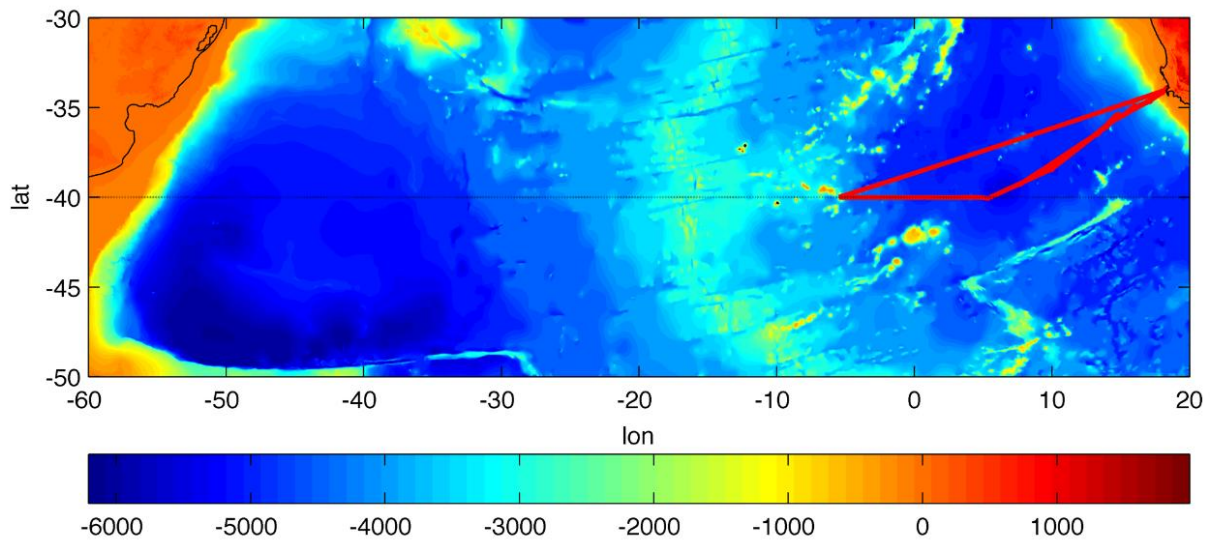


# CRUISE REPORT

## D357 / GA10E UK-GEOTRACES 40°S

D357 science party members



**UK GEOTRACES**

RRS Discovery  
18/10/2010 - 22/11/2010  
Cape Town – Cape Town



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## OVERVIEW

The cruise forms part of the international GEOTRACES Programme ([www.geotraces.org](http://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 left Cape Town in South Africa on 18th October 2010, aiming to sail  $\approx$ SW towards 40oS and then due west to end in Montevideo, thereby providing a zonal South Atlantic section along the band of high productivity at this latitude.

About one third of the way across the Atlantic, after 7 full science stations had been completed, a medical emergency required the ship to return directly to Cape Town. This first out and back from Cape Town is termed Leg 1 in this report.

Following this medical evacuation, there was insufficient time to complete the section, but remaining ship-time was used to increase the resolution of sampling along the original line during a second out-and-back from Cape Town (Leg 2).

Although the cruise therefore did not go as planned, the ability to reoccupy the same section did offer significant unexpected scientific reward. It allowed an increase in spatial resolution in the Cape Basin, and for some of the original stations to be reoccupied to provide information about changing conditions during the onset of the spring bloom.

This cruise report presents information from both Leg 1 and Leg 2 of D357.

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 conducted 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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Principal Scientist

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Robin Why, Third Officer  
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Steve Bell, Second Engineer  
Gary Slater, Third Engineer  
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John McDonald, Seaman 1A  
Graham Bullimore, Purser  
Mark Preston, Head Chef  
Lloyd Sutton, Chef  
Jeffrey Orshorn, Steward

## OBJECTIVES

The D357 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. <sup>231</sup>Pa/<sup>230</sup>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 AND SAMPLING STRATEGY

Seven stations and one test station were occupied between Cape Town and 40°S, 5°W before the medical evacuation forced a return to port. Six further stations were occupied after the port call, along with a number of reoccupations of the initial stations.

Typical stations consisted of three rosette deployments generally followed by a core, with interspersed deployment of the VMP-750

- A full depth deployment of the stainless-steel rosette allowed recognition of basic oceanographic properties and collection of all chemical samples not prone to contamination
- A full depth deployment of the titanium rosette, with all bottle handling conducted in a clean container on the aft deck, allowed collection of chemical samples prone to contamination
- A 400m cast of the stainless steel rosette allowed high-resolution collection of biological parameters, and some additional large volume sampling for chemical measurements.
- Coring, with the megacorer (Leg 1) or box corer (Leg 2) allowed for sediment recovery
- The VMP was deployed once or twice during rosette change-overs to assess ocean mixing state

At the three superstations (3, 6, 11) additional deployments were made as follows:

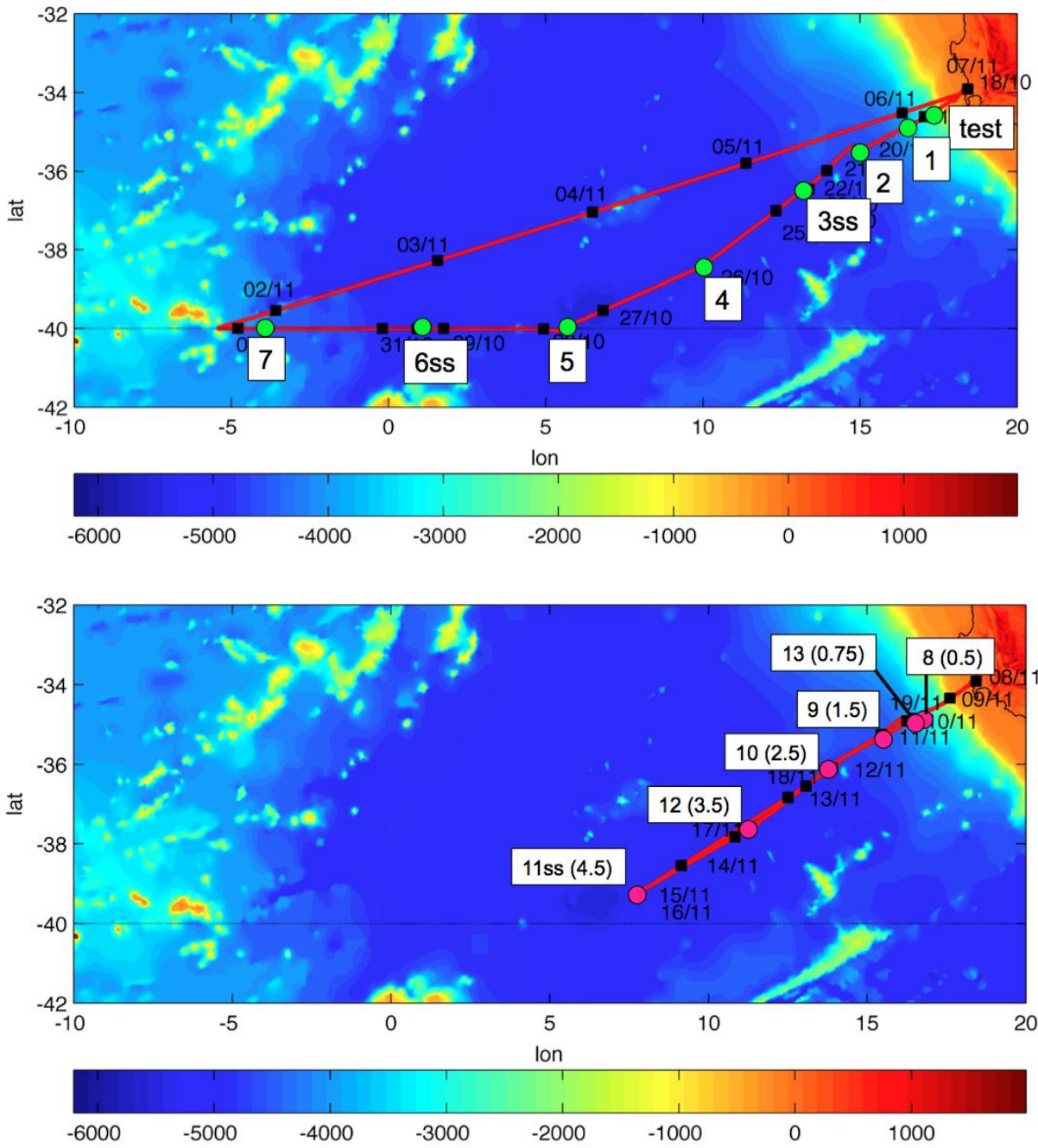
- Stand Alone Pumps (SAPs) were deployed in pairs, with up to four pairs at a time, to collect particulates from large volumes of seawater and radionuclides on Mn cartridges. In each pair, one SAP was used for trace metal analysis (with Supor filters), and the other for <sup>234</sup>Th (glass fibre 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

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

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 1:** Station locations





**Figure 1:** Cruise tracks for Leg 1 (upper) and Leg 2 (lower) superimposed on GEBCO bathymetry in metres. Dates are midnight start of day. Station locations and numbers are shown in white boxes.

## DEPLOYED EQUIPMENT: SUCCESSES AND PROBLEMS

This section presents a brief overview of the equipment deployed during D357. Further details of much of this equipment is provided in the NMFSS Technical Cruise Report as Appendix D.

