Preliminary Cruise Report for Knorr 204-01 (November 6- December 11, 2011)

The U.S. GEOTRACES North Atlantic Transect – 2011 Shipboard Team

January 26, 2012

Prelude:

This cruise resumed the first U.S. survey section as part of our participation in an international program named GEOTRACES. In October 2010, the section began, departing Lisbon towards Mauritanea (and ultimately intended, Bermuda and Woods Hole), but problems with the ship's propulsion system terminated the 2010 cruise in the Cape Verde Islands. The section completion effort resumed again in November 2011, sailing in the reverse direction (Woods Hole to Bermuda to the Cape Verde Islands).

As before, a major challenge in organizing this cruise was the fact that requests from participating groups were made for ~10 berths more than the ship's capacity of 32. Fortunately, compared to the previous year's cruise where only 31 science berths were available because of accommodation of a foreign observer, we had the full 32 available in 2011. In addition, two of 2010's scientists developed sample storage methods that eliminated the need to do shipboard analyses, so in effect we had three berths more available than the previous year. During the pre-cruise planning meeting at Old Dominion University (ODU) in March 2011, discussion focused around how we would accomplish cruise objectives within this improved berthing limitation. We established three core groups whose responsibilities included (1) four individuals (Morton, Fitzsimmons, Bundy, and Shelley, one more than the previous year) staging for and sampling of the trace-metal clean GO-FLO carousel, (2) three individuals (Pahnke, Hayes, and Longworth) staging Niskin rosette casts and sampling with the assistance of the ODF team, and (3) five individuals staging McLane pumping casts (Morris, Ohnemus, Pike, Rigaud, and Owens, one more than the previous year), and (4) Four berths for the ODF rosette, nutrient, salinity, and data management effort (one extra compared to the previous year; Johnson, Miller, Palomares, and Schatzman). There was common effort towards these and other jobs, but each group was responsible for organizing itself and its helpers during deck activities. In addition to these teams, Geoff Smith maintained an underway fish for clean trace metal samples. Aguilar-Islas and Shelley undertook atmospheric aerosol sampling. Standard hydrographic analyses (salinity, dissolved oxygen, and micromolar nutrients) were carried out by the Ocean Data Facility (ODF) group, along with CTD data reduction and archiving, as well as primary data management operations. We felt that this latter function was extremely important for a GEOTRACES cruise from the viewpoint of metadata assembly and data submission requirements to BCO-DMO and ultimately to the GEOTRACES data assembly center at BODC. Low-level nanomolar nutrient analyses were carried out by Cutter's ODU group. Sampling for properties such as stable isotopes, dissolved inorganic carbon, radiocarbon, etc. was accomplished by designated cruise participants in addition to their own programmatic responsibilities. At the ODU planning meeting, sampling protocols and a skeleton cast plan were slightly revised from the previous year's efforts, which were further refined on board as the scope and scale of sampling requirements became clearer.

Prior to the KNORR's departure from Woods Hole in November, the Dynacon winch and A-Frame for the GEOTRACES trace metal clean carousel were mounted on the ship. In addition, the chemical reagents required for the cruise were secured in the chemistry van on the 02 level. Early on the first day, six laboratory vans were loaded onto the ship, 4 on the main deck and 2 on the 01 level. Although equipment and supplies were stored in the scientific hold, limited space meant that other items had to be kept in the laboratory space, and packing boxes were left behind in Woods Hole until demobilization when the ship returned in late December. A leased freezer van was mounted on the 02 level, and a bulwark was fabricated and installed on the forward side of the van to protect the machinery from salt spray and waves. Finally, a large number of compressed gas cylinders (nearly 60) were mounted and secured on racks both on the 01 level and in the aft hangar. We are grateful to

Eric Benway, Chad Smith and the Port Office for their assistance in arranging these modifications.
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Please note that the results presented here are both preliminary and proprietary to the individual investigators.

Cruise Narrative and Preliminary Observations:

Cruise mobilization commenced on November 2 in the port of Woods Hole. Space on the ship was at a premium. A major challenge for managing deck space was the large number (48) of pallet boxes required for gear and sample storage. This challenge was met in part by storing some on the main deck while the remainder were deployed on the 02 and 01 levels. Because there was no elevator service to the 02 level, scientists had to carry heavy (~20 liter, literally tons in total) containers up the steep stairway; it would be better if there were some mechanical way to do this. We are grateful to the ship's crew (and in particular the chief mate) for their patience, assistance, and advice during this trying process.

Over the course of 4 days (Nov. 2-5), the shipboard scientific team and several other scientists and Chad Smith worked hard loading gear on board, securing equipment, setting up the laboratory vans (including connecting electric, water, and compressed air supplies), and assembling the trace metal clean areas (bubbles) using plastic sheeting and HEPA filters. Liquid nitrogen tanks were topped up. Gas tank regulators were installed and tubing connected to equipment. CTD rosettes were assembled and connected to the conducting wires, and various sampling and sample processing systems were set up. Because the first station was just ten hours steaming from the dock, we held our first cruise science meeting in the Smith Building two days before departure. We discussed some changes to the shipboard routine. Pete Morton maintained a "Microsoft Project" document to arrange shipboard events and schedule our time. We also brought shipboard pagers so that in principle we could alert people without having to track them down physically (more about this later in the "lessons learned" section).

