

PROJECT SUMMARY

Criterion 1, Intellectual Merit

Since the GEOSECS program of the 1970s it is clearly recognized that trace elements and their isotopes (TEI) can act not only as nutrients or contaminants, but also as powerful tracers or proxies of oceanographic processes. In this context the new international program GEOTRACES proposes to study the marine biogeochemical cycles of TEIs in the world's oceans. There are new sampling, analytical, and modeling techniques that can be utilized in GEOTRACES, but before sampling transects across ocean basins are started, the efficacy, accuracy and representativeness of these methods must be evaluated. This falls under the category of "intercalibration" and the GEOTRACES Science Plan explicitly states that this must be the first phase of the program. The research proposed here will undertake the U.S. GEOTRACES Intercalibration with four primary objectives: **(1) Develop and test the US GEOTRACES sampling systems and procedures for dissolved and particulate TEIs. This equipment will be a community resource for use in all future US GEOTRACES' cruises; (2) Using these systems, conduct a thorough intercalibration for all the key GEOTRACES TEIs, and as many others as possible, in the dissolved and particulate phases through the participation of the worldwide TEI community; (3) Establish GEOTRACES Baseline Stations in the western North Atlantic and eastern North Pacific Oceans as part of the Intercalibration Cruises; and (4) Fully document the intercalibration results and create "US GEOTRACES Users Manuals and Procedures" for future US-sponsored GEOTRACES cruises.** This research will be a collaborative effort among 3 PIs over 3 years, but participation in the intercalibration component will be international and will involve at least 80 other laboratories. The western North Atlantic and eastern Pacific (oligotrophic deep water sites and mesotrophic margin locations) will be used in these efforts.

Criterion 2, Broader Impacts

The scientific importance of the proposed work is intimately linked to that of GEOTRACES as a whole. However, the development of GEOTRACES infrastructure (sampling systems and procedures) may become most significant in its broader impacts to oceanographic science in general. The creation of Users' Manuals will be invaluable not only to scientists in the US, but also to those in less-developed countries with few resources to devote to basic oceanographic research. Outreach in the form of communicating what environmental scientists do and its relevance to the lay public is also a vital facet of research. In this respect, the PIs will employ a variety of outreach tools including public open houses (particularly on board research vessels) and working with specifically designed outreach programs, notably COSEE at Rutgers (MACOSEE; <http://www.macosee.net/>). Graduate and undergraduate students will be intimately involved in the studies, and Cutter, as a PI on the NSF-funded Hall-Bonner Program for Minority Scholars in Ocean Sciences (<http://www.hamptonu.edu/science/marine/hallbonner.htm>), will work to recruit one of these students (at no charge to this grant). The PIs also maintain university web sites featuring current research endeavors that are designed for public viewing and education.

INTRODUCTION

It is widely recognized that trace elements and their isotopes can function as nutrients, contaminants, and tracers or proxies of various oceanographic processes. Results from the Geochemical Ocean Sections Study (GEOSECS) of the 1970s led to much of this recognition (e.g., Broecker and Peng, 1982). The development of clean sampling protocols and new, highly sensitive analytical methods, combined with advances in modeling tools that can link and synthesize large data sets, have revolutionized our ability to study the marine biogeochemical cycling of trace elements and isotopes on a global scale; we can now go well beyond what GEOSECS started. This seed was nurtured at an international workshop in Toulouse, France in 2003, and after workshops and the inputs/efforts of more than 300 scientists culminated in the international GEOTRACES Program that was recently approved by the Scientific Committee on Oceanic Research (SCOR). GEOTRACES has three primary research objectives (GEOTRACES Science Plan found at www.geotraces.org):

- (1) To determine global ocean distributions of selected trace elements and isotopes, including their concentration, chemical speciation, and physical form, and to evaluate the sources, sinks, and internal cycling of these species to characterize more completely the physical, chemical, and biological processes regulating their distributions;
- (2) To understand the processes involved in oceanic trace-element cycles sufficiently well that the response of these cycles to global change can be predicted, and their impact on the carbon cycle and climate understood; and
- (3) To understand the processes that control the concentrations of geochemical species used for proxies of the past environment, both in the water column and in the substrates that reflect the water column.

A major portion of the GEOTRACES objectives will be met by sampling along ocean basin sections, and as an international program, many countries are already planning (or will be conducting shortly) their GEOTRACES cruises. However, before this major effort is begun in earnest, the Science Plan states that intercalibration activities must take place to assure the accuracy of all the collected data. To avoid confusion, intercalibration is defined as, “The process, procedures, and activities used to ensure that the several laboratories engaged in a monitoring program can produce compatible data. When compatible data outputs are achieved and this situation is maintained, the laboratories can be said to be intercalibrated” (Taylor, 1987). Thus, intercalibration is an active process between laboratories that includes all steps from sampling to analyses, with the goal of achieving the same accurate results regardless of the method or lab.

The ultimate goal for the intercalibration component of GEOTRACES is to achieve the best precision and accuracy possible (lowest random and systematic errors) for the suite of GEOTRACES’ Trace Elements and Isotopes (TEI) as a prelude to the sampling program, and continuing effort throughout the sampling and analysis program. Thus, the primary goal of the work proposed here is to provide the infrastructure and organization required to support the participation by as many U.S. scientists as possible, as well as scientists from many other nations, in this vital intercalibration activity. Specific objectives of this proposal are described in detail in the Proposed Research section. This research will be a collaborative effort between 3 PIs over 3 years, but participation in the intercalibration component will be international and involve at least 80 other laboratories.

Results of Prior NSF Support Related to This Proposal - Cutter

Grants: OCE-9523159 and -0117648 **Project Titles:** Collaborative research: Trace element input and cycling in the western South Atlantic; Biogeochemistry of trace elements in the western Pacific: atmospheric input and surface water processing **Periods:** 11/1995-4/1998; 8/2001-8/2005; **Amounts:** \$134,541; \$277,974.

Summary of Results and Publications: These related grants were collaborative projects between 3 PI's at Old Dominion University, Florida State University, and the University of Hawaii that sought to examine the interaction between inputs (atmospheric, including dust from North Africa and Asia, and riverine), cycling, and transport of Al, As, Fe, Sb, and Se in the western Atlantic and Pacific Oceans. It also was the foundation for the 1996 and 2002 Intergovernmental Oceanographic Commission Contaminant Baseline Surveys, the third and fourth cruises in an UNESCO effort to establish the present day concentrations of trace elements and synthetic organic compounds in the major water masses of the world's oceans (see Cutter et al., 1996). The major results are presented in the papers listed in the Reference section (marked with a *) and in 2 special volumes of *Deep-Sea Research II* (vol. 46, No. 5; vol. 48, No. 13) and a special volume of *G³* with results from the 2002 expedition. To date, over 24 papers have been supported directly or indirectly from this grant. Moreover, talks on results from the cruises were presented during three special sessions: 1997 ASLO Aquatic Sciences Meeting, 1998 AGU Ocean Sciences Meeting, and 2002 AGU Fall Meeting.

Development of Human Resources: As a faculty member in an academic department, many aspects of my research programs are incorporated into the graduate and undergraduate courses I teach. Perhaps most significantly, the cruises supported under these grants allowed 6 Ph.D.'s to be completed: M. Charette (URI), K. Conway (UCSC), G. Kim (U. Delaware), M. Ranville (UCSC), K. Rolfhus (U. Conn.), and J. Yuan (U. So. Miss.).

