

GEOTRACES and OCB partner to synthesize knowledge of ocean trace elements

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GEOTRACES is an international study of the global marine biogeochemical cycles of trace elements and their isotopes (TEIs). Its mission is “To identify processes and quantify fluxes that control the distributions of key trace elements and isotopes in the ocean, and to establish the sensitivity of these distributions to changing environmental conditions.” While the mission emphasizes the biogeochemical cycles of TEIs, GEOTRACES was designed with the expectation that the results would impact other oceanographic disciplines. For example, the vital role of trace element micronutrients in regulating the growth of marine organisms, which may influence the structure and composition of marine ecosystems, is now well established. Marine organisms, in turn, influence the biogeochemical cycles of trace elements, much as they impact the biological CO₂ pump and therefore climate.

Benefits of an improved knowledge of the marine biogeochemistry of TEIs extend well beyond marine ecology and biogeochemistry. GEOTRACES findings also contribute to our understanding of the transport

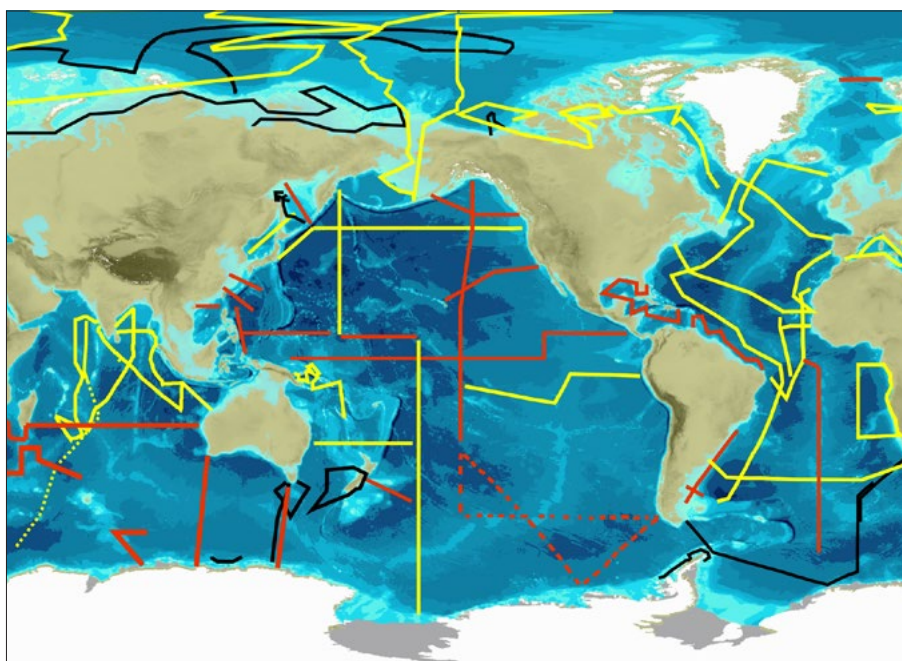


Figure 1. Evolving map of the GEOTRACES global survey. Black lines represent preliminary GEOTRACES sampling on cruises of the International Polar Year; yellow represents completed sections, and red indicates desired sections that have yet to be completed. This map is updated periodically and available for download on the [GEOTRACES home page](#).

and fate of anthropogenic contaminants in the ocean. For example, data from GEOTRACES cruises provide an unprecedented view of the distributions of anthropogenic lead and mercury in the ocean, while documenting the decline in lead concentrations following the phase-out of its use in motor fuels. Furthermore, GEOTRACES is expanding our knowledge of the biogeochemistry of TEIs in marine substrates such as sediments, corals and microfossils, the interpretation of which is so critical to our understanding of past variability in the ocean environment, including the ocean’s role in climate change.

Initiated in 2009, GEOTRACES has now completed about half of its planned global survey (Figure 1). As of mid-2016, 84 cruises on ships of 15 nations have contributed to the collection of GEOTRACES data, including process studies as well as the sections shown in Figure 1. A global survey at this scale exceeds the capabilities and resources of any one nation. Coordinated international collaboration is the only strategy that can provide global coverage of TEI data using sampling and analytical methods that are rigorously intercalibrated, giving confidence that observed spatial and temporal patterns are real and not an artifact of analytical bias.

Coordinated collaboration also enables systematic measurements of a suite of key TEIs consisting of micronutrients, contaminants and tracers of the processes that influence their distributions, together with nutrients and hydrographic parameters that allow their distributions to be interpreted in an oceanographic context. Underlying this approach is the philosophical principle that studying multiple TEIs simultaneously provides information that is inaccessible by examining a single element in isolation. Each element can be understood as a special case in a continuum of geochemical properties, where the similarities and contrasts among the elements offer insights into each individual element. In many cases, the better constrained, or more simply defined, behavior of one element illuminates the behavior of another.

Investigators familiar with the global ocean survey by the WOCE and CLIVAR programs, characterized by a semi-regular grid of meridional and zonal sections, will immediately recognize that GEOTRACES is guided by a different set of principles. Cruise tracks of the GEOTRACES survey are designed, in part, to sample regions thought to represent end-member conditions with respect to supply and removal of TEIs, as well as regions of anticipated intense gradients of TEI concentrations. Thus, with a limited number of cruises, the GEOTRACES field program aims to gather information about TEI distributions across a broad spectrum of environmental conditions that regulate their ocean biogeochemistry.

Prior to reaching the halfway point of the global survey, the GEOTRACES Scientific Steering Committee (SSC) sought to engage the broader oceanographic community to exploit the new results delivered by the program. As a first step, GEOTRACES is preparing organized sets of quality-controlled data. The first data product, released in 2014 (IDP2014), consists of two parts: 1) a [digital compilation of TEIs and classical hydrographic parameters](#), and 2) the *eGEOTRACES Electronic Atlas* providing section plots and animated 3D visualizations of the data. GEOTRACES anticipates the release of a second intermediate data product in 2017, and feedback on IDP2014 will be used to improve the next product.

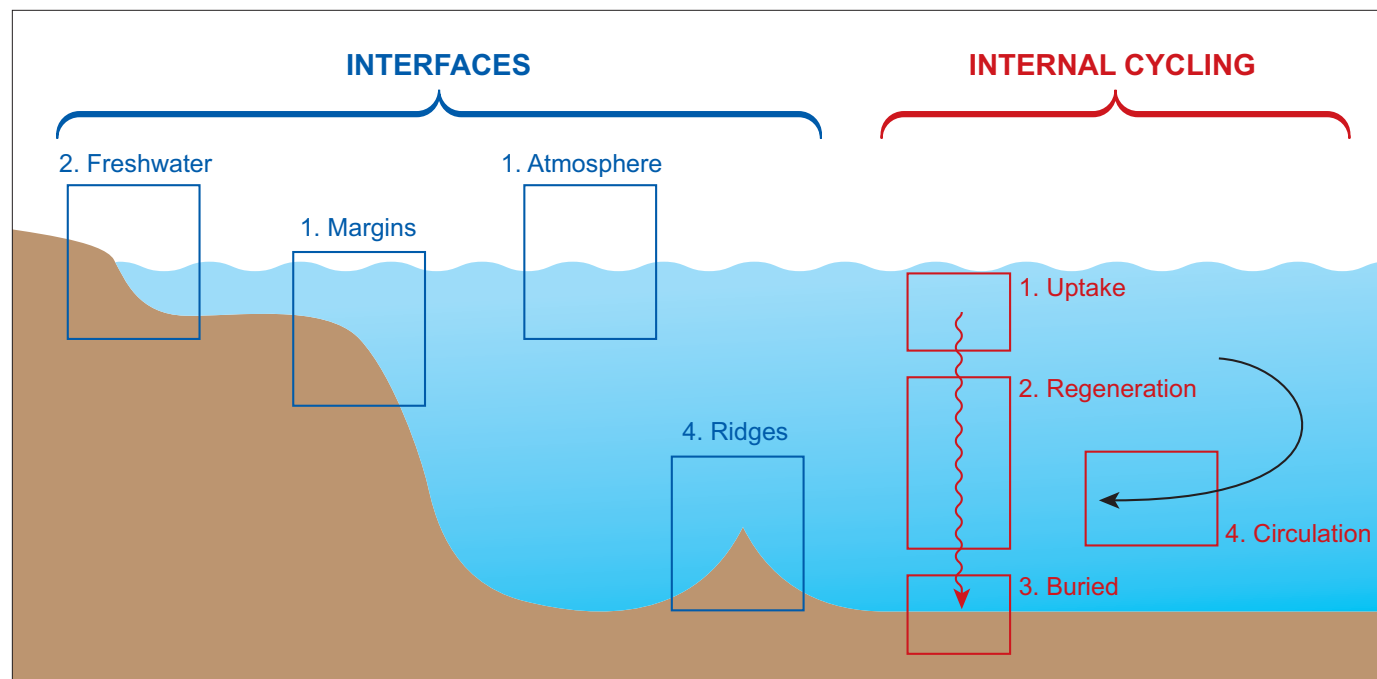


Figure 2. A schematic diagram illustrating the major processes that influence the distribution of trace elements and their isotopes in the ocean. Fluxes across four major ocean interfaces (blue) and four major internal cycling processes (red) are responsible for ocean TEI distributions. Figure reproduced from the GEOTRACES Science Plan.

The second step to engage the broader community is a three-pronged initiative to synthesize GEOTRACES findings, interpreting and modeling multiple data sets at a level beyond that normally achieved by a single-investigator project. This, too, will involve investigators from other fields of ocean research. Synthesis will ramp up while the remainder of the field program is completed.

Distributions of TEIs in the ocean are influenced by supply and removal at ocean boundaries, by internal cycling that involves a variety of chemical and biological processes, and by transport involving advection and mixing (Figure 2). Boundary fluxes, including atmospheric deposition, rivers, exchange with margin sediments, hydrothermal fluxes, and burial in sediments are to some extent independent from internal cycling. Frequently, these processes are investigated by separate populations of the oceanographic community, although there is some overlap among them. The same can be said of the community that exploits TEIs as proxies in paleoceanographic research. Consequently, GEOTRACES elected to approach synthesis of TEI results via three linked but quasi-independent efforts focusing on the themes of boundary fluxes, internal cycling and TEIs used as proxies in paleoceanography.

Synthesis of findings pertaining to the supply and removal of TEIs at ocean boundaries began with two events hosted by the Royal Society of London: A two-day open meeting on “Biological and climatic impact of ocean trace element chemistry” (7-8 December 2015, London, UK) and a two-day workshop on “Quantifying fluxes and processes in trace metal cycling at ocean boundaries” (9-10 December 2015, Chicheley Hall, Buckinghamshire, UK). A special volume of publications from these events will appear in the *Philosophical Transactions of the Royal Society Part A*.

Many of the TEIs that are measured on GEOTRACES sections are used as proxies in paleoceanography, as well as providing information about biogeochemical cycles in the modern ocean. Synthesis of new findings concerning these TEIs will improve our understanding of the relationships between the proxies and the oceanographic conditions that regulate TEI distributions in the modern ocean and thus their imprint on marine sediments. These relationships are the basis for interpreting the geological record, and yet they are often poorly constrained due to the sparse data available for historical proxy calibration. The inaugural event in this synthesis activity will be a special session on “Trace elements and their isotopes as geochemical proxies of past ocean conditions” to be held at the next PAGES (Past Global Changes) Open Science Meeting, 9 – 13 May 2017 in Zaragoza Spain.

The component of synthesis focused on the internal cycling of TEIs within the ocean may be of greatest interest to the [Ocean Carbon and Biogeochemistry \(OCB\)](#) community. This aspect of synthesis incorporates the influence of micronutrient limitation on the growth and metabolism of marine organisms, which has implications for the efficiency of the biological pump. Major facets of internal cycling include the bioavailability and biological uptake of micronutrients (Chappell, this issue) as well as the depth scale and elemental stoichiometry of the regeneration of biogenic debris (Twining, this issue). Scavenging, or abiotic sorption to sinking particle surfaces, affects micronutrients and other trace elements alike. Each of these processes is sensitive to an element's speciation, both in dissolved form (Buck, this issue) and in particulate phases (Lam, this issue). The near-term challenge for the marine biogeochemistry community is to characterize these processes and variables with sufficient accuracy to be incorporated into models that properly reproduce the present-day supply, removal and distribution of TEIs in the ocean (Tagliabue, this issue).

The global database of internally consistent results now being generated by GEOTRACES makes it possible for the first time to assemble these components of TEI biogeochemistry. The ultimate goal is to describe these processes quantitatively, and with sufficient accuracy and precision, to predict the response of the ocean's chemical geography to perturbations such as global warming and its affiliated consequences. With the aid of the best ocean models, this knowledge will also inform investigators interpreting ocean conditions in the past using TEI clues extracted from sediments and other archives.

Much must be done, however, before these next-generation models can be constructed. Bioavailability of micronutrients depends on the organisms of interest, as well as the physical form and chemical speciation of the element. Rates and rate constants for uptake, regeneration and sedimentation must be tested using multiple tracer systems. Investigators must discriminate between local processes operating in a one-dimensional sense and pre-formed signals carried to a study site by ocean mixing and advection. As noted above, the distribution of each chemical tracer supplies unique information about processes common to many TEIs, and our interpretation must be consistent across the full spectrum of tracer information available.

This kind of integrative synthesis, challenging our interpretations to withstand repeated testing by multiple

independent chemical and biological probes, is essential to produce models with genuine predictive capabilities. Just as GEOTRACES accelerated research on ocean distributions of TEIs through an internationally coordinated sampling program, so too can the interpretation of the results be advanced through collaboration that involves multiple tracers, multiple models, and expertise from multiple disciplines.

Much of this required expertise abounds in the OCB community. Recognizing that the chemical-biological coupling of micronutrients and other species is an interest shared by OCB and GEOTRACES, the steering committees of both programs decided to partner in hosting a [synthesis workshop on “Biogeochemical cycling of trace elements within the ocean”](#) taking place 1 – 4 August 2016 at the Lamont-Doherty Earth Observatory. Representatives from both programs made up the planning committee for the workshop, which is being supported financially in equal measures by GEOTRACES and OCB.

Workshop participants were selected by the planning committee to include expertise in the following areas:

- TEI observations (micronutrients and tracers)
- Molecular biology (omics)
- Elemental stoichiometry of uptake and regeneration
- Detection, characterization and dynamics of particles
- Particle scavenging of TEIs
- Physical transport (advection and mixing)
- Modeling on scales from cellular to global
- The role of physical form and chemical speciation in regulating the biological availability, particle scavenging and regeneration of TEIs

Three science themes that integrate these areas of expertise will be emphasized during plenary talks, with working groups to be organized around each topic:

1. Biological uptake and TEI bioavailability, focused on identifying ‘bioavailable’ pools and biological demand (especially with respect to keystone species) and their influence on biological uptake

- Biological uptake and stoichiometry of trace elements in biota
- The role of biology in modifying particle and TEI flux in the twilight zone
- Metal-ligand interactions
- Spatial gradients in TEI uptake and bioavailability, and the factors that control them

2. Export, recycling and remineralization, as mediated by zooplankton and bacteria, considering both photic and aphotic zone processes

- Stoichiometry and remineralization of sinking particulates
- Quantifying sinking TEI fluxes in the global 3D ocean
- Quantifying the role of sinking carbon flux as a vector for TEI transport
- Drivers of spatial differences in export and remineralization of TEIs
- Oxygen Minimum Zone (OMZ) conditions that impact TEI biogeochemistry

3. Abiotic cycling and scavenging, including particulate and dissolved speciation, emphasizing the drivers of chemical speciation, dominant ‘scavengers’, and questions concerning role of desorption (basically, do all TEIs ‘scavenge’ in the same way?)

- Abiotic scavenging of trace elements (including aggregation/disaggregation)
- Particulate-dissolved exchange in the ocean interior
- Nepheloid layer processes, and impacts on interior ocean TEIs

Workshop participants will be tasked with the following products:

- Define strategies that exploit multiple data sets to identify the primary internal cycling processes that regulate TEI distribution and speciation.
- Define strategies that incorporate radiotracers, models, and novel approaches to quantify rates of the processes that regulate TEI distribution.
- Identify objectives pertaining to the internal cycling of TEIs that can be met with existing data and models, and lay out a framework to achieve objectives where existing data and models are insufficient.
- Identify critical processes that are currently not included in models, and the steps needed to incorporate them.
- Identify synthesis papers that can be completed within 12 months and teams to write them, including people not attending the workshop.
- Define criteria for future studies (including time series and process studies) and modifications to remaining GEOTRACES sections that will provide additional essential information about the internal cycling of TEIs.
- Identify new research questions, hypotheses and goals to guide ongoing GEOTRACES research and future programs.
- Document anticipated benefits to other ocean research communities by completing these objectives.

The last two tasks specifically reflect the anticipated benefits of these synthesis activities to broader ocean research goals. For example, the synthesis products will help inform emerging OCB-related programs (e.g., [EXPORTS](#) and collaborative international research on the [Coupled North Atlantic-Arctic System](#)), as well as other initiatives that can be anticipated, such as monitoring programs to assess the

environmental impacts of seabed mining. More generally, the synthesis will develop and refine hypotheses for future process studies focusing on chemical-biological-physical coupling in the ocean.

