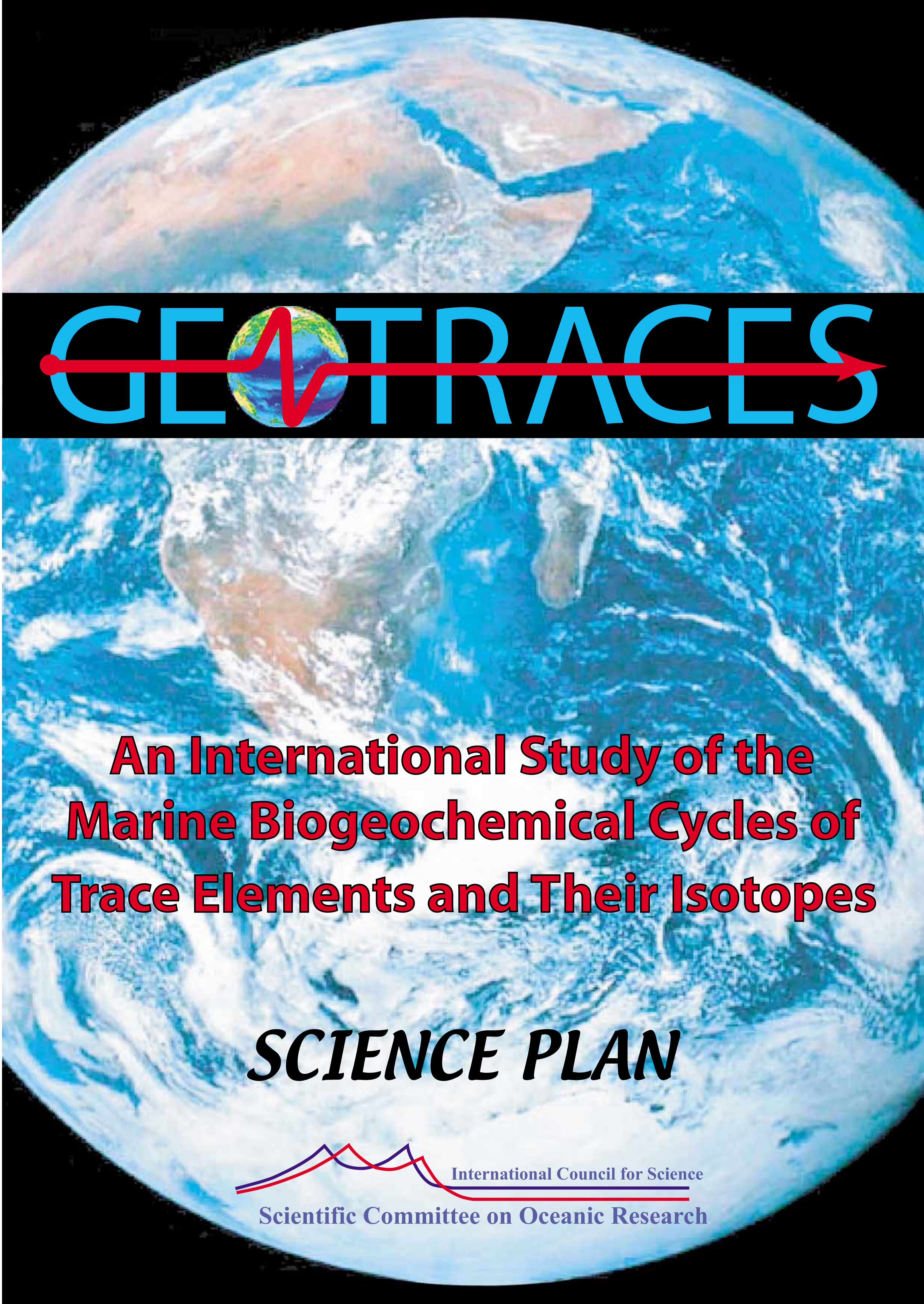
GEOTRACES Science Plan



GEOTRACES

An International Study of the Marine Biogeochemical Cycles of Trace Elements and Their Isotopes

SCIENCE PLAN

International Council for Science

Scientific Committee on Oceanic Research

GEOTRACES Report No. 1

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Preface and Acknowledgements

This Science Plan was prepared by the GEOTRACES Planning Group, whose members are identified in Appendix B of this document, using contributions from many scientists. Planning for a global study of the marine biogeochemical cycles of trace elements and their isotopes was formally launched with an international workshop held in Toulouse, France (April 2003), where the name GEOTRACES was adopted for the programme. Subsequently, regional planning workshops have been hosted by several nations. Input from those workshops has contributed to the preparation of this Plan.

After the workshop in Toulouse, the Scientific Committee on Oceanic Research (SCOR) accepted sponsorship of a Planning Group to further the development of the GEOTRACES programme. The Planning Group met at the University of Oxford, UK (June 2004) where the initial outline for this Plan was drafted. Work on the Plan continued throughout the remainder of 2004, and a draft was made available on the Web for public comment in February 2005. Community input was discussed by the Planning Group at a meeting in Vienna, Austria (May 2005) and used to guide further revision of the Plan, which was delivered to SCOR for review in July 2005. Nine anonymous reviewers provided substantive comments, and their input led to the final revision of this document.

Altogether, more than 300 individuals have participated in planning meetings and/or contributed written material for the planning process. Although it is not possible to thank each individually, their collective contributions are gratefully acknowledged.

Beyond offering financial support for planning meetings, SCOR has provided invaluable assistance in several areas related to the development of GEOTRACES. Members of the SCOR Executive Committee, represented by Robert Duce, contributed constructive comments on organisation and management of the programme as well as on its scientific objectives. Special thanks go to Ed Urban, who has helped with meeting logistics, multiple implementation issues such as data management and coordination with other programmes, as well as by providing comments on drafts of this document.

Many organisations and national funding agencies provided additional support for planning activities, including the US-NSF, CNRS (France), NERC (UK), NSERC (Canada), NSF-China, Université Paul Sabatier, and the Japan Ministry of Education, Culture, Sports, Science and Technology.

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An International Study of the Marine Biogeochemical Cycles of Trace Elements and their Isotopes

Contents

1 Executive summary

Trace elements and isotopes play important roles in the ocean as nutrients, as tracers of processes now and in the past, and as contaminants. Their biogeochemical cycling has direct implications for research in such diverse areas as the carbon cycle, climate change, ocean ecosystems and environmental contamination. This document lays out a plan for a coordinated global research programme, known as GEOTRACES, promising clear benefits to each of these areas by significantly advancing knowledge of the marine biogeochemical cycles of trace elements and their isotopes. The guiding mission of GEOTRACES is:

To identify processes and quantify fluxes that control the distributions of key trace elements and isotopes in the ocean, and to establish the sensitivity of these distributions to changing environmental conditions.

Trace elements serve important roles as regulators of ocean processes, including marine ecosystem dynamics and carbon cycling. Iron, for instance, is well known as an essential micronutrient, the scarcity of which often limits the rate of such vital processes as photosynthesis and nitrogen fixation. Several other trace elements also play crucial roles in cell physiology and in biochemical reactions, and their supply is therefore thought to control the structure and, possibly, the productivity of marine ecosystems. Understanding the biogeochemical cycling of these micronutrients requires knowledge of their diverse sources and sinks, as well as their transport and chemical form in the ocean.

Much of what is known about ocean conditions in the past, and therefore about the processes driving global climate change, is derived from trace element and isotope patterns recorded in marine deposits. Reading the geochemical information archived in marine sediments informs us about past changes in fundamental ocean conditions such as temperature, salinity, pH, carbon chemistry, ocean circulation and biological productivity. These records provide our principal source of information about the ocean's role in past climate change. Understanding this role offers unique insights into the future consequences of global change.

The cycles of many trace elements and isotopes have been significantly impacted by human activity. Some trace elements and isotopes are harmful to the natural and human environment owing to their toxicity and/or radioactivity. Understanding the processes that control the transport and fate of these contaminants is an important aspect of protecting the ocean environment. Such understanding requires accurate knowledge of the natural biogeochemical cycling of these elements so that changes due to human activity can be put into context.

Despite the recognised importance of trace elements and isotopes, our ability to exploit knowledge of their attributes is limited by uncertainties concerning their sources, sinks, internal cycling and chemical speciation within the ocean. For example, the marine biogeochemical cycles of micronutrients are known so poorly that their sensitivity to global change, and the impact of any resulting changes in elemental cycling on marine ecosystems and the ocean carbon cycle, cannot be predicted meaningfully. Similarly, sedimentary records reveal striking correlations between distributions of trace elements in sediments and independent indicators of climate variability; but our ability to use trace elements and their isotopes as reliable palaeoceanographic proxies is limited by incomplete characterisation of their current biogeochemistry. This, in turn, limits our ability to test ocean models against past conditions, and therefore limits our ability to forecast future changes.

Marine geochemists are poised to make significant progress in the biogeochemistry of trace elements. Advances in clean sampling protocols and analytical techniques provide unprecedented capability for measurement of a wide range of trace elements and isotopes. The potential afforded by these advances has not been realised, largely because of a lack of coordinated research in this area since GEOSECS (Geochemical Ocean Sections Study) in the 1970s. New analytical methods that allow high-density sampling, and new modelling strategies (as applied successfully during the WOCE—World Ocean Circulation Experiment and JGOFS—Joint Global Ocean Flux Study programmes) make this the right time to mount a major international research programme to study the global marine biogeochemical cycles of trace elements and their isotopes.

Three overriding goals support the GEOTRACES mission:

1. To determine global ocean distributions of selected trace elements and isotopes – including their concentration, chemical speciation and physical form – and to evaluate the sources, sinks, and internal cycling of these species to characterise more completely the physical, chemical and biological processes regulating their distributions.

2. To understand the processes involved in oceanic trace-element cycles sufficiently well that the response of these cycles to global change can be predicted, and their impact on the carbon cycle and climate understood.

3. To understand the processes that control the concentrations of geochemical species 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 modelling, organised under the following themes:

Theme 1: Fluxes and processes at ocean interfaces

- Atmospheric deposition
- Continental run-off
- The sediment-water boundary
- Ocean crust

Theme 2: Internal cycling

- Uptake and removal from surface waters
- Uptake and regeneration in the sub-surface ocean
- Regeneration at the seafloor
- Physical circulation

Theme 3: Development of proxies for past change

- Factors controlling 'direct' proxy distribution in the ocean
- Factors influencing the distribution of 'indirect' proxies in the ocean
- Palaeoceanographic tracers based on sediment flux

GEOTRACES will be global in scope, consisting of ocean sections complemented by regional process studies. Sections and process studies will combine fieldwork, laboratory experiments and modelling. Sections will be planned to cross regions of prominent sources and sinks (such as dust plumes, major river discharges, hydrothermal plumes and continental margins), to sample principal end-member water masses, and to enter the major biogeographic provinces. Modelling of distributions of measured trace elements will quantify fluxes associated with the principal sources and sinks, as well as those associated with internal cycling processes.

Capacity building will be an important element of GEOTRACES. Beyond achieving the scientific objectives identified above, a natural outcome of this work will be to build an international community of marine scientists who understand the processes regulating trace element cycles sufficiently well to exploit this knowledge reliably in future interdisciplinary studies.

Synthesis and modelling of GEOTRACES findings will produce a more accurate understanding of changing ocean conditions in the past, and it will improve our ability to incorporate trace element cycles into models to predict ocean responses to future global change. Synthesis and modelling activities will benefit from collaborating with contemporary programmes (see below) sharing several common goals.

Early tasks for GEOTRACES, in preparation for the main field activities, will include the creation of a data submission and management strategy, the development and distribution of standard reference materials, and the initiation of intercalibration exercises. These activities will be organised under the direction of an International Programme Office, overseen by the Scientific Committee on Oceanic Research (SCOR). GEOTRACES will collaborate closely with other ocean research initiatives, including CLIVAR, IMBER, SOLAS, LOICZ, IMAGES/PAGES, InterRidge, InterMARGINS, and various modelling programmes. This collaboration will ensure synergy among the different programmes to avoid unnecessary duplication of effort and to ensure that new knowledge of ocean biogeochemical cycles is used effectively across a broad sweep of future environmental science. As one of its first major field efforts, GEOTRACES will collaborate with other projects in both polar regions as part of the International Polar Year. All of these programmes and activities will benefit from new developments within the Global Ocean Observing System, including national and regional ocean observing initiatives (e.g., ORION).

2 Introduction and overview

2.1 Purpose of this document

This document presents a Science Plan for **GEOTRACES—an international study of the global marine biogeochemical cycles of trace elements and their isotopes (TEIs)**. It presents the rationale and motivation for such a study, together with background information about the current understanding of TEI cycles in the ocean and objectives for future research. It develops the framework of a programme to achieve these objectives, and a management scheme to oversee the programme's activities. This document identifies early priorities for the management team, such as establishing a data management plan and implementing other enabling activities (e.g., the preparation of standards and the execution of intercalibration exercises).

This Science Plan also makes recommendations for implementation of the GEOTRACES programme, but it does not provide a complete implementation plan. Separate implementation plans will be developed by regional and national groups that will link specific objectives of this Science Plan to the priorities of their respective ocean research communities, governments and funding agencies. It will be the responsibility of the GEOTRACES Scientific Steering Committee to ensure that a coherent global programme emerges from these individual efforts, and to further ensure that the broader objectives are met through international collaboration and synthesis of the global data set.

2.2 Rationale for a GEOTRACES programme

Trace elements and their isotopes play an important role in oceanography as participants in, and as tracers of, processes of fundamental interest.

Some trace elements (e.g., Fe, Co, Zn) serve as essential micronutrients, the availability of which influences the physiological state and biochemical activity of marine organisms (e.g., Morel *et al*., 2003; Morel and Price, 2003). This effect of TEIs on individual organisms, in turn, is thought to control the structure of ocean ecosystems and their biological productivity, both of which are key factors regulating the ocean carbon cycle and hence have effects throughout the Earth system, responding to and influencing global change. Other trace elements (e.g., Pb and perhaps Hg) are influenced by global-scale anthropogenic emissions. The large-scale distributions of these trace elements are, however, poorly known. This represents a major barrier to understanding their biogeochemical role in the Earth system.

Certain TEIs (e.g., Al, Mn, and the isotopic composition of Nd, Pb, Hf and Os) are diagnostic of specific mechanisms that supply the broader suite of TEIs to the ocean. Other TEIs (e.g., Cd, Ba, Zn, redox-sensitive oxyanions, natural radionuclides and radiogenic isotopes) are exploited to reconstruct environmental conditions in the past (e.g., ocean productivity, patterns and rates of ocean circulation, ecosystem structures, ocean anoxia) and hence inform the debate on past and future global change. In addition, the distributions of natural and artificial radionuclides can be modelled to derive rates of a diverse array of processes, including the flux of particulate material exported from surface waters, the scavenging and removal from the ocean of particle-reactive chemical species (including many contaminants), and rates of ocean transport on timescales not attainable by direct measurement.

Improved understanding of the biogeochemical cycles and large-scale distributions of TEIs will inform many areas of environmental research, from climate science to planning for future global change. This benefit can be further enhanced by collaboration between GEOTRACES and other new programmes such as SOLAS and IMBER.

2.3 Background

The Geochemical Ocean Sections Study (GEOSECS) of the 1970s provides a good illustration of the benefits to be derived from a global study of the chemical geography of the sea. GEOSECS produced the first view of the global oceanic distributions of many dissolved chemical species. This knowledge led to fundamental advances in understanding of ocean circulation and biogeochemical cycles, particularly demonstrating the way in which the large-scale distributions of TEIs such as ^{14}C, ^{210}Pb and ^{226}Ra could allow the rate of ocean processes to be determined (Broecker and Peng, 1982). New tracers have been developed more recently for a variety of ocean processes, including Th and Pa isotopes for scavenging processes (Cochran, 1992) and short-lived Ra isotopes for submarine groundwater discharges (Moore, 1996).

Recognition of the important role of many TEIs has been tied intimately to advances in sampling and analytical technology. The development and application of trace-element 'clean' techniques since the 1970s revealed, for the first time, 'oceanographically consistent' distributions of many trace elements (Figure 1). These findings provided ground-breaking insights into the cycling of trace elements within the ocean (e.g., Bruland and Lohan, 2003). For example, the nutrient-like profiles of many trace elements suggested that they are consumed biologically in surface waters and regenerated at depth along with decomposing biogenic material.

Subsequent advances in analytical technologies have enabled oceanographers to measure concentration

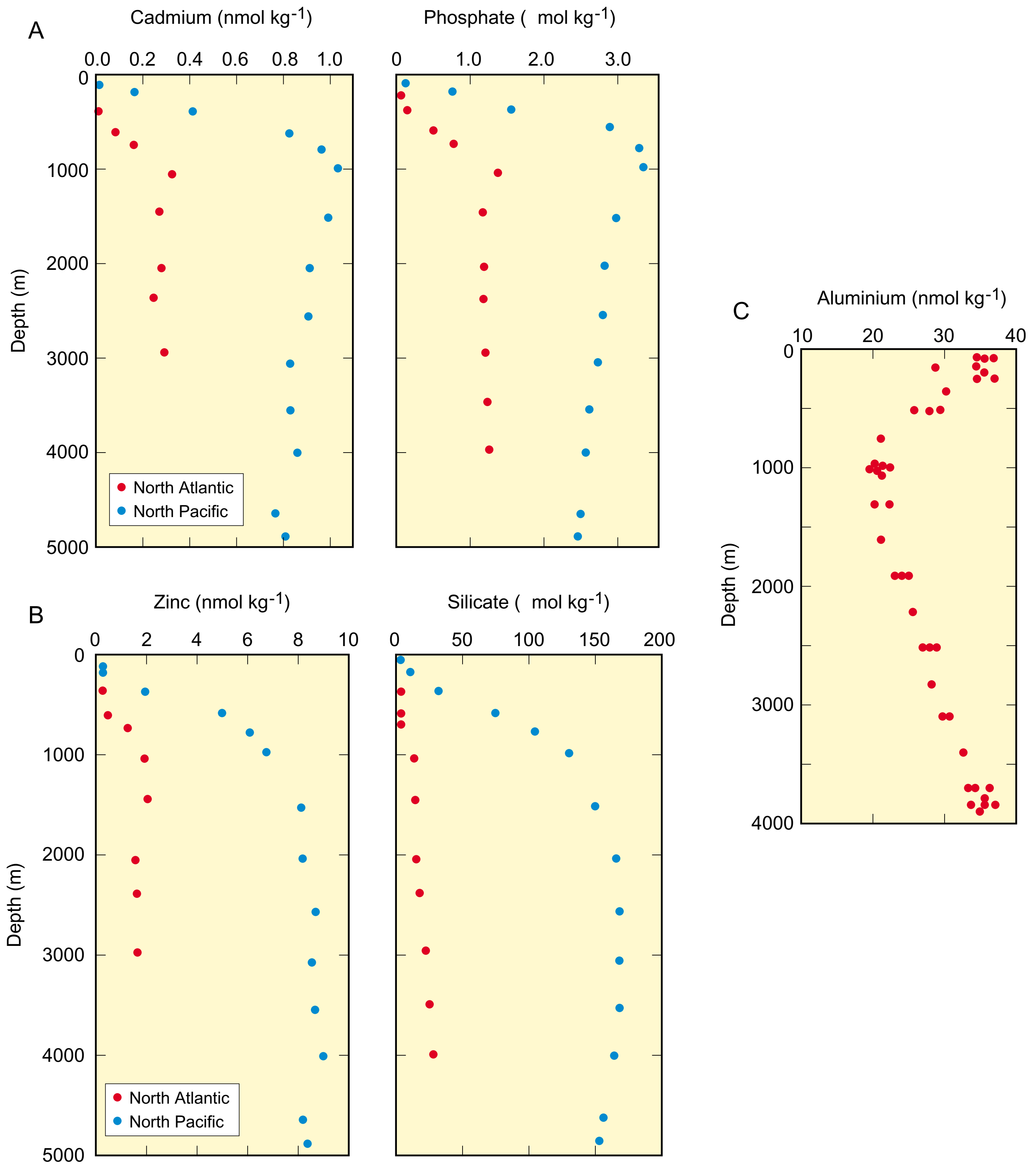

Figure 1. Certain trace elements, such as Cd (A) and Zn (B), have nutrient-like distributions, indicating biological uptake from surface waters and regeneration at depth, as well as accumulation in deep waters along the flow path from the Atlantic Ocean to the Pacific Ocean. Other trace elements, such as Al (C), have mid-depth concentration minima, reflecting sources at the surface and bottom as well as scavenging to particles throughout the water column. Figures reprinted from Chemical Oceanography, Vol. 8, K.W. Bruland, Trace Elements in Sea-water, pages 157–220, Copyright (1983), with permission from Elsevier.

profiles for most of the elements in the periodic table (Figure 2) as well as for many stable and radioactive isotopes. For example, multiple-collector plasma source mass spectrometers (MC-ICP-MS) are now allowing the systematic study of isotopic fractionation for most elements of the periodic table — a young and burgeoning research field. New technologies have also provided insight into the physical and chemical speciation of many trace elements, with the importance of organic complexes and colloids now well established for some

Vertical Profiles of Elements in the North Pacific Ocean

(compiled by Y. Nozaki, 2001)

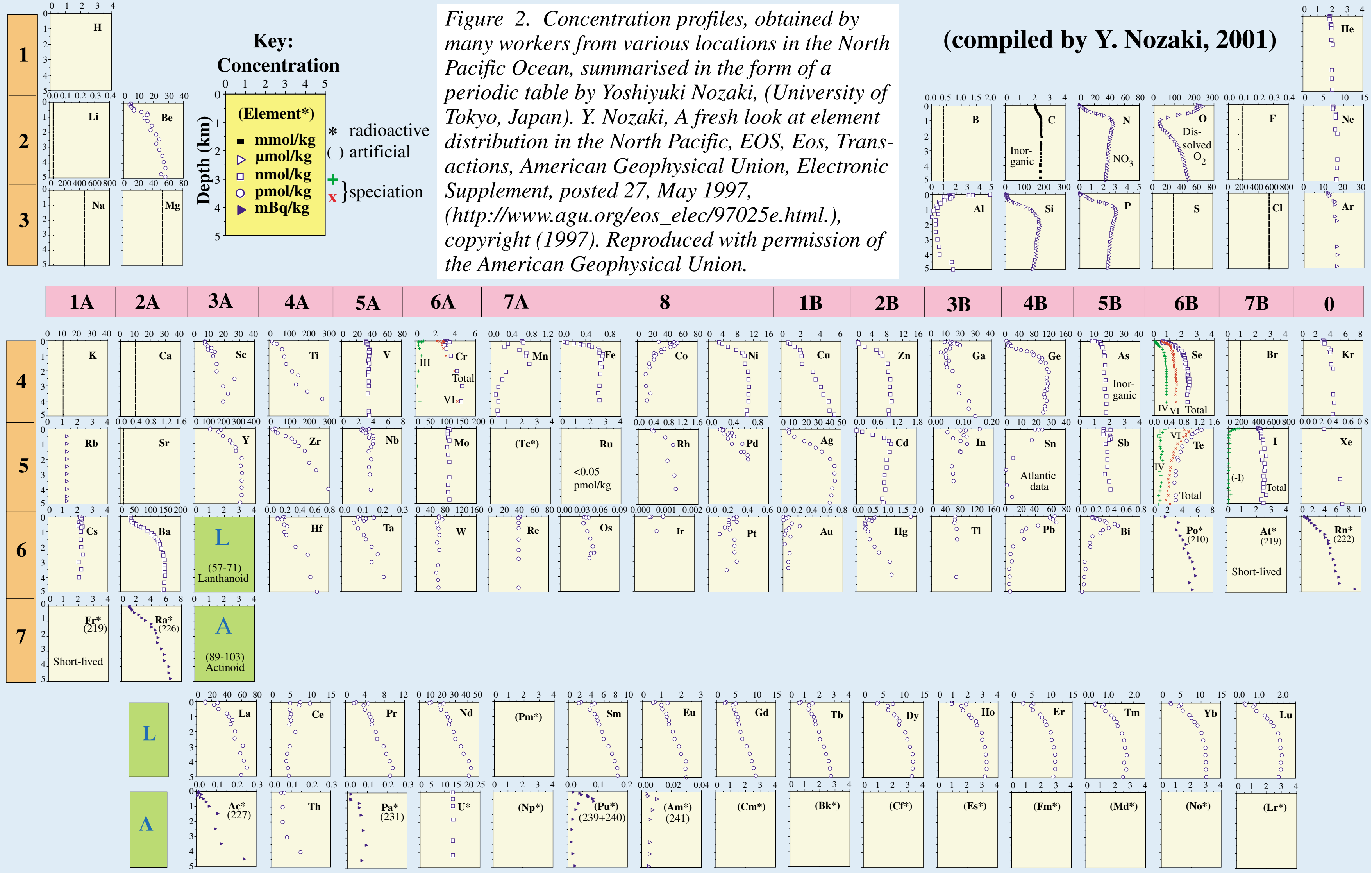

Figure 2. Concentration profiles, obtained by many workers from various locations in the North Pacific Ocean, summarised in the form of a periodic table by Yoshiyuki Nozaki, (University of Tokyo, Japan). Y. Nozaki, A fresh look at element distribution in the North Pacific, EOS, Eos, Transactions, American Geophysical Union, Electronic Supplement, posted 27, May 1997, (http://www.agu.org/eos_elec/97025e.html.), copyright (1997). Reproduced with permission of the American Geophysical Union.

Figure 3. An example of one of several new TEI-clean sampling devices. This rosette consists of 12 Teflon™-coated Go-Flo bottles mounted on a powder-coated rosette frame with 0.38-inch 4-conductor, polyurethane-coated Kevlar line. To prevent contamination from the frame and auxiliary components, bottles are tripped from the deck while the package is moving upwards through clean water at low winch speeds (ca. 10 m/min). The system has been used to collect 12 samples in the upper 1100 m in less than 60 minutes. Sample bottles are removed from the frame and sub-sampled in a laboratory van with HEPA-filtered air. Figure provided by Chris Measures.

elements (Bruland and Lohan, 2003). Improvements have continued in the ability to sample the ocean cleanly so that even the most low-level trace elements can now be sampled with appropriate trace metal-free sampling rosettes (Figure 3) and towed sampling devices.

Despite these technical advances, our understanding of the global biogeochemical cycle of many trace elements has not advanced as much as might be expected. For some, it has been sufficient to think of trace elements simply as 'conservative', 'nutrient-like', or 'scavenged', but there is a growing appreciation that more complex process-based descriptions are required. More significantly, we do not have a good knowledge of the spatial distribution of these elements and isotopes so that assessment of the processes involving lateral transport is frequently limited. Even elements that are known to play a key role in marine ecosystems (e.g., Fe) or are known toxic contaminants (e.g., Pb, As) have been measured only in a few regions (Figure 4). We know even less about the sources, sinks and internal cycling of these and other important TEIs (e.g., other micronutrients such as Zn, Co, Se, or tracers such as isotopes of Pa, Th, or Nd). And there is a similar lack of knowledge about the role that TEI speciation plays in modifying the behaviour of TEIs.

Improved sampling and analytical capabilities for TEIs led, in the 1980s, to an understanding of the role of trace elements as micronutrients regulating ecosystems and the carbon cycle in the ocean and providing a major driver of environmental change. The potential for Fe to serve as a limiting micronutrient in the ocean was recognised long ago, but its significance only began to be fully appreciated in the late 1980s (e.g., de Baar and de Jong, 2001; Bruland and Lohan, 2003 and references therein). It is now suspected that Fe supply may be a major control on ecosystem structure. Consequently, the role of the global Fe cycle within the whole Earth system is now being explored (Jickells *et al*., 2005). During the 1990s, the key role played by many other trace metals in a wide variety of ecosystem functions became increasingly clear (Morel *et al*., 2003; Morel and Price 2003; Table 1). The interaction and competition between these processes, as the availability of various trace metals changes, is only just beginning to be understood (Cullen *et al*., 1999). For example, what happens to individual species, and to ecosystems, when micronutrient A is at low levels, but micronutrient B is plentiful? And how does the ecosystem respond if the situation is reversed? A large amount of fundamental biological understanding will be gathered on this topic in the coming years. The relevance of this information to understanding the ocean will rely on a quantification of TEI distributions, sources, sinks, speciation and internal cycling.

In some cases, the effect of TEIs on organisms is inhibitory rather than nutritional. A good example of this effect is given by Mann *et al*. (2002) who show that the distribution of *Prochlorococcus*, the most abundant photosynthetic organism in the ocean, is affected by Cu toxicity; its abundance is inversely related to the cupric ion activity distribution in the upper water column. In contrast, a closely related organism, *Synechococcus*, is not affected by Cu toxicity and thrives in high-Cu waters that inhibit *Prochlorococcus*.

Parallel to the development of the use of TEI distributions to describe processes in the modern ocean has been the development of new proxies to improve our understanding of palaeoceanography through the study of the trace-element composition of sediment substrates including corals and microfossils (e.g., Henderson 2002). For instance, the Cd/Ca ratio in such records is used as an analogue of phosphate concentration in the past ocean, whereas the Mg/Ca ratio is interpreted as a proxy for palaeotemperatures.

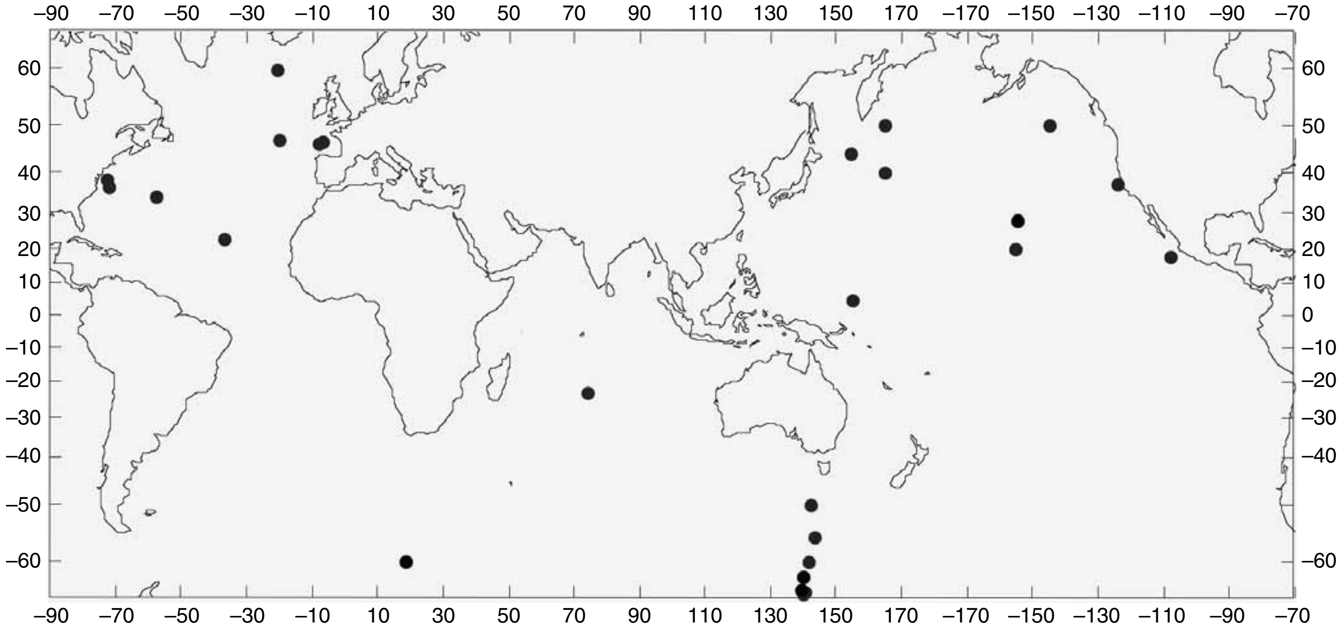

Figure 4. The total number of stations at which concentrations of iron in seawater have been reported for depths 2000 m or deeper, as of 2003. Redrafted from compilation of Payal Parekh, MIT. This figure illustrates the paucity of high-quality data about this key micronutrient in the deep ocean.

To a considerable extent, work on TEIs over the past decades has been performed in isolation and on single cruises so that assessing the relationships among various tracers, as well as the global distributions of many tracers, has been impossible. A more comprehensive understanding of the global biogeochemical cycles of these TEIs is necessary before they can be exploited fully and reliably as tracers of ocean processes; before the sensitivity of marine ecosystems to perturbations of their biogeochemical cycles can be evaluated; before the transport and fate of contaminant species can be assessed; and before their utility as proxies can be realised.

These advances in the 30 years since GEOSECS underpin much of our present understanding of ocean chemistry. An additional measure of the success and impact of GEOSECS is the foundation that it provided for the design and implementation of following programmes. For example, research on ocean circulation, initiated within GEOSECS, continued under programmes such as Transient Tracers in the Ocean (TTO) and the World Ocean Circulation Experiment (WOCE). Research on the carbon cycle, also an important component of GEOSECS, continued under the Joint Global Ocean Flux Study (JGOFS). These advances in geochemical understanding are now being incorporated into model simulations providing valuable and important constraints on ocean processes. By analogy, future studies exploring topics such as metal–biota interactions, their sensitivity to environmental change, and the implications for the carbon cycle and climate variability, can be expected to benefit from and build upon the findings of GEOTRACES.

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), and references therein.

Biogeochemical process	**Important trace elements**
Carbon fixation	Fe, Mn
CO_2 concentration/acquisition	Zn, Cd, Co
Silica uptake – large diatoms	Zn, Cd, Se
Calcifiers – coccolithophores	Co, Zn
N_2 fixation	Fe, Mo (?V)
Denitrification	Cu, Fe, Mo
Nitrification	Cu, Fe, Mo
Methane oxidation	Cu
Remineralisation pathways	Zn, Fe
Organic N utilisation	Fe, Cu, Ni
Organic P utilisation	Zn
Formation of volatile species	Fe, Cu, V
Synthesis of photopigments	Fe and others
Toxicity	Cu, As (?Cd, Pb)

2.4 Timeliness

With the definition of an increasing number of high-priority research questions, described in detail later in this document, the community of marine biogeochemists believes that the time is right to mount a major international research programme to study the global marine biogeochemical cycles of TEIs. Five additional factors favour a coordinated global study at this time:

(1) Advances in sampling techniques and analytical technology.

(2) Understanding of the importance of micronutrients in ocean biogeochemistry and global change, and the need to incorporate this understanding into the development of new proxies of past global environmental change.

(3) Advances in forward and inverse modelling techniques that will provide information not attainable previously.

(4) Implementation of contemporary ocean research programmes (see Section 11) that will provide complementary information of benefit to GEOTRACES, and/or that will utilise and benefit from GEOTRACES findings.

(5) The need to characterise the baseline distributions of TEIs before further perturbation by anthropogenic inputs.

Recent advances in clean sampling protocols and in analytical techniques are providing us with a capability for measuring a wide range of TEIs in the ocean with unprecedented precision and accuracy. Sample size requirements have decreased steadily in recent years as more sensitive analytical instrumentation has become available. With further understanding of the sources of contamination, it has become possible to design sampling methods that are compatible with the sensitivities of multiple analytical protocols. Many of these protocols allow relatively rapid analysis of chemical species that, coupled with the reduced sample sizes, now make it possible to sample at high spatial and temporal resolution. These analytical developments, coupled to improved understanding of the biological roles of trace elements (which will be pursued by IMBER and SOLAS), will allow major advances in global marine biogeochemistry.

An example of the power offered by these recent advances is provided by data collected during a North Atlantic CLIVAR cruise in 2003. Dissolved Fe and Al data, collected at 1 degree (60 nautical mile) spatial resolution in the upper 1000 metres of the water column (Figure 5), demonstrate substantial regional variations and structures, much of which would have been unresolved by only a few profiles. The density of these data is in marked contrast to the entire data set for the deep ocean (Figure 4).

There is agreement that a single element cannot be studied effectively in isolation. Rather, an element can be understood best as a special case in a continuum of behaviours where the similarities and contrasts between the elements enhance the understanding of each individual element. This argument is particularly relevant to Fe, which lacks natural radioisotopes, whose bomb radioisotope has long since decayed away, and whose stable isotope behaviour is only beginning to be explored. Instead, we may look to the better-constrained behaviour of other elements to illuminate the poorly constrained behaviour of iron. The use of Al as a tracer of Fe inputs, even in water where Fe has subsequently been removed (Figure 5), is a powerful demonstration of the need to measure suites of TEIs on the same water samples. Similar reasoning can be applied throughout the suite of TEIs to be studied. Thus, there is great merit in a coordinated multi-element programme where the conclusions that can be drawn far exceed the results from single-element programmes.

Recent advances in modelling capability also make GEOTRACES a timely programme. Improved numerics and parameterisations of sub-grid scale mixing processes now allow for a more realistic description of advective versus diffusive pathways of tracer transport. New adiabatic correction schemes help to reduce systematic circulation errors (Eden and Oschlies, 2006) and emerging oceanic reanalysis and operational oceanography products will further improve our ability to model tracer transport in the ocean realistically. In addition, data assimilation techniques and inverse modelling now allow promising direct data-utilisation methods for the determination of TEI fluxes as well as source and sink terms. This approach has been used successfully during the past decade in analysing results from WOCE, JGOFS and related programmes to derive both vertical and lateral fluxes of carbon and nutrients, as well as regeneration rates of particulate biogenic material (Ganachaud and Wunsch, 2002; Schlitzer, 2002). Inverse models promise to be an important component of ongoing and future studies of ocean circulation, such as those being conducted under the CLIVAR programme. Expanding those activities through assimilation of information about TEI distributions offers a strategy to quantify source and sink terms in the marine biogeochemical cycles of trace elements and their isotopes, as well as rates of internal cycling.

