U.S. GEOTRACES GP17-OCE Cruise Report

1 December 2022 – 25 January 2023

Papeete, Tahiti – Punta Arenas, Chile

R/V *Roger Revelle*

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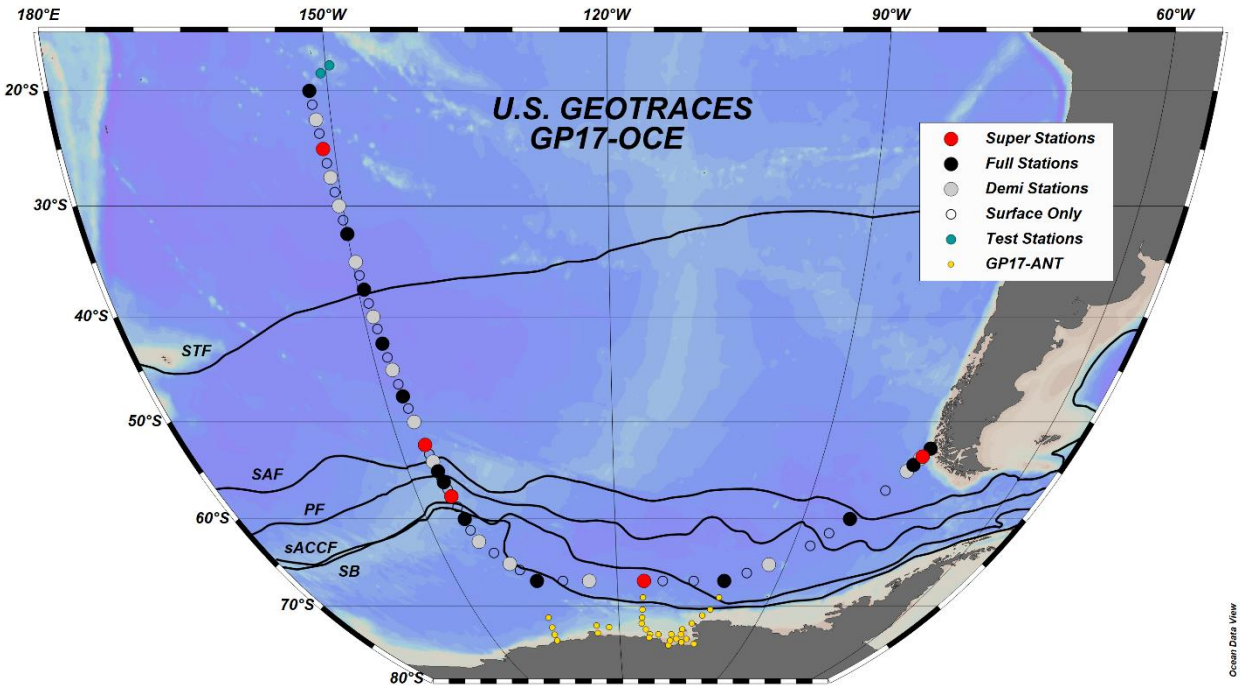

GP17-OCE cruise track

1. Introduction

Trace elements and their isotopes (TEIs) play key roles as micronutrients for marine organisms (Morel & Price, 2003), potentially toxic contaminants (e.g., Mann et al., 2002), and tracers of both modern and past ocean processes (e.g., Anderson et al., 2014; Henderson, 2002). The International GEOTRACES program aims to measure the high-resolution distribution of TEIs across ocean basin sections, which, coupled with mathematical modeling, allows the source fluxes and internal cycling of TEIs to be quantified.

Here, we report on the U.S. GEOTRACES GP17-OCE sampling expedition aboard R/V *Roger Revelle* from Papeete, Tahiti, to Punta Arenas, Chile. The GP17-OCE section encompassed three major transects: a southbound pseudo-meridional section (~152-135°W) from 20°S to 67°S, an eastbound zonal transect from 135°W to 100°W, and a northbound section returning to Chile (100-75°W). In combination with its companion cruise, GP17-ANT, which is slated to sail to the Amundsen Sea on R/V *Nathaniel B. Palmer* in late 2023, the goal of the U.S. GEOTRACES GP17 program is to sample the South Pacific and Southern Oceans from their most oligotrophic waters in the South Pacific subtropical gyre, to their highly productive Antarctic polar region, while also crossing the (paleo)oceanographically relevant Antarctic frontal region. The South Pacific and Southern Oceans sampled by GP17-OCE play critical roles in global water mass circulation and associated global transfer of heat, carbon, and nutrients. Specific oceanographic regions of interest for GP17-OCE include: the most oligotrophic gyre in the global ocean, the Antarctic Circumpolar Current (ACC) frontal region, the previously unexplored Pacific-Antarctic Ridge, the Pacific Deep Water (PDW) flow along the continental slope of South America, and the continental margin inputs potentially emanating from South America. Research questions to be addressed by TEI analysis of GP17-OCE samples include: 1) What are the relative rates of external TEI fluxes to this region, including dust, sediment, hydrothermal, and cryospheric fluxes? 2) What are the (micro)nutrient regimes that support productivity, and what impacts do biomass accumulation, export, and regeneration have on TEI cycling and stoichiometries of exported material? 3) What are TEI and nutrient stoichiometries of subducting water masses, and how do scavenging and regeneration impact these during transport northward?

In total, we sampled at 59 sites, including 2 test stations, 25 surface-only sites, and 32 vertically profiled stations. Three primary sampling systems were deployed at the stations: the GTC (GEOTRACES Trace element Carousel) CTD rosette system for collection of contamination-prone TEIs, the ODF (Oceanographic Data Facility) conventional rosette for collection of non-contamination-prone TEIs, and the in-situ McLane pumps for collection of large-volume particulate TEIs. Vertically-profiled stations were divided into three types: Full stations where samples were collected at 24 depths from surface to bottom (2 GTC casts, 3 ODF casts, and 2 pump casts); Demi stations where samples were taken at 12 depths (1 GTC and 1 ODF cast) in either the upper 1000m (no pumps) or intermediate depths to sample hydrothermal plumes (with pumps); and Super stations where samples were collected at a higher resolution of 32-36 depths using additional casts (3 GTC casts, 4 ODF casts, and 3 pump casts). Surface waters were sampled using a towed fish system (towed from a 20’ aluminum boom extending off the port

side) and the ship's flow-through underway seawater system. The surface samples were taken within one hour of arriving at vertical-profiling stations ("arriving fish") and at "surface-only" stations, either intermediate between stations or in place of vertical profile stations. Finally, specialized sampling for atmospheric aerosols, rain, beryllium-7, and radium isotopes are discussed below in the individual science reports.

We have appended several tables with detailed expedition information. Appendix 1 provides a list of the stations occupied with exact locations, dates, and observed bottom depths. Appendix 2 is a list of science participants on the cruise, as well as funded GP17-OCE projects. Finally, Appendix 3 contains the list of all parameters sampled and to be measured at sea or at PI laboratories back home as part of GEOTRACES GP17-OCE.

GP17-OCE science team in the Strait of Magellan

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2. Cruise narrative

Pre-cruise planning meeting

A pre-cruise planning meeting for principal investigators and cruise participants was hosted at Old Dominion University March 17-18, 2022. The meeting was used to familiarize groups with other funded science, introduce personnel, confirm station locations and types, discuss logistics such as water budgets, and determine the final roster of sailing scientists. Forty-five berths were requested compared to the 37 berths available for science on the Revelle. Prioritization was given to measurements requiring a shipboard analyst and samples for which particularly specialized sampling expertise was required. The PIs (and students!) who did not get a berth were gracious and professional, for which we were grateful, and every effort was made to ensure all samples were collected by others on the ship.

Mobilization

The ship was loaded in San Diego at MARFAC November 9-12, 2022. Eight 20' containers and around 50 pallet boxes were loaded, as well as the U.S. GEOTRACES Dynacon winch, rosette, and custom A-frame. Additionally, 39 floats of four types were loaded: Argo core, BGC Argo, NOAA Deep, and French NEMO/Jumbo. The scientific team benefitted enormously from the assistance of a full complement of SIO ResTechs and ship's crew, and we managed to get everything loaded and strapped down in time for the ship's departure for Tahiti on November 13.

Transit

The ship immediately transited to Tahiti, a two week journey. Several cruise scientists sailed on the transit to continue setting up equipment and instrumentation. Dr. Peter Morton joined the cruise, serving as chief scientist, and led the installation of the underway towfish. Andrew Collins (PMEL/Univ. Washington) set-up the ship's underway pCO2 system. Dr. Yipeng He (Univ. Connecticut) collected underway measurements of Hg in the atmosphere and surface seawater.

The rest of the science party flew to Tahiti for a 7-day quarantine spanning Thanksgiving. On November 27th Revelle arrived in Papeete, and the science boarded on November 29th. It was a great relief to get everyone aboard COVID-free! However, COVID precautions dictated that folks could not leave once they had boarded the ship, and we were grateful for the handful to departing scientists who stayed around and picked-up forgotten and last-minute supplies.

Cruise

Southbound transect

The first five weeks of the expedition were spent conducting a pseudo-meridional transect from 20°S to 67°S. This transect spanned a remarkable gradient in ocean temperature, nutrient availability, productivity, and TEIs. Stations were generally spaced each 2.5° of latitude (ca. 278 km), with surface towfish samples collected intermediate between each station. Tighter station spacing was used around the Antarctic Circumpolar Current (ACC) due to close spacing of fronts. The ship departed Papeete on December 1, 2022 and arrived at the first test station just a few hours later. Two casts of the GTC were conducted to fill all GO-FLO bottles with surface seawater for soaking. We conducted a second test station the following day where the ODF rosette, McLane pumps, and Be pump system were all tested. Two GTC casts were used to collect shipboard dissolved Zn (dZn) and Fe (dFe) samples to test bottle cleanliness.

The first science station – a crossover with GP15 cruise – began on December 3 at 20°S 152°W. Sampling proceeded smoothly until the McLane pump cast, when the squirt boom holding the pump wire block malfunctioned, causing a wire clamp to shear the Vectran jacket. No pumps were lost or damaged, but ca. 800 m of Vectran wire had to be removed. Two floats were deployed on departure from station.

We began station 3 – the first super station, representing the South Pacific gyre, and intended to be a crossover with GP21 – on December 6. Four casts each of the ODF and GTC rosettes provided 32-depth resolution. The monocorer was deployed below the ODF rosette on the deep cast to collect a surface sediment sample. As done on previous US GEOTRACES cruises, a plastic 'cone of silence' was installed to shield the monocorer from the ODF altimeter, however both the cone and the monocorer became wrapped around the CTD above the rosette. No damage was caused, but unfortunately we failed to collect a sediment sample. During the station we realized that the ship had used incorrect station coordinates and that we were about 80 nmiles from the intended crossover with GP21. The bridge acknowledged their error and the ship's coordinates for the remaining stations locations were carefully re-checked, but we decided not to reposition and restart sampling.

We next sampled two demi stations (ca. 3.5 h each). These stations consisted of GTC and ODF casts to approximately 1000 m, as well as arriving fish sampling and surface Ra pumping during the bottle casts. The weather began to pick up, and at station 5 (December 10) the GTC rosette struck the ship's hull on recovery, bending the aluminum rosette frame and damaging two GO-FLO bottles. A crack in the frame was stabilized with a metal splint and fiberglass cast, and both bottles were replaced with back-ups, but we lost a bottle position on the rosette and could only deploy 23 GO-FLO bottles per cast for the remainder of the cruise.

High winds and rough seas continued, and at the next station (station 6, a crossover with GP13 at 32.5°S 150°W) the deep McLane pump cast was aborted due to concerns about wire tension. It was also discovered that the towed fish had been lost from its tether while sitting on station. The AmSteel line and metal thimble were intact, suggesting that a loose shackle was the culprit. It

was a bruising few days for the GTC team! It also became apparent by this point that the sampling event times assumed during pre-cruise planning were unrealistic. Sea conditions consistently requiring slower wire speeds, along with some inexperience in the ship's deck and winch crew, resulted in longer events and station occupations. We therefore decided to convert all planned full-36 stations to full-24 stations in order to stay on schedule.

The weather settled down, and we completed stations 7-9 without incident. A replacement fish was installed on departure from station 7, and we successfully deployed the monocorer at station 8 (37.5°S) after concluding that the 'cone of silence' wasn't needed.

The weather remained calm at station 10, but on December 16th the ship briefly lost all electrical power during a McLane pump cast due to a faulty transition between generators. Following the restoration of power, the DESH5 winch used for the McLane pump Vectran wire could not be restarted. The science team manually pulled in the remaining 320 m of wire, including one McLane pump and the CTD. While this provided an invigorating team-building exercise to pass a Friday evening, it unfortunately marked the beginning of a long saga of electrical struggles with the DESH5 winch that significantly impacted the ability of the pump team to collect samples.

Stations 11-13 were completed despite developing winds and seas as we approached 50°S. The ship's electrician was able to fix the DESH5 in order to conduct pump casts at full station 12. Upon arrival at station 14, rapidly dropping surface salinity and temperature indicated that we had passed the Sub Antarctic Front within the last hour. We decided to steam about an hour north to ensure that super station 14 would be in the Sub Antarctic Zone. Still, thirty-plus knot winds and 20' swells greeted us at station 14. The GTC malfunctioned during the shallow cast and had to be recovered and re-terminated. John Calderwood from the ODF team provided invaluable support on terminations and electrical issues throughout the cruise.

Following demi station 15, we arrived at full station 16 (55°S) on Christmas morning. Wind and seas were moderate, but during the shallow pump cast the ship took an anomalous roll, causing the Vectran wire to slack, catch the top of the block and part when tension was restored. Eight McLane pumps, a CTD, bottom pinger, and an additional 800 m of Vectran were lost. Following the completion of the remaining bottle casts, we made several dragging passes in hopes of catching part of the wire with a hook. Despite a few encouraging tension spikes, we were unable to recover the pumps or wire and had to continue south after about 18 h of dragging.

Three demi stations in the ACC frontal region (stations 17, 19, 21) were sampled with the fish only in order to make up time and also provide some rest for weary sampling teams, as stations 16-21 were each only 40-50 nmiles apart. Station 20 (57.6°S) was south of the Polar Front and was sampled as a super station representative of the Subpolar Region. We saw an iceberg in the distance here – the first of many to come. Unfortunately electronic communication issues with the DESH5 winch resurfaced at station 21 and precluded McLane pump deployments at full station 22. At station 25 – the southern terminus of the pseudo-meridional transect at 67°S – the

four remaining McLane pumps were attached to the steel ODF cable (above the rosette) in order to collect samples for non-contamination prone elements while the DESH5 winch remained inoperative.

Zonal transect along 67°S

On January 6, 2023 we turned east and began a 1-week zonal transect along 67°S. There were abundant icebergs and patches of lingering sea ice, and the captain and mates did an exceptional job navigating the ice and finding clear areas for our casts. The icebergs, occasional pilot whales, and calmer – if colder – weather helped raise spirits on the ship. The towfish was deployed only to sample and then recovered to avoid damage from stray bergy bits. Longer transits between stations provided opportunities for sleep, and extraordinary efforts by the Chief Engineer (Tom Johnson) and Electrician (Dave Woods) brought the DESH5 winch back to life. Super station 27 (67°S 115°W) and full station 29 (67°S 100°W) were sampled and are intended to serve as crossovers with GP17-ANT. Heavy ice coverage caused the ship to deviate north of 67°S, and we decided to sample station 28 with fish only in order catch up on time. Similarly, we did not collect Be samples at stations 27 or 29 or conduct a deep pump cast at station 29. By the time we turned northward towards Chile after station 29 we had caught up from the delays caused by weather and pump loss on the southbound transect.

Northbound transect

On January 12th we began to head towards Chile, crossing the ACC fronts again and hoping to sample Pacific Deep Water at several points, as well as continental margin inputs. However, the heavy winds and large swell characteristic of the ACC quickly reappeared to limit our sampling events. Heavy winds and seas caused us to sample semi station 31 with only the fish, and at full station 32 we were not able to deploy the Be or surface Ra pumps or do McLane pump casts due to weather. Station 33 was planned as a full station, but 40+ knot winds and 20+ foot seas – expected to continue for at least 36 h – led us to collect samples only with the ship's underway system and continue on to station 34.

This provided the opportunity to add both of the 'saddle stations' proposed by Bill Jenkins to characterize the chemical characteristics of PDW. At station 34 we conducted one GTC, ODF and McLane pump cast each centered on the 2500 m isobath to sample PDW and look for possible hydrothermal signatures. Conditions at full station 35 allowed for all sampling events, followed quickly by more 'deep demi' sampling at station 36. Station 37 was sampled as a super station near to the continental margin and above PDW. Finally, station 38 was a shallow (100 m) station over the shelf, followed by less than a day of steaming to the dock in Punta Arenas, Chile. While transiting the Strait of Magellan, surface seawater samples were collected from the ship's underway system for Chilean collaborator Dr. Rodrigo Torres. Sampling within the Chilean EEZ waters (stations 34-38) was enabled by the presence of Chilean observer Ms. Paula Daluz Henríquez, who also helped with pigment and DNA filtrations.

Lessons learned to highlight for future cruises

- Vectran has significant vulnerabilities as a wire for deploying pumps in rough seas; it is worth considering if a new, dedicated block system that holds the line in the shiv should be purchased or developed.
- the ELOGGER event log system worked well
- the Be pumping system was too sensitive to sea state – in particular the ship pitch on the aft deck – for most of the conditions we encountered
- deploying the fish off port side worked well, since it could be left in or not taken out immediately. The fish was visible from the bridge during deployment via the port wing.

3. Hydrography

Hydrography and circulation set first order constraints on the distribution of trace elements and isotopes in the ocean, and the GP17-OCE transect crossed multiple major fronts and sampled within many different water masses in the South Pacific and Southern Oceans. While these fronts and water masses have been called various names in past studies, we recommend the nomenclature of Talley et al. (2011) for consistency within GP17-OCE. This nomenclature will be used in this brief review of the fronts and water masses that we encountered.