Figure 1: *KN204-01 stations*

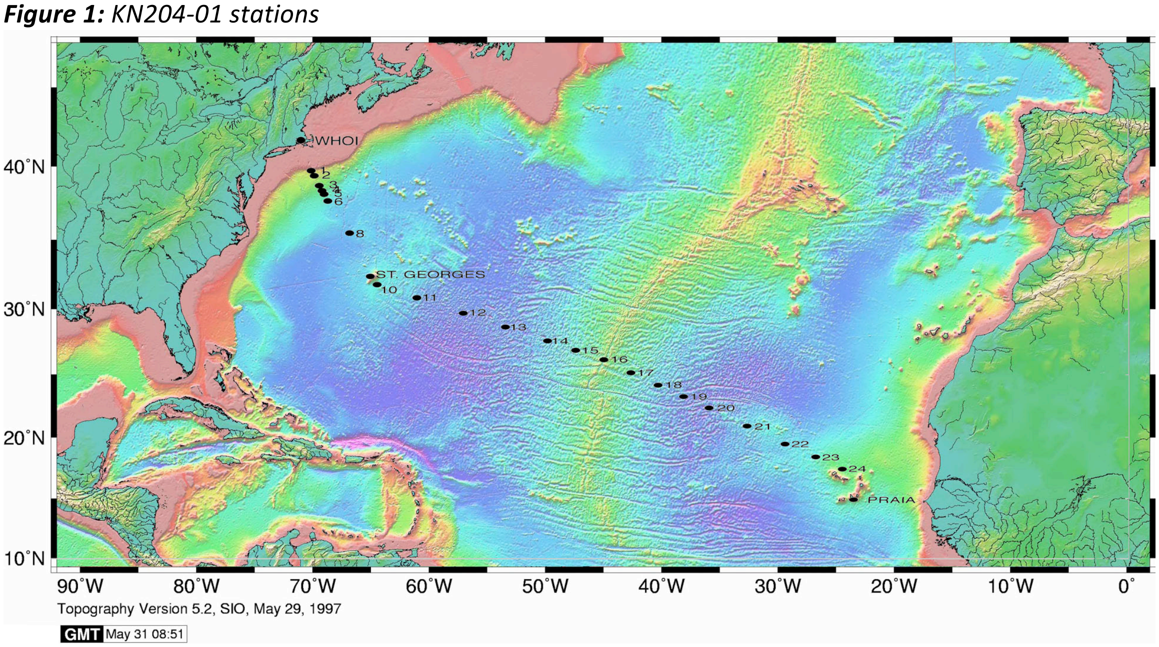


Table 1: US GT-NAT-2011 Stations

Port	US GT NAT-2011 Station Number	Latitude, °N	Longitude, °W	Bottom Depth, m (*)	Arrived on station	Station type	Comments
Woods Hole MA		41.52	70.67				
	1	39.70	69.80	2094	11/6/11 19:30	super	
	2	39.35	69.54	2514	11/8/11 21:30	full	
	3	38.67	69.11	3345	11/9/11 8:00	full	
	4	38.32	68.87	3327	11/12/11 0:20	full-2GTC	
	5	38.09	68.70	3771	11/13/11 14:50	demi	
	6	37.62	68.38	4640	11/13/11 21:30	full+1GTC	bottom nepheloid layer
	8	35.42	66.52	5015	11/16/11 8:00	full+1GTC	bottom nepheloid layer
St. Georges, Bermuda		32.33	64.75				
	10	31.75	64.17	4628	11/19/11 14:30	super+1GTC	BATS;crossover,reoccupation,time-series
	11	30.82	60.78	5512	11/22/11 1:30	demi	
	12	29.70	56.83	5751	11/23/11 1:00	super+1GTC	
	13	28.64	53.23	4283	11/25/11 13:45	demi	
	14	27.58	49.63	4313	11/26/11 10:45	full	
	15	26.86	47.23	3544	11/28/11 1:10	demi	
	16	26.14	44.83	3710	11/28/11 15:15	super	TAG hydrothermal vents
	17	25.14	42.52	3667	11/30/11 21:00	demi	
	18	24.15	40.22	4410	12/1/11 12:45	full	
	19	23.24	38.04	5180	12/3/11 4:00	demi	
	20	22.33	35.87	5940	12/3/11 18:45	super+1GTC	CFC11 rise in bottom waters
	21	20.88	32.63	5404	12/6/11 11:15	demi	
	22	19.43	29.38	5093	12/7/11 8:00	full	
	23	18.39	26.77	4325	12/9/11 2:45	demi	
	24	17.40	24.50	3610	12/9/11 17:15	full	TENATSO; re-occupation, time-series
Praia, CVI		14.92	23.52				

Note: no station 7 or 9 occcupation; pre-cruise plan station numbers were retained to avoid confusion

* Bottom depth for ODF deep cast

The first station occupation began about ten hours after departing Woods Hole the morning of November 6, and was a designated super-station. Fortunately, the weather was relatively warm and the seas were calm, so that given the previous year's experience, operations proceeded smoothly and efficiently from the start. Prior to departure, the GEOTRACES carousel (GTC) GOFlo bottles were filled with low-metal surface seawater stored in cubitainers from the previous year's cruise. Upon arriving on station, the bottles were emptied and the GTC was lowered to ~200 m depth in "blue water" for rinsing, emptied on board, and then sent back down for sample acquisition. We collected samples for shipboard Zn analyses (to assess contamination) by two methods (voltammetry-Carrasco and flow injection fluorescence-Measures/Hatta) to verify trace metal integrity. Measures/Hatta also measured shipboard Fe using flow injection colorimetry. Although there were some slightly high Zn measurements (that did not match between the two methods), no clear problems were identified we concluded that the bottles were working properly from the beginning. Zn analyses by the fluorescence method were continued throughout the cruise and continued to appear satisfactory. The shipboard Fe data was similarly satisfactory.

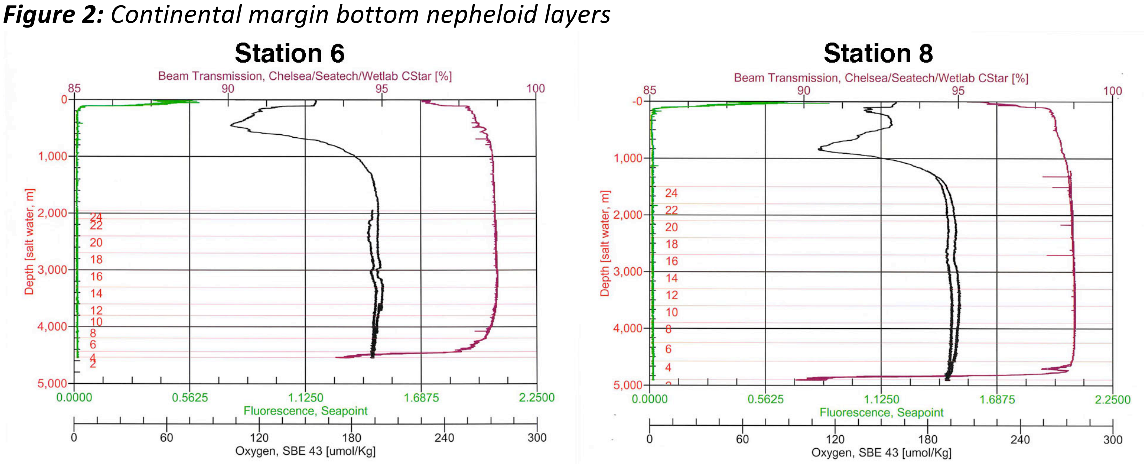
The Niskin rosette was equipped with a nephelometer and an altimeter to enable close bottom approaches. This allowed us to sample full depth profiles to within 10-15 m of the bottom for the rosette casts. The GTC carousel was more problematic, lacking an altimeter, so we generally tried to stay 20-30m about the Knudsen depth although we hit bottle twice despite this precaution.

After 48 hours on "superstation" 1, steaming time between the next three "full" stations was only 2-4 hours, and sample processing and sleep time were inadequate, so up to 8 hours of no deck operations were incorporated into the schedule for these stations. It took some time to work out an optimal schedule of events, so this period was difficult for some of the teams. We skipped two GTC casts at (full) station 4 so that we could do a 3rd GTC cast on the deepest stations (6, 8, 10, 12, 20).

