New insights into the modulation of ocean biogeochemistry by iron

Alessandro Tagliabue[1*], Andrew Bowie[2], Philip Boyd[2], Kristen Buck[3], Kenneth Johnson[4] and Mak Saito[5]

1. University of Liverpool, United Kingdom
2. Institute for Marine and Antarctic Studies, University of Tasmania, Australia
3. University of South Florida, USA
4. Monterey Bay Aquarium Research Institute, USA
5. Woods Hole Oceanographic Institution, USA

[*]Corresponding author: a.tagliabue@liverpool.ac.uk

Preface

Our understanding of the regulation of the magnitude of global and regional primary productivity has been fundamentally altered with the growing recognition of the pervasive role of iron. Observations of this trace metal in the ocean have increased markedly over recent decades, permitting a new synthesis of the processes governing its oceanic cycle. In particular, the inextricable linkages between iron and wider ocean biogeochemistry, including the cycling of carbon and major nutrients are beginning to emerge.

1. The emergence of the 'Iron Hypothesis'

Ocean primary production is crucial to the Earth System, underpinning the functioning of the global carbon cycle, air-sea CO_2 exchange and marine ecosystems[1]. In the past three decades the micronutrient iron has gone from a relative curiosity to emerging 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 as an explanation as to why the major nutrient inventories (nitrogen and phosphorus) were not fully depleted by primary producers in surface waters of much of the Southern Ocean[2-4]. Indeed, early laboratory studies showed that iron enrichment stimulated the growth of phytoplankton[5], providing encouragement that iron could control phytoplankton growth in seawater[6,7]. However, due to the low solubility of iron in the modern oxic ocean[8] and the tendency for iron to be 'scavenged' from the water column by sinking particles[9], dissolved iron was likely to be 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 acknowledged and included in global ocean models[12].

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 pico to nanomolar levels (10^{-12} to 10^{-9} moles L^{-1}). Only in the late 1970s did development of exacting trace metal clean sampling protocols[13] and an appreciation for the rigours of clean analytical methods[14] allow the first reliable oceanic 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 ultra-clean 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 iron to the Southern Ocean during glacial periods led to enhanced utilisation of the major nutrients and a corresponding drawdown of atmospheric carbon dioxide[19] (see also Box 1). Subsequent model simulations showed that if the reserves of major nutrients in the Southern Ocean could be exhausted, then atmospheric CO_2 levels could be reduced significantly by 60 to 100 ppm[20]. Martin's provocative ideas about how iron fertilisation might control past and future climate are now oceanographic folklore and have catalysed research into this field.

Due to the perceived limitations of Martin's shipboard experiments (e.g. exclusion of grazers)[21], only a deliberate *in situ* iron fertilisation was deemed able to satisfactorily corroborate the *in vitro* evidence of iron-limited phytoplankton growth. These 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 Ocean[24]. As of present, more than a dozen mesoscale iron fertilisation experiments have been carried out worldwide, demonstrating phytoplankton iron limitation in the Southern, Equatorial Pacific and subarctic Pacific Oceans[25,26]. Additional shipboard experiments also point to a role for iron limitation in the subpolar North Atlantic Ocean[27], California Current[28] and Humboldt and Peru upwelling systems[29].

The undeniable role for iron in shaping patterns of ocean productivity necessitated an understanding of the processes that regulate the ocean iron cycle itself. In 1997 an important step was made when Johnson and co-workers[30] 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 model[30] assumed that (i) iron-rich aeolian dust input was the major external source of iron to the ocean, (ii) deep ocean iron concentrations were held to a quasi-constant value of approximately 0.6 nmol L^{-1} by uniform levels of the recently quantified organic iron-complexing ligands[31,32] that protected dissolved iron from scavenging and (iii) that despite emerging knowledge of substantial variations in the biological iron demand[33], the uptake of iron and its regeneration from sinking organic matter was closely coupled to phosphorus at basin scales. This synthesis effort[30] (Fig 1) ultimately catalysed the full representation of iron cycling with 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 a large number of global iron models today[38]. Models based on this view of the ocean iron cycle attribute up to half of the 80 ppm glacial decrease in atmospheric carbon dioxide to iron fertilisation[39,40].

In this Review we will explore how the recent expansion of observational data has challenged the prevailing understanding of the ocean iron cycle. New sources and cycling processes are 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 the important linkages to the cycling of carbon and other nutrients. Ultimately we highlight where future advances may be fruitful in advancing our understanding. If this can be achieved, it would substantially reduce uncertainties in our ability to project the impact of environmental change on the ocean carbon cycle.

2. Refining our understanding of the iron cycle and its biogeochemical linkages

In recent years there has been a near 100-fold increase in the number of high quality iron measurements available to explore processes and assess global models[41]. Initially, only a few laboratories worldwide had the capability to sample for and measure iron in the ocean, resulting in relatively sparse datasets. In an effort to remedy this, in the early 2000's the international community galvanised around a global project called "GEOTRACES" (www.geotraces.org) that seeks to systematically document the distribution of trace elements and isotopes, including iron, throughout the oceans[42]. Critical in this regard was an earlier intercalibration effort in 2004 called "Sampling and Analysis of Iron" (SAFe) that sought to intercompare a suite of analytical techniques and trace metal clean sampling methodologies from different laboratories at sea[43]. Importantly, it 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 dynamics[44] and the drivers of "naturally fertilised" regions in the wake of Southern Ocean island systems[45,46]. Thanks to these multi-faceted efforts, there are more than 20,000 available observations of iron from the ocean 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.

2.1 Recognition of external sources and cycling of iron

A key finding from both the GEOTRACES programme and studies of process studies of natural systems was the recognition that there are multiple external sources of iron to the ocean that are significant at both regional and global scales. For example, studies of enhanced biological activity downstream of Southern Ocean island systems[45,46] and offshore from continental margins[47], the ability to track the origins of offshore iron pools via its mineral make up[48] and parallel modelling experiments[49] have emphasised that iron supply from continental margins extends far beyond the coastal zone. Equally, GEOTRACES efforts in the Atlantic[50], Pacific[51], Southern[52] and Arctic[53] Oceans have observed striking signals of iron associated with hydrothermal activity along mid ocean ridges that make a key contribution to the deep ocean iron inventory[49,54]. Due to their important role in the high latitude regions of the ocean crucial for air-sea CO_2 exchange, continental margin and hydrothermal sources play a dominant role in shaping the global carbon cycle[49]. However, the role for dust may have been enhanced during glacial periods typified by greater Southern Ocean dust fluxes.

While the perceived role for dust in regulating the functioning of the ocean carbon cycle via its modulation of high latitude 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 Ocean[55]. The productivity of this region is typically limited by nitrogen[56] and when enough iron is supplied it permits the growth of nitrogen-fixing organisms[57]. More broadly speaking, iron supply has emerged as a major driving force behind the geographic extent and magnitude of nitrogen fixation in the tropics[58-60]. Dust-driven changes in iron supply to the low latitude ocean has therefore emerged as an important component of the maintenance of the oceanic fixed nitrogen inventory[61].