### Winch

Problems controlling the winch used for all starboard side-deployments had developed during the preceding cruise and continued to a lesser extent during D357. Loss of winch power on one station occurred with equipment overboard which was a concern, but the winch was repaired after some hours. In total winch problems cost about 10 hours of ship time.

### 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.

Two minor problems with these deployments were encountered. First, this rosette typically suffered at least 1 bottle per cast that failed to shut completely so it appears critical to cock bottles carefully and that first entry to the water is clean. Second, on one cast (at Station 3), the cable became tangled due to bouncing of the package in high sea-state and required re-termination.

### 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 D357 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.

This plasma-rope approach was generally successful, and was aided by deploying the clean Ti rosette after deployment of the stainless-steel rosette. The latter was deployed on conducting steel cable so provided full information about water-column conditions before the Ti rosette was used.

Two problems were encountered with the plasma-rope approach to deployment, however. The first, and more significant, was that the rope is slightly buoyant so, as depth of deployment increases, the apparent weight of the package decreases. This limited the rate at which the package could be winched, particularly in deep water and particularly as sea-state worsened. This buoyancy problem should be improved before any future cruise that plans such a deployment strategy by addition of more weight to the package.

The second problem was that the Seabird SeaRam pressure trigger failed on three occasions to fire the bottles. The first of these was identified as operator error during the learning process of working with new equipment. The other two occurrences seemed to be due to a faulty unit and this unit was retired from further use on the cruise. This unit should be sent back to Seabird for repair.

### Kevlar rope and dedicated winch

As a back-up to the plasma-rope deployment, 8km of Kevlar rope was purchased with UK-GEOTRACES funds with the plan to spool this on an existing NMF deck winch that was refurbished for the task. Sadly, the diameter of the Kevlar rope was slightly too large (though

within the manufacturers tolerance and the rope could not be spooled neatly . This deployment approach was not used during the cruise.

### Coring

During Leg 1, coring was performed with the NMF megacorer deployed on the plasma-rope. This was very successful with all deployments recovering at least some full tubes.

Unfortunately, the megacorer was unloaded during the mid-cruise port-call in Cape Town to be airfreighted to another cruise. For Leg 2, an NMF box core was used instead. Initial attempts to deploy this failed and the corer returned to the surface untripped. This was caused by the fact that the buoyancy of the plasma rope continued to apply upward force to the trigger mechanism even when the corer hit the sea-floor. To solve this problem, a weight was strapped to the plasma rope above the corer on subsequent deployments. This was time-consuming, but allowed collection of good box cores in the latter stages of Leg 2.

### Stand Alone Pumps

Up to 8 of these were deployed at a time, hung on the CTD cable. This proved successful, although a number of pumps needed to be removed from the ship at the mid-cruise port-call.

### Velocity Microstructure Profiler

Microstructure measurements were made using a Rockland Scientific International manufactured **Velocity Microstructure Profiler** (VMP750) provided by NOC. Full details are provided in the relevant section under WP6 below.

### Summary of lost time during the cruise due to equipment and other problems

Late departure from Cape Town	24 hours
Ship engine loss:	probably minimal
Ship motor and steering control:	24 hours
Winch failure and testing:	10 hours
SeaRam failure to close bottles:	18 hours
High sea state (inability to deploy at Station 3):	28 hours
High sea state (slow deployment on plasma cable):	10 hours
Failure of box corer due to plasma-rope buoyancy:	8 hours
Medical evacuation:	7 days, 11 hours
<b>TOTAL:</b>	<b>12 days, 13 hours</b>

Estimate of time required to get back to point of medi-vac to restart science in initial plan 7 days

Lost time with respect to initial plan 19 days 13 hours

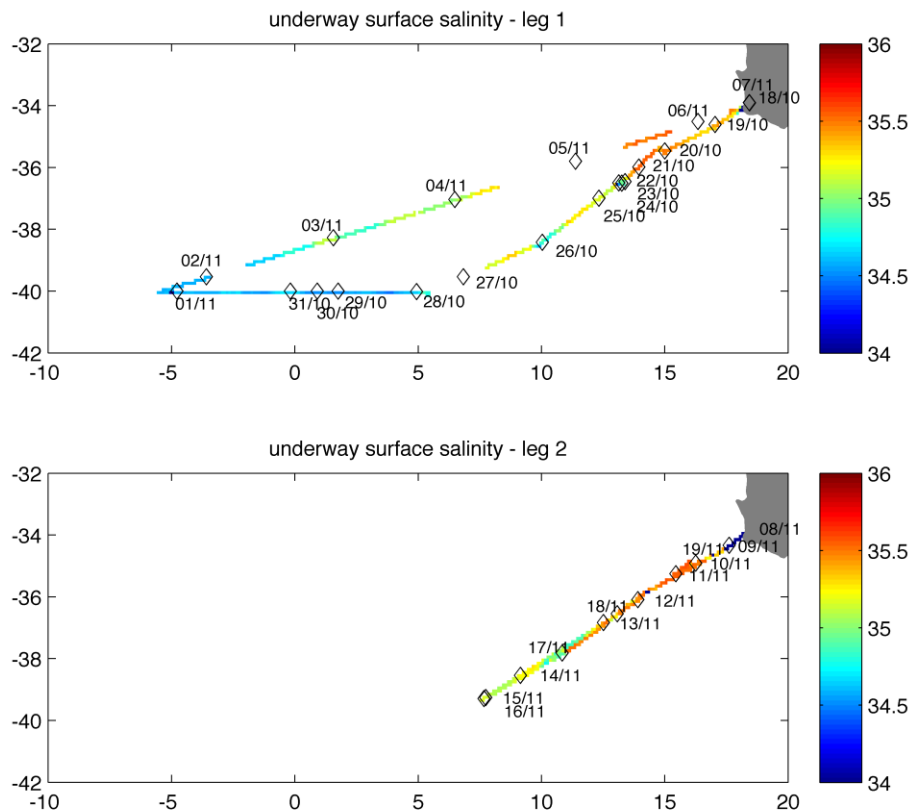
Compared to a contingency for delay in the cruise plan of 5 days

## UNDERWAY DATA OVERVIEW

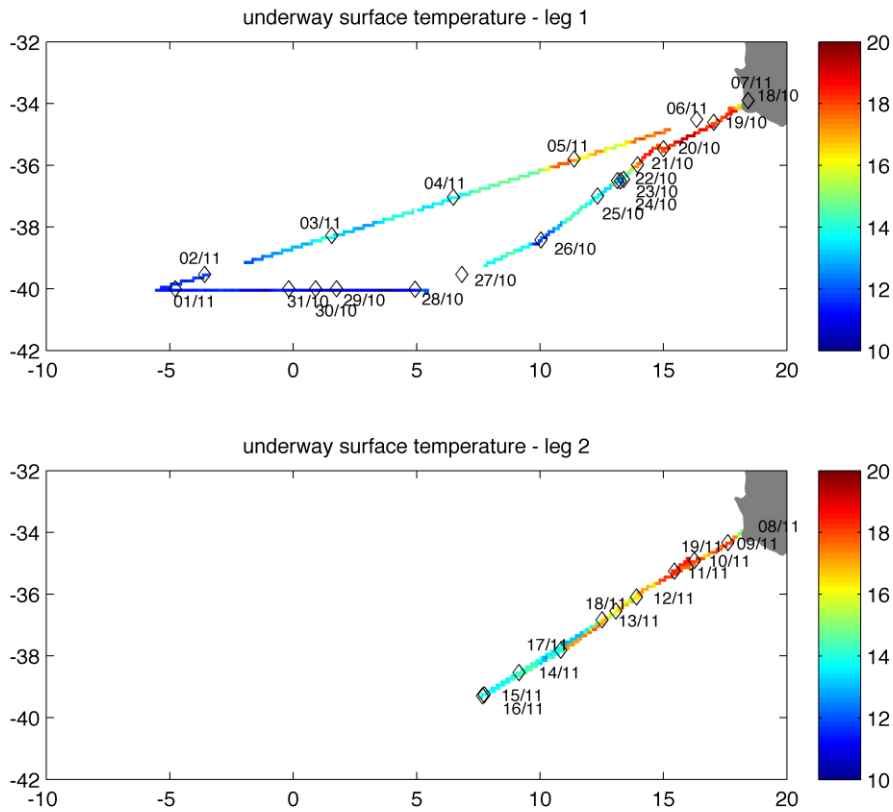
Full plots of underway temperature, salinity, fluorescence, transmittance, meteorology and navigation data are provided in Appendix B, with details of the equipment used to collect the data in Appendix C.

Underway ADCP and bathymetry data is presented with other LADCP data in “Other Research”.

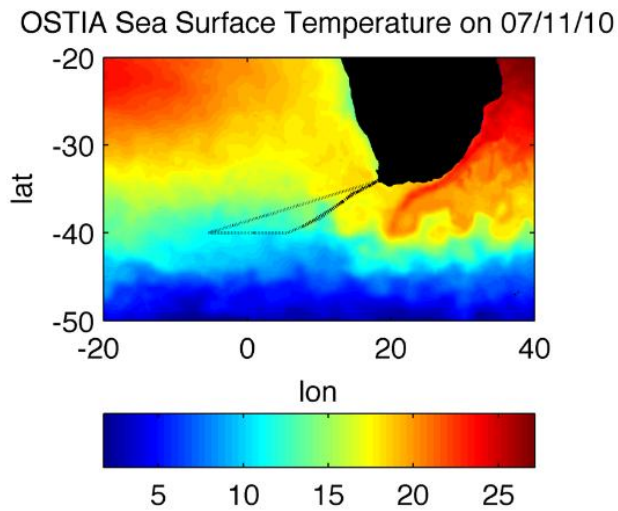
Summary figures of sea-surface salinity, temperature, fluorescence and transmittance are given in this section as back ground for the chemical data that follows.



