CRUISE REPORT

JC068 / GA10W
UK-GEOTRACES 40°S

JC068 science party members

RRS James Cook
24/12/2011 - 27/1/2012
Port Elizabeth to Montevideo

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OVERVIEW

The cruise forms part of the international GEOTRACES Programme (www.geotraces.org) and focused on the marine chemistry of trace elements and isotopes. It was funded by two NERC proposals, and included scientists from eleven institutes.

The cruise was a rescheduled attempt to complete a zonal section across the South Atlantic following the *RRS Discovery* cruise D357 which was prevented from completing this objective by a medical emergency.

JC068 left Port Elizabeth in South Africa on 24th December 2011, called for fuel in Cape Town on 27th December, and then proceeded broadly westward along 40^oS to dock in Montevideo on 27th Janury 2012

The report starts with general information about the cruise, including science objectives, station numbering, and sampling strategy. Then there are two sections covering the science conducting under the two NERC grants, followed by a section on other science. Appendices also present data and other information at the end of the report.

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OBJECTIVES

The JC068 cruise was funded by two NERC funded grants: a consortium grant awarded to ten UK institutes, and a standard grant awarded to three UK institutes. Work to meet these grants dominated the objectives of the cruise, but were augmented by a limited amount of opportunistic additional sampling. The objectives for the funded grants and the additional sampling are as follows:

Ocean Micronutrient Cycles: UK-GEOTRACES

The three major questions we aim to answer are:
1. A prominent region of high productivity occurs at 40°S in the Atlantic in an ocean basin with low concentrations of micronutrients such as Fe. How are micronutrients supplied to support the productivity in this region, and how does this supply influence the nature of the ecosystem across the basin?
2. Deep-water masses in the South Atlantic upwell to the south and north to supply micronutrients to the Fe-starved Southern Ocean, and to the highly productive Equatorial Atlantic. Which processes control the concentration and distribution of micronutrients in deep waters in the South Atlantic, and therefore ultimately the supply of micronutrients to these surface systems?
3. The sources, sinks, and internal cycling of micronutrients in the global ocean remains poorly understood. What are the fluxes of micronutrients in the global ocean, and what are the dominant processes that control these fluxes?

To address these questions, five specific objectives will be addressed within the consortium:
i.   Map the concentration of seven critical ocean micronutrients (Fe, Zn, Co, Cd, Ni, Cu, Mn) at high spatial resolution for the full water column on a zonal section across the Atlantic at 40°S. This to include determination of the variations in physical and chemical speciation of these micronutrients.
ii. Determine the flux of these seven micronutrients to the ocean from the four ocean boundaries, each of which is well represented in the region: atmosphere (the South American dust plume), continent (e.g. the Plata River), sediments (on continental slopes and in the deep ocean), and ocean crust (at the Mid Atlantic Ridge).
iii. Assess, using a range of chemical tracers, together with direct measurements of ocean mixing and ocean modelling, the mixing and advection of these micronutrients away from their sources into the ocean interior to quantify the relative importance of the various sources and ocean processes in setting open-ocean micronutrient concentrations.
iv. Explore the relationship between phytoplankton ecosystem structure and functioning, and the supply of macro- and micro-nutrient concentrations and fluxes.
v.   Use numerical models to gain a comprehensive understanding of micronutrient cycling at 40°S in the Atlantic. Incorporate into these models the fluxes and processes investigated elsewhere in the consortium, and tune the models against micronutrient observations made in the consortium. Use these refined models to assess the controls on micronutrient supply to the surface water at 40°S and the deep-waters that upwell adjacent to the South Atlantic. Also use these models, in conjunction with new data from other research efforts, to assess global understanding of the ocean cycling of micronutrients, and the possible response of these cycles to change.

Comprehensive calibration of critical paleoceanographic proxies

The broad objective is to calibrate and develop geochemical paleoproxies used to provide critical information about the amplitude of possible climate change and the mechanisms causing that change.

Four categories of proxy form the specific targets for this work, and there are a total of fourteen objectives that represent the issues preventing accurate interpretation of these proxies

A. ^{231}**Pa/**^{230}**Th**: We aim to critically assess the use of this high-profile paleoproxy as a tracer of past ocean-circulation rate, and past export productivity. Our results will enable existing and future Pa/Th data to be more robustly interpreted, and limitations placed on the applicability of this proxy.
   Objective 1: Assess the range of water-depth influencing sedimentary Pa/Th
   Objective 2: Assess the optimal location within a water mass to use Pa/Th as a rate tracer
   Objective 3: Assess the role of opal in setting sediment Pa/Th, even in situations where sediment opal contents are low or zero
   Objective 4: Assess the impact of dissolution on sediment Pa/Th
   Objective 5: Assess the role of boundary scavenging on sediment Pa/Th

B. **Silicon isotopes**: The potential of Si isotopes as a powerful proxy for past nutrient utilisation is likely to see widespread future application as a consequence of recent analytical advance. We will evaluate three significant caveats for this proxy to ensure that future results can be accurately interpreted, and that the potential of this proxy can be realized.
   Objective 6: Assess the constancy of Si isotopes in upwelled waters
   Objective 7: Assess isotope fractionation and its variability during biological Si uptake
   Objective 8: Assess the impact of sediment dissolution on Si isotopes

C. **Cd and Cd isotopes**: Cd/Ca is a widely used tracer of past water-mass distribution and nutrient utilisation. We aim to address a number of remaining uncertainties with this tracer that limit its accurate application, and make a first quantitative assessment of the use of Cd-isotope ratios to provide additional information about past nutrient cycling.
   Objective 9: Assess variability of D(Cd/Ca) during growth of benthic forams
   Objective 10: Assess the constancy of Cd/phosphate and Cd isotopes in deepwaters
   Objective 11: Assess covariation in Cd concentrations and isotope ratios in surface waters and planktonic foraminifera

D. **Organic biomarkers**: Diagnostic biomarkers have been identified for most of the major classes of marine phytoplankton and have huge potential for assessment of past phytoplankton community structure. They also provide powerful complementary information for interpretation of inorganic proxies. We will bring together experts in biomarkers with those in inorganic proxies to exploit this potential.
   Objective 12: Assess whether biomarker assemblages in surface waters reflect algal assemblages
   Objective 13: Assess the biases on biomarker assemblages during transport from source to sediment
   Objective 14: Assess the depth range bias in sediment biomarker assemblages

Additional objectives

Opportunistic sampling was also conducted for a range of other chemical and biological parameters, as described under "Other Research" below.

CRUISE TRACK, STATIONS, AND SAMPLING STRATEGY

One test station and 24 numbered stations were occupied during the cruise (Table 1).

Station no.	latitude deg. N	longitude deg. E	water depth m	Notes
test	-34.948	19.347	138	CTD and SAPS tests
1	-34.612	17.054	2595	400 m "Bio" cast only
2	-35.468	14.996	4689	400 m "Bio" cast only
3	-36.341	13.110	4896	Repeat of D357 Super Station (cross over)
4	-38.401	10.402	5155	400 m "Bio" cast only
5	-40.000	5.518	5250	400 m "Bio" cast only
6	-40.015	-0.500	4890	3000m cast only
7	-40.001	-3.034	4450	400 m "Bio" cast only
8	-39.999	-9.666	3378	Standard
9	-40.257	-9.853	1779	1000m cast only (Gough Island)
10	-40.281	-9.892	366	core only (Gough Island)
11	-39.998	-13.000	3213	Standard
12	-40.001	-16.466	3080	Super station (MOR)
13	-39.999	-19.932	3783	Standard
14	-40.000	-23.800	4162	Standard
15	-40.000	-28.000	4233	Standard
16	-39.999	-32.499	4876	Standard
17	-40.000	-37.417	5103	Standard
18	-40.001	-42.416	5144	Super station (Deep Basin) (cross over)
19	-39.994	-47.417	5257	Standard
20	-37.983	-51.029	4791	Standard
21	-37.026	-52.503	3313	Super station (Slope)
22	-36.538	-53.102	1483	Standard
23	-36.338	-53.337	705	Core and VMP only
24	-36.000	-54.000	60	Core only

Table 1: Station locations and overview for JC068

Stations 1-7 follow the name and approximate location of Stations 1-7 on the previous D357 cruise (see Table 2 below). Subsequent JC068 stations are progressively westward to Station 24.

In the portion of JC068 which overlapped with D357, casts were typically only to 400m to capture surface water variability, and no cores were taken. At Station 3, full depth casts were performed to cross-calibrate deep-water values with the previous cruise. At Station 6 a deeper cast was conducted to fill a data gap in D357 sampling.

Name	Alternate name	Lat	Long	Water depth
Test		34o 11'	17o 58'	246
Station 1		34o 37'	17o 03'	2620
Station 2		35o 28'	15o 00'	4681
Station 3		36o 20'	13o 07'	4912
Station 4		38o 24'	10o 24'	5065
Station 5		40o 01'	5o 31'	5200
Station 6		40o 00'	00o 49'	4900
Station 7		40o 00'	-4o 54'	3809
Station 8	Station 0.5	34o 20'	17o 37'	756
Station 9	Station 1.5	34o 59'	16o 01'	4365
Station 10	Station 2.5	35o 57'	14o 05'	4874
Station 11	Station 4.5	39o 13'	7o 48'	5177
Station 12	Station 3.5	37o 27'	11o 39'	5195
Station 13	Station 0.75	34o 22'	17o 33'	1124

Table 2: Station locations for the previous 40°S UK-GEOTRACES cruise – D357 – for reference

West of Station 7, a "standard" station consisted of:
- a full depth cast with the stainless-steel CTD package
- a full depth cast with the titanium CTD package (for trace metals)
- a 400 m cast with the stainless-steel CTD package ("bio" cast)
- a sediment core, taken with the megacorer (for approximately half of the stations)
- deployment of the VMP (Velocity Microstructure Profiler) (for most sites)

The order of these deployments was not fixed but adjusted to suit the schedule of other science operations. The casts were conducted as soon as the ship reached station rather than at a particular time of day.

New superstations were occupied at the mid-ocean-ridge (Station 12); the deep Argentine Basin (Station 18) and the Argentine slope (Station 21). At these stations, additional deployments were made as follows:
- Stand Alone Pumps (SAPs) were deployed in pairs, with up to four pairs at a time, to collect particulates from large volumes of seawater and radionuclides on Mn cartridges. In each pair, one SAP was used for trace metal analysis (with Supor filters), and the other for ^{234}Th (glass fibre filters) and radionuclides (Mn cartridges). SAPs were typically performed twice, once near bottom and once near surface
- An additional full-depth deployment of the titanium rosette allowed collection of large volume water samples for measurement of metal isotopes

Stations 9 and 10 were taken to the east of Gough Island, slightly to the south of the 40oS section. The goal was to make a preliminary assessment of possible trace metal and isotope input from this central Atlantic Island.

Full details of deployments are provided in the Event Log for the cruise in Appendix A

DEPLOYED EQUIPMENT

This section presents a brief overview of the equipment deployed during JC068. Further details of much of this equipment is provided in the NMFSS Technical Cruise Report as Appendix C.

Winch

The ships winches performed well. There were some minor scrolling issues which required slow operation on some occasions but no major delay. Unfortunately a dedicated winch to deployment of a new conducting Kevlar cable was not yet complete and could not be used.

Stainless rosette from conducting steel CTD cable

Standard CTD measurements and water sampling were performed using a 24 position stainless-steel rosette equipped with a full sensor array and 24 20-litre OTE bottles.

This rosette was used to collect all water samples for elements or isotopes not prone to contamination and was generally highly successful.

Early in the cruise this rosette suffered frequent bottle-closure failures, with the bottom of bottles failing to shut completely. Greater care in cocking bottles appeared to remedy this issue.

Problems were experienced with both of the two stainless cables used to deploy this CTD. One was untwisting with the warp apparently opening up and the presence of significant package spin during deployment (as indicated by ADCP data). The other suffered frequent electrical outage damaging CTD data. These issues required several reterminations and care during deployment but did not significantly impair the ability to collect samples and data.

Ti rosette deployed from plasma rope

Funds were provided in the UK-GEOTRACES Consortium grant for the purchase of a dedicated winch and cable for trace-metal ocean chemistry work. This system was designed and tendered for in early 2010 and an order placed with LeBus for a traction winch and with Nexans for a conducting jacked synthetic cable. Unfortunately this equipment was not ready in time for JC068 so an alternative clean sampling approach using existing NMF equipment was deployed.

The plasma rope, normally used for coring, was used to deploy the rosette. This had a significant advantage over conducting steel cable in providing lower contamination of Fe and other metals. The plasma rope is not conducting, however, which means that depths for sampling must be preset and bottles fired with a pressure sensitive trigger. Two Seabird SeaRam units were purchased with UK-GEOTRACES funds for this purpose.

Problems were encountered during the previous D357 cruise with the buoyancy of the plasma-rope. As depth of deployment increases, the apparent weight of the package decreases, limiting the rate at which the package could be winched, particularly in deep water and particularly as sea-state worsened. This buoyancy problem was solved for JC068 by NMF-SS staff by manufacture of new weight stack with Ti fitting which was deployed immediately above the CTD package.

The Seabird SeaRam pressure trigger failed on two occasions due to apparent battery issues. In general, however, these units operated well.

Coring

Coring was performed with the NMF megacorer deployed on a steel coring rope. This was very generally successful and sediment was recovered on most deployments. Notable exceptions were at the mid-ocean ridge and east of Gough Island where, despite attempts to find sediment from the bottom profiler, no sediment was recovered and the sample tubes of the corer damaged.

Stand Alone Pumps

Up to 8 of these were deployed at a time, hung on the CTD cable. This proved successful.

Velocity Microstructure Profiler and Glider

Microstructure measurements were made using a Velocity Microstructure Profiler (VMP) provided by NOC, and a glider equipped with VMP device provided by WHOI. Full details are provided in the relevant section under WP6 below.

Argo floats

UK and US Argo floats were deployed in the western two thirds of the section.

Underway data overview

Summary figures of sea-surface salinity, temperature, fluorescence and transmittance are given in this section as back ground for the chemical data that follows.
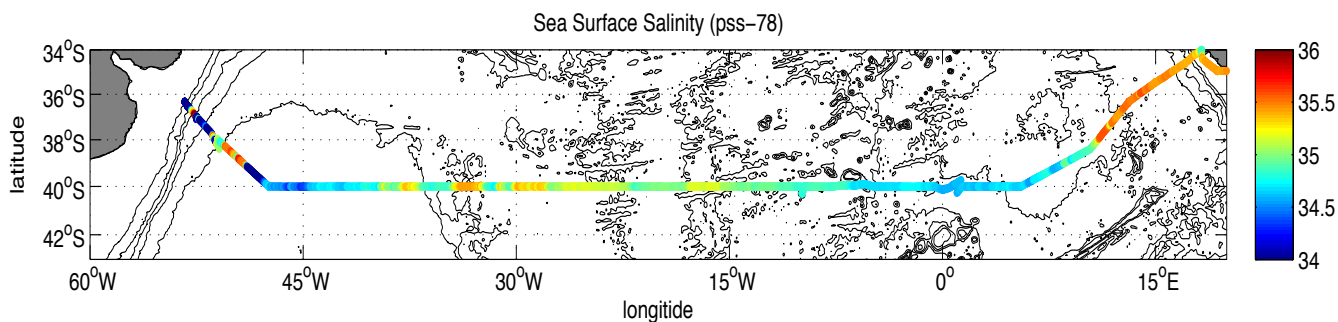
Figure 1: Seabird underway near-surface salinity. The inlet is situated on the underside of the hull, close to the bow, at 5-6 meters depth.
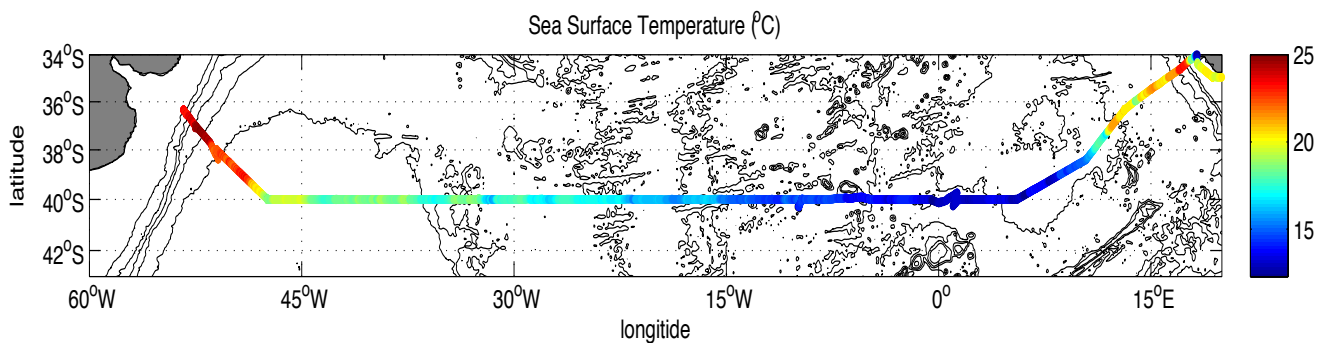
Figure 2: Seabird underway near-surface temperature. The inlet is situated on the underside of the hull, close to the bow, at 5-6 meters depth.
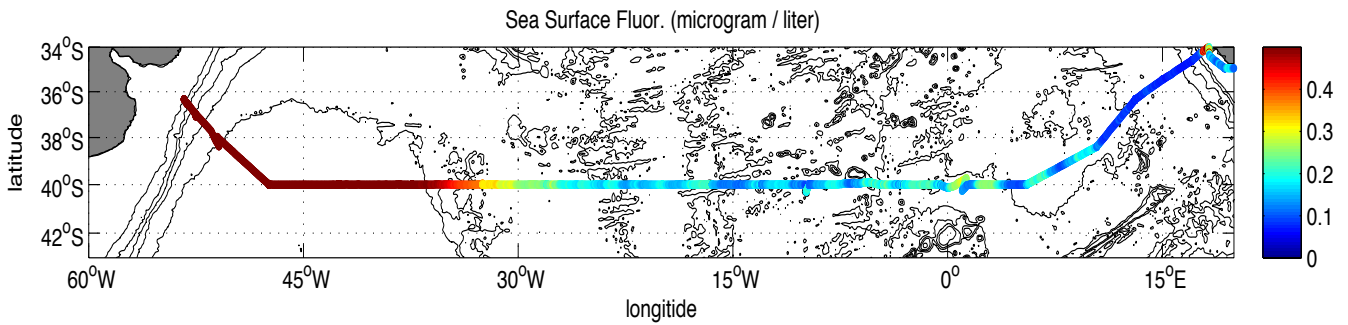
Figure 3: Seabird underway near-surface fluorescence. The inlet is situated on the underside of the hull, close to the bow, at 5-6 meters depth.
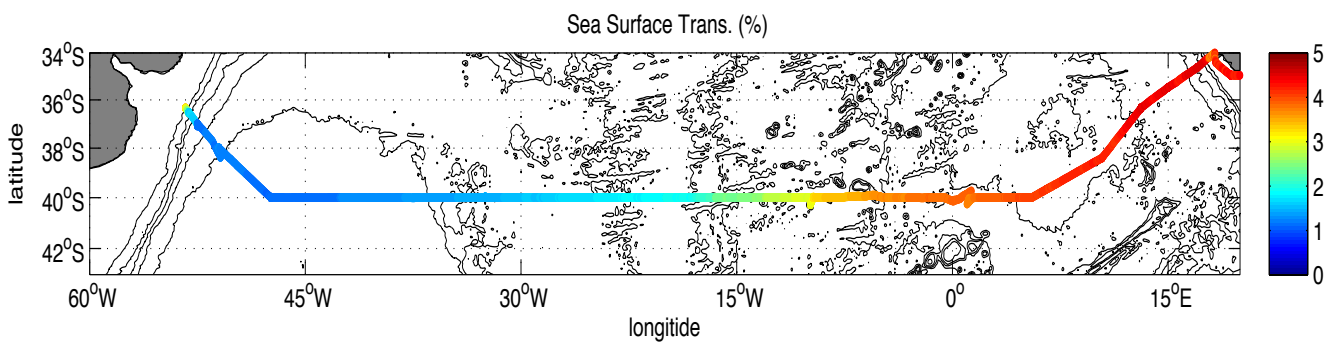
Figure 4: Seabird underway near-surface transmittance (5 minutes low pass filtered). The inlet is situated on the underside of the hull, close to the bow, at 5-6 meters depth.

UK-GEOTRACES Consortium

Ocean Micronutrient Cycles

WORKPACKAGE 1: MICRONUTRIENT MEASUREMENTS IN DISSOLVED AND PARTICULATE CYCLES

Maeve Lohan, Angela Milne, Neil Wyatt, Christian Schlosser, Jessica Klar, Maxi Castrillejo

1.1 TRACE METAL SAMPLING

Sample logs for all Ti-CTD casts are available at www.ukgeotraces.com/restricted. Samples were collected for trace metal analysis both dissolved and particulate fractions (see sections 1.2 and 1.3). In addition, from all Ti-CTD casts, unfiltered samples were collected macronutrients and salinity (see sections 8.1 and 8.4). At stations 3, 8,11,12,13, 16, 18 and 21 filtered samples were collected for iron isotopes. At superstations (Stations, 12,18,21), samples were collected for trace metal isotopes for Zn, Cd, Pb, Cr).

Surface samples from each station were collected by pumping surface seawater into a trace metal clean laboratory using a Teflon diaphragm pump (Almatec A-15, Germany) connected by an acid-washed braided PVC tubing to a towed fish positioned at approximately 2 - 3m depth alongside the ship. Seawater samples were filtered in-line using a 0.2 µm AcroPak Supor membrane filter capsule (Pall). In between each station, surface seawater samples were collected on a 2 or 4 hourly interval. A total of 123 underway surface samples were collected.

1.2 DISSOLVED TRACE METALS

Seawater samples were collected using a titanium CTD frame fitted with 24, 10 L trace metal clean Teflon coated OTE (Ocean Test Equipment) samplers with external springs deployed on a plasma rope. Upon recovery, the OTE bottles were transferred into a class 100 clean air container and lightly pressurized (1.7 bar) with high purity compressed air passed through an inline 0.2 µm cellulose acetate filter capsule (Sartobran P-300, Satorius). Total dissolvable iron samples were collected unfiltered. Samples for dissolved trace metals (Fe, Cu, Cd, Zn, Co, Pb, Ni, Mn, Al) were filtered through 0.2 µm AcroPak Supor polyethersulfone membrane filter capsules (Pall) into 125 mL low density polyethylene bottles (Nalgene). Each sample was acidified to pH 1.7 (0.024 M) by addition of 12 M hydrochloric acid (HCl, UpA, Romil) under a class 100 laminar flow hood and finally stored in polyethylene zip-lock bags. In addition, 1L filtered samples were taken in LDPE bottles for archived samples and acidified on board. These samples were double bagged and stored at Oxford University.

Dissolved Zn and Dissolved Al were analysed on-board ship by Neil Wyatt (University of Plymouth) and Jessica Klar (University of Southampton) respectively. Dissolved Co will be analysed using flow injection analysis at the University of Plymouth (Maeve Lohan and Neil Wyatt), while all other trace metals (Cd, Cu, Pb, Ni, Mn) will be analysed by isotope dilution ICP-MS at the University of Southampton (Christian Schlosser and Eric Achterberg).

Samples Collected:

Total dissolvable metals- 125 ml unfiltered

Stations	1, 2,3,7,8,9,11,12,13,14,16,17,18,19,20,21,22,24
Samples	196
Underway Fish	60

Dissolved Zn and Co - 2 x 125 ml filtered

Stations   1, 2,3,7,8,9,11,12,13,14,16,17,18,19,20,21,22,24

     Samples   374

     Underway Fish   123

Dissolved Al -125 ml filtered

Stations   1, 2,3,7,8,9,11,12,13,14,16,17,18,19,20,21,22,24

     Samples   374

     Underway Fish   123

Dissolved Trace metals- 250 ml

Stations   1, 2,3,7,8,9,11,12,13,14,16,17,18,19,20,21,22,24

     Samples   374

     Underway Fish   123

Archives -1L filtered-held at university of Oxford

Stations, 1, 2,3,7,8,9,11,12,13,14,16,17,18,19,20,21,22,24

     Samples   365

1.2.1 DISSOLVED ZINC

(Neil Wyatt, University of Plymouth)

Samples for dissolved zinc were analysed on-board ship by Neil Wyatt and some of the underway samples were be analysed back in the laboratory at University of Plymouth.

Introduction

Dissolved zinc (Zn) is an essential micronutrient for phytoplankton growth and (*Morel et al.,* 1994; *Lohan et al., 2005*). While it is widely accepted that iron (Fe) limits phytoplankton growth over large areas of the surface ocean [*e.g. Coale et al.*, 1996; *Boyd et* al., 2000], a growing body of evidence suggests that other trace elements such as Zn may limit or co-limit algal growth (*Saito et al.,* 2008; Lohan et al., 2005).

Zinc is a co-factor in the enzyme carbonic anhydrase (CA), which is required by marine phytoplankton for inorganic carbon acquisition (Morel et al., 1994). Some phytoplankton such as centric diatoms are able to substitute Co or cadmium (Cd) for zinc (Zn) in CA. In addition, there is emerging evidence that some forms of alkaline phosphatase (AP), a metalloenzyme that facilitates acquisition of phosphorus (P) from the dissolved organic phosphorous (DOP) pool, that contain Zn as the metal cofactor. Expression of AP is of particular importance in the North Atlantic Subtropical Gyre, where up to 30% of primary production may be supported by the DOP pool (*Mather et al.*, 2008). *Jakuba et al.* (2008) have also provided evidence for important linkages in the biogeochemical cycles of Zn, Co, and P in the phosphorous-poor surface waters of the Sargasso Sea. At present, however, the biogeochemical cycling of Zn and the extent to which this trace element may influence phytoplankton growth and species composition in the surface ocean is not well understood.

Analysis

Dissolved zinc was determined using flow-injection with fluorimetric detection (FI-FL) using a modified version of the methods first described by Nowicki et al. (1994) and more recently by Gosnell et al. (2012). Each sample was run in triplicate as follows. Each sample was buffered in-line to pH 5.2 with 0.3 M ammonium acetate before being passed over a pre-concentration chelating iminodiacetic acid (IDA, Toyopearl AF-Chelate 650 M) column. The column was rinsed using 0.08 M ammonium acetate to remove seawater matrix cations, before zinc was eluted from the column with 0.08 M HCl (SpA, Romil).

Preliminary Results

Samples from all stations were measured at sea (Fig 5). Extremely low (0.01 nM) concentrations of Zn are observed within the upper water column. Many of these samples were below the limit of detection (25 pM) and these concentrations may be limiting phytoplankton growth. Highest concentrations of Zn are observed in the Lower Circumpolar Deep Water (LCDW). A pronounced Zn minimum was observed within the North Atlantic Deep water (NADW).
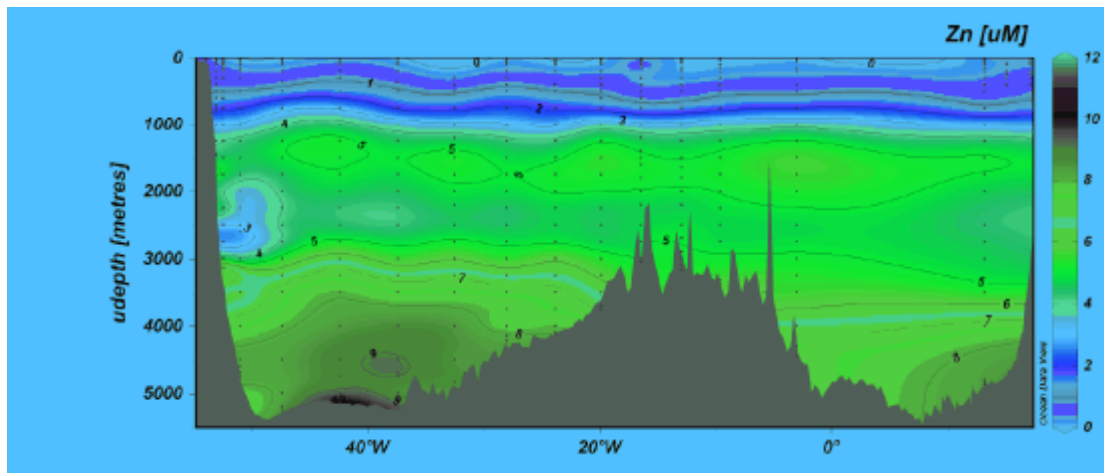
Figure 5 Preliminary dissolved Zinc concentrations along the cruise track.

References

Boyd, P.W., et al. (2000), A mesoscale phytoplankton bloom in the polar Southern Ocean stimulated by iron fertilization, *Nature*, *407*, 695-702.

Coale, K.H., *et al.* (1996), A massive phytoplankton bloom induced by an ecosystem-scale iron fertilzation experiment in the equatorial Pacific Ocean, *Nature*, *383,* 495-501.

Jakuba, R.W., J.W. Moffett and S.T. Dyhrman (2008), Evidence for the linked biogeochemical cycling of zinc, cobalt, and phosphorus in the western North Atlantic Ocean, *Global Biogeochem. Cycles*, *22*, doi: 10.1029/2007GB003119.

Gosnell, K. et al. (2012), Fluorometric detection of total dissolved zinc in Southern Indian Ocean, *Marine Chemistry*, 133, 68-76.

Lohan, M.C. et al. (2005), Iron and zinc enrichment in the northeastern subarctic Pacific: ligand production and zinc bioavailability in response to phytoplankton growth. *Limnol. Oceanogr.* 50: 1427-1437.

Mather, R.L., *et al*. (2008), Phosphorus cycling in the North and South Atlantic Ocean subtropical gyres, *Nature Geosci*, *1*, 439-443.

Morel, F.M.M., *et al*. (1994), Zinc and carbon co-limitation of marine phytoplankton, *Nature*, *369*, 740-742.

Nowicki, J.L. et al (1994), Determination of dissolved zinc in seawater using flow injection analysis with flurometric detection. *Anal. Chem*. 66, 2732-2738.

Saito, M.A., and T.J. Goepfert (2008), Zinc-cobalt colimitation of *Phaeocystis antarctica*, *Limnol. Oceanogr.*, *53*, 266-275.

1.2.2 DISSOLVED ALUMINIUM DISTRIBUTIONS

By Jessica Klar, Christian Schlosser, Maxi Castrilllejo Iridoy, Eric Achterberg, NOC

Introduction

It is widely accepted that an estimation of atmospheric dust deposition to the surface ocean can be carried out through the measurement of dissolved aluminium (dAl) concentrations in surface seawater (Measures and Brown, 1996, Measures and Vink, 2000, Mahowald *et al.*, 2005, Measures *et al.*, 2005). Al is not assimilated by living cells, which makes this element a nearly conservative tracer of dust inputs of Fe and other bio-limiting trace metals, such as Zn, Co and Cu. However, Al is highly particle reactive and scavenges onto sinking particles, and thus its residence time depends on the phytoplankton abundance in the study area. The estimation of atmospheric dust deposition can be complemented with the measurement of other tracers, titanium concentration (Dammshäuser, *et al.,* 2011) and the relation between Th-232 and Th-230 concentrations (Hsieh, *et al.*, 2011). Furthermore, relative concentrations of aluminium to other metals (V, Pb) in aerosol samples can give information about whether the source of atmospheric inputs is crustal (e.g. dust blown from deserts and other arid regions) or industrial (burning of fossil fuels) (Helmers and Van Der Loeff, 1993).

Our aim is to determine the distribution of dAl in surface waters and in the water column along the ships transect. In addition, dAl distributions will be compared to other parameters and tracers measured alongside to improve our understanding of the sources and sinks of dAl throughout the water column.

Methods

Sampling – Water column samples were collected at 19 CTD stations (Figure 6) along the transect using the titanium-frame CTD, which was fitted with trace metal clean 10L OTE (Ocean Technology Equipment) sampling bottles with external springs, modified for trace metal work. At these stations samples were collected at up to 24 depths. The trace metal clean OTE sample bottles were then transferred to a class 100 clean van (sampling container) on the back deck for sample processing (where the OTE bottles were stored until next deployment). OTE bottles were pressurized with air. In addition, underway samples were collected along the transect using a towfish deployed off the port side of the ship. Near-surface seawater (~2 metre depth) was pumped into the sampling container using a Teflon diaphragm pump connected to a clean oil-free compressed air compressor and samples collected every four hours while the ship was in transit.

Sample processing; Al – From the titanium frame rosette bottles, filtered seawater samples were collected in clean 250 mL Nalgene LDPE bottles for shipboard determination of Al and Fe. Prior to filling, the bottles were rinsed with sample three times. Filtered samples were collected through a 0.2mm Supor Acropak filter cartridge (Pall Corp.). All water samples were acidified to pH~1.8 using hydrochloric acid (Romil UpA) within twelve hours of collection.

Analysis – Between one hour and one week after acidification all filtered seawater samples were analysed on board for dissolved Al using flow injection analysis developed by Resing and Measures (1994) (with modifications from Brown and Bruland, 2008), where Al is detected by the fluorescence of a formed chelate by reaction with lumogallion.

Results

Preliminary analysis showed surface concentrations of below limit of detection and up to ~3 nM dAl, in agreement with the extremely low dust inputs this region receives (Figure 7).

Preliminary analysis of the depth profiles showed low dAl at surface (below 1 nM). A subsurface (200 m) maxima is observed, which is more pronounced (5 nM) in the Argentine Basin. From 500 m to 1700 m depth dAl is generally low ranging from 1 to 3 nM. On the eastern side of the ridge, increased dAl concentrations (8 nM) were observed around 3500 m depth. On the western side of the ridge the dAl maxima is observed at 2500 m, which increases significantly towards the Argentine shelf. In deeper waters (below 3000 m), a low dAl core (~2 - 3 nM) is observed in the Argentine Basin. The influence of the Rio Plata Estuary can be observed in a significant increase in dAl in surface waters (up to 300 m) at station 20. The depth section of dAl along the ship's transect is shown in figure 8.
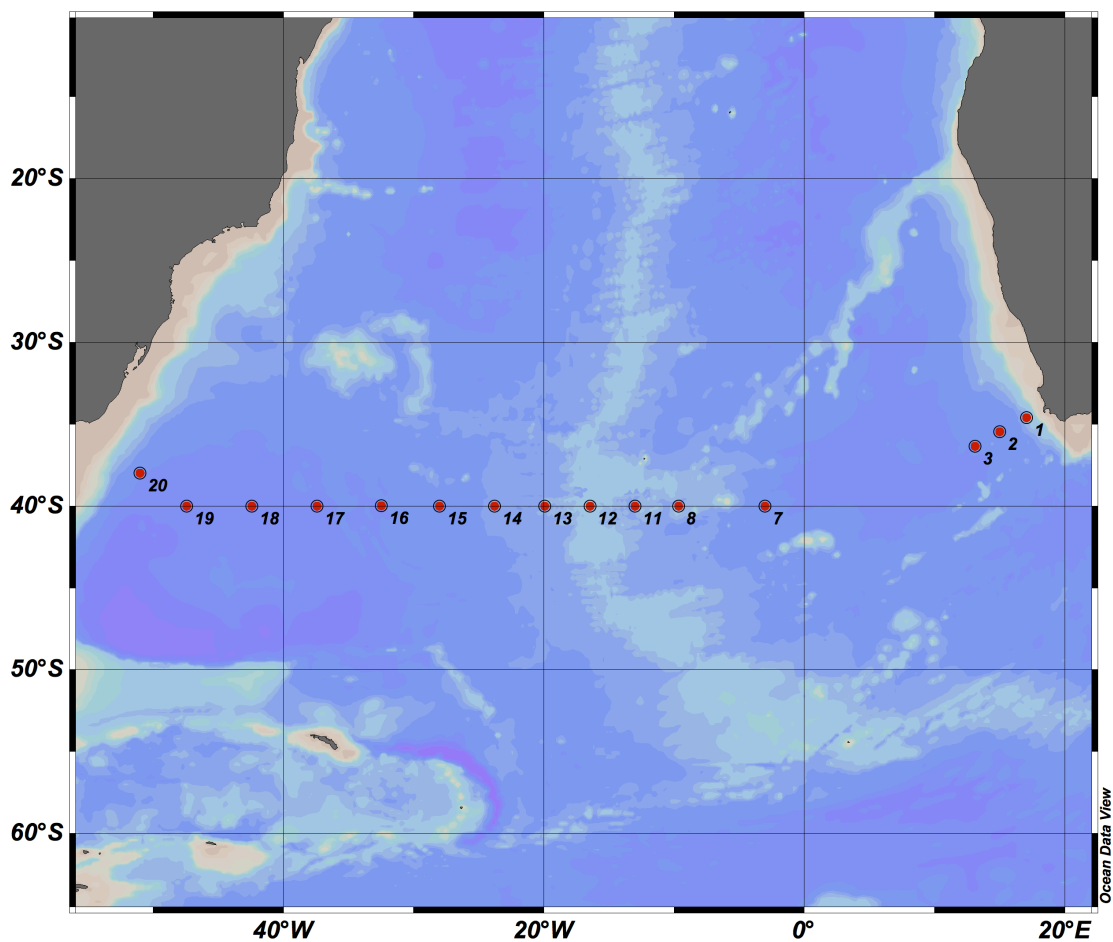
Figure 6:   D361 profile stations (up to Station 20).
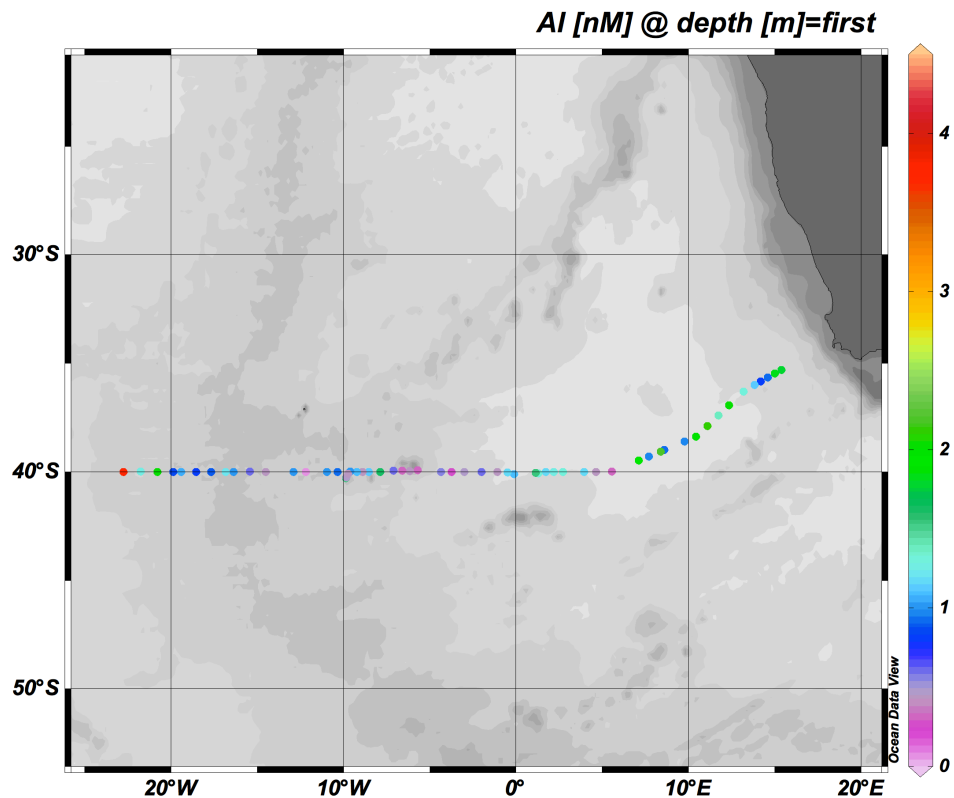
Figure 7:   dAl (nM) concentrations in the underway tow fish samples (every 4h)
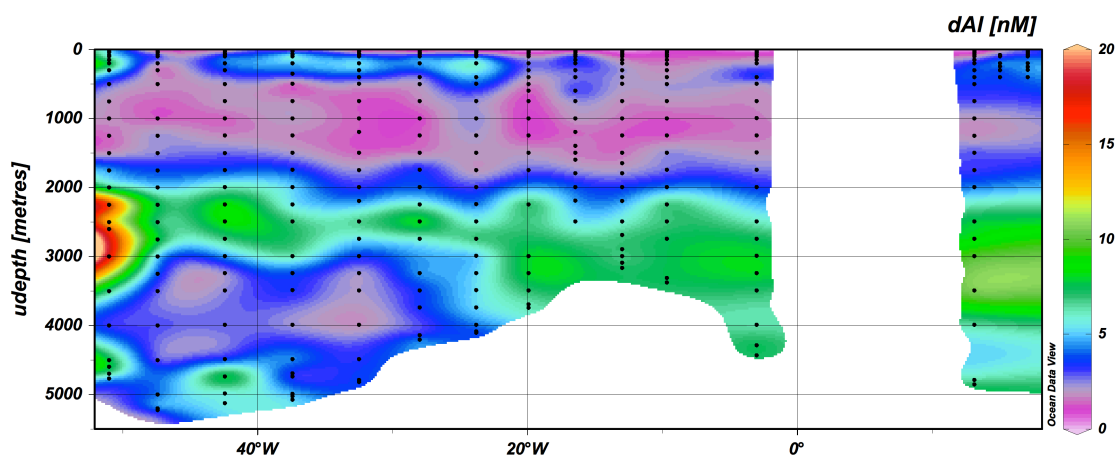
Figure 8:   dAl depth section along the ship's transect (up to station 20).

References:

Bowie, A R, Whitworth, D J, Achterberg, E P, Mantoura, R F C & Worsfold, P J 2002. Biogeochemistry of Fe and other trace elements (Al, Co, Ni) in the upper Atlantic Ocean. *Deep-Sea Research Part I-Oceanographic Research Papers,* 49**,** 605-636.

Boyd, P W & Ellwood, M J 2010. The biogeochemical cycle of iron in the ocean. *Nature Geoscience,* 3.

Brown, M T & Bruland, K W 2008. An improved flow-injection analysis method for the determination of dissolved aluminum in seawater. *Limnology and Oceanography-Methods,* 6**,** 87-95.

Dammshäuser, A, Wagener, T and Croot, P L, 2011. Surface water dissolved aluminum and titanium: Tracers for specific time scales of dust deposition to the Atlantic? *Geophysical Research Letters*, 38.

De Jong, J T M, Boye, M, Gelado-Caballero, M D, Timmermans, K R, Veldhuis, M J W, Nolting, R F, Van Den Berg, C M G & De Baar, H J W 2007. Inputs of iron, manganese and aluminium to surface waters of the Northeast Atlantic Ocean and the European continental shelf. *Marine Chemistry,* 107**,** 120-142.

Helmers, E & Van Der Loeff, M M R 1993. Lead and aluminum in Atlantic surface waters (50 N to 50 S) reflecting anthropogenic and natural sources in the eolian transport. *Journal of Geophysical Research-Oceans,* 98**,** 20261-20273.

Hsieh, Y-T, Henderson, G M and Thomas, A L, 2011. Combining seawater ^{232}Th and ^{230}Th concentrations to determine dust fluxes to the surface ocean. *Earth and Planetary Science Letters,* 312**,** 280-290.

Mahowald, N M, Baker, A R, Bergametti, G, Brooks, N, Duce, R A, Jickells, T D, Kubilay, N, Prospero, J M & Tegen, I 2005. Atmospheric global dust cycle and iron inputs to the ocean. *Global Biogeochemical Cycles,* 19.

Measures, C I & Brown, E T 1996. Estimating dust input to the Atlantic Ocean using surface water Al concentrations. *In:* GUERZONI, S. & CHESTER, R. (eds.) *The Impact of Desert Dust Across the Mediterranean.* Dortrecht: Kluwer Academic Publishers.

Measures, C I, Brown, M T & Vink, S 2005. Dust deposition to the surface waters of the western and central North Pacific inferred from surface water dissolved aluminum concentrations. *Geochemistry Geophysics Geosystems,* 6.

Measures, C I, Landing, W M, Brown, M T & Buck, C S 2008. High-resolution Al and Fe data from the Atlantic Ocean CLIVAR-CO2 repeat hydrography A16N transect: Extensive linkages between atmospheric dust and upper ocean geochemistry. *Global Biogeochemical Cycles,* 22.

Measures, C I & Vink, S 2000. On the use of dissolved aluminum in surface waters to estimate dust deposition to the ocean. *Global Biogeochemical Cycles,* 14**,** 317-327.

Resing, J A & Measures, C I 1994. Fluorometric determination of Al in seawater by Flow-Injection-Analysis with in-line preconcentration. *Analytical Chemistry,* 66**,** 4105-4111.

1.2.3 DISSOLVED TITANIUM

Rosie Chance

Introduction

Little is known about the marine biogeochemistry of titanium. The handful of open ocean measurements reported suggest a dissolved titanium (dTi) concentration range of 5 to 350 pM, with lowest levels in surface waters and a gradual increase with depth (Orians et al., 1990; Croot, 2011). Riverine inputs are thought to be the dominant source (Skrabal et al., 1992), but in the open ocean atmospheric deposition may be important and titanium has recently been suggested as a complementary tracer to aluminium for estimating dust inputs (Dammshauser et al., 2011). In particular, the longer residence time of dTi compared to dAl (which is more rapidly scavenged onto biogenic particles) has led to it being proposed as a tracer of Patagonian dust input.

A new, high sensitivity electrochemical method for the determination of picomolar titanium in seawater was published in 2011 (Croot, 2011). The aim of the titanium work on JC068 was to use this new method to evaluate further the best way of sampling for the element, contribute to a nascent intercalibration exercise, and make surface and profile measurements of seawater titanium concentrations. The 40°S section was considered to be of particular interest because of the possibility of Patagonian dust inputs at the western end of the transect.

Objectives

1. To determine titanium concentrations in the SAFe and GEOTRACES intercalibration samples for comparison with those given in Croot, 2011. As yet consensus values for titanium in these samples have not been reported.

2. To compare samples taken from the standard stainless steel rosette and from the trace metal clean titanium rosette, in order to evaluate which method provides the least risk of contamination. While the latter sampling method is conducted in a more controlled environment, so minimizing the risk of general contamination, the possibility of contamination arising from the rosette itself requires further assessment.

3. To compare filtered vs. unfiltered samples, and acidified vs. unacidified samples and conduct storage tests in order to determine the most appropriate sampling protocol for titanium.

4. To determine titanium concentrations in as many samples as possible along the 40°S transect.

Sampling protocol

All samples were collected in acid cleaned, 125 mL LDPE bottles (Nalgene). The bottles were rinsed three times with a few mL of sample prior to filling. Individual bottles were stored double bagged. Unfiltered samples were collected directly from the stainless steel rosette following a brief rinse of the Niskin bottle tap with MilliQ water. Filtered (Acropak or 0.2 um PES filter) and unfiltered samples were also collected from the trace metal clean titanium rosette and the trace metal clean towed 'fish' according to the protocols described elsewhere. All subsequent sample handling took place under clean conditions, in a laminar flow bench in a container laboratory dedicated to trace metal clean work. Unacidified

samples were analysed within 48 hours of collection. Other samples were acidified using Ultrapure HCl.

Sample analysis

Samples were analysed on board by Dr Rosie Chance, University of East Anglia. Titanium was determined by catalytic cathodic stripping voltammetry, according to the method described in Croot, 2011.

The method carries a significant reagent blank, in this case found to be 44 pM. The blank was determined in two ways: by dilution of the sample with up to 50% MilliQ water and extrapolation of the resultant curve to zero percent sample, and two by spiking of the sample with an extra 50% of each reagent in addition to that used routinely.

Preliminary results

A series of problems limited the number of successful analyses conducted on board ship. These included, but were not limited to: unexplained instability in the sensitivity of the method at the outset, suspected contamination of a working standard, damage to the instrument during rough weather, reagent exhaustion at the end of the cruise.

1. <u>SAFe and GEOTRACES intercalibration samples</u>

For two of the three intercalibration samples analysed during cruise JC068, titanium concentrations were in good agreement with the earlier measurements of Croot, 2011 (table 1). A higher concentration was measured in sample GEOTRACES GS, this is suspected to be due to sample or bottle contamination.

	This work		*Croot, 2011*	
Sample	dTi, pM	n	dTi, pM	n
SAFe D2	129 ± 9	3	127 ± 33	10
GEOTRACES GS	114 ± 5	3	75 ± 12	3
GEOTRACES GD	220 ± 17	2	202 ± 18	3

Table 1. Titanium concentrations in SAFe and GEOTRACES and intercalibration samples

2. <u>Stainless steel vs. Trace metal clean titanium sampling rosette</u>

A comparison of samples collected from two depths at station 11 suggested there was no statistically significant difference between the two different sampling protocols (table 2). However, the sample set was very small and a more extensive comparison is still required.

	Titanium rosette, filtered		*Steel rosette, unfiltered*	
Depth, m	dTi, pM	n	dTi, pM	n
100	78 ± 9	7	166 ± 21	5
3000	75 ± 6	3	138 ± 19	3

Table 2. Comparison of titanium concentrations in samples collected from the trace metal clean titanium rosette and the stainless steel rosette at station 11.

It is noted that no difference was observed between surface water samples collected from the stainless steel rosette and those collected from the towed fish via the outlet in the trace metal clean sampling container. This further suggests that sampling on deck from the stainless steel rosette did not lead to sample contamination (it being highly unlikely that both sampling methods should contribute the same amount of contamination).

3. Comparison of sample handling protocols

Unfortunately, the analytical problems noted above limited the number of comparisons that were successfully carried out, so a full evaluation of sample handling protocols could not be conducted.

No difference in titanium concentration was observed between acidified and un-acidified sub-samples of the same, filtered sample. A direct comparison of filtered and unfiltered sub-samples of the same sample was not successful, but the results shown in Table 2 (for samples from the same depth and station, but different casts) suggest there was unlikely to have been a difference. This is consistent with the findings of P. Croot (*pers. comm.*, 2011).

A 45 hour storage test conducted on a *filtered* sample (1418; Figure 9) suggested un-acidified samples were stable over the 48 hour period following collection. Of four similar storage tests conducted with *unfiltered* samples, two showed no change over ~16 hours (1755 and 1426; Figure 9) while two showed some indication of an increase in concentration, though this was not greater than the errors on repeat measurements (1777 and 1401; Figure 9). Further analyses over longer timescales were not successful with these samples. Profiles analysed over a period of 48 hours (analysing depths in a pseudo-random order) displayed oceanographic consistency, suggesting that significant changes to the samples did not occur over this time frame.
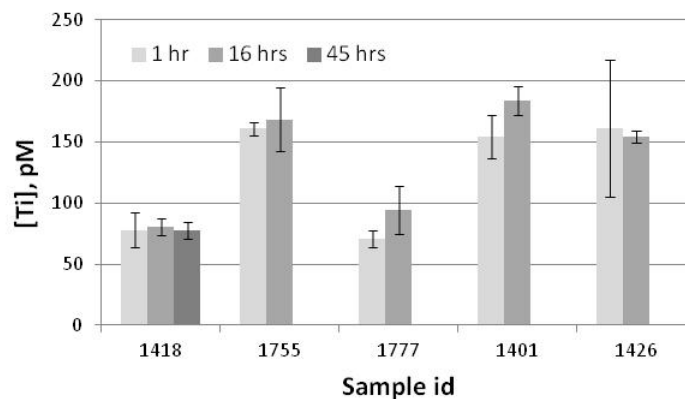
Figure 9. Results of repeat analyses of un-acidified samples following storage at room temperature. Error bars show ± 1 standard deviation. Samples 1418 and 1401 were filtered, all other samples were unfiltered.

4. Titanium concentrations along the 40°S transect.

Samples from stations 7, 8, 11, 12 and 13 were successfully analysed. Concentrations were in line with those expected for the study region (Dammshauser et al., 2011) and the shape of the profiles obtained was also as expected (Orians et al., 1990; Croot, 2011), with lowest values (~50 pM) at the surface and a general increase with depth to 100-150 pm (Figure 10).
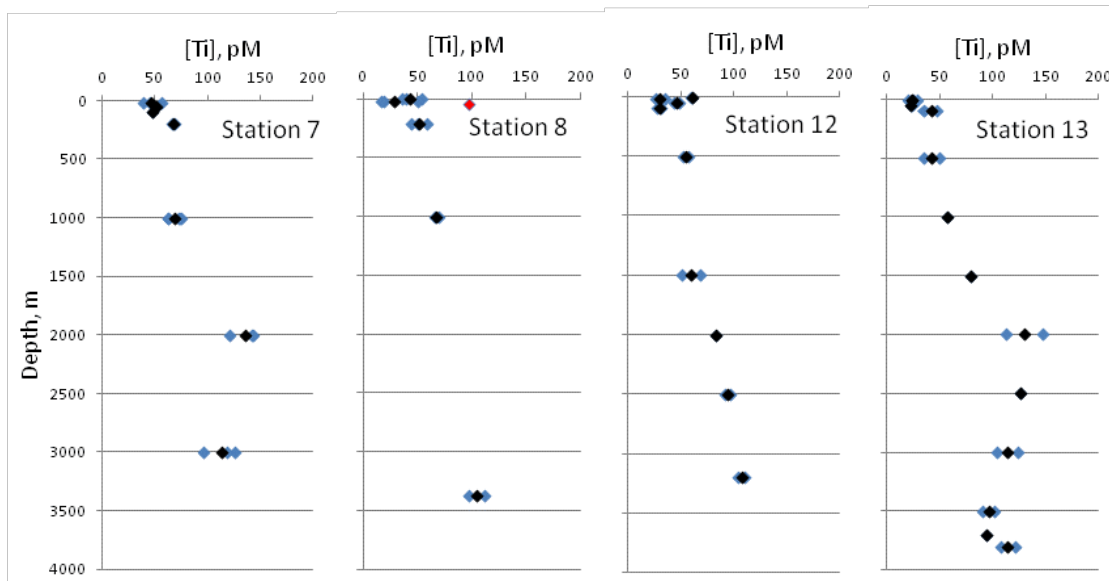
Figure 10. Titanium concentrations in seawater samples collected during cruise JC068 and analysed on board. Black diamonds show average of all replicate analyses, blue diamonds show individual analyses and red diamonds indicate samples suspected to be contaminated. All vales have been corrected for a blank of 44 pM. Stations 7 and 8 were east of the mid-ocean ridge, 12 was above it and 13 was west of it; for exact station positions see elsewhere in cruise report. At stations 7 and 8, filtered water from the trace metal clean rosette was analysed, while at stations 12 and 13 unfiltered water from the stainless steel rosette was analysed.

Additional samples were collected from other stations for return to the UK. However, at present it is not known if it will be possible to analyse these samples, as the work is in addition to the GEOTRACES aerosol analyses to be conducted by Dr Chance at the University of East Anglia, and as such is not funded.

References

Croot, P.L., 2011. Rapid determination of picomolar titanium in seawater with catalytic cathodic stripping voltammetry. Analytical Chemistry, 83, pp. 6395-6400.

Dammshauser, A., Wagener, T. & Croot, P.L., 2011. Surface water dissolved aluminium and titanium: Tracers for specific time scales of dust deposition to the Atlantic? Geophys. Res. Lett., 38, L24601. Doi: 10.1029/2011GL049847.

Orians, K.J., Boyle, E.A., & Bruland, K.W., 1990. Dissolved titanium in the open ocean. Nature, 348, 6299, pp. 322-325.

Skrabal, S.A., Ullman, W.J., & Luther, G.W., 1992. Estuarine distributions of dissolved titanium. Marine Chemistry, 37, 1-2, pp. 83-103.

1.3 PARTICULATE TRACE METALS (ANGELA MILNE AND MAEVE LOHAN)

Samples will be analysed by Angela Mine and Maeve Lohan at the University of Plymouth.

Introduction

Particulate trace metals may occur in several forms, including stable refractory phases or as coatings on surfaces that can be rapidly recycled. Particulate behaviour is metal specific with, for instance, the majority of particulate Fe occurring in refractory phases while Zn is primarily associated with more labile phases (Hurst & Bruland, 2007). Few studies have concurrently measured trace elements in both the dissolved and particulate phases. Furthermore, labile particulate trace metals which are biologically available could be considerably higher than dissolved phase (Berger et al., 2008). Assessment of total biologically available trace elements may thus require the determination of both dissolved and labile particulate metal phases (Lam & Bishop, 2008). A first step towards a quantitative description of the cycling of trace elements between the dissolved and particulate phases required for their realistic incorporation into biogeochemical ocean models is to measure the standing stock of the particulate fraction. To address this, particulate material will be filtered on all water samples collected using the trace metal rosette. In addition sub-samples from the fine and coarse Stand Alone Pumps (SAPs) filters will be taken for particulate trace metals.

Sampling

Profiles were collected from varying depths through the whole water column using twenty-four 10 L OTE bottles mounted on a Ti rosette. On recovery, the OTE bottles were transferred into a clean sampling container where they were immediately sampled for nutrients and salinity before being pressurised to approximately 7 psi with 0.2 μm filtered air using an oil free compressor. Acid clean filter holders (Swinnex, Millipore) were attached to the Teflon taps of the OTE bottles using acid cleaned Bev-A-Line (Cole Parmer) tubing and luer lock fittings. Up to a maximum of 7 L of seawater from each depth was then filtered through acid washed 25 mm (0.2 μm) polyethersulfone filters (PES, Supor, Pall Gellman) housed in the clean filter holders. Following filtration, the filter holders were removed and placed in a laminar flow bench. Using an all polypropylene syringe attached to the top of the filter holder, residual seawater was forced through the filter using air from within the flow hood. The filter holders were gently opened and the PES filter was folded in half using plastic tweezers, the filters were then placed in acid clean 2 mL LDPE vial and frozen at -20°C until analysis. Eight OTE bottles could be pressurised and sampled at one time. Prior to the sampling of the next set of eight, the OTE bottles were inverted three times to gently mix the seawater and re-suspend particulates. Filtration of all twenty-four bottles was completed in approximately nine hours.

The filter housings of the SAPs were fitted with acid washed nylon mesh (10 μm) and paired 293 mm PES filters (0.8 μm, Pall Gelman) and deployed to varying depths in the water column. On recovery, the filter housings were placed in a laminar flow hood for removal of the nylon mesh and PES filters. A clean stainless steel blade was used to cut a quarter section from the nylon mesh which was rinsed with UHP water into a clean plastic jug. This water was then filtered over a 25 mm PES filter (0.2 μm, Supor, Pall Gellman) housed in a clean filter holder (Swinnex, Millipore) using an all polypropylene syringe attached to the top of the filter holder. Residual water was forced through the filter using air from within the flow hood, the filter was then folded in half and placed in acid clean 2 mL LDPE vial. The 293 mm PES filters were folded upon themselves and placed into clean zip-lock plastic bags. Both the 25 mm and 293 mm PES filters were frozen at -20°C until analysis.

To allow for RNA metanomic analyses a sample of the 293 mm PES filter was required. Therefore, prior to the removal of the 293 mm PES filters, a small sub-sample was cut using a clean stainless steel blade. This was then placed into a clean 2 mL LDPE vial, RNA later added and the sample stored at -80°C.

Particulate trace metals from OTE bottles
        Stations   1, 2,3,7,8,9,11,12,13,14,16,17,18,19,20,21,22,24
        Samples   374
Particulate trace metals from SAPS were also collected

Analysis

Samples will be analysed for both labile and refractory particulate Fe, Mn, Al, Co, Zn, Cd, Ba, Ni, Cu, Ti and potentially other trace elements using ICP-MS at the University of Plymouth. For labile particulate trace elements the filter is subjected to a weak acid leach (25% acetic acid at pH 2) with a mild reducing agent (0.02 M hydroxylamine hydrochloride) and a short heating step (10 min 90-95°C). This approach is fully detailed in Berger et al. (2008). After the labile fraction has been determined the refractory trace elements will be determined using methods developed by Robert Sherrell during the GEOTRACES Intercalibration effort. Briefly, the filters will be placed in 15 mL Savillex vials and 1 mL of 50 % HNO_3 & 10 % HF added, the vials are then heated to 130°C for 4 hours. This solution is dried down on a hot plate and 100 µM of concentrated HNO_3 added, the dry down procedure is then repeated. The residue is brought back into solution with 5 % HNO_3 for analysis by ICP-MS. The samples are then spiked with an internal reference material such as In for drift correction. All samples will hopefully be analysed by the end of November 2011.

Samples for RNA analyses will be analysed at Woods Hole Oceanographic Institute by Dr. Mak Saito.

References

Berger et al. (2008), Application of a chemical leach technique for estimating labile particulate Al, Fe   and Mn in the Columbia River Plume and coastal waters off Washington and Oregon. *J. Goephys. Res*. 113, C00B01, doi:10.1029/2007JC004703
Hurst, M. & Bruland, K.W. (2007), An investigation into the exchange of iron and zinc between the   soluble, colloidal, and particulate size fractions in shelf waters using low abundance isotopes   as traces in shipboard incubation experiments. *Mar. Chem*., 103, 211-226.
Lam. P. & Bishop, J. (2008), The continental margin is a key source of iron to HNLC north Pacific
      Ocean, *Geophys. Res. Lettrs*., 35, L07608, doi:10.1029/2008GL033294

1.4 TRACE METAL SPECIATION

Samples for dissolved iron speciation will be analysed by Christian Schlosser and Eric Achterberg at the University of Southampton

Introduction

Understanding the biogeochemistry of Fe, requires the ability to measure their oceanic chemical speciation. Fe is present in seawater as chelates with strong metal-binding organic ligands (Bruland & Lohan, 2004) which dramatically influences their chemical behaviour. These ligands have a stabilising influence, preventing inorganic precipitation (e.g. Liu and Millero, 2002) and increasing the availability of metals for biological uptake. We will characterise the chemical speciation of Fe in surface and deep-waters at chosen stations (super-stations) across the South Atlantic to assess their distribution with variables such as source, depth, and biological environment.