An important hypothesis from the initial view of the ocean iron cycle was the concept of the buffering of dissolved iron to a constant deep-water concentration by uniform concentrations of organic iron-complexing ligands. However, a parallel expansion of ligand observations over recent decades[62,63], including basin scale ocean sections[64,65], reveals that their abundance varies from less than 1 to more than 2 nmol L^{-1} even in the ocean interior. Potential ligand sources associated with iron-limited bacterial and phytoplankton community growth, zooplankton grazing and particle breakdown have emerged[62], as well as potential external inputs associated with dust[66] or rainwater[67] and the microbial production of strong iron-binding siderophores[68]. There is also the likelihood that subduction and equatorward transport of excess ligands from high latitudes can remotely influence the interior distribution of dissolved iron[69]. As they control the residence time of iron in the ocean[70], 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 iron supply[49] and can be responsible for long range transport of iron away from point sources (e.g. hydrothermal vents)[51].

2.2 Biological Iron Cycling

The phytoplankton demand for iron relative to carbon or phosphorus (i.e. 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 between different environments[33,71]. For example, phytoplankton from the low iron waters of the Southern Ocean typically exhibit cellular demands that are more than five-fold lower than those from the iron rich tropical Atlantic[71,72]. This level of stoichiometric plasticity extends far beyond that seen for the major nutrients[73] and is crucial in linking the biological cycling of iron to the assimilation of major nutrients and carbon fixation. Another unique feature for iron is the key role for iron regeneration by zooplankton, bacteria and viruses in supporting iron supply to the biota[74]. A number of process studies have documented regional and seasonal variation in the

importance of regenerated iron in fuelling phytoplankton carbon fixation[74,75] and a potentially important role for higher trophic levels organisms is also emerging[76]. Lastly, specific characteristics associated with remineralisation of particulate iron, relative to major nutrients[77] can decouple the vertical profile of dissolved iron in the ocean from other nutrients[78].

How iron affects rates of carbon and nitrogen fixation is fundamentally linked to the process of iron acquisition by the biota. Early studies demonstrated that only the dissolved iron not bound to iron complexing organic ligands was bioavailable[6,79]. While the sum of these 'free' inorganic species may indeed be the most bioavailable form of iron[80], its concentration in seawater is vanishingly low ($<10^{-15}$ moles L^{-1}). More recently, laboratory[81] and field[82] 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 the iron-poor Southern Ocean[81]. In the dust dominated low latitude regions of the Atlantic Ocean the nitrogen fixing cyanobacterium *Trichodesmium* has been shown to directly access mineral particulate iron[83]. Taken together, this highlights a range of iron acquisition strategies that may be differentially linked to the commonly measured 'dissolved' iron concentration.

When detailed process studies combine measurements of ocean physics, major nutrient distributions and inputs with biological activity the intricate links between the cycling of iron and other nutrients and carbon can be illuminated. 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 plankton[59]. 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 Gyre[84]. 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.

2.3 A new synthesis of the ocean iron cycle and its wider connections

Bringing together these new insights allows an updated synthesis of how the ocean iron cycle operates and its connections with the cycles of carbon and nitrogen (Fig 2). In doing so, we are required to make a broad distinction between the dominance of dust iron at low latitudes and the greater role for sedimentary and hydrothermal iron sources at high latitudes. While iron supply at the high latitudes drives the connections to the wider oceanic 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 subducted from high latitudes and transported equatorward. Previously, close linkages between the cycling of iron and major nutrients such as phosphorus were emphasised (Fig 1). However, as discussed above, multiple unique factors for iron have now been identified, exemplified by the substantial decoupling between observations of phosphate and iron along a meridional section in the West Atlantic Ocean[85] (Fig 3).

Synthesising these new insights provides a more refined picture of the ocean iron cycle and emphasises 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. Due to longer remineralisation length scales, iron export to the ocean interior is more efficient than for major nutrients (phosphorus is emphasised in Fig 2) and decouples subsurface iron reserves from those of major nutrients[78]. 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). 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, dust deposition actually depleted

dissolved iron levels due to the enhanced particle scavenging[86]. In low latitude regions where dust supply is low and upwelling absent, the ensuing iron stress leads to low rates of nitrogen fixation[87]. 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 particles[88]. 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 ligands[69].

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 sections[38]. When models reflect the existence of multiple iron sources and unique aspects to iron's oceanic cycling, simulated glacial iron fertilisation contributes less than a quarter to decrease in the glacial carbon dioxide (despite enhancing Southern Ocean biological activity)[89]. At present, inter-model differences result in iron residence times that range widely, from a few years to a few hundred years[38]. This uncertainty regarding the representation of iron in global models is important as projections of how climate change will affect ocean productivity[90], which has implications for global carbon cycling and marine ecosystems, will be regulated by iron over large swathes of the upper ocean. Reducing uncertainty requires that we are able to dig deeper into the new oceanic survey data to extract quantitative information on the rates and controlling factors of the mechanisms governing the ocean iron cycle to inform accurate model parameterisations.

3. Linking iron to the cycles of carbon and other nutrients: new challenges and opportunities

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 future trends with confidence[38]. The expanding coverage of ocean observations via the GEOTRACES surveys[41] is essential, but alone is insufficient to constrain the key underlying processes.

3.1 Physical linkages across different 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 (e.g. iron regeneration, scavenging, ligand production) 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, interior flow pathways and transit times, which confound interpretation of iron distributions. That said, observed features in iron distributions can themselves be 'fingerprinted' using conservative tracers (either steady state or transient) of specific iron sources and cycling pathways.

Water masses leave the ocean surface via the process of subduction and are transported along lines of constant potential vorticity in the ocean interior[91]. Therefore, water masses provide a framework for the deeper examination of biogeochemical properties. For example, on the recent zonal GA03 GEOTRACES section in the North Atlantic Ocean, an Optimum Multi Parameter Analysis was undertaken whereby the hydrographic and major nutrient data was used to objectively identify nine primary watermasses[92]. Such a physical framework permits the evaluation of how water masses originating from different locations, with specific iron characteristics (e.g. low iron water from the high latitudes and high iron Mediterranean water) affect the distribution of iron throughout the basin. The vertical distributions of iron at a given location should be evaluated in its

proper physical context (i.e. in density space), to account for the physical variability that often complicates interpretations based on absolute depths[78].

Steady state and transient tracers provide an excellent opportunity to fingerprint specific iron sources and assess iron input fluxes or regeneration and scavenging rates. Volcanic helium-3 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 relationship[51]. The radium decay series, which is used to quantify exchanges at ocean boundaries, is also measured on some GEOTRACES sections[93] and may be linked to dissolved iron datasets 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, e.g. by regeneration or scavenging, during the transit of a water parcel subducted from the ocean surface (see: Box 1, Fig 4a) or away from a specific point source (e.g. 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, highlighting distinctions between the cycling of these two nutrients.

Ultimately we require a robust means to isolate the different contributors to the iron cycle within a holistic physical framework (Box 1, Figure 4a), as exists for major nutrients. This would allow the global significance of ocean physics, regeneration and scavenging to iron distributions to be jointly elucidated[69]. With this approach, the first order levels of coupling and decoupling between iron and major nutrients like phosphate may be quantified for use in parameterising the foundations of global models. Furthermore, considering iron observations within their physical context, e.g. water masses, density or potential vorticity, will facilitate the quantification of the rates of key processes. Exploiting the coherent iron-hydrography datasets from GEOTRACES and targeted process studies is needed to achieve this goal.