Plenary sessions during the workshop can be viewed through live streaming (instructions to follow) and will also be recorded for later viewing (instructions to follow).

Biogeochemical cycling of organic iron-binding ligands: Insights from GEOTRACES data in the Atlantic Ocean

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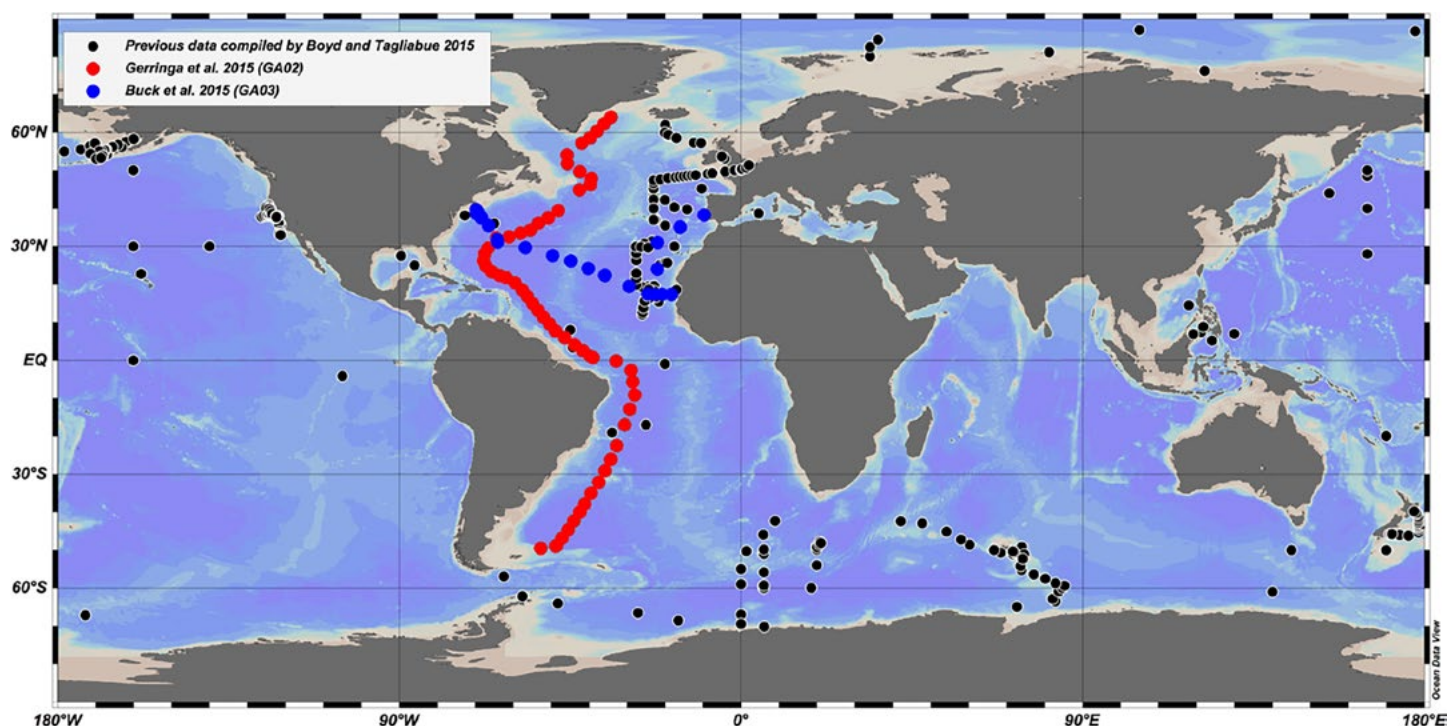


Figure 1. Sampling locations of organic iron-binding ligand measurements to date (10, 11, 66).

Iron is a limiting nutrient for phytoplankton in nearly half of the global surface ocean, and much attention has been paid to the biogeochemical cycling of iron in seawater since suitable trace metal-clean sampling and analysis procedures were developed (1). The organic complexation of dissolved iron, in particular, has emerged as an inherent feature of iron chemistry in the oceans (2-5), and iron speciation measurements are increasingly incorporated into field studies (Fig. 1). The integration of organic iron-binding ligands into biogeochemical models improves their ability to reproduce global dissolved iron distributions (6), and changes in ligand concentrations in the Southern Ocean can have a more pronounced impact on atmospheric CO_2 in model studies than changes in iron supply terms from hydrothermal and dust sources (7). Indeed, field distribution measurements, targeted experimental studies and modeling efforts over the last twenty years have left little doubt that organic ligands are a critical factor in the global biogeochemical cycling of iron. Here we highlight some of the features of iron-binding ligand distributions in

the Atlantic from the unprecedented basin-scale datasets coming out of the GEOTRACES program and attempt to elucidate some of the sources and sinks of iron-binding organic ligands in the oceans.

Dissolved iron speciation

The speciation of dissolved iron (Fe), which describes the chemical forms or species of iron in a filtered (typically $<0.2 \mu\text{m}$) sample, includes both inorganic (Fe^{3+}) and organic (FeL) components. In the oceans, iron speciation studies consistently report that nearly all dissolved iron ($>99.9\%$) is organically complexed (8). This is perhaps not surprising given that the inorganic speciation of iron in oxygenated seawater is dominated by hydrolysis reactions leading to iron precipitation and very low inorganic iron solubility ($\sim 0.1 \text{ nmol L}^{-1}$) under most ocean conditions (9).

Studies of organic iron speciation in seawater use an electrochemical technique, competitive ligand exchange-adsorptive cathodic stripping voltammetry (CLE-ACSV), to determine the concentrations and condi-

tional stability constants of iron-binding organic ligands. This is accomplished by titrating iron-binding ligands in a sample with additions of iron and competing against any natural iron-ligand complexes with an added well-characterized 'competitive' ligand, which forms an electroactive complex with iron that can be measured at the surface of a hanging mercury drop electrode. Titrations often depict no measurable iron bound to the competitive ligand for the first few iron additions, reflecting the presence of excess strong iron-binding ligands in most seawater samples (8). These ligands are described as ligand classes, L_1 , L_2 , L_3 , L_4 , defined by the conditional stability constants determined by CLE-ACSV, with L_1 and L_2 -type ligands the strongest iron-binding organic ligands ($\log K_{FeL_1,Fe'}^{cond} > 12$, $\log K_{FeL_2,Fe'}^{cond} = 11-12$), L_3 and L_4 the weakest ($\log K_{FeL_3,Fe'}^{cond} = 10-11$, $\log K_{FeL_4,Fe'}^{cond} < 10$; (8)).

Iron speciation in the Atlantic: Observations from recent GEOTRACES efforts

The iron speciation datasets emerging from the GEOTRACES program allow a first look at basin-scale distributions of iron-binding ligands in the oceans. Iron speciation datasets from GEOTRACES Sections GA02 (10) and GA03 (11) from the Dutch and U.S. GEOTRACES programs, respectively, document the ubiquitous nature of iron-binding ligands in the Atlantic basin. In

particular, both datasets evince the presence of strong, L_1 -type ligands throughout the water column and no discernible trend with depth in the conditional stability constants for these ligands (10, 11). These observations support the emerging picture from many other field studies of a strong iron-binding ligand pool that is not necessarily restricted to the surface ocean or euphotic zone (Fig. 2) (8).

Elevated dissolved iron and aluminum concentrations in surface waters across the GA03 zonal section, particularly near the center of the basin, demonstrate the widespread contribution of dust deposition to the iron inventory in the Atlantic (12). Iron isotope studies indicate that 71-87% of the dissolved iron along the entire GEOTRACES GA03 section was attributable to dust (13). Water-soluble organic matter characterized from the surfaces of aerosols collected on GA03 exhibited structural differences between aerosol sources that were consistent with their iron solubilities (14), and organic complexation of some of the leached iron was observed in seawater leaches of these aerosols (15). Recent studies using model ligands highlight the particular importance of stronger iron-binding ligands in the stabilization of iron leached from natural aerosols (16).

In the Atlantic GEOTRACES sections, the highest concentrations of ligands in excess of dissolved iron ($[L] - [Fe]$, or L') were often measured at the surface, where

dissolved iron concentrations were low (10, 11). The overall complexation capacity for iron, which is a function of both ligand concentration and the conditional stability constant, also tended to be high in the upper water column. Antarctic Intermediate Water (AAIW) stands out in both datasets as exhibiting higher complexation capacity for dissolved iron than the surrounding water masses (10, 11). These waters originate from highly productive surface waters, and elevated ligand concentrations subducted with these water masses may be the result of higher strong iron-binding ligand concentrations commonly observed in and around chlorophyll maxima and in incubation experiments of iron-stressed diatom communities (see (8) and references therein). In a compilation of three iron speciation

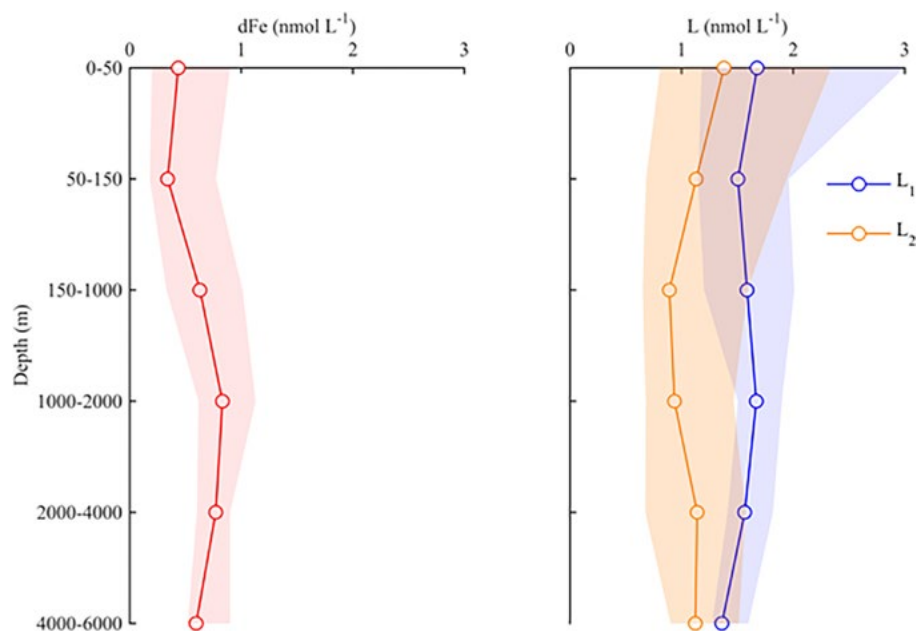


Figure 2. Median profiles of dissolved iron (left) and L_1 and L_2 ligands (right) from all sampling locations shown in Figure 1 binned by depth. The shaded regions represent the lower (25%) and upper (75%) quartile in each dataset. Four samples were excluded from the 2000-4000 depth bin due to very high dissolved iron and ligand concentrations associated with the heart of the TAG hydrothermal plume (11).

datasets that extend from the Arctic (17) down through the Western Atlantic (10) and into the Antarctic (18), higher ligand concentrations were reported at high latitudes relative to low latitudes, with the strongest (highest conditional stability constants) excess ligands measured in the Antarctic (10), and larger excesses of weaker ligands in the Arctic (10, 17).

Excess ligand concentrations in the Atlantic usually decreased with depth as dissolved iron concentrations increased, consistent with saturation of excess ligands with iron (10, 11). A north-south trend of decreasing ligands and excess ligands was reported in the GA02 Western Atlantic meridional section, which was clearly depicted in the samples collected from the North Atlantic Deep Water (NADW) along the section (10). In the GA03 zonal section of the North Atlantic (11), excess ligand concentrations in the water column were on the high end of the two datasets, consistent with the northern end of the GA02 meridional section (10). If anything, organic matter remineralization appeared to be a source of weaker L_3 -type iron-binding ligands in the GA03 zonal section dataset (11).

Excess ligand concentrations in the North Atlantic exhibited local minima in the heart of the oxygen minimum zone west of Mauritania (11), possibly due to scavenging of ligand complexes on sinking particles (19), or elevated reduced iron(II) concentrations complexing the excess ligands (20). It is unclear how much of the iron-binding ligand pool measured by CLE-ACSV may also bind iron(II), or what chemical form of iron(II) is present in these samples, though some may be biogenic (21). One of the most pronounced features in the iron(II) data from GA03 is the exceedingly high iron(II) concentrations in the TAG hydrothermal plume samples, where elevated dissolved iron was ~80% colloidal-sized (0.02–0.2 μm size fraction) iron(II) species (20, 22). These iron(II) colloids are likely pyrite nanoparticles (23), which themselves may be stabilized by organic matter (24).

In the TAG plume samples collected along GA03, excess ligands were at a minimum in the highest iron samples of the plume, but the conditional stability constants of the excess ligands that were detected in these samples were among the highest in the dataset, leading to an elevated complexation capacity for iron around the vent. It is likely that some of the elevated dissolved iron in these samples was not exchangeable with the added competitive ligand during the voltammetry measurements, which would lead to an overestimation of ligand parameters (8). It is also possible that some of this observed increase in complexation capacity in the plume reflects a microbial response

to the iron-enriched plume (25). Several studies have now reported varying degrees of organic complexation of iron in hydrothermal vent plumes (10, 11, 26, 27), and while the cycling of ligands in these systems remains unclear, organic stabilization must be a key factor in determining the chemical speciation and transport of iron from these vents into the deep sea (28–30).

The increasingly rich database of iron-binding ligand distributions from individual field studies and the GEOTRACES program show the widespread organic complexation of iron in the oceans. These datasets also display the inherent complexity of ligand cycling, since ligands are at the interface between the dynamic biogeochemical cycles of both trace metals and organic matter in seawater.

Identity of iron-binding ligands

Electrochemistry (CLE-ACSV) measures ligand concentrations and conditional stability constants from a combination of titration and competition, and is the basis of most of our insights to date into the sources, sinks, and cycling of organic iron-binding ligands in the oceans. Mass spectrometry-based techniques, on the other hand, are increasingly being employed to identify the chemical structures of natural iron-ligand complexes in the oceans. Results from both of these approaches appear to be converging on similar descriptions of the iron-binding ligand pool, one which comprises a mixture of defined biomolecules with high affinities for iron (e.g., siderophores, heme) and weaker iron-binding, ill-defined compounds with high chemical heterogeneity (e.g., humic substances, polysaccharides) (Fig. 3; (8)).

Siderophores are small iron-binding ligands widely produced by bacteria to acquire iron from the environment

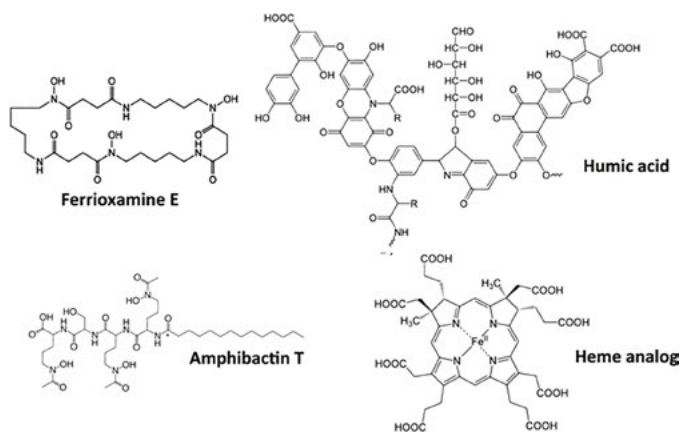


Figure 3. Examples of organic-iron binding ligand identities in seawater (37, 39, 43). The heme analog is siroheme, a relatively soluble iron-containing heme complex (39).