GEOTRACES will contribute to several new and ongoing large-scale ocean research projects. It will, for instance, interact closely with SOLAS in investigating the supply of trace metals to the surface ocean from above and below. It will provide vital information about large-scale distributions and micronutrient supply to programmes studying metal-biota interactions and the consequences for marine ecosystems, such as IMBER. GEOTRACES will make use of increased understanding of ocean circulation and changing conditions from the CLIVAR project and collaborate wherever possible with developing activities within the Global Ocean Observation System (GOOS).

Finally, GEOTRACES provides an opportunity to establish baseline distributions of TEIs before further perturbation of their natural cycles by human activities. The best-documented perturbation involves Pb, for which significant quantities have been mobilised for more than a century by industry and by combustion of leaded fuels in motor vehicles. Rising concentrations of Pb in open-ocean surface waters have been reconstructed by measuring the Pb

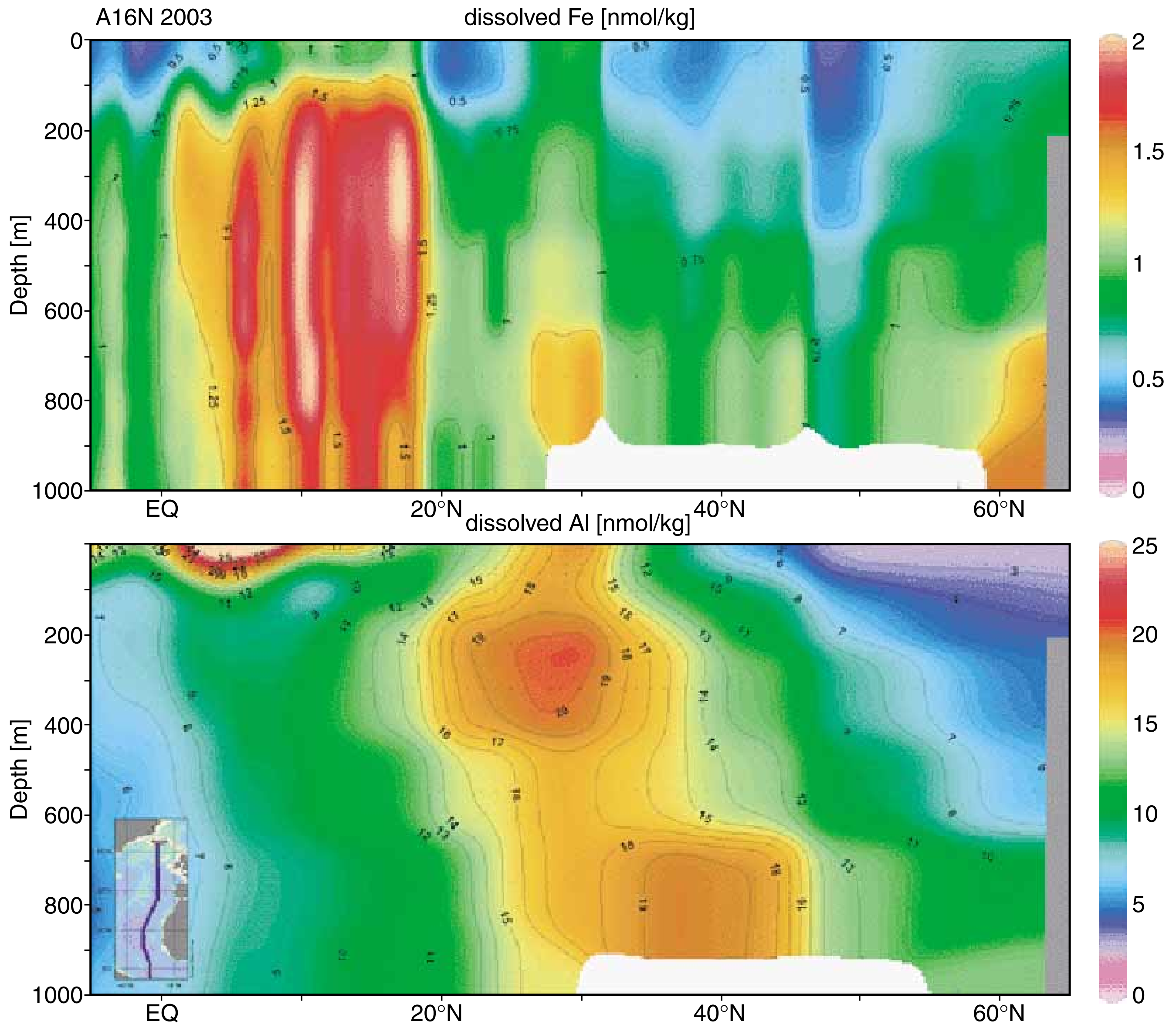

Figure 5. Distributions of dissolved Fe (upper panel) and Al (lower panel) in the upper 1000 m along the CLIVAR A16 cruise track 19 May –11 August 2003 (see inset for location). Al concentrations increase in surface waters under the Saharan dust plume (0–20° N), indicating the addition of TEIs from dissolution of dust. Fe is not particularly enriched in the surface waters here, but is significantly enriched deeper in the water column below this region. This could be explained by the rapid biological use of Fe in the surface waters, followed by settling and regeneration of organic material to return the Fe to intermediate depths. Courtesy of Chris Measures (University of Hawaii) and Bill Landing (Florida State University). Figure used with permission from the International Geosphere-Biosphere Programme (IGBP) and Oceanography. Versions of the figure appeared in Anderson and Henderson (2005) and the IGBP Newsletter #60.

content of corals (Shen and Boyle, 1987; Figure 6). Declining Pb concentrations since the 1970s reflect decreased emissions from industry and, significantly, the removal of Pb from motor vehicle fuels. Evolution through time of the principal sources of anthropogenic Pb is easily traced by changes in the stable isotopic composition of Pb in surface ocean water (Figure 6). Although anthropogenic Pb is delivered to the ocean primarily through atmospheric deposition, its presence can now be detected to great depths in the North Atlantic Ocean (Figure 7) owing to its downward transport by newly formed North Atlantic Deep Water. Timescales for deep-water renewal in other basins are much greater than in the North Atlantic Ocean, so Pb (and other TEI) concentrations in the deep waters of other basins are much less perturbed by anthropogenic sources. This situation will change over time. Other TEIs (e.g., Hg, Cd, Zn) mobilised by human activities have increased fluxes into the ocean through the atmosphere and through freshwater inputs (e.g., Nriagu, 1989). These inputs have presumably followed a similar pathway of introduction to the ocean, but their histories are less well documented than for Pb; a global survey of TEI distributions will provide a

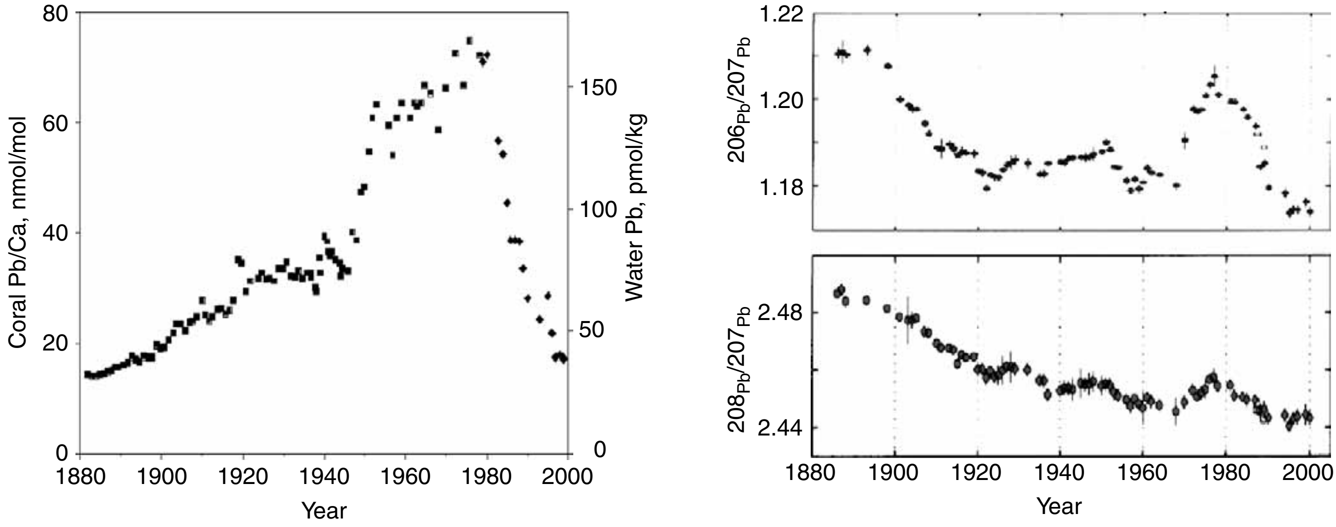

Figure 6. Left: variability of lead (Pb) in surface waters near Bermuda derived from coral measurements (1880–1980) and seawater measurements (1980–2000). Rising Pb from 1880–1980 is due to Pb emissions from smelting, coal combustion and other high-temperature processes during the U.S. industrial revolution (1880–1925) and automobile emissions from use of leaded petroleum. Fine particles from these sources are transported for long distances by the atmosphere and are deposited in the ocean. Decreasing Pb after 1980 results from the elimination of tetraethyl lead gasoline and more stringent emission controls on industrial processes. Surface-ocean Pb is maintained in a steady-state (2 year) balance of the input from the atmosphere and removal onto sinking biogenic particles. Data from 'Centennial-scale elemental and isotopic variability in the tropical and subtropical North Atlantic Ocean' (2002), Ph.D. thesis, Matthew K. Reuer, MIT/WHOI Joint Program in Oceanography.

Right: variability of $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ in surface waters near Bermuda. Pb isotope ratios vary within the Earth owing to generation of these isotopes from U and Th by radioactive decay. Pb isotope ratios vary in the surface ocean owing to changing emission sources. For example, in 1970, the U.S. Pb mining industry shifted from less radiogenic Pb sources in Idaho to more radiogenic sources in Missouri. The decrease since 1980 is due to the increasing dominance of less radiogenic Pb sources from Europe as more radiogenic U.S. emissions decrease. Figure modified from Chemical Geology, Vol. 200, Reuer, M.K., E.A. Boyle, and B.C. Grant, Lead isotope analysis of marine carbonates and seawater by multiple collector ICP-MS, pp. 137–153, copyright 2003, with permission from Elsevier.

baseline for evaluating future changes. Modelling of the changes in Pb distribution has provided valuable constraints on a range of ocean processes (Henderson and Maier-Reimer, 2002).

2.5 GEOTRACES objectives

A global study of the marine biogeochemical cycles of trace elements and isotopes will involve activities of a diverse nature. Nevertheless, these activities will uniformly support three overriding goals:

1. To determine global ocean distributions of selected trace elements and isotopes – including their concentration, chemical speciation and physical form – and to evaluate the sources, sinks, and internal cycling of these species to characterise more completely the physical, chemical and biological processes regulating their distributions.

2. To understand the processes involved in oceanic trace-element cycles sufficiently well that the response of these cycles to global change can be predicted, and their impact on the carbon cycle and climate understood.

3. To understand the processes that control the concentrations of geochemical species 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 modelling, organised under the following themes:

Theme 1: Fluxes and processes at ocean interfaces
- Atmospheric deposition
- Continental run-off
- The sediment-water boundary
- Ocean crust

Theme 2: Internal cycling
- Uptake and removal from surface waters
- Uptake and regeneration in the sub-surface ocean
- Regeneration at the seafloor
- Physical circulation

Theme 3: Development of proxies for past change
- Factors controlling 'direct' proxy distribution in the ocean
- Factors influencing the distribution of 'indirect' proxies in the ocean
- Palaeoceanographic tracers based on sediment flux

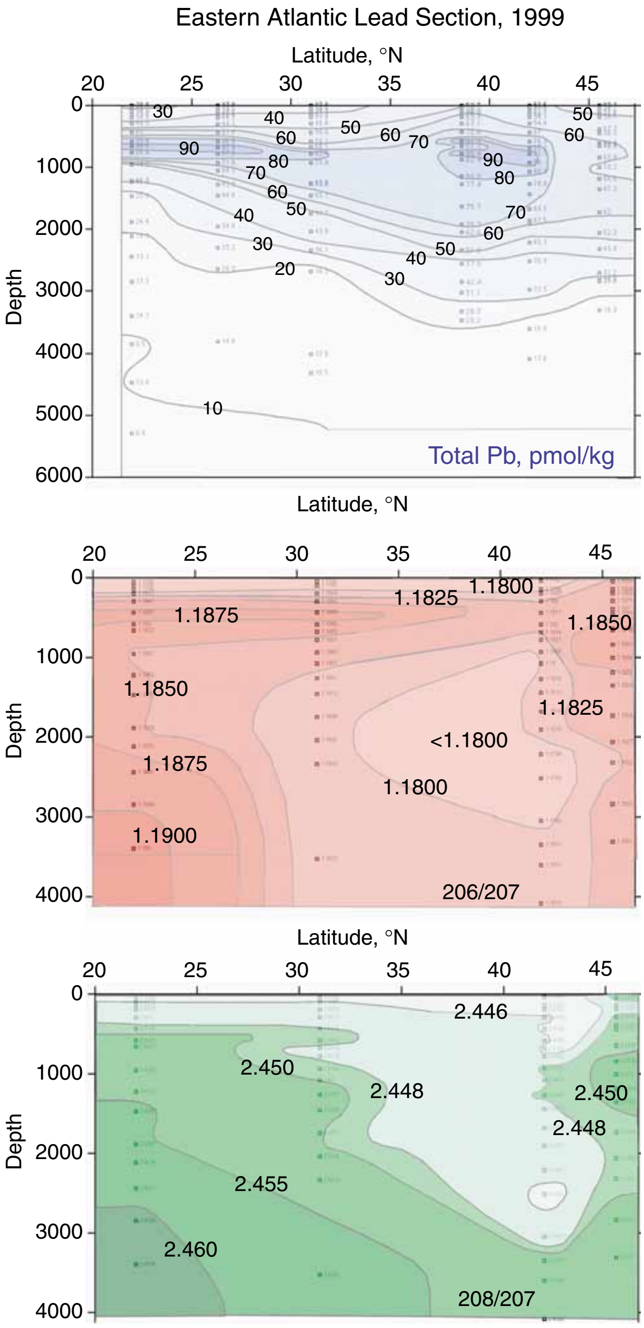

Figure 7. Sections of Pb (top) and Pb-isotope ratios in the water column of the eastern Atlantic Ocean in 1999. The spatial variability of subsurface Pb and Pb-isotope patterns reflects the advection and mixing of surface waters into the deep sea. Water 500–900 m deep in the southern portion of this section sank from the surface decades previously and hence had higher Pb concentrations and a more radiogenic Pb isotope ratio, consistent with surface-water Pb isotope ratios at that time (Figure 6). Deeper waters have less Pb because they are dominated by waters that left the surface many decades ago. For example, at about 3000 m at the southern end of the section, the Pb isotope composition reflects Pb that was at the surface in the 1920s (see Figure 6). Data from 'Centennial-scale elemental and isotopic variability in the tropical and subtropical North Atlantic Ocean' (2002), Ph.D. thesis, Matthew K. Reuer, MIT/WHOI Joint Program in Oceanography.

These research themes are developed in detail in Sections 3, 4 and 5 where, for each theme, specific objectives are identified and guidelines for implementation of research activities are provided. Subsequent sections describe modelling activities that will be an inherent component of each research theme; enabling activities that will provide a foundation for field programmes conducted in support of the research themes; and a management structure to coordinate the various activities and ensure a timely synthesis of GEOTRACES findings.

GEOTRACES will create a unique opportunity for exploration and discovery by determining the distributions of novel TEIs that have received little attention to date, and for accelerated investigation of these TEIs by comparing their distributions to those of better-known species. The primary objective of the GEOTRACES programme is to examine the sources, sinks and internal cycling of particular TEIs that (a) are believed to influence marine ecosystems and, hence, biogeochemical cycles of carbon and related substances, or (b) offer unique insight into past and present ocean conditions, and into the sensitivity of these conditions to perturbation by global change.

2.6 *Anticipated benefits*

Developing a comprehensive understanding of the marine biogeochemical cycles of TEIs, and of the processes and conditions that regulate these cycles, will bring many benefits to be shared across a spectrum of ocean disciplines. This section indicates some of the particular areas where such benefits will be found. These can be considered as deliverables of the programme.

2.6.1 *The role of micronutrients in ocean ecosystems*

The oceanic cycles of the major nutrients (PO_4, NO_3, Si) have been widely studied and are now reasonably well known, although the behaviour of organic forms of N and P (which are associated with DOC-complexed TEIs) are much less well understood. Recognition of the importance of micronutrients is more recent, however, and understanding of the role of such micronutrients is still quite rudimentary. It is now reasonably well established that the supply of Fe limits total productivity in the high-nutrient, low-chlorophyll (HNLC) regions of the surface ocean (e.g., Coale *et al*., 1996). Iron has also been implicated in a range of other ecosystem processes (see Table 1). From laboratory and limited ocean-surface studies, other trace metals are also thought to play a key role in controlling biogeochemical processes in the ocean, particularly Cu, Zn, Co, Cd and Mn (Morel *et al*., 2003; Morel and Price, 2003; Table 1). Cycling of these micronutrients is a key aspect of the whole ocean system, controlling not only the amount of ocean productivity, but also its type, and the functions that it performs. In so doing, micronutrient supply governs key pathways in the chemical cycles of major elements, including N and C. The cycling of micronutrients is therefore fundamental to the behaviour of life and of carbon in the ocean.

Despite this significance, understanding of the cycles of these micronutrients is incomplete. Analytical developments and key discoveries in recent years have advanced our knowledge, but we still lack a good understanding of the distribution of these elements and of the processes that control these distributions.

A good example is provided by present attempts to model the Fe cycle. Motivated by recognition of the importance of Fe as a limiting nutrient, several workers have added Fe to ocean models (Archer and Johnson, 2000; Moore *et al*., 2002; Bopp *et al*., 2003; Parekh *et al*., 2005). Such models have to make broad assumptions about the behaviour of Fe in seawater because of poor knowledge of its distribution and of the ligands that play a fundamental role in its seawater behaviour. These models are producing tantalising maps of the ocean, suggesting regions that are Fe-limited for various taxa (Figure 8). Accurate knowledge of the chemical processes controlling micronutrient distributions would allow such models to be tested and refined, and would allow similar models to be constructed for other important micronutrients. These models could then be used both to improve the interpretation of palaeoceanographic records of the ocean's response to past climate change, and to improve prediction of the ocean's response to global change in the future.

2.6.2 Transport and fate of contaminants

The oceanic cycle of many TEIs has been significantly impacted by human activity (as described above for the case of Pb). Some of these TEIs are harmful to the natural and human environment due to their toxicity and/or radioactivity. Understanding the processes that control the transport and fate of such TEIs is an important aspect of protecting the ocean environment and human health.

Public awareness of the contamination of the ocean was particularly high in 1995 during the controversy about disposal of the Brent Spar oil rig. It was proposed to dispose of the rig after the end of its useful life off the coast of Scotland by sinking it in deep water. Brent Spar was known to contain substantial quantities of Cd, Pb, As, Zn, Hg and low-level radioactive waste. Campaigners against dumping of the rig argued that such metals would be toxic to marine ecosystems, whereas representatives from the oil company to which the rig belonged claimed they would not be. Similar debate is ongoing about the effect of acid mine drainage on marine systems. Such arguments are based on a very limited understanding of typical concentration levels of these TEIs in ocean waters, and of the processes involved in cycling these metals. Full understanding of the biogeochemical cycles of these contaminant TEIs will directly inform such debates about the relative safety of disposal of waste at sea.

For some TEIs, disposal at sea has already occurred, either directly (e.g., dumping of radioactive waste in the North Atlantic Ocean) or indirectly (e.g., release of Pb during industrial processes; Figures 6 and 7). In these cases, assessment of the transport and removal of the TEIs is crucial to understanding their possible eventual incorporation into the human food chain. Mercury provides a good example of an element that has been significantly impacted by anthropogenic emissions and that may represent a significant threat to human food supply by bioaccumulation in fish (Lamborg *et al*., 2002). As noted earlier, several other trace-element cycles have been significantly perturbed by human activity, though the impact of these perturbations on the water column distribution is uncertain. Although many contaminants are found in surface waters, deep waters currently represent a reasonably pristine environment, except in the North Atlantic Ocean (see above). This situation is unlikely to continue for long. Quite apart from deliberate dumping of waste in the deep ocean, natural processes such as advection and particle settling are transporting contaminants from the surface ocean and continental shelves into the deep ocean. For such deep-ocean settings, GEOTRACES will provide a baseline against which future change can be assessed.

This Science Plan does not specifically call for a study of contaminated marine environments. Rather, the emphasis is on understanding fundamental processes regulating the marine biogeochemical cycles of TEIs. An accurate understanding of these fundamental processes is inherent in any effort to predict the transport and fate of contaminants in the ocean, so achieving GEOTRACES objectives offers clear benefits to research on contaminants.

2.6.3 Tracers of present and past ocean conditions

The ocean is a prime driver of the climate system through its capacity to store and transport large amounts of heat and carbon. To understand Earth's climate system therefore requires knowledge of the dynamics of ocean circulation, and of the ocean carbon cycle. In many cases, assessing these processes in the modern ocean can be done by measuring them directly: by measurement of the water movement, for instance, or by direct measurement of dissolved inorganic carbon. Many processes in the modern ocean system cannot, however, be investigated by such direct measurements. For such processes, TEI tracers can provide important constraints. Understanding of the ocean chemistry of these TEI tracers will improve our ability to use these tracers to probe the present ocean system.

For instance, some aspects of ocean mixing are difficult to measure by direct means, such as the long-term rate of

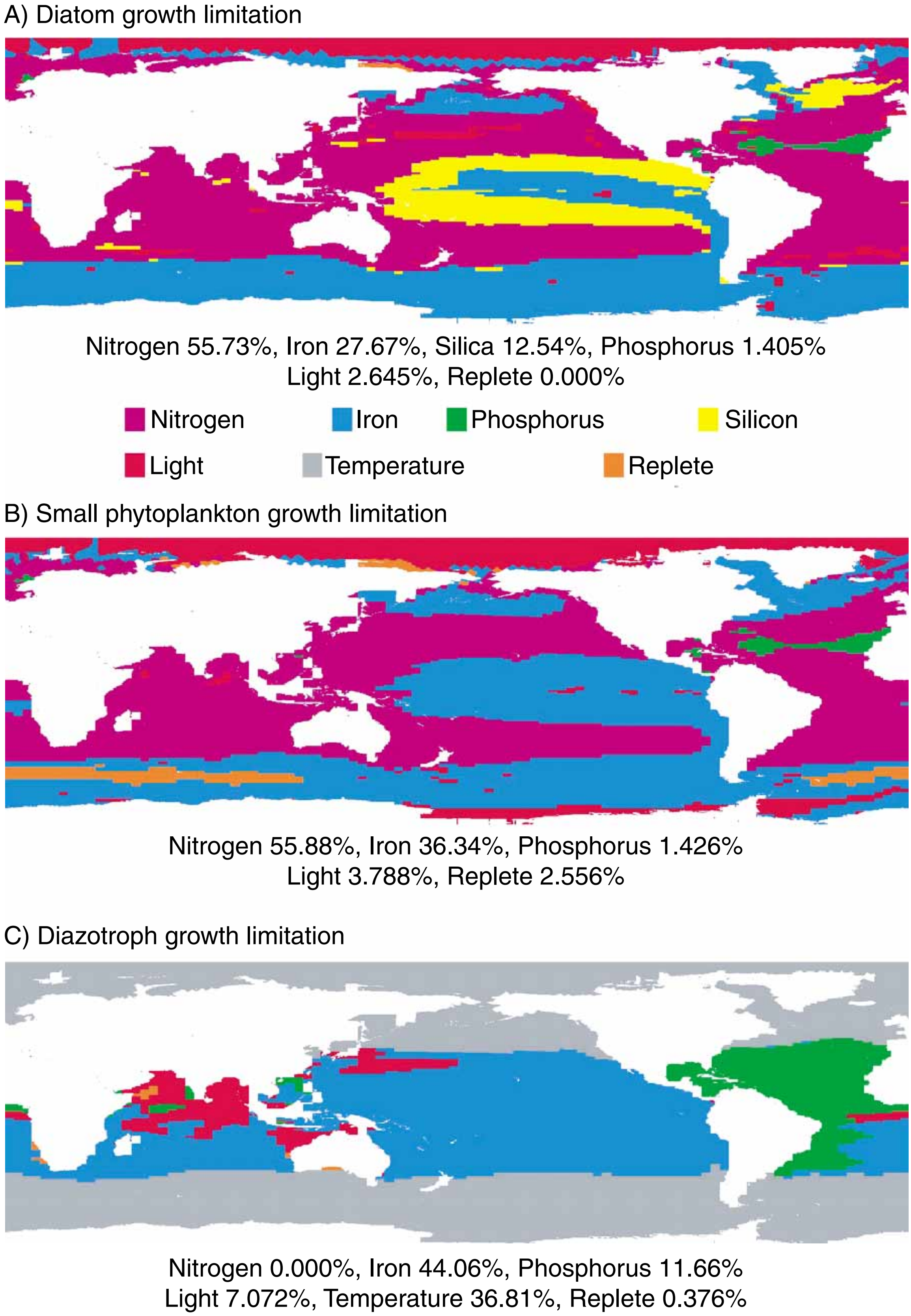

Figure 8. Summer season growth-limitation patterns for diatoms (A), small phytoplankton (B) and diazotrophs (C). The nitrogen-fixing diazotrophs are capable of obtaining nitrogen from dissolved N_2 gas. Their growth is restricted by low sea-surface temperatures at high latitudes. Also shown is the percentage of total ocean area for each growth-limiting factor. Moore, J.K., Doney, S.C., and Lindsay, K., Upper ocean ecosystem dynamics and iron cycling in a global three-dimensional model, Global Biogeochemical Cycles, Vol. 18, GB4028, doi:10.1029/2004GB002220, Copyright (2004) American Geophysical Union. Reproduced by permission of the American Geophysical Union.

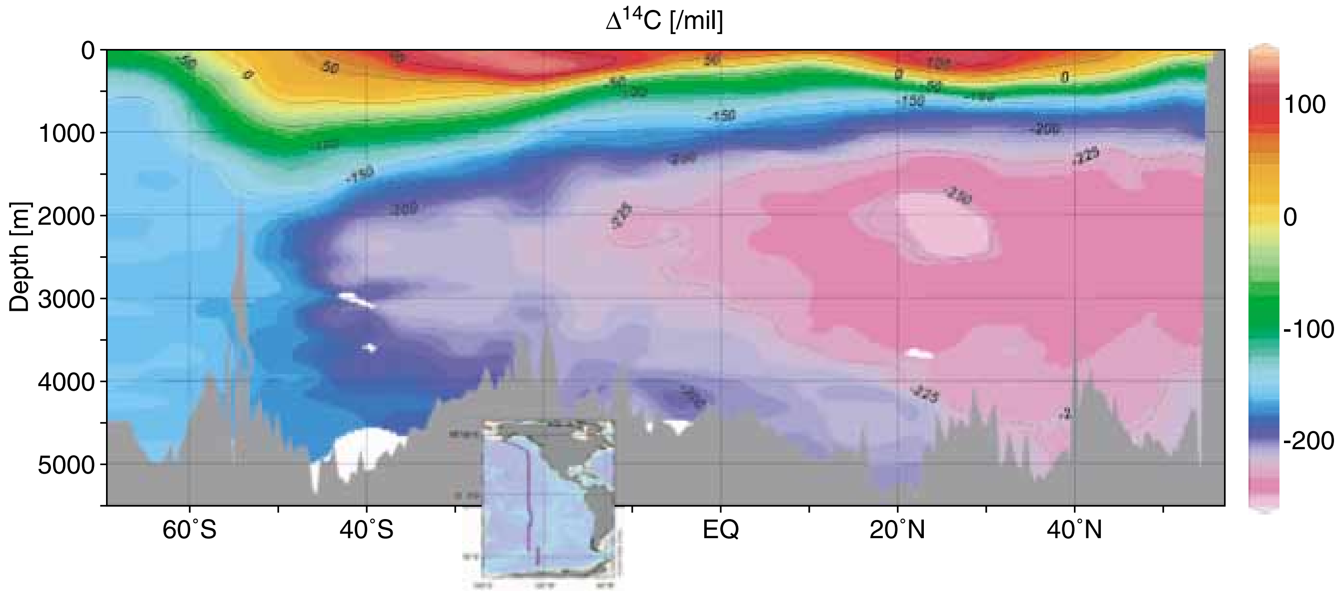

Figure 9. A meridional section of radiocarbon ($\Delta^{14}C$ in permil) through the central Pacific Ocean taken from the GLODAP data set described in Key et al. (2004).

deep-water flow. Measurements of radiocarbon, particularly during the recent WOCE programme, have provided a wealth of information about this flow that could not have been achieved by direct measurement (Figure 9). Such results are used to compare the performance of global ocean circulation models in a way that cannot be accomplished by other observations (England and Maier-Reimer, 2001). Other processes are similarly difficult to measure directly, including long-term mixing rates of deep waters, or shelf-to-open ocean mixing rates. Coupling modern ocean models with observations of natural radionuclides will allow such questions to be addressed, but will rely on a good understanding of the ocean chemistry of these nuclides.

Similarly, important fluxes within the ocean carbon cycle, such as the downward flux of organic carbon, or the dissolution of this carbon in deep waters, are difficult to assess by direct means. Again, there are TEI tracers (e.g., ^{234}Th) that can be exploited to evaluate the rates of such processes, and better understanding of the biogeochemical cycles of these TEIs will improve their use and allow them to be applied more robustly to assess the carbon cycle in its present rapidly evolving state (Benitez-Nelson and Anderson, 2006). For the ocean of the past it is impossible to make direct measurements and we are wholly dependent on tracers to reconstruct past conditions (e.g., Henderson, 2002). Such reconstruction is crucial, however, to assess the processes involved in Earth's climate system, and the possible amplitude of future climate changes. The instrumental record of climate variability is too short to adequately test models used to predict the future, particularly for the most extreme abrupt events which are not sampled within instrumental time series. Accurate understanding of the climate system and prediction of future climate therefore depends on the use of chemical tracers of the past ocean environment.

A wide variety of geochemical tracers have been proposed and, to varying degrees, calibrated against environmental gradients in the modern ocean. These proxies potentially allow reconstruction of past changes of a wide variety of ocean variables, from sea-surface temperature (e.g., using Mg/Ca ratios) to nutrient utilisation ($\delta^{15}N$), and from seawater pH (boron isotopes) to ocean circulation ($^{231}Pa/^{230}Th$ and Nd isotopes). Understanding of many of these proxies is far from complete, however, as is sometimes demonstrated by disagreement between two proxies thought to respond to the same process. An example is provided by the use of $^{231}Pa/^{230}Th$ and ε_{Nd} in the Atlantic Ocean during the last glacial period (Figure 10). Both of these isotope proxies are thought to contain information about the past rates of southward deep-water flow within the Atlantic Ocean, but $^{231}Pa/^{230}Th$ suggests strong flow at the last glacial maximum (McManus *et al.*, 2004) whereas ε_{Nd} suggests much reduced flow at that time (Piotrowski *et al.*, 2004; Figure 10). Both proxies are responding to real environmental change but our understanding of these proxies is insufficient to reconcile them. Such reconciliation can be achieved only through new measurements and modelling to understand the fundamental processes controlling TEI proxies for past change (Figure 11). Calibrating such geochemical proxies, understanding their strengths and weaknesses, and establishing new proxies, represents a primary objective of GEOTRACES and will be a significant benefit to wider study of the climate system.

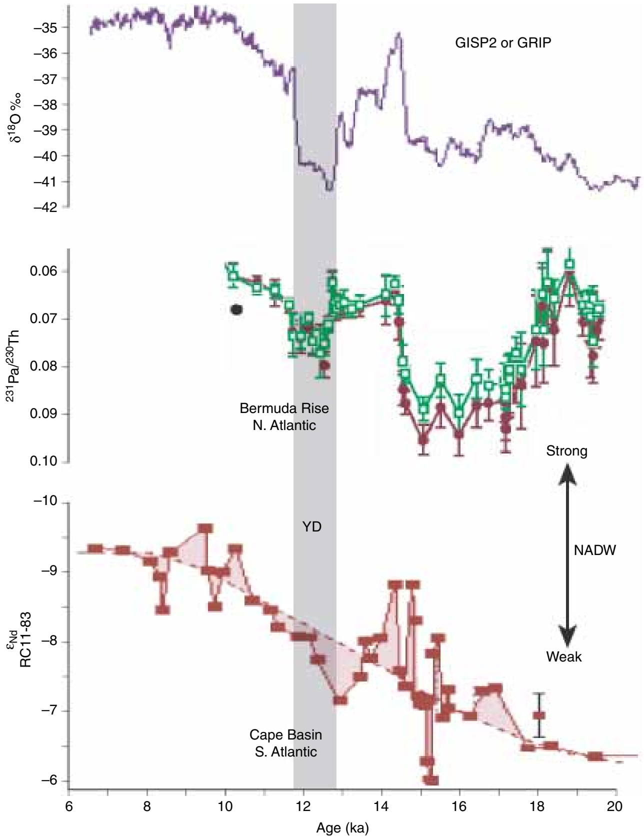

Figure 10. A comparison of two ocean tracers, both thought to provide information about the rate of past flow of North Atlantic Deep Water (McManus et al., 2004; Piotrowski et al., 2004). Although both tracers agree that flow was strong during the Holocene and weak during the Younger Dryas, $^{231}Pa/^{230}Th$ (middle) suggests a high rate of flow at around 19 kyr whereas ε_{Nd} (bottom) suggest a minimum flow rate. This illustrates the need to better understand proxies for past environmental change. The upper panel shows a proxy record for air temperature over Greenland based on the stable isotope composition of the ice (higher $\delta^{18}O$ values correspond to warmer temperatures) for reference. McManus et al. (2004) figure adapted by permission from MacMillan Publishers Ltd: Nature, Copyright (2004). Piotrowski et al. (2004) figure adapted by permission from Earth and Planetary Science Letters, Vol. 225, Piotrowski, A.M., Goldstein, S.L., Hemming, S.R. and Fairbanks, Intensification and variability of ocean thermohaline circulation through the last deglaciation, pages 205–220. Copyright (2004), with permission from Elsevier.

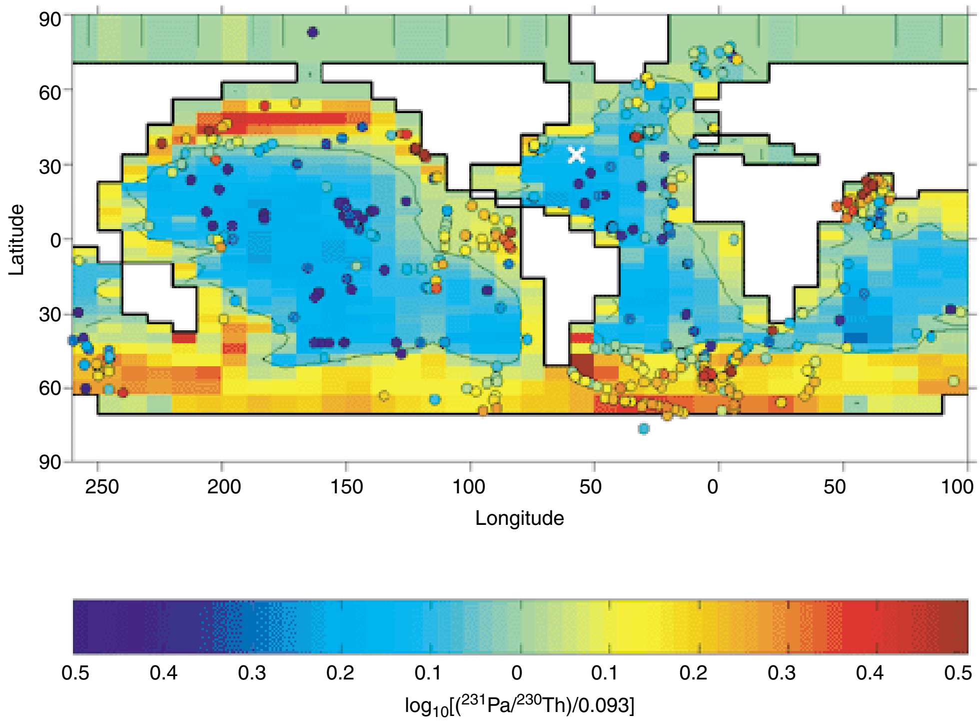

Figure 11. Observation of sediment surface $^{231}Pa/^{230}Th$ (coloured circles; blue represents negative values; i.e., low $^{231}Pa/^{230}Th$ ratios) compared with a model reconstruction of this ratio (background colours) in sediment leaving the ocean. This ratio encodes information about both past ocean circulation rates and past productivity, two important variables in the climate system. By better understanding the ocean behaviour of these nuclides, GEOTRACES will enable these tracers to be used reliably for assessment of past conditions. Reprinted from Earth and Planetary Science Letters, Vol. 237, Siddall, M., G.M. Henderson, N.R. Edwards, M. Frank, S.A. Müller, T.F. Stocker and F. Joos, $^{231}Pa/^{230}Th$ fractionation by ocean transport, biogenic particle flux and particle type, pages 135–155. Copyright (2005), with permission from Elsevier.

3. Theme 1: Fluxes and processes at ocean interfaces

Seawater chemistry reflects the sources and sinks of material to and from the ocean. These sources and sinks result from exchange of material between the solid Earth and the ocean: a process that occurs through four pathways (Figure 12; see also Bruland and Lohan, 2003). In the first pathway, material derived from the continents is transported, in particulate or gaseous form, through the atmosphere to be deposited on the sea surface. Second, continental crust is eroded by chemical and physical processes and transported, in dissolved or particulate form, to the ocean margins by flow in rivers and groundwaters. Third, marine sediments act as a chemical reactor to release and adsorb chemical species to and from seawater. Finally, exchange with the Earth's crust and mantle occurs primarily through interaction with mid-ocean ridge basalts, both at high and low temperature.