Sampling

Profiles were collected from varying depths through the whole water column using twenty-four 10 L OTE bottles mounted on a Ti rosette. On recovery, the OTE bottles were transferred into a clean sampling container where they were immediately sampled for nutrients and salinity before being pressurised to approximately 7 psi with 0.2 μm filtered air using an oil free compressor. After the collection of particulate samples (see section on particulate metals), an Acropak (Pall) filter capsule (0.2 μm) was attached to the Teflon taps of the OTE bottles using acid cleaned Bev-A-Line (Cole Parmer) and silicon tubing. Filtered samples were collected into acid clean sample bottles which had been previously soaked in ultra high purity water. Bottles and caps were rinsed 3 times with filtered sample before being filled two thirds full, all samples were then double bagged and frozen. LDPE (250 mL) bottles were used for Fe speciation.

<u>*Samples Collected*</u>:

Stations	3,7,9,12,16,18,21,22,24
Samples	88

Analysis

Frozen samples will be thawed and analysed in shore based laboratories. The concentrations and conditional stability of Fe ligands, Fe' (soluble inorganic Fe) and free aqueous Fe will be measured at the University of Southampton by competitive ligand exchange cathodic stripping voltammetry (CLE-CSV) with the ligand TAC (Croot and Johansson, 2000).

References

Bruland, K.W. & Lohan, M.C. (2004) Controls of trace metals in seawater. In *The oceans and marine   geochemistry, Treatise on Geochemistry* vol. 6, 23-48.
Croot, P.L. & Johansson, M. (2000), Determination of Iron Speciation by Cathodic Stripping   Voltammetry in Seawater Using the Competing Ligand 2-(2-Thiazolylazo)-p-cresol (TAC). *Electroanalysis*, 8, 565-576.
Liu & Millero, F.M. (2002) The solubility of iron in seawater. *Mar. Chem.* 77, 43-54

1.5 MERCURY SAMPLING AND MEASUREMENTS

by Arne Bratkič

analysed by: Arne Bratkič and Mitja Vahčič

Objectives:

To provide a coherent, high-resolution spatial profile of water column mercury species. These species include dissolved gaseous mercury (DGM), methylmercury (MeHg), total mercury (THg) and dimethylmercury (DMeHg). Such information improves our knowledge of Hg open ocean cycling and provides much needed data for models of global Hg transport and fluxes. Along with other measurements it is also possible to assess (to a certain degree) the influence of biological and chemical mechanisms, governing Hg cycling at this latitude in southern Atlantic Ocean. For more complete picture of environment some sediment samples were also collected when it was possible.

Sample collection and analysis

Only total mercury and dissolved gaseous mercury were analysed on the ship. For DGM, 0.5L of water from each depth was collected from stainless steel rosette into 1L glass beaker and bubbled with nitrogen gas onto gold traps for 5 minutes. Gold traps were afterwards inserted into Hg free argon gas flow (40mL min^{-1}) and heated to release amalgamated DGM from gold. Signal was detected with Brooks Rand model III, connected to portable computer using Mercury Guru 4.1 software.

THg samples were collected into 125mL Teflon bottles, acidified with 0.5mL 37% Suprapur HCl and 1mL of BrCl was added. Samples were irradiated with UV light for no less than 3 hours to oxidize all Hg within. After that, BrCl was inactivated with 0.05% v/v hydroxyl ammonium hydrochloride (aprox. 60μL). 40mL of this solution was poured into Teflon bubblers and 5mL of reducing agent SnCl$_2$ in 5% H$_2$SO$_4$ was added. Then, reduced Hg^0 was bubbled with nitrogen gas onto gold traps and measured in the same manner as DGM.

Samples for MeHg and THg were also collected for subsequent laboratory analyses. Per each sampled depth, filtered and unfiltered sample was collected. Standard Geotraces AcroPak filters with Supor membrane were used for filtering. Samples were collected into 0.5L Teflon bottles, acidified with 1mL 37% Suprapure HCl, packed into double zip-lock plastic bags and frozen at -20°C. THg samples will be analysed with Tekran 2600, 2610 and 2621 modules for THg analysis and MeHg distilled with Tekran 2750 Distillation unit and analysed with Brooks Rand MERX MeHg system, following EPA method 1630 (aqueous ethylation, purge and trap onto Tenax traps, cold vapour atomic fluorescence spectrometry).

Samples for DMeHg were taken only once at Station 20 (CTD #55), when the whole rosette was dedicated for Hg measurements. 2L of seawater was carefully (no turbulent flow!) poured into glass bubbler. It was bubbled with nitrogen for 10 minutes. During that time DMeHg was adsorbed onto Tenax traps. Traps were double-sealed into plastic bags, from which air was evacuated. They were frozen at -20°C. DMeHg will be analysed in the laboratory using thermal desorption and gas chromatography coupled with Brooks Rand model III detector.

As for sediments, a section of sediment profile was put into plastic bag, the atmosphere evacuated and sealed, and then frozen at -20°C. THg and MeHg will be measured in the laboratory upon samples arrival. They will be also measured with Tekran and Brooks Rand equipment.

References:

Horvat M., Kotnik J., Logar M., Fajon V., Zvonaric T., Pirrone N. (2003) Speciation of mercury in surface and deep-sea waters in the Mediterranean sea. *Atmospheric Environment*. **37**, 93-108

WORKPACKAGE 2: AEROSOL SOURCES

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2.1 AEROSOL AND RAIN SAMPLING

Rosie Chance

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Introduction and Cruise Objectives

Atmospheric deposition (dry and wet) is a significant source of both micro- and macronutrients to the oceans, and in some locations, may even be the dominant supply route for certain elements. Due to the episodic nature of deposition events, coupled with a comparatively small number of time series observations and the necessarily 'snap-shot' nature of ship based measurements, atmospheric deposition fluxes to the oceans remain quite poorly constrained. Direct measurements of aerosol and rain chemical composition are particularly sparse for the south Atlantic. In this region, crustal derived mineral aerosol from Patagonia has recently been identified as a potentially important, but as yet rarely sampled, source of trace elements.

The aim of the aerosol and rain sampling on cruise JC068 was to obtain chemical composition information to add to the growing global database of such measurements, and, more specifically, to improve our understanding of atmospheric deposition in the remote south Atlantic.

The specific objectives of the cruise were as follows:

- To collect size segregated atmospheric aerosol samples for the determination of trace metal (TM) and major ion (MI) concentrations.
- To collect bulk atmospheric aerosol for determination of isotope signatures (ISO) and organic biomarkers.
- To collect rain samples for determination of trace metal and major ion concentrations.
- To make ship board measurements of aerosol optical depth.

Planned sample analyses:

- Aerosol and rain trace metals and major ions: Rosie Chance

- Pb, Nd, Zn and Cd aerosol isotopic signatures: Dominik Weiss/Roulin Khondoker, *Imperial College, London, email: roulin.khondoker04@imperial.ac.uk*

- Aerosol organic biomarkers: Maite Hernadez, *University of Bristol, email: maite.hernandezsanchez@bristol.ac.uk*

- Aerosol optical depth: Alexander Smirnov, *Sigma Space Corporation, code 614.4, NASA/Goddard Space Flight Center, Greenbelt, MD 20771. tel.: (301)-614-6626, fax: (301)-614-6695, email: Alexander.Smirnov-1@nasa.gov*

Sampling protocol

Aerosol: Three high volume aerosol collectors (Andersen) were mounted on the monkey island deck of the ship (Figure 11). Each sampler was used for a different set of samples (i.e. TM, MI or ISO). To avoid sampling contaminated air from the ships funnel, power supply to the motors was automatically controlled such that sampling only took place when the relative wind direction was between -80 and 145 degrees. The collectors were also manually turned off during routine testing of the life boat engines, which are forward of the monkey island. Air flow through each collector was calibrated at the beginning of the cruise and the mass flow set to 1 m^3 min^{-1}. Aerosol for TM and MI determination were sampled using a two stage Sierra-type cascade impactor (aerodynamic diameter cut offs of ~2.4 and ~1.6 um) with a back-up filter behind, while that for isotopes was sampled in bulk only. Samples were collected onto Whatman 41 paper filters, which for TM and ISO had been acid washed (HCl then HNO_3) before use. The filters were loaded and unloaded from the sampling cassettes under a laminar flow hood; nitrile gloves were worn and the filters handled by the edges only. Samples were collected over ~48 hours (TM and MI). ISO samples were collected for ~48 hours (ISO) such that one ISO sample covered the same period as two sets of TM or MI filters. Exposed filters were folded in half, placed in sealed plastic bags and frozen at -20°C for return to the UK. Twice during the cruise, TM and MI samples were collected using a six stage impactor. The following blanks were collected for each sample type: Filter blank; Cassette blank; Motor blank.

Rain: Rain was collected using two 40 cm diameter polypropylene funnels with clean sample bottles attached; a new bottle was used for each rain event. The bottles and funnel for TM rain sampling were acid washed and the bottles stored with very dilute HNO_3 in them, while the bottles and funnel for MI rain sampling were detergent washed and the bottles stored with MilliQ water in them. Both funnels were deployed simultaneously on the port side of the monkey island deck during rain events. Following collection, TM samples were acidified using conc. HNO_3 and both samples were frozen at -20°C for return to the UK. Blank samples were prepared by pouring the contents of a cleaned bottle through the funnel and into a second bottle.

Aerosol optical depth: A hand-held sun photometer (Microtops II, Solar Light Co., USA) connected to a GPS was used to measure aerosol optical depth. The instrument was calibrated in advance of the cruise. Readings were taken whenever absence of cloud cover allowed (the solar disk must be completely free of cloud for the instrument to be used).

Aerosol optical depth data was downloaded from the instrument at regular intervals and emailed to Alexander Smirnov for quality control and processing.
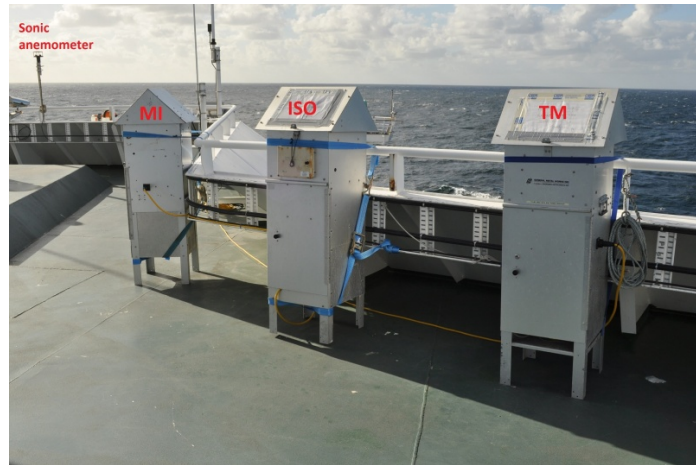
Figure 11. Location of aerosol sampling equipment on starboard wing of monkey island deck during cruise JC068.

Sample ID	Type	Description	START				END*			
			Start time		Start position		End time		End position	
			Date	Time	Latitude	Longitude	Date	Time	Latitude	Longitude
				UT	deg dec.min S	deg dec.min W		UT	deg dec.min S	deg dec.min W
JC068_XX_01	TM, MI, *ISO*	MOTOR BLK	24/12/2011	14:00	34 02.1333	-25 45.7167	24/12/2011	14:00	34 02.1333	-25 45.7167
JC068_XX_02	TM, MI, *ISO*	FILTER BLK	26/12/2011	13:30	n/a	n/a	26/12/2011	13:30	n/a	n/a
JC068_XX_03	TM, MI, *ISO*	CASSETTE BLK	26/12/2011	13:05	34 56.88	-19 20.83	28/12/2011	10:53	35 02.69	-16 00.31
JC068_XX_04	TM, MI, ISO	SAMPLE	28/12/2011	12:00	35 08.69	-15 47.25	30/12/2011	11:05	37 38.65	-11 23.32
JC068_XX_05	TM, MI	SAMPLE	30/12/2011	12:04	37 46.37	-11 13.51	01/01/2012	11:44	40 00.03	-4 50.64
JC068_XX_06	TM, MI, ISO	SAMPLE	01/01/2012	12:49	39 59.96	-4 39.84	03/01/2012	11:48	40 02.27	00 24.34
JC068_XX_07	TM, MI	SAMPLE	03/01/2012	12:47	40 00.89	00 29.99	05/01/2012	12:32	39 57.59	6 18.87
JC068_XX_08	TM, MI, ISO	SAMPLE	05/01/2012	14:49	39 56.25	6 33.63	07/01/2012	09:27	40 15.45	9 51.28
JC068_XX_09	TM, MI	SAMPLE	07/01/2012	10:16	40 13.33	9 49.71	09/01/2012	14:48	39 59.49	15 23.67
JC068_XX_10	TM, MI, ISO	MULTISTAGE	09/01/2012	17:34	40 00.03	16 03.14	11/01/2012	15:13	40 00.35	19 14.90
JC068_XX_11	TM, MI	SAMPLE	11/01/2012	17:01	40 00.07	19 38.49	13/01/2012	14:27	39 59.99	24 19.52
JC068_XX_12	TM, MI, ISO	SAMPLE	13/01/2012	17:51	40 00.00	24 47.55	15/01/2012	14:51	39 59.95	32 27.38
JC068_XX_13	TM, MI	MULTISTAGE	15/01/2012	16:32	39 59.92	32 29.92	19/01/2012	16:14	39 59.99	42 25.00
JC068_XX_14	TM, MI, ISO	SAMPLE	19/01/2012	17:22	40 00.00	42 25.00	22/01/2012	15:29	38 02.53	50 59.56
JC068_XX_15	TM, MI	SAMPLE	22/01/2012	16:46	38 00.10	50 59.95	24/01/2012	15:07	37 01.13	52 29.14
JC068_XX_16	TM, MI, ISO	SAMPLE	24/01/2012	16:23	37 01.15	52 29.48	25/01/2012	18:20	36 31.33	53 07.89
JC068_XX_17	TM, MI, ISO	SAMPLE	25/01/2012	tbc	tbc	tbc	26/01/2012	tbc	tbc	tbc

Table 3. Summary of aerosol samples collected during cruise JC068. Note that end time and position refer only to TM and MI samples; ISO samples typically ran for twice as long, so have the end time and position listed in the row below (except in the case of italicised blanks (*ISO*), which have the end date and position given in the same row. Exact times and positions for final samples (JC068_XX_17) not known at time of writing.

Samples collected

Aerosol: 17 sets of samples were collected for TM and MI and 11 samples were collected for isotopes (see Table 3). This includes three blanks for each sample type.

Rain: Substantial rain events were rare and, when occurring, typically light and/or short lived. Four comparatively small (< 50 mL) sets of rain samples were collected from rain events on 26/12/11, 7/1/12, 13/1/12 and 25/1/12 (see Table 4). Blanks for each sample type were also collected.

| Sample id | Type | Approx. Vol., | Start time | | Start position | |
| | | | Date | Time | Latitude | Longitude |
		mL		UT	deg dec.min N	deg dec.min W
JC068_XX_R01	TM, MI	50	26/12/2011	07:45	34 56.88	-19 20.81
JC068_XX_R02.BLK	TM, MI	100	26/12/2011	12:30	34 56.88	-19 20.83
JC068_XX_R03	TM	35	07/01/2012	20:54	40 00.05	10 57.85
JC068_XX_R04	TM, MI	50	13/01/2012	14:27	39 59.99	24 19.52
JC068_XX_R05	TM, MI	25	13/01/2012	19:48	39 59.94	25 12.36
JC068_XX_R06	TM, MI	10	25/01/2012	04:13	37 01.87	52 30.91

Table 4. Summary of rain samples collected during cruise JC068.

Aerosol optical depth: Cloud cover during much of the cruise prevented many measurements of optical depth being made. In total, only 208 readings were made on 26 separate occasions during the entire cruise.

Sample analysis

Aerosol samples will be extracted into ultrapure water or ammonium acetate and the extracts analysed for soluble TM and MI as described below (Table 5). Rain samples will be analysed by the same methods. Analysis is hoped to be complete by December 2012.

Analyte	Method
Fe, Al, Mn, V, Zn, Na, Mg, K, Ca	ICP-OES
Co, Cd, Ni, Cu, Pb, and Ag and Th if possible	ICP-MS
Total* Fe, Al, Mn *whole filter analysed rather than extract	INAA
Cl^-, NO_3^-, SO_4^{2-}, oxalate, Br^-, plus possibly MSA, formate, acetate	Ion chromatography
NH_4^+	Autoanalyser
PO_4^{3-}	Spectrophotometry
Total soluble N	High temp catalytic oxidation
$\delta^{15}N$ of NO_3^- and NH_4^+	IRMS

Table 5. Summary of analyses to be performed on JC068 aerosol and rain samples by the University of East Anglia.

Additional analyses for aerosol isotopes (mass spectrometry) and organic biomarkers (GC-MS and GC-cIRMS) will be carried out by the project partners listed earlier.

Preliminary results

No aerosol or rain results are available at this time. Aerosol optical depth measurements are shown in Figure 12 and can be obtained from:
http://aeronet.gsfc.nasa.gov/new_web/cruises_new/James_Cook_11_12.html
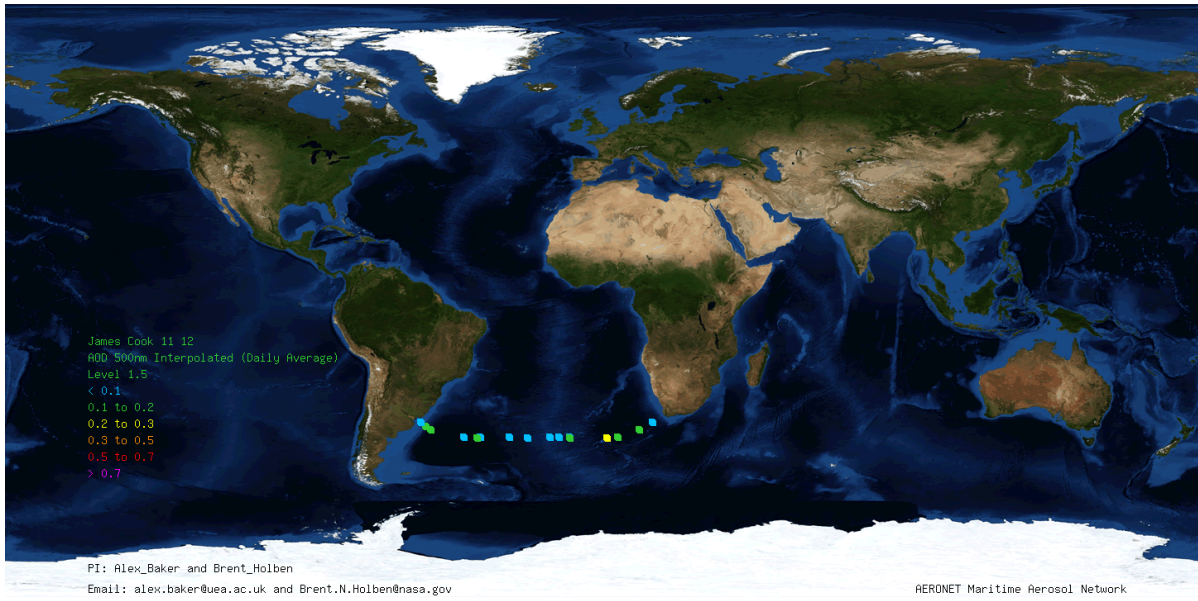
Figure 12. Aerosol optical depth measurements for cruise JC068.

WORKPACKAGE 3: SEDIMENT FLUXES

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3.1 SEDIMENT FLUXES

By William Homoky

Samples collected by Alan Hsieh, Debbie Hembury and Will Homoky

Samples analysed or to be analysed by:

Arne Bratkic (U of Slovenia)	Overlying core water Hg, Sediment Hg
Kate Hendrey (Cardiff)	Overlying core water Si isotopes
Maite Hernandez-Sanchez (Bristol)	Sediment Biomarkers
William Homoky (Southampton)	Sed/Porewater metals, Fe isotopes, bulk properties, O_2, pH
Alan Hsieh (Oxford)	Overlying core water Ra
Seth John (South Carolina)	Overlying core water Fe isotopes
Alex Thomas (Oxford)	Sediment and core water Pa Th
Robyn Turena (Edingburgh)	Particulate organic N
Malcolm Woodward (PML)	Porewater macronutrients

Rationale

The exchange of micronutrients from marine sediments to seawater is scarcely quantified - despite there being substantial gradients in metal concentration between these reservoirs. In the previous decade we have learned shelf-sediments are important sites for micronutrient transport (in particular Fe) to the ocean margins (Elrod et al., 2004). More recently, a modeled approach to understanding the sources of Fe to the oceans has suggested that the deep ocean, as well as the ocean margins, may be an important source of Fe to the water column (Moore and Braucher 2008). Measurements from within 100 m of the seafloor in the Weddell Basin have hinted at a source of Fe from marine sediments (Klunder et al., 2010), and colloidal Fe fluxes have been linked to deep-ocean sediments where labile organic carbon and volcanogenic sediments lead to significant particulate reactions with the porewater (Homoky et al., 2011). The magnitude of Fe supplied to the South Atlantic from either ocean margin or deep-ocean sediments has not been assessed, despite significantly enhanced annual integrated primary productivity in this region of South Atlantic and Southern Ocean mixing. Furthermore, the fluxes of other bio-essential trace metal micronutrients (E.g. Zn, Co and Ni) from any sediment remain largely unconstrained.

Primary Objectives

The primary objective of this work is to quantify the flux of micronutrients between marine sediments and the water column, along the GEOTRACES transect A10. Coring of the intact sediment-seawater interface was necessary to collect sediment and porewater samples for analyses of dissolved trace metals, macronutrients, labile particulate phases, oxygen and pH, in order to constrain the chemical exchanges between surface sediments and the overlying water column. Objective sampling locations can be grouped into 6 regional categories, which collectively describe the sediment interface along the 40°S transect: [1] the South African margin, [2] the Cape Basin [3] volcanogenic (Gough) Island sediments [4] the Mid-Ocean Ridge (MOR), [5] the Argentine Basin and [6] the Uruguayan margin. An earlier cruise (D357) completed in late 2010 sampled regions 1 and 2, leaving regions 3, 4, 5 and 6 as targets for JC068.

Additional sampling objectives

Sediments were also collected to meet the requirements for organic biomarker and palaeoproxy calibrations work funded by the NERC standard grant that provided the ship time for this study. The objectives and rationale for this work are closely aligned with GEOTRACES, and are outlined in a later section of this report - See *Palaeoproxy Calibration* for a description of PaTh, Si isotopes, particulate organic N, and organic biomarkers.

Coring and Sample Recovery

Coring overview
Sediment samples were successfully recovered from 7 of 9 attempted sampling stations. Two core sites failed to recover sediments and succeeded in damaging polycarbonate core tubes. These sites were especially challenging for sediment sampling due to the steep topography typical of Oceanic (Gough) Island and MOR regions. Best efforts were made to use the ships sub-surface profiler and swath bathymetric data to chose level and laminated bottom surfaces at these locations (stations 10 and 12) but were unrewarded.

The successful core sites included East MOR flank sediments from within Antarctic Intermediate Water (AAIW) and a transect of 5 sites from the Argentine Basin (beneath Antarctic Bottom Water - AABW) up the Uruguayan margin, to the shelf top, at just 59 m. This transect also includes two super stations (sites 18 and 21).

The Bowers Connelly Mega Core was the tool of choice used exclusively throughout JC068, as it not only recovered pristine sediment surfaces in approximately 25-75% of cores, but also trapped overlying bottom water, which was sampled throughout this cruise. Eight core tubes mounted to the frame provided an excess of recovered cores from which the best 5 cores were selected for a complete sampling inventory.

Photo log of recovered cores
See Electronic Annex for a photographic record of coring activities on JC068.

Sampling protocol
Mega core samples were removed from the coring frame, photo-documented (see www.ukgeotraces.com/restricted) and immediately transferred to the Controlled Temperature (CT) laboratory, which was set close to bottom water temperatures at 4±2 °C.

Oxygen sampling
For O_2 analyses, a 25 cm long (9.8 cm $\varnothing$) core tube was used, into which a sediment core and its overlying core water was directly extruded by NOCS apparatus. The sub-sampled core was then stopped at its base, wiped clean and transferred to the Unisense microelectrode suite for O_2 profiling of the sediment surface (See *Shipboard Measurements* below for further details).

Overlying core water filtration
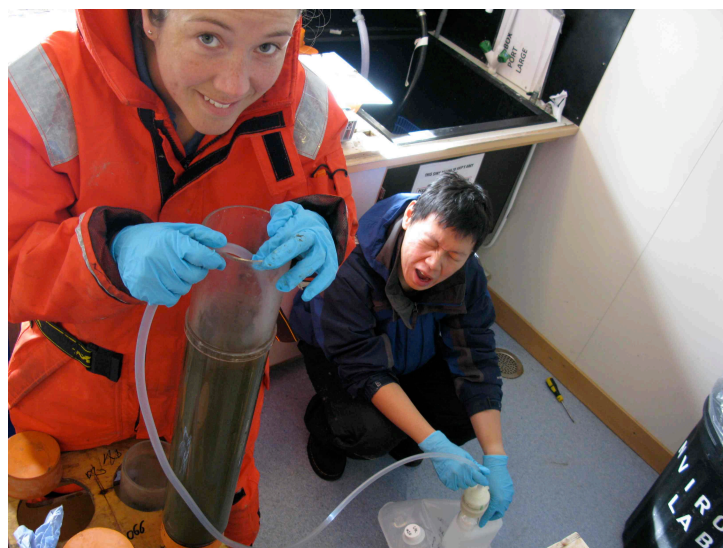
Figure 13. Early morning filtering of overlying core water for an Ra sample.

Water overlying intact Mega Cores was sampled as an in-situ benthic bottom water sample for Ra, Si isotopes, Fe isotopes, PaTh and Hg. Samples were collected by priming a Tygon tube with Milli-Q water and siphoning the overlying core water through a 0.4 µm Acropak filter into clean containers provided by their respective analysts (Figure 13). The Hg sample was collected by the same method, only without the in-line Acropak, to collect unfiltered samples.

Sediment Centrifugation and Filtration

For porewater nutrients and dissolved and colloidal metals, each mega core tube followed a similar extrusion procedure as for O_2: A 35cm core tube (6.5 cm $\varnothing$)
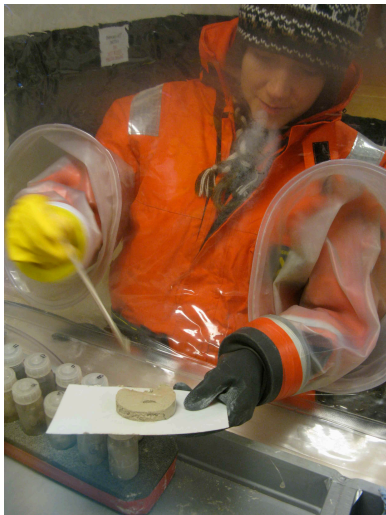
collected a push core subsample to optimise sample depth and permit a manageable size core to fit through the air lock entrance of the table mounted glove bag (Figure 14 top) . The glove bag was pre-purged with Zero grade N_2 gas passed through a Hepa filter. A SensorTech Gas Alert Extreme monitor was used to assess the oxygen concentration in the glove bag. Once anoxic conditions had been established, the core was transferred to a sub-core-sized table mounted extruder. Excess overlying core water was siphoned to waste, and the core was extruded at 1 cm resolution for the surface 0-5 or 0-6 cmbsf, then at 2 cm resolution to the bottom of the core sample, using polycarbonate sectioning rings and a teflon plate and spatula (Figure 14 bottom). Sediment was transferred directly to 85 ml Decon and HCl-cleaned polycarbonate centrifuge tubes. Sealed centrifuge tubes were transferred to a gimbaled centrifuge at 4°C and spun for 10 minutes at 10,000rpm.

Spun sediments were returned to a disposable Cole Palmer glove Bag in the CT lab, and re-opened under an N_2 atmosphere. Supernatant porewater was separated from the sediment using a Teflon tube attached to a Decon, HCl and HNO_3 clean (in this section refered to as "acid clean") 20 ml 'BD Discardit' syringe and then filtered directly through a Whatman Puradisc 0.2 μm Cellulose Acetate 25 mm disposable syringe filter, passing the first 0.5 ml to waste and the remaining sample into 8 ml acid clean LDPE sample pots for trace metals. An aliquot was also transferred to 30 ml HDPE pots for shipboard nutrient analyses by

Figure 14. Top Left: Extruding a sediment sub-core from a Mega Core, in preparation for anoxic pore water extraction. Bottom Left: A Teflon cut section of sediment core being transferred to centrifuge tubes under an N_2 atmosphere at constant temperature (4±2°C).

Malcolm Woodward, or frozen at sea (-20°C) for analysis at PML.

Where porewater volume permitted, additional samples were taken for separation of colloidal metals or preservation of porewater Ligands. For colloidal separation a filter was added inline to the Puradisc for seperation of the colloidal fraction of metals in the porewater (Figure 15). A disposable Whatman Anotop 0.02 μm 25 mm aluminium oxide filter was used for colloidal filtration. All filters were pre-purged with Hepa filtered zero grade N_2 gas prior to sampling to ensure residual oxygen in the filter housing did not produce oxide artifacts. Anaotop filters allowed for 1-4 ml volumes to be passed through the membrane. Used filter housings where internally rinsed with milli-q rinsed and flushed with filtered zero grade N2 gas to remove salts, then stored dark and cold to preserve colloidal fractions for subsequent shore based analyses.

A single full depth Ligand sample profile of 0.2 μm-filtered porewater was transferred to acid clean LDPE and frozen (-20°C) for shore based analyses by Christian Schlosser (Southampton).

The sediment residue from each porewater sample was removed from centrifuge tubes by Teflon spatula, double bagged and refrigerated for later combined analyses of total solid-phase metal concentrations, organic and inorganic carbon concentrations, reactive Fe compositions (Will Homoky) and Pa/Th (Alex Thomas).

Figure 15. Low temperature in-line separation of porewater colloids from the dissolved size fraction under N_2 atmosphere.

Rhizon Filtration
Rhizon samplers have previously been used to measure macro- and micro-nutrients from surface sediments in shelf settings (Homoky et al., 2009; Severmann et al., 2010), and have been favorably compared to centrifuge techniques (Hembury et al., 2012;

Homoky et al., 2012) with a common exception: Nitrate concentrations determined by centrifugation sometimes appear unreasonably elevated - a feature attributed to biological artifacts during spinning (Hammond et al., 1996, Homoky et al., 2012). We made similar observations between spun and rhizon sampled porewater nutrients from D357 the proceeding year, so on JC68 we resorted to using just Rhizons for nutrient sampling.

A sub-core tube 35 cm sub-coring tube was pre-drilled at 1cm intervals along its length to allow for the insertion of 50 mm long, 2.5 mm wide, 0.15 µm membrane Rhizon samplers. Drill holes were sealed with electrical insulation tape, prior to sub-sampling from the mega core (Figure 14, above). The sub-sampled cores either inserted carefully up to a sealed end, to allow the core to be laid horizontally, or left stanging upright in secure racking. The insulation tape was perforated, using a clean stainless steel blade, and individula Rhizons inserted at 1 cm depth intervals at 0-6 cmbsf, and 2, 3 or 4 cm intervals below 6 cmbsf. All Rhizons were attached with Luer lock fittings to the acid clean "BD Discardit" syringes and used to simultaneously draw porewater from the sediment core (Figure 16).

Figure 16. Rhizon samplers drawing porewater for macronutrients.

Drawn samples were collected in 30ml HDPE pots for shipboard nutrient analysis or kept frozen for analysis at PML (Woodward). Where sample volume permitted (Stations 18, 21, 22, and 23) a separate porewater aliquot was preserved in acid clean 8ml LDPE pots for future analysis, such as Zn concentration by chemiluminessence (Maeve Lohan).

Organic Biomarker sampling
Sediment cores for biomarker analyses were frozen whole (-20°C) after the sampling of overlying core water (as described above). Frozen cores were later extruded directly onto pre-ashed aluminium foil, wrapped, bagged and returned to the freezer for return to the UK. One core, from super station 21, was sectioned at 1cm depth resolution using a milli-q rinsed and acetone dried Teflon

sheet. Sectioned samples were individually wrapped in pre-ashed foil and immediately frozen for return to the UK.

Archive core sampling

Archive sediment cores were sub-sampled by push core following the same sub-sampling approach for centrifugation and Rhizon samples (Figure 14). Polypropylene core tubes were individually prepared for the appropriate sample depth, capped at each end and stored refrigerated for return to the UK.

Samples Collected

Seven stations were sampled for sediment, porewater and core water: sufficient for a broad range of bio/geochemical analyses. See documents at www.ukgeotraces.com/restricted for a detailed record of sampling activity.

3.2 SHIPBOARD MEASUREMENTS

By William Homoky

Our transect for WP3 benefitted from shipboard determinations of high-resolution O_2 profiles and some pH profiles of the sediment surface, in addition to porewater nutrient determinations made by Malcolm Woodward. Combined, these ancillary data provide a powerful means for interpreting the behavior of metals such as Fe and Mn in the porewater during early diagenesis. The method used for determination of O_2 and pH by microelectrode is described below followed by a discussion of preliminary results.

O_2 profiling of surface sediment

Figure 17. Surface sediment micro-profiling of O_2 and pH using an M33-2 micromanipulator. The Cal300 chamber sits to the left of the core sample. pH reference electrode and an air stream (to promote surface water mixing) are held in a lab stand to the right of the core sample.

Shipboard dissolved oxygen concentration profiles were measured in surface sediments using Unisense micro-electrode equipment (Figure 17); including micro-sensors with 100 and 50 μm tip diameter, M33-2 micromanipulator, LS18 lab stand, MC-232 motor drive, PA2000 Pico-ammeter, and ProSens software. All analyses were conducted in the controlled temperature laboratory at 4±2°C.

Oxygen micro-sensors were calibrated using a Unisense Cal300 chamber. A 2-point linear dissolved oxygen calibration was obtained from 100% (oxic) and 0% (anoxic) saturated solutions. The 100% oxygen saturation value was determined by placing the micro-sensors in the calibration chamber with an aerated seawater sample of equivalent temperature and salinity to the porewaters. The corresponding oxic voltage was recorded in after a period of stabilisation, which was typically 0.5 to 0.98 V depending on the oxygen sensor used. Anoxic oxygen saturation values were determined by passing nitrogen gas through the chamber for 5 to 10 minutes until the sensor output decreased and stabilised to within 0.001 V. Unisense recommends a calibration only be used when the anoxic voltage is less than 10% of the oxic voltage to ensure sufficient accuracy of analyses. During JC068 anoxic readings were ~0.003 V, ~0.3-0.6% of the oxic value.

Sediment cores were allowed to settle and re-equilibrate for ~20 minutes after sub-sampling. Oxygen profiles were recorded from ~1 mm above the sediment surface to a maximum depth of 90 mm and a sampling resolution of between 100 and 250 μm steps. Recorded oxygen concentration values are converted to molar concentrations directly by Unisense ProSens software, by manually inserting observations of temperature and salinity. Raw and uncalibrated data files are also stored should calibrations need to be adjusted for unforeseen reasons.

pH profiling of surface sediment

The pH profiling of surface sediments was conducted in parallel with the oxygen microsensors (Figure 17). The pH microelectrode (500 μm tip diameter) was first calibrated using a 3-point calibration of buffered standards (4, 7 and 9.2 - Fisher Scientific) following Unisense recommendations. The pH microelectrode was inserted into each pH buffer solution along with a reference electrode. ProSens software recorded the resultant voltage, and three calibration points were taken once the signal had stabilised in each solution (approximately 2-3 minutes). The micro and reference electrodes were Milli-Q rinsed between solutions and profiling. Typical calibrations produced r^2 values of ~0.98.

We did experience some unaccountable drift in pH values, the source of which could not be identified. Despite having an electrical 'ground' reference, it is possible that ships operations produce electrical noise sufficient to cause these occasional disturbances, as the pH microelectrodes are extremely sensitive to electrical interference. In some cases this meant the pH profiles were unusable. In other instances, the pH profiles appear reasonable only offset downcore by ~0.5 pH units from their theoretical true value. These data will need to be explored in more detail to reveal their potential usefulness.

Preliminary results

A comparison of dissolved oxygen concentration profiles between core sites on JC068 is shown in Figure 18. The shallowest oxygen penetration depths have been measured towards the top of the shelf slope - stations 22 and 23 respectively. Station 22 coincides with the depth of a broad and slight oxygen minimum zone (OMZ) and Transmission minimum (suspended particle maxima) identified by CTD (see CTD profile 058/059). The shelf top site (station 24) appears to be more oxygenated in the surface centimetre than stations 22 and 23. This probably reflects (i) the site susceptibility to sediment remobilization, transport and winnowing by bottom currents and (ii) enhanced advection at this site due to the coarser lithology of these sediments (fine-medium sands).
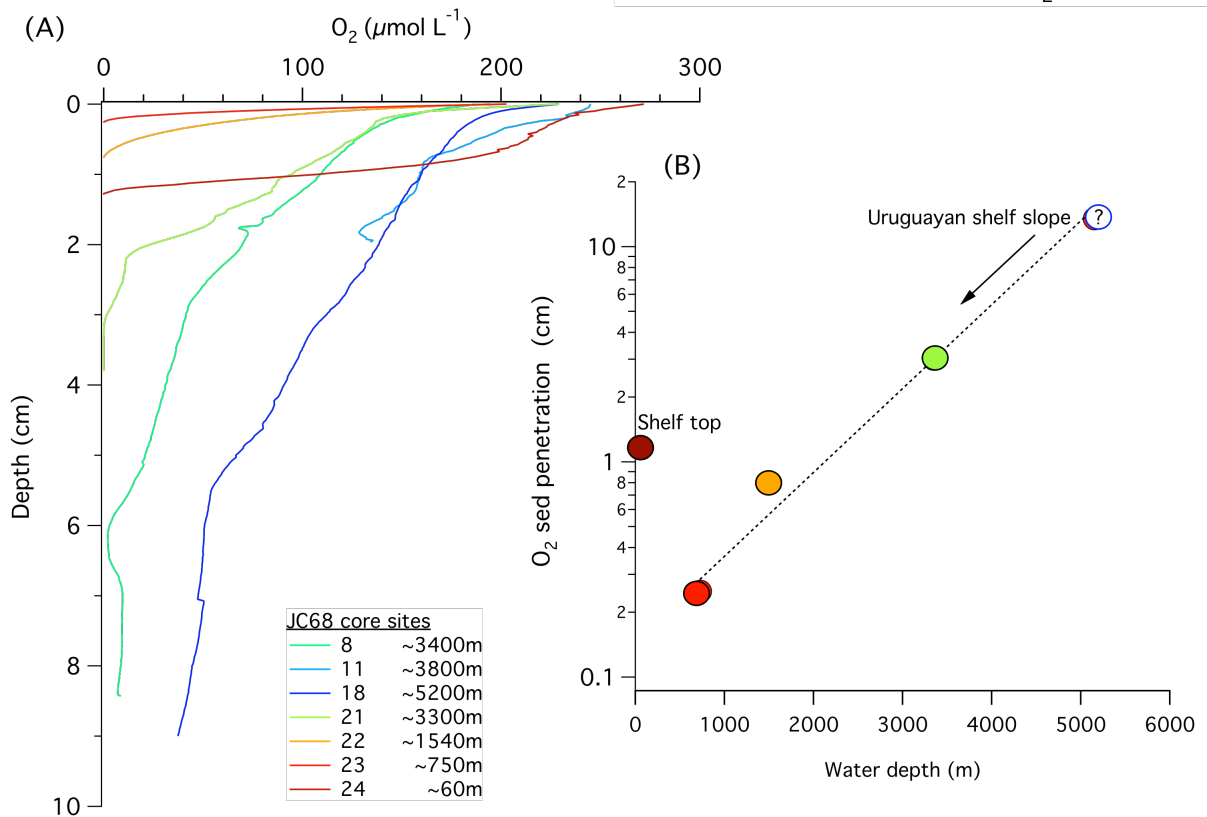
Figure 18. (A) Dissolved oxygen concentration in surface sediments of JC068 core sites, and (B) oxygen penetration depth as a function of water depth on the Uruguayan margin.

Oxygen penetration depths are also consistent with the release of nitrate and its subsequent utilisation during the respiration of organic carbon in surface sediments (Froelich et al., 1979) (Figure 19).

Implications for micronutrient fluxes from sediments

Until the dissolved Fe contents of these porewaters has been determined, the behaviour of Fe at these sites is entirely speculative, and based on the comparison of shipboard determinations for oxygen and nitrate with previous studies of benthic Fe fluxes. Substantial Fe fluxes have been identified from sediments where the oxygen penetration depths lie within a heavily bio-irrigated mixed surface-layer of the sediments (Berelson et al., 2003; Severmann et al., 2010), and where sub-surface Fe maxima (typically 10-100 µM) exist beneath shallow oxygen penetration depths (<1 cmbsf) (Homoky et al., 2012).

Bioirrigating worm tubes were identified in cores from sites 21 (3300m) and 24 (60m) of the Uruguyuan margin. Qualitatively, the presence of this biota indicates that solute exchange at these sites is in part controlled by sediment-irrigation. Oxygen penetration is just 7 and 2.5 mm at sites 22 (1500m) and 23 (750m), respectfully. Figure 18 shows that shelf slope sediments down to ~2000m may have oxygen penetration depths shallower than 1cmbsf – indicating the entire upper shelf slope of the Uruguayan margin may be an important source of macronutrients to 40°S. Although oxygen penetration is deeper on the shelf top (1.2 cm at 59m water depth), advective processes (outlined above) may enhance Fe exchange with the overlying

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seawater - a phenomenon that could make diffusion-reaction modeling of porewater Fe more challenging at this location.
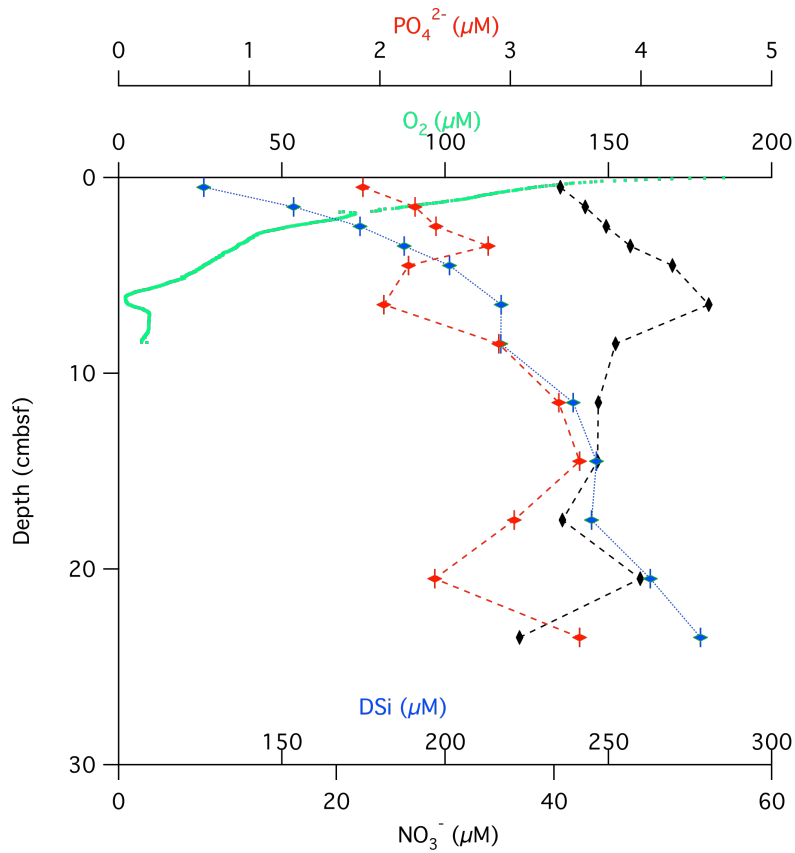
Figure 19. Comparison of station 18 (5156 m) shipboard O$_2$ profile and porewater macronutrient determinations sampled by Rhizons and analyzed by Malcolm Woodward (See WP8).

Acknowledgments

Kevin Smith (NMF)

The sediment team enjoy a Cafe Latte break

References

Berelson, W., McManus, J., Coale, K., Johnson, K., Burdige, D., Kilgore, T., Colodner, D., Chavez, F., Kudela, R., and Boucher, J., 2003. A time series of benthic flux measurements from Monterey Bay, CA. *Continental Shelf Research* **23**, 457.

Elrod, V. A., Berelson, W. M., Coale, K. H., and Johnson, K. S., 2004. The flux of iron from continental shelf sediments: A missing source for global budgets. *Geophysical Research Letters* **31**, art. no.-L12307.

Froelich, P. N., Klinkhammer, G. P., Bender, M. L., Luedtke, N. A., Heath, G. R., Cullen, D., Dauphin, P., Hammond, D., Hartman, B., and Maynard, V., 1979. Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis. *Geochimica et Cosmochimica Acta* **43**, 1075-1090.

Hammond, D. E., McManus, J., Berelson, W. M., Kilgore, T. E., and Pope, R. H., 1996. Early Diagenesis of organic material in Equatorial Pacific sediments: stoichiometry and kinetics. *Deep Sea Research Part II: Topical Studies in Oceanography* **43**(6): 1365-1412.

Hembury, D., Palmer, M.R., Fones. G.R., Mills, R.A., 2012. Comparison of porewater extraction methods for nutrient and trace metal profiles in volcanic sediments. Submitted to *Limnology and Oceanography Methods*.

Homoky, W. B., Hembury, D., Hepburn, L., Mills, R. A., Statham P.J., Fones, G., and Palmer, M., Behaviour of Fe and Mn during the marine diagenesis of volcanogenic sediments. *Geochim. Cosmochim. Acta*, **75**: 5032–5048.

Homoky, W. B., Severmann, S., Riedel, T. E., Statham, P. J., Mills, R. A., Berelson W. M., McManus J., 2012 . The influence of oxygen and suspended particles on the benthic flux of iron determined by *ex situ* shelf sediment and seawater incubation. *Marine Chemistry*, In Press.

Homoky, W. B., Severmann, S., Mills, R. A., Statham, P. J., and Fones, G. R., 2009. Pore-fluid Fe isotopes reflect the extent of benthic Fe redox recycling: Evidence from continental shelf and deep-sea sediments. *Geology* **37**, 751-754.

Klunder, M., Laan, P., Middag, R., and de Baar, H. J. W., 2010. Dissolved Iron in the Southern Ocean. *Deep Sea Research Part II Oceanographic Research Papers* Polarstern ANT XXIV/3 Special issue.

Lohan, M. C. and Bruland, K. W., 2008. Elevated Fe(II) and Dissolved Fe in Hypoxic Shelf Waters off Oregon and Washington: An Enhanced Source of Iron to Coastal Upwelling Regimes. *Environmental Science & Technology* **42**, 6462-6468.

Severmann, S., McManus, J., Berelson, W. M., and Hammond, D. E., 2010. The continental shelf benthic iron flux and its isotope composition. *Geochimica et Cosmochimica Acta* **74**, 3984-4004.

Workpackage 4: Elemental and Isotopic Tracers of Micronutrient Source

4.1 Radium and actinium isotopes in surface waters

By Walter Geibert

Samples to be analysed by Walter Geibert (Edinburgh) and Alan Hsieh (Oxford)

Objectives
The advection of micronutrient-rich water from shelf regions to the open ocean has been identified as an important supply mechanism for micronutrients. Possible sources for micronutrients include river discharge, submarine groundwater discharge, and diffusive release from shelf sediments. Satellite images of ocean colour suggest a potentially large role of shelf or island sources in iron-limited regions, and the importance of these sources has actually been shown for subantarctic islands with underwater shelf-like plateaus (Blain et al. 2007; Charette et al. 2007), partially by means of radium isotopes.
Therefore, radium isotopes were supposed to be studied in surface waters in order to identify potential transport routes of micronutrients from the shelf regions, in particular near the coast of South America, and around Gough Island. Near the coast, micronutrient supply by horizontal mixing of micronutrient rich waters can be quantified with radium isotopes.
In summary, the objectives were
  1) An assessment of offshore mixing rates on the South American shelf
  2) The measurement of radium concentrations (^{223}Ra, ^{224}Ra, ^{228}Ra) in the vicinity of Gough Island, and if possible an assessment of mixing rates
  3) Exploring the potential use of radium isotopes for near-surface mixing studies near South Africa.

Sampling protocol
Three types of samples were collected from surface waters:
  1) from the clean surface water supply (fish)
  2) samples from Niskin bottles of the standard stainless steel CTD rosette
  3) from the standalone pumping systems (SAPS),
Samples for 1) and 2) were collected in LDPE collapsible containers (cubitainers), ~22.5 L volume. Sample volumes range from ~50 L to ~160 L, in most cases the sample volumes were around 160L for samples from the clean surface water supply (fish), and 60-80 L from the CTD. These samples were slowly (flow rate <0.5 L/min) passed over one absorber, consiting of ~25 g MnO_2 coated acrylic fiber
SAPS samples for Ra/Ac and biomarkers usually comprised around 200-500 L, pumped over MnO_2 absorbers in situ. The absorbers consisted of a set of two MnO2 absorbers in series, contained in modified polycarbonate cartridges, each filled with ~10 g of MnO_2 fiber inside (amount reduced to maintain flow rates at an acceptable level for the associated sampling of biomarkers. The sampling was combined with particulate biomarker measurements, which meant the Ac/Ra sampling took place behind two 293 mm GF/F filter (double layer).
SAPS sampling was also performed for particulate trace metals and ^{234}Th on large particles. For the latter samples, a NITEX 53 μm mesh was used, followed by a 1 μm

polyethersulfone (PES) filter (Supor ®). Sample volumes up to 1400 L were achieved with this combination, more regularly around 500 L. Typically, 8 SAPS were deployed in parallel.

The two types of SAPS were always separated vertically by at least 20 m in the water column. Before deployment, filter heads and cartridge holders of the pumps were primed with Milli-Q.

Sampling

1) Samples from the clean surface water supply were taken upon leaving of the station, because the clean supply was switched off when the ship was on station. Sampling of 160 liters took ~50 minutes. Therefore, the surface samples do not represent a single location, but an interval.

2) Samples from the standard CTD rosette were taken from several 20 L Niskin bottles, typically 2-5, triggered at the same depth. Sample depths were adapted to the available water depth and hydrography.

A small volume sample (250mL) was taken for each large-volume sample for the independent analysis of ^{226}Ra via mass spectrometry (Hsieh).

3) Submersible pumps (SAPS, Challenger Oceanic) were used to sample the entire water column by pumping water in situ over two MnO_2 absorbers. After a SAPS test deployment close to South Africa, regular sampling was performed at superstations (12, 18, 21), with two deployments of 8 pumps each for these superstations, separated by at least the time required to recharge the batteries.

Determination of sample mass

Sample mass was determined with a scale (make Kern, max. 35 kg, d=0.02 kg), that provided an averaging/ weight hold function. This function was not sufficient to reach consistent weights with a single averaging cycle when the ship was rolling. Therefore, each cubitainer was weighed 10 times using the hold function, and averages were found to give consistent sample masses.

Determination of sample volume for 3) (SAPS)

Sample volume was determined by a flowmeter. The flowmeter of one pump turned out to display gallons, and an appropriate correction was applied (factor 4.5).

Samples collected

A total of 32 samples were taken for analysis of all 4 Ra isotopes from underway sampling, as well as 16 Niskin bottle samples up to 600 m water depth, consisting of approximately 5000 kg sea water in total. In addition, the concentration of ^{227}Ac will be determined by means of delayed coincidence counting (Geibert et al. 2008) from these samples.

25 samples for Ra/Ac analysis and biomarkers were collected with the standalone pumping systems (SAPS), two of which failed due to electric/electronic problems with the respective SAPS. A full record of SAPS deployments has been made available as a spreadsheet on the server.

Sample analysis

Sample were analysed on board for short-lived radium isotopes by means of a four-channel radium delayed coincidence counter system (RaDeCC, (Moore and Arnold 1996). Briefly, the MnO_2 fiber containing the sample is placed in a recirculated He stream. A connected scintillation counter detects decay events from radon isotopes. Delay times between subsequent decays are used to discriminate between the Rn isotopes, and so indirectly between short-lived Ra isotopes. A second measurement will be required after all excess short-lived radium has decayed.

The counter was calibrated regularly with two standard samples of the short-lived Ra parent nuclides ^{227}Ac and ^{228}Th, which had been obtained from IAEA-MEL Monaco (J. Scholten) in 2009. The counter was run empty with non-recirculated air at regular intervals in order to ensure that the scintillation cell was dry and efficiency was not affected by moisture.

The calculation considers chance coincidence events. Adsorption efficiency of actinium and radium isotopes for the MnO_2 adsorbers is assumed to be 100% for the flow rates used here. For SAPS samples, the efficiency will be assessed by means of an independent measurement of ^{226}Ra, and a transfer of the observed adsorption efficiency to the other Ra isotopes. For Ac, the ratio of the concentration found on two subsequent adsorbers will be used to calculate the efficiency, plus the initial assessment of ^{223}Ra, which can be assumed to be in equilibrium with ^{227}Ac for pelagic conditions.

After the counting for short-lived isotopes has been finished (after all excess ^{223}Ra has decayed to levels supported by ^{227}Ac, approximately three months), the Mn fiber will re-counted for supported activities (reflecting ^{227}Ac for ^{223}Ra, and ^{228}Th for ^{224}Ra), then it will be ashed. The ^{228}Ra/^{226}Ra ratio will be measured by MC-ICP-MS in Oxford. Together with the absolute ^{226}Ra concentration from the subsample, the ^{228}Ra concentration can be calculated. This procedure has already been completed for the samples from GA10E, and a manuscript is in preparation (Hsieh et al. in prep.)

The methods of using MC-ICP-MS to measure ^{226}Ra concentrations and ^{228}Ra/^{226}Ra ratios are followed by Foster et al. (2004) and the new technique developed by Hsieh et al. (2011), respectively. A ^{228}Ra spike is used to determine ^{226}Ra concentrations and chemical blanks. For ^{226}Ra samples, Ra is pre-concentrated by the precipitation of $CaCO_3$ from seawater then sequentially purified by AG1-X8, AG50-X8 and Sr-spec column chemistries. For ^{228}Ra/^{226}Ra samples (Mn-fibers), ashed fibers are leached with 30 mL 6N HCl then centrifuged to remove Ra. The precipitation of $SrSO_4$ in the HCl solution and the following conversion of $SrSO_4$ to $SrCO_3$ are used to purify Ra before column chemistries (AG50-X8 and Sr-spec).

A few samples which would obviously not contain short-lived Ra excess will not be analysed for short-lived Ra isotopes.

Preliminary results

Some excess ^{224}Ra and ^{223}Ra were found in surface waters very close to South Africa. 224Ra supported in surface waters then decreased continuously on the way to Gough Island. Slightly elevated 224Ra total was observed near Gough Island, but at the end of the cruise, it can not yet be clarified whether it is actually due to excess 224Ra. ^{223}Ra is supported by ^{227}Ac (except a potential small depletion in surface waters due to the particle-reactive intermediate ^{227}Th). ^{224}Ra is essentially supported by ^{228}Th, which in turn reflects the distribution of ^{228}Ra, dimished by particulate Th removal over the time scale of this tracer (1.8 years). ^{228}Th is particle reactive, and with a comparatively long half-life of 1.8 years, it is depleted compared to ^{228}Ra, and remineralized at greater depths. This proved to yield interesting information on long-term particulate fluxes in comparison with the ^{228}Ra data in GA10E, and the ^{228}Th-derived particle-flux dataset can be completed with the data from GA10W soon.

4.2 NEODYMIUM ISOTOPES

By Alex Thomas

Samples to be analysed by Alex Piotrowski

<u>Objectives</u>

The isotopic composition of, the rare earth element, neodymium (Nd) has been used as a tracer of water masses. Variability of Nd isotopes exist because of the production of ^{143}Nd from the alpha decay of ^{147}Sm (Samarium, half live = 1.06 x 10^{11} years). Formation of continental crust leads to elevated Nd/Sm elemental ratios due to the compatibility of Sm during mantle melting, and over time this leads to relatively lower amounts of ^{143}Nd in-growth in continental rocks relative to those more recently derived from the mantle. From the limited a data for water column Nd isotope composition available it appears that the oceans water-masses inherit their isotopic composition from the regions where they form. Water from the North Atlantic which is surrounded by old continental rocks, therefore, has a characteristically low ^{143}Nd/^{144}Nd ratio whereas the pacific which is surrounded by young volcanic rocks recently derived from the mantle has a higher ^{143}Nd/^{144}Nd. The residence time of Nd in the oceans is of the order of a few thousand years, which is similar to the circulation time of the oceans. This makes Nd a potential tracer for water mass source. The Nd in the water column is eventually removed to the sea floor by scavenging. Recovery of the Nd isotopic composition from ocean sediments has therefore been used to reconstruct past water mass distributions and therefore reconstruct ocean circulation patterns(Piotrowski et al. 2004; Roberts et al. 2010).

Numerous questions, however, still remain over the use of Nd isotopes as a paleoceanographic proxy(Goldstein and Hemming 2003). The mechanism of how the water masses gain their Nd and how the isotope ratio is preserved and "protected" from further addition of Nd during the history of the water mass is unknown. Also, concentration profiles of Nd show increasing concentrations with depth suggesting a reversible scavenging process. Such and increase of concentration requires a redistribution of Nd through the water column and it is unclear whether this effects the Nd isotope ratio. This transect of data at 40S will be useful in answering these questions especially since the Nd isotope measurements will be augmented with REE concentrations, as well as Fe, Mn, Al, and Th concentrations which will be highlight any potential sources of Nd to the water column (dust, sediment diagenesis, hydrothermal) which could effect the isotope ratio.

<u>Sampling protocol</u>

Water samples
Nd isotopes are to be measured on chemical separated from Pa-Th samples: Up to 10L of seawater was sampled for each depth from 20L OTE bottles, into 10L acid cleaned HDPE bottles. Samples were taken from the rosette on deck, taking special precaution not to put the bottles down on the deck, to reduce risk of contamination from the ship. Large plastic boxes were employed to hold samples during filtration to avoid contact with the ship. Samples were filtered directly from the OTE bottles through 0.45um AcroPak 500 capsules, using PVC tubing. Prior to used each AcroPak was rinsed with filtered surface water from the trace metal clean fish. Capsules were reused until flow rates were noticeably reduced. To reduce cross-contamination AcroPaks were rinsed with ~100mL of sample before rinsing the sample bottle with ~100mL of sample prior to filling. If insufficient sample was

recovered from a single bottle two OTE bottles contents were combined only if they were fired at the sample nominal depth. Occasionally where not near surface water weas available from the rosette a sample from the surface fish was taken. Once filled samples were capped and transferred into the Chemistry Laboratory were they were acidified with 12mL of 10N HCl (quartz distilled), the samples were shaken and the pH checked to be <1.5. Samples bottle caps were sealed with Parafilm and bagged before being stored in boxes for transport back to Oxford.

<u>Samples collected</u>

Details of samples collected are presented in the section for Pa/Th.

<u>Sample analysis</u>

Samples will be processed for Pa and Th analysis, with the Nd and REE fraction being separated along with the Fe used for co-precipitation during anion exchange chromatography. This aliquot will be sent to Cambridge (Piotrowski) for further Nd purification and then measurement of Nd isotope ratio ($^{143}Nd/^{144}Nd$) will be made using a Nu Instruments MC-ICP-MS (Piotrowski et al. 2009).

<u>References:</u>

Goldstein, S. L. and S. R. Hemming (2003). Long-lived isotopic tracers in oceanography, paleoceanography, and ice-sheet dynamics. <u>Treatise on Geochemistry: The Oceans and Marine Geochemistry</u>. H. D. Holland. Elsevier**:** 453-489.
Piotrowski, A. M., V. K. Banakar, et al. (2009). "Indian Ocean circulation and productivity during the last glacial cycle." <u>Earth and Planetary Science Letters</u> **285**(1-2): 179-189.
Piotrowski, A. M., S. L. Goldstein, et al. (2004). "Intensification and variability of ocean thermohaline circulation through the last deglaciation." <u>Earth and Planetary Science Letters</u> **225**(1-2): 205-220.
Roberts, N. L., A. M. Piotrowski, et al. (2010). "Synchronous Deglacial Overturning and Water Mass Source Changes." <u>Science</u> **327**(5961): 75-78.

4.3 NOBEL GASES AND TRITIUM

By Róisín Moriarty

Samples to be analysed by Róisín Moriarty at the University of Manchester
Contact roisin.moriarty@manchester.ac.uk

Objectives

Noble gases, helium and tritium may be used to identify the origins of a water mass. They help elucidate mixing and dilution rates, circulation patterns, ocean ventilation and the changes that occur in water mass characteristics over time. As part of the UK GEOTRACES tracers team our primary role is to collect samples of noble gas isotopes for analysis at the University of Manchester. We are interested in the entire suite of dissolved noble gases, including argon, and tritium (^{3}H, an isotope of hydrogen) but helium (^{3}He and ^{4}He) and, neon (^{20}Ne) are our primary focus.

