THE OFFICIAL MAGAZINE OF THE OCEANOGRAPHY SOCIETY

Oceanography

CITATION

Anderson, R.F., E. Mawji, G.A. Cutter, C.I. Measures, and C. Jeandel. 2014. GEOTRACES: Changing the way we explore ocean chemistry. *Oceanography* 27(1):50–61, http://dx.doi.org/10.5670/oceanog.2014.07.

DOI

http://dx.doi.org/10.5670/oceanog.2014.07

GEOTRACES

Changing the Way We Explore Ocean Chemistry

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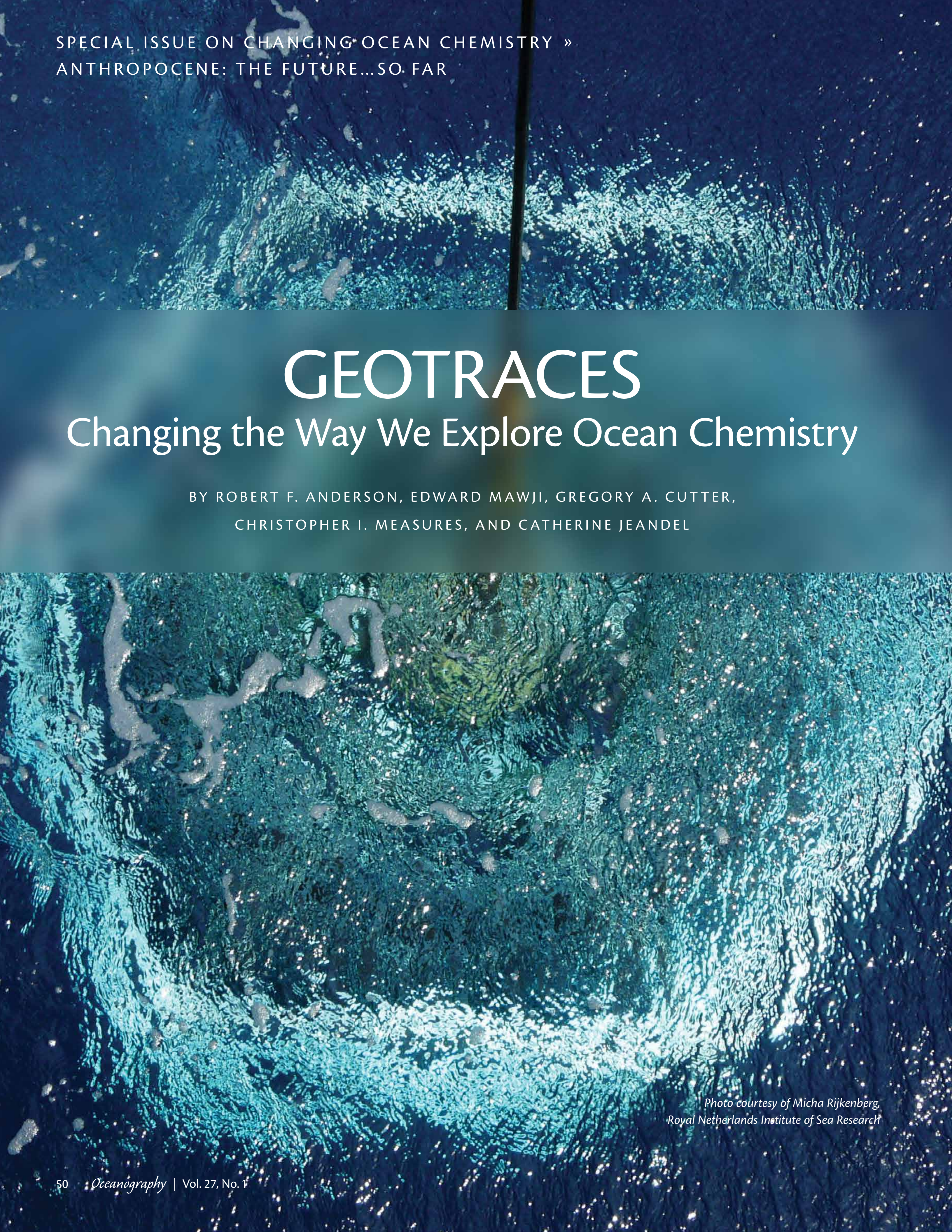

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ABSTRACT. GEOTRACES is an international study of the marine biogeochemical cycles of trace elements and their isotopes (TEIs), designed by marine geochemists to accelerate TEI research under a global program. Combining ocean sections, process studies, data synthesis, and modeling, GEOTRACES will identify and quantify the processes that supply TEIs at ocean boundaries as well as the physical and biological processes that redistribute TEIs within and between ocean basins. Constraining processes that remove TEIs from the ocean will enable complete mass budgets to be generated. Anticipated beneficiaries of GEOTRACES products include scientists studying the sustained health of marine ecosystems and their sensitivity to changes in micronutrient supply; paleoceanographers seeking to reconstruct past changes in the ocean environment, including the ocean's role in climate variability; and scientists and policymakers who seek a better understanding of the transport and fate of contaminants in the ocean. It is hoped that the experiences described here will provide helpful guidance to scientists in other disciplines who wish to advance their fields by organizing coordinated research programs.

INTRODUCTION: THE NEED FOR INTERNATIONAL COLLABORATION

Marine biogeochemical cycles occur on a global scale. Sources of trace elements and their isotopes (TEIs) are diverse, including atmospheric deposition of mineral aerosols, continental erosion and river transport, sediment-water boundary exchange, and hydrothermal fluxes from mid-ocean ridges. Removal processes are equally diverse. Once in the ocean, TEI distributions are influenced by biological uptake and regeneration and by physical transport, as well as by the chemical forms in which the individual TEIs exist. With so many factors involved, and with processes operating in many regions of distinctly different character, a comprehensive understanding of the marine biogeochemical cycles of TEIs can be attained only by a global, coordinated, international effort.

The Geochemical Ocean Sections study (GEOSECS) of the 1970s transformed the field of chemical oceanography as it existed at that time, and it served as a role model for the design of GEOTRACES. Exploiting new technologies available then, scientists pursued novel research on the distribution of dissolved inorganic carbon species, major nutrients (nitrogen, phosphorus, and silicon), a suite of natural and man-made radioisotopes, and noble gases to provide a first view of the chemical landscape of the sea. New insights into ocean mixing and overturning circulation were extracted from the global distribution of radiocarbon and tritium, while uranium-series radionuclides were modeled to constrain rates of vertical transport by sinking particles. A synthesis of GEOSECS results was embodied in the classic textbook by Broecker and Peng (1982), which has since been used to educate a generation of oceanography students.