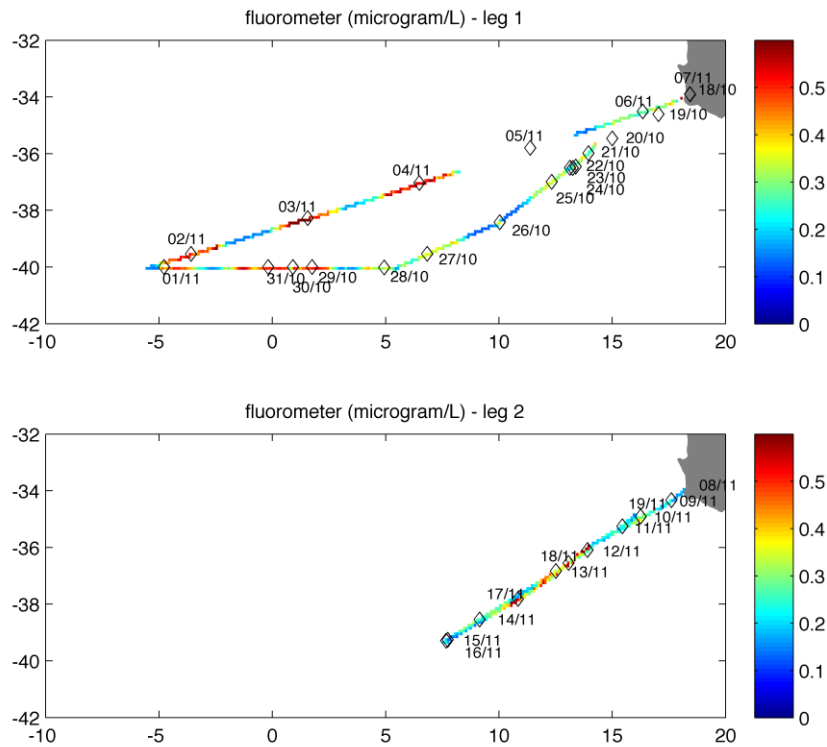
**Figure 2:** Seabird underway near-surface salinity for the two legs. The inlet is situated on the underside of the hull, close to the bow, at 5-6 meters depth. Locations at Midnight start of day are indicated.



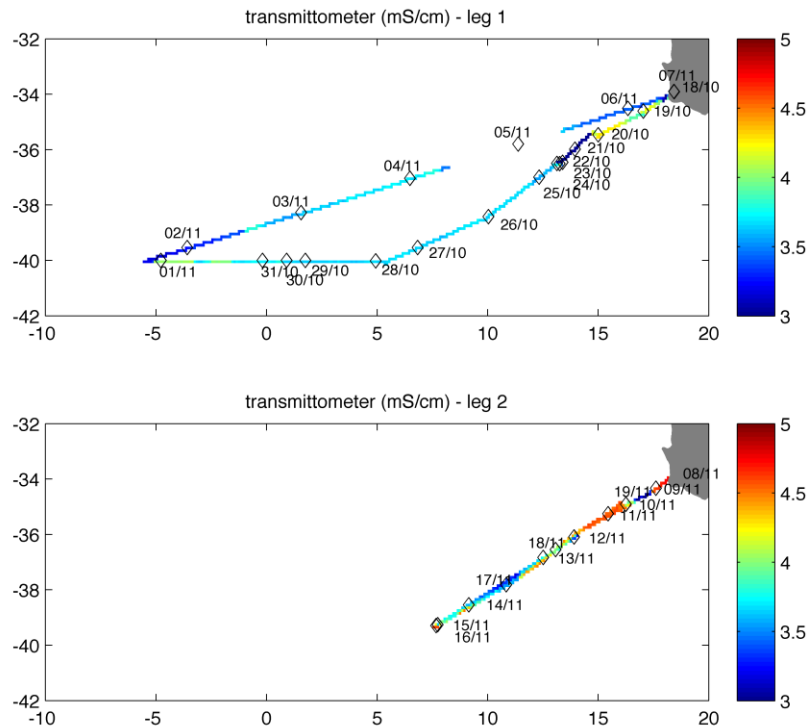
**Figure 3:** Seabird underway near-surface temperature for the two legs. The inlet is situated on the underside of the hull, close to the bow, at 5-6 meters depth. Locations at Midnight start of day are indicated.



**Figure 4:** OSTIA Sea Surface Temperature on 07/11/2010 and the associated error, with the ship track for the duration of the cruise overlaid.



**Figure 5:** Seabird underway near-surface fluorescence for the two legs. The inlet is situated on the underside of the hull, close to the bow, at 5-6 meters depth. Locations at Midnight start of day are indicated.



**Figure 6:** Seabird underway near-surface transmittance (5 minutes low pass filtered) for the two legs. The inlet is situated on the underside of the hull, close to the bow, at 5-6 meters depth. Locations at Midnight start of day are indicated.

# UK-GEOTRACES Consortium

## Ocean Micronutrient Cycles

# WORKPACKAGE 1: MICRONUTRIENT MEASUREMENTS IN DISSOLVED AND PARTICULATE CYCLES

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## DISSOLVED, TOTAL DISSOLVABLE, SOLUBLE, AND COLLOIDAL METALS

By Bronwyn Wake and Marten Klunder

### Introduction

Iron is a critical nutrient for the primary productivity in the ocean. Due to its low solubility iron can be a limiting factor for the growth of phytoplankton in the open ocean as well as in coastal seas (de Baar et al., 1990; Hutchins and Bruland, 1998; Martin and Fitzwater, 1988). There is an increasing interest in resolving the distribution and transport pathways of iron and other micronutrients, such as zinc, cadmium and nickel, into the oceans. Over the past few years it became evident that the atmosphere (Duce and Tindale, 1991), rivers (De Baar and de Jong, 2001), hydrothermal activity (Tagliabue et al., 2010 ; Klunder et al.,2010) and advection of shelf derived sediment to the open ocean (Bucciarelli et al., 2001; Lam and Bishop, 2008) are significant transport pathways for these elements to the ocean. Moreover, in the deep ocean, organic complexation and the distribution over different size fractions determines precipitation and adsorption on particles (Thuroczy et al., 2010). High resolution transects and increasing comparison with other chemical and physical parameters, determination of Fe in different size classes and insight in organic complexation enable scientists to better constrain the distribution and the sources, sinks and biological availability of micronutrients in the Ocean.

### Sampling

#### Sample analysis

Samples to be analysed by:

Total dissolvable metals – University of Southampton, person responsible – Eric Achterberg ([eric@noc.soton.ac.uk](mailto:eric@noc.soton.ac.uk))

Dissolved Fe – University of Southampton

Dissolved Al – University of Southampton

Dissolved Zn and Co – University of Plymouth, person responsible – Maeve Lohan ([maeve.lohan@plymouth.ac.uk](mailto:maeve.lohan@plymouth.ac.uk))

Other dissolved metals – University of Southampton

Soluble and colloidal Fe – University of Southampton

### Sampling protocol

Samples were collected from the titanium rosette, which was fitted with trace metal clean 10L OTE (Ocean Technology Equipment) sampling bottles with external springs, modified for trace metal work. The trace metal clean OTE sample bottles were then transferred to a clean van on the back deck for sample processing. Total dissolvable metals were sampled after nutrients and salinity (both unfiltered). All dissolved metals were sampled after filtration through a 0.2 µm Supor Acropak (Pall Corp.), under compressed air pressure. Soluble Fe was further filtered, in the clean analytical van, through 1000kDa hollow fibre filters. Most samples were acidified to 0.024 M H<sup>+</sup> (pH~1.7) with UpA HCl (Romil, Cambridge, UK). Samples for shipboard analysis of dissolved Fe and Al (125 ml) were acidified to 0.012 M H<sup>+</sup> (pH~2, >24 hrs before analysis).

Samples were also collected from the towed fish (~3 m depth, portside). Surface seawater was pumped into the clean van using a teflon diaphragm pump connected to clean oil free compressed air compressor and samples collected whilst the ship was in transit. Filtered samples were filtered and acidified as stated above.



## **Samples collected**

Samples were collected as follows:

Total dissolvable metals – 125 ml unfiltered

Stations – 6

Samples – 130, including 2 replicate samples

Fish – 12

Dissolved Fe and Al (shipboard) – 125 ml

Stations – 11, plus samples collected at the reoccupation of station 1 and station 3

Samples – 271, including 26 replicate depth samples, excluding reoccupation station

Reoccupation samples – 23, including 2 replicate depth samples at station 1; 2x22 at station 3, one set of samples each for University of Southampton and LEMAR, Brest (intercomparison station with BGH cruise, 2008)

Fish – 60

Dissolved Zn and Co – 125 ml and 60 ml

Stations – 11 plus samples collected at the reoccupation of station 1

Samples – 247, including 3 replicate depth samples, excluding reoccupation station

Reoccupation samples – 23, including 2 replicate depth samples

Fish – 117

Other dissolved metals – 250 ml

Stations – 11 plus samples collected at the reoccupation of station 1

Samples – 247, including 3 replicate depth samples, excluding reoccupation station

Reoccupation samples – 23, including 2 replicate depth samples

Fish – 62

Soluble and colloidal Fe – 250 ml (final volume after ultrafiltration 125 ml)

Stations – 3 plus samples collected at the reoccupation of station 3

Samples – 20, excluding reoccupation station

Reoccupation samples - 6

## **Analysis**

### **Dissolved Fe**

Dissolved Fe ( $<0.2 \mu\text{m}$ ) was measured by flow injection analysis and chemiluminescence detection modified from Obata et al., (1993) and de Jong et al. (1998) as described in Klunder et al. (2010). The chemiluminescence detection follows after pre-concentration on a AF-650M Toyopearl column. The value was corrected for the addition of peroxide by double spiking a SW sample with peroxide. The difference was used as peroxide blank (0.0096 +/- 0.012 nM). The manifold/MQ blank was determined by five times the signal of zero seconds loading and was 0.023 +/- 0.021 nM.