The concentration of helium in the atmosphere is ~5 ppm. It has very low solubility in seawater (2 nmol/Kg). Helium in the atmosphere is a mixture of two stable isotopes ^{3}He and ^{4}He. The isotopic ratio of ^{3}He/^{4}He is 1.4×10^{-6} in air with ^{4}He being one million times more prolific than ^{3}He. Helium in the surface waters of the world ocean is in solubility equilibrium with the atmosphere. Volcanic and hydrothermal activity on the sea floor are a source of helium to intermediate depth waters in the ocean. The ratio of ^{3}He/^{4}He in helium that originates from mantle out gassing is between ten and thirty times greater than the atmospheric ^{3}He/^{4}He ratio. ^{3}He/^{4}He ratios are therefore a useful indicator of the origin of intermediate depth waters.

Alongside hydrothermal inputs of ^{3}He there are also atmospheric inputs of ^{3}He and in order to separate this signal from terrigenic ^{3}He released from the Mid Atlantic Ridge we also measure ^{20}Ne which comes only from the atmosphere.

Argon will be measured as a matter of course and data supplied to Patrick Martin who will use Ar/O$_2$ ratios to estimate net community production in the surface layer.

Tritium was first detected in the environment in the late 1940s. As tritium is an isotope of hydrogen it is oxidized to HTO (tritiated water) and so is the perfect tracer for studies of the natural water cycle. The applications of bomb tritium are limited as an aging tool in waters that have been in contact with the surface oceans after the 1970s and 1980s as concentrations decreased below those which allow the age of water mass to be determined. However, if we measure tritium and it radioactive decay product – tritugenic ^{3}He – simultaneously we can calculate the tritium/^{3}He age of the water mass (the amount of time the water parcel has been isolated from the surface of the ocean). (Clarke et al. 1976). As tritium is a source of ^{3}He in certain water masses there is a non-negligble tritugenic ^{3}He source that needs to be corrected for to separate large-scale background ^{3}He from terregenic sources.

Scientific rational

There are very few measurements of micronutrients at depth in the oceans and information on the distribution and concentration of most micronutrients in the oceans are unknown. Terrigenic or volcanic ^{3}He is produced on the sea floor in hydrothermal vent areas, which are usually found at sea-floor spreading centers, the Mid Atlantic Ridge (MAR) being one such area. Micronutrients are known to be released along mid ocean ridges (MORs) but there are only very sparce micronutrient observations in intermediate and deep waters. Using a ^{3}He as a tracer of hydrothermal source

inputs we hope to identify iron and other micronutrient inputs from hydrothermal sources. Iron is a primary interest on this UK GEOTRACES section. Up until recently it was thought that the amount of dissolved iron supplied to the ocean from mid ocean ridges was limited as iron from hydrothermal vents precipitates out of solution very quickly. Recent work suggests that there is an increase in dissolved iron concentration around mid ocean ridges as iron binding ligands prevent iron from precipitating out of solution (Bennett et al. 2008). In the oceans, ligands usually take the form of organic compounds produced by micro-organisms, but little is really known about their composition and origin. Noble gases (helium ratios and neon) along with tritium allow us to identify source inputs of micronutrient from the MAR and allow us to trace the scavenging of micronutrients away from the hydrothermal vent source. Understanding the distribution of terrigenic [3]He can help to identify the source inputs of micronutrients along 40°S.
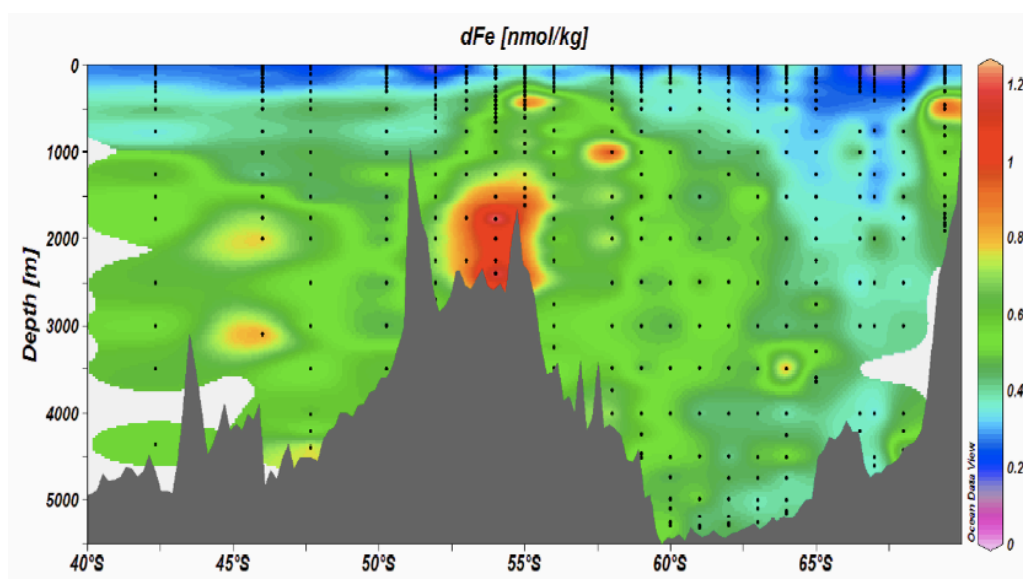
Figure 20: A cross-section showing the concentration of dissolved iron in seawater, with an obvious peak in concentration over the mid-ocean ridge (Klunder personal communication).

With so few observations of micronutrients from intermediate and deep waters it is difficult to assess sources of micronutrients. A recent paper by Middag et al. (in press) has successfully linked manganese (Mn) and [3]He concentrations in the northern Drake Passage to identify South Pacific Deep Slope Water with its Pacific hydrothermal vent signature thus identifying the Mn source at intermediate depths (1500 to 2500m). We hope to increase understanding of micronutrient hydrothermal source inputs along the MAR at 40°S and identify where the MAR is the source of micronutrients.

We hope to identify the hydrothermal plume from the MAR and better understand the transport along this transect. Currently we expect to see the plume in the western section of the transect after results published by Ruth et al. (2000) who identify a westward plume at 11°S, 19°S and 30°S (see Figure 21). This finding is in contrast with those of Reid (1989) who suggests eastward transport near 30°S and along 11°S and meridional transport along 19°S. Once the noble gas samples for the eastern part of the section are analyzed this information will help identify the eastern extent of the hydrothermal vent plume. This will help focus sampling when returning to complete the entire section.
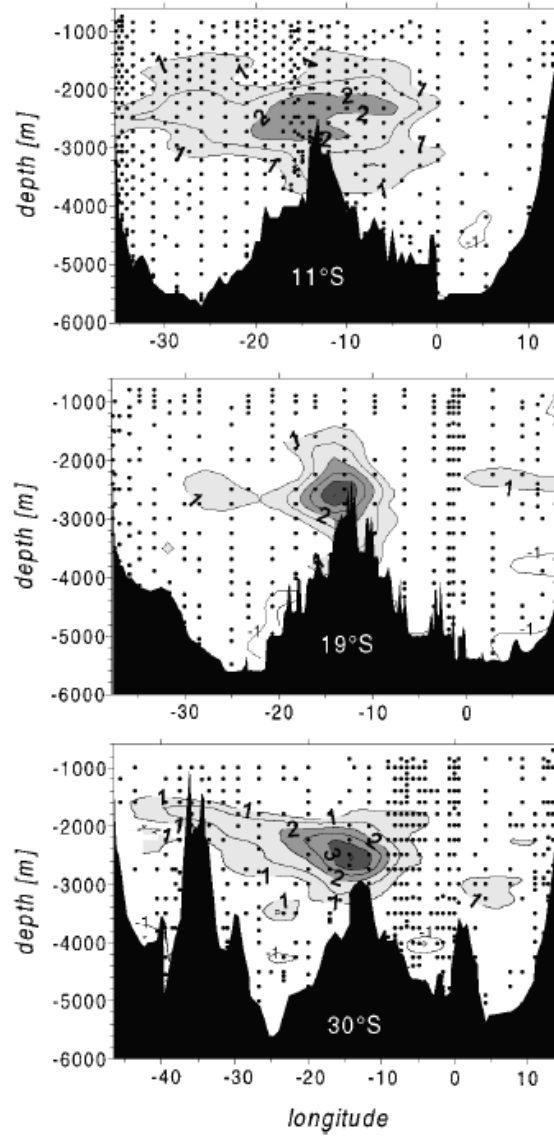
Figure 21: Sections of terrigenic [3]He from the Ruth et al. (2000) showing the hydrothermal vent plume extending to the west.
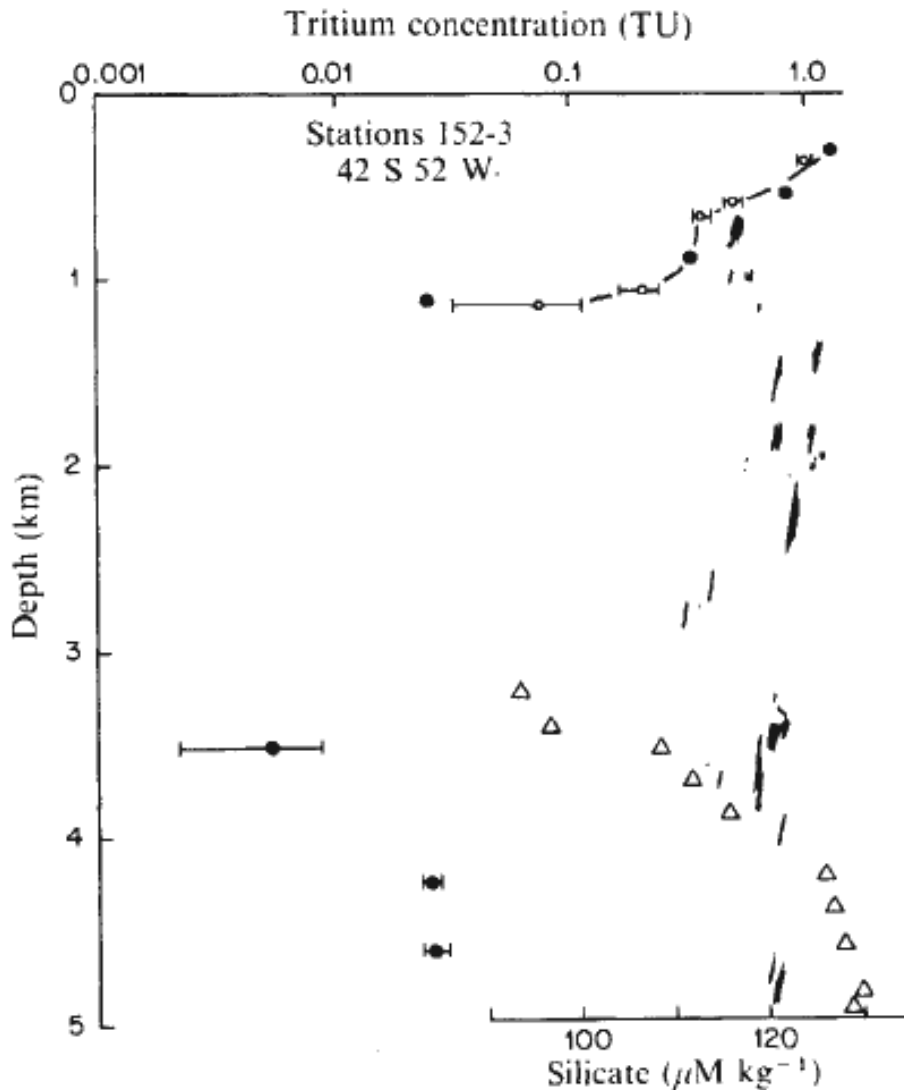
Figure 22: Tritium concentrations near the western section of the UK GEORTACES 40°S transect (Jenkins et al. 1983). Showing low concentrations of anthropogenic tritium at intermediate depths in the NADW and higher concentrations in the surface, AIW and AABW.

Tritium offers another constraint on the identification of water masses and the estimation of flux rates away from source inputs and paired ^{3}He/^{3}H will allow the calculation of water mass age. Identification of tritugenic ^{3}He will help in separating out background ^{3}He concentrations from the hydrothermal vent source signal.

Samples collected
A total of 197 noble gas samples and 180 tritium samples, including duplicates, were collected across the transect. Where duplicates were taken they were taken at one depth (same Niskin bottle) for both noble gas and tritium at each station.

See Table 4 for details of bottles sampled.

Collection details
Noble gas/helium samples will be collected in 80cm long 10mm outside diameter copper pipe (manufactured to EN12735 C106 (formerly BS2781 part 2) refrigeration grade). Noble gases are to be collected first from regular rosette. Water will be

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sampled by attaching tygon tubing to the Niskin bottle and allowing it to flow through the copper tube until there are no longer visible air bubbles.

Tritium samples will be collected in 1,200 ml Argon backfilled bottles (glass bottles, Alpha Sirop, with fitted 28mm white tamper evident cap with Polycine insert, polypropylene with plug seal, amber, 1000ml type II soda lime glass). Bottles have been prepared in an argon environment. Samples will be collected with tygon tubing after all gas phase sampling has taken place from the regular rosette. Bottles will be filled to within 2 inches of the bottleneck to allow room for thermal expansion. There will be no overflow. The sampling tygon need to be rinsed with water from the Niskin before insertion into the sampling bottle.

<u>Sample analysis</u>
Noble gas/helium copper tube samples will be packed and stored in plastic boxes for transport back to the UK. They will be stored until required for gas extraction and analysis on gas source MS.

Tritium water bottles will be packed and stored in plastic boxes for transport back to the UK. They will be stored until required for degassing. Once degassing has taken place sample will be stored in metal canisters (cleaned with Decon90 and distilled water and baked at 160 °C before the sample is introduced) in basement storeroom to prevent build up of helium form cosmogenic sources. After degassing sample will be stored for up to nine months before analysis on gas source MS.

Further details as outlined in Jenkins W. J., D. E. Lott, K. Cahill, J. Curtice, P. Landry 2010. Sampling and measuring helium isotopes and tritium in seawater. The GO-SHIP Repeat Hydrography Manual: A Collection of Expert Reports and Guidelines. IOCCP Report No.14, ICPO Publication Series No. 134, Version 1, 2010.

<u>References</u>
Bennett, S. A., Achterberg, and E. Al. 2008. Earth and Planetary Science Letters **270:** 157–167.
Clarke, W. B., W. J. Jenkins, and Z. Top. 1976. Determination of tritium by mass spectrometric measurement of ^{3}He. The International Journal of Applied Radiation and Isotopes **27:** 515-522.
Jenkins, W. J., D. E. Lott, M. W. Pratt, and R. D. Boudreau. 1983. Anthropogenic tritium in South Atlantic bottom water. Nature **305:** 45-46.
Middag, R., H. J. W. De Baar, P. Laan, and O. Huhn. in press. Signature of Pacific hydrothermal vents visible in the distribution of dissolved Manganese in Drake Passagge.
Reid, J. L. 1989. On the total geostrophic circulation of the South Atlantic ocean: Flow patterns, tracers and transports. Progress in Oceanography**:** 149-244.
Ruth, C., C. Well, and W. Roether. 2000. Primordial 3He in South Atlantic deep waters from sources on the Mid-Atlantic Ridge. Deep Sea Research I**:** 1059-1075.

Station	5			6.1			8			11			11		
CTD	9			10			14			19			20		
Bottle	Depth	ID	Sample	Depth	ID	Sample	Depth	ID	Sample	Depth	ID	Sample	Depth	ID	Sample
1	400	1193	H T	3000	1217	H T D	3372	1313	H T	-10	1423		2200	1447	H T D
2	400	1194			1218			1314		-10	1424			1448	
3	300	1195		2500	1219	H T	3200	1315	H T	3100	1425	H T		1449	
4	300	1196			1220			1316		3000	1426	H T	2000	1450	H T
5	200	1197		2000	1221		3000	1317	H T	2700	1427			1451	
6	200	1198		2000	1222	H T		1318		2500	1428	H T		1452	
7	120	1199		1500	1223	H T	2500	1319	H T D	2200	1429		1800	1453	
8	120	1200			1224			1320		2000	1430		1800	1454	H T
9	100	1201		1250	1225	H T	2000	1321	H T	1800	1431			1455	
10	100	1202	H T	1000	1226	H T		1322		1500	1432		1500	1456	H T
11	80	1203		750	1227	H T	1750	1323	H T	1250	1433			1457	
12	80	1204		500	1228	H T		1324		1000	1434			1458	
13	60	1205		350	1229	H T	1500	1325	H T	750	1435		1250	1459	H T
14	60	1206		200	1230	H T	1250	1326	H T	500	1436			1460	
15	50	1207		100	1231	H T	1000	1327	H T	200	1437	H T		1461	
16	50	1208			1232			1328	H T	100	1438	H T	1000	1462	H T
17	40	1209			1233		700	1329	H T	80	1439			1463	
18	40	1210			1234		500	1330	H T	70	1440			1464	
19	30	1211			1235			1331		60	1441		750	1465	H T
20	30	1212			1236		350	1332	H T	50	1442	H T		1466	
21	20	1213			1237		200	1333	H T	35	1443			1467	
22	20	1214	H T		1238		100	1334	H T	35	1444		500	1468	H T
23	5	1215		5	1239	H T	50	1335	H T	20	1445			1469	
24	5	1216		5	1240		5	1336	H T	5	1446	H T		1470	

Table 6: Samples taken at each station. Table gives Niskin bottle number, approximate depth of sample, UKGEOTRACES ID number and the type of sample taken. H = helium, T = tritium & D = duplicate, wher duplicates were taken they were taken for helium and tritium.

| Station | 12 | | | 13 | | | 14 | | | 15 | | | 16 | | |
| CTD | 21 | | | 25 | | | 26 | | | 33 | | | 36 | | |
Bottle	Depth	ID	Sample	Depth	ID	Sample	Depth	ID	Sample	Depth	ID	Sample	Depth	ID	Sample
1	-10	1471		-10	1561	H T	-10	1635	H T	-10	1755	H T	-10	1827	H T
2	-10	1472	H T	-10	1562		-10	1636		-10	1756		-10	1828	
3	3000	1473		3700	1563	H T	4000	1637	H T	4000	1757	H T	4750	1829	
4	3000	1474		3500	1564		4000	1638		4000	1758		4500	1830	H T
5	2700	1475		3500	1565	H T	3750	1639	H T	3750	1759	H T	4500	1831	
6	2500	1476	H T D	3250	1566	H T	3500	1640	H T	3500	1760	H T	4000	1832	H T
7	2500	1477		3000	1567	H T	3000	1641	H T	3250	1761	H T	3500	1833	H T
8		1478		3000	1568		3000	1642		3000	1762	H T	3250	1834	
9	2000	1479	H T	2750	1569	H T	2750	1643	H T	2500	1763	H T	3000	1835	H T
10	2000	1480		2500	1570	H T	2500	1644	H T D	2250	1764	H T	2750	1836	H T
11	1800	1481	H T	2500	1571		2250	1645	H T	2000	1765	H T	2500	1837	H T
12	1600	1482	H T	2250	1572	H T	2000	1646		1750	1766	H T	2250	1838	
13	1500	1483	H T	2000	1573	H T D	2000	1647	H T	1500	1767	H T D	2000	1839	H T
14	1400	1484	H T	2000	1574		1750	1648	H T	1500	1768		1750	1840	
15	1200	1485	H T	1750	1575	H T	1500	1649	H T	1250	1769	H T	1500	1841	H T
16	1000	1486	H T	1500	1576	H T	1250	1650	H T	1000	1770	H T	1250	1842	
17	750	1487	H T	1250	1577	H T	1000	1651	H T	1000	1771		1000	1843	H T
18	600	1488	H T	1000	1578	H T	750	1652	H T	750	1772	H T	750	1844	
19	500	1489	H T	750	1579	H T	500	1653	H T	500	1773	H T	500	1845	
20	200	1490	H T	500	1580	H T	200	1654	H T	200	1774	H T	200	1846	
21	100	1491	H T	200	1581	H T	100	1655	H T	100	1775	H T	100	1847	
22	50	1492	H T	100	1582	H T	50	1656	H T	50	1776	H T	50	1848	
23	20	1493	H T	50	1583	H T	20	1657	H T	20	1777	H T	20	1849	
24	5	1494	H T	5	1584	H T	5	1658	H T	5	1778	H T	5	1850	

Table 6: continued.

Station	17			18			19			20			21		
CTD	39			45			47			51			56		
Bottle	Depth	ID	Sample	Depth	ID	Sample	Depth	ID	Sample	Depth	ID	Sample	Depth	ID	Sample
1	-10	1899	H T	-10	1975	H T	-10	2023	H T	4804	2119	H	-10	2239	
2	-10	1900		-10	1976		-10	2024		4700	2120		-10	2240	
3	5000	1901	H T	5000	1977		5200	2025	H T	4500	2121	H	-20	2241	
4	5000	1902		5000	1978	H T	5000	2026		4000	2122	H	3300	2242	H T
5	5000	1903		4500	1979	H T	5000	2027	H T	3500	2123	H	3000	2243	H T
6	4500	1904	H T	4000	1980	H T	4500	2028	H T	3000	2124	H	2800	2244	
7	4000	1905	H T	4000	1981		4000	2029	H T	2600	2125		2600	2245	
8	4000	1906		35000	1982	H T	4000	2030		2500	2126	H	2500	2246	H T
9	4000	1907		3000	1983	H T	3500	2031	H T	2250	2127		2250	2247	
10	3500	1908	H T	3000	1984		3000	2032	H T	2000	2128	H	2000	2248	H
11	3250	1909		2500	1985	H T	3000	2033		1750	2129		1750	2249	
12	3000	1910	H T	2250	1986	H T	2500	2034	H T	1500	2130	H	1750	2250	H
13	3000	1911		2000	1987	H T	2000	2035	H T	1250	2131		1500	2251	
14	3000	1912		1500	1988	H T	2000	2036		1000	2132	H	1250	2252	
15	2500	1913	H T	1500	1989		1500	2037	H T	900	2133		1000	2253	H
16	2000	1914	H T	1250	1990	H T	1250	2038		750	2134		1000	2254	
17	2000	1915		1000	1991	H T	1000	2039	H T	500	2135	H	900	2255	
18	2000	1916		750	1992		750	2040		200	2136		700	2256	
19	1750	1917		500	1993	H T	500	2041	H T	160	2137		500	2257	H
20	1500	1918	H T	200	1994		200	2042		100	2138	H	200	2258	
21	1500	1919		100	1995		100	2043	H T	80	2139		100	2259	
22	1500	1920		50	1996		50	2044		50	2140		50	2260	
23	1250	1921		20	1997		20	2045		20	2141	H	20	2261	
24	1000	1922	H T	5	1998	H T	5	2046	H T	5	2142		5	2262	

Table 6: continued.

4.4 NITRATE D15N AND D18O

By Robyn Tuerena
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Modern and palaeoproxy for nitrate cycling

The isotopic composition of sea water nitrate is determined by oceanic N cycling processes and can be used to provide information about the local and global marine nitrogen budget. Stable N and O isotopes can be used to estimate relative proportions of nitrate (NO_3-) utilised by phytoplankton in surface waters, to trace oceanic N_2 fixation, to assess N regeneration, and to determine terrestrial and atmospheric N inputs. The sensitivity of NO_3 isotopes to important biogeochemical fluxes can also help to constrain nutrient budgets and trace the origin and history of water masses.

Sample collection
Samples have been collected from the stainless steel rosette, from every station at each depth. Seawater was filtered through an Acropak (0.4 µm) into acid clean 60 ml Nalgene bottles and frozen at -20 °C. Two bottles were filled at each depth, covering the whole water column at each station.

No further work has been carried out onboard; samples will be taken back to Edinburgh frozen for analysis by the Denitrifier Method. Samples are frozen and not acidified to allow the analysis of δ18O in addition to δ15N.

Sample analysis
Samples will be analysed at the University of Edinburgh and SUERC (Scottish Universities Environmental Research Centre) in East Kilbride using the Denitrifier Method (Sigman et al., 2001, Casciotti et al., 2002).

Outline of method:
- Inoculate agar plates with Pseudomonas *Aureofaciens* (denitrifying bacteria) incubate in dark for 3-4 days and re-streak on new plate.
- Approximately one week prior to sample preparation, inoculate 9ml starter tubes in pairs. Transfer a single colony from freshly grown plate to media using a flamed loop, incubate overnight on shaker.
- Use these starter tubes to inoculate all media bottles. Transfer 0.7ml freshly inoculated bacterial media into each bottle by injecting though seal, put bottles on shaker table for 6-10 days.
- Divide culture evenly between autoclaved 50 ml centrifuge tubes and centrifuge for 30 minutes at 5000 rpm.
- Pink-white bacteria at bottom of bottles should be evident, pour off liquid above cells and add appropriate volume of nitrate free media (NFM) to each centrifuge bottle (0.15 ml NFM per 1 ml original

medium) pour back and forth till all cells re-suspended, add antifoam using sterile pipette.

- Pipette 3 ml of cell concentrate into vials then seal with butyl stopper and crimp seal. Insert venting needles into edge of stoppers.
- Purge vials with He gas by placing all vials on purge needles for ~3 hours
- Rinse syringe then inject seawater sample or standard (30 nmol NO3) into vial through stopper, shake and invert.
- Incubate at room temperature overnight in inverted position.
- Inject 0.1-0.2ml of 10M NaOH into each vial and shake to lyse the bacteria.
- The isotopic composition of N2O will then be measured by isotope ratio mass spectrometry.
- All values will be corrected to standards (USGS32, USGS34 and USGS35).

References:
Sigman, D. M., K. L. Casciotti, M. Andreani, C. Barford, M. Galanter, and J. K Bohlke (2001). "A bacterial method for the nitrogen isotopic analysis of nitrate in seawater and freshwater." Analytical Chemistry **73**(17): 4145-4153.
K. L. Casciotti, D. M. Sigman, M. Galanter Hastings, J. K. Bohlke and A. Hilkert (2002). Measurement of the Oxygen Isotopic Composition of Nitrate in Seawater and Freshwater Using the Denitrifier Method. Analytical Chemistry **74**(19): 4905-4912

WORKPACKAGE 5: BIOLOGICAL RESPONSE AND CYCLING OF MICRONUTRIENTS

5.1 FLUOROMETRIC CHLOROPHYLL-A

By Heather Bouman & Thomas Browning
Department of Earth Sciences, University of Oxford

Objectives
To capture the vertical structure of chlorophyll-a concentration within the surface ocean, measurements of chlorophyll-a were conducted on discrete water samples along the cruise transect. Vertical profiles of chlorophyll-a will be used to calibrate *in vivo* fluorescence profiles made using a Chelsea MKIII Aquatracka fluorometer mounted on the CTD package.

Sampling Protocol
Seawater samples were collected in large (9-20 litre) Nalgene carboys. Each carboy was rinsed three times with sample water and then filled. Triplicate samples of 100 ml were filtered through 25 mm GF/F filters. The filters are placed in 10 ml of 90% acetone in 20ml glass scintillation vials and stored overnight at -20°C to allow pigment to extract.

Sample analysis
The samples were analysed onboard using a Trilogy fluorometer (Turner Designs). Prior to the cruise, the fluorometer was pre-calibrated using spinach chlorophyll-a standard (Sigma). The pigment extract was measured both before and after acidification according to be method of Holm-Hansen et al. (1965).

Preliminary results
Chlorophyll-a concentrations showed significant variation across the transect (Fig 23). The maximum concentration (2.17 mg m^{-3}) was observed at station 19 in the subsurface (43 m). A pronounced subsurface chlorophyll maximum was observed below surface oligotrophic waters within the Argentine basin.

Calibration of CTD fluorometer
The calibration of CTD fluorometer profiles was done using all depths using the upward fluorescence trace. The relationship between *in vivo* fluorescence measured using the Wetlabs fluorometer and in vitro fluorescence measured using the Turner Designs Trilogy fluorometer is shown in Fig 24.
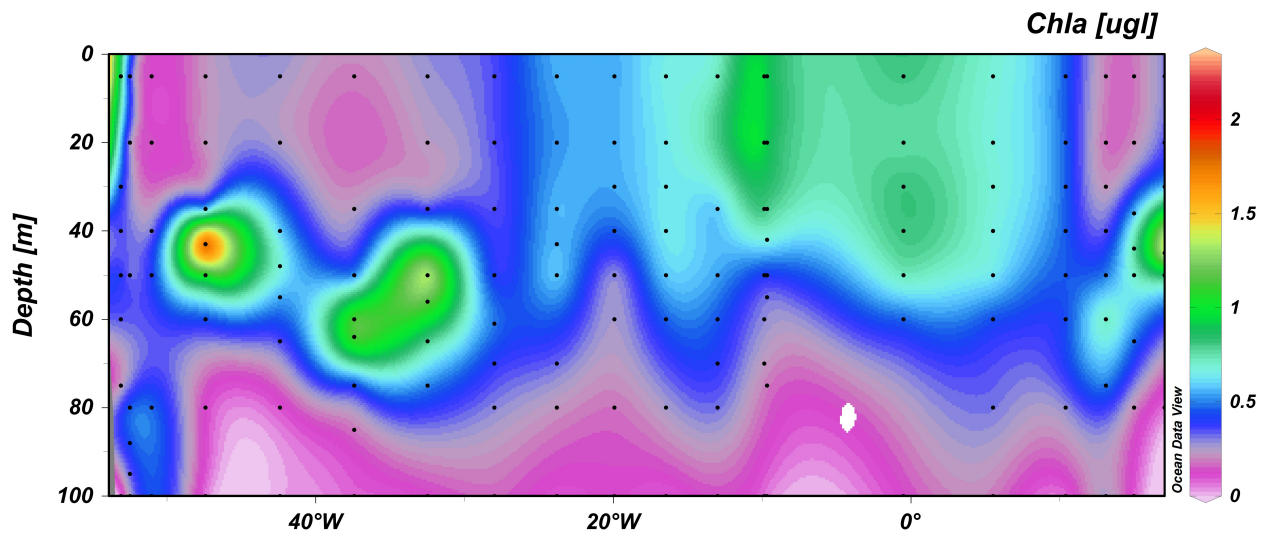
Figure 23: a) Map showing vertical variability in chlorophyll concentration across the GEOTRACES transect.
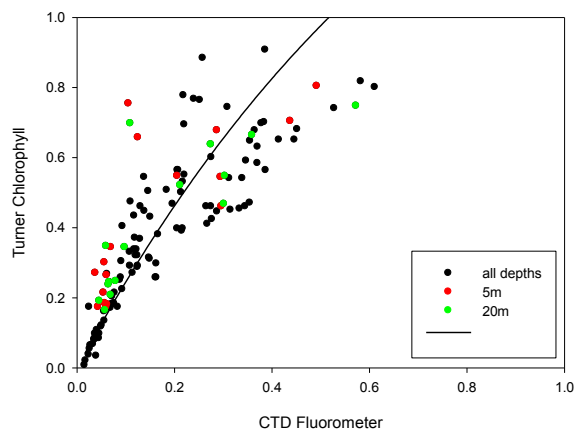
Figure 24: Relationship between extracted chlorophyll pigment measured using a Turner Designs fluorometer and *in vivo* chlorophyll fluorescence using a Chelsea MKIII Aquatracka fluorometer.

5.2 HIGH PERFORMANCE LIQUID CHROMATOGRAPHY ANALYSIS OF ALGAL PIGMENTS

By Heather Bouman & Thomas Browning
Department of Earth Sciences, University of Oxford

Objectives
Phytoplankton pigments can be used as chemotaxonomic markers of key phytoplankton taxonomic groups involved in biogeochemical cycles. These pigments also jointly contribute to the absorptive properties of marine phytoplankton and thus can assist in analysing sources of spectral variation in the shape of the phytoplankton absorption spectra. Thus to examine the spatial and temporal distribution of marine phytoplankton groups and their optical properties seawater samples were collected at 8-10 depths within the photic zone.

Sampling Protocol
Between 500 ml and 1 litre of seawater was subsampled from large (9-20 litre) Nalgene carboys and filtered through 25 mm GF/F filters. The filters were placed in 2 ml cryovials and flash frozen in liquid nitrogen. Filters were then transferred to a -80°C freezer for long-term storage.

Samples Collected
At each station, seawater was collected at 6-8 sampling depths, The depths coincided with those selected for FRRF, phytoplankton *in vivo* absorption, fluorometric and flow cytometric analysis. A detailed list of samples collected may be found in Table 1.

Sample analysis
Frozen samples will be transported back to the Plymouth Marine Laboratory in a dry shipper and stored at -80°C until analysed. Pigment extracts will be analysed using a reverse-phase HPLC column using Thermo-separations and Agilent instruments (Barlow et al., 1997). The instrument is calibrated using pigment standards (DHI Water and Environment, Denmark) on an annual basis.

Phytoplankton pigments will be extracted in 2 to 5 ml 90% acetone by ultrasonication and centrifugation. Extracts will be loaded into a Thermo Separations autosampler (capable of cooling pigment extracts to 2°C) and mixed with 1 M ammonium acetate (1:1, v/v) prior to injection onto a Shimadzu HPLC system (dual LC-GB pumps; SCL-6B controller). Pigments will be detected by absorbance at 440 nm using a Shimadzu SPD-6AV spectrophotometric detector. Pigments will be identified by retention time and on-line visible spectroscopy using a Waters 990 diode array detector.

5.3 ABSORPTION BY MARINE PARTICLES

By Heather Bouman & Thomas Browning
Department of Earth Sciences, University of Oxford

Objectives
Samples were collected to examine the absorptive properties of phytoplankton cells. These data will be used to derive information on the absorptive efficiency of the natural phytoplankton assemblage, which in turn will aid in the interpretation of the photochemical signal obtained by Fast Repetition Rate (FRR) Fluorometry. Another motivation is to test and refine algorithms used to detect the concentration of chlorophyll-a and the presence of algal functional types by ocean-colour remote sensing.

Sampling protocol
Between 500 ml and 1 litre of seawater was subsampled from large (9-20 litre) Nalgene carboys and filtered through 25 mm GF/F filters. The filters were placed in 2ml cryovials and flash frozen in liquid nitrogen. Care was taken to avoid creases or folds in the filter by rolling the filter with the particle laden side facing inwards. Filters were then transferred to a -80°C freezer for long-term storage.

Samples Collected
At each station, seawater was collected at 8-10 sampling depths, The depths coincided with those selected for FRRF, HPLC, fluorometric and flow cytometric analysis. A detailed list of samples collected may be found in Table 1.

Sample analysis
Frozen samples will be transported back to Oxford in a dry shipper and stored at -80°C until analysed. Filters will be scanned using a Shimadzu UV-2550 spectrophotometer equipped with an integrating sphere over the visible range (350-750 nm). A pre-wetted blank filter is placed in the "Sample" holder and scanned against air and save the blank spectrum. The blank filter is then removed and placed in the "Reference" holder and place the sample filter in the "Sample" holder ensuring proper hydration. The sample OD spectrum is then measured from 350-750 nm.

Sample and blank filters will be placed on a filtration system. Approximately 10 ml of hot methanol will be added to filters (sample and blank) by gently pouring down the side of the funnel to minimise re-suspension. The solvent will let stand for 1 minute and then filtered through. Another 10 – 15 ml methanol will be added and allowed to stand for ~1 hour. The funnel will be covered with foil to minimise contamination during extraction. Methanol and dissolved pigments will then be drawn through the GF/F filter. The filter will then be rinsed twice with ~ 20 ml 0.2 μm filtered seawater. Pigment extraction will be complete when the 675 nm chl-a absorption peak is not present in OD spectrum. If present, repeat with successive short (10 min) extractions.

The OD spectrum of the blank and the de-pigmented samples will then be measured on the spectrophotometer, as before (from 350 to 750 nm).

To compute particle absorption $a_p(\lambda)$ in suspension from spectrophotometric OD_{fp} measurements on a filter, it is necessary to adjust the optical pathlength. This includes substituting the geometric optical path length of the particles in suspension, and a scaling factor to account for pathlength amplification due to scattering by the filter. The geometric absorption pathlength (l_s) is given by:

$$l_s = \frac{V}{S}$$

where V is the volume of water filtered (m^3) and S is the clearance area of the filter (mm^2) calculated from the diameter of the coloured part of the filter containing particles.

The absorption coefficient of filtered particles must be corrected for pathlength amplification and the equivalent absorption coefficient in m^{-1} in suspension is computed as:

$$a_p(\lambda) = \frac{2.303 S}{\beta V}[OD_{fp}(\lambda) - OD_{bf} - OD_{750}]$$

where 2.3 is the conversion factor for transforming decimal logarithms to natural logarithms, $OD_{fp}(\lambda)$ is the measured optical density of the sample filter (mean of 10 measurements), $OD_{bf}(\lambda)$ is the optical density of the blank filter (mean of 10 measurements), OD_{750} compensates for baseline offsets and β is a quadratic function used to correct for pathlength increases due to multiple scattering in the filter. We use the quadratic equation proposed by Hoepffner and Sathyendranath (1992):

$$\beta = 0.31[OD_{pf}(\lambda)] + 0.57[OD_{pf}(\lambda)]^2$$

The de-pigmented particle absorption coefficients, $a_d(\lambda)$, is calculated in the same way. The spectral absorption coefficient for phytoplankton, $a_p(\lambda)$, can then be obtained by subtracting the absorption coefficients of detritus $a_d(\lambda)$, from the total particulate absorption spectrum, $a_t(\lambda)$.

$$a_p(\lambda) = a_t(\lambda) - a_d(\lambda)$$

Pigment specific absorption coefficients of phytoplankton can then be calculated by dividing absorption by chlorophyll-a concentration (Turner or HPLC).

5.4 ABSORPTION BY DISSOLVED SUBSTANCES

By Heather Bouman & Thomas Browning
Department of Earth Sciences, University of Oxford

Objectives
Samples were collected to examine the absorptive properties of coloured dissolved organic matter (CDOM), which can be a significant contributor to the visible reflectance signal in coastal waters. The data will be used to determine how the Rio Plata River plume influences the ocean-colour remote sensing signal.

Sampling protocol
250 ml of seawater was collected in glass borosilicate bottles wrapped in foil to protect the samples against photochemical degradation. The samples were immediately stored at 5°C in the dark and analysed within 24 hours of sample collection.

Samples collected
Samples were collected at Standard Stations and Super Stations at the sea surface (5-20m depth).

Sample analysis
The filtration unit was pre-rinsed well with milli-Q water. The filter cup was filled with milli-Q water, and passed through the filtration unit as if it were a sample (only with no filter). Filtrate in the collection flask was swirled and then discarded. This procedure was repeated twice more for a total of 3 Q-water rinses. A 0.2 μm nucleopore filter rinsed with milli-Q, was then placed on the filter support and about 30-50ml of milli-Q water was filtered through the filter. Again, the filtrate was swirled in the collecting flask and discarded. This milli-Q rinse and the sample rinses in the next step get rid of any leachate that might initially come from the filter.

The sample bottle were inverted upside-down 3 times to make sure sample is well mixed (note the bottle is not shaken to prevent breaking up cells and colloids). 10ml of sample was poured into the filter funnel and filtered through. The filtrate was then swirled in the collecting flask and discarded. This rinsing procedure was repeated twice more to get rid of any leachate that might initially come from the filter and to make sure all the milli-Q droplets are out of the filter flask to avoid dilution of the filtered sample. The remaining sample left in the sample bottle was then filtred through the nucleopore filter.

Before the samples were scanned, bottles containing the filtered seawater were allowed to warm to room temperature.   If running at a later time, the bottles were placed back in the refrigerator and store at 4°C until ready to scan. All scans were conducted within 24 hours of sample collection.

Samples were measured using a Shimadzu UV-2550 spectrophotometer. The cuvettes were stored filled with milli-Q-water. Before measurements were made the cuvettes were emptied and rinsed with fresh milli-Q (6 rinses to make sure well-rinsed). An air-to-air baseline is first conducted to ensure a flat spectrum with limited noise. Cuvettes were then filled with milli-Q and all water on outside of cuvettes was wiped thoroughly with kimwipes. The outside of cuvettes were also cleaned with ethanol to ensure the cuvette was optically clean. First, a milli-Q blank is scanned against air reference from 250 to 750 nm to record the absorptive properties of the blank. This is done for both cuvettes. Then a water-to-water baseline is conducted using the two cuvettes filled with milli-Q and the spectrum is recorded. The sample cuvette is then rinsed five times with sample water and placed in the sample

chamber with a milli-Q blank as a reference. The sample is then scanned from 250 to 750 nm. Further details on the protocol may be found in Pegau et al. (2002).

5.5 FLOW CYTOMETRIC ANALYSIS OF PHYTOPLANKTON COMMUNITY STRUCTURE

By Heather Bouman & Thomas Browning
Department of Earth Sciences, University of Oxford

Objectives

Our aim is to measure the concentration of pico- (<2μm) and nano- (2-10μm) phytoplankton over the GEOTRACES cruise transect. Samples were collected at 8-10 depths, which were be chosen based on the downward trace of *in situ* fluorescence from the CTD.

Sampling protocol

Seawater samples were collected from the CTD Niskin or FISH (rinsing carboy three times with sample water before filling). Samples were then fixed paraformaldehyde as soon as feasible. A 2 ml cryovial was filled with 1.875 ml of seawater. 0.125 ml of 16% paraformaldehyde (PFA) was pipetted into each vial, yielding a 1% PFA final concentration. The vials were then mixed using a vortex, and let stand at room temperature for not less than 10 minutes (and not more than about 20-30 minutes). The vials were then flash frozen in liquid nitrogen. The vials were then transferred to an ultra-low temperature freezer (-80°C) for long-term storage.

Samples collected

At each station, seawater was collected at 8-10 sampling depths, The depths coincided with those selected for FRRF, HPLC, fluorometric and flow cytometric analysis. A detailed list of samples collected may be found in Table 1.

Sample analysis

The samples will be analysed at the Plymouth Marine Laboratory using a Becton Dickinson FACSortTM flow cytometer equipped with an air-cooled laser providing blue light at 488 nm (Tarran et al. 2006).

5.6 FIXATION OF MARINE PHYTOPLANKTON FOR LIGHT MICROSCOPY

By Heather Bouman & Thomas Browning
Department of Earth Sciences, University of Oxford

Objectives
Species composition of the microphytoplankton (>20 μm) community will be examined along the 40°S cruise transect using conventional light microscopy.

Sampling protocol
Two 250 ml plastic amber Nalgene bottles were filled with seawater directly from the Nisken bottle tripped at 5m. One bottle was fixed with 5 ml of 20% aqueous solution of formaldehyde (neutralised with hexamethylenetetramine) and the other with 2.5 ml of Lugol's solution. The two preserved samples were then immediately stored at 5°C in the dark.

Samples collected
Samples were collected at Standard and Super Stations at the sea surface (5 -10 m depth).

Sample analysis
Phytoplankton cells will be enumerated and identified following the technique of Uthermöl at 40 and 100 x magnification (Lund et al., 1958). Phytoplankton will be identified to the lowest possible taxonomic level.

5.7 REMOTE SENSING IMAGERY OF PHYTOPLANKTON BIOMAS AND SEA-SURFACE TEMPERATURE

By Heather Bouman & Thomas Browning
Department of Earth Sciences, University of Oxford

Objectives

The strong nutrient gradients observed at ca. 40°S, and the detailed study of Fe cycling planned in the UK GEOTRACES cruise, provide an opportunity to test the relationship between Fe supply, taxonomic response, and ocean colour data. To provide a synoptic view of the physical and ecological state of the surface ocean along the 40°S transect, we requested MODIS Chlorophyll and AVHRR Sea-Surface Temperature images to be sent to the ship in near-real-time from the Natural Environment Research Council (NERC) Earth Observation Data Acquisition and Analysis Service (*NEODAAS*).

Sampling protocol

Daily images of MODIS chlorophyll-a and AVHRR Sea Surface Temperature were sent via email attachment in png format to the ship. 8-day composites of chlorophyll and sea-surface temperature were also provided (see Fig 25).
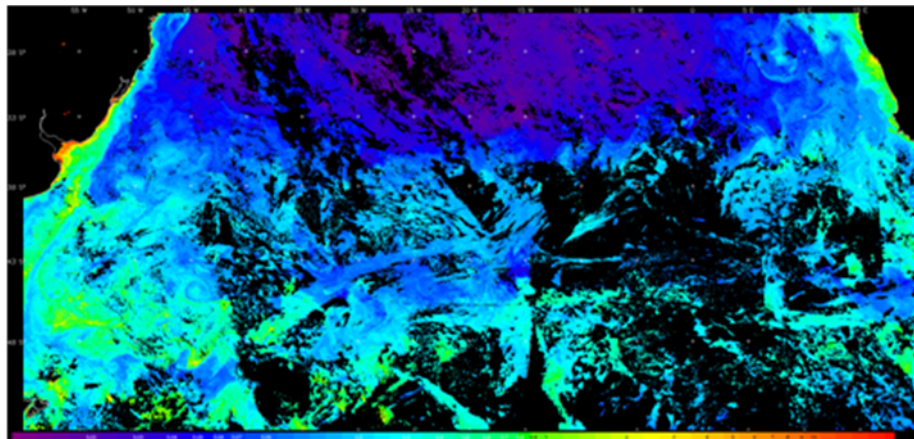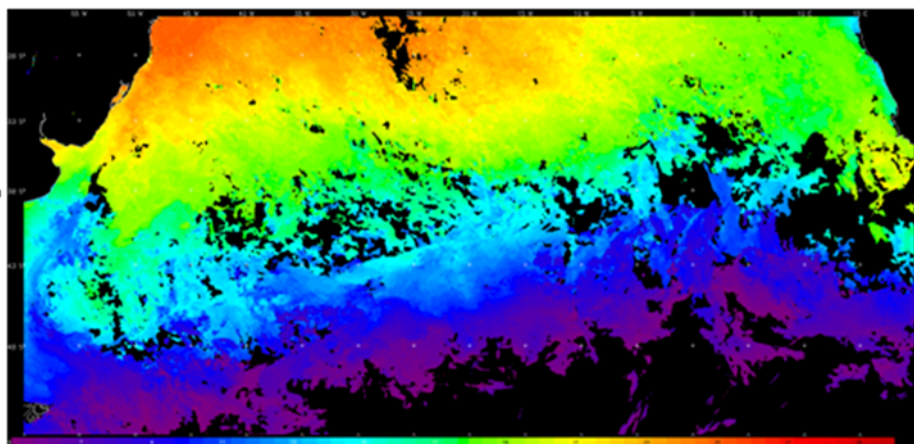
Figure 25: 8-day composites of sea-surface chlorophyll and temperature provided by NEODAAS.

Sample analysis
Corresponding HDF files of chlorophyll-a and sea-surface temperature will be downloaded from the NASA Ocean Color website (http://oceancolor.gsfc.nasa.gov). Analysis of MODIS Chl and sea-surface temperature data will be conducted over a 30° swath crossing the South Atlantic centring on 40°S and will be compared with climatological data.

5.8 FAST REPITITION RATE FLUOROMETRY (FRRF)

By Heather Bouman & Thomas Browning
Department of Earth Sciences, University of Oxford
And C. Mark Moore, NOC

Objectives
The objective was to characterise the along transect phytoplankton photo-physiology with discrete samples using Fast Repetition Rate (FRR) Fluorometry. The sampling strategy was to collect data from multiple depths for each sampling station, together with some inter-station 5m depth fish samples. Results from this analysis are intended to be interpreted on the basis of macro and micro nutrient availability, light climate, and taxonomic composition (see other relevant sections of cruise report).

Sampling protocol
Samples were collected in 250 or 500 mL opaque bottles following 3 rinses with sample water. Samples were then incubated (in opaque bottles – no light) for at least 30 minutes in order for phytoplankton to become dark acclimated. During this period samples were bathed in a continuously flowing water bath of ships underway water to limit sample temperature change.

Samples collected
At 16 stations 8 samples were taken from the depths of interest (stations 1, 2, 3, 4, 5, 8, 11, 12, 13, 14, 15, 16, 17, 18, 19 and 21). The sample depths from station 11 were made up from a combination of 2 CTD casts separated by around 8 hours. At 4 stations 7 samples were taken from the depths of interest (stations 6, 9, 22, 24). 12 samples were taken from depths of interest at station 20, and 9 samples at station 21. The depths of interest were chosen after consultation of the fluorescence trace and temperature/salinity data measured by instruments on the stainless steel CTD. Depths chosen at each station were all less than 160m and the majority were less than 100m.

Fish samples were all taken from 5m depth and were taken between some stations (between stations 7 and 8), on arriving or leaving stations 7, 21 and 23, and at 1 hour intervals on the South American shelf where a significant gradient in chlorophyll concentration was expected

Sample analysis
All sample analysis for this measurement was conducted on ship. After 30 minutes of dark incubation (see sampling protocol section), phytoplankton in samples were assumed to be dark acclimated. For each sample bottle: sample bottle was inverted to homogenise sample, sample water was then used to wash a pyrex test tube 3 times before filling with roughly 3 mL of sample. The filled test tube was then wiped with tissue paper before being inserted into the Fast Repletion Rate Fluorometer (FRRF). The FRRF instrument used was a Chelsea Technologies Group Ltd FAST^{act} sample chamber, FAST^{act} base unit, and FAST$^{tracka\ 2}$ sensor. The sensor water jacket was filled with Milli-Q pumped from a beaker stored in the flow through water bath described previously. FRRF measurements were then taken as follows: single acquisitions were taken for all samples to obtain measurements of, among others, F_v/F_m (the maximum photochemical efficiency of Photosystem II (PS II), dimensionless) and σ_{PS2} (the functional absorption cross section of PS II, nm^2). Rapid Light Curves (RLC) were obtained for samples from 2 depths at each station (in all cases this was from the surface (5m depth) and Deep Chlorophyll Maximum (DCM)). The water jacket pump was run between samples for single acquisitions and continuously at a low rate

during RLC analysis to maintain sample temperature at that of the ships underway water flow. Single acquisitions and RLC were taken for the majority of fish samples. Blanks were run for the majority, but not all, of samples using the following procedure: an aliquot of roughly 3 mL of sample was filtered using a 0.2 μm pore size filter and a single acquisition made using the same FRRF settings as the unfiltered sample.

Preliminary results

Refer to Fig. 26 below. F_v/F_m values generally show a shift from high values off the South African coast to low mixed layer depth values in the central eastern basin to generally high values throughout the water column in the western basin. This trend is thought to be largely controlled by Fe bioavailability. F_v/F_m values are uncorrected for blank measurements and instrument PMT gain setting.
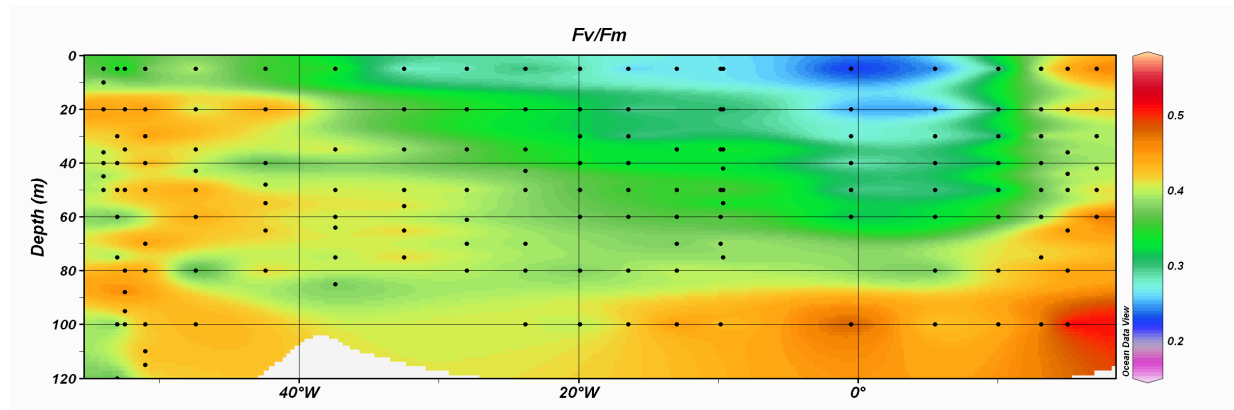
Figure 26: Section of uncorrected F_v/F_m for station samples along the transect.

5.9 FE INCUBATION EXPERIMENTS

By Heather Bouman & Thomas Browning
Department of Earth Sciences, University of Oxford
And C. Mark Moore, NOC

Objectives
The objective was to characterise any surface and Deep Chlorophyll Maximum (DCM) Fe limitation of phytoplankton along the transect.

Sampling protocol and analysis
9 1L polycarbonate bottle were filled with seawater from the trace metal clean fish or the DCM bottle of the trace metal clean CTD rosette. The 1L bottles had previously been rigorously cleaned using soaks in Decon, 3M HCl, 0.5M HCl, with Milli-Q washes in between and were stored in acidified Milli-Q for transport. The bottles were rinsed and filled in a trace metal clean container. The optimum time for filling bottles from the fish was midnight but this varied somewhat depending on the availability of clean fish water at this time (i.e. whether on station or not). The filling time for the 9 1L bottles from the trace metal clean fish was around 10 minutes. 3 bottles were immediately sampled for chlorophyll concentrations and single acquisitions using the FRRF (see relevant sections of cruise report for protocols). 3 bottles were spiked with 2 nM $FeCl_3$ in a 10% HCl solution under a laminar flow hood and 3 control bottles (non Fe spiked) were parafilmed, double bagged and placed in an on-deck incubator which was filled with continuously flowing ships non-toxic flow through water. The incubator was shaded with blue screening to simulate the light field at 5 m water depth. DCM samples were additionally wrapped in black mesh to simulate the lower light environment at this depth. When on station, the incubator was shielded from deck lighting using an opaque black cover. After 24 hours the 3 Fe spiked and 3 control bottles were removed and sampled for chlorophyll concentrations and single acquisitions from the FRRF. Significant increases in F_v/F_m values of Fe amended bottles were used as the signature for Fe limitation of phytoplankton. When not being used directly for a subsequent experiment, incubation bottles were rinsed and left filled with 100-200 mL 5% HCl.

Samples collected
13 fish samples were taken at roughly equal special intervals along the transect. 5 DCM trace metal rosette samples were taken. The DCM experiments were limited in number from the eastern basin as few trace metal CTD casts were carried out in this region.

Preliminary results
Refer to Fig. 27 example below. F_v/F_m values showed significant increases in the Fe amended bottles in the eastern portion of the transect (but away from the South African coast, latitude = -38.30°N, longitude = 9.78°E) indicating Fe limitation of phytoplankton in these waters. No response was seen in the majority of the western basin indicating these waters not to be Fe limiting for phytoplankton. F_v/F_m values shown are uncorrected for blank measurements and instrument PMT gain setting. Chlorophyll concentrations in the control and Fe amended bottles varied from initial concentrations between experiments with the magnitude of this variation varying between experiments. This was thought to be due to bottle effects e.g. the zooplankton concentrations in Fe amended and control bottles.
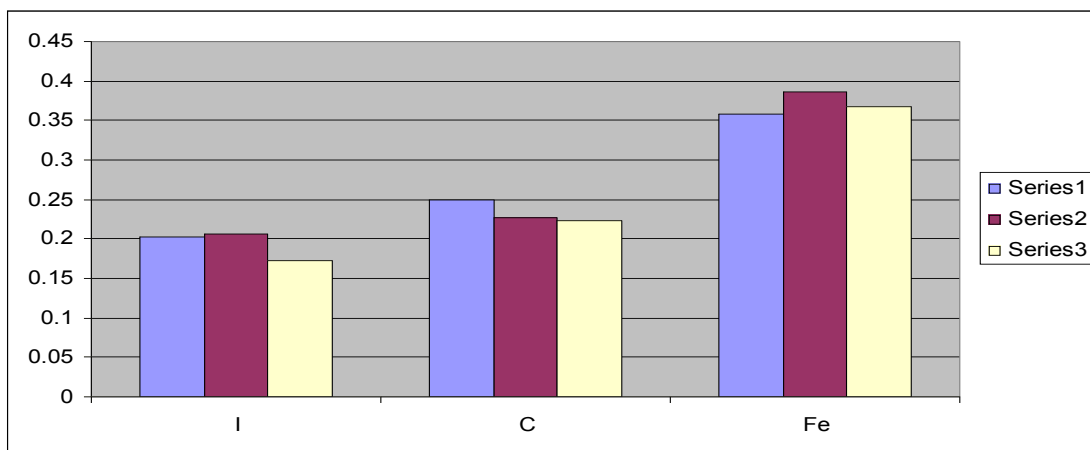
Figure 27: Example F_v/F_m results from a Fe addition experiment (IF3). I = Initial, C = Control, Fe = Fe amended to a final Fe concentration of 2 nM. Series number indicates bottle replicate number. In this particular experiment the Fe amended bottles showed a significant F_v/F_m increase in comparison to the control bottles indicating Fe limitation. F_v/F_m values are uncorrected for blank measurements and instrument PMT gain setting.

5.10 ADDITIONAL MEASUREMENTS TAKEN FOR BIoGEOTRACES

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DNA / RNA analyses of marine diazotroph assemblages
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Objectives
To examine the presence and metabolic activity of marine diazotrophs, seawater samples were filtered for DNA/RNA analysis at six depths within the top 400 m of the water column.

Sampling protocol
Durapore filters (0.22 µm, 47 mm) were placed onto filtration unit using flat-end forceps, taking care to only touch the rim of the filter.
PE bottles were carefully inverted to make sure that cells/particles in the seawater are equally distributed before filtering. The filtration cup was filled to 500 ml (graduated filtration cups). Filtration cups were covered with plastic bags to ensure no dust or debris settled on the filter. When 500 ml was filtered, the filtration cups were filled three times more (total 4 x 500 ml = 2.0 l) or a maximum of 1.5 h filtration time. The final filtration volume was recorded. Filters were folded into halves three to four consecutive times and place it in a 2.0 ml cryotube. The samples were then placed immediately at in a ultra-low temperature freezer at -80°C.

Samples collected
Six samples were collected within the top 400 m of the water column. Surface samples were selected based on the vertical profile of *in vivo* fluorescence obtained from the Biological CTD cast. A detailed list of stations and corresponding sampling depths may be found in Table 4.

Sample analysis
Nucleic acids (DNA and RNA) will be extracted from the sampled filters using commercial kits (Qiagen DNA/RNA AllPrep extraction kit). RNA will be reverse transcribed to cDNA using Superscript III Reverse Transcriptase (Invitrogen). Abundance (DNA) and transcripts (RNA/cDNA) of the *nifH* gene will be determined with real-time quantitative polymerase chain reaction (RT-qPCR) and using an ABI Prism 7000 thermocycler (Applied Biosystems) and Taqman technology (five to seven different phylotypes).

References:
Barlow, R., Cummings, D. G., Gibb, S. W. (1997) Improved resolution of mono- and divinyl chlorophylls a and b and zeaxanthin and lutein in phytoplankton extracts using reverse phase C-8 HPLC. Mar. Ecol. Prog. Ser., 171, 303–307.
Hoepffner, N., Sathyendranath, S. (1992) Determination of the major groups of phytoplankton pigments from the absorption spectra of total particulate matter. J Geophys Res 98:22789-22803.
Holm-Hansen O., Lorenzen C. J., Holmes R. W., Strickland J. D. H. (1965) Fluorometric determination of chlorophyll. J Cons Perm Int Explor Mer 30:3–15
Lund, J. W. G., Kipling, C., Le Cren, E. D. (1958) The inverted microscope method of estimating algal numbers and the statistical basis of estimations by counting. Hydrobiologia, 11, 143–170.
Pegau S. et al. (2002) NASA/TM-2003-211621/Rev4-Vol.IV Ocean Optics Protocols For Satellite Ocean Color Sensor Validation, Revision 4, Volume IV: Inherent Optical

Properties: Instruments, Characterizations, Field Measurements and Data Analysis Protocols

Tarran, G.A., Heywood, J.L., Zubkov, M.V. (2006) Latitudinal changes in the standing stocks of nano- and picoeukaryotic phytoplankton in the Atlantic Ocean Deep-Sea Research II 53 : 1516–1529.

