

Collaborative Research: Management and Implementation of US GEOTRACES Eastern Pacific Zonal Transect

J.W.Moffett (USC), C.R.German (WHOI) & G.A.Cutter (ODU)

RESULTS OF PRIOR SUPPORT

J.W. Moffett: OCE-0136835, *Zinc Biogeochemistry and its Relationship to Cobalt, Phosphate and Phytoplankton Community Structure*, \$344K, 2/02-1/05. **OCE-032727**, *The Speciation of Bioactive Metals in Oxygen Minimum Zones*, \$456K, 9/03-8/06. Fe, Zn and Cu were studied in the three major oxygen minimum zones (Arabian Sea, eastern tropical Pacific and Peru upwelling) and in the Sargasso Sea, the central N. Pacific and Bering Sea, expanding our knowledge of metal speciation in these regions and provided evidence for linkage between their cycling and the phosphorus and N cycles. Broader Impacts include graduation of two Ph.D students, a postdoc who now holds a faculty position, and strong ties with scientists in Chile, Peru and India. Nine publications have resulted from this work (marked with ¶ in the References)

C.R.German & O.Rouxel (with K.J.Edwards, USC): **OCE-0647948**, *Collaborative Research: Hydrothermal fluxes & their impact on the Oceans, EPR 9°N*, \$299k, 04/07-03/10. This project combined geochemical and microbial analyses of sediment trap samples to investigate the impact of hydrothermal Fe on ocean biogeochemistry. The project provided training opportunities for two early career female researchers (including Toner, lead author on the first high-impact paper arising from the project: Toner et al., 2009) and a current PhD student who is using archived splits of samples collected by the project for his studies. **T.M.Shank & C.R.German: ANT-0739675**, *Biogeography and Evolution of Chemosynthetic Ecosystems in the Southern Ocean*, \$395k, 08/08-07/11). This project has been to use the UK ROV Isis to dive to and investigate new hydrothermal fields that had previously been demonstrated to exist in the East Scotia Sea (German et al., 2000) and Bransfield Strait (Klinkhammer et al., 2001). Successful dives in Jan-Feb 2010 on the East Scotia Ridge have revealed the presence of a completely new biogeographic province (Rogers et al., submitted). Broader impacts arising from include a web-based outreach effort, daily, from the 2010 cruise (<http://www.classroomatsea.net/JC042/diary/>) and training opportunities for 2 PhD students associated with the grant.

G.A. Cutter: OCE-0648408, *Collaborative research: GEOTRACES sampling systems and intercalibration*. \$435k, 4/07- 3/11. This grant was for the first phase of the International GEOTRACES Program, Intercalibration. We developed the US GEOTRACES Sampling System and conducted a thorough intercalibration for all the dissolved and particulate key GEOTRACES TEIs (and as many others as possible) on 2 cruises in 2008 and 2009. Three Intercalibration Workshops were conducted, a special session on intercalibration was held at the 2010 Ocean Sciences Meeting, and a special volume in *L&O Methods*, Intercalibration in Chemical Oceanography, is being assembled (paper deadline is July 2011). The lessons learned in this program are compiled into the cruise manual: *Sampling and Sample-handling Protocols for GEOTRACES Cruises* (Cutter et al.; <http://www.obs-vlfr.fr/GEOTRACES/libraries/documents/Intercalibration/Cookbook.pdf>). Aspects of these programs are incorporated into graduate and undergraduate courses taught by Cutter and cruises within these grants enabled 8 postdocs, 15 graduate students, and 3 undergraduate to participate and learn essential trace element sampling and analytical skills.

INTRODUCTION

The International GEOTRACES Program (www.geotraces.org) has an ambitious mission, “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.” (GEOTRACES Science Plan, 2006; or GSP06). This mission is well justified since trace elements can play dual roles as essential micronutrients (e.g., Fe, Zn, Co; Saito et al., 2002; Coale et al., 2003) and as toxicants (e.g., As, Cu; Sunda and Guillard, 1976; Sanders and Vermersch, 1982), and therefore affect biological productivity and carbon cycling, with resulting effects on global climate. Isotopes of these same elements and others can trace many geochemical and biogeochemical processes in the ocean, and allow us to measure the rates of those processes. Within this context, the initial strategy for GEOTRACES is to conduct global scale surveys of trace elements and isotopes (TEIs), with the primary 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.” (GSP06)

In terms of coordinating internationally-led global surveys, basin workshops for the Atlantic (2007; http://www.obs-vlfr.fr/GEOTRACES/libraries/documents/Atlantic_Report.pdf), Indian (2007; http://www.obs-vlfr.fr/GEOTRACES/libraries/documents/Indian_Report.pdf), Arctic (2009; http://www.obs-vlfr.fr/GEOTRACES/libraries/documents/Arctic_Report.pdf), and Pacific Oceans (2007; http://www.obs-vlfr.fr/GEOTRACES/libraries/documents/Pacific_Report.pdf) were held to identify key features and processes to be examined along semi-defined transit lines, and to evaluate which countries could take on selected transects. Following those initial meetings, US GEOTRACES held a Pacific Implementation workshop in October 2008, led by J. Moffett and C. German (http://www.usgeotraces.com/documents/US_GEOTRACES_Pacific_Report_Jun09_001.pdf.) The participants in that workshop recommended that the US GEOTRACES program should pursue two cruises: (i) a Meridional transect at ca. 150° W, and (ii) a Zonal transect that would cross the southern East Pacific Rise, intercepting the large hydrothermal plume that extends west from the ridge-axis near 15° S and the upwelling zone and associated low oxygen waters offshore from Peru. The US GEOTRACES Scientific Steering Committee subsequently endorsed this Implementation Plan, with the recommendation that the Zonal Transect be the first Pacific section to be conducted once the first US GEOTRACES section across the North Atlantic had been completed.

This proposal seeks the necessary core funding to implement the US GEOTRACES zonal transect in the eastern tropical South Pacific (ETSP) from Peru to Tahiti. It is designed to provide the essential support and management structure for acquiring the TEI samples and hydrographic data needed by other investigators, with the following objectives: **(1) plan and coordinate a 52 day research cruise; (2) obtain representative samples for a wide variety of TEIs using conventional CTD/rosette and GEOTRACES Sampling Systems (GO Flo bottles on contamination-free carousel, Kevlar conducting cable, etc); (3) acquire “conventional” hydrographic data (CTD, transmissometer, fluorometer, oxygen sensor, etc) along with discrete samples for salinity, dissolved oxygen (to 1 μM detection limits), plant pigments, redox tracers such as ammonium and nitrite, and dissolved nutrients at micro- and nanomolar levels; (4) ensure that proper QA/QC protocols are followed and reported, as well as fulfilling all GEOTRACES Intercalibration protocols; (5) prepare and deliver all hydrographic-type data to the GEOTRACES Data Assembly Center (via the pertinent US data centers); and (6) coordinate all cruise communications between other investigators, including preparation of a hydrographic report/publication.** Background information and justifications for this transect, and details on its implementation will be elaborated in the sections that follow.

