Collaborative Research: Management and Logistics Operations for the U.S. GEOTRACES Zonal North Atlantic Survey Section

Introduction

The biogeochemical cycling of trace elements and isotopes (TEIs) in the marine environment is an area of active research that has motivated the creation of a major new international program called GEOTRACES (see www.geotraces.org). Trace elements are known to play potentially important roles as nutrients in biological cycling, particularly in regard to enzymatic and catalytic processes in the open ocean. Isotopes are valuable tracers of these and related processes, and of the ocean's interaction with the atmosphere and the solid earth, which in turn play a role in shaping many trace element distributions within the ocean.

Nevertheless, significant gaps exist in both our knowledge of the larger scale distributions of these TEIs in the ocean and in our understanding of the processes responsible for those distributions. This shortfall has implications for numerous scientific endeavors that are relevant to a broad range of intellectual and societal issues, including the carbon cycle and climate change, as well as the marine food web and direct anthropogenic impacts on the oceans. Recent advances in sampling and analytical techniques coupled with a better understanding of the roles of TEIs in ocean biogeochemical cycles present us with an opportunity to rectify this problem. Moreover, we are motivated by the prospect of ongoing global change and the need to understand the present and future workings of the ocean's biogeochemical cycles.

An international planning group formulated the GEOTRACES Science Plan (hereafter referred to as GSP06, http://www.geotraces.org/sciencePlan/documents/GEOTRACESFinalWebVersion.pdf), which was reviewed, modified, and adopted by the broader research community in 2006. The guiding mission of GEOTRACES was formulated:

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

(GSP06, p1). The central observational strategy for GEOTRACES is an internationally-coordinated global-scale survey of key TEIs in the oceans. This central strategy was intended to address the three main GEOTRACES goals (GSP06, p10), and in particular (but not restricted to) the first objective:

> **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 characterize more completely the physical, chemical and biological processes regulating their distributions.**

In 2007 three internationally-attended basin workshops were held to identify critical components to this survey, and to apportion national contributions to this effort. The report of the Atlantic Basin Workshop held in September, 2007 in Oxford, England (ABWR07; http://www.geotraces.org/documents/GEOTRACES_Atlantic_Report.pdf) identified a mid-latitude North Atlantic zonal section as an important U.S. target activity (ABWR07, p 6-10). In response to the U.S. GEOTRACES Scientific Steering Committee's (USGSSC) recommendation, a U.S. planning workshop was held for this section in September, 2008 in Woods Hole, MA. The North Atlantic Zonal Section Implementation Plan (NAZSIP08; http://www.geotraces.org/documents/US_GEOTRACES_Atlantic_Impln_23Dec08c_46083.pdf) arose from this meeting and after community review and comment was adopted in December, 2008 by the USGSSC as a working plan for the first U.S. GEOTRACES activity as part of the Global Survey.

This proposal is in response to the USGSSC's endorsement of the Implementation Plan and represents the first step in carrying out this cruise (NAZSIP08 p 28-29). This proposal is a request for support of management and logistics activities for this first cruise. We request support to:

1. organize and mount a 52 day research cruise,
2. manage on-board sampling, including GO-Flo and Niskin bottle operational QA/QC,
3. Obtain, store, and ship back to the U.S. trace-metal clean water samples,
4. monitor trace-metal clean sampling using on-board Zn measurements,
5. acquire, quality control and manage hydrographic data, including:
    a. CTD, transmissometer, fluorometer, oxygen electrode,
    b. Discrete sample salinity and dissolved oxygen measurements,
    c. Micromolar and nanomolar inorganic nutrients,
6. QA/QC shipboard measurements and submit data to the GEOTRACES data repository,
7. prepare a "framework" hydrographic report/synthesis for cruise participants and publication, and
8. coordinate pre- and post-cruise meetings

In the next two sections of the proposal we describe and justify the Zonal Section from the viewpoint of the GEOTRACES scientific mission and objectives. We then describe the work plan (a detailed explanation of the above list), and follow with a station plan and water budgets. Finally, we describe the data management and dissemination plan.

The North Atlantic Zonal Section

The North Atlantic section (Figure 1) was chosen for a number of reasons. First, the North Atlantic represents the "starting point" for the planetary Meridional Overturning Circulation (MOC), and a complete characterization of "initial" TEI properties is an important step in building an understanding of their global distributions. Second, inasmuch as the North Atlantic appears as an important climate pivot point in past climate-related ocean circulation reorganizations, a better understanding of TEI distributions and behaviors constitutes a significant benefit for paleo-proxy work (GEOTRACES Goal 3, GSP06 p1). Third, the Atlantic basin contains the full suite of physical and biogeochemical processes that affect TEIs, including strong meridional advection, boundary scavenging and sources, aeolian deposition, an input of intermediate waters from the Mediterranean and Labrador Seas, and evidence of anthropogenic impacts (GEOTRACES Goal 2, GSP06, p1). Fourth, the effort is timely: execution of the U.S. zonal Atlantic section in late 2010 fits well within the context of a number of Atlantic sections being carried out by other nations in the time frame of 2009-2011, effectively leveraging international resources and enhancing the value and utility of an approximately synoptic characterization of TEIs within an important ocean basin.

Several attributes of the North Atlantic Ocean can be exploited in fulfilling the GEOTRACES mission to assess the sources, sinks and internal cycling of TEIs. As a relatively small basin surrounded by land masses, the North Atlantic is expected to be influenced by sources of TEIs related to continental weathering to a greater extent than occurs in other major basins. Continental sources are further enhanced by atmospheric deposition, including both natural (*e.g.,* North African dust) and anthropogenic (*e.g.,* industrial emissions from Europe and North America) sources (JICKELLS et al., 2005). The small size of the North Atlantic basin also affects the removal of TEIs that are sensitive to scavenging by particles. The enhanced scavenging that occurs in regions of high particle flux in the vicinity of ocean margins imposes an overall removal rate on scavenged TEIs that is expected to be greater than in other basins.

More than in any other basin, TEI distributions in the North Atlantic are influenced by advective processes. These include southward transport by mode waters and by North Atlantic Deep Water (NADW), together with the counterbalancing northward transport associated with surface waters, Antarctic Intermediate Water (AAIW) and Antarctic Bottom Water (AABW). Lateral injection from quasi-point sources influences TEI distributions as well, including water from Arctic basins delivered as surface transport along the coast of Greenland and water from the Mediterranean Sea, which is injected at mid-depth. Advective transport may serve as both a supply and removal mechanism for TEIs in Eulerian mass budgets, and as an agent for internal cycling by redistributing TEIs within the basin.

The cruise track transects significant regional gradients in biological productivity, starting in seasonally productive waters off the New England coast, moving into the largely oligotrophic subtropical gyre, and then into the highly productive African upwelling region. This track presents investigators with the opportunity to contrast the TEI distributions and inter-relationships among significantly different oceanic biomes. The section also provides an opportunity to contrast the more poorly ventilated deep waters of the eastern basin with those of the western basin. Finally, segments approximately perpendicular to morphologically different continental shelves and slopes permit a characterization of important shelf-slope-open ocean exchange and boundary scavenging processes.

The Section's Relationship to Important TEI Processes

The cruise track and station locations were designed to highlight key processes and identify the major features of key TEIs distributions. In this section we summarize the rationale behind the design. The reader is directed to the Implementation Plan (NAZSIP08) for further details.

