REVIEW

The integral role of iron in ocean biogeochemistry

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The micronutrient iron is now recognized to be important in regulating the magnitude and dynamics of ocean primary productivity, making it an integral component of the ocean's biogeochemical cycles. In this Review, we discuss how a recent increase in observational data for this trace metal has challenged the prevailing view of the ocean iron cycle. Instead of focusing on dust as the major iron source and emphasizing iron's tight biogeochemical coupling to major nutrients, a more complex and diverse picture of the sources of iron, its cycling processes and intricate linkages with the ocean carbon and nitrogen cycles has emerged.

cean primary production is important for the operation of the Earth System, underpinning the functioning of the global carbon cycle, air-sea CO₂ exchange and marine ecosystems¹. In the past three decades the micronutrient iron has been established as a key elemental resource that shapes the magnitude and dynamics of primary production in the global ocean. Oceanographers first became interested in iron in the 1930s, hoping to explain why the major nutrient inventories (nitrogen and phosphorus) were not fully depleted by primary producers in surface waters of much of the Southern Ocean²⁻⁴ (the Antarctic paradox'). Indeed, early laboratory studies showed that iron enrichment stimulated the growth of phytoplankton⁵, providing evidence that iron could control phytoplankton growth in sea water^{6,7}. However, owing to the low solubility of iron in the modern oxic ocean⁸ and the tendency for iron to be 'scavenged' from the water column by sinking particles⁹, dissolved iron was probably a rare commodity for ocean biota. By the early 1980s the crucial role for iron as a co-factor in many cellular enzymes, particularly those linked with photosynthesis, respiration and nitrogen fixation had been identified^{10,11}. Yet, despite this body of knowledge, it was not until the early 2000s that the global importance of iron to ocean productivity and biogeochemistry became widely recognized and included in global ocean models¹².

Emergence of the 'iron hypothesis'

A key issue hindering the study of iron-phytoplankton interactions in the ocean was the need for contamination-free sampling and accurate measurements at the required picomolar to nanomolar levels (10^{-12} to 10^{-9} moles per litre). Only in the late 1970s did development of exacting trace-metal clean sampling protocols¹³ and an appreciation for the rigours of clean analytical methods¹⁴ allow the first reliable ocean iron observations, which showed low surface water concentrations and 'nutrient-like' behaviour through the water column^{15,16}. Results from shipboard iron-enrichment experiments of natural phytoplankton communities conducted with ultraclean methods resurrected the idea that a lack of iron was indeed a key feature of the Southern Ocean^{17,18}. This led John Martin to formulate the 'iron hypothesis', which proposed that greater delivery of dust-derived iron to the Southern Ocean during glacial periods led to enhanced utilization of the major nutrients and a corresponding drawdown of atmospheric carbon dioxide¹⁹ (see also Box 1). Subsequent model simulations showed that if the reserves of major nutrients nitrate and phosphate in the Southern Ocean were to

be exhausted, then atmospheric CO_2 levels could be greatly reduced by 60 to 100 parts per million²⁰. Martin's ideas about how iron fertilization might control past and future climate are now widely accepted and have catalysed research in the field of ocean iron biogeochemistry.

The perceived limitations of Martin's shipboard experiments (for example, inadvertent exclusion of grazers)²¹, meant that only a deliberate large-scale *in situ* iron fertilization was deemed able to satisfactorily corroborate the *in vitro* evidence of iron-limited phytoplankton growth. Such large-scale fertilization experiments were initially performed during the 1990s in iron-limited equatorial Pacific waters^{22,23} and by 2000, results were published from the first test of the iron hypothesis in the Southern Ocean²⁴. At present, more than a dozen mesoscale iron fertilization experiments have been carried out worldwide, demonstrating phytoplankton iron limitation in the Southern, equatorial Pacific and subarctic Pacific oceans^{25,26} and sometimes inducing phytoplankton blooms large enough to be seen from space. Additional shipboard experiments also point to a role for iron limitation in the subpolar North Atlantic Ocean²⁷, California Current²⁸ and Humboldt and Peru upwelling systems²⁹.

The undeniable effect of iron on shaping patterns of ocean productivity necessitated an understanding of the processes that regulate the ocean iron cycle itself. Important progress was made when Johnson and co-workers³⁰ compiled 354 internally consistent iron observations and produced a conceptual view of how the ocean iron cycle operated (Fig. 1), which was supported by a one-dimensional model that reproduced observed profiles from a number of sites (largely in the Pacific Ocean). This model³⁰ assumed (i) that iron-rich aeolian dust input was the major external source of iron to the ocean, (ii) that deep-ocean iron concentrations were held to a quasi-constant value of approximately 0.6 nmol per litre by uniform levels of the recently quantified organic iron-complexing ligands^{31,32} that protected dissolved iron from being scavenged and (iii) that despite emerging knowledge of substantial variations in the biological iron demand³³, the uptake of iron and its regeneration from sinking organic matter was biogeochemically coupled to phosphorus at basin scales (via fixed iron to phosphorus ratios). This view of the ocean iron cycle (Fig. 1) ultimately catalysed the full representation of iron cycling within three-dimensional ocean general circulation models^{34,35}. Subsequent synthesis efforts in the following years^{36,37} echoed this general paradigm for the ocean iron cycle, which still informs most global iron models today³⁸. Models based on this view of the ocean

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Figure 1 | A schematic representation of the first view of the processes governing the ocean iron cycle. The major external source is dust, with the iron supplied from continental margins and hydrothermal activity on mid-ocean ridges thought to be lost from the dissolved pool close to the source. Release of iron from dust or supply of iron from upwelling stimulates biological activity, nitrogen fixation and particulate organic matter fluxes in a constant relationship to major nutrients (that is, they are biogeochemically coupled). In the ocean interior, iron regeneration and scavenging is controlled by fixed concentrations of iron-binding organic ligands.

iron cycle attribute up to half of the glacial decrease (of 80 parts per million) in atmospheric carbon dioxide to iron fertilization^{39,40}.

In this Review we explore how the recent expansion of observational data has challenged the prevailing understanding of the ocean iron cycle. New sources and cycling processes have been identified, which requires an overhaul of the way in which the models we rely on for future projections represent this important resource. These insights permit a new synthesis of the main processes involved in the global ocean iron cycle and intricate linkages to the cycling of carbon and other nutrients. To improve projections of how changes in climate affect the ocean carbon cycle, we suggest that future work should focus on an improved understanding of the interactions between iron cycle processes and ocean circulation and the reactivity (both chemical and physical) of different components of the dissolved iron pool (abiotic and biotic compounds) on different scales.

The iron cycle and biogeochemical linkages

In recent years there has been a nearly 100-fold increase in the number of high-quality iron measurements available, with which to explore processes and assess global models⁴¹. Initially, only a few laboratories worldwide had the capability to sample for and measure iron in the ocean, resulting in relatively sparse data sets. In an effort to remedy this, a global project called 'GEOTRACES' (www.geotraces.org) seeks to systematically document the distribution of trace elements and isotopes, including iron, throughout the oceans⁴². An earlier intercalibration effort called 'Sampling and Analysis of Iron' (SAFe) sought to intercompare a suite of analytical techniques and trace-metal clean sampling methodologies from different laboratories at sea⁴³. SAFe also produced a set of readily available 'reference samples' with consensus values at oceanographically relevant concentrations that could be used by both new and established investigators to evaluate their analytical methods. GEOTRACES has since launched a number of interwoven basin-scale 'sectional' studies, complemented by prior targeted process studies to understand temporal iron dynamics⁴⁴ and the drivers of 'naturally fertilized' regions in the

wake of Southern Ocean island systems^{45,46}. Thanks to these multi-faceted efforts, observations of iron have grown from a few hundred to more than 20,000 at present. This expansion in our ability to observe the system has allowed our understanding of how the ocean iron cycle operates to be refined.