RATIONALE

The US GEOTRACES Scientific Steering Committee used the following criteria in selecting the ETSP Zonal Section:

1. **High Impact Science that would arise from this section, both as a part of the complete program, and from that section alone.** Each GEOTRACES cruise must generate important results on its own, to maintain community support for continuing the program. The diverse array of important regimes in the section (e.g. hydrothermal plumes, oxygen minimum zone), coupled with the importance of the ETSP in climate change science (including paleoceanography) provides an important rationale. OMZs are predicted to expand significantly in many climate change scenarios (Stramma et al., 2008), so this is an important baseline survey. Moreover, the biogeochemistry of the whole region may be altered by changes in the frequency and intensity of ENSO events.
2. **Science product that underscores the value of multiple core parameters being measured on the same ship** (see GSP06). We argue here that the most important processes, like boundary scavenging and the behavior of paleoproxies require multiple TEIs to be measured on a single cruise. Most key objectives in the GEOTRACES Science Plan can not be achieved by individual investigators on single-project cruises. Further, this cruise will offer a unique opportunity to compare and contrast redox-cycling and particle-scavenging processes in a major hydrothermal plume with redox-cycling in the OMZ and boundary scavenging at the high-productivity Peru margin.

The more specific scientific rationale for the section from Peru to the East Pacific Rise centers on the highly productive upwelling region associated with the Peru Current. This is a region characterized by high rates of primary production and C export and one of the world's largest fisheries (Chavez et al., 2008). This feature gives rise to one of the most extensive oxygen minimum zones in the world's oceans, an important sink for fixed nitrogen and important source for N₂O, a radiatively important trace gas. Oxygen depletion results in important redox cycling for many of the GEOTRACES core TEIs. The proposed section is characterized by strong horizontal and vertical gradients in chemical and physical parameters, as well as particle fluxes. West of the East Pacific Rise, the primary scientific rationale for the section changes emphasis to follow the fate of TEIs within a major hydrothermal plume that extends west away from the ridge axis at ~2500m depth and can be traced in ³He enrichments and thermal anomalies out to ~2000km off-axis (Lupton & Craig, 1981; Reid, 1982). While detailed studies have been made on various redox and dissolved-particulate interaction processes in other hydrothermal plumes (as reviewed most recently by German & Von Damm, 2004) this program will undertake the most complete study to-date of dissolved and particulate TEIs in this, one of the world's largest deep-sea hydrothermal plumes (Lupton, 1995). We expect this to mark a significant step forward to test the long-standing hypothesis (e.g. Kadko, 1994) that deep sea hydrothermal systems may impact, significantly, on global ocean chemistry.

TIMELINE

| | |
|-----------------|---|
| Feb. 2011 | Submit Management proposal to NSF |
| Sept. 2011 | Community meeting for <i>any</i> scientist interested in participating in the cruise. |
| Nov. 2011 | Letters of intent to submit proposals posted on US GEOTRACES web site |
| Feb. 2012 | First coordinated submission of science proposals |
| Aug. 2012 | Submission of late-breaking/last-chance proposals for ETSP science/cruise participation |
| Spring 2013 | Cruise planning meeting for all funded PIs |
| Spring 2013 | Management team cruise planning meeting with ship operator |
| Sept. -Oct 2013 | Cruise staged |
| Fall 2014 | Post cruise workshop |

BACKGROUND INFORMATION FOR THE ZONAL SECTION

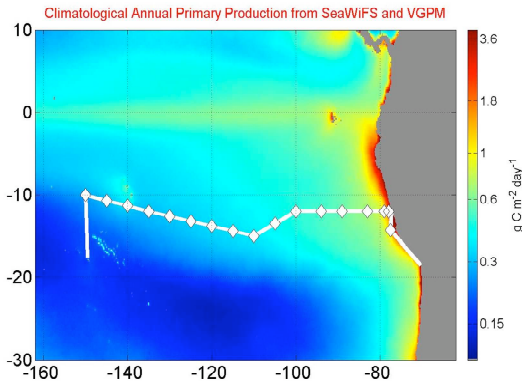


Figure 1. Cruise track & deep stations

the ocean basin from the Peru-Chile coast. The OMZ has been argued to result from the combined effects of high productivity (and export) arising from wind-driven coastal upwelling and reduced ventilation (e.g., Karstensen et al, 2008; Fuenzalida et al, 2009). This system is subject to strong ENSO related inter-annual and longer time-scale variations (e.g. Guilderson and Schrag, 1998; Fiedler and Talley, 2006). The hydrography and shallow circulation of the region has been recently reviewed (Fiedler and Talley, 2006; Kessler, 2006). The upwelling waters in the South Pacific OMZ derive from the Equatorial Undercurrent, which in turn is fed at its western roots by inflowing thermocline waters that have their origins in subducted surface water in the South Pacific (Brown et al, 2007). WOCE-era CFC measurements indicate that the time-scales associated with this pathway for waters with $25 < \sigma_0 < 26.2 \text{ kg m}^{-3}$ are 1-2 decades (Fiedler and Talley, 2006). The slow circulation within the OMZ is a major factor contributing to low oxygen concentrations (Czeschel et al., 2010).

The circulation in this system shows considerable variability, and a single section cannot address this variability as a time-series could. However, given the sluggish circulation within the OMZ, we anticipate that data obtained in this section will be representative of its characteristic chemical properties.