The fluxes of TEIs occurring at each of these ocean interfaces are generally not well known. This lack of knowledge represents a fundamental problem for any of the diverse disciplines that require assessment of regional or global biogeochemical budgets. Improved understanding of the fluxes at each of these four ocean interfaces therefore represents a central theme of the GEOTRACES programme.

Although many of these fluxes can be measured directly, and such measurement programmes are now being implemented in parallel research initiatives (LOICZ, SOLAS, IMBER, etc.), the large spatial and temporal variability of the processes involved renders global integration and budget calculations difficult. GEOTRACES intends to follow a complementary approach, which will take advantage of the fact that the magnitude and pattern of TEI fluxes at ocean interfaces is reflected in the distribution of TEIs within the ocean. Improved knowledge of ocean distributions of TEIs, particularly in regions where such boundary fluxes are of special importance (e.g., dust plumes, estuaries, ocean margins, mid-ocean ridges) will therefore provide direct information about these fluxes.

Knowledge of TEI distributions will also lead to understanding of the processes involved in exchange between the solid Earth, the atmosphere, and the ocean. Mineral dissolution, mineral surface adsorption/ desorption, biological utilisation, element speciation, and a wide range of similar biological and chemical processes ultimately control the fluxes of elements to and from the ocean, and therefore the distribution of TEIs. An important goal of GEOTRACES is to develop sufficient understanding of each of these processes so that changes in TEI cycles in response to future global change can be predicted accurately.

Understanding TEI fluxes and the processes that control these fluxes will rely on an integrated approach that puts new chemical measurements into a rigorous physical and biological framework at each of the ocean interfaces and within the ocean itself. Integration of multiple TEI measurements will also provide important information. Aluminium and Mn, for instance, provide tracers of Fe

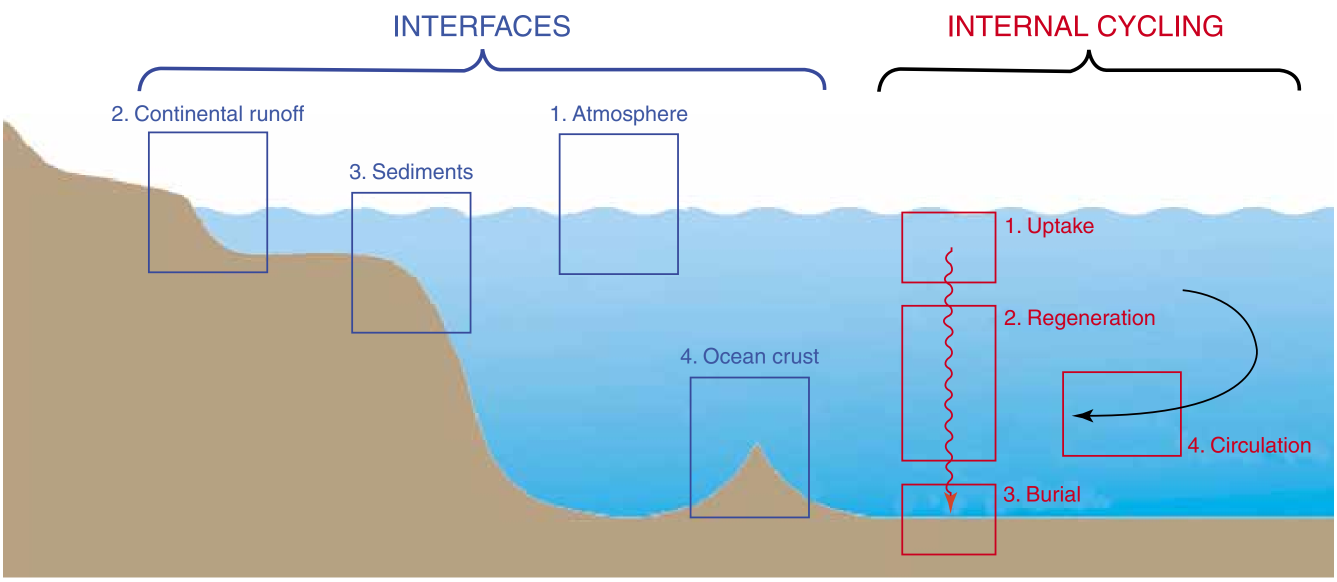

Figure 12. A schematic diagram illustrating the major influences on the distribution of TEIs in the ocean. Four major ocean interfaces (blue) and four major internal processes (red) are responsible for ocean TEI patterns. Within GEOTRACES, interface processes form the basis of Theme 1, while internal cycling processes are the basis of Theme 2.

input that survive in the water column even after Fe has been removed by biological processes. Similarly, isotope systems frequently provide information about the source of TEIs, or about the rates of processes involved in their exchange with particles and sediments. Measurement of a suite of TEIs therefore provides information about interface fluxes and processes that cannot be derived from study of single elements.

Present understanding of TEI fluxes and processes are outlined for each of the four interfaces in the following sections. These sections also detail areas where there is potential for significant advance in our understanding, and provide specific objectives that will be addressed by the GEOTRACES programme.

3.1 Atmospheric deposition

3.1.1 Present understanding

Atmospheric deposition is an important, but poorly quantified, mode of transport of low-solubility TEIs from the continents to the surface waters of the ocean. For the highly insoluble micronutrient Fe, and possibly for others such as Zn and Co, this may be the critical pathway for maintaining biologically necessary concentrations of these elements in surface waters of the open ocean. In fact, it has been proposed that in several large oceanic regions, limited atmospheric deposition of Fe to the surface waters is the principal cause for their HNLC status. It is thought that the lack of available dissolved Fe, an essential micronutrient for phytoplankton growth, prevents complete uptake of surface-water macronutrients in these regions and acts to limit, or co-limit, primary productivity (Martin *et al.*, 1990). Iron supply may also regulate nitrogen fixation in some areas (Falkowski, 1997). Additionally, atmospheric transport is an important vector for transferring anthropogenic materials from the continents to the open ocean (Duce *et al.*, 1991).

Satellite images of optical depth (Figure 13) provide clear synoptic views of the main continental sources of aeolian material to the ocean. While the principal sources of this material are well established as the great desert regions (e.g., Sahara and Asian deserts), large gradients in suspended material occur within the atmosphere in both

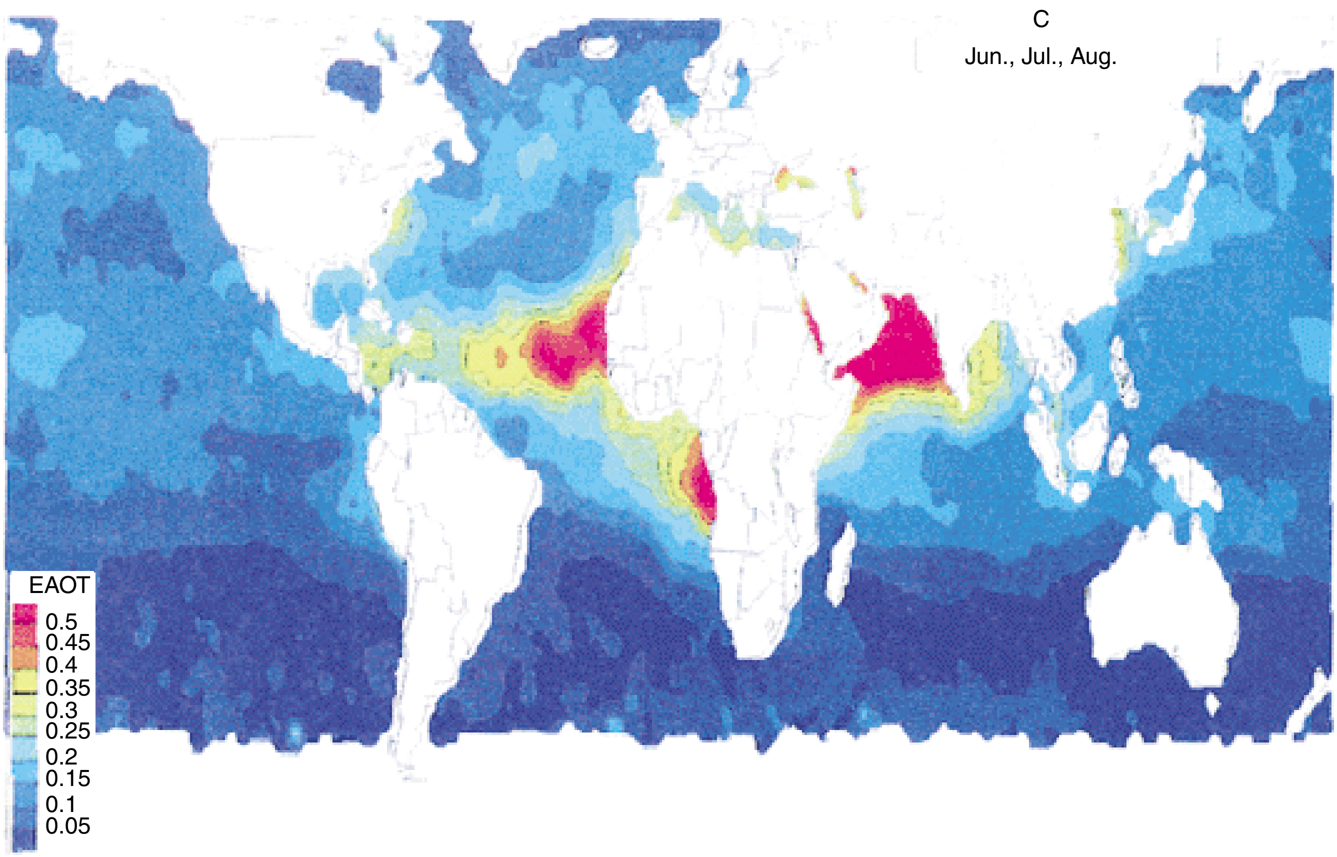

Figure 13. Radiatively equivalent aerosol optical thickness (EAOT X 1000) over the ocean, as derived from the NOAA AVHRR satellites. This figure incorporates the June–August period and therefore misses the Asian outbreaks that occur predominantly in boreal spring. Husar, R.B., Prospero, J.M., and Stowe, L.L. 'Characterization of tropospheric aerosols over the oceans with the NOAA advanced very high resolution radiometer optical thickness operational product'. Journal of Geophysical Research, vol. 102, No. D14, pages 16,889–16,909. Copyright (1997) American Geophysical Union. Reproduced with permission of the American Geophysical Union.

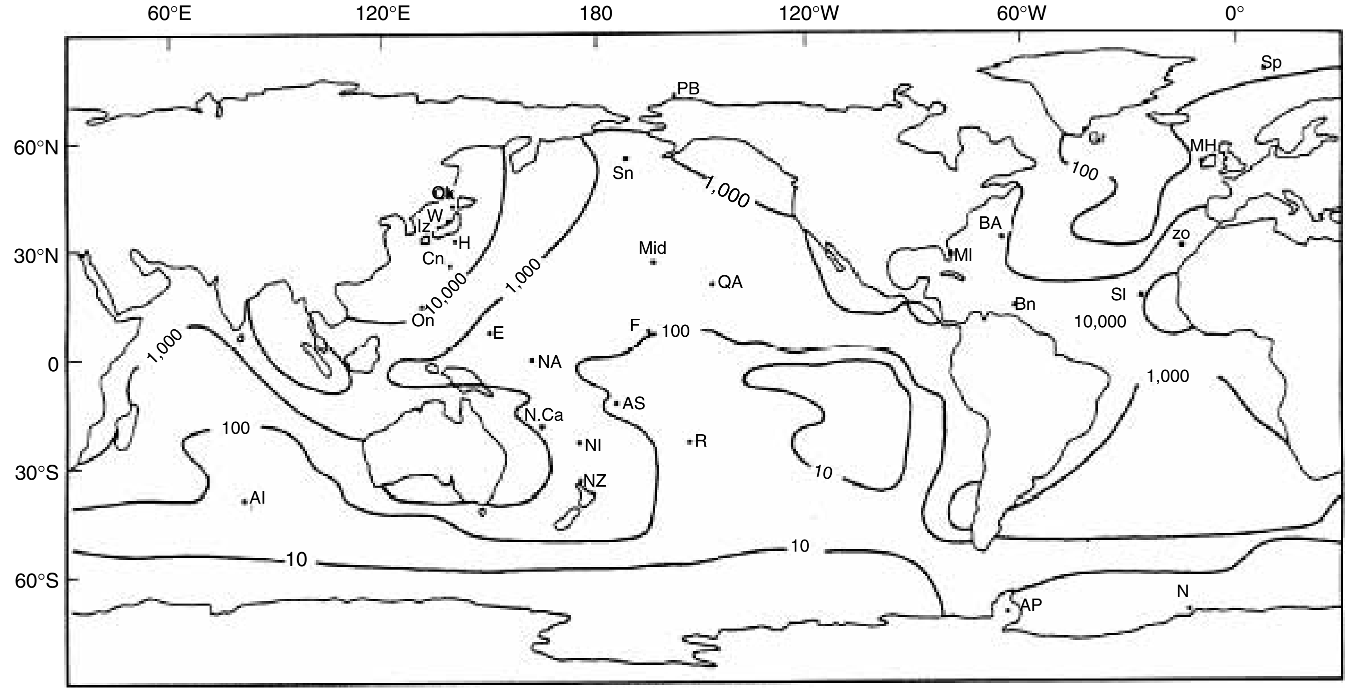

Figure 14. There is a popular misconception that atmospheric inputs to the ocean are well constrained. This misconception is based largely on the frequently cited 'Duce Map' of mineral aerosol fluxes. The figure above from Jickells and Spokes (2001) shows the contours of the Duce Map (Duce et al., 1991), together with the sampling stations on which it is based. Although other information, such as atmospheric transport models, was also used to construct the Duce Map, the scarcity of actual mineral aerosol-flux measurements used in this key study is striking. This figure powerfully illustrates that the flux of material from the atmosphere to the sea surface is actually rather poorly known. Figure reproduced from "Atmospheric iron inputs to the oceans", Jickells, T.D. and L.J. Spokes in The Biogeochemistry of Iron in Seawater. D.R. Turner and K.A. Hunter (editors), Copyright 2001. Copyright John Wiley & Sons Limited. Reproduced with permission.

space and time. Thus, the deposition of wind-transported materials to the surface ocean is highly sporadic geographically and temporally, and source strengths and deposition rates are very uncertain.

In addition to mineral matter, aerosols are added to the atmosphere by sea-spray production and by *in situ* gas-to-particle conversion, for example through condensation of volatile elements (e.g., Pb, Se) for which wet deposition is the primary means for delivery to the sea. Natural radioactive materials produced from interactions between cosmic radiation and atmospheric gases (e.g., ^{7}Be, ^{32}P, ^{33}P and ^{36}Cl) or from the decay of gaseous precursors emanating from the continents (e.g., ^{222}Rn to ^{210}Pb) are also incorporated into aerosols that are delivered to the ocean primarily in wet deposition. Aerosols are also produced by biomass burning and anthropogenic activities that involve high-temperature combustion processes such as coal and oil in energy production, and in the production of industrial raw materials such as cement manufacture and metal smelting. Aerosols produced by different mechanisms have characteristic size distributions that, in turn, regulate their deposition processes, and they have different spatial patterns of deposition reflecting their emission and atmospheric transport pathways.

Currently, only a few geochemical tracers in the surface ocean, such as Fe, Al, ^{210}Pb and stable Pb isotopes, have been systematically investigated and linked to atmospheric deposition (Jickells *et al*., 2005).

3.1.2 Areas for advance

A first-order requirement for assessment of the role that atmospheric deposition plays in global geochemical cycles is to constrain the magnitude and spatial distribution of the atmospheric flux. Because, except in a limited number of places, it is impractical to obtain direct determinations of atmospheric deposition, these estimates have necessarily come from mathematical models of dust source, transport and deposition derived from easily observed parameters. Satellite images document large sources – such as input from deserts – and provide information about suspended loads and variability of load within the atmosphere. Atmospheric sampling at land-based stations has allowed the development of global deposition maps for soil dust and other components. However, the availability of only a few island sampling sites means that these maps are actually based on very sparse deposition data (Figure 14). While satellite sensors that determine optical transparency allow estimation of atmospheric suspended load, it is currently very difficult to transform these values into mineral deposition rates. Estimates of desert dust deposition are thought to be uncertain to a factor of 10.

Models that determine the extent of Fe limitation in the global ocean (for example, Figure 8) are critically dependent on atmospheric flux estimates, as well as estimates of the fraction of dust that actually dissolves in the upper water column. More data are needed for both of these parameters. In the open ocean, models based on reasonable estimates of these parameters have simulated surface water distribution of Fe that are in remarkably good agreement with measured values. In marginal seas, however, this is frequently not the case, especially on seasonal timescales. More data are needed in marginal seas where air mass trajectories are complex and other Fe sources are important.

Improve methods for quantifying dust deposition

Ice core and sedimentary records indicate that large changes have occurred in atmospheric dust loads on glacial to interglacial timescales. The geochemical imprint of changes in deposition to the surface ocean and its propagation through the oceanic interior provides an important palaeoceanographic tool to study changes in palaeo-biogeochemical cycles.

The temporal and spatial variation of dust deposition to the surface ocean needs to be understood on physical scales that encompass major hydrographic provinces and temporal scales that range from seasonal to thousands of years. Predictions of past and future changes in atmospheric TEI supply will require the development of atmospheric transport and deposition models capable of adequately representing these processes.

Characterise processes regulating release of TEIs from aerosols

The underlying processes that regulate the release of TEIs from mineral and other aerosol phases must be understood if meaningful modelling of the impacts of aerosol deposition on surface water biogeochemical cycles is to be undertaken. The biological availability of TEIs is dependent on both the chemical speciation (e.g., redox state and inorganic/organic complexation), as well as their physical (e.g., dissolved, colloidal or particulate) form.

In addition to the problems of quantifying the magnitude of mineral deposition to the ocean, little is known about the effective addition of individual TEIs from mineral dust to the surface waters or their biogeochemical reactivity. Studies have reported that even for the major components of mineral aerosol, such as Al and Fe, the fractional solubility may vary by two orders of magnitude. Consequently, the atmospheric supply of TEIs to the surface ocean may depend as much on the factors that promote the solubility of mineral aerosol as the magnitude of its delivery, and these can change during atmospheric transport and cycling.

Determine the fraction of micronutrient supply to the surface derived from mineral aerosol deposition

In combination with modelling and empirical studies detailed in other sections of this plan, the relative importance of the atmosphere, freshwater inputs, margins and hydrothermal vents in providing TEIs to surface waters needs to be elucidated. The importance of atmospheric deposition processes in global geochemical cycles can only be assessed by quantitative comparison with other major inputs of TEIs to surface waters.

3.1.3 Specific GEOTRACES objectives

1. Develop and refine chemical tracers in the surface ocean for quantification of atmospheric deposition (e.g., Ti, Al, ^{232}Th, plus isotopes of Nd, Pb and Be). The geochemical behaviour of any TEI is the result of a variety of competing processes of addition, removal and transformation, so the power of any tracer is limited by the knowledge and extent of these interactions. To fully develop the systematics and timescales of atmospheric deposition a variety of tracers with differing sensitivity, sources and oceanic residence times will be required (e.g., Al, Ti, Ga).

2. Use measurements of such tracers in surface waters and in the lower atmosphere (in collaboration with SOLAS) to provide global-scale ground-truthing of aerosol deposition models across the major ocean basins and through the major deposition gradients in those basins.

3. Establish the range of fractional solubility of key atmospheric components and the processes that underlie that variability. This range in solubility is a master variable in the delivery of dissolved materials to the surface ocean.

4. Provide a coarse-scale global database quantifying the addition of micronutrients and bioactive elements to the surface ocean (e.g., Fe, P, Co, Zn, Ni, Si, Ge and Cd) so that they can be used in biogeochemical and climate models.

5. Determine the speciation of trace elements added to the ocean by atmospheric deposition and therefore the bio-availability of these elements.

3.1.4 Implementation strategy

It is recommended that GEOTRACES undertake coarse-resolution global surveys of ocean surface waters and atmospheric aerosols in the major ocean basins passing through the major mineral aerosol gradients. Example areas of interest include:

- The North Indian Ocean to characterise the recently observed large anthropogenic plume emanating from the southeast Asia region.

- The North Pacific Ocean to characterise spatially the large desert dust and anthropogenic plume emanating from Asia.

- An Atlantic Ocean transect to allow the characterisation of surface water parameters along the strong deposition gradients that exist from north to south.

- Selected transects in the Southern Ocean (e.g., Tasman Sea, downwind transect from Patagonia) to characterise the extremely low but variable mineral aerosol inputs into this primary HNLC region.

- Transects through the Peru and northwest African upwelling zones to contrast similar upwelling regimes with different dust deposition characteristics.

Natural temporal variability of atmospheric deposition can be exploited at time-series stations to extract information about TEI supply, behaviour and removal. Using existing time-series stations that occur in a variety of hydrographic regimes and dust deposition gradients (HOT, BATS, HiLaTS stations, Station Papa, Canary Island, Kerguelen, Dyfamed) would be particularly efficacious, but does not preclude the instigation of time-series stations specifically positioned to optimise the characterisation of aeolian input. Work at time-series stations would be designed to:

- Determine temporal variations in the magnitude of atmospheric deposition and its coupling to oceanic response.

- Establish the range of fractional solubility of TEIs carried by aerosols, and the factors regulating the variability of the fraction dissolved.

3.1.5 Interaction with other programmes

SOLAS: SOLAS objectives are complementary to those of GEOTRACES. SOLAS will provide valuable information on atmospheric transport and deposition processes and their biogeochemical effects for key nutrients including Fe, but few other TEIs. SOLAS will benefit from high-quality TEI measurements, and from comparison of surface deposition fluxes with those from below and laterally. The global coverage of GEOTRACES will also provide complementary information to SOLAS, which will focus on particular areas. Collaborations on field campaigns provide an excellent opportunity to further the goals of both programmes.

CLIVAR: Adding a TEI component to CLIVAR repeat sections, at least in the upper water column, will provide important insight into temporal variability of mineral aerosol input and impact (e.g., Figure 5). This variability is likely to be more pronounced in shallow waters, where the residence times of particle-reactive elements are shorter.

Ocean Observing Initiatives (e.g., ORION): Global and coastal observatory surface buoys provide a unique opportunity to examine air–sea exchanges and TEI deposition. Of particular importance is the ability to capture deposition events that would generally be missed by ship-based expeditionary sampling, and to provide time-series sampling in regions (such as high latitudes) that are infrequently visited by ships. Automated atmospheric samplers on observatory buoys can supply time-series samples of atmospheric particulate concentrations of TEIs to provide a temporal understanding of input processes and a history of input fluxes and ratios of TEIs, which will be critical to interpreting water column distributions. Furthermore, time series of surface dissolved concentrations, when linked to atmospheric concentrations and deposition models, can supply direct tests of solubilisation models and evaluate wet/dry deposition rates (objectives 2–4 above). Coupling atmospheric and water column sampling with satellite imagery may allow detailed studies of discrete deposition events. Basin-scale transects provided by GEOTRACES will allow the information obtained at specific observatory locations to be placed and interpreted in a larger context.

3.2 Continental run-off

3.2.1 Present understanding

A major source of nutrients and of most TEIs to the ocean occurs at the land–sea interface. Rivers transport TEIs in dissolved, particulate and colloidal form. Partitioning among these phases is dependent on the properties of the element and the riverine environment. In the freshwater/seawater mixing zone, some elements are removed from solution by biological uptake and by chemical scavenging. Coagulation of colloids and small particles also contributes to TEI removal during this mixing process. However, although some portion of the coagulated material is buried in estuarine sediments, the remainder may still be transported to the ocean, albeit in a form potentially quite different from that in which TEIs existed in freshwater. Desorption of particulate TEIs also takes place in this mixing zone, in part because of their displacement from particle surfaces by competition from and complexing by the major ions of seawater.

Submarine groundwater discharges (SGDs) have been recognised in recent years as potentially significant sources of chemical species to the ocean (Figure 15; Moore, 1996). SGDs include freshwater from geological formations away from the coast, and salt water that is either pumped or recirculated through intertidal and subtidal sediments or penetrates into depleted coastal aquifers (Burnett, 1999). As this is a relatively new field, the relevant database is still small.

Cold seeps at active continental margins have become a topic of increased attention in recent years. However, the extent to which they may represent significant sources in oceanic TEI budgets is unknown. Similarly, human-induced coastal erosion may represent a significant local source of TEIs, although the importance of this process in global budgets is unexplored.

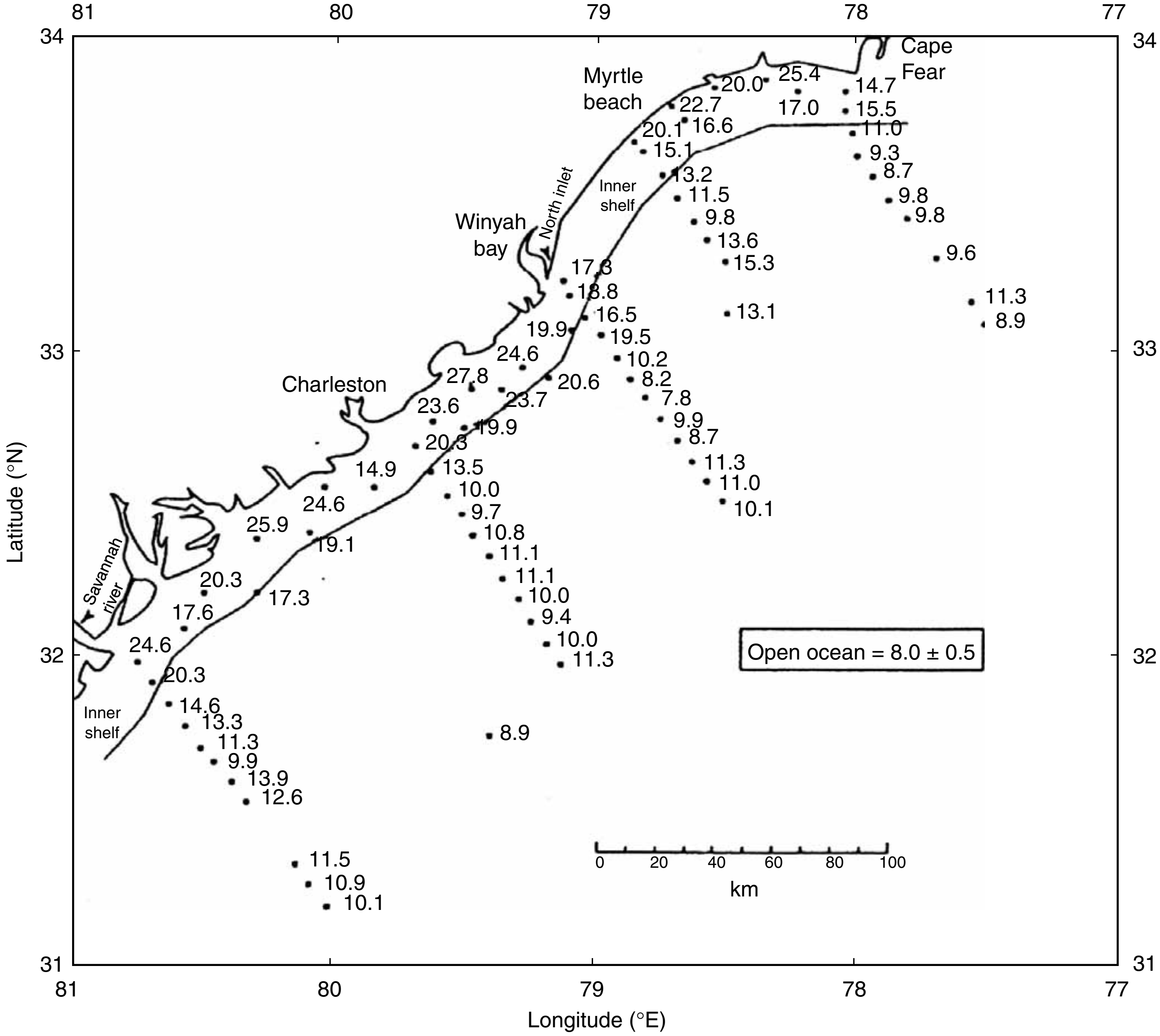

Figure 15. ^{226}Ra concentrations in near-shore waters showing a clear increase towards the coast (Moore, 2000). This increase is evidence for important chemical fluxes occurring between continental aquifers and the coastal ocean. The size of this flux, and the processes controlling it, are currently very poorly constrained. Reprinted from Continental Shelf Research, Vol. 20, W.S. Moore, Determining coastal mixing rates using radium isotopes, pages 1993–2007. Copyright (2000), with permission from Elsevier.

3.2.2 Areas for advance

Understand the behaviour of nutrients and TEIs in the mixing zone

To establish the global fluxes of nutrients and TEIs across the land–sea interface, and the fraction of the fluxes entering the ocean, requires quantitative understanding of the behaviour of TEIs in the mixing zone. Riverine inputs have been studied for many years and data sets exist for some of these fluxes. However, there remain large uncertainties in the riverine contribution to oceanic nutrient and TEI budgets due to their non-conservative behaviour in estuaries and on the shelf. Furthermore, in some systems, transport is dominated by rare but major floods. Many systems have been perturbed by human activities (deforestation, emplacement of dams, growth of agriculture, erosion, etc.). Consequently, it will be necessary to estimate the natural variability and human perturbations of riverine fluxes in order to characterise the riverine sources of oceanic nutrients and TEI budgets. Global change can also affect river and submarine discharges and hence associated fluxes. Therefore, baseline data in present climatic and environmental conditions are required.

Assess the role of glacial weathering of fresh mineral surfaces

Physical weathering in glacial settings such as Greenland and the Antarctic Peninsula delivers 'fresh' mineral surfaces to the ocean where TEIs may be leached by seawater. These processes may be important in basin-scale budgets of TEIs today, and they may have been of greater importance during glacial periods in the past, but they remain largely unquantified. In the Southern Ocean, this source may represent a significant input of iron.

Assess the role of sea ice as a vector transporting TEIs

Although not strictly a form of continental runoff, sea ice may carry a large load of sediment, especially in the Arctic Ocean. Suspended particles may be entrained during formation of frazil ice, while shallow surface sediments are incorporated into fast ice that may later be dislodged and freely move seaward. Sea ice serves as an efficient collector of aerosols. Each of these forms of particulate material is released to the water column when sea ice melts. The impact of these processes on TEI budgets should be evaluated.

Assess the magnitude of chemical fluxes and far-field impact to the ocean from SGD and riverine sources

Research on SGD and cold seeps are new fields and there are no global data sets comparable to those available for riverine fluxes. In most cases, exploratory research is needed simply to assess the order of magnitude of SGD and cold-seep fluxes in oceanic TEI budgets. An example is the Ganges-Brahmaputra river system, which drains a major mountain belt uplift, commonly thought to have played an important role in altering global fluxes to the ocean. Recent work has suggested a large SGD flux of Ba, Ra and Sr from this system that may rival the riverine input. This SGD Sr flux may affect the global seawater $^{87}Sr/^{86}Sr$ ratio (Dowling *et al.*, 2003).

Although land–ocean fluxes are studied in other programmes, the impact of these fluxes on open-ocean chemistry is generally neglected. Other programmes are attempting to better constrain land-derived sources by improving our knowledge of the chemical behaviour of TEIs in the estuary and mixing zone and by directly quantifying estuarine and SGD fluxes.

An example region of interest is the Amazon River system, with huge fluxes of dissolved species and unique fluid muds that are deposited on the continental shelf. The periodic resuspension of these muds may be a substantial source of TEIs to the ocean, and it has been estimated that the flux of Cd to the ocean associated with this process is roughly half that of the global riverine flux. The plume from the Amazon River also reaches a significant distance into the open Atlantic Ocean as shown in Figure 16.

Recent studies suggest that the TEIs in the Bay of Bengal are influenced throughout the water column by desorption of TEIs from particles and sediments.

Studies of SGDs have been performed on the southeastern coast of the United States and Long Island, New York, the coast of southern Brazil, and the coast of southwestern Australia, which therefore make them suitable targets for time-series study or linkage with ocean sections. The Yucatan Peninsula is a region where SGD fluxes are expected to be large and inputs by rivers are low, thereby making it easier to identify far-field impacts of SGD sources of TEIs. And SGD inputs from southern Brazil and in Patagonia may provide a potential source of iron to the Southern Ocean.

A complementary approach would be to identify diagnostic tracers (TEIs or others) characteristic of river and SGD sources and use precise measurements of the distribution of these TEIs to provide integrated estimates of their geographically variable freshwater sources. This approach is complicated by complex ocean circulation in the near-shore environment (Figure 17); it will require collaboration with modellers and integration of real-time satellite data during field programmes involving chemical measurements.

3.2.3 Specific GEOTRACES objectives

1. Develop TEI tracers and multi-tracer approaches that integrate the geochemical fluxes from land to the open ocean.

2. Use these TEI tracers and their global distributions to assess the global pattern of freshwater-derived geochemical fluxes to the open ocean.

3. Integrate chemical data and new measurements with models and physical oceanography data (ship-board and satellite) to constrain the shelf-to-open ocean fluxes of freshwater-derived TEIs (Hutchins and Bruland, 1998; Boye *et al.*, 2003).

3.2.4 Implementation strategy

Spatial and temporal variability of freshwater flux at the land–ocean interface is extremely large. Fluxes of TEIs carried by freshwaters, as well as the processes regulating the fate of these TEIs after they reach the ocean, are expected to be similarly heterogeneous. GEOTRACES will have limited resources to evaluate fluxes of TEIs associated with continental runoff. A judicious strategy to characterise these fluxes must therefore be devised. Such a strategy will include: (1) collaboration with other programmes; (2) evaluation of integrated boundary fluxes by modelling TEI gradients measured in ocean-margin waters; and

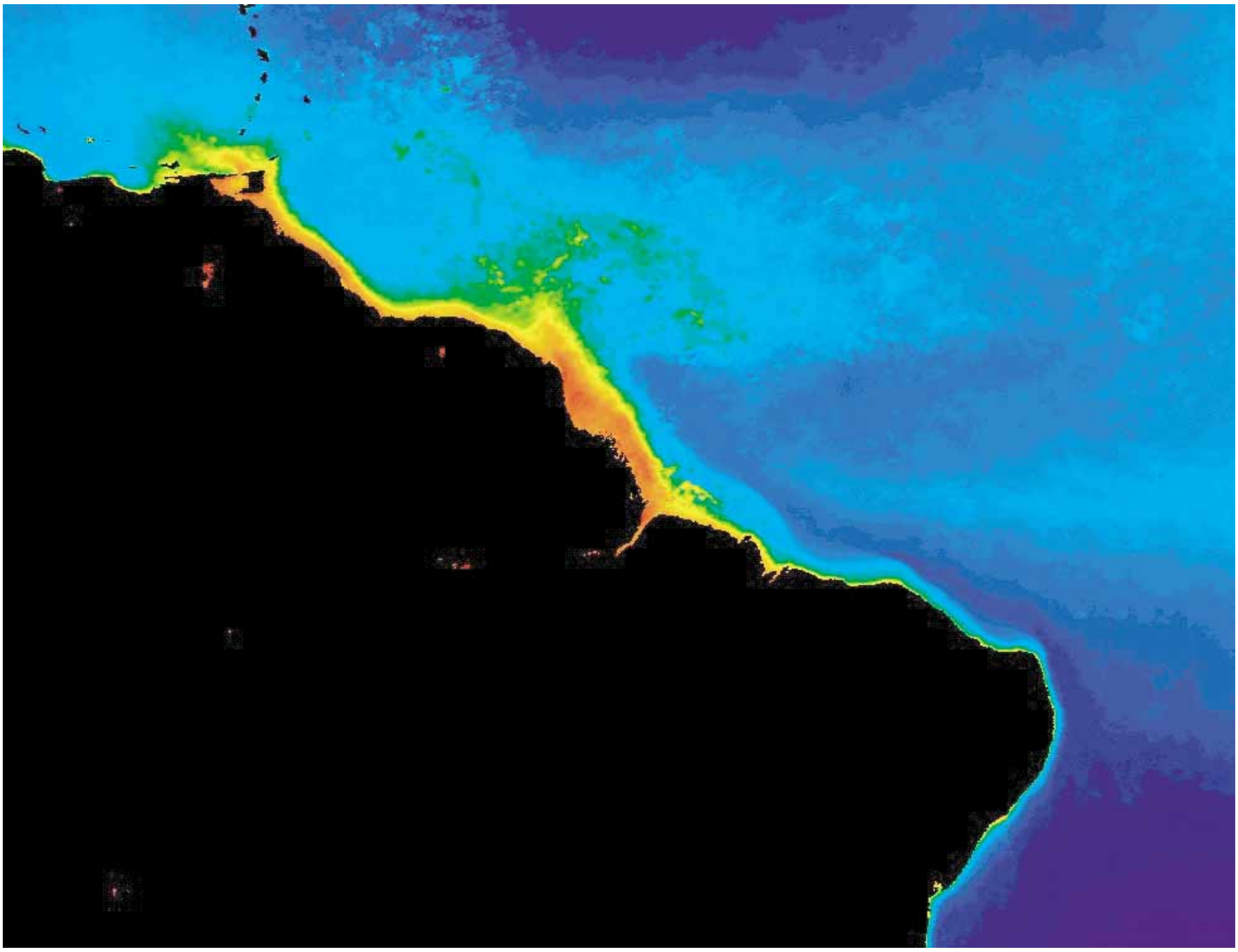

Figure 16. A MODIS composite image of chlorophyll off the northeastern coast of South America from 1 January 2002 to 30 November 2005 (source: oceancolor.gsfc.nasa.gov 4 km grid). Riverine discharge of nutrients from the Amazon River stimulates elevated chlorophyll concentrations extending hundreds of miles from the coast.

