INVITED REVIEW

GEOTRACES – An international study of the global marine biogeochemical cycles of trace elements and their isotopes

SCOR Working Group[*][1]

Abstract

Trace elements serve important roles as regulators of ocean processes including marine ecosystem dynamics and carbon cycling. The role of iron, for instance, is well known as a limiting micronutrient in the surface ocean. Several other trace elements also play crucial roles in ecosystem function and their supply therefore controls 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 past ocean conditions, 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 cycle of many trace elements and isotopes has been significantly impacted by human activity. Some of these 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 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 in context.

Despite the recognised importance of understanding the geochemical cycles of trace elements and isotopes, limited knowledge of their sources and sinks in the ocean and the rates and mechanisms governing their internal cycling, constrains their application to illuminating the problems outlined above. Marine geochemists are poised to make significant progress in trace-element biogeochemistry. Advances in clean sampling protocols and analytical techniques provide unprecedented capability for high-density sampling and measurement of a wide range of trace elements and isotopes which can be combined with new modelling strategies that have evolved from the World Ocean Circulation Experiment (WOCE) and Joint Global Ocean Flux Study (JGOFS) programmes. A major new international research programme, GEOTRACES, has now been developed as a result of community input to study the global marine biogeochemical cycles of trace elements and their isotopes. Here, we describe this programme and its rationale.
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1. Preface

The investigation of trace-element and isotope (TEI) distributions has evolved significantly from the days of Geochemical Ocean Sections Study (GEOSECS) of the 1970s, when some of the earliest "oceanographically

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consistent" trace-element data started to appear in the literature. From sparsely sampled vertical profiles obtained as an ancillary activity during a seagoing project, the determination of trace elements has become an important and sometimes central focus of many research programs that seek information on the nature and rate of biogeochemical processes in the ocean. The study of TEIs has graduated from a curiosity to understand how the chemical diversity of minor and trace elements, in their various redox and chemical speciation states, interacts with the physical and biological processes in the ocean. As a result of the pioneering work of a large number of individuals who have collectively outlined the geochemical cycles of many TEIs in sufficient detail, they can now be used as tools to constrain contemporary and historic oceanic processes.

The development of these tools is important since the distribution of TEIs reflects the net result of the physical and biogeochemical processes, and thus its record in the sediments provides important clues to the historic functioning of the oceanic system under different climate regimes. This is particularly important in the case of micronutrients such as Fe, where the oceanic distributions appear to be an important link to climatic processes (see Section 2.2). In this case, and perhaps for other biologically required TEIs, climate-change-induced perturbations of their cycles may have important consequences for the global carbon cycle and, thus, global climate. However, the historic development of work in this field has meant that much of the advances have been made by individual investigators working in relative isolation. Thus, our ability to link the behaviours of the well-studied TEIs to each other is still in its infancy.

The analytical and sampling advances that have made this progress possible for some TEIs now also open the door to develop new tracers of contemporary and historic oceanographic processes. Thus geochemistry and the geochemical community are at a point where, as a result of community-wide planning, a new era of geochemical exploration is to begin. This will take the form of a new international programme, GEO-TRACES, which will survey critical regions of the world's oceans for TEIs that are known indicators of important biogeochemical and physical processes. In addition to providing a well-calibrated multi-tracer framework of existing TEI for use in constraining our understanding and modelling of oceanic processes, this programme will provide an opportunity to develop new tracers in a rich context of known tracer behaviour, thus enabling the rapid identification and application of novel tracers to oceanic processes.

This manuscript contains the assessment of the current state of the application of TEIs to oceanographic processes, assembled by the SCOR working group for the GEOTRACES science plan. The intention is that by bringing this material to a wider audience who may be unaware of the developments in the tracer applications, it will entrain scientists from other related disciplines who may involve themselves in, and benefit from, this new programme.

2. Introduction and overview

2.1. 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). These effects of TEIs on individual organisms, in turn, are 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 and Hf) 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 time scales 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 GEO-TRACES and other new programmes such as SOLAS and IMBER.

2.2. Background

The 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 and primary references therein). 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 (SGD) (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 (Fig. 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
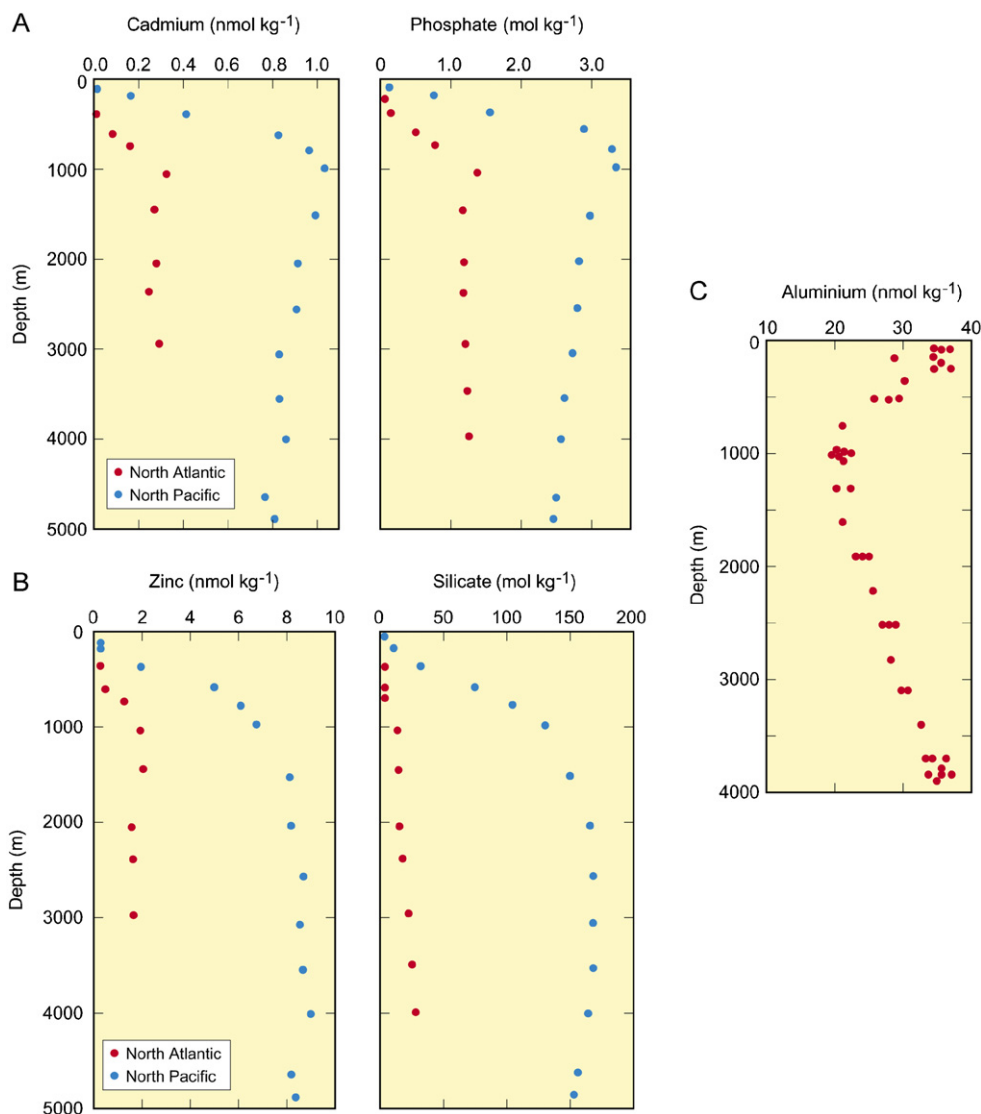

Fig. 1. Trace elements, such as Cd (A) and Zn (B), have nutrient-like distributions, indicating biological uptake from surface waters and regeneration at depth, as well as accumulation in deep waters along the flow path from the Atlantic to the Pacific Ocean. Others, such as Al (C), have mid-depth concentration minima, reflecting sources at the surface and bottom as well as scavenging to particles throughout the water column. Reprinted with permission from Elsevier (Bruland, 1983).

profiles for most elements in the periodic table (Nozaki, 1992) and for many stable and radioactive isotopes. For example, multiple-collector plasma source mass spectrometers are now allowing the systematic study of isotopic fractionation for most elements of the periodic table. 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 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 (see cover image) 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 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 (Fig. 2). 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 oceans and providing a major driver of environmental change. The potential for Fe to serve as a limiting micronutrient was recognised long ago, but its significance only began to be fully appreciated in the late 1980s (e.g., Martin and Fitzwater, 1988; Martin and Gordon, 1988; 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 has become 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.
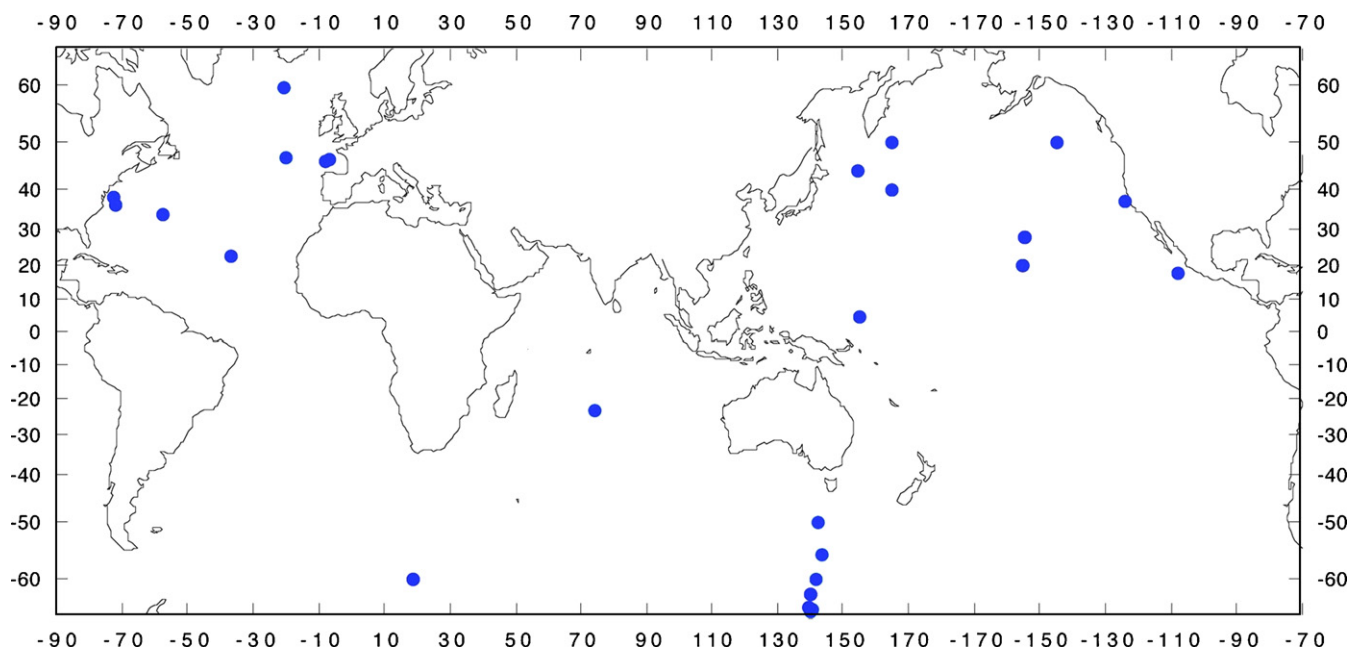
Fig. 2. The total number of stations at which concentrations of iron in seawater have been reported for depths 2000 m or deeper, as of 2003. Redrafted from compilation of Payal Parekh, MIT.

Table 1. Important biogeochemical processes in the ocean and the trace metals thought to be fundamental to their action

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)

Derived from Morel et al. (2003) and Morel and Price (2003), and references therein.

In some cases, the affect of TEIs on organisms is inhibitory rather than nutritional. For example, Mann et al. (2002) showed that the distribution of *Prochlorococcus*, the most abundant photosynthetic organism in the ocean, is affected by Cu toxicity: their 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 paleoceanography 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 proxy for paleotemperatures.

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 distribution of many tracers, has been impossible. A more comprehensive understanding of the global biogeochemical cycles of 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 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 a new marine chemistry programme: GEOTRACES.