3.2 Which iron pools underpin variations in iron cycling?

While the new synthesis (Fig 2) expands our understanding of how iron links to wider biogeochemical cycling, the underlying processes themselves 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 particular process. Biological reactivity (or bioavailability) affects the ability of the biota to acquire iron or how bacteria remineralise iron from organic material, while chemical reactivity will modulate the dissolution of lithogenic iron and the propensity of different forms of iron to be transferred to particulate pools via scavenging or colloidal aggregation. A key contrast between iron and the major nutrients is that while specific chemical forms of nitrogen (e.g. nitrate) or phosphorus (e.g. phosphate) are measured, iron measurements rely on operational definitions. The prime focus of ocean iron observations remains on separating 'dissolved' and particulate iron, i.e. all forms of iron that pass through (or are retained by) a defined filter (normally 0.2 μm). However, somewhere between half and three quarters of dissolved iron does not pass a smaller 0.02 μm filter, which has led to a further distinction between 'soluble' and 'colloidal' dissolved iron[94].

Until relatively recently, most of the focus on the iron present in these different size fractions has been from a geochemical or chemical perspective on inorganic species - emphasising the degree of complexation between iron and ligands in soluble and colloidal pools[94] or the solubility and mineralogy of colloidal and particulate iron[95]. However, due 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 pool[96], while the virus-associated iron may be a non-negligible component of colloidal iron[97]. Additionally, intracellular iron, that is largely associated with metalloenzymes and storage proteins[98] will be 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 (e.g. hemes and iron-sulphur clusters)[99], as well as ferritin and bacteroferritin (iron storage proteins)[98]. While the magnitude of their contribution 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 in different environments. On-going work with new ultra high mass resolution mass spectrometry and 'omics based studies are delving deeper into the 'black box' of 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).

3.3. Transcending the scale window: New frontiers for the ocean iron cycle

Will we see the same step change 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 oceanic cycling, relative to major nutrients, have been identified (Figs 2 and 3). Thus 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 for major nutrients. This would enable progress to be made in the representation of iron cycling in the ocean models we rely on to test hypotheses and appraise the consequences of on-going climate change. Enormous progress has been made in our ability to observe ocean iron distributions thanks to GEOTRACES, but better understanding of the roles played by different biological, chemical and physical processes remains elusive. 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 supply[44]. Two multi-disciplinary experiments focussing on the naturally fertilised Kerguelen plateau region in different seasons were able to develop regional iron budgets[75] and make wider links to physical and biological processes, including downward biogenic carbon export and air-sea CO_2 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[72,92]. More ambitiously, key regions along sections (e.g. downstream of iron sources or across gradients of iron stress) may be targeted and controlled volume experiments performed to elucidate the governing processes. 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 needed to transform our ability to observe variability (e.g. at time-series stations). For instance, this could illuminate how natural climate variations (e.g. El Nino in the Pacific) or seasonal transitions (e.g. at high latitudes or in coastal upwellings) shape biogeochemical cycles via modifications to iron dynamics.

Figure Legends

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 from upwelling stimulates biological activity, nitrogen fixation and particulate organic matter fluxes in a constant relationship to major nutrients. In the ocean interior, iron regeneration and scavenging is controlled by fixed concentrations of iron binding organic ligands.

Figure 2. A revised representation of the major processes in the ocean iron cycle. A broad meridional contrast is emphasised 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 in the low latitudes (although this process can also be restricted by lack of iron outside of 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.

Figure 3. Dissolved phosphate (upper panel) and dissolved iron (lower panel) observations collected along the GA02 GEOTRACES meridional section in the west Atlantic[85] as a function of latitude, with contours of constant potential vorticity overlain.

Figure 4. a) A schematic representation of how 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) An illustration of the different components of particulate and dissolved iron (including the soluble and colloidal components Emphasis is on a fluid continuum of soluble, colloidal and particulate iron, as well as the role of inorganic (bottom half: nano particles and lithogenic species) and organic components (top half: encompassing biogenic and biomolecules that bind iron strongly, as well as weaker diffuse iron-binding ligands such as hemes, saccharides or fulvic acids).

Box 1: 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 constitute 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 (i.e. from sinking organic matter, P_{REG}) pools:

$$P_{TOT} = P_{PRE} + P_{REG} \quad (1)$$

P_{REG} is quantified using apparent oxygen utilisation (*AOU*) and the phosphate:oxygen ratio ($R_{P:O2}$):

$$P_{REG} = R_{P:O2} AOU \quad (2)$$

Equations 1 and 2 then quantify the varying influences of ocean circulation and biological activity on phosphorus cycling[100,101]. As the biological pump shifts phosphorus from the preformed to the regenerated pool, P_{REG}/P_{TOT} (known as *P**) quantifies the efficiency of the biological pump[100]. Observations indicate that the biological pump operates at around one-third efficiency, with a linear relationship between *P** and atmospheric CO_2 levels[100]. This theory underpins the '*iron hypothesis*'[19], whereby additional iron enhances the biological pump efficiency by shifting extra phosphate from the preformed to the regenerated pool and lowering CO_2.

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 iron deposited within the mixed layer affects Fe_{PRE}, but the smaller amount of dust that dissolves in the ocean interior (Fe_{DUST}) must be included:

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

Variability in the iron content of sinking organic matter[71] causes a variable $R_{Fe:O2}$ 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 supply[69] (Fig 2). Importantly, the regeneration and scavenging balance (i.e. 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 impacts total iron[69]. This explains why the slope of the dissolved iron to *AOU* relationship differs from phytoplankton iron contents[72]. While AOU itself may not be the ideal tracer of remineralisation rates, it offers a tractable means for its basin scale quantification.

If Equation 3 were 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[72,77] are allied to ocean tracers (Sec 3.1). For instance, linking subduction timescales determined from transient tracers 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 dissolution of dust may be traced via lithogenic tracers such as aluminium and titanium. Finally, other particle reactive elements that are not biologically active (e.g. thorium) can constrain scavenging.

Ultimately, the role of the each term in Equation 3 is affected by organic iron-binding ligands[69] that are usually in excess of iron[63]. A parallel approach for the total ligand concentration (L_{TOT}) should account for preformed surface produced ligands (L_{PRE}), interior ligand production from both organic matter degradation (L_{REG}) or specific sources (L_{SOURCE}), and ligand loss (L_{LOSS}) from bacterial decay and coagulation:

$$L_{TOT} = L_{PRE} + L_{REG} + L_{SOURCE} - L_{LOSS} \quad (4)$$

484 Equation 4 may be quantified by combining experimental studies and tracers, but an important and
485 confounding issue is the diversity of ligands present (i.e. a blend of iron binding molecules typically
486 represented as distinct 'classes' based on measured binding constants), since each may have a
487 unique provenance and impact(s) on the iron cycle[62-64].
488

References

1 Falkowski, P. & Raven, J. A. *Aquatic Photosynthesis*. 488 (Princeton University Press, 2007).

2 Ruud, J. T. Nitrates and phosphates in the Southern Seas. *Journal du Conseil* **5**, 347-360 (1930).

3 Gran, H. H. On the conditions for the production of plankton in the sea. *Conseil Perm. Internat. pour l'Explor. de la Mer. Rapp. et Proces-Verb.* **75**, 37-46 (1931).

4 Hart, T. On the phytoplankton of the south-west Atlantic and the Bellingshausen Sea, 1929-31. *Discovery Reports* **VIII**, 1-268 (1934).

5 Harvey, H. On the rate of diatom growth. *Journ. 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 diatomThalassiosira weissflogii1. *Limnology and Oceanography* **27**, 789-813, doi:10.4319/lo.1982.27.5.0789 (1982).

7 Brand, L. E., Sunda, W. G. & Guillard, R. R. L. Limitation of marine phytoplankton reproductive rates by zinc, manganese and iron. *Limnology and Oceanography* **28**, 1182-1198, doi:10.4319/lo.1983.28.6.1182 (1983).

