# **U.S. GEOTRACES GP17-ANT Cruise Report**

29 November 2023 – 28 January 2024

Punta Arenas, Chile - Lyttelton, New Zealand

RVIB Nathaniel B. Palmer (cruise NBP24-01)

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Bathymetric map of the Amundsen Sea showing GP17-ANT sampling stations

### **1. Introduction**

Trace elements and isotopes (TEIs) regulate marine primary production and provide key tracers of past and present oceanic processes, such as circulation and particle export. The international research program GEOTRACES aims to identify the processes and quantify the fluxes that control the distributions of TEIs in the oceans, and to establish the sensitivity of those distributions to changing environmental conditions (Anderson & Henderson, 2005; Anderson, 2020). To that end, research expeditions conducted as part of the U.S. GEOTRACES program have collected samples for measurements of a large suite of TEIs together with hydrographic and ancillary data along a series of basin-scale ocean sections in the North Atlantic, North and South Pacific, and Arctic Oceans.

Here we report on the U.S. GEOTRACES GP17-ANT expedition aboard RVIB *Nathaniel B. Palmer* (cruise NBP24-01), which departed Punta Arenas, Chile on 29 November 2023, and arrived Lyttelton, New Zealand on 28 January 2024, with a science party of 35 (Fig. 1). This oceanographic expedition was focused on collecting water-column sampling and hydrographic measurements at stations located over the continental shelf of the Amundsen Sea, as well as several deep-ocean stations located north of the Antarctic shelf break. The GP17-ANT cruise followed a companion expedition, the U.S. GEOTRACES GP17-OCE expedition aboard RV *Roger Revelle* (cruise RR2213), which departed Papeete, Tahiti on 1 December 2022, and arrived Punta Arenas, Chile on 25 January 2023. Together, the two GP17 cruises were designed to document the distribution of TEIs in the South Pacific and Southern Oceans, ranging from the highly oligotrophic waters of the South Pacific subtropical gyre to the highly productive waters of the Antarctic continental shelf, the latter region being the focus of the GP17-ANT cruise.

The Antarctic continental margins are thought to comprise important sources of micronutrient trace elements such as iron and manganese, which may fuel biological production and carbon export over the Antarctic shelves and offshore in the Antarctic Circumpolar Current (Arrigo et al., 2015; Hawco et al., 2023). Furthermore, the Antarctic margins are experiencing rapid environmental changes that are expected to impact ocean circulation and biogeochemical cycling (Kennicutt et al., 2015; Naughten et al., 2018; Dinniman et al., 2023), for which TEIs can provide tracers for the modern and past ocean, as well as important constraints on numerical models of the Earth system (Henderson, 2002; Horner et al., 2021; Jenkins et al., 2023). In this context, the Amundsen Sea is of particular interest because of the pronounced, decadal-scale increases documented in the basal melt rates of its bordering glacial ice shelves, which are being driven by intrusions of warm Circumpolar Deep Water (CDW) onto the continental shelf. This glacial melting has potentially major impacts on global sea level, on the formation of Antarctic Bottom Water in the Ross Sea, and on primary production due to inputs of benthic and glacial iron and other bioactive TEIs that are likely mediated by these melting processes (Rignot et al., 2019; Li et al., 2023; St-Laurent et al., 2017).

Given the importance of the Amundsen Sea for glacial meltwater discharge and associated inputs and mobilization of TEIs, the potential impacts of these inputs, and the rapid pace of environmental changes in this region, it was selected as the focus of the U.S. GEOTRACES GP17-ANT expedition, to complement the open-ocean GP17-OCE cruise. With support from the NSF Chemical Oceanography and Antarctic Oceans and Atmosphere Programs, a cruise management award to Sedwick, Lam, Sherrell and Anderson allowed for the planning and implementation of the 60-day GP17-ANT expedition aboard RVIB *Nathaniel B. Palmer*, which provided a platform for the collection of samples for 23 individual science projects that together encompass measurements of nearly all of the GEOTRACES key TEIs (see Appendix 3 and Tables 1, 2 and 5). These NSF-funded projects address a range of topics aligned with the scientific mission of the GEOTRACES program, including the sources, fate and biological impacts of bioactive trace elements; the distribution and transport of glacial meltwater; the compositional evolution of CDW as it upwells and circulates on the shelf; the rates and elemental stoichiometry of biological and biogeochemical processes; the veracity of paleoenvironmental proxies; and the fidelity of numerical model simulations.

In total, the GP17-ANT cruise sampled 21 stations over the Amundsen Sea continental shelf, 3 stations over the continental slope, and 3 off-shelf stations, including one deep-ocean station that provides a crossover with the preceding GP17-OCE cruise. All of these GP17-ANT stations included collection of samples with a near-surface towfish, a conventional CTD-rosette, a trace-metal clean CTD-rosette, and McLane in situ pumps. Additional sampling activities included collection of aerosols, precipitation, sea ice and snow, as well as sediment cores for pore-fluid extraction, and high-volume pumped seawater samples for radium isotopes and beryllium-7. Although most of the GP17-ANT science goals were achieved, large expanses of heavy sea ice surrounding the Amundsen Sea Polynya prevented access to several of our planned sampling locations, including stations near the Thwaites Ice Shelf, in Pine Island Bay, and over the eastern portion of the outer Amundsen Sea shelf. Nevertheless, the cruise provided us with exciting opportunities to collect samples from stations adjacent to the Dotson and Getz Ice Shelves, as well as on- and off-shelf stations that were impacted by melting sea ice, polynya stations where phytoplankton biomass was extraordinarily high, and a station adjacent to fast ice with near-zero chlorophyll fluorescence in the water column.

Several tables with detailed expedition information are appended to this report. Appendix 1 provides a list of the stations occupied with coordinates, station type, sampling dates, and observed bottom depths. Appendix 2 presents a list of science participants on the cruise, as well as funded GP17-ANT science projects. Finally, Appendix 3 contains a list of all projects and PIs that were funded as part of the GP17-ANT science program.



Figure 1. The GP17-ANT expedition science party and ASC personnel near the Getz Ice Shelf.

## **References**

Anderson, R. F. (2020). GEOTRACES: Accelerating research on the marine biogeochemical cycles of trace elements and their isotopes. *Annual Review of Marine Science*, 12.

Anderson, R. F., & Henderson, G. M. (2005). GEOTRACES. Oceanography, 18(3), 76.

Arrigo, K. R., van Dijken, G. L., & Strong, A. L. (2015). Environmental controls of marine productivity hot spots around Antarctica. *Journal of Geophysical Research: Oceans*, 120(8), 5545-5565.

Hawco, N. J., Tagliabue, A., & Twining, B. S. (2022). Manganese limitation of phytoplankton physiology and productivity in the Southern Ocean. *Global Biogeochemical Cycles*, 36, e2022GB007382. https://doi.org/10.1029/2022GB007382

Henderson, G. M. (2002). New oceanic proxies for paleoclimate. *Earth and Planetary Science Letters*, 203(1), 1-13. https://doi.org/10.1016/S0012-821X(02)00809-9

Horner, T. J., Little, S. H., Conway, T. M., Farmer, J. R., Hertzberg, J. E., Janssen, D. J., et al. (2021). Bioactive trace metals and their isotopes as paleoproductivity proxies: An assessment using GEOTRACES-era data. *Global Biogeochemical Cycles*, 35, e2020GB006814. https://doi.org/10.1029/2020GB006814

Kennicutt, M. C., Chown, S. L., Cassano, J. J., Liggett, D., Peck, L. S., Massom, R., ... & Allison, I. (2015). A roadmap for Antarctic and Southern Ocean science for the next two decades and beyond. *Antarctic Science*, 27(1), 3-18.

Li, Q., England, M. H., Hogg, A. M., Rintoul, S. R., & Morrison, A. K. (2023). Abyssal ocean overturning slowdown and warming driven by Antarctic meltwater. *Nature*, *615*(7954), 841-847.

Naughten, K. A., Meissner, K. J., Galton-Fenzi, B. K., England, M. H., Timmermann, R., & Hellmer, H. H. (2018). Future projections of Antarctic ice shelf melting based on CMIP5 scenarios. *Journal of Climate*, 31(13), 5243-5261.

Rignot, E., Mouginot, J., Scheuchl, B., Van Den Broeke, M., Van Wessem, M. J., & Morlighem, M. (2019). Four decades of Antarctic Ice Sheet mass balance from 1979–2017. *Proceedings of the National Academy of Sciences*, *116*(4), 1095-1103.

St-Laurent, P., Yager, P. L., Sherrell, R. M., Stammerjohn, S. E., & Dinniman, M. S. (2017). Pathways and supply of dissolved iron in the Amundsen Sea (Antarctica). *Journal of Geophysical Research: Oceans*, *122*(9), 7135-7162.

## 2. Cruise Narrative

The cruise track and all stations, including soak and test stations, are shown in Figure 2.

#### 2.1 Pre-cruise Planning Meeting

A pre-cruise planning meeting was held at Old Dominion University on 13-14 March 2023, and attended by principal investigators, cruise participants, and others involved in the cruise organization. The meeting was used to provide attendees with updated information on the plans and scientific context of the expedition, discuss cruise logistics, introduce personnel and funded science projects, and gather information for the required Support Information Package, which was subsequently completed by the cruise management team and submitted to the USAP Antarctic Support Contractor (ASC) in April 2023. Several ASC personnel joined the meeting via Zoom, although the cruise management team was disappointed that no ASC staff were permitted to participate in person, given the complexity of the cruise and the many logistical questions that were raised during the meeting. Also undertaken at the pre-cruise meeting was

discussion of the science berthing available on the RVIB *Palmer*, which resulted in an initial assignment of 18 berths for the cruise management team, 10 berths for ASC personnel, and 17 berths for science project participants, the latter having been reduced from initial requests totaling 25. This was the final breakdown of science berths that ultimately sailed on GP17-ANT, although subsequent adjustments to the management team and ASC personnel rosters were required in order to balance the shipboard workload and include an enhanced medical professional on the ASC team, per NSF requirements.



Figure 2. Map of GEOTRACES GP17-ANT cruise track and stations (Google Earth).

# 2.2 Mobilization and Departure

Mobilization commenced with the arrival of 13 key personnel in Punta Arenas on 15 November 2023, ostensibly to facilitate the early onload of large equipment, although that was ultimately not feasible due to unanticipated sea trials of the RVIB *Palmer* (which had recently had its four engines rebuilt) on 16-17 November. The early-arriving group embarked the ship on 18 November, and began loading and staging breakbulk science cargo. Most of the remaining cruise participants and portcall personnel arrived on November 17, and embarked the ship on

November 19, after completing required COVID testing. Fortunately, all cruise participants and portcall personnel tested negative.

Loading of science cargo and equipment, and shipboard setup of science equipment continued during the week of 20 November, although the onload process was substantially delayed by high winds that shut down the port on a number of days, a required relocation of the ship during a day of high winds, and on-site modifications to the winch support platform that had been fabricated for the cruise, which did not fit in the ship's deck sockets. In addition, the extraordinarily large volume of science cargo and equipment that was loaded for both our cruise and a subsequent geophysics cruise contributed to a more than six day delay in our cruise departure date.

The RVIB *Palmer* departed Punta Arenas on the afternoon of 29 November 2023, soon after which we conducted successful test deployments in the Straits of Magellan, using the newly installed winches for the trace-metal CTD-rosette and the McLane submersible pumps. We then got underway for Palmer Station, which the ship was required to visit in order to avoid tax charges for fuel taken on in Punta Arenas. To offset some of the science time lost due to cargo loading and this unanticipated diversion, NSF allowed the ship to use four engines while underway, to save us some transit time. Nonetheless, these delays resulted in a loss of around 5 science days, which translated to a lesser number of sampling stations than initially planned.

#### 2.3 Transit, Soak- and Test Stations

We experienced favorable winds and seas during our crossing of the Drake Passage on 1-2 December 2023. On 2 December we conducted "soak" casts to 1000 m depth at Station 1, north of the Antarctic Peninsula in the Antarctic Circumpolar Current (ACC), with the GEOTRACES trace metal clean CTD-rosette (two casts were used to close all 44 Go-Flo bottles at ~200 m depth) and the ODF conventional CTD-rosette (one cast was used to close all 36 Niskin-type bottles at ~250 m depth, and all bottles were sampled for shipboard salinity determinations in order to identify any leaking bottles). On 3 December we enjoyed fair weather and scenic views along the Gerlache Strait en-route to Palmer Station, where the ship paused briefly before beginning the transit westward across the continental shelf towards the Amundsen Sea area.

Favorable weather continued through 4 December 2023, which allowed us to complete the setup and an initial test deployment of the towfish clean underway surface water sampling system west of the shelf break at Station 1.5. The towfish test deployment was successful, and allowed the collection of large volumes of uncontaminated near-surface seawater for the shipboard analysts. Shipboard measurements indicated relatively low dissolved iron concentrations (~0.1 nM) in this seawater. Continuing westward along ~65°S under generally favorable sea conditions, we conducted a test sampling station near 79°W on 5 December, where we successfully completed two shallow casts with the GEOTRACES clean CTD-rosette, one shallow cast with the ODF

CTD-rosette, and a test deployment of the McLane in-situ pumps and radium surface-sampling pump. Samples from the clean rosette Go-Flo bottles were analyzed for dissolved iron to check for potential contamination of the samplers, and for salinity to check for leaking bottles.

#### 2.4 Cruise and Sampling Operations

After completing the test station, we continued the transit west to arrive on the evening of 7 December 2023 at Station 3, which was a deep-ocean (~4700 m depth) crossover station with the GP17-OCE cruise located at 67°S, 100°W. This station was occupied from the evening of 7 December through early morning of 10 December, and included towfish surface-water sampling, two casts with the GEOTRACES clean CTD-rosette, three casts with the ODF CTD-rosette, two casts with the McLane submersible pumps, and deployment of pumped sampling systems for radium and beryllium-7. Hard work by the science team, ASC personnel and the ship's crew saw all sampling operations completed with success, despite high winds and moderate, shifting sea ice cover. With broad swathes of melting sea ice and numerous icebergs in the vicinity, conditions at Station 3 were very different from the previous, late January 2023 occupation during GP17-OCE in largely ice-free conditions.



**Figure 3**. Maps showing sea-ice concentration (%) estimated from AMSR2 and AMSR-E satellite microwave data for (a) 11 December 2023, as we approached the Amundsen Sea shelf, and (b) 7 January 2024, as we began a transit west to sample our last few stations (Fig. 2). Shown are the Pine Island Polynya (PIP), Amundsen Sea Polynya (ASP), and iceberg B-22A (B). Note the heavy sea ice cover (purple) that prevented the ship's access to the Pine Island Polynya. Images: University of Bremen.

After completing Station 3, with heavy sea ice blocking our planned approach to the Amundsen Sea shelf between ~102° and 104°W (Fig. 3a), we followed a narrow band of light ice cover and open water southwest to the shelf break at 71°S, 113°W, where we occupied Station 4 in approximately 2740 m water depth. Located in a polynya to the northeast of iceberg B-22A, this station was characterized by extremely high phytoplankton biomass (~30  $\mu$ g L<sup>-1</sup> chlorophyll-a, based on CTD fluorometer measurements) in the shallow surface mixed layer. Sampling was completed between the afternoon of 12 December and early morning of 14 December 2023, and included two casts with the GEOTRACES clean CTD-rosette, three casts with the ODF CTD-rosette, two casts with the McLane submersible pumps, and deployment of pumped sampling systems for radium and beryllium-7. After sampling Station 4, we headed west into sea ice floes and deployed a Zodiac for possible sea ice sampling, however the ice proved unsuitable for sampling, being an unstable mixture of old and young ice with a heavy snow cover. We had planned to head south from Station 4 to occupy stations near the shelf break at 113-114°W, however satellite imagery indicated that our proposed path to the east of iceberg B-22A and proposed stations beyond had become impassable due to heavy, D5-type sea ice cover.

Instead, we continued west through navigable sea ice floes and patches of open water, and skirted the western edge of iceberg B-22A across the shelf break near 116°W. Station 5 was occupied in open water just north of the shelf break near 71°31'S, 116°21'W, with a water depth of ~1020 m. We commenced sampling at Station 5 on the evening of 14 December 2023, with operations including an arriving towfish surface-water collection, a GEOTRACES clean CTD-rosette cast, two casts with the ODF CTD-rosette, one cast with the McLane submersible pumps and the radium surface-water pump, sediment sampling using the multicorer (which recovered twelve complete cores), and beryllium-7 sampling in the upper water column. Station 5 was characterized by very high phytoplankton biomass (more than 20  $\mu$ g L<sup>-1</sup> chlorophyll-a, based on CTD fluorometer measurements). After completing sampling at Station 5 on the evening of 15 December, we conducted a sea ice sampling operation during the transit south from the station, with the successful collection of several ice cores.

We then continued south to occupy four shelf stations (Stations 6-10) along ~116°W, with the aim of completing a meridional transect extending from the shelf break through the highly productive Amundsen Sea Polynya and up to the Getz-A Ice Shelf. Each of these stations included surface-water collection using the towfish, a clean CTD-rosette cast, two casts with the ODF rosette, and one cast with the McLane submersible pumps and the radium surface-water pump, with other sampling activities performed at selected stations. Station 6 was located amongst sea ice floes on the northern flank of the northwest-southeast trending Dotson Trough (ca. 72°30'S, 116°W, 530 m depth). There we completed our core water-column sampling operations late on 16 December 2023, under challenging conditions of increasing winds and drifting sea ice floes. The Vectran line used for the McLane pumps was damaged during

deployment, and had to be cut and re-terminated, after which the pumps were deployed with success.

In deeper waters of the central Dotson Trough, we sampled Station 7 (ca. 72°58'S, 115°45'W, 680 m water depth) on 17 December 2023, as a reoccupation of a station that was previously sampled during the ARTEMIS program in early 2022. Drifting sea ice floes again complicated our sampling operations. This station was designated as a "super station", with collection of additional water-column samples to provide for a number of high-volume sample requests. After successful collection of a monocore using the ODF CTD rosette, the multicorer was deployed and again recovered twelve full sediment cores and a near-bottom water sample. Sea ice sampling was attempted, however sea ice in the area again proved unsuitable for coring.

Station 8 was located on the southwest flank of the Dotson Trough (73°20'S, 116°W, 500 m water depth) in ice-free waters with very high phytoplankton biomass. After sampling this station on 18 December, 2023, we continued south to Station 9, which was located in ice-free waters immediately adjacent to the western end of the Getz-A ice shelf (74°04'S, 116°W, 1070 m water depth). Station 9 was sampled on 19 December, with our final operation being the deployment of an instrumented surface drifter buoy, as part of the management team's STEM education effort. Stations 10 (ca. 73°39'S, 115°59', 730 water depth) and 11 (ca. 73°44'S, 114°W, 530 m water depth) were sampled on 20 and 21 December 2023, respectively. Both these stations were located in the Antarctic Coastal Current (AACC), which we identified using underway shipboard ADCP surveys. The AACC flows westward close to the coast and glacial ice shelves, and may be an important vector for transporting glacial meltwaters and bioactive trace elements to other areas on the Antarctic margin. Both of these stations were characterized by very high phytoplankton biomass.

On 21-22 December 2023, we conducted an underway survey with the ship's ADCP while heading eastward along the Dotson Ice Shelf, under favorable conditions with light winds. Areas of surface outflow and deep inflow were identified, consistent with observations collected during the ARTEMIS project in early 2022, and we planned to return and sample stations at those locations after completing sampling at Station 12 (~74°5'S, 110°16'W, 460 m water depth), which was located in the AACC to the east of the Bear Peninsula and to the west of an area of heavy sea ice, fast ice and icebergs that extended north from the Crosson and Thwaites Ice Shelves. This station was distinguished by remarkably low phytoplankton biomass (near-zero signal on the CTD fluorometers) in the surface waters that emerged from beneath the ice to the east, and may provide key information on the composition of AACC waters prior to the onset of seasonal primary production. All sampling at Station 12 was completed on 22 December 2023.

After Station 12, we moved east and positioned the ship in fast ice during the early hours of 23 December 2023, where conditions allowed science personnel to disembark for the collection of

sea ice, snow and brine samples. This seven-hour sampling operation was led by Laura Whitmore (UAF), assisted by rotating shifts of the science party, and included collection of snow, ice and brine samples for physical parameters, trace elements, beryllium-7, radium isotopes, inorganic carbon, noble gases and tritium, as well as an entertaining visit from a waddle of Adelie penguins. With the ice station sampling completed, we headed west to the Dotson Ice Shelf to sample stations selected based on our earlier ADCP survey. After another targeted ADCP survey confirmed southward flow at around 700 m depth, adjacent to the ice shelf near 112°20'W, we commenced sampling "inflow" Station 13 (~74°15'S, 112°20'W, 1070 m depth) seaward of the ice shelf on the afternoon of 23 December. Sampling operations comprised the standard suite of towfish, clean CTD-rosette cast, two casts with the ODF rosette, and one cast with the McLane submersible pumps and radium surface-water pump. Overnight, the pump cast was complicated by a significant ice calving event and associated waves that impacted the ship. This necessitated a rapid relocation with pumps in tow while dealing with shoaling bottom topography. Fortunately, all equipment was successfully recovered without damage, thanks to the able and quick response of the ASC marine techs and ship's winch operators.

After completing Station 13 on the morning of 24 December 2023, we undertook a targeted ADCP survey of the western extent of the Dotson Ice Shelf, and confirmed a strong northward flow in the upper 400 m of the water column near 74°10'S, 113°19'W (~550 m water depth), adjacent to a protrusion of the ice shelf dubbed Penguin Point. Here we commenced sampling "outflow" Station 14 on the afternoon of 24 December. This station was designated a super station, with an additional clean-CTD rosette cast allowing collection of higher-volumes of water-column samples from 16 depths instead of the usual 12. In addition, seafloor sediments were collected using both the monocorer attached to the ODF rosette, and the multicorer, which collected eight complete cores and a near-bottom seawater sample in a trace-metal clean Niskin-X sampler that was mounted on the corer frame. The final operation at Station 14 was the deployment of another surface drifter buoy, with the aim of obtaining information on the path of surface waters north of the ice shelf outflow.