While GEOSECS was an unmitigated success, its scope was limited by several factors. For example, technologies had not yet been developed to permit sampling without contamination for a broad suite of trace elements. Furthermore, although there was some international collaboration in GEOSECS, it was largely the responsibility of a single nation, thereby limiting the geographical coverage that was feasible within the lifetime of the program. Both the successes and the limitations of GEOSECS weighed heavily in the design of GEOTRACES.

RATIONALE AND ANTICIPATED BENEFITS

Research on trace elements in the ocean was revolutionized in the 1970s by the development and application of technology to collect and analyze uncontaminated seawater samples. Early results showed nutrient-like profiles for many trace elements, suggesting that these elements are consumed biologically in surface waters and regenerated at depth along with decomposing biogenic material (Bruland and Lohan, 2003). The vital role of marine organisms in the cycles of a number of trace element micronutrients is now recognized (Table 1). Nonlinear biological responses due to interactions among multiple limiting micronutrients are now being explored, as are synergistic and antagonistic effects associated with metal substitution and co-limitation. New techniques in molecular biology offer the promise of assessing micronutrient limitation in field studies (Sunda and Huntsman, 1998). There is great potential for revealing the fundamental role of micronutrients in regulating marine ecosystems in coming years. However, success in these endeavors, and in assessing the sensitivity of marine ecosystems to perturbations of marine micronutrient cycles, depends critically on developing a complete knowledge of micronutrient distributions, together with a quantitative understanding of the processes that regulate their supply, removal, and transport within the ocean. A quarter century of research following the development of contamination-free methods to measure trace elements in seawater produced insufficient information (Figure 1) to fully characterize the marine biogeochemical cycles of essential micronutrients (e.g., Boyd and Ellwood, 2010). Early in the new millennium, it was evident to marine chemists that a new strategy would be required to accelerate research on trace metals.

A need to accelerate research was also recognized for geochemical proxies used in paleoceanography. Our understanding of past variability in the ocean environment, including the ocean's role in climate change, has been advanced through the application of a variety of TEI proxies archived in marine substrates such as sediments, corals, and microfossils (Henderson, 2002). However, despite their importance for paleoclimate reconstructions, by necessity, these geochemical proxies have been calibrated in an ad hoc way. Many were developed using samples that do not necessarily reflect modern oceanic conditions, while others are based solely on lab studies. Furthermore, paleo-proxy calibrations are generally empirical, based on limited understanding of the processes that link the measurable proxy to the variable that it is intended to represent. Consequently, there is a critical need for more comprehensive assessment and testing of geochemical proxies, both to develop and calibrate new proxies for environmental variables that are presently difficult to reconstruct and to reduce the uncertainties associated with proxies currently in use.

Benefits to be derived from GEOTRACES extend beyond the study of micronutrients and paleo-proxies. For example, the oceanic distributions of many TEIs have been impacted by human activities. Anthropogenic emissions from automobiles and industry represent the dominant source of lead in the surface ocean worldwide and in deep waters of the North Atlantic (Schaule and Patterson, 1981; Boyle et al., 2014, in this issue). Mercury has been influenced significantly by anthropogenic emissions as well and may represent a significant threat to human food supply (Lamborg et al., 2002, and 2014, in this issue). Although research on contaminants is not a specific focus of the program, knowledge of fundamental processes regulating the supply, removal, and internal cycling of TEIs to be gained through GEOTRACES research can be applied to improve predictions of their transport and fate in the ocean.

A number of factors favor coordinated and simultaneous study of multiple TEIs. With decreasing sample size requirements from improved sensitivity of new instrumentation, it has become possible to design sampling strategies that are compatible with multiple analytical procedures. More importantly, studying multiple TEIs simultaneously provides information that cannot be derived by examining a single element in isolation. Each element can be understood as a special case in a continuum of geochemical properties, where the similarities and contrasts among the elements offer insights into each individual element. In many cases, the better constrained, or more simply defined, behavior of one element illuminates the behavior of another. Clearly, there is great merit in a coordinated multi-tracer program. Information to be derived about the marine biogeochemical cycles of TEIs will far exceed that which could be achieved by multiple studies of a single element.

International collaboration on TEI research extends beyond sharing the workload involved with sampling globally. It includes the development of new technologies to accelerate the collection and analysis of samples, the intercalibration of those technologies to ensure internal consistency among the

Table 1. Important biogeochemical processes in the ocean and the trace metals thought to be fundamental to their action. *Derived from Morel et al. (2003) and Morel and Price (2003)*

Biogeochemical Process	Important Trace Elements
Carbon fixation	Fe, Mn
CO_2 concentration/ acquisition	Zn, Cd, Co
Silicate uptake – diatoms	Zn, Cd, Se
Calcification – coccolithophores	Co, Zn
N_2 fixation	Fe, Mo (?: V)
Denitrification	Cu, Fe, Mo
Nitrification	Cu, Fe, Mo
Methane oxidation	Cu
Remineralization of organic matter	Zn, Fe
Organic N utilization	Fe, Cu, Ni
Organic P utilization	Zn
Formation of volatile species	Fe, Cu, V
Synthesis of photopigments	Fe and others
Toxicity	Cu, As (?: Cd, Hg)

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participating labs, the development of a data management system to facilitate access to the results by the entire oceanographic community, and a broad collaborative effort to model, synthesize, and interpret the results. An International Project Office, located in Toulouse, France, coordinates these activities.

SCIENTIFIC OBJECTIVES

GEOTRACES was designed to achieve three overarching goals:

- Determine global ocean distributions of selected trace elements and isotopes, including their concentration, chemical speciation, and physical form; and evaluate the sources, sinks, and internal cycling of these TEIs to characterize more completely the physical, chemical, and biological processes regulating their distributions.
- Understand the processes involved in oceanic trace element cycles sufficiently well that the response of these cycles to global change can be predicted.
- Understand the processes that control the concentrations of TEIs used for proxies of the past environment, both in the water column and in the substrates that reflect the water column.

These goals will be pursued through complementary research strategies, including observations, experiments, and modeling. Conceptually, these objectives are subdivided into studies of the supply and removal of TEIs at ocean interfaces and research on the internal cycling of TEIs within the ocean (Figure 2).