The southbound pseudo-meridional (135-152°W) section captured the most significant water mass gradients of the GP17-OCE cruise and compares well to the GO-SHIP P16S transect along 150°W (last occupied in 2014; CLIVAR and Carbon Hydrography Data Office – CCHDO). GP17-OCE began on the north side of the South Pacific subtropical gyre in warm, salty Subtropical Surface Waters, which persisted across the upper 400 m of the gyre. Nitrate was fully drawn down in the upper 125m of Stations 1-6 crossing the gyre, though phosphate was only fully drawn down in the upper ~100m of Stations 3-5, representing the most oligotrophic stations of the gyre. At these stations, deep chlorophyll maxima were as deep as 175 m. Chlorophyll in the surface mixed layer was extremely low (~1 μg/L) and dominated by small flagellated cells (based on Imaging Flow Cytobot, IFCB, imagery) and cyanobacteria. In the gyre, surface circulation was dominated by the anticyclonic subtropical gyre. Notably, at Station 1 at depths of ~40-100m, South Pacific Subtropical Underwater (S>36, T>25°C) was also recorded.

At approximately Station 7 (~35-36°S), we crossed the Subtropical Front (STF), as demarcated by significant meridional gradients in temperature (≥4°C) and salinity (≥0.5) over short distances in the upper ocean, with steep thermoclines and haloclines in section view. Station 6 had the strongest eastward currents indicative of the South Pacific Current. After Station 7, surface phosphate concentrations rose considerably, along with surface fluorescence, and surface nitrate was above detection limits by Station 8. All of these point to our entering the Subantarctic Zone north of the STF. Surface chlorophyll rose to 0.3-0.5 μg/L at points, and IFCB imagery shows increasing abundance of larger flagellates and diatoms, as well as the presence of lightly-silicified diatoms.

The next major front crossed on the southbound transect was the Subantarctic Front (SAF), which is traced by the latitude at which the sharp 4-5°C isotherm lies at ~200 m depth (Orsi et al., 1995). On GP17-OCE, this occurred between Stations 14 and 15, at ~53°N, which is very near where it was found on prior GO-SHIP P16S cruises. Importantly, while nitrate and phosphate concentrations rose sharply at ~Station 9 on GP17-OCE and stayed replete throughout the Subantarctic Zone, silicate concentrations remained quite low until we crossed the SAF. Stations 15 and 16 in the Polar Frontal Zone recorded surface fluorescence >2 μg/L, and the IFCB indicated the presence of more heavily silicified diatom taxa such as *Fragilariopsis* and *Coscinodiscus*.

Between Stations 16-18 (55-56°S), we crossed the Polar Front, which is defined as the northernmost extent of the 2°C isotherm surrounding the temperature minimum in the upper 200m. By Station 18 (56°S) we had also crossed the southern ACC Front (sACCF), which is indicated by a θ<0°C in the temperature minimum. The chlorophyll fluorescence dropped appreciably south of the PF. Then between Stations 18 and 20 (~57°S), we crossed the Southern Boundary (SB) of the ACC, which is defined as coincident θ_{max} of 1.5-2.5°C and oxygen minimum of <180 μmol/kg. South of the SB, we entered Antarctic waters ("Subpolar Region"). Once into the Subpolar Region, surface nitrate and phosphate were increasingly drawn down. In this region, surface circulation was dominated by the eastern edge of the cyclonic Ross Sea Gyre.

In the subsurface, we tracked two intermediate water masses throughout the southbound meridional transect. The first was Subantarctic Mode Water (SAMW), which falls within the sigma-theta (σ_θ) contours 26.8-27.05 kg/m^3 (Hartin et al., 2011). SAMW forms seasonally across the Southern Ocean north of the SAF via subduction of deep winter mixed layers and thus can be traced via an oxygen maximum (Talley et al., 2011). Due to the drawdown of nitrate but not silicate in surface waters of the Subantarctic Zone where SAMW forms, SAMW was also traced on GP17-OCE by a negative Si* (= [silicate] – [nitrate]). Stations 13 and 14 were observed to have thick SAMW layers approaching the surface.

Below SAMW is Antarctic Intermediate Water (AAIW), which is identified at its formation region by the σ_θ contours 27.05-27.15 kg/m^3, but it extends down through σ_θ of 27.5 kg/m^3 (Talley et al., 2011). The top of the AAIW can be tracked as a minimum in salinity. AAIW has a variety of local formation regions that can be identified via their salinity on the σ_θ of 27.1 kg/m^3 isopycnal (Bostock et al., 2013), and while most of our AAIW appears to have formed in the Southeastern Pacific, there may also be some influence from AAIW formed in the Southern Ocean. We tracked AAIW across the southbound meridional transect, and Stations 15 and 16 had thick AAIW layers closest to the surface.

Circumpolar Deep Water is the combination of North Atlantic Deep Water, Indian Deep Water, and Pacific Deep Water, all mixed together in the deep waters of the ACC. The upper portion of CDW is called Upper Circumpolar Deep Water (UCDW), which is differentiated from AAIW at σ_θ of 27.5 kg/m^3 (Talley et al., 2011). UCDW can also be recognized as an oxygen minimum layer (dissolved oxgeyn < 180 μmol/kg). The ACC's Southern Boundary (SB) front is defined as the southern boundary of UCDW upwelling.

On the same isopycnal as UCDW is Pacific Deep Water (PDW), which forms in the deep Pacific as a mixture of modified UCDW and upwelled bottom waters (Talley et al., 2011). PDW can be traced by low oxygen concentrations (like UCDW), high macronutrients, no CFCs, and a very high radiocarbon age (it is in fact the oldest water mass in the ocean). Along GP17-OCE, it is best distinguished from UCDW by its high macronutrient concentrations, which peaked at 2000-3000m depth at Stations 1-8.

The lower half of CDW is called Lower Circumpolar Deep Water (LCDW). LCDW is traced as a low silicate, high salinity water mass that upwells south of the ACC's Southern Boundary but never reaches the surface. Instead, it mixes with dense Antarctic abyssal waters before downwelling again. LCDW is the densest water mass to extend northward into the Pacific Ocean, although these waters are often called Antarctic Bottom Water (AABW). Indeed, pure AABW is distinguished from CDW at the neutral density 28.27 kg/m^3 (Talley et al., 2011). Pure AABW is thus denser than CDW and also warmer than the freezing point. Pure AABW is confined to the Southern Ocean by the ridges of the Southern Ocean, which for GP17-OCE is the Pacific-Antarctic Ridge. Thus, we sampled pure AABW at Stations 22, 25, 27, and 29, at least.

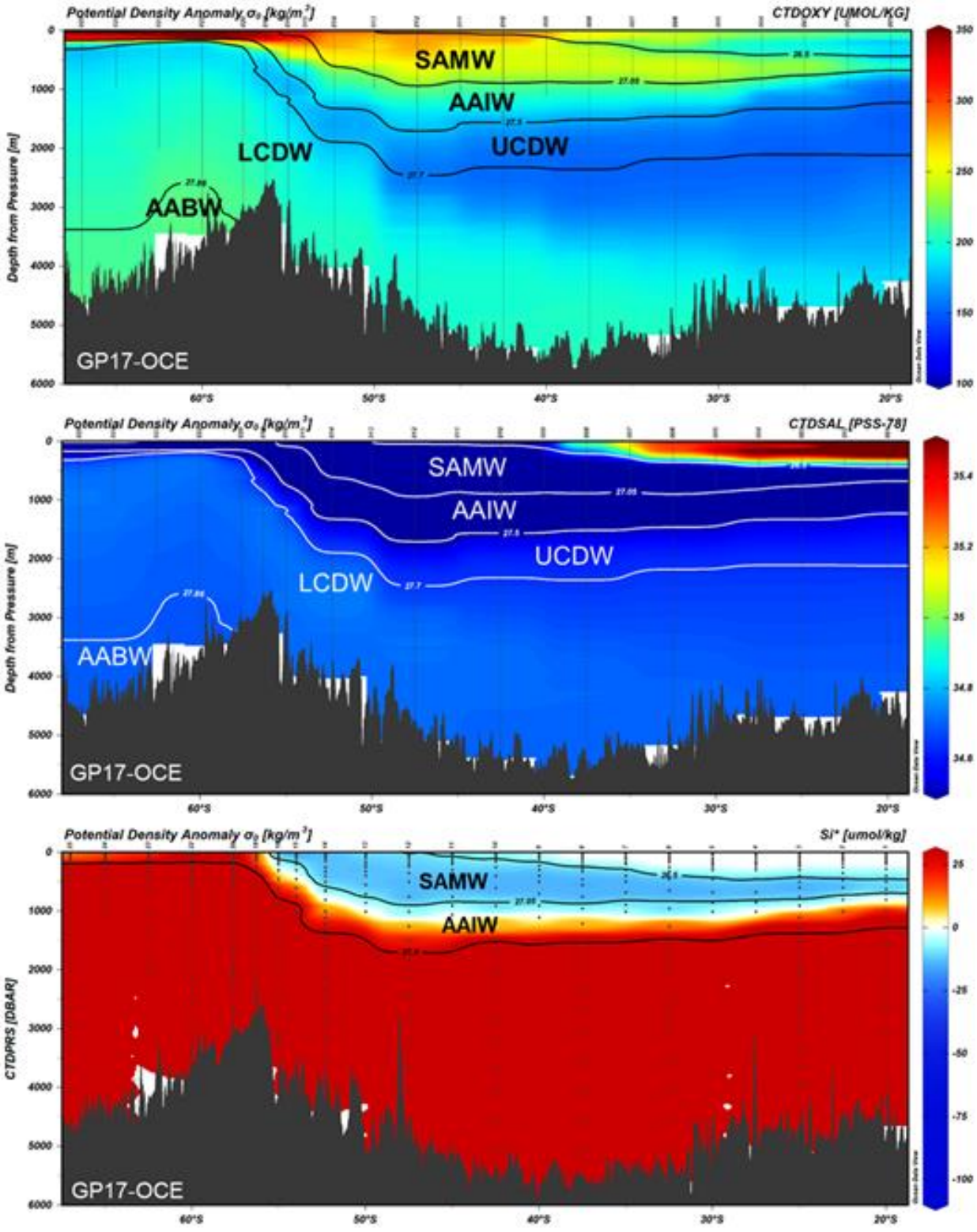

Figure 1: Southbound meridional hydrographic sections from GEOTRACES GP17-OCE, with water masses identified.

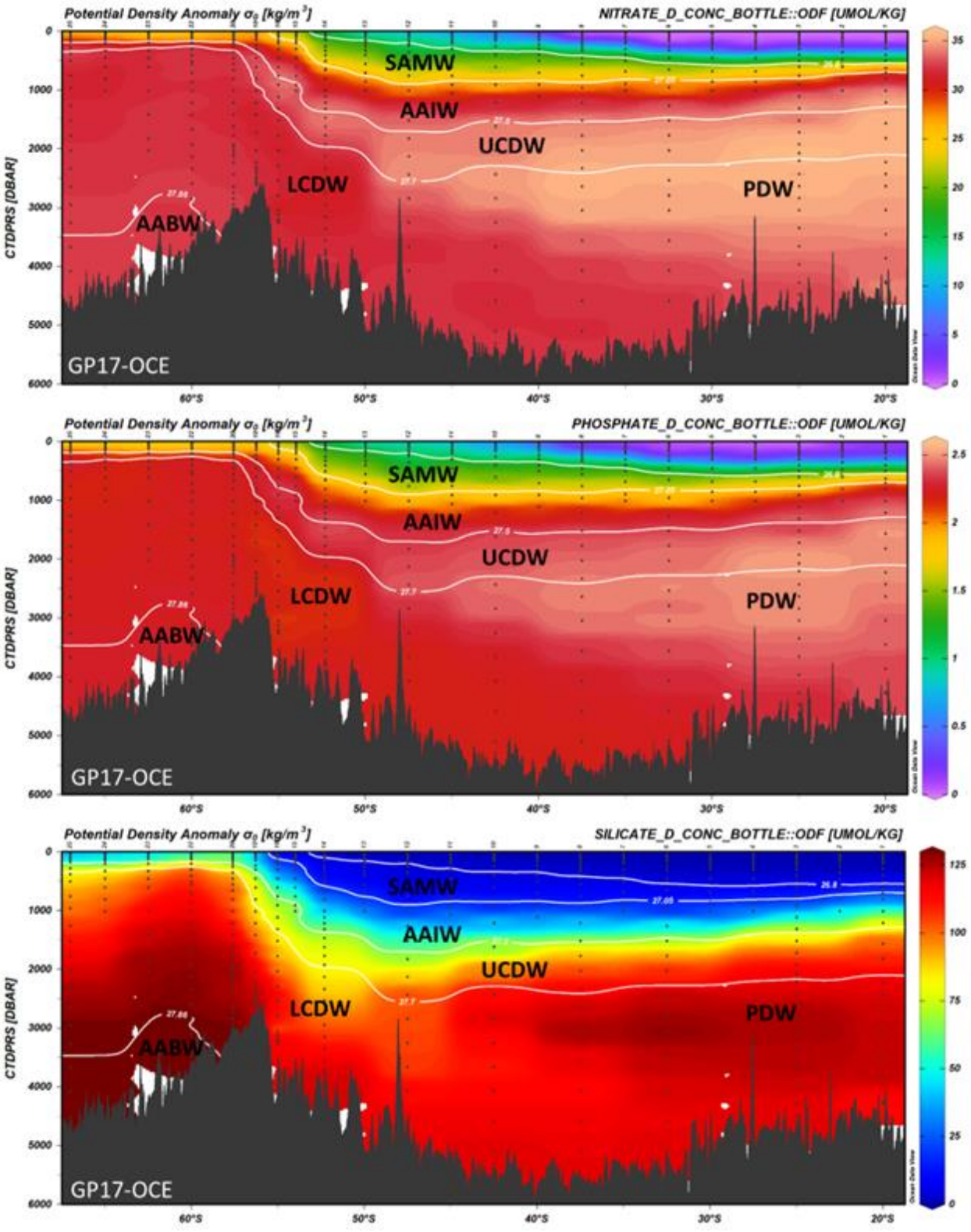

Figure 2: Southbound meridional sections of macronutrients from GEOTRACES GP17-OCE, with water masses identified.

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4. Sampling systems

4.1 GTC rosette

The Cutter group (ODU) and the East Coast van and winch pools provided the GEOTRACES Trace Element Carousel sampling system (GTC), including the A-frame, Dynacon winch with 7300 m of Vectran cable with conductors, clean lab van, and Seabird 9/11+ carousel/CTD with 24 x 12L Go-Flo bottles (+spares). The clean lab van was newly serviced and renovated since the last GEOTRACES cruise (GP15), including new floors and HEPA filters. The Barnstead and MilliQ ultrapure water systems were entirely replaced/upgraded prior to the cruise, and they required much lower water flow than on prior cruises. While the clean van's HVAC systems had been serviced prior to the cruise, only one system (top) was operational during the GP17-OCE cruise. Additionally, the GTC A-frame was also modified before the cruise for easier (dis)assembly and transport, which was successful. The CTD computer was also replaced with a brand new Onlogic micro-computer, and the rosette had been rewelded, stripped, and newly powder coated. Finally, the winch was re-valved for better operation at low temperature, and the Vectran cable was brand new and freshly spooled. All other components remained the same as on prior GEOTRACES cruises.

The GTC system was constructed on *Revelle* during mobilization by Greg Cutter and Chris Powell (ODU), with help from the GTC team and Brian Guest (WHOI, East Coast winch pool manager). The shipboard GTC team was made up of six individuals: Jessica Fitzsimmons (TAMU) ran the CTD console; "super technicians" Dylan Halbeisen (USF), Phil Kong (USC), and Yerim Kim (TAMU) did the Acropak filtration and staged/unstaged bottles; and particle team Laura Sofen (Bigelow) and Emily Frett (ODU) did the membrane particle filtration. Dylan Halbeisen and Phil Kong alternated running the winch, and Laura and Emily handled the tag lines.

The GTC sensor array was re-calibrated immediately prior to the GP17-OCE cruise. The sensor array consisted of dual SBE-9 temperature and salinity sensors (calibration date: 23 June 2022),

an SBE-43 dissolved oxygen sensor (calibration date: 9 Aug 2022), a Seapoint fluorometer, a Benthos altimeter, and a WetLabs C-Star transmissometer (calibration date: 12 July 2022). The "Salinity-2" sensor on the CTD physically broke after Station 36 and was replaced with a spare calibrated from the same set (and calibration values updated accordingly). The Bishop (UC Berkeley), Lam (UC Santa Cruz), and Ohnemus (UGA Skidaway) groups also installed on the GTC a birefringence sensor that detects particulate inorganic carbon (PIC) at all stations/depths (observed as "Voltage 7" in the GTC CTD data). The Fitzsimmons lab (TAMU) also installed a logging, non-conducting MAPR (Miniature Autonomous Plume Recorder) sensor suite on the rosette frame at deep casts of Stations 18 and 20 in order to collect turbidity and oxidation-reductional potential data near the hydrothermal plumes.

In total, 58 GTC hydrocasts were conducted on GP17-OCE. At all stations except the super stations, 2 Go-Flo bottles were triggered per depth. At super stations, 3 Go-Flo bottles were triggered per depth in the shallow casts to accommodate larger sample volume requests; at the first super station (station 1), intermediate and deep casts had 3 Go-Flo bottles triggered per depth.