8 Cooper, L. H. N. Iron in the Sea and in Marine Plankton. *Proceedings of the Royal Society B: Biological Sciences* **118**, 419-438, doi:10.1098/rspb.1935.0064 (1935).

9 Goldberg, E. D. Marine Geochemistry 1. Chemical Scavengers of the Sea. *The Journal of Geology* **62**, 249-265, doi:10.1086/626161 (1954).

10 Williams, R. J. P. The Bakerian Lecture, 1981 - Natural-Selection of the Chemical-Elements. *Proc R Soc Ser B-Bio* **213**, 361-397, doi:10.1098/rspb.1981.0071 (1981).

11 Raven, J. A. The iron and molybdenum use efficiencies of plant growth with different energy, carbon and nitrogen sources. *New Phytologist* **109**, 279-287, doi:10.1111/j.1469-8137.1988.tb04196.x (1988).

12 Moore, J. K., Doney, S. C., Glover, D. M. & Fung, I. Y. Iron cycling and nutrient-limitation patterns in surface waters of the World Ocean. *Deep-Sea Res Pt Ii* **49**, 463-507, doi:10.1016/S0967-0645(01)00109-6 (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. *Analytica chimica acta* **105**, 233-245, doi:10.1016/s0003-2670(01)83754-5 (1979).

14 Settle, D. & Patterson, C. Lead in albacore: guide to lead pollution in Americans. *Science* **207**, 1167-1176, doi:10.1126/science.6986654 (1980).

15 Gordon, R. M., Martin, J. H. & Knauer, G. A. Iron in Northeast Pacific Waters. *Nature* **299**, 611-612, doi:10.1038/299611a0 (1982).

16 Landing, W. M. & Bruland, K. W. The contrasting biogeochemistry of iron and manganese in the Pacific Ocean. *Geochimica et Cosmochimica Acta* **51**, 29-43, doi:10.1016/0016-7037(87)90004-4 (1987).

17 Martin, J. H., Gordon, R. M. & Fitzwater, S. E. Iron in Antarctic Waters. *Nature* **345**, 156-158, doi:10.1038/345156a0 (1990).

18 Martin, J. H., Fitzwater, S. E. & Gordon, R. M. Iron deficiency limits phytoplankton growth in Antarctic waters. *Global Biogeochemical Cycles* **4**, 5-12, doi:10.1029/GB004i001p00005 (1990).

19 Martin, J. H. Glacial-Interglacial Co2 Change: The Iron Hypothesis. *Paleoceanography* **5**, 1-13, doi:10.1029/Pa005i001p00001 (1990).

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, doi:10.1038/349772a0 (1991).

21 Cullen, J. J. Hypotheses to explain high-nutrient conditions in the open sea. *Limnology and Oceanography* **36**, 1578-1599, doi:10.4319/lo.1991.36.8.1578 (1991).

22 Martin, J. H. *et al.* Testing the Iron Hypothesis in Ecosystems of the Equatorial Pacific-Ocean. *Nature* **371**, 123-129, doi:10.1038/371123a0 (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, doi:10.1038/383495a0 (1996).

24 Boyd, P. W. *et al.* A mesoscale phytoplankton bloom in the polar Southern Ocean stimulated by iron fertilization. *Nature* **407**, 695-702, doi:10.1038/35037500 (2000).

25 Boyd, P. W. *et al.* Mesoscale iron enrichment experiments 1993-2005: Synthesis and future directions. *Science* **315**, 612-617, doi:10.1126/Science.1131669 (2007).

26 de Baar, H. J. W. *et al.* Synthesis of iron fertilization experiments: From the Iron Age in the Age of Enlightenment. *Journal of Geophysical Research* **110**, doi:10.1029/2004jc002601 (2005).

27 Moore, C. M. *et al.* Iron limits primary productivity during spring bloom development in the central North Atlantic. *Global Change Biology* **12**, 626-634, doi:10.1111/j.1365-2486.2006.01122.x (2006).

28 Hutchins, D. A., DiTullio, G. R., Zhang, Y. & Bruland, K. W. An iron limitation mosaic in the California upwelling regime. *Limnology and Oceanography* **43**, 1037-1054, doi:10.4319/lo.1998.43.6.1037 (1998).

29 Hutchins, D. A. *et al.* Phytoplankton iron limitation in the Humboldt Current and Peru Upwelling. *Limnology and Oceanography* **47**, 997-1011, doi:10.4319/lo.2002.47.4.0997 (2002).

30 Johnson, K. S., Gordon, R. M. & Coale, K. H. What controls dissolved iron concentrations in the world ocean? *Marine Chemistry* **57**, 137-161, doi:10.1016/s0304-4203(97)00043-1 (1997).

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. *Marine Chemistry* **47**, 41-54, doi:10.1016/0304-4203(94)90012-4 (1994).

32 Rue, E. L. & Bruland, K. W. Complexation of iron(III) by natural organic ligands in the Central North Pacific as determined by a new competitive ligand equilibration/adsorptive cathodic stripping voltammetric method. *Marine Chemistry* **50**, 117-138, doi:10.1016/0304-4203(95)00031-l (1995).

33 Sunda, W. G. & Huntsman, S. A. Interrelated influence of iron, light and cell size on marine phytoplankton growth. *Nature* **390**, 389-392, doi:10.1038/37093 (1997).

34 Archer, D. E. & Johnson, K. A model of the iron cycle in the ocean. *Global Biogeochemical Cycles* **14**, 269-279, doi:10.1029/1999gb900053 (2000).

35 Parekh, P., Follows, M. J. & Boyle, E. A. Decoupling of iron and phosphate in the global ocean. *Global Biogeochemical Cycles* **19**, doi:10.1029/2004gb002280 (2005).

36 Jickells, T. D. *et al.* Global iron connections between desert dust, ocean biogeochemistry, and climate. *Science* **308**, 67-71, doi:10.1126/Science.1105959 (2005).

37 de Baar, H. J. & de Jong, J. T. in *The biogeochemistry of iron in seawater* Vol. 7 (eds D. R. Turner & K. A. Hunter) 123-254 (2001).

38 Tagliabue, A. *et al.* How well do global ocean biogeochemistry models simulate dissolved iron distributions? *Global Biogeochemical Cycles*, doi:10.1002/2015gb005289 (2016).

39 Hain, M. P., Sigman, D. M. & Haug, G. H. Carbon dioxide effects of Antarctic stratification, North Atlantic Intermediate Water formation, and subantarctic nutrient drawdown during the last ice age: Diagnosis and synthesis in a geochemical box model. *Global Biogeochemical Cycles* **24**, doi:10.1029/2010gb003790 (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, doi:10.1038/35037561 (2000).

41 Mawji, E. *et al.* The GEOTRACES Intermediate Data Product 2014. *Marine Chemistry* **177**, 1-8, doi:10.1016/j.marchem.2015.04.005 (2015).

42 Anderson, R. & Henderson, G. GEOTRACES—A Global Study of the Marine Biogeochemical Cycles of Trace Elements and Their Isotopes. *Oceanography* **18**, 76-79, doi:10.5670/oceanog.2005.31 (2005).

43 Johnson, K. S. *et al.* Developing Standards for Dissolved Iron in Seawater. *Eos, Transactions American Geophysical Union* **88**, 131, doi:10.1029/2007eo110003 (2007).

