Controls and distributions of trace elements in the ocean

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Abstract

The concentration of chemical elements in seawater ranges from the molar (mol kg^{-1}) to the femtomolar (1×10^{-15} mol kg^{-1}), with distributions determined by a combination of biogeochemical processes including elemental physiochemistry, addition from external sources (atmosphere, rivers, sediments, hydrothermal venting), removal at sinks (sediments, hydrothermal systems), and redistribution within the oceans. Here we review the state of knowledge on the modern distributions of the marine trace elements and the processes that shape these distributions, especially recent insights into sources and sinks, and the role of biological cycling and advection of ocean water masses in setting the vertical distributions of these elements.

Keywords

Atmosphere; Cryosphere; GEOTRACES; Hydrothermal; Isotope; Regeneration; Rivers; Scavenging; Sediments; Sink; Source; Trace element; Trace metal

Key points

- The general field of marine trace element biogeochemistry and its history are introduced.
- The modern oceanic distributions of the trace elements are described, with the role of the Southern Ocean and multiple boundary sources updated in line with recent findings from the GEOTRACES Program.
- Boundary sources, sinks, and internal processes affecting the concentration of trace elements are introduced.

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Dissolved trace elements in seawater

Introduction

The chemical composition of seawater represents the long-term integration of the effects of a large range of biogeochemical and physical processes on each chemical element (Fig. 1), including external 'sources' that add elements to the ocean at oceanic boundaries (e.g. rivers, sediments, atmospheric deposition, and hydrothermal venting), 'sinks' where elements are removed at ocean boundaries (e.g. sediments, precipitation in hydrothermal processes), and internal cycling processes that redistribute elements throughout the ocean (biological uptake, regeneration, particle scavenging). The ultimate sink for most elements is burial in ocean sediments. The oceanic distribution of each element is thus unique, controlled by a combination of its specific physicochemical behavior in seawater combined with the effect of each of these processes, superimposed on ocean circulation. For elements which have two or more stable isotopes, their isotopic ratios may also be shaped by these processes. Thus, much information can be gleaned about the behavior and chemistry of each element by investigation of concentration and stable isotope distributions (e.g. Fitzsimmons and Conway, 2023; Anderson et al., 2014; Anderson, 2020). Further, decay of radionuclides and subsequent production of daughter isotopes, often with different chemical properties, mean that radionuclides can act as useful tracers for source/sink processes and rates (e.g. Hayes et al., 2018b; Anderson et al., 2016; Homoky et al., 2016; GEOTRACES SCOR Working Group, 2007; Garcia-Orellana et al., 2021).

With the notable exception of the elements that only have radionuclides with very short half-lives, almost the entire periodic table of the elements can be found dissolved in seawater, at a range of different concentrations. Elements can be classified based on their concentration range in seawater, or their 'residence time' (the average time an atom of an element would be expected to remain in the ocean). Elemental concentrations range from the major elements such as sodium (Na^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+), chloride (Cl^-), which are present at molar (mol kg^{-1}) levels, to 'trace' elements that are typically defined as present at less 10 μmol kg^{-1}. These major elements, together with bicarbonate (HCO_3^-) and sulfate (SO_4^{2-}), comprise most of the ~35 g kg^{-1} of salt which defines the 'salinity' of the oceans. Trace elements, by contrast, are often only present at femtomolar to nanomolar levels (fmol kg^{-1} to nmol kg^{-1}), while inorganic nutrients are an intermediate group of elements which are typically present in seawater at micromolar levels (μmol kg^{-1}), N principally as nitrate (NO_3^-), P as phosphate (PO_4^{3-}), and Si as orthosilicic acid or silicate ($SiOH_4$). Thus, the trace elements are defined by concentration range in seawater rather than distribution or physiochemical characteristics, and as such span all the major groupings of the periodic table. However, such trace elements are mostly metals, and so the term 'trace element' and 'trace metal' are often used interchangeably to describe this group of elements in seawater. Latterly, the international GEOTRACES programme (www.geotraces.org) refers to these elements as TEIs to denote trace elements and their isotopes. Here, we will use the term 'trace element' to be inclusive of non-metallic elements, and will refer to the inorganic nutrients nitrate, phosphate and silicate as 'the macronutrients'. We also follow the typical chemical oceanographer's operational definition of 'dissolved' in discussing the distribution of trace elements in this chapter: namely that which will pass through a 0.2 μm filter pore size is 'dissolved', and that which will not is 'particulate', where both the dissolved and particulate fraction can sometimes be further divided based on other pore sizes.

Since the very first reliable measurements of trace elements such as Zn and Cd by pioneers such as Bruland, Boyle, and Martin in the late 1970s (e.g. Martin et al., 1976; Bruland et al., 1978; Bruland et al., 1979; Boyle et al., 1976), there has been great interest in the biogeochemical processes that determine the distributions of trace elements throughout the ocean, as well as the role such elements play in oceanic biogeochemical cycles, influencing primary productivity, and ultimately acting as a lever on the global carbon cycle. As such, measurement of trace elemental concentrations can provide valuable insight into many modern biogeochemical oceanic processes, as well as insight into past ocean processes. The trace elements most notably studied to date include transition metals (e.g. Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Ti, Hg), the lanthanide rare earth elements (REE), the actinides (e.g. Th, Pa, U),

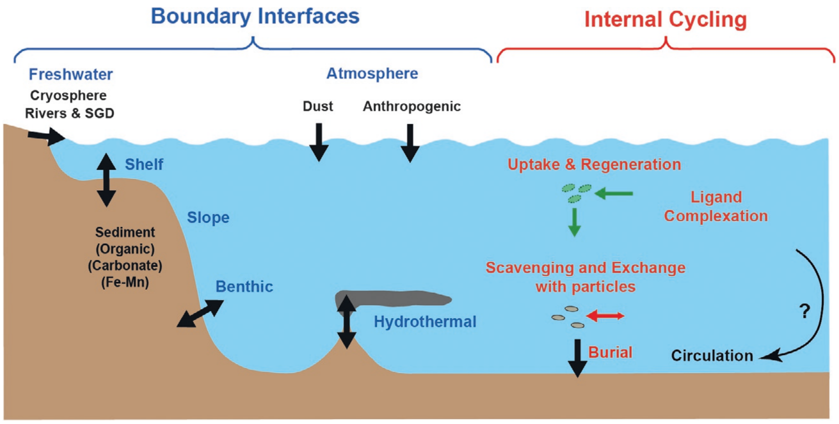

Fig. 1 Conceptual view of trace element cycling in the ocean, showing boundary interfaces and internal cycling processes. Cartoon schematic based on the GEOTRACES science plan (GEOTRACES Group, 2006).

post-transition metals (e.g. Al, Ga, Pb), noble gases (e.g. He, Rn), and other metals (e.g. Ba, Ra). Others that are of interest, present as oxyanions in seawater, include As, Ge, I, Mo, Sb, Rh, Se, Te, V, and W.

Six of the transition trace elements (Fe, Zn, Mn, Cu, Ni, Co), often referred to as the bioactive trace elements, serve as vital micronutrients for life in the ocean, essential for enzymes and proteins needed for a range of metabolic processes such as photosynthesis, elemental uptake, nitrogen fixation, respiration, and carbon uptake (e.g. Morel et al., 2003; Morel and Price, 2003; Morel et al., 2020; Anderson et al., 2014; Sunda, 2012). A seventh, Cd, also appears to behave as a bioactive element, although its role as a micronutrient is subject of ongoing research, as only few species have an absolute need for this element and it is toxic at high levels (Morel et al., 2020; Xu and Morel, 2013). Distributions of these micronutrient elements, as well as the macronutrients, thus play an important role in determining patterns of surface productivity, including phytoplankton community structure (Schoffman et al., 2016; Snow et al., 2015; Hutchins and Boyd, 2016; Moore et al., 2013). Arguably the most important of these elements, Fe, acts to limit growth in the oceans under a range of circumstances, while other elements such as Mn and Co are thought to co-limit or even limit growth themselves (Moore et al., 2013; Wu et al., 2019b; Saito et al., 2008; Sunda and Huntsman, 1995; Sunda, 2012). Accordingly, much research has focused on the distributions and the processes that control the cycling of these elements (Anderson, 2020; Anderson et al., 2014). The stable isotope ratios of these bioactive elements (δ^{56}Fe, δ^{60}Ni, δ^{65}Cu, δ^{66}Zn, δ^{114}Cd; sadly, Co and Mn have just one stable isotope) provide further insight into modern biological processes, but alongside other tracers such as δ^{13}C, δ^{15}N, δ^{39}Si, δ^{53}Cr and δ^{138}Ba may also be useful proxies to provide information on the paleo-productivity of the oceans (recently reviewed in detail by Farmer et al. (2021) and Horner et al. (2021)). Although other trace elements may have no direct role as nutrients, knowledge of their distributions and isotope ratios do provide invaluable information to chemical oceanographers. For example, Al and Pb act as useful tracers of dust and anthropogenic activity, while isotope ratios of elements such as He (δ^{3}He), Th (^{232}Th), Pb, and Ra (^{223}Ra, ^{224}Ra, ^{228}Ra) act as powerful tracers of boundary sources of trace elements to the ocean, whereas isotopes of elements such as Pa (^{231}Pa), Th (^{230}Th, ^{234}Th), Nd (εNd) provide invaluable chemical information about past and present particle scavenging, sources, ocean circulation, and rates of processes (GEOTRACES Group, 2006). Trace elements present as oxyanions (and their stable isotope ratios) such as Se and Mo may be bio-essential elements or useful anthropogenic (As, Sb, Se, and V) or paleo-oceanographic (Mo, Os, Rh, and Se) tracers. In Table 1, we summarize useful TEI tracers typically used for investigating different oceanic sources, sinks, and biotic/abiotic internal cycling processes - though it should be noted that this list is not exclusive and will most likely change as our knowledge of biogeochemical cycles and different trace elements and their isotopes continues to evolve.

This chapter provides a broad overview on the elemental classifications of different elements, their modern distributions in the open ocean, and the external and internal source/sink processes which shape those distributions (see Lyons, 2024, for discussion of elemental distributions and their controls on longer, geological, time scales). While we do discuss sources related to nearshore and coastal processes, we do not provide an overview of trace element distributions in coastal regions. This review is an update of previous Treatise of Geochemistry Chapters (Bruland and Lohan, 2003; Bruland et al., 2014), and accordingly will introduce and focus largely on the controls and distributions of the so called 'trace elements' which have seen great advances in understanding and data availability in the last ten years, facilitated and inspired by the International GEOTRACES Program (Anderson et al., 2014; Anderson, 2020; Conway et al., 2021). We also deliberately do not provide a detailed description of trace element sampling and analytical methods here, but instead point readers to a recent detailed chapter by Middag et al. (2023), as well as the GEOTRACES 'cookbook' (Cutter et al., 2017).

Our chapter is intended to function as an introduction, while more detail on aspects of elemental distributions, their isotopes, their behavior in seawater, interaction with biological cycles, and the processes which influence them can be found in multiple other chapters in this edition, especially Turner (2024), Little et al. (2024), and Twining and Shaked (2024). Further, the particulate aspects of elemental distributions, scavenging processes and tracers are extensively covered in Lam and Xiang (2024) and Marcantonio et al. (2024). Geochemistry of sediments is covered by Hayes (2024), while discussion of past and present redox chemistry, the past Fe cycle, paleo-productivity and paleo-circulation can be found in Hardisty and Lau (2024), Dauphas (2024), Farmer et al. (2024), and Marchitto and Lynch-Steiglitz (2024) respectively. In the case of other trace elements and their isotopes that have found use as paleo-proxies for redox, productivity, and other aspects of past ocean chemistry (e.g. Ag, Ba, Cd, Cr, Cu, Fe, I,

Table 1 Diagnostic Elemental and Isotopic Tracers for different oceanic processes and boundaries.

Oceanic source or process	*Diagnostic TEIs*
Atmosphere	Al, Fe, Mn, δ^{56}Fe, ^{232}Th
SGD and rivers	Ba, Fe, εNd, REE, ^{223}Ra, ^{224}Ra, ^{228}Ra
Cryosphere	Si, Fe
Hydrothermal vents	δ^{3}He, ^{223}Ra, ^{224}Ra, ^{228}Ra, Mn, Fe, δ^{56}Fe
Sediments	Fe, REE, εNd, ^{232}Th, ^{223}Ra, ^{224}Ra, ^{228}Ra
Anthropogenic contaminants	Pb, Hg, Cs, I, aerosol (δ^{56}Fe, enrichment factors of As, Cd, Cu, Ni, Pb, Sb, Se, Sn, V, Zn)
Biological uptake and cycling, nutrient utilization	Cd, Co, Cu, Fe, Mn, Mo, Ni, Zn δ^{13}C, δ^{15}N, δ^{30}Si, δ^{114}Cd
Ocean circulation, scavenging, particle dynamics, and export	CFCs, SF_6, εNd, ^{210}Po, ^{210}Pb, ^{231}Pa, ^{230}Th, ^{234}Th/^{234}U, δ^{13}C

Mo, Ni, Os, Se, Zn, U, V) we also point the reader to some recent reviews (Dauphas et al., 2017; Horner and Crockford, 2021; Horner et al., 2021; Hlohowskyj et al., 2021; Huang et al., 2015; Lau et al., 2021; Lu et al., 2021; Nielsen, 2021; Peucker-Ehrenbrink and Ravizza, 2020; Stueken and Kipp, 2021).

History of marine trace element measurements ('GEOSECS' to 'GEOTRACES')

Accurate measurement of many of the trace elements in seawater lagged measurement of the macronutrients and other chemical parameters in seawater by decades, with macronutrients being relatively well understood in the 1930s but the first reliable measurements of most trace elements not coming until the 1970s. This lag was driven by a combination of the vanishingly-small concentrations of many of these trace elements in seawater, coupled with the substantial challenges that arise from avoiding contamination during sampling from metal ships and in the typical laboratory environment. The required advances were facilitated by the development of the concept of 'clean laboratories' in the mid-late 1970s for trace metal sample processing by Clair Patterson (Patterson et al., 1976), allowing environmental samples to be processed without contamination from the laboratory environment. The 1970s were also the era of 'GEOSECS' (Geochemical Ocean Section Studies), the first widespread research program (1972–1978) to investigate the distributions of chemical, isotopic, and radionuclide tracers throughout the oceans, while focused on the carbon cycle (Chester, 1990; Craig and Turekian, 1980). For many nutrients, trace elements and isotopes, GEOSECS was instrumental in changing our understanding of their oceanic cycling and ocean circulation (e.g. the macronutrients, Ba, ^{3}H, ^{14}C, δ^{13}C; Broecker and Peng, 1982). At the time, vertical distributions of contamination prone elements such as Fe and Ni from GEOSECS were considered to be major advances in data quality (Sclater et al., 1976); however, later measurements have shown that these profiles overestimated the concentration of some elements to different degrees, likely due to contamination and the limits of the equipment and techniques available. For example, Fig. 2 shows North Atlantic vertical profiles of Fe and Ni concentrations from GEOSECS and the more recent 'GEOTRACES' program published 35 years apart, highlighting how collection, processing, and analytical techniques have improved, leading to lower concentration, oceanographically consistent (i.e. smooth, non-noisy profiles) profiles. However, the role of GEOSECS in inspiring much research into contamination prone elements, including programs like GEOTRACES, should not be underestimated (Anderson, 2020). The first accurate concentration measurements and oceanic profiles of Ni, Cu, Zn, and Cd followed soon after GEOSECS, published in the mid 1970s—early 1980s, and led to groundbreaking developments in our understanding of the marine trace elements (Boyle et al., 1976; Bruland et al., 1978, 1979), with the more challenging contamination-prone element Fe following in the 1980s and 1990s (e.g. Landing and Bruland, 1981; Gordon et al., 1982; Landing and Bruland, 1987; Martin et al., 1990b).

The pioneering research and clean techniques developed in the late 1970s stimulated a growing field of trace element science that led to many significant advances in our understanding of trace element cycling and oceanic distributions through the 1980s and 1990s, with the first reliable profiles of the very contamination-prone trace element Fe coming only in 1981–1982 (Landing and Bruland, 1981; Gordon et al., 1982; Landing and Bruland, 1987). Highlights of this period were a growing understanding of the crucial role Fe plays in determining primary productivity in areas of the ocean, as well as influencing the carbon cycle in the past (e.g. Moore et al., 2002, 2004; Moore and Braucher, 2008; Martin and Michael Gordon, 1988; Bruland and Lohan, 2003; Martin and Fitzwater, 1988; de Baar and de Jong, 2001; Martin et al., 1990a, b; Martin, 1990; Boyd and Ellwood, 2010), as well as a formative understanding of the importance of a mix of external sources in supplying trace elements such as Fe (Johnson et al., 1997, 1999; Elrod et al., 2004). Reasonably accurate example vertical profiles for most of the periodic table were available by the early 1990s (Nozaki, 1997, 1992), although there was only limited knowledge of spatial variability, with profiles often limited to the North Pacific and North Atlantic. Despite such research, however, by the early 2000s, the challenges of sampling and analysis as well as the diverse range of collection and analytical methods used by different research groups meant that there were

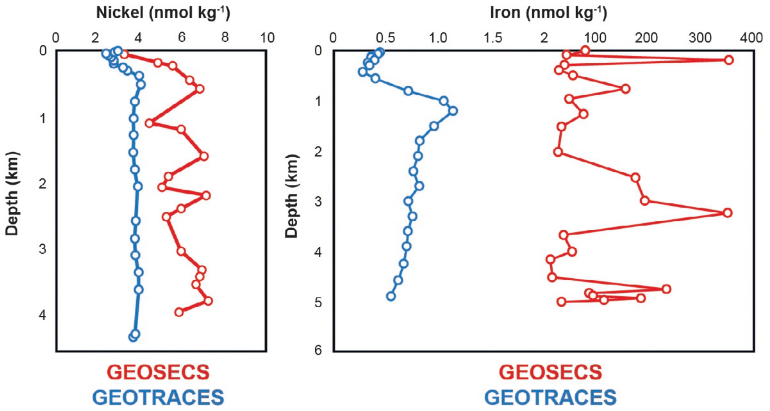

Fig. 2 State of the field—comparison of dissolved Ni and Fe vertical concentration profiles from the North Atlantic Ocean obtained via GEOSECS (1970s) and GEOTRACES (2010) Programs. Data are reproduced from comparison in Middag et al. (2023), with data from Brewer et al. (1972), Sclater et al. (1976), Rijkenberg et al. (2014), and Middag et al. (2020).

still only a small number of ocean profiles available for each trace element. Further, such profiles were dispersed geographically, and not always comparable (GEOTRACES SCOR Working Group, 2007; Anderson and Henderson, 2005). Although successful efforts were made to intercompare data generated on the same samples by multiple groups (e.g. Johnson et al., 2007) in order to allow a global picture to be drawn, the range of methods and the challenges of collection and analysis meant that knowledge of the distribution of the trace elements lagged severely behind hydrographic parameters such as temperature and salinity, as well as the macronutrients, for which high-resolution 2D ocean distribution 'sections' were already available from the World Ocean Circulation Experiment (1990–2002; Woods, 1985; Lehman, 2021).

In the early 2000s, the International GEOTRACES Program was conceived in order 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*" (Anderson and Henderson, 2005; Anderson et al., 2014; GEOTRACES SCOR Working Group, 2007; Frank et al., 2003). Driven by a Science Plan (GEOTRACES Group, 2006; GEOTRACES SCOR Working Group, 2007) that considers the ocean in terms of boundary exchange processes and internal cycling (see Fig. 1), the GEOTRACES Program is a group of scientists from over 35 countries that has come together to characterize the oceans for the full suite of TEIs simultaneously, generating WOCE-style 2D ocean sections and 3D visualizations of TEIs throughout all the major oceans (Mawji et al., 2015; Schlitzer et al., 2018; GEOTRACES Intermediate Data Product Group, 2023). These datasets are then used to provide new insights into (and questions about) the processes that determine elemental distributions, the sources and sinks that are important for each element, and how elements may act as paleo-proxies for past oceans and are designed to stimulate smaller-scale 'process' study endeavors (Anderson et al., 2014).

This large, data-intensive program has built on the pioneering clean collection techniques of earlier researchers and has made rigorous intercalibration of both collection/processing and analytical methods a core objective (Cutter, 2013), providing a 'cookbook' of instructions (Cutter et al., 2017), carrying out intercalibration exercises and making use of 'crossover stations' or re-occupations of the same location by different expeditions for comparison (e.g. Cutter and Bruland, 2012; Anderson et al., 2014; Middag et al., 2015a). For example, different programs all make use of similar CTD carousel 'rosette' systems for water collection which have been designed and found to be non-contaminating (US, Japanese, and Dutch systems are shown in Fig. 3). Such rosette systems make use of Teflon-coated GO-FlO or Niskin-X, PVDF or polypropylene bottles, mounted on frames which are comprised of Ti or epoxy-powder coated metal, with no sacrificial Zn anodes and all exposed metal parts made of Ti (Cutter and Bruland, 2012; Rijkenberg et al., 2015). Sampling is carried out using non-contaminating cables and dedicated winches, and bottles (or in the case of NIOZ, the entire sampling system) are brought within custom built clean laboratories for further processing and filtration of samples (typically via a 0.2 or 0.4 μm pore-size membrane filter or cartridge where 0.2 μm is the GEOTRACES standard). While early trace element concentration measurements relied on techniques such as Graphite Furnace Atomic Absorption Spectroscopy (GF-AAS), and then Flow-Injection (FIA) analytical techniques, most groups now measure trace element concentrations by inductively-coupled plasma mass spectrometry (ICP-MS) (Sohrin and Bruland, 2011; Worsfold et al., 2013). Typically, multi-element analysis is carried out by ICP-MS following a cation resin separation and purification step (e.g. ESI's SeaFAST system), with prior UV-digestion for some complexed elements such as Co or Cu (Lagerström et al., 2013; Wuttig et al., 2019). However, element-specific methods are still used for some elements, and FIA techniques remain useful tools for shipboard analysis

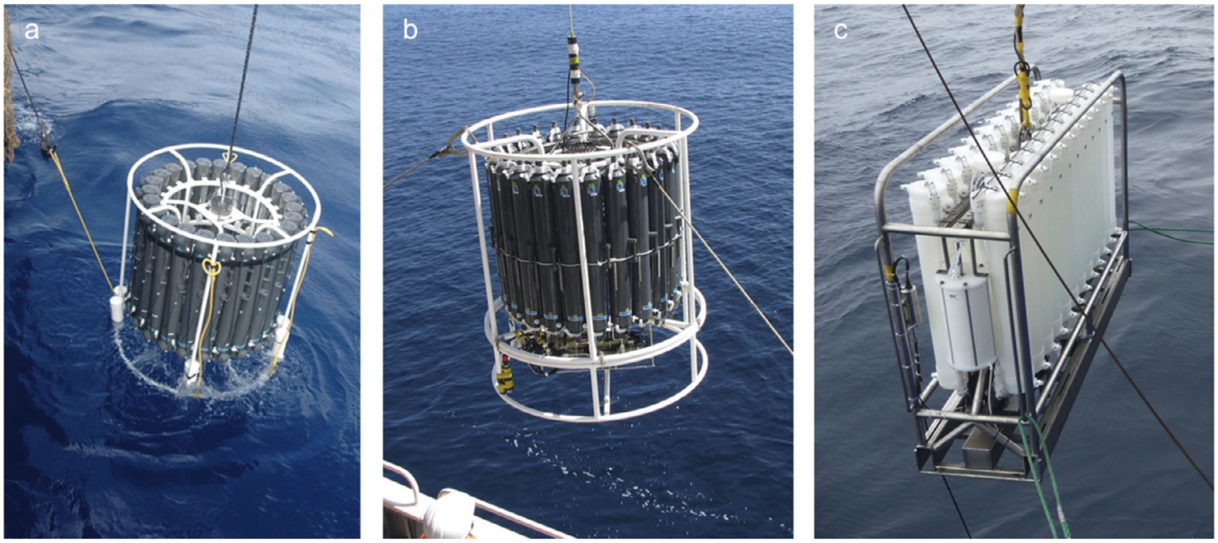

Fig. 3 The U.S. (a), Japanese (b), and Dutch (c) trace metal clean sampling systems developed for the GEOTRACES Program. The US system uses 24 each 12-L Teflon-coated GO-FLO samplers, the Japanese system uses 24 each 12-L Teflon-coated Niskin-X samplers, while the Netherlands system uses 24 each 23-LPVDF PRISTINE samplers (a light-proof version of the PRISTINE samplers made of polypropylene is also in use). These sampling systems utilize clean conducting wires and clean areas for sample processing. The U.S. and Japan remove the sampling bottles from the rosette and move them into a clean van or clean "bubble," whereas the NIOZ system moves the entire sampling unit into a clean van. Figure reproduced from Bruland et al. (2014).