External sources and cycling of iron

A key finding from both the GEOTRACES programme and process studies of natural systems is that there are multiple external sources of iron to the ocean that are important at both regional and global scales. For example, studies of enhanced biological activity downstream of Southern Ocean island systems^{45,46} and offshore of continental margins⁴⁷, the ability to track the origins of offshore iron pools via its mineral composition⁴⁸ and parallel modelling experiments⁴⁹ have emphasized that iron supply from continental margins extends far beyond the coastal zone. Equally, GEOTRACES efforts in the Atlantic⁵⁰, Pacific⁵¹, Southern⁵² and Arctic⁵³ oceans have observed striking signals of iron associated with hydro-thermal activity along mid-ocean ridges, adding to the deep-ocean iron inventory^{49,54}.

The prevailing circulation pathways (upwelling of deep water and lateral transport away from shelves) at the high latitudes crucial for air–sea $\rm CO_2$ exchange mean that continental margin and hydrothermal sources of iron are important in these regions⁴⁹. Nevertheless, during glacial periods, fluxes of dust-derived iron to the high-latitude Southern Ocean were much greater than is the modern dust supply^{55–58}. The mechanisms shaping the glacial carbon cycle remain uncertain, but presumably involve parallel changes in ocean circulation, whereby modifications to Southern Ocean overturning affect the partitioning of major nutrients between preformed and regenerated pools (see also Box 1) as well as deep-ocean carbon storage^{56,57}.

Although the perceived role of dust in regulating the functioning of the contemporary ocean carbon cycle via its modulation of Southern Ocean productivity has diminished in recent years, it remains a key supply mechanism to the low-latitude ocean. This is illustrated by new high-precision iron isotope studies that have, via the distinct isotopic signal associated with crustal iron, quantified the contribution of dust to dissolved iron in the tropical Atlantic Ocean⁵⁹. The productivity of this region is typically limited by nitrogen⁶⁰, and when enough iron is supplied it permits the growth of nitrogen-fixing organisms⁶¹. Broadly speaking, iron supply has emerged as a major driving force behind the geographic extent and magnitude of nitrogen fixation in the tropics^{62–64}. Dust-driven changes in iron supply to the low-latitude ocean must therefore be important to the maintenance of the ocean's fixed nitrogen inventory⁶⁵.

In the initial view of the ocean iron cycle, an important hypothesis was that deep-water dissolved iron levels are buffered to a constant upper bound set by uniform concentrations of organic iron-complexing ligands. However, an expansion of ligand observations over recent years^{66,67}, including basin-scale ocean sections^{68,69}, reveals that their abundance varies from less than 1 nmol per litre to more than 2 nmol per litre even in the ocean interior. Potential ligand sources associated with iron-limited bacterial and phytoplankton community growth, zooplankton grazing and particle breakdown have emerged⁶⁶, as well as potential external inputs associated with dust⁷⁰ or rainwater⁷¹ and the microbial production of strong iron-binding siderophores⁷². It is also probable that subduction and equatorward transport of excess ligands from high latitudes remotely influence the interior distribution of dissolved iron⁷³. As these exert a major control on the residence time of iron in the ocean⁷⁴, the cycling of organic iron-complexing ligands has also emerged as a crucial component of the ocean iron cycle. For instance, modelling indicates that variations in ligand concentration have a larger influence on contemporary atmospheric carbon dioxide levels than dust-derived iron supply⁴⁹ and can be responsible for long-range transport of iron away from point sources (for example, hydrothermal vents)⁵¹. However, our understanding of the production and consumption of iron-complexing ligands is evolving rapidly and uncertainties persist regarding the relative roles and rates of different processes.



Figure 2 | A revised representation of the major processes in the ocean iron cycle, with emphasis on the Atlantic Ocean. We draw attention to a broad meridional contrast between the iron-limited Southern Ocean and the major nutrient-limited low-latitude regimes. Dust remains dominant in the low latitudes, but continental margin and upwelled hydrothermal sources are more important in the Southern Ocean. Flexible iron uptake and biological cycling, along with the production of excess iron-binding ligands, dominate the Southern Ocean, whereas nitrogen fixation occurs

Biological and chemical iron cycling

The phytoplankton consumption of iron, relative to carbon or phosphorus (that is, their 'stoichiometry') is a common way of evaluating the coupling between the biological cycling of different resources. Despite its initial representation in numerical and conceptual models (Fig. 1) as a constant quantity^{30,35}, it is now well established that phytoplankton can exhibit substantial variations in their iron stoichiometry in different environments^{33,75}. For example, phytoplankton from the low-iron waters of the Southern Ocean typically exhibit iron to phosphorus stoichiometries that are more than fivefold lower than those from the iron-rich tropical Atlantic^{75,76}. This level of stoichiometric plasticity extends beyond that typically seen for the major nutrients⁷⁷ and is crucial in linking the biological cycling of iron to the assimilation of major nutrients and carbon fixation. An emerging feature for iron is the key role for iron regeneration by zooplankton, bacteria and viruses in supporting iron supply to the biota⁷⁸. A number of process studies have documented regional and seasonal variation in the importance of regenerated iron in fuelling phytoplankton carbon fixation78,79 and a potentially important role for organisms at higher trophic levels is also emerging⁸⁰. Lastly, specific characteristics associated with effective remineralization of particulate iron (that is, the net release of dissolved iron to the wider ocean), relative to major nutrients⁸¹ can decouple the vertical profile of dissolved iron in the ocean from other nutrients⁸².

The influence of iron on rates of carbon and nitrogen fixation is fundamentally linked to the process of iron acquisition by the biota. Early studies proposed that only the dissolved iron not bound to iron-complexing organic ligands was bioavailable in the ocean^{6,83}. Although the sum of these 'free' inorganic species may indeed be the most bioavailable form of iron⁸⁴, its concentration in seawater is vanishingly low ($<10^{-15}$ moles per litre), although it can be more abundant in some regions, such as the cold waters of the Southern Ocean⁸⁵. In addition, dissolved iron can occur in ferric (+3) and ferrous (+2) oxidation states in sea water, although the extent to which ferrous iron is used by the biota is not well known. Ferrous iron is mainly produced photochemically and although it is generally rapidly oxidized⁸⁶, transient daytime accumulations have been modelled⁸⁷, even in warm waters⁸⁸ and have been observed to persist on

in the low latitudes (although this process can also be restricted by lack of iron outside the North Atlantic subtropical gyre). The particulate organic iron flux is decoupled from that of phosphorus at high latitudes and the flux of lithogenic material is important at low latitudes influenced by dust. Subduction of excess organic iron-binding ligands from the Southern Ocean has a remote influence on the interior ocean at low latitudes. Contrasts for the Pacific Ocean are mentioned in the text.

longer timescales in low-temperature⁸⁹ and low-oxygen⁹⁰ systems, as well as along GEOTRACES sections⁹¹. More recently, laboratory⁹² and field⁹³ experiments have demonstrated that phytoplankton are also able to access the more dominant organically complexed iron pool via high-affinity acquisition systems, such as ferric reductases, and this strategy appears to be prevalent in organisms adapted to the iron-poor Southern Ocean⁹². In the dust-dominated low-latitude regions of the Atlantic Ocean the nitrogen-fixing cyanobacterium *Trichodesmium* has been shown to access mineral particulate iron directly⁹⁴. Taken together, this highlights a range of iron acquisition strategies that may be differentially linked to the commonly measured 'dissolved' iron concentration that is usually assumed to represent the bioavailable pool. More recent work seeks to unify concepts of the phytoplankton uptake across different iron substrates⁹⁵ within a 'bioavailability envelope' in which uptake rate constants are strongly linked to the surface area of different phytoplankton species⁹⁶.