2.3. Timeliness

With the definition of an increasing number of high-priority research questions, 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: (a) advances in sampling techniques and analytical technology; (b) 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; (c) advances in forward and inverse modelling techniques that will provide information not attainable previously; (d) implementation of contemporary ocean research programmes that will provide complementary information of benefit to GEOTRACES, and/or that will utilise and benefit from GEOTRACES findings; and (e) the need to characterise the baseline distributions of TEIs before further perturbation by anthropogenic inputs. It is realised though that for TEIs whose fluxes have been strongly impacted by anthropogenic activities over long periods of time, pristine baseline values may be unobtainable.

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 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 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. Data on dissolved Fe and Al, collected at 1 degree (60 nautical mile) spatial resolution in the upper 1000 m of the water column (Fig. 3), demonstrate substantial regional variations and structures, much of which would have
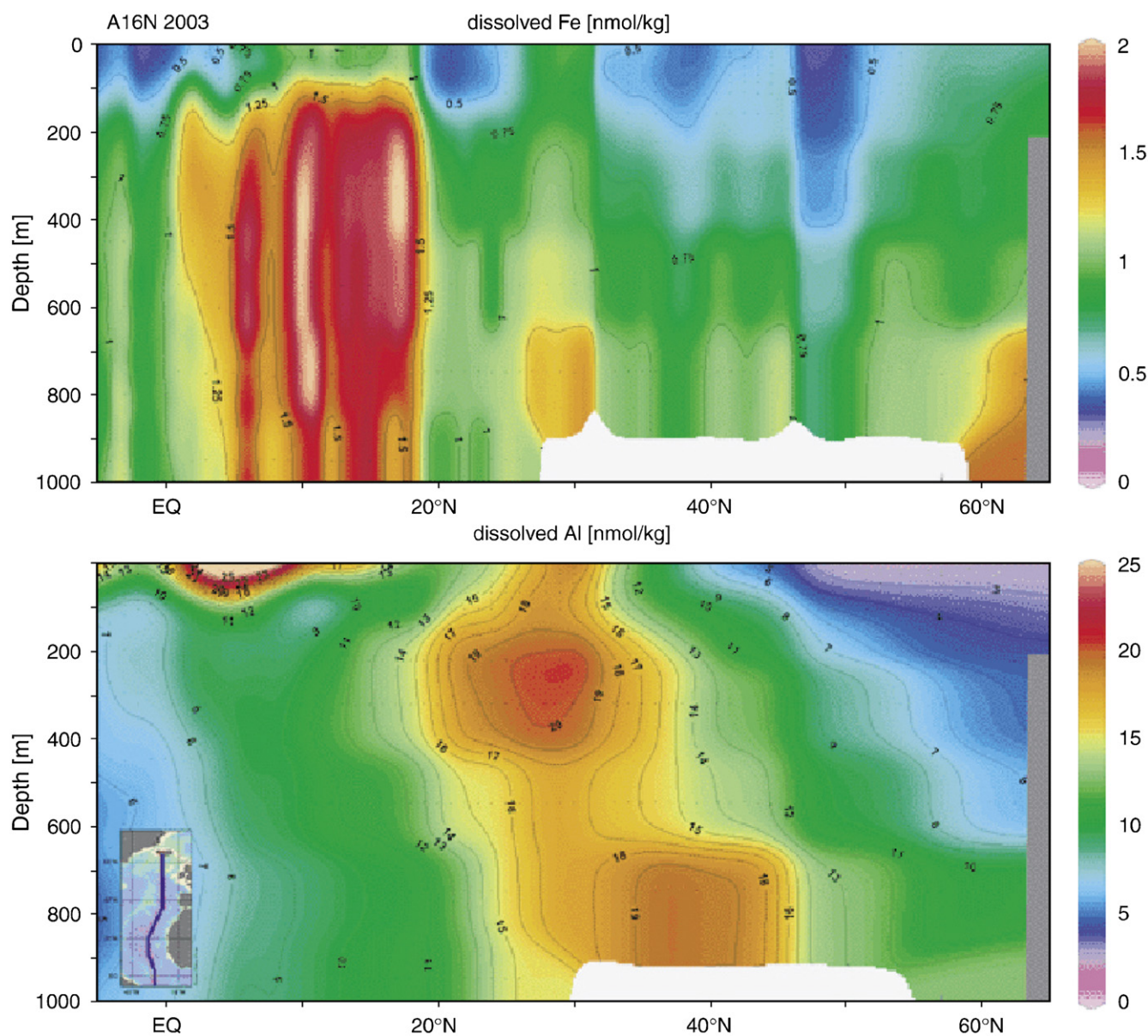
Fig. 3. Distributions of dissolved Fe (upper panel) and Al (lower panel) from 682 samples in the upper 1000 m along the CLIVAR A16 cruise track May 19–August 11, 2003 (see inset for location). Al increases in surface waters under the Saharan dust plume (0–20°N), indicating the addition of TEIs from dissolution of dust. Fe is not particularly enriched in the surface waters, but is significantly enriched deeper in the water column. 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). Reproduced 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.

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 (Fig. 2).

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 (Fig. 3), 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 subgrid-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 the 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 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 programmes within the Global Ocean Observation System.

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 content of corals (Shen and Boyle, 1987; Fig. 4). 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 (Fig. 4). Although anthropogenic Pb is delivered to the ocean primarily via atmospheric deposition, its presence can now be detected to great depths in the North Atlantic Ocean (Fig. 5) due to its downward transport by newly formed North Atlantic Deep Water. Time scales for deep-water renewal in other basins are much greater than in the North Atlantic Ocean, so Pb (and other TEIs) concentrations in 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 via freshwater inputs (e.g., Niragu, 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 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).

2.4. 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 over-riding goals:

- 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.
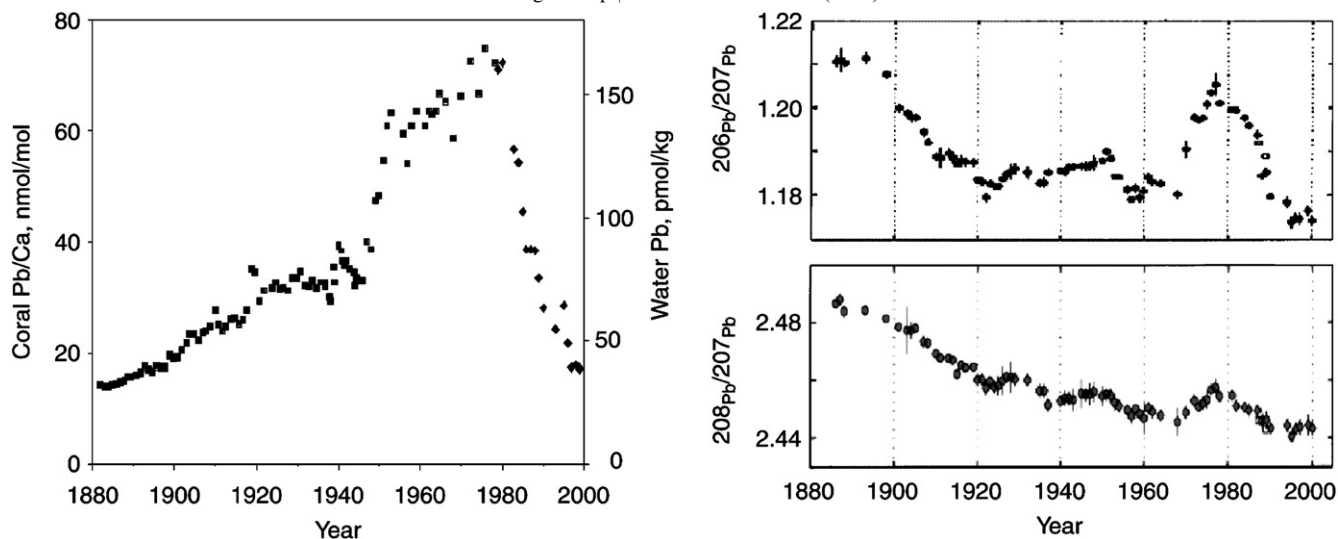
Fig. 4. Left: variability of lead (Pb) in surface waters near Bermuda derived from coral measurements (1880–1980) and seawater measurements (1980–2000). Rising Pb from 1880 to 1980 is due to Pb emissions from smelting, coal combustion and other high-temperature processes during the US industrial revolution (1880–1925) and automobile emissions from leaded gasoline utilisation. 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 years) balance of the input from the atmosphere and removal onto sinking biogenic particles. Data from Reuer (2002).

- 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.
- 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 runoff; the sediment–water boundary; ocean crust).
Theme 2 – Internal cycling (uptake and removal from surface waters; uptake and regeneration in the subsurface 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; paleoceanographic tracers based on sediment flux).

2.5. Anticipated benefits

2.5.1. The role of micronutrients in ocean ecosystems

The oceanic cycle of the major nutrients (PO_4, NO_3, Si) has been widely studied and is now reasonably well understood, 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 their role is still quite rudimentary. It is now reasonably well established that the supply of Fe limits total productivity in the HNLC regions of the surface ocean (e.g., Coale et al., 1996). Fe has also been implicated in a range of other ecosystem processes (Table 1). From laboratory and limited ocean-surface studies, other trace metals are also thought to play a key role in controlling biogeochemical processes, particularly Cu, Zn, Co, Cd and Mn (Morel et al., 2003; Morel and Price, 2003). Cycling of these micronutrients is a key aspect of the whole-ocean system, controlling not only the amount of ocean productivity, but 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 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 (Moore et al., 2002;
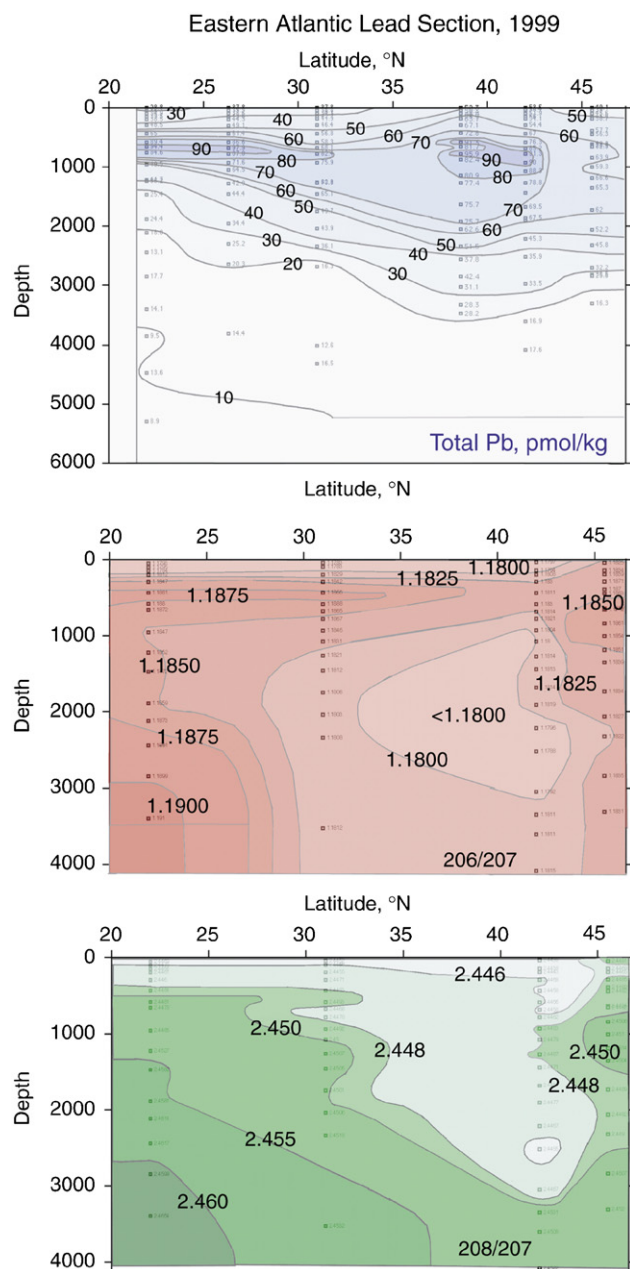
Fig. 5. Sections of Pb (top) and Pb-isotope ratios in the water column of the eastern Atlantic Ocean in 1999. The spatial variability of subsurface Pb and Pb-isotope patterns reflects the advection and mixing of surface waters into the deep sea. Water 500–900 m deep to the south of this section sank 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 (Fig. 4). Deeper waters have less lead because they are dominated by waters that left the surface many decades ago. For example, at ~3000 m at the southern end of the section, the Pb-isotope composition reflects lead that was the surface in the 1920s (see Fig. 4). Figure from Reuer (2002).