44 Boyd, P. W. *et al.* FeCycle: Attempting an iron biogeochemical budget from a mesoscale SF6 tracer experiment in unperturbed low iron waters. *Global Biogeochemical Cycles* **19**, doi:10.1029/2005gb002494 (2005).

45 Blain, S. *et al.* Effect of natural iron fertilization on carbon sequestration in the Southern Ocean. *Nature* **446**, 1070-U1071, doi:10.1038/Nature05700 (2007).

46 Pollard, R. T. *et al.* Southern Ocean deep-water carbon export enhanced by natural iron fertilization. *Nature* **457**, 577-580, doi:10.1038/nature07716 (2009).
47 Elrod, V. A., Berelson, W. M., Coale, K. H. & Johnson, K. S. The flux of iron from continental shelf sediments: A missing source for global budgets. *Geophysical Research Letters* **31**, doi:10.1029/2004gl020216 (2004).
48 Lam, P. J. & Bishop, J. K. B. The continental margin is a key source of iron to the HNLC North Pacific Ocean. *Geophysical Research Letters* **35**, doi:10.1029/2008gl033294 (2008).
49 Tagliabue, A., Aumont, O. & Bopp, L. The impact of different external sources of iron on the global carbon cycle. *Geophysical Research Letters* **41**, 920-926, doi:10.1002/2013gl059059 (2014).
50 Saito, M. A. *et al.* Slow-spreading submarine ridges in the South Atlantic as a significant oceanic iron source. *Nature Geoscience* **6**, 775-779, doi:10.1038/Ngeo1893 (2013).
51 Resing, J. A. *et al.* Basin-scale transport of hydrothermal dissolved metals across the South Pacific Ocean. *Nature* **523**, 200-203, doi:10.1038/nature14577 (2015).
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 Research Part II: Topical Studies in Oceanography* **58**, 2678-2694, doi:10.1016/j.dsr2.2010.10.042 (2011).
53 Klunder, M. B. *et al.* Dissolved iron in the Arctic shelf seas and surface waters of the central Arctic Ocean: Impact of Arctic river water and ice-melt. *J Geophys Res-Oceans* **117**, doi:10.1029/2011jc007133 (2012).
54 Tagliabue, A. *et al.* Hydrothermal contribution to the oceanic dissolved iron inventory. *Nature Geoscience* **3**, 252-256, doi:10.1038/ngeo818 (2010).
55 Conway, T. M. & John, S. G. Quantification of dissolved iron sources to the North Atlantic Ocean. *Nature* **511**, 212-215, doi:10.1038/nature13482 (2014).
56 Moore, C. M. *et al.* Processes and patterns of oceanic nutrient limitation. *Nature Geoscience*, doi:10.1038/ngeo1765 (2013).
57 Falkowski, P. G. Evolution of the nitrogen cycle and its influence on the biological sequestration of CO2 in the ocean. *Nature* **387**, 272-275, doi:10.1038/387272a0 (1997).
58 Moore, C. M. *et al.* Large-scale distribution of Atlantic nitrogen fixation controlled by iron availability. *Nature Geoscience* **2**, 867-871, doi:10.1038/ngeo667 (2009).
59 Schlosser, C. *et al.* Seasonal ITCZ migration dynamically controls the location of the (sub)tropical Atlantic biogeochemical divide. *Proceedings of the National Academy of Sciences of the United States of America* **111**, 1438-1442, doi:10.1073/pnas.1318670111 (2014).
60 Dutkiewicz, S., Ward, B. A., Monteiro, F. & Follows, M. J. Interconnection of nitrogen fixers and iron in the Pacific Ocean: Theory and numerical simulations. *Global Biogeochemical Cycles* **26**, doi:10.1029/2011gb004039 (2012).
61 Weber, T. & Deutsch, C. Local versus basin-scale limitation of marine nitrogen fixation. *Proceedings of the National Academy of Sciences of the United States of America* **111**, 8741-8746, doi:10.1073/pnas.1317193111 (2014).
62 Gledhill, M. & Buck, K. N. The organic complexation of iron in the marine environment: a review. *Frontiers in microbiology* **3**, 69, doi:10.3389/fmicb.2012.00069 (2012).
63 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. *Marine Chemistry* **173**, 52-66, doi:10.1016/j.marchem.2014.12.003 (2015).
64 Buck, K. N., Sohst, B. & Sedwick, P. N. The organic complexation of dissolved iron along the U.S. GEOTRACES (GA03) North Atlantic Section. *Deep Sea Research Part II: Topical Studies in Oceanography* **116**, 152-165, doi:10.1016/j.dsr2.2014.11.016 (2015).
65 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. *Marine Chemistry* **177**, 434-446, doi:10.1016/j.marchem.2015.04.007 (2015).
66 Wozniak, A. S., Shelley, R. U., McElhenie, S. D., Landing, W. M. & Hatcher, P. G. Aerosol water soluble organic matter characteristics over the North Atlantic Ocean: Implications for iron-binding ligands and iron solubility. *Marine Chemistry* **173**, 162-172, doi:10.1016/j.marchem.2014.11.002 (2015).
67 Cheize, M. *et al.* Iron organic speciation determination in rainwater using cathodic stripping voltammetry. *Analytica chimica acta* **736**, 45-54, doi:10.1016/j.aca.2012.05.011 (2012).

68 Mawji, E. *et al.* Production of siderophore type chelates in Atlantic Ocean waters enriched with different carbon and nitrogen sources. *Marine Chemistry* **124**, 90-99, doi:10.1016/j.marchem.2010.12.005 (2011).

69 Tagliabue, A., Williams, R. G., Rogan, N., Achterberg, E. P. & Boyd, P. W. A ventilation-based framework to explain the regeneration-scavenging balance of iron in the ocean. *Geophysical Research Letters* **41**, 7227-7236, doi:10.1002/2014gl061066 (2014).

70 Völker, C. & Tagliabue, A. Modeling organic iron-binding ligands in a three-dimensional biogeochemical ocean model. *Marine Chemistry* **173**, 67-77, doi:10.1016/j.marchem.2014.11.008 (2015).

71 Twining, B. S. & Baines, S. B. The trace metal composition of marine phytoplankton. *Annual review of marine science* **5**, 191-215, doi:10.1146/annurev-marine-121211-172322 (2013).

72 Twining, B. S., Rauschenberg, S., Morton, P. L. & Vogt, S. Metal contents of phytoplankton and labile particulate material in the North Atlantic Ocean. *Progress in Oceanography* **137**, 261-283, doi:10.1016/j.pocean.2015.07.001 (2015).

73 Martiny, A. C. *et al.* Strong latitudinal patterns in the elemental ratios of marine plankton and organic matter. *Nature Geoscience* **6**, 279-283, doi:10.1038/ngeo1757 (2013).

74 Boyd, P. W. *et al.* Why are biotic iron pools uniform across high- and low-iron pelagic ecosystems? *Global Biogeochemical Cycles* **29**, 1028-1043, doi:10.1002/2014gb005014 (2015).

75 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, doi:10.5194/bg-12-4421-2015 (2015).

76 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, doi:10.1371/journal.pone.0114067 (2014).

77 Twining, B. S. *et al.* Differential remineralization of major and trace elements in sinking diatoms. *Limnol. Oceanogr* **59**, 689-704, doi:10.4319/lo.2014.59.3.0689 (2014).