Detailed process studies that combine measurements of ocean physics, major nutrient distributions and inputs with biological activity shed light on the intricate links between the cycling of iron and other nutrients and carbon. Across the tropical Atlantic Ocean it has been demonstrated that synoptic variation in dust input, linked to variations in the Inter-Tropical Convergence Zone, controls the 'biogeochemical divide' between phosphorus and iron limitation of nitrogen-fixing plankton⁶³. In the Pacific Ocean, metaproteomic techniques find gradual transitions from nitrogen to iron stress between the subtropical Pacific gyre and the equatorial Pacific that are linked to the underlying physics, with continuing iron stress in the south Pacific gyre⁹⁷. These approaches provide basin-scale perspectives on how the distinct environmental characteristics of different ocean biomes translate into gradients in the resource regulation of biological activity.

Drivers in the ocean iron cycle

Bringing together these new insights allows an updated synthesis of how the ocean iron cycle operates and its connections with the cycles of carbon, nitrogen and phosphorus (Fig. 2). In doing so, we are required to make a broad distinction between the dominance of dust-borne iron at low latitudes and the greater role for sedimentary and hydrothermal



Figure 3 | Observations from a meridional section in the west Atlantic Ocean as a function of latitude and depth. The section is GEOTRACES GA02⁹⁸. Dots show sample locations. **a**, Dissolved phosphate (colour scale). **b**, Dissolved iron (colour scale). Contours of constant potential vorticity $(\times 10^{-12} \text{ m}^{-1} \text{ s}^{-1})$ are shown on both panels.

iron sources at high latitudes. Whereas iron supply at the high latitudes drives the connections to the wider ocean cycling of carbon and air-sea carbon dioxide exchanges, low-latitude dust supply contributes to the maintenance of the fixed nitrogen inventory of the ocean. The drivers of the interior distribution of iron are more complicated than for major nutrients (see Box 1), with roles played by deep-ocean iron sources, the independent regeneration of iron from sinking particles and scavenging, as well as by the remote influence of water masses with distinct iron and ligand signatures subducted from high latitudes and transported equatorward. Previously, apart from dust sources and scavenging, close biogeochemical linkages between the cycling of iron and major nutrients such as phosphorus were emphasized (Fig. 1). However, as discussed above, multiple factors unique to iron have now been identified, exemplified by the substantial decoupling between observations of phosphate and iron along a meridional section in the West Atlantic Ocean98 (Fig. 3).

Synthesizing these new insights provides a more refined picture of the ocean iron cycle and emphasizes key meridional contrasts (Fig. 2). At high latitudes, upwelling and mixing of iron into surface waters is the major supply mechanism fuelling biological activity that is sustained via iron recycling by zooplankton and bacteria. Owing to longer effective remineralization length scales (that is, the depth at which particles are remineralized and returned to the dissolved inventory), iron export to the ocean interior is more efficient than for major nutrients (phosphorus is emphasized in Fig. 2) and decouples subsurface iron reserves from those of major nutrients⁸². As high latitudes are often iron limited, ligand production by iron-stressed communities and depletion of dissolved iron stocks leaves an excess of iron-complexing ligands that can be subducted and transported equatorward (dashed arrows in Fig. 2). This is similar to the idea that fluctuations in the consumption of major nutrients in response to changing iron delivery affect adjacent regions⁹⁹. In contrast, low latitudes are strongly affected by dust and the associated iron supply fuels nitrogen fixation by Trichodesmium, Crocosphera and other

diazotrophs. Dust may act as a source or sink for iron both in the surface ocean and during its sedimentation into the ocean interior. For example, in the iron-replete Mediterranean Sea, dust deposition actually depleted dissolved iron levels owing to enhanced particle scavenging¹⁰⁰. In lowlatitude regions where dust supply is low and upwelling is absent, the ensuing iron stress leads to low rates of nitrogen fixation¹⁰¹. Subsurface iron at low latitudes will be affected by the balance between local iron regeneration from sinking organic material and scavenging onto lithogenic and organic particles¹⁰². As scavenging rates are closely linked to the amount of iron not organically complexed, subsurface iron in the low latitudes can also be remotely controlled by subduction and equatorward transport of high-latitude waters with excess ligands⁷³, regulated by the lifetime of iron-complexing ligands. Although this view emphasizes the Atlantic Ocean, the meridional ocean circulation in the Pacific is also dominated by high-latitude deep-water sources that will drive similar processes. In the equatorial Pacific, sedimentary iron can also be an important source via the equatorial undercurrent¹⁰³, while dust deposition is more prevalent in the western sub-Arctic Pacific region³⁶. Just as in the Atlantic Ocean, hydrothermal and sediment sources are also important in the high-latitude Pacific Ocean^{48,104}.

This integrated view of the ocean iron cycle places additional challenges on the global ocean models we rely on for testing hypotheses and projections of change. For example, those global models that more closely track the developments in our understanding of the ocean iron cycle encapsulated in Fig. 2 are better able to reproduce observed features emerging from the iron data collected along large GEOTRACES ocean sections³⁸. When models represent the existence of multiple iron sources and specific aspects of iron's ocean cycling (for example, varying biological demands, dynamic cycling of ligands and iron recycling), simulated glacial iron fertilization contributes less than a quarter of the decrease in the glacial carbon dioxide (despite enhancing Southern Ocean biological activity)⁵⁸. Examinations of the parallel role of past changes to ocean circulation and dust delivery tend to suggest that iron fertilization indeed

BOX I Using theory to identify first-order governing processes.

A suite of interleaving processes controls the distributions of nutrients in the ocean. Biological uptake and chemical removal are sinks, whereas external inputs and regeneration are sources. Physical transport also transfers nutrients between surface and deep waters and throughout the ocean interior. Thus, interior ocean phosphate (P_{TOT}) is the sum of preformed (physically transported into the ocean interior, P_{PRE}) and regenerated (that is, from sinking organic matter, P_{REG}) pools:

$$P_{\text{TOT}} = P_{\text{PRE}} + P_{\text{REG}}$$

P_{REG} is quantified using apparent oxygen utilization (AOU) and the phosphate:oxygen ratio (r_{P:O2}):

$$P_{\rm REG} = r_{\rm P:O_2} \times \rm AOU \tag{2}$$

Equations (1) and (2) then quantify the varying influences of ocean circulation and biological activity on phosphorus cycling^{117,118}. As the biological pump shifts phosphorus from the preformed to the regenerated pool, $P_{\text{REG}}/P_{\text{TOT}}$ (known as P^*) quantifies the efficiency of the biological pump¹¹⁷. Observations indicate that the biological pump operates at around one-third efficiency, with a linear relationship between P^* and atmospheric CO₂ levels¹¹⁷. This theory underpins the 'iron hypothesis'¹⁹, whereby iron fertilization enhances the biological pump efficiency by moving phosphate from the preformed to the regenerated pool and lowering CO₂.