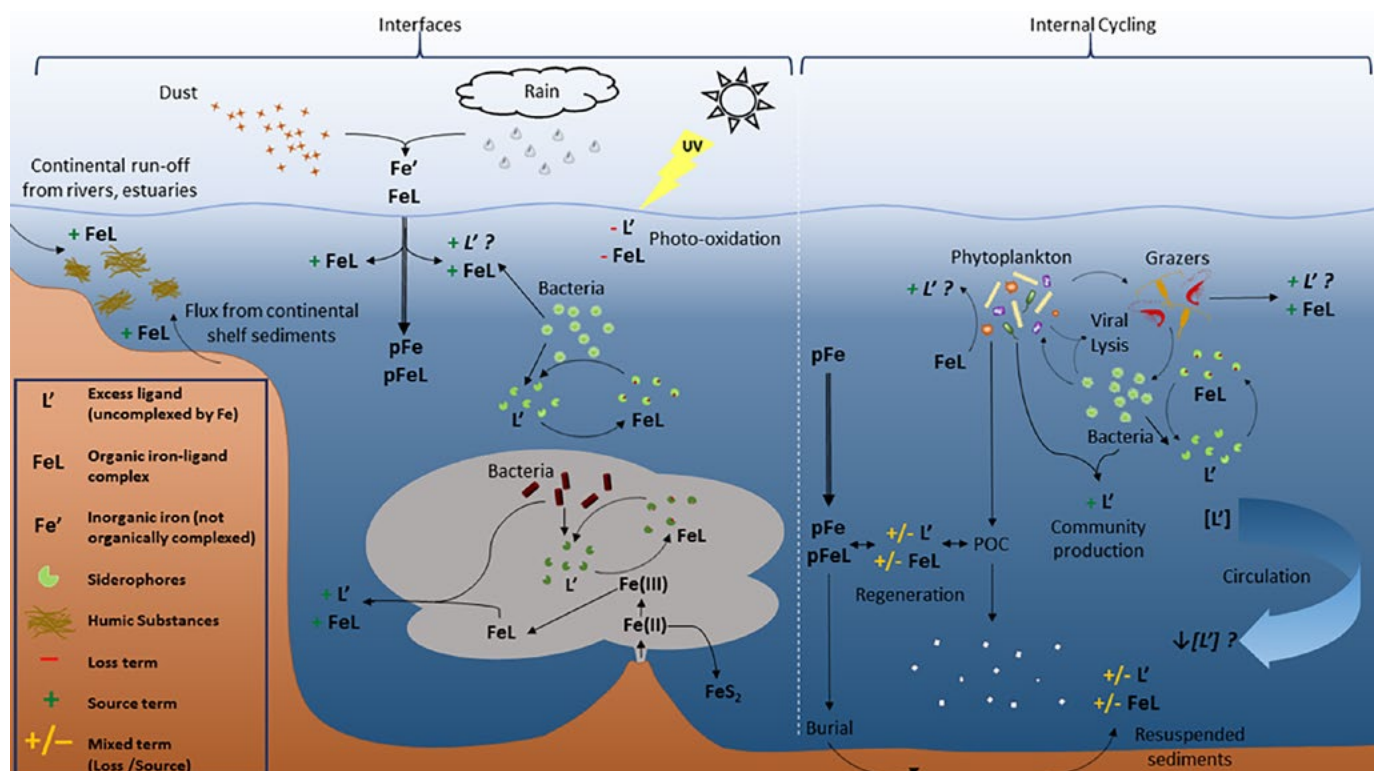


Figure 4. Schematic of iron-binding ligand cycling in the ocean.

(31), including the marine environment (32, 33). Model siderophores are typically, though not exclusively, characterized as among the strongest L_1 -type ligands measured in CLE-ACSV (3, 8). Iron complexed by these discrete biomolecules can usually be chromatographically resolved, although isolation of these compounds from seawater is notoriously difficult. Ferrioxamines and amphibactins have been the most widely reported from the water column (Figure 3; (34–36)) and shipboard incubations (37), though marine bacteria cultures have produced a broader suite (32). The limited diversity and only picomolar concentrations of siderophores extracted from seawater compared to marine bacteria cultures likely reflects limitations in sampling, the extraction procedures available (8, 32), and detection of certain siderophore functional groups that are preferentially photodegraded in surface waters (38). Importantly, siderophores have been observed to persist throughout the water column below the euphotic zone (36) and are not restricted to low-iron waters (34). Additional discrete biomolecules, like heme or intracellular iron storage proteins, are also expected to contribute to the strong iron-binding ligand pool in seawater, though they may be prone to particle adsorption and aggregation processes, making them more likely to be found in the colloidal and particulate phases (8, 39). Because of their role as intracellular iron-binding ligands, these molecules are

usually released to the extracellular environment as iron complexes, rather than as free ligands. Similarly, viruses may even constitute a component of colloidal organically complexed iron (40).

Unlike siderophores, humic substances and polysaccharides are complex molecules with high heterogeneity and complexity (Fig. 3), which cannot generally be resolved chromatographically, but represent a large component of the natural organic matter pool (41). Some of these molecules actually form electroactive complexes with iron and have been directly measured by electrochemistry in estuarine, coastal, and deep open ocean waters (42–44). Suwannee River Fulvic Acid (SRFA), a suspected component of the refractory dissolved organic matter pool (45), has been identified as a model ligand that can be used to reproduce the peak of natural electroactive iron complexes (46); exopolymeric substances can similarly form electroactive iron complexes (47). The conditional stability constants for exopolysaccharides and SRFA determined by CLE-ACSV generally fall under the L_2 to L_4 ligand class definitions (8).

Ligand processes at ocean interfaces (Fig. 4)

Photochemical degradation of natural iron-binding ligands is variable in field studies (48, 49), and may account for sea surface minima in ligand concentrations

observed in some profiles (8). Experimental studies indicate that siderophore photolability depends on chemical structure and whether the siderophore is bound to iron (FeL) or not (L') (38). Humic substances, on the other hand, are universally photoreactive by the nature of their molecular structure (50), though the iron-binding ability of their photoproducts is unknown. Dust deposition and rainfall may serve as ligand sources if depositing strong iron-binding ligands in addition to their iron loads (14, 51–54), or stimulating ligand production by surface microbial communities (55, 56), which may be critical for stabilizing atmospherically-derived iron in surface waters (16). Inorganic iron additions in mesoscale fertilization experiments have also been shown to stimulate ligand production in the fertilized waters (8, 57). Similarly, a microbial iron cycle fueled by hydrothermal iron inputs at the crust-ocean interface has recently been suggested (25) to support the organic stabilization and transport of dissolved iron in plumes extending remarkable distances from vent systems (28, 30).

Along the coastal margins, organically complexed iron is delivered to the coastal ocean from river plumes, estuaries, and shelf sediments, often along with excess weaker iron-binding ligands, including humic substances (8, 42, 44, 58). Elevated excess iron-binding ligands were observed in bottom waters of several of the GA03 stations in the North Atlantic (11) that were also local maxima in excess copper-binding ligands (59), indicating overlap in the ligand pool between these two bioactive elements (44).

Internal ligand cycling (Fig. 4)

The low solubility of inorganic iron, and the overwhelming organic complexation of the dissolved iron pool by a diverse suite of ligands has significant implications for iron bioavailability to marine phytoplankton (60, 61). The high biological demand for iron by phytoplankton and heterotrophic bacteria in turn supports a myriad of iron acquisition strategies, which are largely mediated by organic complexation (33, 61). High excess ligand concentrations in low-iron waters may potentially result from ligand production, iron uptake from a ligand complex, or both. Production of excess iron-binding ligands has been observed under a range of iron conditions, with iron additions in large-scale iron fertilization experiments (57), and in iron-stressed diatom communities (49, 62, 63), perhaps indicative of a community iron cycle including diatom-associated bacterial communities (64).

Grazing, viral lysis, and organic matter remineralization are likely important sources of weaker iron-binding

ligands (e.g., humic-like substances, exopolysaccharides, or intracellular organic iron complexes like heme) to the ocean interior (8, 19). Mounting evidence points to bacterial production of the strongest ligands observed in seawater as an iron uptake strategy (8, 49, 57). Organic matter remineralization may similarly be a source of strong iron-binding ligands to the entire water column, given that siderophore production by heterotrophic bacteria is not necessarily restricted to the surface ocean and may be associated with 'hot spots' of sinking organic matter in the deep sea (65).

The extent to which iron-binding ligands are remineralized themselves is unknown. Excess ligand concentrations tended to decrease with depth in the Western North Atlantic as dissolved iron concentrations increased (10, 11). Decreasing total ligand concentrations in NADW samples were negatively correlated, albeit weakly, with apparent oxygen utilization (AOU) along the GA02 meridional section (10), implying some ligand remineralization during circulation since dilution was not expected to impact ligand concentrations. Gerringa et al. (2015) calculated a residence time on the order of 10^3 years for iron-binding ligands in the NADW, up to four times longer than that of dissolved iron, suggesting that particles must scavenge iron from strong organic complexes in the deep sea (10). Overall, the interactions between iron-binding ligands and sinking particles, whether lithogenic or biogenic in origin, are largely uncharacterized. These particles likely serve as both sources and sinks of iron-binding ligands (19) depending on the nature of the ligands, particles and biological communities involved.

Conclusions

Detailed large-scale datasets from the Atlantic Ocean have given us an unparalleled view of ligand cycling in this basin. These studies have enabled us to take a holistic look at ligand sources and sinks and internal cycling for the first time, and new paradigms have emerged. Biological contributions to the ligand pool are clear across nearly all ligand datasets. Although the direct connection between the organisms responsible for ligand production and the compounds they produce is still uncertain, marine microorganisms appear to be active producers of strong iron-binding ligands that influence iron cycling through the water column. Expansion of basin-scale datasets to the other basins and collaborative experimental studies to elucidate the mechanisms of ligand cycling behind the basin-scale distributions, some of which have been described here for the Atlantic, will improve under-

standing of the cycling of organic iron-binding ligands and inform global biogeochemical models of iron and carbon cycles.

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References

1. K. W. Bruland *et al.*, *Analytica Chimica Acta* **105**, 233-245 (1979).
2. M. Gledhill, C. M. G. van den Berg, *Marine Chemistry* **47**, 41-54 (1994).
3. E. L. Rue, K. W. Bruland, *Marine Chemistry* **50**, 117-138 (1995).
4. C. M. G. van den Berg, *Marine Chemistry* **50**, 139-157 (1995).
5. J. Wu, G. W. Luther III, *Marine Chemistry* **50**, 159-177 (1995).
6. A. Tagliabue *et al.*, *Global Biogeochemical Cycles* **30**, 149-174 (2016).
7. A. Tagliabue *et al.*, *Geophysical Research Letters* **41**, 920-926 (2014).
8. M. Gledhill, K. N. Buck, *Frontiers in Microbiology: Microbiological Chemistry* **3**, Article 69 (2012).
9. X. Liu, F. J. Millero, *Marine Chemistry* **77**, 43-54 (2002).
10. L. J. A. Gerringa *et al.*, *Marine Chemistry* **177**, 434-446 (2015).
11. K. N. Buck *et al.*, *Deep-Sea Research II* **116**, 152-165 (2015).
12. C. Measures *et al.*, *Deep-Sea Research II* **116**, 176-186 (2015).
13. T. M. Conway, S. G. John, *Nature* **511**, 212-215 (2014).
14. A. S. Wozniak *et al.*, *Marine Chemistry* **154**, 24-33 (2013).
15. K. N. Buck, A. M. Aguilar-Islas, (unpublished).
16. M. P. Fishwick *et al.*, *Global Biogeochemical Cycles* **28**, 1235-1250 (2014).
17. C.-E. Thuróczy *et al.*, *Journal of Geophysical Research* **116**, C10009 (2011).
18. C.-E. Thuróczy *et al.*, *Deep-Sea Research II* **58**, 2695-2706 (2011).
19. P. W. Boyd *et al.*, *Limnology and Oceanography* **55**, 1271-1288 (2010).
20. P. N. Sedwick *et al.*, *Deep-Sea Research II* **116**, 166-175 (2015).
21. B. P. von der Heyden *et al.*, *Environmental Science & Technology Letters* **1**, 387-392 (2014).
22. J. N. Fitzsimmons *et al.*, *Deep-Sea Research II* **116**, 130-151 (2015).
23. M. Yücel *et al.*, *Nature Geoscience* **4**, 367-371 (2011).
24. B. M. Toner *et al.*, *Nature Geoscience* **2**, 197-201 (2009).
25. M. Li *et al.*, *Nature Communications* **5**, 3192-3199 (2013).
26. S. A. Bennett *et al.*, *Earth and Planetary Science Letters* **270**, 157-167 (2008).
27. J. A. Hawkes *et al.*, *Earth and Planetary Science Letters* **375**, 280-290 (2013).
28. J. N. Fitzsimmons *et al.*, *Proceedings of the National Academy of Sciences* **111**, 16654-16661 (2014).
29. S. G. Sander, A. Koschinsky, *Nature Geoscience* **4**, 145-150 (2011).
30. J. A. Resing *et al.*, *Nature* **523**, 200-203 (2015).
31. J. B. Neilands, *Journal of Biological Chemistry* **270**, 26723-26726 (1995).
32. J. M. Vraspir, A. Butler, *Annual Review of Marine Science* **1**, 43-63 (2009).
33. M. Sandy, A. Butler, *Chemical Reviews* **109**, 4580-4595 (2009).
34. E. Mawji *et al.*, *Environmental Science & Technology* **42**, 8675-8680 (2008).
35. R. M. Boiteau, Massachusetts Institute of Technology-Woods Hole Oceanography Institution, (2016).
36. R. M. Bundy *et al.*, *Limnology and Oceanography*, (in prep).
37. M. Gledhill *et al.*, *Marine Chemistry* **88**, 75-83 (2004).
38. K. Barbeau *et al.*, *Limnology and Oceanography* **48**, 1069-1078 (2003).
39. S. L. Hogle *et al.*, *Metallomics* **6**, 1107-1120 (2014).
40. C. Bonnain *et al.*, *Frontiers in Marine Science* **3**, article 82 (2016).
41. L. I. Aluwihare *et al.*, *Nature* **387**, 166-169 (1997).
42. R. M. Bundy *et al.*, *Marine Chemistry* **173**, 183-194 (2015).
43. L. M. Laglera, C. M. G. Van den Berg, *Limnology and Oceanography* **54**, 610-619 (2009).
44. M. M. Abualhaja *et al.*, *Marine Chemistry* **172**, 46-56 (2015).
45. N. Arakawa, L. Aluwihare, *Environmental Science & Technology* **49**, 4097-4105 (2015).
46. L. M. Laglera *et al.*, *Analytica Chimica Acta* **599**, 58-66 (2007).
47. C. S. Hassler *et al.*, *Proceedings of the National Academy of Sciences* **108**, 1076-1081 (2011).
48. K. Barbeau, *Photochemistry and Photobiology* **82**, 1505-1516 (2006).
49. R. M. Bundy *et al.*, *Frontiers in Marine Science* **3**, Article 27 (2016).
50. P. G. Coble, *Chemical Reviews* **107**, 402-418 (2007).
51. A. C. Saydam, H. Z. Senyuva, *Geophysical Research Letters* **29**, 1524 (2002).
52. M. Cheize *et al.*, *Analytica Chimica Acta* **736**, 45-54 (2012).
53. J. N. Fitzsimmons *et al.*, *Marine Chemistry*, (2015 in press).
54. J. D. Willey *et al.*, *Limnology and Oceanography* **53**, 1678-1684 (2008).
55. T. Wagener *et al.*, *Geophysical Research Letters* **35**, L16601 (2008).
56. L. J. A. Gerringa *et al.*, *Marine Chemistry* **102**, 276-290 (2006).
57. C. L. Adly *et al.*, *Limnology and Oceanography* **60**, 136-148 (2015).
58. M. E. Jones *et al.*, *Limnology and Oceanography* **56**, 1811-1823 (2011).
59. J. E. Jacquot, J. W. Moffett, *Deep-Sea Research II* **116**, 187-207 (2015).
60. F. M. M. Morel *et al.*, *Limnology and Oceanography* **53**, 400-404 (2008).
61. Y. Shaked, H. Lis, *Frontiers in Microbiology* **3**, Article 123 (2012).
62. K. N. Buck *et al.*, *Marine Chemistry* **122**, 148-159 (2010).
63. A. L. King *et al.*, *Marine Chemistry* **128-129**, 1-12 (2012).
64. S. A. Amin *et al.*, *Microbiology and Molecular Biology Reviews* **76**, 667-684 (2012).
65. F. Azam, F. Malfatti, *Nature Reviews* **5**, 782-791 (2007).
66. P. W. Boyd, A. Tagliabue, *Marine Chemistry* **173**, 52-66 (2015).

Exploring molecular methods for assessing trace element bioavailability in phytoplankton

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This summer OCB and GEOTRACES are co-sponsoring a [synthesis workshop on the biogeochemical cycling of trace elements in the ocean](#). The overall goal of the workshop is to bring together expertise from across the field of oceanography to take advantage of the growing [datasets of trace elements in the ocean](#) and explore biological-chemical-physical underpinnings of trace element cycling within the ocean. One of the three main themes that will be addressed at the workshop is “biological uptake and trace element bioavailability.” Part of this theme will include a discussion of how molecular markers have been used to address questions of trace element bioavailability in the past and the exciting future for continued efforts in this area given the growing molecular toolkit.

As a starting point to open the door to this broad discussion topic, let us turn our attention to how molecular methods have been used to evaluate iron (Fe) bioavailability to certain phytoplankton groups. Marine phytoplankton play a key role in the global carbon cycle by performing a significant fraction of global primary production (1). Since John Martin’s groundbreaking work introduced the concept that Fe is a limiting nutrient for phytoplankton growth (2), numerous studies have shown that insufficient Fe limits primary productivity in the major high-nitrate, low-chlorophyll (HNLC) regions of the ocean, and that Fe availability can regulate phytoplankton processes in many other oceanic settings (3, 4). Fe is a critical micronutrient required by phytoplankton for a

multitude of cellular tasks, including electron transfer in photosynthesis and respiration, as well as macronutrient acquisition and assimilation (5). Studies of Fe limitation in marine environments beyond the traditional HNLC regions suggest that Fe limitation may be driven not simply by low Fe concentrations, but a combination of low Fe bioavailability coupled with high macronutrient supply (e.g., 6, 7). In an admittedly overly simplified summary, the different pools of Fe present in the ocean are defined based on filter pore-size cut-offs and chemical interactions with organic compounds (3). Knowledge of the distribution of these various forms of Fe in the oceans has increased dramatically in recent years thanks to coordinated sampling efforts like [GEOTRACES](#).