The system overall performed very well despite rough seas. However, we did damage several Go-Flo bottles and required several cable re-terminations:

- On demi Station 5 (shallow Cast 2) in rough seas, we lost communication with the CTD and had to recover the GTC (no bottles fired). Upon recovery, a miscommunication on deck resulted in the CTD hitting the hull of the ship twice, resulting in a severe bend and crack in the rosette frame (vertical pole and tee to bottom of frame) and damage to 3 Go-Flo bottles (2 irreparable damage to spigot neck and 1 with reparable damage to the plunger assembly). John Calderwood (SIO ODF) re-terminated the original electrical termination done by Chris Powell during mobilization. We could not re-weld the aluminum rosette frame with shipboard tools, and we opted not to try to bend it back into position due to a fear that cracks in the frame would weaken the rosette's strength. Instead, we installed a brass tee brace (welded out by the ship's engineers) filled with epoxy putty to strengthen the weakest tee in the frame, and we coated it with fiberglass wrap. However, due to the bend in the rosette frame, we could no longer fit a Go-Flo bottle in rosette position #2, so all subsequent casts were completed with only 23 Go-Flo bottles for the remainder of the expedition. We did not repeat the cast at this station due to the time required for these repairs.
- At full Station 10 (deep Cast 7), one bottle was irreparably damaged during a fall on deck, as the PVC neck to the spigot was sheared.
- At super Station 14 (shallow Cast 2) in rough seas, we lost communication with the CTD after firing bottles at 4 of 8 total depths. Upon recovery, troubleshooting by Calderwood (ODF) pointed to an issue with a CTD cable, which was swapped out. Thus, we re-deployed at Cast 6, and while communications were OK on deck, once the GTC hit the water, communications were lost once again (no bottles fired). Upon recovery, Calderwood did a complete electrical re-termination, and the aborted cast 6 was replaced with Cast 8.

- Station 18 (Cast 3) suffered noisy transmissometer data because of a cable that came loose part way through the cast.
- Station 22 (Cast 2) was aborted when communications were lost in rough seas. After troubleshooting, John Calderwood re-terminated the electrical connection, but that did not fix the issue. Further troubleshooting revealed that the junction box on the Dynacon winch had flooded, so we removed the terminal block, cut back the wiring, and soldered the wires together; this also did not fix the issue. Further troubleshooting revealed that the cable between the junction box and the slip ring was spliced, and the connection had become wet. We opened that splice, cut back the cables, and re-soldered and re-wrapped that section, at which point CTD communications were resumed.
- After Station 32 (Cast 3), two Go-Flo bottles were recovered with broken connections between the Go-Flo bottle body and the small PVC tee that supports the spigot. It is not clear what those bottles hit, as the rosette was not further bent, nor did anyone on deck notice a collision. No re-termination was required, and the Go-Flo bottles were replaced with spares.
- At Station 34 (Cast 2), the rosette hit the ship's hull during recovery. A vertical post on the rosette was bent, and blue paint from the ship was visible on the rosette's powder coating. No Go-Flo bottles were damaged, and no re-termination was required.
- At Station 35, the GTC rosette again hit the ship's hull during recovery. This time, the bottom of the rosette was still in the water, likely slowing the velocity of the package, and fortunately the rosette and Go-Flo bottles were not damaged.

Once samples were brought into the clean van, unfiltered samples were collected immediately before connecting the Go-Flo bottles to the air pressure system (which was maintained at 12 psi). Acropak filtration was completed using Acropak-500 0.8/0.2 µm capsule filters; this is the same filter material but a larger capsule than the Acropak-200 capsules used on prior U.S. GEOTRACES cruises (which were not available for GP17-OCE due to COVID manufacturing delays). Membrane filtration was completed using 25mm 0.45 µm Supor membranes in a Swinnex filter holder, which at select euphotic zone samples was preceded by filtration through a second Swinnex filter holder containing a 25mm 5 µm polycarbonate filter.

In total, 12,943 bottles were filled from the GTC system (Table 1). The sampling order at each station is designated by the order of samples on the cast sheets.

Table 1. Number of bottles filled for each type of sample

Sample parameter (PI name) – Bottle volume	Unfiltered	Filtered
Salinity (ODF) – 200 mL	1242	
Macronutrients (ODF) – 30 mL	1242	
Dissolved oxygen (ODF, for sensor calibration) – 100 mL	23	
Single-cell metals ICPMS (Hawco, unfunded) – 15 mL	22	
Cell quotas SXRF (Twining) – 1 L	14	
Iodine speciation (Hardisty) – 125 mL amber		616
Nanonutrients (Cutter) – 30 mL		51
Barium (Horner) – 60 mL		616
Dissolved trace elements (Shiller, unfunded) – 125 mL		613
Dissolved cobalt (Saito) – 60 mL		616
Labile cobalt (Saito) – 60 mL		520
Shipboard zinc (Cutter) – 60 mL		448
Zinc speciation (Hawco) – 250 mL		616
Nickel/cadmium speciation (Hawco) – 250 mL		556
Shipboard Al & Mn (Resing) – 100 mL		616
Shipboard dissolved iron (Sedwick) – 125 mL		556
Dissolved iron (Sedwick) – 125 mL		555
Dissolved metals (Fitzsimmons) – 250 mL		616
Ultrafiltered soluble metals (Fitzsimmons) – 500 mL		483
Iron ligands (Bundy/Buck) – 500 mL		483
Fe, Zn, Cd isotopes (Conway) – 2 L		588
Ultrafiltered Fe isotopes (Conway/Fitzsimmons) – 2.5 L		45
Lead isotopes (Boyle/Marcantonio) – 2 L		535
Copper & nickel isotopes (John) – 1 L		533
Mercury speciation (Lamborg) – 2 L	14	505
Siderophores (Repeta/Boiteau) – 4 L		542
Dissolved metals (John) – 125 mL		84
Labile metals (John) – 1 L		52
Ultrafiltered Cu and Ni isotopes (John) – 2.5 L		34
Ultrafiltered soluble Th (Anderson) – 3.5 L		62
0.45 µm Supor membrane samples		601
5 µm Polycarbonate membrane samples		142
0.45 µm Supor membrane procedural blanks		42
5 µm Polycarbonate membrane procedure blanks		14

4.2 ODF Rosette

The 36-place Scripps ODF rosette was used to sample water for less contamination-prone elements (Table 2). Cutter (ODU, co-cruise leader), along with Marty Fleisher (LDEO) and Jule Middleton (WHOI) were responsible for managing the water budget and overall sampling of the ODF rosette. The ODF group was responsible for maintenance and calibration of the rosette

bottles and instrumentation. Costs associated with management of the rosette and sample collection on this cruise was covered by a sub-award to G. Cutter (NSF Grant OCE-2023315).

Sampling order for gas and unfiltered samples was: CFCs, He, ODF O2, O_2/Ar (where collected, see ODF sample log appendix), $\delta^{15}N$-N_2O (where collected), pH, DIC, $\delta^{13}C$-DIC, H_2S (in the upper 1500m of the water column), ^3H (where collected), salts and nuts, total alkalinity, and $\delta^{18}O$-H_2O. These samples were collected from the first bottle of each depth.

Table 2. PI, parameters, and samplers of ODF rosette. For samples collected by the ODF technicians, total number of bottles filled is provided.

Role/PI	Parameter	Total bottles	Sampler
Leader/Bottle cop			Greg Cutter
Super tech			Marty Fleisher
Super tech			Jule Middleton
	ODF O_2		Susan Becker/Andrew Barna
	ODF salts and nuts		Susan Becker/Andrew Barna/Mike Kovatch
Chappell	DNA/RNA		Ben Twining
Twining	Pigments		Ben Twining/Paula Daluz
Repeta	Fe isotopes, Genomics		Iulia Streanga
Middleton/German/Jenkins	^3He		Jennifer Middleton
Casciotti/Bourbonnais/ Hemming	N_2O	1416	Jim Happell/ODF super techs
Happell	CFCs		Jim Happell
Woosley	pH, DIC, TA	748, 712, 714	Jiyoung Moon
Charette	Ra		Margot Debeyser
Cutter	H_2S, DOS	520	Nicole Buckley
Buesseler	^{237}Th		Wokil Bam
Anderson/Hayes	Th/Pa	537	ODF super techs
Basak/Hemming	Nd/REE	526	ODF super techs
Brzezinski	$\delta^{32}Si$	526	ODF super techs
Knapp	$\delta^{15}N$-NO_3	67	ODF super techs
Quay	$\delta^{13}C$-DIC, O_2/Ar	668/89	ODF super techs
Sigman	$\delta^{15}N$-NO_2, $\delta^{15}N$-NO_3	872	ODF super techs
Sikes/Wagner	$\delta^{18}O$-H_2O	722	ODF super techs

Cast types included ‘Demi’ station casts to 1000 m, and for Full and Super stations, shallow casts to 800-1400 m, intermediate casts from 1000-2600 m, and deep casts to within 15 m of the

bottom. At each full and Super station, an additional cast of the ODF rosette was conducted to sample large volumes for pigments, Radium, and Thorium isotopes (PigRaTh cast). On the PigRaTh casts, eight depths were selected to match the shallowest eight pump depths. Another four depths were chosen for resolution of Th-234, and a surface bottle was tripped for a 13th sample depth. The surface bottle was used primarily to sample dissolved gases at the sea surface, rather than drawing these samples from the tow fish or the ship's underway system. Surface bottle sampling also occurred at demi stations (13 depths sampled instead of 12).

Pigments were sampled from the shallowest 4-6 depths on every PigRaTh cast; typically the surface sample was taken via the arriving fish to free-up water on the rosette. Pigments were collected into 2L amber bottles, triple rinsed with sample prior to filling. They were immediately filtered under vacuum through 25 mm GF/F filters. They were folded and placed inside aluminum foil packets, labeled with appropriate GEOTRACES numbers, and frozen at -80 °C.

For details on CTD instrumentation, data processing, nutrient, salts, and oxygen measurements at sea, please see ODF report.

Table 3. Overview of samples taken by the ODF Super Techs. Note that this overview does not account for samples taken by the Towed Fish. Towed Fish samples are accounted for in the GTC sample log.

Stn #	Cast Type	Casciotti $\delta^{15}N$-N_2O	Quay $\delta^{13}C$-DIC	Quay O_2/Ar	Marconi $\delta^{15}N$-NO_3	Knapp $\delta^{15}N$-NO_3	Wagner $\delta^{18}O$-H_2O
1	ODF Shallow	24	12	0	18	7	13
1	ODF Deep	24	12	0	12	0	13
1	PigRaTh	2	1	7	2	1	1
2	Demi	0	13	2	19	7	14
3	ODF Shallow	48	12	0	18	7	13
3	PigRaTh	4	1	2	2	1	1
3	ODF Intermediate	48	12	0	12	0	13
3	ODF Deep	48	12	0	12	0	13
4	Demi	0	13	2	19	7	14
5	Demi	0	13	7	19	7	14
6	ODF Shallow	24	12	0	18	7	13
6	PigRaTh	2	1	2	2	1	1
6	ODF Deep	24	12	0	12	0	13
7	Demi	0	13	2	19	7	14
8	ODF Shallow	25	12	0	18	7	13
8	PigRaTh	2	1	2	2	1	1
8	ODF Deep	24	12	0	12	0	13
9	Demi	0	13	7	19	7	14

10	ODF Shallow	24	12	0	18	0	13
10	PigRaTh	2	1	2	2	0	1
10	ODF Deep	24	12	0	12	0	13
11	Demi	0	13	2	19	0	14
12	ODF Shallow	24	12	0	18	0	13
12	PigRaTh	2	1	2	2	0	1
12	ODF Deep	24	12	0	12	0	13
13	Demi	0	13	7	19	0	14
14	ODF Shallow	48	12	0	18	0	13
14	PigRaTh	4	1	2	2	0	1
14	ODF Deep	48	12	0	12	0	13
14	ODF Intermediate	48	12	0	12	0	13
15	Demi	26	13	2	19	0	14
16	ODF Shallow	24	12	0	18	0	13
16	PigRaTh	2	1	2	2	0	1
16	ODF Deep	24	12	0	12	0	13
17	Changed to Tow Fish only	0	0	0	0	0	0
18	ODF Deep	24	12	0	12	0	13
18	PigRaTh	2	1	2	2	0	1
18	ODF Shallow	24	12	0	18	0	13
19	Changed to Tow Fish only	0	0	0	0	0	0
20	ODF Shallow	48	12	0	18	0	13
20	PigRaTh	4	1	2	2	0	1
20	ODF Intermediate	48	12	0	12	0	13
20	ODF Deep	48	12	0	12	0	13
21	Changed to Tow Fish only	0	0	0	0	0	0
22	ODF Shallow	24	12	0	18	0	13
22	ODF Deep	24	12	0	12	0	13
22	PigRaTh	2	1	7	2	0	1
23	Demi	0	13	2	19	0	14
24	Demi	0	13	2	19	0	14
25	ODF Shallow	24	12	0	18	0	13
25	PigRaTh	2	1	5	2	0	1
25	ODF Deep	24	12	0	12	0	13
26	Demi	0	13	2	19	0	14
27	ODF Shallow	48	12	0	18	0	13

27	PigRaTh	4	1	2	2	0	1
27	ODF Intermediate	48	12	0	12	0	13
27	ODF Deep	48	12	0	12	0	13
28	Cancelled due to ice	0	0	0	0	0	0
29	ODF Shallow	24	12	0	18	0	13
29	ODF Deep	23	12	0	12	0	13
30	Demi	0	13	2	19	0	14
31	Changed to Tow Fish only	0	0	0	0	0	0
32	ODF Shallow	24	12	0	18	0	13
32	PigRaTh	2	1	2	2	0	1
32	Radium Cast	4	2	0	4	0	2
32	ODF Deep	20	10	0	10	0	11
33	Changed to Underway sampling only	0	0	0	0	0	0
34	Deep Demi	24	12	0	12	0	13
35	ODF Shallow	24	12	0	18	0	13
35	PigRaTh	2	1	5	2	0	1
35	ODF Deep	24	12	0	12	0	13
36	Deep Demi	24	12	0	12	0	13
37	ODF Shallow	48	12	0	18	0	13
37	PigRaTh	4	1	2	2	0	1
37	ODF Intermediate	40	10	0	10	0	11
37	ODF Deep	48	12	0	18	0	13
38	Shelf	12	6	2	12	0	7
Total Samples Collected		**1416**	**668**	**89**	**872**	**67**	**722**

ODF Rosette-Filtered Water Samples

Filtered samples were collected from a separate Niskin bottle. The order of collection for filtered samples was NO_2^-/NO_3^-, $\delta^{32}Si$ (where collected), Th/Pa, and Nd/REE. Filtered samples were collected through Acropak filters (nested 0.8, 0.45 um filter capsules). These filters were reused on similar casts (shallow, intermediate, or deep), drained, and kept refrigerated between uses. Tubing for filters was reused for every cast, rinsed with milliQ water between casts. There were 36 filters in use at any one time, with 12 in use for shallow and demi cast depths, 12 in use for intermediate cast depths, and 12 in use for deep cast depths. One filter was used exclusively for all depths on the shelf stations, and then discarded.

Nutrients were sampled from every bottle from which a sample was taken. O_2 and salts were collected from one (usually the first) bottle at every depth. The range of samples collected in this way were:

1) $^{15}N\text{-}NO_3$ (60 ml bottles) samples in the oligotrophic gyre (stations 1-9) were collected for Angie Knapp at the shallowest 8 depths from each station; 7 depths from the shallow cast and the surface water sample from the PigRaTh cast. Samples were stored frozen at -20°C. Total number of samples collected was 72.
2) $^{15}N\text{-}NO_3$ (60 ml bottles) samples at all depths and all stations were collected for Dario Marconi/Danny Sigman. Total number of samples collected was 872.
3) Dissolved Mn (60 ml bottles) samples were taken on selected casts at a few stations to assist Jess Fitzsimmons track potential hydrothermal plume signals.
4) Si isotope samples (2 liter bottles) were collected for Mark Brzezinski. He requested 4 liter samples (2 x 2 liter bottles) at depths shallower than 400 m for stations North of ~57° S and 2 liter samples at all other depths and stations. Water was collected and stored at ambient temperatures on the ship in pallet boxes provided by the Brzezinski group. Total number of samples collected was 532.
5) Nd isotope and Rare Earth Element (REE) samples were collected for Chandranath Basak and collaborators. Samples were collected in 5 liter cubitainers at the rosette, Samples were acidified with 20 ml of 6M Hydrochloric Acid, caps were parafilmed and the cubitainers were double bagged before being stored at ambient temperatures in pallet boxes on the main deck. A few samples for Nd and REE were collected from the arriving fish at select stations. Post sample collection treatment was identical to the rosette samples. Total number of samples collected was 536.
6) Th isotope (^{232}Th and ^{230}Th) and ^{231}Pa samples were collected for Chris Hayes and collaborators. Sampling procedures and sample processing was identical to Nd/REE methods. Total number of samples collected was 547.

Reported sampling issues:
Water budgets were prepared based on requested water amounts from each group. In some instances, the 'gas' bottle contained less than the expected amount of water. In such cases, water was sometimes borrowed from the bottle used for filtered samples.

On occasion, when a 30-L Niskin bottle deployed with the McLane pumps did not close properly, water was collected from the ODF Niskin rosette at the appropriate depths.

4.3 Monocorer

Brief history of monocorer
Since the GP16 cruise in 2013, the monocorer, a small gravity coring device made and sold by the folks at NIOZ, has been used to collect surface sediments at station locations on US GEOTRACES cruises (GP16, GN01, GP15, and now GP17-OCE). A cloaking device (six triangular pieces of plastic) was used with the monocorer to allow its use with an altimeter (a device attached to the CTD rosette frame which measured the distance between the rosette and the seafloor, starting when the distance is less than 100 meters).

Early problem
The monocorer had been borrowed by a colleague and made it back to Lamont only a few days before all of our gear was shipped to San Diego for mobilization at the SIO Marine Facility. To

make shipping back to us easier, the cloaking device was disassembled. Reconfiguring the cloaking device took longer than expected, so the monocorer was first deployed at Station 3, cast 13. As seen in Figure 3, somehow the monocorer and cloaking device wrapped themselves around the 0.322 CTD conducting cable. Our best guess is that this occurred very early in the deployment, as the altimeter data from the CTD never showed a bottom depth of 25-27 meters. The 0.322 conducting cable was brand new, and it's likely that the entire rosette was rotating as it was lowered through the water. While there is no evidence that it had ever happened before, it appears that the cloaking device acted as a kite and, combined with the motion of the rosette, the entire monocorer floated above the rosette, leading to what is seen in Figure 3.