After departing Station 14 early on 25 December 2023, we headed northwest to the next station at reduced speed, to allow the hardworking science party some time to rest and enjoy the Christmas lunch and dinner. After the relatively modest levels of phytoplankton biomass observed along the Dotson Ice Shelf, Station 15, located in the mostly ice-free waters of the central eastern Dotson Trough (73°20'S, 115°W, 890 m water depth), marked a return to very high algal biomass as estimated by our CTD fluorescence measurements. We completed our standard sampling suite of towfish, CTD rosette casts, and in-situ pump deployment on 25-26 December, as well as sediment sampling using the monocorer and multicorer. With the multicorer, we collected twelve complete sediment cores and another near-bottom seawater sample. Interestingly, the sediment cores included a surface layer of fluffy, orange-colored material, suggesting oxidation of sediment-derived iron(II) near the seafloor.

On 26-27 December 2023 we sampled Station 16 in the northeast Dotson Trough (~73°S, 113°47'W, 470 m water depth), among scattered sea ice and within several miles of a very large tabular iceberg. This station was again marked by exceptionally high phytoplankton biomass as estimated from the CTD fluorometers and the ship's continuous surface-water fluorometer, and marked the start of stations along an eastward zonal transect into a thick band of D4/D5 sea ice that has prevented us from entering the Pine Island Polynya. After completing our standard suite of sampling operations at Station 16, we continued east to Station 17, which was located in relatively shallow waters over Bear Ridge (~73°S, 112°W, 420 m depth). Here biomass was again exceptionally high, with surface waters visibly green against the numerous ice floes. This station was sampled as a super station on December 27-28, and included a second clean CTD-rosette cast in addition our standard sampling operations to satisfy requests for large-volume seawater samples. More sediment samples were collected with the monocorer and the multicorer, with the latter recovering eleven cores and a near-bottom seawater sample.

From Station 17, we pushed further east toward Station 18, which was initially planned for 110°W. However, the ship encountered impassably thick sea ice near 111°W, at the western edge of the large swath of D4/D5-type ice separating the Amundsen Sea and Pine Island Polynyas. Given this, we chose to occupy Station 18 nearby (~73°03'S, 111°12'W, 320 m depth) amongst ice floes and bergs, on 28 December 2023. Here we undertook our standard suite of sampling operations, although with the towfish sampling conducted while departing from station rather than arriving. A planned sea ice sampling to the east of Station 18 on the evening of 28 December was cancelled due to adverse weather (35+ knot winds, poor visibility) and unsuitable ice. With heavy sea ice preventing any further transit east, we chose to head back west along ~73°S, and occupied Station 19 (~73°S, 118°W, 410 m depth) on 29-30 December. There, in relatively shallow, high-biomass waters, we completed our standard sampling operations comprising towfish, clean CTD-rosette cast, two casts with the ODF CTD-rosette, and deployment of the McLane submersible pumps and radium surface-water pump.

On 30 December 2023 we transited south to Station 20 (~73°51'S, 118°21'W, 1240 m depth), at the edge of a several-mile-wide band of compacted sea ice floes, bergs and brash ice that abutted the western portion of the Getz-B Ice Shelf (following the nomenclature of Lee et al., 2024). This station location was chosen following a shipboard ADCP survey along the ice edge, which revealed the consistent westward flow of the AACC in the upper water column, as well as intermittent northward flows that may have reflected outflow from the adjacent ice shelf. After completing our standard suite of sampling operations on 30-31 December, we moved northwest along the sea ice edge to search for larger ice floes that were amenable to sea ice sampling. After locating a suitable floe, the ship pulled alongside and three members of the science party (Whitmore, Marsay and Passcantando) were deployed using a personnel basket for three hours of ice and snow sampling on 31 December.

We then headed north to begin a second meridional transect along the western edge of the Amundsen Sea Polynya, occupying Station 21 (~73°29'S, 118°22'W, 580 m depth) on 31 December 2023-1 January 2024. There a deployment mishap necessitated a re-termination of the clean CTD-rosette conducting cable, after which we completed our standard sampling operations in calm conditions amid ice floes and welcome glimpses of sunshine. We also collected seafloor sediments at this station, which marks the eastern end of a trough that extends west then northwest toward the shelf break. A monocore was collected using the ODF CTD-rosette, followed by twelve complete cores and a near-bottom water sample collected with the multicorer. Finally, a third instrumented surface drifter buoy was released before departing station on New Year's Day.

Further north at Station 22 (~72°59'S, 118°50'W, 400 m depth), on the western perimeter of the Amundsen Sea Polynya, phytoplankton biomass was notably lower than at previous stations (< 2  $\mu$ g/L chlorophyll-a, based on fluorescence measurements from the CTDs and ship's underway system). There we completed our standard sampling operations on 1-2 January 2024, amid thin ice floes and several icebergs, and enjoyed continued fine weather and light winds. We then moved north to occupy Station 23 (~72°34'S, 118°56'W, 470 m), near the northern edge of the shelf and on the southern flank of the Dotson Trough outlet. Phytoplankton pigment samples were distinctly orange, perhaps suggesting dominance by diatoms rather than *Phaeocystis antarctica*, which appear to have dominated our previous high-biomass stations (to be confirmed by post-cruise pigment analyses). After completing our standard sampling operations on 2 January 2024, we attempted to sample nearby sea ice floes, however these again proved unsuitable for sampling, with slushy ice encountered under thick overlying snow.

On 3 January 2024 we pushed northwards through heavier sea ice to the shelf break to begin sampling operations at Station 24 (~71°58'S, 119°08'W, 1410 m depth). With preliminary shipboard measurements from samples at shelf-break Station 5 suggesting offshore transport of dissolved iron and manganese from shallower shelf sources, we chose to sample Station 24 as a super station, with higher volume samples collected from 16 depths. Weather conditions quickly deteriorated during the day, with the combination of 35-40 knot winds and shifting sea ice floes forcing the early termination of a McLane pump deployment and preventing us from attempting a second clean CTD rosette cast and beryllium-7 pumping operations; subsequent sampling operations were limited to ODF CTD rosette casts. After completing those deployments in continuing high winds on the evening of 3 January, we got underway northwards to Station 25.

We reached Station 25 (~71°31'S, 119°W, 2060 m depth) early on 4 January 2024, and commenced sampling operations with two ODF rosette casts. This station was characterized by relatively high chlorophyll fluorescence, and was sampled as an off-shelf full station. With winds decreasing after completion of the two ODF rosette casts, we moved off station to collect

underway towfish samples, then repositioned to complete two clean CTD rosette casts, the ODF rosette pigments-radium-thorium (PigRaTh) cast, and two McLane pump deployments, the latter in the lee of an iceberg to reduce problems associated with drifting sea ice floes. Station 25 sampling also included collection of pumped seawater for beryllium-7 analysis, and deployment of the multicorer, which recovered ten full cores and an associated near-bottom seawater sample. We then returned to shelf-break super Station 24 (ca. 71°58'S, 119°08'W, 1410 m depth) on the evening of 5 January and in the early hours of 6 January began the sampling operations that had been previously curtailed by poor weather: McLane pumps and radium surface pump, an ODF rosette PigRaTh cast (repeated for comparison with the McLane pumps), a second clean CTD rosette cast, and beryllium-7 pumping operations. With this work completed on the evening of January 6, we began heading northwest, stopping to collect samples from a sea ice floe, which was completed around midnight.

With access to the Pine Island Polynya and eastern Amundsen Sea still blocked by large expanses of D4 and E4 sea ice (Fig. 3b), and after consultation with the ship's Captain, we made the decision to transit west in the early morning hours of 7 January 2024, with the aim of occupying stations in the West Getz Trough and adjacent to the western portions of the Getz Ice Shelf during our final week of sampling operations. However, the transit proved much more difficult and longer than anticipated, with the ship encountering large areas of C4- to D5-type sea ice en-route. After two days of working through ice floes as thick as several meters, and numerous course adjustments to avoid heavy ice, the ship finally entered a polynya north of the western portions of the Getz Ice Shelf on the morning of 9 January. Due to the heavy sea ice cover, our plans to sample two stations on the outer shelf were cancelled.

On the afternoon of 9 January 2024, we conducted a shipboard ADCP survey along the western edge of the Getz-E Ice Shelf (following the nomenclature of Lee et al., 2024), and identified an area of apparent outflow from beneath the glacial ice shelf near Grant Island. Here we occupied Station 26 (~74°22'S, 130°56'W, 470 m depth), the first of a series of planned stations running northward along the eastern side of the West Getz Trough. After completing our standard suite of shelf-station sampling operations – towfish, clean CTD rosette cast, two ODF CTD rosette casts, and deployment of the McLane submersible pumps and radium surface-water pump – in sunny conditions and brisk winds, we deployed a fourth instrumented drifter on the morning of 10 January, and then headed northwest along the ice shelf toward Station 27, which was located to the west of Dean Island.

Station 27 (~74°21'S, 128°34'W, 820 m depth) was selected as another location of possible glacial outflow in the upper water column, based on our shipboard ADCP observations, as well as possible inflow of modified Circumpolar Deep Water (mCDW) at depth. We completed our standard suite of sampling operations at Station 27 on 10-11 January 2024, with the addition of a multicorer deployment that was again successful, recovering twelve complete cores with well-

preserved sediment-water interfaces and a near-bottom seawater sample in a Niskin-X sampler. We then headed further northwest along the Getz-D Ice Shelf (following the nomenclature of Lee et al., 2024) to Station 28 (~73°55'S, 127°23'W, 780 m depth), which was located near the juncture of the ice shelf and Siple Island. This location was selected after a shipboard ADCP survey revealed active inflow under the ice shelf, and thus complements Stations 26 and 27 in terms of assessing the chemical modification of mCDW that interacts with the glacial ice shelf. After completing standard shelf-station sampling at Station 28 in fine weather on 11 January, we hurriedly departed the site later in the evening, as northwesterly winds began pushing a band of heavy sea ice toward the ice shelf.

Moving west overnight, we paused for a sea-ice sampling operation, during which snow, iceedge seawater and ice slush were collected, although the ice floes themselves proved too soft for conventional ice coring. With the sea ice sampling completed on the morning of 12 January 2024, we got underway for Station 29 (~73°28'S, 132°54'W, 1590 m depth), which was located beyond the shelf break near 133°W. Although located to the west of the West Getz Trough and not directly connected to the inner-shelf Stations 26-28, Station 29 will provide us with another view of the water-column distributions of trace elements and isotopes in an off-shelf location, in addition to Stations 4 (near 113°W) and 25 (near 119°W). Station 29 was occupied as a "semisuper" station, with samples collected from additional depths (a total of 17 water-column depths), but without the extra volume of a third Go-Flo bottle at each depth from the clean CTD rosette. Commencing mid afternoon on 12 January, our sampling operations included towfish surface-water collection, two clean CTD-rosette casts, two conventional CTD-rosette casts, and deployment of the McLane submersible pumps and the radium surface-water pump. Sampling conditions were challenging, with winds exceeding 25 knots, drifting ice floes, blowing snow and poor visibility.

Sampling at Station 29 was completed during the afternoon of 13 January, and, with winds dropping, a zodiac was deployed for sea ice sampling, although no suitable floes were identified in the vicinity. After completing some crane-assisted cargo movements in the relatively calm afternoon conditions, we commenced our transit northward to New Zealand in the evening of 13 January 2024. Our return transit began 1-2 days earlier than we had initially planned, in order to accommodate a required inspection and possible cleaning of the ship's hull in Nelson, New Zealand, ahead of demobilization in the port of Lyttelton. During our transit north the ship maintained a good speed of 10-12 knots through mostly moderate seas, apart from a period of rough weather on January 17-18. Shipboard sample processing, experiments, analyses and some packing of science equipment and samples were completed during the transit, and the collection of aerosols and precipitation, samples for mercury and proteins from the ship's underway seawater supply, and underway sensor measurements continued until we reached the New Zealand EEZ on 20 January 2024.

### 2.5 Arrival in New Zealand and Demobilization

On 24 January 2024 the ship was positioned in Tasman Bay, offshore of Nelson, New Zealand, where relatively calm conditions allowed for packing and movement of science cargo, including some larger items that required use of the ship's cranes. On 25 January, the ship docked in Nelson for refueling and the hull inspection required by the New Zealand Ministry for Primary Industries. It was subsequently determined that no hull cleaning was required, and the ship got underway for Lyttelton that evening, arriving offshore of Lyttelton Harbor on the morning of 27 January. With no berths available in the port of Lyttelton, the ship remained offshore on 27 and 28 January, until berthing at a cruise ship dock in Lyttelton on the evening of 28 January. Much of the demobilization of science cargo and cruise samples was completed on 29 and 30 January, and all of the science party were required to disembark by the evening of 30 January. Unloading of the remaining science cargo and samples was completed by ASC personnel and ship's crew on 31 January 2024.

### References

Lee, J. I., Hillenbrand, C. D., Wellner, J. S., Kim, H. J., Rhee, H. H., Yoo, K. C., ... & Lee, M. K. (2024). Seafloor geomorphology of the Wrigley Gulf shelf, Amundsen Sea, West Antarctica, reveals two different phases of glaciation. *Earth Surface Processes and Landforms*.

## 3. Major Sampling Systems

#### 3.1 ODF Rosette

A 36-place CTD-rosette (hereafter the ODF rosette) with Niskin-type water samplers was provided by the Scripps Oceanographic Institution Ocean Data Facility (SIO-ODF) and used for the water-column sampling of less contamination-prone chemical species (Table 1). The ODF rosette was deployed and recovered by the ASC Marine Technicians (Ken Block, Heather Jackson, Stuart Siddons and Henry Thoreen) and the winch was operated by ship's crew (Bienvenido Aaron, Louie Andrada and Ronnie Carpio), with profiling and sampling overseen by the ASC Electronics Technicians (Chris Linden and Ben Rosen-Filardo), SIO-ODF team members (Andrew Barna, Aaron Mau and Gabriel Matthias) and Chief Scientists, with assistance from ODF Supertech Martin Fleisher (LDEO) for monocorer deployments. Subsampling from the Niskin-type samplers was managed and performed by the ODF Supertech team Martin Fleisher, Katherine Kouba (OSU) and Kameko Landry (Boston College). Laboratory Supervisors Bettina Sohst (ODU) and Laura Whitmore (UAF) coordinated sample requests and sample log sheets, and served as water cops with assistance from Rebecca Miller (Physician) and April Abbott (CCU). The SIO-ODF team of Andrew Barna, Kelcey Chung, Gabriel Matthias and Aaron Mau were responsible for maintenance and calibration of the CTD-rosette system, and for the subsampling and measurements of dissolved oxygen (from all depths sampled), salinity

(from all bottles sampled) and nutrients (from all depths sampled). Costs associated with provision and management of the ODF rosette system and associated oxygen, salinity and nutrient analyses were covered by a sub-award to Co-Chief Scientist Phoebe Lam, and the ODF Supertech and Lab Supervisor teams were overseen by Chief Scientist Peter Sedwick.

All water-column sampling stations included at least one "primary cast" and at least one additional "PigRaTh cast" using the ODF rosette. For the ODF primary casts, typically 3 Niskintype samplers were closed at each of the 12 sampling depths, with the subsampling order for Shelf- and Full Stations as follows: (1) unfiltered samples from the first Niskin-type bottle at each depth: noble gases, noble gas isotopes (when collected), dissolved oxygen, DIC, pH, alkalinity, nutrients, salinity,  $\delta^{15}$ N in nitrate and TDN,  $\delta^{18}$ O and  $\delta^{2}$ H in H<sub>2</sub>O, and tritium (at selected stations/depths), then (2) filtered samples from the second Niskin-type bottle at each depth:  $\delta^{15}$ N in nitrate and TDN,  $\delta^{15}$ N in ammonium (at selected stations/depths), vitamin B12 (at selected stations/depths), DMn (at selected stations/depths), and DOS (at selected stations/depths); then (3) filtered samples from the third Niskin-type bottle at each depth: Th isotopes and <sup>231</sup>Pa, Nd isotopes and REEs. The filtered samples were gravity filtered through pre-cleaned Acropak 500 0.8/0.45 µm Supor filter capsules that were initially rinsed with ~500 mL from each Niskin-type bottle, with a single filter capsule used for each separate cast. In the case of 16-depth primary ODF casts that were conducted at super stations, subsamples were not taken for some of the parameters that were collected at only selected stations/depths, which allowed subsamples for all regularly sampled parameters to be collected using only 2 Niskintype samplers at each sampling depth in just one single cast. At most of the Shelf Stations, the ODF primary cast was performed last (after the ODF PigRaTh cast, which is described below), and in such cases a monocorer was suspended on a line below the rosette to collect short cores (~30 cm) of surface sediment. The monocorer deployments were mostly successful, with intact sediment cores recovered from 23 of 27 sampling stations (further details are provided in the SIO-ODF group's separate report and in section 4.8). The monocorer was also deployed with the ODF PigRaTh cast at stations where that cast happened to be the final ODF rosette cast.

At all sampling stations, the additional cast of the ODF rosette termed the PigRaTh (pigments, radium and thorium) cast collected water-column samples from 13 depths to provide: a near-surface sample (~4 m depth) for ODF-rosette parameters analogous to the samples collected from the towfish for GTC-rosette parameters; large-volume samples for radium isotopes, <sup>234</sup>Th and  $\delta^{30}$ Si from 8 depths corresponding to the McLane in-situ pumps (see section 3.3); and samples for <sup>234</sup>Th from an additional 5 depths (including the near-surface) in addition to the depths of the McLane pumps, typically focused on the euphotic and upper mesopelagic zones. Samples for phytoplankton pigments were taken from the uppermost six sampling depths (typically <150 m), along with samples for measurements of phytoplankton photosynthetic efficiency (F<sub>v</sub>/F<sub>m</sub>) at selected stations. For the 13-depth ODF PigRaTh casts, typically 3 or 4 Niskin-type samplers were closed at the near-surface depth, 3 samplers were closed at each of

the 8 McLane-pump depths, and 1 sampler was closed at each the remaining 4 sampling depths. The subsampling order was the same as for the ODF primary casts for the 3 near-surface Niskin-type bottles, with the addition of filtered samples for DIC, pH and alkalinity from the first near-surface Niskin-type bottle, and samples for phytoplankton pigments and <sup>234</sup>Th from the second near-surface Niskin-type bottle. For samples collected from the 8 depths corresponding to the McLane pumps, the subsampling order was (1) unfiltered samples from the first Niskin-type bottle for dissolved oxygen, nutrients, salinity, pigments (upper six depths),  $F_v/F_m$  (upper six depths at selected stations), <sup>234</sup>Th, radium isotopes and silicon isotopes (filtered) from the first Niskin-type bottle. For the remaining four depths, the subsampling order was dissolved oxygen, nutrients, salinity, pigments (upper six depths or second and third Niskin-type bottles. For the remaining four depths, the subsampling order was dissolved oxygen, nutrients, salinity, pigments (upper six depths or second and third Niskin-type bottles. For the remaining four depths, the subsampling order was dissolved oxygen, nutrients, salinity, pigments (upper six depths only) and <sup>234</sup>Th, all unfiltered and taken from a single Niskin-type bottle.

Role/PI(s)	Parameter	Sampler
Bottle cops	_	Sohst/Whitmore/Miller/Abbott
ODF Supertechs	_	Fleisher/Kouba/Landry
SIO-ODF team	dissolved oxygen	Barna/Chung
SIO-ODF team	salinity, nutrients	Matthias/Mau
Loose, Seltzer	noble gases, noble gas isotopes	Passacantando
Woosley	DIC, pH, alkalinity	Woosley
Wang	$\delta^{15}$ N in nitrate, TDN, ammonium	ODF Supertechs
Wagner, Loose	$\delta^{18}$ O and $\delta^2$ H in H <sub>2</sub> O	ODF Supertechs
Loose	<sup>3</sup> H	Passacantando
Saito	vitamin B-12	ODF Supertechs
Resing	DMn	ODF Supertechs
Cutter	DOS	ODF Supertechs
Hayes	Th isotopes and <sup>231</sup> Pa	ODF Supertechs
Zheng	REEs	ODF Supertechs
Management team	pigments	ODF Super techs
Sherrell	F <sub>v</sub> /F <sub>m</sub>	Passacantando
Buesseler	<sup>234</sup> Th	Bam
Charette	Ra isotopes	ODF Supertechs/Debyser
Debyser	δ <sup>30</sup> Si	ODF Supertechs/Debyser

 Table 1. PI, parameters, and samplers of ODF-rosette system.

For both the primary and PigRaTh ODF casts, samples for shipboard measurements of dissolved oxygen, nutrients and salinity were taken from a single Niskin bottle (generally the first) from each depth sampled. For details of the ODF rosette CTD instrumentation and sensors, data processing, and measurements of dissolved oxygen, salinity and nutrients, the reader is referred

to the SIO-ODF group's report. The ODF PigRaTh cast samples for phytoplankton pigment analyses were collected in 1 L brown high-density polyethylene bottles that were rinsed with sample prior to filling, then samples were vacuum filtered through 25 mm GF/F filters under low ambient lighting by Sofia Moutinho or Peter Sedwick. The filters were then folded and placed into labelled polypropylene cryovials; once all samples had been filtered, the cryovials were flash frozen by immersing them in a dewar of liquid nitrogen, and then stored at -80°C.