78 Tagliabue, A. *et al.* Surface-water iron supplies in the Southern Ocean sustained by deep winter mixing. *Nature Geoscience* **7**, 314-320, doi:10.1038/ngeo2101 (2014).

79 Hudson, R. J. M. & Morel, F. M. M. Iron transport in marine phytoplankton: Kinetics of cellular and medium coordination reactions. *Limnology and Oceanography* **35**, 1002-1020, doi:10.4319/lo.1990.35.5.1002 (1990).

80 Morel, F. M. M., Kustka, A. B. & Shaked, Y. The role of unchelated Fe in the iron nutrition of phytoplankton. *Limnology and Oceanography* **53**, 400-404, doi:10.4319/lo.2008.53.1.0400 (2008).

81 Strzepek, R. F., Maldonado, M. T., Hunter, K. A., Frew, R. D. & Boyd, P. W. Adaptive strategies by Southern Ocean phytoplankton to lessen iron limitation: Uptake of organically complexed iron and reduced cellular iron requirements. *Limnology and Oceanography* **56**, 1983-2002, doi:10.4319/lo.2011.56.6.1983 (2011).

82 Maldonado, M. T. & Price, N. M. Utilization of iron bound to strong organic ligands by plankton communities in the subarctic Pacific Ocean. *Deep Sea Research Part II: Topical Studies in Oceanography* **46**, 2447-2473, doi:10.1016/s0967-0645(99)00071-5 (1999).

83 Rubin, M., Berman-Frank, I. & Shaked, Y. Dust- and mineral-iron utilization by the marine dinitrogen-fixer Trichodesmium. *Nature Geoscience* **4**, 529-534, doi:10.1038/ngeo1181 (2011).

84 Saito, M. A. *et al.* Multiple nutrient stresses at intersecting Pacific Ocean biomes detected by protein biomarkers. *Science* **345**, 1173-1177, doi:10.1126/science.1256450 (2014).

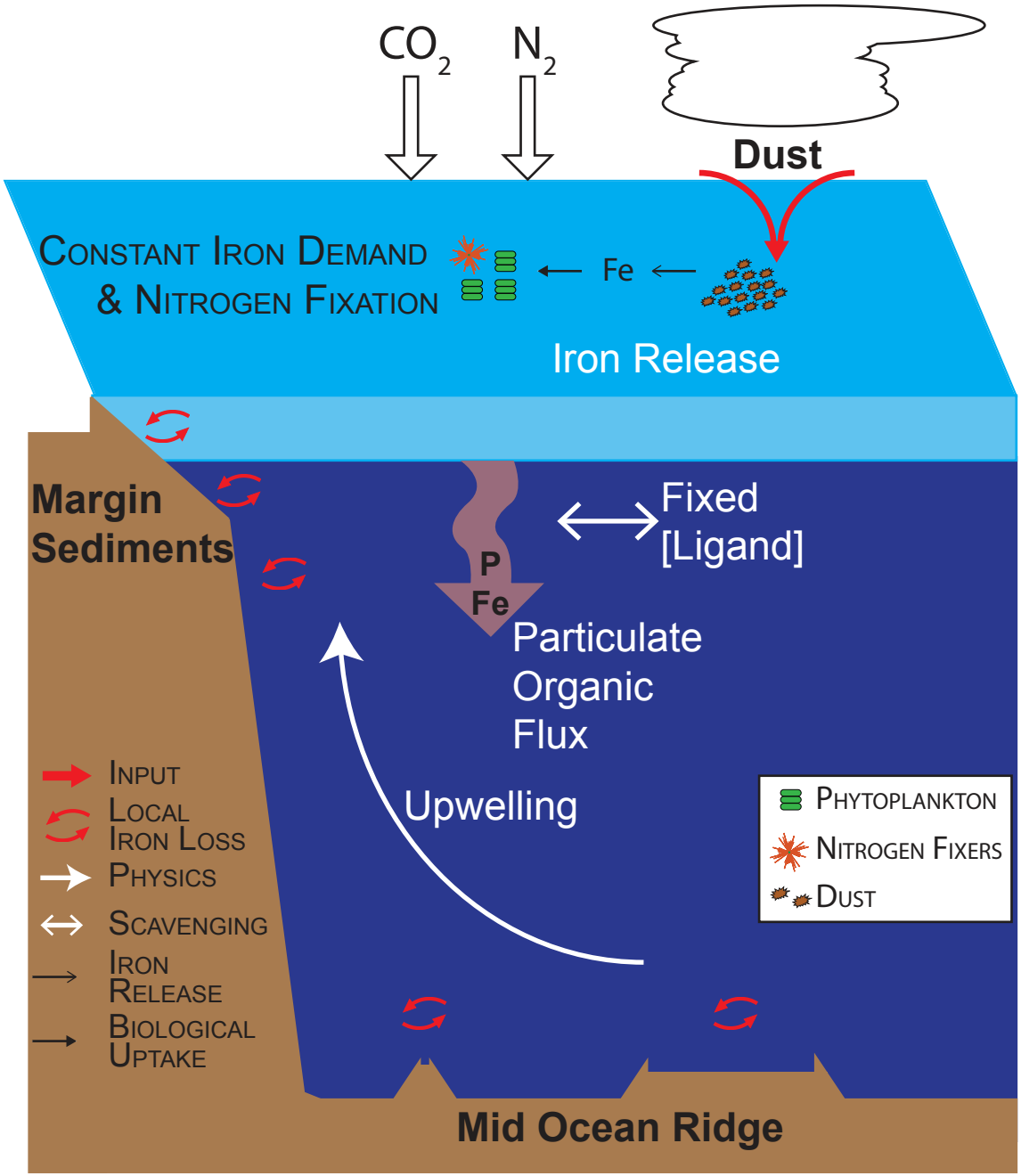
85 Rijkenberg, M. J. *et al.* The distribution of dissolved iron in the West Atlantic Ocean. *Plos One* **9**, e101323, doi:10.1371/journal.pone.0101323 (2014).