Several serious discussions took place at this point, including the suggestion that use of the monocorer be abandoned for the remainder of the cruise. Given the number of funded and unfunded projects that would make use of monocore samples, it was decided to modify the cloaking device to make it less likely to kite in the above manner. This involved drilling multiple two-inch diameter holes in each panel and retying the panels to each other, with a larger gap between them. A test deployment at a demi station (rosette maximum depth of 1,000 m in 4,000 m water column) followed, and while the monocorer pre-tripped, there was no evidence that the monocorer had kited up during this test deployment.

Figure 3. Chief Engineer working to remove the monocorer after it was deposited on top of Rosette carousel at Station 3, cast 13. Notice the loose wrap of the 5/8" diameter white line around the 0.322" conducting cable.

Ultimately, it was decided that the cloaking device would be completely removed from the monocorer to ensure that there was no repeat of the events that occurred at Station 3. The

downside to this choice was that the altimeter was going to reflect the distance between the monocorer and the altimeter for most of the deployment. As can be seen in Table 4, we were very successful (>90% successful rate) coring after removing the cloaking device. The only unsuccessful deployment was at Station 37, a continental margin site, where a significant slope made it difficult for the altimeter to even see a consistent bottom depth.

Table 4. Monocore deployments on GP17-OCE. Success rate was >90% after removing the cloaking device from the monocorer system between stations 3 and 8.

Station	Cast	Latitude (N)	Longitude (E)	Water Depth (m)	GEOTRACES #	Core Length (cm)
3	13	-25.00018	-151.24956	4658	16247	No core
8	10	-37.50024	-149.2803	5620	16639	20.3
10	9	-42.4989	-148.47194	5359	16798	19-19.5
12	10	-47.50289	-147.5176	5060	16957	19-20
14	12	-52.31024	-146.40088	4000	17159	10-11
16	8	-55.00814	-145.66114	3220	17343	12
20	14	-57.6006	-144.85502	3130	17593	8.5
22	8	-59.9969	-143.9992	3425	17688	9.5
25	10	-66.99992	-135.00062	4590	17921	23.5
27	12	-66.99626	-115.00492	4741	18113	23.8
29	8	-66.99832	-100.00236	4688	18215	25.5
35	10	-54.3519	-76.54824	3994	18544	11-12.5
37	3	-53.49912	-75.75098	3345	18652	No Core

Figure 4 shows the cores arranged by Station number. There is a clear lithology change from station 12 to Station 14 and then again between Stations 22 and 25, between the Sub-Antarctic Front and the Southern Boundary of the Antarctic Circumpolar Current. Stations 25-29 should show the strongest influence of inputs from Antarctica. It will be interesting to see if we find evidence of ice-rafted debris and other continental inputs in those three cores. Perhaps there was also a change as we moved from our West-East transect at 67°S up towards the southern tip of South America, at Station 35. Unfortunately, we ran into steep topography as Station 37, which likely played a role in our unsuccessful coring attempt at that location.

Figure 4. GP17-OCE cores arranged by Station number. The shortest cores (Stations 14-22) occur in the region of the fronts. In almost all cases, the cores showed evidence that there was loss of the bottom portion of the core, possibly at the seafloor.

This suite of cores represents an important addition to the monocores that we have already collected on previous US GEOTRACES cruises. Our goal is to split the cores, x-ray, photograph, measure physical properties, and use the LDEO XRF Scanner to make measurements of major and trace elements. The working halves of the cores will be sectioned at 1cm intervals, freeze-dried, and then made available, first to GEOTRACES investigators, and then to the wider community for other analyses.

Thanks are due the following GP17-OCE participants for their help with deployment/recovery of the monocorer, and the on-board processing of the cores themselves; Mason Schettig, Doug Penny, John Calderwood, Mike Kovatch, and Andrew Barna (ODF group SIO), Nicole Buckley and Greg Cutter (ODU), Jenny Middleton (LDEO), and Dan Ohnemus (Skidaway). Mason Schettig and John Calderwood were instrumental in helping to make modifications to the monocore system, before and after removal of the cloaking device. Craig Hunt, from the Revelle crew, welded some modifications onto the monocorer that improved its performance. Thanks are

also due the Captain and Crew of R/V Roger Revelle for all their help with the ship operations involved in the deployment and recovery of the CTD/monocorer.

4.4 McLane Pumps

The McLane pumping operations were part of Daniel Ohnemus' (Univ. of Georgia) science proposal with co-PI Phoebe Lam (Univ. of California Santa Cruz) and a subcontract to Steve Pike (WHOI). The McLane pumps were used to collect size-fractionated small (~1 to 51 micron) and large (>51 micron) particles using "mini-MULVFS" filter holders. Short-lived radionuclides (Ra quartet, Th-228, Ac-227) were collected simultaneously over two Mn-coated cartridges attached downstream of the filter holders.

4.4.1 Equipment:

In-situ pumps, wire, 30 L Niskins

WHOI provided 12 dual-flow battery-operated McLane pumps with two cartridge holders (modified WTS-LV-upright) from the WHOI UNOLS pump pool, and 6200 m of 0.322" OD Hytrel-coated non-conducting Vectran wire, MBS=5700 lbs (property of Ken Buesseler at WHOI and spliced from two previously cut sections). Two titanium pressure casings (rated to 6000 m depth; vs the 5000 m regular casings) were among the pumps brought on board.

The Vectran was spooled onto powder-coated SIO drum at MarFac prior to the cruise and deployed from the DESH-5 winch and squirt boom on Revelle. Up to eight McLane pumps were deployed at a time on a cast. The remaining four pumps were used for parts and as spares, until an incident at station 16 when all eight primary pumps were lost (see below). WHOI also supplied eight 30L Niskin bottles, plus one spare, that were mounted on the pump wire on intermediate and deep casts.

SBE 19-plus SeaCAT CTD with optical sensors

Co-PI Lam provided a SBE 19-plus SeaCAT self-recording CTD that was shackled to the end of the non-conducting Vectran wire for each pump cast until the loss of the string. The SeaCAT CTD was outfitted with the following optical sensors:

- WetLabs ECO-AFL/FL Fluorometer (S/N FLNTURTD-870) (Voltage 0)
- A Seapoint Turbidity Meter, S/N 12809 (Bishop—UCB) (Voltage 1)
- A UC Berkeley-produced prototype Particulate Inorganic Carbon sensor (S/N PIC 011) modified by collaborator Dr. Bishop from a WetLabs transmissometer (Voltage 2)
- WetLabs C-Star Transmissometer (S/N CST 1450), also on loan from Dr. Jim Bishop (UC Berkeley) (Voltage 3)

These instruments were lost at the wire-loss incident at Station 16.

Pinger

A Benthos BFP312 12 KHz pinger— provided by the WHOI SSSG pool and loaned to Steve Pike for use with the pumps—was used on near-bottom casts to determine proximity of the SeaCAT CTD to the ocean floor. The pinger was attached by hose clamps and shackles onto the SeaCAT CTD frame. When not in use, the pinger was un-powered and remained attached to the CTD. This instrument was lost in the wire-loss incident at Station 16.

4.4.2 McLane pump team:

The pump team consisted of a McLane pump "supertech", Steve Pike (WHOI), pump team PI Daniel Ohnemus (UGA Skidaway), Mariah Ricci (UGA Skidaway), Margot Debyser (WHOI-radium isotopes group), and Wokil Bam (WHOI, Thorium isotope group). Pike was responsible for pump programming and maintenance; Ohnemus led the particle processing and subsampling with help from Ricci and oversaw pump team operations; Debyser was responsible for Ra sampling from Mn-coated cartridges attached to the pumps and sampled the 30L Niskins for Ra isotopes; Bam was responsible for sampling Th isotopes and related parameters from the 30L Niskin bottles. Bam also sampled all Niskins for nutrients and salts, which were analyzed shipboard by the ODF group. All team members helped with pump deployments and recoveries.

4.4.3 McLane pump operations:

McLane pumps were programmed to fire at a pre-scheduled time, decided typically 15 to 30 minutes before taking the deck. Firing time was determined based on our best estimate of the time required to hang equipment and to wire down to final target depth (at 30 m/min), plus a small (usually ~10 minute) cushion. Until the pump loss incident at station 16, the SeaCAT CTD was deployed first and allowed to de-bubble for 1 minute just below the surface.

On intermediate and deep casts, a 30L Niskin was mounted above each pump to collect water for the radium and short-lived thorium groups. Niskin bottles were typically not mounted above pumps on the shallow casts because water for these groups was collected on the ODF PigRaTh cast that typically followed each shallow McLane pump cast. After the pump loss incident at Station 16, eight Niskins were deployed on intermediate and deep casts, hung alone without an associated McLane pump. Niskins were deployed on shallow casts at Stations 32 and 35 to compensate for depth gaps present in the GEOTRACES depths taken on other casts.

On shallow casts, the McLane pumps were mounted at wire-out readings determined from target sampling depths. On intermediate and deep casts, a 30L Niskin was mounted first, then a McLane pump was mounted 1-2 m below the Niskin. A Teflon-coated messenger with a long lanyard to bypass the pump was attached to the Niskin and the messenger was clipped below the pump, thereby bypassing the Niskin and pump pair. After loss of an incompletely attached messenger at Station 8, the ship's Chief Engineer helpfully drilled out a spare 0.25" diameter messenger (which didn't fit the wire) to fit the Vectran. On casts with Niskin bottles, a blank messenger was dropped halfway (2 h) through the pumping time to close the Niskin bottles. (At Station 3, during an intermediate cast, the messenger was instead dropped near the end of the cast but before final recovery.)

McLane pumps are typically attached to the tension-member using a pump-mounted clamp (top clamp) and a free clamp (bottom clamp) which is attached to the wire just before the pump. After loss of the string (and all associated clamps) at Station 16, only two spare clamps remained aboard, limiting the number of pumps that could be deployed to three: two on clamps and one shackled to the bottom of the wire. Ship's engineers arranged the welding of a set of clamp inserts to a ship-owned book clamp (Fig. 5) to allow deployment of all four remaining McLane pumps (three on clamps and one shackled to the bottom of the wire above a 200 lb pig weight).

Figure 5. Pump clamp welded by ship's engineers following loss of McLane pumps and associated clamps.

4.4.4 McLane pump cast statistics:
Summary of how many and where McLane pumps were deployed:

- A full set of 8 McLane pumps was deployed on 14 casts (8 stations) including the loss of the string at Station 16.
- At reduced set of 3 McLane pumps was deployed on 7 casts (4 stations).
- A single pump was deployed to sample the mixed layer at Stations 18 and 20.
- At stations 27 through 37, four McLane pumps were deployed on all casts.
- The total number of pumps deployed was 169.
- Including dipped blank filters, we collected 209 of each of QMA pairs, Supor pairs, QMA-prefilters (Qp), and Supor-prefilters (Sp).
- The total volume filtered in-situ by pumps was about 171,316 L over the whole cruise.

4.4.5 Particle Sample collection:
Each pump contained two "mini-MULVFS" style filter holders (Bishop et al. 2012) plumbed into the pump head. One holder was loaded with a 51-micron polyester mesh prefilter (underlain by a 150-micron polyester mesh support filter) above paired 0.8-micron polyethersulfone Supor membrane filters on a separate stage (0.8-51-micronsize fraction) for contamination prone TEIs; the second holder was loaded with a 51-micron polyester mesh prefilter (underlain by a 150—micron polyester mesh support filter) above paired Whatman QMA quartz fiber filters underlain by a 150-micron polyester mesh support filter on a separate stage (1-51-micron size fraction) for particulate organic carbon and TEIs requiring higher volumes (e.g. short-lived radionuclides). The 51-micron prefilters over the Supor and QMA filters are referred to with the suffixes "Sp" and "Qp", respectively. Typically, the volumes filtered through the Supor and QMA sides were ~400 L and 1100 L, respectively. One of the pumps ("Pump 3") had a larger top plate that

allowed the attachment of two additional filter holders loaded with a Supor set and a QMA set of filters, each filter set overlain by a 0.2 –micron Supor to act as a particle prefilter. These holders were not plumbed into the pump head, but were exposed to seawater for the duration of the cast and functioned as seawater/process blanks ("dipped blanks") for each filter type (i.e., Sp, Qp, Supor, QMA).

Please refer to the narrative from the Radium group for details and statistics about the Mn-coated cartridge sample collection.

4.4.6 Particle sample handling and subsampling:

Excess seawater in the headspace of filters holders was sucked down on deck using an aspirator pump before removing filter holders from the pump. Filter holders were brought into the main lab bubble, and sample processing began within an hour (usually within half an hour) of recovery of all pumps.

In the bubble, filter holders were again connected to a vacuum pump to remove excess seawater before disassembling. Digital photographs were taken under constant lighting conditions of each of the four filters to come off a pump (Qp, Sp, Q, S for QMA prefilter, Supor prefilter, QMA, and Supor, respectively). Dipped blank samples were processed first, then filters were processed from shallow to deep.

Table 5 summarizes the recipients of particle subsamples, the TEIs measured, and processing requirements. A total of 16 groups will receive particle subsamples to analyze over 23 TEIs. Filter subsamples that needed to be frozen or rinsed were subsampled immediately. Remaining QMA filters were dried in a 55°C oven in a 150 mm petri dish. Qp and Supor samples that could be stored dry were first dried in a laminar flow hood on egg crate grids for >12 hrs, and then subsampled and bagged for distribution.

Table 5. Particle subsamples

PI(s)	Parameter(s)	Filter(s) Sub-sampled	At-Sea Personnel
Basak	eNd, REEs	Qp, Supor	None
Brzezinski	Si isotopes	Supor	None
Buesseler	234-Th, 228-Th	Sp, QMA	Bam, Pike
Charette/Horner	226-Ra, Ba isotopes	QMA, Supor	Debyser
Cutter	Sulfides (acid-volatile and Cr-reducible)	QMA, Supor	Cutter, Buckley
Hardisty	Iodine	QMA	None
Hayes/Anderson	230-Th, 231-Pa	Qp, Supor	Fleisher
John	TM isotopes	Supor	None
Lam/Ohnemus	Particulate TEIs	Qp, Supor	Ohnemus
	Part. Inorganic Carbon	Qp, QMA	Ohnemus
	Biogenic Silica	Qp, Supor	Ohnemus
	Particulate C and N isotopes	Qp, QMA	Ohnemus

Mason/Lamborg	Particulate Hg	Qp, QMA	Despins
Repeta	Particulate ligands	QMA	Streanga
Saito	Proteins	Qp, QMA	None
Stephens	7-Be	QMA	He

4.4.7 Transmissometer Maintenance:

Transmissometer windows were cleaned before and after each deployment with a Kimwipe wetted with dilute Dawn detergent, a liberal MQ water rinse, and wiped dry with a Kimwipe. On-CTD readings of Vair (unblocked beam) and Vdark (blocked beam) were taken every few stations. Windows were cleaned until Vair was maximized.

Transmissometers from the three main systems (GTC, ODF, McLane pumps) were intercalibrated off-CTD by taking readings of Vair and Vdark powered by a 12V power supply and read by a multimeter pre-cruise and at the end of the cruise. On-instrument readings for these values were taken after attachment to their respective systems immediately after the pre-cruise in-laboratory calibration.

4.4.8 Problems encountered:

Initial spooling onto the drum, bad wraps:

Shore-side level-winding onto the drum at MarFac prior to the cruise appears to have left several bad wraps near the base of the drum, which disturbed the lay of the wire on the drum at sea. This problem was exacerbated by poor behavior of the Vectran at the cheeks of the drum. No casts on the cruise were deep enough to fully spool-off the offending wraps, so the Chief Engineer (Tom Johnson), who helped oversee the initial spooling at MarFac, was thankfully present at the winch drum to monitor and adjust spooling during nearly all pump recoveries on the DESH-5 winch.

Wire damage incident due to squirt boom "creep" (03-Jan-2022, Station 1):

During recovery of the first full pump cast on the Vectran, boom "creep"—slow continued inboard movement of the squirt boom after stop—led to the wire imperceptibly lowering during recovery of the first pump. The tension of the seven submerged pumps and CTD dragged a still-attached pump clamp up the wire, damaging the Hytrel coating at around 789 m of payout. The Vectran tension core did not appear damaged, but the core was exposed for several inches. Given the high expected use of that section of wire, the decision was made to cut and remove the ~800 m of Vectran below the damaged section and re-terminate.

DESH-5 winch issues:

Several problems with the DESH-5 winch led to delays and difficulties deploying scientific equipment on the Vectran hydrowire, cancelation of pump casts, and temporary movement of the pump deployments to a metal hydrowire. (These issues are separate from the pump loss incident described in the next section.)