(e.g. Jensen et al., 2019; Rijkenberg et al., 2018). For much greater detail on sampling systems and analytical techniques, see the recent review by Middag et al. (2023).

Careful international efforts to make representative accurate measurements, together with work by GEOTRACES Data Management and Standards and Intercalibration Committees have meant that data from many groups worldwide can be successfully intercompared and synthesized into publicly-available data products and electronic atlases (Schlitzer et al., 2018; GEOTRACES Intermediate Data Product Group, 2023); http://www.egeotraces.org). GEOTRACES Intermediate Data Products launched in 2014, 2017, and 2021 have included data from over 50 expeditions and over 50,000 samples. GEOTRACES, together with other international endeavors such as CLIVAR, SOLAS and IMBER, has thus facilitated an 'explosion' of oceanic TEI data allowing for dramatic advances in understanding trace element distributions and the processes that shape them (Conway et al., 2021; Anderson, 2020); for example, we now have access to 2D ocean sections, and data for over a thousand water column 'stations', compared to ~25 vertical profiles >2000 m depth for dissolved Fe or Zn in 2003 (Anderson et al., 2014; Schlitzer et al., 2018; GEOTRACES Intermediate Data Product Group, 2023). Through GEOTRACES and other process studies, the community has also begun to be able to assess temporal changes by reoccupation of time series stations for trace elements (e.g. Tagliabue et al., 2023). In Section "Current knowledge of the marine distributions of trace elements and isotopes", we provide a review of how large programs and process studies have both driven forward data coverage and knowledge.

Physiochemical speciation and organic complexation

The trace elements exist in a range of physiochemical forms in seawater, ranging from free ions to species complexed with a range of inorganic ions and organic molecules, to particulate matter that can include lithogenic minerals, biogenic material, and elements adsorbed, precipitated, onto, or incorporated into any of these particle types. This complexity obviously raises many challenges for measuring distinct species of trace elements, and so operational definitions are often used. The simplest of these is the division between 'dissolved' and 'particulate', which is typically based on a 0.2 μm pore size filter; anything passing through this filter is referred to as 'dissolved', and anything larger is classified as particulate, which can then be subdivided further (Cutter et al., 2017). In reality, this 'dissolved' pool actually includes a veritable 'soup' of free ions, inorganic and organic complexed species, inorganic and organic colloids, and even nanoparticles, which variably interact with, and are 'bioavailable' to, marine micro-organisms.

The speciation and concentration of each dissolved trace element in seawater are dictated by an element's redox state and 'solubility' in seawater and the environmental conditions. Depending on the element, species can be free cations, oxyanions, or complexed to inorganic ligands such as OH^-, Cl^-, $CO_3{}^{2-}$, or present as organic complexes. The inorganic speciation of trace elements can be calculated in seawater as a function of variables such as pH and temperature (Turner et al., 1981; Byrne et al., 1988); for example, the inorganic speciation of major elements and some trace elements such as Zn, Mn, Co, and Ni are considered to be dominated by free cations, elements such as Be, Al, Fe, Ti and Ga are present predominately as hydrated complexes (e.g. $FeOH^{2+}$ or $Fe(OH)_3$), Cd, Ag and Pd are typically present complexed with Cl^- ligands, elements such as Cu, Sn, U and the REE are predominantly complexed with CO_3^{2-}, and As, Cr, Ge, Mo, Sb, Rh, Se, Te, V, and W are typically present as oxyanions (e.g. Mo as $MoO_4{}^{2-}$, V as $HVO_4{}^{2-}$, and W as $WO_4{}^{2-}$). The speciation of Hg in seawater is perhaps unique, with Hg present as not only the mercuric ion Hg^{2+} (that is typically complexed to inorganic and organic ligands) but also elemental Hg^0 and methylated Hg: dimethylmercury ($(CH_3)_2Hg$) and monomethylmercury (CH_3Hg^+)) (Fitzgerald et al., 2007); the latter is of most concern to human health, especially via bioaccumulation in, and then later consumption of, fish (Fitzgerald and Clarkson, 1991; Fitzgerald et al., 2007). This is a significant modern concern, since Hg, like Pb, is an element that has been dramatically perturbed by anthropogenic activity and consequent atmospheric addition to the oceans, with anthropogenic Hg penetrating most of the oceans (Lamborg et al., 2014). For a table of the inorganic speciation of the trace elements see Bruland et al. (2014), and for more details on elemental physiochemical speciation in seawater see Turner (2024).

The concentration of the inorganic species of each element is ultimately driven by its physiochemical 'solubility' in seawater. For example, at the typical pH and redox conditions of open-ocean seawater, Fe^{2+} added to seawater is preferentially oxidized to Fe^{3+} and progressive hydration through $FeOH^{2+}$ and $Fe(OH)_2^+$ to $Fe(OH)_3^0$ is favored (Millero, 1998; Millero et al., 1987). These hydrated forms of Fe(III) have solubility limits of around 0.1 nmol kg^{-1} in seawater at pH 8.1 and 25 °C (Millero, 1998; Liu and Millero, 2002) meaning that precipitation of $Fe(OH)_3$ is favored and inorganic Fe can only remain present at picomolar levels in seawater. However, and fortuitously for phytoplankton who require Fe, operationally-defined dissolved Fe concentrations can reach several nmol kg^{-1} in open ocean waters, and up to several hundred nmol kg^{-1} near reducing sediments or in hydrothermal plumes (Schlitzer et al., 2018; GEOTRACES Intermediate Data Product Group, 2023). In these latter cases, unique environmental conditions such as low dissolved oxygen or low pH may facilitate the presence of much of the dissolved Fe as Fe^{2+}, but across the open ocean elevated dissolved Fe(III) levels are thought to be sustained by complexation with organic molecules (Boyd and Ellwood, 2010). Indeed, it has been argued that >99.9% of dissolved Fe is present bound to organic ligands, taking the form of siderophores, humics, porphyrins, exopolysaccharides, and other organic molecules (Moffett and Boiteau, 2024; Rue and Bruland, 1995; Gledhill and Buck, 2012). However, the operational definition using a 0.2 μm cutoff by definition also includes Fe present as both inorganic and organic colloids, and it has long been known these are also an important player in the Fe cycle, studied by further filtration of seawater with a 0.02 μm or 10 kDa filtration, present as 0–90% of the dissolved Fe, and likely exchanging with the ligand-bound pool over a range of timescales (e.g. Fitzsimmons and Boyle, 2014; Fitzsimmons et al., 2015a, b, c; Bergquist et al., 2007; Cullen et al., 2006; Wu et al., 2001). Further, many studies have suggested that a substantial fraction of the organically-complexed or ligand bound Fe exists in the colloidal fraction (i.e. the fraction <0.2 μm but larger than the additional 0.02 μm or 10 kDa filter used (Hurst and Bruland, 2007; Thuroczy et al., 2010; Nishioka et al., 2001, 2005; Cullen et al., 2006; Bergquist et al., 2007; Nishioka and Takeda, 2000).

For recent comprehensive reviews of organic speciation of trace elements in seawater, we point the reader to Moffett and Boiteau (2024) and to Twining and Shaked (2024), and as such only give a short overview here. Dissolved Fe is not the only trace element that is strongly influenced and maintained above inorganic solubility limits by organic complexation, especially in surface waters. For example, while arguably not as well studied as Fe, research has pointed to the importance of complexation for Cu, Zn, Ni, Co and Cd in surface waters, with studies showing a majority of these to be bound to strong organic ligands. For example, based on electrochemical techniques, greater than 99% of dissolved Cu is bound to organic complexes, 98% of Zn in surface water has been estimated to be complexed, $<90\%$ of cobalt is bound to strong Co-binding ligands, and around 80% of Cd in surface waters is complexed (e.g. Moffett et al., 1990; Coale and Bruland, 1988; Bruland, 1989, 1992; Donat and Bruland, 1990; Ellwood and Van Den Berg, 2000; Saito et al., 2017). Organic complexation thus plays an important role in determining elemental concentrations, speciation, solubility and reactivity (Vraspir and Butler, 2009). Ni, in contrast to some of the other elements, is only thought to be complexed at around 30–50%, but this complexation has been argued to be key for keeping surface dissolved Ni concentrations at near 2 nmol kg^{-1} in surface waters (Van Den Berg and Nimmo, 1987; Saito et al., 2004; Morel et al., 2014; Glass and Dupont, 2017; Achterberg and Van Den Berg, 1997; Mackey et al., 2002; Wen et al., 2006).

Dissolved Cu and Co are especially interesting elements when it comes to organic complexation, considering both are bio-essential trace elements, despite Cu being toxic at even relatively low concentrations. Here, complexation of Cu with strong organic ligands is actually thought to lower the concentration of free Cu^{2+} in seawater by several orders of magnitude (Ruacho et al., 2022), to levels of around 1 nmol kg^{-1} in surface waters, which is not high enough to be toxic to phytoplankton. Studies have even shown that cyanobacteria may produce strong Cu binding ligands when stressed (Moffett and Brand, 1996). As such, complexation is key to keeping the dissolved Cu in surface waters at just the right levels; this has led to Cu being known as a 'goldilocks' element, and means that Cu does not fully deplete at the surface like other micronutrients (Bruland and Lohan, 2003; Schlitzer et al., 2018; GEOTRACES Intermediate Data Product Group, 2023). While distributions of dissolved Co in seawater are considered to be controlled by a mix of uptake, scavenging, and sources (e.g. Tagliabue et al., 2018, Saito et al., 2017), a portion of the dissolved Co is so strongly complexed to organic ligands that great care must be taken to oxidize (using UV and/or hydrogen peroxide) samples prior to analysis in order to get accurate concentration measurements of total dissolved Co (e.g. Lagerström et al., 2013; Rapp et al., 2017; Wuttig et al., 2019; Biller and Bruland, 2012; Middag et al., 2015a). Similarly, the strong ligands that bind Cu mean that oxidation may also be required prior to analysis of seawater for accurate dissolved Cu measurements (e.g. Little et al., 2018; Lagerström et al., 2013; Rapp et al., 2017; Wuttig et al., 2019; Biller and Bruland, 2012; Middag et al., 2015a).

To determine the organic complexation or speciation of trace elements, different voltammetry methods have often been applied (Middag et al. (2023) and references therein). Such electrochemical techniques have been used for the estimation of ambient organic ligand concentrations and conditional stability constants using Competitive Ligand Exchange (CLE) that is based on establishing a competitive equilibrium between a competing (artificial) ligand and the natural ligands (L) in a seawater sample. Such studies have now been widely used to characterize the strength and presence of natural ligands, including along GEOTRACES sections (e.g. Thuroczy et al., 2011; Gerringa et al., 2015, 2017; Slagter et al., 2017; Buck et al., 2015, 2018), and to identify metal-specific ligand production in incubations (e.g. Smith et al., 2022; Gledhill et al., 2004; Gledhill and Buck, 2012). However, care must be taken when interpreting electrochemical methods; for example, Gerringa et al. (2021a) recently argued that the results of such methods for both the ligand concentration as well as the conditional stability constant depend on the choice of the added competing ligand, complicating the interpretation of the results obtained by these methods. Variability likely arises from differences in detection windows between methods, as well as not reaching equilibrium between natural and added ligands, and kinetic artefacts (Gerringa et al., 2021a; Moffett and Boiteau, 2024). Much insight has been obtained from CLE based methods, but results should be evaluated critically (Moffett and Boiteau, 2024). Further, while electrochemically-identified metal-binding ligands are ubiquitous in the marine environment at nanomolar levels, making up an important component of the dissolved organic matter pool, their identity and structure remain relatively-poorly constrained.

Fortunately, novel methods based on molecular characterization and quantification of naturally occurring marine organic ligands in the ocean are emerging. Such characterization and quantification can be done via various methods such as excitation-emission matrix (EEM) fluorescence combined with parallel factor analysis (PARAFAC; Yamashita et al., 2011), nuclear magnetic resonance (NMR; Hertkorn et al., 2006; Rehman et al., 2017), Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS; Pohlabeln and Dittmar, 2015) and high-performance liquid chromatography mass spectrometry (HPLC-MS; Boiteau et al., 2016b; Mawji et al., 2008; Velasquez et al., 2016). Notably HPLC based methods have provided recent insight in the distribution of strong iron-binding ligands known as siderophores, as well as identifying other Cu and Ni specific ligands (Boiteau et al., 2019, 2016b; Boiteau and Repeta, 2022; Gledhill et al., 2022), but this is still very much a developing method and challenges remain as still only a small fraction of all ligands can be extracted and identified (Moffett and Boiteau, 2024). However, studies have already identified over 20 different marine siderophores, with diversity varying between oceanic regions and Fe availability, as well as observing the production of siderophores and ligands for multiple elements in seawater incubations (e.g. Boiteau et al., 2013; Bundy et al., 2018; Moffett and Boiteau, 2024; Gledhill et al., 2004; Mawji et al., 2011; Velasquez et al., 2011, 2016; Boiteau et al., 2016a, b, 2019). For a more detailed discussion on the role of organic speciation of trace elements in seawater in influencing trace element biogeochemistry, bioavailability, and uptake into micro-organisms, see Twining and Shaked (2024).

Classical concentration distribution patterns and residence times

As soon as the first reliable vertical profiles of the bioactive trace elements were available in the 1970s, patterns in the distributions of the different trace elements emerged, related to the biogeochemical processes that shaped such distributions. Early studies of dissolved Ni, Zn and Cd showed clear similarities between the vertical profiles of these trace elements and the dissolved inorganic macronutrients phosphate, nitrate, and silicate, while Cu profiles demonstrated evidence of scavenging of dissolved Cu to particles (Bruland, 1980; Boyle et al., 1976; Martin et al., 1976; Bruland et al., 1978, 1979). Such observations continue to be largely confirmed (and built upon) as our understanding and datasets grow (Fig. 4 shows examples vertical profiles of macronutrients and trace elements). These early studies also permitted the identification of apparent distinct correlations between dissolved Cd and dissolved phosphate (and nitrate), dissolved Zn with dissolved silicate, and dissolved Ni with an intermediate of phosphate and silicate, as well as the observation that the Pacific was more enriched at depth than the Atlantic (e.g. Bruland, 1980; Boyle et al., 1976).

Early studies also noted that while Cd correlated best with phosphate and nitrate, Zn correlated better with silicate, leading to the hypothesis that Zn might be co-located more strongly with siliceous diatom frustules while Cd is co-located more with organic tissue (Bruland et al., 1978). In this view, Zn and Si both regenerate more slowly than Cd or phosphate, and thus exhibit a deeper maximum in concentrations, as observed in their vertical profiles—however, this idea was later shown to be at odds with most diatom Zn being associated with organic tissue (Twining and Baines, 2013). For Cd, it was also soon realized that its relationship with phosphate in the Atlantic could not be described by a simple linear correlation, but that there was a break or 'kink' in the slope at ~1.3 μmol kg^{-1} phosphate, dividing the relationship into two correlations with different slopes for surface and young North Atlantic waters vs older waters (Cullen, 2006; De Baar et al., 1994). However, even with just a handful of vertical profiles by two labs in 1980, it was possible for Bruland to summarize that the distributions of the different trace elements were the result of '*the involvement of these metals in the internal biogeochemical cycles of the sea*', that such distributions are '*predictable on the basis of oceanographic parameters*', and to calculate oceanic residence times for each element (Bruland, 1980). It was also quickly realized that such tight modern correlations between elements such as Cd and phosphate, or Zn and silicate might not only allow predictive

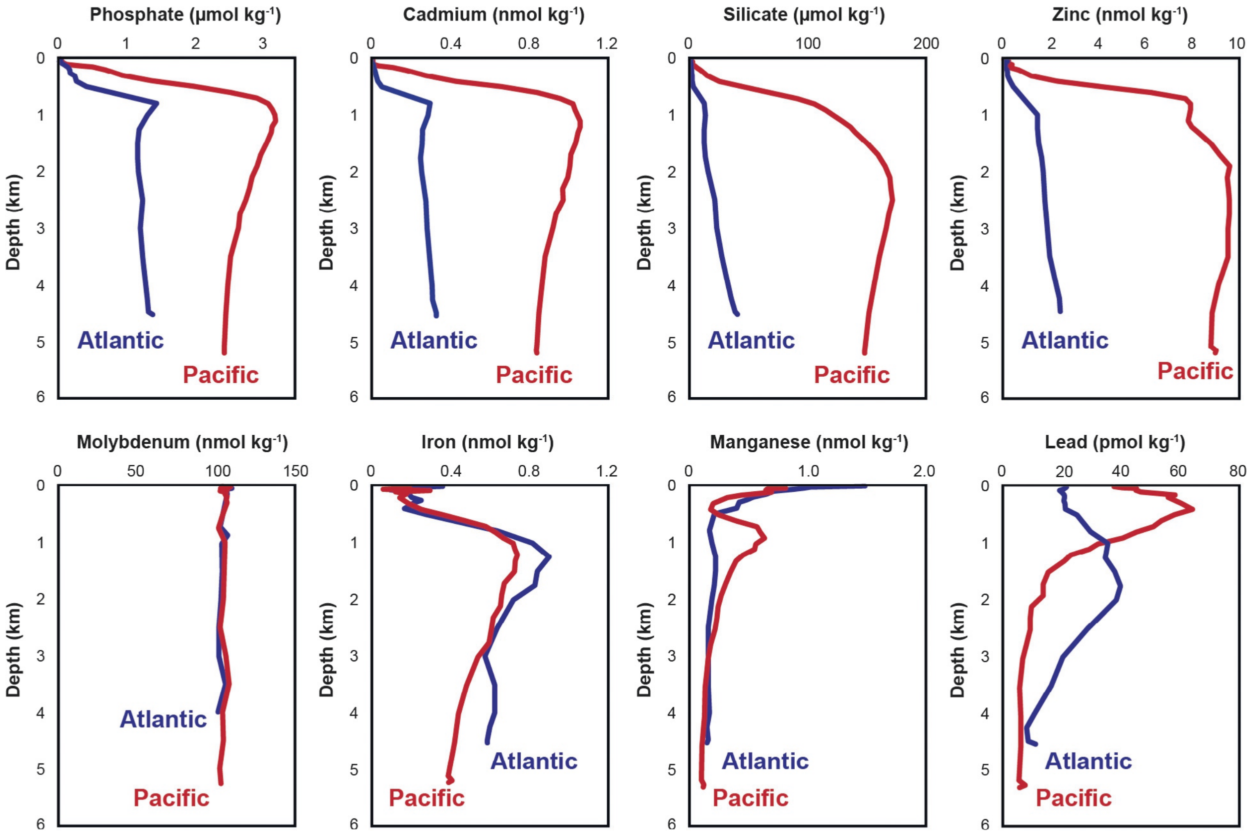

Fig. 4 Typical vertical oceanic concentration profiles of dissolved macronutrients (phosphate and silicate), nutrient-type trace elements (Cd and Zn), conservative trace element (Mo), and hybrid-scavenged trace elements (Fe, Mn, and Pb) for the North Atlantic and North Pacific. For profile geographic locations, refer to maps in Fig. 6. North Atlantic data come from the 2010 GEOTRACES GA02 Dutch Occupation of the Bermuda Atlantic Time Series Site in the Northwest Atlantic (31°N, 64°W; Middag et al. (2015a), except for Mo which come from the same location from 2008 (Nakagawa et al., 2012)). North Pacific data come from the 2018 US GEOTRACES GP15 Station 14 in the Northeast Pacific (32°N, 152°W; Lanning et al., 2023; Sieber et al., 2023a, b), except for Mo which come from the Northwest Pacific (44°N 155°E; Nakagawa et al., 2012).

power for the distribution of these elements in the modern oceans, but also permit measurements of these metals preserved in sediment microfossil archives to be used to reconstruct past ocean nutrient concentrations (e.g. Elderfield and Rickaby, 2000; Marchitto et al., 2002; Delaney and Boyle, 1987; Boyle, 1988).

Insights were not limited to trace elements with distributions similar to the macronutrients, however; for example, the first profiles of dissolved Mn highlighted the importance of Mn addition from sources, the role of oxygen in determining Mn concentrations, and the importance of particle scavenging (Landing and Bruland, 1980; Klinkhammer and Bender, 1980), while the earliest measurements of dissolved Pb in seawater helped to demonstrate the prevalence of this anthropogenic pollutant in the marine environment (Schaule and Patterson, 1983, 1981). Continued measurement of dissolved Pb over the next three decades documented the decline in Pb concentrations in the ocean following the phasing out of leaded gasoline in North America and Europe for human health reasons, highlighting an example of where science and policy can work together to solve an environmental problem (Fig. 5; Olivelli et al., 2023; Bridgestock et al., 2016; Boyle et al., 2014).

Following on from the first vertical profiles of trace elements, in addition to elements being classified by their concentration range in seawater, there was a tendency to classify trace elements by the shape of their vertical distribution profiles in the ocean. As the reader will see from the following section (Section "Current knowledge of the marine distributions of trace elements and isotopes"), this initial, relatively simplistic 1D approach has been largely replaced by a more informed 3D approach in the modern era, as data quantity for the trace elements has caught up with the macronutrients, and full ocean sections are available (Figs. 6 and 7). However, while a 1D approach is inherently more simplistic, it does have the benefit of implicitly including information about the processes that shape the vertical profiles, whether elements be invariant with depth (relative to salinity), scavenged quickly to particles, dependent on point sources and sinks, or controlled by biological uptake in surface waters and later release at depth. Additionally, much of the accurate insights gleaned from a 1D approach have shaped our understanding as the field has advanced.

The main simple distribution classifications that have been applied to trace elements are conservative-type (invariant with depth relative to salinity), nutrient-type (depleted at surface, enriched at depth), scavenged-type (enriched near sources, low at depth or away from sources), hybrid-type (exhibiting features of multiple types), and mixed type (where different species of the same element have different distributions). We will briefly describe the first three types here, together with examples. In understanding these different profile types, it is useful to grasp the concept of oceanic residence time. Residence time can be thought of as the time that an atom of an element may be expected to remain in the ocean, and at steady state, is defined as the total mass of an element in the ocean divided by the flux of that element into or out of the ocean. Residence times can be calculated for an element, or for different chemical species of an element, and as such can vary from less than a second, to many millions of years (see Hayes et al. (2018a) for a recent assessment of residence times). Residence times can also be compared to the whole ocean mixing time (~1000 years; Döös et al., 2012; Khatiwala et al., 2013), where elements with much longer residence times (>100,000 years) than

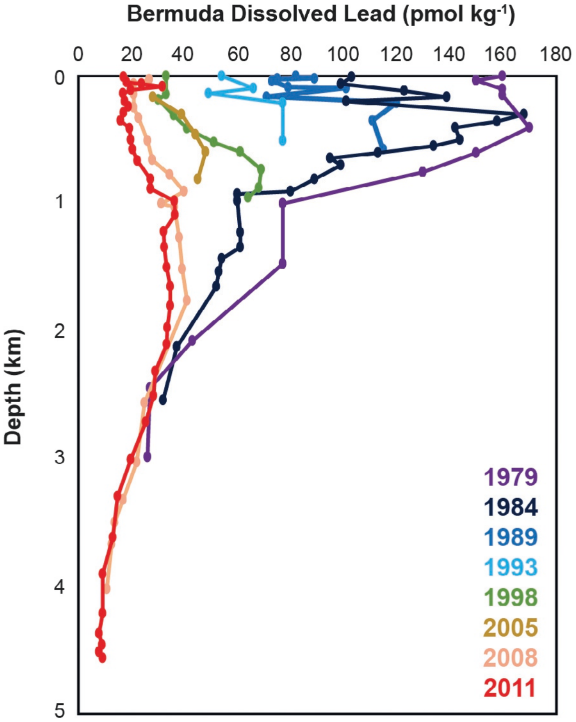

Fig. 5 Changing dissolved Pb concentrations from occupations of the Bermuda Atlantic Time Series station (31°N, 64°W) over the period 1979–2011, showing the influence of the phasing out of anthropogenic Pb in gasoline on North Atlantic Pb concentrations, and the value of ocean time series data. Data are from multiple laboratories and are reproduced from Boyle et al. (2014).