(3) a limited number of process studies, where other programmes cannot provide necessary information.

Other programmes have devoted substantial effort to evaluating riverine fluxes of TEIs. An important 'enabling' activity (see Section 8.1) to be performed early in the GEOTRACES programme will be to communicate with such programmes and complete a synthesis of past and present studies of riverine TEI fluxes. Although study of SGDs is in its infancy, some work in this area is beginning (Burnett *et al*., 2003) and this should be included in the synthesis. Two principal objectives of this synthesis will be to produce up-to-date estimates of global freshwater fluxes of TEIs to the ocean, and to identify gaps in the available information that can be used to set priorities for sampling during the GEOTRACES programme.

For TEIs with residence times comparable to, or less than, the mixing time of the ocean, spatial gradients in nearshore waters carry information about net fluxes. Concentrations of TEIs measured along sections close to the coast will be modelled to derive quantitative estimates of fluxes at the land-ocean boundary. Examples of regions where existing data suggest that riverine and SGD sources may have significant impact on far-field oceanic TEI distributions include the Ganges–Brahmaputra river system and the Amazon River.

Process studies will be limited to those that elucidate processes known to be important for TEIs, but where present understanding is limited. Examples include the release of TEIs from particulate material in rivers with high particle loads, and the fluxes of TEIs transported by SGDs. Because no other programme is investigating the role of these processes for TEI cycles, and because they have direct relevance to the goals of GEOTRACES, they will be high priority for process studies within the programme. These process studies should, if possible, be linked to the ends of open-ocean sections, encouraging participation of coastal countries not involved in open-ocean transits. Locations for such process studies will be identified during

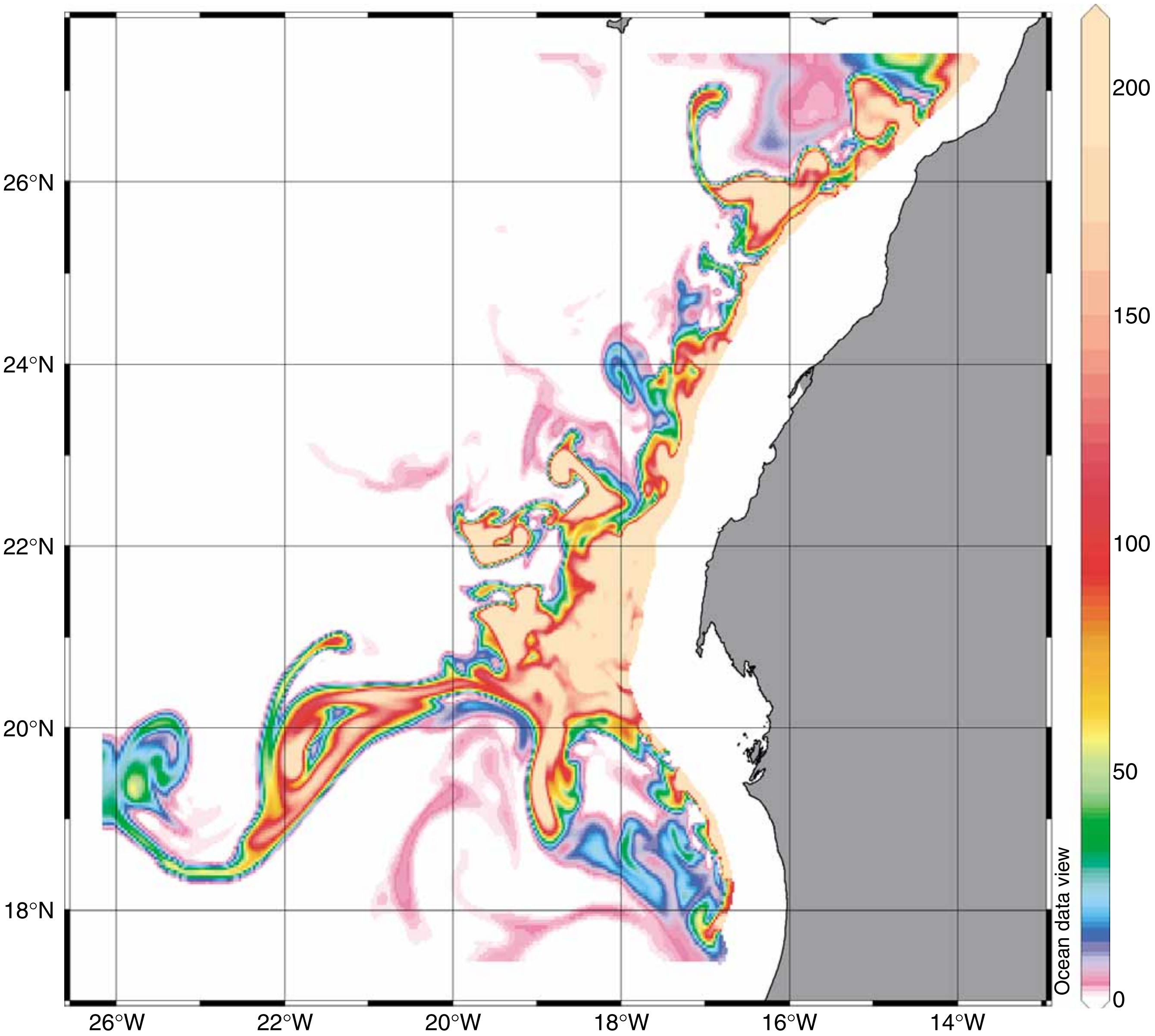

Figure 17. Snapshot from a high-resolution model showing particles eroded from the northwest African shelf and transported toward the open ocean by complex and highly variable ocean currents (Karakas et al., 2006). To extrapolate from measurements of TEIs to realistic flux estimates in such settings will require use of such modelling and of relevant monitoring studies, including satellite data. Journal of Geophysical Research. Copyright (2006) American Geophysical Union. Reproduced with permission of the American Geophysical Union.

national and international implementation planning (see Section 8). Possible locations include:

- the Southeast coast of the United States,
- the coast of southern Brazil,
- the coast of east Asia where rivers carry a large suspended load,
- the Yucatan Peninsula,
- Patagonia,
- high-latitude regions to evaluate the source of TEIs associated with physical weathering by glaciers, and
- high-latitude ocean areas to evaluate the transport of TEIs by sea ice.

3.2.5 Interaction with other programmes

LOICZ: Work within the remit of LOICZ provides complementary information to achieve these research objectives. Compilation of existing river flow data (e.g., GLORI) for instance, provides important flux estimates. Near-shore modelling of ocean circulation conducted within LOICZ will provide ideal background information for assessment of TEI fluxes from the shelf to the open ocean.

National River/Estuarine Programmes: Links to regional programmes will be essential to the successful estimate of freshwater inputs of TEIs. This will provide an opportunity for scientists from coastal nations to contribute to GEOTRACES. This will also represent one of the capacity-building aspects of GEOTRACES, since the exchange of scientists and expertise with nations without a large oceanography infrastructure will provide training and knowledge.

Ocean Observing Initiatives (e.g., ORION): Coastal observatories established as part of the Global Ocean Observing System provide opportunities for time-series sampling to constrain temporal variability of TEI fluxes associated with freshwater runoff. Inputs in the mixing zone may be tied to rare events (such as storms and floods) that are rarely sampled by shipboard measurements. Observatories can provide a sustained observational presence to examine the frequency of events and through automated samplers provide samples of suspended and dissolved materials when ship-based sampling is not possible. Also, sustained observations provided by observatories provide a means of assessing long-term trends.

3.3 The sediment–water boundary

3.3.1 Present understanding

Chemical fluxes between sediments and the overlying water column include net sources and sinks for dissolved TEIs in seawater as well as being a significant component of the internal cycling of TEIs in the ocean (Section 4.3). For some TEIs, sediments may alternately serve as a source or a sink, depending on local conditions. However, most TEIs introduced into the ocean are ultimately removed by burial in marine sediments.

Little is known about the net supply of TEIs from sediments. The clearest evidence for a sedimentary source comes from soluble members of the natural U and Th decay series (e.g., isotopes of Ra, Rn and ^{227}Ac) that are released into solution after radioactive decay of their sediment-bound parent nuclides. Unequivocal evidence for sedimentary sources also comes from Nd isotopes, which label the source of rare earth elements (REEs) in the water column. The strongest sources of Nd isotopes seem to be in ocean margin sediments, from which distinct Nd isotope compositions can be traced considerable distances into the ocean interior (Lacan and Jeandel, 2001). Such a boundary source is actually required to balance the global budget of both Nd and Nd isotopes (Tachikawa *et al*., 2003).

Diagenetic transformation of continental detritus in coastal and hemipelagic sediments may similarly release other TEIs into ocean margin waters. This is particularly true where chemically reducing conditions mobilise iron and manganese oxides formed on land, releasing oxide-bound TEIs into solution (Haley and Klinkhammer, 2004). Although the release of TEIs from ocean-margin sediments has been documented for some first-row transition metals (Elrod *et al*., 2004; Johnson *et al*., 2003) the extent to which this represents a net source, by diagenetic mobilisation of continentally derived material versus the regeneration of biogenic and authigenic marine phases, remains undetermined.

Several generic types of process contribute to the removal of TEIs from seawater and their burial in marine sediments. The simplest of these is the passage of continentally derived particles through the water column, whether supplied by the atmosphere or by runoff, without any further solid-solution reaction. TEIs bound within aluminosilicate minerals are included in this category. Organisms incorporate TEIs into marine particles, as do abiological solid–solution exchange reactions (e.g., adsorption, complexation). A fraction of these TEIs delivered to the seabed by sinking particles is preserved and buried in sediments. Dissolved TEIs in bottom waters may also be removed by direct sorption to surface sediments (Nozaki, 1986). Finally, precipitation from pore waters removes some dissolved TEI species that diffuse into sediments from the overlying water column. Most commonly this category of reaction is important for redox-sensitive TEIs (e.g., U, Mo, V, Re) that are soluble in the presence of oxygen but insoluble when reduced to lower oxidation states in anoxic sediments (Crusius *et al*., 1996).

Each of the removal processes identified above is generally more active (in terms of rate per unit area) near ocean margins than in the open ocean. Biological productivity is typically greater in coastal waters than in the open ocean. Consequently, rates of active biological uptake of TEIs as well as rates of abiological sorption of TEIs to biogenic detritus tend to be greater near ocean margins. Fluxes of lithogenic particles eroded from continents are also greater near ocean margins, reflecting the proximity of the source. Therefore, rates of scavenging of TEIs by lithogenic particles, as for biogenic particles, are expected to be much higher near ocean margins.

High biological productivity near ocean margins has an indirect effect on TEI cycles through its impact on redox conditions in underlying sediments. In particular, the eastern boundaries of the Atlantic and Pacific oceans, as well as the Arabian Sea, are locations where coastal upwelling of nutrient-rich water induces some of the highest biological productivity in the world ocean. Respiration in subsurface waters and in continental slope sediments of the organic by-products of this high productivity gives rise to strong oxygen minimum zones (OMZs). Low concentrations of dissolved oxygen in bottom waters coupled with high rates of respiration in surface sediments create chemically reducing conditions close to the sediment–water interface. Reduction of iron and sulphate may occur at sub-bottom depths as shallow as a few millimetres. The shallow depths of reducing conditions in sediments in contact with OMZ waters allows substantial fluxes across the sediment–water interface, with TEIs mobilised by reducing conditions diffusing from the sediments into the water column and species precipitated under reducing conditions moving in the opposite direction.

Enhanced removal of TEIs at ocean margins, coupled with diffusive and advective exchange of water masses between shelf/slope regions and the open ocean, produces a net flux from the open ocean to ocean margins for some dissolved TEIs, a process known as boundary scavenging (Spencer *et al*., 1981; Bacon, 1988). Boundary scavenging represents an important component of the overall removal of some TEIs from the ocean (Lao *et al*., 1992), but to date the preferential removal at ocean margins has been assessed quantitatively only for a few natural radionuclides (e.g., ^{210}Pb, ^{231}Pa, ^{10}Be). Boundary sources may be important as well. For example, recent results demonstrate that the boundary scavenging of REE is likely balanced by boundary sources. This type of boundary exchange is required to explain the observation that the Nd isotopic composition of water masses can be modified significantly without a corresponding increase in the dissolved Nd concentration (Lacan and Jeandel, 2005; Jeandel *et al*., submitted; Arsouze *et al*., submitted).

3.3.2 Areas for advance

Determine TEI fluxes between sediment and the water column

Sediments serve as the primary sink for TEIs in the sea, but rates of removal vary spatially and, under certain conditions, sediments may serve as a net source of TEIs to the water column. Closure of TEI budgets for the ocean will require accurate estimates for the fluxes of TEIs removed to the sediments, with spatial coverage sufficient to provide a meaningful average of the natural spatial variability. Evaluating TEI fluxes between sediments and the water column, and their spatial variability, is only a first step. The long-range goal is to predict the sensitivity of these fluxes to changing environmental conditions. Developing such a mechanistic understanding will require knowledge of how these fluxes vary with oceanographic environment (e.g., temperature, sedimentation rate, oxygen levels) and with the type of biogenic (opal, carbonate) and lithogenic (mafic or felsic origin, crust material or weathering product) sediment involved.

Quantify fluxes in OMZ regions

Redox reactions at shallow depths within sediments in contact with OMZ waters are particularly effective at mobilising certain TEIs and sequestering others (see above). Although there is strong evidence that fluxes of certain TEIs in OMZ regions are greater than elsewhere, the quantitative significance of these fluxes in ocean-wide biogeochemical cycles remains undetermined. Therefore, evaluating TEI fluxes in OMZ regions should be targeted as a high priority within the larger programme to evaluate the exchange of TEIs between sediments and the water column globally.

Establish the extent of boundary scavenging for particle-reactive TEIs

Thus far, the importance of boundary scavenging has been clearly established for a few natural radionuclides with relatively simple source terms, including some originating from the U-decay series. As emphasised by results from recent studies of Nd, the importance of this process for TEIs with more complex source functions still needs to be established. There is also a need to distinguish between the influence of particle flux and particle composition in driving boundary scavenging. Theoretical considerations suggest that boundary scavenging should be more pronounced for TEIs with longer residence time but much remains to be done to quantify this relationship. In particular, it will be important to quantify the effect of boundary scavenging on the removal of ^{230}Th, which is used as a normalising tool to estimate sedimentary fluxes in palaeoceanography (Section 5).

Compare fluxes at active and passive margins

Ocean margins can themselves also be divided into two categories: active margins (that is, margins where subduction takes place) and passive margins. These have very different topographies, with active margins characterised by a narrow continental shelf and steep slope, whereas the opposite is true for passive margins. The different settings of active and passive margins result in differences in the importance of certain processes. Active margins typically have greater sediment supply, no shelf on which to store sediment, but a nearby trench to collect sediment as it migrates downslope. The nature of the sediment is also often rather different, featuring a higher concentration of volcanic material at active margins. Active margins can also feature active fluid venting from accretionary prisms and more common cold seeps. Continental shelves on passive margins often extend over 100 km into the ocean. Here, coarse-grained relic sediments typically cover thick sequences of sedimentary or fractured rocks having high permeability. Seawater may circulate through these shelves in response to geothermal heating. This circulation has the potential to add or remove TEIs (Wilson, 2003). These differences make active and passive margins end members with a range of different processes dominating TEI exchange between seawater and sediments.

3.3.3 Specific GEOTRACES objectives

1. Evaluate burial (removal) fluxes of TEIs globally, and discriminate between TEIs contained in detrital phases and those that were removed from solution.

2. Determine the spatial variability of TEI removal fluxes as well as their dependence on sediment composition, sediment accumulation rate, rain rate of biogenic particles, bottom water composition, redox conditions, and other environmental parameters.

3. Evaluate net sedimentary sources of TEIs in regions where such sources are anticipated to exist (e.g., oxygen minimum zones), and characterise the processes responsible for supplying the TEIs.

4. Evaluate the net lateral exchange of TEIs between ocean margin sediments and the open ocean (boundary sources and boundary scavenging).

5. Establish TEIs that serve as tracers for dissolution of lithogenic sediments for which the signal can be determined unambiguously well into the water column.

3.3.4 Implementation strategy

Many features of the oceanic distributions of TEIs are influenced simultaneously by fluxes at multiple interfaces, or by internal cycling that occurs together with net removal. For example, TEIs mobilised from coastal sediments mix with dissolved TEIs carried by rivers and SGDs (Section 3.2). Similarly, TEIs delivered to the seabed by sinking particles, following chemical scavenging or biological uptake in the water column, may be regenerated (Section 4.3) or removed permanently by burial. The processes removing dissolved TEIs from the water column are the same in either case, while the factor determining whether a particular TEI is regenerated or buried may be nothing more than the rate of sediment accumulation (i.e., the timescale available for TEI regeneration). Therefore, while it is helpful conceptually to consider these processes individually, in practice the TEI distributions measured at any location will have been influenced by fluxes at multiple boundaries and by multiple internal cycling processes.

Insight into the relative importance of these different processes can be gained by studying TEI distributions in end-member situations, where one source, sink or recycling process is more likely than others to be important. As noted above, many of these end-member situations occur at ocean margins. Examples of end-member margin types that should be examined include:

(1) margins with high particulate organic carbon fluxes and intense oxygen minimum zones, for example, the upwelling regions off Peru and Chile, West Africa, and the Costa Rica Dome;

(2) margins with large lithogenic inputs, for example, Papua New Guinea, the Bay of Bengal, New Zealand, the Amazon Basin, and East Asia; and

(3) margins with high-energy conditions leading to periodic resuspension of sediments, for example, Papua New Guinea and the Oregon coast.

3.3.5 Interaction with other programmes

LOICZ: Running GEOTRACES sections into margins where LOICZ activities have been or are being performed offers obvious synergy. Modelling and observation of water-mixing processes in the coastal zone, performed within LOICZ, will provide important background to the interpretation of TEI results collected within GEOTRACES.

InterMARGINS: Assessing sedimentary fluxes in margin settings is a major goal of the InterMARGINS programme. Fluxes of sediment components into and out of the margin setting therefore represent a natural shared interest with GEOTRACES.

Ocean Observing Initiatives (e.g., GOOS and ORION): Establishment of observatories at coastal and ocean margin locations is a priority for the ORION Project. Temporal variability is enhanced near boundaries and the dynamics of individual transport processes in general cannot be resolved from ship-based expeditionary studies. Working together, GEOTRACES and ORION can provide unique new insights into the exchange of elements at ocean boundaries. The water-column distribution measurements provided by GEOTRACES reflect the net result of all the processes influencing concentrations while the dynamics provided by sustained, real-time, high-frequency measurements from observatories from the ORION programme may be used to examine the role of individual transport processes and sources.

3.4 Ocean crust

3.4.1 Present understanding

Seafloor hydrothermal circulation was first observed in a submarine mid-ocean ridge (MOR) environment in 1977 and is now recognised to play a significant role in the cycling of heat and chemicals between the solid Earth and the ocean (German and Von Damm, 2003). Hydrothermal circulation occurs when seawater percolates downward through fractured ocean crust along the 50,000–60,000 km of the global mid-ocean ridge system. Seawater is heated and undergoes chemical modification through reaction with the host rock as it percolates downward, reaching maximum temperatures that can exceed 400°C. At these temperatures the fluids are extremely buoyant and rise rapidly back to the seafloor, where they are expelled into the overlying water column. Important enrichments and depletions are imparted to high-temperature vent fluids relative to ambient seawater (Figure 18). To date, more than 100 individual hydrothermal fields have been investigated on the seafloor and evidence has been collected for the existence of at least double this number (Figure 19). Even this is likely to be a conservative estimate because more than 50% of the global MOR system remains completely unexplored. Even though we do not know the precise

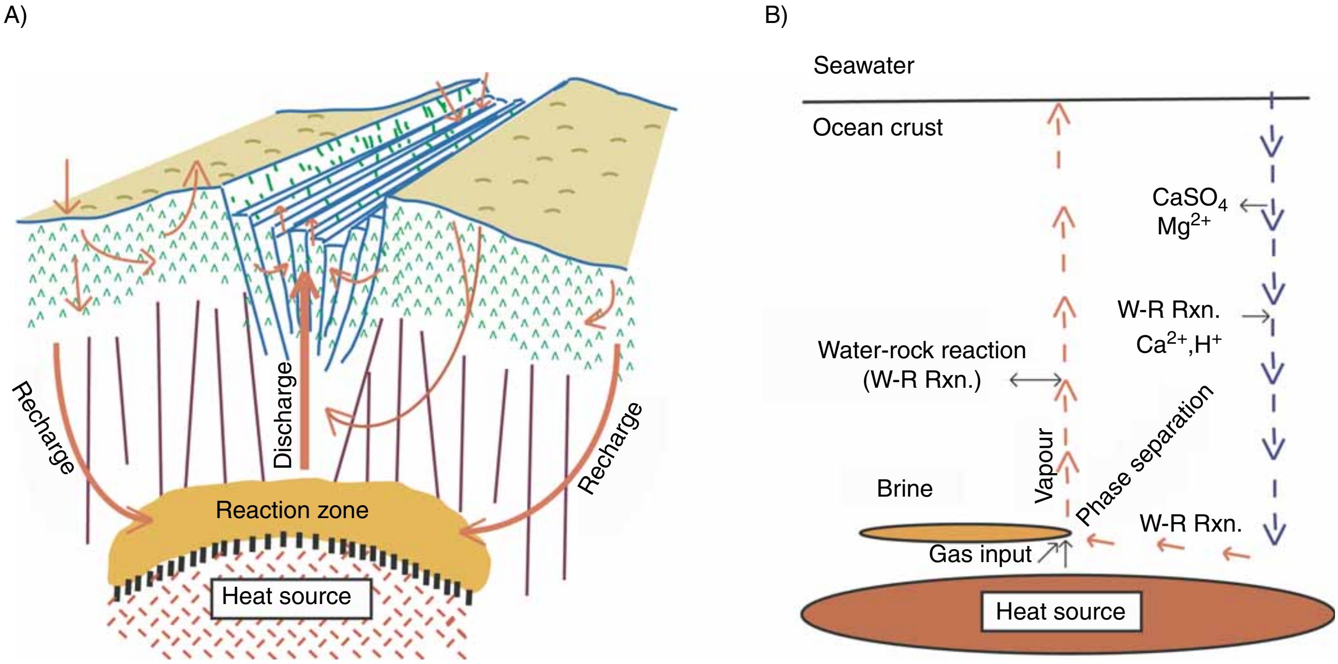

Figure 18. A simplified representation of the processes occurring at mid-ocean ridges. Seawater is drawn down and interacts with warm ocean crust causing significant chemical exchange. Hot altered vent water is then returned to seawater to influence its chemistry both directly and through the resulting hydrothermal plume. Figure reprinted from Treatise on Geochemistry, Vol. 6, German, C.R. and Von Damm, K.L., Hydrothermal processes, pages 181–222. Copyright (2003), with permission from Elsevier.

number and location of individual vent sites on the seafloor, we do know the global fluxes of key conservative tracers (e.g., $^{87}Sr/^{86}Sr$ ratio) to within approximately one order of magnitude (Elderfield and Schultz, 1996).

Approximately 25% of the total global heat flux from the Earth's interior (about 43 TW) occurs in the form of hydrothermal circulation through 0–65 Ma age ocean crust. A significant component of this heat flow occurs at the ridge axis itself (0–1 Ma), where hydrothermal heat release is estimated at 2.8 ± 0.3 TW (Elderfield and Schultz, 1996; Mottl, 2003). The remainder occurs through older oceanic crust (1–65 Ma) where heat fluxes associated with hydrothermal circulation are estimated at 7 ± 2 TW (Mottl, 2003). The most spectacular manifestation of seafloor hydrothermal circulation is that of high-temperature (≤400°C) 'black smokers' that expel fluids from the seafloor at the ridge axis. Although earlier summaries suggested that 90% of axial heat flux might be in the form of lower temperature 'diffuse' fluids, recent work has suggested that the proportion of heat released through high-temperature circulation may be closer to 50%. This is important because it is only in *high-temperature* hydrothermal systems that many chemical species escape from the seafloor in high abundance. When they do, the buoyancy of the high-temperature fluids carries them hundreds of metres up into the overlying water column where they rapidly entrain ambient seawater in proportions close to 10,000 : 1 (Helfrich and Speer, 1995) and form non-buoyant plumes that contain a wide variety of both dissolved chemicals and freshly precipitated mineral phases. It is the processes active within these dispersing hydrothermal plumes that determine the net impact of hydrothermal circulation upon the ocean and marine geochemistry.

Best estimates for hydrothermal circulation suggest that, while the entire volume of the ocean is only cycled through the subsurface hydrothermal circulation cells of mid-ocean ridges every 20–30 Ma, the cycling through hydrothermal plumes is much more rapid. If 50% of high-temperature fluids expelled from black smokers were to form buoyant hydrothermal plumes, for example, then the associated entrainment of ambient seawater would be so large that the total volume flux through those hydrothermal systems would be an order of magnitude greater than all other hydrothermal fluxes *and* the global riverine flux to the ocean. At its most conservative, the associated residence time for the global ocean with respect to cycling through hydrothermal plumes has been calculated as 4–8 kyr, comparable to the characteristic timescale of the meridional overturning circulation (~1 kyr; Broecker and Peng, 1982). Consequently, we anticipate that hydrothermal circulation should play an important role in the marine geochemical cycle of many TEIs.

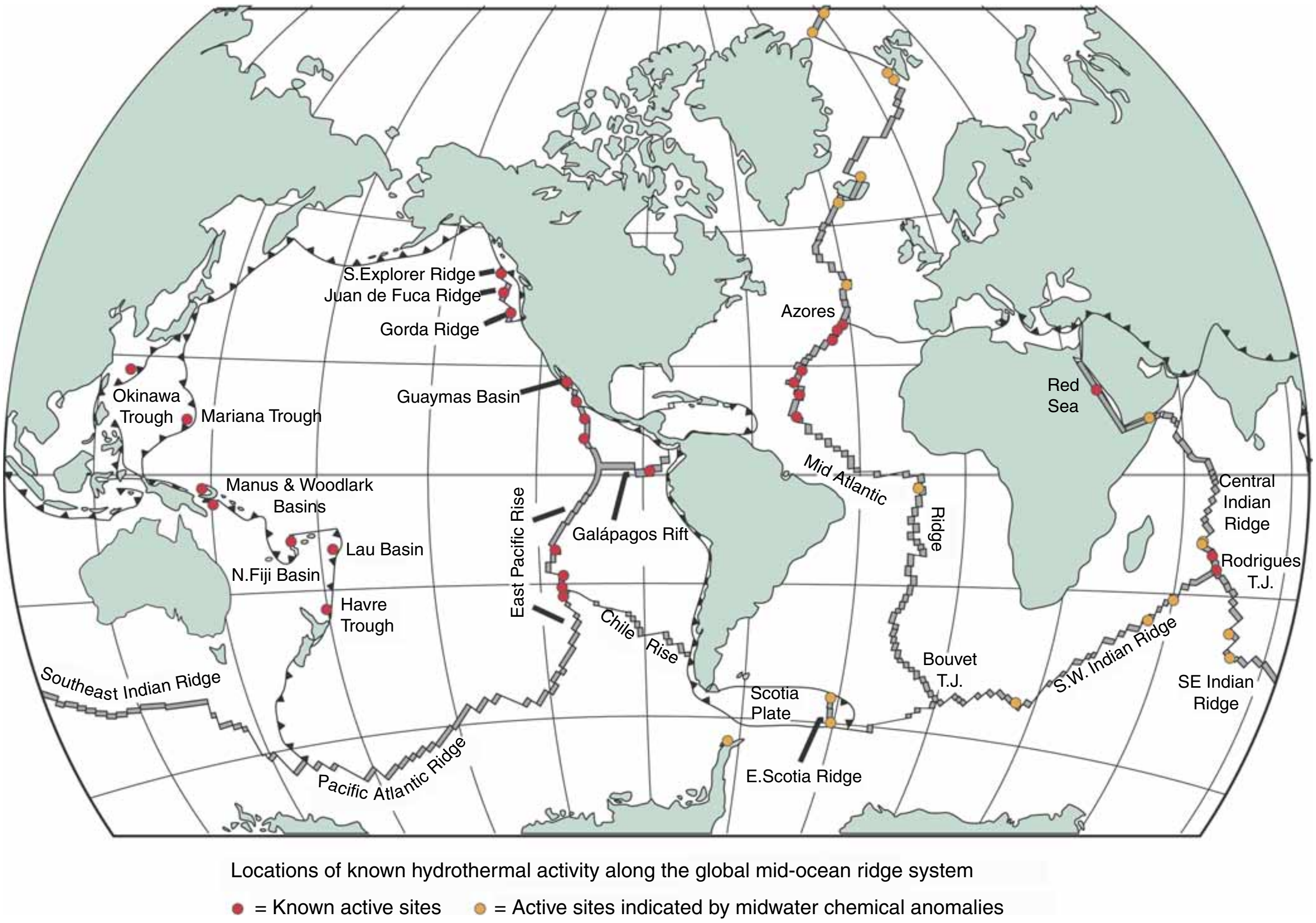

Figure 19. The global mid-ocean ridge system showing known activity. Figure reprinted from Treatise on Geochemistry, vol. 6, German, C.R. and Von Damm, K.L., Hydrothermal processes, pages 181–222. Copyright (2003), with permission from Elsevier.

3.4.2 Areas for advance

What is the impact of hydrothermal circulation on the ocean budget of short-residence-time tracers?

In particular, what is the extent to which ocean compositions may be altered and/or buffered through formation of high-temperature hydrothermal vent fluids and, potentially even more important, through the large volumes of seawater that are cycled through the resultant chemically reactive hydrothermal plumes? Such hydrothermal plumes have been shown to exhibit strong removal of some particle-reactive tracers from the ocean (e.g., REE, ^{230}Th, ^{231}Pa, ^{10}Be), even when compared with high-productivity ocean-margin scavenging. What requires evaluation now, therefore, is whether such hydrothermal scavenging is sufficiently widespread along the 50,000–60,000 km global MOR system that it is quantitatively important to global ocean chemical cycles of other elements, both in the present day and throughout past ocean history.

Where do the key reactions take place that determine the fate of TEIs emitted from hydrothermal systems to the ocean?

A limitation of most hydrothermal plume process studies is that they have been conducted in few locations and using restricted resources. Specifically, much of our understanding is based upon a series of detailed studies using surface-ship sampling in the North Atlantic Ocean. This is unfortunate because in the North Atlantic Ocean, oxidation kinetics of dissolved Fe in hydrothermal plumes are at their most rapid and likely not representative of the conditions that prevail along faster-spreading ridges of the Indian and south Pacific oceans, where the majority of the gross hydrothermal Fe flux is expected to occur. This is a significant problem because the key findings from North Atlantic studies were (a) that Fe oxidation was indeed rapid (e.g., Rudnicki and Elderfield, 1993) and (b) that such Fe-oxyhydroxide precipitation played a dominant role in regulating the net flux of other dissolved TEIs to the ocean at those locations (German *et al*., 1991). To a first approximation previous work predicted that key reactions that constrain the impact of hydrothermal fluxes to ocean chemistry (e.g., sulphide precipitation, Fe-oxyhydroxide colloid formation and aggregation) must occur within the rising 'buoyant' portion of a hydrothermal plume that could only be sampled by submersible. With the recognition that Fe oxidation kinetics vary significantly along the global thermohaline conveyor (Field and Sherrell, 2000; Statham *et al*., 2005) there is a pressing need to conduct repeat experiments under conditions more representative for the world's fastest-spreading ridges (e.g., southeastern Pacific Ocean) where most of the gross hydrothermal flux occurs. The slower oxidation kinetics anticipated in these regions suggest that important processes in these systems may predominantly occur in the dispersing non-buoyant plume, more amenable to surface ship sampling, and different from prior North Atlantic Ocean investigations.

What is the role of hydrothermal plumes in global nutrient cycles (e.g., as a source of Fe and as a removal mechanism for P) and in deep-water carbon cycling?

With the advent of techniques for measurement of new elemental and isotopic compositions comes the opportunity to evaluate the role of hydrothermal systems on marine geochemical budgets. Such technological advances can shed surprising new light on systems that were previously believed to be well constrained. For example, measurements of Fe isotopic compositions could give useful information about whether a significant amount of Fe in the deep Pacific Ocean is hydrothermally derived. In contrast to the micronutrient Fe, dissolved P is extensively removed from solution in seawater by adsorption onto hydrothermal Fe-oxyhydroxides (Feely *et al*., 1990). The global P removal flux associated with this process is comparable to the global riverine flux of dissolved P to the ocean and may show systematic variations along the global thermohaline conveyor (Feely *et al*., 1998). The influence of this removal on global nutrient cycles now and in the past requires further study.

Hydrothermal fields on the deep seafloor play host to abundant high-biomass chemosynthetic communities. Furthermore, carbon fluxes (per unit area) to the seafloor close to these vent sites are comparable to terrestrial fluxes beneath rainforest canopies. An important future development, therefore, will be to quantify the impact that hydrothermal cycling may have, cumulatively, on the global carbon cycle, both through these fluxes and through the supply and removal of nutrients.

How important are microbial/biogeochemical interactions in hydrothermal systems?

Historically, much hydrothermal research has been focused on interactions with the seafloor and young oceanic crust. Consequently, many studies of hydrothermal systems have been geologically/mineralogically influenced, with a tendency to treat these systems as largely inorganic reaction systems. Increasingly, however, the mid-ocean ridge community has come to recognise that biological and biogeochemical cycling plays an important role in all aspects of seabed and subsurface hydrothermal interactions from the deep hot biosphere to the role of microbiota in regulating oxidising/reducing and pH conditions within the fabric of high-temperature hydrothermal sulphide structures and associated mineralogical deposits. Future work should examine the role that (micro)biological activity may play in regulating the cycling of TEIs released from hydrothermal venting to the ocean. There is clear evidence that hydrothermal plumes enriched in TEIs are also enriched in microbial content (cell counts) and that such organisms are different in characteristics (bacteria versus archaea) from open-ocean deep waters. An important open question is to what extent such microbial systems interact with, depend upon, or perhaps even regulate, the cycling of TEIs released by and/or taken up into deep-ocean hydrothermal plume systems.

3.4.3 Specific GEOTRACES objectives

1. Determine the fluxes, mechanisms and rates of advective and eddy-diffusive dispersion of hydrothermal fluids and TEIs associated with plume waters.

2. Determine the processes responsible for supply and removal of the TEIs dissolved within hydrothermal plumes. This will be equally important for 'conservative' and 'quasi-conservative' tracers added to the ocean through hydrothermal systems (e.g., dissolved ^{3}He, ^{222}Rn and Si) against which we will be able to compare the behaviours of species with shorter residence times. Understanding supply and removal processes will be key to identifying those elements and isotopes for which hydrothermal circulation is important with respect to their global ocean cycles.

3. Determine the role of particle formation in partitioning of hydrothermally affected TEIs among dissolved, colloidal and particulate phases. Key sub-objectives will include: (a) comparison of particulates in buoyant versus non-buoyant plumes (e.g., domination of sulphide versus oxyhydroxide phases); (b) the modification of gross dissolved hydrothermal fluxes through precipitation of hydrothermal particles; (c) impact on ambient seawater of scavenging onto hydrothermal particles; and (d) rates of particle advection (e.g., using $^{234}Th/^{230}Th$, $^{210}Pb/Pb$ disequilibria) which could also be extended to studies of settling and transfer to underlying sediments.

4. Determine the importance of (micro) biological interactions to the chemical cycling of hydrothermally affected TEIs (already known, for example, to dominate oxidation of dissolved Mn in hydrothermal plumes) and, conversely, the importance of hydrothermally sourced TEIs to broader whole-ocean productivity and the global carbon cycle.