While the bioavailability of Fe to phytoplankton is believed to be different for the various Fe pools, there is still no clear consensus as to which, if any, pools of Fe are always bioavailable and which, if any, are completely unavailable (8, 9). Additionally, it is known that all phytoplankton are not created equal with respect to their ability to persist under low-Fe conditions (10) and access different Fe pools (9). These factors make it difficult to accurately predict how changing concentrations of the different pools of Fe may impact phytoplankton productivity in a changing ocean. One way to address questions about biological availability is to use phytoplankton themselves as *in situ* indicators of Fe stress. An approach that appears promising in addressing these questions of bioavailability of Fe

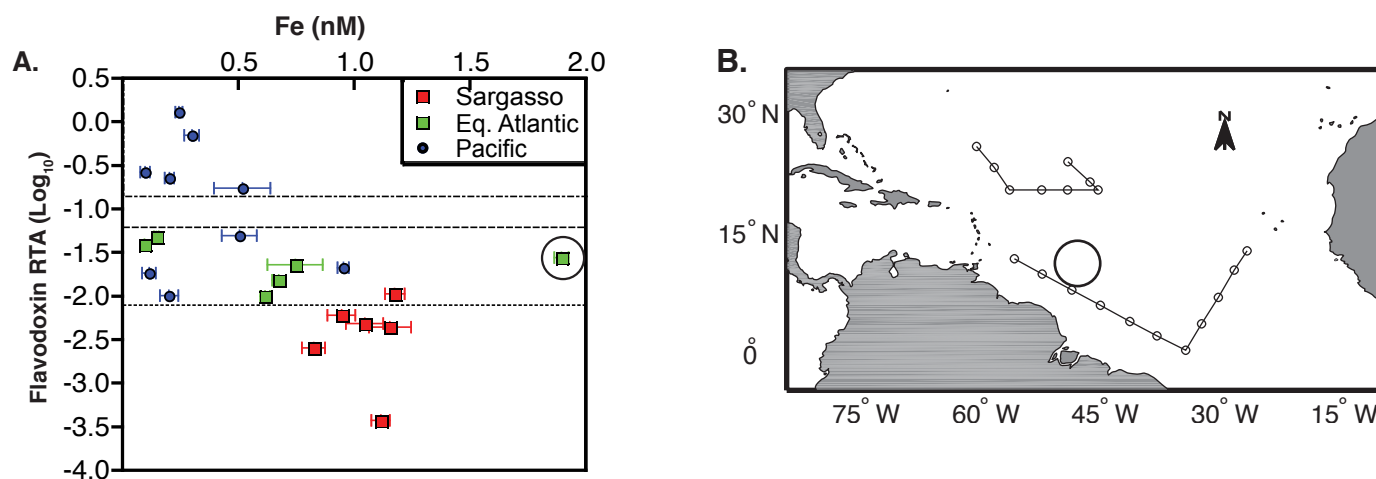


Figure 1. A. *T. thiebautii* flavodoxin expression relative to the housekeeping gene actin (RTA = Relative Transcript Abundance) and dissolved Fe from (15). Circled data point represents the gene expression at the Amazon plume station referenced in the text. **B.** Map of sampling locations in the Sargasso Sea and equatorial Atlantic Ocean for the data points shown in A. Circled station shows the location of the Amazon plume sampling. Modified from (15).

to individual phytoplankton species is the development of species-specific molecular markers of Fe limitation such as those that have been developed for the oceanic diatom *Thalassiosira oceanica* (11), and for the two main groups of the nitrogen-fixing cyanobacterial genus *Trichodesmium* (12). These assays in particular follow the expression of genes that encode flavodoxin, a non-Fe-containing protein that phytoplankton are known to substitute for the Fe-containing ferredoxin protein to maintain photosynthetic electron transport under Fe-limiting conditions (13). They focus on gene expression analysis rather than protein analysis, as many phytoplankton have multiple genes that encode for flavodoxin proteins and, at least in diatoms, not all gene copies are sensitive to Fe (14).

The *Trichodesmium* assays were calibrated using cultures grown with six different concentrations of Fe in the media. In laboratory cultivation experiments, gene expression was shown to be inversely proportional to Fe present in the media and expression was downregulated when Fe was fed back to Fe-limited cultures (12). The *Trichodesmium thiebautii* assay was further used to evaluate field populations from open ocean samples collected globally (15), providing insights into Fe bioavailability to wild populations of *Trichodesmium*. Overall, there was an inverse correlation between gene expression and total dissolved Fe concentrations (Fig. 1). Comparing the results with the laboratory calibration led to the conclusion that most of the dissolved Fe, including organically bound Fe, was available to *T. thiebautii*. An intriguing result from this study was that one sample collected in the plume of the Amazon River had significantly higher gene expression than would be expected based on the measured dissolved Fe at that site (Fig. 1; 15). These findings suggest that there is a fraction of the dissolved Fe in the Amazon River plume that is not bioavailable to *T. thiebautii*, the clade of *Trichodesmium* that is more abundant and active in the open ocean (15, 16).

The *T. oceanica* assay is also highly sensitive to Fe with high gene expression in cultures that were Fe-limited, a rapid reduction of gene expression following an Fe pulse to Fe-limited cultures, and no induction of expression by macronutrient limitation (11). Using this method on field samples from the northeast Pacific Ocean, *T. oceanica* flavodoxin expression was found to be highest in samples with low measured dissolved Fe and vice versa (11). Two notable exceptions to this trend were samples collected along the shallow shelf of Haida Gwaii, stations 26 and 27, which showed anomalously high expression of both genes despite high measured dissolved Fe (Fig. 2), suggest-

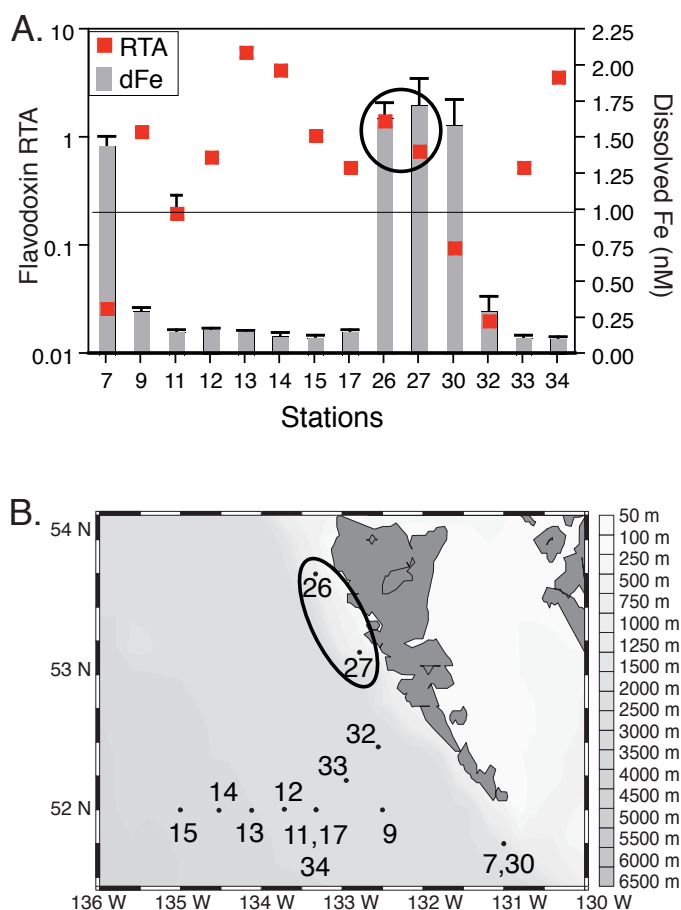


Figure 2. A. *T. oceanica* flavodoxin expression relative to the housekeeping gene actin (RTA = Relative Transcript Abundance) and dissolved Fe from stations identified in panel. **B.** Black line in A indicates expression level associated with Fe limitation. The circled stations are the shallow shelf stations referenced in the text. Modified from (11).

ing that something about the dissolved Fe in these shallow coastal stations made it unavailable to the *T. oceanica* in these waters. It should be noted that *T. oceanica* is an oceanic diatom species, so both sets of findings suggest that there is a fraction of dissolved Fe from a terrestrially influenced water sample that was not bioavailable to a species of oceanic phytoplankton.

While these two datasets are intriguing, they are limited in scope and admittedly raise more questions than they answer. There are a variety of questions that stem from these results, including what, if anything, is different about the dissolved Fe at these stations? Was this coastal/terrestrially sourced Fe unavailable because only oceanic phytoplankton, which rarely encounter dissolved Fe from terrestrial sources, were queried? Did coastal phytoplankton simply outcompete the oceanic phytoplankton for access to the dissolved Fe perhaps because they have

different or more efficient Fe uptake mechanisms? Would an assay targeting coastal phytoplankton reveal the same results? We know that coastal diatoms have significantly higher Fe requirements (10). What if coastal and oceanic phytoplankton also differ in their abilities to access Fe from different sources? A recent study in the Sea of Okhotsk yielded a significant correlation between a bulk diatom community indicator of Fe stress and dissolved Fe with increasing distance from the mouth of the Amur River, suggesting that the riverine Fe was bioavailable to the community that was dominated by coastal diatoms (17).

A number of recent advances in molecular microbial oceanography are making it increasingly possible to start answering these types of questions on a broader scale. A major sequencing effort that was completed in 2014, the Marine Microbial Eukaryote Transcriptome Sequencing Project (MMETSP), added a wealth of data on the functional genetic diversity of marine microeukaryotes (18). The project resulted in [over 650 publically available transcriptomes from over 250 genera of marine microeukaryotes](#). Even before all the transcriptomes from the project were released, data mining of a limited portion of the MMETSP publically available dataset yielded valuable information as to the varied Fe management strategies utilized by different species of marine diatoms, creating a list of additional potential molecular markers for evaluating Fe nutritional status of diatoms in the field (19). Another data mining technique that has proven useful in identifying coordinated transcriptional responses in diatoms has involved the application of clustering algorithms to evaluate publically available microarray data for two of the more commonly studied diatom species, *Phaeodactylum tricornutum* and *Thalassiosira pseudonana*, grown under a wide variety of conditions (20). New insights into the diatom Fe stress response and Fe uptake mechanisms have also been gained through combining physiological experiments with genetic knockdowns of previously uncharacterized Fe

responsive genes (21). These new molecular advances are providing a suite of new potential targets for querying the physiological status of phytoplankton present throughout the global ocean. At the [OCB/GEOTRACES synthesis workshop on the biogeochemical cycling of trace elements in the ocean](#), the conversation will include a discussion of how to effectively combine these new analyses with the growing datasets of bioactive trace elements to answer questions regarding the biological availability of different trace element pools. While this mini-review has focused on Fe, additional trace elements will be discussed at the meeting in August.

References

1. C. B. Field et al., *Science* **281**, 237-240 (1998).
2. J. H. Martin, S. Fitzwater, *Nature* **331**, 341-343 (1988).
3. P. W. Boyd, M. J. Ellwood, *Nature Geoscience* **3**, 675-682 (2010).
4. P. W. Boyd et al., *Science* **315**, 612-617 (2007).
5. F. M. M. Morel, N. M. Price, *Science* **300**, 944-947 (2003).
6. K. W. Bruland, E. L. Rue, G. J. Smith, *Limnol. Oceanogr.* **46**, 1661-1674 (2001).
7. A. L. King, K. N. Buck, K. A. Barbeau, *Marine Chem.* **128-129**, 1-12 (2012).
8. E. Breitbarth et al., *Biogeosci.* **7**, 1075-1097 (2010).
9. Y. Shaked, H. Lis, *Frontiers Microbiol.* **3** (2012).
10. W. G. Sunda, S. A. Huntsman, *Marine Chem.* **50**, 189-206 (1995).
11. P. D. Chappell et al., *ISME Journal* **9**, 592-602 (2015).
12. P. D. Chappell, E. A. Webb, *Envir. Microbiol.* **12**, 13-27 (2010).
13. J. LaRoche et al., *J. Phycol.* **31**, 520-530 (1995).
14. L. P. Whitney et al., *Frontiers Microbiol.* **2** (2011).
15. P. D. Chappell et al., *ISME Journal* **6**, 1728-1739 (2012).
16. A. M. Hynes, Massachusetts Institute of Technology (MIT) (2009).
17. K. Suzuki et al., *Biogeosci.* **11**, 2503-2517 (2014).
18. P. J. Keeling et al., *Plos Biol.* **12** (2014).
19. R. D. Groussman, M. S. Parker, E. V. Armbrust, *PloS One* **10** (2015).
20. J. Ashworth et al., *Marine Genom.* **26**, 21-28 (2016).
21. J. Morrissey et al., *Curr. Biol.* **25**, 364-371 (2015).

Marine particles: Distribution, composition, and role in scavenging of TEIs

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GEOTRACES and particles in the ocean

GEOTRACES is an international program to study the global marine biogeochemical cycles of trace elements and their isotopes (TEIs). The program's guiding mission is to "identify processes and quantify fluxes that control the distributions of key TEIs in the ocean" (1).

Particles represent a key parameter for the GEOTRACES program because of their role as sources, sinks, and in the internal cycling of so many TEIs (1, 2). Particles in the ocean fall into two classes: 1. Those that have sources external to the system such as lithogenic material carried by atmospheric transport, river, or lateral transport from continental margin sediments; and 2. those that are produced internally in the system, primarily by biological production, but also by authigenic mineral precipitation (2).

External particle sources such as mineral dust deposition and sediment resuspension act as sources of dissolved TEIs when they partially dissolve in seawater. Conversely, dissolved TEIs are removed by active biological uptake or passive adsorption onto particles surfaces, followed by particle removal by aggregation and sinking. Indeed, the biological and abiotic interactions of dissolved TEIs with particles determine the residence time of a dissolved TEI.

In most open ocean basins away from ocean floor boundaries, external sources of particles are dwarfed by the much greater biological production and destruction of particles. Particle cycling in most open ocean basins is thus dominated by the biological pump, the processes by which suspended particles are produced by photosynthesis in the euphotic zone at the surface, and are then abiotically or biologically aggregated into larger particles that can sink into the abyss (3).

As particulate organic carbon (POC) cycles through processes such as aggregation, disaggregation, remineralization, and sinking (collectively referred to here as particle dynamics), other particle phases are swept along for the ride, including

other major components such as biologically precipitated minerals (especially CaCO_3 and opal), as well as lithogenic and authigenic particles, and scavenged TEIs adsorbed to the surfaces of other particles (Fig. 1).

In this article, I will briefly review the role of particle composition on the scavenging of TEIs.

Scavenging: A two-step removal process

Most adsorption of TEIs likely occurs onto small, suspended particles, which are usually more abundant, and have a longer residence time in the water column than large, sinking particles. For TEIs to be removed from the water column, the suspended particles must then be aggregated into larger, sinking particles. There are thus two distinct steps for the removal of a dissolved TEI by scavenging: 1) adsorption onto suspended particle surfaces, followed by 2) removal via the aggregation of suspended particles onto larger particles that sink out of the water column. Fig. 1 shows a very simple schematic illustrating these basic processes. The adsorption step is governed by the affinity of a TEI for a particular particle surface, and the removal step is governed by the particle dynamics that package suspended particles into large, sink-

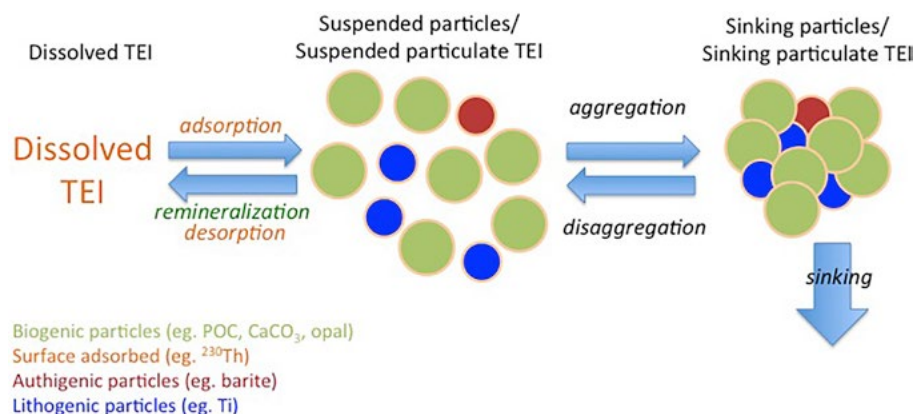


Figure 1. Schematic illustrating a conceptual adsorption and particle cycling model. A dissolved TEI adsorbs onto suspended particles with a certain rate constant, depicted as an orange coating surrounding particles of different compositions and origins. Example particle types indicated: green for biogenic particles, red for authigenic particles, and blue for lithogenic particles. This particle-associated TEI can return to the dissolved phase if the particles remineralize and/or if the TEI desorbs from the particle surface. Particle-associated TEIs can then be aggregated into larger, sinking particles, which can sink and be removed from the water column, or disaggregate back to suspended particles.