## 3.2 GTC Rosette

The U.S. GEOTRACES trace element carousel sampling system (hereafter the GTC rosette), including the Dynacon winch with 7300 m of sheathed conducting cable with Vectran strength member, block, clean laboratory van, SeaBird custom-built carousel (newly purchased) and SBE-9/11plus CTD/deck unit, and 24 x 12 L Go-Flo bottles (plus spares), were provided by the Cutter group (ODU) and the UNOLS East Coast Van and Winch Pools. The clean van had been stored in the USAP storage yard and the winch and cable in the USAP warehouse, in Punta Arenas, Chile, since the completion of the GP17-OCE cruise in January 2023. Accessing the interior of the clean van required opening the escape hatch because the door key, which had been transferred to USAP personnel, had been misplaced in the interim. The clean lab van had been newly serviced and renovated before GP17-OCE, including new floors and HEPA filters. We discovered that the drain in the back left corner of the clean area, near the sink and MilliQ system, had been covered with vinyl flooring, so early in the cruise the flooring was neatly cut to reveal the drain. The Barnstead and MilliQ ultrapure water systems had been serviced at ODU before the cruise; these were reinstalled during the mobilization, using all new cartridges. We found during the cruise that the MilliQ system really needs a water pressure regulator installed just upstream of the unit; we had to adjust flow by carefully manipulating the ship's freshwater inlet valve, and even so the MilliQ pump motor never seemed happy with the pressure control. The clean van's HVAC systems had been serviced prior to GP17-OCE, and was configured for heating only, not cooling (nor dehumidifying). The HVAC system performed very well, but the portable dehumidifier supplied by ODU was much too small to be effective on time scales shorter than several days. The CTD computer was also replaced with a brand new Onlogic microcomputer, which had to be affixed to the brass window frame of the aft control room to improve cooling, following problems that arose due to overheating of the unit early in the cruise.

Prior to GP17-OCE, the winch had been re-valved for better operation at low temperature, and worked well without issues during GP17-ANT. The U.S. GEOTRACES A-frame was not shipped or used, because the RVIB *Nathaniel B. Palmer* has a starboard A-frame that was determined to work adequately with the rest of the GTC rosette hardware. Due to concerns about possible ice buildup in the sheave of the GTC block (a problem on the U.S. GEOTRACES Arctic cruise), we initially used a Nylatron 0.68 block loaned by the East Coast Winch Pool; however, ice buildup was not significant, so we switched back to using the GTC block during the

latter part of the cruise. All other components remained the same as used on prior U.S. GEOTRACES cruises. During installation of the vans at dockside, it was realized that the planned position of the USAP clean van immediately next to the mercury lab van on the starboard side of the aft deck was not going to work because the electrical connection would not fit in the narrow gap between the two vans. As there were no alternative deck sockets, the USAP clean lab van was moved to the starboard side, just aft of the A-frame, and the U.S. GEOTRACES clean van was moved next to the mercury van on the aft deck. This change necessitated a longer walk to carry Go-Flo bottles to and from the van, but because many people pitched in to accomplish this task, it did not present a problem. One advantage to this necessary change was that the USAP clean van, which contained the sampling manifold for the towfish system, was located very close to the towfish deployment location, making a shorter tubing run and easier communication between van and deck personnel during deployment, sample collection, and recovery.

The GTC rosette was assembled on the ship during mobilization by Greg Cutter (ODU), with help from the GTC Supertech team, Kate Kouba (ODF Supertech), Gabe Matthias (SIO-ODF team) and Jessica Fitzsimmons (TAMU). The shipboard GTC rosette sampling team comprised six individuals: Supertechs Eleanor Bates (UH-Manoa), Hannah Hunt (USF) and Laura Moore (UW) did the Acropak filtration and staged/unstaged bottles, while Supertech Hannah Inman (UConn) and Co-Chief Scientist Rob Sherrell (Rutgers) performed the membrane particle filtration and sampling of the associated filtrate seawater, as well as other sampling from the "particle side" Go-Flo bottles. Laboratory Supervisors Bettina Sohst (ODU) and Laura Whitmore (UAF) worked on deck to complete the GTC hydrocast log sheets and ensure that the Go-Flos were mounted in correct positions, cocked correctly, and moved into the GTC lab van in proper order at the end of the cast. The winch was very ably run by the Able-Bodied Seamen of Edison Chouest Offshore (Bienvenido Aaron, Louie Andrada and Ronnie Carpio) and the GTC CTD-rosette was deployed by the ASC Marine Technicians (Ken Block, Heather Jackson, Stuart Siddons and Henry Thoreen).

The GTC system sensor array consisted of dual SeaBird SBE-3 temperature and SBE-4C conductivity sensors, an SBE-43 dissolved oxygen sensor, a Seapoint fluorometer, and a WetLabs C-Star transmissometer. Sensors were calibrated during summer 2023, immediately prior to the GP17-ANT cruise, together with maintenance and repair of some sensors and the pylon, pump and deckbox, following damage and some problems encountered during the GP17-OCE cruise. The GTC rosette also included a Benthos altimeter, which ceased functioning during the latter part of the cruise and was replaced with a Valeport altimeter borrowed from shipboard USAP equipment, and a Seapoint turbidity sensor that was provided by Joe Resing (UW/PMEL). Because the GTC rosette was stored on deck between casts, the oxygen sensor was installed within 30 minutes of starting each cast and removed within 20 minutes of recovery, to protect it from freezing. The routine deployment procedure was to load all Go-Flo bottles

except those in rosette positions 1-4, then mount the oxygen sensor, then load the remaining four Go-Flos. Costs associated with the GTC Supertech team and for preparing the GTC rosette and the backup USAP trace metal clean sampling system were covered by the cruise management awards to Sherrell and Sedwick.

All 44 operable Go-Flo bottles (4 additional bottles were mechanically compromised at the start, and were set aside) were filled with seawater during the soak cast at Station 1 on 2 December 2023, early in the transit from Punta Arenas to the Amundsen Sea. In this cast the GTC rosette was lowered to 1000 m depth, then all bottles were closed at ~200 m depth with the rosette slowly moving up through the water column. The filled bottles were allowed to soak while stored on racks in the GTC clean van until 5 December 2023, when they were emptied and deployed again during the test cast at Station 2. Bottles were again tripped at ~200 m depth (base of chlorophyll-a fluorescence layer), and then seawater was filtered through an Acropak 0.2 µm filter capsule (see below) for shipboard analysis of dissolved iron by Joe Resing. Most of the filtered Go-Flos samples had similarly low dissolved iron concentrations < 100 pM (mean:  $78 \pm 12$  pM, 1SD). However, samples from 14 bottles had concentrations of 103-209 pM, and were thus not accepted as fully "clean", although some samples gave values of < 100 pM upon repeat analysis. This left 30 nominally clean Go-Flo bottles, of which 24 were selected as the "A team" for use on the GTC rosette. During the cruise, various mechanical issues with specific bottles meant that, occasionally, a Go-Flo bottle was replaced with another "A-team" bottle, or in a few cases with a "B-team" bottles that had yielded samples with dissolved iron slightly higher than 100 pM in the initial shipboard analysis. Further information regarding Go-Flo sampler issues and substitutions are available from the Chief Scientists upon request. Because of delays in shipping of their equipment, the Saito team was not able to perform shipboard dissolved zinc analyses (which were used on GP17-OCE) as a contamination test. Nevertheless, based on the shipboard dissolved iron results, the cruise management team were satisfied that the Go-Flo bottles employed were suitably trace-metal clean for use at the subsequent sampling stations during the cruise.

In total, 38 GTC rosette hydrocasts were conducted on GP17-ANT, including soak and test casts. At all stations except the "extra-volume" super stations, 2 Go-Flo bottles were triggered at each depth. At extra-volume super stations, 3 Go-Flo bottles were triggered at each depth in order to accommodate requests for larger sample volumes. From a total of 372 Go-Flo bottles triggered, 3 returned no samples, either because they did not close (pylon issue) or were lost on deck due to a leaking Go-Flo ball valve or broken spigot. Shipboard measurements of salinity performed by the SIO-ODF group were compared to corresponding CTD salinity sensor data at the nominal bottle triggering depths to identify Go-Flo bottle miss-trips. Discrepancies were typically interpreted as bottles closing either early (lanyard releasing before pylon position was triggered) or late (ball valves not closing fully until bottle had risen to a shallower depth) during the upwards cast; based on these comparisons, mis-trips occurred for only 7 samples throughout the

cruise (GEOTRACES sample numbers corresponding to these mis-trips are 19007, 19783, 19784, 19785, 20206, 20632 and 20634). Other salinity mismatches were interpreted to result not from bottle malfunctions but rather to reflect rapid changes in salinity with depth, typically in near-surface or near-bottom samples (further details are provided in section 8.3 of the SIO-ODF cruise report).

Once the Go-Flo bottles were secured in the clean van and labeled with GEOTRACES numbers, sampling began with three or four of the GTC team personnel. Starting with the "membrane-side" Go-Flos, dissolved oxygen samples were collected first, typically from 2-3 Go-Flos per cast, and immediately passed, un-stoppered, out of the clean van to one the SIO-ODF team for pickling in the Baltic Room. Immediately following oxygen sampling, a 0.8  $\mu$ m/0.2  $\mu$ m pore-size Acropak 200 Supor cartridge filter was rinsed with 500 mL of seawater and used to collect time-sensitive Fe(II) samples from each Go-Flo, which were transferred in batches of 6 (on ice, in darkness) to Alexis Floback (USC) for immediate shipboard analysis. Next, unfiltered samples (salinity,  $\delta^{18}$ O, cellular metals, diatom frustule Zn) were drawn from all Go-Flos. The Acropak 200 capsule was then replaced and again rinsed prior to sampling each Go-Flo, and filtered samples for Hg speciation and Cu/Ni isotopes were drawn. Finally, the Go-Flos were gently mixed to resuspend any settled particles, and Swinnex 25 mm filter holder(s) for Go-Flo particle filtration were attached, rinsed, and used to collect 0.45  $\mu$ m filtered samples for solid phase extraction of ligands.

Filtration continued until 2 hours time elapsed, or when filter clogging caused filtration rate to decrease to one drop per second, following GEOTRACES protocols. If the 4 L ligand sample was not full at this point, filtration continued using the assigned Acropak filter cartridge for that Go-Flo, noting the approximate volume that had passed through each type of filter. For particle-rich surface waters, ligand samples were sometimes taken through the Acropak cartridge filter only, and this was noted, and remaining volume in the Go-Flo was then used for particle filtration. Particles were thus collected on 0.45  $\mu$ m Supor filter membranes, with size-fractionation achieved in the upper 4-6 depths by mounting 5  $\mu$ m polycarbonate membranes in a separate 25 mm Swinnex filter holder plumbed upstream of the Supor filter. The Swinnex filter holders were initially joined by a female-to-male adapter and a small length of C-flex tubing (as per the Twining group on GP17-OCE), but early in the cruise we discovered that the filter holders could be attached together directly and securely by friction-fit of their opposite-gender Luer connections. All filtration was carried out using ~0.5 atm over-pressure of filtered air.

For Go-Flo bottles on the "Acropak-side" of the GTC van, sampling proceeded as follows. First, salinity and nutrient samples were drawn unfiltered. Then the Acropak 0.8/0.2 µm Supor filter cartridge was attached, rinsed with 500 mL of seawater, and filtered seawater drawn in the following order to collect samples for dissolved V/Ga/Ba, dissolved Zn ligands, archived dissolved samples for ICP-MS/flow-injection analysis, shipboard dissolved Al, shipboard

dissolved Fe/Mn, dissolved and colloidal trace elements, dissolved Fe/Zn/Cd isotopes, dissolved CSV ligands, dissolved total and labile Co, and dissolved Pb isotopes. Further details are provided in Table 2. For super stations, three Go-Flos were closed simultaneously at a single depth by attaching lanyards to a single rosette pylon trigger, thus sampling 8 depths per cast. This allowed a third Go-Flo to be used for additional large-volume samples. Unfiltered samples were collected for ligand incubation studies and Hg speciation incubation experiments, then Acropak cartridge filters were used to collect filtered samples for ligand-isotope exchange experiments, ultrafiltered Fe/Zn/Cd isotopes, and ultrafiltered Th/Pa isotopes, depending on requests for specific stations.

<u>Membrane side</u>			Acropak side			
<u>PI</u>	Sample type		<u>PI</u>	Sample type		
Becker	Oxygen*		Becker	Salinity*		
Moffett	Fe(II), I**		Becker	Nutrients*		
Becker	Salinity*		Whitmore	V, Ga, Ba		
Loose	$\delta^{18}$ O of seawater*		Hawco	Zn ligands		
Twining	Cell quotas SXRF*		Resing	Archive ICP-MS, FIA		
Morton	Diatom frustule Zn*		Resing	Shipboard DAl, DMn, DFe		
Mason	Hg speciation**		Fitzsimmons	Dissolved TMs		
John	Cu/Ni isotopes**		Fitzsimmons	Colloidal TMs		
Mix Go Flos	Attach 25 mm		Conway	Fe/Zn/Cd isotopes		
	Swinnex filter holder		Collway			
Boiteau	SPE ligands***		K. Buck/Bundy	Ligands (CSV)		
Complete particle	2 h or filter clogs***					
filtration –	(Acropak used to		K Buck/Bundy	Ligands (CSV)		
Sherrell/Morton	finish SPE ligand		K. DUCK/DUNUY			
	sample as necessary)					
*unfiltered sample			Saito	DCo		
**Acropak filtered			Saito	Labile Co		
			Boyle	Pb isotopes		

Table 2. GTC rosette Go-Flo sub-sampling order.

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The GTC rosette system performed well throughout the cruise, despite the frequent presence of heavy sea ice. However, a number of issues and events are noted:

- 1. Mobilization took an inordinately long time, affecting the availability of some essential components of the GTC system which required considerable pre-cruise preparation time.
- 2. The plastic support ring for the pylon trigger assembly was found missing upon unpacking equipment, and a replacement had to be fabricated by ASC personnel. This replacement worked, but the positioning of mounting bolt holes meant that the bail on the top of the rosette interfered occasionally with the release of the nearest pylon triggers,

which led to a few Go-Flo mistrips. However, early in the cruise the missing original plastic support ring was located and mounted, preventing further such Go-Flo mistrips.

- 3. The plinth (steel support frame for the GTC-rosette and McLane-pump winches) that was designed and manufactured for the cruise by the East Coast Winch Pool and shipped to Punta Arenas, was found not to fit the container pockets on the ship's 02 (helo) deck. With assistance from Hannah Gray and Matt Louis (ASC) and the ASC marine technicians (MTs), a team of welders was hired and worked over two days to fabricate adapter plates to attach and secure the plinth to the deck.
- 4. The alignment of the winches with the starboard A-frame was not ideal, so that considerable time was required to align the cables and sheaves with appropriate tangs on the A-frame cross-member, and to test those arrangements dynamically, for both the GTC rosette (Dynacon) winch and McLane pump (MASH4k) winch. The eventual positioning of the GTC rosette sheave on the forward-most tang meant that a block and tackle arrangement for the tag line, and considerable effort by the MTs, were required to pull the full rosette aft during recovery thereby avoiding contact with the A-frame.
- 5. Re-termination of the cable was required at Station 21, due to a miscommunication among deck personnel, which led to tension being put on the cable before its release from a securing line. The cable was stretched and distorted, and so was cut and ably reterminated by Supertech Kate Kouba and the MTs. The cable performed flawlessly for the remainder of the cruise.
- 6. The GTC rosette frame suffered a few minor knicks from minor contact with the A-frame on recovery. This resulted from the need to hang the block on the forward tang on the A-frame cross member, rather the central tang, because of the cable and winch alignment issues noted in point 4 above. Knicks were covered in white electrical tape.
- 7. The Dynacon winch and conducting cable generally performed very well, but poor wraps on the winch drum beyond ~3500 m of line out (inherited from the previous GP17-OCE cruise) made recovery slow and difficult during the first deep cast at Station 3. To address this, we stopped en-route to Station 4 and deployed ~4000 m of the cable, then slowly retrieved it taking care to align wraps evenly and inserting short sections of line to fill voids (as was done more abundantly during the preceding cruise). This largely alleviated any issues with cable spooling during the remainder of the cruise, although the ASC MTs recommended that the winch be respooled under tension after the cruise. We had no other serious issues with the GTC winch and cable.
- 8. The GTC lab van did not drain well, with water tending to collect from sampling spillage and leaking bottles. It was discovered that the floor drain near the sink, which happened to be the low corner of the van, had been covered with vinyl flooring, which was carefully cut away to reveal the drain. Drains worked better without the plastic grids, so grids were unscrewed and removed for the cruise period, then replaced.
- 9. Maintaining sufficient air pressure to sample seawater through Acropak cartridge filters, while not exceeding GEOTRACES recommendations for membrane filtration, was an

issue requiring compromise throughout the cruise. Air pressure in the lab van must be individually regulated for each "side" of Go-Flos, so that higher pressure can be used as needed for Acropak filtration, while keeping membrane filtration overpressure at 0.5 atm. It would be helpful to install a large fluid-filled pressure gauge (0-15 psi) for each side of van, downstream of a fine-control regulator, so that pressure is more easily monitored.

10. Two Go-Flos had spigots broken off at base of the grey PVC boss due to accidental bumps or drops, and these samplers were retired for the remainder of the cruise.

#### 3.3 Near-bottom Water Sampling on the Multicorer

To supplement investigation of water-column TEIs near the seafloor, Co-Chief Scientist Sherrell worked with ASC MTs and April Abbott to devise a plan for mounting a trace metal-clean external-closure Niskin (Niskin-X) bottle to the stainless steel frame of the multicorer. The Niskin-X sampler was mounted vertically using stand-off blocks and stainless steel hose clamps, after careful cleaning of the multicorer frame, with the middle of the bottle positioned at ~1m above the seafloor. This sampling method was carried out successfully on the ARTEMIS cruise in early 2022 and improved upon for GP7-ANT. Specifically, the tripping mechanism was made more reliable, and the number of different subsamples collected from the 12 L volume samples were optimized for GEOTRACES. The Niskin-X bottle used was from Sherrell's equipment, as was also used for particle filtration from towfish samples, and a single Niskin-X sampler (#15) was used for each multicorer deployment. The bottle was mounted only after the multicorer was fully prepared for deployment and was cocked (opened) only at the last minute before deployment commenced. Similarly, the full Niskin-X was removed from the frame and moved to the rack in the USAP clean van immediately after recovery of the multicorer. The Niskin-X was handled only by Sherrell or one of the GTC Supertechs; at no point did any other personnel touch the Niskin-X bottle. The Niskin-X closed successfully and returned samples for 8 of the 9 multicorer deployments, at Stations 7, 10, 14, 15, 17, 21, 25, and 27.

It is critically important that the Niskin-X water sample does not collect sediments resuspended when the multicorer frame contacts the seafloor. The tripping mechanism was initiated by the initial descent of the multicore tubes and associated lead weights, which occurred immediately upon landing and loss of tension on the deployment cable. For six of the deployments, a video camera and light were mounted on an adjacent vertical member of the multicorer frame, continuously recording during the deployment. This allowed both the closing of the Niskin-X bottle and the plume of disturbed sediment to be visualized, and the timing estimated. From our analysis of these videos, the Niskin-X bottles generally closed approximately 2-3 seconds after initial contact (although as long as 8 seconds for one deployment), and the observed plume of resuspended sediment never reached the bottom of the Niskin-X bottle before the end caps closed. Analysis of particulate samples from the Niskin bottle may help to verify the absence of sampling artefacts from resuspended sediments, relative to samples taken at 10 m above the

seafloor using the GTC rosette. Further, salinity samples and CTD sensor data confirmed that all of these Niskin-X tripped at the bottom; no late trips were detected. These multicorer Niskin-X samples are thus designated as 1 m above bottom, and are expected to be a useful in comparison to the deepest GTC rosette Go-Flo samples, which were typically taken 10 m above the seafloor.

Thus, in combination with CTD and towfish samples, water-column samples at 8 of the 9 multicoring stations can be considered to be 14-depth profiles, with excellent coverage of the near-bottom environment (samples at  $\sim$ 1, 10 and 35 m above bottom). Subsamples from the Niskin-X sampler were taken for as many parameters as possible, so that multi-element near-bottom gradients can be used to explore benthic sources or sinks.

Subsampling was carried out by the GTC Supertechs, with Sherrell carrying out the particle filtration and collection of filtered samples from that filtrate stream for some of the deployments. Subsampling commenced within minutes of the full Niskin-X sampler being transferred from the multicorer into the USAP clean laboratory van. The limited sample volume meant that not all parameters could be subsampled, however most were. The sampling order is listed in Table 3.

<u>PI</u>	Subsample type	<u>PI</u>	Subsample type
1. Becker	Salinity (unfilt.)	Acropak-filtered	(continued)
2. Becker	Nutrients (unfilt.)	12. Saito	DCo
3. Loose	$\delta^{18}$ O of seawater (unfilt.)	13. Saito	Labile Co
Attach Acropak filter		14. Basak	REE
4. Moffett	Fe(II), I	15. K. Buck/Bundy	Ligands (CSV) -1
5. Whitmore	V, Ga, Ba	16. K. Buck/Bundy	Ligands (CSV) -2
6. Hawco	Zn ligands	17. Mason	Hg speciation, Acropak
7. Resing	Archive ICP-MS, FIA	18. John	Cu/Ni isotopes
8. Resing	Shipboard DAl, DMn, DFe	Mix Niskin-X sampler	Attach 0.45 μm Supor membrane filter
9. Fitzsimmons	Dissolved TMs	19. Mason	Нg
10. Fitzsimmons	Colloidal TMs	20. Boiteau	SPE ligands
11. Conway	Fe/Zn/Cd isotopes	21. Sherrell/Morton	Particles on 0.45 µm Supor membrane

**Table 3**. Order of subsampling from the single Niskin-X sampler deployed on the multicorer.

# 3.4 Towfish Underway Sampling

Towfish underway sampling for uncontaminated near-surface water (upper  $\sim 2$  m depth) was initiated with test Station 1.5 (Fig. 2), and then performed upon arrival at each station, starting with crossover Station 3. One exception was Station 18, where towfish sampling was carried out on departure rather than arrival, a necessary change forced by sea ice conditions. The second exception was Station 25, where an ODF rosette deployment was carried out first, then towfish sampling, followed by GTC rosette deployment. The compressed cruise schedule did not allow for any high-spatial-resolution surface water transect sampling using the towfish.