To validate the results, the international standard reference water samples (SAFe and GS) were measured. To ensure an equal pH in the SAFe (acidified to  $\text{H}^+$  0.024 M) as in the samples, 280  $\mu\text{l}$  of a 2 M  $\text{NH}_4\text{Ac}$  buffer was added to the SAFe standard waters. The concentrations found were: 0.10 +/- 0.03 nM (n=3) for SAFe S -12; 0.92 nM for SAFe D2 -502 and 0.46 nM for GS 146. To correct for Fe in the buffer added, buffer was spiked in MQ and the difference with a non-spiked MQ sample was considered buffer blank, this was 0.004 +/- 0.004 nM (n=4).

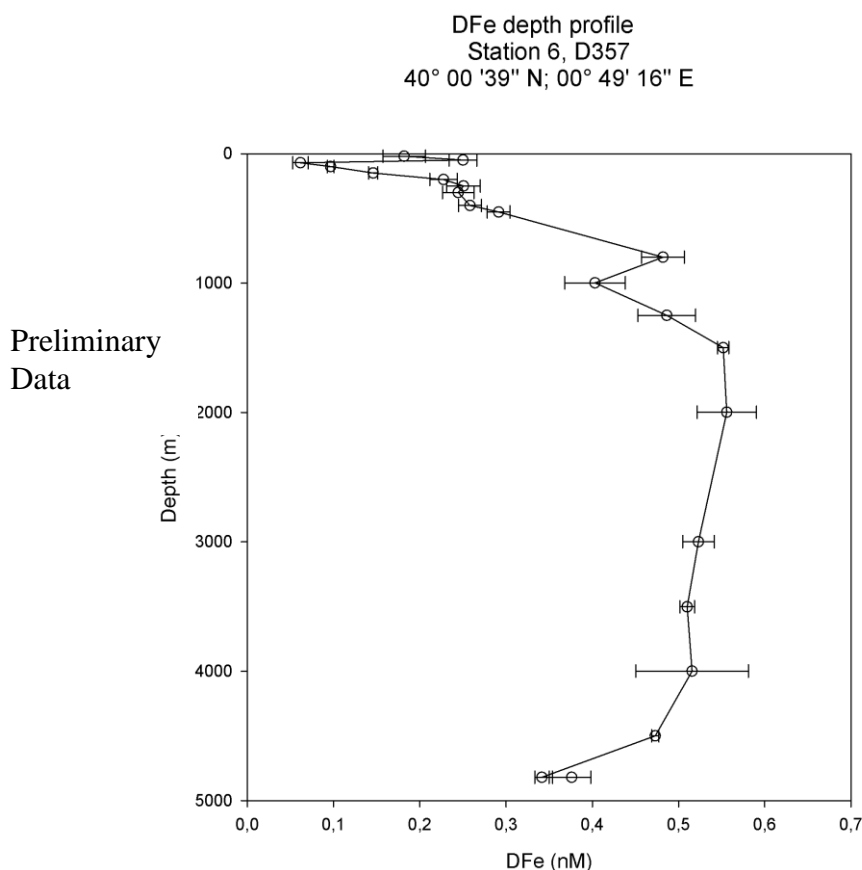
### **Soluble Fe**

Samples for Fe-Soluble were filtered on-board according to the following protocol (Nishioka et al., 2001; Thuroczy et al., 2010). Tubing was acid rinsed for 30 min before starting, using 0.024 M  $\text{HNO}_3$ . Then the hollow fibre filters were placed in the tubing and rinsed with MQ (~210 ml). After rinsing, 250 ml bottle of Seawater (sample) was introduced. The first 125 ml is to rinse the filter and was thrown away. After that, Fe soluble sample was filtered, depending on the filter filtrate volume is 80 -125 ml. After the sample filtration, filter was MQ rinsed again before the new sample was introduced. After the last sample, tubing was MQ rinsed (~210 ml). Per filter 2-3 samples were filtered.

Samples are acidified with 125  $\mu\text{l}$  of UpA HCl in 125 ml, final  $\text{H}^+$  concentration of 0.012 M. If the sample is not 125 ml, acidification is done by comparison with MQ in a similar bottle. Sample bottles are stored in the grey crates to be transported back to NOCS. Samples will be analysed by Fe FIA as described above.

## Preliminary results

During the cruise samples from the first occupation of the transect (Station 1-6) and 23 surface samples obtained by towed fish were measured.



**Figure 7:** Preliminary depth profile of dissolved Fe (+/- st. dev), indicative of the shipboard results.

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# PARTICULATE METALS

By Angela Milne

Samples will be analysed by Maeve Lohan and Angela Milne at the University of Plymouth, SoGEES, Portland Square, Plymouth, PL4 8AA.

**Objectives:** 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, 2005). 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 protocol:** 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.

**Samples collected:** Particulates from OTE bottles: a total of 259 samples were collected from 12 stations spanning the whole water column from 5 m to approximately 5200 m. The amount of

samples collected at each station varied between 12 and 24, this variation was either due to bottom depth, water budget requirements or the necessity to soak replacement OTE bottles before use.

At station 1 a partial (12 samples) and full (23 samples) water column profiles were collected. Time restraints on the first occupation of the station prevented particulates from being collected from the entire profile. Re-occupation of the station three weeks later allowed for the collection of samples from the full water column. As a consequence there are some duplicate samples from the upper water column though these were collected three weeks apart. Full profiles were collected from stations 2 (24 samples), 3 (21 samples), 4 (23 samples), 5 (24 samples), 6 (24 samples), 8 (12 samples), 9 (24 samples), 10 (24 samples), 11 (24 samples) and 12 (24 samples).

On recovery of the loaded filters after filtration, it was discovered that the silicone o-ring was not fully secured over 4 of the particulate filter samples. These samples were 382 (station 6), 482 (station 1 re-occupied), 622 (station 10) and 895 (station 8 re-occupied). The volume of water passed over the filter for these samples will potentially be compromised.

Particulates from SAPS: a total of 25 samples were collected from varying depths at station 1 (4 samples), station 3 (8 samples), station 6 (8 samples) and station 11 (5 samples). In addition, a small sub-sample for RNA analyses from each PES filter was taken.

**Sample 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<sub>3</sub> & 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<sub>3</sub> added, the dry down procedure is then repeated. The residue is brought back into solution with 5 % HNO<sub>3</sub> 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. M. Saito.

# METAL SPECIATION AND LIGANDS

By Angela Milne

Samples will be analysed by Maeve Lohan and Angela Milne at the University of Plymouth, SoGEES, Portland Square, Plymouth, PL4 8AA.

**Objectives:** Understanding the biogeochemistry of Fe, Zn and Co requires the ability to measure their oceanic chemical speciation. Fe, Zn and Co are 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 these three micronutrients 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 protocol:** 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  $\mu\text{m}$  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  $\mu\text{m}$ ) 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. LDPE (250 mL) bottles were used for Fe speciation whereas FPE (500 mL) bottles were used for Zn/Co speciation.

Eight OTE bottles could be pressurised and sampled at one time. Filtration of all twenty-four bottles was completed in approximately nine hours. All samples collected were stored unacidified at  $-20^{\circ}\text{C}$  within nine hours of sampling until analysis.

**Samples collected:** Speciation samples were only collected at the 4 super-stations. For Fe speciation, a total of 49 samples were collected spanning the full water column; station 3 (14 samples), station 6 (14 samples), station 11 (14 samples) and station 8 (re-occupied, 7 samples). The sampling protocol above was followed for all samples.

For Zn/Co speciation, a total of 44 samples were collected spanning the full water column; station 3 (12 samples), station 6 (12 samples), station 11 (12 samples) and station 8 (re-occupied, 7 samples). The sampling protocol above was followed for all samples.

**Sample analysis:** Frozen samples will be thawed and analysed in their respective shore based laboratories. The concentrations and conditional stability of Fe ligands, Fe' (soluble inorganic Fe) and free aqueous Fe will be measured at NOCS by competitive ligand exchange cathodic stripping voltammetry (CLE-CSV) with the ligand TAC (Croot and Johansson, 2000). Concentrations and conditional stability of Zn and Co ligands, Zn' and Co' (soluble inorganic Zn and Co) and free aqueous Zn and Co will be measured at the University of Plymouth using CLECSV with the ligand APDC (Lohan et al., 2005) for Zn and DMG (Saito & Moffett, 2001) for Co. All samples will hopefully be analysed by the end of March 2012.