Fluxes of TEIs at ocean interfaces with land, the atmosphere, and the oceanic crust are poorly known. This lack of information represents a fundamental limitation for research in any discipline that requires knowledge of regional or global biogeochemical budgets. Improved understanding of chemical fluxes at each of these ocean interfaces therefore represents a central theme of the GEOTRACES program.

"Internal cycling" refers to a complex suite of transport and transformation processes that influence the marine distributions of TEIs. Transformations include TEI exchange among dissolved, colloidal, and particulate forms, as well as conversions between chemical species (e.g., oxidation/reduction). Paramount among these processes is the uptake of TEIs into biological material and their subsequent regeneration when this material decays. Ocean circulation transports TEIs, while gravitational settling of particulate material provides a unique vector delivering TEIs to their ultimate repository in marine sediments. Therefore, internal cycling plays a role in regulating the distributions of TEIs in the ocean that is at least as significant as the processes controlling their supply and removal.

PROGRAM IMPLEMENTATION

A suite of complementary activities was identified as necessary to achieve the objectives of GEOTRACES. These activities can be divided broadly into the following categories: enabling activities (standards and intercalibration; data management); ocean observations (sections and process studies); synthesis and modeling; capacity building; and program philosophy and management.

Enabling Activities

Certain enabling activities must be completed to allow international cooperation and to ensure that results produced by different groups are comparable, internally consistent, and readily available to the oceanographic community.

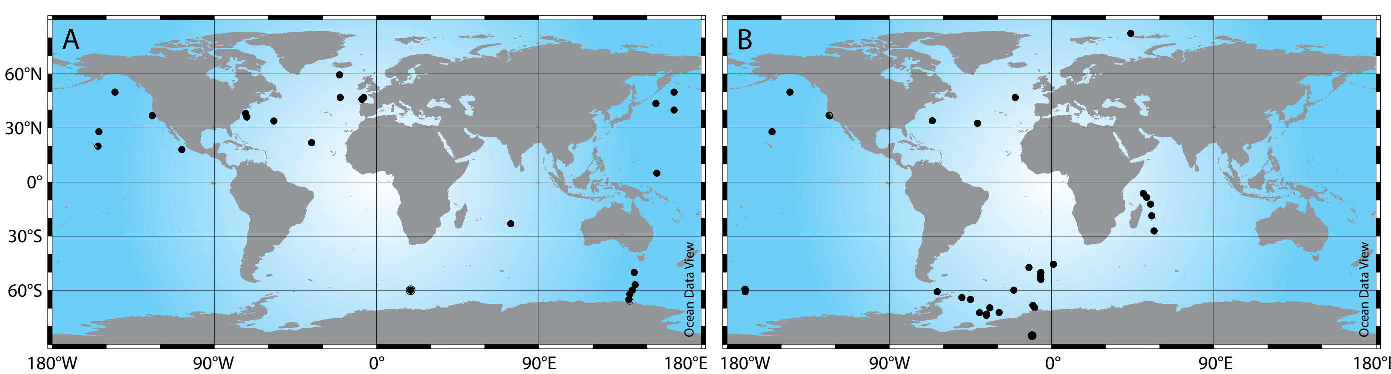

Figure 1. (A) A global map of stations where concentrations of iron in seawater had been reported for depths of 2,000 m or deeper, as of 2003. *Redrafted from a compilation by Payal Parekh, Massachusetts Institute of Technology and initially presented in the GEOTRACES Science Plan* (B) A global map of stations at which concentrations of zinc in seawater had been reported for depths of 2,000 m or deeper, as of 2009. *Information compiled by Maeve Lohan*. These maps illustrate the paucity of high-quality data needed to define the marine biogeochemical cycles of these key micronutrients. *Figure produced using Ocean Data View (R. Schlitzer, http://odv.awi.de, 2011)*

Intercalibration

In determining the concentrations of certain trace elements, accuracy can be compromised during sample acquisition, handling, processing, storage, and analysis. Consequently, GEOTRACES implemented a standards and intercalibration initiative with two principal goals: (1) to establish procedures and protocols for sampling at sea that will ensure that samples are collected, handled, and stored without contamination or other sources of bias, and (2) to produce samples of seawater containing TEIs at levels representative of open ocean conditions and for which concentrations are established through multiple independent analyses with sufficient reliability that the water can be used as a consensus reference material. Prior to GEOTRACES, available certified reference materials for seawater had concentrations of TEIs that are 5 to 10 times higher than oceanic values, so developing a new set of reference samples representative of open ocean conditions was afforded high priority. The purpose of the GEOTRACES intercalibration initiative is to ensure that different methods used to measure a parameter give accurate, precise, and internally consistent results, not necessarily to establish a single method for each parameter to be used by all investigators on all GEOTRACES cruises.

With support primarily from the US National Science Foundation, the GEOTRACES intercalibration initiative involved two cruises. The first cruise (Atlantic Ocean, June–July 2008) focused on testing a newly designed US sampling system for rapid collection of contamination-free seawater samples (Cutter and Bruland, 2012). Shipboard analyses of a number of contamination-prone elements (Al, Fe, Hg, Pb, and Zn), as well as nutrients and salinity, were used to evaluate the performance of the system by comparing results against those obtained using more traditional, but slower, procedures (individual GO-FLO bottles deployed on a Kevlar line; MIT vane sampler). Water samples were also archived for shore-based analyses.

Following the cruise, intercalibration samples were distributed worldwide to participating labs. To facilitate the process, the full suite of TEIs submitted to intercalibration was divided into 15 categories, each led by a point person, or elemental coordinator. GEOTRACES had advertised the intercalibration initiative for more than a year leading up to the first cruise, inviting interested parties to identify themselves. Elemental coordinators distributed samples to labs that had indicated an interest in participating in the intercalibration. Some categories involved as many as 20 labs. Some labs participated in multiple categories. Intercalibration results are published in a special volume of *L&O Methods* (http://www.aslo.org/lomethods/si/intercal2012.html).

Both shipboard measurements and the analysis of archived samples demonstrated that the new US GEOTRACES carousel system collects uncontaminated samples and produces results that are consistent with those obtained by the more traditional methods (Figure 3). The internal consistency among measurements indicates reliable intercalibration among analytical labs as well as contamination-free sampling across several different sampling systems.