The towfish system employed was loaned by Jessica Fitzsimmons (Texas A&M), and was a scaled-up version of a previous design employed by Co-Chief Sherrell, modified in minor ways from that used on GP17-OCE to better fit the specifics of deployment using the ship's starboard A-frame. The system uses 3/4" OD/1/2" ID kink-resistant Bev-a-Line tubing, mated with Nylon cable ties and PVC electrical tape to an Amsteel synthetic line as a strength member. The relatively large diameter of the inlet tubing allowed for high flow rates (~4 L/min unfiltered), which in turn allowed two or three different types of samples to be collected simultaneously from the sampling manifold inside the USAP clean van, thus decreasing the time and distance over which various surface water samples were collected. Deployment was from the painted steel boom that inserts into a welded steel socket on the aft face of the aft vertical arm of the starboard A-frame. The tubing was guided through a 90° elbow of 1" ID hard PVC electrical conduit to avoid kinking at the transition from the strength member and the towfish body, which was secured to the robust PVC towfish body using stainless steel hose clamps. A small painted steel block (ship-supplied) was secured to the end of the boom, and used initially to raise or lower a larger-diameter aluminum block with a sheave and throat that could accommodate both the tube and strength member as a pair. Early in the cruise, however, it was determined that deployment and recovery were easier and quicker if the strength member went through the steel block only, while the inlet tube diverged from the line near deck level, via another hard PVC elbow to prevent kinking, for securing at the rail. A second safety line ran directly from the towfish to a lateral position on the rail, aft of the A-frame. The sample inlet tubing then ran to an a pneumatic, Teflon and polypropylene, double-diaphragm pump which was secured to small a wooden platform sitting on the deck. The tubing outlet from the pump was led vertically about 2 m to an upper pass-through on the forward starboard corner of the USAP clean van, through the anti-room, and into the starboard side of the clean van, where sampling was carried out. The sampling manifold consisted of three metal-free hand-operated valves for filtered or unfiltered sampling. Rinsing seawater was caught in a shallow plastic tray on the lab bench that was plumbed to a floor drain. All filtered samples were collected through 0.8/0.2 µm Acropak 500 Supor cartridge filters, so that filtration pore size was identical to that of samples taken from Go-Flo bottles. The USAP lab van was mounted on the starboard deck with its door facing forward just a few meters aft of the A-frame, so that sample tubing runs were minimized. The entire towfish system had been acid-cleaned by the Fitzsimmons lab at Texas A&M, and the Acropaks were pre-cleaned by the Sedwick group at Old Dominion University.

Towfish deployment procedures were typically started approximately 3 nautical miles from the nominal station locations, so that all samples could be taken within ~2 nautical miles of station, ending sampling at closest proximity to the station. The ship was slowed to ~2 knots and the towfish deployed by the ASC MTs, with help from the GTC Supertechs, Lab Supervisor Bettina Sohst (ODU), and Chief Scientists Sedwick and Sherrell, depending on who was on watch. When the towfish was deemed to be towing well at its furthest extension from the hull (A-frame

fully out), the pump was started by turning on the compressed air regulator. Priming typically took only a few minutes, with the tube between the rail and the pump inlet held in a position to allow gravity as a priming aid, and it was never necessary to pump water down the tube to achieve priming. The whole inlet system was flushed for several minutes before sampling began, including valves and Acropak cartridge filters. Generally, sampling could be achieved with two GTC Supertechs, with a third available to assist for part of the time. The mercury team joined the sampling team in the clean van at some stations, to assist with the large volume samples collected for Hg isotopes and speciation studies. Unfiltered seawater for particulate samples and limited sampling from the associated filtrate was led across the van into a clean externally-closing Niskin bottle (Co-Chief Sherrell's equipment) mounted on the wall rack. After filling to ~6 L by opening the top end cap, the Niskin was closed, bar-clamped, and pressurized to collect a filtered sample (always by co-Chief Sherrell or GTC Supertech Hannah Inman). Early problems with leaking at compression fittings in the sampling manifold were resolved by replacing plastic ferrules and fittings, and cleanly cutting new sections of Bev-a-Line tubing to replace those that had been distorted by previous use. Still, back-pressure induced by partially-used Acropak filters induced leaking at some connections, so sampling rate was sometimes reduced because of the need to reduce inlet pressure by adjusting the outlet valve leading from the manifold to the drain. The towfish sampling order is summarized in Table 4.

PI		Sample type	PI		Sample type
1.	Becker	Salinity (unfilt.)	(co	ntinued)	
2.	Becker	Nutrients (unfilt.)	18.	K. Buck/Bundy	Ligands (CSV)-1
3.	Loose	$\delta^{18}$ O of seawater (unfilt.)	19.	K. Buck/Bundy	Ligands (CSV)-2
4.	Sherrell	Particulate TMs (unfilt.)	20.	Conway	Fe/Zn/Cd isotopes
5.	Morton	Diatom frustule Zn (unfilt.)	21.	John	Cu/Ni isotopes
6.	Resing	TDFe (unfilt.)	22.	Hawco	Zn ligands
7.	Wang	$\delta^{15}$ N in nitrate, TDN, NH <sub>4</sub>	23.	Hawco	Ni/Cd ligands
8.	Boiteau	SPE ligands	24.	Saito	DCo
9.	K. Buck/Bundy	Siderophores	25.	Saito	Labile Co
10.	Boyle	Pb isotopes	26.	Whitmore	V, Ga, Ba
11.	Lam	Pump rinses (as needed)	27.	Mason	Hg speciation
12.	Moffett	Fe(II), I	28.	Boiteau*	Isotope exchange experiments
13.	Resing	Shipboard DMn, DFe	29.	Boiteau*	Large volume SPE ligands
14.	Resing	Shipboard DAl	30.	Boiteau*	Laboratory experiments
15.	Resing	Archive ICP-MS, FIA	31.	Moffett*	Aged seawater experiments
16.	Fitzsimmons	Dissolved TMs	32.	Lam*	Incubation experiments
17.	Fitzsimmons	Colloidal TMs	33.	Mason*	Hg isotopes

**Table 4**. Order of sampling from the towfish deployments. All filtered at  $0.2 \mu m$  unless noted. Some samples were collected simultaneously from individual sampling valves on the manifold.

\*These samples taken only at select stations.

After gaining experience at early stations and streamlining procedures, all towfish sampling could generally be achieved within one hour. Sampling was slowed at some stations, where ice floes and bergy bits required stopping the pump temporarily and raising the towfish into the air to hop over floating ice pieces. These maneuvers, when necessary, often coincided with adjusting planned station stations to a relatively ice-free region for GTC rosette deployments, which typically followed towfish sampling. Towing speed during sampling was generally  $\sim 2$ knots, but sometimes increased to ~4 knots if conditions suggested that faster towing was required to avoid use of the ship's bow thruster, thereby avoiding contamination of seawater seawater at the inlet on the towfish body. Sampling depths varied from  $\sim 1-2$  m, depending on conditions. Between deployments, the pump was allowed to continue running as the towfish was raised in the air, clearing most of the seawater from the tube. After towfish recovery, the sample inlet tube was detached from the pump inlet and remaining seawater was gravity-drained from the inlet portion of the tubing by stretching it out over the deck (requiring 2-3 people for several minutes) without allowing the tubing to touch the deck. The tube was then reattached to the pump, and the towfish body, pump and coiled tubing were stored in a plastic fish box secured to the rail and bulwark immediately aft of the A-frame. The tubing from the outlet of the pump was fed out and under the lid of the fish box so that the pump-to-sampling manifold section of the tube was not disconnected. The compressed air hose, which was connected to a supply tap in the helo hangar (02 deck), was removed from the pump, coiled and stored in the antechamber of the USAP lab van. This storage routine successfully prevented seawater freezing in the tubing between deployments, and no heater was needed for the fish box.

To summarize, the towfish sampling was very efficient because the design worked well and the deck and van crews coordinated closely. The towfish was monitored on deck by one or two ASC MTs for the duration of the sampling period. The entire team was devoted to keeping the system clean, providing high confidence in uncontaminated sampling throughout the cruise. That said, records from the ship's underway sensors, and some replicate sampling for shipboard Fe and Mn analyses, suggest significant lateral gradients in surface water composition over the towfish sampling distance, so care should be taken in comparing towfish samples taken up to one hour apart, and in comparing towfish surface samples to the upper water-column samples collected by the subsequent GTC rosette cast on station.

## 3.5 McLane Pumps

The McLane in-situ pump operations were part of Phoebe Lam's (UCSC) portion of the GP17-ANT management proposal with a subcontract to Steve Pike (WHOI). The McLane pumps were used to collect size-fractionated small (~1  $\mu$ m-51  $\mu$ m) and large (>51  $\mu$ m) particles through two 142 mm diameter filter holders, short-lived radionuclides (the Ra quartet – <sup>223</sup>Ra, <sup>224</sup>Ra, <sup>226</sup>Ra, <sup>228</sup>Ra – and <sup>227</sup>Ac) using 1-2 Mn oxide-coated cartridge(s) attached downstream of the filter holders, and finally DNA samples using Sterivex cartridges and  $>0.8 \mu m$  particles on 47 mm diameter Advantec filter holders on an unmetered third flow path.

#### Equipment

#### McLane In-situ Pumps, 30 L Niskin Bottles.

The WHOI UNOLS pump pool (managed by Steve Pike) provided 8 dual-flow battery-operated McLane pumps (5 WTS-LVDF, 3 modified WTS-LV-upright). Daniel Ohnemus (co-PI on Lam's GP17-ANT particle geochemistry award) provided 4 additional WTS-LVDF pumps. Eight active pumps (5 from the WHOI pump pool; 3 from the Ohnemus supply) were modified to accommodate two cartridge holders plumbed between the main 142 mm filter holders and the pump head. The WHOI UNOLS pump pool also provided 18 McLane vertical-intake 142 mm filter holders. Up to eight McLane pumps were deployed at one time on a cast. The remaining four pumps were used for parts and as spares. WHOI also supplied eight 30 L Niskin bottles that were mounted on the pump wire on deep casts. Prior U.S. GEOTRACES cruises used modified WTS-LV-upright pumps and 142 mm "mini-MULVFS" filter holders. Many of these were lost at sea during GP17-OCE. This was the first U.S. GEOTRACES cruise to use the new McLane WTS-LVDF design as well as the new 142 mm McLane vertical-intake filter holders. Both the new McLane pump and filter holder were based on the designs tested and intercalibrated by the U.S. GEOTRACES pumping group. However, small differences in the final implementation of these new products posed some issues, which are described further in the "Problems Encountered" section.

#### Vectran Wire.

Steve Pike/Ken Buesseler at WHOI provided 5494 m of 0.322" OD Hytrel-coated nonconducting Vectran wire with MBS = 5000 lb. This wire was spliced on GP15 to include a length bought for the GEOTRACES GP16 cruise in 2013 and a length bought for the Arctic GEOTRACES cruise in 2015. A 5x safety factor set the safe working load to be 1000 lb. The Vectran was spooled onto the East Coast Winch Pool's MASH4k winch at WHOI in July 2023. The Vectran was terminated with a Yale grip and pull tested to 2000 lb. The pumps were deployed from the ship's starboard A-frame using the USAP trace metal block hung on the center tang. During deployment at Station 6, pump 6 got caught on the deck under tension and part of the Hytrel jacket was stripped from the wire, exposing the Vectran strength member with 477 m of wire out. Pumps were recovered and wire was cut at 477 m line out. Final wire length at the end of the cruise was 5017 m. The splice in the wire is now at 1859 m on the MASH4k wire out reading, which is probably around 1788 m of actual wire out (see "McLane Pump Operations").

#### MASH4k Winch

The MASH4k winch was mounted on a turntable on a support plinth attached to the helo deck aft of the GEOTRACES Dynacon winch. A remote control was installed in the aft control room.

# SBE 19-plus v2 Seacat CTD with Optical Sensors

Lam provided an SBE 19-plus v2 Seacat self-recording CTD that was shackled to the end of the non-conducting Vectran wire for each pump cast. The Seacat CTD was fitted with the following optical sensors:

- WetLab ECO-FLUOR-BB fluorometer/backscatter meter (S/N FLBBRTD-8391) (V0fluor; V1-BB)
- WetLabs C-Star transmissometer (S/N CST 2486) (V2)
- prototype WetLabs/UC Berkeley particulate inorganic carbon sensor (S/N PIC 010) from Dr. Jim Bishop, UC Berkeley (V3)
- Seapoint turbidity meter (S/N 18043) (V4)

# Transmissometer Maintenance

Transmissometer windows were cleaned at the beginning of the cruise with a Kimwipe wetted with dilute Dawn detergent, a liberal MQ water rinse, and wiped dry with a Kimwipe. Subsequently, the windows were rinsed liberally with MQ after each cast and capped. On-CTD readings of Vair (unblocked beam) and V0 (blocked beam) were taken every few stations. Windows were wiped with a dry kimwipe until Vair was maximized. Transmissometers from the three main sampling systems (GTC rosette, ODF rosette, McLane pumps) were intercalibrated on a lab bench by powering the instruments with a 12 V power supply and taking readings of Vair and V0 powered by a 12 V power supply and read by a multimeter at the beginning and end of the cruise (Table 5).

Date	Local time (UTC - 3 h)	Temperature (°C)	Instrument	V0	Vair
11/28/23 (pre-cruise)	09:04	17.2	ODF#1 CST1874DR	0.0072	4.7994
	9:09	17.2	ODF#2 CST1873DR	0.0035	4.8200
	9:19	17.4	GTC#1 CST1035DR	0.0029	4.8148
	9:25	17.6	Lam CST2486	0.0056	4.8080
01/14/24 (post-cruise)	16:14	15.3	ODF#2 CST1873	0.0037	4.8117
	16:20	15.3	Lam CST2486	0.0056	4.8183
	16:25	15.3	GTC#1 CST1035	0.0030	4.8159

Table 5. In-lal	o V0 and	Vair readings	of transmissor	meters from	the three main	systems.
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# Pinger

An Oceanographic Instrument Systems (OIS) model 6000 high powered pinger from the OSU tech pool was used on the cruise to determine proximity of the Seacat CTD to the seafloor. The pinger was attached by hose clamps to the Seacat CTD frame.

# Depth Sensor

A STAR-ODDI depth sensor provided by the ASC Electronics Technicians (ETs) was attached to a pump in the middle of the string as a back-up depth recorder and to help determine if the wire angle was straight or curved. The STAR-ODDI Starmon Compass (S/N SCL0009) was attached to a pump on stations 4D-17S. A STAR-ODDI TDR DST centi-TD (C7847 or C7848) was attached to a pump on stations 19S-29S. These were programmed, mounted, and dismounted by the ETs.

## McLane Pump Team

The pump team consisted of the two McLane pump Supertechs – Steve Pike (WHOI) and Allison Laubach (UCSC) – and Lauren Hearn (UCSC), Phoebe Lam (UCSC), Margot Debyser (WHOI, radium isotopes), and Wokil Bam (WHOI, <sup>234</sup>Th). Pike was responsible for pump programming and maintenance, and was at the rail for all deployments and recoveries. Lam, Laubach, and Hearn were on overlapping 16-hour shifts so that two persons were always awake to cover pump deployments, recovery, particle processing and subsampling; Debeyser was responsible for radium sampling from Mn oxide-coated cartridges attached to the pumps, and assisted with pump deployments and recovery; Bam assisted on pump deployments and recoveries when 30 L Niskins were deployed.

## McLane Pump Operations

McLane pumps were programmed with a trigger delay time that was determined based on our best estimate of the deployment time from start to finish (reaching of final target depth). Trigger times were typically 45 minutes-1 hour for shallow casts and 1.5-3.5 hours for deep casts. Pumping times were typically set to 4 hours, but were occasionally shortened at the request of the bridge if conditions were bad (see Table 4). The most frequent cause of bad conditions for pumping was if the bridge could not create or maintain position in an opening in the sea ice for the duration of the pump cast, usually due to sea ice drifting in a different direction to the wind.

At Station 17S, the ship's sewage tanks were expected to exceed their holding capacity prior to the completion of the pump cast, and sewage was discharged while pumps were still in the water. After Station 17S, we generally shortened the pumping time to 3.5 hours so as not to exceed the ship's 6-hour sewage tank holding capacity. Sewage was discharged towards the end of the pump time on all deep casts, which typically extended beyond the sewage holding capacity.

We occasionally observed what was later confirmed to be small paint chips on pump filter samples. Starting at Station 13S, we instituted a wipedown of the bottom of the pump frames with wet paper towels after each pump was attached to the wire. The wipedown confirmed that there was a coating of paint chips on the bottoms of all of the pump frames from dragging the pumps around on the deck in the Wetlab and out onto the weather deck. The wipedown protocol reduced but did not eliminate paint chips in the samples. Around Station 18S, a sheet of plywood was placed in the Wetlab for the pumps to sit on to reduce the generation of paint chips as the pumps were moved around. This further reduced the paint chips in the samples, although a rogue paint chip was observed at Station 24, but none afterwards. A sample of the dried paint was taken for analysis.

All packages (CTD plus each pump) were allowed to debubble for ~1 minute below the surface before sending down. McLane pumps were attached to the wire at wire out readings determined from target sampling depths, which were subsets of the depths sampled by the GTC and ODF rosette casts. As with previous cruises, we zeroed the wire with the CTD on deck to facilitate calculation of attachment intervals between CTD and pumps; 7 m was added to the final wire-out reading to account for the distance between the deck and the surface of the water. The MASH4k wire-out readings were found to be 3-5% higher than the actual wire out, based on wire-out comparisons to pressure-derived depth readings from the CTD and STAR-ODDI. Starting at station 4S, an adjusted wire-out with a 3-5% correction was used to better achieve target depths.

For the deep casts at the three full stations (Stations 3, 4, 25), a 30 L Niskin was mounted above each pump to collect water for the radium and <sup>234</sup>Th groups. The 30 L Niskin was mounted first, then a pump was mounted 1-2 m below the Niskin. A long lanyard with Teflon-coated messenger was attached to the Niskin and the messenger was clipped below the pump, thereby bypassing the Niskin and pump pair. On these deeper casts, a messenger was dropped halfway (2 hours) through pumping to trigger the Niskin bottles to close. On the first deep cast at Station 3, the maximum tension with 8 pumps and 8 Niskins was 1350 lb, exceeding the safe working load. At Station 4, only 5 pumps and 5 Niskins were deployed and the maximum tension was 824 lb. At Station 25, 6 pumps and Niskins were deployed and maximum tension was 1049 lb.

## Particle Sample Collection

Each pump contained two McLane vertical-intake holders plumbed into the pump head. One holder was loaded with a 51  $\mu$ m polyester mesh prefilter (underlain by a 150  $\mu$ m polyester mesh support filter) above paired 0.8  $\mu$ m Supor polyethersulfone membrane filters on a separate stage (0.8-51  $\mu$ m size fraction) for contamination prone TEIs; the second holder was loaded with a 51  $\mu$ m polyester mesh prefilter (underlain by a 150  $\mu$ m polyester mesh support filter) above paired Whatman QMA quartz fiber filters underlain by a 150  $\mu$ m polyester mesh support filter on a separate stage (1-51  $\mu$ m size fraction) for particulate organic carbon and TEIs requiring higher volumes (e.g. short-lived radionuclides). The 51  $\mu$ m 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. Pump 4 had an additional top plate that allowed the attachment of two additional McLane vertical-intake filter holders loaded with a Supor set and a QMA set of filters, each 51  $\mu$ m filter set overlain by a 0.2  $\mu$ m Supor filter 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).

Refer to the narrative from the radium group for details and statistics about the Mn oxide-coated cartridge sample collection.

# McLane Pump Cast Statistics

Table 6, below, and the bullet points that follow it provide a summary of how many and where McLane pumps were deployed.

McLane	UTC date	UTC time	Station/cast	# pumps/cast	Pump time	Total volume
deployment#	at mid-cast	at mid-cast	type (S or D)		(h)	pumped/cast
1	12/8/23	11.50	38	8	4	7324
2	12/0/23	5:16	3D	8	4	11331
3	12/10/23	7:24	48	8	4	8408
4	12/13/23	7.24	4D	5	4	6460
5	12/15/23	11.28	58	8	4	7831
6	12/13/23	5.11	6S	7	1.5	3396
7	12/17/23	17:35	78	7	2	4113
8	12/18/23	17:34	85	8	4	6529
9	12/10/23	17:34	9S	8	4	6564
10	12/20/23	15.37	10S	8	4	5655
11	12/21/23	15:38	11S	8	4	6092
12	12/22/23	21.12	128	8	4	11641
13	12/24/23	5:55	138	8	4	9214
14	12/25/23	2:08	14S	8	4	10279
15	12/26/23	9:25	158	8	4	7804
16	12/27/23	5:01	16S	8	4	6237
17	12/27/23	23:41	17S	8	4	6881
18	12/28/23	18:41	18S	8	3.5	7731
19	12/30/23	4:21	19S	8	3.75	5337
20	12/31/23	3:53	20S	8	3.5	5813
21	1/1/24	7:21	21S	8	3.5	7747
22	1/2/24	4:39	22S	8	3.5	8025
23	1/2/24	21:50	238	8	3.5	7555
24	1/3/24	19:19	24Sabort1	8	2	4425
25	1/5/24	0:08	258	8	3.5	8272
26	1/5/24	13:53	25D	6	4	6889
27	1/6/24	10:58	24S	8	3.5	8659
28	1/10/24	10:07	268	8	3.5	7991
29	1/11/24	5:56	278	8	3.5	7770
30	1/12/24	3:21	285	8	2.5	4561
31	1/14/24	9:15	298	8	2.5	4981

**Table 6**. McLane pump cast statistics ("S" casts were shallow casts with no Niskins and "D" casts were deep casts with a 30 L Niskin deployed with each pump).