While a similar theory for iron (Fe_{TOT}) would include preformed (Fe_{PRE}) and regenerated (Fe_{REG}) components, it must also consider subsurface sediment (Fe_{SED}) and hydrothermal (Fe_{HYD}) input, alongside iron scavenging loss (Fe_{SCAV}). The dust-mediated iron supply within the mixed layer affects Fe_{PRE}, but any dust that dissolves in the ocean interior (Fe_{DUST}) must be included:

$Fe_{TOT} = Fe_{PRE} + Fe_{REG} + Fe_{SED} + Fe_{HYD} + Fe_{DUST} + Fe_{SCAV}$ (3)

Variability in the iron content of sinking organic matter⁷⁵ causes a variable $r_{Fe:O_2}$ that must be combined with AOU to derive Fe_{REG}. Using equation (3) within a model finds that Fe_{PRE} interacts with interior sources to shape the magnitude of surface iron supply⁷³ (Fig. 2). Importantly, the regeneration and scavenging balance (that is, Fe_{REG} – Fe_{SCAV}) is decoupled from the gross rates of regeneration inferred from AOU because upstream subduction of excess ligands places an upper limit on how regeneration affects total iron⁷³. This scavenging loss of regenerated iron explains why the slope of the dissolved iron to AOU relationship differs from phytoplankton iron contents⁷⁶. While AOU itself may not be the ideal tracer of remineralization rates¹¹⁹, it offers a tractable means for such basin-scale efforts.

If equation (3) was linked to observations, the first-order drivers of the ocean iron cycle could be identified. This can be achieved if estimates of phytoplankton iron content^{76,81} are allied to ocean tracers (see subsection 'Linkages across space and time scales'). For instance, linking subduction timescales determined from transient tracers¹²⁰ to density-based or potential vorticity flow pathways can track preformed iron and its modification. Source-specific tracers, such as helium or radium, may isolate hydrothermal and sediment pools. Interior dust dissolution may be derived from lithogenic tracers such as aluminium and titanium. Finally, other particle-reactive, but biologically inactive elements (for example, thorium) can constrain scavenging rates.

Ultimately, the role of the each term in equation (3) is affected by organic iron-binding ligands⁷³ that are usually in excess of iron⁶⁷. A parallel approach for the total ligand concentration (L_{TOT}) should account for preformed surface-produced ligands (L_{PRE}), interior ligand production from organic matter degradation (L_{REG}) or specific sources (L_{SOURCE}), and ligand loss (L_{LOS}) from bacterial decay and coagulation:

$L_{\text{TOT}} = L_{\text{PRE}} + L_{\text{REG}} + L_{\text{SOURCE}} - L_{\text{LOSS}}$

(4)

(1)

Equation (4) may be quantified by combining experimental studies and tracers, but an important and confounding issue is the diversity of ligands present (that is, a blend of iron-binding molecules typically represented as distinct 'classes' based on measured binding constants), since each may have a unique provenance and impact on the iron cycle⁶⁶⁻⁶⁸.

has a small effect¹⁰⁵, which may have then combined with changes to ocean ventilation and carbon storage⁵⁶ to shape past changes in glacial carbon dioxide levels. Other emerging ideas, such as variations in hydro-thermal iron supply over glacial timescales^{106,107}, which may modulate the ocean iron inventory, and the decoupling between iron and major nutrient pools, which can affect partitioning between preformed and regenerated pools of iron (Box 1), remain to be tested within a glacial context.

At present, inter-model differences result in iron residence times that range widely, from a few years to a few hundred years³⁸. This uncertainty is a concern, because projections of how climate change will affect ocean productivity¹⁰⁸, which has implications for global carbon cycling and marine ecosystems, will be regulated by iron over large swathes of the upper ocean. To reduce this uncertainty we need to be able to extract quantitative information from the new ocean survey data on the rates and controlling factors of the mechanisms governing the ocean iron cycle to inform more accurate model parameterizations of the key processes of external iron supply and internal cycling.

Linking iron to other nutrient cycles

The rapid increase in iron observations over recent decades has led to a much clearer understanding of the myriad processes underpinning the

ocean iron cycle and its connections to the cycling of carbon and major nutrients (Fig. 2). However, a complete theoretical framework for how iron cycling embeds within the broader context of ocean biogeochemical cycling is still lacking, which limits our ability to project the future evolution of ocean productivity and the carbon cycle in iron-limited regions with confidence³⁸. The expanding coverage of ocean observations via the GEOTRACES surveys⁴¹ is essential, but alone is insufficient to constrain the key underlying processes.

Linkages across space and time scales

The new proliferation of full-depth, basin-scale ocean sections for iron have been instrumental in advancing our understanding of the ocean iron cycle (Fig. 2). However, the 'biogeochemical' processes of interest (such as iron regeneration, scavenging and ligand production rates) operate on the backdrop of different physical processes that must be taken into consideration to extract information on the underlying biogeochemical processes (see Box 1). For instance, a given oceanic section is overlain with signatures of different water masses reflecting their individual end-member conditions, mixing between water masses, interior flow pathways and transit times, which confound the interpretation of iron distributions. That said, such iron distribution signatures can themselves be 'fingerprinted' and hence tracked using conservative tracers





a, Physical linkages in the iron cycle. Iron cycle processes can be placed within a holistic physical framework. Subduction of a water mass between density layers (σ_1 and σ_2) and subsequent spreading along lines of constant potential vorticity transports iron signals. This remote impact will then affect the interpretation of observed local phenomena. The terminology of the iron and ligand pools is described in Box 1. **b**, The components of particulate and dissolved iron pools (including the soluble and colloidal

(either steady-state or transient) of specific iron sources and cycling pathways.

Steady-state and transient tracers provide an excellent opportunity to fingerprint specific iron sources and thus assess iron input fluxes or regeneration and scavenging rates. Volcanic ³He has been used to identify iron plumes associated with mid-ocean ridges^{50,51,54}, as well as derive large-scale hydrothermal fluxes when estimates of global helium efflux are combined with the slope of the iron versus helium relationship⁵¹. The radium decay series, which is used to quantify exchanges at ocean boundaries, is also measured on some GEOTRACES sections¹⁰⁹ and may be linked to dissolved iron data sets to estimate a range of iron boundary fluxes. A particularly promising avenue may be the combination of such tracers with iron isotope studies. Tracers of ocean ventilation, such as chlorofluorocarbons or tritium, and diagnostics of interior ocean flows, such as potential vorticity, can be used to provide a coherent context within which to quantify how iron concentrations are modified—such as by regeneration or scavenging—during the transit of a water parcel subducted from the ocean surface along lines of constant potential vorticity (see Box 1 and Fig. 4a) or away from a specific point source (for example, a mid-ocean ridge or continental margin). As shown in Fig. 3, phosphate distributions are almost always closely linked to lines of constant potential vorticity following the major physical flows, whereas the distributions of iron have little obvious connection to potential vorticity, highlighting distinctions between the cycling of these two nutrients. The ventilation approach we advocate (Box 1, Fig. 4a) would enable the remote signal associated with iron (and ligands) subducted as preformed tracers to be isolated from the patchwork of interleaving processes that dictate the measured dissolved iron concentration.

Ultimately, we require a robust means of isolating the different contributors (both sources and internal cycling) to the iron cycle within a holistic physical framework (Box 1, Fig. 4a), such as exists for major nutrients. This would allow the global influence of ocean physics, regeneration and scavenging on iron distributions to be elucidated⁷³. With this approach, the first-order levels of coupling and decoupling between iron and major nutrients like phosphate may be quantified for use in parameterizing the foundations of global models. Furthermore, considering iron observations within their physical context—such as water masses, density or potential vorticity—will facilitate the quantification of the rates of key processes. To achieve this goal, we must exploit the coherent iron-hydrography data sets from GEOTRACES and targeted process studies.



components). Emphasis is on a fluid continuum of soluble, colloidal and particulate iron, as well as the role of inorganic (nanoparticles, authigenic iron and lithogenic species) and organic components (encompassing biogenic pools and biomolecules that bind iron strongly, as well as weaker diffuse iron-binding ligands such as hemes, saccharides or fulvic acids). We draw attention to the cycling of different inorganic and organic iron species within and across operationally defined boundaries.