After station 4 (Nov. 11-Nov. 15), weather conditions deteriorated, with a hurricane passing between our position and Bermuda (influencing our weather for about 2 days), followed by three more days of sustained winds in excess of 25 knots. These winds did not prevent station work but slowed the ship to a maximum speed of less than 9 knots during this period (7.5 knots during station 6 steam-backs). Station 6 in the Gulf Stream required a lot of steaming back to station given our drift during each cast, so this station required much more time than planned for (51 hours compared to 29 in the original plan). Between these two factors (weather and steaming back to station), we lost more time than was built into the station plan and had to eliminate 6 hours of demi stations (7 and 9). We retained the original station numbering-position plan to avoid confusion, but it should be clear that stations numbered 7 and 9 were not occupied.

At station 6, we encountered a very strong bottom nepheloid layer, detectable below 4200m but most strongly expressed below 4400m, where the beam transmission on the GTC carousel dropped from ~98.5% in the deep clearwater layer to ~93% near the bottom (figure 2). The near-bottom nepheloid layer was even stronger at station 8 which had a minor transmission minimum at 4600m but the strongest near the bottom (~90% beam transmission at ~5900m). These nepheloid layers were easily visible on the pump cast filters.

Figure 2: *Continental margin bottom nepheloid layers*



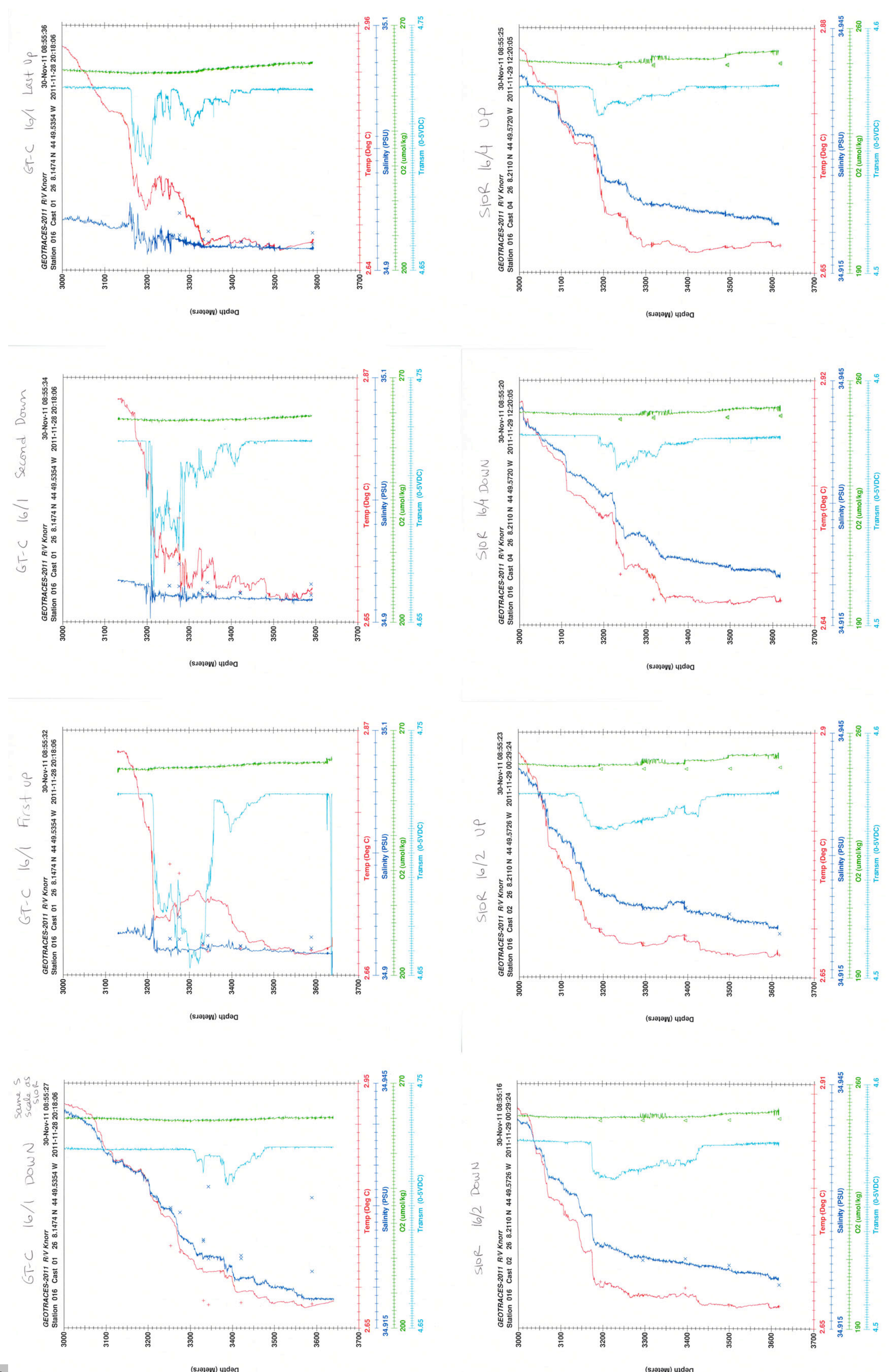
After a much-appreciated rest day during the Bermuda port stop (Friday morning, November 18, for the purpose of unloading some samples, and taking on fuel and food), we resumed our work on Saturday morning, November 19. The day began with news that the -20°C freezer van compressor had an electrical short, but after a brief return to the dock it was established that no spare parts or repair would be possible on short notice, so we steamed to Station 9 (BATS) to continue science work on the assumption that we could steam back to Bermuda after the station if a freezer van repair option became available. As it developed, there was no viable freezer van repair or replacement option, so we then continued steaming along the cruise track as planned with hopes that the van would survive the trip (with a backup of other science freezers and the ship's galley's freezer). The crew found that the problem was a short in one of the fans that blow air across the cooling coils into the freezer van, and that the compressors themselves were functioning. By minimizing access to the freezer van, a single fan proved adequate until the ship returned to Woods Hole.

Stations 9-15 were carried out as planned with no surprises. Station 9 was at the BATS site and represents the trifecta as a re-occupation station (from the 2008 GEOTRACES IC 1 cruise), a crossover station (with the Netherlands meridional section), as well as a forming a connection to ongoing BATS time-series observations.