- A total of 31 McLane pump casts were deployed over 36 days at all 27 sampling stations (i.e., Stations 3-29). Stations 3, 4 and 25 were full stations, which had a shallow and a deep cast at each station; the other stations were on the continental shelf and had only 1 McLane cast per station. There were two casts at Station 24: the first was aborted 1 hour into pumping due to concerns from the bridge about deteriorating weather and encroaching ice (Station 24sabort1). A successful repeat cast was completed upon return to Station 24 after the weather died down (Station 24S).
- Most pump casts had 8 pumps and a set of blanks. The number of pumps was restricted to 5 pumps and Niskins at the deep cast at Station 4 (station 4D) and 6 pumps and Niskins at the deep cast at Station 25 (station 25D) due to concerns from ASC about exceeding the safe working load on the wire under dynamic tension (1000 lb).
- A total of 241 pump samples were collected.
- Including dipped blank filters, we collected 272 of each of QMA pairs, Supor pairs, 51 µm QP prefilters, and 51 µm SP prefilters.
- The total volume filtered in-situ by pumps was 221,514 L over the whole cruise.

# Particle Sample Handling and Subsampling

Shower caps were placed over the tops of 142 mm filter holders upon removal of the pump from the wire. Pumps were wheeled inboard from the wire on a flat dolly, then placed on deck, being careful to keep the pump (and filter holders) horizontal. 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 transported in and out of the shipboard clean bubble in Sterilite totes that each held 2 holders. Filter holders were brought into the clean bubble and sample processing began within an hour of recovery of all pumps.

In the clean 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, starting with the QMA side. Total processing time ranged from 3-6 hours.

Table 7 summarizes the recipients of particle subsamples, the TEIs that will be measured, and processing requirements. A total of 13 groups will receive particle subsamples to analyze dozens of TEIs. All filter subsampling was done on board and preserved according to PI requirements. All samples were dried for >12 hours before being stored away.
PI	parameter	Sample fraction and processing notes	container	representative at sea
Hayes/Anderson/ Edwards	<sup>230</sup> Th/ <sup>231</sup> Pa	<sup>1</sup> / <sub>4</sub> Qp, 5/16 Supor: laminar dry	cleanroom bags	Marty Fleisher
Zheng	εNd, REE	3/16 Qp: laminar dry; Supor: share w/ Th/Pa	cleanroom bag	Marty Fleisher
Buesseler (CafeTh)	<sup>234</sup> Th	<sup>1</sup> /4-7/8 Sp: CafeTh rinse onto Ag then oven dry; 25 mm QMA: oven dry	150mm petri (from CafeTh)	Wokil Bam, Steve Pike
Wang/ Sigman	$\delta^{15}N$	32 mm QMA, 1/8 Sp: laminar dry	cleanroom bag	Kameko Landry
Charette	<sup>226</sup> Ra	"rest of QMA": oven dry	Ziploc bag	Margot Debyser
C. Buck/Marsay	<sup>7</sup> Be	"rest of QMA": oven dry	Ziploc bag	Chris Marsay
John	TM isotopes	Supor: laminar dry	cleanroom bag	none
Ohnemus	pTM total	1/16-1/8 Qp: rinse onto 0.8 μm Supor then laminar dry; 3/16 Supor: laminar flow dry	Qp: leached petrislide; Supor: cleanroom bag	Phoebe Lam, Allison Laubach
Lam	pTM leach	1/16 Qp, 1/16 Supor: laminar dry	cleanroom bag	Phoebe Lam, Allison Laubach
	XRF	1/16 Supor: laminar dry	cleanroom bag	Phoebe Lam, Allison Laubach
	bSi	1/16 Qp, 1/16 Supor: laminar dry	cleanroom bag	Phoebe Lam, Allison Laubach
	PIC	1/16 Qp: laminar dry; 25 mm QMA: oven dry	cleanroom bag	Phoebe Lam, Allison Laubach
	C/N+ isotopes	Sp, QMA: post <sup>234</sup> Th	see <sup>234</sup> Th	Phoebe Lam, Allison Laubach
	archive	0-1/16 Qp, 0-3/4 Sp, 4*1/16 Supor: laminar dry; 32 mm QMA: oven dry	cleanroom bag	Phoebe Lam, Allison Laubach
Mason/Lamborg	pHg	2*1/16 Qp, 2*25 mm QMA: laminar dry	Qp: cleanroom bags; QMA: petrislides	Carl Lamborg, Marissa Despins
Moffett	Ι	25 mm QMA: oven dry	60 mm petri dish	Alexis Floback
Boiteau/Repeta	ligands	32 mm QMA: -80°C	teflon-lined Ziplocs	Nicole Coffey
Saito	proteins	1/8 Qp, 47 mm QMA: -80°C	Qp, QMA: 5 mL cryovials; QMA leftovers: Ziploc bags	Annie Stefanides

Table 7. McLane pump particle subsamples.

**Notes**: All "oven dry" QMA samples were dried on reused 150 mm polystyrene petri dishes in the Cafe-Th oven set at 55°C. All "laminar dry" samples were dried on leached eggcrate grids on eggcrate shelves in a Mystair laminar flow bench inside the bubble. The "rest of QMA" samples were the leftovers after punching out all subsamples. These were oven dried for <sup>226</sup>Ra (Charette) at 11 stations (Stations 3-10; 24, 25, 29); at the remaining 16 stations (Stations 11-23, 26-28), the "rest of QMA" samples were folded and placed fresh into Ziplocs into the fridge, then subsequently into -80°C for proteins (Saito). At Stations 3, 4, 24, 25, 29, the upper 200 m samples will be first counted for <sup>7</sup>Be (Buck/Marsay) by Mark Stephens before sending to Charette for <sup>226</sup>Ra.

#### Problems Encountered

#### McLane Vertical-Intake Filter Holder Issues

This was the first U.S. GEOTRACES cruise to use the new McLane vertical-intake filter holder. This design is the commercial product based on the "mini-MULVFS" design that was tested and intercalibrated on the 2008 and 2009 GEOTRACES intercalibration cruises and used for all U.S. GEOTRACES cruises to date. The new holders retained the dimensions of the mini-MULVFS design and generally produced very good particle distributions on the filters. Several modifications were made by McLane to solve some of the inconveniences from the original mini-MULVFS design; unfortunately, some of these modifications created new problems. The mini-MULVFS design had 32 4"-long acrylic tubes glued into an acrylic top plate as the first "baffle" for particle retention and distribution. Having glued tubes facilitated cleaning, as the entire top module could be acid cleaned, but the top module was difficult to fix if a tube cracked. The new McLane design compresses the 32 tubes between two plastic (HDPE) plates, using a silicone o-ring in the HDPE plates on either end of each tube for a seal. The two plates are held together by 4 plastic (Ultem) 1/4-20 thread hex-head screws on each plate that screw into four 4"long plastic (HDPE) standoffs between the plates. While this facilitates tube replacement, it makes cleaning for trace metal applications more difficult. The insides of the 4"-long tubes and the bottom of the bottom HDPE plate see the most sustained contact with sample. It is thus desirable to be able to acid clean these parts thoroughly for trace metal applications. Because of the o-rings embedded in the HDPE plates, the module needs to be completely disassembled for cleaning and then reassembled, and the many small plastic parts can experience stress if not reassembled precisely and lead to failure. Issues we encountered are described below:

- Pre-cruise cleaning: the silicone o-rings (red) that come with the McLane vertical-intake holders have poor resistance to HCl. Given the 64 silicone o-ring seals on each holder's top module, we did not want to risk even a quick dunk of the fully assembled top module into acid, since small amounts of acid would likely get stuck in the o-ring grooves even after copious rinsing and slowly degrade the seal.
  - a. For the ten existing WHOI vertical-intake holders, we disassembled the pieces, gave the HDPE plates with embedded silicone o-rings a very quick dunk in 10% HCl followed by extensive rinsing and soaking in milli-Q water to remove as much acid as possible. We gave the acrylic tubes and other HDPE and Ultem pieces a full overnight 10% HCl acid soak.
  - b. For the eight new McLane vertical-intake holders that were purchased immediately before the GP17-ANT cruise, we requested that the top module be shipped to us disassembled, with HDPE plates \*without\* embedded silicone orings. We bought replacement viton o-rings, which have much better acidresistance, acid leached all parts fully (10% HCl overnight followed by MQ rinsing) and reassembled the parts.

- 2) Failures in Ultem screws and HDPE standoffs: of the 18 McLane vertical-intake filter holders that we shipped, 4 arrived at the ship with broken parts:
  - a. 5Q: failure in an HDPE standoff just below the end of the top Ultem screw
  - b. 8Q: failure in a top Ultem screw above the standoff
  - c. 5S: failure in a top Ultem screw above the standoff
  - d. 6S: hairline fracture on an acrylic tube (this top module became a dipped blank holder)
  - e. 8S: failure in both a standoff and the top Ultem screw (snapped both the screw and standoff together); failure in an additional top Ultem screw just above the standoff

We did not have any replacement standoffs and did not have enough replacement Ultem screws. To mitigate these failures, we 3D-printed some replacement standoffs onboard ship (Lulzbot TAZ 3D printer) by printing a tube of height 86.1 mm, 2.42 mm inner radius, 5.7 mm outer radius out of PETG 2.85 mm filament, which was subsequently tapped for ¼-20 thread by an MT. Our first attempt was printed vertically, but we found that this was not strong enough. We subsequently printed the tubes horizontally, which were stronger to tensile stresses experienced by the standoff. We used as many replacement Ultem screws as we had and replaced the other broken ones with some plastic ¼-20 bolts provided by another scientist on board. We consolidated as many of the replacement parts as possible into the "dipped blank" filter holders that were not connected to plumbing. The black knob on the thumb screws provided to attach the holders to the pumps frequently separated from the stainless steel bolt. This was solved by epoxying the stainless steel bolt to the black plastic knob. We suggest that thumb screws with a smaller diameter knob may be less prone to breaking off.

3) The female thread on the 3 legs of the filter holder that the thumb screws attached to was made of relatively soft plastic and was easily cross-threaded. It would be preferable if the female thread on the legs could be made of a harder plastic. Unscrewing the thumb screws from the legs had a tendency to also unscrew the legs from the holders. This was worsened if the threads in the legs had been cross-threaded, as this increased the resistance between the thumb screws and the legs, and tended to then unscrew the legs from the holders.

We suspect that uneven tightening of the 4 Ultem screws holding the top plate to the 4 standoffs created strain on these pieces that caused their failures. There is unfortunately no easy way to tell whether the holder reassembly has been done in a way to minimize this strain. Given the need to disassemble the filter holders for acid cleaning for trace metal applications, the frequency at which this failure occurred in our experience is a considerable drawback to this design. At minimum, users should be supplied with many replacement standoffs and Ultem screws.

#### **Pumping Issues**

This was the first US GEOTRACES cruise to use the new McLane WTS-LVDF design. Several key differences between this design and the previous upright design (WTS-LVUP) may negatively affect sample quality compared to previous U.S. GEOTRACES samples:

- 1) the WTS-LVDF design has a significantly shorter distance between the water intake to the 142 mm filter holders and the bottom of the pump ( $\sim$ 2') compared to the modified WTS-LVUP pump ( $\sim$ 4'). This is for two reasons: 1) the WTS-LVDF pressure case is mounted horizontally instead of vertically, so the frame height is shorter, and 2) the filter holders now sit inside the frame rather than on top of it. The shorter frame of the WTS-LVDF greatly facilitates moving the pump around, and placing the holders inside the frame protects them better, but the reduced distance between water intake and the bottom of the pump has increased sample contamination issues. As described in the McLane Pump Operations section above, we observed paint chips in the filter samples, especially in the first half of the cruise prior to instituting a wipedown of each pump frame base prior to deployment. The outlet of the final exhaust hose points to the bottom of the frame, which may have helped to remobilize particles (such as paint chips) stuck to the bottom of the frame. Given that our exhaust contains high Mn from passing through the Mn oxide-coated cartridges, there is also concern about potential Mn contamination in our samples. For users concerned about contamination, it may be worth considering mounting filter holders on top of the frame.
- 2) The new pump design incorporates many PVC connectors in the path between the filter holder connector and the flowmeter that create two issues: 1) it is often quite difficult to fit the plumbing through the hole in the support plate to plug into the filter holders, and these also have a tendency to loosen while plugging holders in. We found that the check valve beneath the filter holder connection is a common place for leaks to develop. For example, there was an undiscovered leak on the Supor side of pump 7 for 7 casts, leading to Supor volumes recorded by the flowmeter that were much higher than normal (and higher than what was filtered). For these samples, we applied an average Supor:QMA volume ratio to better estimate the actual volume filtered through the Supor side.

# MASH4k Winch Issues

Connection issues were experienced with the remote control any time the power was cycled. During one deployment, the level wind stopped hard over to the aft side. Error on drive display read "motor overload". After power was cycled, the issue was resolved.

# 4. Cruise Participant Reports

# **4.1 Cruise participant: April Abbott** (Coastal Carolina University)

**Project title**: Collaborative Research: US GEOTRACES GP17-ANT: Iron redox cycling in the Amundsen Sea in the water column and shelf sediments **Project PI(s)**: Silke Severmann, James Moffett

# Brief Description of Shipboard Activities

The megacorer was deployed at 9 stations (Stations 5, 7, 10, 14, 15, 17, 21, 25, and 27) with a 100% success rate in retrieving sediment core samples on every deployment. An external-closure Niskin bottle attached to the megacore frame was successful in collecting near-bottom seawater in 8 of the 9 deployments. Between 8 and 12 cores met visual quality standards for each station and were processed for a combination of pore water and sediment samples (Table 8). Each core was assigned its own GEOTRACES number with all samples (solid and fluid) from that core sharing the same number. At each site, at least one core was extruded whole into 4-in PVC to be kept as an archive. A second core was also used for solid phase only, sectioned into 1 cm (top 10 cm) and 2 cm (10-20 cm) intervals for porosity, Pb isotopes, ligands, and an aliquot to be freeze dried and distributed later. A minimum of 5 cores were used for Rhizon-based porewater sampling and a 6<sup>th</sup> core was sectioned in a nitrogen glove bag and centrifuged for pore water to be used for rare earth element (REE) analysis and potentially for other species adsorbed by the Rhizon material. Additional successful cores were split between Ra incubation experiments, bulk porewater collection (all depth intervals combined) for dimethyl mercury, and an acidified pore water samples for post-cruise analyses. Fe(II) and total Hg concentrations were measured on board, the rest of the measurements will be made post-cruise.

Station	Cores collected	Pore water	Pore water	Sectioned	Cores used
	(of possible 12)	intervals	intervals	solid-phase	for radium
		sampled	sampled for REE	samples	incubation
5	12/12	12	10	15 intervals	3 cores
7	11/12	13	10	15 intervals	1 core
10	11/12	12	12	15 intervals	1 core
14	8/12	11	12	15 intervals	—
15	12/12	12	12	15 intervals	1 core
17	11/12	11	12	15 intervals	1 core
21	12/12	12	12	15 intervals	1 core
25	10/12	11	9	13 intervals	_
27	12/12	12	10	15 intervals	_

Table 8.	Summary of cores	collected during th	ne cruise and cor	e subsampling details.
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Station	Intervals	Intervals	Intervals	Intervals	Intervals	Intervals
	sampled for	sampled	sampled for	sampled for	sampled for	sampled for
	acidified	for Hg in	Fe(II) in	ligands* in	N isotopes in	nutrients in
	pore waters	pore waters				
5	12	12	11	11	12	12
7	13	11 + bulk	10	11	12	12
10	12	11	10	9	11	11
14	11	11	11	10	11	11
15	12	12	10	9	11	12
17	11	10 + bulk	10	11	11	10
21	12	11 + bulk	11	11	11	11
25	11	10 + bulk	11	11	10	11
27	12	11 + bulk	10	11	12	11

Table 8 (continued). Summary of cores collected during the cruise and core subsampling details.

\*this is the maximum number intervals sampled for the two groups measuring ligands

#### List of Parameters to be Measured:

Pore water: Hg (total, methyl, dimethyl); Fe/Zn/Ni/Cu isotopes; ligands; rare earth elements; Pb isotopes; N isotopes; dissolved Ga, Ba, V; nutrients; Fe(II); I; Rn/Ra fluxes; sweep of periodic table for concentrations of other elements.

Solid phase: Pb isotopes; ligands; rare earth elements; porosity; sweep of periodic table for concentrations of other elements.

**4.2 Cruise participants: Wokil Bam and Steven Pike** (Woods Hole Oceanographic Institution) **Project title**: Export and remineralization rates of bioactive and particle reactive trace elements using thorium-234

Project PI(s): Ken Buesseler, Claudia Benitez-Nelson, Laure Resplandy

# Total <sup>234</sup>Th (Particulate and Dissolved) Collection and Analyses

The goal of the project is to quantify spatial variability in particle flux from the well-lit surface layer (euphotic zone, EZ), and its attenuation with depth into the mesopelagic across biogeographical and TEI gradients in the highly productive Amundsen Sea and its polynyas using <sup>234</sup>Th (half-life = 24.1 d). For this, seawater samples were collected into approximately 2 L FLPE Nalgene bottles from each Niskin for the total <sup>234</sup>Th analysis for all the 27 stations from the PigRaTh (pigments, radium, and thorium) ODF cast. For deeper depths at Stations 3, 4 and 25, seawater was collected from 30 L Niskins incorporated into the McLane pump casts at depths that coincided with pump depths. PigRaTh ODF 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. Each sample was spiked with 1 mL of a

50.03 dpm/g <sup>230</sup>Th standard for future chemical recovery calculations. Total <sup>234</sup>Th was precipitated via additions of KMnO<sub>4</sub> and MnCl<sub>2</sub> 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 after 5 months. Total <sup>234</sup>Th samples will be coupled with particulate <sup>234</sup>Th data (as well as other particulate trace metal and isotope data) in order to produce flux calculations. In summary, 385 total <sup>234</sup>Th (unfiltered 2 L seawater samples), 270 small-size fraction (<51 µm) particulate <sup>234</sup>Th, and 272 large-size fraction (>51 µm) particulate <sup>234</sup>Th samples were collected and processed onboard. See section on pump operations for more detail on particulate analyses. Overall, the preliminary data showed deficits of <sup>234</sup>Th with respect to <sup>238</sup>U within upper euphotic zone suggesting the export of particulate matter. An excess of <sup>234</sup>Th was observed in few stations between the base of the euphotic zone and 200 m indicating particle remineralization. The magnitude and depth of export fluxes and remineralization varied with sampling locations.

# Underwater Vision Profiler (UVP)

The UVP (French CNRS patent) is a high-resolution underwater camera designed to study large (from 60 to 1000 micrometers) particles and zooplankton simultaneously. This instrument was mounted on the ODF CTD rosette. The UVP was operated for all the regular ODF and PigRaTh CTD casts.

4.3 Cruise participant: Eleanor Bates (University of Hawaii at Manoa)
Project Title: Mapping zinc speciation in the Southern Ocean overturning circulation to test the zinc scavenging hypothesis
Project PI(s): Nicholas Hawco, University of Hawaii at Manoa

For this project, 430 filtered samples were collected throughout the water column for post-cruise analysis of zinc speciation; 27 filtered surface water towfish samples were also collected for post-cruise analysis of nickel speciation.

4.4. Cruise Participant: Teagan Bellitto (Texas A&M University)
Project Title: Collaborative Research: GEOTRACES GP17-ANT: Dissolved concentrations, isotopes, and colloids of the bioactive trace metals
Project PI(s): Tim Conway, Jessica Fitzsimmons, Seth John

# <u>Ultrafiltration</u>

Samples were collected from the Towfish, GTC rosette, and the Niskin-X mounted to the multicorer frame and then processed on board. 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). Large volume samples (>2 L) from the GTC at each of the superstations were also ultrafiltered onboard through a crossflow filtration system for collaborators Conway and Hayes.

Ultrafiltered samples from both systems, along with the  $<0.2 \,\mu$ m dissolved samples collected from the GTC, will be analyzed in the Fitzsimmons laboratory at Texas A&M University using ICP-MS techniques for Fe, Mn, Cu, Cd, Zn, and Ni concentrations. The three size fractions from each depth 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.

A total of 405 total dissolved (<0.2  $\mu$ m) 250 mL samples and 1,099 total dissolved (<0.2  $\mu$ m) 60 mL samples were collected from the Towfish, GTC rosette, and the Niskin-X mounted on the multicorer. Additionally, 291 x 60 mL samples were collected through the Anopore membrane system (20 nm). 808 x 60 mL samples were collected through the 10 kDa crossflow filtration system (3 nm) – with one permeate 60 mL bottle and one retentate 60 mL bottle from each of 405 sampling depths.

# 4.5 Cruise Participant: Nicole R. Coffey (University of Minnesota)

**Project Title**: Molecular speciation of trace element-ligand complexes in the Southern Ocean and Antarctic Shelf

Project PI(s): Rene Boiteau, Daniel Repeta

# Description of Shipboard Activities

Shipboard activities consisted primarily of sample collection and preparation; no analyses were conducted during the duration of the cruise, although six separate incubations were completed.

# Sample Collection

Sediment, porewater, and particulate samples were frozen shipboard for transport and analysis back in our laboratory at University of Minnesota. Filtered seawater samples from the surface ( $\sim$ 3 m) and mid-water column ( $\sim$ 300 m) were frozen shipboard for transport back to the lab for use in photochemical degradation experiments. All other samples underwent some degree of shipboard processing before preservation. Table 8 summarizes all samples that were collected.