Figures 1 and 2 show the proposed sections superimposed over surface nitrate and dissolved oxygen at 250m, respectively, along with major station locations. Figure 3 shows the same station locations superimposed on the deep-water ^3He hydrothermal plume. Note that the westernmost station at 10° S , 150° W will be designated an Intercalibration station, to be reoccupied by other, future GEOTRACES Sections including the recommended US GEOTRACES Meridional Section along 150° W

Circulation and Hydrography

The shallow water column in the ETSP is dominated by the intense oxygen minimum zone (OMZ) extending into

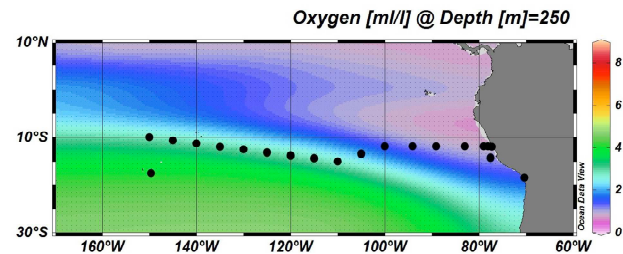


Figure 2. Section showing OMZ

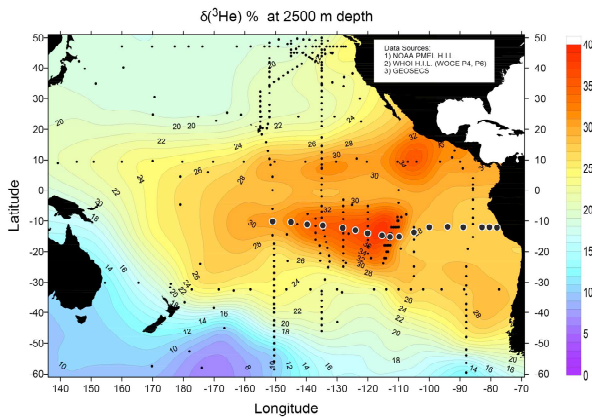


Figure 3 Cruise track showing ^3He plume at 2500m

Across the East Pacific Rise (EPR) near 15° S , a major and highly asymmetric plume is observed that extends less than 50km to the East but can be traced readily to $\sim 3000\text{ km}$ off axis (to at least 150° W), in both ^3He and (less markedly) thermal anomalies (Lupton & Craig, 1981; Reid, 1982; Lupton, 1995). Contrary to the Arons-Stommel model (Stommel & Arons, 1960) which predicted generally south- and eastward direction of flow across the SE Pacific Ocean, these data imply westward transport of water away from the ridge-crest at $0.2\text{-}0.5 \text{ cm/s}$ with the distinct possibility that this deep-ocean flow is actively *driven* by the buoyancy flux and resulting entrainment/vertical-pumping caused by ridge-crest hydrothermal activity

(Stommel, 1982; Hautala & Riser, 1993). This tongue of water injects between two other major water masses in the region that enter the South Pacific from the South and can be recognized from extrema in their salinities (Reid, 1982). One is the intermediate water which is evident from a minimum in salinity that extends north, to lower latitudes while the other, at greater depths, is the Lower Circumpolar Water (LCPW), a mixture of Antarctic Bottom Water formed in the Weddell Sea and North Atlantic Deep Water, which is present below 4000m. Bottom waters in the Peru Basin originate in the Chile Basin. Oxygen is higher and nutrients are lower in the abyssal waters than in the overlying deep waters.

The Nitrogen Cycle.

The N cycle provides an important rationale for this section. The cruise track crosses one of the three main regions for denitrification in the ocean, and a nitrate-depleted region offshore that has been proposed to be an important area for N fixation (Deutsch, 2007). The coupling of N-cycle processes with TEIs is largely understudied as well, yet important relationships may exist. For example, regions of active denitrification have elevated Fe concentrations associated with high nitrate depletion. Residual, elevated iron present in these waters when they reach the surface may fuel N fixation. Strong lateral and vertical gradients in many core parameters are anticipated, requiring an intense but realistic sampling plan. The Peruvian OMZ region is important for the global N budget, with nitrogen loss through sedimentary and water column denitrification (Codispoti et al., 2001). As a result of denitrification, some of the highest enrichments of $\delta^{15}\text{N}$ (and $\delta^{18}\text{O}$) in NO_3^- are observed there and the processes enabled by the extremely low oxygen content of these waters play a critical role in the distribution of $\delta^{15}\text{N}$ - NO_3^- (and $\delta^{18}\text{O}$ - NO_3^-) in the Pacific (Casciotti and McIlvin, 2007; Sigman et al., 2005;).

Oxygen Minimum Zone and Trace Element Redox Cycling.

Considerable attention has been paid to TEIs in oxic and anoxic waters, but much less so to these same elements under the more globally-prevalent suboxic conditions such as those found in the Eastern Tropical South Pacific (for consistency, suboxic is defined, here, as waters that have dissolved $\text{O}_2 < 2\mu\text{M}$ and nitrate reduction/denitrification: Morrison et al., 1999). Many elements utilized by microbes as terminal electron acceptors exist in these areas in reduced forms, even though nitrate and traces of oxygen are still present. Examples include Fe(II), Mn(II) and I(-I) (Farrenkopf et al., 1997; Lewis and Luther, 2000; Moffett et al. 2007). Fe(II) seems largely confined to regions with high nitrite (i.e. active denitrification), while Mn(II) and iodide persist beyond these regions, perhaps because of slower oxidation kinetics. Dissolved Mn and Fe increase in OMZs because the reduced forms are less particle reactive, but their sources and mechanisms of generation and removal are unresolved. Dissolved Mn profiles exhibit maxima in the northern-most sections of the eastern tropical Pacific's suboxic zone, and reactive/leachable particulate Mn distributions show minima in these same waters (Landing and Bruland, 1987; Rue et al., 1997; Nameroff et al., 2002). Dissolved iron distributions also exhibit maxima in suboxic waters, (Landing and Bruland, 1987; Nameroff et al., 2002; Blain et al., 2008). Local maxima in dissolved Fe profiles coincide with maxima in Fe(II) and nitrite, leading to an Fe enriched zone observed in all three of the world's major OMZs (ETNP: Hopkinson and Barbeau, 2007); Arabian Sea: Moffett et al., 2007; Peru: Croot et al., 2010).

Subsurface maxima could arise from *in situ* reductive dissolution of particulate Fe and Mn from overlying waters, but Knauer and Martin (1984) argued that an alternative explanation for Mn maxima that persist well beyond denitrifying zones could be that they result from horizontal advection off-shore, following release from reducing shelf sediments. Conversely, Johnson et al. (1996) have attributed subsurface dissolved Mn maxima to *in situ* remineralization coupled with oxidative scavenging. Our study will take advantage of the opportunity to analyze multiple TEIs in concert to provide new insights into this unresolved problem. For example, westward-flowing subsurface currents should presumably transfer some Fe and Mn offshore, whereas *in situ* reduction must be invoked to explain the persistence of Fe(II).