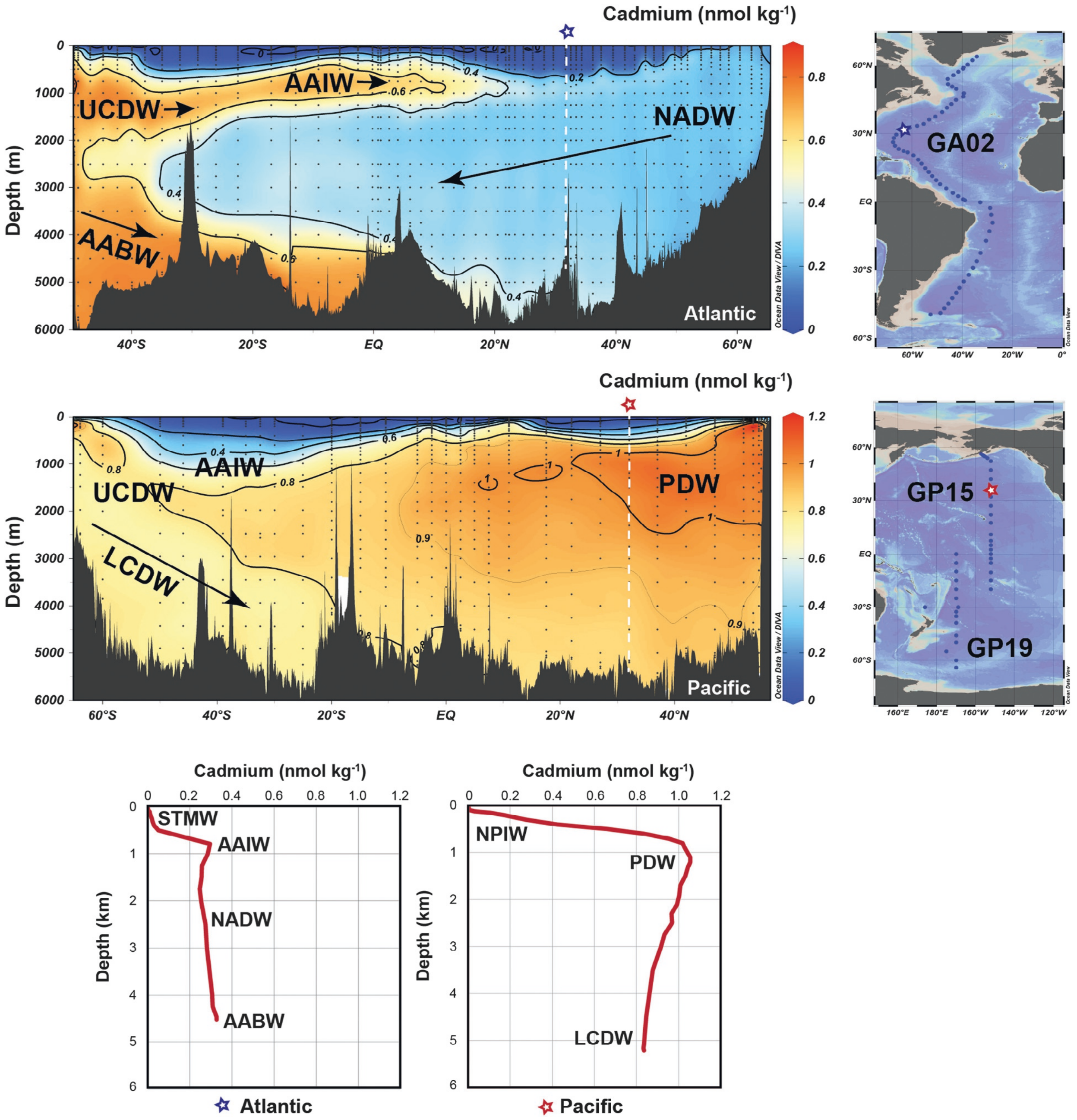

Fig. 6 GEOTRACES meridional sections of dissolved Cd concentrations through the Atlantic (GA02) and Pacific (GP15 & GP19) Oceans, showing main water mass features. Dots denote sample depths and locations. STMW = Subtropical Mode Water, NADW = North Atlantic Deep Water, AAIW = Antarctic Intermediate Water, AABW = Antarctic Bottom Water, UCDW = Upper Circumpolar Deep Water, LCDW = Lower Circumpolar Deep Water, PDW = Pacific Deep Water, and NPIW = North Pacific Intermediate Water. Maps indicate station sampling locations for each section. Vertical profiles of Cd concentration are shown from the locations denoted by the stars/dashed vertical lines and indicate the importance of water masses to the vertical structure. Starred locations also denote locations of vertical profiles shown in Fig. 4. Data are sourced from Middag et al. (2018), Sieber et al. (2019a), and Sieber et al. (2023b).

the mixing time will typically be well-mixed and thus invariant and conservative (relative to salinity) throughout the ocean, while concentrations of elements with short residence times will be highly variable between locations.

The conservative-type distribution is the simplest vertical profile shape, with distributions invariant in concentration in the ocean relative to salinity, meaning that they exhibit relatively narrow concentration ranges, and have no detectable *in situ* production or consumption. As such, conservative elemental concentrations only vary significantly as salinity changes occur due to evaporation, precipitation, brine rejection, and physical mixing of water masses. Conservative elements include the major ions which make up salinity (Na^+, Mg^{2+}, K^+, Cl^-), as well as other ions such as Li^+, Sr^{2+}, F^-, Br^-, with the most classic examples being Cl^- with a residence time of approximately 100 million years, and Na^+ at around 68 million years (Pytkowicz, 1976; Bruland, 1983;

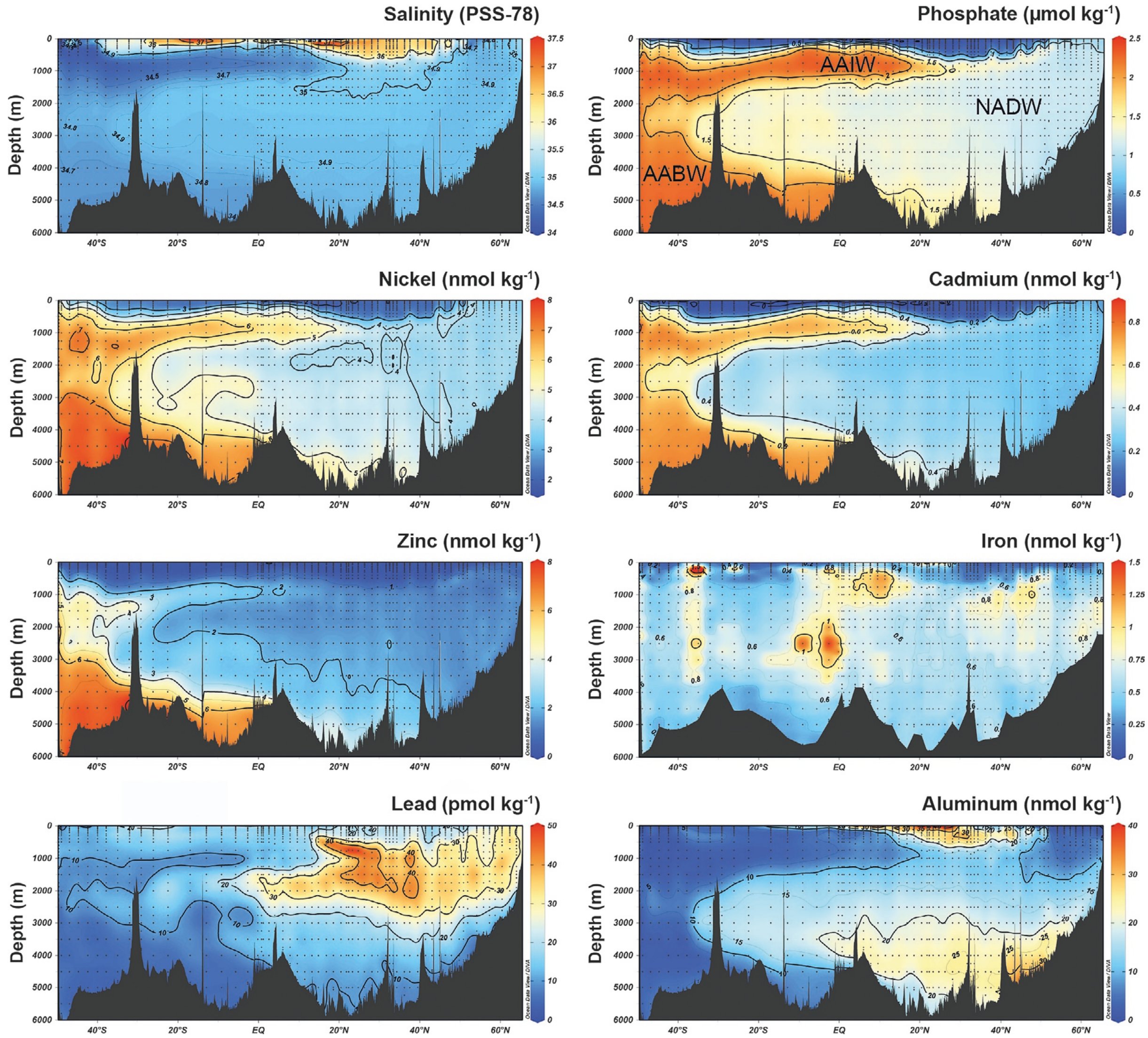

Fig. 7 Atlantic meridional sections (GEOTRACES GA02) of salinity, phosphate, and dissolved trace element (Ni, Cd, Zn, Fe, Pb, and Al) concentrations. Dots denote sample depths and locations. Water mass labels denote positions of major water masses; AABW = Antarctic Bottom Water, AAIW = Antarctic Intermediate Water, NADW = North Atlantic Deep Water. Refer to Atlantic map in Fig. 6 for station locations. Data are from the Dutch GEOTRACES GA02 section (Fe, Rijkenberg et al. (2014); Cd, Middag et al. (2018); Ni, Middag et al. (2020); Zn, Middag et al. (2019) and Vance et al. (2017); Pb, GEOTRACES Intermediate Data Product Group (2023); Al, Middag et al. (2015b)).

Broecker and Peng, 1982). Some trace elements are also conservative, typically those found as oxyanions (e.g. Mo, W, Rh, Os, U) or as large monovalent cations (e.g. Cs^+, Rb^+). Molybdenum (Mo) is a good example of a conservative trace element, mainly present as molybdate (MoO_4^{2-}), exhibiting concentrations of near 105 nmol kg^{-1} throughout the oceans, and having a residence time of 440,000 years (Firdaus et al., 2008; Miller et al., 2011). Similarly, Vanadium (V) is present as VO_4^{2-} with a conservative concentration of 30–36 nmol kg^{-1} (e.g. Collier, 1984; Emerson and Huested, 1991; Wu et al., 2019a). Oxyanions such as molybdate have a very low particle reactivity in seawater and so are not easily particle scavenged. Further, while Mo does play a biological role in cells, the very small requirement of Mo in phytoplankton relative to other nutrients (Ho et al., 2003), combined with high ambient Mo concentrations (Nakagawa et al., 2012), means that uptake and regeneration do not dramatically influence the shape of Mo's vertical concentration profiles (Fig. 4). Interestingly, while the element Germanium (Ge) typically has a nutrient-like distribution (see below), some methylated forms of Ge are conservatively distributed ($CH_3Ge(OH)_3$ and $(CH_3)_2Ge$; Lewis et al., 1998).

Measurement of the distribution of inorganic macronutrients in the ocean pre-dates accurate trace element profiles by almost half a century, with the classic paper by Redfield et al. (1963) describing how carbon, nitrate, and phosphate are present in oceanic waters (and taken up into phytoplankton) following an expected average ratio (the Redfield Ratio). Although these elements (together with silicate) have intermediate residence times that are longer than the mixing time of the oceans but shorter than conservative elements (~1000–100,000 years), their vertical distributions are not conservative; instead, their distributions are highly perturbed by biological activity that partitions these elements between the surface and deep oceans. Nutrients are assimilated into phytoplankton during growth in the surface ocean, then released by degradation and oxidation of organic matter (termed regeneration, remineralization or recycling; in this chapter we use the term regeneration), either in the near-surface, or as organic matter sinks with depth, leading to depletion of nutrient concentrations in surface waters, and enrichment with depth as particulate organic matter regenerates. Like the macronutrients, Barium (Ba) is present at relatively high concentrations (~30–100 nmol kg^{-1}) in seawater and displays a nutrient-type distribution with distinct variability between ocean basins (Chan et al., 1976; Horner and Crockford, 2021). However, in the case of Ba, distributions are thought to be driven by barite precipitation related to microbial oxidation of sinking organic matter, and not biological assimilation and regeneration (Chow and Goldberg, 1960; Bishop, 1988; Dehairs et al., 1980).

Some bioactive trace elements (e.g. Ni, Zn, Cd, Ag), in addition to having intermediate-length residence times of ~100,00 years, also have vertical distributions that closely resemble those of the macronutrients (Fig. 4) and are hence termed 'nutrient-type' profiles or elements. Several of the trace elements present in seawater as oxyanions also demonstrate 'nutrient' type distributions. For example, the dominant form of Germanium (Ge) in seawater is Germanic acid, which displays a nutrient-like distribution which shows a tight correlation with Si (Froelich and Andreae, 1981). Similarly, Selenium (Se), which can be both toxic and bioessential, and exists in several oxidation states ($Se(VI)O_4^{2-}$ and $Se(IV)O_3^{2-}$, has a nutrient-like distribution (Cutter and Bruland, 1984; Cutter and Cutter, 1995). The first profiles of dissolved Cr, which exists in seawater in the forms of Cr(III) and Cr(VI) as the particle-reactive $Cr(VI)(OH)_2^+ \cdot 4H_2O$ and the soluble oxyanion $Cr(III)O_4^{2-}$, also indicated nutrient-type behavior, albeit more muted than the other nutrient-like trace metals (Elderfield, 1970; Cranston and Murray, 1978; Campbell and Yeats, 1981; Semeniuk et al., 2016). However, the challenges of analysis and quality control with Cr's complicated redox chemistry have meant that Cr data quality has lagged the other metals (Horner et al., 2021). More recently, δ^{53}Cr studies have shed more light on Cr cycling, continuing to highlight the dominant role of redox in Cr cycling, but also the importance of biological mediation of Cr and δ^{53}Cr distributions (Moos et al., 2020; Horner et al., 2021; Janssen et al., 2020a). Overall, however, Cd and Zn are perhaps the best examples of nutrient-type trace elements, with extreme depletion in surface waters of the open ocean gyres (down to pmol kg^{-1} levels for Zn and fmol kg^{-1} for Cd), and enrichment with depth up to 11 nmol kg^{-1} for Zn and 1.2 nmol kg^{-1} for Cd in the North Pacific (Figs. 6–8; Schlitzer et al., 2018; GEOTRACES Intermediate Data Product Group, 2023).

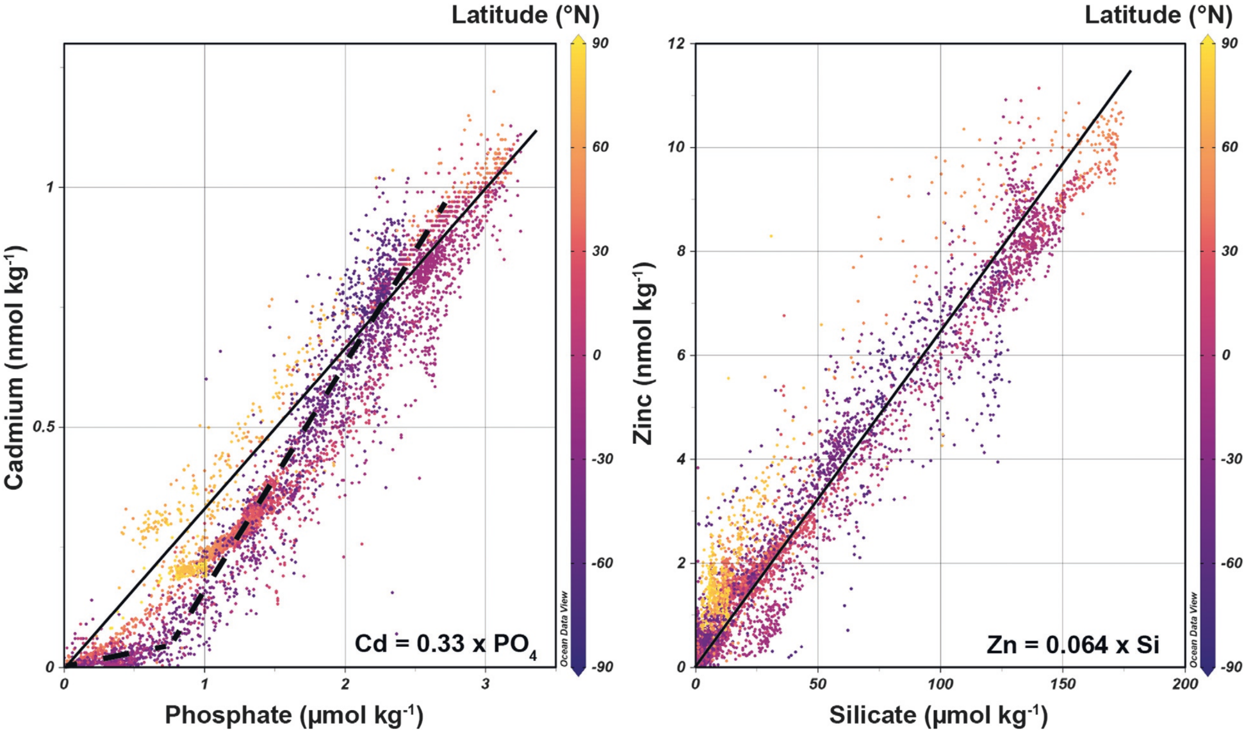

Fig. 8 Global relationships between oceanic macronutrients and micronutrients. Left panel shows oceanic dissolved Cd and dissolved phosphate, and right panel dissolved Zn and dissolved silicate. Black lines denote slopes based on the relationship of these elements in deep waters (de Souza et al., 2022; Vance et al., 2017). The dashed lines on Cd/P panel shows an example of how the Pacific Cd/P relationship can be described with two lines of different slopes in surface and deep waters (Sieber et al., 2019), but overall complexity to the global Cd/P graph arises from the mixing of different water masses with different preformed Cd:P ratios (Middag et al., 2018). Notably, Cd:P and Zn:Si are both strongly elevated in Arctic waters (Jensen et al., 2019; Zhang et al., 2019). Data are taken from the GEOTRACES Intermediate Data Product 2021 (GEOTRACES Intermediate Data Product Group, 2023) and Sieber et al. (2023a,b).

As with the macronutrients, since nutrient-type trace elements are not highly scavenged to particles, their concentrations are higher in 'older' waters. Water mass age is calculated relative to the last time the water was at the surface where it was able to exchange gases with the atmosphere and where nutrients were last depleted due to biological uptake. As such, older water masses have accumulated more nutrients from regeneration of particles settling from above into the water masses as they travel through the deep ocean. Nutrient type elements typically have an intermediate depth maximum, reflecting a required circulation component in addition to the simple vertical processes of uptake and regeneration (Bruland et al., 2014). This noted enrichment at intermediate depths can be clearly observed when comparing the relatively young North Atlantic and the much older North Pacific water in Fig. 4 for macronutrients and nutrient-type trace elements (Cd is 0.3 nmol kg^{-1} at 1000 m in the Atlantic and 0.9 nmol kg^{-1} at 1000 m in the Pacific, while Zn increases from ~2 to 8 nmol kg^{-1}).

A third group of trace element distributions are the 'scavenged' distributions, that exhibit a very different profile shape to those of the macronutrients. These elements have very short residence times (<50 to 1000 years), driven by their chemical reactivity and thus more intense interaction with particles leading to removal via adsorption or precipitation (particle scavenging). Classic examples of trace elements with scavenging-type profiles are Al, Mn and Pb, where concentrations are only high near-source (e.g. atmospheric input, bottom sediments, hydrothermal vents, oxygen minimum zones) and decrease with distance from source. A variety of dominant sources between ocean basins (e.g. dust in the North Atlantic vs subsurface sediments in the North Pacific for Mn), means that concentrations tend to vary between basins at surface and intermediate depths, while continuous particle scavenging drives concentrations down in deep waters, leading to negligible inter-basin variability between the deep Pacific and Atlantic (Fig. 4). For example, Mn can reach concentrations of 1–2 nmol kg^{-1} in the surface/sub-surface but is uniformly low (~100 pm kg^{-1}) in deep waters in both profiles shown in Fig. 4. Similarly, Pb, which is very particle-reactive, is present at <10 pmol kg^{-1} at depth in both the North Atlantic and North Pacific (Fig. 4; Lanning et al., 2023; Boyle et al., 2014). Aluminum profiles are often dominated by input from atmospheric dust (Measures et al., 2008), meaning that Al is present at high concentrations in the surface of the tropical Atlantic, where dust deposition is high, but lower in regions such as the North Pacific which receive little dust (Orians and Bruland, 1986; Measures et al., 2015; Middag et al., 2015b). For example, Al concentrations can reach as low as 0.1 nmol kg^{-1} in surface Antarctic Waters (Middag et al., 2011b, 2012), to 50 nmol kg^{-1} in surface North Atlantic waters (Measures et al., 2015) to ~180 nmol kg^{-1} in Mediterranean Waters which receive high dust levels of dust deposition (Rolison et al., 2015). Particle scavenging generally drives down deep-water Al concentrations in deep and older waters (Orians and Bruland, 1986). Intriguingly, dissolved Al, while generally displaying scavenged type behavior, can also display a nutrient-like behavior. However, while such behavior was initially thought to be due to Al incorporation in diatom frustules and subsequent release with dissolution, reversible scavenging is now deemed more important in driving this (Van Hulten et al., 2014; Xu and Weber, 2021).

Some trace elements exhibit vertical distributions that reflect a mix of nutrient-type and scavenging behavior, and thus have been described as 'hybrid' type distributions. For example, while Co was originally thought to be a scavenged-type element (Jickells and Burton, 1988), it is now considered to be hybrid, with a mix of biological cycling, scavenging, organic-complexation, and sources all being important in setting Co's distribution (Tagliabue et al., 2018; Saito and Moffett, 2002; Noble et al., 2008, 2012; Saito et al., 2017). However, perhaps the most classic example of a hybrid type distribution is dissolved Fe, which is strongly influenced by both biological cycling and particle-interactions. In some regions of the surface ocean, such as the Southern Ocean, Fe concentrations are strongly depleted in surface waters (down to <20 pmol kg^{-1}) by biological uptake, and then increase with depth up to values of up to 0.8 nmol kg^{-1} in intermediate depth (~1000 m) waters (e.g. Martin and Michael Gordon, 1988; Johnson et al., 1997; Blain et al., 2008; Sarthou et al., 2008). Unlike the nutrient-type elements, however, Fe does not show a clear increase in deeper waters or from the Atlantic to the Pacific, displaying near-identical vertical profiles in the North Atlantic and North Pacific (see Fig. 4). The hybrid profile shape of Fe was initially interpreted as atmospheric addition and biological uptake in the surface, intermediate depth regeneration, and deep-water concentrations of Fe controlled by a mix of regenerating particles, particle scavenging, and ligand complexation setting the deep ocean to 0.6–0.7 nmol kg^{-1} (Johnson et al., 1997). In the oligotrophic gyres, particularly the North Atlantic, where productivity is nutrient-limited and dust deposition adds dissolved Fe to surface waters, Fe exhibits surface concentration maxima and subsurface decline, like the scavenged elements. For example, western subtropical North Atlantic surface waters can reach values of up to 2 nmol kg^{-1} from dust deposition in summer, and as low as 0.1 nmol kg^{-1} in the subsurface (or at the surface in winter) from scavenging and biological activity (Sedwick et al., 2005). While we now know that dissolved Fe profiles are more heavily influenced by a mixture of sources than were considered in the late 1990s view of Fe cycling (see Section "Current knowledge of the marine distributions of trace elements and isotopes"), it is notable that many of the insights gleaned about Fe cycling in these early studies from just a small number of profiles have been confirmed by larger Fe datasets. Further, even in early datasets it was possible to see the importance of deep sources such as margin sediments in contributing to intermediate depth Fe maxima (Johnson et al., 1999); the difference is then they were thought to be the exception, now we know them to be commonplace.

