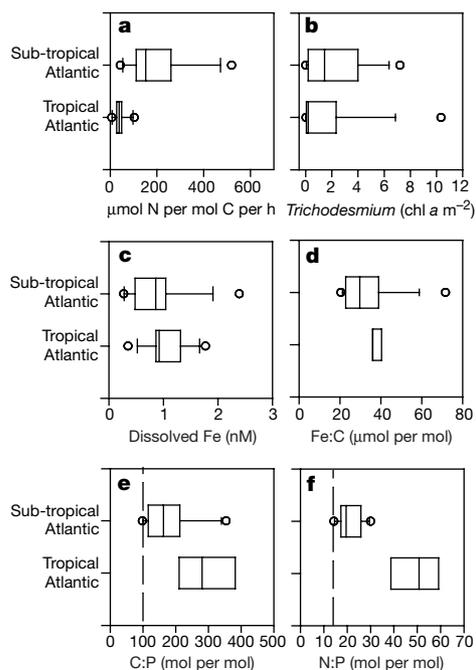


Figure 1 Box plots of N₂ fixation, dissolved Fe levels and elemental composition (C, N, P, Fe) in field-collected *Trichodesmium* colonies of the central Atlantic ocean. **a**, Nitrogen fixation. **b**, *Trichodesmium* biomass. **c**, dissolved Fe levels. **d**, Fe:C ratios. **e**, C:P ratios. **f**, N:P ratios. The tropical and subtropical areas represent our 0–6° N and 10–16° N latitude transects respectively. The line within the box is the median, and the boundary of the boxes indicates the 25th and 75th percentiles. Error bars to the left and right of the box indicate the 90th and 10th percentiles. Open circles show outlying points. Dashed line in **e** and **f** represent Redfield ratios. This figure shows that N₂ fixation (**a**) was considerably higher in the subtropical transect although the levels of dissolved Fe (**c**) in both transects were essentially the same. The Fe:C ratio (**d**) in the *Trichodesmium* colonies was relatively constant, but the C:P (**e**) and N:P (**f**) ratios were different in the subtropical and tropical transects. Those differences were caused by differences in the P content of the colonies (about two times higher in the subtropical transect). All of the data used in this figure is available in the Supplementary Information.

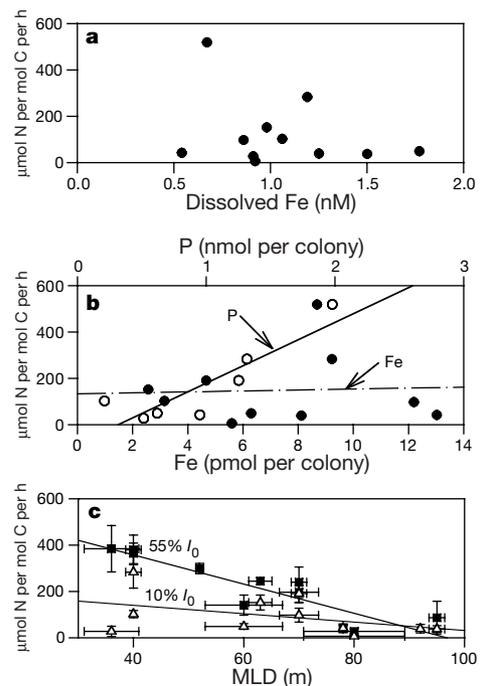


Figure 2 Relationship of N₂ fixation with dissolved Fe, with Fe and P composition in the *Trichodesmium* colonies, and with mixed-layer depth (MLD). **a**, N₂ fixation versus dissolved Fe. **b**, N₂ fixation versus Fe (filled circles) and P (open circles) content in the *Trichodesmium* colonies. Regression equation: N₂ fixation = 262 (± 65) × [P] – 83 (± 72); r² = 0.77, P < 0.01. **c**, N₂ fixation versus upper-ocean mixed-layer depth, calculated according to ref. 28. Squares represent N₂ fixation calculated at 55% I₀ and triangles indicate N₂ fixation calculated at 10% I₀. Irradiance. Bars denote ± 1 s.d. (MLD, n = 2; N₂ fixation, n = 3). **a** and **b** show that N₂ fixation was independent of Fe (in the water column and in the colonies) and strongly correlated with the P content in the *Trichodesmium*. **c** shows that N₂ fixation was higher at shallower mixed-layer depth and at higher irradiance.