Iron pools underpin variability in the iron cycle

A key contrast between iron and the major nutrients is that iron measurements more strongly rely on operational definitions because iron is present in multiple chemical forms and redox states. The prime focus of ocean iron observations remains on separating 'dissolved' and 'particulate' iron, by means of a defined filter (normally 0.2 µm). However, somewhere between half and three-quarters of dissolved iron does not pass through a much smaller 0.02-µm filter, which has led to a further distinction between 'soluble' and 'colloidal' dissolved iron¹¹⁰. Although much progress has been made in understanding how iron links to wider biogeochemical cycling (Fig. 2), the underlying processes themselves that affect the sources and sinks of iron are ultimately governed by the particular functional forms of iron that define its 'reactivity'. It is important to consider reactivity in different ways depending on the particular process. Biological reactivity (sometimes called bioavailability) affects the ability of the biota to acquire iron or how bacteria remineralize iron from organic material and varies depending on the iron acquisition strategy and its kinetics. Chemical reactivity will modulate the dissolution of lithogenic iron and the propensity of different forms of iron to be organically complexed or transferred to particulate pools via scavenging and colloidal aggregation.

Most of the focus on the iron present in these different size fractions has been from a geochemical or chemical perspective on inorganic speciesemphasizing the degree of complexation between iron and ligands in soluble and colloidal pools¹¹⁰ or the solubility and mineralogy of colloidal and particulate iron¹¹¹. However, owing to the scarcity and bio-essential nature of iron, much of the iron reservoir must be associated with the biota and their biochemical components. For instance, phytoplankton and bacteria are a notable fraction of the small particulate iron pool¹¹², whereas the virus-associated iron may be a non-negligible component of colloidal iron¹¹³. Additionally, intracellular iron, which is largely associated with metalloenzymes and storage proteins¹¹⁴, is released to the dissolved phase following microbial grazing and viral lysis of biogenic particles. Notable examples of biomolecules that may contribute to the dissolved or colloidal iron pool when released from cells include numerous metalloenzymes and their iron-binding constituents (for example, hemes and iron-sulfur clusters)¹¹⁵, as well as ferritin and bacteroferritin (iron-storing proteins)¹¹⁴. Although the magnitude of the contribution of biomolecules to measured iron levels and their lifetime in the dissolved phase remain unknown, these biogenic iron species will contribute to the biological and chemical reactivity of iron differently across a range of environments. On-going work with ultrahigh-resolution mass spectrometry

and genomic and proteomic studies is investigating what makes up different iron pools, which will be crucial in better understanding the biological and/or chemical reactivity of iron. A key challenge in this regard is the transient nature of these different components of the ocean iron pool, which is affected by the specific attributes of distinct environments and will ultimately regulate the linkages between iron and other biogeochemical cycles (Fig. 4b).

New frontiers of the ocean iron cycle

Will we see another change of similar magnitude in our understanding of the ocean iron cycle over the next decade? The importance of iron in regulating ocean productivity and biogeochemical cycling is well established and as we have discussed, important aspects unique to its ocean cycling, relative to major nutrients, have been identified (Figs 2 and 3). To be able to project the impacts of ocean change with confidence, iron needs to be fully integrated into a theoretical framework where the main drivers of its distribution and cycling are identified, as they are for major nutrients. This would enable progress to be made in the representation of iron cycling in the ocean models that we rely on to test hypotheses regarding the functioning of ocean biogeochemical cycles and to appraise the consequences of on-going climate change on marine productivity. Enormous progress has been made in our ability to observe ocean iron distributions thanks to GEOTRACES, but the roles of different biological, chemical and physical processes still require clarification. In part, this is due to our fragmentary picture of ocean iron cycle variability and the linkages to global biogeochemical cycles.

When iron measurements are conducted at similar scales to other biogeochemical tracers during targeted experiments, budgets and fluxes can be quantified, which yield insight into the linkages that ultimately regulate the functioning of the ocean's biogeochemical cycles. For example, the FeCycle experiment followed iron dynamics in a labelled patch of the subantarctic Southern Ocean, documenting the parallel roles of ocean physics, biology and chemistry in governing links between iron and broader aspects of biogeochemical cycling, including dust iron supply⁴⁴. In particular, a key finding of FeCycle was that apparent uniformity in dissolved iron profiles concealed the rapid internal recycling that drives around 90% of the biological demand in iron-limited waters⁴⁴. Two multidisciplinary experiments focusing on the naturally fertilized Kerguelen plateau region in different seasons were able to develop regional iron budgets⁷⁹ and make wider links to physical and biological processes, including downward biogenic carbon export and air-sea CO₂ exchange. We recommend future work that expands such efforts to the ocean-basin scale, coupling ocean sections with insights into the associated physical, chemical, biochemical and ecological processes. This may be achieved in its simplest sense by expanding the biological, biochemical and physical measurements conducted on GEOTRACES sections, as for the GA03 North Atlantic section^{76,116}. More ambitiously, key regions along sections (for example, downstream of iron sources or across gradients of iron stress) may be targeted and controlled volume experiments performed to elucidate the processes governing the sources and sinks for iron

Finally, expanding the temporal scale of iron sampling requires advances in analytical chemistry, which may ultimately yield the autonomous sensors or remote samplers for iron that are needed to revolutionize our ability to observe variability (for example, at time-series stations or in remote inhospitable regions such as the Southern Ocean during winter). Efforts to expand the temporal scale of sampling using deployable sensors may be particularly important for iron given its short residence time, relative to major nutrients. For instance, this could illuminate how natural climate variations (for example, El Niño in the Pacific) or seasonal transitions (for example, at high latitudes or in coastal upwellings) shape biogeochemical cycles via modifications to iron dynamics. Ultimately, the ability to link deployable iron sensors alongside multi-disciplinary ocean surveys and process studies would transform our understanding of the ocean iron cycle over the next decade by linking parallel variations in iron to changes in nitrogen and carbon cycling.