Other TEIs examined in suboxic waters of the eastern tropical Pacific include Cr (Murray et al., 1981; Rue et al., 1997), I (Rue et al., 1997), Se (Cutter and Bruland, 1984; Rue et al., 1997), and Mo, Re, U, and V (Nameroff et al., 2002). Of these, only iodine shows a very pronounced change in redox speciation, with the quantitative conversion of iodate (+V) to iodide (-I) exactly paralleling the drop in oxygen (Rue et al., 1997). Iodine is an excellent indicator of suboxia since both the oxidized and reduced species are measurable, and there is no loss or change in reactivity between the oxidized and reduced forms (as opposed to nitrate/nitrite, and CrVI/III). Both Se and Cr show reductions in dissolved selenate and chromate under suboxia, but the reduction products (Se0 and Cr III, respectively) are either insoluble (Se0) or too particle reactive (CrIII) to persist in solution (Murray et al., 1981; Cutter and Bruland, 1984; Cutter, 1992; Rue et al., 1997). Thus, the redox cycling of Se and Cr is somewhat obscured by the changes in reactivity of the reactants to products. The other TEIs examined to date (Ba, Cd, Cu, Mo, Re, U, V) show no change in speciation or abundance within suboxic waters (Nameroff et al., 2002), as one would expect based on equilibrium thermodynamic calculations.

Because the biogeochemical cycling of certain key GEOTRACES TEIs (Fe, Mn) and others (e.g., Cr, I, Se) are affected by suboxic conditions, their horizontal and vertical fluxes to other water masses may be similarly affected. This also has implications for their use as paleotracers. Revealing the mechanisms and rates of these suboxic influences are relevant to GEOTRACES objectives (see *Introduction*), particularly if in global change scenarios, both the extent and intensity of oxygen minimum zones are set to increase in the near future (Stramma et al., 2008). Furthermore, the use of tracers such as iodine speciation may help to better delineate the extent of suboxic conditions in conjunction with more typical tracers (oxygen, nitrate deficit/nitrite, nitrous oxide).

The upper water column.

The upper water column is characterized by huge spatial gradients in physical, chemical and biological parameters (Pennington et al., 2006). Cold, freshly upwelled waters sustain exceedingly high levels of primary production. Suboxic to anoxic conditions in the underlying waters lead to exceedingly high concentrations of iron and other metals that are solubilized under reducing conditions (Bruland et al., 2000). At the surface, westward transport of nutrients supports elevated productivity well offshore. But nitrate is highly depleted relative to phosphate, reflecting removal of nitrate by denitrification before the water is upwelled (World Ocean Atlas). It has been proposed (Deutsch, 2006) that such conditions lead to very high rates of nitrogen fixation but rates reported to date are very slow. This could be due to Fe limitation of N fixation, since surface Fe concentrations are less than 100pM. High surface phosphate and OMZ conditions persist out to 110°W, but the westerly direction of the cruise track skirts the highly oligotrophic SE subtropical gyre (Fig.1). This area was surveyed recently by the French BIOSOPE program (Blain et al., 2008). It is characterized by low nutrients, low Fe and the lowest light attenuation of any region. The extension of the cruise along the axis of the deepwater ³He/hydrothermal plume (Fig.3) enables us to probe the NW corner of this area, a vast region where few prior TEI analyses have been performed.

The Peru Margin as a source/sink of TEIs.

Evaluating the importance of sediment sources of TEIs in OMZ regions was identified as a high priority objective in the science plan (GSP06, p26). The complex physical oceanography in the region makes this difficult in a single zonal section. However, the measurement of multiple TEIs will help us to constrain many uncertainties that arise from the complex circulation. For example, distinguishing the contribution of lateral transport and vertical remineralization to metal enrichments within the OMZ can be resolved by examining a suite of the core GEOTRACES parameters (for instance radium isotopes and particulate

metals). This is an example of the type of problem that can only be solved by measuring all of these parameters on a single cruise.

Of particular interest is the exchange of materials between the Peru margin and the interior of the basin. The proposed section will provide an opportunity to examine exchange of water and materials between the eastern boundary and the northeastern-most corner of the SE subtropical gyre associated with these water masses (Figure 1). We will be able to observe the metal signatures associated with each of these water masses and examine processes involved in their exchange.

High rates of particle export from waters beyond the continental shelf are important in the transport of TEIs to deep waters and also contributes to the large size of the OMZ. Many trace elements are also enriched within the OMZ and help sustain high populations of microbes involved in denitrification. Elevated metals could be supplied from surface waters by (1) remineralization of sinking biogenic materials or (2) through lateral advection, since the shelf and slope waters are strong sources because of reducing conditions. Czeschel et al. (2010) suggest that transport within the OMZ, while sluggish, contains westward-flowing filaments of the SEC interspersed with eastward flowing currents. Moreover, eddies generated over the shelf are another important mechanism for moving water depleted in oxygen (and presumably enriched in metals) across the shelf. Siedlacki and Archer (2010) showed that episodic relaxation in Ekman pumping contributes to offshore transport of subsurface plumes in upwelling regimes; they used iron as a specific example in their model. This may also be important off Peru.

Boundary Scavenging.

The high POC export in the Peruvian margin and steep gradient in POC export along this section provide an end member for thorium-based assessments of POC export and for study of scavenging of other particle-reactive TEI. Indeed, $^{230}\text{Th}/^{231}\text{Pa}$ data from the Panama and Guatemala Basins, to the north of the proposed study area (Anderson et al., 1983), suggest that this may be one of the best places in the world to study the sensitivity of trace element scavenging to variability in the flux and composition of particles. Furthermore, very preliminary results from the U.S. GEOTRACES North Atlantic section indicate much weaker lateral concentration gradients (i.e., boundary scavenging) into the high productivity region of the Canary Current than were observed in the eastern tropical Pacific (R.F. Anderson, *pers. comm.*), providing an opportunity to identify and quantify the factors that regulate the intensity of boundary scavenging by comparing results from these two contrasting regimes. Other core parameters such as Ra isotopes will provide important information about margin sources versus internal cycling for elements like Fe and Mn that are enriched in low oxygen regimes.

TEIs and the Carbon Cycle.

An important objective of GEOTRACES is to understand the relationship between the utilization of bioactive metals by phytoplankton and the linear relationships between dissolved metal concentrations and nutrients. This provides insight into their utilization and potential for biolimitation, and is important for metals used as paleoproxies. Large gradients in surface particulate and dissolved metals are anticipated from the Peruvian shelf to the oligotrophic subtropical gyre. The Atlantic section also afforded this opportunity, but with a crucial difference. *In the oligotrophic ETSP, N is strongly depleted relative to P, and is invariably the limiting nutrient, whereas in the Atlantic, P is strongly depleted and is often the limiting nutrient (Casey et al., 2009).* Metals required for P acquisition mechanisms involving alkaline phosphatase, like Zn and Co, may be utilized preferentially in the Atlantic under low P conditions. The proposed section enables us to study this contrast, and also to study metal:C and metal:P relationships across large gradients in CO_2 concentration.