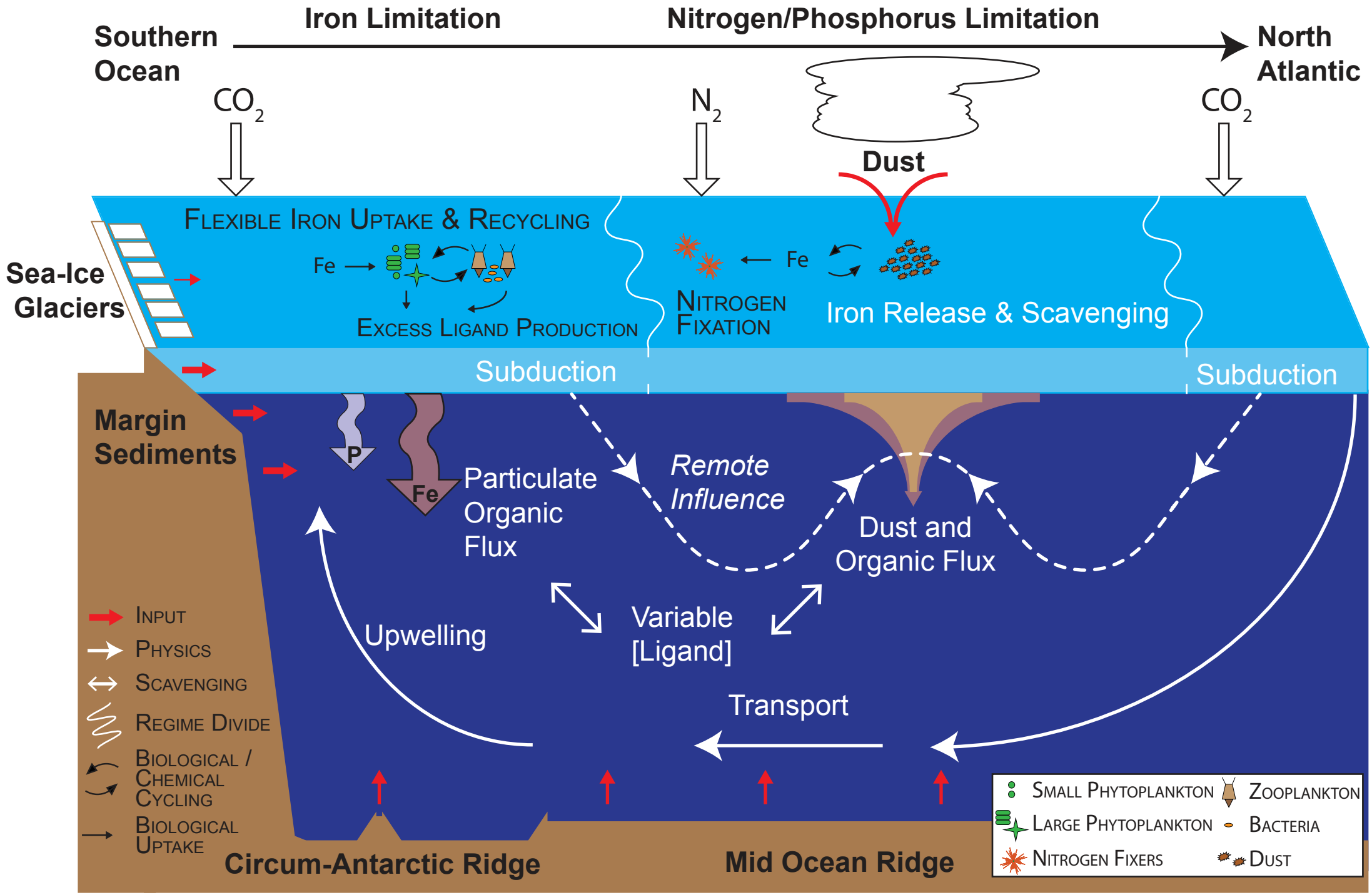
86 Wagener, T., Guieu, C. & Leblond, N. Effects of dust deposition on iron cycle in the surface Mediterranean Sea: results from a mesocosm seeding experiment. *Biogeosciences* **7**, 3769-3781, doi:Doi 10.5194/Bg-7-3769-2010 (2010).

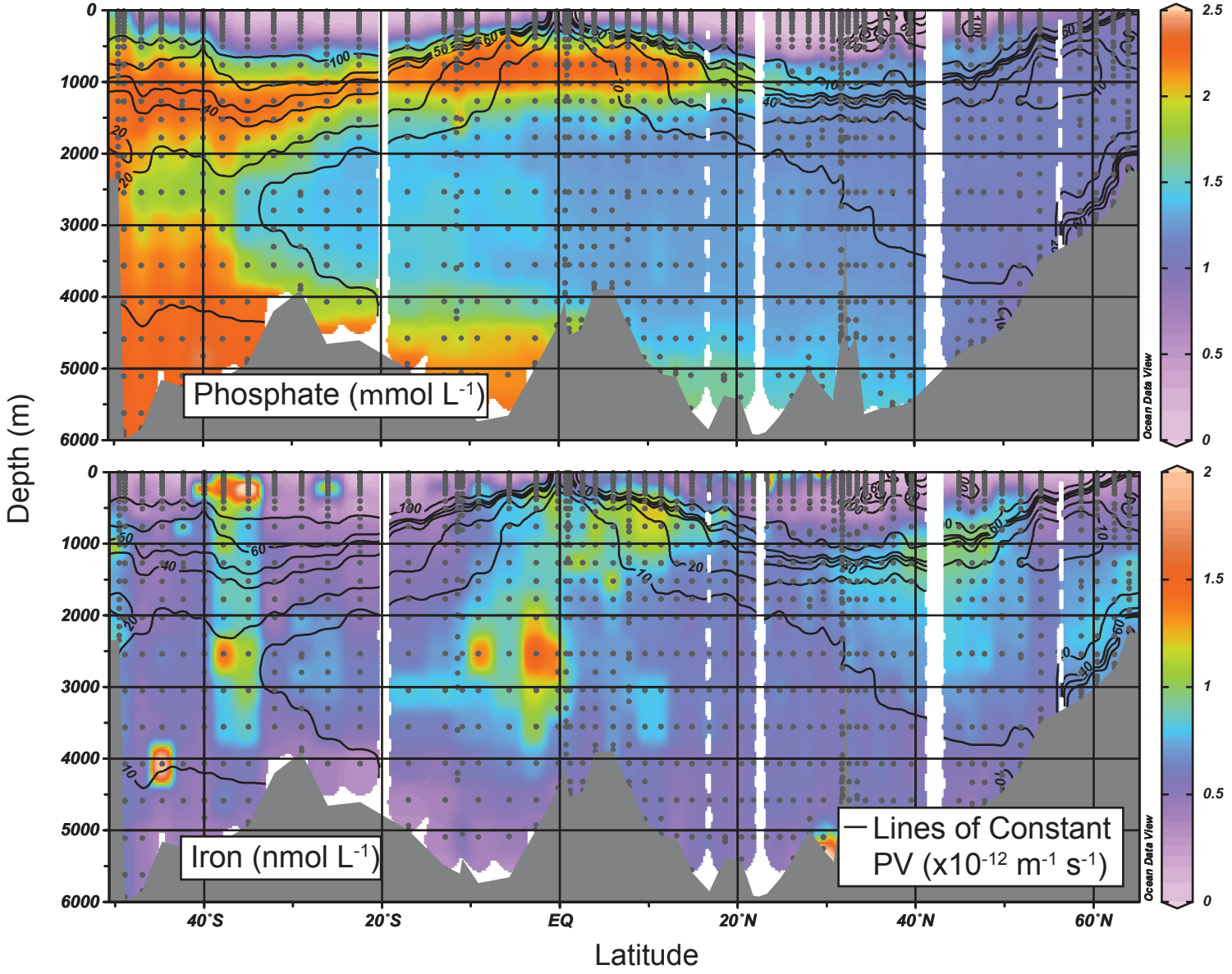
87 Sohm, J. A. *et al.* Nitrogen fixation in the South Atlantic Gyre and the Benguela Upwelling System. *Geophysical Research Letters* **38**, doi:10.1029/2011gl048315 (2011).

88 Boyd, P. W. & Ellwood, M. J. The biogeochemical cycle of iron in the ocean. *Nature Geoscience* **3**, 675-682, doi:10.1038/ngeo964 (2010).