Station 16 was sited at TAG hydrothermal field at coordinates provided by Peter Rona, and we spotted the hydrothermal plume on first (deep) GTC cast. This was very exciting, but during this first cast we also banged the GTC onto a small basalt glass peak that did not show on Knudsen sonar scan or SeaBeam (the basalt glass identification was established by rock fragments embedded into the GTC powder coating upon returning to the deck). Some repairs were required on some sensors and the upper Ti harness was bent, but the GTC was restored to full functioning by the next station. The hydrothermal plume was clearly evident as a chocolate brown layer on the pump cast sample. The transmissometers encountered the plume eight times (on two down and up cycles of the GTC on the first cast, and two down and up casts of the ODF rosette. The plume transmission was variable in intensity and depths between these encounters, no doubt a result of the extreme near-field siting.

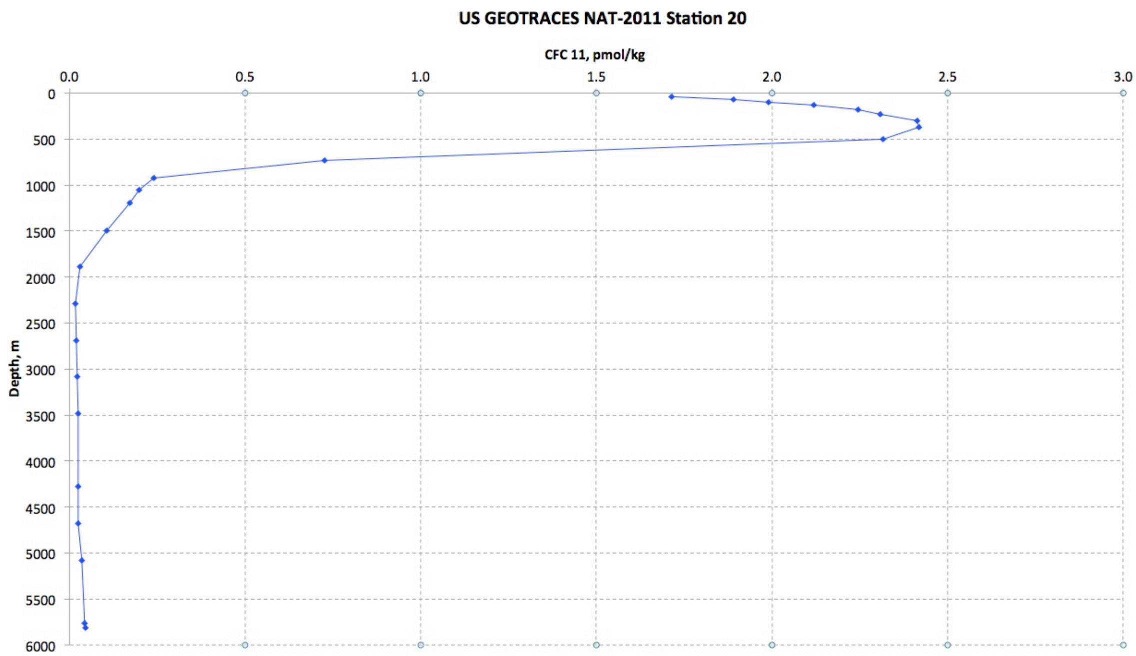
We should also note that out of concern that the hydrothermal plume might contaminate the GOFlo samplers, we used 12 "B" (reserve) team GOFlos for the plume GTC cast.

Figure 3. CTD casts through TAG hydrothermal plume. Top row: GTC casts; down and up casts from a single deployment. Bottom row: ODF casts, down and up casts from two deployments.



At our deepest station in the eastern basin (station 20), Eugene Gorman observed a small but significant increase in CFC-11 in the nearest bottom samples (detectable at 5100m, but higher at 5700m, figure 4) . This station was south of the eastward expression of the Kane Fracture Zone (figure 1) and these higher CFC-11 concentrations must reflect transport of a component of a relatively recent bottom water component formed within the past 6 decades, perhaps through that fracture zone or perhaps through the Vema Fracture Zone to the south (McCartney ref.).

Figure 4: Plot of CFC-11 at Station 20. Measurements were made by Eugene Gorman of Bill Smethie's laboratory. Data are preliminary and may change by as much as 1-2%. Note the significant rise in concentration near the bottom (5940 m).



The rest of the stations went well with no particular surprises, although we had a problem on the station 22 pump cast where a messenger hung up on worn Vectran® pump cable and would have run into the shiv were it not for the sharp eyes of Amy Simoneau ,who stopped the winch just in time.

We finished the cruise with station 24 at the TENATSO time series site, providing an overlap with both an ongoing time series as well as our US-GT-NAT-2010 cruise from the previous year.

Sampling and Analysis Accomplished:

Not counting test casts for mechanical evaluation and rinsing of bottles, a total of 39 casts were made with the GEOTRACES carousel, and 65 ODF-Niskin rosette casts were completed. For the former system, 924 salinity and nutrient measurements were made for evaluation of bottle integrity, calibration check on the CTD, and generation of property profiles. For the latter casts, ≥773 oxygen, nutrient and salinity samples were drawn and analyzed for similar reasons. In addition, 100 nutrient, salinity and oxygen samples were drawn from the deep pump cast Niskin bottles. Having this data nearly real- time after the analyses were completed was a real boon to the chief scientist, as it provided rapid assessment of sampling quality and strategies.

Reports on sampling activities and individual groups participating in the cruise:

(1) GEOTRACES carousel sampling: The Cutter (ODU) group provided the GEOTRACES sampling system, including the Dynacon winch with 7800m of Kevlar cable with conductors, A-frame, clean lab, and Seabird carousel/CTD with 24 12L GO-Flo bottles (and 14 spares). Peter Morton (FSU), Jessica Fitzsimmons (MIT) and Randelle Bundy (SIO) were the "super technicians" in charge of the trace element sampling logistics with assistance from Rachel Shelley, while Ed Boyle and Greg Cutter were in charge of the overall operation. In total, 39 hydrocasts were conducted and 2 GO-Flos per depth were triggered, one for filtration with 0.2µm Acropak capsules and one for 25mm membrane filtration (Supor, 0.4 µm). An average of 17 sample bottles were filled from each Acropak-filtered GO-Flo, and 6 from the membrane-filtered GO-Flo. The membranes were then stored for subsequent particle analyses by Ben Twining (Bigelow Lab) and Bill Landing (FSU). For the 21 stations occupied, this represented the acquisition of 8940 trace element samples! Shipboard analyses of Al, Fe, and Zn indicated multiple sporadic (e.g., not confined to a single GO-Flo or element) contamination events in the first 2 stations, but with very few questionable results.