## WORKPACKAGE 2: AEROSOL SOURCES

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### AEROSOL AND RAIN SAMPLING

By Dr Rosie Chance

Laboratory for Global Marine and Atmospheric Chemistry, School of Environmental Sciences, University of East Anglia, Norwich, NR4 7TJ, UK, email: r.chance@uea.ac.uk

#### **Samples to be analysed by**

- Rosie Chance (aerosol and rain - trace metals and major ions)
- Dominik Weiss (Pb, Nd, Zn and Cd aerosol isotopic signatures) *Imperial College, London*
- Kate Hendry (Si aerosol isotopic signatures) *Woods Hole Oceanographic Institution (via University of Oxford)*
- Maite Hernandez (aerosol organic biomarkers) *University of Bristol, email: maite.hernandezsanchez@bristol.ac.uk*
- Alexander Smirnov (aerosol optical depth) *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*

#### **Objectives**

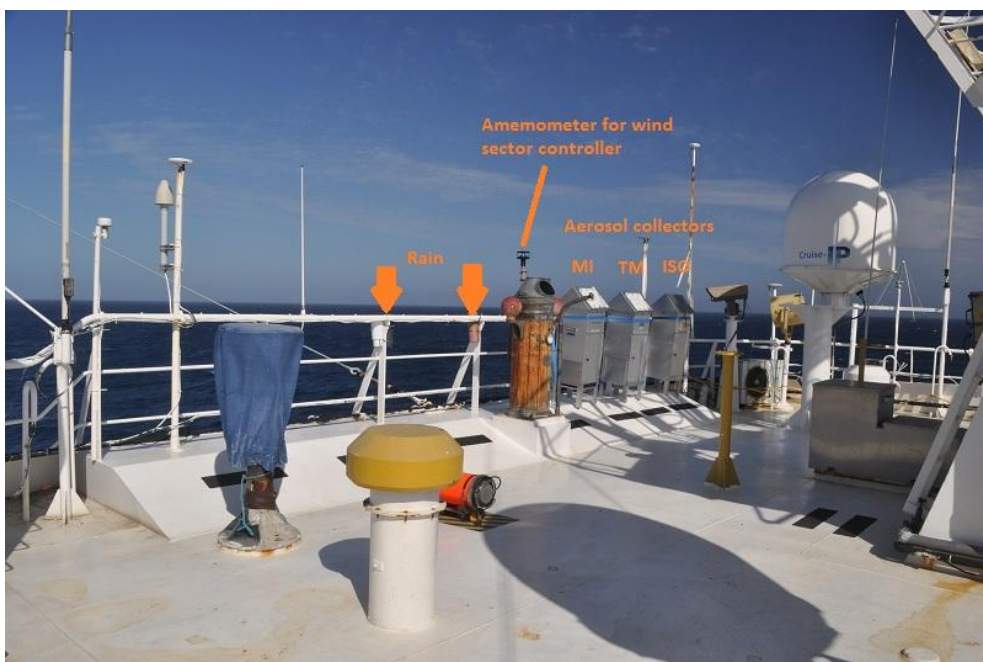
- To collect size segregated atmospheric aerosol samples for the determination of trace metals (TM) and major ion (MI) concentrations.
- To collect bulk atmospheric aerosol for determination of isotope signatures (ISO) and organic biomarkers .
- To collect rain samples for determination of trace metal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

#### **Sampling protocol**

Aerosol: Three high volume aerosol collectors (Andersen) were mounted on the monkey island deck of the ship (figure 1). Each sampler was used for a different set of samples (i.e. TM, MI or ISO). To avoid sampling contaminated air from the ships chimney, power supply to the motors was automatically controlled such that sampling only took place when the relative wind direction was between -45 and 135 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  $1 \text{ m}^3 \text{ min}^{-1}$ . Aerosol for TM and MI determination were sampled using a two stage Sierra-type cascade impactor (aerodynamic diameter cut offs of  $\sim 2.4$  and  $\sim 1.6 \text{ }\mu\text{m}$ ) 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 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  $\sim 48$  hours (TM and MI) or  $\sim 96$  hours (ISO) such that the ISO samples 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  $-20^\circ\text{C}$  for return to the UK. Twice during the cruise, TM and MI samples were collected using a six stage impactor deployed for 96 hours. The following blanks were collected for each sample type: Filter blank; Cassette blank; Exposure 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<sub>3</sub> 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 at the front of the monkey island deck during rain events (see figure 1 for locations). Following collection, TM samples were acidified using conc. HNO<sub>3</sub> 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 up to three times a day, where absence of cloud cover allowed.



**Figure 8.** Location of aerosol and rain sampling equipment on monkey deck of RRS Discovery during cruise D357.

### Samples collected

*Aerosol:* 15 sets of samples were collected for TM and MI and 10 samples were collected for isotopes. This includes four blanks for each sample type. Unfortunately, at least some of the isotope samples are thought to have become contaminated.

*Rain:* rain events were rare and, when occurring, very light and/or short lived. Only four small (<20 mL) sets of rain samples were collected from rain events on 22/10, 30/10, 8/11 and 19/11/10. Blanks for each sample type were also collected.

*Aerosol optical depth:* A total of 197 readings were made during the cruise.

### Sample analysis

Aerosol samples will be extracted into ultrapure water and the extracts analysed for soluble TM and MI as described below. Rain samples will be analysed by the same methods. Analysis is expected to take place between summer 2011 and March 2012.

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	INAA



*whole filter analysed rather than extract	
Cl <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> , oxalate, Br <sup>-</sup> , plus possibly MSA, formate, acetate	Ion chromatography
NH <sub>4</sub> <sup>+</sup>	Autoanalyser
PO <sub>4</sub> <sup>3-</sup>	Spectrophotometry
Total soluble N	High temp catalytic oxidation
<input type="checkbox"/> <sup>15</sup> N of NO <sub>3</sub> <sup>-</sup> and NH <sub>4</sub> <sup>+</sup>	IRMS

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

Aerosol optical depth data was downloaded from the instrument at regular intervals and emailed to Alexander Smirnov for quality control and processing.

### **Preliminary results**

No aerosol or rain results are available at this time. Aerosol optical depth data from the cruise is available at [http://aeronet.gsfc.nasa.gov/new\\_web/maritime\\_aerosol\\_network.html](http://aeronet.gsfc.nasa.gov/new_web/maritime_aerosol_network.html)

## WORKPACKAGE 3: **SEDIMENT FLUXES**

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### SEDIMENT FLUXES

By William Homoky

Samples to be analysed by: William Homoky (Southampton); Maite Hernandez-Sanchez (Bristol); Alan Hsieh (Oxford); Alex Thomas (Oxford)

#### **Rationale**

Marine sediment is perhaps the largest physical interface with the oceans, yet the exchange of micronutrients from marine sediments to seawater is scarcely quantified. In the previous decade we have learned shelf-sediments are important vectors for micronutrient transport (in particular Fe) to the ocean margins (Elrod et al., 2004). More recently, water column measurements from within 100 m of the seafloor in the Weddell Basin have also indicated 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 pore-fluids (Homoky et al., submitted). However, the magnitude of Fe fluxes in the South Atlantic from ocean margin and deep-ocean sediments have not been assessed, and the fluxes of other micronutrients 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 pore-fluid samples for analyses of dissolved trace metals, macro-nutrients, labile particulate phases and oxygen, 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 with the 40°S transect: [1] the South African margin, [2] the Cape Basin [3] volcanogenic (Gough) Island sediments [4] the Mid-Ocean Ridge, [5] the Argentine Basin and [6] the River Plata-dominated Argentine/Uruguayan shelf.

#### **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 is outlined below in a later section - See Organic Biomarkers, Pa/Th, Ra, and Si isotopes in later section *Palaeoproxy calibration*.

#### **Coring and Sample Recovery**

##### **Coring overview**

Sediment samples were successfully recovered from 7 Stations, which represent 2 of the 6 intended regions along the GTA10 transect, the South African Margin, and the Cape Basin.

Two types of coring apparatus were used to collect sediments on D357, the Bowers Connelly Mega Core and the Box Core. The Mega core was successfully deployed 4 times using 8 core tubes prior to the Discovery's return to Cape Town: at one test station on the Cape shelf (Station 0, 236m), once on the Shelf slope (Station 1, 2602m), and at both Cape Basin Super Stations (Stations 3 and 6, 4900-5000m). Single deployments of the Megacore were sufficient to obtain enough sediment to meet our sampling objectives. Sample recoveries ranged from 6-8 cores per

deployment, typically ~ 30% of recovered cores showed signs of slight physical disturbance - indicated by either turbid overlying core water, or visible mixing of air during surface handling of the corer.

Due to changes to shipping times of shared coring and sampling apparatus, between D357 and the upcoming JC55 cruise, the Mega Core was replaced by the Box Core for the second leg of D357. The Box core was used for 3 successful recoveries: One from another Cape Basin Super station (Station 11) at 5269 m, and two from the Cape Shelf slope, Station 8 (reoccupation) at 733 m, and Station 13 at 1183 m, where sediment is likely to directly underlie an oxygen minimum zone (OMZ), and thus provide optimum conditions for Fe(II) release from shelf sediments (Lohan and Bruland, 2008; Severmann et al., 2010).

An initial Box core deployment at Station 7 (~4500m) was unsuccessful, and later shown to result from the ~200 kg upward force of the buoyant Plasma Rope used for trace metal clean deployments on this cruise that applied upward pressure to the release mechanism of the Box core and inhibited its functionality. A successful recovery from Station 11 (5269m) was achieved by the addition of ~170kg weight to the plasma rope ~ 30m above the box core, using a siemens splice knot and protective sheath's around the plasma line. The modification added ~1.5 hours to the total deployment and recovery time of the Box core. The Station 8 (733 m) deployment was successful without the addition of weight to the plasma rope, while the Station 13 (1183 m) deployment failed to trigger without the additional weight.