The Rare Earth Elements (REE), which compromise the lanthanides (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) and Sc and Y, are a group of elements with interesting chemistry and distributions in rocks, rivers, and seawater (Piper and Bau, 2013). Typically subdivided arbitrarily based on atomic mass into 'heavy', 'middle', and 'light, or just 'light' (LREE) and 'heavy' (HREE), these elements all have similar overall chemistry in seawater, generally at 3^{+} oxidation states complexed with carbonate (CO_3^{2-}) or phosphate ions and present at fmol kg^{-1} to pmol kg^{-1} concentrations (Piper and Bau, 2013; Elderfield and Greaves, 1982; Byrne and Sholkovitz, 1996). However, an effect known as the lanthanide contraction means that the atomic radius of these elements increases more than might be expected across the periodic table, which has a fundamental effect on their aquatic chemistry. Notably, the strength of the dissolved REE-CO_3^{2-} complex increases across the period, increasing stability and reducing the propensity to be scavenged to particles (Byrne and Kim, 1990; Luo and Byrne, 2004; Turner et al., 1981; Goldberg et al., 1963). As such, it is much easier to particle-scavenge light REE such as La than heavy REE such as Lu, with the effect of the ocean being relatively enriched in HREE over LREE compared to the continental crust (e.g. Sholkovitz and Schneider, 1991; De Baar et al., 1985). It also means that the REE, while having similar overall chemistry, display a range of residence times and distributions in the ocean; HREE such as Lu have near-conservative vertical profiles and a residence time of ~3000 years, while LREE such as La have profiles that strongly reflect source addition (atmosphere and sediments), scavenging, and water masses, and a residence time of ~500 years (Nozaki, 2001; Elderfield and Greaves, 1982). The difference in concentration in deep waters of the Pacific and Atlantic is only a factor of 2–3, in comparison to much larger differences for nutrient-like elements (De Baar et al., 1985). A notable exception to the other REE is Ce, which typically forms 4+ ions in seawater and is easily particle-scavenged, leading to a residence time of only 50 years, and profiles that are dominated by source-addition and relatively rapid removal (Piper and Bau, 2013). Measurement of the pattern or 'curve' of REE (their relative distributions) in seawater or seafloor rocks can be useful for investigating the exchange of REE between dissolved and particulate phases, or during hydrothermal alteration, while the radiogenic isotope ratios of elements such as Nd (εNd) and Hf trace terrestrial sources to the ocean and thus have found utility as water-mass tracers (van de Flierdt et al., 2016; Piper and Bau, 2013; Marchitto and Lynch-Steiglitz, 2024).

Current knowledge of the marine distributions of trace elements and isotopes

The GEOTRACES program and a range of other research efforts in the last ~20 years has led to many advances in our understanding of trace elements and their isotopes in the oceans. It is not our intention to review them all here, but we do point the reader to recent reviews (e.g. Anderson, 2020; Horner et al., 2021) which provide more detail. Here we aim to describe how large datasets have allowed for a more complete picture of the distributions of the bioactive trace elements throughout the oceans, as well as the processes which shape them. GEOTRACES and other works have also led to dramatic advances in our knowledge of the global distributions and behavior of rare earth and radionuclide trace elements which have utility as rate, circulation, or process tracers. These trace elements are discussed further in Sections "Inputs of trace elements to the oceans (sources)" and "Dissolved to particulate exchange processes and ocean sinks" in the context of their utility in investigating sources, sinks, and internal cycling processes, and the use of these radionuclides is described further by Marcantonio et al. (2024).

Even from the first vertical profiles of the nutrient-type bioactive trace elements, it was clear to early researchers that profile shapes could not be simply explained by local uptake and regeneration, but that ocean-circulation was required to explain why elements were more enriched in the older waters of the Pacific than the Atlantic (Section "Classical concentration distribution patterns and residence times"). Some studies also recognized the importance of the Southern Ocean in influencing global trace elements distributions, especially for the Atlantic 'kink' in the Cd-P relationship (e.g. Frew and Hunter, 1992; De Baar et al., 1994; Cullen, 2006; Broecker and Peng, 1982), where sub-Antarctic waters giving rise to mode and intermediate waters are depleted in dissolved Cd relative to phosphate, while other deep water masses are similar to the global ocean dissolved Cd:P ratio. The reason for preferential uptake of Cd over phosphate in these regions is still not fully understood, though it has been attributed to increased Cd uptake under Fe-limited conditions (Sunda and Huntsman, 2000; Cullen, 2006; Twining and Baines, 2013; Quay et al., 2015). However, an extreme paucity of trace element data that was needed to fill in the jigsaw meant that there was a tendency to continue to interpret distributions dominantly in terms of vertical cycling processes of uptake, regeneration and/or scavenging. Similarly, dissolved Fe profiles were typically interpreted as a combination of surface addition from dust, biological uptake, ligand-complexation, and scavenging (Boyd and Ellwood, 2010). However, with the onset of the International GEOTRACES program, and the veritable explosion in data that has come with it, it has been confirmed that interpreting trace element distributions largely only in terms of their vertical profiles fails to capture the entire picture.

Accordingly, since the publication of the previous version of this chapter in 2014 (Bruland et al., 2014), our view of the controls on the distributions of trace elements and their isotopes have evolved to align closer with understanding of the controls on the macronutrients, following Sarmiento et al. (2004), with the Southern Ocean acting as a global 'hub' that drives global nutrient distributions (e.g. Vance et al., 2017; Sieber et al., 2019b; Middag et al., 2018, 2019, 2020). Upwelling of deep waters around Antarctica brings nutrients to the surface, while preferential uptake and regeneration of different nutrients within zones of the Antarctic Circumpolar Current (ACC) impart distinct 'pre-formed' nutrient signatures to subducting water masses such as subantarctic Mode Water (SAMW) and Antarctic Intermediate Water (AAIW) which form from different regions of the Southern Ocean (Talley et al., 2011; Talley, 2013; Orsi et al., 1995; Sarmiento et al., 2004). These water masses then advect northward carrying nutrients (P and N), leaving the Southern Ocean and influencing low latitude thermocline nutrient distributions (Marinov et al., 2006; Sarmiento et al., 2004). In this view, the deeper maximum seen in silicate compared to phosphate or nitrate in the typical low-latitude nutrient-type profile (Fig. 4), is not driven principally by differing rates of local regeneration of phosphate and silicate, but by the advection of Southern Ocean sourced water masses with preformed Si:P ratios that are set in the surface of the Southern Ocean where diatom utilization of Si preferentially traps Si within the Antarctic Zone, while a greater portion of the P and N escape northward into AAIW and SAMW, feeding the low latitude thermoclines (Sarmiento et al., 2007, 2004). Local and accumulated regeneration may then act to gradually overprint these signals, influencing nutrient ratios as water masses advect and mix.

With the availability of larger trace element datasets, it has become clear that similar mechanisms are driving the global distributions of trace elements and their isotopes as well as any relations between trace elements and the macronutrients. As such, the varying global distribution of the nutrient-type trace elements and their similarities or differences relative to the macronutrients both arise principally from variable use of different nutrients by phytoplankton in different regions, where the uptake stoichiometry is for example different in the formation region of North Atlantic Deep Water compared to waters of the Southern Ocean where water masses such as AAIW or AABW form. Notably in the different zones of the ACC, this effect is driven by Southern Ocean diatoms that take up elevated Zn and Si—and to a lesser extent Cd—relative to phosphate (Twining and Baines, 2013), leaving a biochemical fingerprint on surface waters; Zn and silicate are both preferentially used and thus trapped in the Antarctic zone, while phosphate—and to a lesser extent Cd—remains present into the surface waters of the Polar Frontal Zone and into the sub-Antarctic zone, from where subducting AAIW and SAMW form, respectively (Sieber et al., 2020; de Souza et al., 2018; Zhao et al., 2014; Vance et al., 2017). As such, these water masses are clearly depleted in Zn relative to phosphate when sampled at lower latitudes (e.g. Wyatt et al., 2014; Middag et al., 2019). Cd is also strongly sequentially depleted through the zones of the ACC, with AAIW and SAMW carrying lower Cd:P dissolved ratios than upwelling UCDW (0.30 and 0.25 vs 0.35; Baars et al., 2014; Sieber et al., 2019b). However, a slower depletion of Cd relative to Zn (and later mixing with UCDW in the Atlantic) means that both AAIW and SAMW remain relatively Cd-rich water masses compared to Zn or Si (Middag et al., 2018, 2019; Sieber et al., 2020; Croot et al., 2011; Baars et al., 2014)—and hence why vertical profiles of Cd more strongly resembles P at lower latitudes while Zn resembles Si (Fig. 4).

In the Atlantic Ocean, northward proliferation of Southern Ocean water masses such as SAMW and AAIW carrying preformed trace element concentrations dominate the lower-latitude trace element vertical distributions, while local uptake and regeneration only act to overprint the influence of regional circulation of water masses with different nutrient contents (Abouchami et al., 2014; Xie et al., 2015; Middag et al., 2018). This can be very clearly seen in a compilation of two meridional sections of dissolved Cd from the Atlantic and Pacific Oceans (Dutch GA02, and Japanese GP19 & US GP15), where example vertical profiles can be seen to be simply an expression of the 3D circulation (Fig. 6). The Atlantic is characterized by very-depleted Cd in gyre surface waters due to biological uptake and the presence of nutrient depleted SAMW and STMW, but the dominance of the high-Cd southern water masses AAIW, UCDW and AABW vs the lower-nutrient NADW are clear at depth (Abouchami et al., 2014; Middag et al., 2018). Analysis of water masses from the GA02 section have highlighted the fact that the Atlantic Cd-P relationship is not merely characterized by a simple 'kink', but instead is a combination of mixing lines between a range of different water masses with distinct preformed dissolved Cd:P ratios that are determined by uptake/regeneration stoichiometry and formation location (Baars et al., 2014; Quay et al., 2015; Middag et al., 2018; Xie et al., 2015).

In the Pacific Ocean, a lack of regional deep-water formation means that Southern Ocean Cd-P systematics and Southern-Ocean sourced water dominates, with the dataset characterized by two slopes: a shallow slope in shallow waters and a steeper slope for intermediate and deep waters (Sieber et al. (2019b); shown as dashed lines in Fig. 8). In the North Pacific, however, old PDW at intermediate depths contains the highest Cd concentrations in the ocean, and reflects southern sourced waters complemented with *in situ* regeneration over time. For instance, Sieber et al. (2023b) recently estimated that 30% of the Cd and P in PDW comes from *in situ* regeneration in the Pacific, at an integrated Cd:P ratio lower than the dissolved Cd:P of the deep Pacific (set by Southern Ocean water masses such as LCSW), and thus PDW data lies offset from the rest of the data in Fig. 8—hence in the Pacific a range of processes and water masses come together to create a scatter rather than a distinct correlation or single kink in Cd-P, as seen in the most recent global compilation of Cd and phosphate (Fig. 8). This complexity that we now know exists in both dissolved Cd-P and Zn-Si (Fig. 8) is driven by multiple processes, meaning that great care must be used in interpreting local or regional changes in the change of one element relative to the other, and also for regression lines with a non-zero intercept, such as the Cd-PO_4 relationship, care should be taken to differentiate between the slope of regression and the dissolved or 'spot' ratio (Baars et al., 2014; Middag et al., 2018). Recently, parameters such as Cd* and Zn* have also been used to identify deviations in the behavior of Cd and P or Zn and Si from an expected ratio due to variable stoichiometry during uptake or removal of one element or the other from the dissolved phase (e.g. Baars et al., 2014; Janssen et al., 2014). Such parameters have been defined as $Cd^* = 0.33^*[Cd/P]_{local}$ and $Zn^* = 0.064^*[Zn/Si]_{local}$ based on the global mean ratios of the nutrients in the deep ocean (e.g. Vance et al., 2017; de Souza et al., 2022). Again, such parameters are useful, but it must be stressed that changes in these parameters are arbitrary, and do not necessarily imply local loss or gain of one of the elements. In interpreting local deviations in Cd* or Zn* and spot ratios, it has to be stressed that the preformed structure of the ocean (i.e. differences in Cd*, Zn*, Cd:P and Zn:Si due to discrete water-masses) must be considered.

Trace element isotopes have also played a key role in understanding the global distributions of the nutrient-type trace elements (see Little et al. (2024) for more details), which are typically seen to fractionate towards higher isotopic ratios in surface waters as kinetic isotope fractionation favors uptake of lighter isotopes (e.g. Cd; Ripperger et al., 2007). For example, the distribution of dissolved δ^{114}Cd in the Atlantic and Pacific highlights the fact that uptake of isotopically light Cd in Southern Ocean waters imparts a distinct isotopically-heavy, Cd depleted, signature to AAIW relative to deep water (+0.4 to +0.6‰ relative to +0.2‰), which is then advected northwards and dominates intermediate depths of the South Pacific and the Atlantic (Sieber et al., 2019a, b; Abouchami et al., 2014; Conway and John, 2015a; Xue et al., 2012). Silicon isotopes (δ^{39}Si) within dissolved silicate shows similar behavior (de Souza et al., 2012a, b). In contrast, measurement of δ^{66}Zn distributions have shown no obvious nutrient type fractionation towards heavy surface values, which led to the suggestion that reversible scavenging must be playing a role in the marine Zn and δ^{66}Zn cycle (Weber et al., 2018; John and Conway, 2014). Most recent Zn isotope work, while continuing to highlight the dominance of the Southern Ocean in setting the global Zn distributions and the Zn/Si correlation (Fig. 8) over much of the ocean, still highlights a need for other processes, especially in the North Pacific (Weber et al., 2018; Sieber et al., 2023a), where *in situ* regeneration of Zn coupled to phosphate, as well as regenerative scavenging decoupled from Si have been invoked to explain both Zn and δ^{66}Zn distributions (Sieber et al., 2023a). While questions remain, these examples highlight the utility of trace element isotope systems in informing our understanding. However, while δ^{114}Cd systematics are now well studied, the systematics of other trace element isotope systems in relation to biological uptake (e.g. δ^{53}Cr, δ^{56}Fe, δ^{60}Ni, δ^{65}Cu, δ^{98}Mo) remain unclear and are thus in need of further data and study to establish their potential utility for understanding modern and past oceans (Horner et al., 2021; Fitzsimmons and Conway, 2023), in conjunction with other isotope systems such as δ^{13}C, δ^{15}N, δ^{39}Si, and δ^{138}Ba.

Meridional GEOTRACES ocean sections such as the Atlantic GA02 section also provide illumination of the distribution of a range of other trace elements. From such sections (Fig. 6), we can see the contrasting behavior of the trace elements and the role of mixing of water masses in setting their distributions. For the nutrient-type elements, Cd somewhat resembles phosphate with a distinct 'tongue' of AAIW extending well into the North Atlantic, while Zn is much more subdued in AAIW and more strongly present in AABW. Ni follows a similar pattern to Cd, but never depletes fully and maintains a stubborn ~2 nmol kg^{-1} in surface waters which has been recently attributed to a slower depletion of Ni relative to other nutrients in upwelling regions (John et al., 2022). Sections of Al, Fe and Pb look very different to the nutrient-type elements, highlighting the individual chemical processes affecting these elements. For Pb, concentrations are most strongly elevated in intermediate depth waters at ~1000 m (Labrador Seawater) in the North Atlantic, coincident with elevated CFCs and representing Pb that was added to the ocean decades ago via atmospheric deposition in formation regions. Although this Pb has been partially scavenged since addition, enough remains to be advected southward and visible at depth, while surface waters reflect lower addition of Pb combined with effective scavenging (Fig. 5; Boyle et al., 2014). The elevation at intermediate depths in the Atlantic is also clear from Fig. 4, while the Pacific has elevated Pb at ~500 m, reflecting the input of Pb from Asia into North Pacific Intermediate Water (Lanning et al., 2023). Lower Pb levels in the very deep Atlantic and Pacific reflect water (e.g. AABW, LCDW) that has not been influenced by human activity, and Pb is kept low by particle scavenging. For Al, clear addition can be seen from atmospheric dust from the Sahara within tropical latitudes, as well as large, and unexpected addition from benthic sediments in the northern part of the section (Van Hulten et al., 2013; Middag et al., 2015b) which highlights the importance of local sources.

Similarly, our knowledge of the distribution of Fe has evolved dramatically since 2010, moving from the prevalent 1990s view—surface addition of Fe from dust combined with regeneration at intermediate depths and organic-complexation keeping deep concentrations at near 0.6 nmol kg^{-1} (see Section "Classical concentration distribution patterns and residence times")—to a view where Fe distributions are shaped by a wide range of sources and processes (Tagliabue et al., 2017). The GA02 dissolved Fe section highlights this, with a range of different Fe hotspots visible, attributed to Fe released from a mix of sediments, venting on the Mid-Atlantic Ridge, the Amazon River, and deposition of desert dust (Rijkenberg et al., 2014): Fig. 7). Prior to recent datasets, although there were studies that hinted at the importance of the transport of Fe from reducing sediments (Pollard et al., 2007; Johnson et al., 1999; Elrod et al., 2004; Blain et al., 2007), it was often assumed that Fe from sources such as sediments or hydrothermal vents would be dominantly lost near-source. Perhaps one of the great advances of GEOTRACES is to enhance this picture, showing that in fact sediments and hydrothermal venting are can in fact be pervasive deep sources of Fe, which can be transported great distances through the intermediate-deep ocean, shaping vertical distributions and potentially impacting surface productivity (Resing et al., 2015; Tagliabue et al., 2017; Anderson, 2020; Nishioka et al., 2020). Indeed, studies have shown that both sediment- and hydrothermally-sourced plumes of Fe can travel thousands of kilometers, sustained by a—still incompletely understood—mix of organic ligand complexation and/or particle-interactions (Saito et al., 2013; Fitzsimmons et al., 2014, 2017; Conway and John, 2014b; Resing et al., 2015; Nishioka et al., 2007, 2020), but intriguingly, long range transport is not always observed for hydrothermal or sedimentary derived Fe.

There are other surprises from recent research—for example, while reducing sediments have been confirmed to be important sources of Fe due to release of dissolved Fe^{2+} from porewaters (produced by reduction of Fe(III) associated with microbial breakdown of organic matter) to bottom waters, ocean sections have also shown that non-reducing sediments can also be large sources of dissolved Fe (Conway and John, 2014b; Anderson, 2020; Radic et al., 2011), inspiring changes to our understanding of how sediments add Fe to the ocean in the form of colloidal lithogenic weathering products (Homoky et al., 2021). Measurement of dissolved stable Fe isotopes (δ^{56}Fe) has helped with assessing the importance of different sources, by allowing sources to be fingerprinted and dissolution mechanisms to be interrogated (Fitzsimmons and Conway, 2023). For example, very different δ^{56}Fe compositions are seen in the Atlantic (+0.1‰) vs the Pacific (−0.5 to −1‰) for the 0.7 to 0.8 nmol kg^{-1} maximum in Fe concentrations at 1000 m (Fig. 4), highlighting the fact that transport of different Fe sources (non-reductive sediment vs reductive sediment plumes) are influential in producing equivalent features in two different basins (Conway and John, 2014b, 2015b). This demonstrates how different Fe sources can vary in importance, locally, regionally, and globally; for example, paired sections of Fe and δ^{56}Fe highlight the relative and varying importance of multiple distinct sources to different regions of the subtropical Atlantic GA03 section (Fig. 9).

The importance of considering a mix of Fe sources that vary regionally is beautifully highlighted in Fig. 10 by a 3D compilation of GEOTRACES ocean sections that shows how prevalent different margin sources of Fe are through the Atlantic and Pacific Oceans (http://www.egeotraces.org; Schlitzer et al., 2018; GEOTRACES Intermediate Data Product Group, 2023). Thus, while important questions remain about the form of Fe released by each source, its longevity in the ocean, and thus the potential for such Fe to influence productivity in surface waters, the importance and prevalence of these deep sources is now undeniable. As a sense of how our view of Fe sources to the ocean has changed, biogeochemical models even go as far to suggest that dust—contrary to the original paradigm that it was the dominant source of Fe to the oceans—may even be the least important Fe source to the overall water column as well as for driving carbon export in most areas of the ocean (excluding the low latitudes), favoring upwelling of deep sediment or hydrothermal sources instead (Tagliabue et al., 2014a, 2017). Despite these impressive advances in our understanding of the Fe cycle in the four decades since the first measurements were made, much of

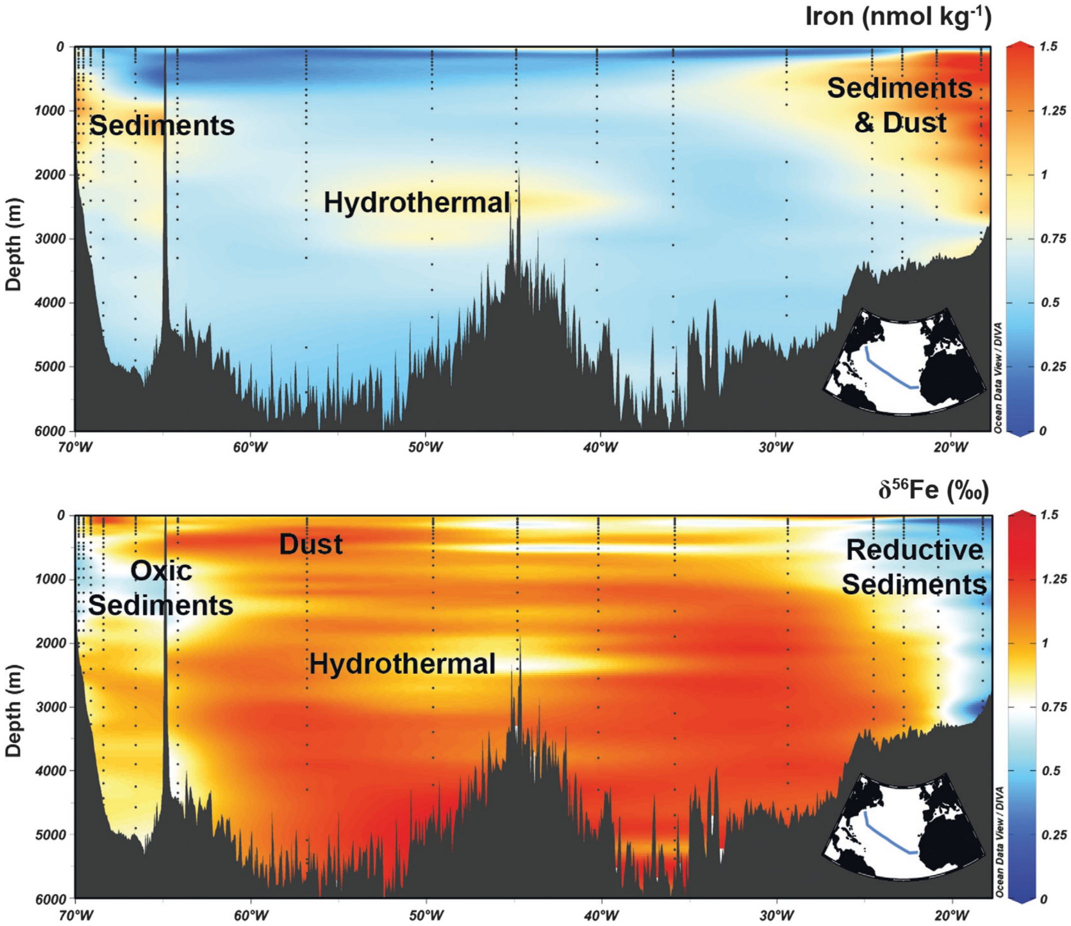

Fig. 9 Subtropical North Atlantic Zonal Section (GEOTRACES GA03) of dissolved Fe concentrations and stable isotopes (δ^{56}Fe relative to IRMM-014). Dots indicate sampling and station locations, and map shows station locations. Hydrothermal Plume at station 16 over the Mid Atlantic Ridge is excluded. Data are reproduced from Conway and John (2014b). Labels denote the influence of external boundary sources on the distribution of both parameters.

dissolved Fe chemistry remains something of a 'black box', with many questions remaining. For example, we have only recently been able to characterize specific natural Fe-binding ligands such as siderophores *in situ*, and shown that they make up only a tiny fraction of the operationally-defined Fe-binding ligand pool (Gledhill and Buck, 2012; Moffett and Boiteau, 2024). Similarly, the importance of (inorganic) colloids and particles, and not just organic ligands, in facilitating Fe cycling, especially in dusty regions, continues to be recognized and (only recently) incorporated into models of ocean biogeochemistry (e.g. Fitzsimmons et al., 2015b; Homoky et al., 2021; Tagliabue et al., 2023). As such, we anticipate that our understanding of the processes that set dissolved Fe distributions will continue to evolve.