Table 2: GTC samples

Number of Samples	Size (ml)	Property	P.I.
488	125	Fe, Al, Mn, Zn	Measures & Hatta
623	60	Total & reactive Co	Saito & Noble
470	2000	Hg & Hg speciation	Lamborg
187	125	Nanomolar nutrients	Cutter
434	425	Fe speciation	Buck
35	425	Fe speciation	Bundy
336	850	Cu speciation	Moffett & Jacquot
924	500	Salinity	ODF
924	30	Nutrients	ODF
370	125	Fe	Sedwick
350	60	Fe(II)	Sedwick
350	125	Multi-element trace metal	Landing
584	1000	Fe, Mn, Cu, Cd, Zn	Wu
74	1000	Zr, Hf, Nb, Ta	Orians & McAlister
350	500	Al, Sc, Ti, Mn, Fe, Co, Ni, Cu, Zn, Ga, Cd, Pb	Bruland & Smith
115	500	Total As, As(III), monomethyl and dimethyl As	Cutter
38	60	Os	Sharma
288	150	N- and O-isotope analysis of NO3	Casciotti
48	300	Shipboard Zn analysis for contam.	Boyle & Carrasco
27	500	Zn speciation	Boyle & Carrasco
376	2000	Total Pb, Pb isotopes	Boyle
82	500	Total Pb, Pb isotopes, demi stations	Boyle
28	1000	Cr(total) and Cr(III) isotopes	Boyle
1492	30	Fe colloids	Boyle & Fitzimmons
12	1000-2000	Fe colloid isotopes	Boyle & Fitzimmons
350	125	Mn, V, REE, Ga	Shiller
38	500	Ti	Murray
931	1000	Fe isotopes	John
465	2000-8000	Particulate samples for trace metals	Twining

(2) Sampling on the ODF (30 liter Niskin) rosette was performed for non-contamination prone elements and compounds. Filtered samples for non-contamination prone elements were collected from the ODF Niskin rosette (12 x 30L Niskin bottles) using AcroPak 500 filter cartridges with a Supor 0.45/0.8µm membrane attached to Teflon-lined Tygon tubing. The samples for radioactive and radiogenic isotopes (Th, Pa, Nd, Pb, Po, Pu) were acidified with 6 N hydrochloric acid (optima grade: Pa, Th, Nd; trace-metal grade: Pb, Po, Pu) to a pH of ~2 within two hours of collection. These samples were parafilmed, double-bagged, and stored in pallet boxes. In addition to depths from the ODF casts, 5 L filtered samples were taken for the Th/Pa and Nd isotopes groups from the towed surface fish at stations for which this sampling system was available. All samples for nitrogen isotopes were frozen at -20°C. At three stations (1, 10, 16), we separated 15mL from 14-16 the Th-Pa samples into 50mL centrifuge tubes containing an Amicon Ultra centrifugal filter insert (UltraCel - 10K) and centrifuged the samples for 20 mins at 3,500 rpm. The filter inserts were then removed and the centrifuges capped and parafilmed. These filtrates were acidified with 60 µl of 6 N optima grade hydrochloric acid and will be analyzed for colloidal 232Th.

TABLE 3. ODF rosette samples

Number of Samples	Size (ml)	Property	P.I.
339	500	Dissolved inorganic carbon & alkalinity	Millero & Bates
335	500	^{13}C and ^{14}C	Quay
58		O_2/Ar	Quay
431	50	$^{3}He/^{4}He$, dissolved He, Ne	Jenkins
433	1000	^{3}H	Jenkins
773	30	Nutrients	ODF
774	250	Dissolved oxygen	ODF
796	500	Salinity	ODF
433	500	CFCs and SF6	Smethie
344	25	^{18}O in H_2O	Coleman
24	100	^{17}O in H_2O	Luz
333	125	Hg Thiols	Hammerschmidt
333	30	Ba concentration	McManus
298	5000	^{232}Th, ^{230}Th, ^{231}Pa, ^{232}Th colloids	Anderson, Edwards, Moran, Robinson, Pahnke, Scher, Goldstein
298	5000	Nd isotopes	Anderson, Edwards, Moran, Robinson, Pahnke, Scher, Goldstein
238	5000	Rare Earth Elements	Anderson, Edwards, Moran, Robinson, Pahnke, Scher, Goldstein
81	20000	^{210}Pb, ^{210}Po	Church
154	2000	Si isotopes	Brzezinski
107	20000	^{239}Pu, ^{240}Pu, ^{137}Cs, ^{237}Np	Kenna
120	4000	HPLC pigments	Hooker
385	4000	^{234}Th	Buesseler
385	20	^{238}U	Buesseler
96	500	flow cytommetry, metagenomic and qPCR	Chisholm
107	2000	NIF-H RNA analysis	LaRoche
333	60	^{15}N-NO_3	Casciotti/Sigman

(3) Pumped Sampling of size-fractionated suspended particulate matter: Size-fractionated suspended (<51 micron) and sinking (>51 micron) particulate matter was collected via dual-flowpath in situ pumps at fourteen stations, up to 16 depths per station. The dual flowpath design allowed simultaneous collection of particles on quartz fiber *(QMA)* filters for particulate organic carbon and other analyses and on Supor (polyethersulfone) filters for trace element, isotopic, and biogenic silica analyses. Typical volumes filtered were ~1100L through the quartz filter and ~500L through the Supor filter over a 4 hr pumping period. Filters were processed at sea using trace-metal clean techniques in a clean space. All filters were photographed, misted lightly to remove salts, subsampled for distribution to groups that required fresh samples, and the remainder dried for later subsampling and analysis on land. QMA filters were dried at 60°C overnight, and supor filters were dried at room temperature overnight in a laminar flow hood and then frozen at -20°C to retard potential aging of amorphous oxyhydroxides.

Particle subsamples were or will be distributed to nine groups for analysis of major particulate phase composition (Lam) proteins (Saito), and a broad suite of particulate trace elements and isotopes including e_{Nd} and rare earth elements (Pahnke, Scher, Goldstein), $^{231}Pa/^{230}Th$ AND ^{232}Th (Anderson, Edwards, Moran, Robinson), ^{234}Th AND ^{228}Th (Buesseler), Pu/Cs/Np (Kenna), Hg (Lamborg and Hammerschmidt), $^{210}Pb/^{210}Po$ (Baskaran, Church, Stewart), Fe isotopes (John), Bioreactive trace metals (Twining), and total and acid leachable trace metals (Lam).