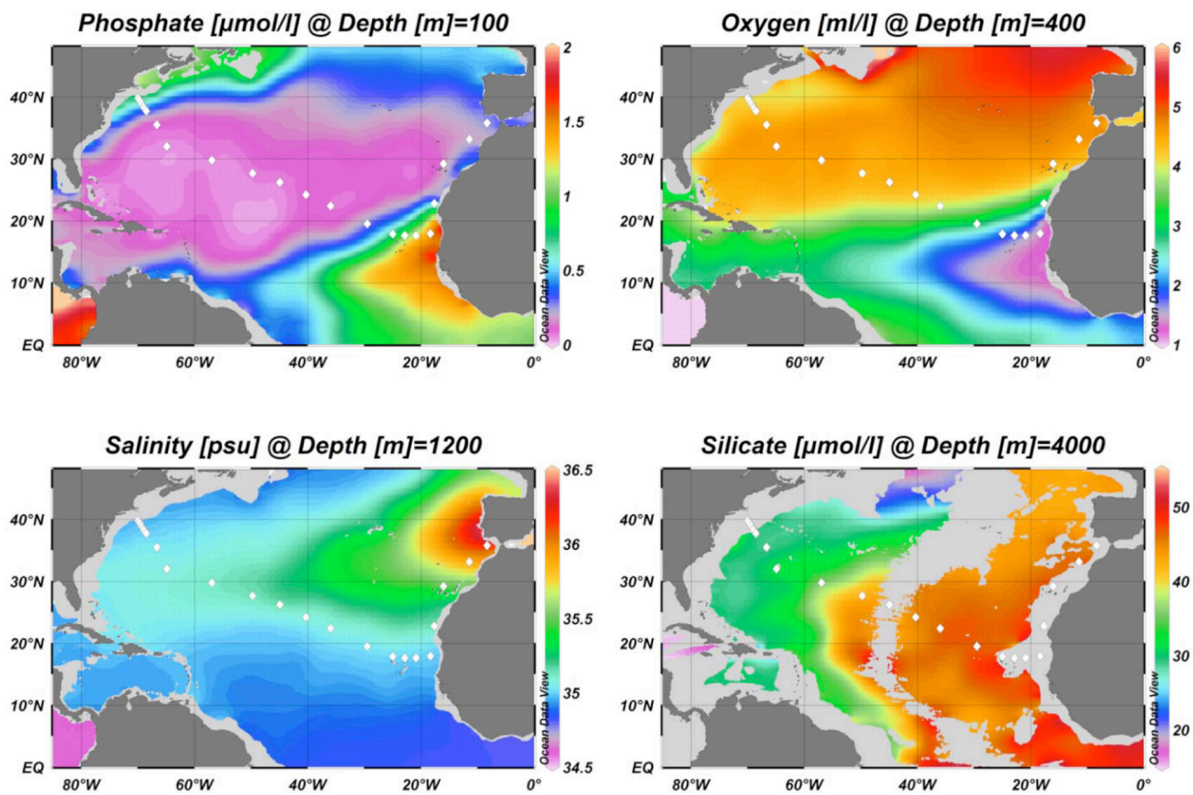

Figure 1: The planned location of full "GEOTRACES compliant" stations (white diamonds) for the proposed North Atlantic Zonal Section shown on some representative property distributions. Approximately 20 additional shallow and limited sampling stations (not shown) will be occupied as well. These and subsequent maps in this document were created using Ocean Data View, courtesy of Reiner Schlitzer (see ODV.awi.de). Data plotted here are from the World Ocean Atlas (Garcia et al, 2006).

Meridional Advection and the MOC: The proposed section cuts across both the dominant northward-bound returning limb of the Meridional Overturning Circulation (MOC) embodied in the Gulf Stream and also the westward-intensified, southward-flowing deep western boundary currents (DWBC) constituting the lower limb of the MOC. The newly ventilated DWBC is highlighted by elevated levels of anthropogenic tracers (Schlitzer, 2007). Simultaneously determining the abundances of TEIs in these currents is important for characterizing the fluxes, budgets, and transformation rates for these properties. The section also extends diagonally across the deep western basin of the North Atlantic, permitting the measurement of TEIs in the abyssal, zonally-oriented recirculation gyres that are known to "buffer" and influence the net southward transport of TEIs in the lower limb of the MOC (Doney and Jenkins, 1994; Henderson et al., 1999). Low concentrations of ^{230}Th and ^{231}Pa carried by recently ventilated deep waters are reported to influence dissolved concentration profiles of these TEIs throughout the North Atlantic basin (Moran et al., 2002). Similarly, concentrations and the isotopic composition of dissolved Pb reflect the history of atmospheric deposition over North Atlantic regions of deep water formation and the penetration of the anthropogenic Pb signal into deep waters (Alleman et al., 1999). Other TEIs are expected to have their distributions influenced similarly by deepwater ventilation.

In shallow waters, the proposed cruise transects the relatively well-ventilated subtropical gyre recirculation region, including the south-westward advection of subtropical mode waters from their formation region north-east of the Gulf Stream extension (Istoshin, 1961; Worthington, 1959). Mode water formed along the northern fringe of the subtropical gyre carries a distinct chemical signature into the ocean interior (Palter et al., 2005). For example, elevated concentrations of dissolved Al observed at depths of 200 to 400 m, between 20° and 35° N along a meridional section in the eastern N Atlantic (Figure 2), are attributed the dissolution of mineral dust in surface waters throughout the region of mode water formation, and spreading of the Al signal into the thermocline (Measures et al., 2008). Sampling along the proposed cruise track will allow investigators to assess the impact of these processes on other TEIs. Including transient tracers such as CFCs and ^{3}H will add information about the time scales for transport of the TEI signal into the thermocline (Jenkins, 1998). The eastward extent of the section (particularly east of 25°W) penetrates the so-called "shadow zone" which is excluded from direct ventilation by subducted waters (Luyten et al., 1983)

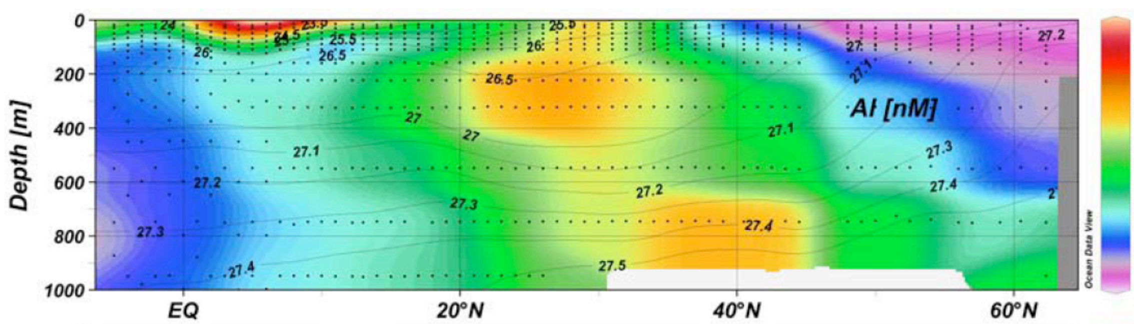

Figure 2. Dissolved Al concentrations (nM) along the CLIVAR A16 section in the eastern N Atlantic Ocean. High concentrations at the surface between the equator and 10°N reflect dissolution from recent dust deposition. The elevated concentrations between 200 and 400 m (20°N to 35°N) are associated with Mode Water advection, while the elevated concentrations between 800 and 1000 m (30° to 45°N) are associated with high salinity water from the Mediterranean Sea. From Measures et al., (2008).

TEIs and the Carbon Cycle: A number of trace metals serve as essential micronutrients (*e.g.,* GSP06, p3). This can be inferred from the fact that their distributions mimic macronutrients; for example, Cd and phosphate, Zn and silicic acid (Bruland and Lohan, 2004). Departures from constant trace metal-nutrient relationships further inform us about processes that have a specific impact on a particular trace element, and about the regions where these processes are important (e.g., (BOYLE, 1988; ELDERFIELD and RICKABY, 2000; FREW and HUNTER, 1992). Benefits of studying these relationships range from developing more reliable interpretations of TEIs used as paleoceanographic proxies to new insights into the metabolic function of trace metals in marine biota. In particular, extending studies of metal-nutrient relationships to ultra-low nutrient concentrations, and to simultaneous studies of multiple TEIs, may reveal synergistic as well as antagonistic relationships among macro and micro nutrients, as well as taxa-dependent preferences for specific micronutrients (e.g., preferences for Co by cyanobacteria and for Zn by diatoms; (MOREL et al., 2004; SAITO and MOFFETT, 2002; SUNDA et al., 1995).