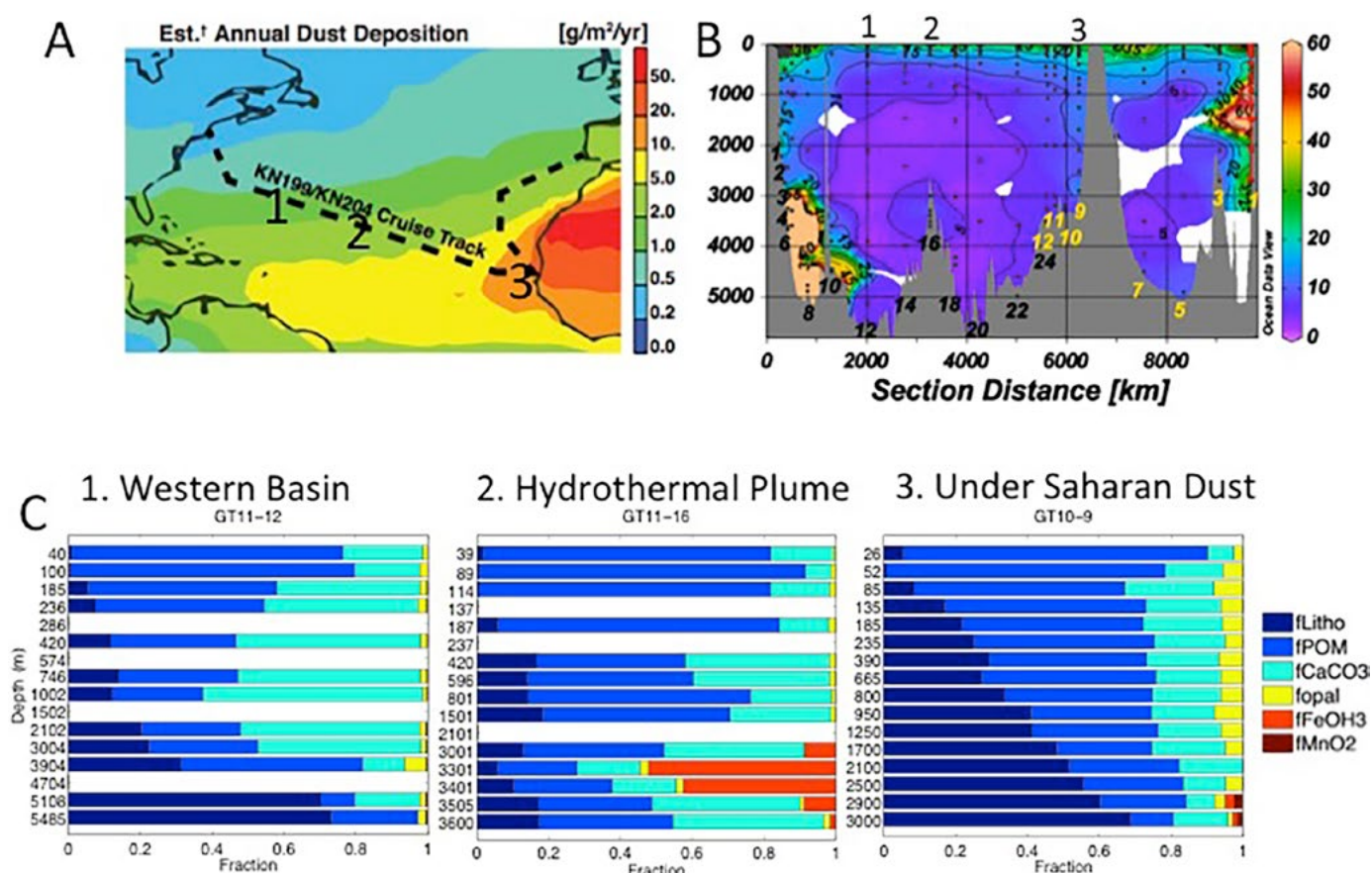


Figure 2. **A.** Cruise track of GA03 overlaid on estimated annual dust deposition from the AEROCOM model. **B.** Total suspended particulate mass along GA03, in µg/L. **C.** Particle composition in small (<51µm) size fraction at three stations along GA03 as indicated in panels **A** and **B**. Figures modified from (4) and (30).

ing aggregates, and are the focus of studies of the biological pump. The removal of TEIs by scavenging thus intimately links one of OCB's scientific goals, the understanding of the biological carbon pump, to GEOTRACES's mission to identify processes and quantify fluxes that control the distributions of key TEIs in the ocean.

Particle concentration and composition: horizontal and vertical variations

Particles collected in the ocean are a heterogeneous mixture of biogenic, lithogenic, and authigenic (precipitated in-situ) components. The relative proportions of these different components vary geographically and with depth. Fig. 2 shows the distribution of total particle concentration from GA03, the U.S. GEOTRACES North Atlantic Zonal Transect cruise in 2010/2011, as well as the changing composition of small (<51 µm) particles at three stations along the transect (4). Particle concentrations are highest at the surface and at the margins, where biological production is highest. It is clear that particulate organic

matter (POM) dominates particle composition in the upper 100 m, making up more than 70% of the suspended particle mass at all three stations. The balance in the upper 100 m is mostly made of other biogenic components such as CaCO₃ and opal, with a small contribution from lithogenic particles directly under the Saharan dust plume. At all stations, the inorganic components (everything except for POM) become relatively more important with depth as POM is remineralized. In the eastern half of the basin, lithogenic particles make up the largest fraction of particle mass, accounting for >50% of particle mass below 1500 m. In the western half of the basin, further from the Saharan dust source, lithogenic particles are not as important, and CaCO₃ makes up the largest fraction (~50%) of particle mass between 500 – 3000 m. A special case is found in a station over the Mid-Atlantic Ridge, where iron oxyhydroxides from the hydrothermal plume make up ~50% of the particle mass. Iron and manganese oxyhydroxides are rarely dominant components of particle mass, except in special situations such as hydrothermal

plumes, but may exert a particularly large influence on TEI adsorption (5, 6).

Studies suggest that particle composition may affect both the affinity of dissolved TEIs for adsorbing onto particle surfaces (2), and the vertical flux of particles from the water column (7-9). Horizontal and vertical changes in particle composition thus allow us to test hypotheses of the importance of particle composition on both steps in the scavenging of TEIs.

Effect of particle composition on adsorption of TEIs

The affinity of TEIs to particles has typically been characterized by a partition coefficient, K_d , which is calculated empirically as:

$$K_d = \frac{(\text{mass of particulate TEI})/(\text{mass of particles})}{(\text{mass of dissolved TEI})/(\text{volume of seawater})}$$

Prior to the GEOTRACES program, the effect of particle composition on TEI adsorption affinity had been studied in the field using sediments and sinking particles collected in sediment traps. The affinity of trace metals to marine sediments of different compositions varied: Some trace metals (Cs, Be, Sn, and Fe) had a higher affinity to sediments dominated by aluminosilicate clay minerals, and others (Ba, Cd, Zn, Mn, and Co) had a higher affinity to sediments enriched in Mn oxyhydroxides (10). In the water column, correlations between the partition coefficient of ^{230}Th and particle composition in sediment trap particles from around the world have variously implied that the scavenging efficiency of ^{230}Th is controlled by CaCO_3 (11, 12), lithogenic material (13, 14), and/or Mn oxyhydroxides (15). Studies that span strong opal gradients across the Polar Front in the Southern Ocean show higher partition coefficients for ^{231}Pa scavenging in areas of high opal content (11, 16). ^{231}Pa is generally not as particle-reactive as ^{230}Th in the open ocean, but is often removed with equal efficiency as ^{230}Th in near-margin areas (e.g., 17), presumably because opal is more important in margin settings. The Arctic, on the other hand, displays the opposite $^{230}\text{Th}/^{231}\text{Pa}$ removal signal, with ^{231}Pa removal less efficient relative to ^{230}Th at the margins compared to the open ocean (18).

Since TEIs adsorb primarily onto suspended particles rather than sinking particles, studying the correlations between partition coefficients and suspended particles may resolve some of the discrepancies observed in the sediment trap studies (c.f., 2).

The GEOTRACES GA03 North Atlantic Zonal Transect has provided the first opportunity to investigate

the correlation between partition coefficients of various TEIs and the particle composition of suspended particles in the ocean. Thus far, this has been done for ^{230}Th and ^{231}Pa partition coefficients, with Mn and Fe oxyhydroxides emerging as key controlling phases and opal having no controlling effect (5). The North Atlantic is very opal-poor (Fig. 2), so particles collected from more diatom-rich regions are needed to examine the potential of opal as a controlling phase. Other studies are underway to study the particle affinities of Hg (19), Po (20), and Pb (6) on this same North Atlantic transect. Subsequent U.S. GEOTRACES sections (GP16—Eastern Tropical South Pacific Zonal Transect and GN01—Western Arctic) will also have full ocean depth size-fractionated particle concentration and composition, allowing us to examine samples from different biogeochemical provinces, and hopefully expanding the range of particle compositions.

TEIs as tracers of scavenging rates and particle dynamics

The unprecedented data sets from GEOTRACES are also allowing us to estimate adsorption and desorption rate constants (Fig. 1) from inverse modeling of the observations of dissolved and particulate TEIs and particle concentrations (19, 21, 22). This gives us a kinetic view of the scavenging process to complement the empirically-derived partition coefficients, which are often viewed as representing equilibrium constants.

Applying inverse modeling approaches to observations of the distributions of size-fractionated particles and particulate TEIs can also allow us to estimate rates of particle remineralization, aggregation, disaggregation, and sinking (21, 23). This approach requires only that a conceptual model relating the suspended and sinking particle size fractions be applied to observations of particle mass and particulate TEIs, and does not require knowledge about which specific physical or biological processes are responsible for particle transformations. For example, Fig. 1 illustrates a simple conceptual model in which a pool of suspended particles can be lost to the dissolved phase through remineralization, or by aggregation into sinking particles; conversely, sinking particles can sink, or can be disaggregated back into suspended particles. By assuming that particulate TEIs are simply part of the overall particle pool (e.g., a coating on organic particles in the case of radiogenic TEIs such as ^{230}Th or as part of a lithogenic particle in the case of a TEI such as Ti) and thus are subject to the same rates of particle transformations as the major phases such as POC, we can apply the same conceptual model to observations of particle mass and

to observations of particulate TEI to better constrain the rates of these transformations (23). As some of these rates such as aggregation and disaggregation are notoriously difficult to measure directly, these inverse approaches offer a way forward to quantify these important processes.

Particle composition and the biological pump

In addition to its effect on scavenging efficiency, particle composition has also been implicated as an important factor in the strength and efficiency of the biological pump. Several meta-analyses of global deep (>1000 m) sediment trap data showed strong correlations between POC flux and mineral flux (7-9), leading to the development of the “ballast hypothesis.” The mechanisms to explain the correlations, which are still being debated (24, 25), range from mineral protection of POC (8), mineral contribution to particle excess density (7), scavenging of mineral particles by POC (26), and minerals as proxies for particle packaging, POC lability, and ecosystem structure (9, 27-29).

Although the GA03 dataset is based on size-fractionated particle samples collected by in-situ filtration rather than sinking particles collected by sediment traps, we can nonetheless examine whether there is a correlation between POC and ballast minerals in small or large particle size fractions. We found that POC concentration in large (>51 μm) particles was not consistently correlated with any of the potential ballast minerals CaCO_3 , opal, and lithogenic particles (4). The lack of strong correlations within this regional dataset is consistent with the idea that ballast mineral correlations with POC may only emerge in global datasets that combine different biogeochemical provinces (25).

Outlook

The GEOTRACES program is not only rapidly expanding global observations of dissolved TEIs, but it is also the latest major program to systematically sample particle distributions since JGOFS and GEOSECS (2). These particle measurements are not only helping us understand the processes controlling TEI distributions, but the TEI measurements can also be used as tracers for quantifying key processes of particle cycling. Both GEOTRACES and OCB can benefit from the insights gained in each program.

References

1. GEOTRACES, Scientific Committee on Oceanic Research, Ed. (Baltimore, Maryland, 2006).
2. C. Jeandel *et al.*, *Progress in Oceanography* **133**, 6 (4//, 2015).
3. C. L. De La Rocha, in *Treatise on Geochemistry*, H. Elderfield, K. K. Turekian, Eds. (Elsevier, 2003), vol. 6: The Oceans and Marine Geochemistry, pp. 83-111.
4. P. J. Lam *et al.*, *Deep Sea Research Part II: Topical Studies in Oceanography* **116**, 303 (6//, 2015).
5. C. T. Hayes *et al.*, *Marine Chemistry* **170**, 49 (3/20/, 2015).
6. E. A. Boyle *et al.*, paper presented at the 2016 Ocean Sciences Meeting, New Orleans, LA, USA, 2016.
7. C. Klaas, D. E. Archer, *Global Biogeochemical Cycles* **16**, 1116 (Dec 5, 2002).
8. R. A. Armstrong *et al.*, *Deep-Sea Research Part II-Topical Studies in Oceanography* **49**, 219 (2002).
9. R. François *et al.*, *Global Biogeochemical Cycles* **16**, (Oct-Nov, 2002).
10. L. S. Balistrieri, J. W. Murray, *Geochimica Et Cosmochimica Acta* **48**, 921 (1984).
11. Z. Chase *et al.*, *Earth and Planetary Science Letters* **204**, 215 (Nov 30, 2002).
12. Z. Chase *et al.*, *Deep-Sea Research Part II-Topical Studies in Oceanography* **50**, 739 (2003).
13. S. D. Luo, T. L. Ku, *Earth and Planetary Science Letters* **220**, 201 (Mar, 2004).
14. M. Roy-Barman *et al.*, *Earth and Planetary Science Letters* **286**, 526 (2009).
15. M. Roy-Barman *et al.*, *Earth and Planetary Science Letters* **240**, 681 (2005).
16. H. J. Walter *et al.*, *Earth and Planetary Science Letters* **149**, 85 (1997).
17. R. F. Anderson, M. P. Bacon, P. G. Brewer, *Earth and Planetary Science Letters* **66**, 73 (1983).
18. H. N. Edmonds *et al.*, *Earth and Planetary Science Letters* **227**, 155 (Oct, 2004).
19. C. H. Lamborg *et al.*, *Philos T R Soc A*, (accepted).
20. Y. Tang *et al.*, paper presented at the 2016 Ocean Sciences Meeting, New Orleans, LA, USA, 2016.
21. O. Marchal, P. J. Lam, *Geochimica Et Cosmochimica Acta* **90**, 126 (2012).
22. P. Lerner *et al.*, *Deep Sea Research Part I: Oceanographic Research Papers* **113**, 57 (7//, 2016).
23. P. J. Lam, O. Marchal, *Annual Review of Marine Science* **7**, 159 (2015).
24. P. Boyd, T. Trull, *Progress in Oceanography* **72**, 276 (2007).
25. J. D. Wilson, S. Barker *et al.*, *Global Biogeochemical Cycles* **26**, GB4011 (2012).
26. U. Passow, *Geochemistry Geophysics Geosystems* **5**, (Apr 6, 2004).
27. P. J. Lam *et al.*, *Global Biogeochem. Cycles* **25**, GB3009 (2011).
28. S. A. Henson *et al.*, *Global Biogeochem. Cycles* **26**, GB1028 (2012).
29. S. Z. Rosengard *et al.*, *Biogeosciences* **12**, 3953 (2015).
30. D. C. Ohnemus, P. J. Lam, *Deep Sea Research Part II: Topical Studies in Oceanography* **116**, 283 (6//, 2015).

Using GEOTRACES data to appraise iron cycling as represented within global ocean models

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We rely on global ocean models to predict how climate change might affect the evolution of ocean productivity, acidification, and deoxygenation (1). Such platforms are also used to test hypotheses regarding the controls on ocean biogeochemical cycling and to understand past change (both on historical and geologic timescales). Ocean biogeochemistry models began with relatively simple formulations of a carbon export flux that involved restoring to observed phosphate distributions, but have more recently evolved into complex multi-element representations of the ocean. In line with our understanding that the trace micronutrient iron (Fe) limits phytoplankton productivity over large areas of the world ocean (2), most global models that aim to project future change also explicitly represent the Fe cycle.

Datasets regarding the major limiting nutrients (nitrate, phosphate, and silicate) have been available as gridded ‘climatologies’ since the early 1990s (3). This has greatly facilitated the development and evaluation of modelled distributions over the past two decades. However, over this period there has been little comprehensive evaluation of how different models represent the ocean Fe cycle. Over recent years, there has been a marked increase in the availability of iron measurements in the ocean (4), largely driven by the international [GEOTRACES](#) effort to conduct full depth, basin-scale surveys. This led us to initiate the first-ever attempt to critically compare a range of global ocean iron models against the largest global datasets, as well as against the newly emerging ocean section data (5).

The Fe Model Intercomparison Project (FeMIP) sought to be as inclusive as possible in this first step and therefore did not seek to standardize the underlying ocean circulation or external inputs. Instead, we simply asked each of the thirteen models to provide their best representation of dissolved iron in three dimensions at monthly resolution. We then compared these models against each other, a global iron database of over 20,000 observations and against five unique basin-scale sections from the GEOTRACES intermediate data product 2014 (IDP2014) (6).