Results from Prior NSF Support Related to This Proposal - Bruland

Grant: OCE-0324727 **Project Title:** Collaborative Research: Sampling and Analysis of Iron (SAFe), an International Collaboration. K. Johnson was the PI and Bruland was one of the co-PIs. **Period:** 10/1/03-3/30/06; **Amount:** \$175,037.

Summary of Results and Publications: The NSF-funded Sampling and Analysis of Fe (SAFe) program brought together marine chemists who study iron from around the world on one ship in the eastern region of the North Pacific subtropical gyre in October-November 2004 to 1) compare shipboard analytical methodologies, sampling strategies, and sample storage techniques appropriate for iron concentrations in seawater, and 2) obtain large volumes of uncontaminated seawater for the production of seawater reference samples at appropriate concentrations to assist investigators in future technique development and global surveys. The University of California at Santa Cruz (UCSC) and Moss Landing Marine Laboratories (MLML) were responsible for the collection and distribution of the large volume filtered and acidified seawater samples for the SAFe program that were aliquoted into small bottles (0.5 L) and made available to researchers in the oceanographic community. This funding supported publications listed in the Reference section (marked with a *) and two meeting presentations to date. A SAFe email list (safe@ucsc.edu) is now available where scientists can share results from the SAFe samples and post analytical developments, or problems encountered, related to the analysis and sampling of iron and other trace metals in seawater. Additionally, an email address was created to facilitate requesting the SAFe seawater standard reference materials (requestsafestandard@ucsc.edu).

Development of Human Resources: As a faculty member in an academic department, many aspects of my research programs are incorporated into the graduate and undergraduate courses I teach. The cruise allowed the participation of 2 of my Ph.D. students (Ana Aguilar-Islas and Kristen Buck, who will complete their theses during calendar year 2006) and one post doctoral researcher (Maeve Lohan) who is now a faculty member at the University of Plymouth, UK.

Results from Prior NSF Support Related to This Proposal – Sherrell

Grant: OCE 9902660 **Project Title:** *Trace Metal Limitation of Phytoplankton Productivity: Combined Immunological, Geochemical, and Growth Assay Approaches in Lake Superior*. Collaboration: R. Sterner was the lead PI, Sherrell was a co-PI **Period:** 7/99 – 6/03 **Amount:** \$339,970 (\$93,506 Sherrell share).

Summary of Results and Publications: This project generated the first comprehensive trace metal data for Lake Superior, with complete spatial coverage and 3 year temporal coverage, using new direct injection ICP-MS methods (Field and Sherrell, 2003; full citation marked with a * in the References). We demonstrated for the first time that Lake Superior has sufficiently low Fe that it can at times be near co-limitation for Fe and P (Sterner et al., 2004), and that Cu and Mn interact to control Cu toxicity (*Twiss et al., 2004). Sherrell's chemical results for dissolved and colloidal Fe were compared to co-PI McKay's novel bioreporter determination of Fe availability (McKay et al., 2004; 2005). Work supported by this grant led to the development of a new ongoing OCE-funded project (ending 2/07) on the dynamics of nitrate accumulation and its relationship to Fe and P dynamics in the lake. We have developed a freshwater version of the MAGIC method for low-level SRP determination (Anagnostou, 2005), and compared these results to new assays of pool size using P-33 uptake experiments, confirming the mean open lake SRP of ~2nM. New ICP-MS methods demonstrate that DOP levels in the lake are lower than in any oceanic system studied to date (~10-30nM). The results have also been reported in several international meetings.

Development of Human Resources: This project funded graduate student Yongcheng Ji, who will defend his Ph.D. in Sept 2006. He showed through field measurements and lab culture experiments that phytoplankton in Lake Superior are unusually enriched in Zn, in part as a result of enzymatic responses to limiting P availability, demonstrating for the first time a macronutrient-micronutrient link in field assemblages. The subsequent NSF funding supported M.S. student Eleni Anagnostou (now a Ph.D. student in Sherrell's lab), who developed a new low-level P method for Lake Superior and, in collaboration with field efforts of Environment Canada, determined DIP and DOP distributions throughout the lake, showing that DOP is a very actively cycled P pool. In addition, this project supported summer internships in 2005 and 2006 for high school student Mgbechi Erondu, who will start as a Freshman at Princeton in Fall 2006.

BACKGROUND

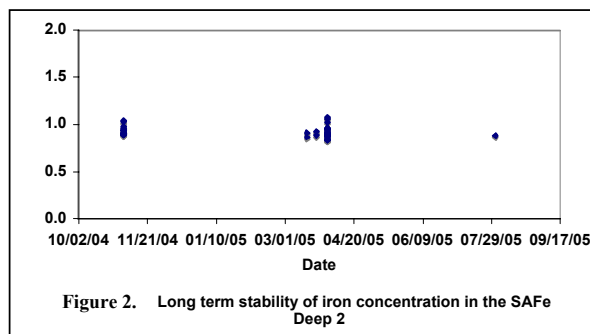
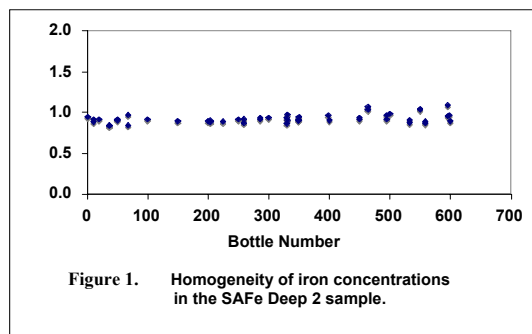
In order for the goals of GEOTRACES to be met, TEI data must be as accurate as possible (where accuracy includes random errors, precision, and systematic ones; see Taylor, 1987). The works of Bruland et al. (1979) and Schaule and Patterson (1981) showed that for certain trace elements, accuracy could be compromised at each step in determining elemental concentrations in seawater - sample acquisition, handling/processing, storage, and finally analysis. Importantly, these authors also demonstrated that with care and clean techniques, accurate data could be obtained. In the recent past, most intercalibration efforts have been directed at the last step - analysis - and for many TEIs the effects of sample handling and storage have hardly been addressed. In terms of determining TEIs, the use of representative primary standards and certified reference materials are crucial, and a series of recommendations on this aspect are provided in the GEOTRACES Standards and Intercalibration Plan (available on www.geotraces.org). While valuable, reference materials do not validate sampling and handling methods used at sea. Moreover, currently available certified reference materials for the dissolved phase have concentrations of TEIs that are 5-10x higher than oceanic values, and no reference materials are available for chemical speciation of dissolved constituents (trace elements, nutrients). Although certified ocean reference materials are relevant to GEOTRACES, it is beyond the scope of this proposal to create them (refer to NRC, 2002). Instead, the focus will be on the use of real seawater samples to conduct intercalibrations. This section will review the state-of-the-art in evaluating and assuring accuracy for oceanographic measurements of TEIs in the dissolved and particulate phases.