Table 7

Date	Station	Event	CTD	ID	Depth	Bottle	Long	Lat	Time In	Tchl	FRRF	Abs	HPLC	FCM	FluorEx	DNA (Kiel)	DNA (Le
26/12/2011	Test	001	0		5		19.343	-34.948	07:15	3X300 ml	Y	N	N	N	N	N	N
27/12/2011	1	005	001S	1023	5	23	17.054	-34.612	01:32	3X300 ml	Y	1000	1000	2	1000	2000	2000
27/12/2011	1	005	001S	1020	20	21	17.054	-34.612	01:32	3X300 ml	Y	1000	1000	2	1000	N	N
27/12/2011	1	005	001S	1019	30	19	17.054	-34.612	01:32	3X300 ml	Y	1000	1000	2	1000	2000	N
27/12/2011	1	005	001S	1016	45	16	17.054	-34.612	01:32	3X300 ml	Y	500	1000	2	1000	2000	2000
27/12/2011	1	005	001S	1014	50	14	17.054	-34.612	01:32	3X300 ml	Y	1000	1000	2	1000	N	N
27/12/2011	1	005	001S	1012	60	12	17.054	-34.612	01:32	N	Y	1000	1000	2	N	2000	N
27/12/2011	1	005	001S	1010	80	10	17.054	-34.612	01:32	3X300 ml	Y	1000	1000	2	1000	2000	N
27/12/2011	1	005	001S	1008	100	8	17.054	-34.612	01:32	3X300 ml	Y	1000	1000	2	1000	N	N
27/12/2011	1	005	001S	1006	200	6	17.054	-34.612	01:32	N	N	N	N	N	N	N	N
28/12/2011	2	007	003S	1072	5	24	14.996	-35.468	16:20	3X300 ml	Y	1000	1000	2	1000	2000	N
28/12/2011	2	007	003S	1068	20	21	14.996	-35.468	16:20	3X300 ml	Y	1000	1000	2	1000	N	N
28/12/2011	2	007	003S	1067	36	19	14.996	-35.468	16:20	3X300 ml	Y	1000	1000	2	1000	2000	N
28/12/2011	2	007	003S	1064	44	16	14.996	-35.468	16:20	3X300 ml	Y	500	680	2	500	2000	4000
28/12/2011	2	007	003S	1062	50	14	14.996	-35.468	16:20	3X300 ml	Y	1000	1000	2	1000	N	N
28/12/2011	2	007	003S	1060	65	12	14.996	-35.468	16:20	3X300 ml	Y	1000	1000	2	1000	2000	N
28/12/2011	2	007	003S	1058	80	10	14.996	-35.468	16:20	3X300 ml	Y	1000	1000	2	1000	N	N
28/12/2011	2	007	003S	1056	100	8	14.996	-35.468	16:20	3X300 ml	Y	1000	1000	2	1000	2000	N
28/12/2011	2	007	003S	1054	200	6	14.996	-35.468	16:20	N	N	N	N	N	N	1850	N
29/12/2011	3	012	007S	1167	5	23	13.106	-36.343	22:46	3X300 ml	Y	1000	2000	2	1000	2000	4000
29/12/2011	3	012	007S	1165	20	21	13.106	-36.343	22:46	3X300 ml	Y	1000	2000	2	1000	2000	N
29/12/2011	3	012	007S	1163	30	19	13.106	-36.343	22:46	3X300 ml	Y	1000	2000	2	1000	N	N
29/12/2011	3	012	007S	1161	40	17	13.106	-36.343	22:46	3X300 ml	Y	1000	2000	2	1000	2000	N
29/12/2011	3	012	007S	1160	50	16	13.106	-36.343	22:46	3X300 ml	Y	1000	2000	2	1000	N	N
29/12/2011	3	012	007S	1157	60	13	13.106	-36.343	22:46	3X300 ml	Y	1000	1000	2	1000	2000	4000
29/12/2011	3	012	007S	1155	75	11	13.106	-36.343	22:46	3X300 ml	Y	1000	2000	2	1000	N	N
29/12/2011	3	012	007S	1153	100	9	13.106	-36.343	22:46	3X300 ml	Y	1000	2000	2	1000	N	N
29/12/2011	3	012	007S	1151	120	7	13.106	-36.343	22:46	3X300 ml	Y	1000	2000	2	1000	2000	N
29/12/2011	3	012	007S	1148	200	5	13.106	-36.343	22:46	N	N	N	N	N	N	2000	N
30/12/2011	4	013	008S	1192	5	24	10.402	-38.401	18:16	3X300 ml	Y	1000	1000	2	1000	2000	4000
30/12/2011	4	013	008S	1189	20	22	10.402	-38.401	18:16	3X300 ml	Y	1000	1000	2	1000	N	N

30/12/2011	4	013	008S	1180	80	12	10.402	-38.401	18:16	3X300 ml	Y	1000	2000	2	1000	N	N
30/12/2011	4	013	008S	1178	100	10	10.402	-38.401	18:16	3X300 ml	Y	1000	2000	2	1000	2000	N
30/12/2011	4	013	008S	1174	200	6	10.402	-38.401	18:16	N	N	N	N	N	N	1000	N
01/01/2012	5	014	009	1216	5	24	5.518	-40.000	06:41	3X300 ml	Y	1000	1000	2	1000	2000	N
01/01/2012	5	014	009	1214	20	22	5.518	-40.000	06:41	3X300 ml	Y	1000	1000	2	1000	N	N
01/01/2012	5	014	009	1212	30	20	5.518	-40.000	06:41	3X300 ml	Y	1000	1000	2	1000	2000	N
01/01/2012	5	014	009	1210	40	18	5.518	-40.000	06:41	3X300 ml	Y	1000	1000	2	1000	2000	N
01/01/2012	5	014	009	1208	50	16	5.518	-40.000	06:41	3X300 ml	Y	1000	1000	2	1000	N	N
01/01/2012	5	014	009	1206	60	14	5.518	-40.000	06:41	3X300 ml	Y	1000	1000	2	1000	2000	N
01/01/2012	5	014	009	1204	80	12	5.518	-40.000	06:41	3X300 ml	Y	1000	2000	2	1000	N	N
01/01/2012	5	014	009	1202	100	10	5.518	-40.000	06:41	3X300 ml	Y	1000	2000	2	1000	2000	N
01/01/2012	5	014	009	119?	300	?	5.518	-40.000	06:41	N	N	N	N	N	N	2000	N
03/01/2012	6.5	015	010	1239	5	23	-0.500	-40.015	12:48	3X300 ml	Y	1000	1000	2	1000	2000	N
03/01/2012	6.5	015	010	1238	20	22	-0.500	-40.015	12:48	3X300 ml	Y	1000	1000	2	1000	2000	N
03/01/2012	6.5	015	010	1237	30	21	-0.500	-40.015	12:48	3X300 ml	Y	1000	1000	2	1000	N	N
03/01/2012	6.5	015	010	1236	40	20	-0.500	-40.015	12:48	3X300 ml	Y	1000	1000	2	1000	2000	N
03/01/2012	6.5	015	010	1234	50	18	-0.500	-40.015	12:48	3X300 ml	Y	1000	1000	2	1000	N	N
03/01/2012	6.5	015	010	1233	60	17	-0.500	-40.015	12:48	3X300 ml	Y	1000	1000	2	1000	2000	N
03/01/2012	6.5	015	010	1234	100	15	-0.500	-40.015	12:48	3X300 ml	Y	1000	2000	2	1000	2000	N
03/01/2012	6.5	015	010	1230	200	14	-0.500	-40.015	12:48	N	N	N	N	N	N	2000	N
04/01/2012	FISH 11:55	N/A	FISH	N/A	5	N/A			11:55	3X300 ml	Y	1000	1000	2	1000	N	N
05/01/2012	FISH 07:41	N/A	FISH	N/A	5	N/A			07:41	3X300 ml	Y	1000	1000	2	1000	Y	N
05/01/2012	FISH 15:15	N/A	FISH	N/A	5	N/A			15:15	3X300 ml	Y	1000	1000	2	1000	N	N
06/01/2012	8	020	012	1287	5	23	-9.666	-39.999	11:13	3X300 ml	Y	1000	1000	2	1000	2000	N
06/01/2012	8	020	012	1286	20	22	-9.666	-39.999	11:13	3X300 ml	Y	1000	1000	2	1000	2000	N
06/01/2012	8	020	012	1283	35	19	-9.666	-39.999	11:13	3X300 ml	Y	1000	1000	2	1000	N	N
06/01/2012	8	020	012	1280	42	16	-9.666	-39.999	11:13	3X300 ml	Y	1000	1000	2	1000	2000	N
06/01/2012	8	020	012	1278	50	14	-9.666	-39.999	11:13	3X300 ml	Y	1000	1000	2	1000	N	N
06/01/2012	8	020	012	1276	55	12	-9.666	-39.999	11:13	3X300 ml	Y	1000	1000	2	1000	2000	N
06/01/2012	8	020	012	1274	75	10	-9.666	-39.999	11:13	3X300 ml	Y	1000	2000	2	1000	N	N
06/01/2012	8	020	012	1271	100	7	-9.666	-39.999	11:13	3X300 ml	Y	1000	2000	2	1000	2000	N
06/01/2012	8	020	012	1270	200	6	-9.666	-39.999	11:13	N	N	N	N	N	N	2000	N
07/01/2012	9	024	015	1360	5	24	-9.853	-40.257	03:12	3X300 ml	Y	1000	1000	2	1000	2000	N
07/01/2012	9	024	015	1358	20	22	-9.853	-40.257	03:12	3X300 ml	Y	1000	1000	2	1000		N
07/01/2012	9	024	015	1356	35	20	-9.853	-40.257	03:12	3X300 ml	Y	1000	1000	2	1000	2000	N
07/01/2012	9	024	015	1354	50	18	-9.853	-40.257	03:12	3X300 ml	Y	1000	1000	2	1000	2000	N
07/01/2012	9	024	015	1352	60	16	-9.853	-40.257	03:12	3X300 ml	Y	1000	700 &	2	1000	N	N

													1000				
07/01/2012	9	024	015	1350	70	14	-9.853	-40.257	03:12	3X300 ml	Y	1000	2000	2	1000	2000	N
07/01/2012	9	024	015	1347	100	12	-9.853	-40.257	03:12	3X300 ml	Y	1000	2000	2	1000	2000	N
07/01/2012	9	024	015	1346	200	10	-9.853	-40.257	03:12	N	N	N	N	N	N	2000	N
08/01/2012	11	028	017	1387	60	14	-13.000	-40.000	10:31	3X300 ml	Y	1000	1000	2	1000	N	N
08/01/2012	11	028	017	1385	70	12	-13.000	-40.000	10:31	3X300 ml	Y	1000	1000	2	1000	N	N
08/01/2012	11	028	017	1383	80	10	-13.000	-40.000	10:31	3X300 ml	Y	1000	1000	2	1000	N	N
08/01/2012	11	028	017	1381	100	8	-13.000	-40.000	10:31	3X300 ml	Y	1000	2000	2	1000	N	N
08/01/2012	11	028	017	1380	120	6	-13.000	-40.000	10:31	3X300 ml	Y	1000	2000	2	1000	N	N
08/01/2012	11B	031	019	1446	5	24	-13.000	-40.000	17:45	3X300 ml	Y	1000	1000	2	1000	N	N
08/01/2012	11B	031	019	1443	35	21	-13.000	-40.000	17:45	3X300 ml	Y	1000	1000	2	1000	N	N
08/01/2012	11B	031	019	1442	50	20	-13.000	-40.000	17:45	3X300 ml	Y	1000	1000	2	1000	N	N
08/01/2012	11B	031	019	1441	60	19	-13.000	-40.000	17:45	3X300 ml	Y	1000	1000	2	1000	N	N
08/01/2012	11B	031	019	1440	70	18	-13.000	-40.000	17:45	3X300 ml	Y	1000	1000	2	1000	N	N
10/01/2012	12	038	023	1542	5	24	-16.465	-40.002	11:35	3X300 ml	Y	1000	1000	2	1000	Y	4000
10/01/2012	12	038	023	1540	20	22	-16.465	-40.002	11:35	3X300 ml	Y	1000	1000	2	1000	N	N
10/01/2012	12	038	023	1538	30	20	-16.465	-40.002	11:35	3X300 ml	Y	1000	1000	2	1000	Y	N
10/01/2012	12	038	023	1535	40	17	-16.465	-40.002	11:35	3X300 ml	Y	1000	1000	2	1000	Y	N
10/01/2012	12	038	023	1533	50	15	-16.465	-40.002	11:35	3X300 ml	Y	1000	1000	2	1000	N	N
10/01/2012	12	038	023	1531	60	13	-16.465	-40.002	11:35	3X300 ml	Y	1000	1000	2	1000	N	N
10/01/2012	12	038	023	1529	80	11	-16.465	-40.002	11:35	3X300 ml	Y	1000	1000	2	1000	Y	N
10/01/2012	12	038	023	1527	100	9	-16.465	-40.002	11:35	3X300 ml	Y	1000	2000	2	1000	Y	N
10/01/2012	12	038	023	1525	140	7	-16.465	-40.002	11:35	N	N	1000	2000	N	N	N	N
10/01/2012	12	038	023	1523	200	5	-16.465	-40.002	11:35	N	N	N	N	N	N	Y	N
12/01/2012	13	046	027	1631	5	23	-19.930	-40.000	05:19	3X300 ml	Y	1000	1000	2	1000	Y	3000
12/01/2012	13	046	027	1629	20	21	-19.930	-40.000	05:19	3X300 ml	Y	1000	1000	2	1000	Y	N
12/01/2012	13	046	027	1628	30	20	-	-40.000	05:19	3X300 ml	Y	1000	1000	2	1000	N	N

12/01/2012	13	046	027	1626	40	18	-19.930	-40.000	05:19	3X300 ml	Y	1000	1000	2	1000	Y	N
12/01/2012	13	046	027	1625	50	17	-19.930	-40.000	05:19	3X300 ml	Y	1000	1000	2	1000	N	N
12/01/2012	13	046	027	1623	60	15	-19.930	-40.000	05:19	3X300 ml	Y	1000	1000	2	1000	Y	N
12/01/2012	13	046	027	1622	80	14	-19.930	-40.000	05:19	3X300 ml	Y	1000	2000	2	1000	N	N
12/01/2012	13	046	027	1620	100	12	-19.930	-40.000	05:19	3X300 ml	Y	1000	2000	2	1000	Y	N
12/01/2012	13	046	027	1618	200	10	-19.930	-40.000	05:19	N	N	N	N	N	N	Y	N
13/01/2012	14	051	030	1704	5	22	-23.800	-40.000	08:54	3X300 ml	Y	1000	1000	2	1000	Y	4000
13/01/2012	14	051	030	1702	20	20	-23.800	-40.000	08:54	3X300 ml	Y	1000	1000	2	1000	N	N
13/01/2012	14	051	030	1700	35	18	-23.800	-40.000	08:54	3X300 ml	Y	1000	1000	2	1000	Y	N
13/01/2012	14	051	030	1697	43	15	-23.800	-40.000	08:54	3X300 ml	Y	1000	1000	2	1000	Y	N
13/01/2012	14	051	030	1695	50	13	-23.800	-40.000	08:54	3X300 ml	Y	1000	1000	2	1000	N	N
13/01/2012	14	051	030	1693	70	11	-23.800	-40.000	08:54	3X300 ml	Y	1000	1000	2	1000	Y	N
13/01/2012	14	051	030	1691	80	9	-23.800	-40.000	08:54	3X300 ml	Y	1000	2000	2	1000	N	N
13/01/2012	14	051	030	1689	100	7	-23.800	-40.000	08:54	3X300 ml	Y	1000	2000	2	1000	Y	N
13/01/2012	14	051	030	1687	200	5	-23.800	-40.000	08:54	N	N	N	N	N	N	Y	N
14/01/2012	15	053	031	1729	5	23	-28.000	-40.000	09:15	3X300 ml	Y	1000	1000	2	1000	Y	Y
14/01/2012	15	053	031	1727	20	21	-28.000	-40.000	09:15	3X300 ml	Y	1000	1000	2	1000	N	N
14/01/2012	15	053	031	1725	35	19	-28.000	-40.000	09:15	3X300 ml	Y	1000	1000	2	1000	Y	N
14/01/2012	15	053	031	1723	50	17	-28.000	-40.000	09:15	3X300 ml	Y	1000	1000	2	1000	Y	N
14/01/2012	15	053	031	1721	61	15	-28.000	-40.000	09:15	3X300 ml	Y	1000	2000	2	1000	Y	N
14/01/2012	15	053	031	1719	70	13	-28.000	-40.000	09:15	3X300 ml	Y	1000	1000	2	1000	N	N
14/01/2012	15	053	031	1717	80	11	-28.000	-40.000	09:15	3X300 ml	Y	1000	2000	2	1000	N	N
14/01/2012	15	053	031	1715	100	9	-28.000	-40.000	09:15	3X300 ml	Y	1000	2000	2	1000	Y	N
14/01/2012	15	053	031	1715	200	5	-28.000	-40.000	09:15	N	N	N	N	N	N	Y	N
15/01/2012	16	058	034	1802	5	24	-	-39.999	15:14	3X300 ml	Y	1000	1300	2	1000	N	3500

32.499																	
15/01/2012	16	058	034	1800	20	22	-32.499	-39.999	15:14	3X300 ml	Y	1000	1000	2	1000	N	N
15/01/2012	16	058	034	1798	35	20	-32.499	-39.999	15:14	3X300 ml	Y	1000	1000	2	1000	Y	N
15/01/2012	16	058	034	1796	50	18	-32.499	-39.999	15:14	3X300 ml	Y	1000	1000	2	1000	Y	N
15/01/2012	16	058	034	1793	56	15	-32.499	-39.999	15:14	3X300 ml	Y	1000	2000	2	1000	Y	N
15/01/2012	16	058	034	1791	65	13	-32.499	-39.999	15:14	3X300 ml	Y	1000	1000	2	1000	N	N
15/01/2012	16	058	034	1789	75	11	-32.499	-39.999	15:14	3X300 ml	Y	1000	1000	2	1000	N	N
15/01/2012	16	058	034	1787	100	9	-32.499	-39.999	15:14	3X300 ml	Y	1000	2000	2	1000	Y	N
15/01/2012	16	058	034	1787	200	5	-32.499	-39.999	15:14	N	N	N	N	N	N	Y	N
16/01/2012	17	063	037	1872	5	22	-37.417	-40.000	22:05	3X300 ml	Y	1000	1600	2	1000	1560	3000
16/01/2012	17	063	037	1871	35	21	-37.417	-40.000	22:05	3X300 ml	Y	1000	1000	2	1000	N	N
16/01/2012	17	063	037	1868	50	18	-37.417	-40.000	22:05	3X300 ml	Y	1000	1000	2	1000	1520	N
16/01/2012	17	063	037	1867	60	17	-37.417	-40.000	22:05	3X300 ml	Y	1000	600	2	1000	N	N
16/01/2012	17	063	037	1865	64	15	-37.417	-40.000	22:05	3X300 ml	Y	1000	600	2	600	1800	N
16/01/2012	17	063	037	1864	75	14	-37.417	-40.000	22:05	3X300 ml	Y	1000	1000	2	1000	N	N
16/01/2012	17	063	037	1863	85	13	-37.417	-40.000	22:05	3X300 ml	Y	1000	2000	2	1000	1220	N
16/01/2012	17	063	037	1860	100	10	-37.417	-40.000	22:05	3X300 ml	Y	1000	2000	2	1000	1640	N
16/01/2012	17	063	037	1858	200	8	-37.417	-40.000	22:05	N	N	N	N	N	N	1480	N
18/01/2012	18	073	043	1949	5	23	-42.416	-40.002	17:48	3X300 ml	Y	1000	1000	2	1000	Y	3660
18/01/2012	18	073	043	1947	20	21	-42.416	-40.002	17:48	3X300 ml	Y	1000	1000	2	1000	N	N
18/01/2012	18	073	043	1945	40	19	-42.416	-40.002	17:48	3X300 ml	Y	1000	1000	2	1000	Y	N
18/01/2012	18	073	043	1943	48	17	-42.416	-40.002	17:48	3X300 ml	Y	1000	1000	2	1000	Y	N
18/01/2012	18	073	043	1941	55	15	-42.416	-40.002	17:48	3X300 ml	Y	1000	1000	2	1000	N	N
18/01/2012	18	073	043	1939	65	13	-42.416	-40.002	17:48	3X300 ml	Y	1000	1000	2	1000	N	N
18/01/2012	18	073	043	1937	80	11	-42.416	-40.002	17:48	3X300 ml	Y	1000	2000	2	1000	Y	N
18/01/2012	18	073	043	1935	100	9	-	-40.002	17:48	3X300 ml	Y	1000	2000	2	1000	Y	N

18/01/2012	18	073	043	1931	200	5	42.416 / -42.416	-40.002	17:48	N	N	N	N	N	N	Y	N
21/01/2012	19	089	049	2093	5	23	-47.417	-39.988	10:40	3X300 ml	Y	1000	1000	2	1000	Y	3000
21/01/2012	19	089	049	2092	20	22	-47.417	-39.988	10:40	3X300 ml	Y	1000	1000	2	1000	Y	N
21/01/2012	19	089	049	2089	35	19	-47.417	-39.988	10:40	3X300 ml	Y	1000	1000	2	1000	N	N
21/01/2012	19	089	049	2087	46	17	-47.417	-39.988	10:40	3X300 ml	Y	1000	1000	2	1000	Y	N
21/01/2012	19	089	049	2085	50	15	-47.417	-39.988	10:40	3X300 ml	Y	1000	1000	2	1000	N	N
21/01/2012	19	089	049	2083	60	13	-47.417	-39.988	10:40	3X300 ml	Y	1000	1000	2	1000	Y	N
21/01/2012	19	089	049	2081	80	11	-47.417	-39.988	10:40	3X300 ml	Y	1000	2000	2	1000	N	N
21/01/2012	19	089	049	2079	100	9	-47.417	-39.988	10:40	3X300 ml	Y	1000	2000	2	1000	Y	N
21/01/2012	19	089	049	2075	200	5	-47.417	-39.988	10:40	N	N	N	N	N	N	Y	N
22/01/2012	20	092	050	2117	5	23	-51.029	-37.981	08:32	3X300 ml	Y	1000	2000	2	Y	Y	N
22/01/2012	20	092	050	2116	20	22	-51.029	-37.981	08:32	3X300 ml	Y	1000	2000	2	Y	N	N
22/01/2012	20	092	050	2115	30	21	-51.029	-37.981	08:32	N	N	1000	2000	2	Y	N	N
22/01/2012	20	092	050	2114	40	20	-51.029	-37.981	08:32	3X300 ml	Y	1000	2000	2	Y	Y	N
22/01/2012	20	092	050	2113	50	19	-51.029	-37.981	08:32	3X300 ml	Y	1000	2000	2	Y	N	N
22/01/2012	20	092	050	2112	70	18	-51.029	-37.981	08:32	N	N	1000	2000	2	Y	Y	N
22/01/2012	20	092	050	2111	80	17	-51.029	-37.981	08:32	3X300 ml	Y	1000	2000	2	Y	N	N
22/01/2012	20	092	050	2109	100	15	-51.029	-37.981	08:32	3X300 ml	Y	1000	2000	2	Y	Y	N
22/01/2012	20	092	050	2108	110	14	-51.029	-37.981	08:32	N	N	1000	2000	2	Y	N	N
22/01/2012	20	092	050	2107	115	13	-51.029	-37.981	08:32	3X300 ml	Y	1000	2000	2	Y	N	N
22/01/2012	20	092	050	2104	140	10	-51.029	-37.981	08:32	N	N	1000	2000	2	Y	Y	N
22/01/2012	20	092	050	2103	160	9	-51.029	-37.981	08:32	3X300 ml	Y	1000	2000	2	Y	N	N
22/01/2012	20	092	050	2099	200	5	-51.029	-37.981	08:32	N	N	N	N	N	N	Y	N
24/01/2012	21	111	059	2310	5	24	-52.501	-37.001	10:56	3X300 ml	Y	1000	1600	2	Y	Y	N
24/01/2012	21	111	059	2309	20	23	-	-37.001	10:56	3X300 ml	Y	1000	2000	2	Y	N	N

							52.501										
							-										
24/01/2012	21	111	059	2308	35	22	52.501	-37.001	10:56	3X300 ml	Y	1000	2000	2	Y	Y	N
24/01/2012	21	111	059	2307	50	21	-52.501	-37.001	10:56	3X300 ml	Y	1000	1500	2	Y	Y	N
24/01/2012	21	111	059	2306	80	20	-52.501	-37.001	10:56	3X300 ml	Y	1000	1000	2	Y	N	N
24/01/2012	21	111	059	2304	88	18	-52.501	-37.001	10:56	3X300 ml	Y	1000	1000	2	Y	Y	N
24/01/2012	21	111	059	2303	95	17	-52.501	-37.001	10:56	3X300 ml	Y	1000	1000	2	Y	N	N
24/01/2012	21	111	059	2298	100	12	-52.501	-37.001	10:56	3X300 ml	Y	1000	2000	2	Y	Y	N
24/01/2012	21	111	059	2297	120	11	-52.501	-37.001	10:56	3X300 ml	Y	1000	2000	2	Y	N	N
24/01/2012	21	111	059	2294	200	8	-52.501	-37.001	10:56	N	N	N	N	N	N	Y	N
25/01/2012	22	115	061	2357	5	24	-53.102	-36.536	11:42	3X300 ml	Y	1000	2000	2	Y	1750	N
25/01/2012	22	115	061	2355	30	21	-53.102	-36.536	11:42	3X300 ml	Y	1000	2000	2	Y	2000	N
25/01/2012	22	115	061	2354	40	20	-53.102	-36.536	11:42	3X300 ml	Y	1000	1000	2	Y	N	N
25/01/2012	22	115	061	2352	50	18	-53.102	-36.536	11:42	3X300 ml	Y	1000	1000	2	Y	2000	N
25/01/2012	22	115	061	2351	60	17	-53.102	-36.536	11:42	3X300 ml	Y	1000	1000	2	Y	N	N
25/01/2012	22	115	061	2350	75	16	-53.102	-36.536	11:42	3X300 ml	Y	1000	2000	2	Y	2000	N
25/01/2012	22	115	061	2349	100	15	-53.102	-36.536	11:42	3X300 ml	Y	1000	2000	2	Y	2000	N
25/01/2012	22	115	061	2348	200	14	-53.102	-36.536	11:42	N	N	N	N	N	N	2000	N
26/01/2012	24	120	063	2404	5	22	-54.000	-36.000	07:12	3X300 ml	Y	500	1000	2	500	N	N
26/01/2012	24	120	063	2402	10	20	-54.000	-36.000	07:12	3X300 ml	Y	500	1000	2	500	N	N
26/01/2012	24	120	063	2396	20	14	-54.000	-36.000	07:12	3X300 ml	Y	500	1000	2	500	N	N
26/01/2012	24	120	063	2394	30	12	-54.000	-36.000	07:12	3X300 ml	Y	500	1000	2	500	N	N
26/01/2012	24	120	063	2392	40	10	-54.000	-36.000	07:12	3X300 ml	Y	500	1000	2	500	N	N
26/01/2012	24	120	063	2390	45	8	-54.000	-36.000	07:12	3X300 ml	Y	500	1000	2	500	N	N
26/01/2012	24	120	063	2384	50	2	-54.000	-36.000	07:12	3X300 ml	Y	500	1000	2	500	N	N
26/01/2012	FISH		12:55		5				12:55	3X300 ml	Y	500	1000	2	500	N	N
26/01/2012	FISH		13:56		5				13:56	3X300 ml	Y	500	1000	2	500	N	N

26/01/2012	FISH	14:55	5		14:55	3X300 ml	Y	500	1000	2	500	N	N
26/01/2012	FISH	15:56	5		15:56	3X300 ml	Y	500	1000	2	500	N	N
26/01/2012	FISH	17:56	5		17:56	3X300 ml	Y	500	1000	2	500	N	N
26/01/2012	FISH	18:55	5		18:55	3X300 ml	Y	500	1000	2	500	N	N
26/01/2012	FISH	20:01	5		20:01	3X300 ml	Y	500	1000	2	500	N	N
26/01/2012	FISH	20:54	5		20:54	3X300 ml	Y	500	1000	2	500	N	N
26/01/2012	FISH	21:46	5		21:46	3X300 ml	Y	500	1000	2	500	N	N

5.11 DOWNWARD PARTICLE FLUXES ALONG TRANSECT 40°S TRANSECT: APPLICATION OF 234TH:238U DISEQUILIBRIA TECHNIQUE

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<u>Objective</u>

Using ^{234}Th:^{238}U disequilibria technique and deployments of Stand Alone Pump Systems (SAPS), measure vertical fluxes of particulate organic carbon and nitrogen (POC and PON), particulate inorganic carbon (PIC), and biogenic silica (BSi) along 40S parallel of the Southern Atlantic to estimate the amount of primary production exported from the surface of the ocean to its interior.

<u>Methods</u>

^{234}Th:^{238}U Disequilibria Approach. Rationale

^{234}Th is widely used as a natural tracer of marine particle formation, transport, and dissolution. ^{234}Th is a naturally occurring isotope, produced by radioactive α-decay of ^{238}U. Unlike conservative ^{238}U ($t_{1/2}$=4.5x10^9 yr), ^{234}Th has a short half-life ($t_{1/2}$=24.1 days) and a strong scavenging affinity, i.e. it is readily scavenged onto particles surfaces and exported with them out of the euphotic zone. In the absence of ^{234}Th uptake onto particles, a secular equilibrium between ^{234}Th and ^{238}U is expected (^{234}Th=^{238}U). Since ^{234}Th is scavenged and then removed from the surface of the ocean as particles descend, a deficiency in ^{234}Th relative to ^{238}U occurs in the upper water column (^{234}Th > ^{238}U, also known as ^{234}Th : ^{238}U disequillibrium) (Santschi, Murray et al. 2006; Verdeny, Masque et al. 2009; Maiti, Benitez-Nelson et al. 2010). An opposite process takes place at depth where particles are solubilized and remineralized supplying ^{234}Th back into the water column and causing ^{234}Th excess relative to ^{238}U (^{234}Th < ^{238}U) (Maiti, Benitez-Nelson et al. 2010).

Assuming steady state of the system (no advective or diffusive turbulent transport), ^{234}Th flux from surface to depth can be calculated from its activity profile integrated from surface to depth z where ^{234}Th and ^{238}U secular equilibrium is reached:

$$Th \, flux = \int_0^z \lambda_{Th}(A_U - A_{Th}) \, dz$$

where λ_{Th} is ^{234}Th decay constant ($\lambda_{Th} = 0.20876 d^{-1}$); A_U is ^{238}U activity (dpm m^{-3}) calculated from the salinity; A_{Th} is ^{234}Th activity (dpm m^{-3}) (measured by beta-counting). Detailed description of ^{234}Th analytical procedures is given in Ruetgers van der Loeff *et al.* (2006) (Rutgers van der Loeff, Sarin et al. 2006).

To derive particulate fluxes, ^{234}Th fluxes are multiplied by the known concentration ratio of a particle-associated element (e.g. C, N, P, etc.) to ^{234}Th on large particles collected with either sediment traps or *in situ* filtration systems. For example, ^{234}Th-derived POC flux (export) is calculated as follows in (Rutgers van der Loeff, Sarin et al. 2006):
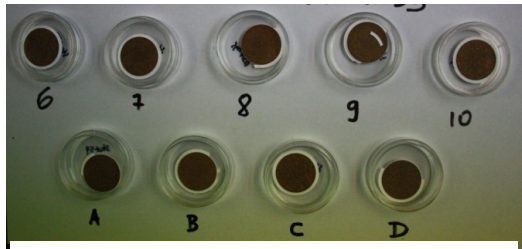
$$POC\ flux = 234Th\ flux * {POC}/{234Th} \qquad \text{(eqn 1)}$$

<u>On-board work</u>

Total [234]Th collection and processing

To determine total [234]Th activity in seawater, 'small volume' technique (Pike, Buesseler et al. 2005) was used. [234]Th was scavenged onto MnO_2 co-precipitate in 4L of seawater collected at 11-12 different depths on a stainless CTD rosette. The method allowed immediate on-board beta-counting of [234]Th activity and enhanced both spatial and temporal resolution of particle export.

Within ~1 hour of collection, seawater samples were acidified to pH 1-2 with concentrated HNO_3 at 1.5ml/L to separate [234]Th from parental [238]U and shaken vigorously. 50µl (0.35Bq/g) of [230]Th yield tracer was then added to each sample bottle. The samples were vigorously shaken again and left to equilibrate for 6-8hrs. After equilibration, 7-8ml of HN_4OH was added per sample to bring the pH to 8.0-8.1. To form suspension of MnO_2, 50µl (7.5mg/L) of $KMnO_4$ and 50µl (7.5mg/L) of $MnCl_2$ were subsequently added to seawater samples. The MnO2 precipitate was then allowed to scavenge [234]Th for 6-8hrs. The bottles where precipitation of MnO2 took place were then attached to a specially designed filter-holders and the content was precipitated onto ashed 25mm QMA (Whatman) filter (Fig.28). Filter precipitates were dried for 12-24hrs at 60°C

and then mounted onto Risø beta-counter filter holder under layer of Mylar film and Al foil in order to shield alpha-particles and low energy beta-emitters. [234]Th was quantified by counting daughter [234m]Pa ($t_{1/2}$=1.2min) on a low-level Argon gas-flow 5-sample GM-25 beta-counter manufactured by Risø National Laboratories (Roskilde, Denmark). The counter utilized an anti-coincidence shield above 25mm-diameter sample windows. The unit was completely shielded by lead bricks to reduce background count

Figure 28: QMA filters with MnO2 precipitate

rates. To assess efficiency of beta-counter, deep water (from >1000m depth) was collected and analyzed for [234]Th activity. The activity of parental [238]U was calculated from water salinity according to Chen et al (1986)(Chen, Edwards et al. 1986):

$$^{238}U = 0.07081 \times S(‰) \qquad \text{(eqn 2)}$$

Initial counting will be followed by a final background radiation count after >7 half-lives of [238]Th decay (~6 months).

Stand Alone Pumping Systems (SAPS) Deployments

When measuring particle export fluxes with [234]Th disequillibrium approach, it is important to know the ratio of the element of interest on sinking particles (eqn 1).

Sinking particles were collected below the mixed layer (Table 9) onto a prefilter (53µm Nitex mesh) and a main filter (0.8 µm PES filter dedicated completely to trace metal analysis) (Fig.29). SAPS were set to pump for 1.5 hrs with a delay time of 0.6-1.3 hrs, as a result pumping between 400-2000 L of seawater. When recovered, a piece of Nitex mesh was cut for particulate trace metal analysis. The remaining particles were rinsed off the Nitex mesh with

exactly 1L of filtered FISH seawater (0.4 µm Polycarbonate Whatman filters). Resulting particle concentrated solution was split into subsamples with Folsom splitter. Split sizes were normally as follows: ¼ for POC and PON, ¼ for [234]Th, 1/8 for PIC and 1/8 for BSi; ¼ was given for analyses of ^{14}C isotopes and amino acids to Robyn Tuerena and Amandine Sabadel, respectively. The splits were then filtered onto pre-combusted (12hrs @ 450 °C) 25mm GF/F (Whatman) filters for POC and PON analyses, onto pre-combusted 25mm QMA (Whatman) filter for [234]Th analysis, and onto 25mm membrane polycarbonate (Whatman) filters for PIC and BSi analyses. All filters were then dried for 12-24hrs in the oven at 60°C. [234]Th filters were immediately counted on beta-counter (as described in 2.2.1), while POC (PON), PIC and BSi were stored for further analysis in land laboratory. Blanks for POC, PON, PIC and BSi were obtained by filtering 200ml of the seawater used for rinsing the particles off the Nitex mesh.

Figure 29: Particles collected onto PES filter (distant) and Nitex mesh (front). In this deployment Nitex mesh 'caught' a lot of krill

Future on-land analysis will include background counting of particulate [234]Th. POC and PON will be determined by fuming respective filters with HCl for 24hrs, drying them for 24hrs and then analyzing on CHN analyzer. PIC filters will be leached with 1 M acetic acid for 24hrs and analyzed for Ca with inductively-coupled plasma atomic emission spectroscopy (ICP-AES). BSi samples will be digested in 0.2 M NaOH for 3 h at 90°C and measured as Si with an autoanalyzer.
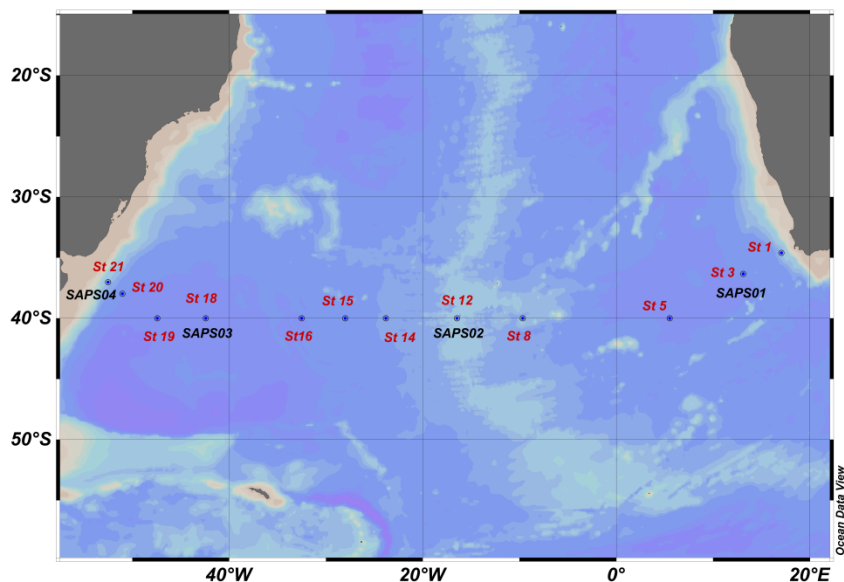
Figure 30: Stations sampled for total [234]Th and SAPS deployed

<u>Results</u>

Collected samples

12 stations were sampled to measure total [234]Th activity (Fig.30, Table 8). 11-12 samples were collected between surface and 400m depth at stations 3, 5, 8, 12, 14, 16, 18, 20. 14; station 21 included 11 samples coming from the surface to 400m and 3 samples from 1000 to 20m above the seafloor; 5 deep samples (from >100m depth) were collected at station 15; 6 deeps samples (3 from ~3000m and 3 from 4000m depth) were collected at station 19. The summary of all the total [234]Th samples are given in the Table 8.

Table 8: Stations sampled for total [234]Th during JC068

Station #	Date	Lon E	Lat N	Depths sampled [m]
1	28/12/2011	17.053826	-34.612418	4.3, 18.9, 29.1, 44.0, 49.2, 58.6, 78.8, 98.2, 198.7, 297.7, 396.7
3	29/12/2011	13.106173	-36.343107	3.1, 17.6, 26.9, 46.4, 58.2, 71.9, 97.3, 117.5, 297.2, 37.5, 396.3
4	01/01/2012	5.517732	-39.99972	4.6, 20.1, 29.9, 41.2, 49.2, 60.3, 79.6, 99.3, 123.9, 298.4, 398.3
8	06/01/2012	-9.666384	-39.999299	4.1, 19.3, 34.3, 41.2, 48.6, 54.1, 74.0, 99.6, 199.2, 298.1, 396.9
12	10/01/2012	-16.465105	-40.001732	0.3, 15.8, 26.0, 35.6, 45.7, 55.8, 75.0, 96.0, 136.6, 196.1, 294.3, 393.4
14	13/01/2012	-23.800013	-39.999978	0.8, 15.9, 35.5, 41.1, 48.0, 68.3, 78.1, 98.1, 118.8, 198.6, 298.2, 397.6
15	14/01/2012	-27.999989	-40.000013	994.2, 1491.2, 2491.3, 2993.0, 3491.5
16	15/01/2012	-32.498563	-39.998592	4.5, 19.9, 34.1, 49.6, 56.0, 65.2, 74.6, 99.5, 119.1, 199.7, 299.3, 398.0
18	18/01/2012	-42.41579	-40.001206	6.1, 20.4, 40.8, 48.0, 55.7, 64.6, 79.6, 100.9, 119.3, 200.1, 299.8, 398.9
19	21/01/2012	-47.41667	-39.993915	3990.1, 3990.1, 3990.1, 2989.4, 2989.4, 2989.4
20	22/01/2012	-51.029353	-37.982839	5.4, 20.5, 30.7, 49.9, 79.9, 90.0, 114.9, 120.4, 149.8, 199.6, 299.3, 396.9
21	24/01/2012	-52.502528	-37.025569	0.0023, 15.0, 30.2, 45.0, 74.8, 82.6, 89.5, 95.1, 114.5, 194.6, 393.3, 985.7, 2564.5, 3316.9

SAPS deployments were performed during the cruise (Table 9). Deployment depths were chosen in a way that the shallowest SAPS was located right below the base of mixed layer depth and the deepest one at 400m depth. Additional samples from deep SAPS deployments were taken at station 21 to investigate possibility of [234]Th scavenging by resuspended sediments. Most of the shallow SAPS deployments were successful with an exception of stations 12 (100m) and station 18 (400m) where pumps misfired (see low volumes pumped in Table 9).

Table 9: Summary of SAPS deployments during JC068 (pump misfires are in red)

Station #	S/N SAPS	Depth [m]	Delay [hrs]	Pump [hrs]	Volume [L]
3	03-02	75	0.8	1.5	1351
3	03-05	175	0.6	1.5	1936
3	02-003	425	0.6	1.5	2122
12	02-002	400	1.3	1.5	506
12	03-04	150	1.3	1.5	1123
12	02-003	100	1.3	1.5	5
12	03-005	60	1.3	1.5	843
18	02-003	400	1.2	1.5	1
18	03-04	250	1.2	1.5	947
18	03-005	150	1.2	1.5	899
18	03-02	50	1.2	1.5	445
21	03-04	3260	2.4	1.5	949
21	03-02	2600	2.4	1.5	540
21	03-005	1000	2.4	1.5	870
21	03-03	400	1.2	1.5	1562
21	03-04	250	1.2	1.5	1250
21	03-005	150	1.2	1.5	1128
21	03-02	100	1.2	1.5	719

Preliminary results

[234]Th activity profiles from stations 1-21 (Fig. 31, station 21 is not shown) were estimated based on first activity counts performed on board 2-3 days after sample collection. Here, for all the samples, background activity and recovery were assumed to be 0.3cpm and 95% respectively. The profiles of stations 1-18 showed a relatively high depletion of [234]Th in the upper water column (surface to ~50m depth), and a secular equillibria regained just below 100m. Weaker [234]Th:[238]U disequilibria were also observed in Station 20. Stations 3, 5 and 20 showed [234]Th excess between 200m and 400m indicating remineralization processes. [234]Th depletion at 300m and 400m was observed in stations 3, 14, and 16.

[234]Th first-count data for Station 21 still has to be processed, and therefore was not presented in this report.
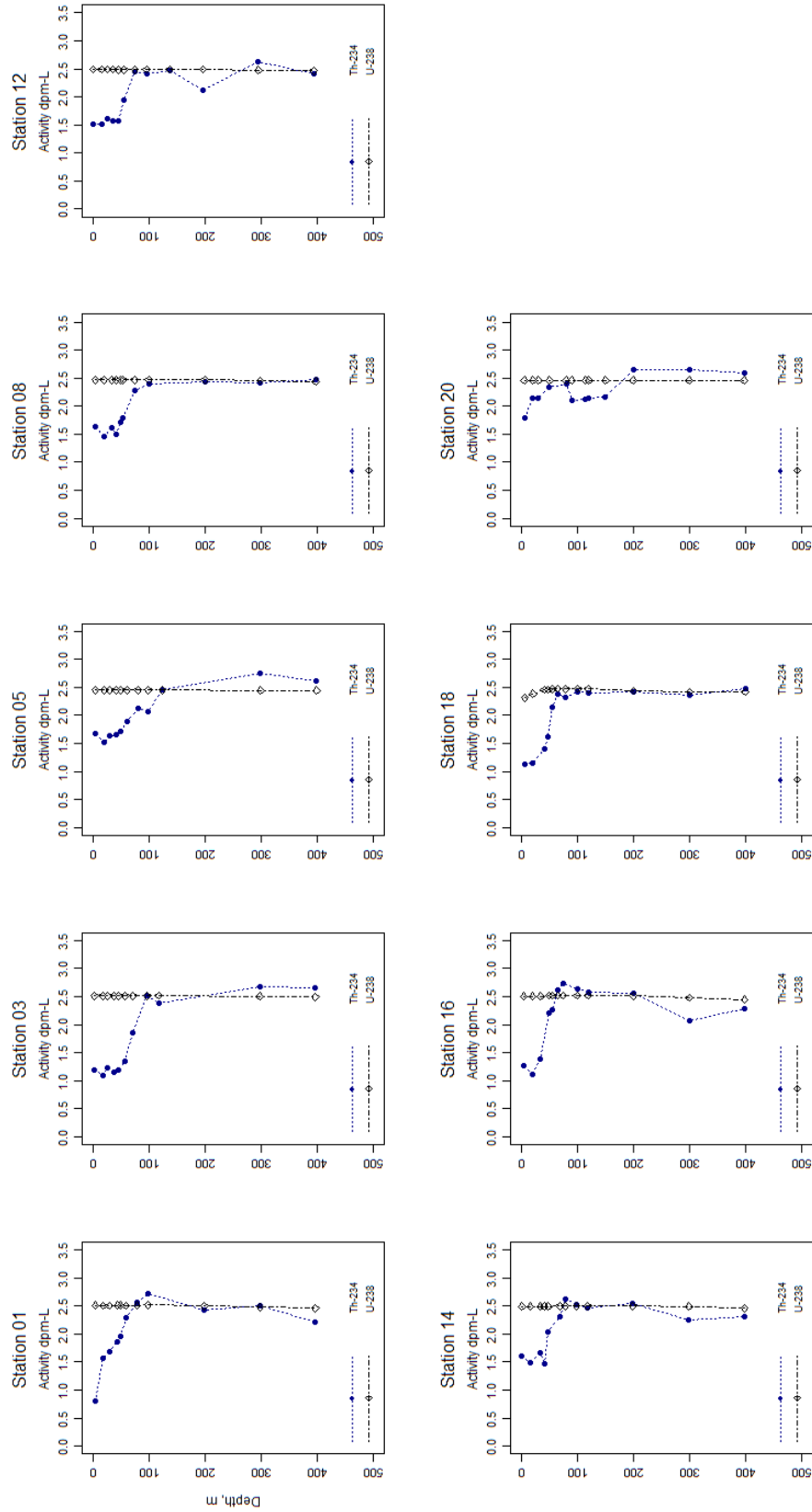
Figure 31: Estimated ^{234}Th Activity profiles with assumed background count rate of 0.3 cpm and recovery of 95%. Error for U-238 activity is about 3%.

References

Chen, J. H., R. L. Edwards, et al. (1986). "238U, 234U and 232Th in seawater." EarthandPlanetaryScienceLetters(80): 241-251.

Maiti, K., C. R. Benitez-Nelson, et al. (2010). "Insights into particle formation and remineralization using the short-lived radionuclide, Thoruim-234." Geophys. Res. Lett. 37(15): L15608.

Pike, S. M., K. O. Buesseler, et al. (2005). "Quantification of Th-234 recovery in small volume sea water samples by inductively coupled plasma-mass spectrometry." Journal of Radioanalytical and Nuclear Chemistry 263(2): 355-360.

Rutgers van der Loeff, M., M. M. Sarin, et al. (2006). "A review of present techniques and methodological advances in analyzing 234Th in aquatic systems." Marine Chemistry 100(3-4): 190-212.

Santschi, P. H., J. W. Murray, et al. (2006). "Thorium speciation in seawater." Marine Chemistry 100(3-4): 250-268.

Verdeny, E., P. Masque, et al. (2009). "POC export from ocean surface waters by means of Th-234/U-238 and Po-210/Pb-210 disequilibria: A review of the use of two radiotracer pairs." Deep-Sea Research Part Ii-Topical Studies in Oceanography 56(18): 1502-1518.

5.12 MICRONUTRIENT ISOTOPE RATIOS

Samples were collected for a number of scientists and returned to their respective institutions for analysis, the elements and the institutions are detailed below:

Cr isotopes   Ken Amor, Department of Earth Sciences, University of Oxford, South Parks Road, Oxford, OX1 3AN.

Fe isotopes   Seth John, Department of Earth and Ocean Sciences, University of South Carolina, Columbia, SC 29208.

Cu/Zn isotopes Derek Vance, School of Earth Sciences, Wills Memorial Building, Bristol, BS8 1RJ.

Cd isotopes   Gideon Henderson, Department of Earth Sciences, University of Oxford, South Parks Road, Oxford, OX1 3AN.
Mark Rehkamper, Department of Earth Science & Engineering, Imperial College, Prince Consort Road, London, SW7 2AZ.

Pb isotopes   Dominik Weiss, Department of Earth Science & Engineering, Imperial College, Prince Consort Road, London, SW7 5PD.

Sampling

Profiles were collected from varying depths through the whole water column using twenty-four 10 L OTE bottles mounted on a Ti rosette. On recovery, the OTE bottles were transferred into a clean sampling container where they were immediately sampled for nutrients and salinity. Unfiltered samples for Pb were collected prior to the OTE bottles being pressurised to approximately 7 psi with 0.2 µm filtered air using an oil free compressor. An Acropak (Pall) filter capsule (0.2 µm) was then attached to the Teflon taps of the OTE bottles using acid cleaned Bev-A-Line (Cole Parmer) and silicon tubing for the collection of filtered samples. Samples were collected into clean sample bottles which varied in size and make depending on the isotopic element of interest (see metadata sheets for the respective element). Bottles and caps were rinsed 3 times with seawater sample before being filled. All isotope samples collected were stored unacidified. All samples were double bagged within the clean container before storage.

Samples Collected:

Iron Isotopes- 1L filtered
        Stations   8,11,12,13,16,18,21
        Samples   160
Cu/Zn Isotopes- 2 x 1L filtered or 2 x4L Filtered in surface waters
        Stations   12,18,21
        Samples   68
Cd Isotopes- 1L filtered at depth, 1 x 5L mid water column, 2 X 10L surface waters
        Stations   12,18,21
        Samples   68
Cr Isotopes- 500 ml filtered
        Stations   12,18,21
        Samples   68

Analysis

Samples will be analysed at the respective institute for the isotope of interest. Various methodologies will be followed as detailed in the metadata sheets.

5.13 Particulate d^{15}N, d^{13}C, and POC/PON

By Robyn Tuerena
School of Geosciences, University of Edinburgh.
Email: r.e.tuerena@sms.ed.ac.uk

Modern and palaeoproxy for nutrient content and ocean circulation

NO_3- utilization results in an increase in the d^{15}N of residual NO_3-, this signal is then transferred to PON which can be traced as it sinks through the water column. Mapping the d^{15}PON values across this transect both at the surface and at depth can provide information on productivity rates and the transfer of isotopic signals to the deep ocean. Isotopic data can also be used to investigate relative proportions of marine and terrestrial organic matter in suspended and bottom sediments and in combination with grain size analysis and productivity proxies can be used to unravel processes that govern the distribution at 40ºS.

Sample collection
Particulate samples were collected onto ashed, pre weighed GF/F microfibre filters (0.7µm pore size, 25 mm diameter). Water was primarily collected from the biological rosette in the surface 400m, when the water budget allowed, deeper samples were also taken from the regular rosette. 2-4 litres were taken from the high chlorophyll surface waters and 8-10 from deeper waters depending on chlorophyll levels from the CTD.

Eight depths were sampled from each rosette, and pressure filtered simultaneously using a compressor (at ~10 psi) and an 8-way manifold system. Each sample was filtered within half an hour of collection. Once the total volume for each depth was filtered, the filters were extracted from the filter holder, placed in labelled aluminium foil and dried at 50 °C for ~12 hours. Once dried, filters were placed in ziplock bags and frozen at -20 °C. Bottles were rinsed three times with Milli-Q between samples.

Sample analysis
Analyses will be conducted at the School of Geosciences. filter samples will be analysed using a Carlo Erba NA 2500 elemental analyser in-line with a VG PRISM III isotope ratio mass spectrometer for elemental POC/PON and $\delta^{13}C_{POC}$ and $\delta^{15}N_{PON.}$,. To prepare for analysis filters will be defrosted, re wet with Milli-Q water and placed in a dessicator containing an open beaker of HCl for 48 hours to dissolve any carbonates present. Filters will then be dried, cut in half and packed in to tin cups for analysis.

References:
D.Carson, 2008. Particulate barium transformations and fluxes in the continental shelf Antarctic sea ice environment (Thesis).

MJ Lourey, Trull TW and Sigman DM, 2003. Sensitivity of d[15]N of nitrate, surface suspended and deep sinking particulate nitrogen to seasonal nitrate depletion in the Southern Ocean. <u>Global Biogeochemical Cycles</u>, **17 (**3) 1081

5.14 DISSOLVED BARIUM

By Robyn Tuerena

Contact:
Dr Raja Ganeshram
School of Geosciences, University of Edinburgh.

Dissolved Ba (Ba^{2+}) is removed from seawater as barite which is formed in association with opal and decaying organic matter. Vertical profiles of dissolved barium will help to provide information about how the Ba budget is influenced by biogenic particle formation.

Sample collection
Dissolved Ba samples were collected from each station. Samples were taken from approximately 12 depths on the stainless steel rosette. Seawater was filtered through an Acropak (0.4 μm) into 30 ml Nalgene bottles. The bottles were pre-acidified at the University of Edinburgh with ultra pure HCl. After collection samples have been stored at room temperature in labelled ziplock bags.

Sample Analysis
Dissolved Ba will be analysed by inductively coupled plasma optical emission spectroscopy (ICP-OES) at the School of Geosciences, University of Edinburgh. Samples will be resuspended in HNO_3 for analysis.

References:
D.Carson, 2008. Particulate barium transformations and fluxes in the continental shelf Antarctic sea ice environment (thesis chapter).

Ganeshram, R.S, R. Franc, J. Commeau and S.L Brown-Leger, 2003. An Experimental Investigation of Barite Formation in Seawater. Geochimica et Cosmochimica Acta **67** (14) 2599–2605.

WORKPACKAGE 6: ASSESSING MIXING AND CIRCULATION
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6.1 VELOCITY MICROPROFILER
The VMP device was overseen by Kurt Polzin, Woods Hole Oceanographic Institute

6.2 ARGO FLOATS
Deployment info; GA10 line; JC068

SOLO #1
WHOI Float #   1118
PTT ID# 104048
Lat: 39 59.98' S
Lon: 13 00.32' E
Deployed: 03:35 9 Jan 2012 UTC
Station 11

SOLO #3
WHOI Float #   1121
PTT ID# 104051
Lat: 39 59.81' S
Lon: 19 56.62' W
Deployed: 07:11 12 Jan 2012 UTC
Station 13

SOLO #5
WHOI Float # 1091
PTT #   104022
Lat: 39 59.470 S
Lon: 32 29.410 W
Deployed: 02:36 16 Jan 2012 UTC
Depth: 4806 m
Station 16

SOLO #2
WHOI Float #   1108
PTT ID#   104038
Lat: 40 0.075' S
Lon: 16 28.474' W
Deployed: 22:15 10 Jan 2012 UTC
Station 12

SOLO #4
WHOI Float #   1097
PTT ID# 104028
Lat: 39 59.91' S
Lon: 23 48.28' W

Deployed: 09:54 13 Jan 2012 UTC
Station 14

APEX #1
UK Float # 5555
Lat: 40 00.00' S
Lon: 37 25.00' W
Depth: 5102m
Magnet Swipe: 13:12 Jan 17 UTC Deployed: 14:34 Jan 17 2012 UTC
Conditions: 2m swell, 25 knot winds, cloudy sky
Air Temp: 14.3 C
Station 17

SOLO #6
WHOI Float #   1105
PTT ID# 104036
Lat: 40 00.300' S
Lon: 37 24.905' W
Deployed: 14:34 UTC Jan 17 2012
Depth: 5148m
Station 17

SOLO #7
WHOI Float #   1090
PTT ID# 104021
Lat: 40 00.00' S
Lon: 42 35.00' W
Deployed: 05:21 Jan 20 2012 UTC
Depth: 5156m
Station 18

SOLO #9
WHOI Float #   1096
PTT ID# 104027
Lat: 39 59.28' S
Lon: 47 26.51' W
Deployed: 12:27 Jan 21 2012 UTC
Depth: 4926 m
Station 19

APEX #2
UK Float # 5556
Lat: 40 00.00' S
Lon: 42 35.00' W
Depth: 5156m
Magnet Swipe: 04:43 Jan 20 UTC
Deployed: 05:20 Jan 20 2012 UTC
Conditions: 2m swell, 20 knot winds, partly cloudy sky
Air Temp: 18.1 C
Station 18

SOLO #8
WHOI Float # 1111
PTT ID 104047
Lat: 40 00.00 S
Lon: 44 53.10 W
Deployed: 14:25 UTC Jan 20 2012
Depth: 5136m
Station #: N/A (Between Stations 18/19)

APEX #3
UK Float # 5554
Lat: 39 58.26 S
Lon: 47 26.53 W
Depth: 4928m
Magnet Swipe: 1112 Jan 21 UTC
Deployed: 1125 Jan 21 2012 UTC
Conditions: 1m swell, 5 knot winds, clear sky
Air Temp: 18.35 C
Station 19

APEX #4
UK Float # 5553
Lat: 38 13.46' S
Lon: 51 01.91' W
Depth: 4895 m
Magnet Swipe: 1129 Jan 23 UTC
Deployed: 1154 Jan 23 2012 UTC
Conditions: 1m swell, 6 knot winds, clear sky
Air Temp: 21.72 C
Station 20

SOLO #10
WHOI Float #   1109
PTT ID# 104039
Deployed: 11:55 Jan 23 2012 UTC
Lat: 38 13.59' S
Lon: 51 01.72' W
Depth: 4895 m
Station 20

On this cruise there were 9 WHOI Argo floats deployed. They are Series 1 SOLO floats. They were activated after being shipped but prior to loading on the ship. Each float received a physical inspection prior to deployment. The deployment method for these 9 floats was by using a slip line attached to the water release bridle. The float was lowered over the stern while the ship was moving at about 1-2 knots. It was possible to simply let the box containing the float slide over the stern as the deployment box protects it from the possibility of banging against the ship. The float would sit in the water for 5-15 seconds before the mechanism released and the float, inside of its deployment box, would float away.

There were 4 UK Argo floats deployed as well. They are APEX floats from Webb/Teledyne. These were started up from 1 hour to 20 minutes before deployment. Their function was verified using a receiver or "beeper" which emits a noise each time the float transmits a signal, confirms the float is running. These floats were lowered over the starboard rail of the stern again using a slip line. The crane could have been used but wasn't necessary. The deployment of these floats was a bit more delicate as they were not housed in anything. Extra care was required while lowering them over the rail so as not to collide with the ship while in motion. It would be advisable if in the future necessary equipment like the small disposable receivers were shipped in doubles. There was a point where the receiver, which functions on the ARGOS frequency, stopped working. For the APEX version float, if it cannot be confirmed that the float is successfully transmitting messages then the float will not be deployed. In this instance a receiver was sourced from Spray glider equipment, which allowed the remaining floats to be deployed. Had this not been the case 3 APEX floats would have never been launched.

The floats deployment locations were chosen based on areas which were lacking current float coverage. This area of the South Atlantic is normally sparse with Argo floats due to strong currents which tend to move any floats away from the area. The float deployments were also doubled up in areas of diverging currents and higher interest. In the four locations where an APEX float was deployed a SOLO float was deployed as well.

Further information regarding the Argo floats deployed on this cruise may be found here:

http://argo.whoi.edu/argo.whoi_indexes.html
http://www.bodc.ac.uk/projects/international/argo/uk_floats/

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6.3 GLIDER

A Spray glider was deployed during the JC068 cruise as well. The Glider was being used to collect micro-turbulence data using a Rockland Scientific MicroRider sensor. The deployments also collected useful data concerning the flight dynamics of the Spray glider with the MicroRider attached. There have been few instances where a Spray has been deployed and recovered in this manner. A new deployment device was created which made deployments possible from a ship of this size. The deployment device was simply a hook/cradle with bars on the back to protect the wings in the event of a collision with the ship.

While deployment is very similar to that which is done on a regular basis from a smaller boat the recovery is another issue. Recoveries are usually performed by using a steadying pole and the same device the glider was deployed from. When in the "Roaring 40's" as they are known recovery is not that simple. A small boat recovery using a Rigid Inflatable Boat, or RIB, is normally what is done for recovery. The James Cook is not equipped with such a boat. Recoveries need to be performed using the ships jet rescue boat. The Sprays' larger extremities make this type of recovery difficult due to the small amount of open space in the boat. This is compounded by the high, solid sides of the boat and as well the delicate nature of the antennae in the wings and tail.

The crane used for deployments was positioned on the rear starboard quarter. The placement of the crane was less than ideal for deployments. When deploying the glider, and many other instruments, it is best to keep it at least 1/3 of the distance of the line paid out between the instrument and the ship. This keeps the instrument, in this case the glider safely away from the side of the ship. The ships layout put the glider at a position which obstructed the view of the crane operator as it neared the water. While the crew still managed to perform well, this is a less than ideal condition for glider work. A crane placed mishaps would also be preferable for glider work, as the ships movement would be a little less drastic from wave action.

Anytime a crane will be used for recovery it is important to have a pole or some connection to the floating instrument. In this case there was a long carbon fiber pole which proved to be too unwieldy with the safe distance that the ship needed to keep from the glider. A small boat recovery was the only real option. This was always contingent on good weather which was the biggest concern for recovery.

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6.4 ASSESSING MIXING AND CIRCULATION IN DEEP WATERS WITH [227]AC AND [223,224,226,228]RA

By Walter Geibert

Samples to be analysed by Walter Geibert, Alan Hsieh

Objectives

The mixing of deep waters on annual to decadal time scales is a process of eminent importance for global biogeochemical cycles. It moderates temperatures between deep and surface waters, thus affecting global overturning circulation, and it provides a mechanism by which micronutrients released from deep ocean sediments can eventually reach surface waters and trigger productivity. The parameterization of ocean mixing, especially its vertical component, has been shown to strongly influence the outcome of global climate models (Brierley et al. 2008); however, it is only poorly constrained.

One way of studying mixing is the measurement of related physical properties, which is the approach of the ADCP and VMP measurements that were also conducted during this cruise. While being highly precise, these analyses only reflect the mixing at the exact time of measurement.