Archer and Johnson, 2000; 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 species (Fig. 6). 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 paleoceanographic 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.
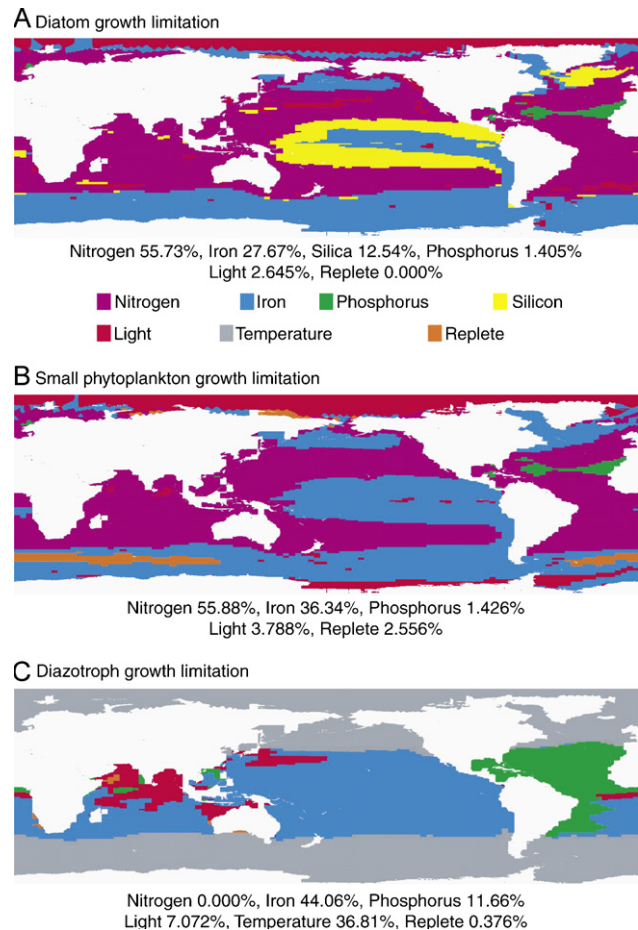
2.5.2. Transport and fate of contaminants

The oceanic cycle of many TEIs has been significantly impacted by human activity. Some 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.

Public awareness of the contamination of the ocean was particularly high in 1995 during the controversy surrounding disposal of the Brent Spar oil rig. 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, while 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 contaminants and TEIs will directly inform debates such as this into 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 accidentally (e.g., release of Pb during industrial processes; Fig. 4 and 5). 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 (Mason et al., 1994; Mason and Sheu, 2002) 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 presently 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

A Diatom growth limitation

Nitrogen 55.73%, Iron 27.67%, Silica 12.54%, Phosphorus 1.405%
Light 2.645%, Replete 0.000%

■ Nitrogen ■ Iron ■ Phosphorus ■ Silicon
■ Light ■ Temperature ■ Replete

B Small phytoplankton growth limitation

Nitrogen 55.88%, Iron 36.34%, Phosphorus 1.426%
Light 3.788%, Replete 2.556%

C Diazotroph growth limitation

Nitrogen 0.000%, Iron 44.06%, Phosphorus 11.66%
Light 7.072%, Temperature 36.81%, Replete 0.376%

transporting contaminants from surface ocean and continental shelves into the deep ocean. Of particular importance in this regard are materials that are mobilised under reducing conditions commonly found in near-shore sediments. For deep-ocean settings, GEOTRACES will provide a baseline against which future change can be assessed.

The 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.

2.5.3. 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

Fig. 6. 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 et al. (2004), Copyright (2004), American Geophysical Union. Reproduced with permission of American Geophysical Union.

$\Delta^{14}C$ [/mil]
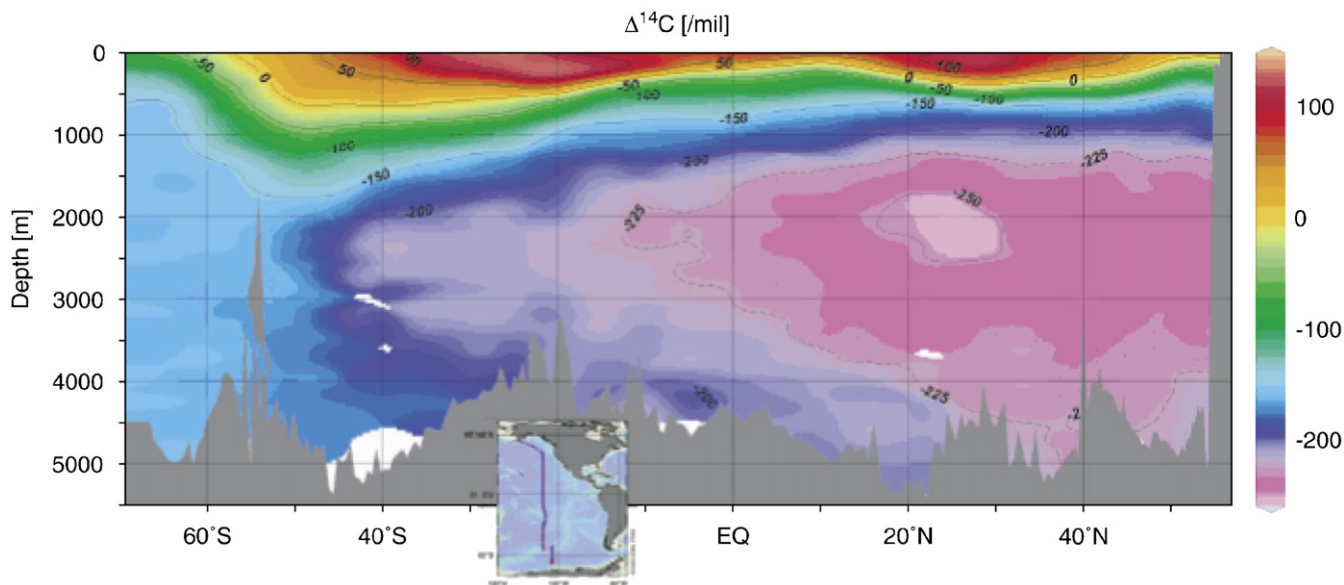
Fig. 7. A meridional section of radiocarbon ($\Delta^{14}C$ in permil) through the central Pacific Ocean taken from the GLODAP data set described in Key et al. (2004).

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. In such settings, 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 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 (Fig. 7). 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 directly measure, 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 Moore, 2006). For the ocean of the past it is impossible to make direct measurements and we are wholly dependant 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 that 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 in a wide variety of ocean variables, from sea-surface temperature (e.g., using Mg/Ca ratios) to nutrient utilisation (δ^{15}N), and from seawater pH (boron isotopes) to ocean circulation (^{231}Pa/^{230}Th or 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 the use of ^{231}Pa/^{230}Th and ε_{Nd} in the Atlantic Ocean during the last glacial period (Fig. 8). Both 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 (Piotrowski et al., 2004; Fig. 8). Both proxies are responding to real environmental change but our understanding is insufficient to reconcile them. Reconciliation can be achieved only through new measurements and modelling to understand the fundamental processes controlling TEI proxies for past change (Fig. 9) and so unravelling the cause of these differences. 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.

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 (Fig. 10; 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 (MOR) basalts both at high and low temperature.

The fluxes of TEIs occurring at each of these ocean interfaces are generally not well known. This 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.

While many of these fluxes can be measured directly, and such measurement programmes are now being implemented in parallel research initiatives (LOICZ, SOLAS, etc.), the large spatial and temporal variability
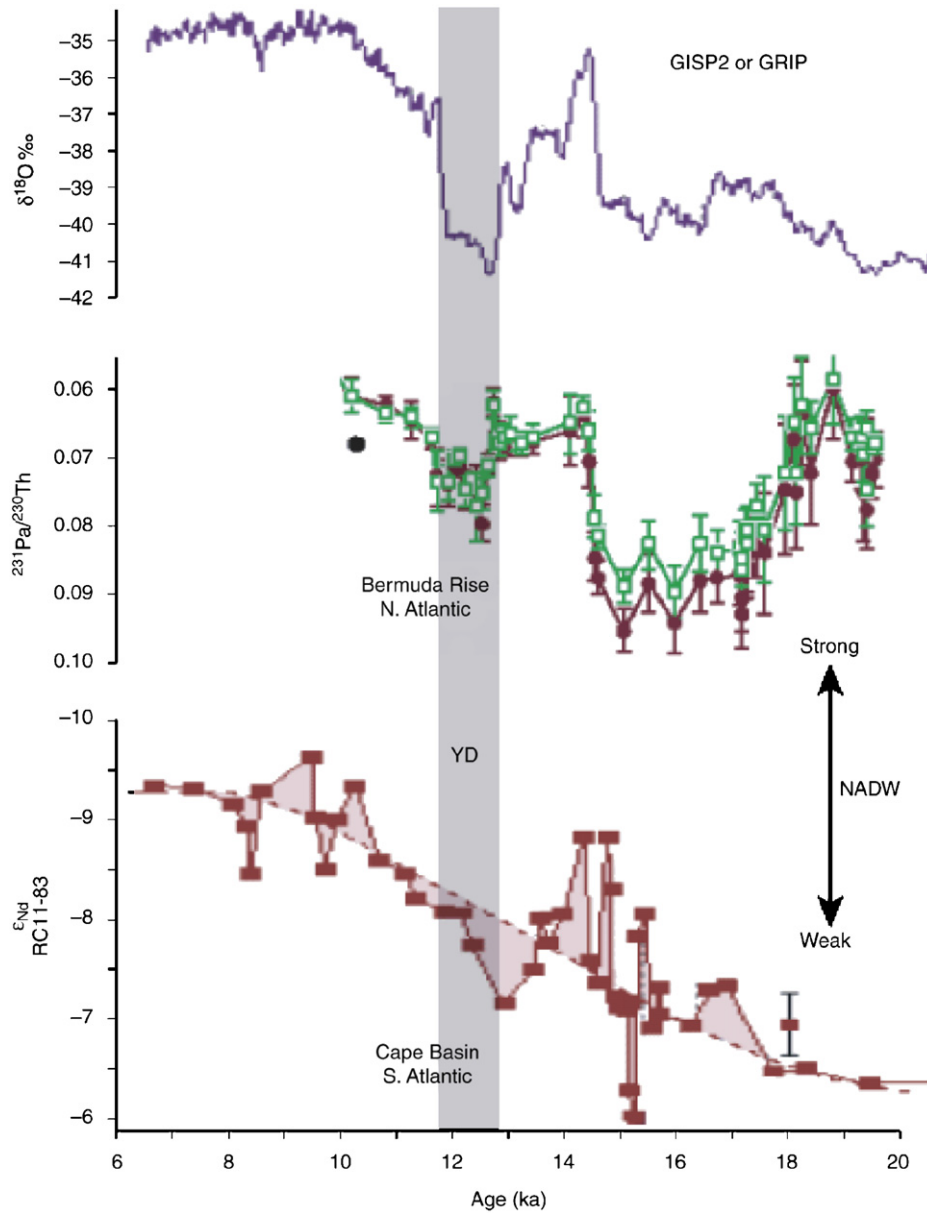
Fig. 8. Comparison of two ocean tracers, both thought to provide information about the rate of past flow of North Atlantic Deep Water (McManus et al., 2004; Piotrowski et al., 2004). Although both tracers agree that flow was strong during the Holocene and weak during the Younger Dryas, ^{231}Pa/^{230}Th (middle) suggests a high rate of flow at around 19 kyr while 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 δ^{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 et al. (2004), Copyright (2004), reprinted with permission from Elsevier.