Firstly, it is apparent that even when the underlying iron cycles of the different models are evaluated, a substantial degree of inter-model discord exists. The total iron

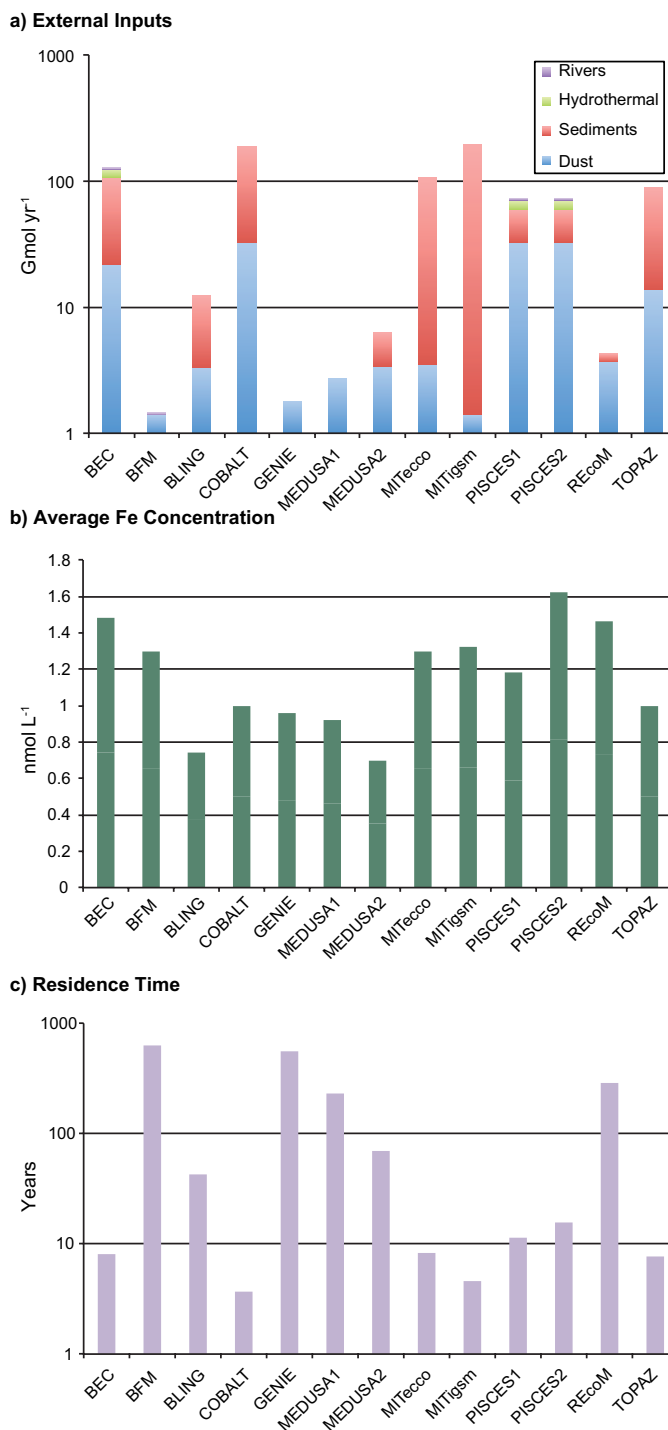


Figure 1. The (a) input of iron to the ocean (Gmol yr^{-1} , with colors representing the different specific sources), (b) average ocean concentration of iron (nmol L^{-1}) and (c) the residence time of iron (years) across the suite of FeMIP models. Note the logarithmic scale for panels (a) and (c).

input varies from around 2 to 200 Gmol yr⁻¹ across the thirteen models (Fig. 1a). Even for ‘well known’ sources like atmospheric deposition, the inter-model variability is around an order of magnitude. On the other hand, the average concentrations of dissolved Fe between the models is much less variable and ranges from 0.35 to 0.81 nmol L⁻¹ (Fig. 1b), or an average of 0.58±0.14 nmol L⁻¹. This apparent constancy reflects an initial view of the ocean Fe cycle in which interior Fe concentrations were held at a quasi-constant value of 0.6 nmol L⁻¹ assuming a constant concentration of Fe-binding ligands (7). Thus the FeMIP models are balancing widely varying Fe input fluxes against relatively constant overall Fe concentrations by tuning the Fe scavenging rate, which is a crucial but poorly known parameter. This results in residence times for Fe that range from <5 to >500 years across the FeMIP models (Fig 1c). This difference is important, as it represents substantial inter-model deviation concerning the timescales over which the different models respond to a perturbation in Fe supply.

When compared statistically against the global dataset, similar levels of variability arise. Some models display correlation coefficients of >0.5, whereas others are slightly anti-correlated. When the FeMIP models are compared against the five GEOTRACES sections, it becomes apparent that those models that represent the newly emerging features of the iron cycle perform much better. For instance, having Fe scavenging rates that vary in space and time, including variable Fe:carbon (C) stoichiometry, multiple Fe sources, and representing ligand concentrations in a dynamic manner, all act to improve the representation of different observed features in the models. Importantly, the IDP2014 provided the opportunity to demonstrate that the issues at hand were specific to Fe, since the models could represent the observed distributions of major nutrients with a much greater degree of skill (5).

The next stage of FeMIP will be a deeper comparison of the processes themselves. Of particular interest is whether GEOTRACES datasets can provide broader assessments of the rates of Fe scavenging – e.g., using other particle-reactive, non-biological tracers such as thorium (8, 9). Equally, the emerging database of GEOTRACES process studies provides an important opportunity to appraise the way different models represent biological iron cycling and in particular, the often-observed importance of recycled and remineralized sources of Fe (10, 11). Finally, the new GEOTRACES intermediate data product 2017 will also facilitate further evaluation of models, providing new section data from the Atlantic, Pacific and Arctic Oceans.

References

1. L. Bopp et al., *Biogeosci.* **10**(10), 6225-6245, doi:10.5194/bg-10-6225-2013 (2013).
2. C. M. Moore et al., *Nature Geosci.*, doi:10.1038/ngeo1765 (2013).
3. S. Levitus et al., *Prog. Oceanogr.* **31**(3), 245-273, doi:10.1016/0079-6611(93)90003-v (1993).
4. A. Tagliabue et al., *Biogeosci.* **9**(6), 2333-2349, doi:10.5194/bg-9-2333-2012 (2012).
5. A. Tagliabue, A. et al., *Glob. Biogeochem. Cycles*, doi:10.1002/2015gb005289 (2016).
6. E. Mawji et al., *Marine Chem.* **177**, 1-8, doi:10.1016/j.marchem.2015.04.005 (2015).
7. K. S. Johnson, R. M. Gordon, K. H. Coale, *Marine Chem.* **57**(3-4), 137-161, doi:10.1016/s0304-4203(97)00043-1 (1997).
8. C. T. Hayes et al., *Geochim. Cosmochim. Acta* **169**, 1-16, doi:10.1016/j.gca.2015.07.019 (2015).
9. N. Rogan et al., *Geophys. Res. Lett.* **43**(6), 2732-2740, doi:10.1002/2016gl067905 (2016).
10. P. W. Boyd et al., *Glob. Biogeochem. Cycles* **29**(7), 1028-1043, doi:10.1002/2014gb005014 (2015).
11. R. F. Strzepek et al., *Glob. Biogeochem. Cycles* **19**(4), GB4S26, doi:10.1029/2005gb002490 (2005).

Trace metal uptake and remineralization and their impact on upper ocean stoichiometry

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1. Stoichiometry of metals in the ocean

The close relationship between the stoichiometry of nutrients dissolved in the upper ocean and the planktonic organisms that grow in these waters has long been recognized (1, 2). The stoichiometry of 106 C:16 N:1 P first summarized by Redfield has become a fundamental concept of marine biogeochemistry, with numerous studies using the ratio as a benchmark to assess ecosystem function. Decades after the work of Redfield, with the implementation of trace metal-clean techniques, oceanographers produced the first meaningful measurements of dissolved trace metals in the open ocean (3-5), and they found that many of the bioactive metals such as Fe, Zn, Ni, Cu and Cd are also depleted in surface waters and enriched at depth, similar to the macronutrients. Such nutrient-like behavior supported not only a growing understanding of the physiological roles that these metals play in phytoplankton physiology (6), but it also indicated that biological uptake and sub-surface remineralization were important processes for controlling the distributions of these bioactive metals in the ocean. Thus, the biogeochemical behavior of the micronutrient metals is in many ways analogous to that of the macronutrients N, P and Si.

In the open ocean far from coastal and shelf influences, dissolved concentrations of bioactive metals increase with depth at relatively consistent ratios to macronutrients (5), and these metal:nutrient remineralization ratios have been used to approximate the composition of sinking biogenic material and euphotic zone phytoplankton (7, 8). These 'extended Redfield ratios' have been compared to average compositions of marine phytoplankton species grown in culture (9-12),

and the general agreement between these approaches further supports the importance of biological uptake and subsequent remineralization of trace metals in the upper ocean as key processes impacting trace metal geochemistry. Average metal:nutrient stoichiometries for phytoplankton have also been compared to dissolved stoichiometries in the ambient water, and relationships between these fractions have been used to estimate nutrient limitation and deficiency in the ocean (13). Thus, there is significant interest in controls on upper ocean metal stoichiometries, as well as the relationships between cellular/biological, particulate and dissolved fractions.

Analogous to macronutrients, there are also relationships between metal stoichiometries in phytoplankton

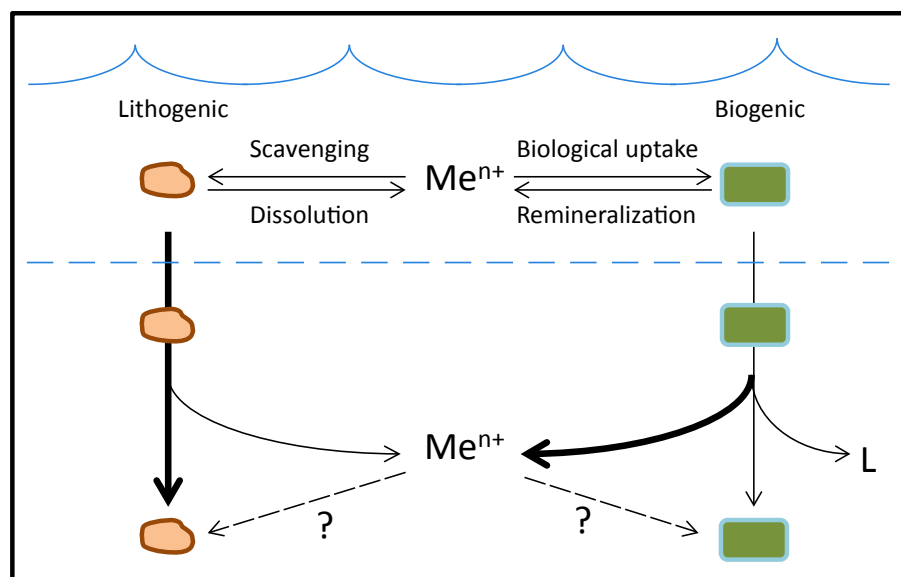


Figure 1. Diagram representing the chemical and biological processes controlling the partitioning of elements between dissolved and particulate forms in the upper ocean. The brown particle represents lithogenic matter, likely sourced from aeolian dust, continental run-off or sediment resuspension. The green particle represents biologically derived material. Arrows indicate the primary routes of metal uptake into/onto particles and release from particles into the dissolved phase (Me^{n+}). As these model particle types sink in the ocean they are likely to be affected to differing degrees by thermodynamic and biological remineralization processes; this is represented by the relative thicknesses of the arrows. Degradation of biological material also results in the potential release of metal-binding organic ligands (L). The processes of differential remineralization vs. (re) scavenging are difficult to discern and are largely unconstrained. The horizontal blue dashed line corresponds roughly to the bottom of the euphotic zone.

and those in deeper waters of the ocean. Departures from these relationships are likely to provide insights into the internal biogeochemical cycling of metals in the ocean. Morel and Hudson (7) noted differences in the extended stoichiometries of plankton and the water column and concluded that they must reflect the relative efficiency of remineralization of the elements, as well as the propensity of elements to be scavenged onto sinking particles in the sub-surface ocean. Similarly, the rapid remineralization of trace metals from sinking plankton was addressed in seminal work by Collier and Edmond (14). Using carefully collected data on surface plankton material, and with more computational rigor than (7), they compared surface particle stoichiometries to deep water dissolved

stoichiometries and calculated the relative remineralization of plankton-associated elements in sinking biogenic material. They noted significant differences among the behaviors of biogenic metals such as Cd, Ni and Fe due to their scavenging and remineralization behaviors. More recently, Morel (15) mused about these processes and their relationships to cellular biochemistry and evolution of phytoplankton physiology and ocean biogeochemistry. Through the GEOTRACES program, the data to test and extend these early, relatively simple box models and stoichiometric comparisons are now available. Metal concentrations and stoichiometries for phytoplankton, bulk and size-fractionated particulate material, and co-located dissolved species have been measured in the North Atlantic and South Pacific Oceans thus far.

Combined with data for non-bioactive metals such as Ti and Th, these data also provide the opportunity to discern the behavior and contributions of lithogenic vs. biogenic matter, as well as the processes of remineralization and scavenging.

2. Processes affecting dissolved and particulate stoichiometries of trace metals

Vertical profiles of dissolved macronutrients show characteristic depletion at the surface and enrichment at depth due to remineralization, and dissolved micronutrients often show the same behavior. However, the internal cycling of metals in the ocean is expected to differ from that of macronutrients for a few salient reasons. Some metals such as Fe are significantly less soluble than macronutrients and are prone to abiotic adsorption onto particulate surfaces (16). This process is driven by thermodynamics, and the accompanying process of desorption also occurs; the net observed process is typically called 'scavenging' (Fig. 1). Scavenging in the deep ocean causes concentrations of less soluble metals such as Fe and Al to decrease along the path of thermohaline circulation, in contrast to macronutrients and more soluble

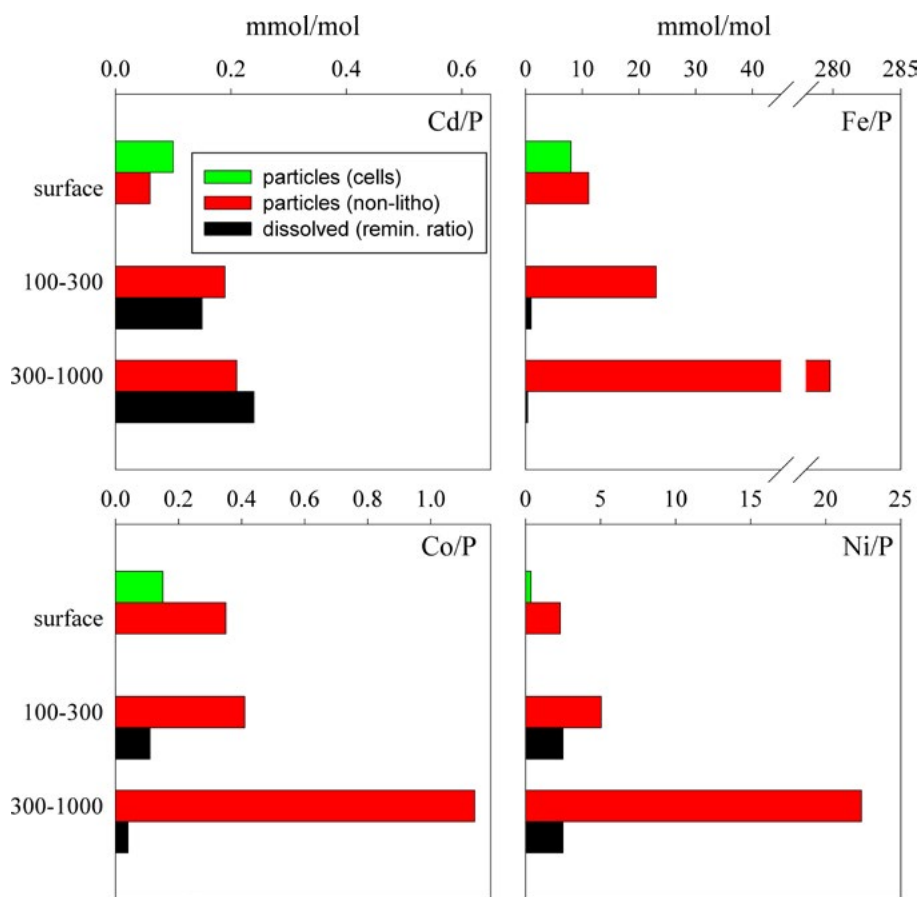


Figure 2. Metal:phosphorus ratios in dissolved and particulate fractions in the upper ocean. Data were collected as part of US GEOTRACES North Atlantic Zonal Transect cruise (19; Noble et al. in prep; C. Parker and K. Bruland unpublished, 35-37) and are available online through the GEOTRACES Intermediate Data Product 2014 (38). Cellular ratios (green) were measured directly with synchrotron x-ray fluorescence analysis (except for Cd:P, which was estimated from digests of labile particulate material). Bulk particulates (red) have been corrected for lithogenic material using Ti (see text for details) and are median values for cruise stations 12-22. Remineralization ratios (black) have been calculated with linear regressions of dissolved data (see text for details) and are mean values for these cruise stations. Depth ranges are given in meters.

metals that may mimic macronutrient behavior such as Cd and Zn (17). In the absence of significant lateral nutrient inputs, the balance of scavenging and remineralization will influence the resulting vertical profiles of dissolved elements (18).