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- Falkowski, P. & Raven, J. A. Aquatic Photosynthesis 488 (Princeton Univ. Press, 1.
- 2007) 2. Ruud, J. T. Nitrates and phosphates in the Southern Seas. J. Conseil 5, 347-360 (1930).
- Gran, H. H. On the conditions for the production of plankton in the sea. Conseil 3 Permanent International pour l'Exploration de la Mer. Rapports et Procès-Verbaux des réunions 75, 37-46 (1931).
- 4 Hart, T. On the phytoplankton of the south-west Atlantic and the Bellingshausen Sea, 1929-31. Discov. Rep. VIII, 1-268 (1934).
- 5 Harvey, H. On the rate of diatom growth. J. Mar. Biol. Assoc. 19, 253-276 (1933)
- 6. Anderson, M. A. & Morel, F. M. M. The influence of aqueous iron chemistry on the uptake of iron by the coastal diatom Thalassiosira weissflogii. Limnol. Oceanogr. 27, 789-813 (1982).
- 7. Brand, L. E., Sunda, W. G. & Guillard, R. R. L. Limitation of marine phytoplankton reproductive rates by zinc, manganese and iron. Limnol. Oceanogr. 28, 1182-1198 (1983).
- Cooper, L. H. N. Iron in the sea and in marine plankton. Proc. R. Soc. Lond. B 8. 118, 419-438 (1935).
- 9 Goldberg, E. D. Marine geochemistry. 1. Chemical scavengers of the sea. J. Geol. 62, 249-265 (1954).
- 10. Williams, R. J. P. The Bakerian Lecture, 1981-Natural selection of the chemical elements. Proc. R. Soc. B 213, 361-397 (1981).
- Raven, J. A. The iron and molybdenum use efficiencies of plant growth with 11. different energy, carbon and nitrogen sources. New Phytol. 109, 279-287 (1988)
- Moore, J. K., Doney, S. C., Glover, D. M. & Fung, I. Y. Iron cycling and nutrient-12. limitation patterns in surface waters of the World Ocean. Deep Sea Res. Part II 49.463-507 (2002).
- 13 Bruland, K. W., Franks, R. P., Knauer, G. A. & Martin, J. H. Sampling and analytical methods for the determination of copper, cadmium, zinc, and nickel at the nanogram per liter level in sea water. Anal. Chim. Acta 105, 233-245 (1979)
- Settle, D. & Patterson, C. Lead in albacore: guide to lead pollution in 14. Americans. Science **207**, 1167–1176 (1980). Gordon, R. M., Martin, J. H. & Knauer, G. A. Iron in Northeast Pacific waters.
- 15. Nature 299, 611-612 (1982)
- 16. Landing, W. M. & Bruland, K. W. The contrasting biogeochemistry of iron and manganese in the Pacific Ocean. Geochim. Cosmochim. Acta 51, 29-43 (1987).
- Martin, J. H., Gordon, R. M. & Fitzwater, S. E. Iron in Antarctic waters. Nature 17. 345, 156-158 (1990).
- 18. Martin, J. H., Fitzwater, S. E. & Gordon, R. M. Iron deficiency limits phytoplankton growth in Antarctic waters. Glob. Biogeochem. Cycles 4, 5-12 (1990)
- Martin, J. H. Glacial-interglacial CO2 change: the iron hypothesis. 19 Paleoceanography 5, 1–13 (1990). This paper presented the iron hypothesis-that past variations in atmospheric carbon dioxide were driven by greater iron supply to the Southern Ocean.
- 20. Joos, F., Sarmiento, J. L. & Siegenthaler, U. Estimates of the effect of Southern Ocean iron fertilization on atmospheric CO₂ concentrations. Nature 349, 772-775 (1991)
- Cullen, J. J. Hypotheses to explain high-nutrient conditions in the open sea. 21 Limnol. Oceanogr. 36, 1578–1599 (1991).
- 22. Martin, J. H. et al. Testing the iron hypothesis in ecosystems of the equatorial Pacific Ocean. Nature 371, 123-129 (1994).
- 23. Coale, K. H. et al. A massive phytoplankton bloom induced by an ecosystem scale iron fertilization experiment in the equatorial Pacific Ocean. Nature 383, 495-501 (1996).
- Boyd, P. W. et al. A mesoscale phytoplankton bloom in the polar Southern 24. Ocean stimulated by iron fertilization. Nature 407, 695-702 (2000). This paper reported results from the first in situ iron fertilization experiment from the Southern Ocean.
- 25. Boyd, P. W. et al. Mesoscale iron enrichment experiments 1993-2005: synthesis and future directions. Science 315, 612-617 (2007).
- 26 de Baar, H. J. W. et al. Synthesis of iron fertilization experiments: from the Iron Age in the Age of Enlightenment. J. Geophys. Res. 110, C09S16 (2005).
- 27. Moore, C. M. et al. Iron limits primary productivity during spring bloom development in the central North Atlantic. Glob. Change Biol. 12, 626-634 (2006).
- 28. Hutchins, D. A., DiTullio, G. R., Zhang, Y. & Bruland, K. W. An iron limitation mosaic in the California upwelling regime. Limnol. Oceanogr. 43, 1037-1054 (1998)
- Hutchins, D. A. et al. Phytoplankton iron limitation in the Humboldt Current 29. and Peru Upwelling. Limnol. Oceanogr. 47, 997-1011 (2002).
- 30 Johnson, K. S., Gordon, R. M. & Coale, K. H. What controls dissolved iron concentrations in the world ocean? Mar. Chem. 57, 137-161 (1997) This paper put forward the first conceptual and numerical model of the main processes driving the ocean iron cycle.
- 31. Gledhill, M. & van den Berg, C. M. G. Determination of complexation of iron(III) with natural organic complexing ligands in seawater using cathodic stripping voltammetry. Mar. Chem. 47, 41-54 (1994).

RESEARCH REVIEW

- Rue, E. L. & Bruland, K. W. Complexation of iron(III) by natural organic ligands 32. in the Central North Pacific as determined by a new competitive ligand equilibration/adsorptive cathodic stripping voltammetric method. Mar. Chem. 50, 117-138 (1995).
- 33. Sunda, W. G. & Huntsman, S. A. Interrelated influence of iron, light and cell size on marine phytoplankton growth. Nature 390, 389-392 (1997) This paper demonstrated how different environmental factors led to large
- variations in the phytoplankton iron uptake. 34. Archer, D. E. & Johnson, K. A model of the iron cycle in the ocean. Glob. Biogeochem. Cycles 14, 269-279 (2000).
- Parekh, P., Follows, M. J. & Boyle, E. A. Decoupling of iron and phosphate in the 35. global ocean. Glob. Biogeochem. Cycles 19, GB2020 (2005).
- 36. Jickells, T. D. et al. Global iron connections between desert dust, ocean biogeochemistry, and climate. Science 308, 67-71 (2005).
- de Baar, H. J. & de Jong, J. T. in The Biogeochemistry of Iron in Seawater Vol. 7 37. (eds Turner, D. R. & Hunter, K. A.) 123–254 (2001).
- Tagliabue, A. *et al.* How well do global ocean biogeochemistry models simulate dissolved iron distributions? *Glob. Biogeochem. Cycles* **30**, 149–174 (2016). 38 This paper was the first to critically appraise how well a range of state-of-the-art ocean models represented the ocean iron cycle.
- Hain, M. P., Sigman, D. M. & Haug, G. H. Carbon dioxide effects of Antarctic 39 stratification, North Atlantic Intermediate Water formation, and subantarctic nutrient drawdown during the last ice age: Diagnosis and synthesis in a geochemical box model. Glob. Biogeochem. Cycles **24,** GB4023 (2010).
- 40. Watson, A. J., Bakker, D. C. E., Ridgwell, A. J., Boyd, P. W. & Law, C. S. Effect of iron supply on Southern Ocean CO2 uptake and implications for glacial atmospheric CO2. Nature 407, 730-733 (2000).
- The GEOTRACES Group. The GEOTRACES Intermediate Data Product 2014. 41. Mar. Chem. 177, 1-8 (2015).
- This paper reported the first release of high-quality iron data, alongside a range of other important datasets, from the GEOTRACES programme. Anderson, R. & Henderson, G. GEOTRACES—A global study of the marine 42
- biogeochemical cycles of trace elements and their isotopes. Oceanography 18, 76-79 (2005).
- Johnson, K. S. et al. Developing standards for dissolved iron in seawater. 43 Eos 88, 131-132 (2007).
- Boyd, P. W. et al. FeCycle: attempting an iron biogeochemical budget from a 44. mesoscale SF₆ tracer experiment in unperturbed low iron waters. Glob. Biogeochem. Cycles 19, GB4S20 (2005).
- Blain, S. et al. Effect of natural iron fertilization on carbon sequestration in the 45. Southern Ocean. *Nature* **446,** 1070–1074 (2007).
- 46. Pollard, R. T. et al. Southern Ocean deep-water carbon export enhanced by natural iron fertilization. Nature 457, 577-580 (2009).
- Elrod, V. A., Berelson, W. M., Coale, K. H. & Johnson, K. S. The flux of iron from 47 continental shelf sediments: a missing source for global budgets. Geophys. Res. Lett. 31, L12307 (2004).
- Lam, P. J. & Bishop, J. K. B. The continental margin is a key source of iron to 48.
- the HNLC North Pacific Ocean. *Geophys. Res. Lett.* **35**, L07608 (2008). Tagliabue, A., Aumont, O. & Bopp, L. The impact of different external sources of 49 iron on the global carbon cycle. Geophys. Res. Lett. 41, 920-926 (2014).
- Saito, M. A. *et al.* Slow-spreading submarine ridges in the South Atlantic as a significant oceanic iron source. *Nat. Geosci.* **6**, 775–779 (2013). 50.
- 51. Resing, J. A. et al. Basin-scale transport of hydrothermal dissolved metals across the South Pacific Ocean. Nature 523, 200-203 (2015). This paper was the first to demonstrate that the longevity of iron from hydrothermal vents was much longer than previously estimated.
- 52. Klunder, M. B., Laan, P., Middag, R., De Baar, H. J. W. & van Ooijen, J. C. Dissolved iron in the Southern Ocean (Atlantic sector). Deep Sea Res. Part II 58, 2678-2694 (2011).
- Klunder, M. B. et al. Dissolved iron in the Arctic shelf seas and surface waters of 53. the central Arctic Ocean: impact of Arctic river water and ice-melt. J. Geophys. Res. Oceans 117, C01027 (2012).
- Tagliabue, A. et al. Hydrothermal contribution to the oceanic dissolved iron 54 inventory. Nat. Geosci. **3**, 252–256 (2010). Martinez-Garcia, A. *et al.* Iron fertilization of the Subantarctic ocean during the
- 55 last ice age. Science 343, 1347-1350 (2014).
- 56. Jaccard, S. L., Galbraith, E. D., Martinez-Garcia, A. & Anderson, R. F. Covariation of deep Southern Ocean oxygenation and atmospheric CO $_2$ through the last ice age. Nature ${\bf 530},$ 207–210 (2016).
- Sigman, D. M., Hain, M. P. & Haug, G. H. The polar ocean and glacial cycles in 57. atmospheric CO2 concentration. Nature 466, 47-55 (2010).
- 58. Lambert, F. et al. Dust fluxes and iron fertilization in Holocene and Last Glacial Maximum climates. Geophys. Res. Lett. 42, 6014-6023 (2015).
- Conway, T. M. & John, S. G. Quantification of dissolved iron sources to the 59. North Atlantic Ocean. Nature 511, 212-215 (2014). This paper was the first to use iron isotopes to fingerprint the importance of
- different iron sources in the North Atlantic Ocean. Moore, C. M. et al. Processes and patterns of oceanic nutrient limitation. 60 Nat. Geosci. 6, 701–710 (2013).
- Falkowski, P. G. Evolution of the nitrogen cycle and its influence on the 61. biological sequestration of CO₂ in the ocean. Nature 387, 272–275 (1997).
- 62. Moore, C. M. et al. Large-scale distribution of Atlantic nitrogen fixation controlled by iron availability. Nat. Geosci. 2, 867-871 (2009)
- Schlosser, C. et al. Seasonal ITCZ migration dynamically controls the location 63. of the (sub)tropical Atlantic biogeochemical divide. Proc. Natl Acad. Sci. USA 111, 1438-1442 (2014).