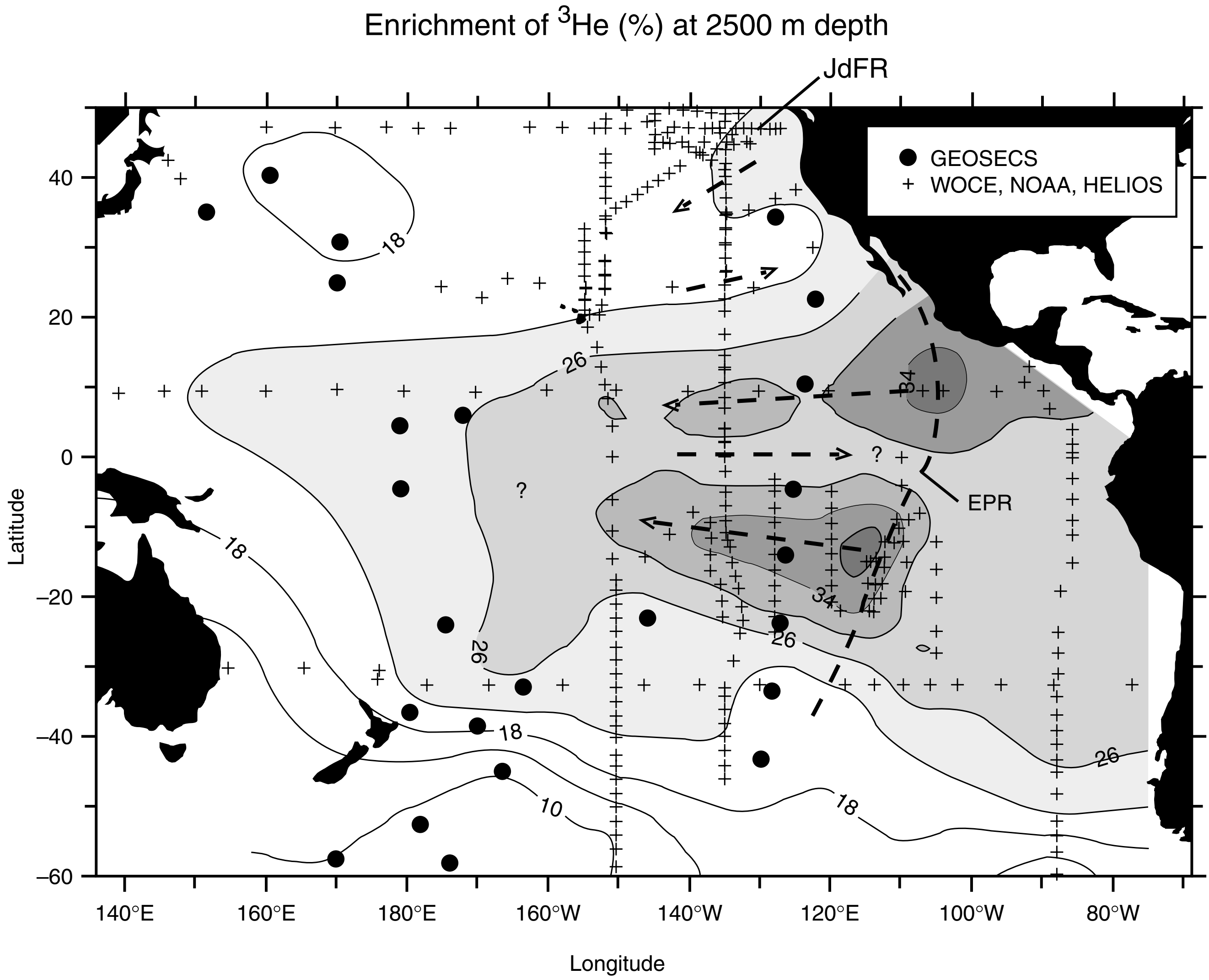

Figure 20. Map illustrating the enrichment of ^{3}He relative to the atmospheric standard (%) contoured on a surface at 2500 m depth in the Pacific. Contour interval is 4%. The major helium sources lie along the East Pacific Rise (EPR) and Juan de Fuca Ridge (JdFR) systems. The dashed arrows indicate areas where the helium plumes define regional circulation patterns. Data from along WOCE sections P4 and P6 from W.J. Jenkins (unpublished data). All other data from Lupton (1998). Reprinted from Ocean Circulate and Climate, P. Schlosser, J.L. Bullister, R. Fine, W.J. Jenkins, R. Key, J. Lupton, W. Roether and W.M. Smethie Jr, 'Transformation and age of water masses', pages 431–452. Copyright (2001), with permission from Elsevier.

3.4.4 Implementation strategy

GEOTRACES should be mindful of sources and sinks at mid-ocean ridges when interpreting results from ocean sections. Where sections pass near mid-ocean ridges, sampling for ^{3}He (Figure 20) will provide a measure of the relative influence of hydrothermal vent fluid among samples collected along the section, and thereby aid in interpreting TEI sources and sinks associated with these systems.

The Southern East Pacific Rise (SEPR) provides a desirable target for evaluation of the sources and sinks of TEIs at mid-ocean ridges. The SEPR is a rapid spreading centre with a well-defined and stable plume that is amenable to study over long distance and time scales (Figure 20). This plume therefore makes a good target for study as part of an ocean section that would address TEI evolution in the hydrothermal plume as it is advected away from the SEPR site. A process-study approach would also be beneficial to characterise near-vent source material injected into the EPR plume.

3.4.5 Links to other programmes

InterRidge: Links to continuing international study of the ridge environment are clear. As well as their possible involvement in process studies at the EPR, a new InterRidge Working Group, 'Biogeochemical Interactions', is focusing on understanding chemical-(micro)biological interactions within hydrothermal systems, particularly at the seafloor. Interaction between this group and GEOTRACES would extend this work into the open ocean.

IODP: GEOTRACES also offers opportunities that complement possible future International Ocean Drilling Programme (IODP) objectives. For example, a significant volume flux and low-temperature heat flux occurs through mid-ocean ridge flanks. These 'flank fluxes' probably play only a minor role in marine geochemical cycles of TEIs, but will be at a maximum on the EPR. Future IODP investigation of sub-seafloor fluid flow and hydrothermal circulation, extending west away from the SEPR axis, would complement the GEOTRACES section in the overlying water.

Ocean Observing Initiatives (e.g., GOOS and ORION): Emanations from ridge spreading centres are generally episodic. The ORION Programme plans to establish a regional, cabled observatory on the Juan de Fuca Plate that would include sensor and sampling instruments on the associated ridge system. Capturing and following the chemistry of specific eruption events will provide unique insights into the input of associated TEIs to oceanic deep water, which will assist in the interpretation of distributions globally.

4. Theme 2: Internal cycling

Marine biogeochemical cycles of TEIs are influenced by a complex suite of transport and transformation processes, which together are referred to here as 'internal cycling'. Transformations involve TEI exchange among dissolved, colloidal and particulate forms, including the uptake of TEIs into biological material and their regeneration when this material decays. TEIs are redistributed by ocean circulation, while gravitational settling of particulate material provides a unique vector transporting TEIs toward their ultimate repository in marine sediments. During their residence time in the ocean, which may range from decades to millions of years, TEIs can be expected to undergo numerous transformations and, except for TEIs with the shortest residence times, to be transported long distances, thus separating the location of their initial source from that of their final removal into marine sediments. Internal cycling therefore plays a role in establishing the distributions of TEIs in the ocean, which is at least as significant as the processes controlling their sources and sinks. Identifying the physical, chemical and biological processes that regulate the internal cycling of TEIs, and quantifying their rates, is therefore crucial in establishing the roles played by TEIs as regulators and recorders of ocean processes.

The principal features of internal cycling are well established for the major nutrient elements, including carbon, in large part as a result of the GEOSECS programme and related work that followed (e.g., Broecker and Peng, 1982). For example, P is incorporated into organic tissue in surface waters. Although most organic tissue is consumed and respired within days of its production, a substantial fraction is exported as sinking detritus to the deep sea, where it is subsequently regenerated. Ocean circulation returns the regenerated inorganic phosphorus to surface waters to be utilised again by phytoplankton, and the cycle is repeated. Phosphorus supplied to the ocean from rivers is recycled in this fashion on average approximately 50 times before finally being buried in marine sediments.

The role of such cycling for TEIs, including important micronutrients and potential contaminants, is currently poorly understood. That uptake and regeneration influence the behaviour of TEIs is, however, evident in their vertical profiles (Bruland and Lohan, 2003). As with the major nutrients, vertical profiles of micronutrients exhibit minimum concentrations in surface waters and values that increase with depth (Figure 2). Even the most insoluble TEIs, as illustrated by Th, are exchanged between dissolved and particulate forms scores of times before finally being removed to the sediments and buried (Bacon and Anderson, 1982).

Although these features were first recognised more than a quarter of a century ago, much remains to be learned about the internal cycling of most TEIs, including the factors controlling their internal cycling, their rates of uptake and regeneration, the impact of these processes on marine ecosystems and the ocean carbon cycle, and the sensitivity of these processes to global change. One of the primary goals of the GEOTRACES programme will be to fill this important gap in our knowledge of marine biogeochemistry.

4.1 Uptake and removal from surface waters

4.1.1 Present understanding

Concentration profiles of many TEIs demonstrate that dissolved elements are removed from surface waters and added at depth (Figure 2). Removal from surface waters occurs by a combination of biological uptake, both into organic tissue and into biogenic minerals, and by abiotic sorption to particle surfaces. In some cases, inorganic precipitation of minerals may occur as well, such as the formation of barite within aggregates of decomposing organic matter. Each of these forms of particulate TEI is subject to regeneration at depth through a combination of processes that include desorption, dissolution and respiration.

Biological uptake of TEIs, as well as their affinity for sorption to particles, depends on their chemical speciation. Many dissolved TEIs exist as complexes, both with organic and inorganic ligands, rather than as free aqueous ions (Bruland and Lohan, 2003). Complexation by dissolved ligands competes for TEIs with sorption to particle surfaces, and the balance between these competing processes influences the overall biogeochemical behaviour of each element. Transformations between dissolved and particulate phases in surface waters often occur through colloidal intermediaries (see Wells, 2002; Doucet *et al*., submitted). Binding by colloids, like complexation by dissolved ligands, affects the bioavailability of TEIs and their affinity for sorption to particles.

Whether dissolved TEIs (normally defined as those that pass through a 0.4 μm filter) in surface waters actually exist as colloids or as truly dissolved species, it is large rapidly sinking aggregates of particulate material that transport TEIs from the ocean surface to depth. A suite of aggregation processes in surface waters transfers TEIs up the particle size spectrum, converting colloids and even suspended cells into forms that sink into the deep sea. These processes include packaging by zooplankton grazers as they filter smaller particles from the water column as well as the binding of particles when they collide as a consequence of Brownian motion, shear and differential settling.

4.1.2 *Areas for advance*

How do uptake and removal vary with chemical speciation and physical form?

Changes in the inorganic and organic composition of seawater may affect the uptake and removal of TEIs in surface waters by altering the fraction of TEIs held in dissolved complexes. For example, many trace elements in surface waters exist predominantly as complexes with strong organic ligands (e.g., Bruland and Lohan, 2003). This complexation will affect both the biological availability of these elements and their affinity for sorption to non-living particles. Our understanding of these effects is currently undergoing a substantial change. Whereas it was once thought that free metal ions were the forms predominantly available to organisms, it is now known that certain organic ligands are engineered to facilitate metal uptake (Morel *et al*., 2003). Much remains to be learned about the impact of organic ligands on the marine biogeochemical cycles of TEIs, and of the sensitivity of these factors to changing environmental conditions.

The chemical speciation of many TEIs and, consequently, their affinity for sorption to marine particles is also known to be pH dependent (Stumm and Morgan, 1996). During peak glacial conditions the carbonate ion concentration and pH of surface waters were both greater than during the pre-industrial modern period. In contrast, the carbonate ion concentration and pH of surface waters today are decreasing due to the ocean's uptake of anthropogenic CO_2 (Feely *et al*., 2004). Thus, the behaviour of TEIs may have changed with the CO_2 content of the atmosphere in the past, and likely will change even more in the future. The extent to which the fundamental properties of TEIs, such as their bioavailability and their residence time in the ocean, changed (or will change) in response to changes in pCO_2 and pH remain unknown.

Spatial and temporal variability of TEI speciation, the sensitivity of TEI speciation to long-term changes in environmental conditions, and the impact on marine biogeochemical cycles of TEIs caused by these changes are largely unexplored. The role of speciation in the marine biogeochemical cycles of TEIs should be studied in a systematic manner, and the results of these studies incorporated into models used to simulate the ocean's response to global change.

How do uptake and removal vary with the supply of lithogenic particles?

Lithogenic particles serve as sources of TEIs to the surface ocean, through desorption and dissolution, while they also serve as agents for removal, through sorption to surface reaction sites. Lithogenic particles also act as 'ballast', increasing the density and sinking rate of marine aggregates, thereby accelerating their removal from surface waters along with their associated TEIs.

Lithogenic particles are delivered to the surface ocean by the atmosphere, as aerosols, by rivers, and by resuspension of coastal sediments. Fluxes of lithogenic particles to the surface ocean have changed in the past, they are changing now, and they will change in the future. Ice-core and marine sediment records inform us that fluxes of mineral aerosols (dust) were greater than today during cold stages of glacial cycles. Lower sea levels during glacial times eliminated many of the estuaries that trap riverine particles today, allowing for the delivery to the open ocean of greater fluxes of lithogenic particles eroded from the continents. Human activities have altered the supply of lithogenic material to the ocean as well. Agriculture and forestry have accelerated erosion rates in many areas, with mobilised soils being carried to the sea by rivers. Supply of lithogenic particles has been reduced, on the other hand, by the construction of dams that trap suspended solids in reservoirs. Changes in the hydrological cycle expected to accompany global warming may also affect the delivery of lithogenic material to the ocean, through processes ranging from increased erosion and runoff in some areas to desertification in others.

The sensitivity of marine TEI cycles to the changes described above is largely unexplored. A quantitative and mechanistic understanding of the supply and removal of TEIs by lithogenic particles is needed, and this understanding must be incorporated into models used to simulate the ocean's response to global change.

How do uptake and removal vary with the structure of marine ecosystems?

Uptake and removal of TEIs from surface waters are sensitive to the composition and structure of marine ecosystems as well as to the abundance of organisms in the water column. An increase in biomass, both autotrophs and heterotrophs, will increase the demand for essential micronutrients, while simultaneously creating more particles capable of removing TEIs by abiotic scavenging. The latter is evident, for example, in the observed increase in disequilibrium between ^{234}Th and ^{238}U with increasing biomass and primary production. In addition to simple biomass, the composition of the autotrophic community (diatoms, cyanophytes, etc.) affects the physiological demand for micronutrients, while the types of heterotrophic grazers (copepods, salps, etc.) largely control the biogenic flux out of surface waters. Large grazers, microbial heterotrophs (e.g., protists) and bacteria all affect particulate TEI regeneration. Thus, biological uptake and removal of TEIs will vary with the composition and structure of marine ecosystems. Ecosystem structure, in turn, is sensitive to many environmental variables that include TEI concentrations and speciation. For example, the demand for iron may be greater when the supply of dissolved silicic acid is sufficient to support the growth of diatoms (Bruland *et al*., 2001).

Although each of these relationships is known from past work, or can be predicted from first principles, there have been few systematic studies of the sensitivity of TEI uptake and removal to variability in the structure of marine ecosystems. Palaeoceanographic studies inform us that marine ecosystems have changed in response to climate variability in the past, so we can anticipate future changes in marine ecosystems as well. How marine biogeochemical cycles of TEIs have responded to past changes in marine ecosystems, and how they will respond to future changes, is largely unexplored. Thus, the rates of TEI uptake, regeneration, and flux in the modern ocean should be determined, together with the sensitivity of these rates to changes in the composition and structure of marine ecosystems. This information, in turn, should be incorporated into models to portray accurately the TEI-related feedback mechanisms that link ecosystem structure and the ocean carbon cycle to global change.

How do biological uptake and regeneration affect the isotopic fractionation of micronutrients?

As we have seen for N (Sigman *et al*., 1999) and Si (de la Rocha *et al*., 1998), isotope fractionation of micronutrients has the potential of providing important and unique information on their cycling in the marine environment and their interaction with the marine biota. Metals such as Fe, Zn, Cu, Cd, Mo, Se, which are utilised in biological processes, have the potential to leave an isotopic fingerprint of these transformations. This potential needs to be assessed.

4.1.3 Specific GEOTRACES objectives

1. Determine the effect of speciation on the uptake and removal rates of TEIs in surface waters.

2. Determine the impact of the abundance and composition of colloids on the uptake and removal of TEIs in surface waters.

3. Determine the sensitivity to supply of lithogenic material of the uptake and removal rates of TEIs in surface waters.

4. Determine the sensitivity to changes in ecosystem structure of the uptake and removal rates of TEIs in surface waters.

4.1.4 Implementation strategy

Many of the above objectives are shared with parallel ocean biogeochemistry programmes (e.g., SOLAS and IMBER; see below), with which GEOTRACES will seek mutually beneficial collaboration. In some areas (e.g., TEI fluxes, chemical speciation) GEOTRACES will be best suited to take the lead. Research in other areas (e.g., TEI bioavailability; the purposeful generation of ligands by organisms, for example, to sequester micronutrients or for detoxification purposes) is best led by programmes having greater emphases on marine biology and ecosystem research.

A multifaceted approach of basin-wide sections and specific process studies is required to achieve the above objectives. Substantial progress can be made by exploiting natural spatial and temporal variability of TEI uptake and removal from surface waters. This will require a combination of measurements along ocean sections that span

- end-member water masses;
- regions expected to have high rates of TEI transformation;
- spatial gradients in ecosystem structure (Figure 21);
- spatial gradients in lithogenic particle supply (Figure 13); and
- spatial gradients in chemical speciation;

as well as measurements at time-series stations (Figure 22) where these parameters change in known, if not predictable, patterns. Such changes occur, for example, following the seasonal cycle of biological productivity or associated with events such as dust storms.

4.1.5 Interaction with other programmes

IMBER, SOLAS and Time-Series Stations: GEOTRACES shares an interest in understanding metal-biota interactions with IMBER (Theme 1, Issues 1 and 2; Theme 2, Issue 2 and 3) and SOLAS, and will seek collaborative efforts. It would be mutually beneficial if studies of the chemical speciation of TEIs and their rates of cycling and transformation in surface waters could be coordinated with complementary research on the structure of marine ecosystems and on the rates of biological processes. Indeed, the *IMBER Science Plan and Implementation Strategy* (http://www.imber.info/products/IMBER_SPIS_Final.pdf) lists specific collaborations with GEOTRACES on transects (IMBER, pp. 47, 50 and 63), and we envision a similar opportunity for collaboration on their process studies (IMBER, p. 48) and 'sustained observations' at time-series stations such as HOT and BATS (IMBER, pp. 48–49; Fig. 22). The linkage of the two programmes will be mutually beneficial, providing crucial TEI concentration and speciation information for them, and biological rate and mechanistic information for GEOTRACES, resulting in a truly interdisciplinary approach to studying biogeochemical (i.e., internal) cycling. It is hoped that the establishment of open ocean observatories will serve as locations for time-series and process studies associated with the IMBER and SOLAS programmes and thus be important locations for examining the biogeochemistry of TEIs.

Powerful new tools in the emerging fields of genomics and proteomics provide an opportunity to integrate many

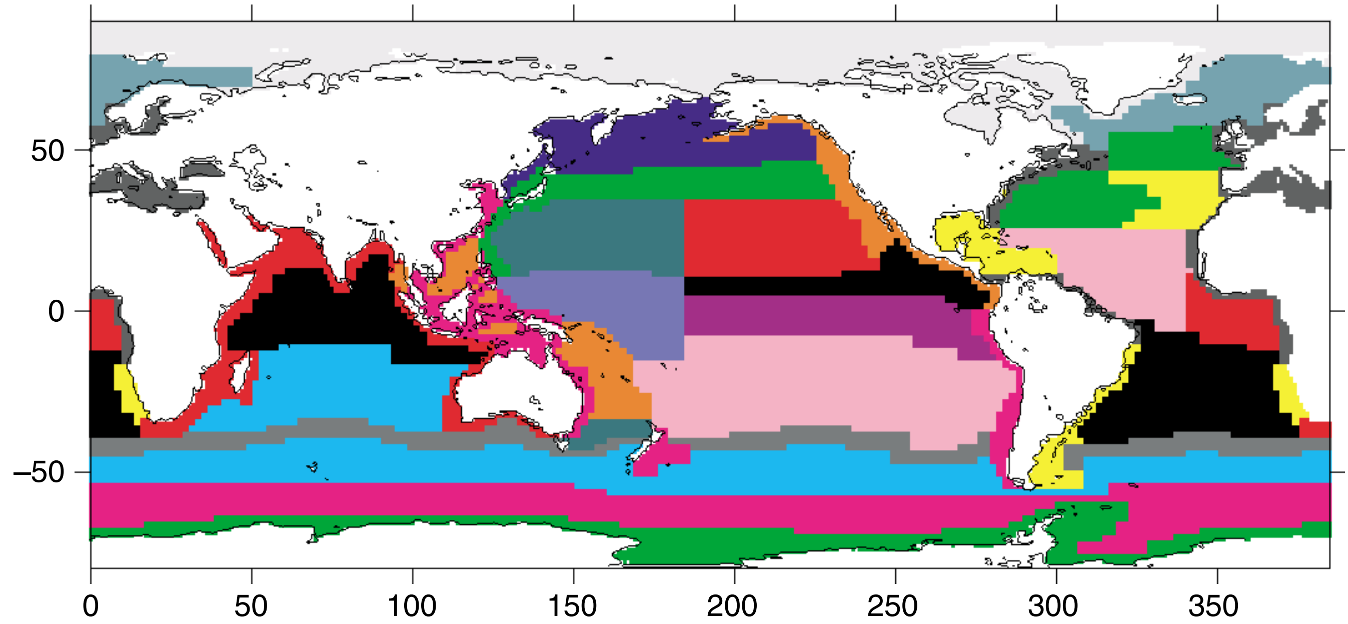

Figure 21. A division of the ocean into 57 biological provinces based on surface and vertical distribution of chlorophyll, mixed-layer depth and surface nutrients (Longhurst, 1998). Modified from Ecological Geography of the Sea, A.R. Longhurst. Copyright (1998), with permission from Elsevier.

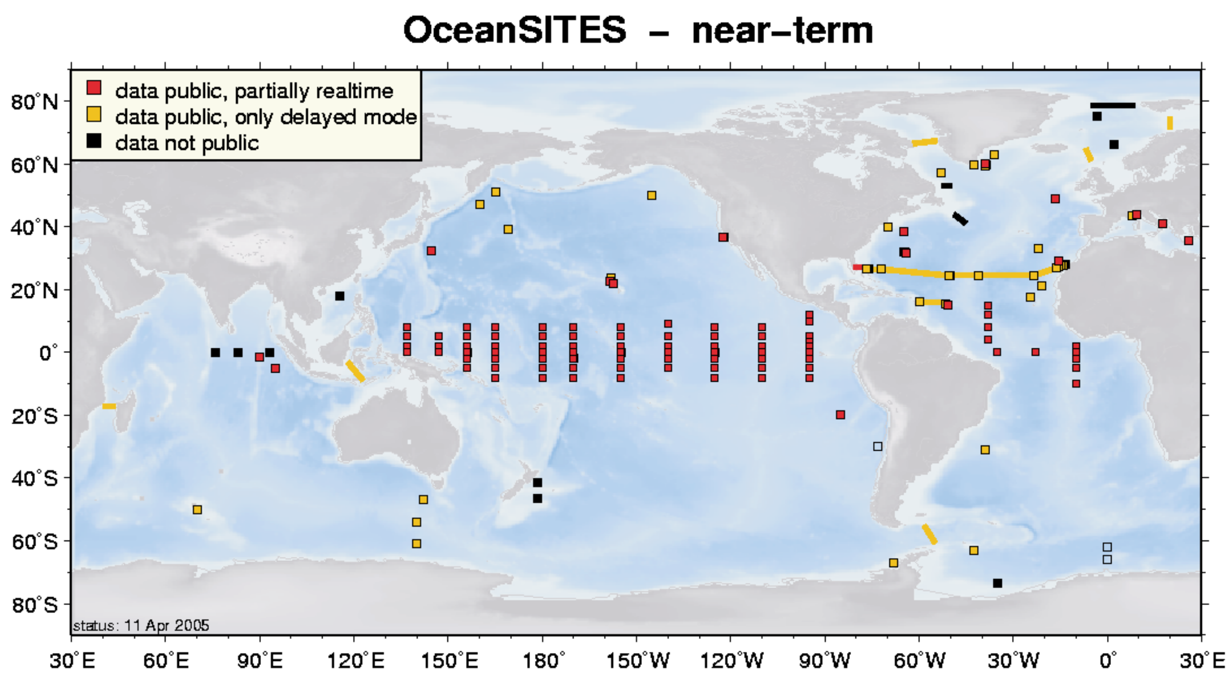

Figure 22. The locations of existing or planned time series. Source http://www.oceansites.org/OceanSITES/docs/pogo4.pdf.

common objectives of these programs. This is because molecular diagnostics of physiological conditions such as Fe or P limitation can replace time-consuming process studies that are inconsistent with the survey/section approach of GEOTRACES (LaRoche *et al.*, 1996; Webb *et al.*, 2001; Dyhrman *et al.*, 2006). Techniques that involve rapid sample collection and freezing for subsequent analysis ashore will be a small burden logistically, but will provide useful data on the relationship between TEI distribution and wide-scale ecosystem effects. Such information will enable GEOTRACES to play a critical role in refining the boundaries of biogeochemical regimes in the oceans, like those proposed by Moore *et al*. (Figure 8).

4.2 *Uptake and regeneration in the subsurface ocean*

4.2.1 Present understanding

Particulate TEIs exported from surface waters through sinking particles are regenerated in the subsurface ocean through a combination of oxidation, dissolution and desorption processes. Concentration profiles of some TEIs provide first-order information about these processes (Bruland, 1983). For example, the relatively shallow concentration maxima of certain TEIs, such as Cd, are interpreted to indicate regeneration by a relatively rapid process, such as the oxidation of organic matter. Deeper concentration maxima of other TEIs, such as Zn, Ba and Ge, suggest regeneration through slower processes, such as the dissolution of more refractory biogenic minerals.

Particles remove dissolved TEIs from the water as well as serving as a source. Evidence for deep removal by adsorption on settling particles (scavenging) comes primarily from the study of natural U-series radionuclides (e.g., ^{230}Th, ^{231}Pa and ^{210}Pb) (Cochran, 1992). Analysis of particulate material collected by sediment traps shows that the fluxes of these isotopes increase with depth, indicating active scavenging of these nuclides over the entire water column (Anderson *et al*., 1983). Most of the biogenic particles that survive their transit through the water column are eventually regenerated at the seabed. Many TEIs carried by these particles are regenerated also. Regeneration of TEIs in surface sediments is discussed in the next section.

4.2.2 Areas for advances

There is a need to learn more about the rates and processes of uptake and regeneration in the subsurface ocean, and their sensitivity to environmental variables. For instance, an increase in scavenging rate or a decrease in regeneration rate of a TEI acting as a micronutrient will increase the efficiency of its removal from the ocean, thereby decreasing its inventory and rate of supply to surface waters. Many TEIs also have tremendous potential as tracers and integrators of relevant oceanic processes, both in the modern ocean (e.g., suspended barite accumulation in the mesopelagic zone to quantify apparent oxygen utilisation rate) and past ocean (e.g., Hf, Pb, Nd isotopes as water mass tracers). Changes in environmental conditions, however, could decouple TEIs from the processes they are used to trace and induce misleading interpretations. There is thus a need to gain a quantitative understanding of the mechanistic underpinning of these relationships, to clearly identify and take into account these possible effects.

How does chemical speciation affect uptake and regeneration in the subsurface ocean?

Speciation has a profound effect on the biogeochemical attributes of poorly soluble elements (e.g., Fe, Th). The chemical speciation of dissolved TEIs, particularly organic complexation, must influence their abiotic adsorption on particles (Quigley *et al*., 2001, 2002). The effective solubility of iron is much enhanced by complexation with organic ligands, as its deep water concentration (0.7–1 nM; Johnson *et al*., 1997) is much greater than its solubility (estimated to be about 0.1 nM; Liu and Millero, 2002). A balance between solubilisation by organic ligands and scavenging must form the basis for the deep water distributions of Fe, which does not appear to conform to the usual pattern of nutrient behaviour with enrichment from the deep Atlantic Ocean to the deep Pacific Ocean. An accurate knowledge of the speciation of TEIs in deep water is thus critical to our understanding of their internal ocean recycling. Likewise, the physical and chemical forms of particulate TEIs must influence their rates of regeneration from particles. Knowledge of the partitioning of TEIs among the different particle constituents should thus be a priority for understanding the regeneration cycle of TEIs.

How does particle composition affect scavenging of TEIs in the subsurface ocean?

Empirical evidence has indicated that certain TEIs adsorb preferentially to specific solid phases. This represents a fundamental aspect of the marine biogeochemical cycles of TEIs, and a better characterisation of these relationships is a necessary first step toward assessing the sensitivity of these cycles to global change. Recent work has produced conflicting evidence about the relative affinity for sorption by certain TEIs to major particulate phases (e.g., Luo and Ku, 1999, 2004; Chase *et al*., 2002; Chase and Anderson, 2004), as well as about the role of water composition (e.g., pH, and concentrations of TEI-complexing ligands) in the absorption of TEIs to particles (Geibert and Usbeck, 2004). These discrepancies must be resolved and the relative affinity of all important TEIs for major particulate phases must be determined unambiguously.

How do particle dynamics affect uptake and removal in the subsurface ocean?

The internal cycling of TEIs is significantly affected by partitioning between suspended and sinking particles (Figure 23). Particles sinking to the seafloor and particles suspended in the water column are both sources and sinks of TEIs. Sinking particles also transport TEIs from shallow to deeper water. The trade-off between uptake, regeneration and removal is strongly dependent on particle aggregation, disaggregation, degradation and sinking rates (Murnane *et al*., 1996). Accurate representations of particle dynamics and their sensitivity to changes in the composition and flux of particles are thus vital for understanding and modelling the marine biogeochemical cycles of TEIs.

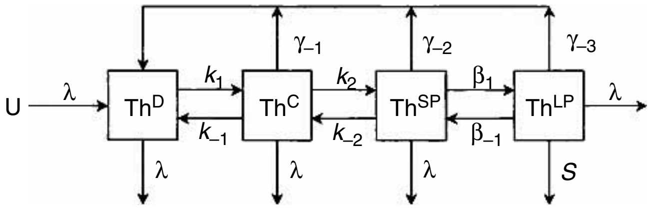

Figure 23. A schematic representation of the particle scavenging of an insoluble element such as Th (Cochran and Masque, 2003). Understanding and correctly modelling such particle dynamics is key to accurately capturing the cycling of many trace elements in the ocean. In the figure above, U and Th refer to parent–daughter pairs (either ^{238}U–^{234}Th or ^{234}U–^{230}Th). Superscripts D, C, SP and LP refer to dissolved, colloidal, small-particle and large-particle forms of Th, respectively. Rate constants k_1, k_2 and β_1 refer to the forward processes of adsorption to colloids, coagulation of colloids, and aggregation of small particles into large particles, respectively. Rate constants with negative subscripts refer to the reverse processes. Greek symbols "λ" and "γ" refer to the rate constants for radioactive decay and for particle regeneration, respectively. The sinking rate of large particles is represented by S. Reproduced with permission from the Mineralogical Society of America.

What are the depth scales for particulate TEI regeneration and what is their sensitivity to environmental variables?

The depth scale for regeneration of particulate TEIs is a fundamental parameter influencing their marine biogeochemical cycles. Regeneration in the thermocline allows TEIs to be returned to the surface ocean on timescales of years to decades. Regeneration in deeper waters, or at the seabed, can extend the timescales for return to the surface to centuries or even millennia.

The depth scale over which particulate TEIs are regenerated depends on the rate at which the particle carriers sink, as well as on the rates of the regeneration processes themselves. Particle sinking rates vary with the size, morphology and density of particles. These parameters, in turn, depend on particle aggregation, disaggregation and composition. Thus, determining the depth scale of regeneration and its dependence on environmental variables requires study of particle dynamics (see above). Particle regeneration rates vary with the composition of the particles and with the concentrations of certain dissolved species in ambient seawater (e.g., oxygen, carbonate ion, silicic acid, pH). Temperature affects the rates of these processes as well. The sensitivity to each of these factors of the time and depth scale for regeneration of particulate TEIs must be established, and these parameters must be encoded in models, to simulate the response of marine biogeochemical cycles of TEIs to global change.

4.2.3 Specific GEOTRACES objectives

1. Determine the partitioning of TEIs among dissolved, colloidal and particulate (adsorbed and lattice-held) forms in the subsurface ocean, and the sensitivity of that partitioning to changes in particle composition and in the dissolved speciation of the TEIs.
2. Determine the regeneration depth scales of TEIs in the subsurface ocean, their spatial variability, and their sensitivity to changes in the composition and flux of particles.
3. Determine particle aggregation, disaggregation and sinking rates, and their sensitivity to changes in the concentration, flux, size distribution and composition of particles.

4.2.4 Implementation strategy

Achieving the objectives above will require careful coordination of ocean sections, time-series work, laboratory experiments and modelling. As for the study of internal cycling in surface waters (Section 4.1), substantial progress can be made by exploiting natural spatial and temporal variability of TEI uptake, removal and regeneration. This will require a combination of measurements along ocean sections that span:

- spatial gradients in seawater composition (e.g., oxygen minimum zones) that are expected to influence the chemical speciation of TEIs as well as the behaviour of particulate-carrier phases;
- spatial gradients in biological productivity;
- spatial gradients in ecosystem structure (Figure 21); and
- spatial gradients in lithogenic particle supply (Figure 13).

Time-series stations will complement the survey work by exploiting:

- natural temporal (especially seasonal) variability to assess the sensitivity to changes in particle composition of the partitioning of TEIs between dissolved and particulate forms;
- the contrasting chemical composition of suspended and sinking particles to provide insight into exchange of materials between these two particle pools; and
- natural stable and radioactive isotopes to constrain aggregation, disaggregation and sinking rates of particulate material.

Regeneration of TEIs will be evaluated by applying inverse models to their measured distributions, while controlled laboratory experiments can be envisioned to study the sensitivity to respiration, mineral dissolution, temperature, pH, oxygen concentration, and other variables of the partitioning of TEIs between dissolved and particulate phases.

4.2.5 Interaction with other programmes

Time-series stations and global observatories: Existing time-series stations have regular programmes to collect sinking particles in sediment traps while planned global observational networks (e.g., ORION) will provide additional opportunities to exploit natural temporal variability in the study of TEIs (Figure 22). These stations would be well suited for partnering with GEOTRACES studies of TEI regeneration in the subsurface ocean.

4.3 Regeneration at the seafloor

4.3.1 Present understanding

Diagenetic processes in surface sediments change the composition of incoming particles radically. For example, most of the biogenic particles that survive their transit through the water column are eventually regenerated on the seabed. The major part (order 99%) of the organic material reaching the seabed is respired. A large but variable fraction of biogenic minerals (e.g., opal, calcite, aragonite, barite) is dissolved at the seafloor. The fraction dissolved depends in part on bottom water chemistry, but also on the rate of sediment accumulation, with preservation generally increasing with increasing sediment accumulation rate. Regeneration of biogenic carrier phases will release some TEIs to solution. Other TEIs may be mobilised by desorption, reduction, or complexation due to the changing chemical environment. Upon release by these various diagenetic processes, TEIs may either adsorb to other surfaces in their sedimentary surroundings or return to the water column, where they may participate once again in the cycle of uptake and regeneration.

As the upper sediment layer is usually bioturbated, particles remain in contact with the bottom water until they are buried below this mixed layer after a period that varies from decades to thousands of years. Thus, the timescale for reactions that lead to regeneration of TEIs on the seabed can be quite large.

Studies of diagenesis have concentrated on the dissolution of biogenic minerals, the regeneration of organic material and the resulting behaviour of a series of trace elements influenced by these processes. For some elements, extensive pore water analysis has been done (Mn, Fe, N, P, Si, etc.). Similarly, diagenetic fluxes into and out of the sediments have been evaluated for some TEIs using benthic flux chambers. However, existing data are still insufficient to assess the impact of benthic recycling on biogeochemical cycles at a global scale for most of the TEIs.

4.3.2 Areas for advance

A complete understanding of the internal cycling of TEIs in the subsurface ocean requires knowledge of the fraction of each particulate TEI reaching the seabed that is regenerated and returned to the water column, versus the fraction that is buried. Equally important is knowledge of the processes and conditions that regulate the fraction of each TEI that is regenerated, so that the sensitivity of these important recycling processes to changing environmental conditions can be assessed accurately. For most TEIs, the ratio of the fraction returning to the water column to the fraction buried is unknown. Spatial variability of this ratio, and factors regulating its variability, are unknown as well. Quantifying the regeneration and burial of TEIs in marine sediments is an essential step toward characterising their biogeochemical cycles.

4.3.3 Specific GEOTRACES objectives

1. Determine the fraction regenerated at the seafloor for particulate TEIs of interest.
2. Identify specific processes responsible for TEI regeneration.
3. Characterise the spatial variability of the fraction of particulate TEIs regenerated as well as the sensitivity of this variable to sediment composition, sediment accumulation rate, rain rate of biogenic particles, bottom water composition (e.g., pH, temperature, and the concentration of oxygen, carbonate ion and dissolved silicic acid), redox conditions and other environmental parameters.

4.3.4 Implementation strategy

Two complementary approaches can be used to constrain recycling of TEIs at the seafloor:

1. The composition of particles reaching the seafloor can be compared with the composition of the sediment that accumulates at any given site to estimate the fraction of each TEI that is buried versus the fraction regenerated. Applying the ^{230}Th normalisation method to correct for sediment focusing will further allow actual burial rates and regeneration fluxes to be derived; and
2. Fluxes induced by diagenetic reactions can be determined by measuring and modelling TEI distributions in pore waters, and by measuring TEI fluxes across the sediment–water interface using benthic flux chambers.

Sites selected for study of TEI regeneration at the seabed should encompass a range of conditions. Much larger fluxes of biogenic particles typically occur at ocean margins, compared with the central ocean gyres, often leading to intense oxygen minimum zones within the water column and chemically reducing conditions within surface sediments at ocean margins. Transects from the ocean interior towards different types of margins, with different productivity, bottom water oxygen concentrations, lithogenic input, sediment resuspension and nepheloid transport, would thus be ideal to study the influence of these factors on the regeneration of TEIs.

Similar studies of TEI burial and regeneration should be carried out at pelagic sites crossing strong lateral productivity gradients such as found at the Equator or across polar and subpolar fronts. Comparing results from these diverse regions will elucidate the relative importance for TEI recycling and burial in the large areas covered with pelagic sediments and the much smaller zone covered with margin sediments.

4.3.5 Interaction with other programmes

Studies of deep-sea particle fluxes using sediment traps have been conducted at many sites throughout the ocean over the past quarter century. Some of these have been one-time efforts whereas others have been incorporated into time-series studies of longer duration. Many of these studies have archived samples of sediment trap material that could be used as a vital component of a systematic study of TEI regeneration at the seabed.