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, MORs) 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
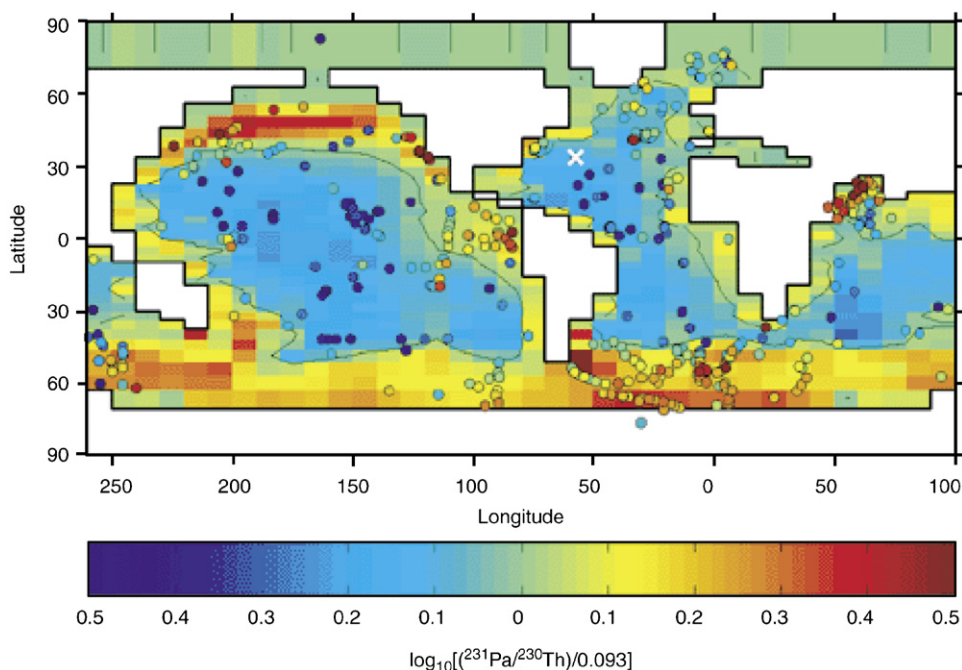
Fig. 9. Observation of sediment surface $^{231}Pa/^{230}Th$ (coloured circles) compared to a model reconstruction of this ratio (background colours) in sediment leaving the ocean. This ratio encodes information about both past ocean circulation rates and past productivity – two important variables in 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 Siddall et al. (2005), *Earth and Planetary Science Letters*, Copyright (2005), with permission from Elsevier.

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 accurately predicted.

Understanding of TEI fluxes and of the processes that control them 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. Al and Mn, for instance, provide tracers of Fe 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 proposed 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 (Fig. 11) 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, Asian deserts), large
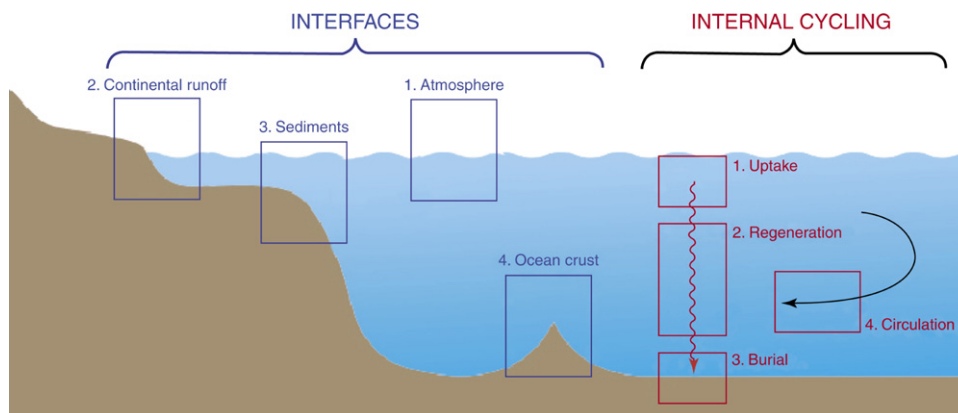
Fig. 10. Schematic illustrating the major influences on the distribution of TEIs in the oceans. Four major ocean interfaces (blue) and four major internal processes (red) are responsible for ocean TEI patterns. Within GEOTRACES, interface processes form the basis of Theme 1, while internal cycling processes are the basis of Theme 2.
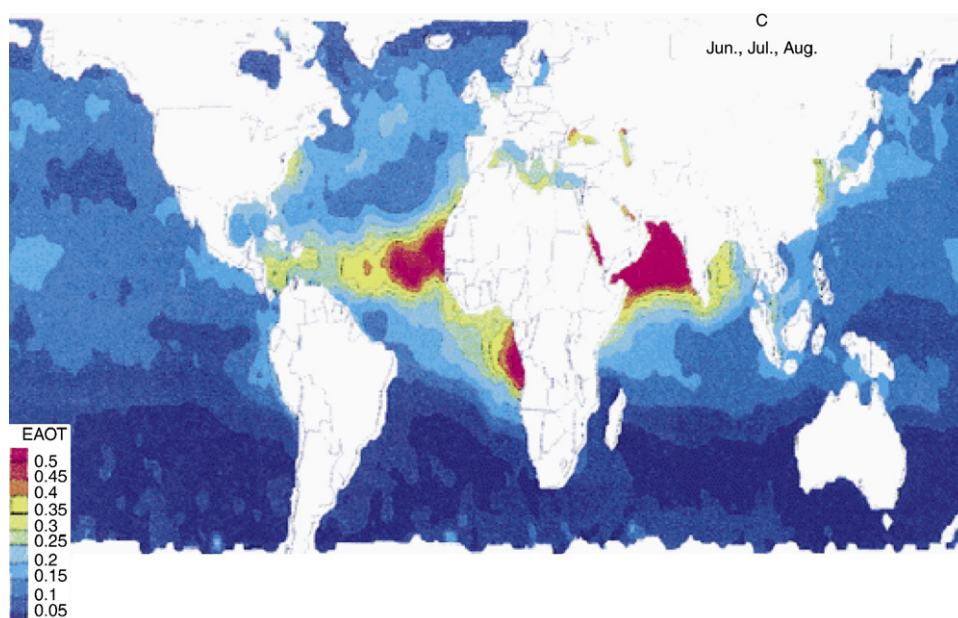
Fig. 11. Radiatively equivalent aerosol optical thickness (EAOT X 1000) over the ocean, as derived from the NOAA AVHRR satellites. It incorporates the June–August period and therefore misses the Asian outbreaks that occur predominantly in boreal spring. Husar et al. (1997), Copyright (1997) American Geophysical Union. Reproduction with permission of American Geophysical Union.

gradients in suspended material occur within the atmosphere in both space and time. Thus, the deposition of aeolian 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, ^{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 probably 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 distribution that, in turn, regulate their deposition processes, and they also have different spatial patterns and deposition reflecting 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).

Dissolved Al in surface waters has been qualitatively associated with atmospheric deposition since the earliest reports of its distribution in seawater (e.g., Hydes, 1979; Measures et al., 1984; Orians and Bruland, 1986; Moran and Moore, 1991; Yeats et al., 1992; Helmers and Rutgers van der Loeff, 1993). Using these and other results, Measures and Brown (1996) developed a model that used dissolved Al concentrations of the surface layer to estimate dust deposition fluxes to surface ocean waters. Measures and Vink (2000), found that this model compared well with absolute determinations and predictions from the atmospheric data-based GESAMP model of Duce et al. (1991). However in the western North Pacific a major discrepancy in the results from these two approaches has underlined the need for more ground-truthing of model-based deposition estimates as well as the need to develop new tracers with differing sensitivities to the time scales of deposition (Measures et al., 2005). In addition, since the biogeochemical impacts are dependant upon the fractional solubility of aerosols, it is important to identify and quantify the processes that control it.

The importance of understanding the atmospheric transport deposition and partial solubility of continental mineral dust is exemplified by the case of Fe, whose availability in surface waters and its role in ecosystem control (see above) appears to be coupled directly with the importance of its atmospheric transport route to, and partial solubility in, the surface oceans (Jickells et al., 2005). In addition to Fe, many of the other trace elements that are believed to play fundamental roles in biogeochemical processes in the ocean (see above and Table 1) are likely to have important aeolian transport routes whose perturbation may have far-reaching global biogeochemical consequences.

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 (Fig. 12). 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 worlds oceans (for example, Fig. 6) are critically dependant on atmospheric flux estimates, and of the fraction of dust that actually dissolves in the upper water column. More data are need for both of these parameters. In the open ocean, models based on reasonable estimates of these parameters have simulated surface water distribution of Fe in remarkably good agreement with measured values. In marginal seas, however, this is frequently not the case, especially on seasonal time scales. 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 time scales. The geochemical imprint of changes in deposition to the surface ocean and its propagation through the oceanic interior provides an important paleoceanographic tool to study changes in paleogeochemical and 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 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 dependant 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
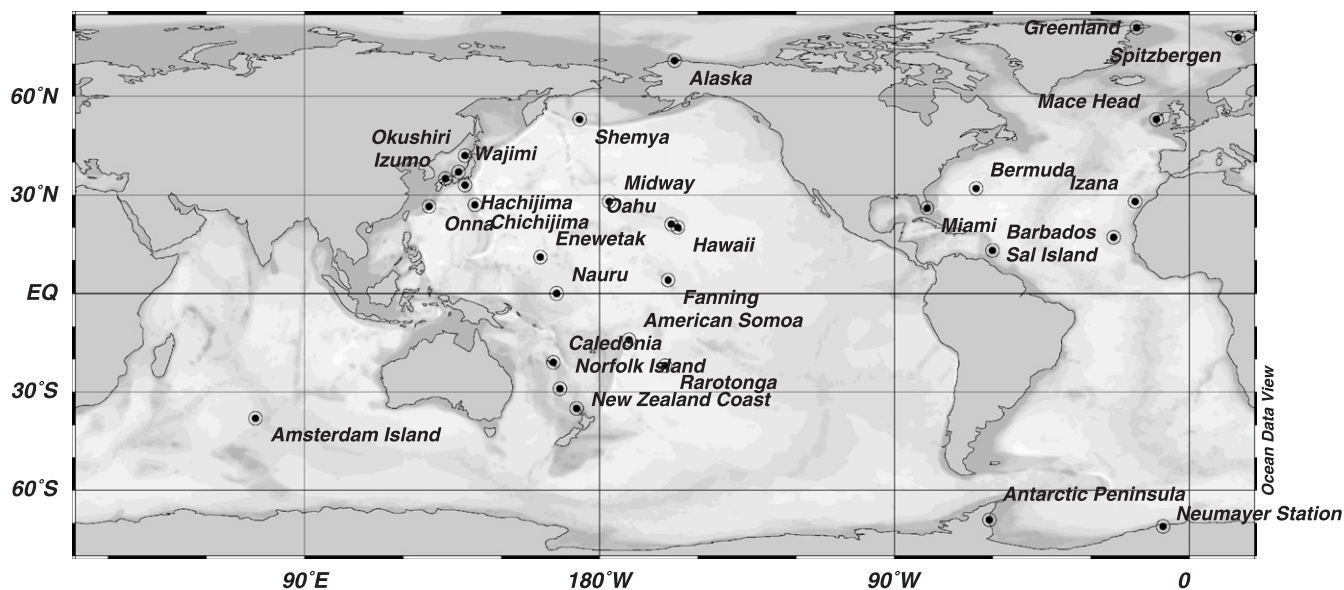
Fig. 12. There is a popular misconception that atmospheric inputs to the ocean are well constrained. This is based largely on the frequently cited "Duce Map" of mineral aerosol fluxes. The figure (Jickells and Spokes, 2001) shows the contours of the Duce Map in mg mineral dust $m^{-2} yr^{-1}$ (Duce et al., 1991), 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 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 and Spokes, (2001), Copyright (2001), Copyright John Wiley & Sons Limited. Reproduced with permission.

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

(a) Develop and refine chemical tracers in the surface ocean for quantification of atmospheric deposition (e.g., Ti, Al, ^{232}Th, isotopes of Nd, Pb, 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 time scales of atmospheric deposition, a variety of

tracers with differing sensitivity, sources and oceanic residence times will be required (e.g., Al, Ti, Ga).

(b) 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.

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

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

(e) Determine the speciation of trace elements added to the ocean by atmospheric deposition and therefore the bioavailability of these elements.

3.2. Continental runoff

3.2.1. Present understanding

A major supply 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 dependant on the properties of the element and the riverine environment. In the fresh-water/seawater mixing zone, some elements are removed from solution by biological uptake and by chemical scavenging. Coagulation of colloids and small particles also contribute to removal during this mixing. In this zone, desorption of particulate TEIs also takes place, in part due to their displacement from particle surfaces by competition from and complexing by the major cations of seawater.

SGD have been recognised in recent years as potentially significant sources of chemical species to the ocean (Fig. 13; Moore, 1996). SGD include fresh-water 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.