For certain TEIs, differences among labs were identified during the intercalibration, indicating unrecognized blanks as well as some systematic offsets. In each case where differences were detected, members of the group used the findings to identify the cause(s) of inconsistency and make necessary corrections.

The second intercalibration cruise (Pacific Ocean, May 2009) continued many of the comparisons initiated during the first cruise and added tests for sampling, storage, and analytical methods used to determine the chemical speciation of selected TEIs, including organic complexes of Fe and Cu as well as the oxidation state of Fe. Good agreement was found among different groups in determining conditional stability constants and concentrations for Fe- and Cu-binding ligands. Results also indicated that freezing seawater at –20°C for

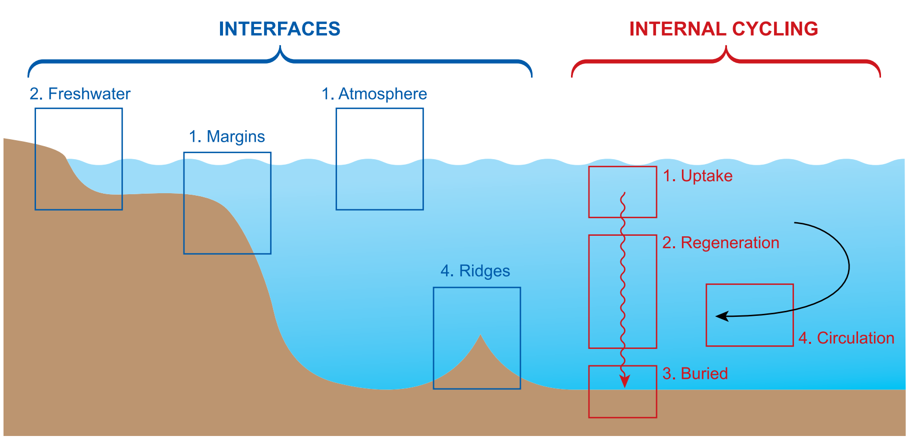

Figure 2. A schematic view of the major processes influencing the distribution of trace elements and their isotopes (TEIs) in the ocean. Fluxes across four major ocean interfaces (blue) and four major internal processes (red) are responsible for ocean TEI patterns. GEOTRACES is designed to quantify these fluxes and characterize the internal cycling. *Reproduced from the GEOTRACES Science Plan*

shore-based ligand analysis introduced no detectable artifacts, although freezing at –80°C introduced biases. For Fe (II), results indicated that decay rates are slow enough that sampling from a clean rosette system as part of a normal sampling sequence introduces no detectable artifacts.

Intercalibration of particulate TEIs involved not only the elements themselves, but also three different sampling systems (two in situ pumping systems and filtration directly from GO-FLO bottles), three different filter materials, different filter diameters, and different pore sizes. In addition, contamination of the filtrate by the filter and filter holder was examined. Whereas most filters tested showed little evidence for contamination, there was clear evidence that the type of filter used can affect the measured particulate TEI concentrations, presumably due to differences in the effective size fractions and particle subpopulations sampled by each filter type. Clearly, particulate metal concentrations are operationally defined, and for this reason consistent filtration methods should be used throughout a cruise and, ideally, among cruises.

Reference Materials

Collection and distribution of seawater samples to be used as reference materials began under the Sampling and Analysis of Fe (SAFe) program (SAFe station, 30°N, 140°W) and continues under GEOTRACES. These reference samples are intended for use as working standards during the analysis of seawater for a subset of TEIs that are particularly prone to contamination or other analytical difficulties (Al, Cd, Co, Cu, Fe, Mn, Ni, Pb, Zn). Current consensus values for the concentrations of selected dissolved trace metals for the SAFe reference samples can be found on the GEOTRACES website (http://www.geotraces.org/science/intercalibration/322-standards-and-reference-materials). Results are being updated as new information becomes available. A variety of newer GEOTRACES reference samples are also available, including surface and deep water from the Atlantic (Bermuda Atlantic Time Series Station [BATS]) and Pacific (SAFe station) Oceans. Information about obtaining these reference materials and instructions for reporting results is provided via the web link above.

Participants in all GEOTRACES cruises are expected to use SAFe/GEOTRACES reference samples as a primary reference standard when analyzing seawater samples for those TEIs for which consensus concentration values have been produced. Implementing the reference samples has proven to be a crucial step to ensure internal consistency among the results.

Crossover Stations

Cruise leaders are advised to incorporate crossover stations into their cruise plans as a further measure of intercalibration. With advance planning, a crossover station can be implemented at any location where the track of one cruise intersects that of another, provided that each cruise collects samples at that location. Concentrations of most dissolved TEIs in the deep ocean are not expected to change significantly on the time scale between cruises, so comparing results from crossover stations provides a measure of internal consistency for all parameters.