# Sample Preparation

The majority of our samples collected during this cruise were prepared using a solid phase extraction (SPE) technique. Briefly, solid phase extraction columns were pre-primed with

methanol, 0.1% HCl, and ultrapure water prior to departure for the cruise. Shipboard, filtered samples were pumped over the pre-primed ENV resin SPE at a flow rate of 13 mL/min. The flowthrough from these columns was either discarded as waste or collected and acidified (0.1% optima grade HCl) for further processing. The ENV columns were rinsed with ultrapure water, and frozen for transport back to our lab for further processing. Post-cruise, the organic matter trapped on the resin will be eluted with methanol, dried down, rehydrated with ultrapure water, and analyzed by LC-MS and LC-ICP-MS to characterize and quantify trace element-ligand complexes. For samples selected for further shipboard processing, acidified sample was pumped over pre-primed ENV-CHAR columns at a flow rate of 13 mL/min. These columns were rinsed with 0.1% HCl and frozen for shipment back to our lab, and further processing and analysis as above. Infrequently, locations were selected as candidates for metagenomic analyses. At these sites, 1 L of unfiltered seawater was passed through a Sterivex filter. These filtered with Sterivex filters, which were preserved as above, and extracted with ENV resin as above. Sample types are summarized in Table 9.

Sample Type	Sample Origin	Number
ENIV columns, frozon (20%C)	Depth profile (GTC, towfish, Multicorer Niskin-X)	440
ENV columns, nozen (-20 C)	Sea ice	4
	Incubations	49
ENV CAPP columns frozen (20°C)	Depth profile (GTC)	95
ENV-CARD columns, nozen (-20 C)	Sea ice	4
	Depth profile (towfish, ODF rosette)	7
Sterivex filters, frozen (-80°C)	Sea ice	1
	Incubations	36
Filtered seawater, 4 L bottles, frozen (-20°C)	Depth profile (GTC, towfish)	8
Sediment, 5 g bags/tubes, frozen (-20°C)	Coring efforts	90
Porewater, 10 mL in 50 mL tubes, frozen (-20°C)	Coring efforts	90
QMA filter pieces with particulates, frozen (-20°C)	Depth profile (McLane Pumps)	274

Table 9. Summary of samples collected for Boiteau and Repeta project.

**4.6 Cruise Participant: Margot Debyser** (Woods Hole Oceanographic Institution) **Project Title**: US GEOTRACES GP17-OCE and GP17-ANT: Sources and rates of trace element and isotope cycling derived from the radium quartet **Project PI(s)**: Matthew Charette

# Large Volume Ra/Th/Ac Sample Processing and At-Sea Radium Counting

MnO<sub>2</sub>-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. <sup>224</sup>Ra ( $t_{1/2} = 3.7$  d) and <sup>223</sup>Ra ( $t_{1/2} = 11.4$  d) were measured on the Radium Delayed Coincidence Counter (RaDeCC) system and typically counted within 24 h of sample collection. A second count was conducted onboard after 3 weeks for correction from <sup>228</sup>Th. Scavenging efficiencies of the cartridge filters for Ra and Th is validated by a discrete seawater sample taken in parallel with every pump depth: 21.5 L seawater was passed over a column of MnO<sub>2</sub> impregnated acrylic fiber on deck, and recirculated for >3 h, which removes radium at 100% efficiency. These filter samples will be analyzed for <sup>226</sup>Ra through its daughter, <sup>222</sup>Rn in land-based laboratories. For shallow pump cast depths, these discrete <sup>226</sup>Ra samples were collected by the ODF Niskin rosette from PigRaTh casts by the ODF Supertechs; for deep pump casts, they originated from a 30 L Niskin bottle that was hung next to each McLane pump and triggered by messenger at mid-cast. In total, 242 cartridges from seawater and 10 fiber samples from sediment core-top water and sea-ice were counted onboard through the RaDeCC system by Margot Debyser.

# Surface Sampling for Ra Isotopes

At all stations, ~1500 L of surface water was collected using a surface pump deployed by hand over the starboard quarter of RVIB Nathaniel B. Palmer to ~3 m depth. The seawater was filtered through 10 and 1  $\mu$ m pre-filters, then through MnO<sub>2</sub>-coated acrylic cartridges to collect radium isotopes as per the McLane pumps, as well as an unfiltered 21.5 L sample for <sup>226</sup>Ra. In total, cartridge and fiber samples were collected from the surface at 27 stations. Samples were processed in a similar manner to McLane pump cartridge samples and were analyzed for shortlived Ra isotopes on the ship-board RaDeCC systems by Margot Debyser.

# Seawater Sampling for Dissolved Silicon Isotopes (δ<sup>30</sup>Si, Unfunded)

From PigRath casts, seawater was gravity filtered through pre-cleaned Acropak 500 0.8/0.45  $\mu$ m Supor filter capsules into 60 mL acid-cleaned Nalgene bottles and stored at +4°C for future analysis of dissolved Silicon isotopes ( $\delta^{30}$ Si). For this, 243 seawater samples were collected in total by Margot Debyser and ODF supertechs.

4.7 Cruise participants: Marissa Despins (University of California Santa Cruz), Hannah
Inman (University of Connecticut) and Carl Lamborg (University of California Santa Cruz)
Project Title: US GEOTRACES GP-17-OCE and -ANT Sections: External sources, cycling and processes affecting mercury speciation in the South Pacific and Southern Oceans
Project PI(s): Rob Mason, Carl Lamborg, Silvia Newell; collaborators Sarah Janssen, Mike Tate

The ANT leg of this project sailed on the RVIB NB Palmer from Punta Arenas, Chile on November 29, 2023 for 60 days of research and transit time in the Amundsen Sea, Antarctica and surrounds. The on-board mercury (Hg) team engaged in several activities during the cruise.

These included: 1) shipboard analysis of Hg species in a variety of sample types, 2) maintenance of underway surface water and atmospheric Hg speciation instruments, 3) collection of air and water samples for Hg isotopes, 4) working with the Lam Lab (UCSC) to collect particulate material for Hg species and genomic analysis and 5) work as a GEOTRACES Supertech (Inman). The goal of these activities, when coupled with remaining on-shore analyses is to gain an understanding of the distribution and dynamics of Hg species in a poorly studied and rapidly changing region of the ocean. Of particular interest was the influence of sea-ice, large freshwater inputs and the upwelling of Circumpolar Deep Water on air-sea exchange and biogeochemistry of Hg. As an important aspect of these processes is the behavior of the dissolved gaseous elemental Hg (Hg<sup>0</sup>) and dimethylmercury ((CH<sub>3</sub>)<sub>2</sub>Hg), and as these species cannot be easily stored for later analysis, on-board and underway determination of Hg<sup>0</sup> and (CH<sub>3</sub>)<sub>2</sub>Hg was a major component of on-board activities. Total dissolved Hg (HgT) was also measured on-board in a variety of media both to avoid the need to return large numbers of samples and to also conduct crucial real-time quality assessment of the collection and processing of samples performed by GEOTRACES technicians.

Sample types analyzed on-board included surface waters for  $Hg^0$  and  $(CH_3)_2Hg$  by underway equilibrators (>1000 individual measurements for  $(CH_3)_2Hg$  and >6000 for  $Hg^0$ ), atmospheric  $Hg^0$  and reactive gaseous Hg, aerosol Hg and ozone concentrations by a continuous atmospheric system (>6000), discrete profiles of HgT,  $Hg^0$ ,  $(CH_3)_2Hg$  (~442 measurements), profiles of porewater and overlying water HgT from multicore-collected sediment (103 measurements) and single-per-core measurements of porewater  $Hg^0$  and  $(CH_3)_2Hg$  (~4 measurements). For later, on-shore analysis, we collected 442 samples for dissolved MMHg, 26 samples for total methylated  $(MMHg+(CH_3)_2Hg)$  Hg, >300 samples for particulate HgT and MMHg and 7 surface water, 10 atmospheric and 5 dissolved gaseous  $(Hg^0+(CH_3)_2Hg)$  samples for isotopic analysis, 500 Sterivex filter capsules for DNA sequencing from water and ice. Finally, several liters of water were collected for distribution as a consensus standard for intercomparison exercises.

Preliminary findings include: 1) prominence of  $(CH_3)_2Hg$  in surface and subsurface waters unlike most regions of the ocean, 2) large swings in Hg<sup>0</sup> saturation with respect to the atmosphere from subsaturation in open waters south of the Antarctic Front to high levels of supersaturation in waters recently isolated from contact with the atmosphere under ice sheets, 3) possible ice melt and benthic flux signatures in HgT profiles, and 4) first ever measurements of dissolved gaseous Hg species in marine porewaters that indicated elevated Hg<sup>0</sup> concentrations compared to overlying water and an absence of  $(CH_3)_2Hg$ .

Following the cruise, the team will receive sediment subsamples from Silke Severmann of Rutgers University and begin analyzing water, air, sediment, ice and DNA samples to complete what should be an exciting dataset.

# **4.8 Cruise participant: Martin Fleisher** (Columbia University) **Project title**: Collaborative Research: U.S. GEOTRACES GP17-OCE and GP17-ANT: quantifying trace element sources and sinks using <sup>230</sup>Th, <sup>231</sup>Pa and <sup>232</sup>Th **Project PI(s)**: Chris Hayes, Larry Edwards, Bob Anderson

Work for the project on board was mainly the collection of 5 liter water samples for Th and Pa at every depth at every station from the ODF rosette. We also collected separate 5 liter samples for Xinyuan Zheng and Michael Bizimis, who were funded to measure Nd isotopes and rare earth elements (REEs) on the cruise. Samples were acidified to pH~2 with redistilled 6N HCl, then double bagged and stored in the ship's science hold.

We also deployed the NIOZ Monocorer from the rosette on the Deep ODF cast at every station. This corer is used to collect small sediment cores at each station as a service to the community at large, as has been done on previous GEOTRACES cruises. We successfully recovered cores at 23 of the 27 sampling stations on the cruise.

We stored 832 samples and 20 Blanks (2 liter aliquots of Milli-Q from LDEO in 5 liter cubitainers, acidified at sea along with samples) in the ship's science hold for a total volume of about 4.2 m<sup>3</sup> of samples. Twenty four of the samples were extras collected at Station 29 just for the Th/Pa group. The remaining 808 cubitainers represent a suite of 404 samples each to be analyzed by the Th/Pa group and for the Nd/REE group.

The Pa/Th group will measure two long-lived Th isotopes: <sup>232</sup>Th, which is supplied mainly from dust and other terrigenous inputs such as dirty ice and other ice shelf and iceberg inputs, and <sup>230</sup>Th, which is produced in the water column from the decay of <sup>234</sup>U, and is used as a constant flux proxy for water column processes. We will also measure <sup>231</sup>Pa, produced in the water column from the decay of <sup>235</sup>U, whose ratio to <sup>230</sup>Th can inform us about the particulate phases most responsible for trace metal scavenging.

The same suite of isotopes will be analyzed for colloids from 3.5 L samples collected at 6 depths on each of the 4 super stations. These water samples came from the GTC rosette Go-Flos and were processed for colloids by Teagan Bellitto from Texas A&M, using their cross-flow filtration (CFF) system. In addition to the 1 L permeate and retentate fractions from the CFF system, we also took a 1 L sample of Acropak-filtered water from the GTC Go-Flos to compare with 5 L ODF rosette sample from the same station/depth, and to measure the source water for the 1 L aliquots from the CFF system.

All of this work would not have been possible without the help of the crew of the *Palmer*, both on the ECO side and the ASC side. The Supertechs from both rosette systems worked very hard

to get us the water we had requested. In particular, I'd like to give special thanks to everyone working on the ODF rosette; Andrew Barna, Kelcey Chung, Gabe Matthias, and Aaron Mau from ODF; Bettina Sohst and Laura Whitmore who prepared cast sheets and acted as bottle cops for the ODF rosette; Becky "Pam" Miller who filled in as bottle cop on a regular basis; Molly Passacantando and Ryan Woosley for their camaraderie around Gladys as we all patiently waited for our turns to take our samples. And finally, I can't thank the other two ODF Supertechs, Kate Kouba and Kameko Landry enough for all of their help and friendship. They made the cruise for me. And thanks to all of the scientists on GP17-ANT, especially Phoebe Lam, Rob Sherrell, and our fearless leader, Pete Sedwick, for making this a memorable experience.

# 4.9 Cruise participant: Alexis Floback (University of Southern California)

**Project title**: Collaborative Research: US GEOTRACES GP17-ANT: Iron redox cycling in the Amundsen Sea in the water column and shelf sediments **Project PI(s)**: James Moffett, Silke Severmann

# Brief description of shipboard activities

Shipboard analysis of Fe(II) by chemiluminescence and collection of samples for post-cruise analyses of iodine species and inert copper. Table 10 summarizes all samples that were collected.

Analyte	Number of Samples
DFe(II)	410 water column
	93 sediment porewater
	12 sea ice differential melt timepoints
Iodide/iodate	410 water column
	93 sediment porewater
	12 sea ice differential melt timepoints
Inert Cu (unfunded)	56 water column

Table 10. Summary of samples collected for Moffett and Severmann project.

An overall trend in the results shows enrichment of DFe(II) at the surface and sediment-water interface, and often a mid-water column enrichment. These trends were not observed at every station, but suggest that photoreduction of DFe(III) at the surface, sea ice melt, and release from sediments are important sources of DFe(II). Figure 4 shows examples of the DFe(II) concentration profiles from the water column and sediment pore waters at Station 27. Oxidation kinetics experiments showed that the half-life of DFe(II) in waters at these low temperatures range from  $\sim$ 1.5-2 hours. Future analysis of iodine species will help constrain benthic sources.



**Figure 4**. Vertical profiles of dissolved iron(II) concentrations in the water column (left) and sediment pore waters (right) from Station 27.

**4.10 Cruise participants: Phoebe Lam** (University of California Santa Cruise) **Project title**: Collaborative Research: US GEOTRACES GP17-ANT: Characterizing the composition, scavenging efficiency and bioavailability of size fractionated particles **Project PI(s)**: Phoebe Lam, Dan Ohnemus

Particulate Fe bioassays were conducted as part of Phoebe Lam's project. Incubations were designed by Katherine Mateos. Incubations were conducted at sea by Phoebe Lam and Allison Laubach, with assistance from Lauren Hearn. We conducted three incubations towards the end of the cruise, which are summarized in Table 11.

	Incubation A	Incubation B	Incubation C
Station#, GT#	24, GT20476	29, GT20963	28 ice, GT20958
#treatments	6	6	5
Treatments	Ctrl, +FeCl <sub>3</sub> , +Bt,	Ctrl, +FeCl <sub>3</sub> , +Bt,	Ctrl, +FeCl <sub>3</sub> , +Bt,
	+Phaeo, +Out, +NB	+FhGA, +Out, +NB	+Out, +NB
+Out:	GT20232PC, Stn	GT19775PC, Stn14S,	GT20799PC, Stn 26,
	20S, 139 m	114 m	235 m
+NB:	GT19716PC, Stn	GT19964PC, Stn	GT20319PC, Stn 21,
	13S, 1004 m	16S, 437 m	541 m
#replicates	3	3	3
Volume of each	1 L	1 L	250 mL
incubation			
Start date	01/03/24	01/12/24	01/13/24
End date	01/10/24	01/18/24	01/18/24
Filtrate for Boiteau	400-500 mL from	800 mL from	N/A
lab?	duplicates of Ctrl,	duplicates of Ctrl,	
	+FeCl <sub>3</sub> , +NB	+FeCl <sub>3</sub> , +Bt, +Out,	
		+NB	

Table 11. Summary of shipboard particulate iron-addition bioassay experiments.

Incubations A and B were started with 25 L of unfiltered TM-clean towfish water collected by the GTC Supertechs. Incubation C was started with 50 mL of meltwater from the high-biomass slush sample taken by Laura Whitmore at Station 28, diluted to 250 mL with filtered seawater from the Station 29 TM-clean towfish.

The treatments were:

Control (Ctrl): nothing added

+FeCl<sub>3</sub>: 2nM of FeCl<sub>3</sub>

+Bt: crushed biotite mineral, equivalent to 2 nM of leachable pFe

+Phaeo: freeze-dried *Phaeocystis* EPS, equivalent to 2 nM of leachable pFe

+FhGA: freeze-dried ferrihydrite that was co-precipitated with glucuronic acid, a model monosaccharide

+Out: particles collected at a putative glacial outflow depth

+NB: particles collected near-bottom

All incubations had a "sacrificial bottle" that was a +FeCl<sub>3</sub> treatment from which we monitored Fv/Fm and Fm daily.

The "+Out" and "+NB" particles were collected on 47 mm 0.8 µm polycarbonate filters on the unmetered third flow path of the McLane pumps and kept frozen until use. Duplicate filters were typically collected. For incubations A and B, half of one of the duplicate filters was kept for future total and leachable particulate trace metal analysis by ICP-MS as well as mineralogical Fe analysis by synchrotron X-ray techniques (STXM, XAS). The other 1.5 filters were

resuspended in filtered seawater and added to the treatment bottles. For incubation C, a single particle filter was collected for the "+Out" treatment, and duplicate particle filters were collected for the "+NB" treatment. One quarter of a filter was resuspended in filtered seawater and added to the treatment bottles. The remaining 1.75 (+NB) or 0.75 (+Out) filters were kept for additional analysis.

We collected samples for nutrient and pigment analysis at T0 and Tfinal for later analysis. Nutrient samples were syringe filtered through a precombusted GF/F filter into 20 mL scintillation vials and frozen at -20°C. Pigment samples were filtered onto precombusted GF/F filters, flash frozen in cryovials in LN2, and stored at -80°C.

We monitored the  $F_v/F_m$  and Fm daily from the sacrificial bottle on the mini-FIRE, and from all treatments 3-4 times over the course of the incubation using the sacrificial bottle results to guide time of measurement.

For incubations A and B, we collected the filtrate from a subset of treatment bottles for the Boiteau lab to analyze for ligands by mass spectrometry.



**Figure 5**.  $F_v/F_m$  for the various experimental treatments after day 5 for Incubation A (left panel) and day 6 for Incubation B (right panel).

Preliminary experimental results are shown in Figure 5. Both Incubations A and B showed an increase in  $F_v/F_m$  in the positive control (2 nM FeCl3), demonstrating iron limitation at these stations. Interestingly, both experiments showed the greatest response to the +NB treatment (near-bottom particles), even larger than for the positive control, perhaps suggesting limitation by one or more additional micronutrients supplied by the near-bottom particle addition. Incubation B also showed some enhancement in  $F_v/F_m$  compared to control in the +Out and +Bt treatments. Incubation C showed final  $F_v/F_m$  above the control for all treatments, but most significantly the +NB treatment. In contrast to the other incubations, although  $F_m$  increased in all treatments over time,  $F_v/F_m$  decreased (Fig. 6). The +NB treatment was most able to retain its

original  $F_v/F_m$ , while the control and other treatments became increasingly stressed. The slush water was likely high in Fe, so the Fe additions did not prevent stress. This further suggests the presence of a beneficial non-Fe micronutrient in near-bottom particles.



Figure 6. Time-course of  $F_v/F_m$  for the different treatments during Incubation C.

# 4.11 Cruise participant: Kameko Landry (Boston College)

**Project title**: Nitrogen isotope dynamics on the Amundsen Sea continental margin **Project PI(s)**: Daniel Sigman and Xingchen (Tony) Wang

#### Description of Shipboard Collection

About 838 NO<sub>3</sub><sup>-</sup>  $\delta^{15}$ N and  $\delta^{18}$ O 60 mL samples were collected from the ODF rosette from the primary casts (standard 12 depths) as well as a surface sample from the PigRaTh cast. Two NO<sub>3</sub><sup>-</sup>  $\delta^{15}$ N and  $\delta^{18}$ O 60 mL samples were collected from each depth: one filtered and the other unfiltered. 27 unfiltered NO<sub>3</sub><sup>-</sup>  $\delta^{15}$ N and  $\delta^{18}$ O 60 mL samples were collected from the surface towfish when towfish operations were feasible. All samples will be analyzed for the  $\delta^{15}$ N and  $\delta^{18}$ O of NO<sub>3</sub><sup>-</sup> as well as total dissolved nitrogen (TDN) using the denitrifier method. Unfunded collection of NH<sub>4</sub><sup>+</sup> consisted of taking three 500 mL water samples from the primary ODF cast and one 500 mL sample from the surface depth of the PigRaTh at each station, besides Station 3 and Station 29 where full depth profiles were sampled. The NH<sub>4</sub><sup>+</sup> isotope samples were acidified

with 0.5 mL of 4N HCl. Both NO<sub>3</sub><sup>-</sup>  $\delta^{15}$ N and  $\delta^{18}$ O and NH<sub>4</sub><sup>+</sup> isotope samples were frozen after collection.

Sediment, porewater, and particulate samples also collected onboard will be divided between Princeton's and Boston College's labs for  $\delta^{15}$ N analyses.

4.12 Cruise participant: Léo Mahieu (Oregon State University)
Project title: Collaborative Research: U.S. GEOTRACES GP17-OCE and GP17-ANT: Characterizing iron-binding organic ligands in the Southern Ocean and implications for iron cycling in the global ocean
Project PI(s): Kristen N. Buck (OSU), Randelle M. Bundy (UW)

Onboard electrochemical characterization of iron-binding ligands in seawater samples was performed employing the method described in Buck et al. (2007, 2015, 2018) and Mahieu et al. (2024). The dataset collected onboard will be completed by the analysis of porewater and sea-ice samples by Léo Mahieu in the Buck lab at OSU and multiple analytical window analysis by the Bundy lab at UW for a more holistic view of the sources and sinks of iron-binding ligands in the studied area. Seawater particle samples were also collected to investigate the distribution of iron-binding ligands between dissolved and particulate material in subsequent analysis by Léo Mahieu at OSU. The composition of the iron-binding ligand pool in the seawater samples will be further resolved by the electrochemical characterization of exopolymeric substances by NSF OPP-funded postdoctoral researcher Laura Moore in the Buck lab at OSU. In parallel, organic matter has been concentrated for siderophore and molecular characterization of other metal-binding ligands at UW. Samples collected are summarized in Table 12. Preliminary results of the iron-binding ligand concentration ( $L_{Fe}$ ) and binding-strength (log K), calculated using shipboard DFe measurements (see section 4.15), show an increase in both parameters from open ocean waters to shelf waters (Fig. 7).