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 that 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.
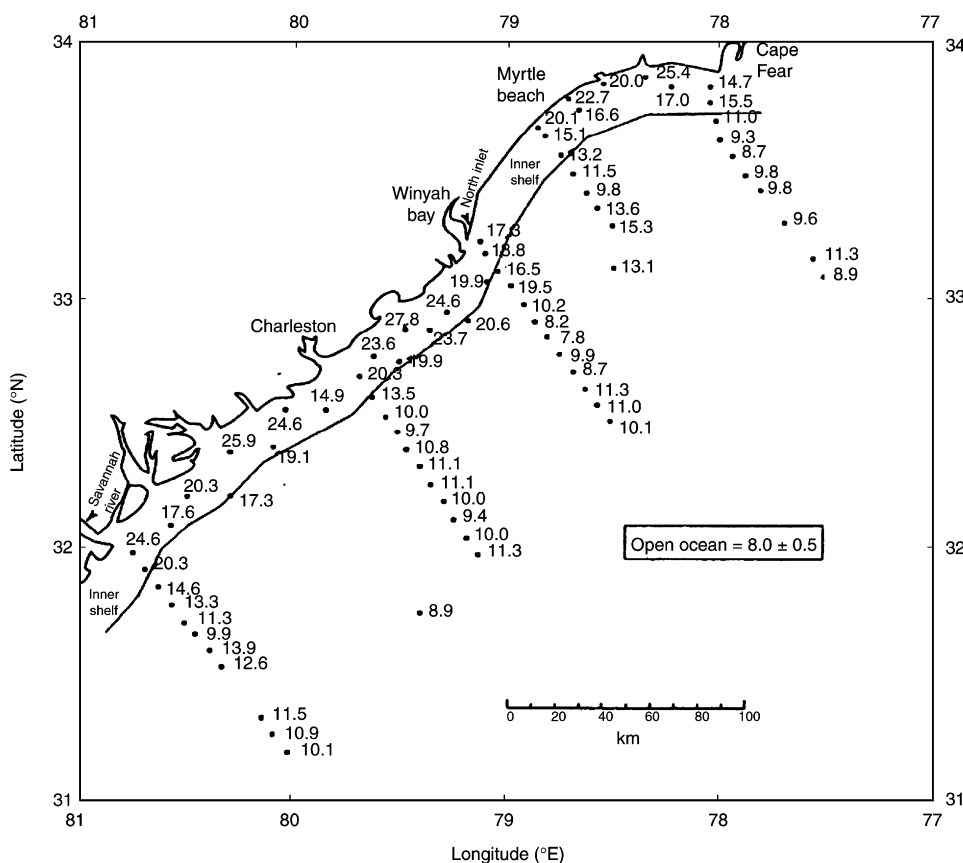
Fig. 13. ^{226}Ra concentrations in near-shore waters showing a clear increase towards the coast (Moore, 2000). This increase is evidence for important chemical fluxes occurring between continental aquifers and the coastal ocean. The size of this flux, and the processes controlling it, are presently very poorly constrained. Moore (2000), Copyright (2000), with permission from Elsevier.

- Assess the role of glacial weathering of fresh mineral surfaces

  Physical weathering in glacial settings (e.g., Greenland, 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 may represent a significant source of iron.

- Assess the role of sea ice as a vector transporting TEIs

  While 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 the 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 oceans. 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 $^{87}Sr/^{86}Sr$ (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 programs 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 is the Amazon 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 associated with this process is roughly half that of the global riverine flux. The plume from the Amazon also reaches a significant distance into the open Atlantic (Fig. 14).

Recent studies suggest that the TEIs in the Bay of Bengal are influenced throughout the water column by desorption of TEIs from these particles and sediments (Moore, 1997).

Studies of SGD have been performed on the southeastern coast of the United States and Long Island, NY, southern Brazil and 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 (Fig. 15) and will require collaboration with modellers and integration of real-time satellite data during chemical measurements programmes.

3.2.3. Specific GEOTRACES objectives

(a) Develop TEI tracers, and multi-tracer approaches, which integrate the geochemical fluxes from land to the open ocean.
(b) Use these TEI tracers and their global distributions to assess the global pattern of freshwater-derived geochemical fluxes to the open ocean.
(c) Integrate chemical data and new measurements with models and physical oceanography data (ship-board or satellite) to constrain the shelf-to-open-ocean fluxes of freshwater-derived TEIs (Hutchins and Bruland, 1998; Boye et al., 2003).

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 and 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)
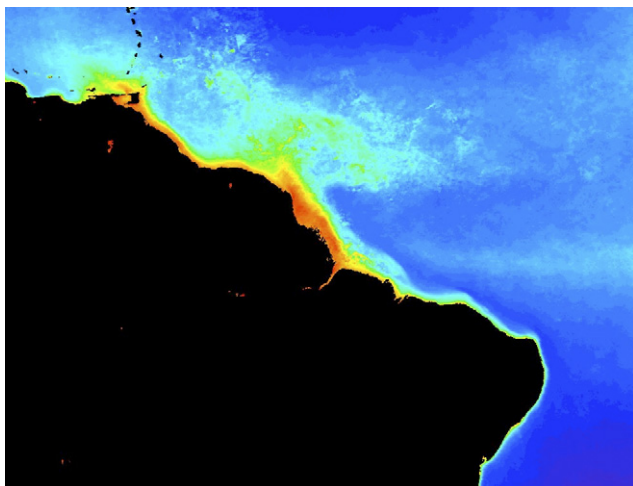
Fig. 14. A MODIS composite image of chlorophyll off the northeastern coast of South America from 1 January 2002 to 30 November 2005 (source: oceancolor.gsfc.nasa.gov 4 km grid). Riverine discharge of nutrients from the Amazon River stimulates elevated chlorophyll concentrations extending hundreds of miles from the coast.

that are released into solution following 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 (REE) in the water column. The strongest sources of Nd isotopes seem to be in ocean margin sediments, for which the evidence 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 (Johnson et al., 2003), the extent to which this represents a net source, by diagenetic
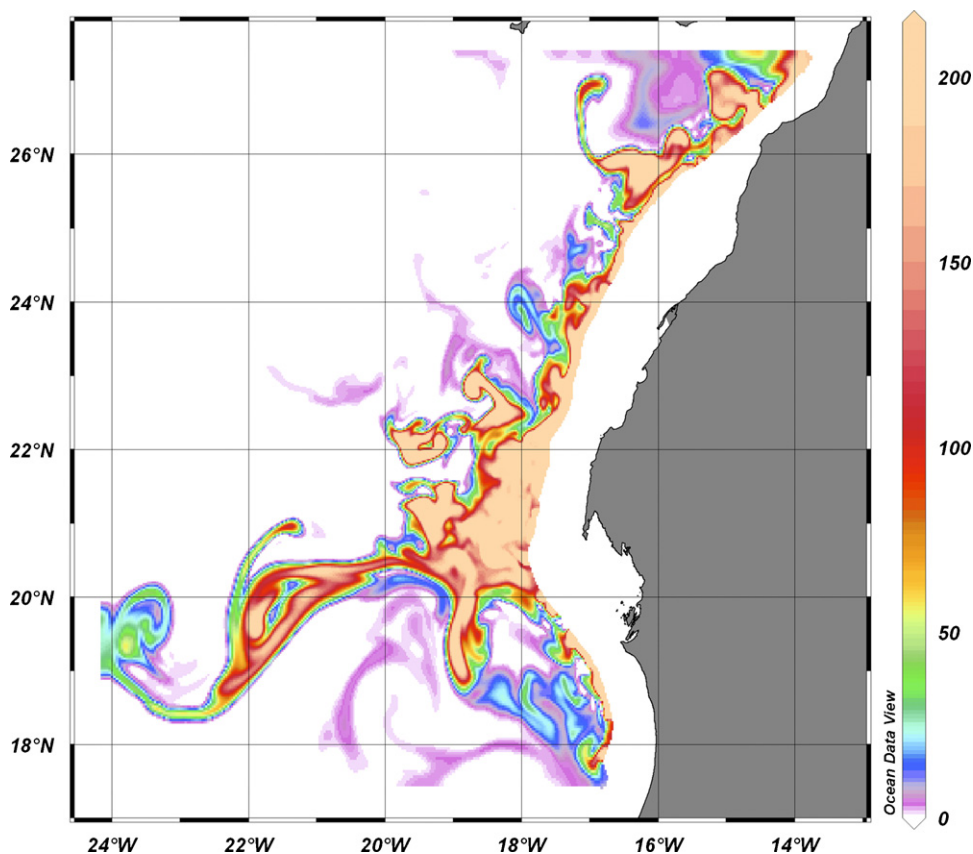
Fig. 15. Snapshot from a high-resolution model showing relative distribution of particles eroded from the NW African shelf and transported towards the open ocean by complex and highly variable ocean currents (Karakas et al., 2006). To extrapolate from measurements of TEIs to realistic flux estimates in such settings will require use of such modelling and of relevant monitoring studies, including satellite data. Copyright (2006) American Geophysical Union. Reproduced with permission of American Geophysical Union.

mobilisation of continentally derived material versus the regeneration of biogenic and authigenic marine phases, remains undetermined.

Historic and ongoing studies off major river mouths in Papua New Guinea (Kineke and Sternberg, 2000; Aller et al., 2004), and on the Equatorial Undercurrent in the Mid Pacific (Kaupp, 2005; Measures and Yang, pers. comm., 2005) suggest that the diagenetic and resuspension processes in the mobile mud belts that form in these regions might provide significant fluxes of biogeochemically important TEIs to the upwelling zones of the central Pacific (Wells et al., 1999). Additional work in the Drake Passage (Measures et al., 2006) suggests that the resuspension of shelf sediments results in Fe addition to Antarctic Circumpolar Current Water. This process is believed to be responsible for fuelling the large increases in phytoplankton biomass observed downstream in the Scotia Sea by satellites.

Several generic types of processes contribute to the removal of TEIs from seawater and their burial in marine sediments. The simplest is the passage of continentally derived particles through the water column, whether supplied via the atmosphere or by runoff, without any further solid-solution reaction. TEIs bound within aluminosilicate minerals would be 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 sea bed 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 these removal processes is generally more active (in terms of rates 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, and 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 byproducts of this high productivity gives rise to a strong oxygen minimum zone (OMZ). 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 permits 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 (Bacon, 1988; Spencer et al., 1981). 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., 2007, Arsouze et al., 2007).

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 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 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, their quantitative significance in ocean-wide biogeochemical cycles remains undetermined. In addition, the magnitude and location of OMZ regions has probably varied significantly over geologic time. 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 paleoceanography (Section 5).

- Compare fluxes at active and passive margins
Ocean margins can be divided into active margins (i.e., where subduction takes place) and passive margins. These have very different topographies, with active margins characterised by a narrow continental shelf and steep slope, while the opposite is true for passive margins. These different settings 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

(a) Evaluate burial (removal) fluxes of TEIs globally, and discriminate between TEIs contained in detrital phases and those that were removed from solution.
(b) 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.
(c) Evaluate net sedimentary sources of TEIs in regions where such sources are anticipated to exist (e.g., OMZs), and characterise the processes responsible for supplying the TEIs.
(d) Evaluate the net lateral exchange of TEIs between ocean margin sediments and the open ocean (boundary sources and boundary scavenging).
(e) Establish TEIs that serve as tracers for dissolution of lithogenic sediments for which the signal can be determined unambiguously well into the water column.