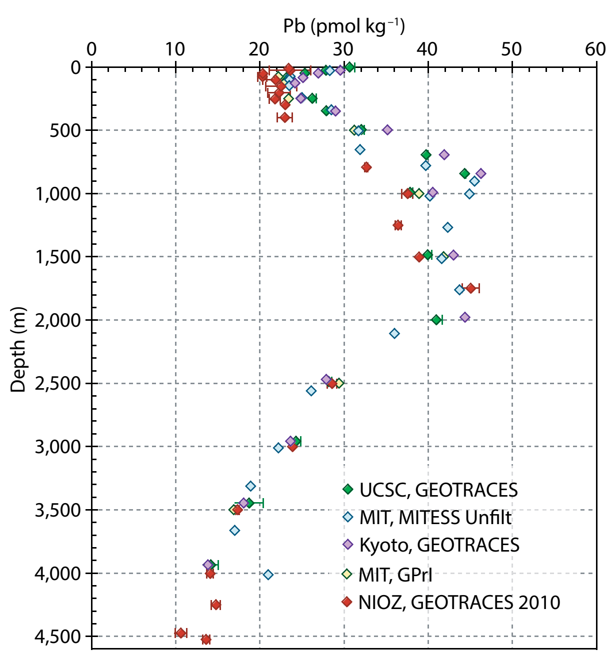

Figure 3. Concentration profiles of dissolved Pb at the Bermuda Atlantic Time Series (BATS) station. Similar concentrations in deep water (2,000–4,000 m) found in different sets of analyses indicate internal consistency among different sampling systems, different laboratories, and different cruises. "UCSC, GEOTRACES" indicates samples collected by the US GEOTRACES system in June 2008 and analyzed at the University of California, Santa Cruz. "Kyoto, GEOTRACES" samples were collected using the same system, on the same cruise, and analyzed at Kyoto University. "MIT GPrI" indicates samples collected with the US GEOTRACES carousel from a different cast on the June 2008 cruise and analyzed at the Massachusetts Institute of Technology (MIT). "MIT MITESS" samples were collected in June 2008 using the MIT vane sampling system (MITESS, Bell et al., 2002), previously demonstrated to collect contamination-free samples, and analyzed at MIT. Unlike the other samples, these vane samples were unfiltered. The BATS site served as the first crossover station for GEOTRACES and was re-sampled in June 2010 during a GEOTRACES cruise of the Royal Netherlands Institute for Sea Research (NIOZ). Data indicated as "NIOZ, GEOTRACES" involve samples collected in June 2010 by the Netherlands GEOTRACES system (de Baar et al., 2008) and analyzed at the University of California, Santa Cruz. *Figure courtesy of Ken Bruland, University of California, Santa Cruz*

Results from the first crossover station of the GEOTRACES program, at the BATS site, illustrate the value of this approach. Concentrations of Pb in deep water measured during the first intercalibration cruise (June 2008) agree well with concentrations measured in June 2010 aboard a section cruise of the Netherlands (Figure 3). Good agreement in deep waters between cruises indicates that the generally lower concentrations of Pb measured at intermediate depths in 2010 reflect the true decline in the concentration of dissolved Pb at intermediate depth and not an analytical bias. The GEOTRACES Standards and Intercalibration (S&I) Committee is tasked with making an annual review of the results from crossover stations as part of the overall intercalibration and quality-control effort that will continue throughout the program.

Methods Manual

Recommended methods for sampling and storing seawater are detailed in the GEOTRACES "Methods Manual" (available at http://www.geotraces.org/libraries/documents/Intercalibration/Cookbook.pdf). The S&I Committee will periodically update this document as new information becomes available. The guide is intended to serve as a resource for any investigator who wishes to initiate or improve upon the analysis of seawater for any of the parameters that are regularly measured within the GEOTRACES program, regardless of whether or not the analyses will be carried out within the context of a GEOTRACES project.

Data Policy and Data Management

A data management infrastructure is required to ensure completeness, quality, and consistency of a global data set. GEOTRACES responded to this need by establishing a Data Management Committee (DMC) comprised of data originators (i.e., observational scientists), data managers, and data users (including modelers) and by creating an international GEOTRACES Data Assembly Centre (GDAC) hosted by British Oceanography Data Centre (BODC), Liverpool, UK (http://www.bodc.ac.uk/geotraces). GDAC reports to the DMC on the status of data and metadata from all the participating nations. The DMC and GDAC are involved in all GEOTRACES data activities from start to finish, including providing recommendations on how to manage data and, just as importantly, the metadata.

Endorsement of a scientific activity by GEOTRACES requires the cruise Principal Scientist (PS) to act in accordance with the data policy, which includes ensuring that all metadata and data documentation are completed and delivered to GDAC. Expectations for submitting this material are posted on the website (url above). Post-cruise metadata and data should be submitted within two years after samples have been analyzed, but this could be extended when analytical procedures have inherent built-in delays. Failure of a PS to submit metadata is considered reason to remove GEOTRACES endorsement. It is strongly recommended that at least one berth on every GEOTRACES cruise be allocated to an individual with data management experience to serve as a Shipboard Data Specialist.

The GEOTRACES website posts all cruise summary reports (CSR), where available, and cruise reports for completed GEOTRACES cruises. Information about planned cruises is posted as well, normally after a funding commitment for a cruise has been made. Investigators seeking additional information about planned GEOTRACES cruises may either contact the International Project Office (ipo@geotraces.org) or contact the PS directly.

GDAC was created in 2008 to provide a centralized hub to interact between national data centers and the DMC and, ultimately, to guarantee that GEOTRACES data are accessible to scientists. Post-cruise data will be submitted initially to national data centers to meet national funding obligations and then transferred to BODC when deemed appropriate by the PS and by the regional data manager (within the two-year period). If a country does not have a national data center, then GDAC will act as the primary recipient. Data will become open access when all data restrictions have been removed, normally within two years after analysis. Global data sets will be created for all key parameters and mapped to BODC ontology, allowing participants to search and access information related to data collection.

Observations

Ocean Sections

Measurement of a suite of TEIs along full-depth ocean sections, traversing each of the major ocean basins, is a core activity of the GEOTRACES program. This effort will identify, at a global scale, the wide range of chemical, physical, and biological processes involved in the cycling of TEIs. It will map the present distribution of TEIs and allow prediction of future changes to their distribution, with relevance to global-change research. It will allow relationships between different TEIs to be exploited to better understand their chemical behavior, and will also allow use of TEIs as proxies for past change. Global data sets, of certified quality (via intercalibration), from these ocean sections will be one of the major legacies of the program and will provide important information to a wide variety of related disciplines, including global carbon cycle modeling, climate modeling, ocean ecosystem studies, and research into ocean contaminants.

The process of defining ocean sections to be sampled by GEOTRACES began during the drafting of the GEOTRACES Science Plan (available at http://www.geotraces.org/images/documents2/Science_plan.pdf) with the identification of regions of the ocean where specific processes were believed to dominate the supply, removal, or internal cycling of TEIs. Principal water masses and major biogeographic provinces were identified as well. Potential target regions were located on a map of the global ocean (Figure 4) and lines were simply added to illustrate the concept of sections that would span multiple regions of interest.

With these principles in place, GEOTRACES held a series of international planning workshops in 2007, one each for the Pacific, Atlantic, and Indian Oceans. An Arctic planning workshop was held in 2009. Each workshop served to match recommendations from the Science Plan with the priorities of individual nations. Although many section cruises are expected to involve international participation, cruise planning at national levels is necessary to secure ship time and logistical support from national funding sources. National leaders coordinate their planning through the international Scientific Steering Committee (SSC) to cover the principal regions of interest while avoiding unnecessary redundancies.

Recognizing that GEOTRACES would have opportunities for a limited number of cruises, it became a high priority to sample multiple areas of interest within a single section. Consequently, unlike other ocean surveys (e.g., CLIVAR Carbon and Hydrographic Sections; http://www.clivar.org/resources/data/clivar-carbon-and-hydrographic-sections), GEOTRACES sections often do not follow straight lines (Figure 5), thus enabling each cruise to sample as many high-priority targets as possible.