Sample characteristic	Sample characteristic Sample collection		Number of samples collected for		
_	_	Intercalibration and	Onboard analysis		
		EPS measurement			
Seawater	GTC	369	369		
Surface seawater	Towfish	29	29		
Sea ice	Sea-ice operations	12			
Porewater	Megacorer	92			
Seawater 1 m above seafloor	Niskin-X sampler	6			
Seawater particle	McLane pumps	8			
Concentrated organic matter	Towfish	30			

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I ante	14.	Samples	conected	IOI	Charac	ierza	uon	01 ГС-	-DIHUHIB	organic	nganus.
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Figure 7. Iron-binding ligand characteristics (log K and L<sub>Fe</sub>) for Stations 3 to 10 analyzed at sea.

Buck, K.N., Lohan, M.C., Berger, C.J.M., Bruland, K.W., 2007. Dissolved iron speciation in two distinct river plumes and an estuary: Implications for riverine iron supply. *Limnology and Oceanography* 52, 843–855. <u>https://doi.org/10.4319/lo.2007.52.2.0843</u>

Buck, K.N., Sohst, B., Sedwick, P.N., 2015. The organic complexation of dissolved iron along the U.S. GEOTRACES (GA03) North Atlantic Section. *Deep Sea Research Part II: Topical Studies in Oceanography* 116, 152–165. <u>https://doi.org/10.1016/j.dsr2.2014.11.016</u>

Buck, K.N., Sedwick, P.N., Sohst, B., Carlson, C.A., 2018. Organic complexation of iron in the eastern tropical South Pacific: Results from US GEOTRACES Eastern Pacific Zonal Transect (GEOTRACES cruise GP16). *Marine Chemistry*, The U.S. GEOTRACES Eastern Tropical Pacific Transect (GP16) 201, 229–241. <u>https://doi.org/10.1016/j.marchem.2017.11.007</u>

Mahieu, L., Omanović, D., Whitby, H., Buck, K.N., Caprara, S., Salaün, P., 2024. Recommendations for best practice for iron speciation by competitive ligand exchange adsorptive cathodic stripping voltammetry with salicylaldoxime. *Marine Chemistry*, 104348. <u>https://doi.org/10.1016/j.marchem.2023.104348</u>

# 4.13 Cruise participant: Chris Marsay (University of Delaware)

Project title: Atmospheric deposition and aerosol fractional solubility in remote ocean regionsProject PI(s): Clifton Buck (University of Georgia), Chris Marsay (University of Delaware)Project title: Quantifying the properties of atmospheric trace elements and their fluxes to the Amundsen Sea

Project PI(s): Yuan Gao (Rutgers University)

The aim of the Buck and Marsay project was to collect aerosol and precipitation samples for analysis of a suite of trace elements, and to collect upper water column samples and snow from sea ice cover to determine the inventory of beryllium-7 (a tracer of atmospheric deposition). Aerosols were collected on board using up to five high volume aerosol samplers (Tisch 5170-

BL) operated under wind sector control to avoid sampling emissions from the ship. One sampler was loaded with GFF filters, one with a five-stage Sierra-style slotted cascade impactor, and up to three with W41 filters. Frequent snow events proved to be a big problem for the high-volume samplers, with snow blowing up inside the sampler and collecting on the aerosol filters – several samples were discarded because of this issue. A total of three precipitation samples were also collected for trace element measurements using an N-CON automated wet deposition sampler, and five snow samples were collected specifically for beryllium-7 analysis using buckets secured on deck. Atmospheric sample collection is summarized in the Table 13. Water column sampling for beryllium-7 was completed at six stations, and snow samples were collected at five sea ice stations, as summarized in Table 14. In addition, aerosol sampling was conducted for Yuan Gao's project, using MOUDI and Anderson size-fractionated impactors, a Partisol aerosol sampler, and a setup to collect aerosols for individual particle analysis. Sample collection for this project is also summarized in Table 13.

Sample type	Number of successful deployments
HiVol aerosol – W41	8
HiVol aerosol – GFF	7
HiVol aerosol – five-stage impactor	5
MOUDI impactor aerosol	6
Anderson impactor aerosol	6
Partisol aerosol	5
"Individual particle" aerosol	5
Falling snow – trace elements	3
Falling snow – beryllium-7	5

 Table 13. Atmospheric sampling summary.

Extractions of aerosol-laden W41 filters were carried out while at sea, using ultrapure water (UPW) or filtered surface seawater from the towfish (each using a 0.2  $\mu$ m polycarbonate backing membrane), or using filtered towfish seawater with a 0.02  $\mu$ m Anodisc backing filter. Each extraction was carried out on three separate, replicate filters from each deployment. These leaches included:

- UPW  $21 \times 100$  mL sample leaches and  $9 \times 100$  mL blanks; subsamples also taken from one UPW leach per deployment for major anion analysis.
- 0.2  $\mu$ m filtered seawater 24 × 100 mL sample leaches and 6 × 100 mL blanks.
- 0.02  $\mu$ m filtered seawater 12 × 100 mL sample leaches and 6 x 100 mL blanks.

Additional replicate W41 filters from each deployment will be digested with concentrated acids back onshore for analysis of total concentrations of a suite of trace elements by ICP-MS. Aerosol sample leaches will also be analyzed by ICPMS and used with digest data to determine fractional solubility of the aerosols collected.

Station #	Samples collected
3	Water column – 6 depths
4	Water column – 6 depths
5	Water column – 6 depths
5	Snow
12	Snow
20	Snow
24	Water column – 6 depths
24	Snow
25	Water column – 6 depths
28	Snow
29	Water column – 6 depths

 Table 14. Water column and sea ice beryllium-7 sampling summary.

Beryllium-7 samples will be analyzed by colleagues at Florida International University and the data used with aerosol concentration data to calculate deposition fluxes of trace elements.

# 4.14 Cruise participant: Mollie Passacantando (University of Rhode Island)

**Project title**: Collaborative Research: US GEOTRACES GP17-OCE and GP17-ANT: Properties and processes impacting other trace element and isotope cycles using noble gas and stable isotope tracers

Project PI(s): Chris German, Wiliam Jenkins, Brice Loose, Jennifer Middleton, Gisela Winckler

# Brief Description of Shipboard Activities

Collection of seawater samples for noble gas, tritium, and  $\delta^{18}O$  analysis. Collection of sectioned ice cores and snow samples for tritium analysis. Analysis of discrete phytoplankton  $F_v/F_m$  in water-column samples.

# Samples Collected During the Cruise

800 x 30 mL water samples for  $\delta^{18}$ O analysis.

414 cold-welded copper tubes with 414 duplicates with 200 mL of water for noble gas analysis.

128 x 800 mL water samples for tritium analysis.

4 snow samples for tritium analysis.

6 ice samples for tritium analysis.

146 x 10 mL samples analyzed on board for Fv/Fm measurements.

# 4.15 Cruise participant: Joseph Resing (University of Washington) Project title: Collaborative Research: US GEOTRACES GP17-ANT: Shipboard Measurements of Fe, Mn, and Al in the Amundsen Sea Sector of the Antarctic Continental Margin PI(s): Joseph Resing, Peter Sedwick

# Shipboard Dissolved Iron Measurements

Approximately 440 samples were analyzed for dissolved iron (DFe) using a modification of the shipboard flow-injection analytical technique of Measures et al. (1995). All samples were filtered through a 0.2  $\mu$ m Acropak capsule prior to analysis. Samples collected for analysis include near-surface and water-column (29 stations), near-seafloor (9 samples; not all were analyzed during the cruise), and snow/ice (8 samples). All samples were collected as outlined elsewhere in the cruise report. Three DFe samples were taken over the course of each towfish deployment (spanning ~40 minutes) to assess small-scale spatial variations in near-surface DFe concentrations.

Preliminary results indicate that the distribution of DFe on the Amundsen Sea shelf is dynamic and variable in the near-surface ocean, where it may be influenced by a number of processes including input from sea-ice, bottom sediments and glacial melt water. The largest enrichments were near the seafloor. Several examples of the water-column profiles are presented in Figure 8. At Station 12, characterized by extremely low phytoplankton biomass, DFe was relatively constant throughout the water column, and elevated relative to Station 16, where chlorophyll biomass was very high and DFe was considerably lower, especially within the euphotic zone (~0.15-0.25 nM); DFe was not as low at the surface, which may reflect sustained inputs from melting sea ice, which was observed over much of our study area. Interestingly, DMn concentrations appear to reflect greater removal in the upper water column relative to DFe at station 16, possibly as a result of the relative enrichment of sea-ice meltwater in DFe (e.g., Lannuzel et al., 2011, 2014).

Stations 13 and 14 are thought to be located near the inflow to (at depth) and outflow from (at ~200-600 m) the Dotson Ice Shelf, respectively. The putative inflow waters are enriched in DFe at depth, with relatively low concentrations over the rest of the water column. At Station 14, DFe is comparably higher in the upper 600 m than at Station 13, reflecting elevated DFe in the outflow derived from the deep inflow waters and/or glacial meltwater; further analysis and information from other tracers (e.g., radium and oxygen isotopes) may allow us to assess the relative magnitudes of these processes.



**Figure 8**. Dissolved Fe concentration profiles from (A). Stations 12 on the inner shelf northeast of Bear Island (low biomass) and 16 on the inner shelf in the Amundsen Sea Polynya (high biomass); and (B). sites adjacent to the Dotson Ice Shelf: Stations 13 (inflow) and 14 (outflow).

#### Shipboard Dissolved Manganese Measurements

Approximately 450 samples were analyzed for dissolved manganese (DMn) using a modification of the shipboard flow-injection analytical technique of Resing and Mottl (1992). All samples were filtered through a 0.2  $\mu$ m Acropak capsule prior to analysis. Samples include near-surface and water-column (29 stations), near-seafloor (9 samples), and snow/ice (8 samples). Water-column samples were collected using Go-Flo bottles mounted on the GEOTRACES trace metal clean CTD-rosette, and near-surface samples were collected using a trace-metal clean towfish system. Three DMn samples were taken over the course of each towfish deployment (spanning ~40 minutes) to assess small-scale spatial variations in near-surface DMn concentration. Near-bottom samples were collected within ~ 1 m of the seafloor using a Niskin-X sampler mounted to the frame of a multicorer. Sea-ice cores and snow samples were collected using trace-metal clean coring/sampling protocols and were melted prior to filtration.

Preliminary results indicate that the distribution of DMn on the Amundsen Sea shelf is highly dynamic and influenced by a number of processes. Several examples of the water-column profiles are provided in Figure 9. At Station 12, located in the Antarctic Coastal Current (AACC) to the northeast of Bear Peninsula and on the western edge of a large expanse of fast ice, was characterized by extremely low phytoplankton biomass. Here DMn concentrations are highly enriched in the surface and upper water column (~3-7 nM), perhaps reflecting inputs from glacial outflow or sea ice melt to the east; there is also a mid-depth minimum of below 2 nM suggesting removal via scavenging, and a modest maximum of ~2 nM toward the seafloor suggesting benthic inputs (panel A in Figure 9). Stations 15 and 16 in the Amundsen Sea Polynya were characterized by high phytoplankton biomass, and exhibit sub-nanomolar concentration minima at the surface and in the shallow sub-surface, which likely reflect biological uptake (panel B in Figure 9); both stations also show strong maxima toward the seafloor, suggesting sedimentary sources of DMn on the inner shelf.



**Figure 9**. Dissolved Mn concentration profiles from (A). Station 12 on the inner shelf northeast of Bear Island (low biomass); (B). Stations 15 and 16 on the inner shelf in the Amundsen Sea Polynya (high biomass); and (C). Stations adjacent to ice shelves: Station 13 (Dotson inflow), Station 14 (Dotson outflow), and Station 26 (Getz-E outflow).

Panel C in Figure 9 shows three examples of profiles adjacent to glacial ice shelves. Stations 13 and 14 are thought to be located near inflow to (at depth) and outflow from (at ~200-600 m) the Dotson Ice Shelf, respectively. Both stations show elevated DMn toward the surface, similar to Station 12, with the putative outflow station 14 showing higher concentrations in the ~300-500 m depth range, implying that DMn is enriched in the glacial outflow. Station 13, in much deeper water, also shows highly elevated DMn near the seafloor that likely reflect benthic inputs to the modified Circumpolar Deep Water as it intrudes southwards onto the shelf. Curiously, Station

26, located near the putative outflow of the Getz-E Ice Shelf shows nearly uniform DMn concentrations near 1 nM over the entire water column, suggesting minimal glacial/benthic inputs, and possibly biological uptake in surface waters as they are carried eastwards in the AACC. Other tracers measured as part of GP17-ANT (e.g., radium isotopes and thorium-234) are expected to provide information that will improve our understanding of these DMn data.

Lannuzel, D., Bowie, A. R., van der Merwe, P. C., Townsend, A. T., & Schoemann, V. (2011). Distribution of dissolved and particulate metals in Antarctic sea ice. *Marine Chemistry*, 124(1-4), 134-146.

Lannuzel, D., Chever, F., van der Merwe, P. C., Janssens, J., Roukaerts, A., Cavagna, A. J., ... & Meiners, K. M. (2016). Iron biogeochemistry in Antarctic pack ice during SIPEX-2. *Deep Sea Research Part II: Topical Studies in Oceanography*, 131, 111-122.

Resing, J. A., & Mottl, M. J. (1992). Determination of manganese in seawater using flow injection analysis with on-line preconcentration and spectrophotometric detection. *Analytical Chemistry*, 64(22), 2682-2687.

# 4.16 Cruise Participants: Rob Sherrell (Rutgers University)

**Project title:** Collaborative Research: US GEOTRACES GP17-ANT: Answering key questions in marine particle trace element biogeochemistry in the Amundsen Sea **Project PI(s):** Rob Sherrell, Peter Morton

The main goal of this project is to determine the distribution and elemental composition of suspended particulate matter, at high spatial resolution, collected from the Go-Flo bottles deployed on the GTC rosette. We will test hypotheses related to glacial delivery of mineral particles and the very high productivity of the polynyas. A second goal is to determine the Zn content of diatom frustules using synchrotron XRF methods, to better constrain the role of biogenic silica frustules in the overall cycling of Zn in Antarctic waters.

We collected particles from volumes ranging from 0.2 L to ~6 L, dependent on filter clogging and water budget. The filter type used for all samples was a Supor (Pall) 0.45  $\mu$ m pore size, 25 mm diameter, in keeping with established GEOTRACES methods. At the 6 uppermost samples at each station (euphotic zone and major remineralization zone), the particles were sizefractionated by placing a 5.0  $\mu$ m polycarbonate filter upstream of the primary 0.45  $\mu$ m filter, in a separate filter holder. In total, particulate matter was collected from 372 seawater samples at 27 stations (Stations 3-29). Of these, 162 were size-fractionated. Three stations had 16 depths sampled, three had 24, and the remainder were of 12 depths. Particles were not sampled from Stations 1 and 2, which were dedicated to Go-Flo bottle cleaning and testing. In addition, particles were collected from 27 surface towfish samples (all size-fractionated), and from 8 deployments of a clean external-closure Niskin bottle mounted vertically on the frame of the multicorer. Finally, we collected 41 samples of particulate matter from sectioned sea ice cores, on 0.45  $\mu$ m Supor filters, in collaboration with Dr. Laura Whitmore. In total, PIs Sherrell and Morton will have 610 individual filters to analyze in the coming months. The filters will be cut in half and subjected to both a total digestion and a weak acid leach, and will be analyzed by ICP-MS for a suite of trace elements: Be Al P Ca Sr Sc Ti V Cr Mn Fe Co Ni Cu Zn Y Zr Mo Ag Cd Sn Sb Ba REEs Pb Th-232 U (GEOTRACES key parameters in **bold**).

In addition to these efforts, we collected and froze 30 mL samples of unfiltered seawater from both the towfish (2 m) and uppermost CTD/rosette sample (10 m), at all stations. These will be prepared at Texas A&M UNiversity for analysis of Zn and Si in diatom frustules by a combination of SXRF and conventional techniques.

These samples, and all GTC water samples, were collected successfully thanks to the expertise and hard work of the GTC Supertechs Eleanor Bates, Hannah Hunt, Hannah Inman, and Laura Moore, who did a fantastic job staging for stations, sampling in the clean van, trouble-shooting equipment and organizing all the resulting samples collected for many of the 23 funded projects on GP17-ANT.

PI Sherrell also provided for the cruise a MiniFire instrument (fluorescence induction and relaxation system), on loan from Dr. Max Gorbunov (Rutgers University). This instrument is used to measure photophysiological parameters of the phytoplankton assemblage, which can be related to nutrient (e.g. Fe) stress. It was configured in flow-through continuous mode, measuring surface water along the entire cruise track, using seawater from the ship's underway seawater system (the "water wall"). It was also employed in discrete mode by PhD student Mollie Passacantando (see section 4.14) to measure the same parameters through the euphotic zone using samples from the conventional ODF CTD/rosette, and by PI Phoebe Lam (see section 4.10) and her group to determine the photophysiological response to Fe additions in various physico-chemical forms, in two multi-day incubation experiments.

4.17 Cruise participant: Annie Stefanides (Woods Hole Oceanographic Institution)
Project title: US GEOTRACES Cobalt Biogeochemical Cycling and Phytoplankton Protein Biomarkers in the Pacific and Southern Oceans
Project PI(s): Mak Saito
Project title: US GEOTRACES GP17-OCE and GP17-ANT: Particulate and biogenic trace elements in the South Pacific and Southern Ocean
Project PI(s): Ben Twining

#### Cobalt and Protein Biomarkers

Shipboard electrochemical analysis of total (samples were UV irradiated prior to analysis) dissolved cobalt (DCo) and labile (samples were not UV irradiated) DCo using cathodic stripping voltammetry (CSV) and a hanging mercury drop electrode as outlined in Saito et al. 2001. Samples were collected in duplicate in acid-washed 60 mL LDPE bottles using the GEOTRACES trace-element rosette and trace-element clean towfish for both on board and post-cruise DCo analysis. Samples were then filtered using 0.2  $\mu$ M Acropak filters. Archived duplicate samples were stored in gas impermeable plastic bags for sample preservation and all samples were stored at 4°C. In total, about 802 60 mL sample bottles were collected (400 samples collected in duplicate) from 27 stations, and all samples were analyzed for labile DCo during the cruise. Roughly 150 samples from 9 stations were analyzed for total DCo while aboard the ship, and the remaining 250 samples will be analyzed post-cruise for total DCo. Intralaboratory seawater standards were run periodically and with each new batch of reagents to determine instrumentation consistency and precision, and blank analysis was performed with each new batch of reagents which were found to be within the acceptable limits of <10 pM DCo. GEOTRACES standards will be run post-cruise for intercalibration.

In addition to DCo analysis on board, filter samples were collected from the ship's underway system for proteomic and genomic analysis post-cruise. The volume of seawater that flowed through the system depended on the oligotrophy of the seawater, but did not exceed 45 L. Three different filter sizes were collected in tandem (3  $\mu$ m, 51  $\mu$ m, and 0.2  $\mu$ m), and each filter was divided into the following fraction sizes of the total filter: 1/8 for archival, 3/8 for DNA analysis, and  $\frac{1}{2}$  for proteomic analysis. In total, 189 filter fractions were collected for post-cruise analysis and stored at -80°C.

McLane pump samples were also collected on board the ship for post-cruise metaproteomic analysis. About 270 QMA filters were collected and then divided into various fractions sizes. In addition to the QMA filter, 270 pre-filters (Qp) were collected for each station and pump as well as the remaining scraps from the filter punches. There were roughly 143 scrap samples collected from the McLane pump filters, and all McLane samples were stored at -80°C.

Lastly, 78 x 400 mL seawater samples were collected from the ODF rosette for post-cruise analysis of cobalamin (vitamin B12) availability/ limitation in the Southern Ocean and its implications for Co uptake in Antarctic bacteria and the demand for bioavailable Co in this region. Samples were stored at -20°C.

#### Particulate and Biogenic Trace Elements

Shipboard collection of pre-concentrated and raw seawater samples for post-cruise analysis of single-cell trace element analysis using synchrotron x-ray fluorescence (SXRF) in dried phytoplankton samples mounted on silicon microscope grids. Samples were collected at 11 stations of various environment types (oceanic, shelf, and ice) with each station getting a pre-concentrated and raw treatment. Each treatment was preserved in duplicate for a count of four sample windows per station (two pre-concentrated samples and two raw samples). In total, 46 sample windows were collected as two stations resulted in five sample windows.

Specific GT Parameters to be analyzed post-cruise: CELL\_VOLUME\_BOTTLE CELL\_TYPE\_BOTTLE Fe\_CELL\_CONC\_BOTTLE Si\_CELL\_CONC\_BOTTLE P\_CELL\_CONC\_BOTTLE S\_CELL\_CONC\_BOTTLE Mn\_CELL\_CONC\_BOTTLE Co\_CELL\_CONC\_BOTTLE Ni\_CELL\_CONC\_BOTTLE Cu\_CELL\_CONC\_BOTTLE Zn\_CELL\_CONC\_BOTTLE

4.18 Cruise participant: Laura Whitmore (University of Alaska Fairbanks)Project title: US GEOTRACES GP17-ANT: Dissolved Ga, Ba, and V as interface, process, and circulation tracers in the Amundsen SeaPI(s): Laura Whitmore

There were 5 sea ice stations in which samples were collected. Snow was sampled at every station. Three stations had bulk cores melted for community samples (Mason, Woosley, Boiteau, K. Buck, Conway/Fitzsimmons, Resing, Whitmore). The sea-ice stations and associated sampling are summarized in Table 15.