Sampling and Analysis of Iron – the SAFe Program

The most recent intercalibration effort for a trace element in seawater was the SAFe program with Ken Johnson (MBARI) as the PI. Co-PI's included Ed Boyle (MIT), Ken Bruland (UCSC), Chris Measures (U of H), Kenneth Coale (MLML), and Jim Moffett (WHOI). The SAFe Program involved 32 scientists representing 17 laboratories from 7 countries on the R/V Melville in the eastern North Pacific in Oct/Nov 2004 for an intercalibration effort determining dissolved iron in seawater. A variety of clean trace metal samplers were tested in low Fe (<0.1 nM) surface seawater. It was reassuring to observe that there were no significant differences between the dissolved Fe concentrations determined on samples collected with a trace metal-clean surface pumping system (Bruland et al., 2005), the “old fashioned” Teflon-coated 30L GO-Flo bottles deployed on Kevlar hydrowire and tripped with Teflon messengers (Bruland et al., 1979), MITESS samplers (Bell et al., 2002; Boyle et al., 2005), and a trace metal-clean rosette system of 12L GO-Flo bottles deployed on Kevlar conducting line and sub-sampled in a clean lab (Landing and Measures system used on CLIVAR cruises). These systems were tested in both near-surface waters and at 1000 m (except the pump system). There were, however, elevated dissolved Fe concentrations observed on samples collected using a trace metal-clean rosette system with Niskin bottles deployed on standard hydrowire.

The SAFe Program also developed a large volume tank system (Bruland/Smith) composed of two 500L fluorinated polyethylene tanks utilizing Teflon plumbing and pumps to homogenize large volume filtered samples for intercalibration studies. The SAFe program produced ~600 0.5L samples of dissolved ($<0.2\mu\text{m}$), acidified surface water and an equivalent number of samples from a depth of 1000 meters. Combined data to date for multiple analysis methods from all the various participants yield consensus values of 0.91 ± 0.17 nM for the 1000 meter sample and 0.097 ± 0.043 nM for the surface sample (Johnson et al., article submitted to EOS). These samples are currently being distributed and are available to the community for use as seawater reference materials for open ocean iron measurements at requestsafestandard@ucsc.edu.

Figure 1 shows the concentrations of dissolved Fe in different aliquot bottles from the SAFe Deep 2 (D-2) sample determined by a subset of experienced analysts using a variety of methods both on board the ship and in shore-based laboratories. Figure 2 shows the long-term stability of dissolved iron in the acidified 0.5L D-2 samples (0.92 ± 0.06). Similar results were obtained for the surface S-1 sample (0.092 ± 0.015). These results demonstrate that we were able to meet our goal of collecting, bottling, and distributing well-characterized surface and deep seawater samples with oceanographically consistent iron concentrations.



The SAFe 0.5L samples have additional value for intercalibrations of trace elements other than iron. Evaluation of the Deep and Surface samples for other trace elements has been completed using

organic extraction concentration and ICP-MS analysis. Results from Mike Gordon (MLML) indicate that the samples are homogeneous and contain an appropriate range of trace element concentrations:

<u>Dissolved trace element</u>	<u>Surface 1 concentration</u>	<u>Deep 2 concentration</u>
Zinc	0.05 ± 0.01 nM	6.60 ± 0.33 nM
Copper	0.50 ± 0.02 nM	1.95 ± 0.13 nM
Nickel	2.35 ± 0.03 nM	8.62 ± 0.12 nM
Cobalt	2.6 ± 0.5 pM	25.1 ± 1.0 pM
Lead	40.5 ± 1.2 pM	25.3 ± 1.6 pM

The concentrations of these elements are consistent with previous measurements at nearby stations (e.g., Bruland, 1980 and VERTEX-IV data of John Martin) and therefore may be an excellent set of reference samples for other TEIs in addition to Fe. While the 0.5L samples collected and available by the SAFe program can serve the needs of some of the TEI community for dissolved metal determinations, they cannot meet the needs of a wide variety of TEIs. Many of the stable and radiogenic isotope determinations require larger sample sizes and some measurements require different preservation techniques. Nevertheless, the SAFe program does provide models for the design of a GEOTRACES Intercalibration Program for other TEIs. Importantly, it also provides confidence that the development of a trace metal-clean rosette and clean sampling van modeled after that used for CLIVAR's Al and Fe measurements will be able to meet the goals of GEOTRACES (note that CLIVAR's goals are climate-related and the carbon cycle is a major focus). In this respect, Landing (pers. comm.) reports that their system has also obtained oceanographically-consistent profiles for Cd, Co, Cu, Mn, Ni, Pb, and Zn, although there may be slight Zn contamination in near surface samples, an issue that will be addressed in the proposed work.

Particle and Colloid Sampling

With a few very notable exceptions, much of what we understand about the association of trace metals with particles in the ocean has been inferred from gradients in dissolved metal distributions. For example, there have been very few studies of particulate distributions of most of the metals identified as "key parameters" in the GEOTRACES Science Plan (Al, Fe, Mn, Zn, Cu, and Cd). Much of the research on the role of particles and their dynamics in determining the global distributions of TEI in the ocean has focused on the isotopes of Th and Pb, and on Fe, elements that are strongly partitioned into the particulate phase. The multi-element studies published to date have sampled the suspended particle population by obtaining relatively large samples using in situ pumping (e.g., Sherrell and Boyle, 1992; Boyd et al., 1999; Moran et al., 2003; Buesseler et al., 2005; Lam et al., 2006) or large volume continuous-flow centrifugation (Kuss and Kremling, 1999). While large samples of particles are necessary for some parameters (e.g., Th isotopes), modern analytical methods like ICP-MS are capable of very sensitive multi-element analyses, reducing theoretical sample requirements for a suite of trace elements including key trace metals (as above) to suspended particles filtered from only 1-4 L of seawater (Cullen and Sherrell, 1999), although isotope ratio determinations often require larger samples. Even with modest sample volumes there is a critical need for low blank, yet efficient, filter materials, an issue that has been briefly explored (Cullen and Sherrell, 1999) to arrive at optimum filter types for determination of particulate TEIs.

It is well understood that separation of particles from natural waters is an operationally defined process, and that there is no ideal filter type or pore size for all analytes and scientific questions. It will be our goal in the GEOTRACES Intercalibration Cruises to establish a "default" filtration protocol that will be used for the key TEI throughout the Program. Interested GEOTRACES investigators can then elaborate and expand on these standard procedures as needed to address all analytical goals that will ultimately be part of the Program.

Intimately tied to the issue of accurate sampling of suspended particles is the importance of colloidal material to the distribution and transport of TEIs. Great effort was expended some years ago to investigate and reconcile numerous methods for separating colloidal material, with an emphasis on Th isotopes and carbon (e.g., Buesseler et al., 1996). The findings revealed a large dependence on operational factors and led to no clearly superior technique. It is now broadly recognized that particulate elements comprise a continuum from small macro-molecules all the way to large sinking particles. The colloidal fraction, nominally and variably defined as >1000 kDa but <0.2 μm , seems to be a larger relative pool for some elements than others (roughly as predicted theoretically by the Irving–Williams order). However, there has been no published comprehensive determination of the open ocean colloidal pool for the key elements in GEOTRACES, the difficulty of avoiding contamination or processing artifacts largely accounting for the dearth of data. Among the transition elements, most of the work has focused on Fe (e.g., Wu et al., 2001), although progress has been made for a number of metals in estuaries and coastal waters (Guo et al., 2000; Wells et al., 2000).