Power loss to the DESH5 winch at Stn 10:

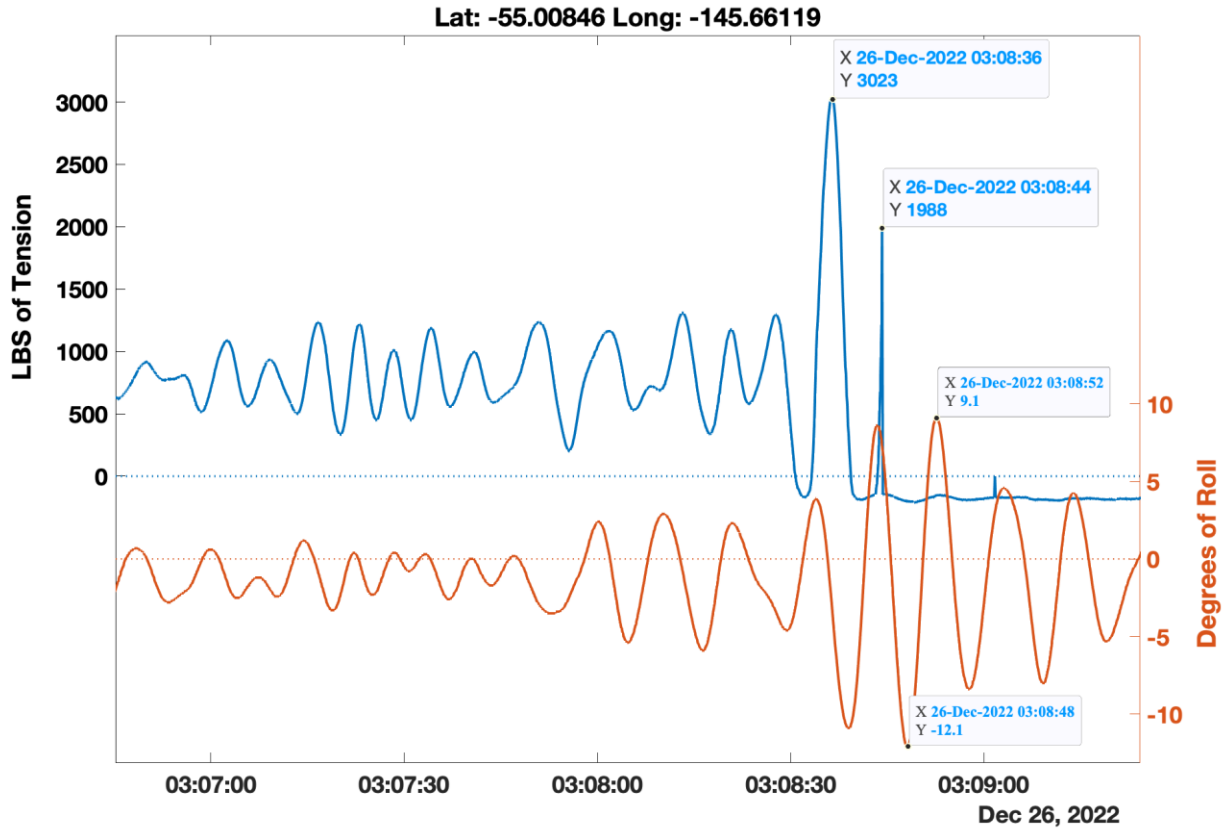
During recovery of the final pump and CTD at Station 10 on 16-Dec-2022, with 309 m of wire still in the water, loss of primary ship's power due to an unrelated engineering incident

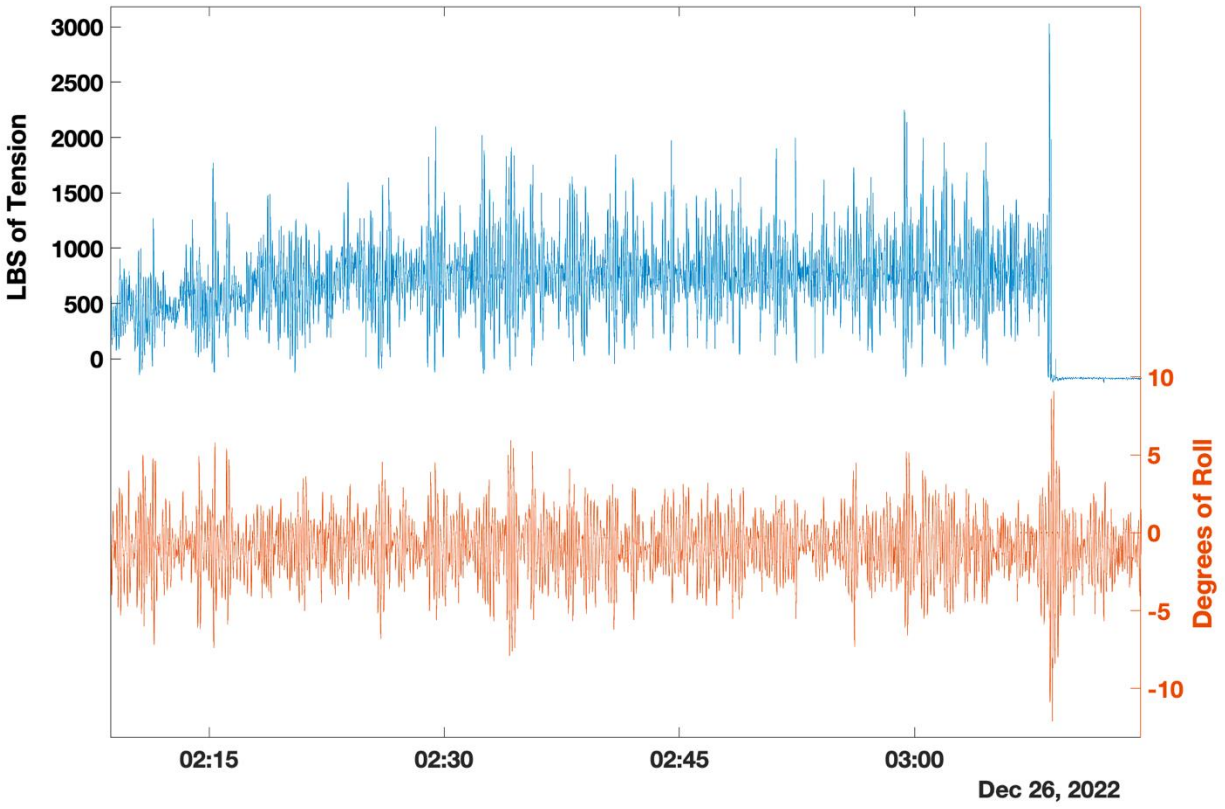
interrupted power to the DESH-5 winch. After ship's power was restored, the winch could not be restored to operating condition within a few hours. The final ~300 m of wire, McLane pump, and CTD/pinger were hauled aboard by hand by the science party and deck crew after redirecting the wire to the deck using a snatch block. The deep pump cast at this station was canceled due to inoperability of the DESH-5 winch. After extensive communication with shore-based support teams over the next few days, the DESH-5 winch was restored to working condition before the next planned pump station (station 12).

Payout/Speed Indicator Problems with the DESH-5 during Stn 22 and 25:
Beginning at station 22 on 01-Jan-2023, the DESH-5 winch began showing intermittent payout/speed readout failures. Due to the non-conducting nature of the Vectran wire, payout and speed readings from the winch are required to deploy the pump equipment, so this failure at first delayed and ultimately canceled deployment of the pumps on the trace metal Vectran wire for several casts. A deep pump cast at station 22 was canceled. Pumps were deployed at Station 25 on the (metal, 0.322") ODF hydrowire as a stopgap measure. Deployment on the metal hydrowire allowed collection for organic/biological parameters but contaminates for many trace metal GEOTRACES parameters, reducing value of the pumped particle samples at Station 25.

Pump loss incident (12/25/2022):
During the soak of eight McLane pumps and the SeaCAT CTD at station 16 on 25-Dec-2022, with 800 m of Vectran out at 55.00846ºS/145.66119ºW—during Christmas dinner—a series of unexpected swells across the beam of the ship led to the parting of the Vectran tension-member. Lost were eight McLane pumps and batteries, the SeaCAT profiling CTD (Lam, UCSC) and all attached optical equipment provided by UC Berkeley, the WHOI SSSG Benthos pinger, eight bottom McLane pump clamps, and 18 mini-MULVFS filter holders and filters. At the time, no 30L Niskin bottles were on the wire.

Sea state and weather conditions at the time were not especially poor relative to conditions already experienced on the cruise: sea state 4, 25-kn winds, and otherwise consistent swell direction. Surface currents measured by shipboard ADCP were approximately 0.5 knot moving south. Figures detailing the measured tension on the DESH-5 winch (recorded at 10 Hz) and the degrees of roll of the ship are shown in the following pages in the (upper panel) two minutes before the wire loss, and (lower panel) the hour before the wire loss. Annotation boxes in the figures show specific values for tension and roll at key times.


Lat: -55.00846 Long: -145.66119
X 26-Dec-2022 03:08:36
Y 3023
X 26-Dec-2022 03:08:44
Y 1988
X 26-Dec-2022 03:08:52
Y 9.1
X 26-Dec-2022 03:08:48
Y -12.1
LBS of Tension
Degrees of Roll
3000
2500
2000
1500
1000
500
0
10
5
0
-5
-10
03:07:00
03:07:30
03:08:00
03:08:30
03:09:00
Dec 26, 2022


LBS of Tension
Degrees of Roll
3000
2500
2000
1500
1000
500
0
10
5
0
-5
-10
02:15
02:30
02:45
03:00
Dec 26, 2022

Wire tension during the deployment and first hour of soak were typical for the sea state, reaching peaks of ~1500-2000 lbs of tension during larger rolls and with a static load of ~800 lbs typical of eight-pump casts. The largest tension spike before the wire loss, reaching 3023 lb at 03:08:36 GMT, was followed by a gradual decrease indicating the wire was still intact. A second rise in tension occurred approximately ten seconds later and is interrupted by a much sharper loss of tension when the wire parted. The tension data therefore seems to indicate that the wire did not fail due to tension alone.

Visual inspection of the wire suggests wire failure was in part due to mechanical slicing or severing, likely when tension returned (measured at 03:08:44 as an instantaneous loss of tension). Inspection of the remaining ship-board section of wire shows a clear slice through the wire's jacket and approximately half of the strength-member fibers (see photos below). Longer, tension-stretched fibers are also present, likely stretched to failure after the rest of the tension core was cut.

No saved video footage of the incident exists, which would have improved our ability to discern the exact mode of wire failure. A likely scenario is that slacking of the wire under low tension allowed it to jump the sheave into or onto the small gap between the sheave and the block cheek. When tension returned, the upper edge of the sheave cut the wire. The shipboard section of the wire snapped over to the port side of the ship and was found laying on the roof of the CFC analytical van on the 02 Deck. Nobody was hurt in the incident.

After the wire loss, the ship's Restech (Mason Schettig) and Captain (Tom Desjardins) prepared a dragging apparatus (two quad-hooks chained to an 800 lb pig weight) which was deployed from the traction winch in an attempt to recover some or all of the equipment. Over 12 hours the ship made three slow passes over the loss site and slightly south of the loss coordinates at slightly different angles of attack. Wire tension was monitored during each drag and was fairly stable during the dragging, indicating a level bottom. The only tension increase was noticed during the third pass and was consistent with the weight of the gear (approximately 800-1000 lbs in water). The wire was recovered each time to inspect for recovered gear, but ultimately no gear was recovered.

CTD issues:
Several casts in the first few stations were plagued by "Stop CMD received" errors from the SeaCAT CTD, leading to no data below a few meters of depth at the start of the cast, likely due to shorting of the communications pigtail. After several unsuccessful attempts to re-seat and re-route the communications pigtail, replacement of the pigtail dummy with a used spare seems to have corrected the problem.

The CST-1450 transmissometer suffered from intermittent data outages at depth on several casts, likely due to a bad Y-cable. Wiggling/re-orienting the cable in specific directions at the transmissometer could reproduce the drop-outs on deck, so the transmissometer-end of the cable was resecured in several different positions between casts to fix the drop-outs but without much success. (No shipboard spare of the Y-cable existed to allow full replacement.) Full removal and cleaning of the Y-data cable and all connectors and re-seating/re-running seems to have fixed the issue at Station 12.

McLane Pump issues:
a) The sum of the QMA and Supor flowmeters should be within 5% or so of the reading of the final (pump exhaust) flowmeter. If the final flowmeter is significantly greater than the sum of the QMA and Supor flowmeters, this indicates a leak in the plumbing, often associated with a Mn cartridge holder that is not sealed. In these cases, the QMA and Supor volumes are generally lower than usual, but should be OK. However, the appropriate volume to be used for the Mn cartridges may not be easily recoverable depending on which cartridge holder leaked.
b) the ratio of volume filtered through the Supor/QMA sides is typically 0.38. If the ratio deviates significantly from this a leak in the Supor or QMA flowmeters may be indicated.
c) We had 25 failed (zero or low-volume) pumps out of a total of 169 deployed (14.7% failure rate). Failed pumps were generally due to one of the following problems:

i) corrosion and/or seawater-shorting of the pump motor pins which connect the pressure casing to the pump motor. The McLane pump error for this is typically "sudden flow obstruction", "sudden pressure release" or indicated by a pre-mature "normal shutdown" after only a few liters of pumping (due to low flow indicated by the pump motor). These failure modes worsen in cold deck air temperatures waters when the cabling fits were poor. After the pump loss incident at station 16, already under-performing/flaky pumps were brought into service and spare cables (from unused pumps) were not available. The only solution was to carefully clean all pins and make sure the plugs were dry and properly seated between casts. This frequent re-seating of the cables helped to some degree, as did keeping the pumps in a plastic-sheeting "tent" between casts, heated using a small space heater. Starting after Station 27, when 3 of 4 pumps failed on a deep cast, all pump motor cable terminations were again cleaned and the cables "sealed" to the pump motor and pressure casing using a silicon caulking bead spread inside the end of cable. This improved connectivity and reduced failures in the final third of the cruise.

ii) corrosion in the communication pins on the pressure casing: the McLane pump error message for this is "stopped by user". The solution is to carefully clean the comms pins and make sure the dummy plug was dry, properly seated, and sealed.

30L Niskin issues:

Several 30L Niskin bottles failed to trip, typically due to the messenger lanyard getting caught underwater on various pump or Niskin bottle hardware after release. When this happened, water for the Ra and short-lived thorium groups was often obtained from the ODF rosette cast.

4.5 Tow-fish

The Fitzsimmons group (TAMU) provided the tow-fish clean sampling system for obtaining trace metal clean surface water samples. The system was newly constructed and, for the first time by U.S. GEOTRACES, was used instead of the aging "GeoFish" system originally built by Geoffrey Smith at UC Santa Cruz. The Fitzsimmons lab tow-fish system consisted of a weighted torpedo (PVC) connected to deck with Amsteel blue line via a urethane-coated aluminum block (Sherman-Reilly, 74 Series, 16'' diameter) and 19' powder-coated aluminum boom mounted to the port side of the vessel on the main deck. While the Amsteel blue line held the tension, a ¾'' OD Bev-a-line tube (non-load-bearing) was taped to this line at regular intervals and passed through the block to the torpedo, where it was attached to the torpedo's front through a PVC elbow and secured with a PVDF compression fitting. The boom was attached to a purpose-built mount that was bolted to the deck on the port side of the ship, just aft of the Hydro Lab. A forward stay was attached on the 01 deck, and the boom was lifted with a deck plate mounted on the 02 deck just aft of the CASS-5 winch. The boom also had an aft line attached to the port side of the ship (primarily used for recovering the boom), and an Amsteel "safety" line was also attached from the back of the torpedo to the tip of the boom.

Seawater was drawn through the tubing with a Teflon bellows pump. The pump was powered by the ship's compressed air located just aft of the Hydro Lab. A length of Bev-a-line tubing ran from the bellows pump, through the pass-through into the Hydro Lab, across the Hydro Lab, through the pass-through across the "Route 66" hallway, through the pass-through into the Wet Lab on top of the staging bubble, through the pass-through to the starboard main deck, along the inboard bulkhead, through the pass-through into the Main Lab, and into the main lab bubble. At the start of the cruise, the pressure on the bellows pump was set at 35 psi for priming and then lowered to 30 psi for pumping, which averaged 4 L per minute. By the end of the cruise, the pressure on the bellows pump has been raised to 60 psi to prime and then set at 50 psi to maintain the same flow.

Tow-fish sampling was led by Yerim Kim (TAMU), and deployment, recovery, and general fish maintenance was done by Yerim Kim (TAMU), Jess Fitzsimmons (TAMU), Dylan Halbeisen (USF), Kristie Dick (TAMU), and Phil Kong (USC), with the generous assistance of many others. Tow-fish sampling occurred just before arrival at every station ("arriving fish," also called "Cast 1") and when possible at the halfway point between stations ("intermediate fish," with a "0.5" station number).

One of the most significant issues with the tow-fish was the significant swell on the GP17-OCE transect. While we were able to control the porpoising and inboard/outboard position of the fish by changing how much tubing/line was out from the tip of the boom to the torpedo, the high

swell still put a lot of tension on the fish. Unfortunately, we lost one fish torpedo to the sea in rough seas on 12 December between Stations 6 and 7. The Amsteel blue line remained intact, but the torpedo and its shackle were missing, suggesting that the shackle gave way, despite its zip tie mousing. We rebuilt the tow-fish with a spare torpedo, and we moused every shackle with stainless steel mousing line. We also changed the operations so that we recovered the fish anytime the true wind speed exceeded 30 knots. We also deployed the fish for the minimal amount of time required for sampling when we were in areas that might have had sea ice; this assuaged the concerns of the bridge and the tow-fish teams.

Inside the main lab bubble, a new style of sampling manifold was constructed whereby three sampling stations were teed off through PTFE ball valves (PlastOmatic, TruBlue): one for permanent Acropak-1500 filtration (0.8/0.2 µm), one for permanent unfiltered sample collection, and one for flexible use. There was an additional ball valve downstream of the sampling tees to force water through the tees when necessary (the "throttle"). Unfortunately, the TruBlue valves did not have a perfect fit into the ¾''-1/2'' adapter fittings through which they were led, which contributed to significant leaks that were a constant struggle with the fish sampling system. Yerim Kim worked very hard to prevent contamination via leaking drops in this system; slower overall flow rates did help. The Acropak-1500 capsule filters were changed before the cruise, on 12/18/2022 (before Station 10.5), on 12/27/2022 (before Station 18), and on 1/12/2023 (before Station 29).

In total, 1169 bottles were filled from the GTC fish system. The sampling order at each station is designated by the order of samples on the cast sheets.

Table 5. Total bottles filled from towfish.