The cruise track offers excellent opportunities to examine these relationships. The section cuts through both regions of very high and very low productivity. The contrast is best seen in the distribution of phosphate at 100 m depth shown in Figure 1. Down-welling and subduction of nutrient depleted waters throughout the subtropical gyre lead to low nutrient availability for winter convection, resulting in oligotrophic conditions in the central gyre. Upwelling off the African coast, on the other hand, leads to high productivity. Also, advection brings many water masses to the North Atlantic region. Stations are well positioned to sample metal-nutrient relationships in subpolar and subtropical mode waters, while also characterizing any departures from metal-nutrient relationships in North Atlantic water masses relative to Si-rich water from the Southern Ocean in the deepest part of the basin and salty Mediterranean outflow water injected into the eastern side of the basin (Figure 1). Phytoplankton taxa also vary markedly along the proposed section. For example, cyanobacteria dominate in low-nutrient waters of the central gyre while diatoms are abundant in the upwelling region off NW Africa (OLSON et al., 1990; PARTENSKY et al., 1999). Incorporating measurements of nanomolar nutrient concentrations together with simple measures of phytoplankton taxa (e.g., HPLC pigments) along the section will enable investigators to interpret spatial variability in metal-nutrient relationships, as well as relationships among TEIs, in the context of the range of different phytoplankton taxa that may influence the uptake of TEIs.

The salinity map in Figure 1 and the aluminum section in Figure 2 highlight the intrusion of Mediterranean Water into the North Atlantic and its contrast to surrounding water masses. Key questions can be asked about the relative contributions of the three dominant intermediate water masses (*i.e.,* Mediterranean Outflow, Labrador Sea Water, and Antarctic Intermediate Water) to the distributions of TEIs in the North Atlantic. For example, the northward transport of water masses originating in the Southern Ocean may influence TEI distributions as far north as the proposed section. The northward penetration of Antarctic Bottom Water plays a potentially important role in ultimately affecting the TEI characteristics of the NADW, and hence the lower limb of the MOC. Although Antarctic Bottom Water has been modified extensively by mixing before it enters the North Atlantic Ocean (SCHLITZER, 2007), high dissolved Si concentrations provide a diagnostic chemical signature of southern sourced deep water masses, as evident in the silica map in Figure 1, where Si-rich deep water can be seen penetrating northward at 4000 m against the Mid Atlantic Ridge along the eastern margin of the western basin. At this depth, the entire eastern basin has deep water enriched in Si, indicating admixture of a component of southern sourced deep water. Comparing TEI-Si relationships across gradients in Si concentration will aid in identifying advective sources of TEIs associated with NADW and/or with AABW. These relationships will be expanded spatially by combining results from the U.S. section with those from sections undertaken by other nations to the north and south of the U.S. section.

Exchange with Ocean Margins: Continental shelves act to filter the supply of TEIs introduced to the ocean by continental weathering. Some TEIs are removed on continental shelves whereas others are thought to be mobilized (*e.g.,* Fe and, perhaps, other micronutrients). The east coast of North America is incised by estuaries while being surrounded by a broad continental shelf. The west coast of North Africa, in contrast, has no large estuaries and a narrow continental shelf. The proposed cruise track intersects these margins with higher than average spatial resolution (Figure 1) allowing investigators to quantify continental sources in these contrasting continental shelf regimes. Continental sources of dissolved TEIs, whether by direct river influx or submarine discharge or exchange, can be traced seaward by measuring dissolved Ra isotopes. Short-lived isotopes (^{223}Ra, ^{224}Ra) trace coastal inputs to shallow waters over time scales of several days to weeks (MOORE, 2000a; MOORE, 2000b; MOORE, 2007). Concentrations of ^{228}Ra in the thermocline can be (and has been) used to estimate average subsurface groundwater inputs over decadal time scales (MOORE et al., 2008). In each case, the Ra isotopes are used in conjunction with measured gradients of other TEIs to estimate fluxes from the continent as well as in situ processes.

Detached nepheloid layers represent another process introducing continental material into the interior of the ocean. Whereas evidence for these layers has accumulated for decades in transmissometer data (e.g., (PAK et al., 1980), little work has been done to assess their contribution to dissolved TEI distributions in the ocean. Detached nepheloid layers are common along Line W, the western portion of the proposed cruise track (see NAZSIP08, p 10-11), extending hundreds of kilometers into the ocean basin. This section will allow investigators to evaluate the role of shelf-basin exchange of both dissolved and suspended forms to TEI budgets by careful sampling within and across the features. Moreover, characterizing the TEI composition (and evolution) of suspended particles is diagnostic of their origins (OLIVAREZ et al., 1991). High-resolution sampling of bottom waters for concentrations of dissolved Al, ^{232}Th, and other refractory TEIs will allow the significance of potential sources to be evaluated.

Complementing the studies of benthic sources of TEIs, Nd isotopes will be used to estimate the net effect of exchange reactions along the flow path of deep water in contact with the sediments (LACAN and JEANDEL, 2005). Regional variability of Nd isotopic composition in continental sources of lithogenic material offers a unique opportunity to evaluate solid-solution exchange processes at the sea floor in the absence of net fluxes (JEANDEL et al., 2007). This strategy will be most effective when combining results from this section with those of other GEOTRACES sections collected at additional points along the flow path of NADW (see ABWR07). Along the west coast of North Africa, Nd isotope results will provide additional constraints on sediment-water exchange fluxes in the absence of strong lateral transport.

Atmospheric Deposition: Atmospheric deposition is particularly important as a source of TEIs in the North Atlantic Ocean due to the combined effects of anthropogenic emissions from industrial and agricultural sources together with mineral dust mobilized in the North Africa. Mineral aerosols are thought to be a significant source of Fe and other micronutrients for much of the central North Atlantic Ocean , while atmospheric deposition may be a significant source of fixed nitrogen in some regions and may affect the upper ocean nitrogen isotope budget (KNAPP et al., 2008) . Where that is true, the isotopic composition of aerosol nitrogen can be diagnostic of its source (HASTINGS et al., 2003).

Radiogenic isotopes can be exploited to constrain the provenance of selected aerosol constituents. For example, Pb isotopes readily discriminate between European and American sources of Pb, while Nd isotopes are diagnostic of the age of source rocks from which mineral dust is generated, thereby constraining its source as well (PATTERSON and SETTLE, 1987);(NAKAI et al., 1993). Aerosol deposition is seasonal (see NAZSIP08, p11-13), so that sampling during a cruise could give a biased view of the mean annual supply of TEIs by atmospheric deposition. Consequently, a clearer picture of the mean and variability of atmospheric deposition can be derived by studying aerosol-derived TEIs having a range of residence times in surface waters. For example, by analogy with ^{234}Th, lithogenic ^{232}Th that dissolves from mineral aerosols is expected to have a residence time of a few weeks (WAPLES et al., 2006), whereas Al mobilized by similar processes is thought to have a residence time in surface waters of a few years (MEASURES and BROWN, 1996). Other lithogenic TEIs (e.g., Fe, Nd) are expected to have intermediate residence times. In addition, comparing ^{210}Pb with lithogenic TEIs may help resolve the relative importance of wet and dry deposition (KIM et al., 1999). The strong seasonality of dust deposition should be considered in choosing the timing of the cruise. Furthermore, peak dust deposition occurs at different times of the year along different segments of the section. For example, near the Cape Verde

Islands, in the vicinity of the eastern end of the section, dust deposition begins to rise in the boreal autumn and peaks in winter (CHIAPELLO and MOULIN, 2002). Thus, a cruise beginning in Woods Hole in mid-autumn would reach the eastern portion of the section at about the time of the initial seasonal increase in dust deposition, allowing investigators to assess the immediate response of TEIs to increasing dust flux.

Sampling along the proposed cruise track will enable investigators to examine potential causes for the enigmatic "reverse zonal gradient" in surface concentrations of dissolved aluminum identified by Measures et al (2008); see also NAZSIP08, p11-13), as well as the implications for sources of other aerosol-derived TEIs. The proposed cruise track is well located to examine this problem.

Hydrothermal Sources and Sinks: Hydrothermal fluids vented at the crest of mid-ocean ridges bear a chemical composition created by reaction of seawater with host rocks at high temperature. This interaction may result in biogeochemically significant fluxes of TEIs either into, or from the circulating seawater, and may play a role in the long term control of the chemical composition of the oceans. Products of rock-water interactions vary with the composition of the rock, which, in turn, differs between slow spreading ridges such as the Mid-Atlantic Ridge and fast spreading ridges such as the East Pacific Rise.