- Dutkiewicz, S., Ward, B. A., Monteiro, F. & Follows, M. J. Interconnection of 64. nitrogen fixers and iron in the Pacific Ocean: theory and numerical simulations. Glob. Biogeochem. Cycles 26, GB1012 (2012).
- 65 Weber, T. & Deutsch, C. Local versus basin-scale limitation of marine nitrogen fixation. Proc. Natl Acad. Sci. USA 111, 8741-8746 (2014).
- 66. Gledhill, M. & Buck, K. N. The organic complexation of iron in the marine environment: a review. Front. Microbiol. 3, 69 (2012).
- 67. Boyd, P. W. & Tagliabue, A. Using the L* concept to explore controls on the relationship between paired ligand and dissolved iron concentrations in the ocean. Mar. Chem. **173**, 52–66 (2015). Buck, K. N., Sohst, B. & Sedwick, P. N. The organic complexation of dissolved
- 68. iron along the U.S. GEOTRACES (GA03) North Atlantic Section. Deep Sea Res. Part II 116, 152–165 (2015).
- 69 Gerringa, L. J. A., Rijkenberg, M. J. A., Schoemann, V., Laan, P. & de Baar, H. J. W. Organic complexation of iron in the West Atlantic Ocean. Mar. Chem. 177, 434-446 (2015).
- Wozniak, A. S., Shelley, R. U., McElhenie, S. D., Landing, W. M. & Hatcher, P. G. 70. Aerosol water soluble organic matter characteristics over the North Atlantic Ocean: implications for iron-binding ligands and iron solubility. Mar. Chem. 173, 162–172 (2015).
- Cheize, M. et al. Iron organic speciation determination in rainwater using 71. cathodic stripping voltammetry. Anal. Chim. Acta 736, 45-54 (2012).
- Mawji, E. et al. Production of siderophore type chelates in Atlantic Ocean 72. waters enriched with different carbon and nitrogen sources. Mar. Chem. 124, 90–99 (2011).
- Tagliabue, A., Williams, R. G., Rogan, N., Achterberg, E. P. & Boyd, P. W. A 73. ventilation-based framework to explain the regeneration-scavenging balance of iron in the ocean. *Geophys. Res. Lett.* **41**, 7227–7236 (2014).
- 74 Völker, C. & Tagliabue, A. Modeling organic iron-binding ligands in a three-dimensional biogeochemical ocean model. Mar. Chem. 173, 67-77 (2015).
- Twining, B. S. & Baines, S. B. The trace metal composition of marine 75. phytoplankton. Annu. Rev. Mar. Sci. 5, 191-215 (2013). This paper provides a state-of-the-art summary of the iron content of marine phytoplankton determined using a variety of different techniques.
- Twining, B. S., Rauschenberg, S., Morton, P. L. & Vogt, S. Metal contents of 76. phytoplankton and labile particulate material in the North Atlantic Ocean. Prog. Oceanogr. 137, 261–283 (2015).
- Martiny, A. C. et al. Strong latitudinal patterns in the elemental ratios of marine 77. plankton and organic matter. Nat. Geosci. 6, 279-283 (2013).
- Boyd, P. W. et al. Why are biotic iron pools uniform across high- and low-iron 78. pelagic ecosystems? Glob. Biogeochem. Cycles 29, 1028-1043 (2015).
- 79 Bowie, A. R. et al. Iron budgets for three distinct biogeochemical sites around the Kerguelen Archipelago (Southern Ocean) during the natural fertilisation study, KEOPS-2. Biogeosciences 12, 4421-4445 (2015)
- 80. Ratnarajah, L., Bowie, A. R., Lannuzel, D., Meiners, K. M. & Nicol, S. The biogeochemical role of baleen whales and krill in Southern Ocean nutrient cycling. PLoS One 9, e114067 (2014); correction 10(4), e0125134 (2015)
- Twining, B. S. et al. Differential remineralization of major and trace elements in 81. sinking diatoms. Limnol. Oceanogr. 59, 689-704 (2014).
- 82. Tagliabue, A. et al. Surface-water iron supplies in the Southern Ocean sustained by deep winter mixing. Nat. Geosci. 7, 314-320 (2014).
- 83 Hudson, R. J. M. & Morel, F. M. M. Iron transport in marine phytoplankton: kinetics of cellular and medium coordination reactions. Limnol. Oceanogr. 35, 1002-1020 (1990).
- 84. Morel, F. M. M., Kustka, A. B. & Shaked, Y. The role of unchelated Fe in the iron nutrition of phytoplankton. Limnol. Oceanogr. 53, 400-404 (2008)
- Schlosser, C., De La Rocha, C. L., Streu, P. & Croot, P. L. Solubility of iron in the 85 Southern Ocean. Limnol. Oceanogr. 57, 684-697 (2012).
- Liu, X. & Millero, F. J. The solubility of iron in seawater. Mar. Chem. 77, 43-54 86. (2002).
- Tagliabue, A. & Arrigo, K. R. Processes governing the supply of iron to 87. phytoplankton in stratified seas. J. Geophys. Res. 111, C06019 (2006).
- Weber, L., Völker, C., Schartau, M. & Wolf-Gladrow, D. A. Modeling the 88 speciation and biogeochemistry of iron at the Bermuda Atlantic Time-series Study site. Glob. Biogeochem. Cycles 19, GB1019 (2005).
- Croot, P. L. et al. Retention of dissolved iron and Fe-II in an iron induced 89 Southern Ocean phytoplankton bloom. Geophys. Res. Lett. 28, 3425-3428 (2001).
- Moffett, J. W., Goepfert, T. J. & Naqvi, S. W. A. Reduced iron associated with 90. secondary nitrite maxima in the Arabian Sea. Deep Sea Res. Part I 54, 1341-1349 (2007).
- 91. Sedwick, P. N., Sohst, B. M., Ussher, S. J. & Bowie, A. R. A zonal picture of the water column distribution of dissolved iron(II) during the U.S. GEOTRACES North Atlantic transect cruise (GEOTRACES GA03). Deep Sea Res. Part II 116, 166-175 (2015).
- Strzepek, R. F., Maldonado, M. T., Hunter, K. A., Frew, R. D. & Boyd, P. W. 92. Adaptive strategies by Southern Ocean phytoplankton to lessen iron limitation: uptake of organically complexed iron and reduced cellular iron requirements. Limnol. Oceanogr. 56, 1983-2002 (2011).
- Maldonado, M. T. & Price, N. M. Utilization of iron bound to strong organic 93. ligands by plankton communities in the subarctic Pacific Ocean. Deep Sea Res. Part II 46, 2447-2473 (1999).
- Rubin, M., Berman-Frank, I. & Shaked, Y. Dust- and mineral-iron utilization 94. by the marine dinitrogen-fixer Trichodesmium. Nat. Geosci. 4, 529-534 (2011).