Sample parameter (PI name) – Bottle volume	Unfiltered	Filtered
Salinity (ODF) – 200 mL	54	
Macronutrients (ODF) – 30 mL	55	
DNA samples (Chappell) – 10-20 L	54	
Pigments (Twining) – 2-4 L	39	
Cell quotas SXRF (Twining) – 1 L	18	
Dissolved inorganic carbon (Woosley) – 250 mL	2	
Alkalinity (Woosley) – 250 mL	2	
Spectrophotometric pH (Woosley) – 100 mL	34	
Radium (Charette) – 20 L	1	
Dissolved organic nitrogen & isotopes (Knapp) – 30 mL		17
Iodine speciation (Hardisty) – 125 mL amber		55
Nanonutrients (Cutter) – 30 mL		18
Barium (Horner) – 60 mL		55
Dissolved trace elements (Shiller) – 125 mL		37
Dissolved cobalt (Saito) – 60 mL		37
Labile cobalt (Saito) – 60 mL		37
Shipboard zinc (Cutter) – 60 mL		36
Zinc speciation (Hawco) – 250 mL		56

Nickel/cadmium speciation (Hawco) – 250 mL		35
Shipboard Al & Mn (Resing) – 100 mL		38
Shipboard dissolved iron (Sedwick) – 125 mL		54
Dissolved iron (Sedwick) – 125 mL		54
Dissolved metals (Fitzsimmons) – 250 mL		55
Ultrafiltered soluble metals (Fitzsimmons) – 500 mL		21
Iron ligands (Bundy/Buck) – 500 mL		37
Fe, Zn, Cd isotopes (Conway) – 2 L		45
Lead isotopes (Boyle/Marcantonio) – 2 L		32
Copper & nickel isotopes (John) – 1 L		36
Mercury speciation (Lamborg) – 2 L		22
Siderophores (Repeta/Boiteau) – 4 L		37
Th & Nd isotopes (Anderson) – 5 L		12
Dissolved sulfides	27	27
Silicon isotopes (Brzezisnki) – 2 L		7

5. Individual labs/PI reports

5.1 ODF

Please see the accompanying file "GP17-OCE_ODF_cruise_report.pdf" for the full report on activities from the Ocean Data Facility group.

5.2 Bottle particles

PI: Ben Twining
At sea: Laura Sofen and Emily Frett

Suspended particulate matter samples were collected at all stations and nearly all depths using the GTC system (following damage to the GTC rosette, one bottle position became unusable, and the bottle particle team thus gave up one depth on each cast). Particulate samples were collected directly from GO-FLO bottles pressurized with 10-25 psi 0.2-um filtered air onto 25-m membranes that were mounted in Swinnex polypropylene filter sandwiches. South of Station 8, two size fractions (0.45 – 5 um and > 5 um) were collected at the surface-most 4-7 depths, chosen by the depth where chlorophyll fluorescence measured by the CTD approached 0 and the beam transmission approached its maximum. For these depths, two Swinnex filter holders were connected by a ca. 2" piece of tubing; the upstream filter held a 5 um polycarbonate membrane and the downstream filter held a Supor 0.45μm polyethersulfone membrane. At all other depths, all particulates were collected directly onto a Supor 0.45μm polyethersulfone membrane. An average of 6 L of water (range 1.5 – 10.5 L) was filtered through each membrane. Filters were frozen at -20°C until analysis at the home laboratory.

Table 6. Number of bottle particle samples and process blanks (PB) collected onto either 0.45um Supor membranes or 5um polycarbonate (PC) membranes

Station	type	0.4um Supor	5um PC	Supor PB	PC PB
1	full	23		2	
2	demi	12		1	
3	super	32		6	
4	demi	12		2	
5	demi	0			
6	full	24		4	
7	demi	12		2	
8	full	24	24	2	2
9	demi	12	12	1	1
10	full	12			
11	demi	12	6	1	1
12	full	24	7		
13	demi	11	5	2	2
14	super	33		1	
15	demi	11	4	1	
16	full	23	6	1	
17	fish	0			
18	full	22		1	
19	fish	0			
20	super	30	7	1	1
21	fish	0			
22	full	23	5		
23	demi	12	5	1	
24	demi	12	7		
25	full	24	5		
26	demi	12	4	1	1
27	super	33	6	1	1
28	fish	0			
29	full	24	4	2	2
30	demi	12	5		
31	fish	0			
32	full	24	5	1	
33	underway	0			
34	deep demi	11			
35	full	23	4	3	
36	deep demi	12		1	
37	super	33	1	2	
TOTAL		590	122	41	11

5.3 Underway Proteomics

PI: Mak Saito

At sea: Ben Twining

Filtered particulate samples for proteomic and genomic analysis by the Saito lab were collected from the underway seawater system by Ben Twining. Particulate samples were first filtered through a 51 µm Nitex filter, followed by a 3 µm Versapore filter and then onto a 0.2 µm Supor filter. All filters were 142 mm diameter. The volume of seawater filtered varied between 31 L and 51 L, depending on the oligotrophy of the seawater. The 51 µm filter was collected whole, while the 3 µm and 0.2 µm filters were each sub-sampled into proteomics samples and DNA samples, with 1/8 of the filter collected for DNA analysis and 7/8 of the filter collected for proteomic analysis. Samples were stored at -80ºC. samples were taken at all full and super stations, as well as the final shelf station, resulting in 138 total samples.

5.4 Plankton biogeography and eukaryotic metatranscriptomics

PIs: Dreux Chappell and Sophie Clayton
At sea: Ben Twining

DNA and RNA samples were collected at all tow-fish sampling points and from the mixed layer and DCM at all demi, full, and super stations. Mixed layer samples were collected via the arriving fish, and DCM samples were collected from the ODF CTD. Samples were immediately passed through Sterivex filters (4-6 liters per filter). DNA/RNA preservation solution was added and filters were frozen at -80C. One hundred sixty-six total Sterivex filters were collected. Samples will be analyzed by Dreux Chappell (ODU) to assess eukaryotic phytoplankton biogeography (amplicon sequencing) in the context of hydrographic, macro- and micro-nutrient distributions. A metatranscriptomic bioassay approach will also be developed to determine what macro- or micronutrient limits eukaryotic phytoplankton capable of impacting carbon export (diatoms, dinoflagellates, haptophytes). Additionally, a machine learning approach will be applied to identify the minimal subset of measured physical and chemical variables necessary to reconstruct regional nutrient limitation patterns.

5.5 Plankton imaging

PI: Ben Twining
At sea: Laura Sofen

A McLane Research Laboratories Imaging FlowCytobot (IFCB) was brought by Twining group and used to characterize the surface phytoplankton community via automated single-cell imaging. The IFCB was plumbed into the ship's underway seawater system in the hydrolab. The IFCB operated between stations 4 and 21, allowing examination of the shift in microplankton community composition across this major nutrient gradient. After station 21, mechanical and/or electrical problems developed that precluded subsequent operations.

5.6 Phytoplankton cell quotas

PI: Ben Twining
At sea: Ben Twining

Samples for synchrotron x-ray fluorescence (SXRF) analysis of the elemental composition of individual phytoplankton cells were collected at

Unfiltered water samples were taken for SXRF analysis from select depths (surface and DCM) of the GEOTRACES GO-FLO rosette. Samples were preserved with 0.25% trace metal clean buffered glutaraldehyde and centrifuged onto SiN TEM windows. Using an upright Olympus microscope, transmitted light (differential interference contrast) images of the windows were collected.

Phytoplankton samples for flow cytometric sorting with subsequent ICP-MS analysis were collected during arrival at 10 stations. Unfiltered water from the towed fish was preconcentrated in parallel over a 0.4 um polycarbonate filter (approx. 100-200 mL) and a 5 um polycarbonate filter (approx. 0.6 – 1 L) to 4 – 4.5 mL. The concentrated seawater and filter were transferred to a 5 mL cryovial, preserved with filtered TM-clean buffered glutaraldehyde, frozen in liquid nitrogen, and stored at -80 deg C. A 2 mL whole seawater sample was also preserved and frozen.

5.7 Hydrogen sulfide as a strong ligand affecting the speciation and solubility of key trace metals

PI: Gregory Cutter
At sea: Nicole Buckley

Shipboard Determinations of Total Dissolved Sulfide and Free (Uncomplexed) Sulfide
Samples of unfiltered water from the ODF Niskin bottles and the tow-fish pump were collected for at-sea sulfide determinations of total dissolved sulfide (TDS) and carbonyl sulfide (OCS) using acidification, helium gas stripping, liquid nitrogen-cooled cryotrapping and determination using an Agilent 8890 gas chromatograph with flame photometric detector (Radford-Knoery and Cutter, 1993). All determinations were made within 6 hours of sampling.
Shipboard sulfide measurements were made in the upper 1500 m of the water column at 30 stations (1-6, 8, 9, 12-18, 20, 22-30, and 32-38). Approximately 260 TDS and OCS samples were collected and measured in duplicate or triplicate analyses. Concentrations of TDS rarely exceeded 50 pmol/L in the near surface waters through Station 14 before dropping below detection limits until Station 25. TDS concentrations in the surface generally increased as we approached the Chilean shelf. TDS maximums were typically in the upper 50m and then decreased with depth. OCS concentrations did exceed 100 pmol/L occasionally but saw maximums typically in the upper 50m and then decreased with depth, similar to TDS.
Free sulfide ($H_2S+HS^-+S^{2-}$ not complexed with metals) samples were collected from the tow-fish pump at 22 stations and measured in duplicate or triplicate (Radford-Knoery and Cutter, 1994). Concentrations of free sulfide were mostly below detection limits except at three stations (1, 25, and 35).

Particulate Sulfide Sampling
Unfiltered water from the ODF was also collected and filtered for nanoparticles at select stations near hydrothermal vents for analyses back at ODU. In addition to those particles, particles from the Supor and QMA filters from the McLane pumps were also collected for analyses back at ODU.

Approximately 220 samples of Supor (slices, collected in duplicate) and QMA (single punches) filters from the McLane pumps were collected by the Ohnemus Pump Team. These filter subsamples were placed cryovials and then stored in heat-sealed Tedlar bags with oxygen scrubbers and kept at -80°C. Unfiltered water samples from the ODF Niskins were collected at 4 stations (18, 20, 35, and 37) from intermediate and deep casts for determinations of sulfide nanoparticle concentrations in near and distant hydrothermal vent plumes. Within a nitrogen-purged glove bag these plume samples were sequentially filtered within 5 hours of collection through 0.2 and 0.05 µm Nucleopore membranes. Each membrane was then placed in a petri slide and stored in heat-sealed Tedlar bags with oxygen scrubbers and kept at -80°C for the duration of the cruise. All of these filter samples will be returned to the ODU lab via coolers with dry ice for shipping and then stored in a -80°C for determinations of pAVS (CdS, ZnS, NiS, etc.) from the Supor filters and pCRS (FeS_2, CuS) from the QMA filters.

Dissolved Organic Sulfur

Samples of 0.45 µm-filtered water from the ODF Niskins were collected at depths from 25-4600 meters from 18 stations (1, 3, 6, 8, 10, 12, 14, 16, 18, 20, 22, 25, 27, 29, 32, 35, 37, 38) for dissolved organic sulfur analyses. These samples were immediately -20°C frozen upon collection and stored frozen; they will be shipped back to the United States in a refrigerated container. DOS determinations will be made back at the ODU lab (Cutter et al., 2004).

References

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Radford-Knoery, J., & Cutter, G. A. (1993). Determination of carbonyl sulfide and hydrogen sulfide species in natural waters using specialized collection procedures and gas chromatography with flame photometric detection. *Analytical Chemistry*, *65*(8), 976–982. https://doi.org/10.1021/ac00056a005.

5.8 Shipboard determinations of dissolved zinc (dZn)

PI: Gregory Cutter (management grant)
At Sea: Ekaterina Bulygina

Samples (filtered through 0.2 µm AcroPak Supor) were collected from the trace metal-clean carousel (GTC) at Stations Test 2, 1, and 2 to check for GO FLO contamination (ca. 100 samples). These samples were run without acidification as soon as they were collected and thus the data do not represent total Zn. For the rest of the cruise, samples were collected from the GTC and trace metal-clean fish (filtered through 0.2 µm AcroPak Supor) and run after acidification (0.024 M q-HCl) and 24-hour holding time. All samples were analyzed shipboard for dZn using a Lab-on-Valve, GlobalFIA MiniSIA-2 analyzer and FloZF software, as described in Grand *et al.* (2016). Data generated onboard served primarily to validate the sample collection methods by highlighting any potential contamination sources in near real-time. Samples were collected from all bottles in a given cast to access bottle replicates when they were run for contamination. Ultimately, the precision of the system made it a good tool for assessing GO-FLO bottle contamination. However, the method will need some revision to be useful for accurate sample quantitation in a timely manner. We analyzed 374 samples from Stations 6, 10, 12, 14, 15, 16, 18, 20, 22, 23, 25, 27, and 29 for total Zn (acidification and >24 hour holding).

References
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5.9 Nanomolar-level nutrient analyses

PI: Gregory Cutter (management grant)
At Sea: Ekaterina Bulygina

Samples were collected from the uppermost depths using the GTC and from the trace metal-clean tow fish. All samples were filtered (0.2 μmAcroPak Supor) into acid-cleaned polyethylene 25 mL scintillation vials then refrigerated until analyses. Samples were held refrigerated until ODF analyses determined whether the nutrient concentrations were below their detection limit of 0.2 mM. Samples were analyzed on an Astoria-Pacific Segmented Flow Analyzer using World Precision Instruments Waveguides as detector cells with three channels: PO_4, NO_2, and NO_3+NO_2. In total we analyzed 48 samples for nanomolar level of nutrients, and the concentration ranged from 0-200 nM for nitrate+nitrite, 0-100 nM for nitrite, and 0-100 nM for phosphate.

5.10 Helium isotopes

PIs: Chris German, Jennifer Middleton, William Jenkins, Gisela Winckler, Brice Loose
At sea: Jennifer Middleton

Helium samples were collected from every depth of the ODF Shallow, Intermediate, and Deep casts. Samples were also collected at every surface bottle of the ODF PigRaTh casts. In total, samples were taken from 663 discrete depths. Every sample was collected in duplicate (in tubes labeled A and B, or C and D in cases where A and B tubes were compromised), except for 15 samples in which one duplicate tube was compromised. Both replicates wer compromised during the copper tube-sealing process in only 12 samples. A second set of duplicate samples was collected at 27 depths (tubes labeled A2 and B2), for interlaboratory comparison.

Sampling method:
Samples were collected using the copper tube method. In this method 2 ~45” sections of tygon tubing is attached to a 29.5” section of 5/8” soft copper refrigeration tubing (Cambridge-Lee Industries, LLC) that has been straightened, sectioned, deburred, and marked into 2x12” sections with 2.75” spare length at each end. Both sections of tygon tubing have a clamp placed ~18” from the copper tube. While flushing with sample water, the copper tube is thumped with a bat to remove bubbles from the walls of the tube. After flushing roughly 1 liter of water through them, the clamps are closed. The sample filled copper tube is then cut into the 2 predefined 12” lengths using pneumatic jaws. This means that each sample is collected in duplicate. The samples are then rinsed and cleaned thoroughly with fresh water and dried to inhibit corrosion on the copper surface during storage.

Samples will be analyzed at the Helium Isotope Lab at Woods Hole Oceanographic Institution and in the Trace Isotope and Noble Gas Lab at Lamont-Doherty Earth Observatory.

5.11 Tritium

PIs: William Jenkins, Brice Loose, Chris German, Jennifer Middleton, Gisela Winckler
At sea: Jennifer Middleton, Marty Fleischer

Tritium samples were collected from a total of 31 samples throughout the water column at the three GP17OCE-ANT cross-over stations (Stations 25, 27, 29).

Sampling method:
Tritium samples were collected in one-quart flint glass bottles that were pre-treated with argon. Tygon tubing was connected directly to the niskin spigot and held with exhaust end up to allow water to liberally rinse the outside of the tube. The bottle was then carefully filled, with minimal disturbance to the argon inside, within 1'' of the bottle neck, capped, and sealed tight with electrical tape. Care was taken to ensure potential sources of tritium contamination (such as tritiated watch dials) were not present during sampling. After sampling, bottles were wiped clean with a freshwater towel and stored in wooden boxes.

Samples will be analyzed at the Tritium Lab at Woods Hole Oceanographic Institution.

5.12 Mercury speciation

PIs: Carl Lamborg (UCSC), Rob Mason (UConn), and Chad Hammerschmidt (WSU)
At sea: Marissa Despins (UCSC), Yipeng He (UConn)

1) Trace Metal Rosette
    a. Received samples from the GEOTRACES Clean Rosette (GTC) for on-board analysis of dissolved total mercury, elemental mercury, dimethylmercury, and monomethylmercury. Samples for monomethylmercury were archived for on-shore analysis. Analytical problems prevented dimethylmercury to be analyzed at a number of stations, these stations elemental mercury and dimethylmercury were analyzed together as dissolved gaseous mercury. Given bottle allowances and time demi stations were skipped. We also participated in GTC deployment and recovery. Number of samples: 495.
    b. Collected water for intercomparison with colleagues. Samples were collected in triplicate and archived.
2) Arriving FISH
    a. Received filtered arriving FISH samples for Hg speciation. Analyzed for dissolved total mercury, elemental mercury, and dimethylmercury on-board and stored for monomethylmercury analysis shore side. Contamination in the bubble prevented accurate reporting in a few stations.
    b. Mercury isotope samples were collected at 7 arriving fish stations (including station 3, 8, 14, 20, 25, 29 and 30). Pre-concentration and elution occurred on-board. Samples were then archived for analysis shore side. Contamination was not an issue as an air-tight sampling apparatus was built.
    c. Mercury isotope particles were collected over one long transit in the South Pacific.
3) McLane *in-situ* pumps

a. Samples were collected, both large and small fraction particulate samples for monomethylmercury and total mercury analyses. Filter samples were dried and stored for future analyses shore-side. Number of pump stations: 169
b. Sterivex filters were attached to manifolds on the pumps and deployed at 8 stations. Sterivex samples were stabilized to be analyzed on-shore.

4) Atmospheric Samples
    a. Continuous atmospheric elemental mercury and reactive gaseous mercury concentrations were measured during the duration of the transect and the cruise (Dec 1, 2022 – Jan 25, 2023) using a Tekran speciation system (1130/1135/2537B), deployed on the bow. Ozone concentrations were also measured in tandem with atmospheric mercury.
    b. Atmospheric elemental mercury isotope sampler was deployed on the bow in San Diego, CA and ran during the entirety of the transit and cruise. 3 transect samples with duplicates were collected and archived to be analyzed on-shore.
5) Mercury Underway System
    a. The elemental mercury and dimethylmercury underway systems were deployed at the beginning of the transit in San Diego, CA and collected sample data continuously until port in Punta Arenas, Chile. Samples were collected (Dec 1, 2022 – Jan 25, 2023).
    b. The dissolved elemental mercury isotope samples were collected during the whole cruise. Totally, 7 transect samples were collected and archived to analyzed on-shore.
6) Sampling
    a. Assisted with deployment and recovery of GTC, Beryllium pumps, FISH, and McLane *in-situ* pumps.