### **Photo log of recovered cores**

See Electronic Annex for a photographic record of coring activities on D357.

### **Sampling protocol**

Mega core samples were removed from the coring frame and immediately transferred to the Constant Temperature (CT) laboratory set close to bottom water temperatures.

For O<sub>2</sub> analyses, a 25 cm long 6.5 cm i.d. core tube was inserted into the megacore tube and stopped by a neoprene bung, prior to extruding the mega core using the NOCS extrusion kit. The sub-sampled core was then stopped at its base, wiped clean and transferred to the Unisense microelectrode suite for O<sub>2</sub> profiling of the sediment surface (See Sample analysis below for further details).

### *Centrifugation and Filtration*

For porewater dissolved/colloidal metals and nutrients, a mega core tube followed the same extrusion procedure as for O<sub>2</sub>, using a 35cm core tube to optimise sample depth and still remain a manageable size to fit through the air lock entrance of the table mounted glove bag. The glove bag was pre-purged with Zero grade N<sub>2</sub> gas, brought into the CT lab via a 1/4" o.d. copper line, and 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 table mounted extruder. Excess overlying core water was siphoned to waste. The core was then 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. Sediment was transferred directly to 125 ml acid cleaned polycarbonate centrifuge tubes. Sealed centrifuge tubes were transferred to a gimbaled centrifuge at 4°C and spun for 6 minutes at 10,000rpm.

Spun sediments were returned to a disposable Cole Palmer glove Bag in the CT lab, and re-opened under a nitrogen atmosphere. Supernatant porewater was separated from the sediment using a teflon tube attached to an acid cleaned 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 1st ml to waste and the remaining sample into 8 ml HCl clean LDPE sample pots for trace metals. An aliquot was also transferred to 30 ml HDPE pots for shipboard nutrient analyses by Malcolm Woodward. Lastly, where porewater volume permitted, an additional filter was added inline to the Puradisc for separation of the colloidal fraction of metals in the porewater. Either a

disposable Whatman Anotop 0.02  $\mu\text{m}$  25 mm Aluminium oxide filter, or a Whatman Nucleopore (track-etched polycarbonate) 0.015  $\mu\text{m}$  25 mm membrane in reusable filter housings was used for this purpose. Anaotop filters allowed for larger volumes to easily be passed through the membrane (1-7 ml), whereas Nucleopore membranes (max 1-2 ml sample) could be removed from their housings and preserved frozen for shore based analyses of any colloidal fractions.

All trace metal samples (filtered and double filtered), were acidified using Sigma Aldrich Trace Select concentrated HCl, diluted with Milli-Q to 6M, and added to the sample in the ratio 6  $\mu\text{l}$  HCl to 1 ml sample to achieve a pH of  $\sim 1.7$ . All metal samples were stored cold and transported back to the UK for analyses.

Sediment residue was removed from centrifuge tubes, double bagged and refrigerated for transport back to the UK, for shared analyses of total solid phase metal compositions, TIC and TOC, reactive Fe concentrations (Homoky), Pa/Th (Thomas), Ra (Hsieh) and Si(Hendrey).

#### *Rhizon Filtration*

An alternative method for extracting porewaters was necessary for sampling from Box cored sediments due to the early shipping of the Glove bag and gimbaled centrifuge from D357. 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), although they are not widely used in comparison to centrifugation techniques.

Polycarbonate core tubes of 6.5 cm i.d,  $\sim 35$  cm long, were pre-drilled at 1cm intervals along their length to allow for the insertion of 50mm 0.2  $\mu\text{m}$  rhizon samplers. Drill holes were sealed with electrical tape, prior to sub-sampling from the box-core. The sub-sampled cores were brought directly to the CT lab, and mounted in a tabletop core stand. The electrical tape was then perforated, using a small pipette tip, and the rhizons inserted at 1 cm depth intervals at 0-6 cmbsf, and 2, 3 or 4 cm intervals below 6 cmbsf. All rhizons had been pre-flushed with Milli-Q. Syringes (HCl clean) were attached with Luer lock fittings to the rhizons and used to simultaneously draw porewater from the sediment core, passing the 1st ml of sample (diluted by residual Milli-Q) to waste. Between 18 ml and 3 ml of fluid was extracted after 20 minutes, at which point syringes were removed and quantitatively acidified directly in the syringe to pH 1.7 as for Centrifugation and filtration method - this is important, as Fe(II) is vulnerable to oxidative precipitation in the syringe. Samples were then transferred to sample pots and store as for the method above. Meaningful assessment of colloidal fractions cannot be achieved using the rhizon samplers unless under a nitrogen atmosphere as either a non-acidified sample may partially oxidise in the syringe prior to secondary filtration, or an acidified sample in the syringe dissolves the metal colloids prior to sampling.

A separate sub-core adjacent to that used for metals was used to extract porewaters for nutrients, following the approach above without the acidification step.

#### **Samples Collected**

In total 7 stations were sampled for sediment. Providing enough sediment for a broad range of geochemical analyses: Dissolved and colloidal porewater metals, porewater nutrients (nitrate + nitrite, phosphate and silicate), pore-water Si isotopes, solid-phase metals, reactive Fe phases, TIC and TOC, Pa/Th, Ra, organic biomarkers, and particulate organic nitrogen isotopes.

Summary tables are presented below for all samples collected from each Megacore and Box core event. Please refer to appendix for original log sheets.

Station/ Event No.	Core No.	Samples Collected	Analyst	Shipboard analysis
<b>0 (Test)</b> D357_006 (Megacore)	2	Porewater metals	Homoky	
	2	Porewater nutrients	Homoky, Woodward, Reynolds	✓
	2	Oxygen profile	Homoky	✓
	2	Solid-phase metals	Homoky	
	2	Sold-phase Pa/Th	Thomas	
	2	Solid-phase Ra	Hsieh	
	2	Solid-Phase Si isotope	Hendrey	
	8	Archive core		
	3	Biomarkers	Hernandez-Sanchez	
	3	PON	Tuerena	
<b>1</b> D357_014 (Megacore)	5	Porewater metals	Homoky	
	5	Porewater nutrients	Homoky, Woodward, Reynolds	✓
	7	Oxygen profile	Homoky	✓
	5	Solid-phase metals	Homoky	
	5	Sold-phase Pa/Th	Thomas	
	5	Solid-phase Ra	Hsieh	
	5	Solid-Phase Si isotope	Hendrey	
	8	Archive core		
	4	Biomarkers	Hernandez-Sanchez	
	4	PON	Tuerena	
<b>3</b> D357_31 (Megacore)	3	Porewater metals	Homoky	
	3	Porewater nutrients	Homoky, Woodward, Reynolds	✓
	5	Oxygen profile	Homoky	✓
	3	Solid-phase metals	Homoky	
	3	Sold-phase Pa/Th	Thomas	
	3	Solid-phase Ra	Hsieh	
	6	Solid-Phase Si isotope	Hendrey	
	4	Archive core		
	8	Biomarkers	Hernandez-Sanchez	
	8	PON	Tuerena	
6	Micrometeorites	Giebert		
<b>6</b> D357_058 (Megacore)	8	Porewater metals	Homoky	
	8	Porewater nutrients	Homoky, Woodward, Reynolds	✓
	1	Oxygen profile	Homoky	✓
	8	Solid-phase metals	Homoky	
	8	Sold-phase Pa/Th	Thomas	
	8	Solid-phase Ra	Hsieh	
	7	Solid-Phase Si isotope	Hendrey	
	7	Ra flux incubation exp.	Henderson, Giebert, Hsieh, Thomas, Homoky	
	6	Archive core		
	2	Biomarkers	Hernandez-Sanchez	
2	PON	Tuerena		
7	Micrometeorites	Giebert		

Station/ Event No.	Core No.	Samples Collected	Analyst	Shipboard analysis
<b>11</b> D357_108 (Box core)	1	Porewater metals	Homoky	
	2	Porewater nutrients	Homoky, Woodward, Reynolds	✓
	3	Oxygen profile	Homoky	✓
	1	Solid-phase metals	Homoky	
	1	Sold-phase Pa/Th	Thomas	
	1	Solid-phase Ra	Hsieh	
	BC	Solid-Phase Si isotope	Henderson, Hendrey	
	BC	Porewater Si isotope	Henderson, Hendrey	
	6	Archive core		
	4	Biomarkers	Hernandez-Sanchez	
	4	PON	Tuerena	
7	Micrometeorites	Giebert		
<b>8 (re-oc.)</b> D357_123 (Box core)	1	Porewater metals	Homoky	
	2	Porewater nutrients	Homoky, Woodward, Reynolds	✓
	3	Oxygen profile	Homoky	✓
	1	Solid-phase metals	Homoky	
	1	Sold-phase Pa/Th	Thomas	
	1	Solid-phase Ra	Hsieh	
	BC	Solid-Phase Si isotope	Hendrey	
	BC	Porewater Si isotopes	Henderson, Hendery	
	5	Archive core		
	4	Biomarkers	Hernandez-Sanchez	
	4	PON	Tuerena	
<b>13</b> D357_123 (Box core)	2	Porewater metals	Homoky	
	2	Porewater nutrients	Homoky, Woodward, Reynolds	✓
	3	Oxygen profile	Homoky	✓
	2	Solid-phase metals	Homoky	
	2	Sold-phase Pa/Th	Thomas	
	2	Solid-phase Ra	Hsieh	
	BC	Porewater Ra	Henderson, Thomas	
	BC	Porewater Si isotope	Henderson, Hendrey	
	6	Archive core		
	4	Biomarkers	Hernandez-Sanchez	
	4	PON	Tuerena	

# SHIPBOARD MEASUREMENTS

By William Homoky

WP3 has benefitted from shipboard determinations of high-resolution O<sub>2</sub> profiling of the sediment surface, in addition to porewater nutrient determinations made by Woodward and Reynolds (See WP8 for methods of nutrient analyses). Combined, these ancillary data provide a powerful means for interpreting the behavior of Fe in the porewater during early diagenesis. The method used for determination of O<sub>2</sub> by microelectrode is described below followed by a discussion of preliminary results.