The proposed cruise track intersects the Mid-Atlantic Ridge at a well-studied hydrothermal vent site, the TAG hydrothermal Field (GERMAN et al., 1993; GOTO et al., 2003; RONA et al., 1983). Hydrothermal fluids at the TAG site on the Mid Atlantic Ridge have low sulfur content, thereby allowing relatively high concentrations of iron in the effluent fluids (FOUSTOUKOS and SEYFRIED JR., 2005). Oxidation of iron (and manganese) and its subsequent precipitation as the effluents mix with surrounding seawater generates an abundance of oxyhydroxide phases (approximately tens of nanomolar Fe at a depth where plumes reach neutral buoyancy compared to surrounding seawater (GERMAN and VON DAMM, 2004)), capable of scavenging numerous TEIs from seawater. Samples collected at a station located within the hydrothermal plume "downstream" from the TAG vents will enable investigators to evaluate TEI/Fe and TEI/^{3}He (to characterize dilution) relationships for a wide range of TEIs, while also evaluating the depletion of dissolved TEIs within the plume. Examining dissolved and particulate TEIs together will offer a more complete view of TEI removal than would be obtained by investigating either phase alone.

Hydrothermal systems may also serve as a source for certain TEIs. For example, both the concentration and speciation of Hg may be uniquely influenced by hydrothermal systems (AMYOT et al., 2005). Sampling at the TAG site will allow sources to be identified as well as sinks, and will provide investigators with the opportunity to examine chemical speciation of TEIs associated with hydrothermal systems.

The Work Plan: Responsibilities of the Management and Logistics Team

Summary- The PIs for this management proposal will be responsible for the basic logistics of the cruise, including interaction with UNOLS, ship operators, agents, and State Department clearances. The Management Team will coordinate a pre-cruise organizational meeting and communicate with cruise participants regarding ship-board requirements and operation. We will provide "water catching" support as outlined in the U.S. Atlantic Section Implementation Plan, including acquisition, quality control and archival of the appropriate operational metadata (navigation, event logs, etc) as well as hydrographic data. Water sampling will be done using both the GEOTRACES trace metal-clean 24 x 12L GO-Flo carousel and Kevlar cable winch developed and used during the GEOTRACES Intercalibration Exercise (see detail discussion below) along with a clean-lab van, and also using a "traditional" 12 x 30L Niskin rosette on the standard hydro winch. The Team will take responsibility for coordination of on-board water sampling activity and to ensure smooth and efficient operation of station-related procedures. They will enforce appropriate GEOTRACES sampling protocols (developed as part of the Intercalibration Program), and those established during the pre-cruise planning meeting (e.g., the correct order of bottle sampling and recording), as well as maintaining the cruise event log.

By hydrographic data we mean CTD and related sensor data (fluorometer, transmissometer, oxygen electrodes), discrete water sample measurements (micromolar inorganic nutrients, dissolved oxygen, salinity), and nanomolar nutrients. The Team, along with ODF technicians, will be responsible for establishing and monitoring GO-Flo and Niskin integrity using the discrete hydrographic measurements. They will also be responsible for quality control and archival of the ship-board measurement data, as well as making it available to on-board participants during and after the cruise.

Cruise participants are required to provide their own suitably cleaned and prepared sample containers for shore-based TEI analysis, and will be responsible for transporting these containers to the ship at its departure port (tentatively Woods Hole). The Team will provide shipping and logistics support for the return of water samples obtained from routine Niskin and GO-Flo casts between Lisbon, the likely terminus of the cruise, and Norfolk VA. Individual cruise participants will be responsible for shipment from there. Furthermore, international shipment of samples requiring special conditions (e.g., refrigeration) will be the responsibility of those participants requiring it. On the ship, we will provide a dispensing system for and coordinate testing of a trace metal clean automated HCl acid dispensing system for sample preservation for those PIs who wish to use it. The Team will also perform on-board Zn measurements on bottle samples to establish GEOTRACES Go-Flo and carousel sample integrity and will continue to monitor for contamination throughout the cruise (see later section).

Finally, the Team will be responsible for quality control and submission of the ship-board acquired data and metadata to the appropriate GEOTRACES agency (Biological and Chemical Oceanography Data Management Office in Woods Hole; BCO-DMO) and will make the data available to the cruise participants on a web page. The Team will be responsible for creating a final cruise report based on this data and a preliminary description of the ship-board data and hydrography that may be useful for the interpretation of TEI data obtained from shore-based analysis (and later publication). The Team will also host a post-cruise "synthesis meeting" to promote collaboration and discussion among the participants. It is anticipated that funding for the synthesis meeting will be provided through the U.S. GEOTRACES project office award.

Trace Element Sampling- Depth profiles for dissolved and suspended particulate TEIs will be obtained using the GEOTRACES carousel sampling system operated by Cutter's group in combination with those from a conventional rosette. The GEOTRACES carousel is a Seabird aluminum frame with polyurethane powder coating that holds twenty four, 12 L GO-Flo bottles capable of firing up to 3 at once. The bottles are mounted onto pivoting polyethylene blocks with titanium pins to facilitate easy removal. The carousel has a Seabird 9+ CTD with dual temperature and conductivity sensors, SBE 43 oxygen sensor, a Seapoint fluorometer, and a Wet Labs transmissometer; all of the pressure housings and pylon are titanium, eliminating the need for zinc anodes and resulting contamination. The carousel itself is attached to a 14 mm OD, 7800 m long Kevlar conducting cable spooled onto a Dynacon traction winch with slip rings. The bottles are fired (up to 3) on the upcast while moving into clean water at ca. 3 m/min in order to minimize contamination from the frame and sensors.

After recovery the bottles are transferred into the HEPA-filtered, positive pressure clean lab van where they are sub-sampled for dissolved and particulate TEIs (the GO-Flos are also stored in the clean van). Specifically, assuming that two GO-Flo bottles will be fired at each depth (see below), one GO-Flo will be pressurized (<8 psi) with filtered, compressed air (can be nitrogen for suboxic or anoxic waters) and the water directly passed through a capsule filter (e.g., 0.45 μm Osmonics) and into sample bottles (low density polyethylene, Teflon, etc depending on the analyte) for contamination-prone elements (e.g., Fe, Zn). In addition, if a TEI cannot be filtered due to contamination (e.g, perhaps Pb isotopes), unfiltered samples can be taken from this GO-Flo. The second GO-Flo will be devoted to particulate samples where the entire volume (ca. 11.5 L) is passed directly through a membrane filter (to be determined after Intercalibration Cruise 2, but likely a 0.45 μm polysulfone Supor filter, or 0.45 μm cellulose acetate Millipore membrane) under <8 psi pressure (not vacuum). The filtrate from this membrane filter is then used for TEIs that are not as prone to contamination (e.g., Al, Mn), and the filter used for total metal determinations via acid digestion and ICP-MS analysis. All water samples from the carousel system are completely processed in the Class 100 clean van, including acidification under a HEPA laminar flow bench. During the first Intercalibration Cruise (June-July 2008) both ship-board and stored sample analyses showed no contamination for any of the key dissolved or particulate TEIs with this system (Dec. 2008 Intercalibration Workshop).

Examining the tentative water budget given in the Implementation Plan, it is possible to cover (also see below) all of the key TEIs with two GO-Flos (for contamination-prone elements) and water from the conventional CTD/rosette for TEIs not prone to contamination (e.g., Nd and Th isotopes). However, an additional GO-Flo can be fired if the water budget for contamination-prone elements is too large (> 22 L). Finally, to assess the integrity and representativeness of the TEI samples, salinity and nutrient samples, and aliquots for shipboard determinations of dissolved Zn, are taken from each GO-Flo. Comparisons of salinity and nutrients concentrations with those from the conventional rosette (with bottles that are not prone to leaking) allow leaking or misfiring to be easily identified (e.g., Cutter and Measures, 1999).

To evaluate potential TEI contamination, shipboard determinations of dissolved Zn are utilized since this metal is amongst the most contamination prone due to galvanization on most of the ship's exposed steel and the use of zinc sacrificial anodes as well as natural and synthetic rubber. For underway surface samples, we will use a trace metal-clean "fish" (e.g., (DE JONG et al., 1998; VINK et al., 2000) that is deployed ca. 8-10 m from the ship's quarter using an Al boom, and to which is attached Teflon-lined tubing that leads to a deck-mounted Teflon diaphragm pump. This system provides flow rates of up to 5L/min while steaming at 10+ knots and the water is capsule filtered (as above) or taken unfiltered. In addition to rosette sampling while on station, large volume samples in the upper 50 m can be obtained with this pumping system.