Tracer studies have the potential to integrate mixing over longer time scales. This can either be done by release of artificial stable tracers (Ledwell et al. 2000), or by use of naturally occurring radioactive isotopes. A unique tracer in this context is [227]Ac, which has a pronounced source in deep sea sediments, and has an ideal half-life (21.8 years) to trace vertical mixing in the deep-sea (Nozaki 1984). Complimentary information can be obtained by studying the longer-lived radium isotopes 228 and 226. In regions of pronounced deep upwelling, [227]Ac can also be used to constrain rates of deep upwelling (Geibert et al. 2002), and the combination of Ac and Ra can potentially be used to constrain the age of water masses. However, no measurements from the South Atlantic north of the Polar Front were available. This Geotraces cruise provided a unique opportunity to study deep-ocean mixing in direct comparison with micronutrient supply and supporting [231]Pa activities, in a context of varying mixing regimes (deep-sea plains, mid ocean ridge, continental slopes).

The objective of this work package was therefore:

To quantify deep ocean mixing and the associated biogeochemical fluxes on a transect along 40 degrees South.

Sampling protocol and sample analysis

Samples were collected with the standalone pumping systems (SAPS), manufactured by Challenger Oceanic systems, supported by NERC Marine Facilities. The systems pumped sea water in situ over a GF/F filter and subsequent absorbers for radium and actinium.

Samples usually comprised around 300 L, pumped over MnO_2 absorbers in situ. The absorbers consisted of two perspex tubes filled with MnO2-coated acrylic fiber in series. The sampling was combined with particulate biomarker measurements, which meant the Ra sampling took place behind a 293 mm GF/F filter.

After recovery of the pumps, the absorbers were immediately taken out of the filter cartridge, labelled (including absorber sequence) and the fibre was partly dried manually (squeezing) to remove sea water. This process was repeated three times with added Milli Q to remove salt. The samples were then counted with a four channel Radium Delayed Coincidence Counting system (RaDeCC, Moore and Arnold 1996) within the next three-four days, as quickly as the counting capacity allowed, in order to detect potential [223]Ra or [224]Ra excess near the sea floor, if present. The counter was calibrated regularly with two standard samples of the short-lived Ra parent nuclides [227]Ac and [228]Th, which had been obtained from IAEA-MEL Monaco (J. Scholten) in

2009. The counter was run empty with non-recirculated air at regular intervals in order to ensure that the scintillation cell was dry and efficiency was not affected by moisture.

The calculation considers chance coincidence events. Adsorption efficiency of actinium and radium isotopes for the MnO_2 adsorbers is assumed to be 100% for the flow rates used here. For SAPS samples, the efficiency will be assessed by means of an independent measurement of ^{226}Ra, and a transfer of the observed adsorption efficiency to the other Ra isotopes. For Ac, the ratio of the concentration found on two subsequent adsorbers will be used to calculate the efficiency.

The samples will be re-counted when back in the home laboratory (Jan-Mar 2011), and then processed for ^{228}Ra/^{226}Ra in Oxford. The methods for measuring ^{228}Ra/^{226}Ra ratios and ^{226}Ra and ^{228}Ra concentrations are described above (see sample analysis in WP4).

Preliminary results

Shipboard results indicate that the deepest samples are enriched in ^{227}Ac, and to a lesser extent in ^{228}Th, which is a non-quantitative indicator of ^{228}Ra.

^{227}Ac activity levels, estimated from ^{223}Ra, turned in general out to be lower than previously found South of the Antarctic Circumpolar Current (ACC), approximately by a factor 3, a result which had not been expected, at least not that pronounced. The systematic decrease in ^{223}Ra/^{224}Ra (total) with water depth suggests that we should still be able to further constrain vertical mixing in the deep Atlantic with our approach, as anticipated.

A surprising finding were high ^{223}Ra/^{227}Ac activities at the deepest SAPS sample from the mid-ocean ridge. A preliminary estimate of the activity is 5.32 ± 0.82 dpm/m^3, an activity which has so far only been reported from the deepest part of the Weddell Gyre, and an additional ^{227}Ac source is required to explain these activities. In contrast, ^{224}Ra on this sample was at deep ocean background levels (1.32 ± 0.25dpm/m^3), which results in a very exceptional and specific ^{223}Ra/^{224}Ra (total) ratio of >3 (typical ranges are 0.03 – 0.15 for shelf/slope sediments).

In the Argentine basin, a profile consisting of 10 data points could be collected at STN 18, which is an exceptional resolution for ^{227}Ac, which should allow a comparison with constraints on mixing from the vertical mixing profiler operated by Kurt Polzin.

References

Blain S, Queguiner B, Armand L, Belviso S, Bombled B, Bopp L, Bowie A, Brunet C, Brussaard C, Carlotti F, Christaki U, Corbiere A, Durand I, Ebersbach F, Fuda JL, Garcia N, Gerringa L, Griffiths B, Guigue C, Guillerm C, Jacquet S, Jeandel C, Laan P, Lefevre D, Lo Monaco C, Malits A, Mosseri J, Obernosterer I, Park YH, Picheral M, Pondaven P, Remenyi T, Sandroni V, Sarthou G, Savoye N, Scouarnec L, Souhaut M, Thuiller D, Timmermans K, Trull T, Uitz J, van Beek P, Veldhuis M, Vincent D, Viollier E, Vong L, Wagener T (2007) Effect of natural iron fertilization on carbon sequestration in the Southern Ocean. Nature **446**:1070-U1071

Brierley CM, Collins M, Thorpe AJ (2008) The impact of perturbations to ocean-model parameters on climate and climate change in a coupled model. Climate Dynamics:1-19

Charette MA, Gonneea ME, Morris PJ, Statham P, Fones G, Planquette H, Salter I, Garabato AN (2007) Radium isotopes as tracers of iron sources fueling a Southern Ocean phytoplankton bloom. Deep-Sea Research Part Ii-Topical Studies in Oceanography **54**:1989-1998

Foster, D.A., Staubwasser, M. and Henderson, G.M. (2004) 226Ra and Ba concentrations in the Ross Sea measured with multicollector ICP mass spectrometry. Marine Chemistry, **87**:59-71

Geibert W, Charette M, Kim G, Moore WS, Street J, Young M, Paytan A (2008) The release of dissolved actinium to the ocean: A global comparison of different end-members. Marine Chemistry **109**:409-420

Geibert W, Rutgers van der Loeff MM, Hanfland C, Dauelsberg HJ (2002) Actinium-227 as a deep-sea tracer: Sources, distribution and applications. Earth and Planetary Science Letters **198**:147-165

Geibert W, Vöge I (2008) Progress in the determination of ^{227}Ac in sea water. Marine Chemistry **109**:238-249

Ledwell JR, Montgomery ET, Polzin KL, St. Laurent LC, Schmitt RW, Toole JM (2000) Evidence for enhanced mixing over rough topography in the abyssal ocean. Nature **403**:179-182

Moore WS, Arnold R (1996) Measurement of ^{223}Ra and ^{224}Ra in coastal waters using a delayed coincidence counter. Journal of Geophysical Research C: Oceans **101**:1321-1329

Nozaki Y (1984) Excess ^{227}Ac in deep ocean water. Nature **310**:486-488

WORKPACKAGE 7: MODELLING OF MICRONUTRIENT FLUXES AND SYNTHESIS OF DATA

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No work towards this Workpackage was conducted during the cruise. It is included here only for completeness.

WORKPACKAGE 8: CRITICAL SUPPORT MEASUREMENTS

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8.1 NUTRIENTS

By Malcolm Woodward and Amandine Sabadel

Objectives
To investigate the spatial and temporal variations of the dissolved nutrient species; Nitrate, Nitrite, Silicate, Ammonium and Phosphate during the research cruise across the 40 degree South UK-Geotraces transect line between South West of CapeTown, South Africa, and Montevideo, Uruguay. Also to use an innovative analytical technique for measuring nanomolar ammonium concentrations.
Analysis was also carried out for sediment Core water samples for Will Homoky, of NOC. Underway surface water samples were analysed all along the transect from samples taken from the 'trace-metal free' fish, which was during during the inter-station transects.
Overall the aim was to carry out sampling and analysis according to Go-Ship protocols wherever possible, and to compare results with a certified International Nutrient reference materials provided by KANSO, Japan, this being part of a global programme to improve nutrient analysis data quality world-wide.

Sampling and Analytical Methodology
The micro-molar analyser was a 4 channel (nitrate, nitrite, phosphate, silicate) Bran and Luebbe AAIII segmented flow, colorimetric, autoanalyser, and classical proven analytical techniques were used.
The system used for ammonium analysis was a technique based on the gas diffusion of the ammonia across a Teflon membrane due to a differential pH gradient, and there then followed its reaction with a fluorescent reagent and the subsequent detection by a Jasco fluorimeter.
Water samples were taken from either a 24 x 20 litre stainless steel CTD/Rosette system (SeaBird), or an automatically fired (Sea-Ram system, (SeaBird)) CTD 24 bottle system on a trace metal free titanium rosette system. These samples were processed within the trace metal free sampling laboratory container .The CTD bottles were sub sampled into acid clean, 'aged', 60 mls HDPE (nalgene) sample bottles and analysis for the nutrient samples was in most cases complete within 2-3 hours of sampling. That is except for the pore water fluids which were stored in a fridge at 4C, and then had to be diluted before analysis in order to produce sufficient sample volume for analysis.
Clean handling techniques were employed to avoid any contamination of the samples, particularly for the ammonium samples. Gloves used were Dura-Touch, and all people sampling prior to the nutrients from the CTD wore these gloves. Samples were not decanted and kept tightly closed until just before analysis for the ammonium, this to avoid any contamination from external sources.
No water column water samples were frozen or stored in any way.

Table 10: CTD SAMPLES ANALYSED by AAIII AUTOANALYSER.

Date	CTD	Position	CTD or TM bottle analysed
26/12/2011	**Test**		**1,2,3,4,5,6,8,9,10,11,12,13,14,15,16,17,18, 19, 20, 21, 22, 23, 24.**
28/12/2011	**CTD_001 (SS-Bio)**	$34^0$36.74'S $17^0$03.23'E	**1,2,3,4,5,6, 8,9,10,11,12,13,14,15,16,17,18, 19, 20, 21, 22, 23, 24.**
28/12/2011	**CTD_002 (TiT)**	$34^0$36.74'S $17^0$03.23'E	**1,2,3,4, 6,7,8,9,10,11,12,13,14,15,16,17, 19, 20, 21, 22, 23, 24.**
28/12/2011	**CTD_003 (SS-Bio)**	$35^0$28.08'S $14^0$59.77'E	**1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18, 19, 20, 22, 23, 24.**
28/12/2011	**CTD_004 (TiT)**	$35^0$28.08'S $14^0$59.77'E	**1,2,3,4,5,6.**
29/12/2011	**CTD_005 (SS-Bio)**	$36^0$20.16'S $13^0$06.71'E	**1,3,4,6,8,14,15,16,18, 19, 20, 21, 22, 23, 24.**
29/12/2011	**CTD_006 (TiT)**	$36^0$20.97'S $13^0$06.34'E	**TM:1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17, 18, 19, 20, 21, 22, 23, 24.**
29/12/2011	**CTD_007 (SS-Bio)**	$36^0$20.54'S $13^0$06.44'E	**1,2,3,4,6,7,8,9,10,11,13,14,15,16,17,18, 19, 20, 21, 22, 23, 24.**
30/12/2011	**CTD_008 (SS-Bio)**	$38^0$23.94'S $10^0$24.05'E	**1,2,3,4,6,7,9,10,11, 13,14,15,16,17,18, 19, 20, 21, 23, 24.**
31/12/2011	**CTD_009 (SS-Bio)**	$40^0$00.00'S $05^0$30.00'E	**1,3,4,7,8,9,10,11,12,14,15,16,18,19,20,21, 22,23,24.**
03/01/2012	**CTD_010 (SS)**	$40^0$00.89'S $00^0$29.99'W	**1,2,3,4,6,7,8,9,10,11,12,13,14,15,17,18,20,21, 22, 23, 24.**
04/01/2012	**CTD_011 (TiT)**	$40^0$00.00'S $03^0$02.17'W	**1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18, 19, 20, 21, 22, 23, 24.**
05/01/2012	**CTD_012 (SS-Bio)**	$39^0$59.98'S $09^0$39.95'W	**2,3,4,5,6,7,10,11,12,13,14,15,16,17,18, 19, 21, 22, 23.**
05/01/2012	**CTD_013 (TiT)**	$39^0$59.98'S $09^0$39.94'W	**1,3,4,6,7,8,10,11,13,14,16,18, 19, 20, 21, 23, 24.**
05/01/2012	**CTD_014 (SS)**	$39^0$59.95'S $09^0$40.05'W	**1,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18, 20, 21, 22, 23, 24.**
07/01/2012	**CTD_015 (SS-Bio)**	$40^0$15.44'S $09^0$51.19'W	**1, 2, 3, 4, 5, 7, 8, 9, 10, 11, 14, 15, 16, 18, 19, 20, 22, 23, 24.**
08/01/2012	**CTD_017 (SS-Bio)**	$40^0$00.00'S $09^0$51.19'W	**1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14.**
08/01/2012	**CTD_018 (TiT)**	$40^0$00.00'S $12^0$59.92'W	**1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24.**
08/01/2012	**CTD_019 (SS)**	$39^0$59.98'S $12^0$59.95'W	**3, 4, 6, 15, 16, 18, 19, 20, 21, 22, 24.**
08/01/2012	**CTD_020 (SS)**	$39^0$59.99'S $12^0$59.99'W	**1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 13, 14, 15, 16, 18, 19, 20, 21, 22, 23, 24.**
09/01/2012	**CTD_021 (SS)**	$40^0$00.04'S $16^0$27.96'W	**1, 2, 3, 5, 6, 7, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24.**
10/01/2012	**CTD_022 (TiT)**	$40^0$00.01'S $16^0$27.79'W	**1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24.**
10/01/2012	**CTD_023 (SS-Bio)**	$40^0$00.10'S $16^0$27.91'W	**1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24.**
10/01/2012	**CTD_024**	$40^0$00.00'S	**7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19,**

	(TiT)	$16^0$27.99'W	20, 22, 23, 24.
11/01/2012	CTD_025 (SS)	$39^0$59.96'S $19^0$55.94'W	1, 2, 3, 5, 6, 7, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24.
12/01/2012	CTD_026 (TiT)	$40^0$00.02'S $19^0$55.81'W	1, 2, 3, 4, 5, 6, 7, 8, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24.
12/01/2012	CTD_027 (SS)	$40^0$00.02'S $19^0$55.82'W	8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24.
13/01/2012	CTD_028 (SS)	$40^0$00.02'S $23^0$48.00'W	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24.
13/01/2012	CTD_029 (TiT)	$40^0$00.00'S $23^0$48.00'W	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24.
13/01/2012	CTD_030 (SS-Bio)	$40^0$00.00'S $23^0$47.99'W	1, 3, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23.
14/01/2012	CTD_031 (SS-Bio)	$40^0$00.01'S $27^0$59.99'W	1, 2, 3, 4, 5, 6, 7, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24.
14/01/2012	CTD_032 (TiT)	$40^0$00.00'S $27^0$59.99'W	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24.
14/01/2012	CTD_033 (SS)	$40^0$00.00'S $28^0$00.00'W	1, 2, 3, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24.
15/01/2012	CTD_034 (SS-Bio)	$39^0$59.96'S $32^0$29.94'W	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 13, 14, 15, 16, 17, 18, 19, 20, 22, 23, 24.
15/01/2012	CTD_035 (TiT)	$39^0$59.99'S $32^0$30.00'W	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24.
16/01/2012	CTD_036 (SS)	$40^0$00.01'S $32^0$29.99'W	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24.
16/01/2012	CTD_037 (SS-Bio)	$40^0$00.00'S $37^0$25.00'W	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24.
17/01/2012	CTD_038 (TiT)	$39^0$59.99'S $37^0$24.99'W	1, 2, 3, 4.
17/01/2012	CTD_039 (SS)	$40^0$00.00'S $37^0$25.00'W	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24.
17/01/2012	CTD_040 (TiT)	$40^0$00.00'S $37^0$25.00'W	Failure
17/01/2012	CTD_041 (Tit)	$40^0$00.00'S $37^0$25.00'W	5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 20, 21, 22, 23, 24.
17/01/2012	CTD_042 (Test)	$40^0$00.00'S $42^0$24.93'W	Test cast – no sampling.
18/01/2012	CTD_043 (SS-Bio)	$40^0$00.10'S $42^0$24.93'W	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24.
19/01/2012	CTD_044 (TiT)	$40^0$00.00'S $42^0$25.01'W	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24.
19/01/2012	CTD_045 (SS)	$40^0$00.00'S $42^0$25.01'W	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24.
20/01/2012	CTD_046 (TiT)	$40^0$00.00'S $42^0$34.89'W	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 23, 24.
21/01/2012	CTD_047 (SS-Bio)	$39^0$59.96'S $47^0$24.93'W	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24.

21/01/2012	CTD_048 (TiT)	$40^000.00$'S $47^025.00$'W	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24.
21/01/2012	CTD_049 (SS-Bio)	$39^059.22$'S $47^025.00$'W	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 22, 23, 24.
22/01/2012	CTD_050 (SS-Bio)	$37^058.85$'S $51^001.76$'W	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24.
22/01/2012	CTD_051 (SS)	$38^000.03$'S $50^059.97$'W	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23.
22/01/2012	CTD_052 (TiT)	$38^000.07$'S $50^059.97$'W	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24.
24/01/2012	CTD_056 (SS)	$37^000.01$'S $52^030.00$'W	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24.
24/01/2012	CTD_057 (TiT)		Aborted
24/01/2012	CTD_058 (TiT)	$37^000.01$'S $52^029.52$'W	1, 2, 3, 4, 5, 6, 7, 8, 9, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24.
24/01/2012	CTD_059 (SS-Bio)	$37^000.04$'S $52^030.04$'W	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24.
24/01/2012	CTD_060 (TiT)	$37^000.10$'S $52^029.96$'W	4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24.
25/01/2012	CTD_061 (SS-Bio)	$36^032.16$'S $53^006.09$'W	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 23, 24.
25/01/2012	CTD_062 (TiT)	$36^032.16$'S $53^006.09$'W	6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24.
26/01/2012	CTD_063 (SS-Bio)	$36^000.00$'S $54^000.00$'W	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24.
26/01/2012	CTD_064 (TiT)	$36^000.00$'S $54^000.00$'W	1, 2, 3, 4, 5, 6.

Table 11: CTD SAMPLES ANALYSED for NANOMOLAR AMMONIUM.
(samples were not analysed from the Trace metal CTD due to its method of sampling)

Date	CTD	Position	CTD bottle analyzed
26/12/2011	Test		None
28/12/2011	CTD_001 (SS-Bio)	$34^036.74$'S $17^003.23$'E	1, 3, 5, 8, 9, 11, 13, 15, 16, 17, 18, 20, 22, 23.
28/12/2011	CTD_002 (TiT)	$34^036.74$'S $17^003.23$'E	None, TM
28/12/2011	CTD_003 (SS-Bio)	$35^028.08$'S $14^059.77$'E	1, 3, 5, 7, 9, 11, 13, 16, 17, 19, 22, 23.
28/12/2011	CTD_004	$35^028.08$'S	None, TM

	(TiT)	$14^0 59.77$'E	
29/12/2011	CTD_005 (SS-Bio)	$36^0 20.16$'S $13^0 06.71$'E	1, 3, 4, 6, 8, 14, 15, 16, 18, 19, 20, 21, 22, 23, 24.
29/12/2011	CTD_006 (TiT)	$36^0 20.97$'S $13^0 06.34$'E	None, TM
29/12/2011	CTD_007 (SS-Bio)	$36^0 20.54$'S $13^0 06.44$'E	1, 2, 3, 4, 5, 6, 7, 8, 10, 13, 15, 17, 18, 20, 22.
30/12/2011	CTD_008 (SS-Bio)	$38^0 23.94$'S $10^0 24.05$'E	1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 23.
31/12/2011	CTD_009 (SS-Bio)	$40^0 00.00$'S $05^0 30.00$'E	1, 3, 7, 9, 11, 14, 15, 18, 19, 21, 23.
03/01/2012	CTD_010 (SS)	$40^0 00.89$'S $00^0 29.99$'W	1, 3, 6, 7, 9, 10, 11, 12, 13, 14, 15, 17, 18, 20, 21, 22, 23.
04/01/2012	CTD_011 (TiT)	$40^0 00.00$'S $03^0 02.17$'W	None, TM
05/01/2012	CTD_012 (SS-Bio)	$39^0 59.98$'S $09^0 39.95$'W	2, 3, 5, 7, 10, 11, 13, 15, 18, 21, 22.
05/01/2012	CTD_013 (TiT)	$39^0 59.98$'S $09^0 39.94$'W	None, TM
05/01/2012	CTD_014 (SS)	$39^0 59.95$'S $09^0 40.05$'W	1, 3, 5, 7, 9, 11, 12, 14, 15, 16, 18, 20, 21, 22, 23, 24.
07/01/2012	CTD_015 (SS-Bio)	$40^0 15.44$'S $09^0 51.19$'W	1, 3, 5, 7, 9, 10, 11, 14, 15, 18, 19, 22, 23.
08/01/2012	CTD_017 (SS-Bio)	$40^0 00.00$'S $09^0 51.19$'W	1, 3, 4, 7, 9, 11, 13.
08/01/2012	CTD_018 (TiT)	$40^0 00.00$'S $12^0 59.92$'W	None, TM
08/01/2012	CTD_019 (SS)	$39^0 59.98$'S $12^0 59.95$'W	3, 4, 6, 15, 16, 18, 19, 20, 21.
08/01/2012	CTD_020 (SS)	$39^0 59.99$'S $12^0 59.99$'W	3, 6, 9, 10, 13, 16, 19, 22.
09/01/2012	CTD_021 (SS)	$40^0 00.04$'S $16^0 27.96$'W	2, 6, 7, 9, 10, 11, 12, 13, 14, 15, 16, 18, 19, 20, 21, 22, 23, 24.
10/01/2012	CTD_022 (TiT)	$40^0 00.01$'S $16^0 27.79$'W	None, TM
10/01/2012	CTD_023 (SS-Bio)	$40^0 00.10$'S $16^0 27.91$'W	2, 5, 7, 9, 11, 13, 15, 17, 18, 20, 22, 24.
10/01/2012	CTD_024 (TiT)	$40^0 00.00$'S $16^0 27.99$'W	None, TM
11/01/2012	CTD_025 (SS)	$39^0 59.96$'S $19^0 55.94$'W	2, 5, 7, 9, 11, 13, 15, 17, 18, 19, 20, 21, 22.
12/01/2012	CTD_026 (TiT)	$40^0 00.02$'S $19^0 55.81$'W	None, TM
12/01/2012	CTD_027 (SS)	$40^0 00.02$'S $19^0 55.82$'W	5, 6, 7, 8, 9, 10, 13, 14, 16, 17, 19, 22, 24.
13/01/2012	CTD_028 (SS)	$40^0 00.02$'S $23^0 48.00$'W	1, 3, 6, 8, 10, 13, 15, 17, 19, 20, 21, 22, 23, 24.
13/01/2012	CTD_029 (TiT)	$40^0 00.00$'S $23^0 48.00$'W	None, TM

13/01/2012	CTD_030 (SS-Bio)	$40^000.00$'S $23^047.99$'W	1, 3, 5, 6, 7, 9, 11, 13, 15, 18, 20, 22.
14/01/2012	CTD_031 (SS-Bio)	$40^000.01$'S $27^059.99$'W	1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 23.
14/01/2012	CTD_032 (TiT)	$40^000.00$'S $27^059.99$'W	None, TM
14/01/2012	CTD_033 (SS)	$40^000.00$'S $28^000.00$'W	1, 3, 6, 8, 9, 11, 14, 16, 19, 21, 22, 23, 24.
15/01/2012	CTD_034 (SS-Bio)	$39^059.96$'S $32^029.94$'W	1, 3, 5, 7, 9, 11, 13, 14, 15, 17, 19, 22, 23.
15/01/2012	CTD_035 (TiT)	$39^059.99$'S $32^030.00$'W	None, TM
16/01/2012	CTD_036 (SS)	$40^000.01$'S $32^029.99$'W	1, 5, 6, 7, 9, 11, 13, 17, 19.
16/01/2012	CTD_037 (SS-Bio)	$40^000.00$'S $37^025.00$'W	1, 3, 5, 7, 8, 10, 13, 14, 15, 17, 18, 21.
17/01/2012	CTD_038 (TiT)	$39^059.99$'S $37^024.99$'W	None, TM
17/01/2012	CTD_039 (SS)	$40^000.00$'S $37^025.00$'W	1, 3, 7, 11, 14, 17, 21, 24.
17/01/2012	CTD_040 (TiT)	$40^000.00$'S $37^025.00$'W	Failure
17/01/2012	CTD_041 (Tit)	$40^000.00$'S $37^025.00$'W	None, TM
17/01/2012	CTD_042 (Test)	$40^000.00$'S $42^024.93$'W	Test cast – no sampling.
18/01/2012	CTD_043 (SS-Bio)	$40^000.10$'S $42^024.93$'W	1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 23.
19/01/2012	CTD_044 (TiT)	$40^000.00$'S $42^025.01$'W	None, TM
19/01/2012	CTD_045 (SS)	$40^000.00$'S $42^025.01$'W	1, 3, 4, 5, 6, 8, 9, 11, 13, 15, 17, 18, 19, 20, 21, 22, 23, 24.
20/01/2012	CTD_046 (TiT)	$40^000.00$'S $42^034.89$'W	None, TM
21/01/2012	CTD_047 (SS-Bio)	$39^059.96$'S $47^024.93$'W	1, 3, 5, 7, 11, 12, 13, 15, 17, 19, 20, 21, 22, 23, 24.
21/01/2012	CTD_048 (TiT)	$40^000.00$'S $47^025.00$'W	None, TM
21/01/2012	CTD_049 (SS-Bio)	$39^059.22$'S $47^025.00$'W	1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 22, 23.
22/01/2012	CTD_050 (SS-Bio)	$37^058.85$'S $51^001.76$'W	1, 3, 5, 8, 9, 10, 11, 12, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23.
22/01/2012	CTD_051 (SS)	$38^000.03$'S $50^059.97$'W	1, 2, 3, 4, 6, 8, 10, 12, 14, 16, 17, 19, 20, 21, 22, 23.
22/01/2012	CTD_052 (TiT)	$38^000.07$'S $50^059.97$'W	None, TM

24/01/2012	CTD_056 (SS)	$37^0$00.01'S $52^0$30.00'W	1, 3, 4, 5, 8, 10, 11, 15, 19, 21, 22, 23.
24/01/2012	CTD_057 (TiT)		Aborted
24/01/2012	CTD_058 (TiT)	$37^0$00.01'S $52^0$29.52'W	None, TM
24/01/2012	CTD_059 (SS-Bio)	$37^0$00.04'S $52^0$30.04'W	1, 6, 7, 8, 10, 11, 17, 19, 20, 21, 22, 23, 24.
24/01/2012	CTD_060 (TiT)	$37^0$00.10'S $52^0$29.96'W	None, TM
25/01/2012	CTD_061 (SS-Bio)	$36^0$32.16'S $53^0$06.09'W	1, 3, 4, 6, 9, 14, 15, 16, 17, 19, 20, 21, 23.
25/01/2012	CTD_062 (TiT)	$36^0$32.16'S $53^0$06.09'W	None, TM
26/01/2012	CTD_063 (SS-Bio)	$36^0$00.00'S $54^0$00.00'W	None
26/01/2012	CTD_064 (TiT)	$36^0$00.00'S $54^0$00.00'W	None, TM

Core samples for pore water nutrients

These samples were from Will Homoky and details of the sampling techniques etc can be seen in his cruise report.

Before analysis the samples were diluted due to their high concentrations of nutrients and also because of the small volume of samples provided.

The normal volume provided to us was around 3 mls, making a dilution of x10, but this did vary and corrections were applied accordingly to calculate the exact concentrations of the original samples.

Sediment Core 1:11th January 2012: Samples analysed for nutrients and ammonium, these weer stored in refrigerator until ready for analysis.

Cores 2 and 3: 24th January 2012, both cores analysed at same time and again for nutrients and ammonium. Storage again in refrigerator.

Underway sampling from Trace Metal Fish

Samples were taken for nutrients on a regular basis throughout the cruise between CTD stations. The event log for this activity will detail times and dates along with other sampled parameters.

Nutrients were analysed for underway samples numbered: C.Fish 1001 – 1113.

Cruise results and summary

The 4-channel autoanalyser worked very well except for the autosampler which went up in smoke with 2 weeks to go until the end of the cruise. This was a terminal electrical melt-down and so the sampler was configured in a manual mode and was moved by hand from sample to sample but at the specific timings required by the AACE software on the autoanalyser. This was to allow normal computer data handling following completion of the analysis.

All preliminary data handling and work-up was carried out on the cruise. Likewise all the data for the nanomolar ammonium analyser was also worked up in its preliminary form.

Initial results for the cruise up until station 18 are shown below using ODV plotting software. These are for the full depth sections and also for the top 500 metres of the section showing greater detail of the water masses and their nutrient signatures.

High nutrient wasters, particularly the silicate can be seen below 4000 metres and this is the Antarctic bottom water which is on its northerly flow into the Atlantic. Shallower in the water column other water masses can be identified.

These profiles showed good correlations with last year's cruise nutrient profiles and also show close agreement to previous international voyages in the region.

Silicate [uM/L]

Silicate [uM/L]

Phosphate [uM/L]

Phosphate [uM/L]
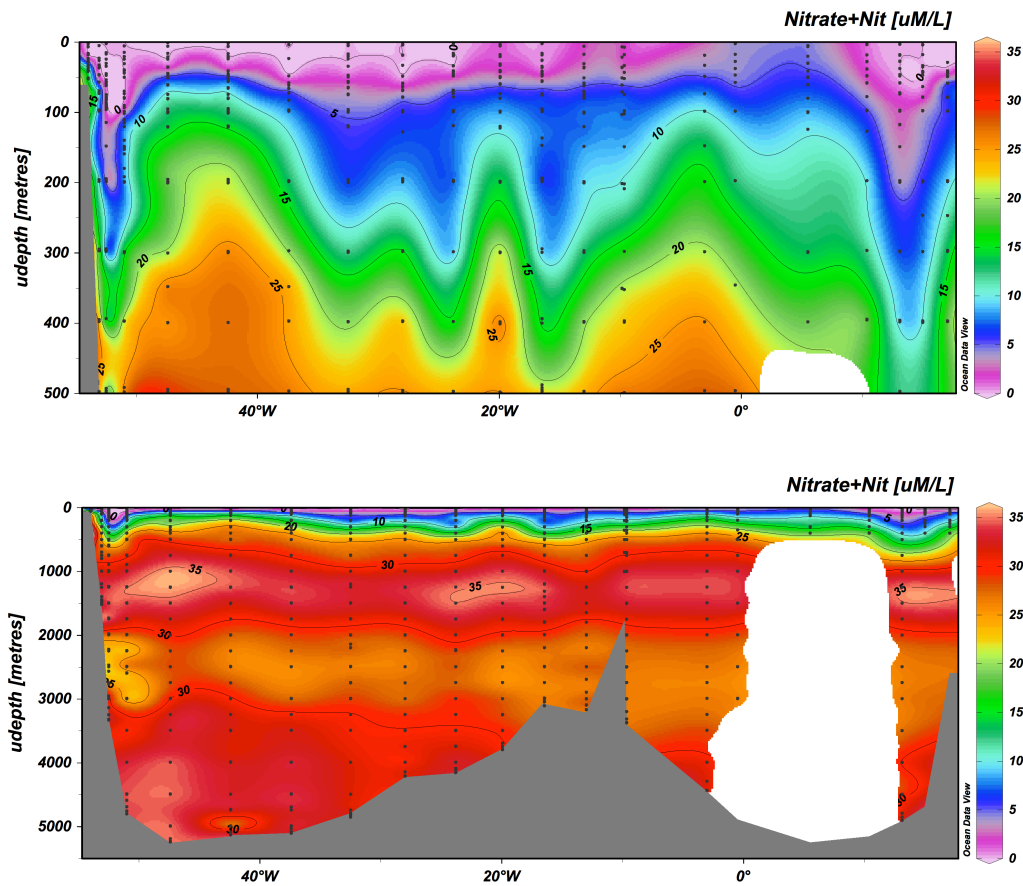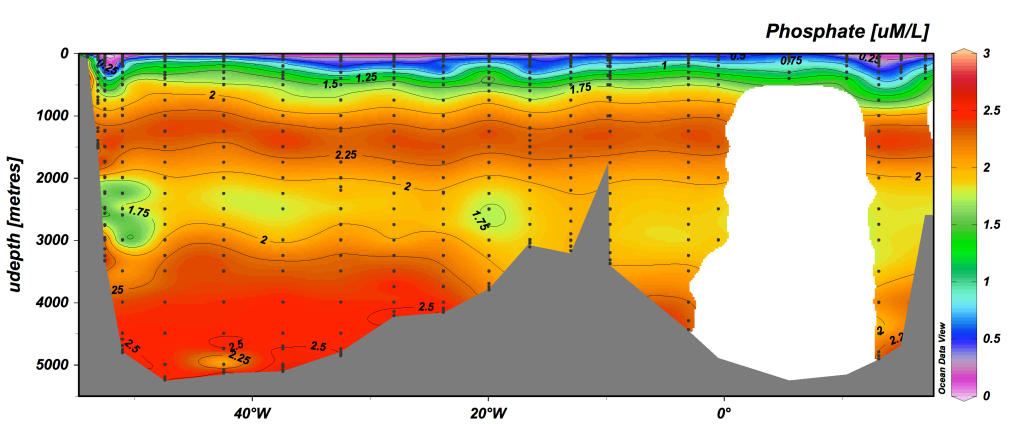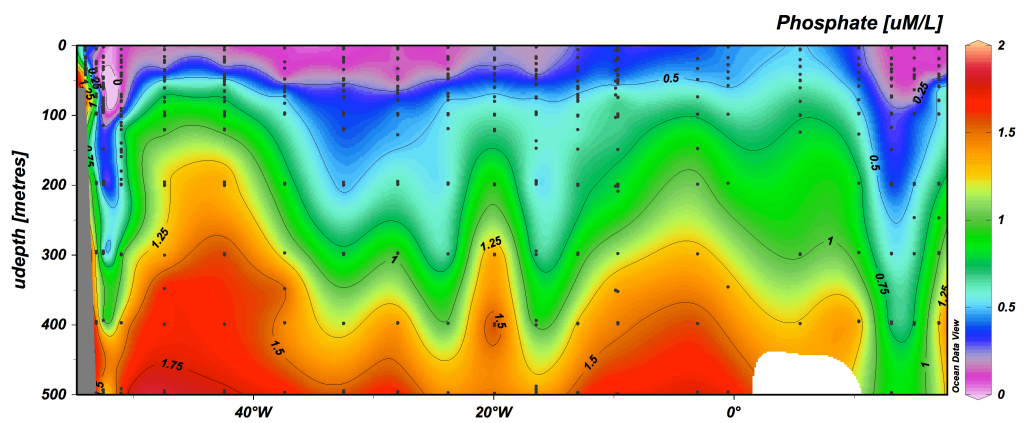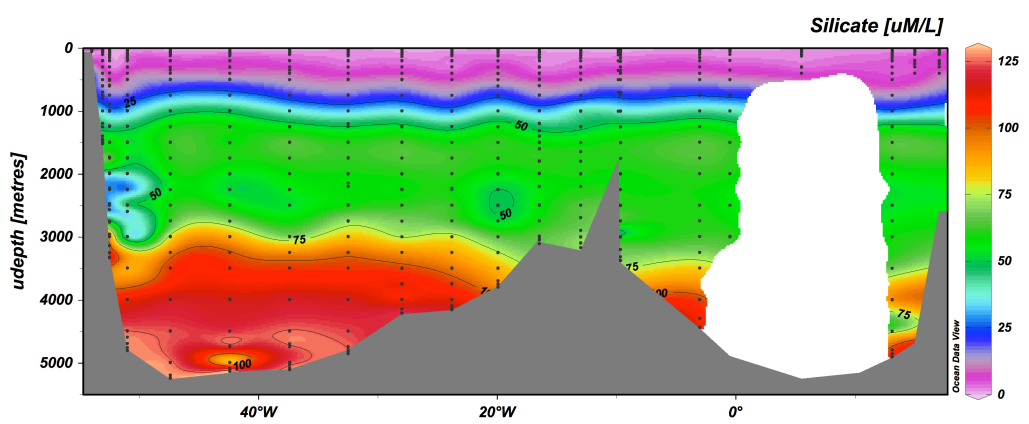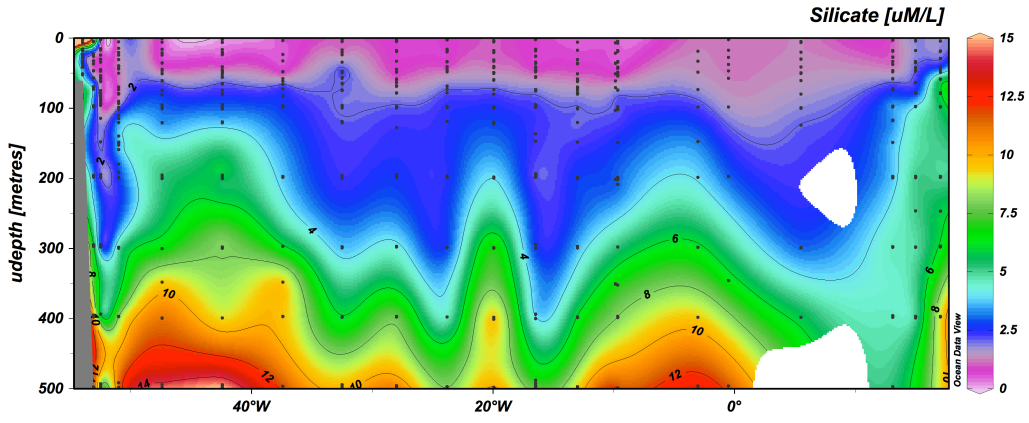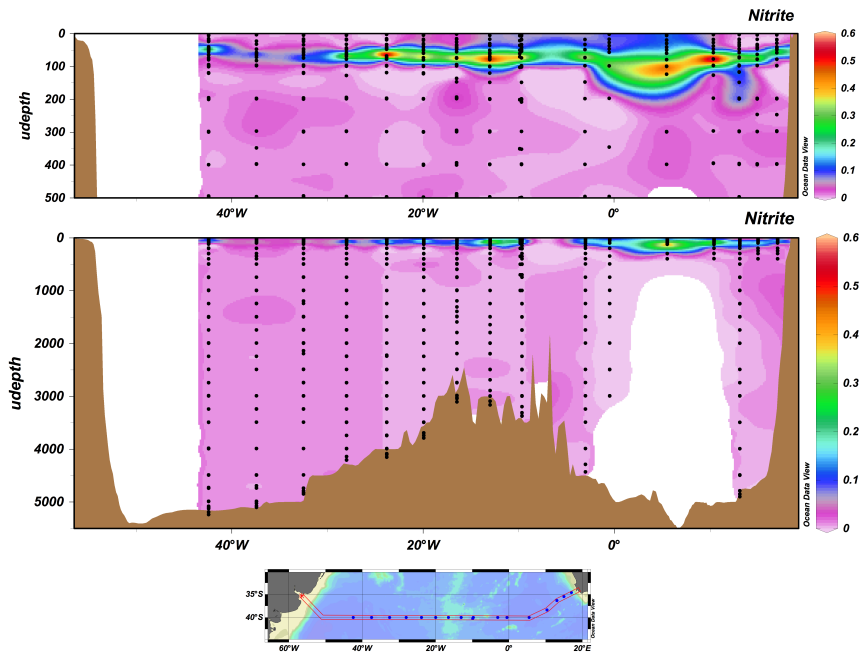
Figure 32: ODV plots of nutrient data

Thanks:

To the RRS James Cook, her officers, crew, and catering superstars for making it all possible, particularly the great efforts made over the Christmas and New Year which was not an easy time for many to be away from home and families. At least this was made bearable and a good time was had with the celebrations.

Thanks to Otago University in allowing Amandine to come to the cruise to help with the nutrients alongside sampling and analysing for her PhD project.

Thanks particularly to all those who helped by being 'human autosamplers' following the melt-down of the autoanalyser sampler.

And finally special thanks to all the other cruise scientists for making this cruise a pleasure to be a part of, a great team effort.

8.2 AMINO ACIDS

By Amandine Sabadel

Objectives

Objectives of this cruise are to understand the role of the amino acids – either dissolved free amino acids (DFAAs) or bounded amino acids – within oceanic food webs of the nutrient-depleted waters of the oligotrophic Oceans. As part of the UK-Geotraces program, the investigation took place along the 40°transect in the Southern Atlantic Ocean, where bioactivity is yet, relatively important. The main purpose of this cruise was to collect seawater samples and particles in order to develop new methodologies to determine:

1> DFAAs bulk concentrations
2> Individual DFAAs concentrations
3> Compound specific δ^{15}N, all the AAs found in particles
4> Compound specific δ^{15}N analysis of individual DFAAs

The work resulting from these samples is essential to set up a working methodology for future analysis. A horizontal and vertical profile of the DFAAs concentrations will also be generated and used as a reference in the future. Finally, these results will give us an idea of the role of the DFAAs in oligotrophic oceans.

Sampling methodology

Seawater samples from a dozen of depths for DFAAs concentration and eventually compound specific δ^{15}N of individual DFAAs analysis have been collected on each sampled Station; when water for particles collection was sampled every other station (see fig 33 below).

Water samples were poured directly from the CTD/Rosette system into clean, 30 ml HDPE (Nalgene) sample bottles for DFAAs. Fine filtration (0.2 μm) was applied straight away to the sample by syringe filtration and each seawater sample was individually stocked in brand new 30 ml HDPE Nalgene bottles.
For particles, 10L of seawater were used to collect a sufficient amount of matter from each sample. Once the seawater filtered though GF/C 0.45 μm filters, they were dried for 48h at 45°C, then stored at -20°C until further analysis onshore.
Clean handling techniques, including wearing gloves during the whole procedure, were employed to avoid any contamination of the samples.

<u>Where did we sample?</u>

17 stations were sampled for DFAAs and 11 for particles collection including 2 extra for SAPs.

Table 11 - List of the samples depth per station for DFAAs analysis. In red, bottom samples and in green, deep chlorophyll maximum (DCM) samples. 313 samples in total.

Station 01	Station 03	Station 05	Station 06	Station 08	Station 11	Station 12	Station 13	Station 14	Station 15	Station 16	Station 17	Station 18	Station 19	Station 20	Station 21	Station 22
34°36 S 17°03E	36°20 S 14°06E	40°00 S 05°30E	40°00 S 00°30E	40°00 S 09°40 W	40°00 S 13°00 W	40°00 S 16°30 W	40°00 S 20°00 W	40°00 S 23°48 W	40°00 S 26°00 W	40°00 S 32°30 W	40°00 S 37°30 W	40°00 S 43°00 W	40°00 S 48°00 W	38°00 S 51°00 W	37°00 S 52°30 W	36°32 S 53°06 W
5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
20	50	30	30	20	35	20	20	20	20	20	35	20	20	20	20	30
42	60	50	40	35	50	30	30	35	35	35	50	40	35	30	35	40
60	100	80	60	42	60	40	40	43	50	50	60	48	46	40	50	50
100	300	100	100	50	70	50	60	50	61	56	64	55	50	50	80	100
200	400	300	200	55	80	60	80	70	70	65	75	65	60	70	100	200
400	500		500	75	100	80	100	80	80	75	85	80	80	90	120	400
	750		750	100	200	100	120	100	100	100	100	100	100	100	200	600
	1000		1000	200	300	140	200	120	130	120	200	120	120	120	300	800
	1250		2000	300	400	200	300	200	200	200	300	200	200	200	400	1000
	1500		2500	350	2500	300	400	300	300	300	400	300	300	300	500	1500
	3500		3000	400	3000	400	500	400	400	400	750	400	400	400	600	Bottom
	4500			500		500	750	500	500	500	1000	750	500	500	750	
	Bottom			700		750	1000	750	750	750	1500	1000	750	750	900	
				1000		1000	1500	1000	1000	1000	2000	1500	1000	1000	1000	
				1250		1200	2000	1500	1500	1500	2500	2000	1500	1500	1250	
				1500		1400	2500	2000	1750	2000	3000	2500	2000	2000	1750	
				1750		1500	3000	2500	2000	2500	3500	3000	2500	2500	2000	
				2000		1800	3500	3000	2500	3000	4000	3500	3000	3000	2500	
				2500		2000	Bottom	3500	3000	3500	4500	4000	3500	3500	3000	
				3000		2500		3750	3250	4000	5000	4500	4000	4000	Bottom	
				3200		2750		4000	3700	4500	Bottom	5000	4500	4500		
				Bottom		3000		Bottom	4000	Bottom		Bottom	5000	Bottom		
						Bottom			Bottom				5000			
													Bottom			

Table 12 - List of the samples depth per station for particles collection. In red, bottom samples and in green, deep chlorophyll maximum (DCM) samples whenever it was possible to get 10 L of seawater of each of the listed depth below. Highlighted in yeallow, particles coming directly from SAPs. 110 samples in total.

Station 01	Station 03	Station 05	Station 06	Station 08	Station 12	Station 14	Station 16	Station 18	Station 20	Station 21
34°36S 17°03E	36°20S 14°06E	40°00S 05°30E	40°00S 00°30E	40°00S 09°40W	40°00S 16°30W	40°00S 23°48W	40°00S 32°30W	40°00S 43°00W	38°00S 51°00W	37°00S 52°30W
5	5	5	350	5	40	43	56	48	50	88
20	50	40	1500	35	60	70	65	60	90	100
42	60	50	2500	42	100	100	100	80	115	200
100	75	80	3000	55	140	200	200	120	150	300
200	100	100		200	200	300	300	150	200	600
400	175	400		300	300	1250	750	200	300	1000
	300			700	600	2000	2150	300	1250	1250
	400			1500	1400	3000	3250	400	1750	1750
	425			2000	1600	4000	4500	1500	2500	2600
	1000			2500	2000	Bottom	Bottom	3000	3500	2800
	Bottom			3000	2500			4000	Bottom	Bottom
				3200				Bottom		

Fig 33 - Station vs. depth (m) profile of sampled seawater (30 ml, 0.2 μm filtered seawater in Nalgene bottles) for DFAAs concentration analysis (top graph) and particles samples (bottom graph) with a representation of the transect South Africa to Uruguay, along the 40°S (middle graph) showing the physical positions of each sampled station.
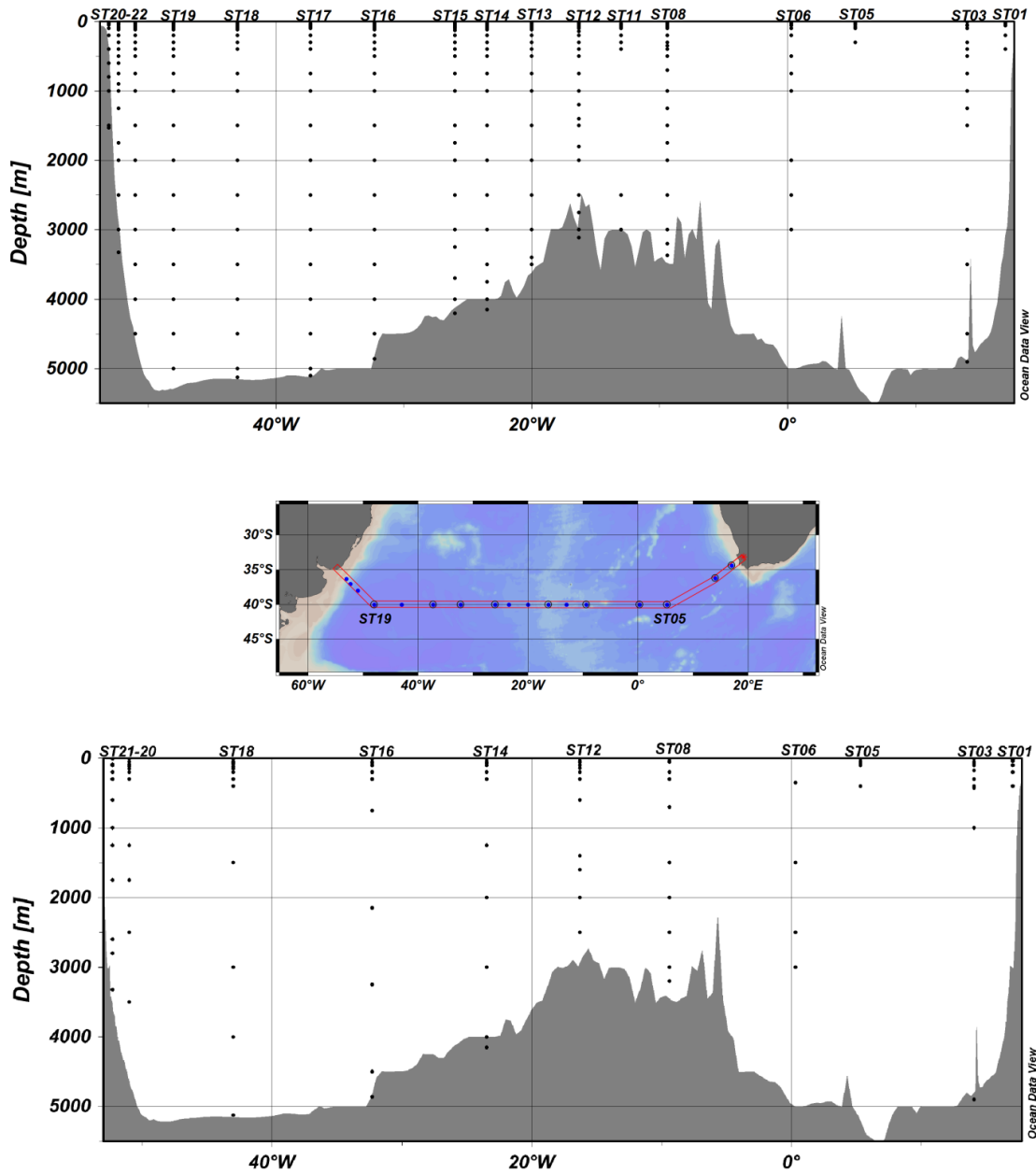
8.3 DISSOLVED OXYGEN

By Debbie Hembury, School of Ocean and Earth Science, National Oceanography Centre, Southampton

Objectives
To sample seawater from Niskin bottles fired during stainless steel CTD deployments, and analyse those samples by Winkler titration to determine dissolved oxygen (DO) concentration. These data will be used to calibrate the CTD oxygen sensor for cruise JC068, a transect at 40°S from Port Elizabeth, South Africa to Montevideo, Uruguay. In addition to calibration of the CTD oxygen sensor, water temperature (measured during sampling) and DO concentration (analysed by Winkler titration) are useful indicators of CTD bottle misfiring.

Sampling methods
Dissolved oxygen samples were taken by Debbie Hembury and Katsia Pabortsava (with the exception of CTD 061, which was sampled by Katsia Pabortsava and Gideon Henderson). Water samples were taken from 20 litre Niskin bottles mounted on the stainless steel CTD rosette. Before sampling, (if DO samples were the first to be taken from that Niskin bottle) the Niskin bottle was checked for leaks by opening the spigot; if the bottle has sealed well, water should not flow from the spigot. One the bottle has been tested for leaks, the air vent at the top of the bottle is opened to allow sampling.

WOCE dissolved oxygen sampling and analysis methods are described in full in Holley and Hydes (1994). In brief, water samples for DO analysis were collected in gravimetrically calibrated BOD bottles of 120ml nominal capacity via a length of silicon tube attached to the Niskin bottle spigot. The silicon tube is inserted into the bottom of the bottle, which is held upside down to allow the water to flow down the inside of the bottle whilst the tubing is checked for air bubbles. If there is air trapped in the silicon tubing, it may be necessary to pinch the tubing to clear the air. The sample bottle is then turned upright, and allowed to overflow by ~3 times its own volume. The tube is then drawn to the top of the bottle, and the flow of water stopped before the tube is gently removed from the bottle, taking care to avoid disturbing the surface of the water. Immediately, the temperature of the water is measured using a hand held thermometer, and reagents are added to fix the dissolved oxygen. 1 ml of manganous chloride followed by 1 ml of alkaline iodide are added to the sample, ensuring that the tip of each dispenser is below the water when adding the reagents. The stopper is inserted with a twisting motion into the bottle, and the bottle is checked to ensure that there are no trapped air bubbles before being shaken thoroughly. Once all samples have been taken from the CTD rosette, the bottles are kept in the dark, in the laboratory for 30 minutes before being re-shaken, allowed to settle for another 30 minutes, and then analysed immediately. Routinely, sample analysis was started one hour after sampling, and although it was aimed to complete analysis within two hours of sampling, as per WOCE guidelines, this was not always possible due to the number of samples and the length of time (~5 mins) taken to analyse each sample.

Analysis methods
Blank measurements and thiosulphate standardisation were performed at the beginning of the cruise, whenever reagents were changed, and on a couple of other occasions during the cruise in order to monitor any change or drift in the reagents. Reagent blanks were analysed using Carpenters' (1965) method of reverse 1 ml reagent addition, using an OSIL Iodate Standard (0.01N, 1.667mM) in Milli-Q deionised water. Sodium thiosulphate standardisation was performed using 10 ml OSIL Iodate

Standard in Milli-Q deionised water, in order to determine the thiosulphate normality. These blank and titre volumes were used to convert sample titration volumes to DO concentrations.

To analyse a sample, a stirrer bean and 1 ml of 5M sulphuric acid were added to the water sample bottle, and the bottle placed on a magnetic stirrer. One the precipitate had dissolved (i.e. the solution was no longer cloudy), the solution was titrated with sodium thiosulphate to a dead stop using amperometric end point detection with a Metrohn Titrino unit. Titration volume was recorded, and used to calculate dissolved oxygen concentration in the water sample.

Table 14: CTD Samples analysed for dissolved oxygen

Date	CTD	Position	Niskin bottles sampled
28/12/11	CTD001		1,2,4,5,6,8,9,10,11,12,13,14,15,16,17,18,19, 20,21,23,24
28/12/11	CTD003		1,2,3,4,6,7,9,10,11,12,13,14,15,16,17,18,19, 20,22,23,24
29/12/11	CTD005		1,3,4,6,8,14,15,16,17,18,19,20,21,22,23,24
30/12/11	CTD008		1,2,3,5,6,7,9,10,11,12,13,14,15,16,17,18,19, 20,21,23,24
01/01/12	CTD009		1,3,4,7,8,9,10,11,12,14,15,18,19,20,21,22,23 ,24
03/01/12	CTD010		1,2,3,4,6,7,8,9,10,11,12,13,14,15,17,18,20,2 1,22,23,24
06/01/12	CTD012		2,3,4,5,7,10,11,12,13,14,15,17,18,19,21,22,2 3
08/01/12	CTD017		1,2,3,4,5,6,7,8,9,10,11,12,13,14
08/01/12	CTD019		3,4,6,15,16,18,19,20,21,22,24
10/01/12	CTD021		2,6,7,9,10,11,12,13,14,15,16,17,18,19,20,21, 22,23,24
10/01/12	CTD023		1,3,4,6,8,10,12,14,16,18,20,22,24
11/01/12	CTD025		1,2,3,5,6,7,9,10,11,12,13,15,16,17,18,19,20, 21,22,23,24
13/01/12	CTD028		1,2,4,5,6,8,9,10,11,13,14,15,16,17,18,19,20, 21,22,23,24
13/01/12	CTD030		1,3,5,6,7,10,12,14,15,18,20,23
14/01/12	CTD031		1,3,5,7,9,11,13,15,17,19,21,23
14/01/12	CTD033		1,2,3,5,6,7,8,9,10,11,12,13,15,16,18,19,20,2 1,22,23,24
15/01/12	CTD034		1,3,5,7,9,11,13,14,15,18,20,22,24
16/01/12	CTD036		1,3,5,6,7,8,9,10,11,12,13,14,15,16,17,18,19, 20,21,22,23,24
16/01/12	CTD037		1,2,3,5,7,8,9,10,13,14,15,17,18,21,22
17/01/12	CTD039		1,3,6,7,10,11,12,15,16,19,20,23,24
18/01/12	CTD043		1,3,5,7,9,11,13,15,17,19,21,23
19/01/12	CTD045		1,3,4,5,6,8,9,11,12,13,14,16,17,18,19,20,21, 22,23,24
21/01/12	CTD049		2,4,6,8,10,12,14,16,18,20,22,24
22/01/12	CTD050		1,3,5,7,8,9,10,11,12,14,15,16,17,18,19,20,21 ,22,23
22/01/12	CTD051		1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18, 19,20,21,22,23

24/01/12	CTD056		1,3,4,5,6,7,8,9,10,11,14,15,17,18,19,20,21,22,23,24
25/01/12	CTD059		1,6,7,8,10,11,12,17,18,20,21,22,23,24
25/01/12	CTD061		1,3,4,5,6,7,8,9,13,14,15,16,17,18,20,21,23
26/01/12	CTD063		1,7,9,11,13,19,21

Cruise Results and Summary

The Metrohn Titrino unit (amperometric end point detection) worked very well throughout the cruise. Repeated blank determination and thiosulphate standardisations compared well, demonstrating that the reagents remained reasonably stable throughout the cruise.

Replicates were taken from every CTD cast, with the aim of taking 10% or more of the samples in replicate. The difference in DO concentration between replicates taken from the same Niskin bottle ranged from 0.013 µmol/l to 0.976 µmol/l (average 0.269 µmol/l). N.B. this excludes samples replicates at the first site, where the sampling method wasn't yet polished, and an outlier at CTD061 (difference between replicates 4.97 µmol/l), where it was reported that the reagents were not added properly on the first sample taken.

All data handling and work-up was carried out on the cruise. Dissolved oxygen concentrations were calculated in µmol/l and the data values were available by the end of the cruise. At times, DO values and their corresponding sampling temperatures were useful in indicating CTD Rosette bottle misfires. Preliminary comparisons of the Winkler oxygen concentrations and the CTD oxygen sensor bottle files suggested a consistent offset between the two data sets, which will be corrected for during calibration of the CTD sensor.

References

Grasshoff, K., Kremling, K, and Ehrhardt, M., 1999. Methods of seawater analysis, 3rd edition. Wiley VCH, Wienheim.

Holley, S. E. and Hydes, D.J., 1994. Procedures for the determination of dissolved oxygen in seawater, James Rennell Centre for Ocean Circulation internal document.

8.4 SALINITY

By Roulin Khondoker

Samples analysed by Roulin Khondoker

Objectives
Salinity was measured on waters recovered from the OTE bottles in order to calibrate the CTD and to check that all bottles fired at the expected depth and did not leak subsequently.

Sampling protocol
Samples for salinity measurement were collected and stored in 200-ml glass bottles closed with plastic stopper and a screw cap.
Each bottle (without cap) was rinsed three times with sample water, then filled to the level of the bottle shoulder. It is important to leave enough headspace in order to avoid any breakage due to the expansion of cold samples. The inside of the bottle neck was wiped with a tissue, and the bottle was closed with a clean and dry plastic stopper. The entire bottle was wiped with a tissue, with particular attention around the neck and stopper in order to avoid the formation of salt crystal which could fall into the bottle when opened for analysis. The samples were carried to the salinometer room where they were stored for at least 24 hours to let the sample temperature equilibrate.
After measurement of salinity, the bottles (together with the screw caps) were rinsed (and shaken vigorously) twice with tap water and twice with Milli-Q water. It is recommended to use new plastic stoppers for each samples in order to have a better seal. However, if it was not possible, they were rinsed several times with tap water and with Milli-Q water. Then they were left to dry in air.

Samples collected
Samples were taken for all normal and biological stainless steel casts and for all Ti main casts. Samples were also taken each time the underway water was sampled for other analytes. A total of 1436 sample measurements were made during JC068. All samples were analysed by Roulin Khondoker.