GEOTRACES launched an aggressive field campaign in 2009. Four years into the global survey, sampling of the Atlantic Ocean is the most complete (Figure 5). Atlantic sections are designed, in part, to study the supply of TEIs from large rivers and from Saharan dust, to characterize the exchange of dissolved TEIs with margin sediments, to quantify transport of TEIs by large-scale overturning circulation as well as by the outflow of the Mediterranean Sea and of the Arctic Ocean, and to constrain the exchange of TEIs with the rest of the global ocean via the Southern Ocean.

Coverage of the Pacific Ocean will span the full decade of the field program simply because of the size of the basin. Pacific sections will examine TEI distributions under an extreme range of biological productivity, from the eutrophic eastern boundary current regimes off South America to the hyper-oligotrophic South Pacific subtropical gyre; quantify sources and sinks associated with the intense oxygen minimum zones of the eastern tropical Pacific; quantify TEI supply by various Asian sources, including dust and exchange with the continent as modified by processes in the marginal seas; and define TEI sources and sinks created by the hydrothermal systems associated with mid-ocean ridges. Cruises in the Indian Ocean will examine sources of TEIs via dust, both natural and anthropogenic, major rivers (e.g., Ganges-Brahmaputra), boundary exchange, and hydrothermal systems.

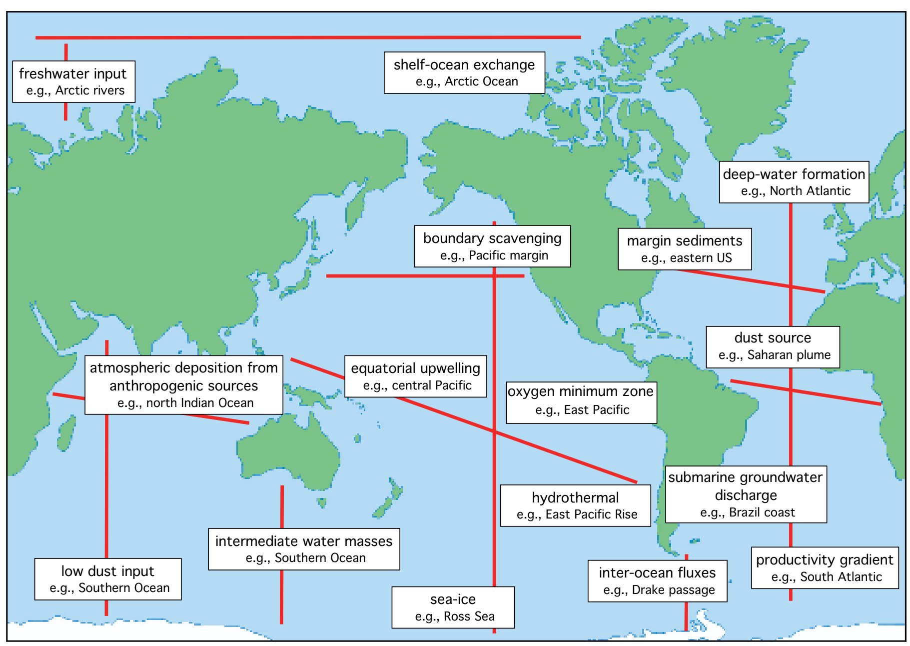

Figure 4. A schematic map indicating the philosophy behind the choice of ocean sections within GEOTRACES. Sections were planned to cover the global ocean and to pass through regions where specific processes were thought to control the distribution and biogeochemical cycling of TEIs. A selection of processes is shown in the figure, together with examples of locations where these processes are expected to have a large impact on TEI biogeochemistry.

International Polar Year

Scientists had an opportunity to begin investigating TEI distributions in the polar oceans in advance of the main GEOTRACES field program by participating in International Polar Year cruises (IPY; 2007–2009). Timing of the IPY posed some difficulties because it occurred before GEOTRACES was fully prepared to mount a complete ocean section study. Nevertheless, implementation was at a sufficient stage of development to permit sampling for a range of TEIs. IPY cruises that have contributed to the GEOTRACES database are illustrated in Figure 5 (black track lines) and tabulated on the GEOTRACES website (http://www.geotraces.org/cruises/cruises-completed/155-geotraces-ipy-cruises-list).

The first full water column GEOTRACES sections, completed as part of the IPY, identified features in TEI distributions at unprecedented resolution (Figure 6). For example, sampling along the prime meridian in the Southern Ocean revealed a plume enriched in dissolved iron that could be traced hundreds of kilometers away from the ridge crest (Figure 6A). The fact that the plume waters are also enriched in Mn (Figure 6B) but not in Al (Figure 6C) indicates a source from hydrothermal solutions emanating from the ridge rather than from resuspended sediments. Comparing the three TEIs measured along a common section illustrates the value of the multi-tracer approach employed by GEOTRACES.

Regional and Process Studies

Although ocean sections will address many of the goals of GEOTRACES, there are other questions that require alternative approaches. For instance, strategies to assess the sensitivity of TEI cycling to variability of environmental conditions include intensive studies of natural temporal and spatial variability, involving process studies that may require sampling at very high spatial resolution, long periods on station, repeat occupation of the same site, or retrieval of significant quantities of sediment.

Biological processes that influence TEI distributions, as well as research on the sensitivity of marine ecosystems to changes in the concentration and speciation of miconutrients, are well suited for GEOTRACES process studies (e.g., Boyd et al., 2012). Efforts to incorporate minimal sampling of relevant biological parameters (http://www.geotraces.org/science/biological-parameters) on GEOTRACES section cruises have been challenging because ships lack sufficient berth space to support both research on a broad range of TEIs and work on the interaction between TEIs and marine organisms. This represents one of the most frustrating limitations for the GEOTRACES program, and it illustrates the need to incorporate larger ships into oceanographic fleets to support exciting new interdisciplinary fields of research, such as chemical-biological coupling. Until larger ships become available, the GEOTRACES SSC recommends that interactions between micronutrients and marine ecosystems be examined using process studies that can focus on a limited suite among the TEIs that are of interest to GEOTRACES.