Stn 4	Start	2023-12-16 04:08 UTC	-71.5345 N, -116.7368 E	Community, TM Sectioned, Seawater,
Stn 4	End	2023-12-16 07:22 UTC	-71.5478 N, -116.7495 E	Brine, DNA, Snow
Stn 12	Start	2023-12-23 06:09 UTC	-74.0674 N, -109.954 E	Community, Fe-differential Melt,
Stn 12	End	2023-12-23 13:28 UTC	-74.0674 N, -109.9539 E	Overflow, Snow (TM, Beryllium,
				Tritium), Tritium, Radium, Temperature
Stn 20	Start	2023-12-31 17:09 UTC	-73.6737 N, -118.4846 E	Snow, TM Sectioned, Brine,
Stn 20	End	2023-12-31 20:33 UTC	-73.6507 N, -118.5042 E	Temperature
Stn 24	Start	2024-01-07 03:06 UTC	-71.9362 N, -119.4478 E	Community, TM Sectioned,
Stn 24	End	2024-01-07 06:26 UTC	-71.939 N, -119.4411 E	Temperature/DNA, Tritium, Radium,
				Snow (TM, Beryllium, Tritium)
Stn 28	Start	2024-01-12 10:16 UTC	-73.9111 N, -128.0697 E	Snow (TM Domilium) Socuetor Sluch
Stn 28	End	2024-01-12 12:15 UTC	-73.9111 N, -128.0424 E	Show (11vi, Berynnuni), Seawater, Siush

Table 1	5. 5	Summary	of se	a-ice	stations	and	associated	sampling.
		2						

In total 123 unique samples were processed and allocated. Temperature cores indicated an isothermal ice structure. All sea ice program samples had nutrient, oxygen isotope, and salinity collected. Sea ice work was conducted under Whitmore's grant with the primary goal of characterizing the geochemical endmember of sea ice. All community, DNA, tritium, radium, Fe(II) and beryllium and were opportunistic and are supported under the individual PIs' grants.

# 4.19 Cruise participant: Tara Williams (Old Dominion University)

**Project title**: Collaborative Research: US GEOTRACES GP17-ANT: Shipboard Measurements of Fe, Mn, and Al in the Amundsen Sea Sector of the Antarctic Continental Margin **PI(s)**: Joseph Resing, Peter Sedwick

# Shipboard Dissolved Aluminum Measurements

Dissolved aluminum (DAl) was measured shipboard using a flow injection analysis method modified from Resing and Measures (1994). A total of 420 unique samples were analyzed. These samples include: (1) near-surface and water-column 0.20  $\mu$ m-filtered seawater samples from 29 stations; (2) 9 near-seafloor 0.2  $\mu$ m-filtered filtered seawater samples collected in the Niskin-X sampler mounted on the multicorer; and (3) 8 snow/ice 0.2  $\mu$ m-filtered meltwater samples.

Water-column profile samples were collected using Go-Flo bottles on the trace metal clean CTD-rosette, and near-surface samples were collected using the trace-metal clean towfish system. Samples collected with the multicorer used the Niskin-X sampler mounted to the corer frame in order to collect seawater ~1 meter above the seafloor. Sea-ice cores and snow samples were melted and filtered after collection.

An internal reference seawater sample was measured throughout the cruise, and yielded a mean DAl concentration of  $2.4 \pm 0.8$  nM (n = 23), suggesting an analytical precision of around  $\pm$  33%. The highest DAl concentration seen in water column samples was ~4 nM, and the average concentration was ~1.4 nM. Snow and sea-ice meltwaters contained up to 11 nM DAl and

averaged 7.5 nM. Figure 10 shows examples of DAl concentration profiles from a super station with multiple clean rosette hydrocasts and a near-bottom multicorer sample (Station 7, left panel), and from a station with a single clean rosette cast (Station 18, right panel). All samples analyzed at sea have been retained for possible re-analysis, alongside duplicate samples collected for post-cruise analyses of DFe, DMn and DAl.



**Figure 10**. Dissolved Al concentration profiles from Station 7 in the central Dotson Trough (left panel) and Station 18 over Bear Ridge (right panel). For Station 7, the orange and blue symbols indicate samples taken from two separate GTC rosette casts, and the gray symbol indicates the multicorer Niskin-X sample.

Resing, J. A., & Measures, C. I. (1994). Fluorometric determination of Al in seawater by flow injection analysis with in-line preconcentration. Analytical Chemistry, 66(22), 4105-4111.

4.20 Cruise participant: Ryan Woosley (Massachusetts Institute of Technology)Project title: US GEOTRACES GP17-OCE and GP17-ANT: Inorganic Carbon Cycling in the South Pacific and Southern Oceans by Direct MeasurementPI(s): Ryan Woosley

#### Discrete pHt Analyses

Sampling. Seawater from all primary ODF casts and the surface bottle from the PigRaTh casts were collected in 150 mL borosilicate glass serum bottles. The bottles and Teflon coated butyl rubber caps were rinsed three times then 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, 2.1 mL of seawater was withdrawn from the bottle using a pipette to create a reproducible headspace of ~1%, followed by the addition of 60  $\mu$ L of saturated HgCl<sub>2</sub> 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 pHt (total scale) 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 (pHt) was measured using an Agilent Cary 8454 UV-vis spectrophotometer according to the methods originally 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  $20 \pm 0.1$  °C. Prior to analysis samples were placed in a Thermo RTE7 water bath to thermostat samples to  $20 \pm 0.1$  °C a minimum of 2 hours before analysis. The 10 cm microvolume 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 6 V 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 pHt 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 sensor on the CTD.

*Reagents.* The purified mCp indicator dye (provided by Dr. Robert H. Byrne, University of South Florida) was prepared in  $\sim$ 0.7 m NaCl to a concentration of  $\sim$ 2.5 mM and pH was adjusted to  $\sim$ 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 199 (Dr. Andrew Dickson, University of California, San Diego), TRIS buffers (DelValls and Dickson, 1998) prepared according to Paulsen and Dickson (2020), and duplicate samples. Measurements of CRM and TRIS were alternative between each set of measurements. Duplicate samples were measured for every primary ODF cast. The mean and standard deviation for the CRMs was  $7.9088 \pm 0.0011$  (n = 15). The mean and standard deviation of the TRIS buffer (Batch 5) was  $8.2429 \pm 0.0011$  (n = 17). The mean and standard deviation of the absolute difference of pHt between duplicate samples was  $|0.0014| \pm 0.0010$  (n = 25).

*Data Processing.* The addition of the indicator affects the pHt of the sample, and the degree to which pHt is affected is a function of the difference in pH<sub>t</sub> 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 pHt (Carter et al. 2013). This adjustment had not yet been applied to the data compiled at the end of the cruise.

A total of 399 unique location/depths were analyzed for  $pH_t$ . Initial quality control flags are 397 good or duplicated analyses, 2 questionable and 0 bad.

*Problems*. No significant problems occurred. If an issue occurred during sample analysis such as bubble within the secretomotor light path the sample was immediately rerun.

# Dissolved Inorganic Carbon

Sampling. Samples for dissolved inorganic carbon (DIC) measurements were drawn from Niskin bottles on all primary ODF casts and the surface niskin for PigRaTh casts into 250 mL borosilicate glass reagent bottles using silicone tubing. The bottles and stoppers were rinsed three times 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 to remove 8.48 mL (leaving a reproducible ~1% headspace after capping the bottle) followed by adding 150  $\mu$ L of saturated HgCl<sub>2</sub> 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 primary ODF cast. A total of 399 unique locations/depths were sampled plus 1 duplicate at each station. In addition 3 samples of sea ice were collected at sea ice stations.

*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).

#### Total Alkalinity

Sampling. At each primary ODF cast and the surface sample of each PigRaTh cast, total alkalinity (TA) samples were drawn from the Niskin-type samplers into 150 mL borosilicate glass serum bottles using silicone tubing. The bottles and caps were rinsed three times, 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, 2.1 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  $\mu$ L of saturated HgCl<sub>2</sub> solution was added to each bottle. The sample bottles were capped with a butyl-rubber stopper and sealed with an aluminum seal. A pair of duplicates were collected at every primary ODF cast. A total of 399 unique location/depths were sampled plus 1 duplicate at each station.

*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).

# <u>Ikaite</u>

*Sampling.* Ikaite is an unstable polymorph of calcium carbonate known to form in polar regions during ice formation. The mineral is unstable above approximately 4°C, making it difficult to detect, particularly since all analysis of the inorganic carbon system occurs at 20°C, meaning any ikaite present will dissolve prior to analysis and artificially increase the inorganic carbon of the system. In order to infer the presence of ikaite, additional filtered sets of samples for pH<sub>t</sub>, total alkalinity, and dissolved inorganic carbon were collected from the surface bottle of the ODF PigRaTh casts. After the normal unfiltered inorganic carbon samples were collected, an Acropak-500 0.8/0.45  $\mu$ m filter catridge was placed on the Niskin-type bottle using silicone tubing. First, all bubbles were removed from the filter catridge, then it was allowed to flush for 20-30 seconds before samples for the three carbon parameters were collected using the same methods as for the unfiltered samples described above. Samples for pH<sub>t</sub> were analyzed with the regular samples, and samples for TA and DIC will be analyzed in the lab at MIT following the protocols as described above. The presence of ikaite will be inferred if there is a decrease in the

inorganic carbon of the filtered samples compared to the non-filtered samples. A total of 28 sets of filtered samples were collected.

Carter, B. R., Radich, J. A., Doyle, H. L. & Dickson, A. G. "An automated system for spectrophotometric seawater pH measurements". *Limnol. Oceanogr. Methods* **11**, 16–27 (2013).

Clayton, T. D. and Byrne, R. H., "Spectrophotometric seawater pH measurements: Total hydrogen ion concentration scale calibration of m-cresol purple and at-sea results," *Deep-Sea Res.*, 40, pp. 2315-2329 (1993).

DelValls, T. A. & Dickson, A. G. "The pH of buffers based on 2-amino-2-hydroxymethyl-1,3propanediol ('tris') in synthetic sea water". *Deep. Res. Part I* 45, 1541–1554 (1998)

Dickson, A. G., Afghan, J. D. & Anderson, G. C. Reference materials for oceanic CO2 analysis: a method for the certification of total alkalinity. *Mar. Chem.* **80**, 185–197 (2003).

Johnson, K.M., A.E. King, and J. McN. Sieburth (1985): "Coulometric DIC analyses for marine studies: An introduction." *Mar. Chem.*, 16, 61-82.

Johnson, K.M., P.J. Williams, L. Brandstrom, and J. McN. Sieburth (1987): "Coulometric total carbon analysis for marine studies: Automation and calibration." *Mar. Chem.*, 21, 117-133.

Johnson, K.M. (1992): Operator's manual: "Single operator multiparameter metabolic analyzer (SOMMA) for total carbon dioxide (CT) with coulometric detection." Brookhaven National Laboratory, Brookhaven, N.Y., 70 pp.

Johnson, K.M., K.D. Wills, D.B. Butler, W.K. Johnson, and C.S. Wong (1993):"Coulometric total carbon dioxide analysis for marine studies: Maximizing the performance of an automated continuous gas extraction system and coulometric detector." *Mar. Chem.*, 44, 167-189.

Liu, X, Patsavas, M. C., and Byrne, R. H., "Purification and characterization of meta-cresol purple for spectrophotometric seawater pH measurements," *Environ. Sci. and Tech.* 45, pp 4862-4868 (2011).

Paulsen, M., and Dickson, A.G. "Preparation of 2-amino-2-hydroxymethyl-1,3-propanediol (TRIS) pHt buffers in synthetic seawater" *Limnol. Oceanogr: Methods*, 100383 (2020)

# **Appendix 1: GP17-ANT Sampling Stations**

For each station, cast locations and associated bottom depths varied to accommodate weather and ice conditions. Here approximate station coordinates and bottom depths are presented to the nearest 0.1' or 10 m, respectively; refer to event log and cast log sheets for cast-specific values.

Station	Latitude (S)	Longitude (W)	Туре	Dates	Depth (m)
1	61°36.6'	62°46.2'	soak	2 December 2023	3450
1.5	65°25.8'	72°55.2'	towfish test	4 December 2023	ND
2	65°13.8'	78°51.6'	test	5 December 2023	4040
3	67°00.0'	100°00.0'	full	7-10 December 2023	4700
4	71°00.0'	113°00.0'	full	12-14 December 2023	2740
5	71°31.5'	116°21.2'	shelf	14-15 December 2023	1020
6	72°20.0'	116°00.0'	shelf	16 December 2023	530
7	72°57.9'	115°45.1'	super	17 December 2023	680
8	73°20.0'	116°00.0'	shelf	18 December 2023	500
9	74°04.0'	116°00.0'	shelf	19 December 2023	1070
10	73°38.5'	115°58.8'	shelf	20 December 2023	730
11	73°44.0'	114°00.0'	shelf	21 December 2023	530
12	74°05.4'	110°16.4'	shelf	22 December 2023	460
13	74°14.7'	112°20.1'	shelf	23-24 December 2023	1070
14	74°11.0'	113°22.0'	super	24-25 December 2023	550
15	73°20.0'	115°00.0'	shelf	25-26 December 2023	890
16	73°00.1'	113°46.7'	shelf	26-27 December 2023	470
17	73°00.4'	112°11.7'	super	27-28 December 2023	420
18	73°02.8'	111°11.7'	shelf	28 December 2023	320
19	73°00.0'	118°00.0'	shelf	29-30 December 2023	410
20	73°50.9'	118°20.5'	shelf	30-31 December 2023	1240
21	73°29.3'	118°22.1'	shelf	31 December 2023- 1 January 2024	580
22	72°59.0'	118°49.9'	shelf	1-2 January 2024	400
23	72°33.5'	118°56.3'	shelf	2 January 2024	470
24	71°58.3'	119°08.1'	super	3 & 6 January 2024	1410
25	71°30.9'	119°00.5'	full	4-5 January 2024	2060
26	74°22.2'	130°56.2'	shelf	9-10 January 2024	470
27	74°21.1'	128°33.5'	shelf	10-11 January 2024	820
28	73°54.5'	127°22.7'	shelf	11 January 2024	780
29	73°27.7'	132°54.0'	semi-super	12-13 January 2024	1590

Participant	Project PIs	Primary task/analytes
April Abbott	Moffett, Severmann	Sediments and porewaters
Wokil Bam	Buesseler, Bentiez-Nelson, Resplandy	Thorium-234
Andrew Barna	Management	SIO-ODF group
Eleanor Bates	Management	GTC Supertech
Tegan Bellitto	Conway, Fitzsimmons, John	Size-fractionated transition metals
Nicole Coffey	Boiteau, Repeta	Metal-binding organic ligands
Kelcey Chung	Management	SIO-ODF group
Margot Debyser	Charette	Radium and silicon isotopes
Marissa Despins	Lamborg, Mason, Newell	Mercury
Martin Fleisher	Management	ODF Supertech/Th/Pa
Alexis Floback	Moffett, Severmann	Iron(II)
Lauren Hearn	Lam, Ohnemus	Pump particles
Hannah Hunt	Management	GTC Supertech
Hannah Inman	Management	GTC Supertech
Kathleen Kouba	Management	ODF Supertech
Phoebe Lam	Management/Lam, Ohnemus	Co-Chief Scientist/pump particles
Carl Lamborg	Lamborg, Mason, Newell	Mercury
Kameko Landry	Management/Sigman, Wang	ODF Supertech/nitrogen isotopes
Allison Laubach	Lam, Ohnemus	Pump particles
Leo Mahieu	Buck, Bundy	Dissolved iron speciation
Chris Marsay	Buck, Marsay, Gao	Aerosols/precipitation/beryllium-7
Gabriel Matthias	Management	SIO-ODF group
Aaron Mau	Management	SIO-ODF group
Laura Moore	Management	GTC Supertech
Sofia Moutinho	Management	Science writer
Mollie Passacantando	Loose, German, Middleton, Jenkins	Noble gases
Steven Pike	Mangement/Lam, Ohnemus	Pump Supertech/pump particles
Joseph Resing	Resing, Sedwick	Dissolved iron and manganese
Peter Sedwick	Management/Resing, Sedwick	Chief Scientist/dissolved aluminum
Robert Sherrell	Management/Sherrell, Morton	Co-Chief scientist/bottle particles
Bettina Sohst	Management	Lab Supervisor
Anne Stefanides	Saito	Cobalt, proteins
Laura Whitmore	Whitmore	Sea ice/snow/Lab Supervisor
Tara Williams	Resing, Sedwick	Dissolved aluminum
Ryan Woosley	Woosley	Inorganic carbon system

# Appendix 2: GP17-ANT Shipboard Science Participants
## Appendix 3: List of NSF Awards Funded as Part of the GP17-ANT Science Program

Collaborative Research: Management and Implementation of US GEOTRACES GP17 Section: Amundsen Sea Sector of the Antarctic Continental Margin (GP17-ANT) PI(s): Peter Sedwick, Bob Anderson, Phoebe Lam, Rob Sherrell

Collaborative Research: RUI: Southeast Pacific and Southern Ocean Seawater Isotopes Determined from US GEOTRACES GP17-OCE and GP17-ANT Samples PI(s): Amy Wagner, Liz Sikes

Collaborative Research: U.S. GEOTRACES GP17-OCE and GP17-ANT: Characterizing Iron-binding Organic Ligands in the Southern Ocean and Implications for Iron Cycling in the Global Ocean PI(s): Randelle Bundy, Kristen Buck

Collaborative Research: US GEOTRACES GP17-ANT: Characterizing the Composition, Scavenging Efficiency and Bioavailability of Size Fractionated Particles PI(s): Daniel Ohnemus, Phoebe Lam

Collaborative Research: US GEOTRACES GP17-ANT: Constraining the Neodymium (Nd) Isotope and Rare Earth Element Cycles near the Amundsen Sea Continental Margin PI(s): Xinyuan Zheng, Howie Scher

Collaborative Research: US GEOTRACES GP17-ANT: Dissolved Concentrations, Isotopes, and Colloids of the Bioactive Trace Metals PI(s): Tim Conway, Jessica Fitzsimmons, Seth John

Collaborative Research: US GEOTRACES GP17-ANT: Iron Redox Cycling in the Amundsen Sea in the Water Column and Shelf Sediments PI(s): James Moffett, Silke Severmann

Collaborative Research: US GEOTRACES GP17-ANT: Nitrogen Isotope Dynamics on the Amundsen Sea Continental Margin PI(s): Xingchen (Tony) Wang, Danny Sigman

Collaborative Research: US GEOTRACES GP17-ANT: Tracing Inputs and Transport of Aluminum, Manganese, and Iron from the Amundsen Sea Sector of the Antarctic Continental Margin PI(s): Joseph Resing, Peter Sedwick Collaborative Research: US GEOTRACES GP17-OCE and GP17-ANT: Export and Remineralization Rates of Bioactive and Particle Reactive Trace Elements Using Thorium-234 PI(s): Ken Buesseler, Claudia Benitez-Nelson, Laure Resplandy

Collaborative Research: US GEOTRACES GP17-OCE and GP17-ANT: Pb Isotopes PI(s): Edward Boyle, Franco Marcantonio

Collaborative Research: US GEOTRACES GP17-OCE and GP17-ANT: Properties and Processes Impacting Other Trace Element and Isotope Cycles Using Noble Gas and Stable Isotope Tracers PI(s): Chris German, Jennifer Middleton, Brice Loose, William Jenkins

Collaborative Research: US GEOTRACES GP17-OCE and GP17-ANT: Thorium-230, Thorium-232 and Protactinium-231 Tracers of Trace Element Supply and Removal PI(s): Chris Hayes, Bob Anderson, Larry Edwards

US GEOTRACES GP17-ANT: Quantifying the Properties of Atmospheric Trace Elements and Their Fluxes to the Amundsen Sea PI(s): Yuan Gao

US GEOTRACES GP17-OCE and GP17-ANT: Atmospheric Deposition and Aerosol Fractional Solubility in Remote Ocean Regions PI(s): Clifton Buck, Chris Marsay

US GEOTRACES GP17-OCE and GP17-ANT: Cobalt Biogeochemical Cycling and Phytoplankton Protein Biomarkers in the Pacific and Southern Oceans PI(s): Makoto Saito

US GEOTRACES GP17-OCE and GP17-ANT: Inorganic Carbon Cycling in the South Pacific and Southern Oceans by Direct Measurement PI(s): Ryan Woosley

US GEOTRACES GP17-OCE and GP17-ANT: Mapping Zinc Speciation in the Southern Ocean Overturning Circulation to Test the Zinc Scavenging Hypothesis PI(s): Nicholas Hawco

US GEOTRACES GP17-OCE and GP17-ANT: Particulate and Biogenic Trace Elements in the South Pacific and Southern Ocean PI(s): Benjamin Twining US GEOTRACES GP17-OCE and GP17-ANT: Sources and Rates of Trace Element and Isotope Cycling Derived from the Radium Quartet PI(s): Matthew Charette

Collaborative Research: US GEOTRACES GP-17- OCE and -ANT Sections: External Sources, Cycling and Processes Affecting Mercury Speciation in the South Pacific and Southern Oceans PI(s): Rob Mason, Carl Lamborg, Silvia Newell

Collaborative Research: US GEOTRACES GP-17-ANT: Molecular Speciation of Trace Element-ligand Complexes in the Southern Ocean and Antarctic Shelf PI(s): Daniel Repeta, Rene Boiteau

Collaborative Research: US GEOTRACES GP17-ANT: Answering Key Questions in Marine Particle Trace Element Biogeochemistry in the Amundsen Sea PI(s): Peter Morton, Rob Sherrell

US GEOTRACES GP17-ANT: Dissolved Ga, Ba, and V as Interface, Process, and Circulation Tracers in the Amundsen Sea PI(s): Laura Whitmore