Sample analysis
The measurements were conducted on board with a Guildline Autosal laboratory salinometer (Model 8400 B), which provided the double conductivity ratio. This instrument was installed in a constant temperature room. The temperature of the bath was set to 21°C, and the room temperature room was about 2°C below the bath temperature.
The Autosal was standardized before each batch of samples with IAPSO Standard Seawater (SSW) provided by OSIL. The SSW were from the batch P151 or P153, the conductivity ratio of which was K_{15}=0.99997 or =0.99989, respectively, corresponding to practical salinity 34.999. After each batch of samples, a SSW was measured in order to verify the stability of the Autosal.
A sample measurement consisted in flushing three times the conductivity cell with sample water, then measuring three times the double conductivity ratio of the sample, the cell being flushed between each measurement. The data standard deviation was set to ± 0.00005, and if a double conductivity ratio value was exceeding this standard deviation, another measurement was done to replace the "outlier" value.
The Autosal was connected to a computer. The software used was "Autosal-2009 V8.5" created by NMF. This software allowed the online recording of the double conductivity ratio, the calculation of the average value for the 3 measurements and the

data standard deviation. The software allowed as well the calculation of the practical salinity, which was done offline.
Results
Graph 34 and 35 show the correlation between the salinity measured with the salinometer and the one obtained by the CTD for the stainless steel (normal and biological) casts (SS) and the Ti main casts respectively.
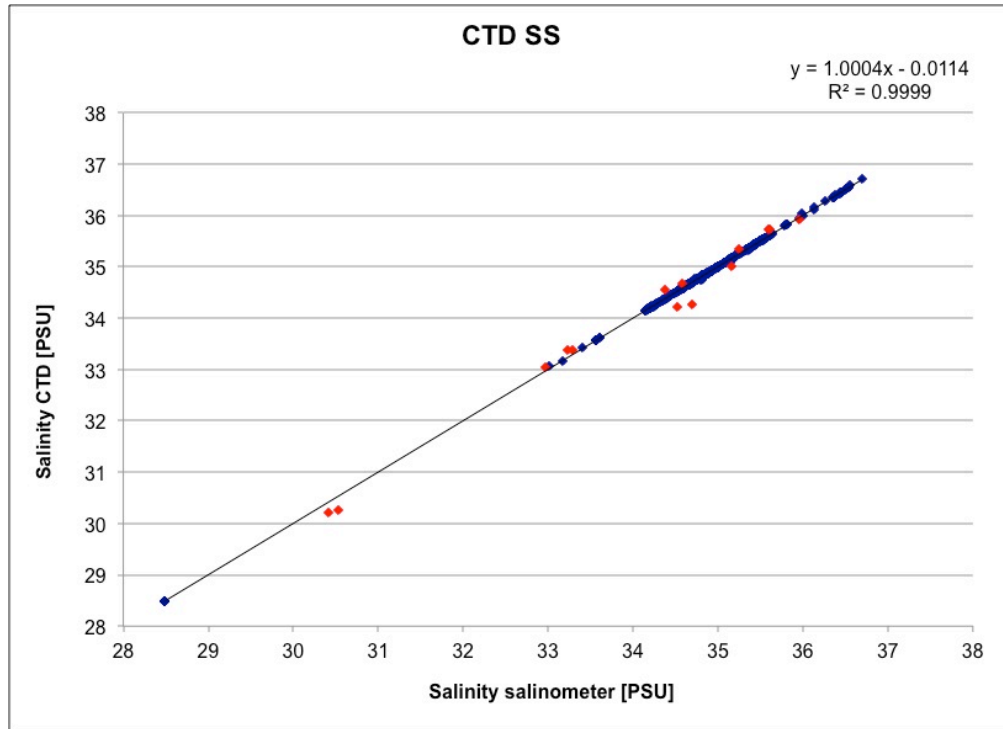
Figure 34: correlation between the salinity measured by the salinometer (x-axis) and the one measured by the CTD (y-axis) for the stainless steel rosette. For the determination of the equation and of the regression coefficient, the flyer points (in red) were not taken in account.

For the stainless steel rosette, there are 14 flyer points (in red). They correspond to the following Geotraces samples:
- 1464 from CTD020_SS
- 1580 from CTD025_SS
- 1978 from CTD045_SS
- 2110, 2102, 2103 and 2113 from CTD050_SS
- 2350, 2355, 2357 and 2358 from CTD061_SS
- 2396, 2399 and 2400 from CTD063_SS
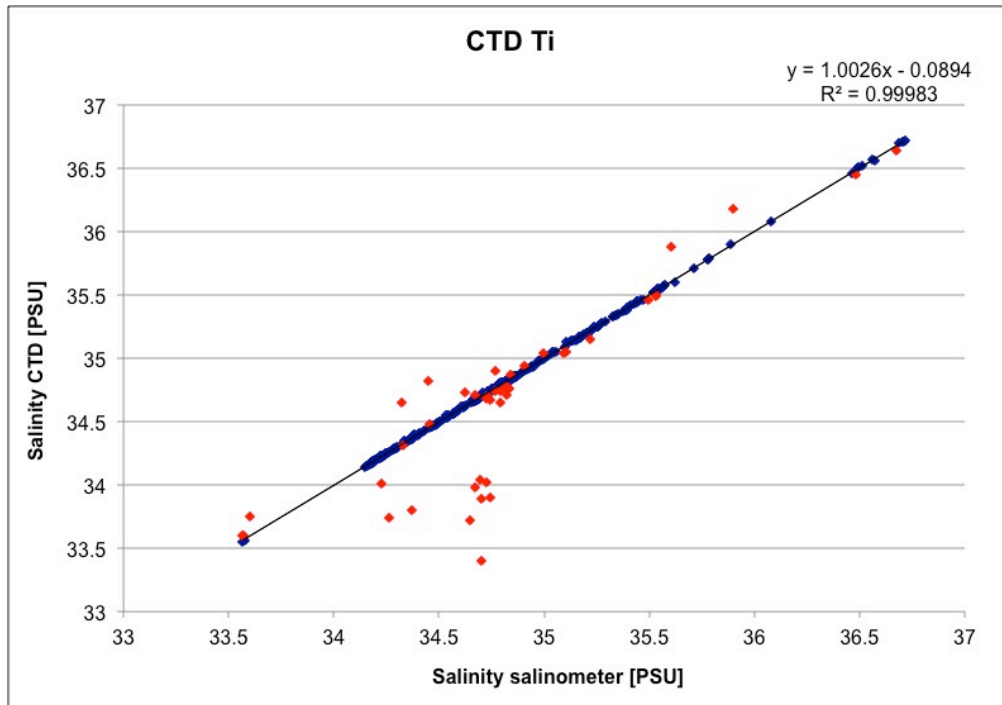
Figure 35: correlation between the salinity measured by the salinometer (x-axis) and the one measured by the CTD (y-axis) for the Ti main casts. For the determination of the equation and of the regression coefficient, the flyer points (in red) were not taken in account.

For the Ti main casts comparison with the CTD, there are 43 flyer points (in red). They correspond to the following Geotraces samples:
- 1089, 1090 and 1091 from CTD004_T
- 1123, 1124 and 1130 from CTD006_T
- 1242 to 1249, 1252 to1256, 1258 to 1264 from CTD011_T
- 1291 from CTD013_T
- 1515 from CTD022_T
- 1603 and 1604 from CTD026_T
- 1675 from CTD029_T
- 1733 and 1749 from VTD032_T
- 2012 to 2014, 2019, 2021 and 2022 from CTD046_T
- 2068, 2069 and 2070 from CTD048_T
- 2166 from CTD052_T
- 2319, 2329 and 2331 from CTD060_T
- 2372 to 2375 from CTD062_T
- 2408 to 2411 from CTD064_T

Graphs 36 and 37 show the deviation between the salinity measured by the salinometer and the one measured by the CTD for the stainless steel casts and Ti main casts, respectively, with respect to the sample number.
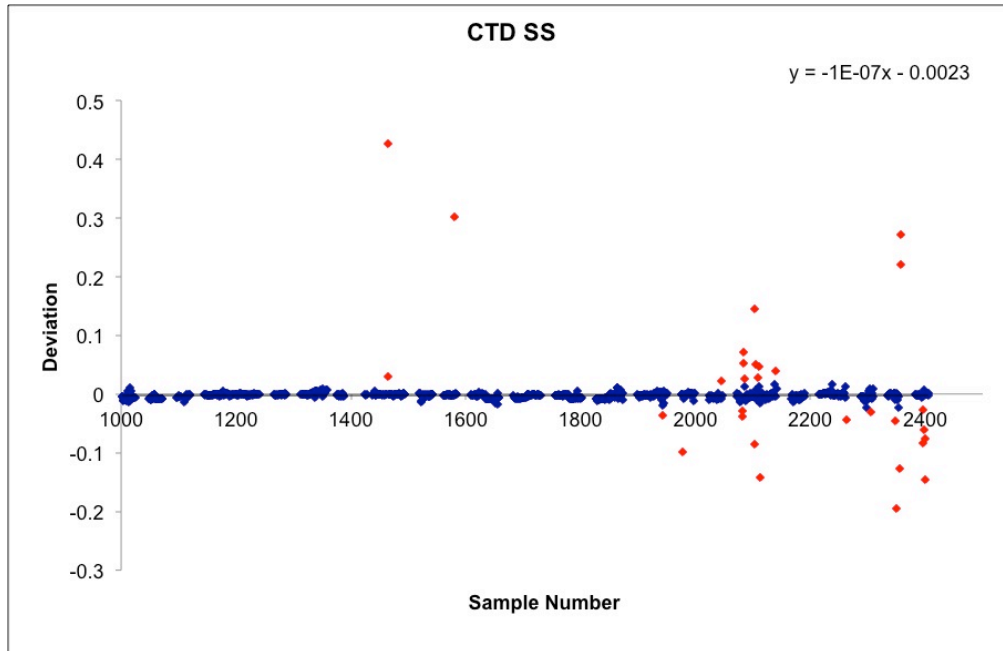
Figure 36: deviation between salinity measured by the salinometer and the one measured by the CTD (y-axis, S (salinometer) – S (CTD)) with respect to the sample number (x-axis) for the stainless steel casts. The flyer points (in red) were not taken in account for the calculation of the equation.
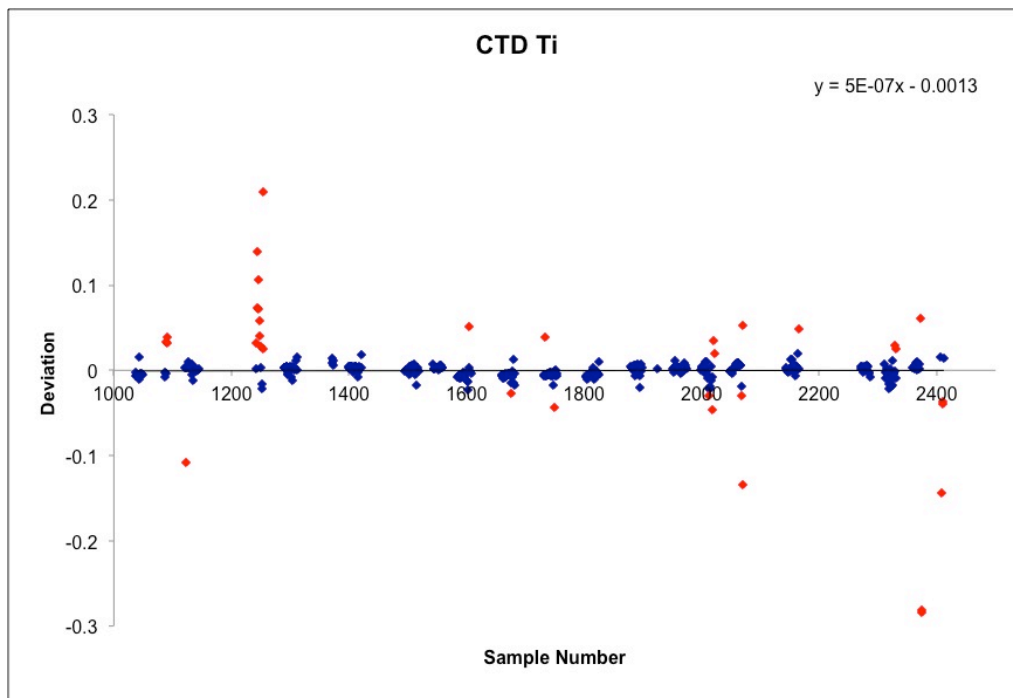
Figure 37: deviation between salinity measured by the salinometer and the one measured by the CTD 1 (y-axis, S (salinometer) – S (CTD)) with respect to the sample number (x-axis) for the main Ti casts. The flyer points (in red) were not taken in account for the calculation of the equation.

References

"Laboratory measurement of salinity", file provided by OSIL during the laboratory measurement of salinity training course.

Kowano T. "The GO-SHIP Repeat Hydrography Manual: A Collection of Expert Reports and Guidelines", IOCCP Report No. 14, ICPO Publication Series No. 134, Version 1, 2010.

8.5 OCEAN CARBONATE SYSTEM

Report, sample collection and analysis by Matthew P. Humphreys

Objectives

To collect samples at all stations for the measurement of:

Dissolved Inorganic Carbon (TCO$_2$) and Total Alkalinity (TA), to be analysed on the cruise

Dissolved Organic Carbon (DOC) and Total Dissolved Nitrogen (TDN), to be analysed at the National Oceanography Centre, Southampton (UK)

Samples for δ^{13}C of TCO$_2$ will also be collected at a few stations, to be analysed after the cruise, to enable an inter-lab calibration with the bigger set of δ^{13}C of TCO$_2$ samples being collected separately by Alex Thomas for Alex Piotrowski (University of Cambridge, UK).

Samples taken

For TCO$_2$ and TA, a sample was taken from one Niskin bottle at each depth on almost every full-depth and shallow (bio) cast of the stainless steel rosette. A similar set of samples was taken for DOC and TDN up to and including Station 12, after which every non-leaking Niskin bottle on the full-depth casts was usually sampled. Samples for δ^{13}C of TCO$_2$ were taken when convenient.

Table 15, below, lists which Niskin bottle numbers were sampled on each cast.

Station	Cast	TCO$_2$ and TA	DOC and TDN	δ^{13}C of TCO$_2$
1	001	1(x2), 3, 5, 8, 9, 11, 13, 15, 18, 20, 22	Unfiltered: 2, 3, 5 Filtered: 8, 9, 11, 13, 15, 18, 20, 22	
2	003	1(x2), 3, 5, 7, 9, 11, 13, 15, 18, 20, 22	Unfiltered: 1(x2), 3, 5 Filtered: 7, 9, 11, 13, 15, 18, 20, 22(x2)	
3	005	1, 3, 4, 6(x2), 8, 14, 15, 16, 18 – 24 (23x2)	Unfiltered: 1, 3, 4, 6(x2), 8, 14, 15, 16, 18, 19, 20 Filtered: 21 – 24	
4	008	1(x2), 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 23	Unfiltered: 1(x2), 3, 5 Filtered: 7(x2), 9, 11, 13, 15, 17, 19, 21, 23	
5	009	1(x2), 3, 7, 9, 11, 14, 15, 18, 19, 21, 23	Unfiltered: 1, 3 Filtered: 7, 9(x2), 11, 14, 15, 18, 19, 21, 23	
6	010	1(x2), 3, 6, 7, 9 – 15, 17, 18, 20(x2), 21, 22, 23	Unfiltered: 1(x2), 3, 6, 7, 9 – 14 Filtered: 15, 17, 20 – 23	
8	012	2, 3(x2), 5, 7, 10, 11, 13, 15, 17, 19, 21, 23		
8	014	1(x2), 3, 5, 7, 9, 11, 12, 14, 15, 16, 18, 19, 21 – 24	Unfiltered: 1(x2), 3, 5, 7, 9, 11, 12, 14, 15, 16, 18, 19, 21 Filtered: 22, 23, 24(x2)	
9	015	1, 3, 5, 7(x2), 11, 14, 15, 18, 19, 22,	Unfiltered: 1, 3, 5, 7 Filtered: 14, 15, 18, 19, 22,	

		23(x2)	23	
11	017	1, 3, 4, 6(x2), 7, 9, 11, 14		
11	019	3, 4, 6, 15, 16, 18, 19, 20, 21, 24	Unfiltered: 3, 4, 6, 15 Filtered: 16, 18, 19, 20, 21, 24	3, 4, 6, 15, 16, 18, 19, 20, 21, 24
11	020	3, 5, 9, 10, 13, 18, 19, 22(x2)	Unfiltered: 3, 5, 9, 10, 13, 18, 19, 22(x2)	3, 5, 9, 10, 13, 18, 19, 22(x2)
12	021	2, 3, 5, 6(x2), 8, 9, 11 − 24	Unfiltered: 2, 3, 5, 6(x2), 8, 9, 11 − 20 Filtered: 21 − 24	
12	022	5		
12	023	1(x2), 3, 4, 6, 8, 10, 12, 14, 16, 19, 21, 23		
13	025	1(x2), 3, 5, 6, 7, 9, 10, 12, 13, 15 − 24	Unfiltered: 1, 2, 3, 5, 6, 7, 9 − 21 Filtered: 22, 23, 24	1, 3, 5, 6, 7, 9, 10, 12, 13, 15 − 24 (24x2)
13	027	8 − 12, 14, 15, 17, 18, 20, 21, 23(x2)		
14	028	1, 3, 5, 6, 7, 9, 10, 11, 13 − 24	Unfiltered: 1 − 11, 13 − 20 Filtered: 22, 23, 24	
14	030	1, 3, 5, 6, 7(x3), 9, 11, 13, 15, 18, 20, 22(x3)		
15	031	1, 3, 5, 7, 9(x3), 11, 13, 15, 17, 19, 21, 23(x3)		
15	033	1, 3, 5, 6, 7 − 13, 15, 16, 18 − 24	Unfiltered: 1, 2, 3, 5 − 20 Filtered: 21 − 24	
16	034	1, 3, 5, 7, 9(x3), 11, 13, 15, 18, 20, 22, 24(x3)		
16	036	1, 3, 4, 6 − 24	Unfiltered: 1 − 20 Filtered: 21 − 24	
17	037	1, 3, 5, 7, 8, 10, 13, 14, 15, 17, 18, 21, 22	Unfiltered: 1, 3, 5, 8 Filtered: 10, 18, 21, 22	
17	039	1, 3, 6, 7, 10, 11, 12, 15, 16, 19, 20, 23, 24	Unfiltered: 1, 3, 6, 7, 10, 11, 15, 16, 19, 20, 23, 24	
18	043	1, 3, 5, 7, 9(x3), 11, 13, 15, 17, 19, 21, 23(x3)		
18	045	1, 3, 5, 6, 8, 9, 11 − 14, 16 − 24	Unfiltered: 1, 2, 3, 5 − 20 Filtered: 21 − 24	
19	047	1, 3, 4, 6, 7, 9, 10, 12, 13, 15 − 23 (19x2)	Unfiltered: 1 − 20 Filtered: 21 − 24	1, 3, 4, 6, 7, 9, 10, 12, 13, 15 − 24 (19x2)
19	049	1, 3, 5, 7, 9, 11, 13,		1, 3, 5, 7, 9, 11, 13,

		15, 17, 19, 22, 23(x2)		15, 17, 19, 22, 23(x2)
20	050	1, 3, 5, 7 – 12, 14 – 22, 23(x2)		1, 3, 5, 7 – 12, 14 – 22, 23(x2)
20	051	1 – 18, 20, 23	Unfiltered: 1 – 19 Filtered: 20 – 23	1 – 4, 6, 7, 9, 10, 12, 14, 16, 17, 20
21	056	1, 3 – 10, 11(x2), 14, 15, 17 – 20, 23(x2)	Unfiltered: 1 – 12, 14 – 20 Filtered: 21 – 24	
21	059	1, 6, 7, 8, 11, 12, 17, 18, 20 – 24 (23x2)		
22	061	1, 3 – 9 (6x2), 13 – 17, 18(x2), 20, 21, 23	Unfiltered: 1 – 9, 13, 14 Filtered: 15, 19, 23	
24	063	1, 7, 9, 11, 13, 19, 21	Filtered: 1, 7, 9, 11, 13, 19, 21	

Sampling protocols

TCO$_2$ and TA

Samples were collected in 250 ml Schott Duran borosilicate glass bottles with glass stoppers that provided an air-tight seal. Samples were collected following trace gases, dissolved oxygen and nutrients, before the Niskin bottles were half empty and within 10 minutes of their opening. Samples were stored in a dark, insulated box and analysed within 24 hours of collection, except for CTD 051, for which this was logistically impossible. These results do not appear to have been affected by the short extra delay.

DOC and TDN

Samples were collected in 20 ml glass ampoules, taken from the Niskin bottles later on in the sampling order. Samples taken in water depths of 150 metres or less were filtered through glass-fibre filters (Whatman, GF/F). All ampoules and filters had been stored in aluminium foil and combusted at 450°C for 4–6 hours before the cruise. Samples were acidified with 35µl of 50% (v/v) hydrochloric acid soon after collection, and then flame-sealed with a propane-butane burner. Between collection and sealing, samples were always covered with aluminium foil to prevent contamination.

δ^{13}C of TCO$_2$

Samples were collected in 100 ml soda-lime glass bottles with ground glass stoppers, taken from the Niskin bottles immediately after TCO$_2$ and TA samples. Preparation for storage was as recommended by Dickson et al. (2007) for TCO$_2$ samples: soon after collection, 1 ml of sample was removed for headspace and 20µl of saturated mercuric chloride added. The stopper was dried and Apiezon L grease was added to improve the air-tight seal. Electrical tape was wrapped around the bottle and stopper to maintain the seal.

Analysis

TCO$_2$ and TA

Measurements of TCO$_2$ and TA were carried out at sea with VINDTA (3C) #038 (Marianda) connected to a CM5015 CO$_2$ coulometer (UIC, Inc.). All samples were

analysed within 24 hours of collection (average time 11 hours). Samples were warmed in a water bath at 25°C for an hour before analysis.

A set volume of the sample is acidified by addition of excess 10% phosphoric acid, which converts all inorganic carbon species to CO_2. This is carried into the coulometric cell by an inert carrier gas (CO_2-free N_2 that is first passed through a magnesium perchlorate and Ascarite II scrubber), and a coulometric titration determines the amount of CO_2, which is equal to TCO_2.

Small increments of 0.1 M hydrochloric acid are added to a set volume of sample while the electromotive force is measured by a glass and reference electrode system. The amount of acid added to reach the carbonic acid equivalence point is equal to the TA.

Regular measurements of both TCO_2 and TA were made from batch 114 Certified Reference Material (CRM) from A. G. Dickson (Scripps Institution of Oceanography) and used to calibrate the results for each session of analysis as follows:

$$TCO_2^{\text{sample, corrected}} = TCO_2^{\text{sample, measured}} \times (TCO_2^{\text{CRM, certified}} / TCO_2^{\text{CRM, measured}})$$
$$TA^{\text{sample, corrected}} = TA^{\text{sample, measured}} \times (TA^{\text{CRM, certified}} / TA^{\text{CRM, measured}})$$

To obtain the final results in units of µmol kg^{-1}, a correction for density (ρ) due to salinity (S) variations was then applied using salinity measured from Niskin bottle samples and an equation of the form (Zeebe & Wolf-Gladrow, 2001):

$$\rho_{\text{sea water, 25°C}} = \rho_{\text{pure water, 25°C}} + AS + BS^{1.5} + CS^2$$

Precision

Precision was monitored by:

5-6 consecutive measurements of the same batch of water from the underway non-toxic seawater supply, carried out several times throughout the cruise

Duplicate samples taken from the same Niskin bottle, analysed consecutively

Triplicate samples taken from the same Niskin bottle, analysed after a range of time intervals (between c. 1 – 24 hours)

CRM results

As the samples were not poisoned with mercuric chloride it was important to establish that no changes to TCO_2 or TA would occur during storage (always <24 hours). Triplicate samples were taken and analysed at a range of time intervals for this purpose. The triplicates were taken from shallow depths (≤100 metres). Results from these analyses demonstrated that (i) there was no systematic variation of TCO_2 or TA with storage time and (ii) precision of measurements was not reduced for samples measured many hours apart compared with consecutively (see Figure 38).
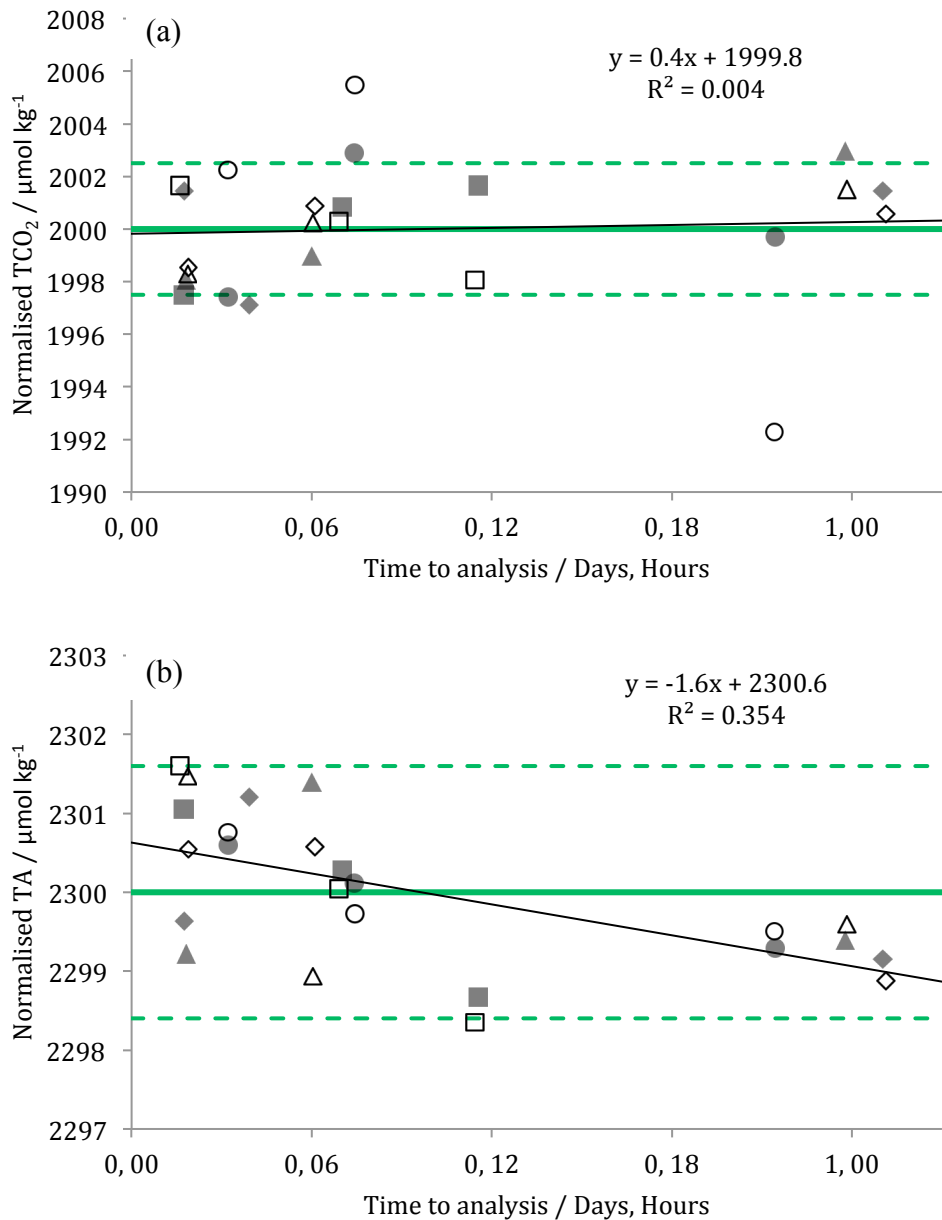
Figure 38. Negligible effect of time between sampling and analysis on (a) TCO_2 and (b) TA measurements. Squares = Station 14, diamonds = St. 15, circles = St. 16, triangles = St. 18. Filled shapes = 100m depth, outlines = 5m. Thick green line = normalisation value, dashed green lines = norm. value ± precision determined from CRMs and duplicates. Black line, equation and R^2 value are for all data.

DOC and TDN

Samples will be analysed by High-Temperature Catalytic Oxidation (Badr et al., 2003) at the National Oceanography Centre, Southampton as soon as possible after the cruise.

$δ^{13}C$ of TCO_2

Samples will be analysed as soon as possible after the cruise.

Preliminary results (TCO_2 and TA only)

Comparison with D357

Measurements from similar locations and depths were compared and found to be in good agreement, as illustrated by Figure 39. In each case the thick red line shows the expected 1:1 trend and the thin black line is the best-fit through the data, corresponding to the equation and R^2 value. The variability seen at lower values for TA is significantly reduced by normalisation to a salinity of 35 (nTA = 35 x TA / Salinity), which implies that the variations are due to changes in freshwater fluxes such as precipitation and evaporation. In general, there is more deviation from the 1:1 line at lower values of TCO_2 and nTA, which corresponds to samples from closer to the surface, where more inter-annual variability is expected.
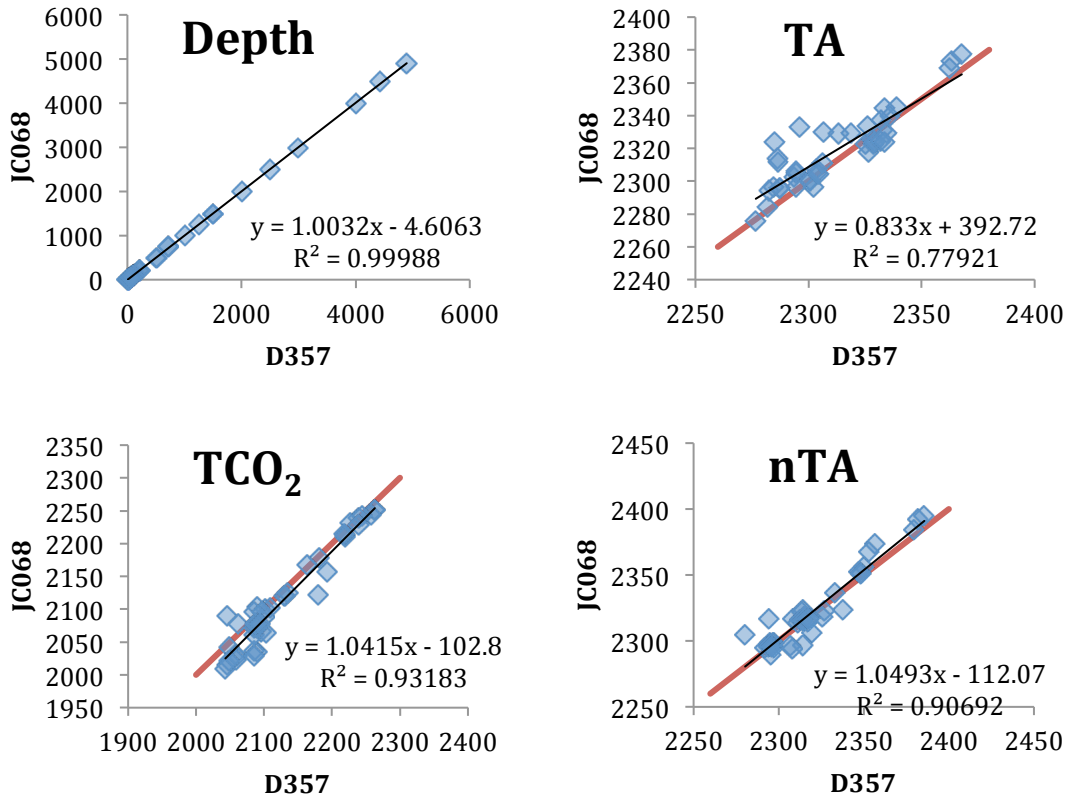
Figure 39. Comparison of TCO$_2$ and TA data from JC068 and D357

References

Badr E. A., Achterberg E. P., Tappin A. D., Hill S. J., Braungardt C. B., 2003. Determination of dissolved organic nitrogen in natural waters using high temperature catalytic oxidation. Trends in Analytical Chemistry, 22, 819-827

Dickson A. G., Sabine C. L., Christian J. R. (Eds.), 2007. Guide to best practices for ocean CO_2 measurements. PICES Special Publication 3, IOCCP Report no. 8

Zeebe R. E., Wolf-Gladrow D., 2001. CO_2 in seawater: equilibrium, kinetics, isotopes. Elsevier Oceanography Series, 65

Comprehensive Calibration of Critical Paleoceanographic Proxies

(NERC Standard Grant)

^{231}PA/^{230}TH

Report by Alex Thomas

Samples to be analysed by Alex Thomas

Objectives

The naturally occurring radioisotopes ^{231}Pa and ^{230}Th are both produced in the ocean from the decay of uranium (^{235}U and ^{234}U respectively). The high solubility and hence long residence time of U in the oceans leads to a uniform (varying only with salinity) concentration of U and only small variations in the isotopic composition of dissolved U in the open ocean(Andersen et al. 2007). Once produced ^{231}Pa and ^{230}Th are rapidly removed from the ocean by scavenging onto particle surfaces and settling. The distribution of ^{231}Pa and ^{230}Th in the oceans it therefore governed by the degree of particle affinity for each ^{231}Pa and ^{230}Th, the flux of particles, and the advection of any ^{231}Pa or ^{230}Th remaining in the dissolved, or "non-sinking" fraction. Measurement of the distributions of the "non-sinking" fraction of ^{231}Pa and ^{230}Th will be made by using a 0.45 μm filter cartridge during sampling. Obtaining a section of ^{231}Pa and ^{230}Th concentrations along 40S in the Atlantic Ocean will allow the investigation of the nature of particle scavenging across different bio-oceanographic settings, with variations of particle flux and type along the section.

The sedimentary record of ^{231}Pa and ^{230}Th is increasingly used as a tracer of past oceanographic conditions. It has been used to infer past rates and modes of ocean circulation(Yu et al. 1996; McManus et al. 2004; Gherardi et al. 2005; Thomas et al. 2007; Gherardi et al. 2009; Negre et al. 2010), and particle fluxes (Kumar et al. 1993; Kumar et al. 1995; Bradtmiller et al. 2007). The use of this proxy is currently controversial with many questions still to be resolved surrounding the transfer of water column ^{231}Pa and ^{230}Th to oceanic sediments. Though coupled measurements of water column and sedimentary ^{231}Pa and ^{230}Th long the 40S transect at localities where the sediment is sited in different water masses with characteristic ^{231}Pa and ^{230}Th concentrations will enable the water depth which is most represented by the sedimentary ^{231}Pa and ^{230}Th to be investigated which remains controversial(Thomas et al. 2006). High resolution ^{231}Pa and ^{230}Th profiles through the surface sediment, coupled with the ^{231}Pa and ^{230}Th concentrations of bottom water, will also be informative as to the control leakage of ^{231}Pa and ^{230}Th from sediment has on the oceanic inventory of ^{231}Pa and ^{230}Th, and how the oceanic signature is "locked" into sediments. The 40S transect will also include sampling close to the African and South American margins which will allow the extent to which enhanced scavenging in these high particle flux regions effects the oceanic ^{231}Pa and ^{230}Th concentrations(Anderson et al. 1983; Anderson et al. 1990), and hence how this might bias paleoceanographic reconstructions.

Sampling protocol

Water samples

Up to 10L of seawater was sampled for each depth from 20L OTE bottles, into 10L acid cleaned HDPE bottles (the lowermost 6 samples were typically sampled in 5L bottles). Samples were taken from the rosette on deck, taking special precaution not to put the bottles down on the deck, to reduce risk of contamination from the ship. Large plastic boxes were employed to hold samples during filtration to avoid contact with the ship, and the sampling bottles were kept within their plastic bags during sampling. Samples were filtered directly from the OTE bottles through 0.45um AcroPak 500 capsules, using PVC tubing. Prior to use, each AcroPak was rinsed with filtered surface water from the trace metal clean fish. Capsules were reused until flow rates were noticeably reduced. To reduce cross-contamination AcroPaks were rinsed with ~100mL of sample before rinsing the sample bottle with a further ~100mL of sample prior to filling. Occasionally where no near surface water was available from the rosette a sample from the surface fish was taken, which was also filtered through a 0.45um AcroPak. Once filled samples were capped and

transferred into the Chemistry Laboratory were they were acidified with 1.2mL/L of 10N HCl (quartz distilled), the samples were shaken and the pH checked to be <1.5. Samples bottle caps were sealed with Parafilm and bagged before being stored in boxes for transport back to Oxford.

Coring Samples

Water was sampled from the mega-corer tubes above the sediment-water interface to get a measure of bottom water in contact with bottom sediment. The temperature of the water was taken with thermocouple thermometer 00. to The mega-core was sampled for water filtered through a 0.4um AcroPak and then acidified with 1.2 mL of 10N HCl per L of water.

Samples for sedimentary Pa and Th analyses will be taken from aliquots of samples taken for pore-water and bulk elemental composition (led by Will Homoky at NOCS). In addition Pa and Th analyses may also be performed on the archive core if deemed appropriate following analysis of the bulk composition aliquats.

Samples collected

Overview of samples: A total of 173 samples were collected. Full depth profiles weer take at: Station 7 (12 samples), Station 8 (13 samples), Station 11 (11 samples), Station 12 (10 samples), Station 13 (12 samples), Station 14 (12 samples), Station 16 (14 samples), Station 18 (18 samples), Station 19 (16 samples), Station 20 (14 samples), Station 21 (12 samples), Station 22 (7 samples) Station 24 (3 samples). 15 samples from the surface fish, were also taken.

Details of samples collected are presented in Table 16 PaTh1.

Station	CTD#	Sampler	Bottle	Target depth, m	PaTh	d13C	Pu	236U	As&Sb	e114Cd	PaTh/ e114Cd Box
1	1	ss	1001	400		y					
1	1	ss	1005	200		y					
1	1	ss	1009	80		y					
1	1	ss	1013	50		y					
1	1	ss	1020	20		y					
1	1	ss	1022	5		y					
3	5	ss	1097	-10				vera109	y		
3	5	ss	1099	4500				vera110	y		
3	5	ss	1100	4000				vera105			
3	5	ss	1104	3000				vera106	y		
3	5	ss	1110	1500				vera001	y		
3	5	ss	1112	1000				vera012	y		
3	5	ss	1114	750				vera033			
3	5	ss	1115	500				vera020	y		
3	5	ss	1116	200				vera035			
3	5	ss	1117	100					y		
3	5	ss	1118	50				vera019			
3	5	ss	1119	20					y		
3	5	ss	1120					vera 003			
3	6	Ti	1126	3000					y		
3	6	Ti	1129	2000				vera 101	y		
3	7	ss	1145	400	y						
3	7	ss	1148	200	y						

Station	CTD#	Sampler	Bottle	Target depth, m	PaTh	d13C	Pu	236U	As&Sb	e114Cd	PaTh/ e114Cd Box
3	7	ss	1152	100		y					
3	7	ss	1159	50		y					
3	7	ss	1164	20		y					
3	7	ss	1166	5		y					
5	9	ss	1193	400		y					
5	9	ss	1201	100		y					
5	9	ss	1207	50		y					
5	9	ss	1213	20		y					
5	9	ss	1215	5		y					
7	11	Ti	1241	4424	y						alt4
7	11	Ti	1242	4300	y						alt4
7	11	Ti	1243	4000	y						alt12
7	11	Ti	1244	3500	y						alt4
7	11	Ti	1246	3000	y						alt12
7	11	Ti	1248	2500	y						alt4
7	11	Ti	1250	1750	y						alt4
7	11	Ti	1252	1250	y						alt4
7	11	Ti	1253	1000	y						alt12
7	11	Ti	1255	500	y						alt12
7	11	Ti	1258	200	y						alt12
7	11	Ti	1261	75	y						alt12
8	14	ss	1313	3372	y	y					alt36
8	14	ss	1315	3200	y	y					alt36
8	14	ss	1317	3000	y	y					alt36
8	14	ss	1319	2500	y	y					alt36
8	14	ss	1321	2000	y	y					alt36
8	14	ss	1323	1750	y	y					alt36
8	14	ss	1325	1500	y	y					alt14
8	14	ss	1326	1250	y	y					alt14
8	14	ss	1327	1000	y	y					alt14
8	14	ss	1329	700	y	y					alt14
8	14	ss	1332	350	y	y					alt14
8	14	ss	1334	100	y	y					alt14
8	14	ss	1336	5	y	y					alt16
11	19	ss	1425	3100	y	y					alt38
11	19	ss	1426	3000	y	y					alt38
11	19	ss	1428	2500	y	y					alt38
11	19	ss	1437	200		y					
11	19	ss	1438	100	y	y					alt15
11	19	ss	1444	35	y	y					alt15
11	20	ss	1452	2000	y	y					alt38
11	20	ss	1456	1500	y	y					alt38
11	20	ss	1460	1250	y	y					alt15
11	20	ss	1464	1000	y	y					alt38
11	20	ss	1466	750	y	y					alt15
11	20	ss	1470	500	y	y					alt15
12	21	ss	1472	-10	y	y			y		alt24
12	21	ss	1476	2500	y	y					alt24
12	21	ss	1477	2500					y		
12	21	ss	1479	2000	y	y					alt24
12	21	ss	1480	2000					y		
12	21	ss	1483	1500	y	y			y		alt24

Station	CTD#	Sampler	Bottle	Target depth, m	PaTh	d13C	Pu	236U	As&Sb	e114Cd	PaTh/ e114Cd Box
12	21	ss	1485	1200	y	y					alt33
12	21	ss	1486	1000	y	y			y		alt33
12	21	ss	1487	750	y	y					alt33
12	21	ss	1489	500	y	y			y		alt33
12	21	ss	1491	100	y	y					alt33
12	21	ss	1492	50					y		
12	21	ss	1494	5	y	y			y		alt33
12	22	Ti	1496	-30						y	alt20
12	22	Ti	1498	2995						y	alt20
12	22	Ti	1502	2495						y	alt20
12	22	Ti	1509	1495						y	alt20
12	22	Ti	1513	995						y	alt20
12	22	Ti	1518	490						y	alt20
12	24	Ti	1546	198						y	alt20
13	25	ss	1561	-10	y	y					alt32
13	25	ss	1563	3700	y	y					alt32
13	25	ss	1565	3500	y	y					alt32
13	25	ss	1567	3000	y	y					alt32
13	25	ss	1570	2500	y	y					alt32
13	25	ss	1573	2000	y	y					alt32
13	25	ss	1576	1500	y	y					alt25
13	25	ss	1577	1250	y	y					alt25
13	25	ss	1578	1000	y	y					alt25
13	25	ss	1580	500	y	y					alt25
13	25	ss	1582	100	y	y					alt25
13	25	ss	1584	5	y	y					alt25
14	28	ss	1636	-10	y	y					??
14	28	ss	1638	4000	y	y					??
14	28	ss	1640	3500	y	y					??
14	28	ss	1642	300	y	y					??
14	28	ss	1644	2500	y	y					??
14	28	ss	1647	2000	y	y					??
14	28	ss	1649	1500	y	y					??
14	28	ss	1651	1000	y	y					??
14	28	ss	1652	750	y	y					??
14	28	ss	1653	500	y	y					??
14	28	ss	1655	100	y	y					??
14	28	ss	1658	5	y	y					??
15	33	ss	1757	4000		y					
15	33	ss	1762	3000		y					
15	33	ss	1765	2000		y					
15	33	ss	1768	1500		y					
15	33	ss	1770	1000		y					
15	33	ss	1772	750		y					
15	33	ss	1773	500		y					
15	33	ss	1774	200		y					
15	33	ss	1775	100		y					
15	33	ss	1776	50		y					
15	33	ss	1777	20		y					
15	33	ss	1778	5		y					
16	36	ss	1828	-10	y	y					alt19
16	36	ss	1829	4750	y	y					alt19

Station	CTD#	Sampler	Bottle	Target depth, m	PaTh	d13C	Pu	236U	As&Sb	e114Cd	PaTh/e114Cd Box
16	36	ss	1831	4500	y	y					alt19
16	36	ss	1832	4000	y	y					alt19
16	36	ss	1833	3500	y	y					alt19
16	36	ss	1835	3000	y	y					alt19
16	36	ss	1837	2500	y	y					alt16
16	36	ss	1839	2000	y	y					alt16
16	36	ss	1841	1500	y	y					alt16
16	36	ss	1842	1250	y	y					alt16
16	36	ss	1843	1000	y	y					alt16
16	36	ss	1845	500	y	y					alt16
16	36	ss	1847	100	y	y					alt28
16	36	ss	1850	5	y	y					alt28
17	37	ss	1851	1000				vera031			
17	37	ss	1852	1000			A33				
17	37	ss	1853	750		y		vera023			
17	37	ss	1854	750			A34				
17	37	ss	1855	400				vera011			
17	37	ss	1856	400		y	A31				
17	37	ss	1858	200				vera027			
17	37	ss	1859	200			A27				
17	37	ss	1861	100		y		vera025			
17	37	ss	1862	100			A28				
17	37	ss	1863	85		y					
17	37	ss	1866	64		y					
17	37	ss	1869	50		y		vera028			
17	37	ss	1870	50			A32				
17	37	ss	1873	5		y		vera010			
17	37	ss	1874	5			A29				
17	39	ss	1901	5000		y					
17	39	ss	1902	5000				vera104			
17	39	ss	1903	5000			A35				
17	39	ss	1905	4000		y					
17	39	ss	1906	4000				vera111			
17	39	ss	1907	4000			A39				
17	39	ss	1910	3000		y					
17	39	ss	1911	3000				vera102			
17	39	ss	1912	3000			A36				
17	39	ss	1914	2000		y					
17	39	ss	1915	2000				vera103			
17	39	ss	1916	2000			A38				
17	39	ss	1919	1500				vera107			
17	39	ss	1920	1500			A37				
17	39	ss	1921	1250		y					
18	44	Ti	1952	-35						y	alt5 (1 in alt28)
18	44	Ti	1962	3995						y	alt5 (1 in alt28)
18	44	Ti	1966	2995						y	alt5 (1 in alt28)
18	44	Ti	1969	2495						y	alt5 (1 in alt28)
18	44	Ti	1972	1995						y	alt5 (1 in alt28)
18	45	ss	1976	-10	y	y			y		
18	45	ss	1977	5090	y	y			y		
18	45	ss	1978	5000	y	y			y		
18	45	ss	1979	4500	y	y					

Station	CTD#	Sampler	Bottle	Target depth, m	PaTh	d13C	Pu	236U	As&Sb	e114Cd	PaTh/ e114Cd Box
18	45	ss	1981	4000	y	y			y		
18	45	ss	1982	3500	y	y					
18	45	ss	1984	3000	y	y			y		
18	45	ss	1985	2500	y	y					
18	45	ss	1986	2250	y	y			y		
18	45	ss	1987	2000	y	y					
18	45	ss	1989	1500	y	y			y		
18	45	ss	1990	1250	y	y					
18	45	ss	1991	1000	y	y			y		
18	45	ss	1992	750	y	y					
18	45	ss	1993	500	y	y			y		
18	45	ss	1994	200	y	y					
18	45	ss	1996	50	y	y			y		
18	45	ss	1998	50	y	y			y		
18	46	Ti	2002	995						y	alt5 (1 in alt28)
18	46	Ti	2011	196						y	alt5 (1 in alt28)
18	46	Ti	2014	96						y	alt5 (1 in alt28)
18	46	Ti	2017	50						y	alt5 (1 in alt28)
18	46	Ti	2018	48						y	alt5 (1 in alt28)
19	47	ss	2024	-10	y	y					??
19	47	ss	2025	5200	y	y					??
19	47	ss	2026	5000	y	y					??
19	47	ss	2028	4500	y	y					??
19	47	ss	2029	4000	y	y					??
19	47	ss	2031	3500	y	y					??
19	47	ss	2032	3000	y	y					alt30
19	47	ss	2034	2500	y	y					alt30
19	47	ss	2036	2000	y	y					alt30
19	47	ss	2038	1250	y	y					alt30
19	47	ss	2039	1000	y	y					alt30
19	47	ss	2041	500	y	y					alt30
19	47	ss	2044	100	y	y					alt20
19	47	ss	2046	5	y	y					alt20
20	51	ss	2119	4808	y	y					alt37
20	51	ss	2120	4700	y	y					alt37
20	51	ss	2121	4500	y	y					alt37
20	51	ss	2122	4000	y	y					alt37
20	51	ss	2124	3000	y	y					alt37
20	51	ss	2125	2600	y	y					alt37
20	51	ss	2127	2250	y	y					alt2
20	51	ss	2128	2000	y	y					alt2
20	51	ss	2130	1500	y	y					alt2
20	51	ss	2132	1000	y	y					alt2
20	51	ss	2134	750	y	y					alt2
20	51	ss	2135	500	y	y					alt2
20	51	ss	2138	100	y	y					alt11
20	53	ss	2167	-10			A03				
20	53	ss	2173	4500			A01				
20	53	ss	2186	3500			A05				
20	53	ss	2188	2000			A07				
20	53	ss	2189	1500			A08				
20	53	ss	2190	1000			A02				

Station	CTD#	Sampler	Bottle	Target depth, m	PaTh	d13C	Pu	236U	As&Sb	e114Cd	PaTh/ e114Cd Box
20	54	ss	2195	600			A09				
20	54	ss	2204	200			A11				
20	54	ss	2213	5			A04				
20	54	ss	2214	5	y						alt11
20	55	ss	2223				y				
20	55	ss	2224				y				
21	56	ss	2239	10	y	y			y		??
21	56	ss	2242	3300	y	y			y		??
21	56	ss	2243	3000	y	y			y		??
21	56	ss	2246	2500	y	y			y		??
21	56	ss	2247	2250	y	y					??
21	56	ss	2248	2000	y	y					??
21	56	ss	2249	175	y	y			y		??
21	56	ss	2252	1250					y		??
21	56	ss	2253	1000	y	y					??
21	56	ss	2256	750	y	y			y		??
21	56	ss	2257	500	y	y			y		??
21	56	ss	2259	100	y	y					??
21	56	ss	2262	5	y	y			y		??
21	58	Ti	2269	2269						y	
21	58	Ti	2276	1993						y	
21	58	Ti	2279	1499						y	
21	58	Ti	2282	995						y	
21	58	Ti	2286	498						y	
21	60	Ti	2320	93						y	
21	60	Ti	2321	91						y	
21	60	Ti	2326	55						y	
22	61	ss	2335	1530	y	y					alt9
22	61	ss	2337	1500	y	y					alt9
22	61	ss	2339	1200	y	y					alt9
22	61	ss	2341	800	y	y					alt9
22	61	ss	2342	600		y					
22	61	ss	2343	400	y	y					alt9
22	61	ss	2347	300		y					
22	61	ss	2349	100		y					
22	61	ss	2351	60		y					
22	61	ss	2353	50	y	y					alt9
22	61	ss	2355	30		y					
22	61	ss	2358	5	y	y					alt9
24	63	ss	2383	50	y	y					??
24	63	ss	2395	20	y	y					??
24	63	ss	2403	5		y					
24	63	ss	2405	5	y						??

Table 17 PaTh1. Details of samples taken for Pa and Th analysis which will also be used for Nd isotope and 10-Be measurements. All samples have paired d13C samples taken from the same bottle unless noted otherwise. Sampler refers to the type of rosette: reg = stainless steel - deep cast; bio = stainless steel – shallow cast; tit = titanium – deep cast; and core = sampled from the overlying water in the mega-corer tube.

Date	Time Start	Time End	PaTh	d13C	Pu	236U	As & Sb	Vol aprox, L	Comments
27/12/11	17:34	17:35				Y		4	VERA007
27/12/11	18:42	18:24	Y					10	
27/12/11	21:11	21:13				Y		4	VERA029
27/12/11	21:22	21:27	Y					10	
27/12/11	23:06	23:08				Y		4	VERA032
27/12/11	23:13	23:18	Y					10	
28/12/11	05:40	05:42				Y		4	VERA024
28/12/11	06:25	06:35	Y					10	
28/12/11	06:36	06:37					Y	0.5	UNFILTERED
28/12/11	06:40	06:41					Y	0.5	FILTERED
28/12/11	19:29	19:31				Y		4	VERA021
28/12/11	19:35	19:35					Y	0.5	UNFILTERED
28/12/11	19:38	19:44	Y					10	
29/12/11	23:49	23:53	Y					10	
29/12/11	19:22	19:26	Y					10	
1/1/12	07:50	07:54				Y		4	VERA030
1/1/12	07:56	07:58					Y	0.5	UNFILTERED
1/1/12	07:58	08:02	Y					10	UNFILTERED
3/1/12	15:46	15:50	Y					10	FILTERED
4/1/12	12:04	12:04					Y	0.5	
4/1/12	12:06	12:06					Y	0.5	
4/1/12	12:07	12:12	Y					10	
6/1/12	23:52	23:52					Y	0.5	UNFILTERED
9/1/12	03:47	03:51	Y					10	
9/1/12	03:51	03:51					Y	0.5	UNFILTERED STN11
9/1/12	03:52	03:53				Y		4	VERA034
14/1/12	20:15	20:23			Y			20	UK#07
14/1/12	20:23	20:25				Y		4	VERA013
14/1/12	20:28	20:33	Y					10	
16/1/12	02:43	02:44				Y		4	VERA036
16/1/12	02:45	02:51			Y			20	UK#08
16/1/12	02:51	02:51					Y	0.5	UNFILTERED STN 17 (ISH)
17/1/12	23:09	23:10					Y	0.5	AFTER MOVE TO TM CAST
21/1/12	13:16	13:24			Y			20	UK#09
21/1/12	13:24	13:24					Y	0.5	
25/1/12	04:20	04:22				Y		4	VERA026
25/1/12	04:22	04:29			Y			20	UK#12
26/1/12	00:23	00:31	Y					10	
26/1/12	12:40	12:49			Y			20	UK#11
26/1/12	12:51	12:52				Y			VERA018
26/1/12	19:00	19:06	Y					10	
26/1/12	21:31	21:35				Y		4	VERA005
26/1/12	21:35	21:35					Y	0.5	UNFILTERED
26/1/12	21:35	21:35					Y	0.5	FILTERED
26/1/12	21:37	21:43	Y					10	

Sample analysis

Samples will be analysed ashore at the University of Oxford, by MC-ICP-MS. Yield tracers of 236U, 229Th and 233Pa will be added to samples prior to processing. Water samples will be equilibrated with their tracer isotopes, and a purified Fe carrier added. Samples will then be neutralised with NH4 and the Fe allowed to precipitate out which will scavenge quantitatively all the U, Th, Pa and REEs. The precipitate will be isolated and redissolved before U, Th, and Pa are separated from each other and the Fe and REEs by anion chromatography. The Fe and REE aliquot will be retained and used for Nd isotope analysis. The U, Pa and Th isotopes will be measured on a Nu Instruments MC-ICP-MS. Methods are further detailed in Thomas et al 2006.

Sediment samples will be totally dissolved using a stepwise HNO_3, HCl, HF digestion using $HClO_4$ to mitigate fluoride formation, and then spiked with the tracer isotopes and then processed as water samples.

Andersen, M. B., C. H. Stirling, et al. (2007). "The tracing of riverine U in Arctic seawater with very precise U-234/U-238 measurements." Earth and Planetary Science Letters **259**(1-2): 171-185.

Anderson, R. F., M. P. Bacon, et al. (1983). "Removal of 230Th and 231Pa at ocean margins." Earth and Planetary Science Letters **66**: 73-90.

Anderson, R. F., Y. Lao, et al. (1990). "Boundary scavenging in the Pacific Ocean: a comparison of [10]Be and [231]Pa." Earth and Planetary Science Letters **96**: 287-304.

Bradtmiller, L. I., R. F. Anderson, et al. (2007). "Opal burial in the equatorial Atlantic Ocean over the last 30 ka: Implications for glacial-interglacial changes in the ocean silicon cycle." Paleoceanography **22**(4): -.

Gherardi, J. M., L. Labeyrie, et al. (2005). "Evidence from the northeastern Atlantic basin for variability in the rate of the meridional overturning circulation through the last deglaciation." Earth and Planetary Science Letters **240**(3-4): 710-723.

Gherardi, J. M., L. Labeyrie, et al. (2009). "Glacial-interglacial circulation changes inferred from Pa-231/Th-230 sedimentary record in the North Atlantic region." Paleoceanography **24**: -.

Kumar, N., R. F. Anderson, et al. (1995). "Increased biological productivity and export production in the glacial Southern Ocean." Nature (London) **378**(6558): 675-680.

Kumar, N., R. Gwiazda, et al. (1993). " [231]Pa/[230]Th ratios in sediments as a proxy for past changes in Southern Ocean productivity." Nature (London) **362**(6415): 45-48.

McManus, J. F., R. Francois, et al. (2004). "Collapse and rapid resumption of Atlantic meridional circulation linked to deglacial climate changes." Nature **428**: 834-837.

Negre, C., R. Zahn, et al. (2010). "Reversed flow of Atlantic deep water during the Last Glacial Maximum." Nature **468**(7320): 84-+.

Thomas, A. L., G. M. Henderson, et al. (2007). "Constant bottom water flow into the Indian Ocean for the past 140 ka indicated by sediment Pa-231/Th-230 ratios." Paleoceanography **22**(4): -.

Thomas, A. L., G. M. Henderson, et al. (2006). "Interpretation of the 231Pa/230Th paleocirculation proxy: New water-column measurements from the southwest Indian Ocean." Earth and Planetary Science Letters **241** 493– 504.

Yu, E. F., R. Francois, et al. (1996). "Similar rates of modern and last-glacial ocean thermohaline circulation infered from radiochemical data." Nature **379**: 689-694.

SILICON ISOTOPES

By Gideon Henderson

Samples to be analysed by Kate Hendry.

Objectives

During upwelling, both nutrients and carbon are brought to the ocean surface. If the nutrients are not fully utilized, then the carbon escapes to the atmosphere. Constraining the fraction of nutrient utilisation in the past is therefore important to assessment of the past carbon cycle. Silicon isotope measurements in opal offer significant potential as a proxy for the past fraction of utilisation of silica (De La Rocha et al. 1998). This proxy has particular relevance due to increasing recognition of the importance of opal production to the ocean carbon cycle. Not only do diatoms represent 40% of net productivity, but their size and density gives them a pivotal role in the packaging of other biogenic material for removal from the surface ocean. Diatoms also compete with carbonate producers so that the Si cycle plays a role in the alkalinity balance of the surface ocean, leading to suggestions that changes in Si cycling may drive glacial-interglacial atmospheric CO_2 cycles (Katsumoto et al. 2002). We have a simple understanding of the $d^{30}Si$ proxy which makes clear its potential for paleoreconstruction. But there are details of the proxy's behaviour which are critical to better understand before we widely apply it and interpret the results.

Three objectives were identified in the NERC Standard Grant, "*Comprehensive calibration of critical paleoceanographic proxies*".

1. *How constant is the $\delta^{30}Si$ of the upwelled nutrient pool?*
To use $\delta^{30}Si$ to assess nutrient utilisation requires knowledge of the isotope composition of input to the surface layer. An existing study has demonstrated that deep waters do not have a uniform value but this issue has not been fully quantified. The $40^{o}S$ profile is ideal for this purpose; recently subducted AIW and AABW are likely to be an end-member composition due to the presence of preformed nutrients, and to contrast with NADW. Collection of waters from each of these water masses will assess the variability of $\delta^{30}Si$ in deep water.

2. *What is the natural isotope fractionation during Si uptake?*
Interpreting sedimentary $\delta^{30}Si$ values in terms of past nutrient utilisation relies on knowledge of the fractionation factor (α) induced by biological uptake of Si. This has been constrained in the laboratory, but a values in the field and variability of α have not been assessed. We will make such assessment by measuring co-existing particulate and dissolved $\delta^{30}Si$ in surface and near surface waters. Synoptic variability along the frontal system and basin-scale productivity gradients will provide a range of nutrient states for this work. Species assemblages, assessed by pigment measurement, may also allow a first assessment of the variation of α with species.

3. *What is the impact of dissolution on $\delta^{30}Si$?*
Different diatom species thrive early in the seasonal bloom relative to late. They therefore have distinct isotope compositions from one another because they grow at times when nutrient utilisation differs. If one of these species dissolves in the water column or sediment more readily than the others (which is likely) this will bias final sedimentary values away from the true annual value. We will measure particulate opal $\delta^{30}Si$ at various depths in the water column (collected by SAPS) and core-top sediment values underlying the water column to assess sediment dissolution effects. Interpretation is made more straightforward because the section is not in an HNLC region so the *a priori* expectation is for $\delta^{30}Si$ equal to upwelled water. $\delta^{30}Si$ measurements on 1cm slices from intact core tops will be used to assess the impact of dissolution through the mixed layer. Core-top opal concentrations may be too low in the eastern basin to allow this work, but those in the western basin are certainly sufficient.

Sampling protocol

Four types of samples were collected for Si isotopes:

i. *Sea-water*: seawater was filtered through an Acropak 500 0.4 micron capsule filter directly from the OTE sampling bottle into precleaned and double-bagged HDPE bottles provided by Dr. Hendry. Bottles were rinsed once before filling. In one case, a water sample was siphoned from the seawater directly overlying an intact megacore. All water samples were left unacidified and were stored at room temperature.

ii. *Pore-waters*: sediment was sliced in approximately 2 cm layers from the revealed face of a box core and placed in a zip-lock bag. The bags were taken directly to the constant temperature lab at a temperature of about 10°C. Sediment was squeezed from each of the bags into between 8x and 16x 50 ml polycarbonate centrifuge tubes. These tubes were centrifuged at 5000 rpm for between 5 and 10 minutes in a chilled centrifuge. Pore-waters were removed from the top of the centrifuged sediments with a 20 ml syringe, and squeezed through a 0.2 micron syringe filter (Puradisc FP30) into prewashed 250 ml HDPE bottles provided by Dr. Hendry. 3 ml of each sample was removed by pipette and used for analysis of the macronutrients by Dr. Woodward. Remaining samples were left unacidified and stored at room temperature.

iii. *Sediments*: The upper ≈1 cm of sediment was scraped from a Megacore into a polycarbonate jar provided by Dr. Hendry. During pore-water sampling, ≥50 g of unprocessed sediment was placed in similar jars or in double-bagged ziplock bags.

iv. *Seawater particulates*: A sector of the trace-metal SAPs filter is intended for Si isotope analysis and will be cut from the filters in clean conditions at University of Plymouth following sample return to the UK (see SAPs section of report).

Samples collected

Samples were taken specifically for Si isotopes at the three new superstation:
Station 12 (MOR): 9 depths
Station 18 (Basin): 12 depths
Station 21 (Slope): 11 depths
Seawater samples span the entire water column at all three sites and capture the major deep-water masses.

In addition, sediment samples at 1 to 2 cm resolution are available for analysis at cored stations should they be required. Portions of SAPs filters are available at all sites where SAPs work was conducted.

Sample analysis

Seawater: Si will be quantitatively separated from seawater using a modified Mg co-precipitation technique (Reynolds et al., 2006). 2% by volume of 1M high purity NaOH will be added to precipitate brucite ($Mg(OH)_2$), shaken, left for 1 hour, centrifuged and the supernatant removed. To ensure quantitative yields, the process is repeated twice (resulting in a total of three precipitations) adding 1% by volume NaOH to the supernatant each time. The samples wil dissolved in 1ml 0.5 M in-house Teflon-distilled HCl and diluted five-fold with Milli-Q water.