Onboard Contamination Monitoring- The Team will be responsible for identifying and hiring a postdoc who will do shipboard Zn analyses to verify that the Go-Flo rosettes are properly working. On the June 2008 GEOTRACES intercalibration cruise, we learned that this Zn screening was extremely important to establishing proper functioning of Go-Flo bottles; bottles that otherwise appeared to be working would show Zn contamination, and Zn was the most sensitive element to problems (i.e., bottles that showed contamination for other elements almost always showed Zn contamination as well). It will be MIT's responsibility to hire a postdoctoral fellow to fill this role. In the first year, this postdoc will be responsible for equipment, reagent, and bottle preparation; in the second year, the cruise and activities associated with it, and in the final year, shorebased analyses of samples to verify the shipboard Zn data and it's relation to other contamination-prone trace elements.

Shipboard "Hydrography"- Good quality hydrographic measurements are necessary not only for bottle quality control (ensuring that the GO-Flo and Niskin bottles are properly sealing and have tripped at the correct depth) but also for interpretation of the origin and character of the water masses being sampled. The Team will be responsible for working with the Ocean Data Facility (ODF) to ensure that high quality hydrographic measurements will be made along with operation of the 12 x 30L "standard" rosette, CTD and transmissometer. Shipboard measurements of micromolar inorganic nutrients (nitrate, silicate, and phosphate), salinity and dissolved oxygen will be made on the standard rosette and the trace-metal clean rosette both for identification of water masses and diagnosis of bottle performance issues. Such measurements will be done to WOCE/CLIVAR standards. These results will be integrated with measurements made by Cutter's lab of nutrients (including ammonia and nitrite) down to nanomolar levels in the upper 200m (see below). Along with ODF, the Team will manage on-going QA/QC of data to identify developing problems during the cruise and will also ensure that the appropriate metadata and shipboard hydrodata will be collected and reported in a timely fashion to the appropriate GEOTRACES data repository (BCO-DMO) and made available to cruise participants both during the cruise and afterward on a suitable web site. In addition, the Team will collaborate with Jim Swift (at SIO) to produce a "hydrographic synthesis", hopefully of publishable quality, describing the basic hydrographic context (water mass structure, major current flows, etc) that will be made available to cruise participants for use in their interpretation of TEI measurements.

Nanomolar Nutrients- Since the GEOTRACES program requires nutrients to be determined at levels comparable to those for the TEIs (i.e., nanomolar) in order to facilitate full biogeochemical integration of the “macro” nutrients (N, P) with those of the micro nutrients (e.g., Fe, Zn), Cutter’s lab will make determinations of ammonium, nitrite, nitrate, and phosphate at nanomolar concentrations for all samples in the upper 200 m (i.e., including underway fish samples). For this, the detection limits on our continuous-flow Astoria Pacific Rapid Flow Analyzer are lowered ca. 100 fold using long path length (2.2 m), liquid core waveguide cells as fully described by (ZHANG, 2000) for nitrite and nitrate, (ZHANG and CHI, 2002) for phosphate, and (LI et al., 2005) for ammonium. These methods have been evaluated (e.g., intercalibrating MAGIC with waveguide phosphates) as a part of the GEOTRACES Intercalibration Cruises. The nanomolar nutrient data will be fully available to all cruise participants in addition to the conventional nutrient determinations at micromolar levels by the ODF hydrography group.

Pigments, Apparent and inherent optical properties - Observations of the AOPs and IOPs of seawater will be made within the euphotic zone for the former and within the mixed layer (as underway sampling) for the latter. In addition, biogeochemical analyses will be made from discrete water samples including a) pigment concentration using high performance liquid chromatography (HPLC), b) particulate absorption, c) dissolved organic carbon (DOC), plus particulate organic carbon and nitrogen (POC and PON, respectively), as well as, d) chromophoric dissolved organic matter (CDOM). The AOP measurements include above- and in-water instruments to determine water-leaving radiances in normalized and exact forms (the latter being essential to remote sensing applications) for 19 channels spanning the ultraviolet to the near infrared (342-865 nm). If only the controllable sources of uncertainty are considered (i.e., if environmental variances are excluded), the quadrature sum of uncertainties is usually to within 3.5% (the current standard for ocean color algorithm validation activities). The IOP instruments measure the in situ spectral absorption across a similarly wide spectral range (360–850 nm), but with higher resolution (1,500 wavelengths), plus the optical backscattering at nine wavelengths and fluorescence at two wavelengths for the determination of chlorophyll and CDOM concentration. The biogeochemical sampling will be a combination of near-surface (primarily underway) samples, the euphotic zone (during or immediately following AOP deployments), and whole water column samples from deep-water casts. The latter will be restricted to CDOM and DOC analyses. The work described in this paragraph will be performed by the NASA group (see Appendix 1 for letter of support) at no direct cost to the proposed grant.

Detailed Station Plan and Water Budgets

By international agreement, participating scientists are expected to measure the full suite of “key” trace elements and isotopes defined in Table 2 of the Science Plan (GSP06) on every GEOTRACES section. Formulation of the sampling plan and budgets described below should be regarded as a “model” plan aimed at demonstrating the feasibility of acquiring the minimum set of core measurements. This is not meant to be an “exclusive laundry list” of a limited number of properties. We plan to accommodate sampling for other related properties that can be argued to contribute toward the GEOTRACES objectives, and this is reflected in the water budgets drawn up for the station plan below. The water budgets are based on experience with the intercalibration exercise and reasonable expectations balanced by pragmatic constraints of ship time and space. In addition, it is expected that a number of ancillary parameters will be measured (see Science Plan).

Taking into account the volumes of water required to support the measurement of key TEIs, and the water needs of ancillary measurements likely to be proposed for the US GEOTRACES section, participants at a planning workshop (22-24 September, 2008, Woods Hole Oceanographic Institution) recommended that three types of stations will be occupied during the cruise:

1) Full water column stations that will include sampling for all key TEIs as well as for most ancillary parameters. These are the stations shown in Figure 1.

2) Shallow stations that will involve one or two casts of the GEOTRACES and conventional systems to a nominal depth of 1000 m, to sample for selected parameters in locations where greater spatial resolution is desired. Shallow stations will be interspersed between full depth stations. Locations of shallow stations, and parameters to be measured, will be determined once funding decisions have been made and more is known about the studies that have been funded.

3) "Super" stations that represent full water column stations with additional sampling to provide water for TEIs that do not require sampling at every station. These may include TEIs that are at an exploratory stage of development, or those for which new insights concerning their sources, sinks and internal cycling can be derived from sampling at a limited number of stations. Potential TEIs in this category include hafnium isotopes, artificial nuclides from nuclear weapons testing and from nuclear fuel reprocessing, and oxygen isotopes in phosphate. Additional casts for high-resolution near-bottom concentration profiles of selected TEIs may be taken at super stations, although these casts may be relocated to other stations if justified by the relevant scientific objectives. In any case, super station sampling and near-bottom casts will take place at the location of normal full water column stations. New stations will not be inserted into the cruise plan to accommodate these sampling needs.

In addition to sampling vertical profiles at the stations defined above, underway samples of surface water for selected TEIs, including micronutrients and tracers of aerosol input, will occur at a nominal spacing of every four hours when the ship is underway between stations (see Trace Element Sampling above). Finally, in a manner analogous to underway sampling of surface water, aerosols will be collected along the full length of the cruise track.

Five general types of sampling devices will be used to fulfill the sampling plan described above: 1) the US GEOTRACES sampling system (as above), 2) a standard ship's rosette with 12 X 30-liter Niskin bottles, 3) *in situ* pumps, 4) a towed fish designed for trace metal-clean sampling of surface waters, and 5) aerosol samplers.

The management team is not requesting support for aerosol and rainfall sampling, nor for *in situ* pumped sampling. However reasonable accommodation (in ship space and station time) will be provided for these activities, and it is anticipated that these sampling systems will be provided by individual PIs with all operating costs covered by their proposal(s). Furthermore, it is anticipated that PIs funded to operate these sampling systems will provide sample aliquots in reasonable amounts to other investigators funded to participate in the cruise. The U.S. GEOTRACES project office will serve as an information center for shared samples.