Table 4: Some samples collected from the McLane casts

Number of Samples	Size (ml)	Particulate Property	P.I.
150		>53 μm 234Th	Buesseler
222		1-53 μm 234Th	Buesseler
100	500	Pump Niskin salinities	ODF
100	30	Pump Niskin nutrients	ODF

(4) Underway trace element clean towed fish sampling: As part of the U. S. GEOTRACES North Atlantic project Professor Ken Bruland's research group was funded to deploy our surface tow-fish (the GeoFish) for the collection of 0.5 liter samples to provide high resolution data along surface transects between and upon arrival at the vertical stations for assaying a suite of contamination prone trace metals (Sc, Ti, Mn, Fe, Co, Ni, Cu, Zn, Ga, Cd, and Pb) in the dissolved (<0.2µm filtered) and unfiltered, weak acid dissolvable (at pH 1.7), phases in surface sea water. Geoffrey Smith was responsible for operating the GeoFish for the collection of our surface samples every two hours during transit between stations. We also were funded to obtain 0.5L samples from each depth of the GEOTRACES rosette vertical profiles as part of a library for future studies and to assay the superstation profile samples for this suite of trace metals to complement the vertical U.S. GEOTRACES profile data obtained by others. Smith provided four hundred sixty two (462) 0.5L bottles for the vertical profile samples to the GEOTRACES sampling team and performed onboard acidification for long term preservation of these samples and those collected for Mukul Sharma. Smith also periodically collected a subset of filtered surface samples between stations for Bill Landing and Alan Shiller. In addition to these samples, Smith supplied large volumes of 0.2µm filtered surface water for Ana Aguilar-Islas and Bill Landing's, and Phoebe Lam's groups for aerosol and particulate leaching experiments respectively.

During the U.S. GEOTRACES North Atlantic 2011 cruise from Woods Hole to the Cape Verde Islands, Nov. 6 to Dec. 11, 2011, Smith performed one hundred and twelve GeoFish sampling events and collected the following samples:

Table 5: Surface trace metal clean "fish" samples

Number of Samples	Size (ml)	Property	P.I.
108	500	Total As, As(III), monomethyl and dimethyl As	Cutter
6	4000	HPLC pigments	Hooker
112	500	Al, Sc, Ti, Mn, Fe, Co, Ni, Cu, Zn, Ga, Cd, Pb	Bruland & Smith
61	125	total dissolvable trace metals	Bruland & Smith
106	50	nutrients	ODF
31	500	salinity	ODF
39	125	Nanomolar nutrients	Cutter
13	125	Multi-element trace metal	Landing
13	125	Mn, V, REE, Ga	Shiller

(5) The coupled biogeochemistries of arsenic and phosphate. Arsenic and phosphorus are chemically and biochemically very similar, so much so that arsenate (AsV) is toxic to phytoplankton due to its substitution in ATP, effectively decoupling energy metabolism. This toxicity is therefore a function of arsenic's chemical speciation, but also the arsenate:phosphate ratio; in oligotrophic waters where phosphate concentrations drop below 10 nmol/L , arsenate is > 10 nmol/L and toxicity is a problem. However, many phytoplankton are able to ameliorate As toxicity by reducing arsenate to arsenite (AsIII) and/or methylating it to mono (MMAs) and dimethyl As (DMAs); these compounds are non-toxic to phytoplankton. Interestingly, in these same conditions of low phosphate phytoplankton are already experiencing P stress or even limitation, so it is possible that reduced and methylated As can function as markers/tracers of P stress. On the transect to date the coupled biogeochemical cycling of As and P were examined by determining the concentrations of reactive phosphate and nitrate+nitrite continuously (every 30 sec) along the cruise track from pumped and filtered"clean towed fish" using colorimetry and liquid core waveguides. Arsenic speciation (total inorganic, arsenite, MMAs, and DMAs) was also determined every 2 hours along the track, together with assays of alkaline phosphatase activity at 6 hour intervals, both from tow fish samples.

(6) Aerosol and Rain Sampling: Aerosol and rainfall samples were collected on the GEOTRACES North Atlantic section cruise (cruise KN204-01) using three high-volume aerosol samplers and two automated rain samplers. Aerosols were collected on acid-cleaned Whatman-41 (cellulosic) filters (for inorganic trace elements and isotopes – TEIs) and pre-combusted quartz microfiber (QMA) filters (for organic species, Hg, and nitrogen compounds). One sampler was equipped with a 5-stage Sierra-style slotted cascade impactor to collect size fractionated aerosols (from >7µm to <0.49 µm). With collaboration from researchers around the world, the 24-hour integrated aerosol samples, and event-based rain samples, will be analyzed for a large suite of TEIs. All aerosol samples will be analyzed for ultra-pure water soluble, seawater soluble, and total (residual) TEIs. The rain samples will be analyzed, both filtered and unfiltered, to quantify the soluble and particulate TEI concentrations. Air mass back-trajectories for all sampling days have been modeled using the NOAA HYSPLIT program. The seawater and ultra high purity (UHP) water aerosol solubility samples will be analyzed at Florida State University for Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb using a shore-based, off-line column extraction method prior to determination by high- resolution magnetic sector ICPMS using isotope dilution.

Replicate samples were obtained from 16 additional aerosol collections (13 x 47mm Whatman-41 filters per collection), and a subset of these replicates were leached on board using instantaneous and slow leaching protocols. The slow leaching protocol uses large volumes (~15 L) of filtered surface seawater, and compares concentrations of iron from leached and unleached filters. The instantaneous leaches were performed with filtered surface seawater (200 ml) and with Milli-Q water (200 ml), and leachates were collected for the analysis of size fractionated iron (<0.02um, and

<0.4um), redox speciation and organic speciation of iron. Organic speciation analysis will be carried-out by Kristen Buck (BIOS) as part of a collaborative study.

In total twelve slow leaches (each in triplicate) and fourteen instantaneous leaches (in duplicate) were carried out on board with freshly collected aerosols (N. American, maritime and N. African origin) and freshly collected filtered surface seawater. Surface seawater was obtained from the UCSC surface sampler (GEOFish). Fourteen instantaneous leaches with Milli-Q water were carried out on replicate filters Filters not leached onboard were frozen and will be taken back to the lab for subsequent leaching and/or analysis of totals. Solutions from leaches and digestions will be analyzed at the University of Alaska Fairbanks.

(7) Fe speciation: A total of 460 samples were collected on the second leg of the cruise: 434 from the full and super station depth profiles (all depths) and 26 from the seawater leaches of aerosols collected by Dr. Ana Aguilar-Islas (University of Alaska, Fairbanks), 12 sets of seawater leaches of collected aerosols, and their associated seawater blanks, will be analyzed for dissolved Fe speciation. Final Fe speciation data (ligand concentrations and conditional stability constants) from station profiles and aerosol leaches will be worked up when dissolved Fe totals are finalized.. All leg 2 samples for Fe speciation were stored frozen (-20º C) following collection. Roughly half of these samples were offloaded during the port stop in Bermuda; the remainder will be retrieved during the R/V Knorr offload scheduled 27 December 2011 in Woods Hole, MA.