In some cases, targets for process studies are readily anticipated. In such cases, process studies can run concurrently with ocean sections. In other cases, the need for process studies will be identified on the basis of new information derived from the ocean sections. In particular, unanticipated features in the distributions of TEIs revealed in ocean sections will identify aspects of TEI biogeochemistry not previously known, and these will serve as targets for process studies. An updated listing

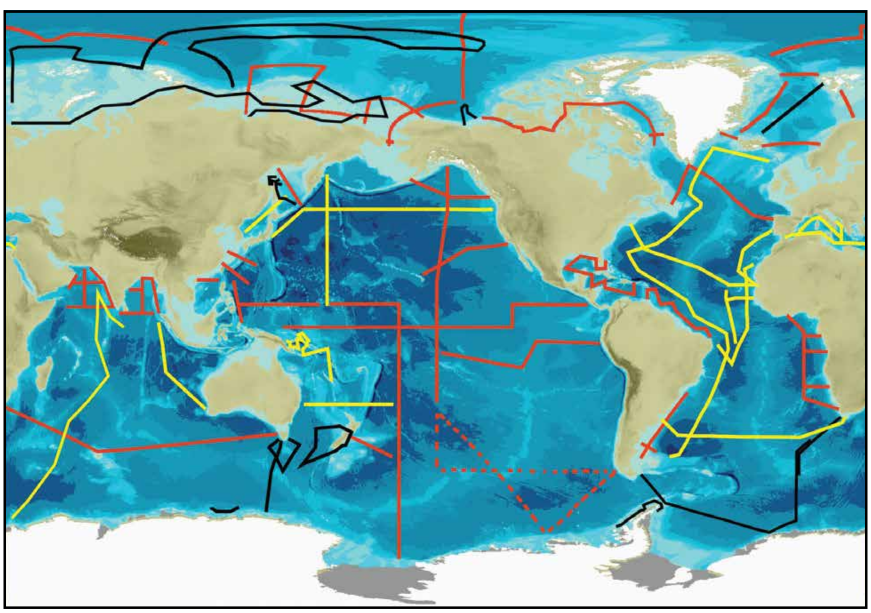

Figure 5. GEOTRACES global survey as implemented (*cf.* Figure 4). Black = sections completed during the International Polar Year. Yellow = full GEOTRACES sections completed by mid-2013. Red = planned future sections. An updated version of this map is maintained on the GEOTRACES home page (http://www.geotraces.org). Information about each section is posted at http://www.bodc.ac.uk/geotraces/cruises as it becomes available.

of GEOTRACES process studies can be found on the GEOTRACES website along with criteria for establishing a GEOTRACES process study.

Synthesis and Modeling

Synthesis and modeling are integral components of the GEOTRACES program. Numerical models offer a strategy to combine information about physical and biogeochemical processes, thereby allowing scientists to infer TEI fluxes (transport terms) from a comparison of simulated TEI fields with measured distributions. In addition, modeling can improve our basic understanding of TEI cycles through sensitivity studies for which selected processes are parameterized in different ways, or excluded altogether. The GEOTRACES observations will be invaluable in constraining existing models and in fostering the development of new dynamic TEI models.

GEOTRACES implemented a series of Data-Model Synergy Workshops in 2007 to facilitate cooperation between the observational and modeling communities while also integrating these activities with data management. The first workshop (Delmenhorst, Germany, September 2007) served largely to introduce each community to the tools, interests, and challenges facing the other. Subsequent workshops have focused on a specific theme selected by an organizing committee with input from the broader GEOTRACES community. For example, the second (Paris, France, December 2009) and third (Barcelona, Spain, November 2011) workshops examined the role of particles in the internal cycling of TEIs in the ocean.

Prior to the first workshop, observational geochemists held the view that modelers could help structure the program by offering guidance in selecting station spacing and perhaps even station location for cruise planning. The first workshop made it clear that we know so little about the cycling and distribution of many TEIs that modelers do not feel able to guide sampling. This freed the observational geochemists to design sampling according to their own intuition and knowledge.

Capacity Building

At the onset of planning for GEOTRACES, access to sampling systems capable of collecting seawater without contamination for trace metals such as lead, iron, and zinc was extremely limited. A carousel system designed by the team at the Moss Landing Marine Laboratory and used successfully during the Joint Global Ocean Flux Study (JGOFS) program in the 1990s (Hunter et al., 1996) demonstrated the technical feasibility of a contamination-free sampling system. Lessons learned during operation of the JGOFS system provided guidance for the design of the next-generation clean sampling system for the CLIVAR program (Measures et al., 2008). Motivated by the richness of features that are becoming apparent in high-resolution trace elements sections (Figure 6), a growing number of marine scientists have sought to develop or to acquire clean sampling systems. Some systems (e.g., those of the US and Canadian GEOTRACES programs) were developed by expanding on the design of the CLIVAR system. Others (e.g., those of