Sediments/particulates: Sedimentary diatoms will be separated from lithics using heavy liquid flotation. Organic matter will be removed by heating three times in H_2O_2 (30% reagent grade) and then three times in distilled concentrated HNO_3, followed by thorough rinsing in 18 MΩ Milli-Q water. The samples will be cleaned in 50% distilled HNO_3/10% distilled HCl, followed by five further Milli-Q rinses. The samples will be dissolved by heating in NaOH (Cardinal et al., 2007). All samples will be passed through a cation exchange column to remove metal cations before analysis by Multi-Collector Inductively Coupled Plasma Mass Spectrometry (MC-ICP-MS; Hendry et al., 2010).

All silicon isotope analysis will be conducted on shore following the cruise.

References:

Cardinal, D., Alleman, L. Y., Dehairs, F., Savoye, N., Trull, T. W., and Andre, L., 2005. Relevance of silicon isotopes to Si-nutrient utilization and Si-source assessment in Antarctic waters. *Global Biogeochemical Cycles* **19**, doi:10.1029/2004GB002364.

De La Rocha, C. L., Brzezinski, M. A., DeNiro, M. J., and Shemesh, A., 1998. Silicon-isotope composition of diatoms as an indicator of past oceanic change. *Nature* **395**, 680-683.

Hendry, K. R., Georg, R. B., Rickaby, R. E. M., Robinson, L. F., and Halliday, A. N., 2010. Deep ocean nutrients during the Last Glacial Maximum deduced from sponge silicon isotopic compositions. *Earth and Planetary Science Letters* **292**, 290-300.

Matsumoto, K, J. L. Sarmiento, and M. A. Brzezinski, *Glob. Biogeochem. Cycles* **16** (3) (2002).

Reynolds, B. C., Frank, M., and Halliday, A. N., 2006. Silicon fractionation during nutrient utilization in the North Pacific. *Earth and Planetary Science Letters* **244**, 431-443.

Reynolds, B. C., Aggarwal, J., Andre, L., Baxter, D., Beucher, C., Brzezinksi, M. A., Engstrom, E., Georg, R. B., Land, M., Leng, M. J., Opfergelt, S., Rodushkin, I., Sloane, H. J., van der Boorn, S. H. J. M., Vroon, P. Z., and Cardinal, D., 2007. An inter-laboratory comparison of Si isotope reference materials. *Journalof Analytical Atomic Spectrometry* **22**, 561-568.

LIPID BIOMARKERS

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Sampling conducted by Roisin Moriaty on JC068

There is a range of phytoplankton lipids (Brassicasterol, C_{28}-alkyl-1,14-diols, dinosterol, 24-methylcholesta-5,24(28)-dien-3β-ol), which are less prone to degradation than other compounds (such as pigments) and can be preserved in the sedimentary record, thus having the potential of being used as proxies for past productivity conditions/phytoplankton assemblages. However, the processes by which those are altered through the water column and sediment water interface are not very well understood and need to be in order to use these lipids as proxies for productivity conditions/in the past. In order to understand these processes and evaluate the use of these lipids as paleo proxies we aim to compare the signature of organic matter found through the water column and in surface sediments. For this purpose, particulate matter has been collected at different depths using stand alone pump systems (SAPS) and also sediment cores using mega coring and box coring techniques.

Besides, 64 surface water samples (4 m depth, ranging from Latitude 34 to 40°S and longitude 18 to 0° E) have been collected on the way along with primary productivity, nutrients and other measurements in order to link lipid and primary production signatures and allowing to better understand lipid sources "in situ" potentially unravelling sources of less specific lipids such as sterols.

In addition, water has been collected from several CTDs (Table 9) and filtered in order to evaluate the range of Intact Polar Lipids (IPLs) present through the water column and under different productivity regimes. These will be analysed at Woods Hole Oceanographic Institution.

Analytical approach

Classic lipid compounds

Lipid markers were collected from surface and deep waters on pre-combusted GFF filters (0.7 μm pore size). GFF filters were wrapped in ashed Al foil and frozen at -70 C. Sediment cores were sliced in 2 cm slices, wrapped in ashed Al foil and frozen at -20 C. Sediment slices were sub sampled for $δ^{13}$C and $δ^{15}$N analysis; briefly a cubic cm of sediment was sampled, stored in a ziplog bag and kept at -20 ^{o}C until analysis in the laboratory at the University of Edinburgh (Robyn Turena; Raja Ganhesram). The most likely protocol to follow for lipid analysis is that of Kawamura et al. (1995). Freeze dried filters and sediments are hydrolysed with 0.1 M KOH in MeOH (5% water) for 4 h and subsequently extracted (x 4 for 15 min) in an ultrasonic bath with a mixture of dichloromethane:methanol (DCM:MeOH, 3:1). Neutral components are separated into four subfractions (*n*-alkanes, aromatic hydrocarbons, ketones and alcohols) using silica gel column chromatography. Subsequently compounds are identify by GC-MS and quantified by CG. Isotopes will be measured By GC-C-IRMS.

Intact Polar Lipids (IPLs)

Generally, 2 L of seawater (from biological cast and FISH underway system) were filtered through 47 mm millipore filters (0.22 μm). These wrapped in ashed aluminium foil and LN_2 frozen and stored at -80C until analysis. IPLs are extracted (back in the laboratory) using a modified Bligh & Dyer extraction: filters are placed in pre-combusted glass vials, phosphate buffer (PBS), methanol, and dichloromethane (DCM) are added together with an internal standard (the synthetic lipid dinitrophenylphosphoethanolamine) to produce a single phase. Tubes are vortexed and sonicated, then more PBS and DCM are added to separate the aqueous and organic phases. Tubes are vortexed again, and then centrifuged, and the lower (organic) phase, containing the IPL, is removed into glass vials. The liquid in the vials is dried under a stream of nitrogen gas, and the samples made up in a 9:1 DCM:methanol mixture, capped with argon, and stored at -80ºC until analysis. IPL are quantified using high-performance liquid chromatography electrospray-ionisation mass spectrometry (HPLC ESI MS).

Stand Alone Pump Systems (SAPS)

SAPS were deployed at the three super stations. Two different sets of SAPS have been deployed. The first set of SAPS aims to collect particles for biomarker analysis using 2 stacked 293 mm diameter pre combusted GFF filters (0.7 µm nominal pore size) and Ra (Walter Geibert, University of Edinburgh;) using filter cartridges filled with Mn fiber(nominal pore size 5 µm). The second set of SAPS aims to collect particles for trace metal analysis (Maeve Lohan, University of Plymouth) using a 293 mm PES filter (0.8 µm nominal pore size) and [234]Th (Patrick Martin, National Oceanography Centre Southampton) suing a 293 mm diameter NITEX mesh (pre filter, 53 µm pore size). Details are given in Table 10.

GFF filters were recovered in a fume hood, wrapped in ashed Al foil and frozen at -70. PES filters and NITEX screens were recovered under laminar flow hood.

Other Research Objectives

ANTHROPOGENIC RADIONUCLIDES (ARNs)

By Alex Thomas

Pu and Np samples to be analysed by Tim Kenna, Lamont-Doherty Earth Observatory
^{236}U samples to be analysed by Stephan Winkler, Fakultät für Physik, Universität Wien

Objectives

The anthropogenic radioisotopes of plutonium (239Pu and 240Pu), neptunium (Np-237), cesium (Cs-137) and 236U were added to the surface ocean, largely, by fallout from nuclear weapons testing in the 1960s-1970s, and subsequently from leakage from the nuclear fuel cycle. The input of these nuclides was spatially non uniform with the South Atlantic being particularly distal from the sites of atmospheric nuclear test in the northern Hemisphere and the Pacific. Once deposited, the different chemical behaviour of Pu, Np and Cs will lead to distinct dispersal vectors into the deeper ocean. The aims of this study are to determine the distributions of these nuclides in the Atlantic at 40S, and then use these distributions – in conjunction with a wider set of ARN data, and other naturally occurring tracers – to understand the processes which control the downward mixing and advection of these contaminants.

Sampling protocol

Water samples

Up to 20L of seawater was sampled from 20L OTE bottles, into 20L acid cleaned cubitainers. Samples were taken from the rosette on deck, taking special precaution not to put the bottles down on the deck, to reduce risk of contamination from the ship. Large plastic boxes were employed to hold samples during sampling to avoid contact with the ship. Samples were not filtered, taking the water directly from the OTE bottles using PVC tubing. If insufficient sample was recovered from a single bottle two OTE bottles contents were combined only if they were fired at the sample nominal depth. Occasionally where not near surface water was available from the rosette a sample from the surface fish was taken. Once filled samples were capped and transferred into the Chemistry Laboratory were they were acidified with 30-40mL of 12N HCl (trace metal grade), the samples were shaken and the pH checked to be <1.5. Samples bottle caps were sealed with Parafilm and double bagged before being stored in boxes for transport.

Samples collected

Collected samples are summarised in the Pa/Th section of this report, and detailed on the CTD Scan Sheets

Sample analysis

Samples will be analysed for Pu-239, Pu240, Np237, and Cs-137 using ICP-MS and gamma counting facilities at Lamont-Doherty Earth Observatory. To each 20L sample will be added a mixed tracer solution of Pu-242, Np236, and Cs-134, and an Fe carrier. Fe oxyhydroxides will be precipitated by raising the pH with ammonia solution, to scavenge the Pu and Np, which will be separated from Fe using anoin chronmatography, and measured by isotope dilution on and Axiom ICP-MS (Kenna, et al 2002). The remaining solution will be re-acidified and Cs separated using an ammonium phosphomolybdate method and gamma counting to determine the Cs-137 concentration (Aoyama et al, 2000, Livingston et al, 1974, and Wong et al. 1994).

236U samples will be analyzed for 236U/U at University of Vienna using accelerator mass spectrometry (AMS), and for total U concentration and 234U/238U (to accurately and precisely determine total 236U and for QC) by ICPMS.
For AMS analysis the bulk sample will be acidified and spiked with 233-U (IRMM-58). A clean (pre-nuclear age) Fe carrier is added and U/Fe precipitated at pH>8 using ammonia solution. U is separated from potentially interfering actinides using UTEVA methods. ~2mg Fe-carrier is added to

the extracted U and then precipitated. The precipitate is dried and calcined (900°C), and then pressed into a cathode for the Cs sputter ion source.

References:
Aoyama, M., Hirose, K., Miyao, T., and Igarashi, Y. 2000. Low level Cs-137 measurenets in deep seawater samples. Applied Radiation and Isotopes 53, 159-162

Kenna, T. C. 2002. Determination of plutonium isotopes and neptunium-237 in environmental samples by inductively coupled plasma mass spectromentry with total sample dissolution. Journal of Analytical Atomic Spectrometry 17, 1471-1479.

Livingston, H. D., Mann, D. R., Fettis, R. C., and Dempsey, B. L. 1974. Radiochemical procedures for the analysis of stronitim, cesium, iron, transuranics and the rare earths in seawater samples: Laboratory Operations Protocol. Woods Hole Oceanoigraphic Institution, Woods Hole, MA.

Wong, K. M., Jokela, T. A., and Noshkin, V. E. 1994. Radiochemical procedures for analysis of Pu, Am, Cs, and Srin seawater, soil, sediments, and biota samples. Technical Report, UCRL-ID-116497. Lawrence Livermore National Laboratory, Berkley, CA.

$\delta^{13}C$ OF DIC

By Alex Thomas

Samples to be analysed by Alex Piotrowski

Objectives

The stable isotopes of carbon in dissolved inorganic carbon will be used as a tracer or biological activity. Biomass production in the surface ocean preferentially incorporates the lighter of the carbon isotopes (C12, C13 , and C14 – C14 is radioactive and is not measured here). This removal of the lighter isotope depletes the surface ocean DIC pool of the lighter isotope. Once produced the biomass is exported from the surface ocean when it sinks into the deeper ocean. As the organic carbon sinks it is returned to the dissolved inorganic carbon pool, largely by bacterial respiration. This not only increases the amount of DIC in the deep ocean but also enriches the deep ocean DIC pool with the lighter isotope if carbon. A simplistic water column profile should have heavier DIC in surface waters and lighter DIC in deeper waters.

Water mass histories also play a role in determining the d13C of DIC. The longer a water mass is isolated from the atmosphere – and re-equilibration of it's carbon isotopes with atmospheric CO_2 – and the greater the amount od organic carbon export the lighter the d13C of that water mass will be. The d13C can therefore be thought of as an integrated carbon export that a water mass has experiences since it left the surface.

The aims of the measurements made here are to use the d13C as a productivity and watermass-history tracer to better parameterise the controls on other tracers (eNd and $^{231}Pa/^{230}Th$), which are related to water mass histories and particle scavenging.

Sampling protocol

Water samples

Samples for the measurement of the stable isotopes of carbon (d13C) in dissolved inorganic carbon (DIC) were collected from the regular (stainless steel) rosette's 20L OTE bottles. The d13C samples were taken immediately after the other dissolved gaseous samples (He, ^3H, $D^{17}O$, O_2), nutrients, and DIC and DOC. d13C samples were taken into 250 mL glass bottles with ground glass stoppers. Water was drained directly into the sample bottle using silicone tubing to the bottom of the bottle to eliminate bubble formation. The bottle and cap were rinsed once with water from the OTE bottle before overflowing the sample bottle by at least 1 bottle volume before withdrawing the silicone tube carefully avoiding bubble formation. The stopper was ten placed in the bottle and then removed so that 2.5 mL of sample could be removed (to allow for thermal expansion) and 50 mL of 100% $HgCl_2$ added to halt any biological activity. The stoppers and the inside of the neck of the bottles were then wiped with tissue to remove any moisture before the stopper – now greased with vacuum grease around the top – is replaced and fixed in place with a foam insert and plastic cover. The samples were then shaken to disperse the $HgCl_2$.

Samples were stored cold (4^oC) and returned to the UK on the *RRS James Cook* at this temperature

Samples collected

Collected samples are summarised in the Pa/Th section of this report, and detailed on the CTD Scan Sheets

Sample analysis

Samples will be measured using a Thermo MAT253 stable isotope mass spectrometer at Cambridge University, equipped with a suitable gas bench.

OXYGEN ISOTOPES

By Gideon Henderson

Water $\delta^{18}O$ samples to be analysed at University of Oxford (contact Gideon Henderson).

Dissolved oxygen $\Delta^{17}O$ to be analysed by Boaz Luz, The Fredy and Nadine Herrmann Institute of Earth Sciences, The Hebrew University of Jerusalem, Jerusalem 91904, Israel, tel. 972-2-6585224; fax. 972-2-5662581, boaz.luz@huji.ac.il

Objectives

Water $\delta^{18}O$: Near-shore, where riverine and submarine groundwater discharge is expected, these freshwater inputs will have distinctive $\delta^{18}O$ values that can potentially be used as a tracer of specific water input to near-surface waters. These values are also more generally useful in understanding and modelling the cycle of oxygen isotopes in the ocean/atmosphere system. In addition, oxygen isotopes of waters will be used for paleoproxy calibration to provide information about the $\delta^{18}O$ profile at the specific site where sediment components (e.g. forams, coccoliths) formed.

Dissolved O_2: $\Delta^{17}O$: Is used in general to provide information about ocean productivity (Luz et al. 1999; Luz and Barkan 2000). Recent work in the tropical Atlantic demonstrates very high $\Delta^{17}O$ values at depths as great as 300 m. This is significantly a greater depth than photosynthesis would be expected, and suggests the transport of a high $\Delta^{17}O$ signal by diapycnal mixing from above, or isopycnal transport. Samples from 40oS will allow the possibility of a high $\Delta^{17}O$ signal being advected in AIW to the tropics, as well as providing more general information about the variability of this relatively new tracer in the ocean.

Sampling protocol

Water $\delta^{18}O$: 10 ml glass vials were filled directly from the OTE bottles with minimal/no air bubble and capped tightly. No filtering or acidification. Vials were sealed with Parafilm, boxed, and stored at $4^{o}C$ on the ship.

Dissolved O_2 $\Delta^{17}O$: Seawater samples were taken with a piece of Tygon tubing and a plastic cone directly into evacuated glass flasks provided by Boaz Luz, following the protocol provided. Flasks were half filled with sea water. Duplicates were taken for all samples. Where two OTE bottle was fired at the same depth, one sample was taken from each OTE. When only one OTE bottle was fired, two samples were taken in succession from that bottle. $\Delta^{17}O$ samples were either the first to be taken from the OTE, or the second, following directly after [3]He sampling (see relevant log sheets for flask by flask details).

Samples collected

Water $\delta^{18}O$: The main stainless cast was sampled at all stations and all depths to give to provide 332 water samples.
A complete list of samples is as follows:

1001, 1003, 1005, 1009, 1011, 1013, 1015, 1018, 1020, 1022, 1049, 1051, 1053, 1055, 1057, 1059, 1061, 1063, 1066, 1068, 1070, 1097, 1099, 1100, 1102, 1104, 1110, 1111, 1112, 1114, 1115, 1116, 1117, 1118, 1119, 1120, 1145, 1147, 1148, 1150, 1152, 1154, 1157, 1159, 1161, 1162, 1164, 1166, 1169, 1171, 1173, 1175, 1177, 1179, 1181, 1183, 1185, 1187, 1189, 1191, 1193, 1195, 1199, 1201, 1203, 1206, 1207, 1211, 1213, 1215, 1217, 1219, 1222, 1223, 1225, 1226, 1227, 1228, 1229, 1230, 1231, 1233, 1234, 1236, 1237, 1238, 1239, 1313, 1315, 1317, 1319, 1321, 1323, 1324, 1326, 1327,

1328, 1330, 1332, 1333, 1334, 1335, 1336, 1425, 1426, 1428, 1437, 1438, 1440, 1441, 1442, 1443, 1446, 1447, 1450, 1454, 1456, 1459, 1462, 1465, 1468, 1472, 1475, 1476, 1479, 1481, 1483, 1485, 1486, 1487, 1489, 1490, 1491, 1492, 1493, 1494, 1561, 1563, 1565, 1566, 1567, 1569, 1570, 1572, 1573, 1575, 1576, 1577, 1578, 1579, 1580, 1581, 1582, 1583, 1584, 1635, 1637, 1639, 1640, 1641, 1643, 1644, 1645, 1647, 1648, 1649, 1650, 1651, 1652, 1653, 1654, 1655, 1656, 1657, 1658, 1755, 1757, 1759, 1760, 1761, 1762, 1763, 1764, 1765, 1766, 1767, 1769, 1770, 1772, 1773, 1774, 1775, 1776, 1777, 1778, 1827, 1829, 1830, 1832, 1833, 1834, 1835, 1836, 1837, 1838, 1839, 1840, 1841, 1842, 1843, 1844, 1845, 1846, 1847, 1848, 1849, 1850, 1901, 1904, 1905, 1908, 1909, 1910, 1913, 1914, 1917, 1918, 1921, 1975, 1977, 1979, 1980, 1982, 1983, 1985, 1986, 1987, 1988, 1990, 1991, 1992, 1993, 1994, 1995, 1996, 1997, 1998, 2023, 2025, 2026, 2028, 2029, 2031, 2032, 2034, 2035, 2037, 2038, 2039, 2040, 2041, 2042, 2043, 2044, 2045, 2046, 2119, 2120, 2121, 2122, 2123, 2124, 2125, 2127, 2128, 2129, 2130, 2131, 2132, 2133, 2134, 2135, 2136, 2137, 2138, 2139, 2140, 2141, 2239, 2241, 2242, 2243, 2244, 2246, 2247, 2248, 2249, 2250, 2252, 2253, 2255, 2256, 2257, 2258, 2259, 2260, 2261, 2262, 2335, 2337, 2338, 2339, 2340, 2341, 2342, 2343, 2347, 2348, 2349, 2350, 2351, 2352, 2354, 2355, 2357, 2383, 2389, 2391, 2393, 2395, 2401, 2403

Dissolved O_2 $\Delta^{17}O$: 24 samples were taken in duplicate (i.e. 48 flasks) at Station 17 in the deep Argentine Basin. Samples spanned the full water column.

Sample analysis

No shipboard analysis of oxygen isotopes was performed.

Water $\delta^{18}O$ will be measured at Oxford using a Thermo Gas Bench connected to a Thermo Delta V mass spectrometer.

$\Delta^{17}O$ will be measured at The Hebrew University of Jerusalem following published protocols (e.g. Luz et al. 1999).

References:
Luz, B., Barkan, E., Bender, M. L., Thiemens, M. H., and Boering, K. A., 1999. Triple isotope composition of atmospheric oxygen as a tracer of biosphere productivity. *Nature* **400**, 547-550.
Luz, B. and Barkan, E., 2000. Assessment of Oceanic Productivity with the Triple-Isotope Composiiton of Dissolved Oxygen. *Science* **288**.

ARSENIC AND ANTIMONY

By Gideon Henderson

Water As/Sb samples to be analysed at the University of Liverpool, School of Environmental Sciences, 4 Brownlow Street, L69 3GP. Contact Pascal Salaun (pascal.salaun@liverpool) or Dominik Weiss (d.weiss@imperial.ac.uk).

Objectives

Surface samples are requested from ~ 18 stations (fish samples) evenly distributed along the cruise and in close proximity of visited stations. Duplicate samples from 5 locations for intercalibration with one other laboratory (TBD) are also requested. All these samples should be unfiltered. At 5 of the 18 stations, filtered samples (0.2 or 0.45 µm) should also be collected. All water for these sampling should be collected in 0.5 l bottles.

Five depth profiles with 6 sampling depth are requested from the following locations along the 40S transect: one on each continental margin (e.g., in the E and the W), one from each deep basin (e.g., in the E and the W) and one close to the mid Atlantic ridge (e.g., vicinity of potential hydrothermal activity). The actual sampling depth should be spread for each profile to capture the main hydrographic features and water masses. As a rough guide we would go for the following depths: 10m, 100m, 300m, 2000m, 3000m and one close to the bottom. These samples should be unfiltered and collected in 0.25 l bottles for 4 depth profiles. The 5th profile should be collected in 0.5 l bottles.

Sampling protocol

LDPE bottles have been acid cleaned and rinsed at Liverpool and are provided individually triple bagged. The box contains 0.5l and 0.25l bottles. 0.25 l bottles should be used for 4 depth profiles (6 depths, 24 bottles) while 0.5 l bottles for fish samples (18 stations, 5 duplicates, 5 filtered) and for 1 depth profile (6 depths). The bottles should be filled with seawater if possible in a clean environment after rinsing the bottle three times before filling them up. Either rosette (SS or Ti) can be used.

Samples collected

A complete list of samples is as follows:

1097, 1099, 1104, 1110, 1112, 1115, 1117, 1119, 1472, 1477, 1480, 1483, 1486, 1489, 1492, 1494, 1976, 1977, 1978, 1981, 1984, 1986, 1989, 1991, 1993, 1996, 1998, 2239, 2242, 2243, 2246, 2249, 2252, 2256, 2257, 2259, 2262

Sample analysis

No shipboard analyses of As or Sb concentrations were performed. All the samples will be processed for As and Sb concentrations in laboratories at Liverpool. The samples will be processed using previously developed methods given in the references below.

References

P. Salaun, K. Gibbon-Walsh, C. M. G. van den Berg, Beyond the Hydrogen Wave: New Frontier in the Detection of Trace Elements by Stripping Voltammetry. *Anal. Chem.* 2011, *83*. 3848-3856, DOI: 10.1021/ac200314q

SULPHUR ISOTOPES

By Gideon Henderson

Water sulphate isotopes to be analysed at Harvard University, 20 Oxford Street, Cambridge, MA 02138, USA (contact David Johnston, Johnston@eps.havard.edu, phone 00 11 617 496 5024).

Objectives

Samples are requested from all depths at three stations, plus an additional mixed layer samples from 10 stations. For the mixed layer samples we would prefer one sample from the surface, one from near the chlorophyll max and a third from near the base of the mixed layer. Assuming 24 depths for a full profile, this represents a sample set of up to 102 samples. In addition, we request a riverine sample from (near) the Rio de la Plata.

Sampling protocol

15 mL Nalgene LDPE in bags of 24 or three are provided and in boxes of about 100 bottles. Two 500 mL Nalgene LDPE bottles are provided for river water sampling, which requires higher sampling volume. Bottles have not been pre-cleaned because sulfate contamination risk is minimal. These bottles should be filled with water from either the stainless or Ti rosettes, filtered through 0.4 micron capsule Acropak filters as samples leave the OTE bottles. No further filtration or other treatment of samples is required following the Acropak filter. Samples can be stored at any temperature.

Samples collected

A total of 46 samples were collected. A complete list of samples is as follows:

1492, 1493, 1494, 1656, 1657, 1658, 1720, 1722, 1724, 1726, 1730, 1943, 1945, 1949, 2023, 2025, 2026, 2028, 2029, 2031, 2032, 2034, 2035, 2037, 2038, 2039, 2040, 2041, 2042, 2043, 2044, 2045, 2046, 2138, 2139, 2239, 2241, 2243, 2246, 2248, 2249, 2254, 2256, 2257, 2259, 2262

Sample analysis

Sulfate will be precipitated from the samples as $BaSO_4$ through the addition of a $BaCl_2$ solution to each sample. The resulting $BaSO_4$ will be converted to H_2S on a distillation line via reduction with a HI-HCl-H_2PO_4 solution and subsequently precipitated as ZnS (Thode et al. 1961, Forrest and Newman, 1977). The ZnS will be later converted to Ag_2S through the addition of $AgNO_3$ solution to the ZnS.

The Ag_2S will then be fluorinated with excess F_2 at 200°C and will be subsequently purified cryogenically and chromatograhically in a specialized gas line (Johnston et al 2005, 2006, 2007). Sulfur isotope measurements (^{32}S, ^{33}S, ^{34}S, ^{36}S) of the clean SF_6 gas will be done on a Thermo Mat 253 Gas Source Mass Spectrometer.

Measurements of the rare S isotopes (^{33}S,^{36}S) are highly specialized and only performed by a handful of labs, mostly for geological and microbial studies. Therefore, there are currently no intercalibration plans. However, we seek out opportunities for intercalibration, using available seawater samples from previous intercalibration cruises.

References:
    Forrest, J., and Newman, L., 1977. Ag-110 microgram sulfate analysis for short time resolution of ambient levels of sulfur aerosol: Analytical Chemistry, v. 49, p. 1579 –1584.

Johnston, D.T., Farquhar, J., Canfield, D.E., 2007. Sulfur isotope insights into microbial sulfate reduction: When microbes meet models. Geochimica Cosmochimica Acta 71, 3929–3947.

Johnston, D.T., Poulton, S.W., Fralick, P.W., Wing, B.A., Canfield, D.E., Farquhar, J., Evolution of the oceanic sulfur cycle at the end of the Paleoproterozoic. Geochimica Cosmochimica Acta 70, 5723–5739.

Johnston, D.T., Farquhar, J., Wing, B., Kaufman, A.J., 2005. Multiple sulfur isotope fractionations in biological systems: A case study with sulfate reducers and sulfur disproportionators. American Journal of Science 305, p. 645– 660.

Thode H. G., Monster J. and Dunford H. B., 1961. Sulphur isotope geochemistry. Geochimica Cosmochimica Acta 25, 159–174.

Vessel Mounted ADCP Instruments

By Alex Forryan

Instrument setup and performance

The two vessel-mounted Acoustic Doppler Current Profilers (ADCPs) onboard RRS James Cook were used throughout the cruise to estimate the horizontal velocity field. These instruments, installed on the port drop keel of the ship, are 75 kHz and 150 kHz Ocean Surveyor (OS) instruments supplied by Teledyne RD Instruments, Poway, California. The different frequencies of the two instruments affect both their depth range and resolution. The 150 kHz allows smaller depth bins and consequently higher vertical resolution, but the signal is more rapidly attenuated and typically only penetrates to ~500 m. The 75 kHz lacks such good vertical resolution but penetrates to ~1000 m.

During JC068, both instruments were run in narrowband single-ping mode. Where depth permitted, both instruments were run in bottom track mode to obtain the most accurate phase and amplitude calibrations. Typically, the instruments were switched between bottom tracking and water tracking close to 1000 m.

The instruments can be operated with the keel either retracted or lowered (hereafter known as 'keel up' and 'keel down' respectively). The keel up position allows greater ship speed, as the vessel is limited to 10 knots with the keel down, but also exposes the instrument to more bubbles, which significantly reduces its profiling range. The instruments were run keel up throughout the cruise.

Fixed calibration

As outlined in the JC029 cruise report, it is known that the OS75 instrument is roughly 9° out of alignment. Consequently, the EA00900 command setting, which sets a rotation angle of 9 degrees, was used in the control file to enable real time monitoring of the currents and for internal VmDas processing.

The best calibration estimates are obtained when the velocity data is collected using the seabed as a reference. However, bottom track calibration estimates are only obtainable when the water depth is within the ADCP profiling range. A table of the bottom tracking calibrations was created (see below) to calculate mean phase and amplitude calibration parameters of the instruments, which were then used as the rotation values in the *q_py.cnt* control file (see below).

ENX file number	phase (median)	amplitude (median)	number of points
10	-0.2666	1.0037	209
11	-0.2542	1.0040	141
12	-0.2463	1.0037	51

Table 18 bottom track calibration data for the OS75 instrument.

ENX file number	phase (median)	amplitude (median)	number of points
10	**-0.6643**	**1.0065**	192
11	**-0.6471**	**1.0047**	99
12	**-0.7066**	**1.0048**	47

Table 19 bottom track calibration data for the OS150 instrument.

The calibrations chosen were as follows for the OS75 rotation angle = -0.25 and amplitude = 1.004, which when combined with the rotation angle set in the control file gives a net rotation angle of 8.75, and for the OS150 rotation angle = -0.68 and amplitude = 1.005.

Performance

A not unexepected consequence of running keel up was that the data quality for both instruments was uniformly poor while underway with wind speeds in excess of a couple of knots. Unfortunately these conditions prevailed for most of the cruise. However, reasonable data quality was achieved while on station and initially after leaving Port Elizabeth (Figures 40 and 41).
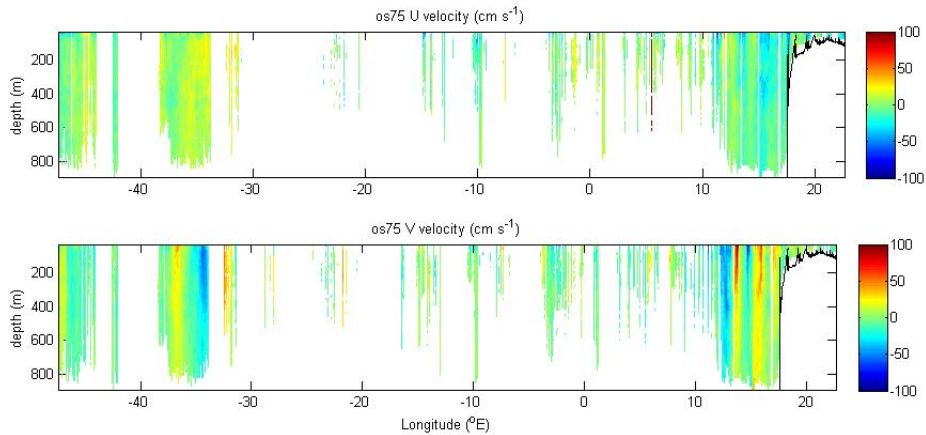
Figure 40 os75 VMADCP velocities from 24th Dec. to 26th Jan. The black line indicates water depth.
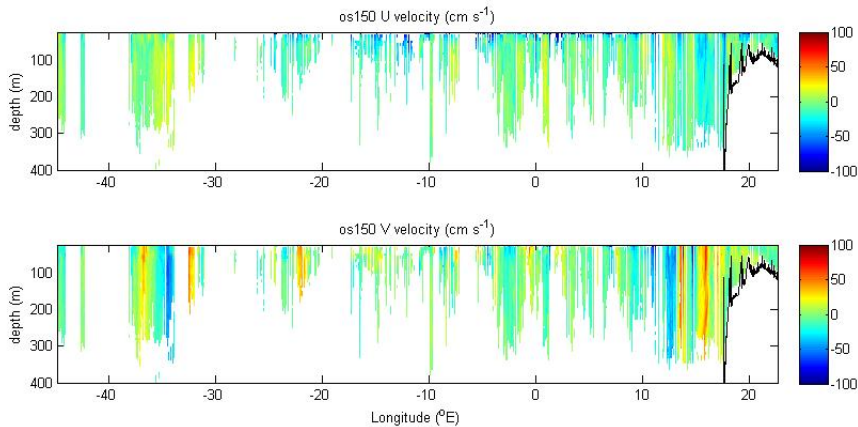
Figure 41 os150 VMADCP velocities from 24th Dec. to 26th Jan. The black line indicates water depth.

Real Time Data Acquisition

The data from the two instruments were acquired using the RD Instruments VmDas software package. This software is installed on two PCs in the main laboratory, which control the 75kHz and 150kHz Ocean Surveyor instruments respectively. The software allows data acquisition in a number of configurable formats and performs preliminary screening and transformation of the data from beam to Earth coordinates.

Files Produced by VmDas

The files we produced have names of the form *os<inst>_jc068<nnn>_<filenumber>. <ext>*, where *<inst>* is the instrument name (75 or 150), *<nnn>* is the file sequence number, *<filenumber>* is the number of the file in the sequence and *<ext>* is the extension.

The list of files produced is given below:
.ENR files are the binary raw data files.
.ENS files are binary ADCP data after being screened for RSSI and correlation and with navigation data included.
.ENX files are ADCP single ping data and navigation data after having been bin-mapped, transformed to Earth coordinates and screened for error velocity and false targets.
.STA files are binary files of short-term average ADCP data
.LTA files are binary files of long-term average ADCP
.N1R files are ASCII text files of raw NMEA navigation data from the NMEA1 stream.
.N2R files are ASCII text files of raw NMEA navigation data from the NMEA2 stream.
.NMS files are binary files of navigation data after screening.
.VMO files are ASCII text files specifying the option settings used for the data collection.
.LOG files are ASCII text files logging all output and error messages.

These files were stored in the following directories:
/vmadcp/jc068_os150   (for 150kHz transducer data)
/vmadcp/jc068_os75   (for 75kHz transducer data)
Post-Processing
The final processing of the data was done using the CODAS (Common Ocean Data Access System) software provided by the University of Hawaii. This suite of Unix and Matlab programs allows manual inspection and editing of bad profiles and provides best estimates of the required rotation of the data, either from water profiling or bottom tracking. The processing was done following the methodology applied on D346.

Setting Up the Directories and loading the data

1. *vmadcp_movescript2* was typed in the Unix command window. This creates a new directory called *rawdata<nnn>* (*nnn* denoting the file sequence) and moves the relevant data to this new location.

2. The command *adcptree.py jc068<nnn>nbenx --datatype enx* was typed at the command window. This command sets up a directory tree for the CODAS dataset and an extensive collection of configuration files, text files and m files.

3. Then the command '*quick_adcp.py --cntfile q_py.cnt*' was used to load the data into the directory tree, perform routine editing and processing and make estimates of both water track and (if available) bottom track calibrations. The raw ping files are also averaged into 5-minute periods. The calibration values are stored in the *adcpcal.out* and *btcaluv.out* files found in the *cal/watertrk* and *cal/botmtrk* directory respectively and are appended each time *quick_adcp.py* is run.

Manual editing
The data were then checked in Gautoedit. The Gautoedit package within CODAS allows the user to review closely the data collected by VmDas and flag any data that is deemed to be bad. These flags can then be passed forward and, using the Unix command "*quick_adcp.py –cntfile q_pyedit.cnt*", the discarded data was removed.

Creating the Output Files
Once the editing and rotations were completed, the final velocities were collated into Mstar files (*.nc) using the Matlab *mcod_01* and *mcod_02*.

The output files produced (*os75_jc068<nnn>nnx.nc)* include the following variables:

time - (in seconds since [2010 1 1 0 0 0])

lon - (0 to 360)
lat - (-90 to 90)
depth - (of bin)
uabs - (absolute *u* velocity in cm/s)
vabs - (absolute *v* velocity in cm/s)
uship - (*u* velocity of ship over ground)
vship - (*v* velocity of ship over ground)
decday - (decimal day of year)

The second file is of the form *os75_jc068<nnn>nnx_spd.nc* and includes, (in addition to the above variables):

speed - (scalar water speed in cm/s)
shipspd - (scalar ship speed over ground in cm/s).

The individual *os75_jc068<nnn>nnx_spd.nc* and *os150_jc068<nnn>nnx_spd.nc* files were then appended together into a single output file for the cruise using a script called *mcod_mapend*. The final output files are *os75_jc068nnx_01.nc* and *os150_jc068nnx_01.nc* which contain appended on-station and underway data.

The files *os75_jc068nnx_01.nc* and *os150_jc068nnx_01.nc* contain the VMADCP data for the whole cruise.

LOWERED ACOUSTIC DOPPLER CURRENT PROFILER (LADCP)

By Alex. Forryan

Instruments Setup and Performance
One RDI 300kHz Workhorse LADCP unit was fitted to each CTD frame used on cruise JC068 in a downward-looking orientation. However, only the unit on the steel frame functioned for the whole cruise. The downward-looking LADCP unit on the titanium frame was fitted for cast 22, diagnosed as being faulty, and removed after CTD cast 41. An upward-looking 300kHz RDI Workhorse was briefly fitted to the steel frame for CTD casts 37 and 39 before also being diagnosed as faulty and removed. All LADCP were configured to have a standard 16 x 10 m bins, one water track and one bottom track ping in a one second ensemble and a 5 m blank at the surface. Data were collected in earth coordinates.

Table 19 summarizes the LADCP configurations for each cast, the level of processing achieved and notes about the quality of the results. It indicates whereas the bottom was tracked by the downward-looking LADCP, which provides independent and more accurate measurements of the current on the bottom 160 m. Bottom tracking is not achieved on the biological casts since the package is only lowered down the top 400 meters.

Date	Time (UTC)	Cast no.	Press (dbar)	Lat. (°N)	Lon. (°E)	Notes
28-Dec-11	16:28	3	401	-35.4684	14.9962	Steel Frame
29-Dec-11	05:38	5	4997	-36.3415	13.1098	Steel Frame
29-Dec-11	22:48	7	401	-36.3431	13.1062	Steel Frame
30-Dec-11	18:19	8	401	-38.4006	10.4016	Time errors synchronizing with CTD cast.
01-Jan-12	06:45	9	403	-39.9997	5.5177	Steel Frame
03-Jan-12	12:55	10	3039	-40.0148	-0.4999	Steel Frame
06-Jan-12	11:13	12	401	-39.9993	-9.6664	Steel Frame
06-Jan-12	20:43	14	3421	-40.0003	-9.6626	Steel Frame
07-Jan-12	03:15	15	1009	-40.2573	-9.8531	Steel Frame
08-Jan-12	10:46	17	403	-39.9983	-13.0001	Steel Frame LDEO unable to read nav. Data used vmadcp to constrain surface currents.
08-Jan-12	17:47	19	3209	-40	-13.0001	Steel Frame
09-Jan-12	01:14	20	2223	-40	-12.9999	Steel Frame
09-Jan-12	20:26	21	3155	-40.0007	-16.4661	Steel Frame
10-Jan-12	08:22	22	3089	-40.0022	-16.4634	Titanium Frame beam 2 suspect.
10-Jan-12	11:37	23	399	-40.0017	-16.4651	Steel Frame
10-Jan-12	21:36	24	405	-40	-16.4667	Titanium Frame beam 2 suspect
11-Jan-12	19:22	25	3855	-39.9993	-19.9324	Steel Frame
12-Jan-12	00:17	26	3807	-40.0004	-19.9302	Titanium Frame beam 2 suspect
12-Jan-12	05:17	27	1515	-40.0004	-19.9303	Steel Frame
12-Jan-12	23:52	28	4227	-40.0001	-23.8001	Steel Frame

13-Jan-12	04:47	29	4211	-40	-23.8	Titanium Frame beam 2 suspect. Processed using 3 beams only
13-Jan-12	08:55	30	403	-40	-23.8	Steel Frame
14-Jan-12	09:15	31	403	-40	-28	Steel Frame
14-Jan-12	10:45	32	4283	-40	-28	Titanium frame beam 2 suspect Processed using 3 beams only
14-Jan-12	15:13	33	4281	-40	-28	Steel Frame
15-Jan-12	15:19	34	403	-39.9986	-32.4986	Steel Frame
15-Jan-12	22:53	36	4943	-39.9941	-32.4927	Steel Frame
16-Jan-12	22:10	37	1005	-40	-37.4167	Steel Frame Uplooker fitted – data file corrupt
17-Jan-12	06:00	39	5207	-40	-37.4166	Steel Frame Uplooker – beam 4 broken
18-Jan-12	17:51	43	403	-40.0012	-42.4158	Steel Frame
19-Jan-12	05:12	45	5229	-40	-42.4167	Steel Frame
21-Jan-12	00:14	47	5347	-39.9939	-47.4167	Steel Frame
21-Jan-12	10:47	49	403	-39.9857	-47.4168	Steel Frame
22-Jan-12	08:35	50	401	-37.9828	-51.0294	Steel Frame
22-Jan-12	11:10	51	4889	-38.0123	-50.9952	Steel Frame
22-Jan-12	20:58	53	4901	-38.0464	-50.9776	Steel Frame
23-Jan-12	01:53	54	595	-38.0864	-50.9812	Steel Frame
23-Jan-12	03:30	55	4915	-38.1092	-50.9766	Steel Frame
24-Jan-12	09:39	56	3379	-37.0256	-52.5025	Steel Frame
25-Jan-12	01:07	59	593	-37.0132	-52.4994	Steel Frame
25-Jan-12	11:44	61	1535	-36.5385	-53.1018	Steel Frame

Table 20 Summary of JC068 LADCP deployments

Issues and Fault Diagnosis

Comparing the absolute velocity estimates from the LADCP unit on the titanium frame to those from the unit on the steel frame for casts from the same station suggested that the titanium LADCP was potentially malfunctioning.

RDI diagnostics indicated that, though all four beams had an acceptable target strength, beam two (bm two below) was showing an unusually high correlation magnitude.

```
Correlation Magnitude: Narrow Bandwidth

               Lag   Bm1   Bm2   Bm3   Bm4
                 0   255   255   255   255
                 1   156   195   170   166
                 2    49   180    86    69
                 3    33   196    39    37
                 4    40   197    19    48
                 5    46   192    14    48
                 6    52   193    14    49
                 7    52   195    13    50


   High Gain RSSI:    70    82    71    74
    Low Gain RSSI:    17    16    18    18

   SIN Duty Cycle:    49    50    51    51
```

```
   COS Duty Cycle:      50    51    50    50

Receive Test Results = $02000000 ... FAIL
```

The abnormally high correlation can be seen in the LDEO diagnostics figure shown below (Figure 42).
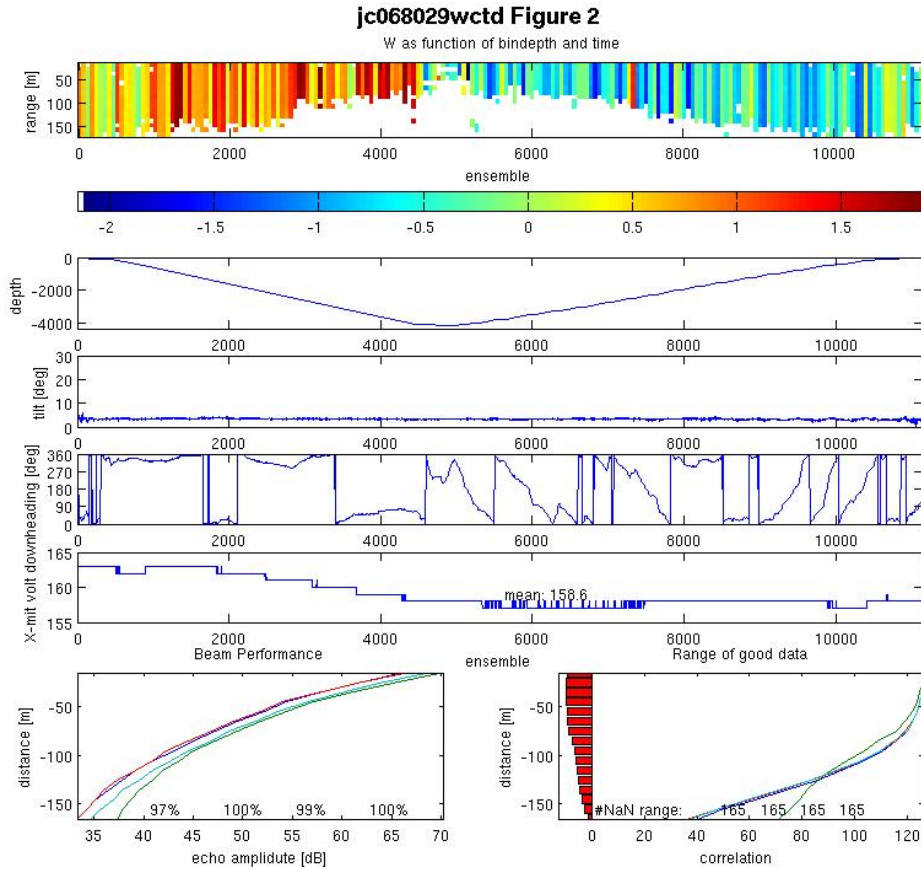
Figure 42 Diagnostics from LDEO processing software. Beam correlation is shown in the bottom right hand panel.

This diagnosis was confirmed by collecting the LADCP data from the titanium unit in beam coordinates then processing without beam two (beam coordinates were selected in the LADCP command file by changing parameter EX11111 to EX00111).

With beam two removed the absolute velocities from the titanium LADCP were in much better agreement with those from the steel LADCP unit (40).
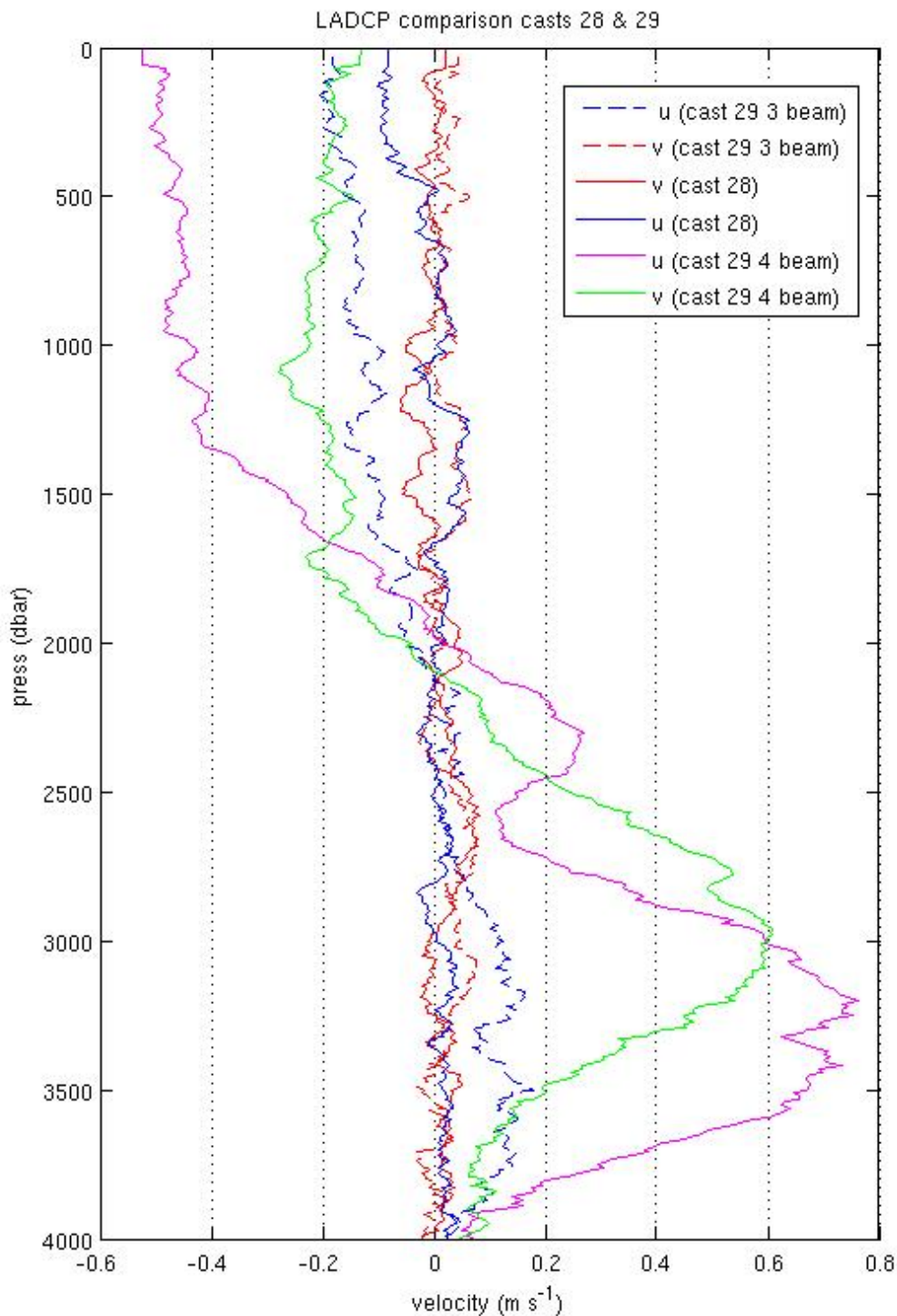
Figure 40 Comparison of LADCP velocities from the steel frame unit (cast 28) with those calculated from the titanium frame unit (cast 29) using all four beams and with beam two excluded.

Data Processing
The data collected by the instrument were downloaded after each cast and stored as RDI binary files and corresponding text files.
The data were then processed using two different tools. Primarily a software package from the University of Hawaii (UH) was used to calculate absolute current velocities using the shear. This also provides information about the heading and tilt of the CTD package. The second piece of software originates from Lamont-Doherty Earth Observatory (LDEO). It calculates velocities using

an inverse method and was also used for obtaining bottom track profiles and to monitor the beams of the instrument. The sequence of the routine processing for the LADCP data is outlined below.

UH Processing

The initial stages of processing allow the user to examine the quality of the data and to calculate relative velocity profiles in the absence of CTD data.

After navigating to the directory ~/cruise/data/ladcp/uh, *source LADall* sets up the paths required for the processing. The raw files downloaded from the LADCP units were copied from the network and symbolic links were created to the required filenames. The software requires a filename of *jnnn_02.000*, where *nnn* is the station number. The suffix 02 refers to the LADCP being downward-looking.

The processing steps were then as follows :

cd proc; perl –S scan.prl nnn_02 : to scan the raw data and create a station specific directory in the proc/casts directory. Data printed to screen should be checked to ensure the details of the cast (i.e. depth, downcast/upcast times) agree approximately with the CTD logsheet.

matlab; m_setup; putpos(nnn,02) gets position of the cast by accessing the TECHSAS data streams; *magvarsm(nnn.02)* applies the magnetic correction to the compass on the LADCP.

perl –S load.prl nnn_02 loads the raw data, applying magnetic compass corrections from *magvar.tab* to start processing. It is very important that this step is only carried out once. If it needs to be repeated the database files (~/proc/casts/dnnn_02/scdb) must be deleted first.

perl –S domerge.prl –c0 nnn_02 to merge the velocity shear profiles from individual pings into full upcast and downcast profiles. The option –c0 refers to the fact that CTD data has not yet been included.

cd Rnav; matlab; make_sm makes a smoothed navigation file for the cast.

cd proc; matlab; plist = nnn.02; do_abs; calculates the relative velocity profiles. Check that these plots look sensible, i.e. reasonable agreement between downcast and upcast and that the vertical velocity changes sign between downcast and upcast (it may be necessary to rescale some of the plots).

Once the CTD data has been processed this can be incorporated into the LADCP processing to make more accurate estimates of depth and sound velocity and to obtain a final absolute velocity profile.The inclusion of CTD data requires an ASCII file containing 1Hz CTD data for the station created in Matlab. If the CTD file is present:

cd proc; cd Rctd and open a Matlab session. Run *m_setup* and the script *mk_ctdfile(nnn).*

cd proc/Pctd; ctd_in(nnn,02) will read the 1Hz CTD data in. *plist=nnn.02; fd* aligns the LADCP and CTD data sets in time.

cd proc; perl –S add_ctd.prl nnn_02 adds the CTD data to the *.blk LADCP files in the scdb directory.

perl –S domerge.prl   -c1 nnn_02 merges the single pings into corrected shear profiles. The -c1 option now states that we have included CTD data.

matlab; plist=nnn.02; do_abs; calculates the velocities again with the merged pings.

The *do_abs* script was re-written to produce high resolution (5 m) output. The UH software calculates vertical shear on 5 m vertical grid but for some reason the original *do_abs* script output was sub-sampled into 20 m bins. The new *do_abs* script also writes out UH values for vertical shear along with absolute velocity, number of pings and variance on vertical shear estimate.

LDEO Processing

The latest version of the LDEO software was installed (ldeoIX) and configured to work within the Mstar environment. The format of the CTD data required is the same for both the LDEO and UH processing paths and when CTD data are available the processing will automatically use it. The LDEO processing also extracts the useful bottom track velocities. The *set_cast_params.m* script which sets up the parameters and file paths for the processing is given below. A additional script was also written (*make_sm_ldeoIX.m*) to extract navigation data from TECHSAS in the same way as the *make_sm* script mentioned above. This script writes an ASCII navigation file with the time field in LDEO Julian date format.

Mstar Formatting

The data from both processing routes were read into Mstar files. Three Mstar files were created for each station: one for the UH profile, one for the full LDEO profile and one for the LDEO bottom track velocities.