PROPOSED RESEARCH

Overall, the GEOTRACES Intercalibration Program needs to establish accurate and non-contaminating sample collection and handling protocols for TEIs. These procedures must be suitable for its planned sampling program (sections and process studies), and the Program should establish GEOTRACES Baseline Stations where the concentrations and speciation of dissolved and particulate TEIs have been intercalibrated and can be used as future references (“in situ reference materials”). In addition, the Program must ensure that methods for the sampling and determinations of essential ancillary/hydrographic parameters, particularly the nutrients (ammonium, nitrite, nitrate, phosphate, and silicate) at nanomolar concentrations, are similarly accurate throughout the duration of field studies. The research proposed here will have four primary objectives:

- (1) Develop and test the US GEOTRACES sampling systems and procedures for dissolved and particulate TEIs. This equipment will be a community resource for use in all future US GEOTRACES cruises;**
- (2) Using these systems, conduct a thorough intercalibration for all the key GEOTRACES TEIs, and as many others as possible, in the dissolved and particulate phases through the participation of the worldwide TEI community;**
- (3) Establish GEOTRACES Baseline Stations in the western North Atlantic and eastern North Pacific Oceans as part of the Intercalibration Cruises; and**
- (4) Fully document the intercalibration results and create “US GEOTRACES Users Manuals and Procedures” for future US-sponsored GEOTRACES cruises.**

It is important to recognize that we are proposing research specifically for the US component of the International GEOTRACES Program, and other countries are developing/have developed their own sampling systems to meet programmatic goals. This is not mutually exclusive, and the Intercalibration Cruises proposed here will be international in scope, including participants and as much as possible, sampling systems. Thus, the proposed efforts will be a key component of the International GEOTRACES program. The other important point is that GEOTRACES identified 12 “key” elements (Al, ^{13}C , Cd, Cu, Fe, Mn, ^{15}N , Zn, and Nd and Pb isotopes) and 3 other parameters (stored/archived samples, particles, and aerosols), and with the exception of the latter, the proposed intercalibration will cover all of these and as many other TEIs as possible. Detailed descriptions of how these objectives will be accomplished follow.

Sampling system, procedures and evaluation

Sampling Equipment. The seawater sampling system for GEOTRACES not only must be non-contaminating and acquire a representative large volume sample, it also must be logistically simple (fast

sampling time) because of long ocean transects with many vertical stations spaced closely together. These criteria suggest that an enlarged version of the Landing and Measures trace metals CLIVAR system (bottles, rosette, winch, and sampling van) that performed successfully during SAFe is the best route to pursue. Because this system will be a community asset to be used on all future GEOTRACES cruises sponsored by the US, the actual purchase of the equipment and spares (ca. \$500,000) will be on a grant submitted by Cutter to the NSF Ocean Sciences' Oceanographic Instrumentation Program (15 October 2006 deadline). That proposal will also detail the management, storage, and maintenance of the systems by ODU.

The rosette (Seabird) will be aluminum that is epoxy powder-coated and holds (24) 12 L Teflon-coated GO-Flo bottles. Seabird is modifying their pylon such that 3 bottles can be simultaneously tripped to collect sufficient water volume. Our sample volume estimate for GEOTRACES transect stations (not the Intercalibration Cruises) is ca. 30 L per depth (5 L for trace elements, 10 L for stable isotopes, 10 L for radioisotopes, 5 L for archive), but 30 L GO-Flo bottles are difficult to handle, particularly in rough weather, and the modified pylon will allow us to get 30 L by simultaneous triggering much lighter, easier to handle bottles; the homogeneity of the sample will be tested (see below). The rosette will have a Seabird CTD (9+) equipped with duplicate temperature, conductivity and pressure sensors, a SBE 43 oxygen probe, and fluorometer and transmissometer with high pressure cases (so they do not have to be removed for deep vs. shallow casts). We will replace all Zn anodes with Mg to minimize Zn contamination (see sampling operations below). The winch will be a Markey or Interocean model holding 8000 m of 0.34" Kevlar cable with 4 conductor wire, and have slip rings and composite rollers on the level-wind. The Kevlar will run over a General Oceanics composite meter wheel with electronic readout in the winch control room. For shipping, the winch and CTD/rosette will be mounted in a standard open-frame container (20x8x8') that also has a 5'(x8x8') dog house on one end that will function as the winch control room. On board ship the winch will be secured to the ship (location depending on the ship; either on deck or still in the container frame) so that the clean rosette casts can be done mid-ships on an existing J-frame.

The 12 L GO-Flos (General Oceanics) will be Teflon-coated, the air bleed valve replaced with a Swagelok fitting to allow pressurization to 6 psi with filtered air and the bottom replaced with a Teflon plug valve. In addition, a Teflon tube (3/8") is run from the plug valve to the silicone skirt of the GO-Flo to allow complete removal of water from the bottom and avoid under sampling settled particles; all of these modifications are identical to those of Bruland et al. (1979) that have proven to be non-contaminating for the GEOTRACES key trace elements. We will have a total of 52 bottles so that 24 can be used on the rosette while 24 are being processed in the sampling van; 4 are spares. The sampling van will be a standard (20x8x8') container to facilitate inexpensive shipping, with the interior made of non-contaminating materials (plastic wall coverings and cabinets, any exposed metal epoxy-coated, etc.) and a heavy duty heating/cooling system. We are still developing the exact design of the van (e.g., so that the GO-Flos can be easily transferred from the deck to the clean area), but it will have racks to hold 24 bottles for active sampling (and 24 for storage/shipping), a Class-100 HEPA clean air bench for filter processing and sample acidification, a table/racks to hold sample containers, and a sink with DI (Milli-Q) water system. The entire working area will be HEPA filtered, and it will have 2 water-tight doors (with one having a small anteroom to allow personnel entry/exit while maintaining positive pressure); this will also meet UNOLS standards for safety. Not only will the sampling van be used for on-board operations, but it will act as the shipping container for all cruise supplies and sample bottles.

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 a crane or 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. While on station, in addition to rosette sampling, large volume samples in the upper 150 m can be obtained with this system. The advantages of

pump sampling are extreme cleanliness (continuous flushing, Teflon-only contact) and the availability of large volumes of water in a relatively short time. Water will be pumped directly into the clean sampling van, where it will be available “on tap” in unfiltered or 0.2 µm cartridge (Sartobran P or similar) filtered form.

To carry out sampling for the full set of key particulate GEOTRACES analytes, we must use in situ pumping as well as filtration from GO-Flos. In situ pumps are necessary for some key TEI’s (e.g. ^{230}Th , ^{231}Pa) which require large samples of water and particles from deeper than 150 m. The community has not adopted a standard type of in situ pump, nor has the filter media used for these devices been standardized. Cross-comparison of results for the full range of TEIs demands that bottle sampling and in situ pumping sample particulate matter with comparable efficiency and size cutoff. To this end, it will be important to carry out parallel particulate filtration using both methods, and to identify a filter type that will work for both collection methods and the full range of TEIs. At this point, however, there is no consensus on the best type of pump to use – there are at least five types (McLane, Challenger, KISP, MULVFS, RAPPID) in use within the last few years. Our proposed strategy is to encourage all interested researchers (i.e., Table 1 and Scientist list on www.geotraces.org) to bring their existing units as “loaners” to the program for Cruise 1. Several researchers have already contacted us expressing their desires to bring their pumping systems. On the basis of side-by-side performance comparisons, while simultaneously evaluating filter types, we will make a decision for purchase of a full set of GEOTRACES in situ pumps shortly following Cruise 1 (separate equipment proposal). In either case, the GEOTRACES-dedicated in situ pumps will be in hand for Cruise 2 where we will fully evaluate and perfect the GEOTRACES particulate sampling routines.