Another key difference between macronutrients and metals is the importance of abiotic particulate fractions such as lithogenic (e.g., aeolian dust and sediment) and authigenic (e.g., Fe- and Mn-oxyhydroxide) phases. While biogenic phases are almost universally produced at the surface and remineralized with depth, abiotic phases can exhibit very different and dynamic internal cycles (19). Dust events, lateral transport and poorly constrained scavenging processes can both deliver and remove specific metals alongside biological processes. Lithogenic phases are generally denser and more refractory than biogenic particles and detritus and are thought to sink more rapidly and remineralize more slowly and at greater depth (Fig. 1; 20). Lithogenic particles may also (re)scavenge metals differently than biogenic material. Efforts to examine these processes in sinking material have been extremely limited to date, with only a few studies examining metals in trace metal-clean sediment traps (21, 22). However, recently published datasets from the GEOTRACES program are shedding new light on the multiple facets of metal partitioning and how they affect subsurface remineralization and scavenging.

A comparison of metal:phosphorus ratios in the upper ocean illuminates some of these processes. Figure 2 displays Cd:P, Fe:P, Co:P and Ni:P ratios in particles in the upper 100m, 100-300m, and 300-1,000m of the water column in the middle of the North Atlantic basin. Particulate material is sub-divided into ratios for phytoplankton cells and non-lithogenic particles (corrected for lithogenic minerals using Ti; 19). Also plotted are dissolved remineralization ratios (that is, the slope of a linear regression between the dissolved metal and phosphate) for these upper ocean depth ranges. The close coupling of Cd and P biogeochemistry has long been recognized (4), and indeed we observe very close agreement (within a factor of about 2) between dissolved Cd:P remineralization and Cd:P in surface ocean particles, as well subsurface particles. Clearly these elements are remineralizing from sinking particles at similar rates. Such comparisons of particulate and dissolved constituents need to carefully consider the different residence times of these fractions and the likelihood for lateral inputs. Here, we have chosen to focus on stations from the mid-North Atlantic gyre, where the upper 700m of the water column consists primarily of a single water mass (23).

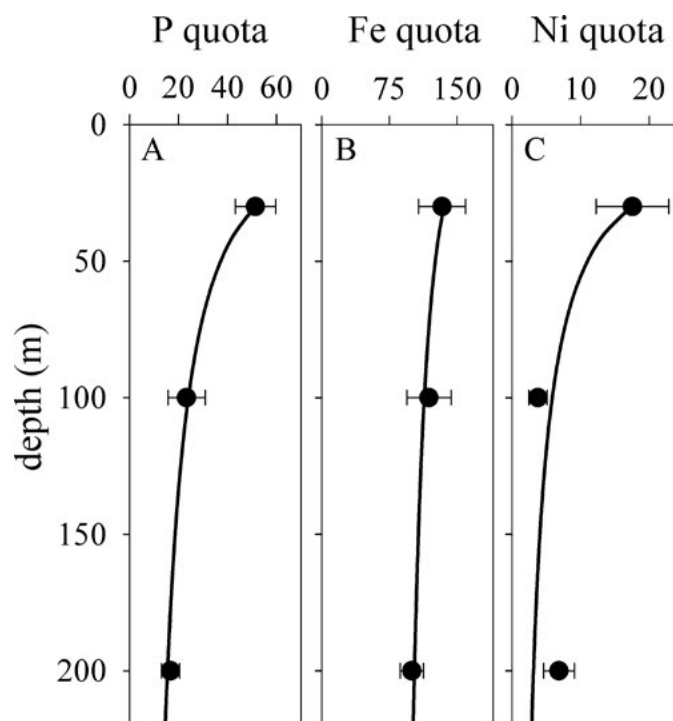


Figure 3. Depth profiles of cellular element quotas for *Asterionellopsis glacialis* diatoms collected during a spring bloom east of New Zealand. Symbols are means $\pm$ SE ($n=5-14$). A power-law function ($\text{flux} = a(\text{depth})^{-b}$; ie. a 'Martin curve') has been fit to each data set. Phosphorus quotas are presented as fmol cell^{-1} , and Fe and Zn quotas are presented as amol cell^{-1} . Modified from (30).

In contrast, the remineralization of Fe and P are quickly decoupled in the water column (Fig. 2). Between 100 and 300m, typically the depth of most rapid regeneration of sinking organic material, labile particulate Fe:P has more than doubled from that in surface waters, and the Fe:P ratio of remineralized dissolved elements (0.98 mmol/mol) is more than 10-fold below that of the labile material that is sinking into these waters. Looking deeper into the water column, Fe and P continue to decouple in labile (i.e., non-lithogenic) particulates, with Fe:P of 300-1,000m particles increasing 10-fold and the dissolved remineralization ratio being nearly 1,000-fold lower (0.35 mmol/mol). Additionally, organic ligands play an important role in stabilizing dissolved Fe (24), so dissolved Fe and P ratios may be further decoupled by biological processes impacting the production and fate of these ligands (20).

A strength of GEOTRACES datasets is their wide coverage of the periodic table, and additional insights can be gained from looking at the behaviors of other bioactive trace metals that are also incorporated into sinking biogenic material. Co:P ratios in particles and remineralized dissolved fractions in the water column follow the

same trend as Fe, but the decoupling of Co and P is much more subtle than with Fe, presumably due to differences in ligand coordination and Co co-oxidation with Mn (25, 26). Dissolved Co:P remineralization ratios at 100-300m generally match those found in phytoplankton and drop only 3-fold below 300m. Similarly, labile particulate Co:P ratios don't change between 0-100m and 100-300m, also indicating that Co and P remineralize in tandem in the upper 300m. Below 300m, labile particulate Co:P increases approximately 3-fold (in contrast with Fe:P, which increases 12-fold), and this depth effect matches the effect in dissolved remineralization ratios. Thus, even though Fe and Co are considered hybrid metals that display both biological uptake and scavenging, there are clear differences in the behaviors of these metals. Nickel provides yet another perspective on the coupling of metals and P. Dissolved remineralization ratios in both subsurface depth ranges closely resemble surface ocean labile particles, supporting the biological coupling of Ni and P (5). However, residual labile particulate Ni:P increases 2- to 4-fold in successive depth ranges, indicating that remineralization is rather decoupled. Given that Ni seems to be associated with both organic material and opal frustules in diatoms (27), it may be that Ni and P are remineralized from particulate organic matter in tandem, but some Ni remains associated with sinking biogenic silica in the ocean.

3. Additional tools to explore and differentiate remineralization processes

The GEOTRACES program has welcomed the application of new analytical approaches that further enable us to study the cycling of metals in the ocean. Spectroscopy and quantitative imaging methods using synchrotron radiation have become more common in the past decade (28), and these allow us to analytically distinguish the behaviors of different fractions of particle assemblages. During the FeCycle II project, a GEOTRACES process study, the fate of Fe was tracked during a spring diatom bloom (29). Diatom cells from the dominant bloom species (*Asterionellopsis glacialis*) were collected in surface waters and from trace-metal clean sediment traps at 100m and 200m in the 48h following the decline of the bloom. Synchrotron x-ray fluorescence (SXRF) analyses of individual cells showed that constituent elements were lost from sinking cells at notably different rates (Fig. 3). Phosphorus was rapidly released from sinking cells, with mean P quotas decreasing 55% and 73% from surface values by 100m and 200m, respectively (30). However, only

25% of cellular Fe was lost from cells sinking through the upper 200m, while 61% of cellular Ni was remineralized. This supports the story told by the bulk biogeochemical data from the North Atlantic: Ni is remineralized largely to a similar degree as P, while Fe is lost more slowly from sinking biogenic material.

Application of microanalytical techniques such as SXRF can be combined with bulk approaches to further advance understanding of subsurface metal remineralization and cycling. In FeCycle II, Fe:P of sinking *A. glacialis* cells increased, on average, only 2.3-fold in the upper 200m, while Fe:P in bulk particulate matter increased more than 13-fold (30). This indicates that the behavior of sinking cells was not representative of the full particle assemblage. Iron and P were likely more completely decoupled in sinking fecal pellets and detrital material (which appears to have contributed significantly to the particulate Fe pool during FeCycle II; 31) than in intact sinking cells. Further application of this approach will allow us to not only distinguish between the behavior of biogenic and lithogenic fractions (Fig. 1), but potentially also between detrital particles. By considering metals such as Mn that are prone to oxidation and scavenging in the subsurface ocean (32, 33), it may also be possible to separate abiotic scavenging from net biological remineralization (Fig. 1). Additionally, 2D (and potentially 3D) mapping of elements within cells and particles also provides information about the spatial and potentially chemical associations of elements with particles (30, 34).

The GEOTRACES program is generating unprecedented data, both in terms of quality and quantity, regarding the cycling of bioactive trace metals in the ocean. Syntheses of these data, and integration of insights from novel microanalytical tools, as well as transcriptomic and proteomic approaches, are resulting in substantial advances in our understanding of metal biogeochemistry. No longer are we limited to a few painstakingly collected dissolved metal profiles. There is now painstakingly collected full-depth coverage of most ocean basins, including in many cases dissolved and particulate fractions of nearly all biogenic elements, enabling testing of early hypotheses about trace metal cycling and parameterization of these processes into next-generation ocean biogeochemical models.

Acknowledgments

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References

1. A. C. Redfield, in *James Johnstone Memorial Volume*, R. J. Daniel, Ed. (Liverpool University Press, 1934), pp. 176-192.
2. A. C. Redfield, *Amer. Scientist* **46**, 205-221 (1958).
3. E. A. Boyle, J. M. Edmond, *Nature* **253**, 107-109 (1975).
4. E. A. Boyle, F. Sclater, J. M. Edmond, *Nature* **263**, 42-44 (1976).
5. K. W. Bruland, *Earth Plan. Sci. Lett.* **47**, 176-198 (1980).
6. J. R. R. Frausto da Silva, R. J. P. Williams, *The Biological Chemistry of the Elements: the inorganic chemistry of life*. (Oxford University Press, Oxford, ed. 2nd, 2001), pp. 575.
7. F. M. M. Morel, R. J. M. Hudson, in *Chemical Processes in Lakes*, W. Stumm, Ed. (John Wiley & Sons, New York, 1985), pp. 251-281.
8. K. W. Bruland, J. R. Donat, D. A. Hutchins, *Limnol. Oceanogr.* **36**, 1555-1577 (1991).
9. T. Y. Ho et al., *J. Phycol.* **39**, 1145-1159 (2003).
10. W. G. Sunda, *Marine Chem.* **57**, 169-172 (1997).
11. W. G. Sunda, S. A. Huntsman, *Limnol. Oceanogr.* **40**, 132-137 (1995).
12. W. G. Sunda, S. A. Huntsman, *Limnol. Oceanogr.* **40**, 1404-1417 (1995).
13. C. M. Moore et al., *Nature Geosci.* **6**, 701-710 (2013).
14. R. Collier, J. Edmond, *Prog. Oceanogr.* **13**, 113-199 (1984).
15. F. M. M. Morel, *Geobiol.* **6**, 318-324 (2008).
16. M. Whitfield, D. R. Turner, in *Aquatic Surface Chemistry: Chemical Processes at the Particle-Water Interface*, W. Stumm, Ed. (John Wiley & Sons, Inc., 1987), pp. 457-493.
17. K. W. Bruland, M. C. Lohan, in *The Oceans and Marine Geochemistry: Treatise on Geochemistry*, H. Elderfield, Ed. (Elsevier, Oxford, 2003), pp. 23-47.
18. P. W. Boyd, M. J. Ellwood, *Nature Geosci.* **3**, 675-682 (2010).
19. D. C. Ohnemus, P. J. Lam, Cycling of lithogenic marine particles in the US GEOTRACES North Atlantic Transect. *Deep-Sea Res. II* **116**, 282-302 (2015).
20. P. W. Boyd et al., *Limnol. Oceanogr.* **55**, 1271-1288 (2010).
21. R. D. Frew et al., *Glob. Biogeochem. Cycles* **20**, GB1S93, doi:10.1029/2005GB002558 (2006).
22. C. H. Lamborg, K. O. Buesseler, P. J. Lam, *Deep-Sea Res. II* **55**, 1564-1577 (2008).
23. W. J. Jenkins et al., *Deep-Sea Res. II* **116**, 6-20 (2015).
24. M. Gledhill, K. N. Buck, *Frontiers Microbiol.* **3**, doi: 10.3389/fmicb.2012.00069 (2012).
25. J. W. Moffett, J. Ho, *Geochim. Cosmochim. Acta* **60**, 3415-3424 (1996).
26. A. E. Noble et al., *Limnol. Oceanogr.* **57**, 989-1010 (2012).
27. B. S. Twining et al., *Glob. Biogeochem. Cycles* **26**, GB4001, doi: 4010.1029/2011GB004233 (2012).
28. P. J. Lam et al., *Prog. Oceanogr.* **133**, 32-42 (2015).
29. P. W. Boyd et al., *Geophys. Res. Lett.* **39**, doi:10.1029/2012GL053448 (2012).
30. B. S. Twining et al., *Limnol. Oceanogr.* **59**, 689-704 (2014).
31. A. L. King et al., *Biogeosci.* **9**, 667-687 (2012).
32. J. P. Cowen, K. W. Bruland, *Deep-Sea Res.* **32**, 253-272 (1985).
33. D. C. Ohnemus et al., *Limnol. Oceanogr.* **In press** (2016).
34. J. Nuester, S. Vogt, B. S. Twining, *J. Phycol.* **48**, 626-634 (2012).
35. B. S. Twining et al., *Prog. Oceanogr.* **137**, 261-283 (2015).
36. M. Hatta et al., *Deep-Sea Res. II* **2015**, 117-129 (2015).
37. S. Roshan, J. Wu, *Glob. Biogeochem. Cycles* **29**, 2082-2094 (2015).
38. E. Mawji et al. *Marine Chem.* **177**, 1-8 (2015).



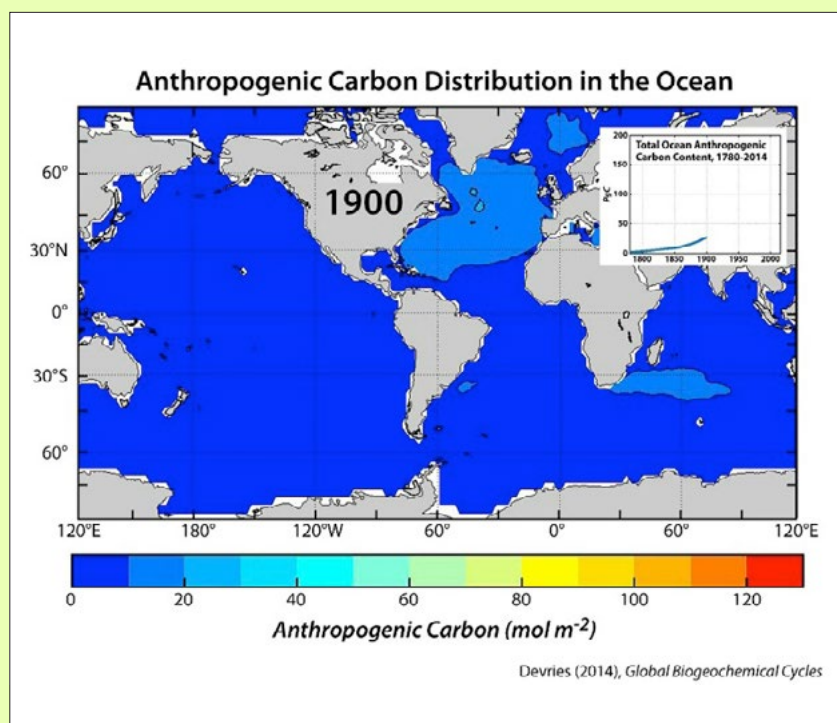
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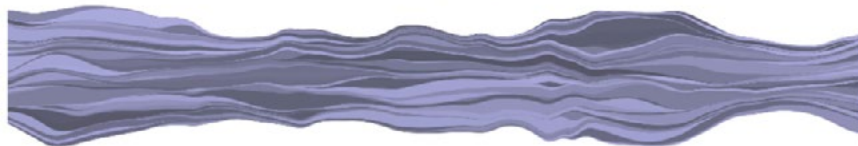
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- Gattuso J.-P. 2016. *An Ocean Scientist at COP21. Limnology and Oceanography Bulletin*. doi:10.1002/lob.10087
- IOCCP Position Paper on Global Ocean Biogeochemistry Data Management
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- U.S.-Canada Joint Statement on Climate, Energy, and Arctic Leadership
- SOLAS article Scientific synthesis and contribution to Earth system science
- GO-SHIP Global Repeat Hydrography review paper (Talley et al., 2016)



Burd, A. et al. (In review). Towards a transformative understanding of the ocean's biological pump: Priorities for future research. Report of the NSF Biology of the Biological Pump Workshop, February 19-20, 2016 (Hyatt Place New Orleans, New Orleans, LA), 36 pp.