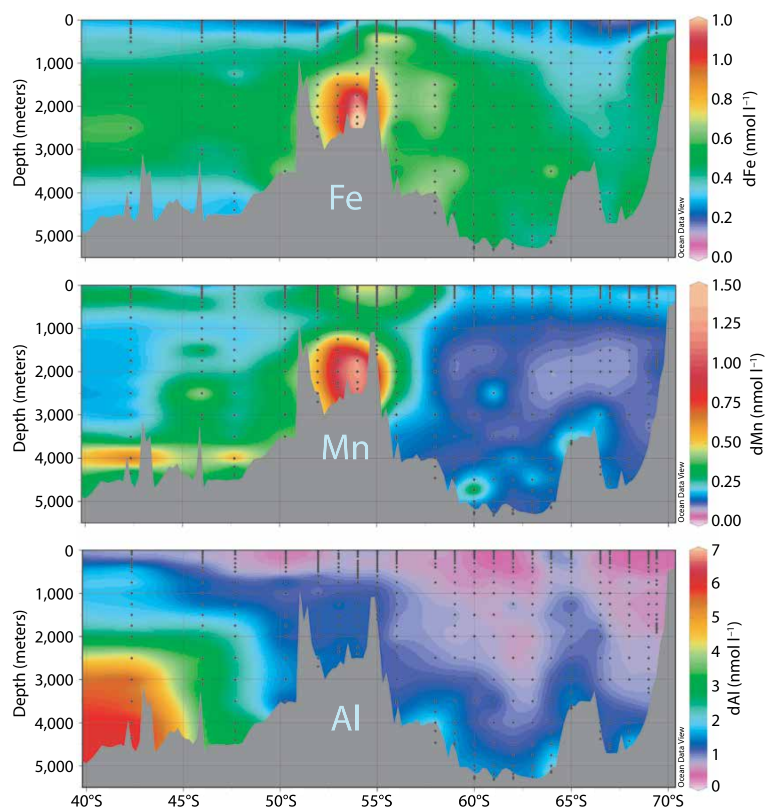

Figure 6. Sections of (A) dissolved iron (Klunder et al., 2011) (B) dissolved manganese (Middag et al., 2011b), and (C) dissolved aluminum (Middag et al., 2011a) along the prime meridian in the Atlantic sector of the Southern Ocean. Data from GEOTRACES International Polar Year cruise GIPY5, *Polarstern* ANT XXIV/3, February–April 2008. The unprecedented resolution of these sections provides a striking contrast to the data available prior to GEOTRACES (Figure 1). *Figure produced using Ocean Data View (R. Schlitzer, http://odv.awi.de, 2011)*

Japan and the Netherlands) evolved from quite different designs. In each case, tests for internal consistency with traditional methods have been made to assess the performance of each system before it is used routinely to sample for TEIs.

In addition to expanding the availability of clean sampling systems, implementation of the GEOTRACES program has required scientists to develop new analytical techniques to cope with the large number of samples collected and the requirement for multi-element and isotope analysis. This has resulted in significant technological advances through the development of in-house and commercial sample pre-concentration and isotope purification systems (e.g., Conway et al., 2013; Lagerström et al., 2013; Sohrin et al., 2008). Improvements in the sensitivity and precision of analytical instrumentation have also been of tremendous benefit to enabling high-resolution sampling along ocean sections.

It is a goal of GEOTRACES that scientists in every nation carrying out oceanographic research should have access to a trace metal-clean sampling system and to appropriate analytical facilities. GEOTRACES offers guidance in the design and construction of sampling systems as well as advice in operating these systems as shared facilities. Even the best analytical chemists find the protocols for trace metal sampling aboard "dirty" research vessels to be a challenge. Therefore, GEOTRACES offers training at sea, both in operating sampling systems and in collecting and handling samples by contamination-free procedures. At-sea training is currently supported by the Scientific Committee on Oceanic Research (SCOR), which enables one investigator each year from a developing nation to receive training aboard a GEOTRACES cruise. Meanwhile, GEOTRACES is searching for international support to establish sea-going training courses that can involve a larger number of investigators.

Program Philosophy and Management

Although GEOTRACES operates internationally under a single Science Plan, each nation contributes to GEOTRACES in accord with its own national priorities, resources, and scientific capabilities. An SSC coordinates implementation and management of the GEOTRACES program, with oversight from SCOR. An International Project Office (IPO), based at the Laboratoire d'Etudes en Géophysique et Océanographie Spatiales (LEGOS) in Toulouse, France, provides operational support. The IPO assists the SSC in implementing the GEOTRACES Science Plan and all related aspects of the program; organizing and staffing meetings of the SSC, working groups, and task teams; liaising with the sponsors and other relevant organizations; seeking and managing program finances; representing the project at international meetings; maintaining the project website; assisting the GDAC in securing information about upcoming cruises; interacting with GEOTRACES national committees and groups; and interacting with other international projects. The GEOTRACES website (http://www.geotraces.org) provides the principal vehicle for communicating information about the program. In addition to general information about the mission and thematic activities of GEOTRACES, the website offers cruise information, a calendar of meetings, information about the latest research findings, a reference list and library of GEOTRACES publications, outreach activities, and program news. Interested persons may subscribe to the GEOTRACES email list and electronic newsletter via the website.

GEOTRACES ocean sections are organized by national committees in collaboration with the SSC. This level of coordination is necessary to ensure that all of the key measurements are covered, to ensure that the objectives of the proposed sections are consistent with the Science Plan, and to avoid unnecessary redundancies or overlap between proposed sections. Regional or process studies, on the other hand, may be proposed by individuals or by groups who wish to contribute to GEOTRACES and thereby benefit from interaction with the global community working on the marine biogeochemical cycles of TEIs.

STATUS AND OUTLOOK

Following a decade of planning and enabling activities, the main phase of GEOTRACES is now underway. Scientists from more than 30 nations have participated in planning meetings and field programs. GEOTRACES cruises (IPY, Process Studies, Sections) have been carried out by 14 nations. More than 800 individual data sets have been produced and more than 220 papers are listed in the GEOTRACES database of peer reviewed publications (http://www.geotraces.org/library-88/scientific-publications/peer-reviewed-papers). At the time this document was prepared, the GEOTRACES data management team is preparing the first data product for public release, including a user-friendly interface that will encourage use of GEOTRACES data by a broad spectrum of the oceanographic community. New data visualization tools are also being prepared to support the use of GEOTRACES results in education and outreach. Many of the experiences and lessons learned in the planning and implementation of GEOTRACES are expected to be relevant to other ocean research programs, so this document was drafted with the intent to aid in the development of new programs as much as to report on GEOTRACES itself. Feedback is welcome and can be submitted via email to any of the authors or to the IPO at ipo@geotraces.org.

ACKNOWLEDGMENTS

Andy Bowie, Philip Boyd, Ed Boyle, Ken Bruland, Kristin Buck, Hein de Baar, Michael Ellwood, Flip Froelich, Maeve Lohan, Jim Moffett, Ben Twining, and Jing Zhang provided helpful input on early drafts of the manuscript. SCOR has supported the planning and implementation of GEOTRACES. Ed Urban, Executive Director of SCOR, has provided exceptional advice and assistance. Support for preparation of this document was provided by the US National Science Foundation (NSF) Chemical Oceanography Program through grants OCE-0938349 and OCE-1243377 to SCOR and OCE-0850963 to the US GEOTRACES Project Office. The GEOTRACES Data Assembly Centre is supported by the UK Natural Environment Research Council, the US NSF, and the Ministry of Earth Sciences, India. The GEOTRACES IPO has received support from the US NSF, Centre National de Recherche Scientifique, Observatoire Midi-Pyrenées, Universitat Autònoma de Barcelona, Kiel Excellence Cluster "The Future Ocean," Swedish Museum of Natural History, The University of Tokyo, University of British Columbia, The Royal Netherlands Institute for Sea Research, GEOMAR-Helmoltz Centre for Ocean Research Kiel, and the Alfred Wegener Institute.

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