- Shaked, Y., Kustka, A. B. & Morel, F. M. M. A general kinetic model for iron acquisition by eukaryotic phytoplankton. *Limnol. Oceanogr.* 50, 872–882 (2005).
- Lis, H., Shaked, Y., Kranzler, C., Keren, N. & Morel, F. M. Iron bioavailability to phytoplankton: an empirical approach. *ISME J.* 9, 1003–1013 (2014).
- Saito, M. A. et al. Multiple nutrient stresses at intersecting Pacific Ocean biomes detected by protein biomarkers. *Science* 345, 1173–1177 (2014). This paper was the first to link data on resource stress from proteomic to field measurements of resource concentrations to demonstrate the transitions between iron and nitrogen limitation in the Pacific Ocean.
 Bilkenberg, M. Let al. The distribution of dissolved iron in the West Atlantic.
- 98. Rijkenberg, M. J. et al. The distribution of dissolved iron in the West Atlantic Ocean. *PLoS One* **9**, e101323 (2014).
- Dutkiewicz, S., Follows, M. J. & Parekh, P. Interactions of the iron and phosphorus cycles: a three-dimensional model study. *Global Biogeochem. Cycles* 19, GB1021 (2005).
- Wagener, T., Guieu, C. & Leblond, N. Effects of dust deposition on iron cycle in the surface Mediterranean Sea: results from a mesocosm seeding experiment. *Biogeosciences* 7, 3769–3781 (2010).
- Sohm, J. A. et al. Nitrogen fixation in the South Atlantic Gyre and the Benguela Upwelling System. Geophys. Res. Lett. 38, L16608 (2011).
- Boyd, P. W. & Ellwood, M. J. The biogeochemical cycle of iron in the ocean. Nat. Geosci. 3, 675–682 (2010).
- Slemons, L. O., Murray, J. W., Resing, J., Paul, B. & Dutrieux, P. Western Pacific coastal sources of iron, manganese, and aluminum to the Equatorial Undercurrent. *Glob. Biogeochem. Cycles* 24, GB3024 (2010).
- Nishioka, J. *et al.* Iron supply to the western subarctic Pacific: importance of iron export from the Sea of Okhotsk. *J. Geophys. Res.* **112**, C10012 (2007).
- 105. Tagliabue, A. *et al.* Quantifying the roles of ocean circulation and biogeochemistry in governing ocean carbon-13 and atmospheric carbon dioxide at the last glacial maximum. *Clim. Past* **5**, 695–706 (2009).
- Middleton, J. L., Langmuir, C. H., Mukhopadhyay, S., McManus, J. F. & Mitrovica, J. X. Hydrothermal iron flux variability following rapid sea level changes. *Geophys. Res. Lett.* 43, 3848–3856 (2016).
- 107. Lund, D. C. *et al.* Enhanced East Pacific Rise hydrothermal activity during the last two glacial terminations. *Science* **351**, 478–482 (2016).
- 108. Bopp, L *et al.* Multiple stressors of ocean ecosystems in the 21st century: projections with CMIP5 models. *Biogeosciences* **10**, 6225-6245 (2013).
- Charette, M. A., Morris, P. J., Henderson, P. B. & Moore, W. S. Radium isotope distributions during the US GEOTRACES North Atlantic cruises. *Mar. Chem.* 177, 184–195 (2015).
- Wu, J., Boyle, E., Sunda, W. & Wen, L. S. Soluble and colloidal iron in the oligotrophic North Atlantic and North Pacific. *Science* 293, 847–849 (2001).
- 111. von der Heyden, B. P., Roychoudhury, A. N., Mtshali, T. N., Tyliszczak, T. & Myneni, S. C. Chemically and geographically distinct solid-phase iron pools in the Southern Ocean. *Science* **338**, 1199–1201 (2012).

- 112. Tortell, P. D., Maldonado, M. T. & Price, N. M. The role of heterotrophic bacteria in iron-limited ocean ecosystems. *Nature* **383**, 330–332 (1996).
- Bonnain, C., Breitbart, M. & Buck, K. N. The Ferrojan horse hypothesis: iron-virus interactions in the ocean. *Front. Mar. Sci.* 3, https://doi.org/10.3389/ fmars.2016.00082 (2016).
- Mackey, K. R. et al. Divergent responses of Atlantic coastal and oceanic Synechococcus to iron limitation. Proc. Natl Acad. Sci. USA 112, 9944–9949 (2015).
- Hogle, S. L., Barbeau, K. A. & Gledhill, M. Heme in the marine environment: from cells to the iron cycle. *Metallomics* 6, 1107–1120 (2014).
 Jenkins, W. J., Smethie, W. M., Boyle, E. A. & Cutter, G. A. Water mass analysis
- Jenkins, W. J., Smethie, W. M., Boyle, E. A. & Cutter, G. A. Water mass analysis for the U.S. GEOTRACES (GA03) North Atlantic sections. *Deep Sea Res. Part II* 116, 6–20 (2015).
- Ito, T. & Follows, M. J. Preformed phosphate, soft tissue pump and atmospheric CO₂. J. Mar. Res. 63, 813–839 (2005).
- Broecker, W. S., Takahashi, T. & Takahashi, T. Sources and flow patterns of deep-ocean waters as deduced from potential temperature, salinity, and initial phosphate concentration. J. Geophys. Res. 90, 6925–6939 (1985).
- Duteil, O. *et al.* A novel estimate of ocean oxygen utilisation points to a reduced rate of respiration in the ocean interior. *Biogeosciences* **10**, 7723–7738 (2013).
- Waugh, D. W., Primeau, F., Devries, T. & Holzer, M. Recent changes in the ventilation of the southern oceans. *Science* **339**, 568–570 (2013).

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