Similarly, many studies have focused on fluxes and processes in surface sediments. This type of work has benefited tremendously from the development of the multi-core device that recovers surface sediments with minimal disturbance. Unlike longer piston and gravity cores that are frequently archived in national and regional repositories, multi-cores are often retained in the personal collections of the investigators who recovered them. GEOTRACES should engage IMAGES and other programmes that have had extensive coring efforts to catalogue available multi-core samples, and to secure access to as many of these as possible to be used within a global survey of TEI regeneration at the seabed.

4.4 Physical circulation

4.4.1 Present understanding

The physical circulation of the ocean is a major determinant of the global distributions of TEIs. Historically, much of what we know about the biogeochemical behaviour of all ocean properties has been diagnosed from their observed distributions combined with our knowledge of circulation and mixing. The fundamental physical principles underlying ocean circulation have been known for some time, and recent global-scale field programmes such as WOCE, combined with advances in satellite observations, have led to a more thorough characterisation of the basic large-scale transport of materials in the ocean. This advance has been complemented by continued progress in higher resolution and coupled global circulation models, particularly those with embedded biogeochemical parameterisations. Measurements of transient tracers have also proved useful in diagnosing mixing, ventilation and circulation, as well as model testing and comparison. We have also made strides in our understanding of what these tracers can and cannot tell us about ocean processes. Tracers have also been used to make more direct inferences of *in situ* biogeochemical rates, for example, for oxygen utilisation and nutrient remineralisation.

The distributions of the TEIs are similarly governed by the interaction of physical and biogeochemical processes as well as by their sources and sinks. The relative importance of these factors depends strongly on the particular TEI's intrinsic biogeochemical attributes, which can vary characteristically in both space and time. Given a determination by GEOTRACES of the distributions of the TEIs on global and regional scales, as well as in areas of enhanced biogeochemical activity, we have the interpretive tools to make quantitatively useful inferences about the biological and geochemical behaviour of many of these substances in the ocean environment.

Planning for WOCE in the 1980s assumed that global hydrographic sections occupied over 5–7 years would form a single global 'snapshot' of ocean circulation, but during the field phase it became clear that ocean circulation is changing even on that timescale. Similarly, it cannot be assumed that global distributions of TEIs will not change during the GEOTRACES field phase. However, even more than for WOCE, our knowledge of global distributions of TEIs is so rudimentary that much will be learned from the global survey.

4.4.2 Areas for advance

Ocean circulation constraints on TEI distributions

Given the above, the primary impediment to progress is our lack of knowledge about the global- and regional-scale distributions of many of the TEIs. Although measurements for some TEIs (notably Al and Fe) are being made on a few ocean transects, we do not yet have even a first-order assessment of the large-scale distributions, gradients and inventories of many TEIs. Regional-scale distributions, particularly in regions of strong biogeochemical or redox 'forcing' (e.g., oxygen minimum zones), as well as the property gradients between regions, are not well documented. With such observations, we will be in a position to answer quantitative questions about the integrated behaviour and characteristics of TEIs in the oceanic environment. Combined with a continuously improving knowledge of large-scale ocean circulation and mixing, it should be possible to diagnose the underlying biogeochemical processes that influence the distributions of many of the TEIs.

In particular, GEOTRACES will address the question of how global- and basin-scale ocean circulation sets up and maintains the global-, basin- and regional-scale distributions of TEIs. This interplay between biogeochemical and physical forcing will differ in character among the individual TEIs, dependent on their particular biogeochemical characteristics. Precisely how they differ provides important information on the underlying processes, and provides us with constraints on mechanistic models of their biogeochemistry. We can ask questions about how the wind-driven circulation (e.g., subduction, upwelling and boundary currents) interacts to create special regional environments, such as oxygen minimum zones, which strongly influence TEI distributions. Studies in these regions may be particularly informative regarding the underlying processes. Finally, it is conceivable that the influence of sub-mesoscale motions on the distributions of rapidly reactive or short-lived TEIs may present us with significant sampling issues. What is the impact of these processes on, for example, offshore transport of reactive elements?

Radiocarbon is an example of a TEI that has been extensively measured in the global ocean as a part of previous observational programmes (e.g., GEOSECS and WOCE), and which shows a rich spatial texture (Figure 9). Despite the complex nature of its history (natural cosmogenic radiocarbon, Suess effect, dilution with 'dead' fossil-fuel carbon, and the transient nuclear bomb input), its long exchange timescale at the sea surface and its involvement in the remineralisation/carbon cycle, the oceanic distribution of ^{14}C has proved useful to effectively constrain and evaluate large-scale ocean models (Guilderson *et al*., 2000). Incorporating other TEIs into these models provides a strategy to constrain their rates of transport and cycling in the deep sea.

Role of ocean circulation in micronutrient supply to surface waters

The pathways whereby major and micro-nutrients that have been regenerated within the water column are returned to the ocean surface layers to support new production is currently not well understood (Williams and Follows, 2003; Sarmiento *et al*., 2004). Depending on the depth at which the nutrients have been remineralised, the timescales over which this transport occurs range from as little as a year to many decades. This process is thus a rate-limiting step in the regulation of new production on decadal timescales, and is often characterised in ocean models by idealised mixing processes that may not represent the true mechanisms. The stable, inert isotope ^{3}He exhibits simple *in situ* behaviour (no chemical or biological sources or sinks). It is created at a known rate by ^{3}H decay in the subsurface region where most nutrient regeneration occurs, whereas it is lost to the atmosphere at the air–sea interface. Helium-3 therefore traces the return pathways in a clear and unambiguous fashion. In combination with its parent, bomb tritium, ^{3}He offers the determination of water mass ventilation timescales, the depth distribution of major and micro-nutrient regeneration, and the return pathway. Figure 24 shows the distribution of these isotopes against potential density anomaly along a meridional section in the Pacific Ocean. Note the upward mixing of ^{3}He across isopycnal surfaces in the tropical region. This highlights the pathways that remineralised nutrients take in their return to the upper ocean. Coupling high-resolution models of TEI distributions with data such as those shown in Figure 24 provides a means to estimate rates of micronutrient supply to surface waters.

Rates of ocean circulation not amenable to direct observation

Finally, the unique boundary conditions and relatively well characterised *in situ* behaviour of some TEIs, for example the four Ra isotopes in coastal regions (Moore, 1996), give prospects for illuminating and quantifying aspects of ocean mixing and transport that are otherwise difficult to characterise. Characterisation and modelling of such isotopes in key areas will likely provide strong constraints on ocean mixing and flow in boundary areas (e.g., Moore, 2000). That these same physical processes are important for several other TEIs makes this approach particularly valuable. In addition, inert gas distributions in the ocean can be used to infer rates of mixing and air–sea gas exchange. Several of the GEOTRACES TEIs can also be used to infer palaeoceanographic changes in circulation (Section 5).

4.4.3 Specific GEOTRACES objectives

The oceanic distributions of TEIs are governed by a combination of physical and biogeochemical processes. Interpretation of TEI distributions given quantitative knowledge of the circulation, mixing and ventilation of the water masses within which they reside can lead to a time- and space-integrated measure of the *in situ* biogeochemical behaviour of these elements. GEOTRACES will attempt to:

1. Evaluate inter-basin and regional fluxes of TEIs.
2. Evaluate TEI fluxes within coastal systems and their exchange with the open ocean, including those characterised by high rates of primary productivity and those with intense subsurface oxygen minima.
3. Develop a model-based context for intelligent interpretation of limited or 'spot' TEI measurements.
4. Extrapolate regional measurements to global-scale TEI fluxes and inventories using a combination of models and complementary tracers.

4.4.4 Implementation strategy

Characterising regional- to basin-scale TEI fluxes requires the simultaneous determination of the distributions of the key TEIs along with the ventilation timescales, as well as the mixing and circulation rates of the water masses within which they reside. Complementary sources of information include:

- Physical transport will be obtained primarily by knowledge of the large-scale flow fields gained through WOCE and CLIVAR programmes, coupled with state-of-the-art models;
- The GEOTRACES global survey will provide the information essential for quantitative estimates of time-mean fluxes of TEIs;

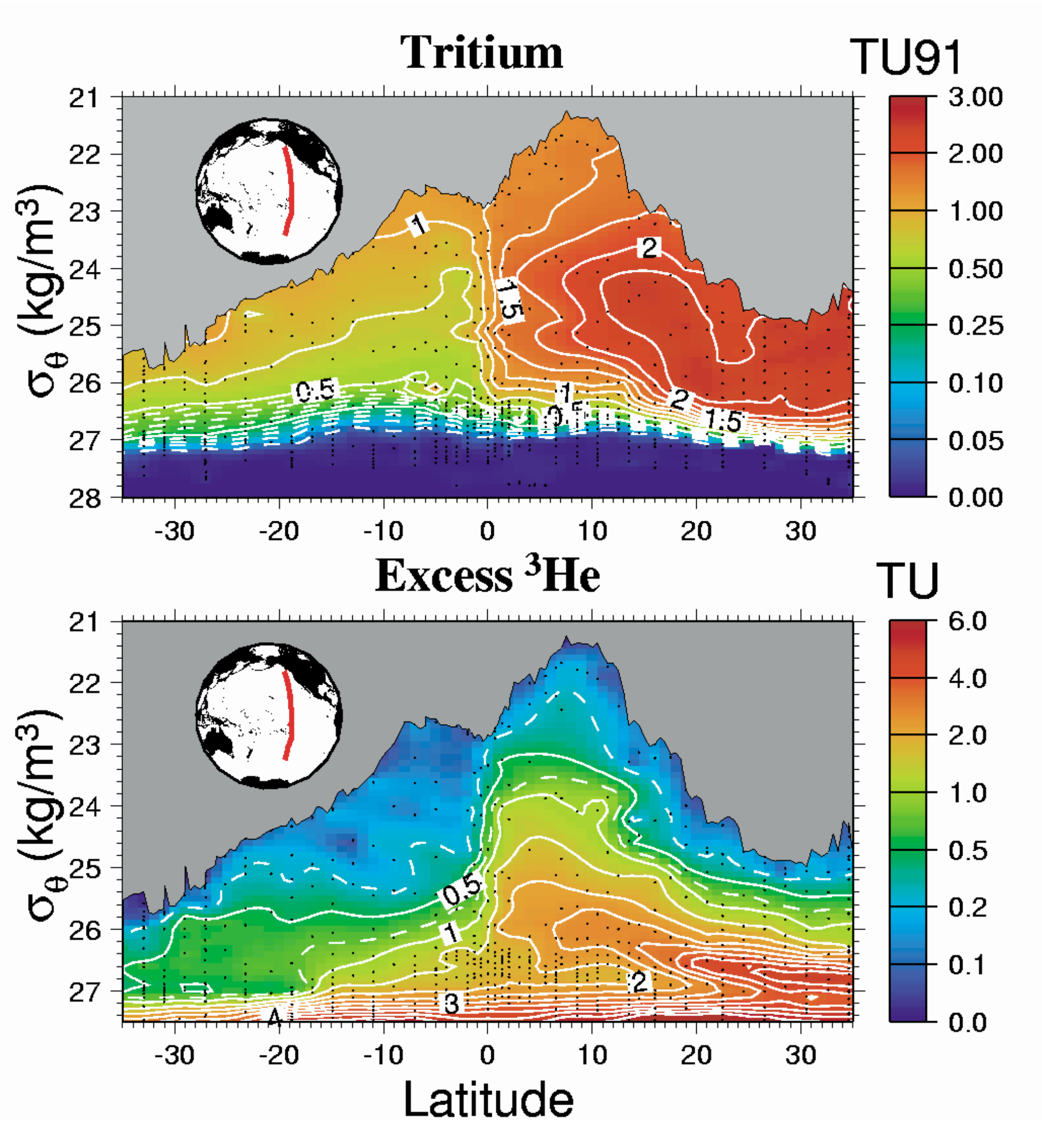

Figure 24. A meridional section of tritium (upper panel) and ^3He (lower panel) in the Pacific Ocean from WOCE. The location of the section is shown in red in the inset of each panel. Figure provided by W. Jenkins.

- Simultaneous measurement of diagnostic TEIs and tracers (e.g., Ra isotopes in margin zones, in some areas inert gases, $^3He/^3H$ and CFCs) will provide additional needed constraints on physical transports.

In addition, high-resolution regional/coastal models will be used along with remote sensing to allow the intelligent interpretation of 'spot' TEI measurements in potentially highly variable, episodic and patchy areas. The inherent difficulty of most TEI measurements almost always leads to a heavily under-sampled system. However, it is possible to embed these intrinsically sparse measurements within a matrix of more highly resolved observations, and an appropriate model, to obtain a realistic estimate of the underlying transport processes influencing measured TEI distributions.

4.4.5 Interaction with other programmes

CLIVAR: The programme with the greatest overlap and synergy in this area is CLIVAR. The GEOTRACES programme will benefit from embedding its observations within the wider space and time framework of tracer and hydrographic observations made within the CLIVAR field programme, and will use model and data products from CLIVAR. Some TEI observations will ultimately be of value in later generations of circulation models, particularly as the latter gain in sophistication.

Ocean Observing Networks: The development of ocean observing networks (e.g., GOOS, ORION) will help to constrain the time-varying circulation and transport terms that influence TEI distributions.

5. Theme 3: Development of proxies for past change

Uncertainty in our ability to predict future climate change is one of the most important problems facing society today. Modern infrastructure is based on a steady-state understanding of global weather patterns. In the United States, for example, there is an efficient transportation grid for the transfer of farm products, grown largely in the centre of the country, to the coasts where most of the people live. Changes in the climate mean state could drastically alter the geography of this arrangement. Elsewhere, in low-lying coastal regions around the world, accelerated sea-level rise due to the combined effects of rising temperatures and melting continental ice threatens the existence of many large cites and rural communities.

A key approach to understanding the range of future climate change is to better constrain the nature of past climate variability. Study of such past change has identified the presence of large-amplitude climate variation and very rapid transitions between climate states. We have also learned that the CO_2 content of the atmosphere, largely set by oceanic processes, has varied in concert with the glacial cycles. Yet we still do not understand the mechanism behind changes in either the mean climate state or its relation to atmospheric CO_2.

Because climatically important ocean variables such as temperature, salinity and macronutrient concentrations cannot be directly measured for the past, we must constrain them by 'proxy'. Proxies utilising geochemistry provide most of our reconstructions of past ocean conditions and have been particularly used to assess two aspects of Earth's climate system: the physics of ocean–atmosphere circulation and the chemistry of the carbon cycle. Of the many variables within the coupled ocean–atmosphere climate system, these two 'state variables' are both relatively poorly known in the past but are accessible by TEI proxies in ocean archives. A comprehensive understanding of the various proxies used to reconstruct these important state variables is therefore of considerable societal importance.

Despite this importance, most proxies (of necessity) have been calibrated in a rather *ad hoc* way. Most calibrations use samples that do not necessarily represent modern conditions, or they have been calibrated solely in the laboratory. And calibration is normally empirical and based on only partial understanding of the processes that relate the measurable proxy to the environmental variable that it encodes. There is therefore an urgent need for more thorough assessment of geochemical proxies to fully understand the uses and limitation of present proxies, and to develop and reliably calibrate new proxies for environmental variables that are currently difficult to reconstruct.

The most widely used palaeoproxies rely on the geochemistry of seawater and on the precipitates that form from seawater (including sediments, corals, microfossils, ferromanganese crusts, etc.). Calibration of proxies therefore belongs naturally in a marine geochemistry programme such as GEOTRACES. Improved understanding of the cycles of TEIs will lead, inevitably, to improved understanding of the proxies that rely on these TEIs. By appropriate design of the measurements made within the programme, pursuit of these complementary objectives will provide considerable new knowledge about proxy reconstruction of the past within a solid process-focused framework, and with considerable cost-effectiveness.

Proxies are captured in a variety of sedimentary substrates and record information about past environmental conditions in three ways:

1. They directly reflect the chemical properties of the water mass in which the substrate forms, where this chemistry reflects an aspect of the past environment (i.e., it has spatial structure that encodes a variable such as nutrient content or water mass distributions). Examples of such 'direct' proxies include Cd/Ca and ε_{Nd}.

2. They record conditions indirectly though fractionation between the water mass and the substrate, where this fractionation is dependent on environmental conditions such as temperature (e.g., Mg/Ca and Ca isotope ratios in $CaCO_3$) or pH (e.g., B isotopes).

3. They provide information about the fluxes of materials to the seafloor as recorded in bulk sedimentary properties (e.g., ^{230}Th, $^{231}Pa/^{230}Th$, Ba and barite accumulation rates).

Prospects for advance in knowledge exist in each of these areas and these are discussed in the following three subsections.

5.1 Factors controlling 'direct' proxy distribution in the ocean

5.1.1 Present understanding

The vertical distribution of a given element in the modern ocean results from a combination of processes such as physical transport, chemical (thermodynamic) control and biological activity. A better understanding of the modern distribution of TEIs is therefore a key component of GEOTRACES' utility to palaeoceanography. Establishing a comprehensive data set of TEIs that are identified as potential palaeoproxies will allow identification of the processes that dominate their distribution. This is particularly true for 'direct' proxies, for which the section approach of GEOTRACES is similar to that often used for palaeoreconstruction.

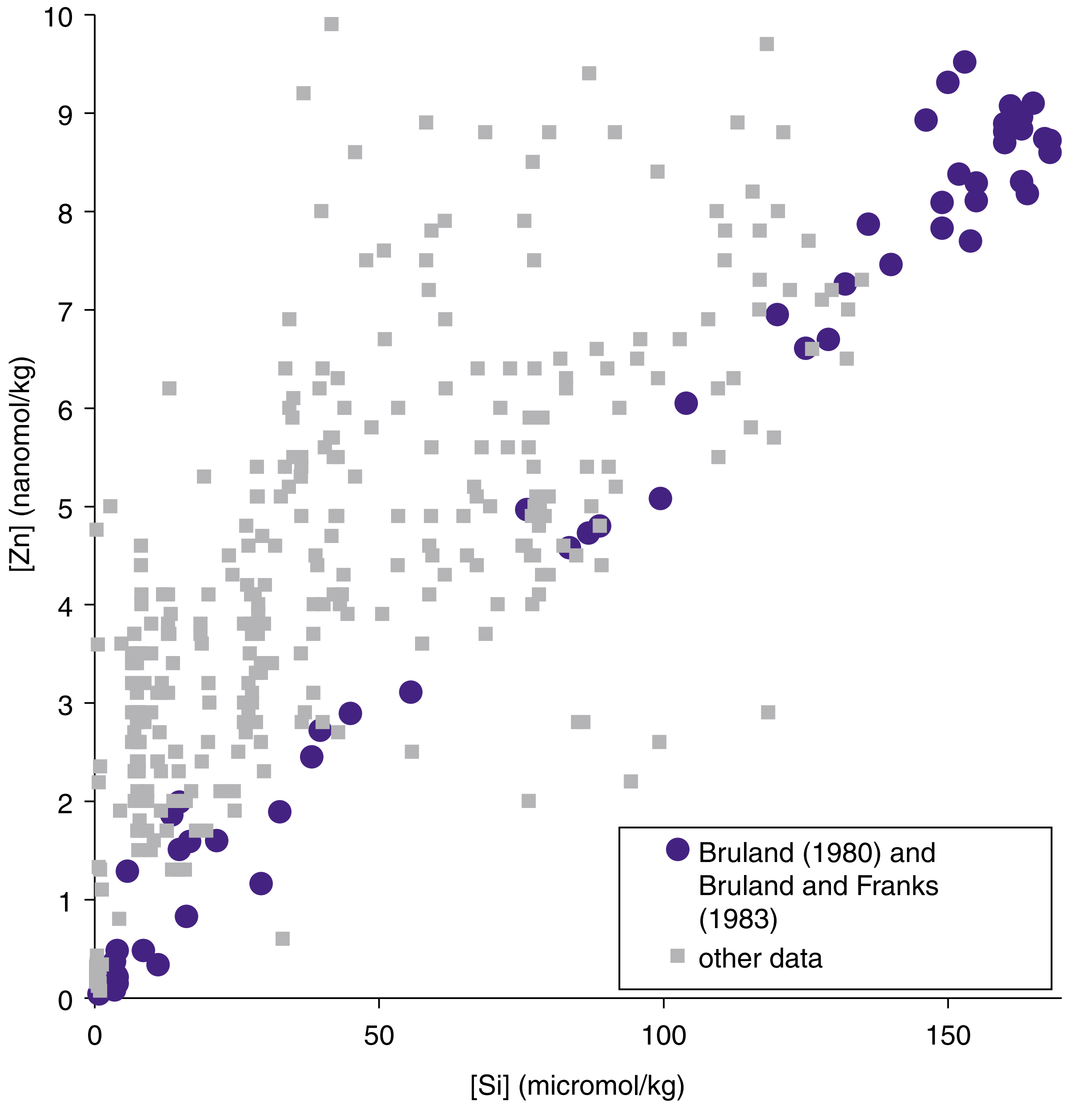

Figure 25. Zn versus Si concentrations reported from ocean water samples. The early data (blue circles) of Bruland (1980) from the North Pacific and Bruland and Franks (1983) from the North Atlantic indicated that there was a strong relationship between Zn and Si. Other data published subsequently (grey squares) do not follow that simple relationship. We cannot determine whether this scatter is due to real variations between different regions of the ocean, or to unresolved problems with contamination or analytical quality control. GEOTRACES is needed to answer this puzzle, with clear implications for the use of Zn as a proxy to reconstruct dissolved Si distributions in the past. Figure provided by Ros Rickaby and Ed Boyle.

A good example is the Cd concentration of seawater, which has a distribution similar to the macronutrient phosphate (Elderfield and Rickaby, 2000). Cadmium concentrations follow those of phosphate because both species are utilised and removed from the surface ocean by biological activity and transported by deep-ocean circulation. The Cd concentration of surface and intermediate waters is therefore a proxy for phosphorus concentrations, with low values indicating that phosphate is being fully utilised. Deep Cd concentration is a proxy for circulation, related to the ageing of water masses along the path of thermohaline circulation. For similar reasons, $\delta^{13}C$ is inversely correlated to phosphate in the present-day ocean. The past distribution of Cd/Ca and $\delta^{13}C$ can therefore help to reconstruct both productivity and deep-ocean circulation.

Just as Cd provides a proxy for phosphate concentrations, there are TEI proxies for the utilisation of the other macronutrients and, perhaps, for some micronutrients. A good illustration is provided by Zn, which preliminary data (Figure 25) suggested might serve as a potential 'direct' tracer of Si concentration. However, questions about the use of Zn as a tracer for Si remain to be addressed. For example, more recent results fail to show the strong correlation between Zn and Si seen in early data (Figure 25). Furthermore, while Zn is incorporated into diatom opal in proportion to the labile Zn concentration {Zn'}, the fraction of total particulate Zn held in opal is quite small, making the observed correlation between Zn and Si puzzling (Ellwood and Hunter, 2000). Other TEIs rely on the kinetic isotope fractionation that occurs during biological incorporation of nutrients, which makes the resulting biogenic phases isotopically light, and the remaining seawater isotopically heavy. The spatial pattern of isotope composition of N (Sigman *et al*., 1999), Si (de la Rocha *et al*., 1998) and, perhaps, Cd and other micronutrients is captured by marine substrates such as microfossils (foraminifera, diatoms, etc.) and provides information about the utilisation of these elements in the past.

Changes in nutrient utilisation and biological productivity are key aspects of the global carbon cycle and represent an important mechanism to explain glacial–interglacial changes in atmospheric pCO_2 (Sigman and Boyle, 2000). Reconstruction of past nutrient utilisation using these TEI proxies is therefore an important goal, but one that cannot be realised without full understanding of these proxies. The distribution of TEIs such as Zn, Cd, Si and (at least) Si and N isotopes along the GEOTRACES sections will provide such understanding and allow accurate reconstruction of the past carbon cycle.

The pattern and rate of ocean circulation also generates spatial variation in ocean TEIs that can be used to reconstruct this circulation. Examples include the use of radiogenic isotopes with residence times less than the oceanic mixing time (Nd, Pb, Hf). These tracers rely on various water masses, particularly those in the deep ocean, being labelled with a distinct composition at its source. For instance, deep-water masses formed in the North Atlantic Ocean are labelled, or were labelled before anthropogenic perturbation in the case of Pb, with relatively low Nd and high Pb isotope compositions, relative to Southern Ocean waters. Although progress has been made recently in understanding how North Atlantic Deep Water (NADW) acquires its Nd signature (Lacan and Jeandel, 2005), the manner in which water masses acquire this composition is only partly understood in the modern ocean and requires further study.

5.1.2 Areas for advance

Processes that link trace-metal concentrations to key environmental variables, and the robustness of these linkages in space and time

That Cd co-varies with phosphate, for instance, is known only from reasonably sparse datasets, and the nature of these relationships is not fully understood. Furthermore, the regions where water-column data exist are not those that have been used to develop the Cd/Ca and $\delta^{13}C$ foraminifera proxy, nor those where the proxies are generally applied. A firmer understanding of the processes that underlie the Cd/Ca and $\delta^{13}C$ to phosphate relationships will come, quite naturally, from better understanding of TEI cycles developed in Theme 1. GEOTRACES will achieve this goal because the relevant TEIs and nutrients will be measured routinely along GEOTRACES sections. In addition, a comprehensive documentation of TEI behaviour along sections and across selected areas (productivity gradients, oxygen minimum zones, etc.) will provide process understanding of the proxies. This will have important scientific impact. For example, it will allow the growing database of past Cd distribution to be 'inverted' to accurately reconstruct aspects of the past carbon cycle. In an analogous manner, new relationships between TEIs (such as Zn, Co, Cd, Ba) and environmental parameters are also expected to be uncovered during the GEOTRACES programme. The processes that generate them, and their spatial robustness, should also be assessed so that they can be reliably used for past reconstruction.

The nature and pattern of isotope fractionation of the nutrient elements

The nature and pattern of isotope fractionation of nutrient elements is under-explored but offers tremendous potential to assess nutrient utilisation in the modern and past oceans. Of all the systems, that of nitrogen has been most extensively studied and a reasonable understanding of the causes of nitrogen fractionation and the spatial pattern of $\delta^{15}N$ in some areas of the surface ocean has been developed (Sigman *et al*., 1999). Even here, coverage of the surface ocean is poor, and of the deep ocean largely absent. This limits the unambiguous use of $\delta^{15}N$ as a tracer for nitrogen fixation and denitrification in the modern ocean, and as a proxy for nitrate utilisation in the past. Silicon isotopes show similar promise to those of N, but with the ability to specifically assess the Si cycle and the production of opal. Silicon isotopes have been studied in only a few sites, however, and new knowledge will rapidly be derived from more comprehensive coverage (de la Rocha *et al*., 2000). The analytical ability to assess isotope fractionation of the micronutrients has only been developed in the past few years, but we are now poised to be able to use isotopes of Cd (Wombacher *et al*., 2003), Cu, Zn (Bermin *et al*., 2006), and potentially Fe, Ni, and other micronutrients to explore micronutrient utilisation now and in the past. This is an exciting prospect for advance in the next decade and will offer significant new insights into the cycles of these elements.

Geochemical labelling of water masses

Understanding of the way in which water masses are geochemically labelled is often insufficient to allow unambiguous interpretation of palaeorecords in terms of either changing ocean circulation or changing continental inputs. Measurements of the radiogenic isotopes of Nd, Pb, Os, and Hf offer significant potential for ocean reconstruction on long timescales, and to address questions that cannot be answered using the nutrient-like proxies or where these proxies disagree (Rutberg *et al*., 2000; Piotrowski *et al*., 2004). These isotope tracers have seen increasing use (Frank, 2002) but can be difficult to interpret because they are influenced by changes in both circulation and in the input to the ocean from the continents caused by changes in the style, amount, or distribution of continental weathering (Lacan and Jeandel, 2005). In many cases, it is clear that there is a strong relationship between a geochemical proxy and climate (e.g., Rutberg *et al*., 2000; Piotrowski *et al*., 2004), but this record cannot be simply interpreted in terms of a particular climatic variable. The ability to interpret such records will be significantly enhanced by a fuller understanding of the chemistry of these elements. Better understanding is needed, for instance, of the manner in which the water masses are initially labelled (e.g., the fraction of the element derived from different sources: rivers, groundwaters, and margin sediments). Improved understanding of the removal of the elements from seawater will also help and, because of the different residence times of these elements, will ultimately allow the various environmental controls to be reliably discriminated using a multi-proxy approach.

Large-scale distribution of ancillary isotopes

Measurements of $\delta^{18}O$, D/H and $\delta^{13}C$ in the water column have been undertaken previously (e.g., GEOSECS, WOCE), but GEOTRACES can still make an important contribution to the palaeoceanographic utility of these tracers. For instance, discrepancies between nutrient reconstructions from Cd and $\delta^{13}C$ in critical areas such as the Southern Ocean require better understanding of the specific behaviours of both tracers. Such information will be provided by the section approach of GEOTRACES. $\delta^{13}C$ data collected during the GEOSECS programme were of high reliability only in the Indian Ocean, with major problems experienced in the Pacific Ocean. WOCE carbon isotope data (contributed as part of the NOSAMS ^{14}C program) only extends to 2000 m depth. So there is still no reliable $\delta^{13}C$ data for deep Pacific Ocean waters, and understanding of the factors regulating $\delta^{13}C$ distributions in deep Atlantic Ocean waters could be improved with more precise data as well. There are also remote regions, with no $\delta^{13}C$ data, where GEOTRACES may collect such data for the first time.

5.1.3 Specific GEOTRACES objectives

1. Identify processes in the modern ocean that create the observed relationships between TEIs and nutrients, for example, Cd-PO_4, $\delta^{13}C$-PO_4, Zn-Si, Ba-Alk.

2. Establish a comprehensive distribution of these TEIs to understand their cycles and to use this improved knowledge to 'invert' their palaeoprofiles into accurate information about past ocean circulation and/or carbon cycle function.

3. Establish the distribution of nutrient isotope fractionation in the global ocean and evaluate isotope fractionation during nutrient utilisation (e.g., N, Si and possibly micronutrient isotope systems such as Cd, Zn and Fe).

4. Understand how water masses are labelled with specific radiogenic isotope ratios by determining the fraction of the elements in each water mass that comes from rivers, from atmospheric deposition, from hydrothermal systems, from exchange with particles and/or sediments.

5.1.4 Implementation

The objectives listed above are linked naturally to the broad objective of Themes 1 and 2 and will therefore be met using the ocean section strategy outlined within these themes. Sections that cross strong oceanographic gradients will be of key importance, particularly gradients of productivity and nutrient utilisation including:

- between near-shore and central gyre regions;

- between open ocean and upwelling regions; and

- between HNLC regions and those where nutrients are efficiently used.

Full water-column work will be an essential component so that the relationship between TEIs and macronutrients in upwelling water masses can be assessed, and so that the uptake and regeneration of TEI proxies and macronutrients can be compared. Stations in extreme end-member situations (e.g., old versus young water masses, oxygen minimum zones, dust plumes) are also required to fully determine if the global average relationships between TEIs and nutrients are robust today and, by implication, in the past.

Collection of particles and the collection of pristine sediment–water interfaces at key locations during the section work will also be important. *In situ* pumping of particles will help to understand processes affecting several TEIs important as direct proxies.

5.2 Factors influencing the distribution of 'indirect' proxies in the ocean

Present understanding

In contrast to the direct proxies discussed above, indirect proxies rely on situations where the fractionation between TEIs dissolved in seawater and those recoverable from sedimentary archives varies with environmental parameters such as temperature (Mg/Ca) or pH ($\delta^{11}B$). Under such circumstances, the resulting sedimentary TEI composition can be used to reconstruct the past environmental conditions.

Often, the principle behind these tracers is based in fundamental thermodynamics and/or kinetics and might be expected to be relatively easy to interpret. Unfortunately, measurements in the ocean show otherwise. Control by more than one environmental variable, and poor

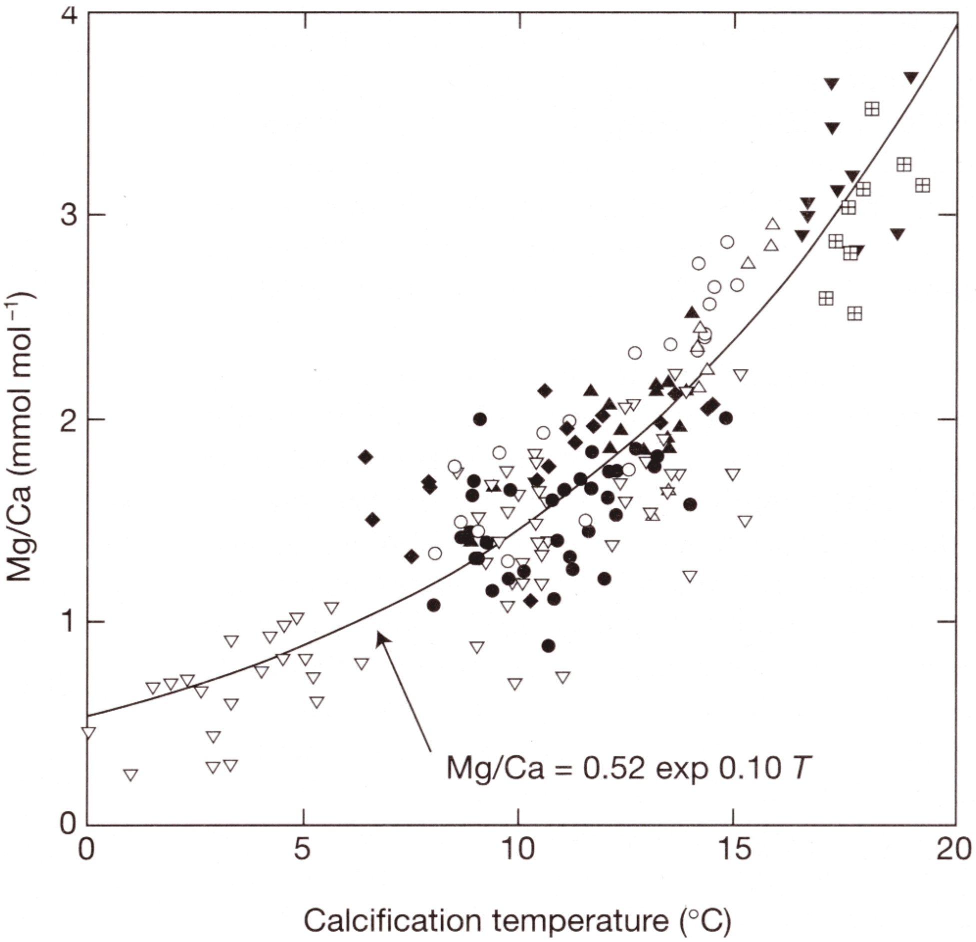

Figure 26. A typical calibration curve of Mg/Ca versus temperature, based on core-top foraminifera (Elderfield and Ganssen, 2000). The clear relationship between Mg/Ca demonstrates that temperature exerts a major control on foraminiferal Mg/Ca. But, the pronounced scatter about this trend hints at additional controls. Mg/Ca is one of the most widely used palaeothermometers, so it is important to assess additional controls and to establish this proxy more firmly. Elderfield and Ganssen (2000); figure adapted by permission from MacMillan Publishers Ltd: Nature, Copyright (2000).

understanding of the processes involved (particularly biochemical pathways), complicate interpretation of TEI proxies. Proxy calibration is therefore crucial but, in the past, much of this work has been performed opportunistically by 'bootlegging' samples from cruises with other major foci, or by making use of archived samples. This has proved cost effective, and demonstrates clearly the usefulness of maintaining good archive collections of core and other material, but it is not without problems. Samples used for existing calibrations are frequently not from the best areas to do the calibration, or from the areas where the calibrations will be applied. Water-column measurements are generally absent so that direct comparison of sediment measurements with those in the overlying water is not possible and most work has been done by extrapolation, sometimes over considerable distances. Furthermore, sediments used for these calibrations are often not collected using optimal procedures, creating questions about sample age and contamination.

In summary, most palaeoproxies have some kind of underpinning calibration but, in virtually every case, this calibration is not ideal and significant refinement of the proxies could be achieved through targeting calibration that seeks to understand the proxies at a process level.

5.2.1 Areas for advance

Discriminating among variables that influence proxy incorporation by substrates

In many areas of the ocean key variables such as temperature, carbonate ion and/or salinity show very similar patterns. Calibrations across such correlated gradients do not allow the influence of the variables to be separated. Sections along which these variables show unrelated changes will allow the proxies to be much more completely understood. One example is the Ca isotope variation in planktonic foraminifera. Early calibration studies from samples grown in controlled cultures showed a strong temperature dependence in the fractionation of Ca isotopes. More recently, several workers have questioned whether carbonate ion and calcification rate might play an important role in controlling this Ca isotope fractionation. In a similar vein, Mg/Ca ratios have been widely interpreted as a proxy for temperature in both surface and deep waters. Not only is the calibration of this tracer scattered beyond the range of analytical precision (Figure 26), but it has also been linked to changes in the concentration of carbonate ion. Such a carbonate-ion control would necessitate re-interpretation of many existing palaeo-SST records, but would also open the way to use Mg/Ca to reconstruct important aspects of the carbon cycle. Separation of the influence of variables on proxies such as Ca isotopes and Mg/Ca is fundamental to their accurate use as palaeoclimate tools.