3.4. Ocean crust
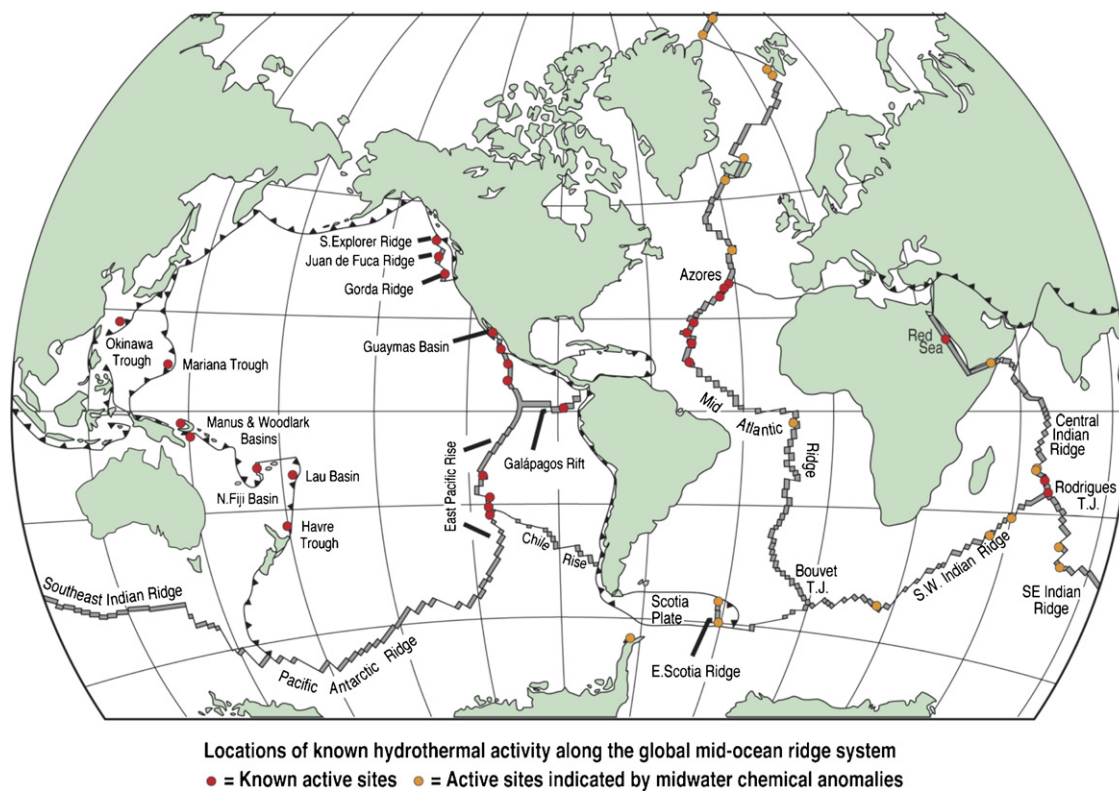
3.4.1. Present understanding

Seafloor hydrothermal circulation was first observed in a submarine 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 MOR system. Seawater is heated and undergoes chemical modification through reaction with the host rock as it percolates downward, reaching maximum temperatures which 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. 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 (Fig. 16). 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 number and location of individual vent sites on the seafloor we do know the global fluxes of key conservative tracers (e.g., $^{87}Sr/^{86}Sr$) to within approximately one order of magnitude (Elderfield and Schultz, 1996).

Approximately 25% of the total global heat flux from the Earth's interior (~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 ($\leqslant 400\,^{\circ}C$) "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 which contain a wide variety of 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 MORs 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 oceans; at its most conservative, the associated residence time for the global ocean with

Locations of known hydrothermal activity along the global mid-ocean ridge system
● = Known active sites   ● = Active sites indicated by midwater chemical anomalies

Fig. 16. The global mid-ocean-ridge system showing known activity. Figure reprinted from German and Von Damm (2003), Copyright (2003), with permission from Elsevier.

respect to cycling through hydrothermal plumes has been calculated as 4–8 kyr, comparable to the characteristic time scale 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.

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 exhibit strong removal of some particle-reactive tracers from the ocean (e.g., REE, ^{230}Th–^{231}Pa–^{10}Be) even when compared to 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 oceans?
  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 systems 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, that 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 which

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 the majority 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 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 focused on interactions with the seafloor and young oceanic crust. Consequently, many studies have been geologically/mineralogically influenced, with a tendency to treat these systems as largely inorganic reaction systems. Increasingly, however, the MOR 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 Eh-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 oceans. 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 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

(a) Determine the fluxes, mechanisms and rates of advective and eddy-diffusive dispersion of hydrothermal fluids and TEIs associated with plume waters.
(b) 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 oceans through hydrothermal systems (e.g., dissolved ^{3}He, ^{222}Rn, Si) against which we will be able to compare shorter-residence-time species' behaviours. This will be key to identifying those elements and isotopes for which hydrothermal circulation is important with respect to their global ocean cycles.
(c) Determine the role of particle formation in partitioning of hydrothermally affected TEIs between dissolved, colloidal and particulate phases. Key subobjectives will include: comparison of particulates in buoyant versus non-buoyant plumes (e.g., domination of sulphide versus oxyhydroxide phases); the modification of gross dissolved hydrothermal fluxes through precipitation of hydrothermal particles; impact on ambient seawater of scavenging onto hydrothermal particles; and 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.
(d) Determine the importance of (micro)biological interactions to the chemical cycling of hydrothermally affected TEIs (e.g., already known 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.

4. Theme 2: internal cycling

Marine biogeochemical cycles of TEIs are influenced by complex transport and transformation processes, which are referred to as "internal cycling". Transformations involve TEI exchange between 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 (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, largely as a result of the GEOSECS programme and related work (e.g., Broecker and Peng, 1982). For example, P is incorporated into organic tissue in surface waters. While 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 P 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 presently 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 (Nozaki, 1992). Even the most insoluble TEIs (e.g., Th), are exchanged between dissolved and particulate forms scores of times before finally being removed to the sediments and buried (Bacon and Anderson, 1982).

While these features were first recognised more than a quarter 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 (Nozaki, 1992). This removal occurs by a combination of biological uptake into organic tissue and biogenic minerals, and by abiotic sorption to particle surfaces. In some cases, inorganic precipitation of minerals may occur, 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, and their affinity for sorption to particles, depends on their chemical speciation. Many dissolved TEIs exist as complexes 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 via colloidal intermediaries (Wells, 2002; Doucet et al., 2007). 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 $0.4\,\mu m$ filter) in surface waters actually exist as colloids or as true 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 does 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 dependant (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 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 systematically, and the results incorporated into models used to simulate the ocean's response to global change.

- How does 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. They 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 via the atmosphere, as aerosols, via rivers, and by resuspension of coastal sediments. Fluxes 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 level during glacial times eliminated many of the estuaries that trap riverine particles today, allowing for the delivery to the 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 does 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 and 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).

While 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. Paleoceanographic 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 so as to portray accurately the TEI-related feedback mechanisms that link ecosystem structure and the ocean carbon cycle to global change.

- How does 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

(a) Determine the effect of speciation on the uptake and removal rates of TEIs in surface waters.
(b) Determine the impact of the abundance and composition of colloids on the uptake and removal of TEIs in surface waters.
(c) Determine the sensitivity to supply of lithogenic material of the uptake and removal rates of TEIs in surface waters.
(d) Determine the sensitivity to changes in ecosystem structure of the uptake and removal rates of TEIs in surface waters.

4.2. Uptake and regeneration in subsurface water

4.2.1. Present understanding

Particulate TEIs exported from surface waters via 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 TEIs such as Cd are interpreted to indicate regeneration via a relatively rapid

process, such as the oxidation of organic matter. Deeper concentration maxima of other TEIs (Zn, Ba, Ge), suggest regeneration via 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 radio-nuclides (e.g., ^{230}Th, ^{231}Pa, ^{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 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 sea bed. Many TEIs carried by these particles are also regenerated.

4.2.2. Areas for advance

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, so as 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 ~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 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 indicates 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 of ^{230}Th, ^{231}Pa and ^{10}Be to major particulate phases (e.g., Chase and Anderson, 2004; Luo and Ku, 2004) and about the role of water composition (e.g., pH; concentrations of TEI-complexing ligands) in the absorption of Th and Pa 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 (Fig. 17). 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 dependant on particle aggregation, dis-aggregation, degradation and sinking rates. 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.

- 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 time scales of years to decades. Regeneration in deeper waters, or at the sea bed, can extend the time scale 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, and on the rates of the regeneration
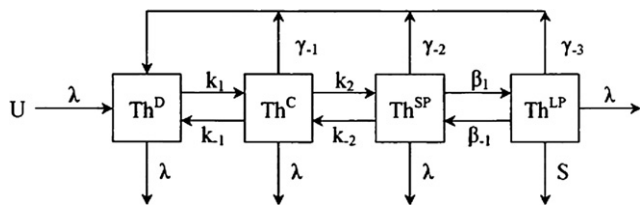
Fig. 17. Schematic of particle scavenging of an insoluble element (Th) (Cochran and Masque, 2003). Understanding and correctly modelling such particle dynamics is key to accurately capturing the cycling of many trace elements in the oceans. Reproduced with permission from the Mineralogical Society of America.

processes themselves. Particle sinking rates vary with the size, morphology and density of particles. These parameters 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. Particle regeneration rates vary with particle compositions and concentrations of certain dissolved species in ambient seawater (e.g., oxygen, carbonate ion, silicic acid, hydrogen ions/pH). Temperature affects these rates as well. The sensitivity to each of these factors of the time and depth scale for regeneration of particulate TEI 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

(a) Determine the partitioning of TEIs between 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.
(b) 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.
(c) Determine particle aggregation, disaggregation and sinking rates, and their sensitivity to changes in the concentration, flux, size distribution and composition of particles.

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 sea bed. The major part (order 99%) of the organic material reaching the sea bed 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 continuous 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 time scale for reactions that lead to regeneration of TEIs on the sea bed can be quite large.

Studies on 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, nutrients, S, some trace metals). 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 sea bed 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. Neither have the spatial variability of this ratio nor the factors regulating its variability been assessed. 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

(a) Determine the fraction regenerated at the seafloor for particulate TEIs of interest.

(b) Identify specific processes responsible for TEI regeneration.

(c) Characterise the spatial variability of the fraction of particulate TEIs regenerated and 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.

4.4. 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 oceans. 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, and 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, e.g., for oxygen utilisation and nutrient remineralisation.

The distributions of the TEIs are similarly governed by the interaction of physical and biogeochemical processes and by their sources and sinks. The relative importance of these factors depends strongly on the particular TEI's intrinsic biogeochemical attributes, which characteristically can vary in space and time. Given a determination by GEOTRACES of the distributions of the TEIs on global and regional scales, and 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 time scale. 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 learnt 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 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., OMZs) 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 regarding 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, we could 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 individual TEIs, dependant on their particular biogeochemical characteristics. Precisely how they differ provides important information on the underlying processes, and provides constraints on mechanistic models of the biogeochemistry. We can ask questions about how the wind-driven circulation (e.g., subduction, upwelling, boundary currents) conspires to create special regional environments such as the OMZs that strongly influence TEI distributions. Studies in these regions may be particularly informative regarding the underlying processes. Finally, it is conceivable that the influence of submesoscale motions on the distributions of rapidly reactive or short-lived TEIs may present significant sampling issues. What is the impact of these processes on, for example, off-shore 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, WOCE), and which shows a rich spatial

texture (Fig. 7). Despite the complex nature of its history (natural cosmogenic radiocarbon, Suess effect, dilution with "dead" fossil-fuel carbon, transient nuclear bomb input), unique long-exchange time scale at the sea surface, and involvement in the remineralisation/carbon cycle, its oceanic distribution 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 micronutrients 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 time scales for this transport range from a year to many decades. This process is thus a rate-limiting step in the regulation of new production on decade time scales, 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, while it is lost to the atmosphere at the air–sea interface. It therefore traces the return pathways in a clear and unambiguous fashion. In combination with its parent, bomb tritium, it offers the determination of water mass ventilation time scales, the depth distribution of major and micronutrient regeneration, and the return pathway. Fig. 18 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 Fig. 18 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, (e.g., 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 a number of other TEIs makes this approach particularly valuable. In addition, inert gas distributions in the oceans can be used to infer rates of mixing and air sea gas exchange. Several of the GEOTRACES TEIs can also be used to infer paleoceanographic 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:

(a) evaluate interbasin and regional fluxes of TEIs,
(b) 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,
(c) develop a model-based context for intelligent interpretation of limited or "spot" TEI measurements,
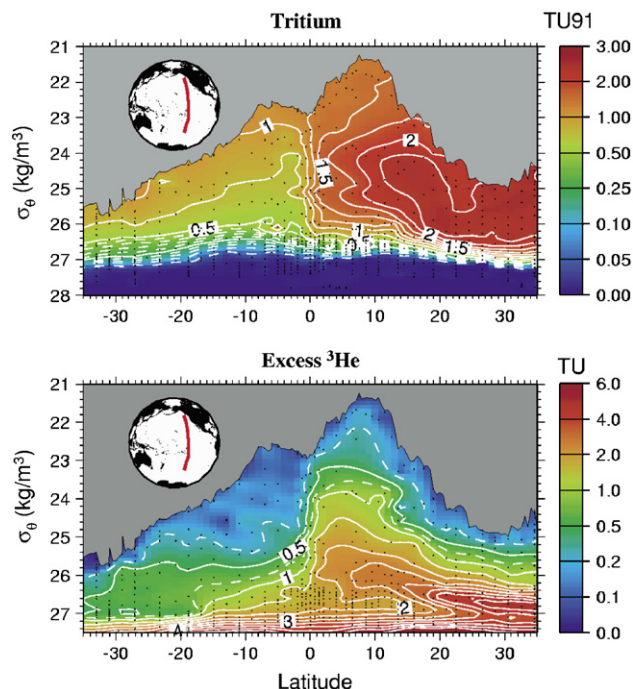
Fig. 18. A meridional section of tritium (upper panel) and ^{3}He (lower panel) in the Pacific Ocean from WOCE. The location of the section is shown in red in the inset of each panel. Figure provided by W. Jenkins.