Inputs of trace elements to the oceans (sources)

Introduction

The composition of seawater over long timescales reflects the balance between addition and removal of a given element from the ocean, while the size of fluxes in/out relative to the reservoir size determines residence time. Elements can enter or leave the ocean at external boundary interfaces, which can function as 'sources' or 'sinks'. It is also important to consider the concept of external 'sources' (e.g. atmosphere, rivers, riverine and lithogenic sediments), and remobilization of elements from particles or sediments as 'internal' sources (e.g. microbial-mediated release of elements from sediments and organic matter to bottom waters during reductive breakdown of organic matter). In this section we briefly introduce and describe the major sources (rivers and submarine groundwater, atmosphere, sediments, hydrothermal, cryosphere) of trace elements to the oceans, with examples of progression from past concepts to recent insights. Historically, understanding of elemental additions to the oceans focused on rivers, with atmospheric sources thought to be most important for some elements with short residence times such as Fe or Pb. While rivers continue to be viewed as major sources of conservative elements which arise from continental weathering, as well as influential for

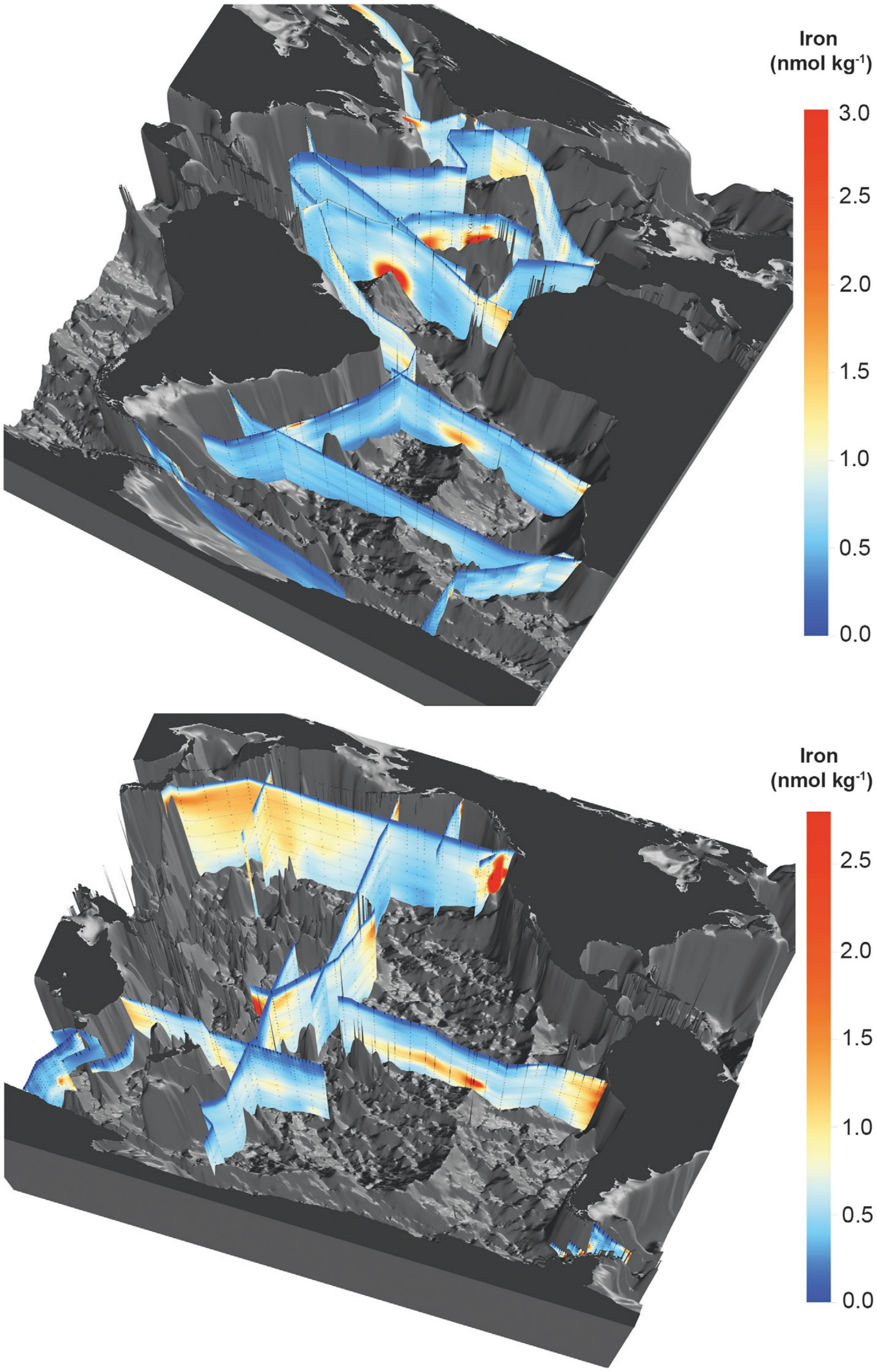

Fig. 10 3D view of multiple GEOTRACES dissolved Fe sections from the Atlantic (top) and Pacific (bottom) Oceans, taken from the GEOTRACES Intermediate Data Product (GEOTRACES Intermediate Data Product Group, 2023) and reproduced from the e-GEOTRACES Atlas (Schlitzer et al., 2018). Low dissolved Fe concentrations can be seen in surface waters, and deeper hotspots of elevated Fe concentrations from external sources are visible near margins. Figure courtesy of Reiner Schlitzer.

the long-term budget of elements with intermediate residence times (e.g. Zn, Ni), more recently, benthic sediment fluxes and hydrothermal venting have emerged as important, and perhaps even dominant, sources of elements such as Fe, while boundary exchange and submarine groundwater at continental margins have also been shown to play an important role for a number of elements (Jeandel, 2016; Tagliabue et al., 2014a). Lastly, though perhaps most poorly constrained, the cryosphere (ice shelves, sea-ice and melting glaciers) may play an important role in the budget of some elements, especially at high latitudes. Fig. 1 shows a schematic view of our current concept of the different sources, sinks, and internal cycling processes, based on the GEOTRACES

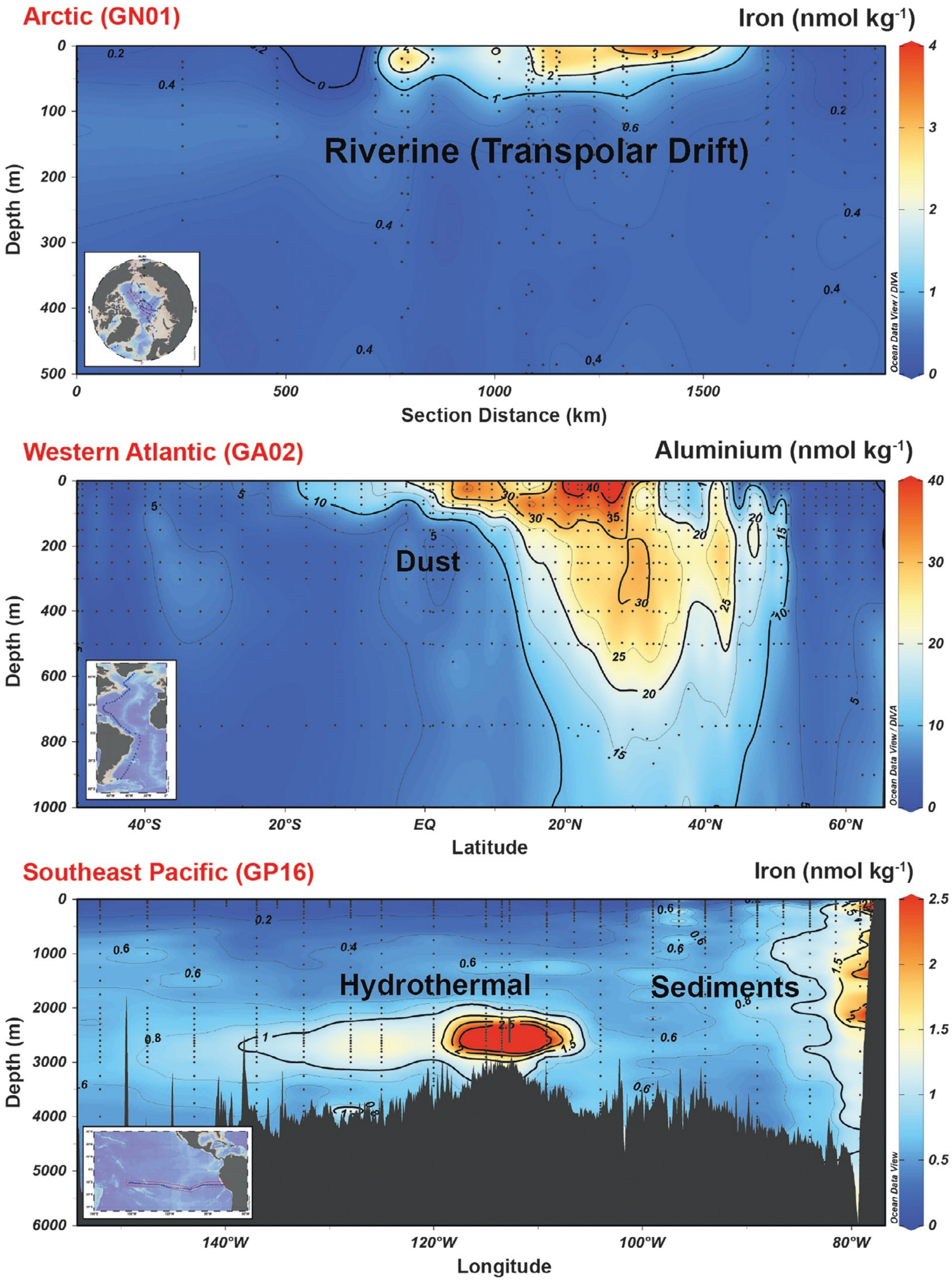

Fig. 11 Boundary sources of trace elements to the Ocean. US GEOTRACES GN01 shows the influence of the Transpolar Drift on trace elements in the surface of the Arctic Ocean (Fe shown). Dutch GEOTRACES GA02 shows the influence of subtropical dust deposition on trace elements in the Western Atlantic Ocean (Al shown). US GEOTRACES GP16 shows the influence of hydrothermal venting on the East Pacific Rise and sediments on the South American margin on trace elements through the Southeast Pacific (Fe shown). Dots indicate sampling and station locations, and maps show station locations. Data are reproduced from the GEOTRACES Intermediate Data Product Group (2023).

Science Plan (GEOTRACES Group, 2006; GEOTRACES SCOR Working Group, 2007), while Table 1 details a non-exhaustive list of which trace elements and their isotopes may be useful for investigating which source/sink or internal cycling process. Fig. 11 shows examples of how ocean sections are proving useful in highlighting the effect of point sources on the Arctic (riverine from the Transpolar Drift), subtropical Atlantic (dust), and South Pacific (hydrothermal), while Figs. 9 and 10 highlights the importance of a mix of Fe sources (dust, hydrothermal, reductive and oxic sediments) to the deep Atlantic and Pacific.

Notably, our view of elemental budgets has evolved to reflect more strongly the fact that the relative importance of each boundary source varies by element, but that it is important to consider all sources in whole ocean and local mass balances for each element. Helping with this, isotopic ratios continue to emerge and develop as powerful source tracers for the ocean system, with radiogenic elements such as Pb, Sr, and Nd, with distinct isotope ratios set at source, long established as dust provenance tracers, while development of different Ra isotopes (^{223}Ra, ^{224}Ra, ^{228}Ra) as non-particle reactive open ocean tracers of hydrothermal venting, submarine groundwater discharge/rivers and sediment release, and ^{7}Be, ^{232}Th/^{230}Th for calculating dust deposition show promise (e.g. Hayes et al., 2013; Charette et al., 2015; Moore et al., 1996). Of course, various uranium decay series radionuclides (^{210}Pb, ^{210}Po, ^{230}Th, ^{231}Pa, ^{234}Th, ^{234}U, etc.) have also long been used as helpful quantitative tracers of particle transport, export fluxes, scavenging, and sediment accumulation/redistribution (see Marcantonio et al. (2024) for a detailed review, and Section "Particle scavenging"). The aspects of Nd which make it a good dust or rock provenance tracer, (namely the radiogenic decay of ^{147}Sm to ^{143}Nd) means that εNd ratios vary significantly between old crustal rocks and young volcanogenic rocks (Robinson et al., 2021); this, combined with the ~500 year residence time of Nd in the ocean, means that εNd varies from basin to basin (and water mass to water mass), and thus is a useful tracer of lithogenic source and water mass circulation (van de Flierdt et al., 2016; Marchitto and Lynch-Steiglitz, 2024). Lastly, in the last decade, research has even advanced to use isotopic tracers such as δ^{66}Zn and δ^{60}Ni to identify and constrain missing sources and sinks and calculate residence times and oceanic mass balances (Little et al., 2014, 2016, 2020), and/or tracers such as δ^{56}Fe to quantify the relative importance of sources to oceanic regions (Conway and John, 2014b); for more information on isotope systematics of oceanic sources and sinks of trace elements see Little et al. (2024).

Rivers and submarine groundwater

For the major ions in seawater, as well as some bioactive trace elements such as Ni, Cu, Zn, and Cd, input from rivers to the oceans is generally considered the dominant long-term source of oceanic elemental budgets (e.g. Cameron and Vance, 2014; Little et al., 2014; Broecker and Peng, 1982), providing a link between the products of terrestrial weathering and the oceans. Riverine fluxes of these trace elements, the isotopic signatures of these fluxes, and rivers' role in oceanic elemental budgets are discussed in more detail in Little et al. (2024). The historical approach to estimate riverine flux of major elements has been to measure their concentrations in both dissolved and particulate forms in the river and multiply these concentrations by the river discharge rate, thus arriving at an input flux of both forms of the elements. For trace elements, however, estimating the riverine flux is more difficult, with major uncertainties arising due to under-sampling of representative river systems, and the non-conservative behavior of some elements. Although large rivers dominate global river inputs to the oceans, such rivers are often located in remote regions and consequently are insufficiently sampled to allow for adequate understanding on the effect of differing chemical processes and sources on trace element concentrations and speciation, as well as to allow for accurate fluxes of dissolved trace element concentrations in relation to season and discharge to be determined (Jickells, 1995). Additionally, it is not unfeasible that small rivers with relatively little discharge could play a large role if the concentration of a specific element is much higher than in other river systems, or if many small individual rivers combined are responsible for substantial discharge (Colombo et al., 2019). Further, much of the historical river data for trace elements may not be accurate, as the use of trace metal clean techniques also needs to be applied to river sampling (e.g. Windom et al., 1991; Guay et al., 2010).

Moreover, riverine concentrations of trace elements upstream of the river mouth may not be the determining factor for the fluvial flux of many elements due to complications that exist under estuarine conditions at the river–sea interface. The increase in salinity occurring at the river–sea water interface, with its concomitant increase in the concentrations of the major seawater cations, can lead to flocculation and sedimentation of trace elements such as Fe or Pb (Boyle et al., 1977; Sholkovitz and Copland, 1981) or to desorption from suspended riverine particles of trace elements such as Ba or Ni (Edmond et al., 1978). Some trace elements like Cu, Ni and Zn have been shown to behave relatively conservatively through some estuaries and river plumes such as the Amazon or Mississippi (Shiller and Boyle, 1991; Hollister et al., 2021), but this may not hold for all estuarine setting. In contrast, however, the removal of Fe has been suggested to be near complete in estuaries due to the flocculation of strongly associated Fe-humic acid colloids in the presence of the increased concentrations of Ca^{2+} and Mg^{2+} found in estuaries (Sholkovitz and Copland, 1981). Estuarine environments are also thought to play a role in enriching the ocean in HREEs over LREEs relative to continental rocks, since LREE are preferentially scavenged in estuaries while HREE may be preferentially released (Sholkovitz et al., 1994; Sholkovitz, 1995). Lastly, many riverine systems may now be partially or highly influenced by anthropogenic activity, either directly into the river, or in the estuarine environment, leading to elevated trace elements such as Cu, Ni, Zn, Cd and Co (e.g. Samanta and Dalai, 2018; Chen et al., 2008; Gao et al., 2013). Overall, varying chemical speciation and behavior of different trace elements within the estuarine environment, coupled with a paucity in representative estuarine sampling, makes it difficult to obtain realistic estimates of the actual river input of dissolved trace elements to the oceans, especially if there is variability between different major river systems.

In addition to the direct supply of dissolved trace elements in river plumes, riverine particles, particle-dissolved exchange, and/or dissolution of estuarine or shelf sediments may themselves be sources of trace elements to the oceans (e.g. Amazon river sediments for Nd; Rousseau et al., 2015), possibly offsetting estuarine losses of dissolved metals and thus complicating global assessment of riverine fluxes. For example, a recent study showed that particle-dissolved exchange (adsorption-desorption) at ocean boundaries may account for almost half of pre-industrial Pb sources to the oceans (Chen et al., 2023). Similarly, recently, the importance of reversible scavenging of Pb for transporting atmospheric Pb from the surface to the deeper ocean has been highlighted (Benaltabet et al., 2020, 2023; Lanning et al., 2023). For riverine particles themselves, while the particulate flux of trace elements in rivers typically vastly exceeds the dissolved flux, most particles are thought to be trapped within estuaries (Chester and Jickells, 2012). Estuarine sediments thus contain both particles and dissolved elements removed to sediments during adsorption and flocculation, in addition to the sediment material itself, all of which can be exported to shelf sediments during periods of high river flow, episodic flushing of estuarine sediments during storms, or spring tides. Fresh particles coated with labile trace elements are also likely to be deposited on the coastal shelf primarily during the highest river discharge (Chester and Jickells, 2012). Coastal sediments are thus a major repository for trace elements derived from rivers and estuaries (Millward et al., 1998). Estuarine or subsequent coastal sediments can then themselves serve as 'sources' of dissolved elements such as Fe remobilized by microbial reductive dissolution (Homoky et al., 2016; Shi et al., 2019; Seyitmuhammedov et al., 2021; Lenstra et al., 2019, 2022), complicating our understanding of how much Fe is lost within estuaries and how much may reach the open ocean, as further discussed in the benthic input section. The answer to this question must rely heavily on an understanding of the form/speciation of the dissolved Fe and thus its longevity through the salinity gradient.

Previously rivers have only been calculated to contribute 3% of the Fe delivered to the surface ocean, with loss in estuarine or nearshore waters leading to assumptions that riverine Fe would have little impact on offshore productivity (Raiswell and Canfield, 2012; Browning et al., 2017). However, recent insights have confirmed that there is much variability between how different river systems might supply trace elements to different ocean basins. Although the influence of rivers on the distribution of particle-reactive elements such as Fe and Mn in the open surface oceans—and thus any effects on primary productivity—may have been assumed to be limited, several studies highlight how this depends on location and ocean circulation. For example, riverine fluxes to the isolated and relatively-land locked Arctic ocean, leads to elevated concentrations of several trace elements, including Fe and Mn, notably in the Transpolar Drift (Fig. 11; Klunder et al., 2012; Middag et al., 2011a; Jensen et al., 2022; Gerringa et al., 2021b; Charette et al., 2020; Colombo et al., 2019; Paffrath et al., 2021), while the Amazon River and Rio de la Plata plumes are clear sources of Fe and Mn to the western South Atlantic (Rijkenberg et al., 2014). Most recently, the Congo River, which is relatively unique in being the only major river that discharges over a narrow shelf on an eastern boundary region (Stramma and England, 1999), has recently been shown to be an important regional source of trace elements to the open ocean where Nd, Hf and Fe were traced 1000 km from the river mouth (Rahlf et al., 2021; Hunt et al., 2022; Vieira et al., 2020), attributed to organic complexation in the case of Fe. Under such conditions, riverine supply of Fe may even act to relieve local Fe-limitation in the South Atlantic (Hunt et al., 2022; Vieira et al., 2020).

Besides continental runoff via rivers, submarine groundwater discharge (SGD) is another pathway for terrestrial macronutrients and trace elements to reach the marine environment (Cho et al., 2018; Garcia-Orellana et al., 2021). Given the challenges of measuring SGD or SGD-driven elemental fluxes directly, tracers need to be used to estimate both the quantity of the water delivered to the ocean this way as well as the associated fluxes. Notably, naturally occurring Ra radionuclides with different half-lives (^{223}Ra, ^{224}Ra, and ^{228}Ra) are excellent non-particle reactive tracers of SGD and sediment input, added to submarine groundwater or coastal waters by decay in rocks and sediments of various members of the Th and subsequent release of soluble Rn and Ra (Charette et al., 2015; Garcia-Orellana et al., 2021). Although the challenges of constraining SGD fluxes has meant SGD has been somewhat overlooked in the past as a source of trace elements to the ocean, early assessments of SGD into the North Atlantic using ^{228}Ra (half life of 6 years) showed the SGD flux to be equivalent to 80–160% of the river flux (Moore et al., 2008). Similarly, SGD has been shown to be an important source of elements, notably to coastal water in the Mediterranean (Trezzi et al., 2016; Tovar-Sánchez et al., 2014b), and is currently receiving much more attention from the scientific trace element community, with Ra-derived SGD fluxes measured in a number of coastal situations (see recent comprehensive review by Garcia-Orellana et al., 2021). A key strength of some GEOTRACES expeditions has been to measure ^{228}Ra alongside other trace elements, the ratio of which can be used together with inverse models of Ra flux to calculate cross-shelf fluxes (including SGD-derived fluxes) of other trace elements to the open ocean (Charette et al., 2016). Despite these efforts, and although the importance of SGD has been established for some major elements and their isotopes (Li, Mg, Ca, Sr, and Ba; Mayfield et al., 2021; Cho et al., 2018), the importance of SGD for the marine budgets and cycling of most bio-essential trace element such as Fe remains poorly constrained. However, given the increasing interest for SGD, its role in the cycling of such elements will undoubtedly be subject of future process studies.