Sampling Procedures. First it should be understood that the procedures described here are proposed and will be adjusted as needed based on intercalibration results (see evaluation below) during the cruises (i.e., **Objective 1**, the sampler intercalibration) and feedback from the other 80+ participating investigators (Table 1). The essential hydrography (salinity, temperature, oxygen, nutrients, POC, pigments) at a station will be established using a conventional rosette/CTD system and subsequent data post-processing; these results will be later compared with the clean GEOTRACES rosette (e.g., matching the salinity and nutrients in both to verify the sampling depth). The 24 GO-Flo bottles will be mounted on the GEOTRACES rosette just prior to deployment; they will never be stored on deck. The package will be lowered through the water at 50-60 m/min, and on the up-cast 3 bottles will be simultaneously triggered while the rosette is moving up slowly into clean water (ca. 2-10 m/min). Upon recovery, all bottles will be transferred into the sampling van, the next set of bottles installed (if needed) and a second cast undertaken while sub-sampling is occurring.

Time sensitive, unfiltered water samples are drawn first (e.g., Hg). In-line 47 mm filter holders are connected to the Teflon valves, 0.2 µm-filtered air lines attached to the bottles, and they are pressurized to 6 psi. The filter pore sizes and materials will be discussed below, but this system will allow filtered water (various size cut offs; see below) and particulate matter samples to be collected simultaneously with minimal handling. Sample storage bottles themselves will be various sizes and materials depending on the TEI (discussed below), but the design of the sampling van will facilitate easy staging and filling of these containers. Acidification (see below) will be done in the sampling van under a HEPA hood. Based on the PIs’ and CLIVAR trace metal team’s experience, we estimate a maximum of 3 hours to process 24 bottles once methods are perfected during the Intercalibration Cruises. Samples from the underway/profiling pump system whose outlet is in the sampling van will be processed in the same fashion as the bottle samples (unfiltered, filtered, sample containers, etc.).

System Evaluation – Sampler Intercalibration. We have selected a clean rosette system to use for the GEOTRACES program, but it has not been tested for the full suite of TEIs (GEOTRACES Science Plan) and therefore during the Intercalibration Cruises our first task will be to assess whether it takes a

representative and uncontaminated sample via a sampling intercalibration. In terms of sampler contamination, the standards of comparison are the Teflon-coated GO-Flo bottle manually deployed on a Kevlar cable and triggered with plastic messengers (Bruland et al., 1979) the MITESS samplers (Bell et al., 2002), and the trace metal-clean pumping system for the upper 150 m (e.g., Bruland et al., 2005); at a minimum these 3 systems will be used, but additional devices brought by other participants (we are actively encouraging this) will be included. Moreover, we will use ship-board analyses of dissolved Fe (using a highly sensitive flow injection method; Lohan et al., 2006) and Zn (using a highly sensitive, adsorptive cathodic stripping voltammetric (ACSV) method; van den Berg, 1985; Donat and Bruland, 1990; Ellwood and van den Berg, 2000; Lohan et al., 2002) as the major evaluation mechanism of whether the GEOTRACES sampling system is collecting uncontaminated samples. Based upon decades of experience, dissolved Fe and Zn are the two most contamination prone trace metals. Nevertheless, other investigators will be determining many other TEIs and will provide data on their elements from the various sampling systems (albeit not necessarily in real time unless they are doing on-board determinations). As a first step after cleaning and flushing the sampling bottles on the trace metal rosette system, they will all be tripped at a common depth and each of the 24 individual bottles will be sampled and analyzed for dissolved Fe and Zn; this will be repeated for the remaining 24 GO-Flo bottles. This will identify contamination within individual bottles and therefore additional cleaning will be undertaken. Subsequently, the bottles will be triggered at the same depths as manually deployed GO-Flos (supplied by Bruland and Cutter), MITESS samplers (supplied by Boyle and Wu), and other sampling systems brought on the cruises. Fe and Zn data (and others) from this exercise will show whether the systems are taking the same clean samples. Furthermore, analyses of salinity and nutrients on the conventional vs. GEOTRACES rosette will indicate whether a representative sample is being taken (i.e., since the GEOTRACES rosette is triggered while moving, are the hydrographic data for the depth at which it was triggered the same as those in the stationary rosette?). All of the hydrographic, Fe, and Zn data between triplicate GO-Flo bottles (i.e., 3 fired simultaneously) will also demonstrate the homogeneity of the sample. This near-real time intercalibration (iterative sample-analysis) will allow for modification of procedures and/or samplers to solve problems that are noted (e.g., rate of ascent during sampling, contamination from anodes, etc.). The system will then be ready for the more extensive intercalibration exercises to follow. It is important to note that our intercalibration of samplers has inherent value far beyond only the GEOTRACES Program since it serves the interests of the worldwide community of trace element biogeochemists.

Intercalibration of dissolved and particulate TEIs

Locations and timing. There are two competing considerations for this activity, one is to do intercalibrations at sites representing the types of regimes that future GEOTRACES will study (e.g., meso- to oligotrophic, high/low suspended particle concentrations). The other consideration is to do them where GEOTRACES Baseline Stations can be located, largely oligotrophic deep water regimes with minimum temporal variability (i.e., so they can be reoccupied and the mid and deep waters are the same). We are proposing to favor the Baseline approach while accommodating the varying regime consideration. SAFe used a similar approach in the eastern North Pacific, arguing that Fe in surface waters would have extremely low concentrations in the offshore site, and be enriched in deep waters. Placing an Intercalibration and Baseline Station in the North Atlantic has a parallel justification, higher surface concentrations for many TEIs and lower (or higher) deep water ones compared to the Pacific. A site such as BATS in the Sargasso Sea is also logistically convenient, has a long temporal record for many GEOTRACES TEIs (e.g. Pb isotopes; Weiss et al., 2003), and is close (3 day steam) to Norfolk, Virginia (second largest shipping port in the eastern US) where Cutter is located and the sampling systems will be built. Therefore, we propose the first Intercalibration Cruise be 30 days in May-June 2008 from Norfolk to BATS at a time when the Sargasso Sea is well-stratified, but before hurricane season and Saharan dust deposition begin (e.g., Sedwick et al., 2005). The focus of this cruise will be to fully test and modify as needed the entire sampling system and procedures (**Objective 1**) at BATS, then perform the first TEI intercalibration using the tested system and SAFe large volume tanks (**Objective 2**; see below). As a

result, this will establish BATS as a GEOTRACES Baseline Station (**Objective 3**). After working at BATS, we will steam west into the mesotrophic waters of the Gulf Stream/shelf break for a more limited intercalibration (and system testing), particularly focusing on particulate matter and particle-reactive TEIs.