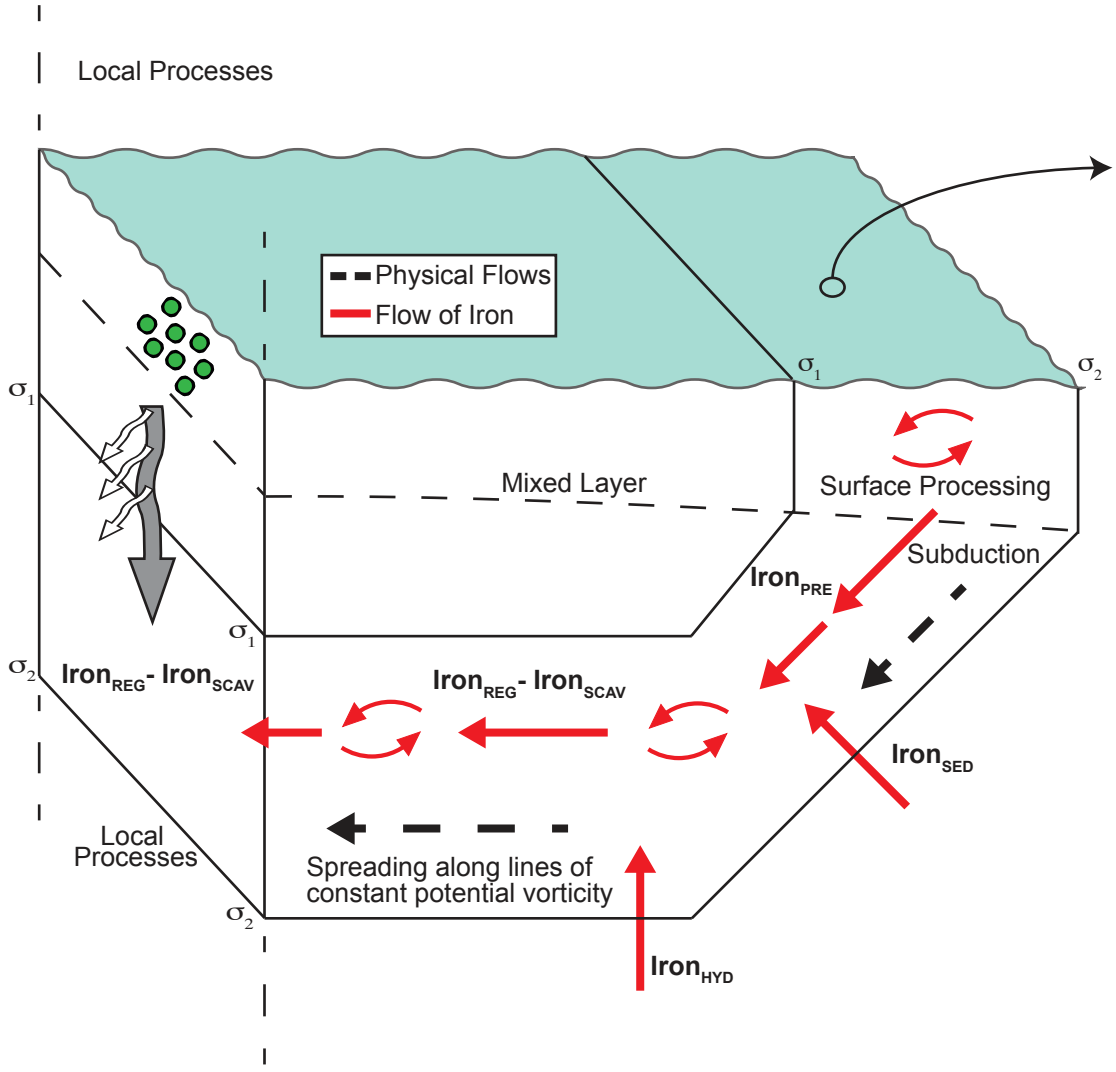
89 Lambert, F. *et al.* Dust fluxes and iron fertilization in Holocene and Last Glacial Maximum climates. *Geophysical Research Letters* **42**, 6014-6023, doi:10.1002/2015gl064250 (2015).
90 Bopp, L. *et al.* Multiple stressors of ocean ecosystems in the 21st century: projections with CMIP5 models. *Biogeosciences* **10**, 6225-6245, doi:10.5194/bg-10-6225-2013 (2013).
91 Keffer, T. The Ventilation of the World's Oceans: Maps of the Potential vorticity Field. *Journal of Physical Oceanography* **15**, 509-523, doi:10.1175/1520-0485(1985)015<0509:tvotwo>2.0.co;2 (1985).
92 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 Research Part II: Topical Studies in Oceanography* **116**, 6-20, doi:10.1016/j.dsr2.2014.11.018 (2015).
93 Charette, M. A., Morris, P. J., Henderson, P. B. & Moore, W. S. Radium isotope distributions during the US GEOTRACES North Atlantic cruises. *Marine Chemistry* **177**, 184-195, doi:10.1016/j.marchem.2015.01.001 (2015).
94 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, doi:10.1126/science.1059251 (2001).
95 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, doi:10.1126/science.1227504 (2012).
96 Tortell, P. D., Maldonado, M. T. & Price, N. M. The role of heterotrophic bacteria in iron-limited ocean ecosystems. *Nature* **383**, 330-332, doi:Doi 10.1038/383330a0 (1996).
97 Bonnain, C., Breitbart, M. & Buck, K. N. The Ferrojan Horse Hypothesis: Iron-Virus Interactions in the Ocean. *Frontiers in Marine Science* **3**, doi:10.3389/fmars.2016.00082 (2016).
98 Mackey, K. R. *et al.* Divergent responses of Atlantic coastal and oceanic Synechococcus to iron limitation. *Proceedings of the National Academy of Sciences of the United States of America* **112**, 9944-9949, doi:10.1073/pnas.1509448112 (2015).
99 Hogle, S. L., Barbeau, K. A. & Gledhill, M. Heme in the marine environment: from cells to the iron cycle. *Metallomics* **6**, 1107-1120, doi:10.1039/c4mt00031e (2014).
100 Ito, T. & Follows, M. J. Preformed phosphate, soft tissue pump and atmospheric CO2. *Journal of Marine Research* **63**, 813-839, doi:10.1357/0022240054663231 (2005).
101 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. *Journal of Geophysical Research* **90**, 6925, doi:10.1029/JC090iC04p06925 (1985).


CO_2
N_2
Dust
Constant Iron Demand
& Nitrogen Fixation
Fe
Iron Release
Margin
Sediments
Fixed
[Ligand]
P
Fe
Particulate
Organic
Flux
Upwelling
Input
Local
Iron Loss
Physics
Scavenging
Iron
Release
Biological
Uptake
Phytoplankton
Nitrogen Fixers
Dust
Mid Ocean Ridge


Southern Ocean
Iron Limitation
Nitrogen/Phosphorus Limitation
North Atlantic
CO_2
N_2
Dust
CO_2
Flexible Iron Uptake & Recycling
Fe
Excess Ligand Production
Sea-Ice
Glaciers
Nitrogen Fixation
Fe
Iron Release & Scavenging
Subduction
Subduction
Margin Sediments
P
Fe
Particulate Organic Flux
Remote Influence
Dust and Organic Flux
Upwelling
Variable [Ligand]
Transport
Input
Physics
Scavenging
Regime Divide
Biological / Chemical Cycling
Biological Uptake
Circum-Antarctic Ridge
Mid Ocean Ridge
Small Phytoplankton
Zooplankton
Large Phytoplankton
Bacteria
Nitrogen Fixers
Dust


Depth (m)
0
1000
2000
3000
4000
5000
6000
Phosphate (mmol L-1)
Iron (nmol L-1)
Lines of Constant PV (x10-12 m-1 s-1)
Ocean Data View
2.5
2
1.5
1
0.5
0
40˚S
20˚S
EQ
20˚N
40˚N
60˚N
Latitude

a) Physical Linkages in the Iron Cycle



b) What makes up the different iron pools?