Carbon system proxies

Proxies developed recently offer significant potential to reconstruct the past operation of the carbon cycle, but present calibrations are sparse, limiting the robustness of such reconstructions. Changes in atmospheric CO_2 on glacial–interglacial and longer timescales are thought to be a major agent forcing climate change. The different pCO_2 states of the past should allow investigation of the response of the whole surface Earth system to changes in radiative balance, but such an approach is complicated by the difficulty of reconstructing pCO_2 (beyond the late Pleistocene where it can be directly measured in ice cores) and of reconstructing other key variables in the carbon system such as ocean pH and carbonate ion concentration. Recent proxies appear to offer significant potential to solve these problems and generate significant new understanding of the operation of the natural carbon cycle. A good example is that of boron isotopes, which provide information about past ocean pH (Sanyal *et al*., 1996; Pearson and Palmer, 2000). Calibrations of this proxy are sparse, however, and there remain major uncertainties in its use. Neither the temperature sensitivity of $\delta^{11}B$ nor the presence or absence of interspecies effects, for instance, have been adequately assessed. The possibility for whole-ocean changes in $\delta^{11}B$ have also been suggested (Lemarchand *et al*., 2000), so that a better understanding of the ocean B isotope cycle is required to use this proxy robustly for the past. Similar uncertainties exist around recently suggested proxies for carbonate ion concentration (e.g., foraminifera mass; Broecker and Clark, 2001). Putting these carbon system proxies onto a firm empirical basis will allow significant new work to understand the operation of the natural carbon cycle.

5.2.2 Specific GEOTRACES objectives

1. Fully assess the relationships between the environmental variables in the water column and the TEI record in biogenic and authigenic phases, both within the water column and in surface sediments. These relationships will later form the basis for detailed studies of the relevant processes, both in nature and in the laboratory.

5.2.3 Implementation

A strategy similar to that for the direct proxies (Section 5.1) will also provide useful information for the indirect proxies. In addition, process studies will be required for the indirect proxies. In most cases, we already understand the modern distribution of the key element, but we do not understand how it is fractionated into the palaeo-archive. Investigation of this fractionation process requires collection of transects of cores and plankton tows from areas of the ocean where the multiple influences on a single tracer can be separated from one another. Process studies will need to examine areas where tracer properties of interest are not positively correlated with one another.

5.3 Palaeoceanographic tracers based on sediment flux

5.3.1 Present understanding

Information about past ocean productivity and circulation can be obtained from the sedimentary burial flux of certain TEIs. The burial flux of biogenic barium or barite, for instance, has been used to infer changes in palaeoproductivity (e.g., Eagle *et al*., 2003). This approach has been prompted by the close empirical correlation that is often found between marine productivity and the flux of Ba measured in sediment traps (Dymond *et al*., 1992). A reliable application of this proxy, however, still awaits a clear understanding of the underpinning mechanism that leads to this correlation.

Likewise, past changes in export production have often been inferred from changes in the accumulation rate of biogenic material on the seafloor. The first-order question for accurate palaeoproductivity reconstruction based on this type of proxy is how best to estimate from the sedimentary archive the vertical flux of material (such as TEIs or biogenic particles) originating from surface water and preserved on the seafloor. This is often complicated by sediment redistribution by bottom currents, which affects mass accumulation rates on the seafloor independently of the flux of material from overlying surface waters. Evaluating preserved fluxes by normalising to ^{230}Th is seeing increasing use as a stratigraphic method for determining sediment accumulation rates. Normalising to ^{230}Th corrects for sediment redistribution by deep-sea currents, is relatively insensitive to small errors in age models, and provides a flux estimate for each sample (Francois *et al*., 2004). This method relies on the assumption that the rapid scavenging and removal of dissolved ^{230}Th from seawater causes its flux to the sediments to be everywhere approximately equal to its known rate of production by radioactive decay of dissolved ^{234}U. Fluxes of other sedimentary constituents can then be estimated by normalising to the known flux of ^{230}Th. This method holds great promise for improving palaeo-flux reconstructions, but questions have been raised about the underlying principle of a constant scavenging flux of ^{230}Th (Thomas *et al*., 2000; Lyle *et al*., 2005). This assumption is known to be an approximation only and its accuracy still needs to be evaluated systematically.

Differential scavenging of radionuclides having varying affinities for sorption to marine particles has also led to the development of radionuclide ratios (e.g., $^{10}Be/^{230}Th$, $^{231}Pa/^{230}Th$) as proxies for past changes in particle flux (Kumar *et al*., 1995). In open-ocean regions, where virtually all particles are of biological origin, sedimentary radionuclide ratios may therefore provide a proxy for past changes in biological productivity.

Although we are equipped with a range of tools to assess the past pattern of ocean circulation (i.e., tracers of water mass structure), proxies for the past rate of circulation are more problematic. To understand the redistribution of heat and carbon requires knowledge of both pattern and rate, so the lack of a good proxy for circulation rate represents a real difficulty in past reconstruction. Here the differential scavenging and residence times of ^{231}Pa and ^{230}Th have been exploited to provide a measure of past changes in the rate of deep-water ventilation based on sedimentary $^{231}Pa/^{230}Th$ ratios (Yu *et al*., 1996; Henderson and Anderson, 2003; McManus *et al*., 2004), as has the past distribution of ^{14}C (e.g., Robinson *et al*., 2005).

Further calibration work is needed to advance each of the applications of radionuclide ratios described above. Recent studies have revealed that the affinity of ^{231}Pa and ^{230}Th for sorption to particles varies substantially from one phase to another (e.g., opal, $CaCO_3$, aluminosilicates, organic matter; Chase *et al*., 2002). Consequently, whereas radionuclide ratios clearly show strong correlations with other indicators of climate change in marine sediments (Figure 10), it is risky to interpret these records in terms of past changes in a single parameter (e.g., particle flux, particle composition or ocean circulation) until a better understanding of the impact of each of these factors on particulate $^{231}Pa/^{230}Th$ ratios has been achieved.

5.3.2 Areas for advance

Accessing the flux of material to deep-sea sediments

There is a need to clearly document the degree to which the scavenging flux of ^{230}Th to the seafloor can deviate from its rate of production in the water column. The underlying causes for these deviations must also be understood, and methods developed to quantify them. For example, do certain particulate phases preferentially scavenge Th? Are regional differences in scavenging intensity sufficient to produce lateral redistribution of dissolved ^{230}Th from regions of low particle flux to regions of high particle flux, thus invalidating the use of ^{230}Th as a tracer to correct for sediment focusing? Resolving these issues will require spatially distributed measurements of dissolved and particulate ^{230}Th distributions in the water column, combined with appropriate models to evaluate the lateral fluxes of ^{230}Th within the ocean.

Differential scavenging of TEIs and their sedimentary ratios

Improving our ability to separate the influence of scavenging and circulation on the $^{231}Pa/^{230}Th$ ratio of particles and sediments is essential for the unambiguous interpretation of past $^{231}Pa/^{230}Th$ variations recorded in sediments. This requires measurements of dissolved and particulate radionuclide distributions under conditions of varying particle flux, varying particle composition and under different circulation regimes (deep-water formation zones, upwelling areas, etc.). We also need to elucidate how scavenging at the seabed affects Th and Pa profiles in the water column as well as their distributions in surface sediments. To achieve this goal, we will need a higher density of measurement of dissolved and particulate ^{230}Th and ^{231}Pa in the water column than currently exist (Figure 27). The introduction of reliable particle fields and TEIs to ocean models, and a better understanding of the chemistry and scavenging of Pa and Th in seawater, are also required.

While the 'ratio' approach has been largely applied to $^{231}Pa/^{230}Th$ and to a lesser extent $^{10}Be/^{230}Th$, other pairs of TEIs with different residence times with respect to scavenging or affinities for major particle phases could conceivably be developed (e.g., Ti/Al) to complement and help separate the effects of particle flux, composition and ocean circulation.

Assess the use of Ba flux as a proxy for past productivity

Laboratory and time-series study to further elucidate the mechanisms of biogenic Ba (or barite) formation in the water column and preservation in sediments are needed to establish if, and under what circumstances, sedimentary Ba fluxes could be used as a quantitative palaeoproductivity proxy. The distribution of particulate Ba and flux estimates by ^{230}Th normalisation in core tops may also provide insights useful for the calibration of this proxy.

5.3.3 Specific GEOTRACES objectives

1. Assess the conditions under which the flux of ^{230}Th to deep-sea sediments is equal to the production of ^{230}Th in the overlying water column, the extent to which the ^{230}Th flux may deviate from its production rate, and the factors responsible for this deviation.

2. Provide a full understanding of the processes controlling ^{231}Pa and ^{230}Th distribution in the ocean and their flux to the sediment.

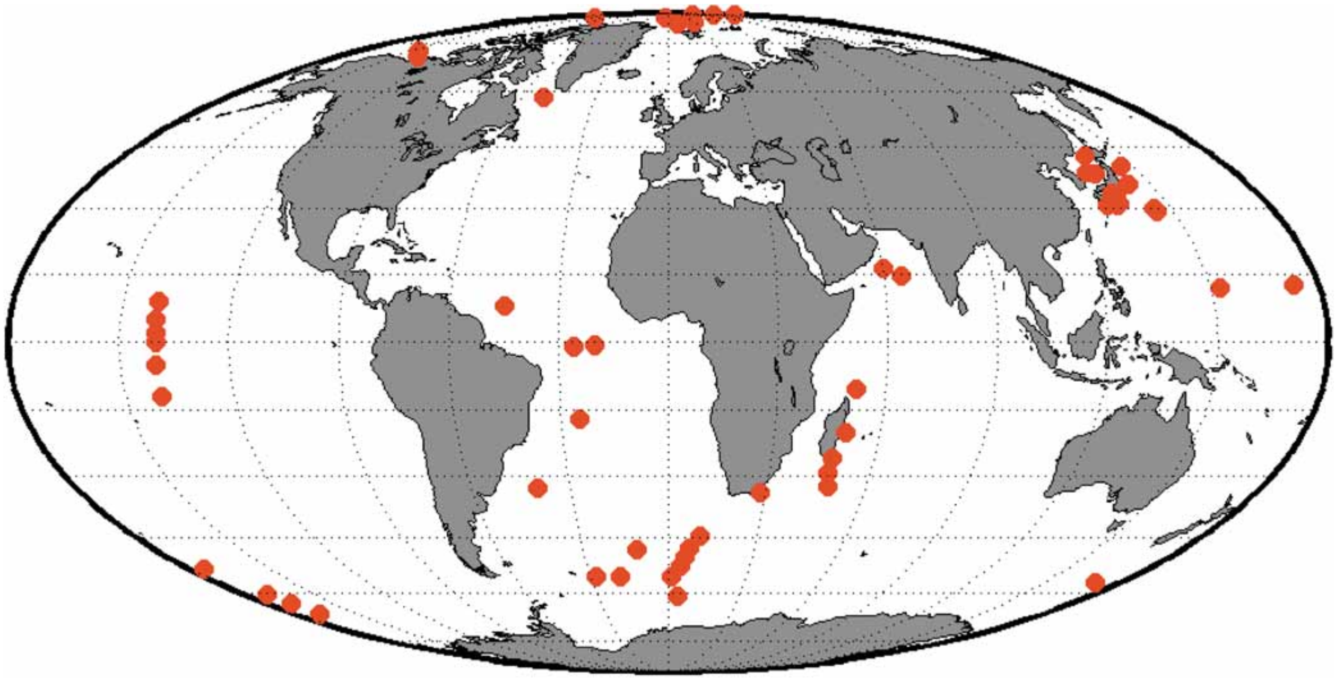

Figure 27. The location of published Pa water-column data demonstrating the poor coverage of measurements of this tracer, despite its increasing use to assess past productivity and ocean circulation. Figure provided by M. Siddall.

3. Investigate the use of other TEI ratios in marine particulates and sediments as proxies for past change.

4. Determine the rates of formation and preservation of barite and, potentially, of other TEI tracers of biological productivity, and the sensitivity of these rates to changing environmental variables.

5.3.4 Implementation

As for the direct and indirect proxies (Sections 5.1 and 5.2), understanding of sediment flux proxies will come from a mixture of measurements made on ocean sections, and those made as specific process studies. For instance, understanding the distribution and control of ^{230}Th and ^{231}Pa will require mapping these isotopes in the water column and forms a natural part of the section work for GEOTRACES. Understanding the flux of these nuclides to the sediment can also use these data, coupled to models, but might also require process studies involving sediment traps and/or coring.

5.3.5 Interaction with other programmes

IMAGES/PAGES, IODP: Many programmes use geochemical proxies to assess past conditions and retrieve long sediment cores from diverse areas in the ocean. Theme 3 of the GEOTRACES programme forms a natural bridge between the TEI cycling goals of Theme 2 and these other programmes. The improved understanding of proxies that will be derived from this study will allow more complete and more confident reconstruction of the past from these coring programmes.

SCOR/IMAGES WORKING GROUPS: SCOR and IMAGES have established two working groups concerned with the calibration and interpretation of palaeoceanographic proxies: PACE: Reconstruction of Past Ocean Circulation (WG 123) and LINKS: Analysing the Links between Present Oceanic Processes and Paleo-Records (WG 124). GEOTRACES will interact with each of these working groups in the development and calibration of palaeoceanographic proxies.

6. Synthesis and modelling

6.1 Introduction

Synthesis and modelling efforts will be an integral component of GEOTRACES throughout the programme. One of the primary objectives of the GEOTRACES programme is to better understand the marine cycles of TEIs and to quantify lateral and vertical transports, as well as biogeochemical sources and sinks. Numerical models offer a strategy to combine and evaluate physical and biogeochemical processes, and allow us to infer TEI fluxes and source/sink rates from a comparison of simulated TEI fields with measured distributions. In addition, modelling can help improve our basic understanding of TEI cycles through sensitivity studies, for which selected processes are parameterised in different ways, or excluded altogether. The GEOTRACES observations will be invaluable in constraining existing models and fostering the development of new dynamic TEI models. Model simulations can reveal the regions as well as spatial and temporal scales of TEI gradients in the ocean, and thus, as the programme develops, can provide guidance for the design of GEOTRACES fieldwork.

Given the large variety of oceanic TEIs considered and the wide range of processes involved, GEOTRACES will apply a hierarchy of models to maximise scientific output. The models will differ in: (1) the geographical coverage and spatial and temporal resolution; (2) the level of complexity and the range of processes explicitly included in the models; and (3) the numerical methods used to obtain model solutions and techniques to utilise TEI data. Examples of models that will benefit GEOTRACES range from box models and water column models to coupled physical/biogeochemical general circulation models, chemical speciation models and inverse models. Recent advances in data assimilation techniques and inverse modelling now allow promising direct data utilisation methods, not previously applied for the determination of TEI fluxes and source and sink terms. This activity will provide a close link between the observational components of GEOTRACES and modelling. Progress in these modelling efforts will both benefit from and inform the ongoing efforts within the IMBER and SOLAS programmes.

6.2 Forward models

Forward modelling will allow assessment of the sensitivity of TEI distributions to many ocean processes such as ecosystem dynamics, biogeochemistry, circulation, and particle interactions. The ability of such models to mimic observed TEI distributions will allow hypothesis testing of our understanding of the key processes controlling TEI cycles. A better understanding of these processes and their climate sensitivities will improve model simulations of future and past climate states and aid interpretation of the palaeoceanographic data.

Existing examples of the application of biogeochemical models to trace element chemistry are:

- The biogeochemistry of Fe: due to its potential role as a limiting micronutrient, Fe has made is way into several global biogeochemical models, allowing assessment of its role in regulating ecosystem structure, carbon cycling, and climate (Moore *et al*., 2002; Aumont *et al*., 2003);
- The coupled biogeochemistry of Al and Si: modelled concentrations of dissolved Al in ocean surface waters provide a means for validating dust fluxes at the air–sea interface, as well as the fluxes of biologically essential elements (e.g., Fe and Si) released from the dust (Gehlen *et al*., 2003);
- The biogeochemistry of ^{230}Th, ^{231}Pa, ^{10}Be, and Al: the sensitivity of these tracers to transport by different particle species has been explored (Siddall *et al*., 2005). Such modelling will allow the particle rain rates and particle composition in the past to be reconstructed from concentrations and ratios of key TEIs in the sediments;
- The biogeochemistry of ^{230}Th and ^{231}Pa in the modern and glacial oceans: the distributions of these tracers in the water column, and their flux to the sediments at any given location, are influenced by the relative contribution of advection and scavenging (Marchal *et al*., 2000). Models of the transport and scavenging of these tracers enable investigators to correct sediment accumulation rates for redistribution by deep-sea currents (from ^{230}Th measurements) and to exploit the ^{231}Pa/^{230}Th ratio in marine sediments for reconstruction of past changes in deepwater ventilation.
- The biogeochemistry of Nd isotopes: the sensitivity of the isotopic composition of dissolved Nd to exchange at ocean boundaries (Lacan and Jeandel, 2005) allows exchange rates to be assessed by coupling Nd sources to spatial gradients in a general circulation model. Preliminary estimates suggest exchange rates of less than one year at the surface and of about 10 years along the deeper part of the continental slope (Arsouze *et al*., submitted; Jeandel *et al*., in press).

Adding tracers to biogeochemical models will obviously benefit model development as well as understanding of TEI cycles. TEIs provide additional means for model validation to give additional constraints to the existing geochemical variables. Such existing variables often occur in Redfield or 'semi'-Redfield stoichiometry (carbon, nutrients, oxygen) so that they strongly co-vary. Adding new tracers such as reactive metals can provide additional 'orthogonal' information to classical marine biogeochemical data sets.

6.3 Inverse models

The principles and methods involved in the inverse modelling approach have been used successfully during the past decade. For example, application of these techniques to the WOCE/JGOFS data set has produced estimates of

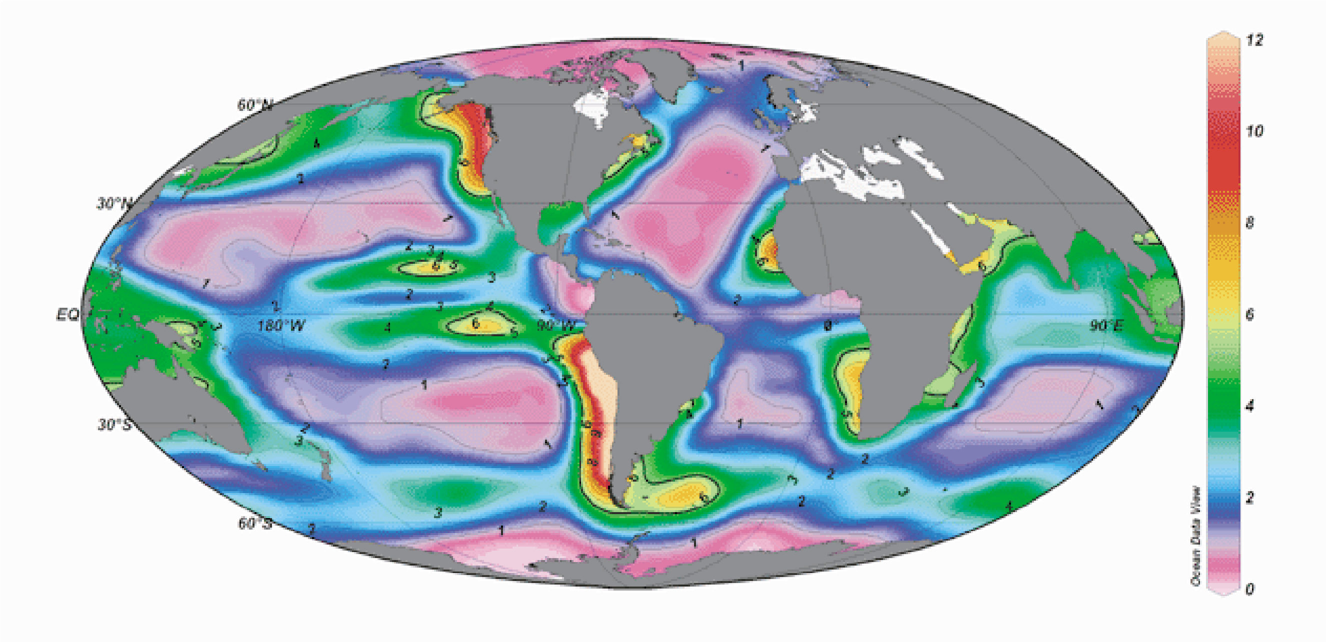

Figure 28. Export production of particulate organic carbon (POC; mol C m^{-2} yr^{-1}) in the world ocean determined by an inverse model from water column oxygen, nutrient and carbon distributions. From R. Schlitzer, Applying the adjoint method for global biogeochemical modelling. In: P. Rayner (editor), Inverse Methods in Global Biogeochemical Cycles. AGU Geophys. Monograph Series, Vol. 114, pp. 107–124, 2000. Copyright (2000) American Geophysical Union. Reproduced by permission of the American Geophysical Union.

horizontal fluxes of nitrate and anthropogenic CO_2 across selected WOCE sections (Ganachaud and Wunsch, 2002; Gloor *et al*., 2003; Macdonald *et al*., 2003). More recently, inverse models have been applied: (1) to estimate the global distribution of the export flux of organic matter sinking to the deep sea (Figure 28; Schlitzer, 2000, 2002, 2004; Schlitzer *et al*., 2004); (2) to estimate particle remineralisation rates in the water column (Usbeck *et al*., 2002); and (3) for a quantitative comparison with sediment trap data (Usbeck *et al*., 2003). Data assimilation methods have also been used for the optimal estimation of ecosystem model parameters at individual time-series and process study sites (Spitz *et al*., 2001; Friedrichs, 2002), and in extrapolations to the basin scale (Oschlies and Schartau, 2005).

Inverse models promise to be an important element of ongoing and future studies of ocean circulation, such as those being conducted under the CLIVAR programme. Expanding those activities through assimilation of information about TEI distributions offers a strategy to quantify source and sink term in the marine biogeochemical cycles of trace elements and their isotopes, as well as rates of internal cycling. Specifically, in addition to evaluating rates of lateral transport, the approach offers constraints on vertical fluxes associated with the uptake and regeneration of TEIs carried by sinking particles.

Inverse models also offer the possibility to quantify TEI fluxes across the sediment–water boundary and from margins into the ocean interior. These fluxes are important for the ocean budgets of many elements, such as Fe, Mn, Ra, Ac and Nd. In the models, the boundary fluxes will be derived from TEI budgets that take into account physical transports arising from bottom and deep water flows, thereby exploiting the measured lateral and vertical TEI gradients.

This approach is particularly crucial for assessing net fluxes across the land–ocean boundary (Sections 3.2 and 3.3). These boundaries are characterised by extreme spatial heterogeneity with respect to both sources (e.g., supply by rivers and submarine groundwater discharges) and sinks (e.g., biological uptake, scavenging to particles, precipitation within sediments) of TEIs. Furthermore, within a single system temporal variability of TEI fluxes may be substantial, for example, where river supply is dominated by extreme flood events. Therefore, the diversity and variability of these processes preclude the evaluation of significant fluxes by direct measurement. As an alternative, integration of heterogeneous boundary fluxes by the diffusive ocean can be used as a powerful tool. For TEIs with residence times less than the mixing time of the ocean, modelling of concentration gradients near ocean boundaries will be used to assess net sources and sinks.

An advantage of the inverse approach is that physical oceanographic and tracer data, collected for example on the CLIVAR/CO_2 Repeat Hydrography sections, can be combined with TEI data to improve the interpretation of both data sets. These modelling techniques also allow data to be distributed irregularly in space and time, thereby allowing data to be collected on separate cruises. Errors in the data are taken into account and can be used to calculate uncertainties in the derived fluxes and source and sink terms.

6.4 Implementation strategy

Synthesis and modelling efforts will start at the beginning of the programme and will extend for several years beyond the end of the field campaigns. Early model development will involve close collaboration with the observational community to determine initial parameterisations and hypotheses regarding the controlling processes of TEIs. Comparisons of model results and observational data will allow for iterative improvements in TEI simulations throughout the programme. As the GEOTRACES database grows, the increased number of constraints on the models will improve their reliability to estimate TEI fluxes and rate constants. As the models improve during the programme, they can highlight key processes or regions, providing guidance to the ongoing fieldwork.

Different modelling tools will be applied to the various aspects of GEOTRACES. Higher resolution regional models and one-dimensional water-column and sediment models may be more appropriate for focused process studies. Computationally efficient box models and intermediate complexity models can explore a wide range of parameter values and sensitivities, allowing for testing and evaluation of numerous hypotheses and parameterisations. Coupled physical–biogeochemical models will simulate global distributions of TEIs that through comparison with the GEOTRACES observations can be used to infer TEI transport, source and sink terms, and the fluxes across ocean interfaces with the atmosphere, ocean margins, and the sediments at the global scale. Processes incorporated in these models will include particle reactivity and removal, micronutrient uptake and regeneration, mineral dust dissolution, and hydrothermal sources, among others. Mechanistic models of TEI cycling in the ocean will be used to predict the responses to global change, and to aid in the interpretation of palaeoceanographic data.

6.4.1 Interactions with other programmes

Much of the model development will benefit from collaborations between GEOTRACES and other ongoing research programmes.

IMBER: The GEOTRACES interest in several key micronutrients complements the focus of IMBER. Ecosystem processes related to the uptake and export of micronutrients exert a strong influence on the TEI distributions. These processes must be considered in the GEOTRACES modelling efforts. IMBER will benefit from the global distributions and flux estimates of key micronutrients generated by GEOTRACES. IMBER will undertake complementary modelling efforts, with special emphasis on biological response to micronutrients in surface waters and on the internal cycling of biogenic material in the mesopelagic zone. These complementary modelling efforts will be coordinated to achieve synergies.

SOLAS: Several of the GEOTRACES TEIs or their precursors have atmospheric sources. SOLAS will provide extensive information on atmospheric inputs of some TEIs (most notably Fe), and will benefit from the GEOTRACES global TEI observations.

CLIVAR: Hydrographic information from CLIVAR in addition to WOCE and other data sources will provide information on the physical transports.

LOICZ: Several TEIs have important coastal zone sources and GEOTRACES will benefit from the LOICZ observational and modelling efforts.

IMAGES/PAGES, IODP: Simulations of past climate regimes that include relevant TEIs will both draw on and benefit interpretations of palaeoceanographic data from sediment cores.

Reanalysis products: Oceanic and atmospheric reanalysis products will help to constrain the time-varying circulation and transports.

Ocean Observing Networks: As for the reanalysis products, the development of ocean observing networks (e.g., GOOS, ORION) will help to constrain the time-varying circulation and transports that affect TEI distributions.

Remote sensing: At the present time, satellite remote sensing offers synoptic global ocean views of several parameters of interest to GEOTRACES, including sea surface temperature, surface salinity (anticipated within the lifetime of GEOTRACES), colour (e.g., chlorophyll concentration, abundance of coccolithophorid-derived $CaCO_3$, coloured dissolved organic matter), atmospheric aerosol loading, wind speed and direction, and altimetry (related to ocean currents and their variability).

7. Standards, sampling protocols and intercalibration

7.1 Rationale

GEOTRACES will produce global-scale property distributions that will be used to identify and quantify sources and sinks of TEIs as well as rates of internal cycling, and provide a baseline against which future changes can be measured. Therefore, it is vital that the data sets that are obtained are accurate, precise and intercomparable. To achieve this goal in a global-scale programme involving multiple laboratories from many countries, it will be necessary to develop an implementation framework that ensures methodological continuity and reproducibility at all levels from sample acquisition and processing through to analytical protocols. It is important that as many as practical of the protocols, standardisations and calibrations detailed below be established before the start of the GEOTRACES field programme. Thus, the establishment of a committee to oversee these activities is a high priority for GEOTRACES.

This section outlines how that framework will be developed and the charges that will be initially made to the committee overseeing implementation. Because many of the techniques that will become an integral part of the project are still in their infancy or have not been used in global-scale sampling efforts, it is likely that the development of protocols and best practices will be an iterative process between the experts in the field and the implementation body.

A standing committee of experts from the field, drawing on the expertise of the TEI community, will need to be established to oversee this process. Because the work of this committee is a critical part of the enabling phase of the project, we recommend that this committee be formed as soon as possible.

The broad outlines of the charge of this committee are detailed here, but it is expected that by necessity the mandate and implementation approach will need to change as the programme progresses. Thus, although the charge is somewhat detailed, it is not meant to be overly prescriptive as it is expected that as the programme progresses the members of that committee will need to modify their approach to ensure that field and laboratory activities meet the overall standards and goals of the GEOTRACES programme.

It is anticipated that this committee will act as both a facilitator and decision maker. It will act as a facilitator by ensuring expert community input into developing protocols, standards and best practices through workshops, sub-committees, etc. In addition, it will act as a decision-making body that will recommend policy to the GEOTRACES Scientific Steering Committee for enactment as policy decisions.

7.2 Sampling and analytical principles

All (core) measurements conducted under the GEOTRACES programme (TEIs and co-parameters) should follow standard protocols. Standard protocols include acceptable sampling and storage methodologies, use of reference standards for laboratory and field calibration, and use of documented methodologies (Dickson *et al*., 2002).

Standard methods must be documented explicitly so that they are transferable among laboratories. Sampling methodology includes:

- collection methods for water (including speciation), sediments and particulates;
- on-board processing protocols such as filtration, pre-concentration and use of yield tracers; and
- storage of samples, including bottle types, pre-cleaning methodology, preservation methods, shelf-life and distribution protocols.

To extend the reach of the GEOTRACES programme, protocols should, wherever practical, be designed so that they can be used readily on volunteer observing ships (VOSs) as well as traditional research vessels.

7.3 Protocols Standing Committee

7.3.1 Membership of the Standing Committee

The expert committee will consist of scientists having collective expertise in all aspects of TEI studies, from sample collection to their analysis. The Chair/ Coordinator of the committee should initially be a member of the GEOTRACES Planning Group, and after that group is replaced, a member of the GEOTRACES Scientific Steering Committee.

The membership will include scientists working in the broad areas of distribution of trace elements, radioactive and radiogenic isotopes, speciation, organics, gases and particulates. Scientists engaged in TEI research and familiar with modern analytical techniques will be preferred.

The committee will be appointed initially by the GEOTRACES Planning Group with as much geographic and gender distribution as is possible, although maintaining relevant expertise will be the highest priority for selection of members. Renewal of terms and later appointments will be handled by the GEOTRACES Scientific Steering Committee after soliciting nominations from the broader TEI community.

Appointment to the committee will be for a term of three years. To maintain continuity between successive committees the term of some members may be extended. Members who perform well and contribute to the overall growth of GEOTRACES will be preferred for extension.

The activities of this committee are central to the GEOTRACES programme. It is expected that the members of this committee may have to devote a significant part of their time to achieve its tasks, including participation in standardisation/calibration cruises, and overseeing the collection and distribution of samples and reference materials for laboratory intercalibrations.

7.3.2 Charge to the Standing Committee

1. Develop and document a series of protocols and best practice methods for use by GEOTRACES scientists in the field and the laboratory to ensure comparable data sets for common parameters by:
    - Establishing a series of reference materials and acceptable reference values for them; and
    - archive of protocols.

2. Implement the above goals through the following steps.
    - Identify existing protocols for measurements and observations and, where appropriate, adopt them as part of the GEOTRACES protocols.
    - Oversee the establishment of appropriate methodologies for TEIs that are inter-calibrated, fully documented and transferable. Where appropriate, the committee should facilitate field and laboratory intercomparisons and intercalibrations (including speciation).
    - Solicit input from experts in the field to establish accepted protocols and to publish them in an easily accessible form, specifically on the GEOTRACES Web site.
    - Develop working relationships with other programmes that rely on measurements of common TEIs. Where appropriate this might also entail developing multi-programme intercalibration exercises and/or reference standards.
    - Identify existing reference materials and promote development of appropriate new standard reference materials (Dickson *et al*., 2002).
    - Coordinate with existing providers of standard reference materials (SRMs) in refining TEI values in existing SRMs and newly developed ones.
    - Coordinate and establish expert accepted values for TEIs in existing reference materials. Recommend the frequency at which primary and secondary standards should be run.
    - Identify and promote the use of deep oceanic stations to allow field calibrations of TEIs.

3. In cases where no SRMs are available the committee should engage community experts to develop alternate strategies, for example, field calibration stations or use of standards added to natural materials, to develop consistent databases.
    - Encourage and facilitate the development and distribution of new and existing reference materials.
    - Where commercial standards are not available, encourage the development, distribution and use of community-based standards.

4. Investigate the feasibility and oversee the development of a sample archiving scheme for water samples from GEOTRACES cruises. Establish protocols for archiving including frequency and volumes, sample container type and preparation, storage conditions, etc.

5. Consider which TEIs require intercalibration of sampling methods, and which require comparison of analytical methods. For the latter, plan intercalibration on the basis of distributed aliquots from a single large-volume sample.

Although standardisation is a necessary component for any large programme it will be important that the committee pay attention to the inherent conflict between standardisation, which provides consistent data sets, and methodological innovation that improves data acquisition through reduced sample volume, improved sensitivity, accuracy, speed and precision. It is expected that the committee will promote continued innovation in methodology to prevent stagnation, while maintaining comparability of measurements worldwide.

8. Programme structure and implementation

8.1 GEOTRACES activities

A suite of complementary activities will be required to achieve the objectives of GEOTRACES (Section 2.5). These can broadly be divided into three categories:

- enabling activities;
- ocean sections (global distributions of TEIs); and
- process studies.

8.1.1 Enabling activities

The global scope of the programme requires international coordination and collaboration. No single nation has the resources to perform a global study of this level of complexity, so cooperation within the worldwide community of marine geochemists is required. Certain 'enabling activities' must be completed to allow such cooperation, and to ensure that results produced by different groups are comparable, internally consistent, and readily available.

Intercalibration and standard reference materials

Many of the TEIs to be studied are difficult to measure. Some are present in seawater at concentrations so low that their measurement pushes the limits of detection of the most sophisticated analytical instruments. Others are exceptionally prone to contamination during the collection of samples and their subsequent handling. Still others are present in seawater in multiple chemical and physical forms, causing different measurement strategies to give divergent estimates of the element's concentration. Success of the programme requires that results from different groups are internally consistent.

Two steps should be taken to ensure such internal consistency: (1) the development, distribution and laboratory measurement of standard reference materials; and (2) the intercalibration at sea of different sampling and analytical strategies. For example, where factors such as differing sensitivities of analytical instruments may lead to systematic differences in measured TEI concentrations, analysis by all participating laboratories of standard seawater with certified TEI concentrations can be used to correct for this bias. In other cases, where sampling methods may influence the measured TEI concentrations due, perhaps, to possible contamination issues, intercalibration of the complete methodology at sea is required. All such intercalibration work is, by its nature, required for the main measurement effort and is therefore one of the earliest objectives of the GEOTRACES programme. A standing committee has been established to refine the needs for intercalibration and standard reference materials (see also Sections 7 and 9).

Data management system

A unique achievement of GEOTRACES will be the global-scale synthesis of oceanic sources, sinks and internal cycling of TEIs. Achieving this synthesis requires that data generated during the GEOTRACES programme are archived and readily available from a data management system. Such a system will be established before the initiation of the GEOTRACES field programme, to be operated by a Data Assembly Centre with oversight from a Data Management Committee (see Section 9).

Coordination of field programmes

To complete the global survey of TEI distributions as efficiently and completely as possible, coordination of field work will be required to avoid redundancies and to ensure that each important target region is covered. Some nations are constrained by national priorities to work within certain regions. Some groups may have pre-existing field programmes that would serve the objectives of GEOTRACES. These and other factors must be considered in the early stages of planning fieldwork. The GEOTRACES Scientific Steering Committee will oversee this coordination, aided by relevant standing committees (see Section 9).

Synthesis of historical data

GEOTRACES will build on the work of earlier programmes, so it is natural that historical data will be used to set priorities for future work. One area in particular, the supply of TEIs by continental runoff, calls for a synthesis of historical data as an enabling activity (see Section 3.2). Many studies of TEIs in river systems have been conducted since the advent of clean sampling techniques. Often this work has been done by individuals who have limited interaction with the marine geochemistry community, so there is a sense that a wealth of data exists which is not in use by marine geochemists. Some of these data could be instrumental in setting priorities for GEOTRACES research on TEI fluxes through continental runoff. Although study of SGDs is in its infancy, work in this area is beginning and should be included in the synthesis as well. Two principal objectives of this synthesis will be to produce up-to-date estimates of global freshwater fluxes of TEIs to the ocean, and to identify gaps in the available information that can be used to set priorities for sampling during the GEOTRACES programme.

Modelling

Modelling will play a key role throughout the programme, including the early enabling phase. One area where modelling can provide useful input before starting measurement campaigns is in guiding sampling density on ocean sections. Such sampling density should be done at a spatial resolution sufficient to allow the identification and quantification of sources and sinks. Where anticipated sources and sinks of TEIs can be identified, sensitivity studies using appropriate models will be conducted as part of the design of the field programmes to address questions such as the optimum spatial resolution for sampling (see also Section 6).

Sample archive

GEOTRACES offers an unprecedented opportunity to define baseline distributions of many TEIs before perturbation by anthropogenic sources or global change. At present, it is impossible to identify all perturbations to TEI cycles that might, in the future, be recognised as significant. Consequently, there is considerable value in establishing an archive of water samples collected during the GEOTRACES programme, which would serve as a resource for future studies. Such an archive would be technically difficult to set up, owing to the need to avoid contamination of the samples, and it would be expensive to maintain. Nevertheless, the value of such an archive is not in dispute. Therefore, an early activity for the GEOTRACES SSC will be to conduct a cost–benefit analysis of options for archiving water samples collected during GEOTRACES cruises.

Satellite remote sensing

Pre-existing knowledge of spatial and temporal scales of variability of key environmental parameters (e.g., surface temperature, phytoplankton biomass) will be crucial for designing the sampling strategies to be used during GEOTRACES cruises, both along ocean sections and during process studies. Such knowledge will be important, as well, in designing models to be used to simulate processes influencing TEI distributions. Much of this information about the surface ocean can be derived from satellite remote sensing. GEOTRACES will engage expertise in relevant satellite data throughout the planning and design of these activities, as well as during the day-to-day sampling aboard cruises as the measurement campaign starts.