(Fig. 1c and d), phosphorus levels in the *Trichodesmium* colonies in the subtropical transect (median was 1.10 nmol P per colony) were two times higher than in the tropical transect (median was 0.51 nmol P per colony; Fig. 1e). Furthermore, although our analyses suggested no relationship between Fe levels and N₂ fixation in the subtropical and tropical Atlantic, rates of N₂ fixation were significantly correlated with the P levels in the colonies (Fig. 2b). Although the importance of P for N₂ fixation in the open ocean has been hypothesized^{4,16}, our data provide the first direct evidence of such a link. The N:P molar ratios measured in the colonies in the tropical (median was 51; range was 35–61) and in the subtropical (median was 21; range was 14–30; Fig. 1f) were higher than the Redfield ratio of 16:1, and these elemental ratios were within the range reported for dissolved NO₃:PO₄ (that is, 20–40) of the Sargasso Sea^{7,16}. Therefore, N₂-fixing diazotrophs may contribute to the high dissolved N:P ratios observed in some areas of the Atlantic¹⁷.

Analysis of the physical regime in the central Atlantic Ocean suggested that N₂ fixation in this region could also be influenced by upper-ocean mixed-layer depth, as previously reported^{1,18,19} (Fig. 2c). The observation that N₂ fixation rates were higher at shallower mixed-layer depth is consistent with the relatively high light requirement of *Trichodesmium*²⁰, suggesting that inadequate mean irradiance for photosynthesis may directly affect the energetically expensive N₂ fixation process²¹. Our results showed that when irradiance was increased, N₂ fixation was also enhanced (Fig. 2c); therefore, light may also have limited N₂ fixation during our cruise. Surface water temperatures in the central Atlantic were relatively constant during our cruise (26.23 ± 1.27 °C) and no relationship with N₂ fixation was observed.

Although the importance of Fe in controlling primary production in high-nitrate, low-chlorophyll regions of the world ocean is well established²², our results suggest that other factors (such as P and light) may control N₂ fixation under the high-Fe conditions of the central Atlantic ocean. Although no other measurements of Fe and P in *Trichodesmium* are available in the literature, the C:N:P:Fe stoichiometry (99.6:18.3:1:3.7 × 10⁻³) in our field-collected *Trichodesmium* colonies (Fig. 3) suggests that P should limit N₂ fixation only after the Fe quota is met. For example, an average ambient dissolved P concentration of 75 ± 42 nM in the Atlantic¹⁶ and our average dissolved Fe of 0.89 ± 0.41 nM yield a dissolved P:Fe ratio of between 1:1.1 × 10⁻² and 1:1.5 × 10⁻². Those dissolved ratios are 3–4 times lower than the ratio measured in *Trichodesmium*, suggesting that the colonies in the Atlantic were not Fe-limited during our study. However, Fe deficiency could limit the growth of this organism in other ocean basins when Fe inputs are much lower. The calculated dissolved P:Fe ratio for the subtropical north Pacific ranges from an Fe-limitation ratio of 1:9.6 × 10⁻⁴ to a near-Fe-limitation ratio of 1:2.1 × 10⁻³ (based on dissolved P and Fe concentrations of 222 ± 14 nM (ref. 16) and 0.2–0.5 nM (ref. 13) respectively).