(d) extrapolate regional measurements to global-scale TEI fluxes and inventories using a combination of models and complementary tracers.

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 US, 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 understand the range of future climate change is to better constrain the nature of past climate variability. Such studies have 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 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 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 lab. 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 presently difficult to reconstruct.

The most widely used paleoproxies directly reflect the geochemistry of seawater and are incorporated in the precipitates that form from seawater (including sediments, corals, microfossils, ferromanganese crusts, etc.). In addition proxies can indirectly record oceanic conditions, e.g., temperature, pH, etc., through fractionation of uptake processes such as Mg/Ca, or B isotopes. Finally, proxies can directly record the fluxes of materials to the seafloor, e.g., ^{230}Th. 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, this complementarity will provide considerable new knowledge about proxy reconstruction of the past within a solid process-focused framework, and with considerable cost effectiveness.

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 paleoceanography. Establishing a comprehensive data set of TEIs that are identified as potential paleoproxies 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 paleoreconstruction.

A good example is the Cd concentration of seawater, which has a distribution similar to the macronutrient phosphate (Elderfield and Rickaby, 2000). Cd 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 aging of water masses along the path of thermohaline circulation. For similar reasons, δ^{13}C is inversely correlated to phosphate in the present day ocean. The past distribution of Cd/Ca and δ^{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, the preliminary data of which (Fig. 19) suggested might serve as a potential "direct" tracer of Si concentration. However, questions remain, e.g., more recent results fail to show the strong correlation between Zn and Si seen in early data (Fig. 19). 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
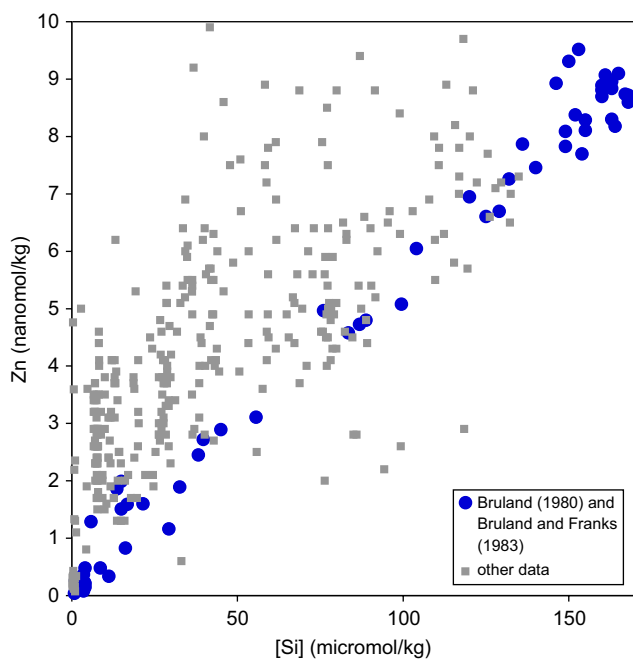
Fig. 19. Zn versus Si concentrations of ocean water samples. The early data (circles) of Bruland (1980) from the North Pacific and Bruland and Franks (1983) from the North Atlantic indicated a strong relationship between Zn and Si. Other data published subsequently (squares) do not follow that simple 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.

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 perhaps a leading candidate 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 prior to anthropogenic perturbation in the case of Pb, with relative low Nd and high Pb-isotope compositions, relative to Southern Ocean waters.

Although progress has been made recently in understanding how NADW acquires its Nd signature (Lacan and Jeandel, 2005), the manner in which water masses acquire this composition is only partially 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 relatively sparse data sets, 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 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, OMZs, 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 N has been most extensively studied and a reasonable understanding of the causes of N 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. Si isotopes show similar promise to those of N but with the ability to specifically assess the silicate cycle and the production of opal. Si isotopes have been studied in only a very limited numbers of 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 last few years but we are now poised to be able to use isotopes of Cd (Wombacher et al., 2003), Cu, Zn (Archer and Vance, 2004) 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 water masses are geochemically labelled is often insufficient to allow unambiguous interpretation of paleorecords of either changing ocean circulation or continental inputs. Measurements of the radiogenic isotopes of Nd, Pb, Os and Hf offer significant potential for ocean reconstruction on long time scales, 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 will make an important contribution to the paleoceanographic 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. $\delta^{13}C$ 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 programme) only extend to 2000 m depth. So there are 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 waters will be improved with more precise data as well. There are also remote regions with no $\delta^{13}C$ data that may be sampled by GEOTRACES.

5.1.3. Specific GEOTRACES objectives

(a) Identify the processes in the modern ocean that create the observed relationships between TEIs and nutrients, e.g., Cd–PO$_4$, $\delta^{13}C$–PO$_4$, Zn–Si, Ba–Alk.

(b) Establish a comprehensive distribution of these TEIs to understand their cycles and to use this improved knowledge to "invert" their paleoprofiles into accurate information about past ocean circulation and/or carbon cycle function.

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

(d) 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, atmospheric deposition, hydro-thermal systems, exchange with particles and /or sediments.

5.2. Factors influencing the distribution of "indirect" proxies in the ocean

5.2.1. Present understanding

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 (δ^{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 real ocean show otherwise. Control by more than one environmental variable, and poor 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 paleoproxies 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.

5.2.2. 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 (Fig. 20), but it has also been linked to changes in the concentration of carbonate ion. Such a carbonate-ion control would necessitate reinterpretation of many existing paleo-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 paleoclimate 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 time scales 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 this 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 (Pearson and Palmer, 2000; Sanyal et al., 1996). Calibrations of this proxy are sparse, however, and there remain major uncertainties in its use. Neither the temperature sensitivity of δ^{11}B nor the presence or absence of interspecies effects, for instance, have been adequately assessed. The possibility for whole-ocean changes in δ^{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
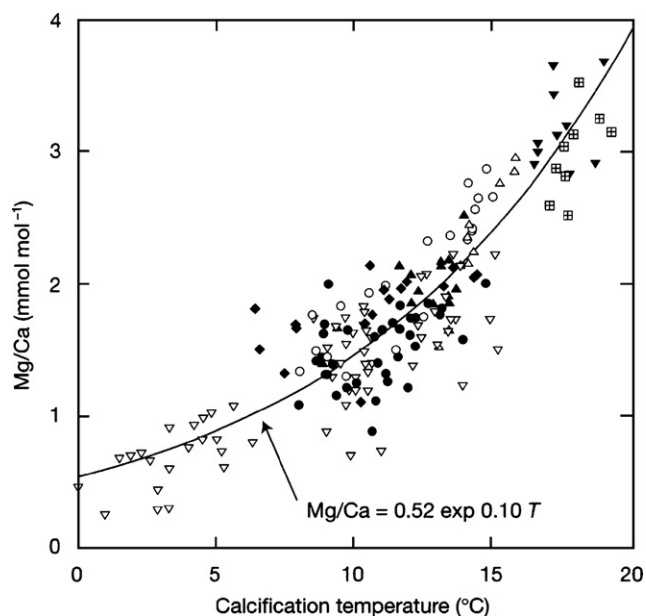
Fig. 20. Typical calibration curve of Mg/Ca versus temperature, based on core-top foraminifera (Elderfield and Ganssen, 2000). The clear relationship demonstrates that temperature exerts a major control on foraminiferal Mg/Ca. But the pronounced scatter about this trends hints at additional controls. Mg/Ca is one of the most widely used paleothermometers so it is important to assess additional controls and to establish this proxy more firmly. Elderfield and Ganssen (2000) figure adapted with permission from MacMillan Publishers Ltd: Nature, Copyright (2000).

these carbon system proxies onto a firm empirical basis will allow significant new work to understand the operation of the natural carbon cycle.

5.2.3. Specific GEOTRACES objectives

The objectives are to 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 in nature and laboratory.

5.3. Paleoceanographic 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. That of biogenic barium or barite, for instance, has been used to infer changes in paleoproductivity (e.g., Eagle et al., 2003). This approach has been prompted by the close empirical correlation often found between marine productivity

and 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 paleoproductivity 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 paleoflux reconstructions, but questions have been raised regarding the underlying principle of a constant scavenging flux of ^{230}Th (Thomas et al., 2000; Lyle et al., 2005). This assumption is 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 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 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 (Fig. 8), 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 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 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 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 variations recorded in sediments. This requires measurements of dissolved and particulate radionuclide distributions under conditions of varying particle flux, particle composition and 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 presently exist. 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 time with respect to scavenging or affinities for major particle phases could conceivably be developed (e.g., Ti/Al) to complement and help separate the effect 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 which circumstances, sedimentary Ba fluxes could be used as a quantitative paleoproductivity 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

(a) 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.
(b) Provide a full understanding of the processes controlling ^{231}Pa and ^{230}Th distribution in the oceans, and their flux to the sediment.
(c) Investigate the use of other TEI ratios in marine particulates and sediments as proxies for past change.
(d) 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.

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 is to better understand the marine cycles of TEIs and to quantify lateral and vertical transports, and 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 and fostering the development of new dynamic TEI models. Model simulations can reveal the regions and 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, GEO-TRACES will apply a hierarchy of models to maximise scientific output. The models will differ in the geographical coverage and spatial and temporal resolution; the level of complexity and the range of processes explicitly included in the models; and the numerical methods used to obtain model solutions and techniques to utilise TEI data. Examples of models that will benefit GEO-TRACES range from box and water-column models to coupled physical/biogeochemical general circulation models, chemical speciation 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.

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 paleoceanographic data.

Examples of the application of biogeochemical models to trace-element chemistry are: (a) 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 (Aumont et al., 2003; Moore et al., 2002). (b) 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, Si) released from the dust (Gehlen et al., 2003). (c) 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. (d) The biogeochemistry of ^{230}Th and ^{231}Pa in modern and glacial oceans: distributions of these tracers in the water column and their flux to 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 enables 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 deep-water ventilation. (e) 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 1 year at the surface and of ca. 10 years along the deeper part of the continental slope (Jeandel et al., 2007; Arsouze et al., 2007).

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 the classical marine biogeochemical data sets.

6.3. Inverse models

The principles and methods of inverse modelling have been used successfully during the past decade. For example, application to the WOCE/JGOFS data set has produced estimates of horizontal fluxes of nitrate and anthropogenic CO_2 across selected WOCE sections (Ganachaud and Wunsch, 2002; Gloor et al., 2003; Macdonald et al., 2003). Inverse models have been applied to estimate the global distribution of the export flux of organic matter sinking to the deep sea (Fig. 21; Schlitzer, 2000, 2002, 2004; Schlitzer et al., 2004); the particle remineralisation rates in the water column (Usbeck et al., 2002); and for quantitative comparison with sediment trap data (Usbeck et al., 2003). Data assimilation methods have also been used for optimal estimation of ecosystem model parameters at individual time-series and process study sites (Friedrichs, 2002; Spitz et al., 2001), 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 (Fe, Mn, Ra, Ac, Nd). In the models, 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, which are characterised by extreme spatial heterogeneity with respect to sources (e.g., supply by rivers and SGD) 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 techniques also permit 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.