Once final funding decisions are made, all funded PIs will work together to finalize the cruise plan and allocation of samples from shared systems. Water depths to be sampled, as well as the distribution of sample aliquots, will be decided at a pre-cruise workshop involving funded PIs. Travel expenses for this workshop will be covered by the U.S. GEOTRACES project office.

A preliminary water budget for the rosette samplers and in situ pumps has been developed with the understanding that these water budgets are likely to be adjusted once the nature of the proposals to be funded is known. Certain parameters will be measured only in surface waters, while others will require telescoping water volumes that either increase or decrease with water depth. Based on reasonable expectations, it is anticipated that two GO-Flo bottles will be tripped at each depth to meet the sample requirements at standard full-depth stations (Table 1). The depth range to be covered by the shallow and deep casts will be decided by funded PIs.

Table 1. Anticipated water volumes from the U.S. GEOTRACES Clean Rosette required to meet the needs for key TEIs and for ancillary parameters. Separate estimates are given for standard full depth stations and for super stations (see text).

Parameter **Shallow GO-Flo**	Full-depth Vol (liters)	Super Vol (liters)	**Deep GO-Flo**	Full-depth Vol (liters)	Super Vol (liters)
Fe, Al, Zn, Mn, Cd, Cu	2	2	Fe, Al, Zn, Mn, Cd, Cu	2	2
Pb isotopes	2	2	Pb isotopes	2	2
Nutrients/sal/oxygen	0.5	0.5	Nutrients/sal/oxygen	0.5	0.5
Low level nuts (surface)	0.5	0.5			
Other properties (e.g. Co, As, V, Ag, ancillary TEIs, Hg, Os, speciation of Cu, Zn, Fe, Co; trace metal isotopes)	19	43	Other properties (e.g. Co, As, V, Ag, ancillary TEIs, Hg, Os, speciation of Cu, Zn, Fe, Co; trace metal isotopes)	19.5	43.5
(particulate TMs share volume)			(particulate TMs share volume)		
TOTAL	24	48	**TOTAL**	24	48

It is anticipated that a standard Niskin rosette with 12 X 30-liter bottles will be used, allowing all sample requirements to be met with a single bottle will be tripped at each depth. The depth range to be covered by the shallow and deep casts will be decided by funded PIs.

Table 2. Anticipated water volumes from the ship's Niskin Rosette required to meet the needs for key TEIs and for ancillary parameters assuming a rosette with 12 30-liter bottles.
Water budget created assuming a total of four shallow casts and three deep casts per super station.

Shallow Ship Rosette	Full-depth Vol (liters)	Super Vol (liters)	**Deep Ship Rosette**	Full-depth Vol (liters)	Super Vol (liters)
15NO3 18O-NO3	0.5	0.5	15NO3 18O-NO3	0.5	0.5
Th, Pa,	5	5	Th, Pa,	5	5
Nd, REE	5	5	Nd, REE	5	5
Nutrients	0.5	0.5	Nutrients	0.5	0.5
O2	0.5	0.5	O2	0.5	0.5
Salt	0.25	0.25	Salt	0.25	0.25
14C/13C	0.5	0.5	14C/13C	0.5	0.5
Other properties (e.g. d30Si, 18O-PO4, 234Th, 226Ra, artificial radionuclides, CFCs/SF6, 3H,3He, 210Pb, 210Po	8	67.75	Other properties (e.g. d30Si, 18O-PO4, 234Th, 226Ra, artificial radionuclides, CFCs/SF6, 3H,3He, 210Pb, 210Po	8	47.75
TOTAL	20.25	80	**TOTAL**	20.25	60

A number of TEIs have been identified for which it will be desirable to measure their concentrations in particulate material as well as in solution. A combination of sampling strategies involving bottles and *in situ* pumps will be used to fill these sample requirements. For contamination-prone TEIs that require only small volumes of water, particles will be filtered from GO-Flo bottles. Several liters of water will be allocated from each depth sampled by GO-Flo bottles (Table 1). Tests conducted during the first U.S. GEOTRACES intercalibration cruise demonstrated that this strategy is feasible (R. Sherrell, personal communication).

In situ pumps will be used to collect particles for TEIs that require sampling from volumes larger than can be accommodated by GO-Flo bottles. Workshop participants developed a tentative water budget to assess the feasibility of filling the anticipated sample requirements using commercially available battery-powered pumping systems (e.g., McLane), which typically filter particles from ~600 liters for each sample. That assessment (Table 3) indicated that battery powered pumps should be capable of meeting the sampling needs for particulate TEIs in deep water, where concentrations are greatest for TEIs requiring the largest sample volumes (e.g., ^{230}Th, ^{231}Pa, Nd isotopes), and where pumping is least likely to be slowed by clogging of filters. In surface waters, where concentrations are lowest for those TEIs requiring the largest volumes, and where filter clogging may limit sample size to substantially less than 600 liters, other strategies may be needed to cover all sample requirements for particles. Options include redesigning battery powered pumps with multiple filter holders to permit filtration of larger volumes of seawater, or using pumping systems that have the capacity to filter volumes of water significantly greater than that provided by battery powered pumping systems that are currently available. A final plan for in situ filtration that meets the needs of funded PIs will be negotiated between the management team and NSF, with advice from the U.S. GEOTRACES SSC, as part of an iterative process to be used in reaching final funding decisions. The management Team is committed to work with PIs responsible for in situ pumping to ensure that pump requirements are accommodated in the cruise plan.

Additional samples of particulate material will be available for TEI analysis by filtration from surface water pumped from the towed fish.

Table 3. Anticipated water volumes from in situ pumps required to meet the needs for key TEIs and for ancillary parameters.

Shallow pump	Volume (liters)		**Deep Pump**	Volume (liters)	
POC, PON	10		POC, PON	10	
BSi	5		BSi	5	
Ca	1		Ca	1	
Al, Ti	10		Al, Ti	10	
Ra isotopes		cartridge *	Ra isotopes		cartridge
228Th	0	non destructive	228Th	0	non destructive
234Th	50		234Th	50	
Transition metals	20		Transition metals	20	
230Th, 231Pa	100		230Th, 231Pa	100	
Nd, REE	300		Nd, REE	300	
Ba	10		Ba	10	
210Pb, 210Po	100		210Pb, 210Po	100	
TOTAL	606		**TOTAL**	606	

*Deep casts are similar to shallow casts except that Ra and Th-228 would not be measured in the mid-gyre sites. Measurement of Ra isotopes and Th-228 are desirable in the margin regions at each end of the section

Station Time and Cruise Duration

Filling the water requirements for each standard full depth water column station identified above in Tables 1 - 3 will require two casts of the clean rosette (one shallow and one deep), two casts of the Niskin rosette (one shallow and one deep) and two casts of in situ pumps at each station. Total station time required to complete these activities is estimated to be 28 hours (Table 4).

Table 4. Station time for a standard full-depth station.

Activity	Duration (hours)	Number per Station	Time per activity (hours)
Shallow GO-Flo rosette cast	1	1	1
Deep GO-Flo rosette cast	5	1	5
Shallow Niskin rosette cast	1	1	1
Deep Niskin rosette cast	5	1	5
Shallow in situ pump	6	1	6
Deep in situ pump	10	1	10
TOTAL (hours)			28

A cruise of 52 days duration is proposed, where 22 days would be required for steaming and 30 days (720 hours) is allocated to station time. A total of 22 standard full depth stations are planned (Figure 1) which, at 28 hours per station, totals 616 hours of station time. The remaining 104 hours of station time are to be divided between shallow stations (nominally one hour each) and super stations. For example, the time available could accommodate one cast to 1000 m at each of 14 shallow stations as well as three deep casts (5 hours each) at each of 6 super stations. Actual station plans and allocation of station time will be determined at the pre-cruise planning workshop, where the management team will ensure that station plans developed by funded PIs are compatible with the overall cruise schedule.

Data Management Plan

Investigators who participate in this cruise, and in particular the Management Team, will comply with the International GEOTRACES data policy, which is compliant with the NSF policy. We will communicate in a timely fashion all data resulting from the cruise including underway systems, instrument deployments, and the shipboard analytical determinations on water samples collected during the cruise to all project participants. We will also report all appropriate meta-data (navigational, meteorological, and event logs as well as data describing methods and protocols). Data will be submitted in a timely manner to BCO-DMO, (http://www.bco-dmo.org). This office will in turn submit it to the International GEOTRACES data office which is currently hosted at the British Oceanographic Data Centre in Liverpool, UK. The International GEOTRACES data office will be ultimately responsible for the permanent archiving of the data sets and their international distribution. See the Implementation Plan (NAZSIP08) for more details. Public release of data will normally be two years from the end of the cruise or field activity, in line with NSF policy.