Our results suggest that N₂ fixation by *Trichodesmium* in the

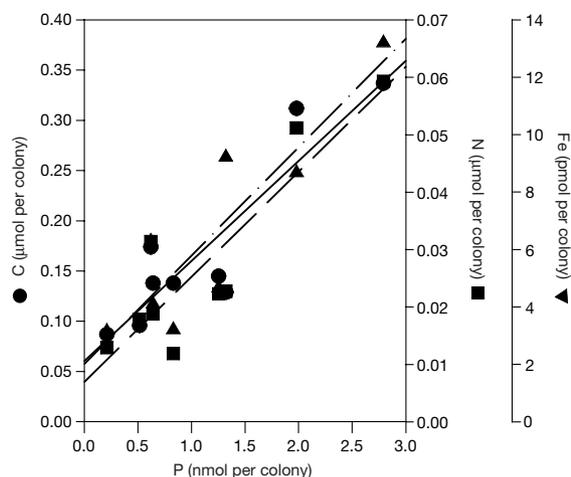


Figure 3 Elemental (C, N, P, Fe) composition of field-collected *Trichodesmium* colonies of the central Atlantic Ocean. Plot of C, N and Fe concentrations versus P concentration (denoted by circles, squares and triangles and corresponding solid, dashed and dashed-dotted regression lines, respectively). Regression equations (in mol per colony): [C] = 99.63 (± 2.1) × [P] + 6.04 × 10⁻⁸ (± 1.4 × 10⁻⁸), r² = 0.82. [N] = 18.3 (± 0.42) × [P] + 6.94 × 10⁻⁹ (± 2.8 × 10⁻⁹), r² = 0.79. [Fe] = 3.72 × 10⁻³ (± 8.7 × 10⁻⁵) × [P] + 2.1 × 10⁻¹² (± 6.2 × 10⁻¹³), r² = 0.79.

central Atlantic Ocean appears to be influenced by a series of factors (such as P or light). However, *in situ* Fe and P addition experiments at various irradiance levels are needed to further substantiate these conclusions. Rising atmospheric CO₂ may result in lower near-surface wind speeds²³ and shallower mixed layers²⁴ in the central Atlantic, consequently allowing more N₂ fixation to occur. Increased N₂ fixation could therefore potentially provide a negative feedback mechanism to climatic warming by sequestering anthropogenic CO₂ from the atmosphere. □

Methods

Surface water samples and *Trichodesmium* colonies were collected from a Zodiac deployed from the RV *Seward Johnson*. Water samples were filtered on-board in a portable class-100 clean unit using 0.45 μm acid-washed polycarbonate filters into acid-washed bottles. Colonies were collected at a depth of about 5 m by towing an acid-washed 102-μm plankton net at about 1 knot. In a class-100 portable bench, an average of about 100 colonies per station were hand-picked from the acid-washed cod-end using a plastic inoculating loop, deposited into 3-ml acid-washed Teflon vials, and digested in acid using a combination of Q-HCl, Q-HNO₃ and Q-HF. Fe content in the *Trichodesmium* colonies was then measured by graphite furnace atomic absorption spectrometry (GFAAS). The Fe blank was 30 ± 11 pmol per vial. Dissolved Fe was also measured using GFAAS after an organic extraction²⁵. Dissolved Fe blanks were 158 ± 88 pM (mean ± 1 s.d.). Phosphorus content in digested colonies was determined by spectrophotometric techniques developed for small volumes of interstitial waters²⁶. Nitrogen fixation was determined on isolated colonies collected between 10 and 20 m by slow (1 knot) plankton tows using a 1-m diameter, 202-μm mesh net using the C₂H₂ reduction technique²⁷. Results were converted to mol N fixed using a 3:1 ratio of C₂H₂ reduced to N₂ fixed. Particulate organic carbon

Table 1 Iron requirements for diazotrophic growth

Diazotrophs	Fe in MoFe protein ²¹ (mol mol ⁻¹)	Fe in nitrogenase complex (mol mol ⁻¹)*	Relative molecular mass of MoFe	Specific activity (nmol C ₂ H ₄ min ⁻¹ per mg MoFe)	N fixed (per mol enzyme s ⁻¹)†	N fixed (per mol enzyme s ⁻¹)‡	Fe required (per mol fixed C s ⁻¹)§
<i>Azotobacter vinelandii</i>	34–38	54–58	216–270K	1,400	3.78	0.065	2.12
<i>Azotobacter chroococcum</i>	>22	42	222K	2,000	4.93	0.117	1.22
<i>Klebsiella pneumoniae</i>	32	52	218K	2,150	5.21	0.100	1.43
<i>Clostridium pasteurianum</i>	24	44	220K	2,500	6.11	0.139	1.03
<i>Rhizobium japonicum</i>	29	49	200K	1,000	2.22	0.045	3.15

* Based on the optimal ratio of 5 mol nitrogenase reductase (Fe protein) to 1 mol nitrogenase (MoFe protein)²⁹, and 4 mol of Fe per Fe protein²¹.

† Calculated using the molecular mass, the specific activities and an ethylene production: N₂ fixation stoichiometry of 3:1.

‡ Mole Fe specifically associated with the nitrogenase complex.