(8) Mercury: The Lamborg and Hammerschmidt groups were funded to receive samples from the various sampling systems, conduct on board determinations of 4 dissolved Hg species and also preserve samples for analysis back on shore (dissolved and particulate thiols and particulate Hg species). The mercury group sent two participants on the US GEOTRACES North Atlantic cruise, including Katlin Bowman, a Master's Student at Wright State University and PI Hammerschmidt. This fieldwork contributes to Ms. Bowman's thesis research, and analysis of the preserved thiol samples will comprise WHOI PhD student Tristan Kading's generals project. The mercury group occupied a UNOLS fleet 20' van outfitted with ceiling HEPA units. The space worked well and suited their needs. In the future, a clean van may not be necessary if they could include equipment to make the space adequately clean. Inside, Bowman and Hammerschmidt operated two Hg species analysis systems, one for mono- and dimethylmercury and the other for total and elemental Hg. The particulate samples will be analyzed for total and monomethylmercury at Wright State, while the thiols will be determined at WHOI.

(9) Particulate Analysis: Samples for Synchrotron X-ray Fluorescence (SXRF) and ICP-MS analyses were collected at 23 stations during the GEOTRACES North Atlantic Section cruise. At each station, unfiltered water samples (250 mL) were taken for SXRF samples from the GEOTRACES GO-Flo rosette from the surface mixed layer and the deep chlorophyll maximum layer. Cells were preservation with 0.25% trace-metal clean buffered glutaraldehyde and centrifuged onto C/formvar-coated Au and Al TEM grids. Using an inverted Leica microscope, transmitted light (differential interference contrast) and chlorophyll autofluorescence images of the cells were collected along with X,Y,Z coordinates on the grids. One-hundred eighty-five grids were prepared for analysis. Bulk particulate samples were collected at each depth sampled using the GEOTRACES GO-Flo rosette. The filtration was performed directly from pressured GO-Flo bottles onto membranes (25mm Supor 0.45µm polyethersulfone) which were mounted in Swinnex polypropylene filter sandwiches. An average of 8.5L of water was filtered through each membrane. Four-hundred sixty-five samples are being stored for analysis via ICP-MS. Before 10 of the stations, bulk particle samples were collected from surface waters with the towed fish. Water from the fish was collected in a 10-L acid-washed carboy and distributed among three, 4L carboys. These were pressurized with 0.2-µm filtered air to force water through replicate 25-mm Supor 0.45µm membranes held in Swinnex polypropylene filter sandwiches. At each station, one of the three replicate filters was oxalate soaked then rinsed with chelexed NaCl, the other two filters remained untreated. These replicate filters will be used to compare methods for isolating trace elements in biogenic particulate matter at a later date.

(10) Copper Speciation: To measure Cu speciation, Jeremy Jacquot used an electrochemical method called competitive ligand exchange adsorptive cathodic stripping voltammetry (CLE-ACSV), which allows one to determine the concentration of organic ligands binding free Cu (Cu^{2+}) and their binding strength. In order to calculate [Cu^{2+}], I will need to find [Cu_T] by using isotope dilution with an inductively coupled plasma mass spectrometry (ICP-MS) system at USC. In total, he obtained 336 850-milliliter filtered samples from the GEOTRACES rosette (125 ml for the totals analysis with ICP-MS and 725 ml for the speciation work) and 96 500-milliliter samples for the Chisholm filtration work.
***(11)* Al, Fe, and Mn onboard measurements:** Sampling for dissolved Al, Fe, and Mn was accomplished using 12 L GO-FLO bottles on the GEOTRACES 24 place rosette. The University of Hawaii group (Measures and Hatta) performed shipboard determinations on subsamples of water taken from these bottles collected using an Acropak filter by the subsampling team. Dissolved trace elements were determined on samples drawn at each of the 11 stations where the GEOTRACES rosette was deployed. Additionally, surface samples were also collected arriving on or departing from station from the UCSC towed fish. In addition, a limited number of samples was collected between stations by this means. In total trace element determinations were made on 249 discrete samples. Data generated onboard were submitted to the shipboard data assembly system and each parameter on each subsample was assigned a quality flag. Dissolved Al, Fe and Mn were determined on these water samples using Flow Injection Analysis. Precisions of each method were established by replicate determination of the same sample at the beginning of a day's run the values were typically: approximately 2% for Al at 10nM; 2% for Fe at 1 nM, and ~ 4% for Mn at 1 nM. In addition to the shipboard determinations 1L samples were collected for shore-based ICPMS determinations of dissolved and dissolvable Fe, Mn, Zn and Cd, by isotope dilution by co PI J. Wu, (University of Miami). These samples were acidified on board, within a few hours of collection. Ultrafiltration of 25 samples was also performed at station 5 for subsequent shore-based determination of the colloidal fraction at the University of Miami.
(12) Cobalt Analysis: The Saito/Noble group collected samples from all GTC casts, and all arriving-on-station Towfish samples, totaling 239 samples. All of these were preserved by storage in a gas-tight sealed bag containing an oxygen scrubber. The samples will be analyzed onshore for total dissolved cobalt after a UV oxidation step using adsorptive cathodic stripping. In addition to total dissolved cobalt, all samples will be analyzed for labile cobalt after an equilibration period with the electroactive ligand, dimethylglyoxime, using adsorptive cathodic stripping voltammetry.
(13) Radium Isotopes: Radium Isotopes: To measure the quartet of radium isotopes (^{224}Ra, ^{223}Ra, ^{228}Ra and ^{226}Ra) to quantify horizontal and vertical transport of dissolved trace elements and isotopes (TEIs), as well as shorter lived thorium isotopes: ^{234}Th and ^{228}Th, used to quantify particle scavenging, vertical fluxes and remineralization rates of bioactive and/or particle reactive TEIs. At all 14 full and super stations a 16 point in situ pump profile was carried out. Eight pumps were deployed for an upper water column shallow pump cast and then turned around to be deployed again for a lower water column deep pump cast. The pumps were hung on a 3/8" plastic coated Vectran line and were programmed to pump for 4 hours, which typically pumped a total of 1500-1700 l of seawater. The pumps used were modified McLane in situ pumps, which were outfitted to accommodate 2 * 142 mm filter heads containing different filter types (see cruise report by Dan Ohnemus). After water had passed through the dual filter heads the streams were joined passed through a MnO_2 impregnated Cuno acrylic cartridge filter for scavenging dissolved radium and thorium isotopes. Three flow meters at various points along the pump plumbing allowed accurate determination of water filtered. After recovering the cartridges from the pumps, they were rinsed with radium-free fresh water to remove salt and then dried to dampness before measurement of the short-lived radium isotopes on board the ship. ^{224}Ra ($t_{1/2}$ = 3.7 d) and ^{223}Ra ($t_{1/2}$ = 11.4 d) were measured on the Radium Delayed Coincidence Counter (RaDeCC) system and were typically measured <24 h after sample collection. All the Cuno cartridge samples for radium were taken and

processed by Paul Morris. The scavenging efficiencies of the Cuno cartridge filters for radium and thorium will be validated by a discrete seawater sample taken in parallel with every pump depth sampled. For shallow pump depths this sample was taken from the niskin rosette and for the deep pump casts a 30 l Niskin bottle was hung next to each pump and triggered with a messenger. For ^{226}Ra, 20-25 l of seawater was passed over a column of MnO_2 impregnated acrylic fiber, which is known to remove radium at 100% efficiency. These samples were bagged and will be analyzed for ^{226}Ra through it daughter, ^{222}Rn back in the lab at WHOI. For details of ^{234}Th determination refer to the ^{234}Th cruise report by Stephanie Owens. Stephanie was responsible for taking both the ^{226}Ra and the ^{234}Th samples, and she is processing the ^{234}Th samples. In total 224 MnO_2 cartridge samples were taken, with 224 corresponding ^{226}Ra calibration samples.