Postdoctoral Researcher Mentoring Plan

The postdoc who will be responsible for the shipboard Zn analyses will be mentored with regard to career development by a combination of institutional seminars and websites (e.g. <http://web.mit.edu/mitpostdocs>, and frequent discussions with the PIs of this proposal. The EAPS department at MIT also mentors postdocs by annual discussions with the department head. In the past our students and postdocs have obtained good positions, and most of them are employed at research universities and research institutions.

Broader Impacts

It is widely agreed that the ocean biogeochemical research community needs a global picture of the key and ancillary GEOTRACES properties; the major impact of this project will be in its service to that community. This service will enable the development of better ocean biogeochemical models so that we can assess the likely impact of future climate change and anthropogenic pollution, and provide a basis for understanding changes observed in past oceans. The development of a reliable platform and procedures for sampling trace metals and isotopes will provide the community with a platform for future oceanographic fieldwork. The development of teams that understand the proper sampling and measurement techniques, many of whom will be graduate students and postdocs, will supply the community with a pool of skills necessary to achieve the goals of the next generation of ocean research programs.

Results from Prior NSF Support

Removed from this file.

References

Alleman, L. Y., Veron, A. J., Church, T. M., Flegal, A. R., and Hamelin, B., 1999. Invasion of the abyssal North Atlantic by modern anthropogenic lead. *Geophysical Research Letters* **26**, 1477-1480.

Amyot, M., Morel, F. M. M., and Ariya, P. A., 2005. Dark oxidation of dissolved and liquid elemental mercury in aquatic environments *Env. Sci. Tech.* **39**, 110-114.

Boyd, P. W., Crossley, A. C., DiTullio, G. R., Griffiths, F. B., Hutchins, D. A., Queguiner, B., Sedwick, P. N., and Trull, T. W., 2001. Control of phytoplankton growth by iron supply and irradiance in the subantarctic Southern Ocean: Experimental results from the SAZ Project. *J. Geophys. Res.* **106**, 31573-31583.

Boyle, E. A., 1988. Cadmium: chemical tracer of deep-water paleoceanography. *Paleoceanography* **3**, 471-489.

Bruland, K. W. and Lohan, M. C., 2004. Controls of Trace Metals in Seawater. In: Holland, H. D. and Turekian, K. K. Eds.), *Treatise on Geochemistry*. Elsevier, Amsterdam.

Chiapello, I. and Moulin, C., 2002. TOMS and METEOSAT records of the variability of Saharan dustr transport over the Atlantic during the last two decades (1979-1997). *Geophys. Res. Lett.* **29**, doi 10.1029/2001GL013767.

De Jong, J. T. M., den Das, J., Bathmann, U., Stoll, M. H. C., Kattner, G., Nolting, R. F., and Baar, H. J. W. d., 1998. Dissolved iron at subnanomolar levels in the Southern Ocean as determined by shipboard analysis. *Anal. Chim. Acta* **377**, 113-124.

Doney, S. C. and Jenkins, W. J., 1994. Ventilation of the deep western boundary current and abyssal Western North Atlantic: Estimates from tritium and 3He distributions. *Journal of Physical Oceanography* **24**, 638-659.

Elderfield, H. and Rickaby, R. E. M., 2000. Oceanic Cd/P ratio and nutrient utilization in the glacial Southern Ocean. *Nature* **405**, 305-310.

Foustoukos, D. I. and Seyfried Jr., W. E., 2005. Redox and pH constraints in the subseafloor root zone of the TAG hydrothermal system, 26 N Mid-Atlantic Ridge *Earth Planet. Sci. Lett.* **235**, 497-510.

Frew, R. D. and Hunter, K. A., 1992. Influence of Southern Ocean waters on the cadmium-phosphate properties of the global ocean. *Nature* **360**, 144-146.

GEOTRACESSCORworkinggroup, 2007. GEOTRACES – An international study of the global marine biogeochemical cycles of trace elements and their isotopes. *Chemie der Erde* **67**, 85-131.

German, C. R., Higgs, N. C., Thomson, J., Mills, R. A., Elderfield, H., Blusztajn, J., Fleer, A. P., and Bacon, M. P., 1993. A geochemical study of metalliferous sediment from the TAG hydrothermal mound, 26 08N, Mid-Atlantic Ridge. *Journal of Geophysical Research* **98**, 9683-9692.

German, C. R. and Von Damm, K. L., 2004. Hydrothermal Processes. In: Elderfield, H. (Ed.), *Treatise on Geochemistry*. Elsevier, Oxford.

Goto, S., Kinoshita, M., Schultz, A., and Von Herzen, R. P., 2003. Estimate of heat flux and its temporal variation at the TAG hydrothermal mound, Mid-Atlantic Ridge 26N. *Journal of Geophysical Research* **108**, doi:10.1029/2001JB000703.

Hastings, M. G., Sigman, D. M., and Lipschultz, F., 2003. Isotopic evidence for source changes of nitrate in rain at Bermuda. *Journal of Geophysical Research-Atmospheres* **108**, doi:10.1029/2003JD003789.

Henderson, G. M., Heinze, C., Anderson, R. F., and Winguth, A., 1999. Global distribution of the ^{230}Th flux to ocean sediments constrained by GCM modelling. *Deep-Sea Research I* **46**, 1861-1893.

Istoshin, Y. V., 1961. Formative area of 'eighteen-degree' water in the Sargasso Sea. *Okeanolgiya* **1**, 600-607.

Jeandel, C., Arsouze, T., Lacan, F., Techine, P., and Dutay, J. C., 2007. Isotopic Nd compositions and concentrations of the lithogenic inputs into the ocean: A compilation, with an emphasis on the margins. *Chem. Geol.* **239**, 156-164.

Jenkins, W. J., 1998. Studying Thermocline Ventilation and Circulation Using Tritium and 3He. *Journal of Geophysical Research* **103**, 15817-15831.

Jenkins, W. J., 2008. The Biogeochemical Consequences of Changing Ventilation in the Japan/East Sea. *Marine Chemistry* **108**, 137-147.

Jenkins, W. J. and Doney, S. C., 2003. The Subtropical Nutrient Spiral. *Global Biogeochemical Cycles* **17**, 1110 doi:10.1029/2003GB002085.

Jickells, T. D., An, Z. S., Andersen, K. K., Baker, A. R., Bergametti, G., Brooks, N., Cao, J. J., Boyd, P. W., Duce, R. A., Hunter, K. A., Kawahata, H., Kubilay, N., LaRoche, J., Liss, P. S., Mahowald, N., Prospero, J. M., Ridgewell, A. J., Tegen, I., and Torres, R., 2005. Global iron connections between desert dust, ocean biogeochemistry, and climate. *Science* **308**, 67-71.

John, S. G., Geis, R. W., Saito, M. A., and Boyle, E. A., 2007a. Zinc isotope fractionation during high-affinity and low-affinity Zn transport in T. oceanica. *Limnol. Oceanogr.* **52**, 2710-2714.

John, S. G., Rouxel, O. J., Craddock, P. R., Engwall, A. M., and Boyle, E. A., 2008. Zinc stable isotopes in seafloor hydrothermal vent fluids and chimneys. *Earth Planet. Sci. Lett.* **269**, 17-28.

John, S. J., Park, Z., Zhang, Z., and Boyle, E. A., 2007b. The isotopic composition of some common forms of anthropogenic zinc. *Chem. Geol.* **245**, 61-69.

Johnson, K. S., Boyle, E., Bruland, K., Coale, K., Measures, C., Moffett, J., Aguilar-Islas, A., Barbeau, K., Bergquist, B., Bowie, A., Buck, K., Cai, Y., Chase, Z., Cullent, J., Doi, T., Elrod, V., Fitzwater, S., Gordon, M., King, A., Laan, P., Laglera-Baquer, L., Landing, W., Lohan, M., Mendez, J., Milne, A., Obata, H., Ossiander, L., Plant, J., Sarthou, G., Sedwick, P., Smith, G. J., Sohst, B., Tanner, S., Berg, S. V. D., and Wu, J., 2007. Developing Standards for Dissolved Iron in Seawater. *EOS Trans. Am. Geophys. Union* **88**, 131-132.