Atmosphere (natural and anthropogenic components)

While riverine, SGD and benthic inputs often dominate the external inputs of trace elements in the coastal zone, and sediments and hydrothermal venting may dominate the deep ocean, an important external source of trace elements and macronutrients to surface waters of the remote oceans is via atmospheric transport of dust, soil, volcanic ash, wildfire products (including entrained soil), and anthropogenic emissions from the continents which can enter the ocean via wet (in rain) or dry deposition (Jickells et al., 2005). Since atmospherically-sourced trace elements are added directly to the surface ocean, they can have an immediate effect on primary productivity, as compared to other sources which may need to be upwelled from deeper waters. However, the effect of atmospheric deposition varies dramatically on both spatial scale and temporal scales, with dust deposition (and elemental solubility) varying by orders of magnitude by location, season, and even discrete dust storms (Hamilton et al., 2020b, 2022; Baker and Croot, 2010). Moreover, processes occurring at the water-atmosphere interface in the so-called surface microlayer (SML), which is particularly rich in trace metals, result in added complexity (Tovar-Sánchez et al., 2014a, 2020; Engel et al., 2017).

With the first measurements of dissolved Fe in seawater, combined with recognition of Fe's role as a limiting nutrient and the first long-term records of atmospheric dust deposition from the Antarctic Vostok ice-core, 'the iron hypothesis' was established (Martin, 1990). This idea suggested that glacial-interglacial changes in the supply of atmospheric Fe to the Fe-limited Southern Ocean (Fe-fertilization) could be influential in regulating productivity and atmospheric carbon dioxide (CO_2) during the Pleistocene glacial cycles (Jaccard et al., 2013; Kohfeld and Ridgwell (2009); Sigman and Boyle, 2000). This link between elevated atmospheric dust (and Fe) deposition to the Southern Ocean during glacial intervals was further strengthened by CO_2, dust, and Fe records from EPICA-Dome C core which provided data from glacial-interglacial cycles over the last 800,000 years (Conway et al., 2015; Wolff et al., 2006; Lambert et al., 2008; Lüthi et al., 2008). While atmospheric Fe is now not thought to be the main driver of glacial-interglacial CO_2 shifts, giving way to other ideas about changing circulation and storage of carbon in the deep ocean, studies still show a role for Fe in influencing the Southern Ocean carbon cycle in the past, especially over millennial time scales (Jaccard et al., 2013; Martínez-García et al., 2014; Sigman et al., 2010; Ai et al., 2020), and have stimulated a range of modern Fe-fertilization experiments across Fe-limited oceanic regions (Yoon et al., 2018; Boyd et al., 2007; De Baar et al., 2005).

Today, while we have confirmed that numerous sources of Fe are important, and atmospheric dust is perhaps considered less important to the whole ocean Fe cycle than previously thought (Tagliabue et al., 2017), dust is still considered an important source of Fe (and Al) to the surface oceans, especially in the 'dusty' subtropical Atlantic (Huang et al., 2022; Conway and John, 2014b). Additionally, although challenging to sample, volcanic ash deposition can have a profound effect on local productivity and trace element cycling (Rogan et al., 2016; Achterberg et al., 2013). Most recently, multiple modelling and observational studies continue to focus on the fact that anthropogenic combustion and biomass burning need to be considered, and may even be the most important aerosol source of highly-soluble trace elements, especially Fe (Myriokefalitakis et al., 2018; Liu et al., 2022a). It has long been known that anthropogenic aerosols are the main route by which certain pollutants such as Pb and Hg enter the ocean (Boyle et al., 2014; Lamborg et al., 2014), and elements such as As, Cd, Cu, Ni, Pb, Sb, Se, Sn, V, Zn can trace anthropogenic inputs to aerosol samples and seawater (e.g. Cutter and Cutter, 1995; Shelley et al., 2015). As the climate continues to warm, modelers have focused more attention on wildfires which are thought to entrain soil and thus provide a vector of both soil- and plant- (and perhaps anthropogenically-) derived trace elements and nutrients to the oceans (Hamilton et al., 2022).

Historically, using a sparse network of field measurements of atmospheric aerosols, Duce and Tindale (1991) were able to provide some of the first global estimates of atmospheric dust input to the oceans. In a review published in 2005, and updated in 2009 (Mahowald et al., 2005, 2009) combined estimates of dust deposition based on observations of dust from in situ measurements, observations from satellites and global atmospheric models, underlined the importance of dust deposition but also highlighted many remaining knowledge gaps. The latter include high spatial and temporal variability of atmospheric deposition, in combination with limited observations, limited understanding of solubilization of particulate elements derived from atmospheric deposition, and the effects of atmospheric processing or dust composition (e.g. Baker et al., 2006, 2016; Baker and Jickells, 2006). While the trace element content of dust can be measured directly on ships or at land-based tower stations following total-digestion of collected aerosol particles, these remain only snapshots of atmospheric deposition. Moreover, it remains challenging both to convert such measurements into fluxes and to leach aerosol dust under representative conditions of the ocean to calculate soluble trace element fluxes, especially as desert dust is relatively insoluble on short timescales (Mahowald et al., 2018).

The issue of estimating trace element solubility and its variability in aerosols in order to assess soluble fluxes of many trace elements has been subject of many studies, yet remains a critical knowledge gap and ongoing research goal (Baker et al., 2016, 2021). Elemental solubility is typically operationally defined, yet controlled by a number of factors such as aerosol source/mineralogy whereby trace elements in aerosol particles associated with anthropogenic activity and/or biomass burning are considered more soluble than those associated with terrestrial soils and desert dust (e.g. Oakes et al., 2012; Schroth et al., 2009; Ito et al., 2019; Liu et al., 2022a; Baker et al., 2006; Spokes et al., 1994). For example, Baker et al. (2006) found that Fe solubility from Saharan dust aerosols is $\sim$1.7%, while aerosols from anthropogenic sources are significantly higher by a factor of 2–10 (Sedwick et al., 2007). However, even determining such operational solubility of trace elements aerosols is not trivial and a wide range of experimental approaches and nomenclature have been used, hindering comparison between studies and underlining the need for standardization (Perron et al., 2020). Compounding this, aerosol solubility is also thought to be driven by a number of other factors including particle size/surface area, atmospheric chemical/photochemical processing, seawater dissolved concentrations, seawater trace element binding ligand characteristics, and aqueous phase dust concentration that all impact trace element solubility (e.g. Baker et al., 2014; Baker and Croot, 2010; Fan et al., 2021; McDaniel et al., 2019; Ingall et al., 2018). Overall, the complex range of factors and interactions affecting deposition and solubility of trace elements such as Fe, makes accurate predictions of both effective fluxes (i.e. the amount actually ending up in solution) as well as the consequences for marine systems an ongoing challenge (Hamilton et al., 2020a, b; Scanza et al., 2018; Jickells et al., 2016; Van Wambeke et al., 2021).

Given such challenges of using direct aerosol observations of trace elements such as Fe, indirect geochemical measurements are often alternately used to inform understanding of sources and atmospheric processes, and to calculate or model eventual deposition of soluble trace elements. For example, dust or Fe deposition fluxes to the surface ocean can be calculated indirectly using fluxes of the cosmogenic ^{7}Be isotope (Kadko et al., 2015, 2020), via estimates of atmospheric deposition of lithogenic elements such as Al, Ti, or ^{232}Th deposition, or from direct particulate or sediment fluxes of lithogenic material, or by using ^{230}Th to estimate lithogenic fluxes (Hayes et al., 2013, 2015b, 2017; Anderson et al., 2016; Jickells et al., 2016). All such indirect approaches have utility as well as potential caveats, often associated with required assumptions about residence times and solubility as well as potential advection of the tracer (i.e. the concentration measured is not just the result of local deposition) and additional uncertainties when the estimate of total deposition are extended to other elements (Anderson et al., 2016). Here, we discuss the use of Al as an indirect tracer for Fe flux in more detail and point the reader to recent excellent reviews covering the state of the field (Hamilton et al., 2022; Baker et al., 2016; Mahowald et al., 2018), as well as a detailed comparison of using these different indirect geochemical techniques and modelling to estimate dust fluxes to the North Atlantic (Anderson et al., 2016).

The trace element Al is a major component of continental materials and is present in seawater at low concentrations in regions devoid of large dust deposition and at high concentrations under dusty regions (Figs. 7 and 11) due to the relatively short residence time of dissolved Al in surface waters (Measures et al., 2008; Middag et al., 2015b). Therefore, dissolved Al concentrations have been used as a tracer of atmospheric inputs to the ocean (Han et al., 2008; Menzel Barraqueta et al., 2019). Despite general agreement between Al-based estimates and other estimates of dust deposition, however, large discrepancies are found as well, notably in regions with other sources of Al (e.g. river run off or sediments) or when there is strong depletion of Al due to scavenging related to the presence of biogenic or other particles (Menzel Barraqueta et al., 2019; Middag et al., 2015b; Benaltabet et al., 2022). For example, a recent study in the Red Sea found that concentrations of Al decreased with increasing aerosol loads as dust storms promoted intense Al scavenging (Benaltabet et al., 2022). Those authors also found that increased dust loads also promoted scavenging removal of other trace metals (Benaltabet et al., 2023), which means that dust inputs may actually lower surface inventories of dissolved metals. Thus, although there can be merit in using Al as a tracer of dust deposition, and Al has indeed provided insight into deposition and subsequent transport of deposited material (e.g. Vink and Measures, 2001), there are certainly caveats associated with this approach. It is thus highly recommended to use multiple techniques and tracers to estimate atmospheric deposition fluxes (Menzel Barraqueta et al., 2019; Baker et al., 2016) as it is unlikely that a single tracer always provides accurate estimates of deposition, notably when the estimate is not only used for the amount of dust, but also to infer the fluxes of other elements. For example, a gradient in surface dissolved Fe concentrations in the Atlantic Ocean reflected dust deposition trends, but was not proportional to the surface dissolved Al gradient nor estimated aeolian input fluxes, likely the result of differences in both residence times as well as latitudinal differences in the fractional solubility (Bergquist and Boyle, 2006; Sedwick et al., 2007). Further, studies have shown the effect of atmospheric input is not limited to the surface ocean as elevated concentrations of Al have also been observed in intermediate depth Atlantic waters such as mode water or Mediterranean outflow water (Rolison et al., 2015; Hatta et al., 2015; Middag et al., 2015b), that received dust deposition in formation regions (Fig. 7). Similarly, elevated anthropogenic Pb (and Hg) added to the ocean in intermediate and deep-water formation regions are visible in downstream subsurface waters in regions of the North Atlantic and North Pacific (Boyle et al., 2014; Lamborg et al., 2014); Figs. 4 and 7). These examples, coupled with the famous example of using anthropogenic CFCs or atomic bomb ^{3}H to trace water mass movement (e.g. see Schlosser et al. (2001) and references therein), illustrate that atmospheric exchange is not only relevant where direct exchange happens, but it can also be imprinted into water masses and moved around the oceans by large scale circulation, dependent on the residence time and removal processes of the trace element of interest. Hence, it is also important to know the inherited or 'preformed' contents of any surface water prior to deposition, if Al (or other tracer) is to be used as a tracer.

In some ways, direct aerosol trace element (TE) measurements have advanced a great deal in recent years, stimulated in part by programs such as SOLAS, AMT, CLIVAR, and GEOTRACES (Morton et al., 2013; Baker et al., 2016). For example, aerosols are now routinely cleanly collected onto filters on CLIVAR, AMT, and GEOTRACES expeditions, and analyzed for trace element contents and solubility, while 'enrichment factor' (ratio of TE:Al in dust relative to the TE:Al signature of the upper continental crust) can provide information about the relative proportions of anthropogenic and natural components in an aerosol sample (e.g. Shelley et al., 2015; Chance et al., 2015; Buck et al., 2006, 2019; Marsay et al., 2018). However, despite these advances, many uncertainties regarding the atmospheric delivery of soluble trace elements remain, largely due to the variable and episodic nature of atmospheric deposition and aerosol content. For example, observation in the Mediterranean have shown the sporadic nature of dust deposition events and that the total annual atmospheric dust deposition for a particular location can be dominated by a single dust storm that may only last a couple of days (Guieu et al., 2010). This is confirmed by model results on a global level that show 30–90% of the annually averaged dust deposition is seen on 5% of the days, underlining the need for sustained observations and that dust models are able to capture deposition in some regions better than others (Mahowald et al., 2009). Even with an enhanced geochemical toolbox to estimate dust fluxes, a recent comparison in the North Atlantic from multiple methods (aerosol collection, ^{7}Be-derived, Al-derived, aerosol ^{232}Th derived, water column ^{232}Th inventory, particulate and sediment ^{230}Th, particle traps, and deposition modelling), illustrated that the calculated dust fluxes spanned over two orders of magnitude (Anderson et al., 2016); those authors themselves commented that much work is still needed to improve uncertainty on dust flux calculations, compounding the work needed to reduce uncertainties on elemental solubility in order to accurately determine soluble fluxes of trace elements to the surface oceans. However, techniques and tracers that can inform these questions continue to develop; for example, *in situ* δ^{56}Fe measurements in collected aerosols have shown that anthropogenic aerosol is remarkably fractionated (−4 to −0.3‰) compared to natural dust (+0.1‰), pointing to the utility of this tracer in calculating source contributions to aerosol samples and informing dust models (Kurisu et al., 2021; Conway et al., 2019).

An additional complication in the high latitude oceans is that atmospheric deposition may occur onto sea ice or ice-shelf derived icebergs, where it can accumulate and release a pulse of trace elements during melting. Dissolution and chemical reactions happening within melt pools on top of ice may also alter the speciation and solubility of aerosol trace elements prior to addition to surface waters (Marsay et al., 2018). Overall, while sea ice is believed to be an important mechanism of delivery of trace elements to surface waters in the Southern Ocean (e.g. Lannuzel et al., 2016; Winton et al., 2014) and Arctic Ocean (e.g. Kadko et al., 2016; Klunder et al., 2012; Aguilar-Islas et al., 2008), it remains a challenge to differentiate whether trace elements originated from the sea water that the ice formed from, from atmospheric dust deposition, or from fluvial input into the region of sea ice formation. With ongoing warming and reduction or melting in sea ice, the ongoing role of sea-ice in delivering atmospheric aerosols to the water column remains unclear and in need of further study.

Benthic sediments (shelf, slope, and abyssal)

Benthic inputs of trace elements to the overlying water column can come from different sources, notably the input of elements from continental derived material that are subsequently released to the dissolved phase, or the release of elements to sediment porewaters and overlying bottom waters from—or related to—breakdown of organic material exported from the surface layer. The first of these may be considered a true external source of elements to the ocean, while the second one can be thought of as remobilization of elements (or an internal source); however, both are often observed as local additions of elements to bottom waters, with elements released by diffusion or during disturbance and resuspension of benthic sediments. As such, it can be difficult to attribute a benthic flux of elements to one of these two sources. This is especially true in coastal and shelf regions, where both riverine inputs of particulate material and biogenic particle and organic carbon export from primary productivity are important for providing particles to sediments. The former supplies lithogenic and organic particulate material directly to sediments, while the latter supplies organic carbon to sediments which is followed by later microbial respiration of organic carbon in sediments by different electron acceptors, leading to production of distinct species such as dissolved Fe^{2+}, Mn, and H_2S by reduction in specific zones of sediment porewaters (Froelich et al., 1979).

Continental or lithogenic particle material that ends up in benthic sediments mainly enters the ocean from riverine sources, as well as from atmospheric dust depending on the region. It is important to remember that these particles only represent a source (or sink) for the ocean when they release elements (or accumulate elements via scavenging), with some component of the lithogenic particle likely simply being buried in sediments. Particles, scavenging processes, and sediments are discussed in much greater detail in other chapters in this volume (Lam and Xiang, 2024; Marcantonio et al., 2024; Hayes, 2024). Generally, trace elements within or associated with continental particulate material can be released into the dissolved phase into benthic sediment porewaters (and then overlying bottom waters) by diagenesis, redox reactions, and organic metal-binding ligands that can solubilize labile particulate material (e.g. Anderson, 2020; Conway et al., 2021; Lenstra et al., 2022). For relatively recent comprehensive reviews of the oceanic particle flux, its fate, and dissolution at sediment boundaries, the reader is refereed to Jeandel and Oelkers (2015) and Jeandel (2016). Riverine input of particulate material typically accumulates along the continental margins and shelves, and resuspension of these fluvial inputs can occur during upwelling events, shear stress imposed by tidal currents, and storms, which are important mechanisms for supplying particles with labile trace elements to surface waters (Bruland et al., 2008). Notably in coastal regions, sediments also often act as "reservoirs" of contaminants, including potentially toxic trace elements, that can re-enter the water column intermittently due to remobilization processes at the sediment-water interface (Pavoni et al., 2021).

Trace elements in particulate matter from rivers are frequently associated with Fe and Mn oxyhydroxides and changes in the sediment redox chemistry near the sediment water interface can lead to alternating periods of reductive dissolution and oxidation of these phases on shelves (Lenstra et al., 2019; Severmann et al., 2008, 2010), often intrinsically linked to total organic carbon supply and bottom water oxygen. On highly productive shelves, where total organic carbon fluxes are high, porewater dissolved concentrations of trace elements can be significantly higher than those observed in the overlying water column. Such elevated porewater concentrations of Fe and Mn from so-called 'reductive dissolution' can lead to benthic diffusion fluxes of dissolved elements out of the sediment, which has been verified by direct measurements (e.g. Elderfield et al., 1981; Westerlund et al., 1986; Elrod et al., 2004; Severmann et al., 2010; Homoky et al., 2011; Shi et al., 2019). In addition to the reductive supply of Fe(II) from shelf sediments, there is a large concentration of readily leachable particulate Fe in resuspended coastal sediments (e.g. Berger et al., 2008; van Manen et al., 2022). It was thought that the concentration of ambient strong Fe(III)-binding organic ligands dictates how much of this leachable suspended particulate Fe is converted into the dissolved phase and represents a source of dissolved Fe to coastal waters (Buck et al., 2007). However recently the importance of organic and lithogenic colloidal phases has gained attention (Homoky et al., 2016, 2021; Jensen et al., 2020b) that contribute Fe to the operationally defined dissolved pool without the need for stabilization via organic complexation.

Such non-reductive dissolution (lithogenic weathering) of particles in sediments to produce colloidal-size dissolved Fe that can be released to the water column during sediment disruption and re-suspension has been shown to be a second important benthic Fe source (Radic et al., 2011; Homoky et al., 2009, 2011, 2013, 2021). Unlike reductive dissolution, which depends strongly on organic carbon and oxygen, this colloidal-size source is likely decoupled from oxygen and thus likely to be more important in the abyssal ocean or where sediment disruption occurs (Homoky et al., 2021). Ocean sections of dissolved Fe parameters in the North Atlantic have shown that such non-reductive release of Fe (likely in the colloidal phase) can also release Fe into the water column on large scales, unrelated to low-oxygen regions (Fig. 9; Conway and John, 2014b; Fitzsimmons et al., 2015b; Rijkenberg et al., 2014). While this mechanism of Fe release still requires further investigation, this long-distance transport may be sustained because colloidal-size lithogenic Fe has a longer residence time than truly dissolved Fe species. Inputs from deep sea sediments have been suggested for other elements as well, notably in regions with benthic nepheloid layers (Gardner et al., 2018a, b) where resuspension of bottom sediments can lead to elevated particulate elements concentrations in nepheloid layers up to a km thick (Lam et al., 2015), but also dissolved elements such as for example dissolved Al (e.g. Xu and Weber, 2021; Middag et al., 2013, 2015b). Non-reductive dissolution of—and exchange of the dissolved phase with—particles and sediments for production of trace elements is perhaps one form of what has been termed 'boundary exchange', and is thought to be critical for the ocean budgets and isotope signatures of elements such as Nd as well as Fe (Lacan and Jeandel, 2005; Jeandel, 2016). Indeed, such exchange with sediments may dominate the oceanic Nd budget (van de Flierdt et al., 2016). Additionally, boundary exchange can be seen manifested in a change in isotopic signature of elements such as Nd or Fe as water masses move along margins (e.g. Lacan and Jeandel, 2001; Radic et al., 2011), if not a significant change in elemental concentrations (likely due to reversible scavenging). Such a mechanism that leads to a change in the isotopic signature of an element like εNd in a water mass is important to constrain, because it may affect the utility of such parameters as water mass tracers. While the mechanism of such processes remains the focus of study, boundary exchange or submarine weathering processes are likely to be important for many lithogenically-sourced elements such as REE, Fe, Sr, Si (Jeandel, 2016).

While authigenic sediments such as carbonates and ferromanganese oxides/crusts have long been considered to be sinks for elements like Cd, Zn and Ni (see Section "Ocean sinks"), recent work suggests that organic sediments are (previously underestimated) important sinks of Cd, Zn, Cu, and Ni (Little et al., 2014, 2015, 2016; Chen et al., 2021), although sediments can also be a return source of these elements to the water column. For example, Zn concentration and Zn isotope anomalies near sediments in oceanic water column profiles have been interpreted as evidence of significant return fluxes of dissolved Zn from sediments, perhaps originally delivered there by export of biogenic material (Lemaitre et al., 2020; Conway and John, 2014a, 2015b). Moreover, GEOTRACES and other work has suggested that there may be extensive remobilization of trace elements such as Cd and Zn from Arctic shelves from biogenic material to the water columns (Jensen et al., 2019; Zhang et al., 2019; Vieira et al., 2019; Cid et al., 2012; Kondo et al., 2016). At a global scale, making use of isotopic mass balance, studies have also identified sediment porewaters as possible return sources of (isotopically heavy) Ni back to bottom waters following diagenesis (Little et al., 2020). In many cases, whether elements diffuse into—or out of—porewaters depends on concentration and diffusion gradient, with porewaters also long documented sources of major elements such as Na and Ca (Sayles, 1979).

Different methods and the state of the field for estimating benthic fluxes of different trace elements from (or particle fluxes to) sediments have been reviewed in detail by Homoky et al. (2016); these methods can take the form of porewater concentration measurements and diffusion calculations, sediment traps, benthic flux chambers and incubations, benthic boundary layer flux calculations using sediment-derived radionuclides such as ^{222}Rn, ^{223}Ra, ^{224}Ra, particle flux and sediment-exchange measurements using ^{232}Th and ^{230}Th, isotope measurements (δ^{56}Fe, δ^{66}Zn), and inverse models. As with SGD, Ra isotopes can be useful as short- or long-distance tracers of benthic sediment input, as well as for constraining fluxes of other trace elements (Charette et al., 2015; Vieira et al., 2019); Section "Rivers and submarine groundwater"). All of these methods provide useful information on different timescales, and all have possible pros and cons. Dissolved Fe isotopes have proved useful in investigating microbial reductive production of Fe^{2+} in sediments, as this dissolved Fe is fractionated via an Fe(II)-Fe(III) equilibrium fractionation that results in the δ^{56}Fe dissolved Fe^{2+} being 1 to 4 permil lighter than the crustal mineral source (+0.1‰; Severmann et al., 2006; Homoky et al., 2009; Fitzsimmons and Conway, 2023). Further, studies show that this distinctive Fe isotope signature survives across the Fe and oxygen gradient into overlying bottom waters (Severmann et al., 2010; John and Adkins, 2012; Hunt et al., 2022), that can potentially be traced through the ocean over large distances (Sieber et al., 2021). Further, δ^{56}Fe were instrumental in the identification of the non-reductive Fe pathway (Radic et al., 2011), where Fe is thought to be released with a near-crustal δ^{56}Fe signature (Homoky et al., 2021). Thus, reductive and non-reductive release of Fe should have diagnostically different Fe signatures which may allow different sediment sources to a basin to be constrained. As an example, by using fixed endmember δ^{56}Fe for reductive and non-reductive dissolution, Conway and John (2014b) constrained the importance of these sediment sources to the dissolved Fe pool in different parts of the North Atlantic. Such work shows potential; however, further study is needed to distinguish the competing effects of various other processes that could fractionate δ^{56}Fe, including ligand complexation and oxidation (Fitzsimmons and Conway, 2023). For example, the addition of dissolved Fe(II) to oxic seawater likely results in oxidation to the less-soluble Fe(III) with the possible subsequent formation of colloidal and particulate oxyhydroxide forms. Further, complexation by dissolved Fe(III)-binding organic ligands can maintain Fe(III) in the dissolved phase (Lohan and Bruland, 2008).