7. Programme implementation

7.1. 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. It will identify, at a global scale, the wide range of chemical, physical and biological processes involved in the cycling of TEIs in the oceans. It will map the present distribution of TEIs and allow prediction of future changes to their distribution, with
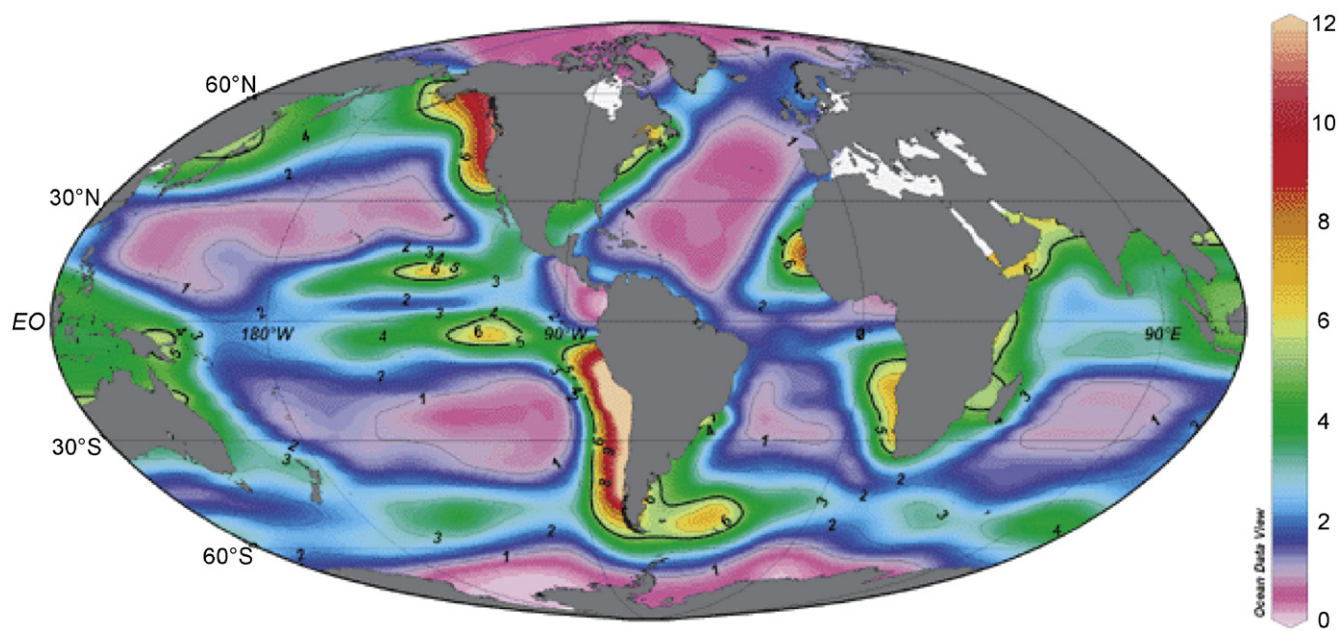
Fig. 21. Export production of particulate organic carbon POC [mol C m^{-2} yr^{-1}] in the world ocean determined by an inverse model from water-column oxygen, nutrient and carbon distributions. From Schlitzer (2000), Copyright (2000) American Geophysical Union. Reproduced with permission of American Geophysical Union.

relevance to global-change research. And it will allow relationships between different TEIs to be exploited to better understand their chemical behaviour and use as proxies for past change. Global data sets, 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.

To maximise the information they provide, Ocean Sections will be designed to intersect regions containing the most significant anticipated sources, sinks and internal cycling of TEIs. 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, hydro-

thermal plumes and continental margins. Ocean Sections will also sample principal water masses as well as the major biogeographic provinces. Keeping in mind that substantial further refinement is needed, a global map containing a number of placeholder sections to identify regions and processes known to be of interest, is shown in Fig. 22.

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 samples are rare.

Parameters to be measured along Ocean Sections can be separated into several categories (Section 7.3), and there will be a hierarchy of sampling frequency
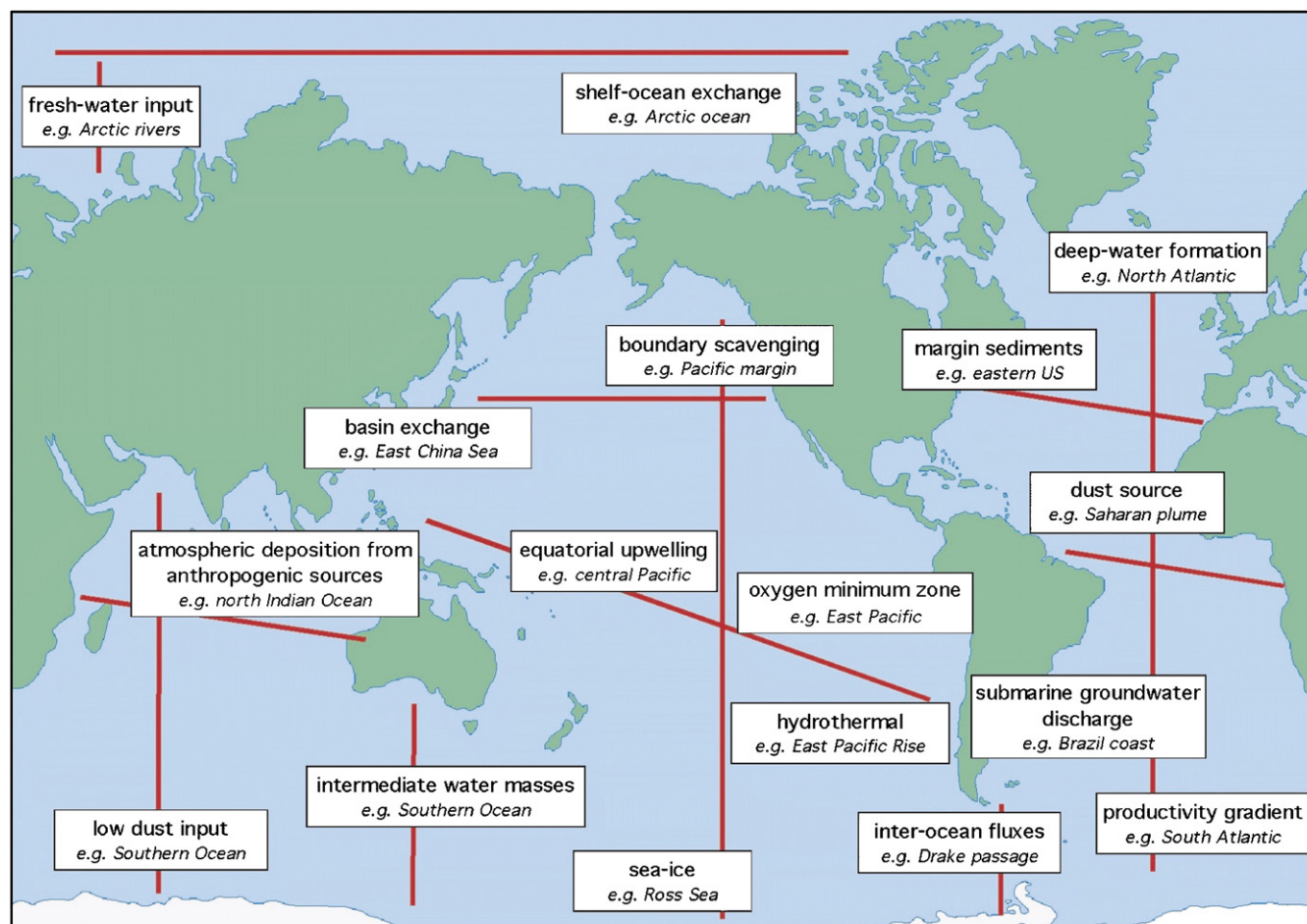
Fig. 22. Schematic map indicating the philosophy behind the choice of ocean sections within GEOTRACES. Sections will be planned to cover the global ocean, and to pass through regions where major processes control the cycling of TEIs. A selection of processes is shown, together with possible locations 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.

depending on the sampling method and type of measurement. For example, total concentrations of TEIs will be measured with greater sampling frequency than the physical form (e.g., dissolved, colloidal, particulate) and chemical speciation of TEIs.

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 cycles models.

7.2. Process studies

Although Ocean Sections will address many of the goals of GEOTRACES, there are other questions that require alternative approaches. For instance, it will be important to assess the sensitivity of TEI cycling to variability of environmental conditions. A viable strategy to investigate this sensitivity is to exploit natural temporal and spatial variability in Process Studies. Process Studies will therefore be designed to run during and after the sections campaign. Particular issues that will require Process Studies include those requiring very high spatial resolution or multiple parallel sections (e.g., to assess SGD discharge on continental shelves); long periods on station (e.g., to assess benthic fluxes at the sediment–water interface; repeat occupation of the same site (e.g., time-series studies; sediment trap studies); and retrieval of significant quantities of sediment with coring equipment.

In some cases, prominent sources and sinks requiring Process Studies are readily anticipated (e.g., near major rivers; in regions of periodic mineral aerosol deposition and where intense oxygen minima intersect continental margins). In such cases, Process Studies can run concurrently with Ocean Sections. Wherever possible, they will be sited to allow comparison of Ocean section results with those from the Process Study (e.g., at one end, or close to, a section). In other cases, new information about the sources, sinks and cycling of TEIs will be identified on the basis of measurements made on the Ocean Sections. This will require additional Process Studies conducted towards the end of the GEOTRACES programme.

7.3. 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.

7.3.1. 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 permit 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 on both Ocean Sections and 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.

Inert gas distributions can be used, along with oxygen data, to evaluate preformed apparent oxygen utilisation to circumvent the required assumption that surface O_2 concentrations are saturated in areas of deep and intermediate water formation. Profiles of inert gases are also valuable for determining the mechanism of deep-water formation and the importance of diapycnal mixing. Inert gases will therefore provide useful process information on some GEOTRACES cruises.

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.

7.3.2. TEI measurements

TEI measurements have a wide range of uses. 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.

Micronutrients: Several trace elements are known to play essential roles in the structure and metabolism of marine organisms. 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, 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. Examples include ^{210}Pb and Al as a tracer of atmospheric deposition; [3]He as a tracer of hydrothermal input; Mn as a tracer of input from margin sediments. Other TEIs provide diagnostic indicators of provenance (e.g., radiogenic isotopes such as Nd, Hf, Pb, Os).

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.

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).

Contaminant tracers: Anthropogenic TEIs also trace the pathways for transport of a variety of contaminants into the ocean. Like Pb, Hg has a geographically distributed atmospheric source. Other anthropogenic TEIs (e.g., Ag, Sn, waste products from nuclear fuel reprocessing) have coastal or even point sources.

Paleoceanographic 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. 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 measurements 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. Amongst these TEIs are some which 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 cruise (Table 2). These "Key Parameters" include trace elements, stable and radioactive isotopes, and other parameters such as

Table 2. Suggested "key parameters" for 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; paleoproxy for nutrient content of waters
Cu	Micronutrient; potentially toxic at high concentration
Stable isotopes	
δ^{15}N (nitrate)	Modern and paleo proxy for nitrate cycling
δ^{13}C	Modern and paleo proxy 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	Paleoproxy 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

This is not a list of all TEIs expected to be measured, but represents those TEIs (and related measurements) which 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 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.

particles and aerosols. They do not require measurement at the same spatial resolution to one another, 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.

8. Proposed timeline

The proposed timeline for the preparation and field work activities of the international GEOTRACES programme is as follows:

- 2005–2008 Enabling Activities,
- 2007–2009 Participation in the International Polar Year,
- 2008–2013 Ocean Sections; initial Process Studies,
- 2013–2018 Process studies; final Ocean Sections.

Acknowledgements

Appendix A

For further details on abbreviations and acronyms, refer Table A1.

Table A1. Abbreviations and acronyms

BATS	Bermuda Atlantic Time Series
CFC	Chorofluorocarbons
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 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 Interaction in the Coastal Zone
MARGINS	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 discharges
SOLAS	Surface Ocean-Lower Atmosphere Study
SRM	Standard reference materials
SSC	Scientific steering committee
SST	*Sea surface temperature*
TEI	Trace elements and isotopes
TRMM	Tropical Rain Measuring Mission

Table A1. (*continued*)

BATS	Bermuda Atlantic Time Series
TTO	Transient Tracers in the Ocean
WCRP	World Climate Research Programme
WOCE	World Ocean Circulation Experiment
WMO	World Meteorological Organisation

Appendix B

The members of the SCOR Working Group and their affiliations are as given in Table B1.

Table B1

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