The second Intercalibration Cruise will be one year later (June 2009) in the North Pacific and will reoccupy the SAFe station (30° N, 140° W) where a growing data set is emerging (see Background above). Like BATS, the SAFe station is logistically convenient to the mainland. This timing will allow all the data from cruise one to be analyzed and compared at planned workshops (below), and modifications to procedures or apparatus made. Thus, the focus of Intercalibration Cruise 2 primarily will be on the intercalibration itself and perfecting the operation of a GEOTRACES station (i.e. sampling sequence and handling to minimize station time; part of **Objective 4**). We will leave from San Diego and after the intercalibration at the SAFe site (and thereby establishing another GEOTRACES Baseline Station), on our return we will occupy another site in the mesotrophic California Current to again focus on particulate matter. This second Intercalibration Cruise will require 21 days.

Participants. The PIs are proposing to build and test the sampling infrastructure for US (and some of international) GEOTRACES, but like SAFe, they require collaborators to do most of the actual TEI determinations. We announced our plans in July 2006 and Table 1 is a summary of the responses as of 14 August 2006. Community interest has been overwhelming; all of the key GEOTRACES parameters are covered along with all other TEIs listed in the Science Plan. A full listing of parameters and investigators is being continuously updated and can be found on the Intercalibration page of the GEOTRACES web site (www.geotraces.org). It should be noted that this grant is not funding their participation, only the infrastructure and ship time.

Table 1. Participant Summary for GEOTRACES Intercalibration Cruises (as of 14 August 2006). A complete and updated list with names and institutions can be found at www.geotraces.org.

TEI (Diss and Part)	# of participants	Countries
Al*	5	USA, Bermuda, Canada, Japan, UK
Cd*	13	USA, Australia, Canada, Japan, UK
Cu*	16	USA, Australia, Canada, Japan, UK
Fe*	20	USA, Bermuda, Canada, Japan, UK
Mn*	12	USA, Australia, Canada, Japan
Zn*	13	USA, Australia, Canada, Japan
¹³ C*	4	USA, China, Japan
¹⁵ N*	5	USA, Japan
²³⁰ Th*	11	USA, Canada, Germany, Japan, UK
²³¹ Pa*	10	USA, Canada, France, Germany, Japan, UK
Pb isotopes*	5	USA, UK, France, Germany
Nd isotopes*	9	USA, France, Japan, Sweden
Other TEI (not “key”)	52	USA, Belgium, Canada, Germany, Japan, Switzerland

* - Listed in the GEOTRACES Science Plan as a “key parameter”

Many of those referred to in Table 1 are asking to go on the cruises. At this point we feel that the priority for direct participation on the cruises (not in ranked order) should be those: (1) doing on-board TEI determinations (including speciation) to provide data for checking contamination (as above) and t=0 concentrations for storage tests; (2) having alternative sampling systems (e.g., MITESS) for the sampler intercalibration; (3) determining short-lived radionuclides or TEIs requiring significant onboard processing; and (4) who have pooled their resources and personnel such that only one of them has to go

(e.g., one person will do everyone's Th preconcentrations). In terms of oversight in the selection of cruise participants, the GEOTRACES Scientific Steering Committee will have to be involved in setting priorities and arbitrating the final selection (see PI Responsibilities, Management Plan, and Intercalibration Workshops below).

SAFe Tank System. We will collect depth profile samples at all intercalibration stations for distribution, therefore creating a data set for the Baseline Stations (**Objective 3**). However, to perform a rigorous intercalibration (and sample storage tests; see below), large homogenous samples are required. We will use a large volume deep sample and a large volume surface sample for this purpose. The deep sample will be collected with either the 30 L GO-Flo samplers (if necessary) or the GEOTRACES rosette system (using the proven "clean" bottles) and filtered through 0.2 μm PCTE membrane filter cartridges (Osmonics) in polypropylene housings to fill the two 500 L SAFe tanks. The surface sample will be collected with the sampling fish (see above) at ~10 meters depth. This homogenized tank water will be available to fill a wide variety of sample bottles of various sizes within the clean van brought along for this purpose (Bruland). Samples for the intercalibration of dissolved Al, Cd, Cu, Fe, Mn, and Zn (and other related trace metals not on the "key parameter" list) will be collected in 0.5 L low-density polyethylene bottles and acidified immediately after filling to pH 1.7 with 2 mL of 6 N quartz-distilled hydrochloric acid (Q-HCl). This is similar to the way the SAFe samples were processed. The majority of responses received from scientists interested in measuring these trace metals (Table 1 and on www.geotraces.org) have indicated that a 0.5 L sample size would be ideal and would allow them to carry out multi-element determinations and/or reanalyze the sample a number of times if required. We will provide, clean and preserved samples for the US and the international community involved in the Intercalibration Program. We propose to provide approximately 200 of these samples at each of the two depths. This will use roughly 150 liters of the large volumes, leaving the remainder for the intercalibrations requiring larger sample sizes (e.g., Nd isotopes, ^{230}Th). For other TEIs such as Hg that require 2 L Teflon bottles, or large containers (e.g. 10 L for Nd isotopes), participants will provide all of the containers prepared in the manner they require and we will coordinate filling, preserving, and distributing these for the intercalibrations.

Sample Storage Tests. Sample storage problems have been worked on and solved for some TEIs, but still remain a problem for others. For example, researchers investigating the chemical speciation of metals and the extent of organic complexation will likely need to carry out preservation and storage studies during these initial Intercalibration Cruises. For example, it may be necessary for speciation studies of dissolved iron to be carried out on fresh ($t=0$) samples and then various storage methods tested over time using different types of sample bottles and preservation (e.g., Teflon vs. other type containers, freezing versus microwaving, and storing refrigerated to preserve the speciation for future analyses in shore-based laboratories). Such detailed studies need to be carried out if samples for speciation measurements are to be collected as part of the GEOTRACES program and analyzed in home laboratories. We will be coordinating such studies in the Intercalibration Cruises in a manner similar to that done during SAFe (e.g., Fig. 2).

Particulate Matter. Overall, the objective of this component of the project will be to determine filter types and procedures that allow rapid, efficient, and contamination-free determination of the key TEIs and particulate ancillary parameters (POC, pigments) while leaving room for expansion and modification as other GEOTRACES particulate goals are addressed. Ideally, in situ pumping will use the same filter type as used with GO-Flo bottles, so that dissolved/particulate partitioning for the fullest range of TEIs can be compared on an equal basis. Particulate matter samples will be collected using 47 mm diameter filter holders for GO-Flo and underway system sampling, and 142-293 mm filtration using in situ pumps. These methods of particle collection will be intercalibrated to verify that equivalent representative samples of the suspended particle pool are sampled. In addition, filter material is a crucial issue, as filter composition and use determines the effective size cut-off of the separation process. We will evaluate a

number of filter materials at sea, following an initial screening of key metal blanks and filtration behavior in the lab (PI Sherrell). Among the selection criteria for filter media are the following: flow rate, clogging tendency with natural particles, metal blanks under various digestion methods, nominal and effective pore size, practical ease of use, and compatibility with filtrate analyses (e.g., contamination). While it is recognized that polycarbonate track-etch filters (Nuclepore, Poretics), have been the standard for trace metal work, this type of “sieve” filter has the disadvantages of low porosity and flow rate, tendency for early and sudden clogging by natural particles, and relatively poor loading characteristics, all leading to limited filtration volumes.