Matlab scripts

Make_sm_ldeoIX.m

```
function make_sm_ldeoIX

m_common

% put ldeoIX functions on path
addpath('/noc/users/pstar/cruise/data/ladcp/ldeoIX/matlab')

if strncmp(Mshipdatasystem,'scs',3)
    data = msload(Mscs_default_navstream);

    lonname = [Mscs_default_navstream '_lon'];
    lonname(strfind(lonname,'-')) = '_';
    latname = [Mscs_default_navstream '_lat'];
    latname(strfind(latname,'-')) = '_';
else % techsas
    data = mtload(Mtechsas_default_navstream);
    time = data.time + Mtechsas_torg;

    lonname = 'long'; latname = 'lat';
end

cmd = ['lon = data.' lonname ';']; eval(cmd);
cmd = ['lat = data.' latname ';']; eval(cmd);
nt = length(time);

% average into 1 minute intervals
% that's got to be accurate enough!
index = 1;
for i = 1:60:nt-60
    time1(index) = nanmean(time(i:i+60));
    lat1(index)  = nanmean(lat(i:i+60));
    lon1(index)  = nanmean(lon(i:i+60));
    time2(index) = julian(datevec(time1(index)));
    index = index + 1;
end

sm = [time2', lon1',lat1'];

% now write it all out
dlmwrite('sm_ldeoIX.asc',sm,'delimiter',' ','precision','%.6f');

end
```

Set_cast_params.m

```
% Simple matlab script to read in
% station time and position data in preparation for
% LDEO ladcp2 processing. Also sets paths to data.

% set cruise_str
cruise_str = 'jc068';

%temporary set for batch runs
run_letter = 'wctd'

% get station number and pad it
if(exist('stn') ~= 1)
```

```matlab
    stn = input('   Type station number: ');
end

% put zeroes in front of statnum
stnstr = sprintf('%03d',stn);

if (exist('first_time') ~=1)
    disp(' ')
    disp(['################## ' 'Processing ' cruise_str ... 'station ' stnstr
' ################']);
end

% get run letter
if(exist('run_letter') ~= 1)
  run_letter = input('Type run letter: ','s');
end

if (exist('first_time') ~=1)
    disp(' ')
    first_time = 1;
end

%%%%%%%% F Values
% paths to BB dataa
% downlooker
f.ladcpdo = ['./ladcp/jc068_',stnstr,'m.000'];
% uplooker
f.ladcpup = [''];
%f.ladcpup = ['./ladcp/jc068_',stnstr,'s.000'];

f.nav = './gps/sm_ldeoIX.asc';
%f.nav_time_base = 1; %yeardays
f.nav_time_base = 2; %Visbeck julian
f.nav_header_lines = 0;
f.nav_fields_per_line = 3;
f.nav_time_field = 1;
f.nav_lat_field = 3;
f.nav_lon_field = 2;

f.res = ['./' cruise_str stnstr '/' cruise_str stnstr run_letter ];

if exist([cruise_str stnstr],'file') ~= 7
    eval(['!mkdir ' cruise_str stnstr ])
end

% ctd time series file
f.ctd = ['./ctd/ctd.' stnstr '.02.asc'];

f.ctd_time_base = 0;%elapsed time
f.ctd_header_lines = 0;
f.ctd_fields_per_line = 4;
f.ctd_time_field = 1;
f.ctd_pressure_field = 2;
f.ctd_temperature_field = 3;
f.ctd_salinity_field = 4;

% checkpoints
f.checkpoints = ['./checkpoints/' cruise_str stnstr run_letter ];

% vmadcp data
% this is converted from MSTAR Combined VMADCP record
% vmadcp on jc is pretty much uniformly rubbish as the wetaher is bad
%f.sadcp = ['./vmadcp/os75_sadcp_jc068.mat'];
```

```matlab
%%%%% P parameters
p.name = [cruise_str stnstr run_letter ];
p.ladcp_cast = stn;
p.cruise_id = cruise_str;
p.whoami = 'A. Forryan';
%p.saveplot = [1:6 9:11 13:14];
p.ladcp_station = stn;

p.btrk_ts = 10;
p.sadcp_dtok = 0;

%p.edit_mask_dn_bins = [1];
%p.edit_mask_up_bins = [1];

% remove all bins > 5 (titanium frame)
%p.edit_mask_dn_bins = [1 32:1:64];
%p.edit_mask_up_bins = [1 32:1:64];

% set magnetic deviation
fname = [ 'postimes/postime' stnstr];
postime = load(fname);
autocat = 1;
intlat = postime(4);
intlon = postime(6);
p.drot = magdev(intlat,intlon);

%level of debugging
p.debug = 1;


% this doesnt do anything unless you're in beam coordinates
disp(' ');
% disp(['######## ATTENTION SET TO IGNORE BEAM 2 IF IN BEAM COORDINATES
#######']);
% disp(' ');
%p=setdefv(p,'ignore_beam',[2 2]);
%p=setdefv(p,'allow_3beam_solutions',1);

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% mostly copied from default.m
% how to get depth from W integration
% getdepth=1 use plain integral of W (mfile getdpth)
% getdepth=2 use inverse method to use bottom reflection
% and integral of W (mfile getdpthi) [default]
%       NB (IX_6): based on a single profile that I've processed,
%                  as well as on comments by Gerd & Martin,
%                  it may well be that getdepth=1 works better
%                  with shallow stations
p.getdepth = 2;

% navigation error in m
p.nav_error = 30;
% average navigation from nav file over a certain fraction of days p.navtime_av
= 2/60/24;

% p.avdz sets the depth interval between adjacent super-ensembles
% default one bin length
% p=setdefv(p,'avdz',medianan(abs(diff(d.izm(:,1)))));

% p.avens overrided p.avdz and sets a fixed number of ensembles to
% average
% default NAN not used
% NB (IX_6): When p.avens == 1,
% p.single ping accuracy has to be set!
```

```
% Otherwise, the software cannot determine the weight of the
% BT constraint.
%p=setdefv(p,'avens',NaN);

% BOTTOM TRACK
%       The are several options to get bottom track data
%
% mode = 1 :   use only RDI bottom track
%        2 :   use only own bottom track
%        3 :   use RDI, if existent, own else (default)
%        0 :   use not bottom track at all
p.btrk_mode = 3;

% p.btrk_ts is in dB to detect bottom above bin1 level
p.btrk_ts = 10;

% p.btrk_below gives binoffset used below target strength maximum
% to make bottom track velocity
p.btrk_below = 1;

% p.btrk_range gives minumum / maximum distance for bottom track
p.btrk_range = [300 50];

% p.btrk_wstd gives maximum accepted wstd for super ensemble
% averages
p.btrk_wstd = 0.1;

% maximum allowed difference between reference layer W and W
% bottom track
p.btrk_wlim = 0.05;

% force to recalculate bottom distance using target strenght
p=setdefv(p,'bottomdist',0);

% Write matlab file
p.savemat = 1;

% produce much more RAW data output
% set to 1 for more data
p.orig = 1;

% save individual target strength
p.ts_save=[1 2 3 4];
% p=setdefv(p,'ts_save',0);
% save individual correlation
p.cm_save=[1 2 3 4];
% p=setdefv(p,'cm_save',0);
% save individual percent good pings
p.pg_save=[1 2 3 4];
%p=setdefv(p,'pg_save',0);

%%%%%%%%%%%%%%%%%%%%%%
% Parameter for inversion   ps.* structure

% Process data using shear based method
% compute shear based solution
% ps.shear=2  ; use super ensemble
% ps.shear=1  ; use raw data
ps.shear=1;

% decide how to weight data
% 1 : use super ensemble std
% 0 : use correlation based field
ps.std_weight = 1;
```

```
% Weight for the barotropic constraint
%ps=setdefv(ps,'barofac',1);

% Weight for the bottom track constraint
%ps=setdefv(ps,'botfac',1);

% Process up and down cast seperately
%ps=setdefv(ps,'down_up',1);

% Depth resolution for final profile
%       default one bin length
%ps=setdefv(ps,'dz',medianan(abs(diff(di.izm(:,1)))));

% Smoothing of the final profile
%ps=setdefv(ps,'smoofac',0.01);

% comment this out to request that shears are small
% (experts only)
ps.smallfac = [1 0];

% weight bottom track data with distance of bottom
% use Gaussian with offset (btrk_weight_nblen(1) * bin)
% and width (btrk_weight_nblen(2) * bin)
% one might set this to [15 5] to reduce the weight of close
% by bottom track data
ps.btrk_weight_nblen = [0 0];

% Weight for SADCP data
% ps.sadcpfac=1 about equal weight for SDACP profile
ps.sadcpfac = 3;

% average over data within how many standart deviations
ps.shear_stdf = 2;

% the minimum weight a bin must have to be accepted for shear
%ps.shear_weightmin = 0.1;

% restrict inversion to one instrument only 1: up+dn, 2:dn only
% 3:up only
%ps=setdefv(ps,'up_dn_looker',1);

% super ensemble velocity error
% try to use the scatter in W to get an idea of the "noise"
% in the velocity measurement
% This is a bit of code used in GETINV.m
% nmax=min(length(di.izd),7);
% sw=stdnan(di.rw(di.izd(1:nmax),:)); ii=find(sw>0);
% sw=medianan(sw(ii))/tan(p.beamangle*pi/180);
%ps=setdefv(ps,'velerr',max([sw,0.02]));
%
%ps=setdefv(ps,'velerr',0.02);

% How to solve the inverse
%     ps.solve = 0  Cholseky transform
%              = 1  Moore Penrose Inverse give error for solution
%ps=setdefv(ps,'solve',1);

% Threshold for minimum weight, data with smaller weights
%       will be ignored
p.weightmin = 0.05;

% Change the weights by
%       weight=weight^ps.weightpower
```

```
%ps=setdefv(ps,'weightpower',1);

% Change remove 1% of outlier after solve
% ps.outlier times
ps.outlier = 1;

% set ps.down_up=1 if up/down cast should be solved seperately
%ps=setdefv(ps,'down_up',1);setdefv(ps,'weightpower',1);

% Weight for the cable drag constraint
% only for experts
%ps=setdefv(ps,'dragfac',0);
%ps=setdefv(ps,'drag_tilt_vel',15);
%ps=setdefv(ps,'drag_lagmax',15);
%ps=setdefv(ps,'drag_zmax',2000);

% Set fixed range for velocity plots
%ps=setdefv(ps,'urange',ur);
%ps=setdefv(ps,'zrange',ax(3:4));

% vertical resoltion (m)
ps.dz = 10;
% for compatability with hawaii method (need for ping data)
%ps.dz = 20;

%%%%%%%%%%
% Some params from Brian
%p.ladcp_station= 4;
%p.drot is now calculated later from position picked out of f.nav
%p.drot=magdev(p.poss(1)+p.poss(2)/60, p.poss(3)+p.poss(4)/60);
%p.btrk_mode = 2;
%Polarstern 23/7 set btrk = 2 and use cd171 version of
%loadrd i. This should select RDI bt vels and post-processed
%bt range

% precentage good threshold
% set to arbitrary value
%p.pglim=0;

%p.elim=0.2;
%p.wlim=0.08;
%p.avdz=ps.dz;
% BAK at SOC 27 Jan 2003; Should set ps.dz to be ladcp bin size.
%ps.dz=10;
%ps.down_up=1;
%ps.botfac = 0;
%ps.barofac = 1;
%ps.shear = 0;
%ps.dragfac = 0;

clear pk
```

do_abs_2.m
(For brevity only the code added to the original *do_abs* script is included)

```
for prof = plist,

    % update logfile
    [profname, station, cast, dbname, prof_dir, prof_integer] = profinfo(prof);

    lat_str = pos_str(prof_xy, prof, 1); % string: degrees N/S
    lon_str = pos_str(prof_xy, prof, 0); % string: degrees E/W
```

```matlab
    pxy = prof_xy(min(find( abs(prof_xy(:,1) - prof) < 1e-6)), [2 3]);
%position:[x y]

    the_title = [titlestr,profname,...
                ', (',lat_str,' ',lon_str,'), ' run_name]   %%%

    fprintf(FID_LOG, '%s\n', the_title);

    merge_dir = ([ dir_profbase,'/',prof_dir,'/merge'])%;
    if(flag_sm == 1)
      smdir = merge_dir;
    else
      smdir = sm_dir;
    end

    % For the current profile, load the up and down merge matlab
    % files, and the matlab smoothr output file, all from the
    % merge directory of the current *profile.

    ld_merge

    disp('files loaded')

    % integrate du/dz, dv/dz, dw/dz, and calculate abs u, v
    uvabs

    % now the hard work is done so its assemble the output time
    % first the original subsampled stuff
    % subsample.  We could use something fancier, like a block average, but we
    % would have to be careful with the masks.
    su_dn_i = real(uvcdn_abs(i_samp));
    sv_dn_i = imag(uvcdn_abs(i_samp));
    su_up_i = real(uvcup_abs(i_samp));
    sv_up_i = imag(uvcup_abs(i_samp));
    su_mn_i = real(uvcmn_abs(i_samp));
    sv_mn_i = imag(uvcmn_abs(i_samp));
    sw_dn_i = w_dn(i_samp)/100;  % back to m/s
    sw_up_i = w_up(i_samp)/100;
    sw_mn_i = w_mn(i_samp)/100;
    sm_dn_i = igm_dn(i_samp);
    sm_up_i = igm_up(i_samp);
    sm_mn_i = igm_mn(i_samp);
    sn_dn_i = ush_dn(i_samp, 2);
    sn_up_i = ush_up(i_samp, 2);
    sn_mn_i = ush_mn(i_samp, 2);
    su_var_dn_i = ush_dn(i_samp, 4);
    sv_var_dn_i = vsh_dn(i_samp, 4);
    sw_var_dn_i = wsh_dn(i_samp, 4);
    su_var_up_i = ush_up(i_samp, 4);
    sv_var_up_i = vsh_up(i_samp, 4);
    sw_var_up_i = wsh_up(i_samp, 4);
    su_var_mn_i = ush_mn(i_samp, 4);
    sv_var_mn_i = vsh_mn(i_samp, 4);
    sw_var_mn_i = wsh_mn(i_samp, 4);

    % bak mod at soc 10 oct 2000
    % asc_out is set in set_da.m. Call ascout.m
    if(asc_out == 1)
        ascout
    end

    save([dir_matprof_base,'/',run_name', '/', profname],...
      'd_samp',...
      'su dn i', 'su up i', 'sv dn i', 'sv up i', 'sw dn i', 'sw up i',...
```

```
       'sm_dn_i', 'sm_up_i', 'sn_dn_i', 'sn_up_i',...
       'su_var_dn_i', 'sv_var_dn_i', 'sw_var_dn_i', ...
       'su_var_up_i', 'sv_var_up_i', 'sw_var_up_i',...
       'su_mn_i', 'sv_mn_i', 'sw_mn_i', 'sm_mn_i', 'sn_mn_i', ...
       'su_var_mn_i', 'sv_var_mn_i', 'sw_var_mn_i', 'txy_start_end', 'pxy');

    % high resolution real deal stuff
    % sample depths (zero is at pos 9)
    d_samp = ush_dn(9:end, 1);
    % u,v and w velocity for up down and mean
    u_dn = real(uvcdn_abs(9:end));
    v_dn = imag(uvcdn_abs(9:end));
    u_up = real(uvcup_abs(9:end));
    v_up = imag(uvcup_abs(9:end));
    u_mn = real(uvcmn_abs(9:end));
    v_mn = imag(uvcmn_abs(9:end));
    w_dn = w_dn(9:end)/100;   % back to m/s
    w_up = w_up(9:end)/100;
    w_mn = w_mn(9:end)/100;
    % mask for the good bins (1 == good)
    smask_dn = igm_dn(9:end);
    smask_up = igm_up(9:end);
    smask_mn = igm_mn(9:end);
    % raw shear estimates of u v w for up down and mean
    shru_dn = ush_dn(9:end, 3);
    shrv_dn = vsh_dn(9:end, 3);
    shrw_dn = wsh_dn(9:end, 3);
    shru_up = ush_up(9:end, 3);
    shrv_up = vsh_up(9:end, 3);
    shrw_up = wsh_up(9:end, 3);
    shru_mn = ush_mn(9:end, 3);
    shrv_mn = vsh_mn(9:end, 3);
    shrw_mn = wsh_mn(9:end, 3);
    % number of estimates per bin
    np_dn_i = ush_dn(9:end, 2);
    np_up_i = ush_up(9:end, 2);
    np_mn_i = ush_mn(9:end, 2);
    % variances for each estimate
    shru_var_dn = ush_dn(9:end, 4);
    shrv_var_dn = vsh_dn(9:end, 4);
    shrw_var_dn = wsh_dn(9:end, 4);
    shru_var_up = ush_up(9:end, 4);
    shrv_var_up = vsh_up(9:end, 4);
    shrw_var_up = wsh_up(9:end, 4);
    shru_var_mn = ush_mn(9:end, 4);
    shrv_var_mn = vsh_mn(9:end, 4);
    shrw_var_mn = wsh_mn(9:end, 4);

    save([dir_matprof_base,'/',run_name', '/', profname,'_hires'],...
     'd_samp','txy_start_end', 'pxy',...
     'u_dn','v_dn','u_up','v_up','u_mn','v_mn','w_dn','w_up','w_mn',...
     'smask_dn','smask_up','smask_mn',...

'shru_dn','shrv_dn','shrw_dn','shru_up','shrv_up','shrw_up','shru_mn','shrv_mn',
'shrw_mn',...
     'np_dn_i','np_up_i','np_mn_i',...

'shru_var_dn','shrv_var_dn','shrw_var_dn','shru_var_up','shrv_var_up','shrw_var_
up','shru_var_mn','shrv_var_mn','shrw_var_mn'...
    );

    % plot a standard set of curves
    if plot_all ~= -1,
      close all
```

```
            pvel
        end

        fprintf(FID_LOG, '\n\n');

end
```

Appendices

A: Event Log
B: Computing and Ship Systems Report
C: NMF-SS Technical Report

Files containing the following are also available:
  Scanned CTD log sheets
  Scanned underway log sheets
  Core summary and photos
  Underway data
  Bottle file for CTD data
These can be downloaded from http://www.ukgeotraces.com/restricted
Or by contacting the PSO (gideonh@earth.ox.ac.uk)

APPENDIX A: EVENT LOG

Cruise JC068 Event Log

Event No.	Date	Station	Latitude	Longitude	Depth (m)	Time IN (GMT)	Time BOTTOM (GMT)	Time OUT (GMT)	Activity	Comments
001	26/12/2011	test	34° 56.89' S	19° 20.83' E	138m	07:15	07:27		Stanless Cast.	Test of stanless rosette.
002	26/12/2011	test	"	"	"	09:05		11:40	SAPS test	
003	26/12/2011	test	"	"	"				camera Ti Cast	Test of Ti rosette
004	26/12/2011	test	"	"	"				Ti Cast	" " " " other reason
005	28/12/2011	1	34° 36.74' S	17° 3.23' E	2595	01:32	01:52	02:40	CTD 001	400m
006	28/12/2011	1	34° 36.44 S	17° 3.13 E	2591	03:59	04:23	05:23	CTD 002	400m
007	28/12/2011	2	35° 28.104 S	14° 59.775 E	4689	16:26	16:52		CTD 003	400m
008	28/12/2011	2	35° 28.10 S	14° 59.7 RE	4684	18:01	18:17	19:10	CTD 004	4000m 5 bottle failures
009	29/12/2011	3	36° 20.166 S	13° 06.707 E	4896	05:37	07:07	09:15	CTD 005	Full depth 8 bottle leaves.
010	29/12/2011	3	36° 20.173 S	13° 06.52 E	4896	09:51	11:52		CTD 006	
011	29/12/2011	3	36° 20.2 S	13° 06.7 E	4890		21:32		SAPS #1	3 274m SAPS ; 1 Mn test
012	29/12/2011	3	36° 20.53 S	13° 06.44 E	4887	22:46	23:04	23:39	CTD 007	400m
013	30/12/2011	4	38° 23.94 S	10° 24.22 E	5135	18:16	18:31		CTD 008	400m
014	1/1/2012	5	40° 00.00 S	5° 30.0 E	5250	06:41	06:58		CTD 009	400m
015	3/1/2012	6½	40° 00.89 S	0° 29.99 W	4890	12:48	13:58	15:27	CTD 010	3000m.
016	4/1/2012	7	39° 59.59 S	3° 02.12 W	4450	06:35			CTD 011	
017	4/1/2012	7			4450				VMP 00	Tethered test of weight drop
018	4/1/2012	7	40° 00.20 S	3° 01.97' W	4463	09:58		11:17	VMP 01	1000m test deployment.
019	6/1/2012	8	39° 58.96 S	9° 39.65' W	3378	10:34			Glider 1	Glider deployment
020	6/1/2012	8	39° 59.97 S	9° 39.94 E	3405	11:13	11:27	11:59	CTD 012	400m
021	6/1/2012	8	39° 59.58 S	9° 40.00 W	3400	12:48	14:01		CTD 013	Full depth Ti cast
022	6/1/2012	8	39° 59.95 S	9° 40.08' W	3409	16:55		20:15	Megacore 1	4 cores full

Cruise JC068 Event Log

Event No.	Date	Station	Latitude	Longitude	Depth (m)	Time IN (GMT)	Time BOTTOM (GMT)	Time OUT (GMT)	Activity	Comments
025	7/1/2012	10	40° 16.87'S	9° 53.52'W	423 366	06:55	07:23		MegaCore #2	415m hit bottom; broken tubes
026	7/1/2012	9	40°15.27'S	9°51'7W	1618	08:38	09:08	09:45	CTD 016	Ti – 1500m only top 4 bottles fired
027	7/1/2012	8	40° 0.79'S	9° 37.62'W				13:10	Glider recovery	No small boat. Some damage to tail.
028	8/1/2012	11	39° 59.87'S	13° 00.06'W	3213	10:38	10:58	11:30	CTD 017	SS – failed CTD communication
029	8/1/2012	11	39° 59.98'S	12° 59.93'W	3183	11:40			VMP 02	
030	8/1/2012	11	40° 00.00'S	12° 59.97'W	3180	12:20	14:10		CTD 018	Ti
031	8/1/2012	11	39° 59.98'S	12° 59.95'W	3192	17:45	18:57	21:05	CTD 019	SS 13 bottles
032	8/1/2012	11	40° 00.00'S	13° 00.00'W	3190	22:40		00:36	MegaCore #3	
033	9/1/2012	11	40° 00.00'S	12° 59.99'W	3190	01:12	02:01	03:08	CTD 020	SS rerun of 031 (CTD019)
034	9/1/2012	12	40° 00.04'S	16° 27.97'W	3080	20:02			VMP 03	
035	9/1/2012	12	40° 00.04'S	16° 27.96'W	3080	20:24	21:38	23:34	CTD 021	SS full depth
036	10/1/2012	12	"	"	3080	00:45		07:10	SAPS #2	8 saps full depth; 2 failed
037	10/1/2012	12	40° 00.00'S	16° 27'49W	3096	08:15	09:35		CTD 022	Ti deep cast
038	10/1/2012	12	40° 00.10'S	16° 27.91'W	3093	11:35	11:53	12:28	CTD 023	400m shimble no leaks
039	10/1/2012	12	40° 00.00'S	16° 28.01'W	"	17:33			MegaCore #4	
040	10/1/2012	12	40° 00.00'S	16° 27.59'W	"	18:03			SAPS #3	4 SAPS – 400m; 1 failed.
041	10/1/2012	12	40° 00.00'S	16° 27.59'W	"	21:22		22:29	CTD 024	Ti shallow cast.
042	10/1/2012	12	40° 00.08'S	16° 28.47'W	"	22:37			ARGO #2	
043	11/1/2012	13	39° 59.96'S	19° 55.14'W	3783			broken	VMP 05	
044	11/1/2012	13	39° 59.96'S	19° 55.74'W	3783	19:21	20:47	23:00	CTD 025	SS full depth
045	12/1/2012	13	40° 00.01'S	19° 55.68'W	3788	00:15	01:47		CTD 026	Ti full depth – 9 leaked.
046	12/1/2012	13	40° 00.02'S	19° 55.81'W	3785	05:19	05:50	06:57	CTD 027	SS 1500m
047	12/1/2012	13	39° 59.81'S	19° 56.62'W		07:11			ARGO #3	
β 33.5	9/1/2012	11	39° 59.98'S	13° 00.32'W	3080	03:33			ARGO #1	
α 38.5	10/1/2012	12							VMP 04	

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Cruise JC068 Event Log

Event No.	Date	Station	Latitude	Longitude	Depth (m)	Time IN (GMT)	Time BOTTOM (GMT)	Time OUT (GMT)	Activity	Comments
048	12/1/2012	14	39° 59.97'S	023° 47.98'W	4162	23:33		24:44	VMP #6	
049	12/1/2012	14	40° 00.01'S	23° 48.00'W	4162	23:48	01:23	07:11	CTD 28	SS full depth
050	13/1/2012	14	45° 00.00'S	25° 48.00'W	4175	04:43	06:45	08:10	CTD 3829	Ti full depth
051	13/1/2012	14	40° 00.00'S	23° 47.99'W	4159	08:54	09:08	09:40	CTD 30	SS 400m
052	13/1/2012	14	39 59.91'S	23° 48.28'W	4168	09:54			Argo #4	
053	14/1/2012	15	40° 00.00'S	28° 00.00'W	4226	09:15	09:28		CTD 31	SS 400m
054	14/1/242	15				10:09		19:45	VMP #7	Stuck in mud for some hours
055	14/1/2012	15	40° 00.00'S	28° 00.00'W	4233	10:42	12:00	14:22	CTD 32	Ti full depth.
056	14/1/2012	15	40° 00.00'S	28° 00.00'W	4232	15:12	16:32	18:33	CTD 33	SS full depth
057	14/1/2012	15	39° 59.30'S	28° 0.29'W	4328	20:03			Argo #5	
058	15/1/2012	16	39° 39.92'S	32° 29.92'W	4791	15:14	15:28	16:08	CTD 34	SS 400m
059	15/1/2012	16				16:18			VMP #8	
060	15/1/2012	16	39° 59.98 S	32° 29.98 W	4876	16:52	18:23	20:40	CTD 35	Ti full depth
061	15/1/2012	16	39° 59.98'S	32 29.98'W	4841	22:51	00:28	02:27	CTD 36	SS full depth
062	16/1/2012	16	39° 59.47'S	32° 29.41'W	4866	02:36			Argo #6	
063	16/1/2012	17	40° 00.00S	37° 25.00W	5103	22:07	22:34	23:17	CTD 37	SS 1000m
064	16/1/2012	17							VMP #9	
065	17/1/2012	17	40° 00.00S	37° 24.99W	5570	00:05	01:39	04:10	CTD 38	Ti full depth only 4 bottles fired
066	17/1/2012	17	40° 00.00'S	37° 25.00'W	5125	05:57	07:36	09:49	CTD 39	SS full depth
067	17/1/2012	17	40° 00.00S	37° 25.00W	5098	10:16	11:48		CTD 40	Ti ≤ 1500m No closed bottles.
068	17/1/2012	17	40° 00.36'S	37° 24.88'W	5095	13:28			Argo #7	
069	17/1/2012	17	"	"	"	13:33			Argo #8	1st UK Argo
070	17/1/2012	17b	40° 00.8'S	38° 15.56W	5163	18.41	20:30	21:42	CTD 41	Ti full depth 3rd time lucky!
071	18/1/2012	18	39° 59.96'S	42° 27.77'W	5144	16:00		19:40 17/1/242	Glider 2	Glider – recovered with small boat

Cruise JC068 Event Log

Event No.	Date	Station	Latitude	Longitude	Depth (m)	Time IN (GMT)	Time BOTTOM (GMT)	Time OUT (GMT)	Activity	Comments
072	18/1/12	18	39° 59.96'S	42° 27.77'W	5145	16:41	16:49		CTD 042	Test dip after failure
073	18/1/12	18	40° 00.10'S	42° 24.93'W	5137	17:48	18:05	18:40	CTD 043	400m bio cast.
074	18/1/12	18	40° 00.65'S	42 85.07'W	5169 MB	18:55		23:58	VMP #10	
075	18/1/12	18	40° 00.00'S	42 25.00'W	5154	19:37		22:35	SAPS #4	Shallow depths
076	18/1/12	18	40° 00.00'S	42 25.00'W	5142	00:18	01:58		CTD 044	Full depth Ti cast
077	19/1/12	18	40° 00.09'S	42 25.07'W	5157 MB	04:37		09:43	VMP #11	
078	19/1/12	18	40° 00.00'S	42 25.00'W	5155	05:10	06:51	09:09	CTD 045	Full depth Stainless
079	19/1/12	18	40° 00.00'S	42 25.00'W	5143	10:25		17:30	SAPS #5	Full depth
080	19/1/12	18	40° 00.00'S	42 35.24'W	5146	20:16		02:26	VMP #12	
081	19/1/12	18	40° 00.00'S	42 35.22'W	5156	21:04	23:17	01:59	Megacore #5	5180 line out at impact 8 cores !
082	20/1/12	18	40° 00.00'S	42 34.84'W	5156	02:15	03:50	04:55	CTD 046	Ti 1500m
083	20/1/12	18	40° 00.00'S	42° 35.23'W	5156	05:20			Argo #9	UK Argo
084	20/1/12	18	"	"	5156	05:31			Argo #10	
085	20/1/12	18.5	40° 00.00'S	44° 53.40'W	5136	14:25			Argo #11	
086	20/1/12	19			5257	11:59			VMP #13	
087	21/1/12	19	40° 00.00'S	47° 25.00'W	5257	00:10	01:56	03:59	CTD 047	Full depth.
088	21/1/12	19	39° 59.16'S	47° 25.00'W	5256	06:02	07:52	10:10	CTD 048	Full depth Ti cast
089	21/1/12	19	39° 59.15'S	47° 25.01'W	5246	10:40	11:00	11:37	CTD 049	Full depth Stainless 400m
090	21/1/12	19	39° 58.36'S	47° 26.30'W	5248	12:23			Argo #12	UK float
091	21/1/12	19	"	"	"	12:25			Argo #13	US who float
092	22/1/12	20	37° 58.85'S	51° 01.76'W	4788	08:33	08:48		CTD 050	400m 1st light high vis
093	22/1/12	20	37 59.274'S	51 01.397'W	4791	10:00			glider #3 deploy	
094	22/1/12	20	38° 00.06'S	51° 00.02'W	4798m	10:33		15:51	VMP #14	
095	22/1/12	20	38° 00.03'S	50° 59.97'W	4797m	11:04	12:47	14:46	CTD 051	Full depth stainless 4308m

Cruise JC068 Event Log ⑤

Event No.	Date	Station	Latitude	Longitude	Depth (m)	Time IN (GMT)	Time BOTTOM (GMT)	Time OUT (GMT)	Activity	Comments
096	22/1/12	20	38° 00.06'S	50° 59.99'W	4794m	16:36	18:00	20:10	CTD #52	Full depth Ti
097	22/1/12	20	38° 02.02'S	50 59.21'W	4825m	20:38		01:31	VMP #15	
098	22/1/12	20	38° 02.38'S	50 58.96'W	4840m	20:56	22:33	00:37	CTD #53	Stainless full depth (Ac + Pu)
099	23/1/12	20	38° 04.96'S	50 58.93'W	4826m	01:48	02:09	02:40	CTD #54	800m stainless cast (Pu)
100	23/1/12	20	38° 05.54'S	50° 58.73'W	4836m	03:29	05:00	07:30	CTD #55	Stainless full depth (Hg).
101	23/1/12	20	38° 22.55'S	50° 53.96'W	4964m	10:08		10:08	Glider recovery #3	
102	23/1/12	21	37° 00.07'S	52° 29.98'W	3313m	21:43		21:43	VMP #16	
103	23/1/12	21	37° 00.05'S	52° 29.97'W	3313m	21:53	23:32:01	00:55	Megacore #6	5 short cores. Corer not fully lowered.
104	24/1/12	21	37° 00.00'S	52° 30.00'W	3320m	~01:35		06:25	SAPS #6	Drifted ~ 6nm from station during (deployment
105	24/1/12	21	36° 59.99'S	52° 29.99'W	3325m	09:21			VMP #17	
106	24/1/12	21	36° 59.99'S	52° 30.00'W	3325m	09:36	11:00	12:58	CTD #56	Full depth stainless
107	24/1/12	21	37° 00.03'S	52° 29.87'W	3291m	14:22			CTD #57	Full depth stainless Ti. restarted after sheave problem
108	24/1/12	21	37° 00.01'S	52° 29.92'W	3323m	15:38	16:50	18:34	CTD #58	Full depth Ti
109	24/1/12	21	36° 59.975	52° 29.986	3325	19:14		00:10	SAPS #7 VMP #18	
110	24/1/12	21	37° 00.00'S	52 29.90'W	3310m			22:25	SAPS #7	
111	25/1/12	21	37° 00.31'S	52 30.07'W	3331m	01:08	01:27	02:07	CTD #59	600m Stainless cast
112	25/1/12	21	37° 00.1'S	52° 30.01'W	3321m	02:40	03:00	03:35	CTD #60	T. shallow 498m
113	25/1/12	22	36° 31.75'S	53° 6.01'W	1483m	09:30	10:26		Megacore #7	
114	25/1/12	22	36° 32.16'S	53° 6.11'W	1520m	11:28		14:10	VMP #19	
115	25/1/12	22	36° 32.16'S	53 6.10'W	1532m	11:42	12:422	13:15	CTD #61	Full depth stainless
116	25/1/12	22	36° 31.79'S	53 6.18'W	1515m	14:40			VMP #20	
117	25/1/12	22	36° 31.81'S	53 6.12'W	1515m	15:31	16:58	17:20	CTD #62	Full depth Ti
101.3	23/1/12	20	38° 13.46'S	51° 01.91'W	4895m	11:54			ARGO #14	U k Argos
101.6	23/1/12	20	38° 13.59'S	51° 01.72'W	4895m	11:55			ARGO #15	US Argos

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APPENDIX B: COMPUTING AND SHIP SYSTEMS REPORT

JC068
NMFSS Sensors and Moorings CTD Report
PSO: Prof. G Henderson
24 December 2011 – 27 January 2012

JOHN WYNAR
Sensors & Moorings Group
National Marine Facilities Division
National Oceanography Centre, Southampton

CTD System Configuration

The initial sensor configuration for the stainless steel (s/s) system was as follows:

- Sea-Bird 9*plus* underwater unit, s/n: 09P-0943
- Frequency 0 - Sea-Bird 3 Premium temperature sensor, s/n: 03P- 2729
- Frequency 1 - Sea-Bird 4 conductivity sensor, s/n: 04C-2450
- Frequency 2 - Digiquartz temperature compensated pressure sensor, s/n: 110557
- Frequency 3 - Sea-Bird 3 Premium temperature sensor, s/n: 03P - 4105
- Frequency 4 - Sea-Bird 4 conductivity sensor, s/n: 04C-3698
- V0 - Sea-Bird 43 dissolved oxygen sensor, s/n: 43-0862
- V2 - Benthos PSA-916T 7Hz altimeter, s/n: 41302
- V3 – WETLabs turbidity sensor, s/n: BBRTD-759R
- V4 – Chelsea UWIRR PAR sensor, s/n: 11
- V5 – Chelsea Aquatracka MKIII fluorometer, s/n: 88-2960-163
- V6 - Chelsea DWIRR PAR sensor, s/n: 10
- V7 – Chelsea Alphatracka MKII transmissometer, s/n: 161048

Ancillary instruments & components:

- Sea-Bird 11*plus* deck unit, s/n: 11P-24680-0587
- Sea-Bird 24-position Carousel, s/n: 32- 31240-0423
- 24 x Ocean Test Equipment 20L water samplers, s/n: 1 through 24

The initial sensor configuration for the trace metal free titanium (Ti) system was as follows:

- Sea-Bird 9*plus* underwater unit, s/n: 09P-0803
- Frequency 0 - Sea-Bird 3 Premium temperature sensor, s/n: 03P- 5277
- Frequency 1 - Sea-Bird 4 conductivity sensor, s/n: 04C- 3873
- Frequency 2 - Digiquartz temperature compensated pressure sensor, s/n: 93896
- Frequency 3 - Sea-Bird 3 Premium temperature sensor, s/n: 03P – 4593
- Frequency 4 - Sea-Bird 4 conductivity sensor, s/n: 04C-3272
- V0 - Sea-Bird 43 dissolved oxygen sensor, s/n: 43-2055
- V2 - Tritech altimeter, s/n: 6196.112522

- V3 – Chelsea Aquatracka MKIII fluorometer, s/n: 088244
- V4 – Free
- V5 – Free
- V6 - Chelsea Alphatracka MKII transmissometer, s/n: 161047
- V7 – WETLabs turbidity sensor, s/n: BBRTD-182

Ancillary instruments & components:

- Sea-Bird 24-position Carousel, s/n: 32- 60380-0805
- SBE 17P SEARAM, s/n: 17P-59976-0326
- SBE 17P SEARAM, s/n: 17P-59976-0327
- 24 x Ocean Test Equipment 10L TMF water samplers, s/n: 1 through 24

CTD Operations

There were 38 s/s CTD casts and 26 Ti casts made. Log sheets were scanned and included with the data from this cruise.

For the s/s system, the pressure sensor was located 10cm below the bottom and approximately 70cm below the centre of the 20L water sampling bottles. The PAR sensors were removed for casts deeper than 500m. The configuration file used was JC068_NMEA.xmlcon (see Appendix A.1) for cast 1S to 63S.

For the Ti system, the pressure sensor was located 30cm below the bottom and approximately 75cm below the centre of the 10L water sampling bottles. The configuration file used was JC68Ti.con (see Appendix A.2) for cast 2 to 11T. From cast 13T to 64T JC68Ti_1.con was used.

Due to the fatigued and corroded state of wire CTD1(the outer armour could be opened up by hand), the operation of the s/s CTD was changed over to CTD2. This wire had a lower "megger" value (approx. 70Mohm at 500V) but significantly better mechanical characteristics. After cutting off 200m of wire, CTD2 megger value increased to >1000Mohm. By cast 10S however, the measurement had reduced to 3 Mohm at 250V. Several hundred modulo errors were being detected during a typical cast caused by communication dropouts between the deck unit and the 9plus producing poor quality data. Hence, after cast 17S it was decided to return to using CTD1 recognising the probable need for re-terminating every few casts. *It should be noted that CTD1 has good electrical characteristics but poor mechanical ones and is considerably shorter than CTD2.* **In my opinion neither ctd wires are fit for purpose.** The large number of sheaves the wire has to travel over probably contributed to the premature ageing of ctd1. This would be greatly mitigated by using a deck-mounted winch.

Casts 17S, 19S and 20S were made without the stabilizing vane and secondary sensors mounted directly on the 9plus fish. Package spin worsened with increased number of rotations on up-cast and now some observed on the down-cast also (where previously there was none). The vane replaced from cast 21S onwards but sensors remained fitted to the fish.

Cast 57T was aborted due to winch problems. CTD recovered and deployed again as 58T.

The Ti system was lowered on the synthetic and non-conducting synthetic rope, the samplers being tripped and data from the sensors stored on the SEARAM 17P units. To compensate for the buoyancy of the rope, a plastic coated weight was hung in-line and connected to the CTD frame via a swivel.

Sensor Failures

During the deployment of cast 11T the vane hit the side of the ship and damaged the vane-fitted sensors. These sensors were removed and the system deployed with only primary T & C sensors. The vane was subsequently removed from cast 13T and secondary sensors (3P-5494 and 4C-3529) fitted inside the frame to the fish (water entrainment not being such an issue using 10L samplers).

Data Processing

CTD cast data was post-processed according to guidelines established with BODC (ref. Moncoiffe 7th July 2010). After plotting oxygen against pressure using Seaplot an oxygen advance of 8 seconds was chosen. WildEdit was not used during processing, it being deemed unnecessary. LoopEdit was employed during processing but saved as a separate file and no further processing carried out on those files.

An error in the cal file for the PAR sensors meant a calibration constant of 10^{11} was used when it should have read 10^{10}. *This should be corrected and taken into account during post-processing.*

Salinity measurement

A Guildline Autosal 8400B salinometer, s/n: 68426, was used for salinity measurements. The salinometer was sited in the Chemistry Lab, with the bath temperature set at 24°C, the ambient temperature being approximately 23°C. A bespoke program written in Labview called "Autosal" was used as the data recording program for salinity values.

In general, a scientist was given the responsibility of taking a salinity sample from each water sampler and making the measurements. Hence detailed results on salinity are given elsewhere in the cruise report.

TRDI LADCP Configuration

The TRDI WHM 300kHz LADCP (s/n: 4275) was deployed in a downward-looking orientation on the s/s CTD frame. Battery voltage could be monitored as the cable was not diode protected. The instrument was configured to ping at intervals of one second, use 16 bins, a blanking distance of 5m and a depth cell size of 10m thus yielding a range of approximately 165m in ideal conditions. The ambiguity velocity was set to 250 cms^{-1} and pings per ensemble to 1.

Built-in pre-deployment tests *(PA, PC2 and PT200)* were run before each cast, and then the following command file sent *(F2)*:

Master command file (WHM_JC68.txt)

PS0
CR1
CF11101
EA00000
EB00000
ED00000
ES35
EX11111
EZ0011101
WM15
WW1
WD111100000
WF0500
WN016
WP00001
WS1000
WV250
SM1
SA001
SW05000
TE00:00:01.00
TP00:00.00
CK
CS

Deployment Comments

Each deployment BBtalk terminal session was logged to a file *(F3)* of the form: *JC68_XX.txt*, where *XX* is the CTD cast number. Downloaded data files were re-named to be of the form: *JC68_XXm.000*.
The real-time clock of the LADCP was checked prior to deployment *(TS?)* and re-synchronised with the ship's GPS clock if it was more than a few seconds in error. The time difference (if any) was written on the log sheet.

Paper log sheets were used for all casts (and scanned for electronic storage), the LADCP file number being defined by the CTD cast number.

There was no LADCP profile recorded during CTD cast 1.

The TRDI WHM 300kHz LADCP (s/n: 13400) was deployed in a downward-looking orientation on the Ti CTD frame from cast 22T to 41T inclusive. The same command file was used as for unit s/n: 4275 on the s/s frame and the same operating procedure adopted as above.
From cast 29T, command file WHM_JC68T.txt was used changing the EX parameter in the command file to:

EX00111
to convert the velocities to beam co-ordinates due to an issue with beam 2. Due to deterioration in data quality recorded from the unit, it was removed after 41T.

For casts 37S and 39S the stainless frame was fitted with two LADCP's in a master/slave configuration (master: s/n 4275; slave: s/n 15288). The command files used were as follows:

Master:	**Slave:**
PS0	PS0
CR1	CR1
CF11101	CF11101
EA00000	EA00000
EB00000	EB00000
ED00000	ED00000
ES35	ES35
EX11111	EX11111
EZ0011101	EZ0011101
TE00:00:01.00	TE00:00:01.00
TP00:01.00	TP00:01.00
WM15	WM15
WD111100000	LD111100000
WF0500	LF0500
WN016	LN016
WP00001	LP00001
WS1000	LS1000
WV250	LV250
WW1	LW1
SM1	SM2
SI0	SA001
SA001	ST0300
SW500	CK
CK	CS
CS	

After cast 39S the data obtained from the slave was too poor to justify using and therefore the unit was removed.

Stand Alone Pumps (SAPs)

The SAPs were deployed on seven occasions, three of them being up to 5000m. Their detailed performance is outlined below:

SAP s/n: 02-02

Used on six occasions with mediocre performance, the batteries capacity to charge being suspect. It's timer board was donated to unit 03-01 which was suspected as faulty. The timer board from 03-01 functioned when fitted to this unit.

SAP s/n: 02-03
Worked well on the first deployment and then failed to start on all but one of the remaining ones. Possible fault of the start reed switch and should be investigated.

SAP s/n: 02-04
Deployed on five occasions and worked reasonably well – no issues.

SAP s/n: 03-01
Deployed six times with reasonable volumes pumped but failed to start twice. Timer board swopped from unit 02-02 but starting issues should be investigated and the sounder replaced (not loud enough).

SAP s/n: 03-02
Used on six of the seven deployments and worked well – no issues.

SAP s/n: 03-03
Only deployed on five occasions but worked reasonably successfully. Battery capacity should be checked as a precaution.

SAP s/n: 03-04
Deployed on six occasions and operated well until it's fourth outing when it failed to pump. The problem was investigated and found to be due to the timer and power supply boards having shaken loose. The boards were refitted and the plastic nuts tightened. On the remaining two deployments the pump worked satisfactorily.

SAP s/n: 03-05
Used on all seven deployments and worked very well, pumping large volumes. There is, however, a fault with the timer display which needs to be investigated.

APPENDIX A.1

Initially, the config file used for the s/s CTD was the following:

Instrument configuration file: C:\Program Files\Sea-Bird\SeasaveV7\JC68\JC068_NMEA.xmlcon

Configuration report for SBE 911plus/917plus CTD

Frequency channels suppressed : 0
Voltage words suppressed   : 0
Computer interface   : RS-232C
Scans to average   : 1

NMEA position data added   : Yes
NMEA depth data added   : No
NMEA time added   : No
NMEA device connected to   : deck unit
Surface PAR voltage added   : No
Scan time added   : No

1) Frequency 0, Temperature

  Serial number : 03P-2729
  Calibrated on : 27 August 2010
  G   : 4.35523958e-003
  H   : 6.41864415e-004
  I   : 2.33690660e-005
  J   : 2.26871883e-006
  F0   : 1000.000
  Slope   : 1.00000000
  Offset   : 0.0000

2) Frequency 1, Conductivity

  Serial number : 04C-2450
  Calibrated on : 22 February 2011
  G   : -1.04350302e+001
  H   : 1.66296359e+000
  I   : -1.86648670e-003
  J   : 2.56279761e-004
  CTcor   : 3.2500e-006
  CPcor   : -9.57000000e-008
  Slope   : 1.00000000
  Offset   : 0.00000

3) Frequency 2, Pressure, Digiquartz with TC

  Serial number : 110557
  Calibrated on : 26 April 2009
  C1   : -6.010548e+004
  C2   : -1.565601e+000
  C3   : 1.823090e-002
  D1   : 2.668300e-002
  D2   : 0.000000e+000
  T1   : 3.020528e+001
  T2   : -6.718318e-004
  T3   : 4.457980e-006
  T4   : 1.203850e-009

T5   : 0.000000e+000
Slope   : 0.99994000
Offset   : -1.08250
AD590M   : 1.280700e-002
AD590B   : -9.299644e+000

4) Frequency 3, Temperature, 2

Serial number : 03P-4105
Calibrated on : 18 February 2011
G   : 4.39420254e-003
H   : 6.47871532e-004
I   : 2.32200702e-005
J   : 2.07133473e-006
F0   : 1000.000
Slope   : 1.00000000
Offset   : 0.0000

5) Frequency 4, Conductivity, 2

Serial number : 04C-3698
Calibrated on : 8 February 2011
G   : -1.01494305e+001
H   : 1.43731532e+000
I   : -2.81457287e-003
J   : 2.88692072e-004
CTcor   : 3.2500e-006
CPcor   : -9.57000000e-008
Slope   : 1.00000000
Offset   : 0.00000

6) A/D voltage 0, Oxygen, SBE 43

Serial number : 43-0862
Calibrated on : 10 March 2009
Equation   : Sea-Bird
Soc   : 4.36200e-001
Offset   : -4.99200e-001
A   : -1.09340e-003
B   : 9.78700e-005
C   : -2.32650e-006
E   : 3.60000e-002
Tau20   : 1.37000e+000
D1   : 1.92634e-004
D2   : -4.64803e-002
H1   : -3.30000e-002
H2   : 5.00000e+003
H3   : 1.45000e+003

7) A/D voltage 1, Free

8) A/D voltage 2, Altimeter

   Serial number : 41302
   Calibrated on : 20 April 2007
   Scale factor : 15.000
   Offset   : 0.000

9) A/D voltage 3, Turbidity Meter, WET Labs, ECO-BB

   Serial number : BBRTD-759R
   Calibrated on : 18 May 2010
   ScaleFactor : 0.003130
   DarkVoltage : 0.048000

10) A/D voltage 4, PAR/Irradiance, Biospherical/Licor

   Serial number   : 11
   Calibrated on   : 14 June 2011
   M   : 0.43350200
   B   : 2.34999500
   Calibration constant : 100000000000.00000000
   Multiplier   : 0.99980000
   Offset   : 0.00000000

11) A/D voltage 5, Fluorometer, Chelsea Aqua 3

   Serial number : 088-195
   Calibrated on : 8 September 2010
   VB   : 0.275800
   V1   : 2.154100
   Vacetone   : 0.313700
   Scale factor : 1.000000
   Slope   : 1.000000
   Offset   : 0.000000

12) A/D voltage 6, PAR/Irradiance, Biospherical/Licor, 2

   Serial number   : 10
   Calibrated on   : 14 June 2011
   M   : 0.47873600
   B   : 1.68992200
   Calibration constant : 100000000000.00000000
   Multiplier   : 0.99970000
   Offset   : 0.00000000

13) A/D voltage 7, Transmissometer, Chelsea/Seatech/WET Lab CStar

   Serial number : 161048
   Calibrated on : 28 May 2008

```
M         : 24.5574
B         : -0.4420
Path length   : 0.250
```

Scan length   : 37

APPENDIX A.2

Initially, the config file used for the Ti CTD was the following:

Instrument configuration file: C:\Program Files\Sea-Bird\SeasaveV7\JC68\JC68Ti.con

Configuration report for SBE 911plus/917plus CTD

```
Frequency channels suppressed : 0
Voltage words suppressed     : 0
Computer interface       : RS-232C
Scans to average        : 1
NMEA position data added     : No
NMEA depth data added      : No
NMEA time added         : No
Surface PAR voltage added    : No
Scan time added         : No
```

1) Frequency 0, Temperature

```
  Serial number : 5277
  Calibrated on : 19/08/2010
  G       : 4.37787181e-003
  H       : 6.38186710e-004
  I       : 2.21796532e-005
  J       : 2.00262477e-006
  F0      : 1000.000
  Slope     : 1.00000000
  Offset    : 0.0000
```

2) Frequency 1, Conductivity

```
  Serial number : 3873
  Calibrated on : 14/09/2011
  G       : -1.01855852e+001
  H       : 1.35578646e+000
```

```
I          : -7.15096189e-004
J          : 1.22353608e-004
CTcor      : 3.2500e-006
CPcor      : -9.57000000e-008
Slope      : 1.00000000
Offset     : 0.00000
```

3) Frequency 2, Pressure, Digiquartz with TC

```
Serial number : 93896
Calibrated on : 12 May 2011
C1         : -8.331332e+004
C2         : -3.281962e-001
C3         : 2.216060e-002
D1         : 2.906000e-002
D2         : 0.000000e+000
T1         : 3.005232e+001
T2         : -3.843669e-004
T3         : 4.436390e-006
T4         : 0.000000e+000
T5         : 0.000000e+000
Slope      : 0.99996000
Offset     : -1.07670
AD590M     : 1.289250e-002
AD590B     : -8.106440e+000
```

4) Frequency 3, Temperature, 2

```
Serial number : 4593
Calibrated on : 29/04/2011
G          : 4.35402714e-003
H          : 6.44517671e-004
I          : 2.17427210e-005
J          : 1.75128984e-006
F0         : 1000.000
Slope      : 1.00000000
Offset     : 0.0000
```

5) Frequency 4, Conductivity, 2

```
Serial number : 3272
Calibrated on : 29/04/2011
G          : -1.02489676e+001
H          : 1.33239316e+000
I          : 8.46740897e-004
J          : 1.06185569e-005
CTcor      : 3.2500e-006
CPcor      : -9.57000000e-008
Slope      : 1.00000000
Offset     : 0.00000
```

6) A/D voltage 0, Oxygen, SBE 43

   Serial number : 2055
   Calibrated on : 15/03/2011
   Equation   : Sea-Bird
   Soc   : 3.74900e-001
   Offset   : -7.06500e-001
   A   : -2.27640e-003
   B   : 6.77830e-005
   C   : -1.32720e-006
   E   : 3.60000e-002
   Tau20   : 2.44000e+000
   D1   : 1.92634e-004
   D2   : -4.64803e-002
   H1   : -3.30000e-002
   H2   : 5.00000e+003
   H3   : 1.45000e+003

7) A/D voltage 1, Free

8) A/D voltage 2, Altimeter

   Serial number : 6196.112522
   Calibrated on : 01/03/2004
   Scale factor : 15.000
   Offset   : 0.000

9) A/D voltage 3, Fluorometer, Chelsea Aqua 3

   Serial number : 088244
   Calibrated on : 11/02/2010
   VB   : 0.236100
   V1   : 2.089100
   Vacetone : 0.287100
   Scale factor : 1.000000
   Slope   : 1.000000
   Offset   : 0.000000

10) A/D voltage 4, Free

11) A/D voltage 5, Free

12) A/D voltage 6, Transmissometer, Chelsea/Seatech/WET Lab CStar

   Serial number : 161047
   Calibrated on : 18/03/2008
   M   : 23.7757
   B   : -0.4636
   Path length : 0.250

13) A/D voltage 7, User Polynomial

 Serial number : 182
 Calibrated on : 17/08/2010
 Sensor name : Turbidity Meter
 A0   : -0.00028950
 A1   : 0.00330100
 A2   : 0.00000000
 A3   : 0.00000000

Scan length   : 30

From cast 13T onwards, the following configuration file was used:

Instrument configuration file: C:\Program Files\Sea-Bird\SeasaveV7\JC68\JC68Ti_1.con

with the following alteration:

4) Frequency 3, Temperature, 2

 Serial number : 5494
 Calibrated on : 15 September 2011
 G   : 4.32408533e-003
 H   : 6.25695430e-004
 I   : 1.92332376e-005
 J   : 1.43221910e-006
 F0   : 1000.000
 Slope : 1.00000000
 Offset : 0.0000

5) Frequency 4, Conductivity, 2

 Serial number : 3529
 Calibrated on : 15 September 2010
 G   : -9.92219785e+000
 H   : 1.57181344e+000
 I   : -2.77902408e-003
 J   : 3.07945801e-004
 CTcor : 3.2500e-006
 CPcor : -9.57000000e-008
 Slope : 1.00000000
 Offset : 0.00000

APPENDIX C: NMF-SS TECHNICAL REPORT

JC068 NMFSS Technical Cruise Report
Cruise Overview

GEOTRACES – Port Elizabeth, South Africa to Montevideo, Uruguay
December 2011 to January 2012

All times given in this report are in UT.

Technicians;

Dave Childs

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Kev Smith (Senior Tech)

John Wynar

Meteorology monitoring package.

The Surfmet system was run throughout the cruise. Please see the separate BODC information sheet JC68_Surfmet_sensor_information_sheet.docx for details of the sensors used and the calibrations that need to be applied. The calibration sheets are included in the directory Ship_Systems\Met\SURFMET\calibrations.

At 03:29 on 25/1/12 the Surfmet logging software partially crashed; valid data was displayed on the screen but invalid values were sent to Techsas and Level-C for air temperature, humidity, air pressure, wind speed and direction and for the PARs and TIRs. The PC was rebooted at 09:00 and logging of the correct data was resumed. This crash did not affect the other underway data variables.

Pumped sea water sampling system [hull bottom intake]. Sea surface monitoring system [salinity, temperature, transmissometer, fluorimeter].

The Surfmet system was run throughout the cruise. Please see the separate BODC information sheet for details of the sensors used and the calibrations that need to be applied. No problems were encountered.

The pumped non-toxic water supply was turned off from 05:00 until 17:32 on 27/12/11 for the Cape Town port call. There was still some air in the system at the end of this period and it would have taken a little while to bleed off.

Ship scientific computing systems.

Data was logged by the Techsas data acquisition system into NetCDF files. The format of the NetCDF files is given in the file NMFSS_NetCDF_Description_Cook.docx. The instruments logged are given in JC68_Ship_fitted_information_sheet_JC.docx. Data was additionally logged into the RVS Level-C format, which is described in the same document. An ASCII dump of each of the Level-C streams was included on the final data disk. The cruise was lucky to have Alex Forryan from NOC Southampton onboard who processed much of the data using the PSTAR package and provided the underway, CTD and LADCP data to whoever needed it making the data processing very easy for the NMFSS technician. The Level-C software was run on the new Sun Enterprise Sparc server. The Enterprise does not have a monitor output and so the fromtechsas program was started remotely and run in the background. This worked well and there were no problems when the xterm that it was started in was closed. As a precaution Level-C was also

run on the old Cook4 Sun Blade 1500. Cook4 hung at 21:52 on 4/1/12. Logging was then started on the Cook3 Sun Blade 1500. The Enterprise worked well and Level-C should perhaps be run from the newer and more reliable Enterprise on future cruises. The Techsas Uninterruptible Power Supply (UPS) failed on 24/1/12 at 20:25. The PC was connected directly to the electrical supply and logging was resumed at 20:32. No data was logged by Techsas or Level-C during this period.

A Drobo network storage device was used to provide a shared storage area for everyone to use. This was copied to the end of cruise data disk.

All acoustic systems were turned off between 05:10 and 16:06 on 27/12/11 for the Cape Town port call.

Kongsberg EA600 12 kHZ single beam echo sounder.

The EA600 single beam echo sounder was run throughout the cruise. The winds were predominantly westerly often reaching 40 knots. The vessel was therefore travelling into the swell and waves for most of the cruise and was pitching heavily. As is typical for this vessel this resulted in lots of aeration under the hull and very poor performance from the acoustic systems, which for this cruise were the EA600 single beam, EM120 multibeam and the 75 and 150 kHz vessel mounted ADCPs. The underway depth data logged was of poor quality with lots of spikes and gaps as a result. The EA600 in particular struggled to get any signal and so the depth values logged in the NetCDF and RVS data files should be examined carefully before use. The single beam data was also logged in Kongsberg raw format and also saved as .bmp bitmap image files. Before using depth data from the EA600's NetCDF file the .bmp files should be consulted to see if the depth data for that time period was reliable.

The EA600 was used with a constant sound velocity of 1500 ms^{-1} throughout the water column to allow it to be corrected for sound velocity in post processing.

At 23:27 on 16/1/12 the EA600 crashed and invalid data was logged until it was restarted at 09:00 on 17/1/12.

Kongsberg EM120 Deep Water Multi beam echo sounder.

Although this was not requested in the cruise agreement it was needed to provide depth, slope and sound velocity inputs to the SBP120. It was also run throughout the cruise to provide general depth information due to the poor performance of the EA600. Once the scientific party had seen the data that it could produce it was left running throughout the cruise and data from certain areas of interest was processed by the Science Systems Technician in CARIS.

 The depth calculated from the EM120's centre beam was logged in the NetCDF and Level-C files. Similarly to the EA600, the EM120 suffered from poor performance due to aeration caused by the vessel's pitching motion, although to a slightly lesser extent than the EA600. The depths in the NetCDF and Level-C files should be treated with caution unless the raw Kongsberg .all files have been consulted first.

Due to the poor data quality the Processing Unit, located in the Transducer Connection Room, would regularly crash when the vessel was pitching. When it has crashed the sonar would not ping and this could be seen on the Synchronisation Unit display in the main lab by a flat line for the EM120. Because only the PU had crashed and the main lab PC was still running, data files were still written but these contain only navigation and sound velocity information and no depths.

Olex was run throughout the cruise and was useful for identifying sites to sample at and the location of the vessel relative to the next station. A JC68 seafloor database was created at the start of the cruise and this was exported to the BODC data disk at the end of the cruise.

At the Gough Island and mid-Atlantic ridge sites Olex's display was useful for identifying suitable coring and sampling sites. Due to the poor quality of the available charts at Gough Island the bridge monitored the EM120 to ensure that the ship was not heading into danger. A planned survey was not run, instead data was captured while the vessel was stationary at stations and when transiting between stations. The vessel was often facing into the wind and waves and consequently pitching and acquiring noisy data.

Data from Gough Island was cleaned by the Science Systems Technician in the Caris package to produce a geo-referenced TIFF image, an ASCII latitude, longitude and depth file of the area at 25 m resolution and a Windows Media Videa .wmv video of a fly over the site. The back scatter data was formed into a mosaic, which is exported as a geo-referenced TIFF mosaic. A sediment analysis was run on the geo-referenced data, but it reported that all areas consisted of "gravel" with a high degree of certainty. This is unlikely to be true as the south-western portion of the surveyed area was rising steeply and was likely to be bare rock.

Data for 24 hours after station 16 was similarly processed. The Caris exports for both of these processed sites are located in Ship_Systems\Acoustics\EM-120\Caris_Processed\ and then either Gough\Export\ or Station16\Export\.

Lines 277, 278 and 279 on 15/1/12 are suspect as the water became deeper than the maximum depth entered in SIS and it tried to fit the signal into this range. The data looks like it could be valid but experience with the system suggests that the depths are too shallow.

Sound Velocity Profiles.

The sound velocity profiles listed in the table below were used in the EM120 and USBL systems. They are included on the data disk. The directory name describes the the CTD cast that the data came from, eg JC68_61 is the CTD cast 61 processed in the Sea Bird software.

Installation Time	Profile
Start of cruise	SVP_Probe\JC066\FinishedProfileAtlantis.asvp
28/12/11 09:12	CTD_Derived\SS01\JC068_SS01_sv_thinned.asvp
30/12/11 08:29	CTD_Derived\JC68_05\JC68_05s_sv_1m_thinned.asvp
6/1/12 18:37	CTD_Derived\JC68_13\20120106_13Ti_thinned.asvp
9/1/12 16:06	CTD_Derived\JC68_19\SoundVelCTD19Jan8_thinned.asvp
15/1/12 13:53	CTD_Derived\JC68_33\soundVelCTD33Jan14_thinned.asvp
16/1/12 15:15	CTD_Derived\JC68_36\soundVelCTD36Jan15_thinned.asvp
17/1/12 17:55	CTD_Derived\JC68_39\soundVelCTD39Jan17_thinned.asvp
19/1/12 15:11	CTD_Derived\JC68_45\soundVelCTD45Jan19_thinned.asvp
21/1/12 11:19	CTD_Derived\JC68_47\soundVelCTD47Jan21_thinned.asvp
22/1/12 19:52	CTD_Derived\JC68_51\soundVelCTD51Jan22_thinned.asvp
24/1/12 15:37	CTD_Derived\JC68_56\soundVelCTD56Jan24_thinned.asvp
25/1/12 15:46	CTD_Derived\JC68_61\soundVelCTD61Jan25_thinned.asvp

Kongsberg SBP120 sub bottom profiler (3°).

The SBP120 was run at each coring to check the sea bed's suitability for coring. Data was saved in SEG-Y format. On previous cruises it has been found that some SEG-Y viewers have different filter options to Kongsberg's SBP120 software and are unable to show the detail that Kongsberg's software achieves. If problems occur viewing the SEG-Y data then Kongsberg should be contacted for advice or a copy of the SBP120 software. The best results were achieved in the SBP120 software by using the following filter options applied to the raw data in the following order:

Gain correction
Transmission loss: 0 dB/m

Filters
Filter type: Matched
Corner frequencies: Auto
Replica shaping: enabled

Attribute processing
Attributes: Inst. amplitude

Automatic gain control
Window length: 10%
Apply point: 0%
Amp. Scaling: 20%

To reduce the need for processing the data in the future JPEG images were produced for each site that the megacorer was deployed at. The topography at station 10 was very undulating and it was difficult to get a good trace on the SBP. It is thought that this was due to the steep angle of the slopes giving a weak reflected signal and also each signal reflecting off multiple surfaces. A plot has been generated but there is little useful information in it. The units of each JPEG's depth scale on the plots are milliseconds. The entire plot is 250 ms long and each division is 10 ms. The plot for station 24 on 26/1/12 is different as the water depth was much shallower. For station 24 the plot is 40 ms long and each division is 5ms. Unfortunately the software does not include an option for showing units on the depth scale of the JPEG plots.

The EM120 multibeam system was run to provide depth and slope and range information for the SBP120. It was found that the EM710 was sending depth datagrams to the SBP120 on the same port number, despite these not being setup in the EM710's configuration. When it was too deep for the EM710 to achieve bottom detection and so its depths were not valid and prevented the SBP120 from sampling the correct section of the water/seabed column. This was fixed by removing the EM710's network cable. The EM710's datagrams should be fixed during the next Kongsberg maintenance visit or when time is available while the vessel is operating in shallow water.

75 kHz and 150 kHz hull mounted ADCP system.
Both ADCP systems were run without problems throughout the cruise. The raw data files and configurations are included on the data disk. A bug was found in the software for both systems; they are currently running VmDas version 1.42. The navigation data feed on the screen would freeze and would no longer be updated, although data would still be written to disk. At the same time the data files would not be closed and so the automatic backup of the data could not happen. When logging was next stopped it would take a long time to do so and the PC would have to be rebooted before logging could be resumed. The physical oceanographer onboard examined the data and found that there had been no effect on the data. While this bug

was being investigated the ADCP 75 kHz PC was rebooted at 17:30 on 28/12/11 and at 20:14 on 1/1/12. The ADCP 150 kHz PC was rebooted at 18:11 on 5/1/12. After this the PCs were allowed to continue until the daily restart to increase the number in the filename. Bottom tracking was enabled on both systems to allow their alignment to be calibrated from the start of the cruise until 06:04 on 28/12/11.

Wave height recorders.

The antenna unit for the Wamos wave radar failed on a previous cruise. A radar engineer in Cape Town was not happy working on the unit due to the access to it being unsafe. Access to the antenna will be improved and the unit fixed during a future refit.

USBL.

The Ultra Short Base Line (USBL) tracking system was not requested for this cruise, but was used on the mega corer at sites shallower than 4000 m to monitor the position of the corer. The Super Sub Mini (serial number 18680-05) and Wideband Sub Mini (serial number 271552-003) beacons onboard were used but are only rated to 4000 m. A 6000m Compatt 5 was left onboard after the previous ROV cruise but was too big to fit on to the mega corer frame. 4000 m is the maximum rating for the entire Sub Mini range. No problems were encountered tracking the beacons when Ranger 1 version 2.04.00 software was used. Their positions were exported in real time for display on the Olex and DP systems.

The positions of the cores taken were recorded by the USBL system and the positions are shown in the table below. The depths were those calculated using acoustics only; the depth sensor on the beacon was not used as tracking was sometimes lost when telemetry was used to send the depth back. The beacon was not fitted during cores 5 and 6 because of the water depth. The bottom times for cores 9 and 10 were obtained from the winch data; the USBL beacon was being tested with the Sonardyne Fusion software package, rather than Ranger and tracking the beacons was found to be difficult, probably due to the shallow depth of the water causing multipath problems and the short duration of the corer's descent to the sea bed not allowing sufficient time to reprogram the beacons for a lower power output.

Station	Core	Date	UT Time	Latitude	Longitude	Depth, m
8	1	6/1/2012	18:39:04	39° 59.93664' S	009° 40.03806' W	3404
10	2	7/1/2012	07:22:42	40° 16.86792' S	009° 53.50698' W	412
11	3	8/1/2012	23:14:00	39° 59.97666' S	012° 59.97834' W	3172
12	4	10/1/2012	15:04:01	39° 59.99124' S	016° 27.98850' W	3083
22	7	25/1/2012	10:25:01	36° 31.99560' S	053° 06.10980' W	1502
23	8	25/1/2012	22:03:53	36° 20.25900' S	053° 20.29980' W	699
24	9	26/1/2012	10:22:09			
24	10	26/1/2012	11:05:50			

The Vertical Microstructure Profiler (VMP) was tracked using a 10 kHz Ixsea pinger connected to either a dunker or the single element of the EA500 single beam echo sounder. Tracking the VMP this way had two disadvantages; the pinger only gave the

depth of the VMP and the slant range and so its distance from the ship could be calculated but not its bearing and the EM120 and EA600 had to be turned off when the VMP was being tracked because they all used frequencies close to 12 kHz. The VMP could be better tracked by fitting it with a USBL beacon. The Sonardyne Wideband Sub Mini (WSM) beacons are a similar size to the Ixsea pingers and their use with the VMP should be investigated when the VMP is operated from an NMFSS vessel using a USBL beacon would give the VMP's latitude and longitude and because it operates in the 18 to 30 kHz band, would not interfere with the echo sounders, which are essential during CTD and coring to provide accurate depths. However, WSM beacons have a maximum depth rating of 4000 m, which is less than the VMP's 6000m maximum depth.

Other Systems.

Several other systems were run as part of the standard instrument suite onboard the vessel. Details of all systems logged are given in the file JC68_Ship_fitted_information_sheet_JC.docx. At 10:12 on 5/1/12 the ADU5's attitude data was found to have crashed overnight and was restarted. At 29/12/11 at 17:16 the gravity meter's dial was reading 10359 but due to the ongoing fault the software read 9541.8. The software was reset to the meter value at this time. At 08:15 on 4/1/12 the dial was reading 10721 but the software was reading 10704.0 and the software was reset to the meter value. On 13/1/12 and 22/1/12 the software and the meter were reading the same.

CTD.

Please see "NMFSS Sensors and Moorings report (above) for further details. The CTD data and relevant documents are included on the data disk in Specific_Equipment\CTD\.