Waters overlying productive shelves with extensive reducing sediments such as the Californian Margin, Peru Margin, Benguela Upwelling can see upwelling fluxes of large fluxes of benthic Fe^{2+} and other trace elements from sediments that drives local productivity and diatom blooms, with nutrients 'trapped' over the shelf (e.g. Biller and Bruland, 2013; Biller et al., 2013; Till et al., 2019; Liu et al., 2022b; Bruland et al., 2005). However, trace elements released from coastal regions in dissolved or colloidal form can also reach off shore regions via long-lived anticyclonic mesoscale eddies transporting Fe from shelf areas as described for the open HNLC region of the Gulf of Alaska. Johnson et al. (2005) examined Haida eddies transporting Fe westward from the British Columbia coast of Canada. Ladd et al. (2009) and Brown et al. (2012) examined Sitka, Yakutat and Kenai eddies transporting Fe from the Alaska coast to the open ocean regions of the northern Gulf of Alaska and the importance of this process for productivity of this otherwise Fe-depleted region. Crawford et al. (2007) showed that during spring months roughly 80% of the chlorophyll in the Gulf of Alaska was associated with mesoscale eddies, which occupied only 10% of the area of pelagic waters in the region. More recently, eddies, specifically Gulf Stream cold-core rings were suggested to play a major role in in the subtropical nutrient and carbon cycling of the Atlantic subtropical northwestern gyre edge (Conway et al., 2018); that study estimated that such eddies could provide a significant portion of the gyre-wide supply of iron that would be comparable to 15% of the median dust deposition flux and that supply via eddies is likely the dominant mechanism of Fe supply in some regions of the gyre. Such eddy-exchange of trace elements is likely to be a feature of ocean currents which separate regions of high and low concentrations of a specific element, with similar observations made for Fe in the Aghulas current (Conway et al., 2016).

In some oceanic regions, recent evidence also suggests that lateral transport of trace elements released from continental margin sediments is an important source of trace elements to the open ocean (Liu et al., 2022b; Homoky et al., 2016; Lenstra et al., 2022;

Seyitmuhammedov et al., 2021; Shi et al., 2019). Beyond shallow productive shelf environments, as discussed in Section "Current knowledge of the marine distributions of trace elements and isotopes", ocean sections have been influential in demonstrating that trace elements sourced by (reductive) dissolution of benthic sediment can be transported long distances through intermediate-depth depth waters in all Oceans, especially through low oxygen waters (e.g. John et al., 2018; Klunder et al., 2011; Noble et al., 2012; Conway and John, 2014b; Nishioka et al., 2020; Zhang et al., 2021; Jensen et al., 2020a). Perhaps the most dramatic example of this is the proliferation of dissolved Fe and other trace elements from reductive sediments in the marginal seas of Japan over ~4000 km within North Pacific Intermediate Water which spreads around the North Pacific at subsurface depths (Wong et al., 2022a, b; Nishioka et al., 2020). As with hydrothermal venting, such long-distance sediment-derived Fe plumes must be sustained by some mechanism that maintains Fe in solution in oxic seawater, which, in the North Pacific, may take the form of organic-complexation with molecules such as humics, or interaction with particles (Yamashita et al., 2020; Misumi et al., 2021; Lam and Bishop, 2008).

Input of sediment-derived trace elements is especially important in iron limited HNLC surface regions such as the subarctic Pacific (Nishioka et al., 2013) or Southern Ocean from both continental margins as well as Antarctic and Subantarctic island margins (e.g. Blain et al., 2001; Bakker et al., 2007, Hatta et al., 2013; Holmes et al., 2019; Janssen et al., 2020b; Sieber et al., 2021). Notably the sediments of Southern Ocean islands and island plateaus provide 'natural Fe fertilization', e.g. studies around the Kerguelen and Crozet Islands have shown that the sediments of these island plateaus represent a significant source of dissolved Fe to surface waters resulting in increased productivity in these regions (Chever et al., 2010; Bowie et al., 2015; Blain et al., 2007; Pollard et al., 2007), consistent with modelling efforts (Robinson et al., 2016). The use of geochemical tracers has suggested that the dissolution of lithogenic material transported by lateral advection might also be a source of dissolved Fe and other trace elements to these regions (Sanial et al., 2014; Zhang et al., 2008; van Beek et al., 2008; Jacquet et al., 2008) and besides direct supply of dissolved Fe, particulate phases can also play an important role as a secondary source of bioavailable Fe (van der Merwe et al., 2019b). Particles can also be a dramatic and important source of elements such as Fe and Mn to other HNLC regions such as the sub-Arctic Pacific (Lam and Bishop, 2008) as well as other areas. Thus, depending on local conditions, a significant component of the external particulate input of trace elements from the continents to the coastal ocean can subsequently be released to the dissolved phase by a variety of mechanisms.

Overall, the differentiation between elements derived from remobilization following benthic recycling or from new external inputs remains a challenge. Regardless, the close proximity of the continental shelf benthos to the productive surface ocean means that this flux is likely to be essential for maintaining ecosystem micronutrient supply (Shi et al., 2019; Homoky et al., 2016). This occurs perhaps most notably underlying highly productive waters, where respiration of this organic material drives the enhanced supply of redox sensitive elements such as Fe and Mn (e.g. Shi et al., 2019; Martin and Knauer, 1984; Landing and Bruland, 1987; Homoky et al., 2016). However, particle resuspension and/or non-reductive dissolution can play a key role too in benthic supply of trace elements, and the interactions in the sediment are frequently modulated by macrofauna through bioturbation and -irrigation (e.g. Lenstra et al., 2019). As such, benthic input is a key component in the biogeochemical cycling of trace elements, whether it constitutes 'new' input or recycling of elements in the ocean domain.

Hydrothermal venting

Hydrothermal systems, driven by mantle heat flux and the interaction of cold seawater with hot oceanic basalt, acts as an important boundary exchange for elements between the ocean lithosphere and the mantle within the oceans. Elements added to 'vent' fluids as they pass through the hot oceanic crust can then be returned to the ocean via the hot buoyant plume, and then dispersed laterally in 'non-buoyant' hydrothermal plumes. A comprehensive discussion of hydrothermal systems can be found in German et al. (2024). It has been estimated, using arguments based upon mantle-derived ^{3}He anomalies and heat flux, that the entire ocean mixes through hydrothermal vent systems, undergoing high-temperature interaction with fresh oceanic basalt every eight to ten million years, leading to the production of high temperature (~3500 °C), acidic (pH 3.5), reducing, sulfide- and metal-rich hydrothermal fluids (Edmond et al., 1979; Von Damm et al., 1985), but importantly also allowing for exchange of elements between the ocean and ocean lithosphere. Indeed, this hydrothermal activity has proven to be the major oceanic sink for some major elements, including Mg and sulfate, and to be a major source for some trace elements such as He, Fe, Mn, and Ra, as well as influencing the budgets of other trace elements via scavenging in oceanic hydrothermal plumes. Our best tracers for overall hydrothermal inputs to the ocean are arguably δ^{3}He anomalies, with primordial ^{3}He-rich He sourced from the mantle into vent fluids (Lupton and Craig, 1975), and He behaving conservatively in seawater once released in hydrothermal plumes—leading to largescale hydrothermal He plumes which were observed by GEOSECS and WOCE (and continue to be observed by GEOTRACES) spreading out and being circulated throughout the intermediate and deep Pacific (Lupton, 1998; Jenkins et al., 2020; Resing et al., 2015). However, it is important to point out that δ^{3}He's use as a tracer is becoming compromised in young water masses, where atom-bomb derived ^{3}He may now overprint hydrothermal signals (Jenkins et al., 2015). GEOTRACES studies have also highlighted the utility of short-lived Ra and Rn isotopes (^{223}Ra, ^{224}Ra, ^{222}Rn) to investigate nearfield plume ages and fate of trace elements, as well as longer-lived Ra isotopes (^{228}Ra) to calculate the age of distal hydrothermal plumes and timescales of delivery of other trace elements to the wider ocean (Kipp et al., 2018; Rudnicki and Elderfield, 1992).

Millimolar concentrations of Fe and Mn concentrations in the hot vent fluids can be a million-fold higher than in the surrounding seawater (Gallant and Von Damm, 2006). However, unlike He, trace elements such as Fe are not conservative. Indeed, much of the Fe (and other metals) is rapidly precipitated; initially either as Fe-sulfides and then oxidized to Fe-oxyhydroxide precipitates, or rapidly oxidized from the soluble Fe(II) form to insoluble Fe(III), and deposited either within the hydrothermal vent system, 'black smoker' chimneys, or as metal-rich particles into sediments near vent sites and over the mid-ocean ridges. Although dissolved Mn may behave in a (pseudo-)conservative fashion and thus is thought to advect further away from the vent source prior to its eventual microbially mediated oxidation and precipitation (Cowen et al., 1998), it was assumed that both hydrothermal Fe and many other elements are almost fully removed due to precipitation and scavenging in the deep sea prior to having a chance to be transported any distance or upwell to surface waters (German et al., 1991). Indeed, German et al. (1991) commented, "*Of the various elements studied here, hydrothermal activity only appears to act as a significant source for dissolved Ca and dissolved Mn.*" However, deep ocean observations of dissolved trace element show that in fact even a small amount of hydrothermal Fe escaping via hydrothermal plumes (the 'leaky vent' hypothesis), can lead to significant anomalies due to the low concentration of dissolved Fe in deep waters (Toner et al., 2012). Indeed, a range of ocean sections and other observational studies show distinct concentration anomalies of Fe and Mn around almost every hydrothermal vent site visited in all the oceans, and that Fe and Mn of hydrothermal origin can be traced 1000s of km from their source given the right circulation and conditions (e.g. Figs. 9–11; Middag et al., 2012; Resing et al., 2015; Fitzsimmons et al., 2014; Jenkins et al., 2020; Wu et al., 2011; Saito et al., 2013; Conway and John, 2014b; Klunder et al., 2011; Middag et al., 2011a). Perhaps the most dramatic example is the plume of dissolved Fe from the East Pacific Rise that the US GEOTRACES GP16 section followed west through the Pacific Ocean for over 4000 km (Resing et al., 2015; Fig. 11). In the Atlantic, by contrast, the general movement of water parallel to the ridge ensures that lateral travel is limited to ~1000 km (Saito et al., 2013; Conway and John, 2014b). The GEOTRACES program has also identified that hydrothermal plumes may be important sources of trace elements such as Zn (Conway and John, 2014a; Lemaitre et al., 2020; Roshan et al., 2016), while confirming that hydrothermal plumes act as important particle-scavenging sites for some elements such as Cd and particle-reactive elements such as Pb, ^{231}Pa, and Th isotopes (Noble et al., 2015; Conway and John, 2015a; Hayes et al., 2015a; Pavia et al., 2019).

Despite first assumptions that Fe would be lost near vent, it now seems a remarkably fair bet that whenever an ocean section crosses a mid-ocean ridge with active venting that resolvable hydrothermal trace element anomalies will be observed (Fig. 10). However, this apparent paradox with geochemical predictions requires explanation. In fact, it appears that Fe from hydrothermal sources can be stabilized and sustained in solution by complexation with organic ligands, or is retained in the dissolved phase as small nanoparticles or colloids, both inorganic and organic (e.g. Hawkes et al., 2013; Yücel et al., 2011; Lough et al., 2019; Fitzsimmons et al., 2017; Tagliabue et al., 2022b; González-Santana et al., 2020).

Dissolved Fe plumes may also be sustained by exchange with particles, with Fitzsimmons et al. (2017) noting that the GP16 East Pacific Rise hydrothermal Fe plume descended in the water column during advection westward, whereas this was not observed for Mn or δ^3He, and thus suggested that reversible exchange of Fe onto slowly sinking particles in combination with organic complexation is an important factor for sustaining this plume over distance. The increasing importance of complexation in sustaining this plume was highlighted by remarkably elevated δ^{56}Fe signals (+0.7‰) that indicated the importance of ligand binding (Fitzsimmons et al., 2017). Such an example highlights the utility of δ^{56}Fe as a tracer of hydrothermal processes. However, the variability in δ^{56}Fe seen in hydrothermal plumes (−4 to +2‰) relative to vent fluids (−0.7 to −0.1‰) only goes to highlight the degree of variability in chemical reactions and the physicochemical speciation of hydrothermal Fe that is known to occur between vent systems and regions (González-Santana et al., 2021; Yücel et al., 2021; Hoffman et al., 2020).

As was commented on in Section "Current knowledge of the marine distributions of trace elements and isotopes", models of ocean biogeochemistry continue to suggest that hydrothermal Fe is one of the two most important sources of Fe to the ocean, and that this source likely dominates the Fe inventory in regions away from sediments or high dust deposition, such as the South Pacific (Tagliabue et al., 2014a). However, as with all other deep sources of trace elements, the question then becomes: to what extent does this Fe reach the surface where it can influence primary productivity? This is a complex question from the geochemical side; poorly-constrained variability in hydrothermally-derived dissolved Fe speciation in the ocean inevitably leads to variability in longevity and residence time of the dissolved Fe. In addition to topography and circulation patterns driving dispersion of hydrothermal Fe, such variability in the form of Fe also likely plays a large role in the differing length scales, transport and isotope signature of distal hydrothermal Fe from different vent sites (Tagliabue et al., 2022b; Fitzsimmons and Conway, 2023). This makes predictions of the amount of hydrothermal Fe that eventually makes it to the surface ocean challenging, relying largely on modelling efforts that include the influence of ocean circulation, which is pivotal for bringing dissolved Fe to the surface before it is lost from solution. As a result, the answer is very region specific, with the impact of hydrothermal venting influenced by the location of vents relative to upwelling. For example, Tagliabue et al. (2010) used a model that suggested that hydrothermal input is an important source of Fe for parts of the surface ocean, particularly in the Southern Ocean where dissolved Fe might reach the surface via upwelling of deep waters; this model calculated that hydrothermal dissolved Fe could contribute 5–15% of the total Southern Ocean carbon export from surface waters, and perhaps even 30% in Fe-limited regions. More recently, it was estimated that at the global scale 3–5% of hydrothermal Fe makes it to the surface ocean, albeit mostly in the Southern Ocean where it contributes 5–15% of total carbon export (Roshan et al., 2020), while in situations where hydrothermal venting is much closer to the surface, the effect may be much greater (Ardyna et al., 2019). Thus, although the hydrothermal supply of Fe to the surface ocean is much lower than atmospheric deposition at the global scale (Roshan et al., 2020), the spatial heterogeneity of both supply mechanism could make hydrothermal supply locally an important driver of primary productivity (Schine et al., 2021; Ardyna et al., 2019; Tagliabue et al., 2022a). Moreover, dissolved Fe from the relatively constant hydrothermal input has been suggested to buffer the oceanic Fe inventory on long timescales against short time scale variability of Fe input from other sources like atmospheric dust input. This, in turn, would have implications for our understanding of how changes in iron supply from variable sources affects global climate via marine productivity and its effect on the carbon cycle (Tagliabue et al., 2010). With on-going efforts in the high-resolution sampling of full depth ocean transects, unravelling of the physicochemical speciation and spatial heterogeneity of hydrothermal input, and the refinement of models, our understanding of the extent and influence of hydrothermal input is likely to improve further in the near future.

Cryosphere

Glaciers and ice shelves can be considered frozen rivers, and when they reach the ocean, they discharge in the form of melt water and icebergs. Icebergs can have an influence on the remote open ocean as they drift and melt far away from their origin. Moreover, icebergs can carry significant amounts of continental debris with them due to glacial erosion. The effects of melting icebergs are episodic but elevated concentrations of dissolved Fe have been observed as far as 10 km away from melting icebergs in the Southern Ocean (Lin et al., 2011). Hence free drifting icebergs have been suggested to be an important source of Fe to the Southern Ocean (Raiswell et al., 2008, 2016; Shaw et al., 2011) that can stimulate primary productivity (Duprat et al., 2016; Schwarz and Schodlok, 2009; Smith et al., 2011); however, it is often hard to constrain the influence of Fe from the iceberg versus ice berg-induced mixing and upwelling of deeper Fe-rich water that has also been suggested to be an important indirect supply mechanism (Randall-Goodwin et al., 2015; Sherrell et al., 2015; Hopwood et al., 2019). Moreover, the Fe supplied by icebergs may not be efficiently used (Boyd et al., 2012), likely related to the patchy distribution of Fe within icebergs that subsequently leads to a heterogenous supply of dissolved Fe into surface waters (Hopwood et al., 2017), also making it extremely challenging to estimate the effects of iceberg-derived Fe on surface dissolved Fe and thus primary productivity (Hopwood et al., 2019).

Besides melting icebergs, direct input of glacial meltwater can form an important source of trace elements to the Southern Ocean (Gerringa et al., 2012; Alderkamp et al., 2012, 2015; Annett et al., 2017; Sherrell et al., 2015; Planquette et al., 2013; Ardiningsih et al., 2021; Seyitmuhammedov et al., 2021; Holmes et al., 2020; van der Merwe et al., 2019b), as well as in other regions, notably around Greenland (Arrigo et al., 2017; Crusius et al., 2017; Ardiningsih et al., 2020; Krisch et al., 2021; Kanna et al., 2020; Hopwood et al., 2020; Bhatia et al., 2013; Hawkings et al., 2021), with large variability in effects between elements and regions observed (Krause et al., 2021). Generally, one might assume that increasing discharge from glaciers, ice shelves and ice sheets under continued climate change has a positive influence on marine primary productivity due to the supply of micronutrients such as Fe (Hopwood et al., 2018). Notably, enhanced weathering under glaciers is thought to have a positive effect on the supply and bioavailability of trace elements. Subglacial supply of trace elements, notably in the colloidal/nano-particulate size range, is linked to biogeochemical processes that occur over relatively long timescales, but is also strongly influenced by sub-ice shelf cavity and estuarine processing (Hawkings et al., 2014, 2020; Raiswell et al., 2018; Li et al., 2022; van Genuchten et al., 2021), including rapid exchange between elements in the particulate and colloidal and/or dissolved phase (Tian et al., 2023; van Manen et al., 2022).

In Antarctica, the dramatic effects of such glacial supply may be largely restricted to coastal regions and polynyas, where the macronutrients are present in abundance and thus glacial supply may act to relieve Fe-limitation and stimulate primary productivity (e.g. Watson et al., 2000; van Manen et al., 2022; Joy-Warren et al., 2022). By contrast, the oceans around Greenland are characterized by relatively low macronutrient concentrations and glacial melt water is relatively poor in nitrate and phosphate, relative to deep ocean concentrations, which may limit the effectiveness of trace element release on primary productivity (Hopwood et al., 2018, 2020). Nevertheless, glacier and ice-shelf interactions can also be an important indirect source of nutrients to the surrounding coastal surface ocean via glacier-induced pumping of deep waters containing macronutrients as well as pre-formed trace elements or benthic sediment-derived trace elements (Cape et al., 2019; Hopwood et al., 2018, 2020; Hendry et al., 2019; Williams et al., 2021; Meire et al., 2017). Such meltwater pumps occur mainly for marine-terminating glaciers where the input of fresh, buoyant water at depth leads to convection and entrainment of deep, relatively nutrient-rich, waters. In the Amundsen Sea, such meltwater pumping has been suggested to bring dissolved trace elements into surface waters of the Polynya (e.g. St-Laurent et al., 2017), where, for many elements including Fe, the actual contribution of Fe in dissolved form from the ice melt has been suggested to be very small (van Manen et al., 2022; Tian et al., 2023). As such, the meltwater itself effectively dilutes the concentrations present in near bottom seawater, but nevertheless, the meltwater-induced upwelling enables supply of Fe-rich near-bottom water to the surface layer where it can be utilized by phytoplankton and thus stimulate productivity (van Manen et al., 2022). By contrast, land-terminating glaciers can not only dilute the macronutrient or trace element content of seawater, depending on the concentration in surface seawater and meltwater, but also lead to increased stratification, potentially suppressing productivity (Hopwood et al., 2018; Meire et al., 2017; Wadham et al., 2016). Overall, the consequences of glacial melt are depend on a myriad of interactions, such as whether the glacier is land or marine terminating, the glacier-bedrock interactions, subglacial water residence times, sub-ice shelf cavity and estuarine processes, the relative supply of trace elements and macronutrients, implying that much more research is needed to further improve our understanding of the role of glacial melt as a source of trace elements to the oceans as well as its role as a driver of marine productivity under continued climate change.

Dissolved to particulate exchange processes and ocean sinks

Introduction

Section "Inputs of trace elements to the oceans (sources)" detailed the main known boundary sources of dissolved trace elements to the ocean. For the oceans to remain in natural steady state for many elements, the inputs of dissolved trace elements inherently need to be balanced by outputs of equal magnitude ('sinks'). As a caveat on this, however, it is important to note that modern estimates of source fluxes (rivers and atmospheric) are likely to be compromised by anthropogenic perturbations, affecting calculations of whole ocean budgets and residence times (Little et al., 2024). Additionally, as Fig. 1 shows, many of the sources that have been already described can also act as sinks; for example, the addition of atmospheric dust, hydrothermal plumes, or resuspended sediment can result in enhanced scavenging, or movement through hydrothermal systems can remove elements such as Mg (Von Damm et al., 1985; Von Damm, 1990). Ultimately though, most trace elements leave the ocean via burial in sediments, whether delivered there by sedimentation of biogenic, lithogenic, or authigenic particles (formation of minerals or particulate phases within the water column), or by direct exchange from the dissolved phase in seawater or in porewaters into authigenic sediments (i.e. sediments which form *in situ* rather than from deposition of marine particles). Thus, exchange with particles, as well as being a potential source of some elements to the ocean, represents an intermediate step in removal of dissolved elements to ocean sinks such as sediments (Lam and Xiang, 2024). As has been discussed in previous sections (and is discussed in more detail in other chapters), removal to particles can take the form of biological uptake of elements into organic matter (Section "Biological uptake, regeneration, and recycling"; Twining and Shaked, 2024), and/or scavenging and precipitation of elements to a range of inorganic and organic particles (Section "Particle scavenging"; Marcantonio et al., 2024). This particulate material can then be recycled, either in the water column or in sediments, with some fraction buried in the sedimentary record (Section "Ocean sinks"; Hayes, 2024). As these topics are covered extensively in other chapters of this treatise volume, our goal here in Sections "Biological uptake, regeneration, and recycling", "Particle scavenging", and "Ocean sinks" is just to provide a general overview of how these processes and sinks affect trace element distributions.

Biological uptake, regeneration, and recycling

A primary conduit to burial in sediments for macronutrients and trace elements is the removal from the water column due to assimilation by phytoplankton, bacteria, or archaea that utilize the elements in their metabolism, notably as co-factors in enzymes that are needed for biochemical functions such as photosynthesis and nutrient acquisition (Sunda, 2012). Many trace elements may also show some degree of particle-reactivity and can be scavenged to biogenic material. As such, trace elements can be carried to the seafloor within (or scavenged to) a range of biogenic particles, including opal, calcium carbonate, and organic matter. Often, however, such uptake that occurs mostly in the surface ocean does not lead to removal from the ocean on long time scales as the majority is returned to the dissolved phase within the water column via regeneration (as described in Sections "Classical concentration distribution patterns and residence times" and "Current knowledge of the marine distributions of trace elements and isotopes"). Nevertheless, a small fraction of the assimilated elements is not regenerated and ends up in the sediments where they can be buried and remain stored for millions of years. The location and magnitude of such burial typically depends on the type of biogenic material and a mix of physical and geochemical factors, with lithogenic material burial typically greatest near continents where sedimentation is highest, organic matter more likely to be buried in productive shelf regions, opal around Antarctica where diatom productivity is high, and carbonate burial is dependent on the flux and ocean saturation state of bottom waters (i.e. relation to the carbonate compensation depth; Allen et al., 2024; Hayes, 2024). Of course, the type, accumulation rate, and geochemistry (oxygen, redox state) of bottom sediments depends strongly on the nature and flux of particles delivered to them, with a synthesis by Homoky et al. (2016) providing a nice overview of how these factors vary across the ocean, and how they may interact with benthic fluxes (see Section "Benthic sediments (shelf, slope, and abyssal)").