5.13 Beryllium-7

PI: Mark Stephens
At sea: Yipeng He

Samples of seawater, aerosols and particles were collected for Be-7 analyses. Seawater was proposed to be sampled at all full stations and superstations (19 planned stations, 114 proposed samples), but only sampled at most of full stations and superstations (12 Be-7 casts, 71 seawater samples, 62% of total proposed samples). Water for Be-7 was pumped into vertical tanks on the back deck (500-700 L) with a centrifugal pump and 1.5-inch PVC hose. Typically, six depths were sampled at each targeted stations, up to a maximum depth of 175 m. A profiling CTD (YSI) was attached to the hose inlet to determine exact depths. The water was then pumped out of the barrels through Fe-coated acrylic fibers. Aerosols will be provided by C. Buck group, and particulate filter samples will be provided by D. Ohnemus group. All samples will be counted by high-resolution, low background gamma spectrometry at FIU. In order to expedite analysis of Be-7 (half-life 53 days), samples will be carried on the flight back to the U.S. by Yipeng He.

Table 7. Detailed information of seawater pumped at six depths for Be-7 at each targeted station, including station and cast numbers, sampling depths (m), and number of depths

Station	Cast	Depth 1	Depth 2	Depth 3	Depth 4	Depth 5	Depth 6	Amount
1	8	14.71	30.20	50.17	100.01	124.93	149.72	6
3	9	5.55	25.13	50.10	79.48	99.02	123.70	6
6	8	32.96	72.79	87.72	102.28	121.69	140.94	6
8	8	20.24	60.12	80.10	99.93	119.90	139.84	6
10	9	10.28	35.07	54.88	80.01	104.91	129.85	6
12	6	21.42	61.25	81.20	101.23	121.21	141.16	6
14	11	33.86	78.12	92.98	107.54	126.56	146.14	6
16								Cancelled
18	7	30.84	80.70	115.75	130.64	145.44	175.23	6
20	7		78.40	108.48	123.32	143.42	173.05	5
22	6	31.34	81.34	96.44	111.54	131.39	161.00	6
25	5	4.88	24.84	49.89	79.85	109.14	139.75	6
27								Cancelled
29								Cancelled
32								Cancelled
33								Cancelled
35	6	17.53	52.48	72.51	92.49	112.41	142.24	6
37								Cancelled
38								Cancelled
							Total	71 (62%)

5.14 Discrete pH_t Analyses

PI: Ryan Woosley (MIT)
At sea: Jiyoung Moon (MIT)

Sampling

Seawater from Arriving FISH and ODF casts were collected in 150 ml borosilicate glass serum bottles. The bottles and butyl rubber caps were rinsed, filled from the bottom using silicone tubing, with care not to entrain any bubbles, then allowed to overflow at least half of the bottle volume. Flow continued while removing the tubing to leave the bottle completely full. Next, 2.105 ml of seawater was withdrawn from the bottle using a pipette to create a reproducible headspace of ~1%, followed by adding 60 µL of saturated $HgCl_2$ solution, to preserve the samples. The sample bottles were crimped closed using an aluminum seal. A pair of duplicates were collected at every ODF cast. One sample per cast was analyzed twice with ~30% more indicator to account for changes in pH_t due to addition of the indicator. This adjustment has not yet been applied to the data. All data should be considered preliminary.

Analysis

The pH on the total scale (pH_t) was measured using an Agilent Cary 8454 UV-vis spectrophotometer according to the methods outlined by Clayton and Byrne (1993) with a custom designed automated system similar to that described by Carter et al. (2013). A VERSACOOL (Thermo-Fischer Scientific, USA) water bath maintained spectrophotometric cell temperature at 25 ± 0.1°C. Another VERSACOOL water bath was used to thermostat samples to

25 ± 0.1°C before analysis. The 10 cm micro-volume flow through quartz spectrophotometer cell (Starna, Inc., Atascadero, CA, USA) was automatically rinsed and filled using a Kloehn 6v syringe pump. The purified sulfonephthalein meta-cresol purple indicator was also injected automatically and mixed by the Kloehn 6v syringe pump. The absorbance was measured at four different wavelengths (434 nm, 578 nm, 730 nm, and 488 nm). The ratios of absorbances at the different wavelengths were used to calculate pH_t using the equations of Liu et al (2011). The isosbestic point (488 nm) will be used to determine the indicator perturbation. Temperature of the samples was measured immediately after spectrophotometric measurements using a Fluke Hart 1523 digital platinum resistance thermometer located in the cell holder immediately adjacent to the cell. Salinity data were obtained from the conductivity 48 sensor on the CTD.

Reagents

The purified mCp indicator dye (Provided by Dr. Robert H. Byrne, University of South Florida) was prepared in ~0.7 m NaCl to a concentration of ~2.0 mM and pH was adjusted to ~7.9 using NaOH. Batch 4 was used for all samples.

Standardization

The precision of the data can be accessed from measurements of certified reference material (CRM) Batch 179 (Dr. Andrew Dickson, University of California, San Diego), TRIS buffers (DelValls and Dickson, 1998) prepared according to (Paulsen and Dickson, 2020), and duplicate samples. A CRM was measured at every odd station, and TRIS and duplicate samples were measured for every cast. The mean and standard deviation for the CRMs was 8.0215 ± 0.0014 (n = 19). The mean and standard deviation of the TRIS buffer was 8.0882 ± 0.0017 (n = 53). The mean and standard deviation of the absolute difference of pH_t between duplicate samples was |0.0019| ± 0.0019 (n = 47).

Data Processing

The addition of the indicator affects the pH_t of the sample, and the degree to which pH_t is affected is a function of the pH_t difference between the seawater and the indicator. Therefore, an adjustment is applied for each batch of the indicator. One sample from each cast was measured twice, once with the normal amount of indicator and a second time with 30% more indicator. The change in the ratio is then plotted versus the change in the isosbestic point to develop an empirical relationship for the effect of the indicator on the pH_t (Carter et al. 2013). This correction has not yet been applied to the data.

Problems

The only significant issue that occurred was bubbles accumulating in the instrument tubing which occasionally interfered with absorbances. It was ensured that samples were reaching thermal equilibrium. The bubbles were cleared by rinsing the sampling tube and cell with air between measurements. If it was determined that bubbles had impacted a measurement, it was immediately rerun.

References

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5.15 Dissolved Inorganic Carbon

PI: Ryan Woosley (MIT)
Sampler: Jiyoung Moon (MIT)

Sampling

Samples for dissolved inorganic carbon (DIC) measurements were drawn from Niskin bottles on ODF casts into 250 ml borosilicate glass reagent bottles using silicone tubing. The bottles and stoppers were rinsed and filled from the bottom with care not to entrain any bubbles, overflowing by at least one-half the volume. Flow continued while removing the tubing in order to keep the bottle completely full. Next, a pipette was used remove 8.48 ml (leaving a reproducible ~1% headspace after capping the bottle) followed by adding 120 µL of saturated $HgCl_2$ solution to preserve the samples. The sample bottles were then sealed with glass stoppers covered with Apiezon-L grease to create a gas tight seal. Finally, stoppers were held in place with a plastic hose clamp and rubber band. A pair of duplicates were collected at every ODF cast. Including the duplicates, 712 samples were collected for DIC, which corresponds to 100% of the depths where Niskins tripped.

Analysis

The sample bottles will be analyzed in the lab at MIT after the cruise. The analysis will be done by coulometry. The system consists of a coulometer (CM5015 UIC Inc., Joliet IL, USA) coupled with a Dissolved Inorganic Carbon Extractor (DICE). The DICE system was developed by Esa Peltola and Denis Pierrot of NOAA/AOML and Dana Greeley of NOAA/PMEL to modernize a carbon extractor called SOMMA (Johnson et al. 1985, 1987, 1993, and 1999; Johnson 1992).

References

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automated continuous gas extraction system and coulometric detector." Mar. Chem., 44, 167-189.

5.16 Total Alkalinity

PI: Ryan Woosley (MIT)
Sampler: Jiyoung Moon (MIT)

Sampling

At each ODF cast, total alkalinity (TA) samples were drawn from Niskin bottles into 150 ml HDPE EPA certified plastic bottles using silicone tubing. The bottles and caps were rinsed with a small volume of seawater, then filled from the bottom and allowed to overflow at least half of the bottle volume, taking care not to entrain any bubbles. Flow continued while removing the tubing in order to keep the bottle completely full. Next, 1.5 ml of seawater is withdrawn from the bottle using a pipette, in order to create reproducible ~1% headspace to allow for thermal expansion. To preserve the samples, 60 µL of saturated $HgCl_2$ solution was added to each bottle. The sample bottles were capped and sealed with parafilm. A pair of duplicates were collected at every ODF cast. Including the duplicates, 714 samples were collected for TA, corresponding to 100% of the depths where Niskins tripped.

Analysis

The samples will be analyzed in the lab at MIT following the cruise. Samples will be analyzed using a custom-built open cell HCl titrator (Dickson et al., 2003) designed and built by the laboratory of Andrew G. Dickson (University of California, San Diego).

References

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5.17 Aerosol and rain sampling

PI: Cliff Buck
At sea: Michael Sheridan

Aerosol samples were collected over two- to three-day periods using five sector-controlled high-volume aerosol samplers (Tisch Environmental, model 5170V-BL). Electrical issues were common onboard, and while every attempt was made to run all five samplers simultaneously, nonoperational samplers necessitated three- and four-sampler runs.

When all five samplers were operational, four samplers were each loaded with twelve 47 mm filters. The fifth sampler was loaded with a five-stage Sierra-style slotted cascade impactor to collect size fractionated aerosols (from >7 µm to <0.49 µm) over periods of four to six days. When fewer than five samplers were operational, at least one sampler was loaded with the cascade impactor while the others were loaded with 47 mm filters.
In total, 16 aerosol filter deployments/retrievals were made yielding:

- 480 x 47 µm Whatman-41 filters (40 groups of 12)
- 192 x 47 µm GFF filters (16 groups of 12)
- 60 x size fractionated filters (10 periods, 6 filters each)

All filters were frozen (-20ºC) and will be distributed to collaborators later in the year (see Buck's Project Description's Table 3).

Leaches of aerosol-laden W41 filters were performed at sea using ultrapure water (UPW) and filtered (0.2 µm) seawater from the towfish. Three leaches per deployment passed UPW through replicate sample filters with a 0.2 µm polycarbonate backing membrane, three leaches per deployment passed seawater through replicate sample filters with a 0.2 µm polycarbonate backing membrane, and three leaches per *every other* deployment passed seawater through replicate sample filters with a 0.02 µm Anodisc backing filter. An aliquot of leachate for major ion analysis was taken from every triad of UPW leaches then frozen (-20ºC). All other leachate was acidified to 0.024M HCl with stock distilled HCl.
Leaches performed on ship included:

- 57 x 100mL UPW leaches (9 blanks, 48 samples)
    - from which 19 x 20mL major ion subsamples were taken (3 blanks, 16 samples)
- 57 x 100mL filtered seawater leaches through 0.2 µm PC membrane (9 blanks, 48 samples)
- 33 x 100mL filtered seawater leaches through 0.02 µm Anodisc filter (9 blanks, 24 samples)

An aethalometer (Magee Scientific Model AE33) took continuous measurements throughout the cruise, but a power outage on December 16, 2022, deleted the first two weeks of unsaved data from the instrument.

Microtops handheld aerosol optical depth measurements were made on clear-sky days then sent to the NASA AERONET program, but regularly cloudy skies only allowed for five days of measurements.

Two automated rain samplers were also mounted to the R/V Revelle's O3 deck, but no rain samples were collected because either high winds and waves made it hazardous to do so or materials were not prepped in time to collect rain.

All work aboard ship was performed by a graduate student in accordance with Buck's Project Description's "Broader Impacts" statement.

5.18 Shipboard dissolved iron

PIs: Peter Sedwick, Joseph Resing
At sea personnel: Bettina Sohst

For the NSF award "Collaborative Research: US GEOTRACES GP17-OCE: Shipboard Measurements of Dissolved Aluminum, Iron, and Manganese – Tracing Inputs to the South Pacific Gyre and Southern Ocean", PI's Sedwick (Old Dominion University) and Resing (University of Washington) proposed to make shipboard and post-cruise measurements of dissolved aluminum, manganese and iron (DAl, DMn and DFe) in water-column and surface-water samples collected by GEOTRACES cruise GP17-OCE. Major goals of the research are to constrain (1) the magnitude of dust deposition to this ocean region and the fidelity of DAl and DMn as tracers of aeolian iron inputs; (2) the origin of deep-ocean DAl and DFe anomalies, and

their implications for deep sources of these elements; and (3) the source and fate of hydrothermal DFe emissions from the deep ocean and their role in supporting Southern Ocean primary production. The shipboard measurements are also intended to provide a check on potential sample contamination, to facilitate adaptive sampling to better define features and processes of interest, and to inform cruise sampling strategies and analyses conducted by other GP17-OCE investigators.

For the ODU component of this research project, Research Specialist Bettina Sohst performed shipboard DFe determinations using flow-injection analysis (FIA) and collected and processed samples for post-cruise analyses of DMn and DFe using inductively-coupled plasma mass spectrometry (ICP-MS). Shipboard FIA was used to measure DFe in 0.2-µm filtered water-column and surface-water samples from 4 (all) super stations, 13 (all) full stations, 8 demi stations, 12 surface fish samplings at the remaining demi stations, and 19 intermediate fish locations, with duplicate samples acidified and stored for post-cruise ICP-MS analyses. Additionally samples from all GTC rosette GoFlo bottles (38) were analyzed at the beginning of the expedition to evaluate cleanliness of the sampling equipment.

In-house reference seawater was analyzed each day to assess precision and accuracy, whereas seawater consensus reference material was only measured for some of the analyses. The analytical limit of detection was 0.07 nM DFe, as estimated from 3 x the standard deviation on 10 replicate analyses of low-concentration filtered seawater sample collected at sea. Analytical precision was generally better than ±10% (one relative standard deviation). All samples were analyzed at least twice (at two separate times of the day). In addition, several samples were re-analyzed on other days to assess precision.

For the shipboard measurements, Sohst faced a number of challenges with the analytical system, including detector failure, manifold contamination and blockages, autosampler malfunctions, and electronics issues, eventually overcoming these hurdles to analyze all planned samples with apparently excellent initial results. Preliminary results of the shipboard DFe analyses are presented in Figures 6 and 7.

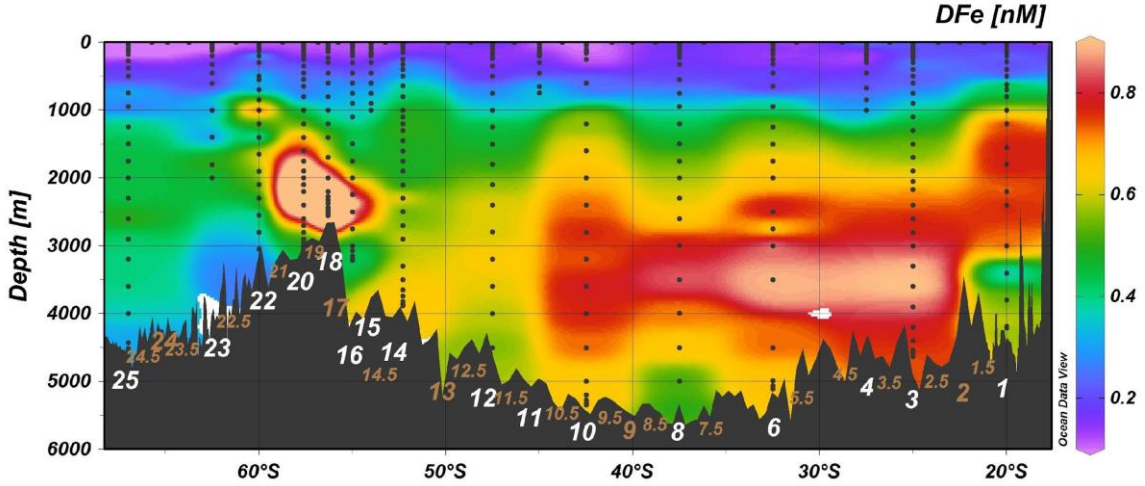

Figure 6. Quasi-meridional section of DFe concentration from Stations 1-25 (preliminary data, Sohst & Sedwick).

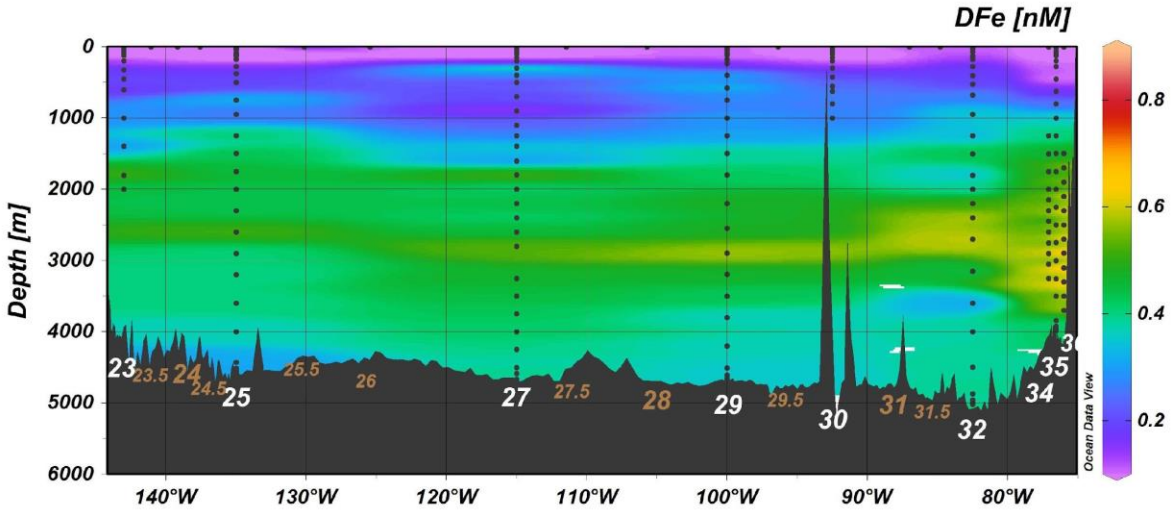

Figure 7. Quasi-zonal section of DFe concentration from Stations 23-36 (preliminary data, Sohst & Sedwick).