## **O<sub>2</sub> profiling of surface sediment**

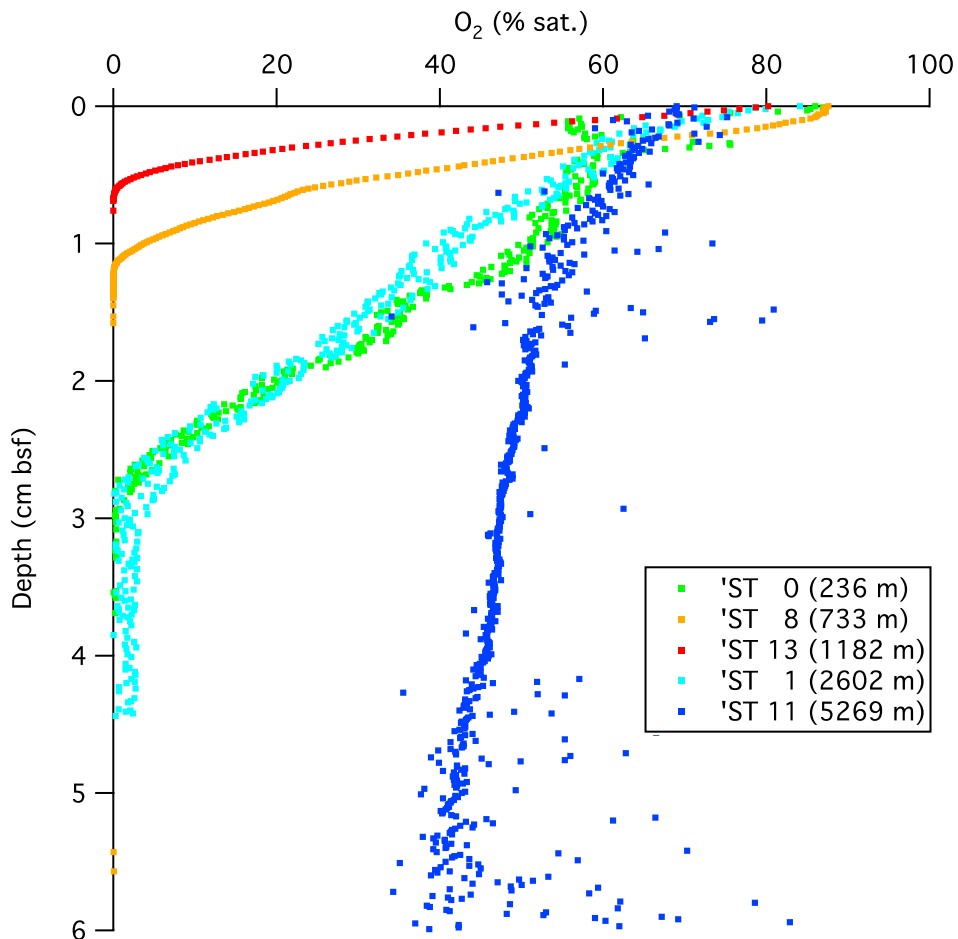
Shipboard dissolved oxygen concentration profiles were measured in surface sediments using Unisense micro-electrode equipment; including micro-sensors with 50  $\mu$ m tip diameter, M33-2 micromanipulator, LS18 lab stand, MC-232 motor drive, PA2000 Pico-ammeter, and Profix software. All analyses were conducted in a controlled temperature laboratory held between 6 and 10 °C.

Micro-sensors were calibrated using a Unisense Cal300 calibration chamber. A two point linear dissolved oxygen calibration was obtained from 100% (oxic) and 0% (anoxic) saturated solutions. Firstly the 100% oxygen saturation value was measured by placing the micro-sensor in the calibration chamber with an aerated seawater sample of comparable temperature and salinity to the sediment pore-fluids. The oxic reading was recorded in Volts following a period of stabilisation from the sensor output (typically ~1.0 V). The anoxic oxygen saturation value was then determined by passing nitrogen gas through the chamber for 5 to 10 minutes until the sensor output had decreased and stabilised to within 0.01 V. Unisense recommends a calibration is only used when the anoxic voltage reading is less than 10% of the oxic voltage reading to ensure sufficient accuracy of analyses. During this cruise anoxic readings were typically 0.005 V, ~0.5% of the oxic value.

Sediment cores were allowed to settle and re-equilibrate for ~30 minutes after sub-sampling. Oxygen profiles were recorded from ~1 mm above the sediment surface to a maximum depth of 60 mm and a sampling resolution of 100  $\mu$ m steps. Recorded oxygen saturation values will be converted to molar concentrations using Unisense conversion tables of empirically derived oxygen saturation values for the appropriate temperature and salinity of the sample, and overlying core water O<sub>2</sub> concentrations will be fitted to bottom water O<sub>2</sub> determinations by CTD cast and Winkler titration (See WP8).

## **Preliminary results**

A comparison of dissolved oxygen profiles between surface sediments from the Cape Shelf, Shelf Slope, and Cape Basin is shown in Figure 1. The shallowest oxygen penetration depths have been measured on the shelf slope at ST 13 and ST 8 respectively. Both ST 8 and ST 13 coincide with a broad oxygen minimum zone (OMZ) measured at ST 1 between 700 and 1100 m in the water column. Changes to oxygen in the water column may be linked to both Antarctic Intermediate Water (AIW) and organic carbon remineralisation at these depths.

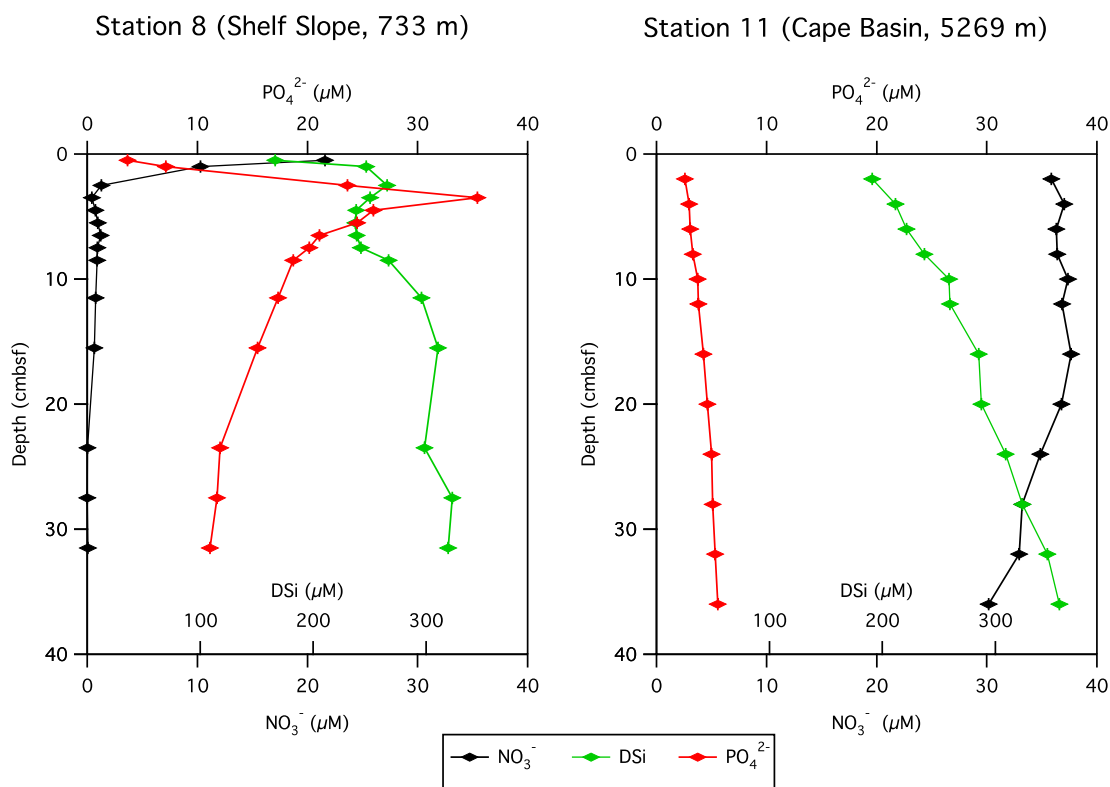


**Figure 9:** Dissolved Oxygen concentrations (percentage saturation) at 100 micron depth intervals in surface sediments from the Cape Shelf (ST 0), Shelf slope (ST 8, ST 13, ST 1), and Cape Basin (ST 11).

Oxygen penetration depths are also consistent with the sequential utilisation of oxidants during the respiration of organic carbon during early diagenesis in surface sediments (Froelich et al., 1979). The rate of  $\text{NO}_3^-$  (nitrate + nitrite) depletion in the porewater is greatest on the shelf slope (Figure 9), presumably where organic carbon supply is greatest. In the Cape Basin, the supply of organic matter to the seafloor is very slow, thus the depletion of nitrate in the porewater is minor by comparison to the shelf slope.