Hydrothermal Processes.

Seafloor hot springs were only discovered toward the very end of the GEOSECS decade (Corliss et al., 1978; Spiess et al., 1979) and hence went almost completely unrecognized by that program. Nevertheless, it was quickly realized that submarine hydrothermal venting may profoundly influence the balances of major and minor elements in the oceans (Edmond et al., 1979) and, hence, is an important subject for GEOTRACES to address (GSP06). While end-member vent-fluids exiting the seafloor may be significantly enriched in a number of TEIs, the *gross* flux from hydrothermal fluids exiting the seafloor can be significantly modified by processes acting in the overlying water column (German et al., 1991b; Lilley et al., 1995; German & Von Damm, 2004) – just as processes acting in estuaries serve to modify riverine fluxes of TEIs to the oceans (Bianchi, 2007). Further, geophysical arguments indicate that the entire volume of the oceans may only be circulated to high-temperatures deep beneath the ocean crust on time scales of ~10Ma (e.g. Elderfield & Schultz, 1996) but - more pertinent to this study - the entire volume of the oceans may also be circulated through deep-ocean hydrothermal *plumes* every few thousand years or less (Kadko et al., 1994; German et al., 2010) – i.e. on timescales that are short compared to thermohaline circulation. Consequently, deep-ocean hydrothermal plumes, despite being physically restricted to only rise hundreds of meters from the seafloor (Lupton, 1995), may significantly impact global ocean chemistry, including upper ocean productivity and global carbon budgets (www.scor-int.org/Working_Groups/wg135.htm).

Typically, when hot supersaturated fluids first exit the seabed, quenching leads to the precipitation of a range of polymetallic sulfide, sulfate and silicate minerals (Feely et al., 1987; Mottl & McConachy, 1990) and these particles are then carried upward - together with their host fluids and an increasing volume of entrained seawater - in ascending plumes that can rise hundreds of meters through the water column before attaining a level of neutral buoyancy (Helfrich & Speer, 1995). The most abundant TEIs in hydrothermal fluids are typically Fe and Mn, which exhibit end-member concentrations ~10⁶-fold higher than the ambient deep-ocean (Von Damm, 1995) although, in the case of Fe, it is estimated that ~ 50% of this gross iron flux is co-precipitated (Mottl & McConachy, 1990; Rudnicki & Elderfield, 1993), together with other chalcophile metals (notably Cu, Zn, Pb). The exact fate of these metals remains uncertain – they may settle rapidly to the seafloor or, alternately, be released back into the deep water column through oxidative dissolution (Trefry et al., 1985; Trocine & Trefry, 1988; Metz & Trefry, 1993). As well as leading to a reduction of the gross fluxes of *hydrothermally-sourced* TEIs, hydrothermal plume processes can also lead to uptake and removal of other TEIs from the surrounding water column. Oxidative precipitation of dissolved Fe to form fine-grained flocs of Fe-oxyhydroxide material can lead to significant uptake of oxyanions such as P, V and As (Feely et al., 1990, 1991) and particle-reactive TEIs including Be, Y, REE, Th, and Pa (German et al., 1990; 1991a, Kadko et al., 1993; Sherrell et al., 1999). In this manner, the resulting impact of hydrothermal circulation can be to act as a net sink in certain TEIs' budgets, even though they are significantly enriched in end-member vent-fluids (German & Von Damm, 2004). A key hypothesis to be tested within the course of this US GEOTRACES section, therefore, is whether “hydrothermal scavenging” above the southern EPR is comparable in its fractionation of key TEIs to the “boundary scavenging” active at the high-productivity Peru margin.

Of course, while the TEI distributions of hydrothermal particles may have received significant past attention, not all hydrothermally-sourced TEIs precipitate readily from solution. Hydrothermal fluids are notable for their enrichments in ³He which, as a noble gas, serves as an inert tracer of the physical dispersion and dilution of hydrothermal fluids released into the ocean. Furthermore, the dissolved Mn released from hydrothermal fluids may be diluted ~10⁴-fold within a buoyant hydrothermal plume, but does not readily co-precipitate to form sulfide phases during the ~1h rise time to reach a level of neutral buoyancy. Consequently, dissolved Mn concentrations of 10s or even 100s of nM are typical in the water column immediately overlying ridge-crests and oxidation of this chemically reduced Mn(II) can be sluggish unless microbially mediated (Cowen et al., 1990; Cowen & Li, 1990; Cowen & German, 2003).

The fate of dissolved Fe in hydrothermal plumes is more complex. Some early work, informed by studies at the northern Mid-Atlantic Ridge, naively assumed that all Fe was quantitatively oxidized and precipitated from solution within the first few minutes of buoyant plume rise (German et al., 1991b, Rudnicki & Elderfield, 1993). While that might be true for hydrothermal fluids erupted into relatively oxidizing North Atlantic Deep Water, it is now recognized that the rate of oxidation of hydrothermally sourced iron decreases, systematically, along the trajectory of the thermohaline circulation from the Atlantic to the Indian and Pacific oceans (Field & Sherrell, 2000; Statham et al., 2005). This is important because the longer that dissolved Fe(II) can persist in the water column prior to oxidative precipitation (order hours in the eastern Pacific) the greater the potential for at least some of this Fe to become stabilized through organic complexation, in dissolved or colloidal form (Bennett et al., 2008; Toner et al., 2009) decreasing the role that Fe oxyhydroxide particle formation may play in modifying other deep ocean TEI budgets. Recent studies have suggested that 10-50% of all Pacific Deep Water dissolved Fe budgets may be hydrothermally sourced (Chu et al., 2007; Bennett et al., 2008), and that hydrothermal activity may supply a significant source of iron to the Southern Ocean.