5.19 Shipboard analysis of dissolved aluminum (dAl) and manganese (dMn)

PI: Joe Resing
At sea: Gabi Weisss

Samples for the shipboard determination of dAl and dMn were obtained from the Geotraces (GTC) trace metal rosette utilizing 24 Teflon-coated, 12L General Oceanic GO-FLO bottles. Shipboard analyses during GP-17 were performed by G. Weiss (on behalf of Dr. Joe Resing, University of Washington) on 0.2µM Acropack- filtered subsamples. Subsamples for dAl and dMn were collected by the GTC supertechs in 100mL acid-cleaned LDPE bottles and acidified to 0.024M HCl for at least one hour prior to analysis. These samples were then analyzed for dAl and dMn using flow injection analysis (Resing and Measures, 1994; Resing and Mottl, 1992 respectively). Dissolved Mn analyses were performed using a modified method based on Resing and Mottle (1992) in which the buffered dAl sample line is used to deliver a partially buffered sample stream to the dMn system. A Miligat pump is used to deliver a small continuous stream of Tris buffer to mix with the partially buffered sample stream that connects the dAl and dMn systems, allowing for an increase in pH for dMn preconcentration. Both dAl and dMn systems used independent Toyopearl AF-650 resin columns for sample preconcentration.

A total of 553 trace metal samples were collected at 31 GEOTRACES stations. This total includes surface samples collected by the GEO Tow Fish, which collected surface seawater at a nominal depth of 5m both at station and between stations (intermediate stations). Intermediate fish were not sampled for shipboard analysis of dAl and dMn by FIA. The surface samples collected by tow fish were also filtered through a 0.2µM Acropak filtered and acidified to 0.024M HCl for an hour prior to analysis. The precision of each of the methods was determined by replicate determination of the same sample throughout the day, with typical values of <5% for dAl and <10% for dMn.

Preliminary dMn data show the existence of a hydrothermal plume at station 20 with two relative dMn maxima around 1750m and 2100m, which was also observed in the GTC transmissometer signal. Surface and waters shallower than 350m had dMn concentrations below the detection limit (~0.05nM dMn).

5.20 Total ^{234}Th (Particulate and Dissolved) Collection and Analyses

PIs: Ken Buesseler, Claudia Benitez-Nelson, Laure Resplandy
Shipboard collection and analyses: Wokil Bam and Steven Pike, WHOI

Total ^{234}Th samples were collected at all stations. For shallow depths, typically less than 1000 m, total 234Th samples were collected from the PigRaTh (pigments, radium, and thorium) cast and the Demi ODF cast where applicable. For deeper depths, seawater was collected from 30 L Niskins incorporated into the McLane pump casts at depths that coincided with pump depths. Typically, 13 water depths were collected during shallow ODF casts and 8 water depths collected per pump cast. Shallow cast seawater samples were collected at depths that coincided with the 8 shallow pump depths, as well as 5 additional depths selected on the basis of interesting features observed on the station's CTD data.

Seawater samples were collected into approximately 2 L FLPE Nalgene bottles from each Niskin. Each sample was spiked with 1 mL of a 50.03 dpm/g ^{230}Th standard for future recovery calculations. Total ^{234}Th was precipitated via additions of $KMnO_4$ and $MnCl_2$ onto QMA filters. Precipitate samples were counted onboard using RISØ Laboratory anti-coincidence beta counters for preliminary first and second counts, with third counts to be completed onshore. Total ^{234}Th samples will be coupled with particulate ^{234}Th data (as well as other particulate trace metal and isotope data) in order to produce flux calculations. In summary, 519 total ^{234}Th, 201 small-size fraction (<51um) particulate ^{234}Th, and 201 large-size fraction (>51um) particulate ^{234}Th samples were collected and processed onboard. See section on pump operations for more detail on particulate analyses.

Additionally, the UVP (French CNRS patent) is a high-resolution underwater camera designed to study large (from 60 to 1000 micrometers) particles and zooplankton simultaneously was mounted on the ODF CTD rosette. The UVP was operated for all the shallow, intermediate and deep CTD cast.

5.21 Zinc speciation along GP17

PI: Nicholas Hawco
At sea: Nicholas Hawco

Samples to determine the speciation of zinc were collected at all FISH and GTC samples (approx. 675 in total). All samples were analyzed at sea by cathodic stripping voltammetry to determine the concentration of labile zinc via a hanging drop mercury electrode with ammonium pyrrolidine dithiocarbamate (APDC) as a competing ligand. In-house consistency standards were measured quasi-daily for the entire cruise, with occasional measurement of GEOTRACES and SAFE standards. Most samples were analyzed were duplicate. All samples were stored refrigerated during the cruise and frozen for transport back to UHM. The survey of labile zinc conducted here is a precursor to future, in-depth analysis for quantification of zinc ligands by

competitive ligand exchange. Duplicate FISH samples were also collected at 36 stations and frozen for later analysis of Zn, Cd, and Ni speciation back on land.

APDC-labile zinc showed high concentrations throughout the deep ocean, and low concentrations (<0.5 nM) in the upper waters of the South Pacific gyre and through the subantarctic zone (Fig. 8). South of the polar front (approximately St. 18) surface zinc concentrations increased dramatically to >2 nM and, in general, remained elevated throughout all Southern Ocean stations (18 – 32). Towards the Chilean margin, labile zinc concentrations decreased once the polar front and subantarctic front were crossed. Slight hydrothermal enrichment was observed at the bottom of Station 18 at the Pacific Antarctic Ridge.

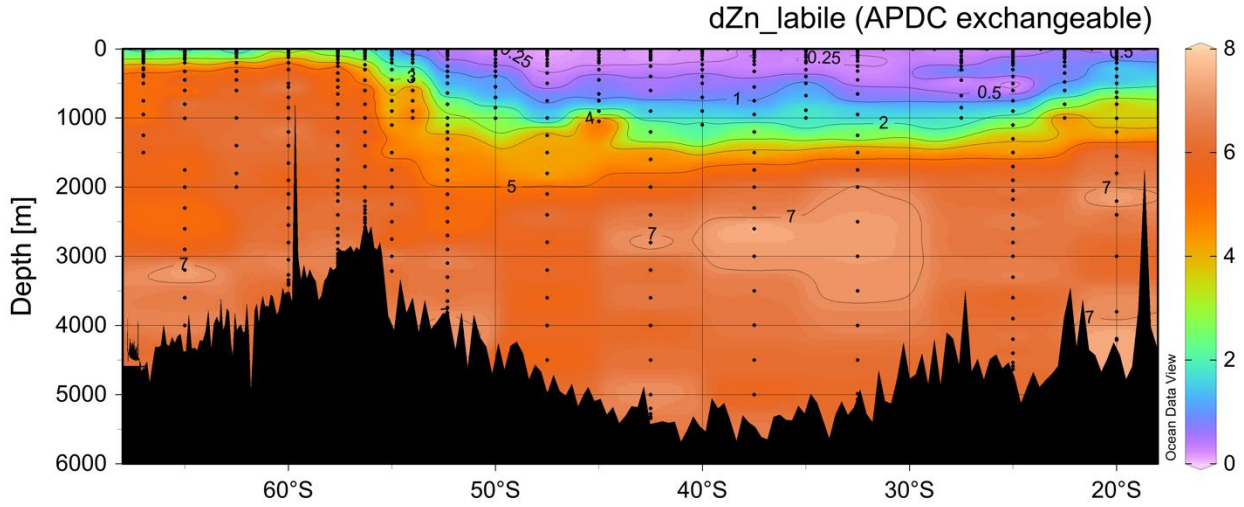

Figure 8. Labile Zn concentration (in nmol L^{-1}) across stations 1-24. Note data is preliminary and final values will continue to be adjusted during post-cruise processing.

Approx. 60 samples were collected for future application toward single cell ICPMS analysis of phytoplankton metal contents. Unfiltered seawater from the Fish was transferred into 4 mL flow cytometry samples, fixed with 100s uL 10% glutaraldehyde, flash frozen and stored at -80 C. In addition, 24 samples were collected from the upper water column GTC casts on Stations 3, 6, and 10 were collected.

Two incubations were conducted to examine the possibility of manganese limitation. One incubation was conducted at Station 12 and bottles were incubated for approx. 60 hours. With 3 control bottles (4L), 3 +Mn bottles (1 nM, 4L), and 3 +Fe bottles (1 nM). The second incubation was conducted at Station 23. Samples were incubated for approx. 130 hrs and only control and +Mn treatments were performed. It was noted that the incubator did not achieve the set temperature (1 C, actual temp ~4-5 C) due to a malfunction in the door latch. For both experiments, initial results did not indicate significant differences in nutrient concentrations at the end of the experiment. Future analyses include pigments, dissolved metals, and cellular metal quotas.

5.22 Ra Isotopes

PI: Matt Charette
At Sea: Margot Debyser

1. Large Volume Ra/Th/Ac Sample Processing and At-Sea Radium Counting
MnO2-impregnated sample cartridges for Ra/Th/Ac radionuclide collection were removed from the pumps after cast recovery and rinsed with radium-free freshwater to remove salt. Cartridges were dried to dampness prior to shipboard measurement of short-lived radium isotopes. ^{224}Ra (t1/2 = 3.7 d) and ^{223}Ra (t1/2 = 11.4 d) were measured on the Radium Delayed Coincidence Counter (RaDeCC) system and typically counted within 24 h of sample collection. All cartridge filter processing and counting for radium was conducted by Margot Debyser. Scavenging efficiencies of the cartridge filters for Ra and Th is validated by a discrete seawater sample taken in parallel with every pump depth sampled. For shallow pump cast depths, this calibration sample was collected by the ODF Niskin rosette; for mid-water and deep pump casts, a 30 L Niskin bottle was hung next to each pump and bottles were triggered by messenger at mid-cast. For ^{226}Ra, 21.5L seawater was passed over a column of MnO2 impregnated acrylic fiber on deck, and recirculated for >3h, which removes radium at 100% efficiency. These filter samples were bagged and will be analyzed for ^{226}Ra through it daughter, ^{222}Rn back in land-based laboratories. Efficiency filter samples were collected and processed by Margot Debyser. In total, 194 cartridges and 291 fiber samples were collected.

2. Surface sampling for Ra isotopes
At all GEOTRACES stations, ~1500 L of surface water was collected using a hand deployable surface pump, and filtered through Mn-oxide coated acrylic cartridges to collect Ra isotopes. In total, 31 cartridge and fiber samples were collected. The pump was deployed over the port side of the R/V Roger Revelle to ~3 m depth. At sea, these surface samples were processed in a similar manner to the MnO2 pump cartridge samples. They were analyzed for short-lived Ra isotopes on the ship-board RaDeCC systems by Margot Debyser.

5.23 Trace metal-organic complexes

PIs: Dan Repeta and Rene Boiteau
At sea: Iulia Streanga

The goal of our sampling is to capture dissolved and particulate organic matter that can be analyzed for trace element organic complexes. In addition, we sought to perform incubations of seawater amended with iron-57 and aluminum-27 labeled siderophores to measure the turnover of these metabolites by the microbial community at different stations along the GP17 cruise track. Our sampling on the cruise was successful. We recovered filtered water samples from the trace metal clean sampler that were subsequently passed through solid phase extraction media to concentrate trace element organic complexed from all samples at all stations. Companion samples were collected at select stations from the conventional rosette that were filtered and preserved for genomic analyses. These samples will inform us of the classification and abundance of bacteria that synthesize and use siderophores. We anticipate that some of the trace element organic complexes we recover will be new to science, and will require nanomole amount of compound for comprehensive spectral characterization. To provide this material, throughout the cruise we took advantage of the ship's clean seawater supply, and surface water sampling from the GEOFISH

sampler to filter ~85L of sea water per day in the expectation that we can recover microgram amounts of target compounds.

We performed 8 incubations along the cruise track of seawater from different depths amended with isotopically labeled siderophores. These samples were incubated for several days at near ambient temperatures and extracted. The extracts will allow us to measure the turnover time and other important details of siderophore cycling along the cruise track. Finally, we expect to receive splits of particulate organic matter from the large volume McLean pumping system that will enable us to analyze trace element organic complexes in particulate matter.

5.24 Cruise outreach

PI: Chrissy Wiederwohl, Jessica Fitzsimmons
At sea: Rebekah Bogdanoff

Rebekah Bogdanoff was in charge of the outreach. She recorded the scientists deploying their equipment; collecting, testing, and storing their samples; and going about daily life on the ship. Some of my footage was posted on social media to keep the public updated on the progress of the cruise and to build interest in the project. She also recorded and recreated parts of the ship for use in a video game that teaches the user about the scientific procedures, about life on the ship, and about the ocean. She took regular photos, videos, and 360 photos and videos. She conducted several interviews with scientists and crew, detailing everything from how fresh water is made on the boat to the history of GEOTRACES. Post-cruise, Rebekah will help make a resource that will be available to the public.

5.25 CFC-11, CFC-12, and SF_6

PIs: Jim Happell and Rana Fine
At sea: Jim Happell

1. Sample Collection

All water samples were collected from the 10.4 liter Niskin bottles on the ODF rosette. A water sample was collected from the Niskin bottle petcock using silicone tubing to fill a 300 ml BOD bottle. The tubing was flushed of air bubbles. The BOD bottle was placed into a plastic overflow container. Water was allowed to fill BOD bottle from the bottom into the overflow container. The stopper was held in the overflow container to be rinsed. Once water started to flow out of the overflow container the overflow container/BOD bottle was moved down so the tubing came out and the bottle was stoppered under water while still in the overflow container. Additional surface water samples were also collected from the ships underway system. Air samples, pumped into the system using an Air Cadet pump from a polyethylene air intake hose mounted high on the foremast were also run Air measurements are used as a check on accuracy.

2. Equipment and technique

Chlorofluorocarbons CFC-11, CFC-12, and SF_6 were measured on 38 stations for a total of ~ 700 samples. Analyses were performed on a custom-built purge and trap gas chromatograph (GC) equipped with an electron capture detector (ECD). This system had recently been rebuilt, with a new gas chromatograph, new values actuators, and new instrument control and data acquisition software. Modifications were also made to measure N_2O, along with the other three

parameters The samples were stored at room temperature and analyzed within 12 hours of collection. Every 6 to 12 samples were followed by a instrument blank and a standard. A subset of samples were held after measurement and was sent through the process again in order to "restrip" it to determine the efficiency of the purging process.

3. Calibration
A gas phase standards, 426505, was used for calibration. The concentrations ofthe compounds in this standard are reported on the SIO 1998 absolute calibration scale. Calibration curves were run over the course of the cruise. Estimated accuracy is +/- 2%. Precision for CFC-12, CFC-11, and SF_6 was less than 2%. Estimated limit of detection is 1 fmol/kg for CFC-11, 3 fmol/kg for CFC-12 and 0.05 fmol/kg for SF_6.

5.26 Float deployments

Thirty-eight floats were deployed during the cruise on behalf of science groups not funded through the US GEOTRACES program. The float deployments are detailed in Table 8.

Table 8. Float deployments during GP17-OCE cruise

Station	Floats deployed
1	Jumbo and BGC ARGO
4	Jumbo (second Jumbo float damaged during deployment and not deployed)
5	ARGO core
6	BGC ARGO
10	BGC ARGO
11	ARGO core
12	BGC ARGO
13	ARGO core
14	BGC ARGO
16	ARGO Core
17	ARGO Core
18	BGC ARGO
20	BGC ARGO
21	ARGO Core
22	BGC ARGO
23	Deep float
24	BGC ARGO
25	BGC ARGO and Deep float
26	BGC ARGO and Deep float
27	BGC ARGO and Deep float
28	Deep float
29	BGC ARGO and Deep float
30	Deep float
31	ARGO Core and Deep float
32	BGC ARGO
33	ARGO Core and BGC ARGO

5.27 Ultrafiltration/Colloids

PI: Jessica Fitzsimmons
At sea: Kristie Dick

Two ultrafiltration methods were used to separate the truly dissolved, "soluble," metal fraction from the colloidal fraction in various samples: 1) a cross flow filtration system (Pellicon XL) and 2) a membrane filtration system (Anodisc). All membrane filters had a pore size of 20 nm, and cross flow filters had a pore size of 3 nm (10 kDa). Ultrafiltered samples from both systems, along with the <0.2 μm dissolved samples collected using the GTC rosette, will be analyzed in the Fitzsimmons laboratory at Texas A&M University using ICP-MS techniques for Fe, Mn, Cu, Cd, Zn, Ni, Pb, and Sc concentrations. The three size fractions will then be analyzed together from a single depth to reveal the relative contributions of small (3-20 nm) and large (20-200 nm) colloids to the dissolved metal fraction.

521 total dissolved (<0.2 μm) 250 mL samples were collected from the GTC rosette. Additionally, 373 x 60 mL samples were collected through the Anopore membrane system (<20 nm). 734 x 60 mL samples were collected through the 10 kDa cross-flow filtration system (3 nm) - one permeate 60mL bottle and one retentate 60mL bottle from each of 373 sampling depths. In addition, ultrafiltered samples were provided collaboratively to several other groups. 104 x 1 L cross flow filtered (<3 nm) samples from the super stations were provided to Marty Fleischer and Bob Anderson (Lamont-Doherty Earth Observatory) to calculate the partitioning of Th isotopes into soluble and colloidal fractions. 64 x 1 L cross flow filtered (<3 nm) samples were provided to Seth John (University of Southern California) for measurement of Ni and Cu isotopes. 38 x 1L cross flow filtered (<3 nm) samples were provided to Tim Conway (University of South Florida) to determine whether soluble and colloidal Fe have variable Fe isotope ratios in seawater, which would suggest different sources or different controlling processes for soluble and colloidal Fe.