- NASA EXPORTS paper in *Frontiers in Marine Science*
- Announcing the 2017 *Limnology and Oceanography* Special Issue “Headwaters to oceans: ecological and biogeochemical contrasts across the aquatic continuum” (Manuscripts due November 7, 2016)

Report on the “Trait-based Approaches to Ocean Life” Scoping Workshop



October 5-8, 2015
Waterville Valley, NH, USA

Report Authors and Meeting Conveners: Andrew Barton (Princeton University, NOAA Geophysical Fluid Dynamics Laboratory) and Stephanie Dutkiewicz (Massachusetts Institute of Technology)

Steering Committee: Ken H. Andersen (Technical University of Denmark), Øyvind Fiksen (University of Bergen), Mick Follows (Massachusetts Institute of Technology), Colleen Mouw (Michigan Technological University), Nick Record (Bigelow Laboratory for Ocean Sciences), Tatiana Rynearson (University of Rhode Island)



SIMONS FOUNDATION

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FOUNDATION  NASA



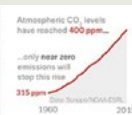
Science Products

- Version 3 - GEOTRACES Intermediate Data Product, IDP2014
- Submit your data for the next GEOTRACES Intermediate Data Product, IDP2017
- New SCOR-JAMSTEC Nutrient Certified Reference Materials (CRMs) will soon be available
- US CLIVAR webinar series
- GLObal Ocean Data Analysis Project version 2 (GLODAPv2) WAVES system
- LDEO (Takahashi) Surface pCO₂ database V2015
- Global Carbon Budget 2015

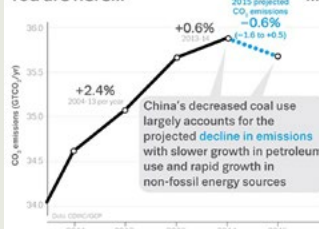
Infographic on the **Global Carbon Budget 2015** released by the Global Carbon Project (Le Quéré et al. (2015), *Earth System Science Data*, DOI:10.5194/essd-7-349-2015).

Global Carbon Budget 2015

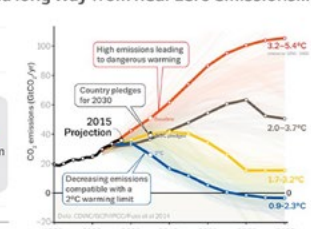
Emissions from fossil fuels and industry **grew +0.6% in 2014**, and are projected to **decline by -0.6% (-1.6 to +0.5) in 2015**. This marks a break in the rapid emissions growth of 2.4% of the previous decade



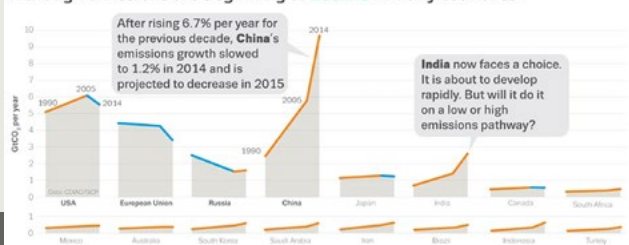
You are here...



...a long way from near zero emissions...



...though emissions are beginning to decline in many countries



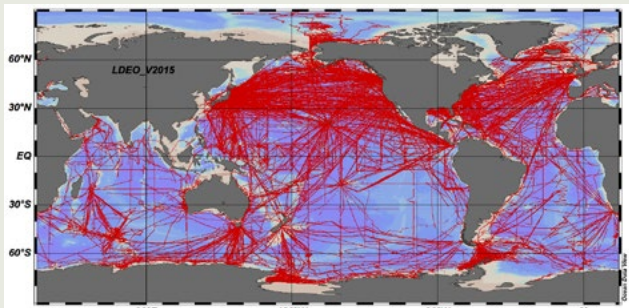
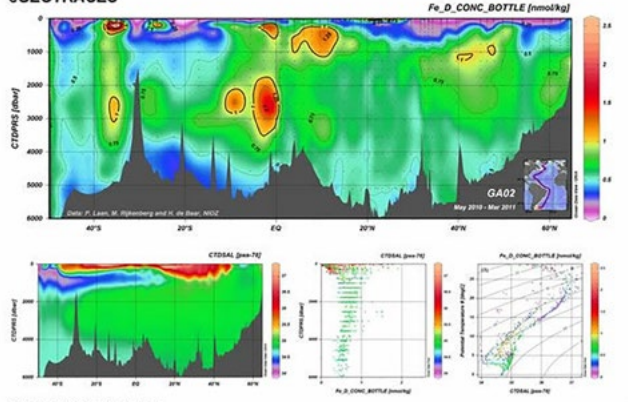
Global emissions must quickly drop to zero to hold to 2°C

Our average per capita emissions are 4.9 tCO₂ each year



Distribution of dissolved iron (Fe) along GEOTRACES North Atlantic GA02 section. Patrick Laan, Micha Rijkenberg and Hein de Baar (Mawji, E., et al. (2015), The GEOTRACES Intermediate Data Product 2014, *Mar. Chem.*, <http://dx.doi.org/10.1016/j.marchem.2015.04.005>).

eGEOTRACES



Location of LDEO V2015 master database of sea surface pCO₂ observations from Takahashi et al. (2016), *Global Ocean Surface Water Partial Pressure of CO₂ Database: Measurements Performed During 1957-2015 (Version 2015)*. ORNL/CDIAC-160, NDP-088(V2015). Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tennessee, doi: 10.3334/CDIAC/OTG.NDP088(V2015).



Ocean Acidification Community News

- 7th *Ocean Acidification Report* from Global Ocean Health
- Latest edition of the OA-ICC Highlights
- New Latin American Ocean Acidification (LAOCA) Network
- Report from international workshop Bridging the Gap Between Ocean acidification Impacts and Economic Valuation
- New open access L&O e-lecture "Combined Effects of Ocean Acidification, Warming, and Hypoxia on Marine Organisms"
- Ocean Acidification International Coordination Centre (OA-ICC) training course on ocean acidification (September 5-10, 2016, Ensenada, Mexico)

Recent Events



Reflections on the 4th International Symposium on the Ocean in a High-CO₂ World: Embrace Complexity

May 3-6, 2016 (Hobart, Tasmania, Australia)

Jessica Cross (NOAA/PMEL) and Heather Benway (WHOI)

The [Fourth International Symposium on the Ocean in a High CO₂ World](#) (High CO₂ IV) was held this year in Tasmania, Australia. Ocean acidification (OA) is an imminent environmental challenge for Australia, which is home to world-renowned coral reef ecosystems. In addition to reduced calcification rates associated with OA (1), this year Australia's iconic wonder - the Great Barrier Reef (GBR) - has undergone the [worst bleaching event on record](#) in response to unrelenting warm ocean temperatures associated with the recent El Niño event. Australian marine resource managers are struggling with how to responsibly balance an economically critical tourism industry with the protection and preservation of the remaining healthy parts of the GBR.

The High CO₂ World meeting series is one of my favorites. It seems like the community saves their best new work

for this conference, so many of the talks are high-impact and highlight important progress in the field. It's more than just individual talks, though: The organizers of these meetings do an excellent job of highlighting the current, cutting-edge trends in ocean acidification research, and focus on the progress that we have made as a community over the previous four years. Overall, a common theme of this meeting implored the OA research community to *Embrace Complexity*.

Similar to the last High CO₂ conference held in Monterey, CA in 2012, much of the research presented focused on organismal responses and ecological effects of ocean acidification. Although the themes might have been similar this year, it was obvious that much progress had been made since the last meeting. The multiple stressor



Katharina Fabricius delivering her plenary talk
(Photo credit: Alastair Bett, F8 Photography)

framework now represents an important benchmark for studying marine ecosystem response to changing climate and ocean conditions. Experimentation is increasingly moving from the laboratory into the field, where an organism can be observed in its natural environment. *In-situ* experiments can often shed light on unexpected fitness, resilience, and vulnerability that may not be present in a sterile, rigidly controlled laboratory setting. Katharina Fabricius gave an excellent plenary talk focusing on the complex methods and benefits of *in-situ* experimentation related specifically to coral reefs. These field-based experiments are accompanied by a unique set of challenges, but new progress is being made in this area (1), especially through the use of mesocosms and long-term ecological research stations.

Linking species and ecosystem responses to models is another rapidly expanding area of OA research. Kristy Kroeker gave one of the best-received plenaries of the week on Tuesday, overviewing the challenges of projecting ecological impacts critical to forecast models. Experimentation and projections are becoming increasingly nuanced, which will hopefully lead to improved model performance in the future. A great example of this process is the J-SCOPE acidification forecast model developed for the Washington and Oregon coasts (2).

However, the tradeoff of increasing specification is the often narrower application of the results. Given the limited available resources to support ocean acidification research, this increasing specialization represents a serious problem, as highlighted by Ken Caldeira in the closing plenary. However, designing experiments that don't have any such limitations is extremely difficult, if not impossible. Instead, the value of these focused studies may lie in their aggregation. Meta-analysis, linking OA impacts to mechanisms and functional groups across species-level barriers was also a prominent theme at the conference. Plenary sessions on the last day by Sam Dupont and Sinead Collins both focused on the applications of ecological theory and evolution to consolidate understanding of OA impacts.

Overall, embracing the complexity and increasing specialization in our field requires enhanced cooperation. This is imperative on the international level, where scientific organizations can collaborate across political boundaries, but also critical between science and other industries. Building trust in scientific research, collaborating on projects to build local community resilience and develop adaptive capacity, and engaging in responsible risk assessment were emphasized in nearly every session. By *working better together*, as Ken Caldeira closed with, we may be able to meet the challenges posed by ocean acidification and other environmental stressors rather than just predict them.



Kristy Kroeker delivering her plenary talk
(Photo credit: Alastair Bett, F8 Photography)

The 3rd Global Ocean Acidification Observing Network Science Workshop

May 8-10, 2016 (Hobart, Tasmania, Australia)

Jessica Cross (NOAA/PMEL) and Heather Benway (WHOI)



The High CO₂ IV conference was followed by the [3rd Global Ocean Acidification Observing Network \(GOA-ON\) science workshop](#), held May 8-10, 2016 at [Commonwealth Scientific and Industrial Research Organisation \(CSIRO\)](#). Involving 130 people from over 40 countries, this truly global workshop was designed to facilitate the clear calls for cooperation we heard at the High CO₂ IV conference. Breakout groups focused on building regional research hubs that facilitate resource sharing and capacity building. The GOA-ON organizing committee also launched the [Pier-2-Peer mentorship program](#), which seeks to link researchers in developing countries with established members of the international OA research community to facilitate professional development, share expertise, and integrate these researchers into the international OA research community via the regional hubs.

Outside the broader discussion periods, the workshop also included breakout sessions for the regional groups.

During these regional breakouts, participants discussed their current observing strengths and weaknesses, which led to avoid discussions of gaps in knowledge and new observing needs. The increasing availability and relative cost-effectiveness of autonomous platforms are increasing the reach of many ocean acidification monitoring experiments, but these platforms and sensors also represent new observing challenges. Understanding how best to incorporate these new technologies into OA research, including robust calibration practices, responsible error analysis, data management, and product generation will be an increasingly important way forward for the OA research community.

References

1. R. Albright et al. *Nature* **531** doi:10.1038/nature17155 (2016).
2. S. Siedlecki et al. *Nature Scientific Reports* 6 doi: 10.1038/srep27203 (2016).



GOA-ON Science Workshop participants (Photo credit: Libby Jewett, NOAA Ocean Acidification Program)

Calendar

Please note that we maintain an *up-to-date calendar* on the OCB website.

2016	
July 4-22	BIOS Modern Observational Oceanography course (BIOS, Bermuda)
July 5-7	Antarctic Science Conference (Norwich, UK)
July 11-15	PRIMER-E Workshop on multivariate statistics for ecologists (Raleigh, NC)
July 16-17	Ocean Global Change Biology Gordon Research Seminar (Waterville Valley, NH)
July 17-22	Ocean Global Change Biology Gordon Research Conference (Waterville Valley, NH)
July 18-20	AtlantOS best practices workshop on trace element measurements in oceanography (Plymouth, UK)
July 24-29**	Gordon Research Conference Unifying ecology across scales (Biddeford, ME)
July 25-28*	2016 OCB Summer Workshop (Woods Hole, MA)
August 1-4*	Joint OCB/GEOTRACES workshop: Internal Cycling of Trace Elements in the Ocean (Palisades, NY)
August 10-11**	Forecasting ENSO Impacts on Marine Ecosystems (San Diego, CA)
August 10-17**	IMBER ClimECO5 Summer School (Natal, Brazil)
August 31-September 4	1st Altimetry for Regional and Coastal Ocean Models Workshop (Pilot ARCOM Workshop) (Lisbon, Portugal)
September 5-10	Ocean Acidification International Coordination Centre (OA-ICC) training course on ocean acidification (Ensenada, Mexico)
September 6-9	2nd International workshop on Air-Sea Gas Flux Climatology (Brest, France)
September 6-8	Colour and Light in the Ocean from Earth Observation (CLEO) workshop: Relevance and Applications Products from Space and Perspectives from Models (Frascati, Italy)
September 12-13	Ocean ventilation and deoxygenation in a warming world (London, UK)
September 18-25	CLIVAR Open Science Conference: Charting the course for future climate and ocean research (Qingdao, China)
September 19-23	ICES Annual Science Conference (Riga, Latvia)
September 26-29	7th EGO (Everyone's Gliding Observatory) conference on Autonomous Ocean Gliders & their Applications (Southampton, UK)
September 26-30	International Global Atmospheric Chemistry (IGAC) Project 2016 Science Conference (Breckenridge, CO)
September 27-29	European Integrated Carbon Observation System (ICOS) 2nd Science Conference on Greenhouse Gases and Biogeochemical Cycles (Helsinki, Finland)
September 30-October 1	Sustainable Oceans Conference – Into the Blue: The Body Connecting Us All (Halifax, Canada)
October 5-7	US GEOTRACES Alaska-Tahiti Planning Workshop (La Jolla, CA)
October 9-14	Dissertations Symposium in Chemical Oceanography (DISCO) XXV meeting (Honolulu, HI)
October 11-13	IMDIS 2016 - the International Conference on Marine Data and Information Systems (Gdansk, Poland)
October 14-16	COME ABOARD! Chemical Oceanography MEeting: A B0ttom-up Approach to Research Directions (Honolulu, HI)
*OCB-led activity **OCB co-sponsorship or travel support	

2016	
October 23-28**	Ocean Optics 2016 (Victoria, BC Canada)
October 23-29	Eco-DAS XII (Honolulu, HI)
October 26-27	SOLAS Science and Society (Brussels, Belgium)
November 1-13	25th Anniversary Annual Meeting of the North Pacific Marine Science Organization (PICES) (San Diego, CA)
November 3-11	2016 Pan Ocean Remote Sensing Conference (PORSEC) (Fortaleza, Brazil)
November 9-12	2016 NAKFI Conference Discovering the Deep Blue Sea: Research, Innovation, Social Engagement (Irvine, CA)
November 14	International Conference on Marine Environment of the Red Sea (ICMERS 2016) (Thuwal, Saudi Arabia)
December 6-8	2nd International Marine Science Communication conference & high-level training workshop (Bruges and Ostend, Belgium)
December 12-16	Fall AGU Meeting (San Francisco, CA)
*OCB-led activity **OCB co-sponsorship or travel support	

2017	
January 9-11	Third Xiamen Symposium on Marine Environmental Sciences (XMAS 3) (Xiamen, China)
January 18-19	Workshop on Environmental Concentrations, Cycling & Modelling of Technology Critical Elements (Rehovot, Israel)
February 26-March 3	2017 ASLO Aquatic Sciences Meeting (Honolulu, HI)
May 21-26	14th International Symposium on the Interactions between Sediments and Water (Taormina, Italy)
May 22-25	International Conference on High Latitude Dust 2017 (Reykjavik, Iceland)
July 22-23	Gordon Research Seminar (New London, NH)
July 23-28	Gordon Research Conference in Chemical Oceanography (New London, NH)
August 13-18	Goldschmidt 2017 (Paris, France)
August 21-25	10th International Carbon Dioxide Conference (Interlaken, Switzerland)
October 2-6	IMBER IMBIZO V: Marine biosphere research for a sustainable ocean: Linking ecosystems, future states and resource management (Woods Hole, MA)
*OCB-led activity **OCB co-sponsorship or travel support	

Upcoming Funding Opportunities

For more information, please visit OCB's *funding opportunities web page*. The *OCB calendar* also lists upcoming deadlines.

- NSF Research Coordination Networks (RCN)
- NSF North Atlantic-Arctic Dear Colleague Letter
- NOAA SBIR Phase I Solicitation for Fiscal Year 2016
- Full list of upcoming NSF proposal deadlines
- NSF Oceanographic Facilities and Equipment Support
- NASA ROSES 2016 solicitation
- NSF Dear Colleague Letter - Seeking Community Input on NSF Polar Programs Realignment

2016	
August 2	NSF full proposal deadline for new LTER site
August 15	NSF Chemical Oceanography , and Biological Oceanography and Physical Oceanography and Marine Geology & Geophysics proposal deadlines (NSF Dear Colleague Letter on North Atlantic-Arctic science)
October 18	NSF Arctic Research Opportunities (NSF Dear Colleague Letter on North Atlantic-Arctic science)
2017	
February 15	NSF Chemical Oceanography , and Biological Oceanography and Physical Oceanography and Marine Geology & Geophysics proposal deadlines (NSF Dear Colleague Letter on North Atlantic-Arctic science)

OCB News

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