The GEOTRACES Science Plan does not include colloidal TEI as a “key parameter” (however, it is listed as important to GEOTRACES goals), but we feel that some exploratory work is appropriate given how little is still known about the distribution of trace elements in this size fraction. We have received interest in quantifying colloidal TEIs from at least three other groups (Table 1 and www.geotraces.org). Recent studies of open ocean colloid Fe have focused on use of simple syringe filtration at 0.02 μm (Anotop Al oxide filters, Wu et al., 2001; Chen et al., 2004; Boyle et al., 2005), while others have used tangential flow filtration (1-10 kDa) for multi-trace element determinations, although largely in coastal waters (Guo et al., 2000; Wells et al., 2000). Recently, Croot and colleagues (P. Croot, IFM-GEOMAR, pers. comm., 2006) have used small sealed tangential flow cartridges (Vivaflow, Sartorius) for rapid processing of 250-2000 mL sized samples (~5 min/100 mL at 10 kDa) with consistent clean results for Fe, and repeated use of one unit for 80 samples in the Southern Ocean. PI Sherrell has initiated applications using these devices at low metal concentrations in oligotrophic Lake Superior, with very promising results (Sherrell, unpubl. data). We will process a subset of samples using Vivaflow cartridges, verifying performance with on-board Zn and Fe determinations, and will invite other participants to augment these efforts in order to begin intercalibrating this critical size fraction in the open ocean.

Ancillary Data. Data for salinity, oxygen, DOC, POC, and nutrients (ammonium, nitrate, nitrite, phosphate, and silicate) are crucial for the success of GEOTRACES objectives (GEOTRACES Science Plan). All of these with one exception are somewhat “standard” and following WOCE or JGOFS protocols will ensure quality data, but we will intercalibrate where possible (particularly in linking the hydrographic and clean rosette bottle data with those of the sensors); 3 groups in the Scientists Table 1 (on www.geotraces.org) want to intercalibrate hydrography and nutrients. However, the Science Plan calls for nutrient data at nanomolar concentrations typically found in oligotrophic surface waters. No data-intensive program has yet accomplished this, and therefore part of the proposed work (by Cutter) will be to test appropriate methods and intercalibrate where possible. The considerations here are that only the upper 200m of the water column will have extremely low nutrient concentrations (i.e., only 10% of the samples are affected, suggesting that extremely costly or elaborate procedures should be avoided), and during GEOTRACES transects a considerable number of samples will have to be analyzed on board (to avoid sample storage issues and to provide a data stream for decision making and assessing the operation of the sampling systems). For these reasons, we will use the standard automated nutrient methods (e.g., Parsons et al., 1984) as used on an Alpkem Rapid Flow Analyzer, but augment the detection limits using long pathlength waveguide cells as fully described by Zhang (2000), Zhang and Chi (2002), and Li et al. (2005). The primary advantage of this approach is that the system can be easily converted from nanomolar to micromolar levels with a change in cell pathlength. Nevertheless, in the year before the first cruise, we will be searching for other possible methods that meet the criteria above; Cutter’s lab has considerable expertise in methods’ development and routine nutrient analyses. For phosphate, we will use the MAGIC method of Karl and Tien (1992) for comparison. At BATS, various investigators have been studying the nitrogen system at nanomolar levels, and we will endeavor to intercalibrate with these measurements on the first cruise (and with other Table 1 participants). After a full evaluation, we will have a working system and users guide for all future US GEOTRACES cruises.

GEOTRACES Baseline Stations

For some of the TEI suite, particularly the radioisotopes and the measurements of chemical speciation, reference materials won't be available. This latter point necessitates not only participation in the US GEOTRACES intercalibration effort, but also the creation of "Baseline Stations." The stations where we perform the complete intercalibrations with large volume samples and vertical profiles will become GEOTRACES Baseline Stations (**Objective 3**). The motivation is that these will provide locations where individuals who are developing new sampling methods or analytical techniques for GEOTRACES can go for testing (particularly in deep waters where temporal variability should be minimized). Also, future GEOTRACES cruises will occupy Baseline Stations on their transects to intercalibrate the sampling, sample storage, and analyses used for that cruise (GEOTRACES Science Plan and Standards and Intercalibration Plan; www.geotraces.org).

Documenting Results and Procedures

Given the scope of GEOTRACES and multitude of laboratories that will be conducting transects and processes studies, it will be absolutely necessary that all aspects of sampling, from the operation of the equipment to sample processing/handling procedures, and the determinations of ancillary parameters, be completely described in GEOTRACES Users' Manuals. Therefore, creating these documents will be our **Objective 4** in the proposed research and will be an ongoing process in which documents are updated as new lessons are learned. These will be placed on the GEOTRACES web site and many of the intercalibration results will of course be documented in the peer-reviewed literature as well.

PI Responsibilities, Management Plan, and Intercalibration Workshops

Cutter will act as the lead PI, coordinating the overall program. He will be responsible for the construction, testing, and intercalibration of the complete sampling system in collaboration with the Co-PIs and with all Intercalibration participants (Table 1). In addition, he will oversee the development of the nutrient system and intercalibration of low-level nutrients, coordinate creation of the Baseline Stations and take the lead in writing the user manuals. He will work with the Co-PIs, the US GEOTRACES SSC, and the GEOTRACES Project Office to organize the Intercalibration Workshops (see below). Bruland will collect, process, and distribute reference seawater samples using the SAFe tank system. He will test the reference water for contamination (especially Fe and Zn) at various points throughout the process. He will also participate in tests to compare the performance of the different water sampling systems. Sherrell will have overall responsibility for particle collection, filter media evaluation, coordination of participants using various filtration methods and particulate TEI intercalibrations. Sherrell will also oversee colloidal fraction sampling and measurements of particulate transition metals at the GEOTRACES Baseline Stations. He will design and purchase/build the underway sampling system, and supervise the evaluation of in situ pumping technologies.

The PIs will oversee the process of synthesizing the intercalibration results, although it is anticipated that other investigators and teams of participants will take the lead in evaluating the results for certain TEIs (other investigators have already expressed an interest in doing so, but no commitments have been made at this time). Cutter will lead the synthesis of results for the metalloids and oxyanions. Following his experience with the IOC Baseline cruises, he will also interact with the ^{13}C , ^{15}N , and Nd and Pb isotope teams in synthesizing their results. Bruland will be responsible for the onboard Fe and Zn determinations, and for the synthesis of results from these contamination-prone TEIs. Following from his past studies of radioactive tracers, he will also work with the teams of participants in evaluating radionuclide intercalibration data sets. Sherrell will lead the synthesis of particulate and colloidal TEI results.

The PIs will work closely with the GEOTRACES SSC to organize and implement this intercalibration program. Keeping in mind that the overall goal is to facilitate participation by as many investigators as possible, some choices must be made along the way, particularly regarding the allocation of berths on the cruises. The SSC is charged (by NSF) with setting priorities that are consistent with the GEOTRACES Science Plan. A first cut at allocating berths and samples will be based on priorities set by the SSC. Peer review will play a role as well. Investigators in need of funding to participate in the intercalibration will be obliged to secure funds through NSF (or other agencies), and those proposals must be ranked highly to be successful.

Although the initial response to the solicitation of interest has been tremendous (over 80 responses), it is anticipated that the number of interested investigators will continue to grow as information about the intercalibration effort spreads. GEOTRACES will publicize the intercalibration opportunity through its newsletters, its web site, its national committees and public meetings. The first public forum will be a town meeting to be held at the Fall 2006 AGU, where the intercalibration program will be one of the main items on the agenda.