§ In order to express the nitrogenase Fe requirements in terms of C fixation, a C:N fixation ratio of 7:1 is assumed as in ref. 6. Therefore, the photoautotrophic Fe requirement for C and N fixation (that is, growth) is the sum of the Fe bound in the nitrogenase complex, the bioenergetic Fe needed for C fixation and respiration to fuel nitrogenase, as well as the Fe needed for net C fixation. For the latter, we used 0.9 mol Fe (per mol C s⁻¹) to compute the estimated Fe requirement for photoautotrophic growth for photoautotrophs as 1.9–4.1 mol Fe (per mol C s⁻¹) (see ref. 6). These enzymatic iron use efficiencies are derived from a variety of terrestrial heterotrophic diazotrophs because these data are lacking for marine photoautotrophic diazotrophs. However, the functional regions of the modelled tertiary structure of *Trichodesmium* Fe protein appear to be highly conserved with respect to a heterotrophic diazotroph such as *Azotobacter vinelandii* (ref. 30).

levels in the field-collected colonies were determined using a Carlo Erba NA1500 NCS system. For *Trichodesmium* chlorophyll biomass, the contents of whole 10-l Niskin bottles from stratified depths were gravity filtered onto 5- to 10- μ m polycarbonate filters and trichome density determined by direct microscopic enumeration using phycoerythrin epifluorescence. *Trichodesmium* trichome density was converted to chlorophyll terms by a factor derived from direct extraction and determination of chlorophyll per trichome and per colony at each station. *Trichodesmium* biomass was then integrated to the upper 50 m. Standard hydrographic parameters (temperature *T*, salinity *S* and density σ_t) were measured by CTD (conductivity–temperature–depth) at each sampling location.

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Preservation of ancient and fertile lithospheric mantle beneath the southwestern United States

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Stable continental regions, free from tectonic activity, are generally found only within ancient cratons—the centres of continents which formed in the Archaean era, 4.0–2.5 Gyr ago. But in the Cordilleran mountain belt of western North America some younger (middle Proterozoic) regions have remained stable^{1,2}, whereas some older (late Archaean) regions have been tectonically disturbed^{1,3}, suggesting that age alone does not determine lithospheric strength and crustal stability. Here we report rhenium–osmium isotope and mineral compositions of peridotite xenoliths from two regions of the Cordilleran mountain belt. We found that the younger, undeformed Colorado plateau is underlain by lithospheric mantle that is ‘depleted’ (deficient in minerals extracted by partial melting of the rock), whereas the older (Archaean), yet deformed, southern Basin and Range province is underlain by ‘fertile’ lithospheric mantle (not depleted by melt extraction). We suggest that the apparent relationship between composition and lithospheric strength, inferred from different degrees of crustal deformation, occurs because depleted mantle is intrinsically less dense than fertile mantle (due to iron having been lost when melt was extracted from the rock). This allows the depleted mantle to form a thicker thermal boundary layer⁴ between the deep convecting mantle and the crust, thus reducing tectonic activity at the surface. The inference that not all Archaean crust developed a strong and thick thermal boundary layer leads to the possibility that such ancient crust may have been overlooked because of its intensive reworking or lost from the geological record owing to preferential recycling.

The North American Cordillera is a broad continental region marked by a long period of tectonic activity, which began in the Palaeozoic era with a series of mountain-forming events and culminated in the Cenozoic era with extension⁵. Deformation appears to be heterogeneously distributed (Fig. 1). The Basin and Range province, which includes much of Nevada and southeastern California, experienced crustal thickening and subsequent large-scale extension (possibly up to 200%)⁶. In contrast, the Colorado plateau, an elevated circular region surrounded on all sides by deformed crust, has remained an island of tectonic quiescence, as evidenced by flat-lying, unfolded and largely unfaulted Palaeozoic sedimentary strata⁷.

Given the relative differences in the degree of deformation seen in the overlying crust⁵ and the correlation between age and stability observed elsewhere in the continents, the more-tectonized Basin and Range lithosphere might be expected to be younger than that beneath the less-tectonized Colorado plateau. However, Sm–Nd model ages indicate that the crust in the southern Basin and Range (referred to here as Mojavia) is older, formed in Palaeoproterozoic to Archaean times (~2.0–2.6 Gyr ago)^{1,2}, whereas the Colorado plateau crust formed subsequently in the middle Proterozoic (1.6–2.0 Gyr ago)^{1,3}. There are two possible explanations for this unexpected relationship. First, the lithospheric mantle beneath Mojavia may not be as old as the crustal model ages indicate. This might

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