Kim, G., Alleman, L. Y., and Church, T. M., 1999. Atmospheric depositional fluxes of trace elements, ^{210}Pb and ^{7}Be to the Sargasso Sea. *Glob. Biogeochem. Cycles* **13**, 1183-1192.

Knapp, A. N., DiFiore, P. J., Deutsch, C., Sigman, D. M., and Lipschultz, F., 2008. Nitrate isotopic composition between Bermuda and Puerto Rico: Implications for N_2 fixation in the Atlantic Ocean. *Global Biogeochemical Cycles* **22**, doi:10.1029/2007GB003107.

Lacan, F. and Jeandel, C., 2005. Neodymium isotopes as a new tool for quantifying exchange fluxes at the continent-ocean interface *Earth Planet. Sci. Lett.* **232**, 245-257.

Li, Q. P., Zhang, J.-Z., Millero, F. J., and Hansell, D. A., 2005. Continuous colorimetric determination of trace ammonium in seawater with a long-path liquid waveguide capillary cell. *Mar. Chem.* **96**, 73-85.

Luyten, J. R., Pedlosky, J., and Stommel, H., 1983. The ventilated thermocline. *Journal of Physical Oceanography* **13**, 292-309.

Measures, C. I. and Brown, E. T., 1996. Estimating dust input to the Atlantic Ocean using surface water Al concentrations. In: Guerzoni, S. and Chester, R. Eds.), *The Impact of Desert Dust Across the Mediterranean*. Kluwer Acad., Dordrecht, Netherlands.

Measures, C. I., Landing, W. M., Brown, M. T., and Buck, C. S., 2008. High-resolution Al and Fe data from the Atlantic Ocean CLIVAR-CO2 Repeat Hydrography A16N transect: Extensive linkages between atmospheric dust and upper ocean geochemistry. *Global Biogeochemical Cycles* **22**, doi:10.1029/2007GB003042.

Moore, W. S., 2000a. The ages of continental shelf waters determined from ^{223}Ra and ^{224}Ra. *Journal of Geophysical Research* **105**, 22117-22122.

Moore, W. S., 2000b. Determining coastal mixing rates using radium isotopes. *Continental Shelf Research* **20**, 1993-2007.
Moore, W. S., 2007. Seasonal distribution and flux of radium isotopes on the southeastern US continental shelf. *J. Geophys. Res.-Oceans* **112**, -.
Moore, W. S., Sarmiento, J. L., and Key, R. M., 2008. Submarine groundwater discharge revealed by ^{228}Ra distribution in the upper Atlantic Ocean. *Nature Geoscience* **1**, 309-311.
Moran, S. B., Shen, C.-C., Edmonds, H. N., Weinstein, S. E., Smith, J. N., and Edwards, R. L., 2002. Dissolved and particulate ^{231}Pa and ^{230}Th in the Atlantic Ocean: constraints on intermediate/deep water age, boundary scavenging, and ^{231}Pa/^{230}Th fractionation. *Earth and Planetary Science Letters* **203**, 999-1014.
Morel, F. M., Milligan, A. J., and Saito, M. A., 2004. Marine Bioinorganic Chemistry: The Role of Trace Metals in the Oceanic Cycles of Major Nutrients In: Holland, H. D. and Turekian, K. K. Eds.), *Treatise on Geochemistry*. Elsevier, Amsterdam.
Nakai, S., Halliday, A. N., and Rea, D. K., 1993. Provenance of dust in the Pacific-Ocean. *Earth Planet. Sci. Lett.* **119**, 143-157.
Olivarez, A. M., Owen, R. M., and Rea, D. K., 1991. Geochemistry of eolian dus in Pacific pelagic sediments - implications for paleoclimatic interpretations. *Geochimica et Cosmochimica Acta* **55**, 2147-2158.
Olson, R. J., Chisholm, S. W., and et al., 1990. Spatial and temporal distribution of prochlorophyte picoplankyon in the North Atlantic Ocean. *Deep-Sea Res.* **37**, 1033-1051.
Pak, H., Zaneveld, J. R. V., and Kitchen, J., 1980. Intermediate Nepheloid Layers Observed Off Oregon and Washington. *J.Geophys.Res.* **85**, 6697-6708.
Palter, J. B., Lozier, M. S., and Barber, R. T., 2005. The effect of advection on the nutrient reservoir in the North Atlantic subtropical gyre. *Nature* **437**, 687-692.
Partensky, F., Hess, W. R., and al., e., 1999. Prochlorococcus, a Marine Photosynthetic Prokaryote of Global Significance. *Microbiol. and Mol. Bio. Revs.* **63**, 106-127.
Patterson, C. C. and Settle, D. M., 1987. Review of data on eolian fluxes of industrial and natural lead to the land and seas in remote regions on a global scale. *Mar. Chem.* **22**, 137-162.
Rona, P. A., Thompson, G., Mottl, M. J., Karson, A., Jenkins, W. J., Graham, D. W., Mallette, M., Von Damm, K., and Edmond, J. M., 1983. Hydrothermal activity at the TAG hydrothermal field, Mid-Atlantic Ridge crest at 26°N. *Journal of Geophysical Research* **89**, 11365-11377.
Saito, M. A. and Moffett, J. W., 2002. Temporal and spatial variability of cobalt in the Atlantic Ocean. *Geochim. Cosmochim. Acta* **66**, 1943-1953.
Schlitzer, R., 2007. Assimilation of radiocarbon and chlorofluorocarbon data to constrain deep and bottom water transports in the world ocean. *Journal of Physical Oceanography* **37**, 259-276.
Stanley, R. H. R., 2007. A Determination of Air-Sea Gas Exchange Processes and Upper Ocean Biological Production From Five Noble Gases and Tritiugenic Helium-3, MIT-WHOI Joint Program in Chemical Oceanography.
Stanley, R. H. R., Baschek, B., Lott, D. E. I., and Jenkins, W. J., 2009a. A method for measuring noble gases and their isotopic ratios using programmed multistage cyrogenic trapping and a combination of quadrupole and magnetic sector mass spectrometers. *Geochemistry Geophysics Geosystems*, Submitted.
Stanley, R. H. R., Jenkins, W. J., and Doney, S., 2006. Quantifying seasonal air-sea gas exchange processes using a noble gas time-series: a design experiment. *Journal of Marine Research* **64**, 267-295.
Stanley, R. H. R., Jenkins, W. J., Lott, D. E. I., and Doney, S. C., 2009b. Noble gas constraints on air-sea gas exchange and bubble fluxes. *J. Geophys. Res.-Oceans*, Submitted.

Sunda, W. G., Huntsman, S. A., and 1995. Cobalt and zinc interreplacement in marine phytoplankton: Biological and geochemical implications. Limnology and Oceanography 40 (8), -. 1995. Cobalt and zinc interreplacement in marine phytoplankton: Biological and geochemical implications. *Limnol. Oceanogr* **40**, 1404-1417.

Vink, S., Boyle, E. A., Measures, C. I., and Yuan, J., 2000. Automated High Resolution Determination of the Trace Elements Iron and Aluminium in the Surface Ocean using a Towed Fish Coupled to Flow Injection Analysis. *Deep-Sea Res. I* **47**, 1141-1156.

Waples, J. T., Benitez-Nelson, C., Savoye, N., Loeff, M. R. v. d., Baskaran, M., and Gustafsson, Ö., 2006. An introduction to the application and future use of Th-234 in aquatic systems *Mar. Chem.* **100**, 166-189.

Worthington, L. V., 1959. The 18 degree water in the Sargasso Sea. *Deep-Sea Research* **5**, 297-305.

Zhang, J.-Z., 2000. Shipboard automated determination of trace concentrations of nitrite and nitrate in oligotrophic water by gas-segmented continuous flow analysis with a liquid waveguide capillary flow cell. **Deep-Sea Res. I**, 1157-1171.

Zhang, J.-Z. and Chi, J., 2002. Automated analysis of nanomolar concentrations of phosphate in natural waters with liquid waveguide. *Environ. Sci. Technol.* **36**, 1048-1053.