Obviously, however, as not all elements have biological functions, not all are actively taken up by biota. Others may be present in such high concentrations that their distributions are not dramatically perturbed by biology; for example, the distribution of conservative elements are typically not visibly affected by the biological cycle in the ocean. Trace elements for which active biological assimilation may be an important factor in controlling surface-water concentrations and distributions include the first-row transition elements Fe, Zn, Mn, Cu, Ni, and Co, along with Cd (Sunda, 2012). For a more detailed discussion of the interplay of trace element biogeochemistry, distributions, and speciation with biological cycling, see Twining and Shaked (2024). Other elements, for example Ag and perhaps Hg, have no known biological role, but are thought to 'hitchhike' with biological cycling, most likely due to inadvertent uptake by biota, or linked to particle scavenging (Boye et al., 2012). Indeed, as described further in Section "Particle scavenging" (and in Lam and Xiang, 2024), bioactive and other particle-reactive trace elements might be removed from the water column due to sorption or scavenging, where the production of biogenic particles by biota and thus increased particle concentrations can lead to increased removal rates from the dissolved phase. Further, bioactive elements such as Zn may also be scavenged to organic matter, which may be later regenerated alongside biogenic material or carried and buried in sediments (Weber et al., 2018; Sieber et al., 2023a).

Since biological uptake is such an important removal process for elements from the dissolved phase, it is important to characterize the trace element and macronutrient composition of biogenic material, and how this varies spatially, as well as to investigate to what degree this biogenic material regenerates (and whether all elements regenerate together) or is changed by scavenging. However, while nitrate and phosphate are assimilated and removed from the surface ocean at a ratio approximating the Redfield ratio (Gruber and Deutsch, 2014), it is challenging to extend the Redfield ratio to other macro and micronutrients because of variable elemental stoichiometry during uptake. This in turn leads to variability both within organic cells and within different water masses, compounded both by differential length scales of regeneration (i.e. depth of regeneration) and scavenging affecting different elements to different degrees (see Sections "Classical concentration distribution patterns and residence times", "Current knowledge of the marine distributions of trace elements and isotopes", and "Particle scavenging"). For example, removal of dissolved Fe in deep waters means that deep waters are typically deficient in dissolved Fe relative to macronutrients such as nitrate, driving much of the Fe limitation in upwelling regions (e.g. Stukel and Barbeau, 2020), while nutrient dynamics in the Southern Ocean and the North Pacific act to decouple the distributions of phosphate and silicate, Zn and silicate, and Cd and phosphate (Sarmiento et al., 2004; Abouchami et al., 2014; Vance et al., 2017; Sieber et al., 2023a, b; Middag et al., 2018); see Section "Current knowledge of the marine distributions of trace elements and isotopes"). Even N and P are not immune from such effects, however, with processes such as N fixation and denitrification affecting the ratio of these nutrients throughout different regions of the ocean and driving deviations from the Redfield Ratio (Gruber and Deutsch, 2014). Overall, while the Redfield Ratio remains a useful average for N and P, and reasonable attempts have been made to extend it to the trace elements (Ho et al., 2003; Ho, 2006), the more extreme plasticity in uptake ratios of trace elements relative to macronutrients by individual species, communities or in different regions, can drive significant variability with implications for exported particle composition (see Twining and Shaked, 2024). For example, at time-series stations in the North Pacific and North Atlantic, while N:P ratios can vary depending upon the source of nitrogen they generally vary by less than a factor of 2 from the Redfield ratio (Martiny et al., 2013a, b; Gruber and Deutsch, 2014); by contrast, Fe/C ratios can vary by several orders of magnitude (Twining et al., 2021), depending upon e.g. the availability of Fe and the taxa as well as whether they are a oceanic or coastal taxon. Phytoplankton such as diatoms can also exhibit luxury uptake where the uptake is 20–30 times higher than what is estimated to be required for maximum growth (Twining et al., 2021; Sunda and Huntsman, 1995); it has been suggested that this high uptake rate and storage capacity in the diatoms allows these species to accumulate excess Fe during periods of high Fe availability, that can then be passed on to their progeny and utilized when the dissolved Fe may later be drawn down to concentrations limiting growth rates. Accumulation and storage of Fe can be an effective strategy for diatom blooms in coastal upwelling regimes, as for example reported for the Oyashio region in the subarctic Pacific (Sugie et al., 2011), while Marchetti et al. (2010) have also shown that pennate diatoms have the ability to store this luxury uptake of Fe as ferritin and pass this Fe stored as ferritin on to their progeny for future use, but other storage strategies besides ferritin exist (Cohen et al., 2018).

Besides Fe, uptake of other trace elements is also known to vary as a function of environmental conditions and phytoplankton are known to regulate their cellular Mn levels in response to Fe availability (Peers and Price, 2004; Wu et al., 2019b), but are also known to acquire up to four times higher levels than needed to support maximum growth (Sunda, 2012), which can lead to convoluted uptake patterns. Additionally, trace elements may substitute for each other if one is absent, with Cd being shown to substitute for Zn in carbonic anhydrase in culture (Price and Morel, 1990). Limited Fe availability is thought to be an important factor driving uptake of other elements, where for example in cyanobacteria it was shown that Zn, Ni, Co, Mn, and Cd to phosphate ratios went up under Fe depleted conditions, indicating enhanced uptake (Cunningham and John, 2017). Such higher metal: phosphate ratios have been attributed to the upregulation of non-specific divalent metal transporters (e.g. Kustka et al., 2007; Lane et al., 2008, 2009) or the increased uptake of P relative to metals ("growth rate dilution"; Cullen et al., 2003), and are important in surface regions such as the Southern Ocean where Fe-limitation is prevalent, with implications passed on to the whole ocean. For instance, enhanced Cd and Zn uptake in zones of the Southern Ocean, attributed to Fe-limitation, is thought to be influential in spatially decoupling these nutrients from phosphate in Southern Ocean surface waters, driving the 'kink' in the Atlantic Cd:P relationship, and, via pre-formed addition to different water masses, much of the global distribution of these elements (see Sections "Classical concentration distribution patterns and residence times" and "Current knowledge of the marine distributions of trace elements and isotopes").

In addition to Fe availability, other environmental conditions such as temperature (Boyd and Hutchins, 2012; Raven and Geider, 1988; Jabre et al., 2021; Andrew et al., 2019), light conditions (Joy-Warren et al., 2022; van Leeuwe and Stefels, 2007; Andrew et al., 2022) and the availability of macronutrients can play a key role in determining the uptake of different trace elements (Finkel et al., 2010; Schoffman et al., 2016; Snow et al., 2015). For example, carrying out nitrogen fixation requires more resources than growth using other nitrogen species (Morel et al., 2014; Schoffman et al., 2016), including a requirement for Fe and Ni (Nuester et al., 2012), while low availability of inorganic phosphate invokes an additional need for Zn that is needed to assimilate organic forms of phosphorus using alkaline phosphatase (Shaked et al., 2006; Mahaffey et al., 2014). Thus, the controls on trace element uptake and the requirements of various biota are complex and a detailed discussion is beyond the scope of this chapter; instead we point the reader to Twining and Shaked (2024) for a more in-depth examination of these aspects of trace metal biogeochemistry. We also note that this is a field of very active research where we can expect insights to continue, for example through the emerging BioGeoSCAPES programme (https://biogeoscapes.org/).

Once fixed into organic material, the degree to which biogenic material survives to reach the sediments is strongly controlled by microbial respiration within the water column, with consequent regeneration and/or recycling of trace elements within the mixed layer, subsurface, and deeper ocean. Such internal recycling is particularly relevant for nutrient-type trace elements that, like the nutrients nitrate, phosphate, and silicic acid, undergo multiple cycles of assimilation into biogenic particulate material within surface waters and release or regeneration at depth during their residence time in the ocean reservoir. In this manner an element can undergo many internal cycles within the ocean prior to ultimate burial in sediments. As an example of the life history of a nutrient-type trace element, imagine an individual Zn atom delivered to the surface waters by upwelling or vertical mixing of deep water. It can be assimilated into a phytoplankton cell, where it might reside a day or two prior to being grazed. In the open ocean the bulk of this phytoplankton Zn and other nutrients will be regenerated in the surface waters and available to undergo perhaps 5 or 10 such assimilation/ regeneration cycles within the surface layer (Hutchins and Bruland, 1994, 1995; Hutchins et al., 1993) prior to removal as an export flux in the form of a fecal pellet excreted from a zooplankter or a larger aggregate of particles. Alternatively, any dissolved Zn could also be scavenged onto settling particles (John and Conway, 2014). The sinking particulate Zn can then be regenerated in the deep sea as the fecal pellet serves as a source of food and nutrition for heterotrophic organisms in the deep sea.

Regeneration of particulate Zn can occur at depth by the degradation of organic matter or the dissolution of the inorganic carrier phases (metal oxides, opal, calcite). This Zn may then be upwelled back into surface waters over the timescale of the mixing of the oceans (~1000 years). Since current estimates of the residence time of dissolved Zn range from 1 to 11,000 years (Horner et al., 2021), numerous cycles such as this may occur. Eventually the Zn atom may be finally buried in lithogenic, organic, or carbonate sediments, or incorporated into ferromanganese crusts (Little et al., 2014). Once this oceanographic journey is complete, a geological journey may then return Zn to the continents after uplifting ocean sediments back to the continents, where it is exposed to continental weathering and makes its way via rivers or aeolian dust input back to the ocean, or it might end up being subducted into the mantle with the descending slab during subduction of the ocean plate.

For Fe, the biologically mediated internal cycling of Fe in surface waters, termed the 'ferrous wheel' (Kirchman, 1996), is considered very important, especially in Fe-limited regions. Particulate biogenic iron in surface waters is rapidly recycled by microzooplankton (Barbeau et al., 1996; Strzepek et al., 2005), mesozooplankton (Laglera et al., 2017; Sarthou et al., 2008), bacteria (Strzepek et al., 2005) and viruses (Mioni et al., 2005; Bonnain et al., 2016; Slagter et al., 2016) all of which can result in the release of bioavailable forms of dissolved Fe (Boyd et al., 2017). Recent work agrees with this idea, suggesting that a combination of upwelled Fe, ligand-binding, and numerous recycling loops are responsible for setting the Fe-isotope signature of surface Fe-limited waters as well as keeping Fe available in the surface ocean for use by phytoplankton (Tagliabue et al., 2014a, b; Sieber et al., 2021; Rafter et al., 2017). Overall, the contribution of new Fe to the total Fe supply, termed the Fe ratio (new Fe/new + regenerated Fe; Boyd et al., 2005), ranges from <10% in HNLC waters (Boyd et al., 2005; Rafter et al., 2017) to 50% in high-Fe waters (Sarthou et al., 2008; Boyd and Ellwood, 2010)—values similar to those observed for nitrogen—underlining the importance and variability of recycling for different elements. However, there does seem to be differences between species and their responses to sources of regenerated Fe (Fourquez et al., 2022), consistent with the notion that bioavailability of Fe depends on both the species of Fe (e.g. free or ligand bound) as well as the species of microbe (Shaked et al., 2021; Fourquez et al., 2023). Further, particulate forms can also be 'bioavailable' and supply required elements to microbes. For example, the N_2-fixing cyanobacterium Trichodesmium has been elegantly shown to capture dust particles inside colonies, reduce the Fe(III) and make use of these particles as sources of Fe and P (Shaked et al., 2023; Rubin et al., 2011). However, generally it is thought there is greater dissolution from biogenic particulate Fe than from lithogenic particulate Fe and that recycling of biogenic particulate Fe is the main source of dissolved Fe and the weaker Fe-binding ligands, whereas lithogenic particulate Fe contributes to dissolved Fe scavenging and ballasting of biogenic particulate iron (Boyd et al., 2010, 2017).

Particle scavenging

In addition to the role of active assimilation of required trace elements by phytoplankton, there is also passive scavenging of trace elements onto the wide variety of relatively high affinity surface sites on both living and dead particulate material existing in the surface waters. The combined process of surface adsorption, followed by particle settling, is termed scavenging (Goldberg, 1954; Turekian, 1977), although the term scavenging is often used more widely to include a range of absorption, adsorption and precipitation processes. For a detailed description of scavenging systematics and tracers see Marcantonio et al. (2024), and for a comprehensive look at how scavenging influences the particulate reservoir of different trace elements, see Lam and Xiang (2024). The binding resulting from scavenging is effectively "passive," in contrast with the active uptake and assimilation of essential trace elements. Such scavenging can be reversible, or irreversible, depending on the trace element and the particle substrate. As discussed in previous sections (Sections "Classical concentration distribution patterns and residence times", "Current knowledge of the marine distributions of trace elements and isotopes", and "Particle scavenging"), 'particle-reactive' elements which are strongly affected by scavenging processes include trace elements such as the REE, Pb, Al, Ga, Fe, Co, Mn, as well as radionuclides such as the ^{210}Po, ^{231}Pa, and the isotopes of Th. Further, reversible scavenging has been invoked to lesser degrees to explain the distributions of elements such as Zn, Ni and Cu (Weber et al., 2018; John et al., 2022; Little et al., 2013; Richon and Tagliabue, 2019), while recent works have shown that reversible particle-scavenging of Pb is an important transfer mechanism of Pb from surface (atmospheric deposition) or coastal waters (sediments and rivers) to deeper waters, and thus a 'source' of both anthropogenic and natural Pb to the deep ocean (Benaltabet et al., 2020, 2023; Chen et al., 2023; Lanning et al., 2023).

Radionuclides have long found use as tracers of fluxes and rates in chemical oceanography (Marcantonio et al., 2024), where perhaps the most useful particle dynamics tracer is the particle-reactive insoluble element Th, with its four different radioactive isotopes (radionuclides) of greatly differing half-lives (Henderson and Anderson, 2003). A key benefit of Th is that the different nuclides are produced via radioactive decay of different parents at different rates, and decay with different half-lives, yet are all reversibly-scavenged to particles in the same way. As such, Th provides insight into the process and rates of scavenging as well as lithogenic addition from dust and sediments. For example, ^{232}Th, with its long half-life of 1.4×10^{10} years, is added to the ocean from external lithogenic sources, while ^{230}Th (half-life 7500 years) is produced within the ocean by the decay of ^{234}U with a conservative-type distribution, yet both are scavenged to particles in the same way. This means that Th scavenging rates can be obtained from measurements of the amount of dissolved ^{230}Th relative to calculated production from radioactive decay of ^{234}U (and decay of ^{230}Th). This can subsequently be combined with measurements of dissolved ^{232}Th in order to calculate lithogenic fluxes of Th—and by extension fluxes of other lithogenic elements such as Fe—from dust or sediments (e.g. Hirose and Sugimura, 1987; Hsieh et al., 2011; Hayes et al., 2013, 2015a, 2017; Anderson et al., 2016). Similarly, the reversible-scavenging behavior of ^{230}Th means that it has long been used to calculate particle settling fluxes to sediments, or to correct accumulation rates for sediment disturbance (Bacon and Anderson, 1982; Francois et al., 2004). As with other geochemical tracers, development of the different Th isotope tracers has also benefitted enormously from the availability of ocean sections providing large Th datasets. These have provided additional detail and have allowed for the calculation of large scale lithogenic fluxes and scavenging rates, as well as the development of paleo-proxies and residence time estimates for other elements (Schlitzer et al., 2018; GEOTRACES Intermediate Data Product Group, 2023; Deng et al., 2014, 2018; Hayes et al., 2018a; Pavia et al., 2019). Such studies have also highlighted the importance of hydrothermal plumes and benthic boundary layers / particle rich 'nepheloid layers' for scavenging of elements, with radionuclides providing rates of scavenging and particle aggregation (Pavia et al., 2019). Lastly, ocean sections have provided new insights on the balance of processes that influence ^{230}Th vs ^{231}Pa and their combined use as a paleoproxy for circulation (Hayes et al., 2015a).

At a shorter-timescale, ^{234}Th, with a half-life of 24.1 days, is continuously produced from ^{238}U in seawater, and acts as an ideal tracer of variable particle scavenging, the strength of 'the biological pump' and the POC export flux in and from surface waters (Coale and Bruland, 1985; Buesseler et al., 1992). For example, the scavenging intensity of ^{234}Th varies dramatically between the oligotrophic gyre of the North Pacific and South Pacific and productive regions such as the subarctic Pacific, the upwelling regime off central California and the equatorial Pacific (Bruland and Coale, 1986). The net scavenging rate constant has been argued to be proportional to new or export production (Coale and Bruland, 1987) and has been observed to be most intense in regimes of high particle production with substantial export of this material from the surface waters, and least intense in regions of lower primary production where regenerated production dominates. However, beside the amount of particles, the nature or composition of the particles plays a key role too (Lerner et al., 2018) where notably authigenic ferromanganese oxides play a key role as scavengers for the natural radionuclides ^{231}Pa and ^{230}Th, while biogenic opal is not as important (Hayes et al., 2015a), yet biogenic opal is deemed to be an important scavenger for Al (Moran and Moore, 1988; Akagi and Nishino, 2021). For a very thorough discussion on the role of particle type, concentration, and other factors on the importance and rate of scavenging for influencing the distribution and dissolved-particulate portioning of the different trace elements, see Lam and Xiang (2024).

Ocean sinks

As discussed in the previous sections, the ultimate sink for elements in the ocean is burial in ocean sediments, or removal to ocean crust by hydrothermal alteration. Trace elements may be delivered to sediments within, or scavenged to, particulate matter, or may be removed to sediments directly in the form of ferromanganese oxides, crusts, and nodules, or by other authigenic and diagenetic reactions occurring within sediment porewaters (Sections "Introduction", "Biological uptake, regeneration, and recycling", and "Particle scavenging"). However, as discussed in Section "Benthic sediments (shelf, slope, and abyssal)", depending on diffusion gradients, there may also be return fluxes of dissolved trace elements from porewaters to bottom waters, or diffusion from bottom waters into porewaters, where elements may be removed to authigenic phases. For example, sediments are thought to be important diffusive sources of Na and Ca, (as well as trace elements such as Fe, Mn, and Ni), while being sinks for K and Mg (Sayles, 1979). Thus, in some ways, constraining the relative importance of each sink for trace metals is more challenging than constraining overall external sources, since most of the outputs happen in the deep ocean over long timescales. Nevertheless, constraining the size of these sinks remains crucial for understanding overall ocean budgets and residence times. Here, ocean mass balances making use of isotopic compositions can be incredibly useful; for example, Tipper et al. (2006) made use of riverine δ^{26}Mg to investigate oceanic sources and sinks of Mg. A similar approach has proven useful for the trace elements, including Zn, Cd, Cu, and Ni (Little et al., 2014, 2015, 2020), where the main sinks for these elements are ferromanganese oxides and crusts, carbonate sediments, and organic sediments. Indeed, such an isotopic approach has allowed for the identification of organic and reducing sediments as important missing oceanic sinks of the bioactive metals, with isotopically light Zn and Cd likely sequestered in these sediments via delivery of biological material and/or during authigenic precipitation (Little et al., 2014, 2015, 2016, 2020; Conway and John, 2014a; Vance et al., 2016). It has also been proposed, and supported by dissolved δ^{114}Cd measurements, that anoxic micro-environments within sinking organic matter may enable removal processes of elements such as Cd and Zn from the dissolved phase, alongside nitrogen and sulfur (Bianchi et al., 2018; Janssen et al., 2014; Conway and John, 2015a). While the jury remains out on both the existence and importance of this process for influencing oceanic trace element distributions (e.g. de Souza et al., 2022), it may ultimately act as an ocean sink to sediments for some elements (Janssen et al., 2014; Guinoiseau et al., 2019). For a recent detailed discussion of oceanic mass balance and the isotopic compositions of the sinks and the sources of all the bioactive trace elements, see Horner et al. (2021) and Little et al. (2024).

Conclusions and future outlook

This chapter presented an introduction to, and review of, our current understanding of trace elemental distributions in the ocean, continuing to update an early principally one-dimensional view of the trace elements with the most recent insights from the last decade. The latter continue to highlight the importance of both ocean circulation and other internal process to the distributions of the trace elements throughout the ocean, as well as a consideration of a mix of different sources and sinks of trace elements (beyond the classic atmospheric inputs) as well as the recognition of previously understudied sources such as SGD and ice sheet melt. After 14 years of the GEOTRACES section program, in addition to a range of non-GEOTRACES studies, high-resolution ocean sections exist for many oceanic regions, and have led to great advances in our understanding of the trace elements. Overall, intermediate data-products and inter-calibration efforts have revolutionized the way the community works together and disseminates high-quality data freely. Some regions, notably the Indian Ocean, remain under sampled, however, and so we anticipate that GEOTRACES ocean sections will continue for the next several years. However, we are now in a position where the many questions posed by these sections must be addressed using smaller-scale experimental studies and field-based process studies, as anticipated by the GEOTRACES Science Plan as the second phase of the program (GEOTRACES Group, 2006; GEOTRACES SCOR Working Group, 2007; Anderson, 2020). There are already excellent examples of these, both within the program and outside. Further, many of the current GEOTRACES section studies, while dramatically improving spatial coverage, provide very little in the sense of temporal variability or the potential consequences of climate change. Long term Oceanic Time Series stations such as the Bermuda Atlantic Time Series (BATS) in the North Atlantic or Station Aloha in the North Pacific have proven their value for hydrographic parameters and particle fluxes (e.g. Conte et al., 2019; Steinberg et al., 2001; Michaels and Knap, 1996; Karl and Lukas, 1996). However, long-time series studies are rarely conducted for trace elements such as Fe, and in the handful of cases where they are, usually only for shorter time periods (Fitzsimmons et al., 2015c; Tagliabue et al., 2023). While crossover stations also provide some measure of temporal variability (e.g. Middag et al., 2015a; Conway et al., 2016; Sieber et al., 2023a), it is clearly challenging in terms of expense and labor to re-occupy ocean sections. We anticipate that higher temporal resolution sampling will be needed to continue to drive forward our understanding of trace element cycling in the oceans, especially in the surface. This is an area of trace element science where autonomous platforms and sensors may become useful as technology develops (Grand et al., 2019; van der Merwe et al., 2019a; Geißler et al., 2021).

At the smaller scale, despite much research, the internal cycling processes that control trace element distributions remain incompletely understood. For example, the speciation of dissolved Fe (and other trace elements) in the ocean remains somewhat elusive. Specifically, our current understanding of the cycling of trace elements is still largely based on observations of what is called dissolved (defined as everything that passes through a filter with 0.2 μm pore size). However, such a sharp boundary does not reflect the continuum in which trace elements are present in seawater, that ranges from truly dissolved molecules to small nanoparticles to colloids and larger particles. Thus, we highlight a need for not only an enhanced understanding of organic-complexation, but also the colloidal pool and exchange between different species, where all components are likely to play varying roles in the overall biogeochemical cycle of trace elements (e.g. Tagliabue et al., 2017, 2023). We also anticipate the continued development of analytical techniques which will permit the identification of the organic species that complex the different trace elements, driving forward understanding. Such aspects of trace element biogeochemistry are critical, not only for understanding longevity and 'bioavailability' of elements, but for accurately capturing trace elements into models of ocean biogeochemistry. For example, current biogeochemical models range widely in their ability to reproduce observations of oceanic Fe distributions accurately and make wide predictions in their estimates of the residence time of dissolved Fe (5 to >500 years, and less than a year in surface waters; Tagliabue et al., 2016; Anderson, 2020). Indeed, the residence time of Fe likely depends on the specific species, an aspect that is key to understanding where and when Fe will be transported over long distances. Moreover, the transformations and exchange processes along the dissolved-particulate continuum are often linked to microbial processes such as regeneration, nutrient uptake, or microbially mediated redox processes (e.g. Boyd et al. (2017)). With these in mind, we eagerly anticipate the development of new programs such as BioGeoSCAPES that will focus on ocean metabolism and nutrient cycling on a changing planet, and undoubtedly provide novel insights on the interactions between marine microbes, trace elements, and the biogeochemical cycles that drive life on our planet.

Overall, while much has been learnt in the first five decades of trace element research, much is still to be understood, no doubt ensuring that marine trace element science as well as marine biogeochemical modeling studies will be an exciting field of research for years to come. We especially look forward to the new insights that will come in the next decade.

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