To address these issues, the current proposal seeks to investigate TEI cycling, down-plume, along the major hydrothermal plume identified from deep-water $\delta^3\text{He}$ anomalies dispersing westward from the crest of the East Pacific Rise near 15°S (Lupton & Craig, 1981; **Fig.3**) consistent with local deep-water flow bathing the ridge axis at these depths (Reid et al., 1982; Hautala & Riser, 1993). While hydrothermal activity is now known to occur in all ocean basins and along ridges of all spreading rates, the Southern East Pacific Rise, 14-19°S, is among the fastest-spreading (hence, highest magma supply-rate) ridges worldwide (de Mets et al., 1994) and hosts the highest known incidence of hydrothermal plume activity overlying any ridge-crest (Baker & Urabe, 1996; Baker & German, 2004). The most recent and systematic studies of the southern EPR have identified extensive plumes all along this section of ridge-axis with maximum concentrations of ~220nM particulate Fe and ~70nM dissolved Mn directly above the ridge-axis at 15°S and concentrations of >30nM pFe and >3nM dMn at distances of >80km off axis to the West (Feely et al., 1996; Ishibashi et al., 1997). Importantly, the hydrothermal plume processes at this location on the southern EPR are both long-lived and consistent. Distributions of particles and dissolved Mn along this section of ridge crest in the above studies compared very closely with those reported a decade earlier at the same latitudes (Shimmield & Price, 1988) while extensive national and international programs conducted throughout the global deep ocean (including Helios, WOCE) have identified the deep SE Pacific $\delta^3\text{He}$ -plume targeted here as the largest ridge-crest hydrothermal plume, worldwide (Lupton, 1995). Importantly, this modern-day plume also directly overlies a lens of metal-rich core-top sediments that was identified, extending west from the same ridge-crest nearly a decade prior to the first discovery of seafloor venting (Bostrom et al., 1969), providing clear evidence that a range of trace metals – both those sourced from hydrothermal fluids (e.g. Pb isotopes: Barrett et al., 1987) and those scavenged from seawater (e.g. REE: Ruhlin and Owens, 1986) have been transported >1000km down-plume along the plume axis throughout the geologically recent past (Fig. 3).

The preservation of these metalliferous sediments at the seafloor in this highly oligotrophic deep ocean basin provides one final motivation for the work proposed here. Previously, it has been argued (notably from P:Fe ratios: Feely et al., 1998) that uptake of key TEIs by hydrothermal particles are linked directly to ambient ocean conditions and, hence, offer important paleoceanographic potential if transferred, reliably, to the underlying sediment record. In the South Pacific, redox-sensitive metals in ridge-crest sediments may represent one of the best ways to reconstruct past ocean conditions at abyssal depths in the absence of alternative proxy records (Mills et al., 2010). While it is actively recognized that such studies require attention to the processes that may alter sedimentary records post-deposition, however, (Schaller et al., 2000; Poulton & Canfield, 2006), what is equally the case – and represents a key goal throughout the broader GEOTRACES program - is that there is an important knowledge gap in how many TEIs behave in *any* hydrothermal system, including a complete absence of knowledge about how the majority of TEIs behave in this, the world's largest mid-ocean ridge hydrothermal plume. The work proposed here will

help fill that gap by expanding our understanding of how hydrothermal activity may impact *modern* global ocean TEI budgets and distributions and, hence, how these same processes may impact the TEI distributions preserved throughout the deep-ocean paleo-record.

IMPLEMENTATION

Cruise Track.

It was decided the section should start on the Peruvian side at 12°S because at this latitude we will be able to begin the section at a time series site maintained by Peruvian oceanographers based in IMARPE (Instituto del Mar del Peru). Furthermore, both ENSO and coastal trapped waves cause a lot of variability in the OMZ further north, while primary production, oxygen depletion and particle export are all substantially lower further south. Wind stress curl is highest during the late austral winter (Bakun and Nelson 1991), so we will initiate the cruise in September or October 2013. Sampling is proposed across the shelf-slope break, where we anticipate strong gradients in primary production, redox gradients and iron concentrations. We anticipate large fluxes of Fe oxides and biogenic particles in this region that may be important in boundary scavenging. However, high density stations are constrained by the turn around time for sample processing – a lesson we learned on the 2010 Atlantic Section Cruise. Detailed dynamic studies of the shelf-slope break will be pursued in the future – for instance a GEOTRACES Process study in collaboration with IMARPE colleagues. Several of these stations will coincide with Peruvian time-series stations inside and outside the upwelling front. For the Western half of the section, the primary information used to guide selection of deep station locations will be the prior work that studied near-vent distributions of Fe and Mn along- and across-axis near the summit of the East Pacific Rise (15°S, 113°W: Feely et al., 1996; Ishibashi et al., 1997) and the more extensive array of meridional sections generated for $\delta^3\text{He}$ anomalies by the Helios and WOCE programs (Lupton, 1995) that also allow the location of the axis of the westward-trending plume to be identified precisely, at regular intervals, at 120°W, 128°W, 135°W and 150°W (Fig.3). As with the case for the eastern portion of the section, it is anticipated that more detailed studies of near-vent processes will also be conducted in the future, to complement the work proposed here, introducing the US GEOTRACES community to the use of deep submergence science (e.g. using the Alvin human occupied vehicle that is currently undergoing a major upgrade) together with CTD-rosettes, to conduct TEI sampling of end member vent-fluids and rising (buoyant) as well as dispersing (neutrally buoyant) hydrothermal plumes.

Responsibilities of the management and implementation team.

Overall – The PIs for this proposal constitute the Management Team who will oversee implementation of the US GEOTRACES East Pacific Zonal Section cruise, including all aspects of logistics, interaction with the ship operator and agents, communication with the science community and data-management. **Prior to the cruise**, we will follow the procedure used for the Atlantic and invite statements of interest from the community well before any proposal deadline. Statements of interest will be posted on the US GEOTRACES web site to facilitate coordination of logistics and creation of scientific collaborations (See the Timeline, above). The section is open to participation by any US Investigator who proposes high quality research that supports the GEOTRACES goals, as defined in the Science Plan. After funding decisions, we will coordinate a PI meeting to determine ship-board requirements and operations including the number, type and precise locations of the stations to be occupied along-section. **At sea**, we will provide for all sample acquisition, quality control and archival of the appropriate operational metadata (navigation, event logs, etc) and hydro-graphic data following previously-established GEOTRACES and WOCE/CLIVAR protocols. The Scripps Ocean Data Facility (ODF) will be in charge

of hydrographic and nutrient data acquisition and will work with the Team on shipboard data management (see Data Management Plan & WHOI Budget). Water sampling will use the GEOTRACES trace metal-clean system (24 x 12L GO-Flo carousel; Kevlar cable winch; clean-lab van - see next section) and a “traditional” 12 x 30L Niskin rosette on a standard hydro winch provided by ODF. The Team will coordinate all on-board water sampling, ensure smooth and efficient operation of all station-related activities and be responsible for acquisition of all essential hydrographic data (CTD, salinity, nutrients, oxygen, and pigments). The Team will also perform on-board Zn measurements on discrete bottle samples to establish and monitor the GEOTRACES GO-Flos and carousel for sample integrity (see later). Working with ODF, the Team will also be responsible for establishing and monitoring both GO-Flo and Niskin integrity using shipboard hydrographic measurements. The Team will be responsible for the quality control and archival of all ship-board measurement data and for making all data and meta-data available to on-board participants. **Post cruise**, the Team will be responsible for ensuring the timely transmission of all data and meta-data acquired during the cruise to the US GEOTRACES data archive (BCO-DMO, WHOI) who, in turn, will be responsible for transferring all such data and metadata to the International GEOTRACES Data Office (see Data Management Plan). The Team will also be responsible, together with Jim Swift (ODF) for creating a final cruise report and a “hydrographic synthesis”, hopefully of publishable quality, describing the basic context (water mass structure, major current flows, etc) that will aid the interpretation of TEI data obtained from shore-based analyses. Finally, the Team will also host a post-cruise “synthesis meeting” to promote collaboration and discussion among the participants which we anticipate will be funded by the U.S. GEOTRACES project office.