At 21 stations (14 full and super stations + 7 demi stations) a surface for radium was collected from a high volume deck pump. 390 l of filtered seawater was rapidly collected into barrels and then subsequently passed through MnO_2 acrylic fiber for determination of all 4 radium isotopes. These samples were processed in a similar manner to the MnO_2 cartridges for short-lived radium isotopes while on board ship. Sampling was carried out by Stephanie Owens and Paul Morris and shipboard analysis was done by Paul Morris. 21 surface samples were taken in this way.

***(14)* Thorium-234 and -228**: On the GEOTRACES 2011 Atlantic Leg, Stephanie Owens and Steve Pike were responsible for the collection and processing of samples for ^{234}Th and ^{228}Th. At each regular and super station, samples for total ^{234}Th were collected from a 30L shallow Niskin cast and Niskin bottles attached to the wire during deep pump casts. All sample processing and preliminary sample analysis by beta counting was completed on board, a requirement because of the short half-life of ^{234}Th (24.1 days). At regular and super stations, 21-point profiles were collected with 16 of those depths matching the *in situ* pump depths while the additional depths were used to obtain higher resolution through the euphotic zone. A surface sample was collected using a pump located on the port side of the ship. At demi-stations, 13-point profiles were collected from the shallow Niskin cast and the surface pump. In all 385 samples (4 L each) were collected for total ^{234}Th at 5 super stations, 9 full stations, and 8 demi-stations. Archive samples for ^{238}U (20 mL) were concurrently collected with all ^{234}Th samples.

Samples for particulate ^{234}Th and ^{228}Th were obtained from the in situ pump casts. Specifically, material from 53 µm screens was rinsed onto silver filters and counted for ^{234}Th (all shallow screens were counted, while deep screens were only counted at super stations, n = 150). All QMA filters (n = 222), shallow and deep, were sub-sampled for ^{234}Th, which was counted immediately while the remainders of the filters were stored for ^{228}Th analysis on shore. These samples will also be analyzed for their organic carbon content in order to determine ^{234}Th/POC ratios. This ratio can be used to estimate the POC export flux based on the ^{234}Th flux determined by the total ^{234}Th measurements described above. The combined measurement of ^{234}Th and ^{228}Th will be used to obtain insight into particle dynamics taking place in the water column.

(15) Biogeotraces Sampling: Jeremy Jacquot collected filters from 12 stations for the Chisholm group that will be used to conduct flow cytommetry and qPCR analyses. He also collected filters for metagenomic samples from 7 stations. Ed Boyle collected 96 samples for the La Roche group and performed reduced-pressure filtration. These samples were kept frozen at -70°C and then shipped to Kiel.

(16) CFC and SF_6 Sampling: was done on deep and shallow Niskin casts at each regular and super-station (for a total of 24 depths per station) and the Niskin cast at all demi-stations (12 depths per station). Samples were analyzed on board and the data reported to the ODF data manager and made available to cruise participants. A total of 240 samples were taken and analyzed.

(17) Tritium and helium sampling: Tritium and ^{3}He sampling were done on all regular, super-, and demi-stations. A total of 431 ^{3}He and 433 tritium samples were taken. The ^{3}He samples were taken in crimped copper tubing and the tritium samples were stored in pre-cleaned, argon-filled 1 liter flint glass bottles.

(18) NASA Sampling: the Cutter group collected 120 four-liter particulate samples that were stored frozen for pigment analyses by the NASA lab of Stan Hooker.
(19) Compilation of samples taken and associated metadata: was accomplished during the cruise by assembling all CTD cast information, cast sheets, and event logs and entering them into a database. ODF staff member Mary Johnson was responsible for this task and for quality checking and merging the relevant information. As a consequence, we have a complete record of all samples taken on the cruise, and their relationship to critical metadata parameters (time, location, etc). Bottle data have been compared to the sensor records in order to check instrument calibration and to establish bottle integrity against pre/post tripping and leakage. The hydrographic data (temperature, salinity, oxygen, nutrients) have been quality controlled and merged into a relational database for use by cruise participants. This data was available in near-real time to cruise participants. For example, CTD data was usually available for plotting within an hour or two of the cast, and the discrete hydrographic measurements (oxygen, nutrients, and salinity) were available within a day or two of the station.

Lessons Learned:

We learned that the experience from the intercalibration cruises and the previous year's cruise have honed the US GEOTRACES team into an efficient and reliable system.

We learned that it would be wise to have an altimeter installed on the GTC to avoid crashing into the bottom, as we did twice with the Knudsen/CTD depth method despite trying to stay 20-30m above the bottom. This is a budget item for the Pacific cruise, so it will be achieved on future US GEOTRACES cruises.

We learned that because of the multiple deep casts for full and super GEOTRACES stations, it is important to incorporate surface current strength into the cruise planning process because its consequences for time spent steaming back to station. On this cruise, we had not planned for this loss of time. Station 6 in the Gulf Stream was the most problematical. That factor combined with bad weather resulted in us being six hours short of station time on the WHOI to Bermuda leg, and hence the cancellation of two demi stations.

We learned that it will be important to treat the Vectran cable (used for the McLane pump casts) more carefully, namely by using a winch that can level-wind the cable rather than spaghetti-wind it. Damage to the cable on this cruise resulted in a stuck messenger, loss of some appropriate Niskin samples to match the pumps, and could have resulted in driving the messenger through the shiv which would damage it and could have been a major safety hazard.

Final Note: We can safely regard this effort as a success. There were a lot of moving parts in the GEOTRACES machinery, and things worked remarkably well. All this was down to a group of motivated, hard working, and cooperative scientists that worked together well. Shipboard science support techs Anton Zafereo and Amy Simoneau performed their duties exceptionally well. It should also be said that the Knorr's crew were extraordinarily helpful and went out of their way to make this a safe and productive cruise. We are grateful to Captains Kent Sheasley (KN204-01A) and Adam Seamans (KN204-01B) for their efforts and hospitality.