Workshops will be essential to the success of the intercalibration program, beginning with steps to organize the sampling at sea and continuing through the final synthesis of the results. The PIs will work closely with the SSC, and will use the resources of the Project Office, to organize these workshops. To the extent possible, they will be held in conjunction with national/international meetings (to save travel costs). The first will be held ca. 5-6 months prior to Cruise 1, likely at the 2007 AGU Fall Meeting, to work out details of cruise activities. By that time the funding decisions will have been made following the 15 February and 15 August 2007 proposal deadlines, so we should have a good idea of who is funded to participate. The second workshop will be held ca. 1 year later to discuss and synthesize Cruise 1 results, and plan/adjust the protocols for Cruise 2. The final workshop will occur 6-9 months after Cruise 2, and will involve not only intercalibration results, but also working on the user manuals and publications.

An Intercalibration list-serve will be established for email discussions, and the GEOTRACES web site has an Intercalibration page where all the cruise results, and eventually the user manuals, will be placed. The workshops, web sites and list-serves are all part of community participation that is an essential part of our **Objective 2**. If one wonders whether this is possible, it is actually something that the TEI community does without any prodding. Indeed, many groups of participants (e.g., ^{230}Th , Si/N isotopes) have already organized themselves to share samples, assign someone to participate on the cruise, etc. This collaborative spirit bodes well for the successful coordination and linkage of all aspects of the program discussed here.

SIGNIFICANCE OF RESEARCH AND BROADER IMPACTS

In as much as GEOTRACES is an internationally-approved science program, and the work proposed here is a crucial first step, the scientific importance of our work is intimately linked with that of GEOTRACES as a whole. Actually, the development of this GEOTRACES infrastructure may have its most significance in its broader impacts to oceanographic science in general. The NSF **Criterion 2** aspects are readily addressed in this proposal. First, the three PIs are in departments having both undergraduate and graduate degrees (<http://www.odu.edu/sci/oceanography/>, <http://www.marine.rutgers.edu/>, <http://oceansci.ucsc.edu/>), and their research findings and excitement are incorporated into the courses they teach. Students from the PIs' universities, but also from the expected participant institutions, can participate directly in this research. Significantly, there are opportunities for minority students to be a part of this research. Cutter is a PI on the NSF-funded Hall-Bonner Program for Minority Scholars in Ocean Sciences (<http://www.hamptonu.edu/science/marine/hallbonner.htm>), and he will try to recruit one of these students (at no charge to this grant as the H-B program provides funding).

In addition to educational impacts, the proposed work will have outreach aspects on scientific and public levels. An additional benefit of creating GEOTRACES Users' Manuals is one of outreach to scientists in developing countries who cannot devote the time and expenses to perfect their own methods. While it is clear that some GEOTRACES sampling gear such as non-contaminating rosettes may not be available, criteria for assessing their own equipments' efficacy will be documented, easily adoptable handling procedures will be described in detail, and the availability of reference materials (e.g., intercalibration water) will allow their own procedures to be validated. Outreach in the form of communicating what environmental scientists do and its relevance to the lay public is also a vital facet of research. In this respect, the PIs have a variety of outreach tools that they will employ during this research. For the last 14 years, Cutter has effectively used ship visitations/open houses just before leaving port as exciting venues for the public to see their tax dollars at work; the proposed Cruise 1 out of Norfolk will definitely include an open house. He also participates in the yearly University Open House, the Virginia Blue Crab Bowl as a moderator (a part of CORE's National Ocean Sciences Bowl, a team competition for high school students in the ocean sciences), and presents lectures to civic groups/clubs. Bruland has a display in the Seymour Discovery Center at the Long Marine Lab at UC Santa Cruz that provides an excellent outreach to K-12 students and the general public, and he will update this display to include highlights of the GEOTRACES Program. He also presents lectures to civic groups/clubs. Sherrell will work closely over the course of this project with the Mid-Atlantic Center for Ocean Sciences Education Excellence (MACOSEE; <http://www.macosee.net/>), which is based at Rutgers-IMCS and directed by IMCS staff specialist Janice McDonnell. Sherrell will specifically accept a role as a "Resource Scientist" and will develop curriculum units for K-12 educators involved in annual summer workshops – a much more effective way of reaching large numbers of children, compared to an annual talk at your kids' school. He will create content on the importance of some of the least abundant chemicals in the ocean, consistent with GEOTRACES goals, and describe and demonstrate some of the approaches to the difficult sampling and analytical techniques used to make accurate measurements, consistent with the goals of this proposal in particular.

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UNOLS Ship Time Request Form - Section ONE

UNOLS Request ID #: 20060808143940GI

Version #: 002

Last Modified: 2006/08/12 15:03 EDT

Date Issued: 2006/08/12 15:03 EDT

P.I. Name Last: Cutter First: Gregory MI: A

Institution: Old Dominion University Research vessel required for:

Address: Dept of Ocean, Earth and Ancillary Only

Atmospheric Sciences Principal Use

Norfolk, VA 23529-0276 No Ship Required

Long Range Planning Document

Phone: 757-683-4929 Fax: 757-683-5303 Email: gcutter@odu.edu

Co P.I. Name Institution Co P.I. Name Institution

Kenneth Bruland UC Santa Cruz Robert Sherrell Rutgers University

Proposal Title:

Collaborative Research: US GEOTRACES sampling systems and intercalibration

Large Program Name: Other Research Purpose: Chemical Oceanography

If Other, specify: GEOTRACES If Other, specify:

New Proposal? Y Agency Submitted to: Foreign EEZ? Y

Funded Grant? N NSF/OCE/CO Bermuda

Institutional Proposal #: Amount Requested: Area(s) of Operation:

1,350,000 NA6,NP9

Agency Proposal #:

Renewal? N Start Date: 1 April Lat/Long: Begin:

2007

Grant #: End Date: 31 March End:

2010

Year	Ship(s) Requested (Name or Size)	# Science Days Req.	Optimum Dates	Alternate Dates
2008	Knorr	30	05/01/2008	06/01/2008
2009	Melville	21	05/01/2009	06/01/2009

Total Science & Ship Days Needed: ----- PORTS -----

59	Start:	Intermediate:	End:
Number in Science Party:	2008, Norfolk;	2008, St Georges	2008, Norfolk;
32	2009, San Diego		2009, San Diego

Equipment Required:

X Vans _ P-Code GPS _ MCS _ Alvin _ DSL 120
_ Dynamic Positioning _ Multibeam _ SCS _ ROV _ 680 Cond.
_ Helicopter Operation

Other Special Equipment; Comments:

This will be a trace element intercalibration cruise requiring ultra clean conditions. The science party will bring 4 vans (20x8x8), including a container-housed Markey winch with 8000 m of Kevlar with conductor, 24 12L bottle clean rosette, and composite meter wheel. This clean rosette will be deployed off one of the ship's J frames (mid-ship); we will also use the ship's standard ctd/rosette system, as well as one ship's winch to spool 6000 m of 1/4" kevlar (and routed to a J frame) for manually deployed 30 L bottle sampling. There will also be underway pumping system (deployed off the quarter using the ship's crane).