8.1.2 Ocean sections

Measurement of a range of TEIs along full-depth ocean sections through each of the major ocean basins represents the core activity of the GEOTRACES programme. This measurement strategy is clearly identified as providing maximum scientific rewards (see, for instance, Section 2.4, and various ‘implementation strategies’ throughout Sections 3–5). It will identify, at a global scale, the wide range of chemical, physical and biological processes involved in the cycling of TEIs in the ocean. For example, measuring multiple diagnostic TEIs in the principal regions for deposition of continental mineral aerosols will lead to an assessment of micronutrient (e.g., Fe) delivery by this process (Sections 2.4 and 3.1). Similar strategies will be exploited during ocean sections to evaluate the net supply of TEIs by continental runoff (Section 3.2); the net supply and removal of TEIs through exchange with ocean margin sediments (Section 3.3); and the sources and sinks of TEIs associated with hydrothermal systems (Section 3.4). Information about the internal cycling of TEIs will be derived by measuring vertical and lateral TEI gradients along ocean sections (Section 4; see also Figure 5 and associated text in Section 2.4). Coupling these measured distributions with ocean-circulation models will also allow the rates of these processes to be constrained (Section 6).

Mapping the present distribution of TEIs along ocean sections will provide a basis for evaluating future changes to their distribution, with relevance to global change research. And it will allow relationships between different TEIs to be exploited to better understand their chemical behaviour, and their use as proxies for past change. Global datasets, of certified quality, from these ocean sections will be one of the major legacies of the programme and will provide important information to a wide variety of related disciplines including global carbon cycle modelling, climate modelling, ocean ecosystem studies, and research into ocean contaminants.

The principal criterion for selecting and approving ocean sections (Section 9) will be their potential to provide insight into the sources, sinks, speciation and internal cycling of TEIs, as well as the sensitivity of these parameters to changing environmental conditions. Although no commitments have yet been made to particular ocean sections, priority will be assigned to regions of prominent sources or sinks, such as dust plumes, major rivers, hydrothermal plumes and continental margins (Figure 29). Ocean sections will also be designed to sample the principal regions of water-mass formation to characterise the TEI composition of each end-member water mass, and to identify the processes regulating these end-member compositions. And sections will be selected to cross major biogeographic provinces and gradients of biological productivity (Figure 29). Precise ocean section locations and ship tracks represent an implementation issue that lies outside the scope of this science plan. This planning will be coordinated by the GEOTRACES Scientific Steering Committee (see Section 9) to ensure global coverage without unnecessary duplication during the ocean sections campaign.

It is anticipated that ocean sections will involve mainly water sampling. Coring, bottom landers, sediment traps, plankton tows, etc. will be used mainly within process studies, although some exceptions will be made, particularly in ocean sections passing into remote regions of the ocean where opportunities to collect sediment samples are rare.

Parameters to be measured along ocean sections can be separated into several categories (see Section 8.2 below),

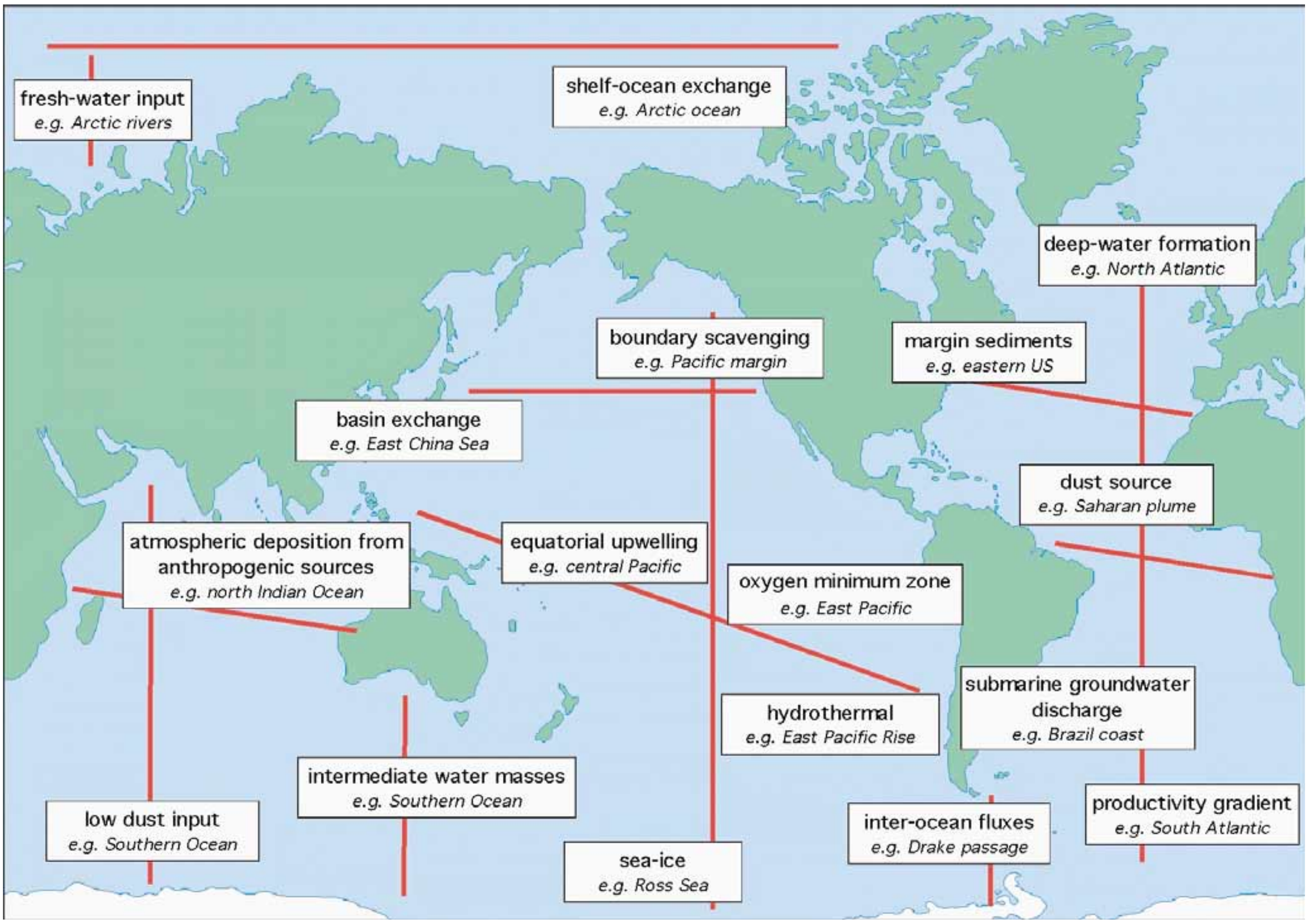

Figure 29. A schematic map indicating the philosophy behind the choice of ocean sections within GEOTRACES. Sections will be planned to cover the global ocean, and to pass through regions where major processes control the cycling of TEIs. A selection of processes is shown in the figure, together with examples of possible locations where these processes might be observed. Most of these processes obviously also operate in other locations (e.g., oxygen minimum zones are well developed on the western coast of Africa and in the Arabian Sea; TEI sources associated with dust and major rivers will be examined in multiple regions). Sections shown are illustrative only. Final section tracks will be selected during the implementation phase of the programme.

and there will be a hierarchy of sampling frequency depending on the sampling method and type of measurement. For example, total concentrations of TEIs will be measured with greater sampling frequency than will be the physical form (e.g., dissolved, colloidal, particulate) and chemical speciation of TEIs. To qualify as a GEOTRACES section, it is anticipated that the key parameters identified in Section 8.2 will be measured, and that measurements will be contributed promptly to the established GEOTRACES data management system.

Modelling will play an integral part in planning the ocean sections, and all resulting measurements will be integrated into models of appropriate complexity. The global view of TEI distributions provided by the section approach will be particularly useful for construction of accurate global models. One example is that improved knowledge of micronutrient cycles will allow their accurate modelling in global carbon cycle models.

8.1.3 Process studies

Although ocean sections will offer insight into many processes of interest to GEOTRACES, in some cases dedicated process studies will be required to fulfil the GEOTRACES mission. Many processes influence the marine biogeochemical cycles of TEIs, far more than can be examined by a single programme. Therefore, while it remains the prerogative of national GEOTRACES programmes and funding agencies to select specific process studies to be carried out (Section 9), some guiding principles will help set priorities in reaching these decisions.

Process studies likely to be of greatest value to GEOTRACES are those that:

- evaluate sources and sinks for TEIs for which large uncertainties currently exist;

- establish the processes that control the recording of geochemical proxies in sedimentary archives;
- establish the sensitivity of critical processes to changing environmental parameters; and
- complement but do not duplicate research conducted by other programmes.

Based on the implementation strategies outlined in Sections 3, 4 and 5, four particular process studies are currently identified as meeting these criteria and therefore as being high priority. This is not an exhaustive list of process studies that would help GEOTRACES meet its goals, but it represents those process studies that can already be identified as of particularly high priority:

- ocean–sediment exchange at oxygen minimum zones (see implementation strategy under Sections 3.3, 4.2 and 4.3);
- release of TEIs from particulate material when high-particulate load rivers discharge to the ocea (see Section 3.2);
- the flux of TEIs to the ocean from SGDs (see Section 3.2);
- recording of geochemical proxies in sediments from regions underlying strong ocean gradients (see Sections 5.2 and 5.3).

In each of these cases, additional work will be required to complement that derived from the ocean section approach. This work will involve tasks such as the collection of sediment or of data on repeat sections that are not planned as part of the ocean section campaign.

Other processes, although important to the goals of GEOTRACES, may be investigated by other programmes. Examples include the processes controlling the fractional dissolution of aerosol material (Section 3.1), which may be investigated by SOLAS, or the chemistry of near-vent hydrothermal fluids (Section 3.4), which may be investigated by InterRidge. The GEOTRACES Scientific Steering Committee will ensure close dialogue with such programmes to ensure that, while there is no duplication, suitable process studies are performed to meet the GEOTRACES goals. Synergies between programmes will also be sought, for instance, by adding new TEI measurements to existing programmes, or by welcoming scientists from other programmes on GEOTRACES cruises.

In general, process studies will run concurrently with ocean section work. However, it is anticipated that the analysis of section results may identify unexpected areas in need of process studies. For example, anomalies in systematic relationships between TEI concentrations and standard hydrographic parameters may indicate the location of previously unknown TEI sources or sinks for which further investigation by process studies is deemed necessary. Therefore, the long-range plan for GEOTRACES should allow for such process studies to occur near the end of the programme.

8.2 GEOTRACES measurements

A fundamental principle underlying GEOTRACES is that measurement of multiple TEIs with varying behaviour will provide insights into processes not attainable from study of a single TEI. There is substantial value added by studying various categories of tracers simultaneously. This principle applies to ocean sections and process studies alike.

8.2.1 Support parameters

New TEI measurements must be set in a broader oceanographic context by combining their measurement with that of other parameters. Standard hydrographic parameters (e.g., salinity, temperature, oxygen) will be measured on all GEOTRACES ocean sections at WOCE quality. Major nutrients (nitrate, phosphate, silicic acid) will also be measured, again at WOCE quality. Where possible and appropriate, new techniques to measure nutrients at nanomolar levels will be employed in low-nutrient surface waters to allow new relationships to be established between the uptake and regeneration of nutrients and TEIs. Similarly, where appropriate, measurements will be made of the inorganic carbon system, both on ocean sections and in process studies.

Transient tracers (e.g., chlorofluorocarbons; ^{3}H–^{3}He) provide valuable information about water mass history and the rates of transport of dissolved chemicals. In some cases, GEOTRACES can rely on data for these tracers generated by other programmes (e.g., WOCE, CLIVAR). In others, it will be beneficial to incorporate these measurements into the design of GEOTRACES cruises where berth space and water requirements allow it.

Distributions of inert gases can be used, along with distributions of oxygen concentrations, to evaluate preformed apparent oxygen utilisation to circumvent the required assumption that surface oxygen concentrations are saturated in areas of deep and intermediate water formation. Profiles of inert gases are also valuable for determining the mechanism of deepwater formation and the importance of diapycnal mixing. Inert gases will therefore provide useful process information on some GEOTRACES cruises.

The strategy for ocean sections calls for selected stations where large volumes of water will be filtered to measure concentrations of particulate TEIs. At these stations, concentrations of major biogenic (e.g., particulate organic carbon, opal, $CaCO_3$) and lithogenic phases will also be measured to establish the role of these phases as carriers of TEIs. It is not expected that organic carbon measurements (dissolved or particulate) will be made routinely at other stations during the programme.

Biological uptake and abiotic scavenging by particles are important processes influencing the internal cycling of TEIs. Optical sensors (calibrated fluorescence, beam transmission) will be used routinely to provide measures of biomass and particle abundance. Samples archived for pigment analysis will be used to identify the principal phytoplankton taxa present at the time of sampling. In developing the implementation strategy for each ocean section or process study, consideration will be given to additional measurements to establish physiological response of organisms to variability in the supply of micronutrients, including measurements to make aboard ship (e.g., fast repetition rate fluorometry) and those that can be made using archived samples (e.g., flow cytometry).

8.2.2 TEI measurements

TEI measurements have a wide range of uses, as outlined throughout this document. The exact suite of TEIs to be measured on each GEOTRACES cruise will depend on the location of the cruise, the processes likely to dominate cycling of TEIs at that location, and on pragmatic issues such as size of ship and personnel involved. This section lists general classes of TEIs that are expected to form important parts of GEOTRACES. This list is illustrative rather than exclusive. At the end of this section is a list of 'key parameters': TEI measurements that are sufficiently central to the broad aims of GEOTRACES that they are expected to be measured on all ocean sections.

Micronutrients

Several trace elements are known to play essential roles in the structure and metabolism of marine organisms (see Section 2.6). Iron has received the most attention, both as a limiting factor in the growth of phytoplankton in high-nutrient low-chlorophyll regions and for its regulation of nitrogen fixation. Other trace elements (e.g., Co, Zn, Ni, Mn and Cu) also serve as essential micronutrients, and investigation of their biogeochemical cycles is a high priority for GEOTRACES.

Source tracers

Certain TEIs provide useful indicators of specific processes supplying TEIs (see Section 3). Examples include ^{210}Pb and Al as tracers of atmospheric deposition; ^{3}He as a tracer of hydrothermal input; Mn as a tracer of input from margin sediments; and Ra isotopes as tracers of SGDs. Other TEIs provide diagnostic indicators of provenance (e.g., radiogenic isotopes such as Nd, Hf, Os, Pb).

Removal tracers

Certain TEIs (e.g., U-series and cosmogenic radionuclides) can be used to constrain rates of biological uptake and scavenging by particles, processes that regulate the internal cycling and eventual removal from the ocean of many TEIs (see Section 4).

Transport tracers

Certain TEIs trace the transport of material from boundary sources to the ocean interior. Surface sources can be traced by natural Nd isotopes or anthropogenic lead isotopes, while bottom sources can be traced by U-series isotopes (e.g., Ra, Ac, Rn; see Section 4.4).

Contaminant tracers

Anthropogenic TEIs also trace the pathways for transport of a variety of contaminants into the ocean. Like lead, mercury has a geographically distributed atmospheric source. Other anthropogenic TEIs (e.g., silver, tin, waste products from nuclear fuel reprocessing) have coastal or even point sources.

Palaeoceanographic proxies

Many TEIs that serve as essential micronutrients, or as diagnostic indicators of supply, transport and removal processes in the modern ocean are exploited to reconstruct past ocean conditions (see Section 5). These include a wide variety of trace elements, stable isotopes, and radiogenic/radioactive isotopes.

Key GEOTRACES parameters

The exact suite of TEI and related parameters to be measured on each GEOTRACES cruise will be tailored to the location and the nature of the processes occurring at that location. A wide selection of parameters from all categories listed in this section is expected to be measured during the programme, including those mentioned throughout the earlier sections of this document. Among these TEIs are some that are of sufficiently wide importance, or for which knowledge of their global distribution would be particularly useful, that they are expected to be measured on all GEOTRACES ocean section cruises (Table 2). These 'key parameters' include trace elements, stable and radioactive isotopes, and other parameters such as particles and aerosols. They do not all require measurement at the same spatial resolution, but are all expected to be measured on at least some stations on all ocean sections. In general, measurement of these key parameters, although not straightforward, is now being performed reliably in enough institutes around the world that widespread measurements of these parameters does not represent a major technical challenge. Nevertheless, these are parameters for which standardisation and intercalibration is a particular priority.

Table 2. A list of suggested 'key parameters' for GEOTRACES ocean sections. This is not a list of all TEIs expected to be measured during GEOTRACES. Rather, it represents those TEIs (and related measurements) that are likely to be particularly fruitful to measure on all ocean sections and for which global coverage is highly desirable. It is not envisaged that each of these parameters will be measured at all stations, but that at least some measurements of these key parameters will be made on all GEOTRACES ocean sections.

Key parameter	**Examples of use**
Trace elements	
Fe	Essential micronutrient
Al	Tracer of Fe inputs (from mineral dust and elsewhere)
Zn	Micronutrient; potentially toxic at high concentration
Mn	Tracer of Fe inputs and redox cycling
Cd	Essential micronutrient; palaeoproxy for nutrient content of waters
Cu	Micronutrient; potentially toxic at high concentration
Stable isotopes	
$\delta^{15}N$ (nitrate)	Modern and palaeoproxy for nitrate cycling
$\delta^{13}C$	Modern and palaeoproxy for nutrient content and ocean circulation
Radioactive isotopes	
^{230}Th	Constant flux monitor in sediments; tracer of modern ocean circulation and particle scavenging
^{231}Pa	Palaeoproxy for circulation and productivity; tracer of modern particle processes
Radiogenic isotopes	
Pb isotopes	Tracer of natural and contaminant sources to the ocean
Nd isotopes	Tracer of natural sources of TEIs to the ocean
Other parameters	
Stored sample	To allow future work
Particles	Essential transport vector for many TEIs
Aerosols	Essential source of TEIs to the surface ocean

9. Programme management

9.1 Background and needs

GEOTRACES represents an unprecedented integration and synthesis on a global scale of research on the marine biogeochemical cycles of trace elements and isotopes. As such, GEOTRACES requires strong coordination and management to address several issues including, but not limited to:

- organising and coordinating the various programme elements to ensure effective communication and a seamless operation of all activities;
- liaison with other research programmes sharing common interests and goals;
- integrating modelling with observational studies to achieve a comprehensive synthesis and interpretation of the findings;
- ensuring the compatibility of analytical methods used by different participating groups;
- collecting, archiving and serving data generated throughout the programme;
- engaging scientists from developing nations to expand the capacity worldwide for marine research on trace elements and isotopes;
- informing the broader oceanographic community, policy makers, educators, and the public at large of principal findings; and
- pursuing complementary funding strategies among various national and international agencies.

An organisational structure to fill these needs is illustrated in Figure 30.

9.2 Scientific Steering Committee

A Scientific Steering Committee (SSC) will have the primary responsibility for coordination and management of international GEOTRACES activities. The SSC will oversee an International Programme Office, a Data Management System/Office, and various standing committees to ensure that the common needs of GEOTRACES activities are met. The SSC will interact with national committees and organise planning workshops as needed to establish research priorities and implement GEOTRACES. Of particular importance, here, is the need to organise ocean sections, both to ensure global coverage of vital regions of interest and to avoid unnecessary duplication of effort. It is anticipated that national GEOTRACES programmes will propose to undertake specific sections. The SSC will review such proposals for compliance with the criteria for ocean sections (Section 8.1), and offer recommendations for adjustments to proposed sections where these are deemed beneficial. In addition, the SSC will foster partnerships where international collaboration is needed to complete a section, or to ensure that all core parameters are measured along a section. Partnering with national committees, the SSC will seek financial resources from national and international funding agencies to support the implementation of GEOTRACES. Later, these same partnerships will play a vital role in disseminating the findings of the GEOTRACES programme. The SSC will provide regular reports to SCOR, the principal body providing oversight of GEOTRACES. SCOR, in turn, will advise the SSC on strategies to achieve GEOTRACES goals. SCOR will also assist GEOTRACES in making contacts with other programmes sharing common research objectives, as well as with national and international funding agencies and with intergovernmental agencies that can offer financial, logistical or political support.

9.3 International Programme Office

An International Programme Office (IPO) will serve as a co-ordination centre for day-to-day operations and logistical matters. The IPO will assist the SSC and its standing committees with all aspects of their work, including the development of a data management policy and with the implementation of a Data Management System/Office. The IPO will facilitate communications among the various components of GEOTRACES (e.g., national committees, standing committees) and will serve as the primary interface for communications with the broader oceanographic community and with the general public. To that end, the IPO will maintain a Web site to post information about GEOTRACES activities and to convey results from the programme in a format that can be understood by non-specialists. Information will be disseminated, as well, through brochures and in articles of newsletters produced by related programmes and organisations. The IPO will produce a GEOTRACES newsletter and will maintain a meta-database for GEOTRACES sections and process studies.

Following the strategy used successfully by previous programmes (e.g., WOCE, CLIVAR), the IPO will hold regional planning meetings involving interested parties to identify contributors to each of the principal ocean sections. Beyond identifying contributors, these meetings will set sampling protocols to ensure intercomparability among results generated by different groups. These meetings will also serve to coordinate activities of process studies to be linked with ocean sections.

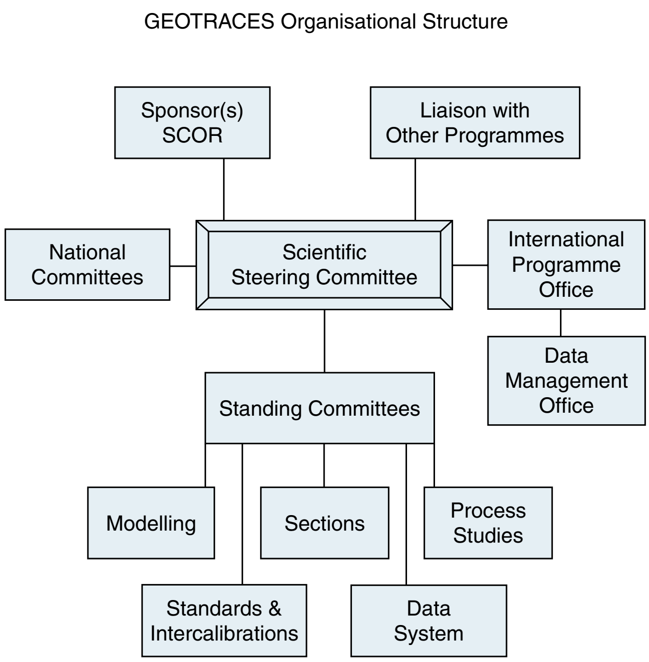

Figure 30. An overview of the organisational structure of the GEOTRACES programme.

9.4 Data management

Throughout the duration of the GEOTRACES programme, data will be generated from all major ocean basins by investigators representing many participating nations. For many TEIs, GEOTRACES will achieve basin-wide to global coverage for the first time. The successful synthesis of these data in working toward a complete knowledge of the global marine biogeochemical cycles of TEIs will require integration of the global data sets, and making them available from a central point of contact.

To ensure completeness, quality and consistency of the global datasets, GEOTRACES will implement a data management infrastructure responsible for the compilation, quality control and dissemination of TEI datasets. At the heart of such a system is an international GEOTRACES Data Assembly Centre (GDAC) that will be established at the start of the programme. The institution that hosts the GDAC must have experience with TEI data and must maintain good contacts with international groups participating in GEOTRACES. The GDAC will handle all GEOTRACES data from all countries participating in the programme. For reliable and efficient data quality control and intercalibration of data from different cruises, the GDAC should seek cooperation with experts in the field, whenever needed.

A GEOTRACES Data Management Committee (GDMC) will be established to: (1) recommend to the SSC standards and formats for submission of data and metadata; (2) recommend to the SSC policies for the submission, archival and dissemination of data; and (3) oversee the activities of the GDAC. The data-sharing policy for GEOTRACES should be consistent with SCOR guidelines and should assure timely and open data access to the scientific community, while respecting the legitimate interests of data producers during the publication rights period. Originating investigators should be strongly encouraged to share their data before the end of the publication rights period.

GEOTRACES will interact with other projects and programmes in two essential data-related activities. First, there are a growing number of national and international efforts to secure and archive historical data from a variety of marine research disciplines. These efforts are designed to encompass a broader suite of parameters than are typically available from World Data Centres, and to serve those data in more user-friendly formats. The GEOTRACES Data Management System will incorporate these historical data, or links to them, and GEOTRACES will make its data available to these developing data initiatives. Second, GEOTRACES will work with other programmes to ensure intercomparability of data (or of metadata).

To ensure timely submission of data, the IPO will track upcoming field programmes, and identify data to be generated as well as the individuals responsible for generating these data. Staff of the IPO will be knowledgeable about the various types of data, including methods used to collect the data. IPO staff will contact scientists involved in upcoming field programmes to inform them of data submission requirements.

9.5 Standing committees

Certain enabling activities (see Section 8) will provide a foundation upon which the subsequent field programmes will be built. Some of these activities (e.g., preparation of standard reference materials, intercalibration of sampling and analytical methods, data management) require a sufficient level of effort and expertise to warrant a standing committee. Standing committees will receive guidance from the SSC and administrative assistance from the IPO. Standing committees are expected to interact with other programmes dealing with similar issues, both to obtain assistance where those programmes are ahead of GEOTRACES in resolving the issues and to ensure compatibility among programmes in terms of solutions that are applied to common problems.

9.6 National committees

While GEOTRACES will be an international study of trace elements and isotopes, the work will be done by individual scientists and groups operating with support from national and regional funding agencies. Funding decisions, in turn, will be influenced by national priorities. Consequently, the formation of national GEOTRACES committees will be encouraged to merge local science priorities and research initiatives with the broader objectives of GEOTRACES, and to pursue financial resources from funding agencies to achieve these shared goals. Extensive interaction between national committees and the SSC will ensure that global coverage of ocean sections is achieved while avoiding unnecessary redundancy of effort. This interaction will also facilitate the development of process studies, both by bringing together nations to work on common studies and by informing nations in the early phases of planning a process study about the lessons learned from previous studies.

Implementation of the global study will be a complex process, the success of which will rely on the strong partnerships among the various national efforts as well as effective coordination by the SSC. Each nation participating in GEOTRACES will develop its own Implementation Plan, using this Science Plan as a basis for design of its research efforts while also ensuring that national priorities are met. The SSC will assist the national committees with the development of their Implementation Plans, while endeavouring to ensure that the sum of the individual national plans meets the objectives of the global GEOTRACES study.

9.7 Liaison with other programmes

GEOTRACES shares research objectives with several existing programmes, and with others currently under development (see Section 11). The SSC will hold responsibility for interaction with these programmes in pursuit of mutually beneficial collaboration. Collaboration may take a variety of forms including, but not limited to, intercalibration of analytically challenging methods, joint sponsorship of process studies, providing sampling opportunities during programme-specific cruises, and shared data management systems. Assistance in liaison relationships will be provided by SCOR.

10. Education and capacity building

A natural outcome of fulfilling the GEOTRACES objectives will be to build and maintain a core community of marine scientists, and to train a new generation of marine scientists who understand the chemical, physical and biological processes regulating the distribution and properties of TEIs well enough to exploit this knowledge reliably in future interdisciplinary studies.

Educating the next generation of marine geochemists will involve more than simply training students in state-of-the-art analytical techniques. Students will experience first hand, through science symposia and data workshops, the synergistic benefits of collaborative interdisciplinary research. Furthermore, modelling will be integrated into GEOTRACES studies to a greater extent than has been the case for previous marine geochemical programmes. Workshops will be designed to inform observationalists about modern techniques in modelling, and modellers about modern techniques in observations. This cross-fertilisation will provide students specialising in any field with an awareness of the opportunities available through complementary approaches, and of the inherent capabilities and limitations of those approaches.

Many coastal nations currently lack the technical capability to measure trace elements and isotopes at natural levels in seawater, whereas others have the capability to measure only a limited suite of TEIs. Training workshops, mentioned above, will include participants from developing nations, from nations with partial capabilities for TEI research, as well as from nations that lead the GEOTRACES field programmes. In addition to the training provided by these workshops, funding will be sought to allow scientists from developing nations to participate in GEOTRACES cruises, and to provide fellowships to enable students and scientists to spend longer periods of time training in established labs. Assistance will be sought from SCOR, the Intergovernmental Oceanographic Commission (IOC), the International Atomic Energy Agency (IAEA), and other sources to perform capacity-building activities.

Outreach and communication will be conducted through various media outlets, the Internet, brochures and by promoting school participation through interactive distance learning Web sites. Teacher participation in cruises has proven to be an effective means of reaching a broader audience in recent years, especially students in elementary and secondary schools. GEOTRACES will explore opportunities to involve teachers in cruises as well as in outreach activities.

GEOTRACES anticipates serving as a resource to policy makers. Communication with policy makers is one of the defined functions of the IPO. Where appropriate, the IPO will call upon members of the SSC, or other scientists participating in GEOTRACES activities, to provide expert testimony concerning topics broadly related to the GEOTRACES mission (e.g., the transport and fate of contaminants; the implications of purposeful ocean fertilisation with biologically limiting micronutrients, such as Fe).

11. Relationship with other programmes and activities

GEOTRACES shares objectives with many other programmes. Some of these are already underway while others remain at early stages of planning. In all cases, efforts will be made to foster mutually beneficial collaboration and to avoid unnecessary duplication of efforts. The following examples are illustrative rather than exhaustive or exclusive.

An improved understanding of marine biogeochemical cycles of biolimiting trace elements is a goal shared with SOLAS (Surface Ocean–Lower Atmosphere Study) and IMBER (Integrated Marine Biogeochemistry and Ecosystem Research), both of which are being developed under joint sponsorship by SCOR (Scientific Committee on Oceanic Research) and IGBP (International Geosphere–Biosphere Programme). (SOLAS is also co-sponsored by the World Climate Research Programme and the Commission on Atmospheric Chemistry and Global Pollution.)

11.1 SOLAS

Atmospheric deposition of trace elements, one of the critical boundary fluxes of interest to GEOTRACES, lies at the heart of the SOLAS programme. GEOTRACES will pursue opportunities for collaborating with SOLAS in areas including, but not limited to, intercalibration of measurement techniques and joint sponsorship of process studies. Furthermore, GEOTRACES will endeavour to provide SOLAS investigators with opportunities for atmospheric sampling aboard its cruises. Because atmospheric deposition may be dominated by episodic events that often escape detection and/or measurement on specific ship-based expeditions, GEOTRACES will also collaborate with the Ocean Observing Initiatives (e.g., GOOS and ORION) that are developing global observatory buoys to provide a continuous record of atmospheric deposition at selected open-ocean and coastal sites.

11.2 IMBER

While the availability of certain trace elements influences the structure of marine ecosystems, as well as the physiological state of individual organisms, the active uptake of trace elements by organisms together with the abiotic scavenging of dissolved elements by biogenic particles regulates the internal cycling and fate of many TEIs. Whereas these two aspects of TEI cycles cannot be studied in complete isolation from one another, neither is it necessarily effective to study the two aspects simultaneously. Here we find potential for synergies in collaboration with IMBER. GEOTRACES will investigate the large-scale impact of biological processes on the marine biogeochemical cycles of TEIs, in the context of other processes that influence these cycles as well. IMBER, on the other hand, will examine the sensitivity of organisms and of ecosystems to variability in the supply of essential TEIs, together with the regeneration of these biogenic materials within the mesopelagic zone. Through collaboration and joint synthesis of findings, GEOTRACES, together with IMBER and SOLAS, will determine the response of marine ecosystems to variability in trace element supply, the sensitivity of these relationships to global change, and the consequences for the global carbon cycle and related concerns.

As described in the *IMBER Science Plan and Implementation Strategy*, IMBER process studies will be co-located at time-series sites. Because observing technologies and infrastructure developed and implemented within Ocean Observing Initiatives may likely serve as the foundation for time-series sites, it is envisioned that synergistic, collaborative efforts will develop among the GOOS, ORION, GEOTRACES, IMBER and SOLAS programmes.

11.3 CLIVAR

Significant opportunity for collaboration also exists with the CLIVAR/CO_2 Repeat Hydrography Programme. Following the WOCE survey, oceanographers have initiated a programme of repeat hydrographic sections to determine changes in hydrography, carbon cycling, and ventilation rates on decadal timescales. This partnership between the CLIVAR (hydrographic) and carbon-cycle research communities is a good example of the mutual benefit that can be derived by sharing limited resources while pursuing common goals. As with the ocean carbon community, trace element geochemists will benefit from collaboration with CLIVAR. Many of the transport terms derived in the study of heat and freshwater budgets apply as well to TEIs. Furthermore, combining the data generated along ocean sections by GEOTRACES with complementary results from CLIVAR will expand the overall database used in support of modelling efforts to characterise the sources, sinks and internal cycling of TEIs and of carbon (see Section 6).

11.4 IMAGES/PAGES

Many trace elements and isotopes are exploited as proxies for past ocean conditions because their records can be readily extracted from sediments, corals and other geological archives. However, proxy-based reconstructions often suffer from uncertainties concerning the relationship between the TEIs and the parameters for which they are intended to serve as proxies. These uncertainties, in turn, are often consequences of the incomplete understanding of the biogeochemical cycles of TEIs in the modern ocean. Completing the goals of GEOTRACES will do much to improve this understanding, effectively providing an improved calibration of many proxies currently in use. Calibration of palaeoproxies is a high priority for IMAGES (International Marine Aspects of Past Global Changes), with whom GEOTRACES anticipates having a close working relationship.

11.5 SCOR/IMAGES working groups

Related investigation of palaeoceanographic proxies is being undertaken by two SCOR/IMAGES working groups: WG 123 (PACE: Reconstruction of Past Ocean Circulation) is examining past ocean circulation, while WG 124 (LINKS: Analysing the Links Between Present Oceanic Processes and Palaeo-Records) is analysing the links between present ocean processes and palaeo-records. TEI proxies play a critical role in reconstructing past ocean circulation, while proxy calibration is the primary objective of WG 124. GEOTRACES will work closely with these working groups to achieve an improved understanding and application of TEI proxies.

Other programmes have a more general interest in material fluxes that hold some overlap with GEOTRACES goals. For example, InterRidge is concerned with the fluxes of material into, and out of, mid-ocean ridge systems. GEOTRACES seeks to establish the role of these fluxes in the global marine biogeochemical cycles of trace elements and their isotopes, thereby sharing a common interest with InterRidge.

Important synergies and potential cost savings can be realised by coordinating GEOTRACES research with that being conducted within other programmes. Substantial benefits can be achieved by coordinating cruises in regions of common interest, sharing modelling resources that are vital to the evaluation of mean and time-varying fluxes, and maintaining a core of skilled seagoing analysts who measure hydrographic and nutrient properties of interest to all parties.

Planning for the International Polar Year (IPY) illustrates the principle above. With oversight from the International Council for Science (ICSU) and the World Meteorological Organization (WMO), planning is underway worldwide for research in both polar regions during 2007–2009. Much of this work will be interdisciplinary, and the objectives of GEOTRACES fit very well within the goals of the IPY. For example, certain TEIs serve as tracers for land–ocean exchange of material in the Arctic Ocean, whereas other TEIs serve as micronutrients that are believed to limit biological productivity in the Southern Ocean. Assessing land–ocean exchanges and the status of polar marine ecosystems is of high priority for IPY, as it is for GEOTRACES. As polar regions are already beginning to show signs of global change, it is particularly urgent to characterise TEI cycles in these regions before further change transpires.

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13 Appendices

Appendix A: abbreviations and acronyms

BATS	Bermuda Atlantic Time Series
CFC	Chorofluorocarbon
CLIVAR	Climate Variability and Predictability
DIC	Dissolved inorganic carbon
EPR	East Pacific Rise
GDAC	GEOTRACES Data Assembly Centre
GDMC	GEOTRACES Data Management Committee
GEOSECS	Geochemical Ocean Sections Study
GLOBEC	Global Ocean Ecosystem Dynamics
GLORI	Global Logistics Research Initiative
GOOS	Global Ocean Observing System
HNLC	High Nutrient, Low Chlorophyll
HOT	Hawaii Ocean Time-series
IAEA	International Atomic Energy Agency
ICSU	International Council for Science
IGBP	International Geosphere–Biosphere Programme
IODP	Integrated Ocean Drilling Program
IPY	International Polar Year
IMAGES	International Marine Aspects of Past Global Change Study
IMBER	Integrated Marine Biogeochemistry and Ecosystem Research
InterRidge	An initiative that promotes interdisciplinary study, scientific communication, and outreach related to all aspects of the globe-encircling, mid-ocean ridge system.
IOC	Intergovernmental Oceanographic Commission
IODP	Integrated Ocean Drilling Programme
IPO	International programme office
JGOFS	Joint Global Ocean Flux Study
LOICZ	Land–Ocean Interactions in the Coastal Zone
InterMARGINS	A coordinated, interdisciplinary investigation of four fundamental initiatives; the Seismogenic Zone Experiment, the Subduction Factory, Rupturing Continental Lithosphere, and Sediment Dynamics and Strata Formation (Source to Sink).

MOR	Mid-ocean ridge
OMZ	Oxygen minimum zone
ORION	Ocean Research Interactive Observatory Networks
NOSAMS	National Ocean Sciences Accelerator Mass Spectrometer
PAGES	Past Global Changes
POC	Particulate organic carbon
POM	Particulate organic matter
SCOR	Scientific Committee on Oceanic Research
REE	Rare earth elements
RIOMAR	River Dominated Ocean Margins
SeaWiFS	Sea-viewing Wide Field-of-view Sensor
SGD	Submarine groundwater discharge
SOLAS	Surface Ocean–Lower Atmosphere Study
SRM	Standard reference material
SSC	Scientific steering committee
SST	Sea surface temperature
TEI	Trace elements and isotopes
TRMM	Tropical Rain Measuring Mission
TTO	Transient Tracers in the Ocean
WCRP	World Climate Research Programme
WOCE	World Ocean Circulation Experiment
WMO	World Meteorological Organization

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