Specific Responsibilities - Moffett will act as lead investigator and sail as co-chief scientist for the cruise with primary responsibility for coordinating sampling activities on the eastern (ocean margin/high productivity) section of the cruise. He will supervise the postdoctoral investigator tasked with shipboard determination of zinc for quality control and will be the primary point of contact with the ship schedulers, overseeing clearance for the Peruvian EEZ (where he has prior experience). **German** will sail as co-chief scientist on the cruise, with primary responsibility for coordinating sampling activities on the western (hydrothermal) section of the cruise. He will be the primary interface with the ODF group, to be subcontracted to WHOI, for acquisition of hydrographic data and with NASA’s Ocean Ecology Branch responsible for pigments/optics determinations (see letter of support). Two “Super-Techs” who will be contracted to oversee TEI sampling and sample handling at sea for all waters collected from the conventional CTD/rosette will be under his supervision. **Cutter**, who runs the GEOTRACES Sampling Facility, will coordinate all trace element sampling and sample handling activities on the cruise (clean lab, winch/CTD-Carousel, GO Flo sampling systems). He will supervise the two “Super-Techs” to be contracted for all trace element sampling from the GEOTRACES system at sea. His team will also be responsible for all nanomolar nutrient determinations and Cutter will also take particular responsibility for coordinating all sampling and handling of low oxygen samples wherever they may occur – at the Peru margin ± in the dispersing hydrothermal plume.

Contamination-prone 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 (below) following the GEOTRACES cruise protocols (<http://www.obs-vlfr.fr/GEOTRACES/libraries/documents/Intercalibration/Cookbook.pdf>). The US 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 carousel uses 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.

The GO Flo bottles are immediately transferred into the HEPA-filtered, positive pressure clean lab van where they are sub-sampled for dissolved and particulate TEIs. Since two GO-Flo bottles will be fired at each depth (see below), one GO-Flo will be pressurized (<8 psi) with filtered, compressed air (will use nitrogen for suboxic waters) and the water directly passed through a 0.4 μm Acropak capsule filter 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 0.45 μm polysulfone Supor filter membrane filter 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 if desired.

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 nutrient 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).

Sampling for non-contamination-prone elements and hydrography.

Work on the two Intercalibration cruises, and the North Atlantic cruise show that a conventional CTD/rosette can be used for all the radionuclide and most of the radiogenic isotopes. For these and conventional hydrography, we will use the 12 position, CTD rosette operated by the SIO Ocean Data Facility (ODF) and overseen by Jim Swift. This unit has 30L Niskin-like bottles that have coated stainless steel springs and Viton o-rings, and will also be equipped for direct, inline filtration (0.4 μm Acropaks just like those on the GO Flo bottles). Sensors on this system include a transmissometer, Seabird SBE-43 oxygen probe, and fluorometer. As far as the need for quality hydrography, not only can GO Flo bottle leaking be identified, the data are crucial for identifying the water masses being sampled. In this respect, shipboard measurements of micromolar inorganic nutrients (nitrate, nitrite, silicate, phosphate, ammonium), 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 nitrite) down to nanomolar levels in the upper 200m (see below). Along with ODF, the PIs 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 hydrographic and sample-analysis are 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 password-protected web-site. In addition, the PIs 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.

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 nitrite, nitrate, and phosphate at nanomolar concentrations for all samples in the upper 200 m. 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, and by Zhang and Chi (2002) for phosphate. These methods have been evaluated (e.g., intercalibrating MAGIC with waveguide phosphates) as a part of the GEOTRACES Intercalibration Cruises. On the North Atlantic cruise in 2010, these data were invaluable in identifying low intensity upwelling/mixing areas that were at the detection limits of conventional methods used by ODF, as well as showing that the area transited was phosphate and not nitrate limited (W.Jenkins, *pers. comm.*). The nanomolar nutrient data will be fully available to all cruise participants in addition to the conventional nutrient determinations made at micromolar levels by the ODF group.

On board determinations of zinc for detecting contamination.

Zinc is the most contamination-prone element, and shipboard determination has often been carried out by previous workers as a quality control. Moffett will supervise a postdoctoral investigator who will make measurements on board. Current plans are to use an anodic stripping voltammetric technique originally developed for cadmium and zinc (Fischer and van den Berg, 1999) modified for zinc speciation by Moffett’s former student Rachel Wisniewski-Jakuba (Jakuba et al., 2008a, 2008b), who did her Ph.D. on zinc. The technique is based on previous anodic stripping voltammetry methods, but the sensitivity is significantly increased through the addition of thiocyanate as a reagent during deposition. Zinc will be measured in shallow samples (where Zn is lowest) to identify Go-Flo bottles that may be contaminated, or the rosette itself. This is not anticipated to be a serious problem, but it has emerged as an important recommendation in GEOTRACES workshops and is a part of the current Atlantic Section. It does not mean that Moffett or the postdoc will inevitably be measuring zinc as a core parameter, and other groups are eligible to submit proposals to measure zinc. We do plan to enable the postdoc to add some basic science to their work plan (with separate funding) for their professional development (see Postdoctorate Mentoring Plan).

Pigments, and apparent and inherent optical properties.

As for the North Atlantic US GEOTRACES Section, we propose to partner with the Ocean Ecology Branch at NASA’s Goddard Space Flight Center. Their group will plan to join the cruise (or, as a fall-back, analyze samples collected by us) for a combination of optical and biogeochemical observations that would allow NASA to improve their remote sensing algorithms and assist in validation of their satellite-derived data-products while, simultaneously, providing us with invaluable upper-ocean data pertaining to biomass and dominant taxa (as derived from pigments) that could be cross-correlated with the nutrient, micronutrient and TEI studies that our US GEOTRACES program will undertake. Observations of the Apparent Optical Properties (AOPs) and Inherent Optical Properties (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 biogeochemical sampling will involve 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 NASA's Ocean Ecology Branch, Goddard Space Flight Center (see Supplemental Material for letter of support) at no direct cost to this proposal.

Detailed Station Plan.

The precise locations and characteristics of our sampling stations will only be decided at the community meeting to be held in Spring 2013, to be convened by the PIs of this proposal but to include *all* the PIs funded to participate in and/or obtain samples from this US GEOTRACES cruise. Nevertheless, the transect to be followed for this section has been established (Figs.1-3) and, based on the speed and endurance of the global class ships available to implement the cruise, we can calculate that the required transit time will be 20-21 days leaving a maximum of 31-32 days available for station work (see later). For this section, therefore, we propose three types of station. The majority of our station work will be dedicated to "standard" full-ocean depth GEOTRACES stations that comprise 2 casts (to 12 depths each) of the GEOTRACES (24 x 10L) carousel (one shallow cast and one deep cast), 2 casts of the ODF (12 x 30L) carousel to the same depths (one shallow cast and one deep) and two casts for pumping/in situ filtration (one deep and one shallow). At a subset of these stations we also anticipate conducting additional casts of one or other CTD-rosette system dedicated to any TEIs for which individual proposals are successful and that require greater volumes of water than can be provided by standard GEOTRACES stations (see water budgets section, below). We anticipate that there should be adequate time within our proposed cruise to occupy ~18 deep water stations in total with ~5 of those sites being selected for extended "super" station sampling. In between these deep-water "standard" and "super" stations, to be occupied between Peru (~80°W) and our most Westerly station at 150°W we will also intersperse shallow stations, as time allows. Typically, we expect such stations would comprise one cast of the GEOTRACES carousel and one cast of the ODF carousel to ≤1000m.

Water Budgets.

Preliminary water budgets for the GEOTRACES and conventional rosette samplers and *in situ* pumps have been developed based on the recent experience with the 2010 US North Atlantic cruise, and anticipated alternations for this Pacific cruise. It is likely that once we know who is funded and their needs, the budgets will be adjusted at the pre-cruise PI meeting (see *Timeline*, earlier). However, we feel that these are conservative estimates and show that we will have sufficient water for all anticipated needs. Based on our experience in the North Atlantic, two GO-Flo bottles (total of 20L) will be tripped at each depth to meet the sample requirements for contamination-prone TEIs at standard full-depth stations (one for cartridge and one for membrane filtration; see Sampling section above). The depth range to be covered by the shallow and deep casts will be decided by the funded PIs. For the other TEIs, including radionuclides, the use of ODF's standard Niskin rosette with 12 X 30-liter bottles, allows all sample requirements to be met with a single bottle tripped at each depth. Like the GO Flos, depth range to be covered by the shallow and deep casts will be decided by funded PIs.

Particulate samples are collected from the GEOTRACES GO-Flo bottles (see *Sampling*, above) and provide sufficient volumes for a number of TEIs (2-10L). For the remaining TEIs, *in situ* pumps will be used, filtering up to 400 L on a standard cast (depending on depth). However, this Management grant does not provide for those pumps and they will need to be funded as part of a dedicated individual proposal. The management Team is committed to working with the PIs responsible for *in situ* pumping to ensure that all pump requirements are accommodated in the cruise plan, and the duration of the cruise requested in support of this proposal already takes account of this.

Station Time and Cruise Duration.

For a standard full depth water column station, the anticipated water requirements will call for two casts of the clean GEOTRACES carousel (one shallow and one deep), two casts of the conventional Niskin rosette (one shallow and one deep), and two casts of *in situ pumps*. Our recent experience on the US N.A. cruise shows this type of station takes 28 hours of shiptime. A super station entails 3 additional casts of the conventional rosette (2 deep, one shallow) and one additional shallow pump cast, making a super station 42 hours in duration. Shallow stations that consist of one cast each of the GEOTRACES carousel and the standard rosette (upper 1000m) take 2.5 hours.

A cruise of 52 days duration is proposed, where 20.5 days would be required for steaming (assuming 11 kts) and 31.5 days (756 hours) is allocated to station time. A total of 18 standard full depth stations are planned (Figures 1-3) which, at 28 hours per station, totals 504 hours of station time. The remaining 252 hours of station time will be divided between shallow stations (nominally 2.5 hours each) and super stations. Actual station plans and allocation of station time will be determined at the pre-cruise planning workshop (see *Timeline* above), where the management team will ensure that station plans developed by funded PIs are compatible with the overall cruise schedule.

Data Management Plan. See attached Supplement.

BROADER IMPACTS

It has been widely recognized that the ocean biogeochemical research community needs a global picture of the key and ancillary GEOTRACES properties for all US and international GEOTRACES sections. Thus, one key contribution from this project will be to provide those data from one of the highest priority sections identified by the US science community and the US GEOTRACES SSC. This work, in turn, will enable the development of better ocean biogeochemical models and a better basis for understanding the roles of a wide variety of processes that contribute to the oceans' regulation of future climate change and the impact of anthropogenic activities on the oceans. As well as providing this input to the work of policy makers, beyond our immediate ocean science community, the continuing development of teams that understand the proper sampling and measurement techniques required (including many graduate students and other early-career scientists), will help equip a new cohort of scientists with the skills necessary to achieve the future goals of US ocean research. At the international scale, this first Pacific section of the US GEOTRACES program also offers strong potential to improve collaborations among various Pacific Rim nations. Lead-PI Moffett has long-standing relationships with workers in Peru and Chile who study oxygen minimum zones. In Peru, his principal contacts are at IMARPE, with Dimitri Gutierrez (paleoceanography) and Michelle Graco (N cycle). He invited 4 IMARPE scientists on a cruise in 2005, and also taught a 2 week short course at a university in Lima in 2009. Likewise, co-PI German has established strong links among the Chilean hydrothermal research community through the Census of Marine Life and was a key-note speaker in their November 2010 South American synthesis meeting timed to coincide with the conclusion of CoML. We are determined to use this section to further the development of observational oceanography and lay the foundations for future collaborations with these nations as part of both the larger international GEOTRACES program and also as part of an emerging pan-South Pacific international deep ocean program being developed as part of the wider *beyond-CoML* program, *INDEEP*. As a co-PI on the Hall-Bonner Program for Minority Doctoral Scholars in Ocean Sciences (<http://sci.odu.edu/oceanography/academics/grad/hall-bonner.shtml> and http://science.hamptonu.edu/mes/hall_bonner.cfm), PI Cutter will utilize this cruise to recruit more Latino/Hispanic students into the Program, and hopefully to participate in GEOTRACES research.