Phosphate dissolution and removal may also indicate a zone of Fe(II) oxidation in the surface 0-3 cmbsf, where  $\text{PO}_4^{2-}$  is strongly scavenged from the porewater by Fe(III)oxyhydroxides.





**Figure 10:** Shipboard determinations of porewater nutrients sampled by Rhizon filtration and measured by M. Woodward and S. Reynolds (See WP8), for ST 8 and ST 11.

### Implications for micronutrient fluxes from sediments

Until dissolved Fe and Mn determinations have been made in these porewaters, their behavior in these sediments is left purely to speculation, and based on the comparison of shipboard determinations for oxygen and nitrate with previous studies of benthic Fe fluxes.

Substantial Fe fluxes have previously been identified from sediments where the oxygen penetration depth lies within the bio-irrigated mixed surface-layer of the sediments (Berelson et al., 2003; Severmann et al., 2010). Sediments at ST 8 and ST 13 were characteristically homogeneous, which often the results from prevalent bioturbation, and contained segmented worm tube structures in the upper 10 cmbsf. Thus, the most probable *sedimentary* source of micronutrients identified from the D357 partial occupation of the Geotraces transect A10, is from the shelf slope sites, ST 8 and ST 13, and to a lesser extent the shelf top (ST 0) and deeper shelf slope (ST 1).

### UK GEOTRACES Nintendo Wii Frisbee Golf Rankings 2010

Disco cruise D357 was also host to the GEOTRACES 2010 Nintendo Wii Frisbee Golf Championships. Results were as follows:

1st Place:	Will Homoky	9-Hole Record: -8;	18-Hole Record: -5
2nd Place:	Robyn Tuerena:	9-Hole Record: -6;	18-Hole Record: +15
3rd Place:	Mounir Luekera:	9-Hole Record: ±0;	18-Hole Record: +12
Last place:	Alex Thomas:	9-Hole Record: +6;	18-Hole Record: +41

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## WORKPACKAGE 4: ELEMENTAL AND ISOTOPIC TRACERS OF MICRONUTRIENT SOURCE

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### 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 ( $^{223}\text{Ra}$ ,  $^{224}\text{Ra}$ ,  $^{228}\text{Ra}$ ) 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 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 ~130 L, in most cases the sample volumes were around 100L. These samples were slowly (flow rate <0.5 L/min) passed over one absorber, consisting of ~25 g  $\text{MnO}_2$  coated acrylic fiber

SAPS samples usually comprised around 300 L, pumped over  $\text{MnO}_2$  absorbers in situ. The absorbers consisted of two 10 inch wound polypropylene filter cartridges (5  $\mu\text{m}$ ) in series, each stuffed with ~25 g of  $\text{MnO}_2$  fiber inside. The sampling was combined with particulate biomarker measurements, which meant the Ra sampling took place behind a 293 mm GF/F filter.

#### 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 100 liters took 30-50 minutes. Therefore, the surface samples do not represent a single location, but an interval, and a certain variation was seen in salinities for one sample.

2) Samples from the standard CTD rosette were taken from several 20 L Niskin bottles, triggered at the same depth. Sample depths were usually 50 m and 400 m. However, the water budget did

not always allow sampling all depths, and in one case, a sample from 700m was taken to have a cross-calibration with a value for the AAIW from the French Bonus-Goodhope cruise.

A small volume sample (250mL) was taken for the independent analysis of <sup>226</sup>Ra via mass spectrometry (Hsieh).

3) Submersible pumps were used to sample the entire water column by pumping water in situ over two MnO<sub>2</sub> absorbers.

#### Determination of sample mass (1) and 2))

Sample mass was determined via a dilution approach. The salinity of each sample was measured with high precision (Autosal, ~0.001 psu standard deviation for a single sample), with an external reproducibility in the cubitainers of 0.004-0.014 psu, determined on replicate samples from the same depth (different Niskin bottles). Then, 100 mL of MilliQ water were added to each cubitainer. The samples were well mixed, and the salinity was measured again for each cubitainer, after letting the initial sample and the diluted sample equilibrate with ambient room temperature in the temperature-controlled salinity lab for ~1 day.

The mass was then calculated as

$$\frac{S_2 \cdot \text{massMQ [g]}}{(S_1 - S_2)} - 250 \text{ g}$$

S<sub>1</sub>: salinity of the sample

S<sub>2</sub>: salinity of the sample after dilution

massMQ: mass of pure water used for dilution (determined volumetrically)

250 g have to be subtracted because this volume was taken from the sample for the determination of salinity.

This method has to my best knowledge not been used before to determine the mass of large sea water samples.

The cubitainers of each sample were then processed sequentially by passing them slowly (<0.5 L/min) over ~25 g of MnO<sub>2</sub>-coated acrylic fiber (pre-washed quality from Scientific Computer Instruments) Then sample, with Ra and Ac now quantitatively adsorbed onto the fiber, was squeezed to remove most of the sea water, and then washed 3x with MilliQ. Eventually, it was squeezed until no further water could be removed mechanically. Before measuring, samples were dried somewhat further in a stream of air (either RaDeCC system, or compressed air).

#### 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 and Niskin bottle samples up to 700 m water depth, consisting of ~3100 kg sea water in total (Table 2). In addition, the approximate concentration of <sup>227</sup>Ac will be determined by means of delayed coincidence counting (Geibert et al. 2008) from these samples.

13 samples for shallow and intermediate water depth were collected with the standalone pumping systems (SAPS), see Table 3.

Station	Lat [°S]	Lon [°E]	depth [m]	mass [kg]	Sampling Date
Test	34°12.724	17°58.168	5	105.2	18/10/2010
Station 1	34°37.66	17°03.98	5	107.5	19/10/2010
Station 1	34°37.66	17°03.98	50	89.0	19/10/2010
Station 1	34°37.66	17°03.98	100	102.5	19/10/2010
Station 1	34°37.66	17°03.98	400	103.9	19/10/2010
Station 2	35°27.68	14°59.69	5	116.4	20/10/2010
Station 2	36°27.68	15°59.69	50	68.1	20/10/2010
Station 2	37°27.68	16°59.69	100	91.8	20/10/2010
Station 2	38°27.68	17°59.69	400	92.0	20/10/2010
Station 3	36°27.65	13°12.30	5	88.9	24/10/2010
Station 4	38°25.46	10°05.17	5	105.6	26/10/2010
Station 4	39°25.46	11°05.17	700	91.8	26/10/2010
Station 5	40°2.572	5°31.482	5	94.5	27/10/2010
Station 5	41°2.572	6°31.482	50	75.1	27/10/2010
Station 5	42°2.572	7°31.482	400	99.7	27/10/2010
Station 6	39°59.66	00°51.25	5	95.5	30/10/2010
Station 7	39°59.69	4°53.53	5	104.3	01/11/2010
Station 8	34°19.82	17°37.02	5	91.3	09/11/2010
Station 9	34°54.21	16°04.49	5	87.8	10/11/2010
Station 9	34°54.21	16°04.49	50	89.5	10/11/2010
Station 9	34°54.21	16°04.49	400	78.6	10/11/2010
Station 3 (2)	36°27.07	13°13.03	400	77.1	10/11/2010
Station 11	39°15.42	7°43.69	5	~105	15/11/2010
Station 11	39°15.42	7°43.69	400	~105	15/11/2010
Station 10 (2)	35°55.06	14°03.83	50	~105	18/11/2010
Station 10 (2)	35°55.06	14°03.83	400	~105	18/11/2010
02Nov2010GMT10			5	~105	02/11/2010
02Nov2010GMT18			5	~105	02/11/2010
03Nov2010GMT02			5	~105	03/11/2010
03Nov2010GMT10			5	~105	03/11/2010
18Nov2010GMT14			5	~105	18/11/2010
19Nov2010GMT00			5	~105	19/11/2010

**Table 2:** Radium samples from clean underway sampling (5 m depth) and Niskin bottles (other depths). Most samples have been measured the first time for  $^{223,224}\text{Ra}$ ; a second measurement of supported activities, to be measured in Edinburgh, still stands out. Based on these results, samples will be selected for measurement of  $^{228}\text{Ra}/^{226}\text{Ra}$  ratios. Subsamples (250 mL) for  $^{226}\text{Ra}$  analysis have been taken for all stations.  $^{227}\text{Ac}$  will be calculated from the results of the second measurement.

Station	Lat	Lon	depth	volume	Sampling Date
Station 3	36°29.73392S	13°6.54662E	10	460	22/10/2010
Station 3	36°29.73392S	13°6.54662E	50	(3771) 0	22/10/2010
Station 3	36°29.73392S	13°6.54662E	100	217	22/10/2010
Station 3	36°29.73392S	13°6.54662E	200	607	22/10/2010
Station 3	36°29.73392S	13°6.54662E	1410	364	22/10/2010
Station 3	36°29.73392S	13°6.54662E	4335	350	22/10/2010
Station 3	36°29.73392S	13°6.54662E	4706	169	22/10/2010
Station 3	36°29.73392S	13°6.54662E	4776	(3312) 0	22/10/2010
Station 6	40°00'50.90''	00°56'25.60'' E	5	306	29/10/2010
Station 6	40°00'50.90''	00°56'25.60'' E	45	301	29/10/2010
Station 6	40°00'50.90''	00°56'25.60'' E	95	409.5	29/10/2010
Station 6	40°00'50.90''	00°56'25.60'' E	195	373	29/10/2010
Station 6	39°59'51.00''	00°54'01.49'' E	1500	340	29/10/2010
Station 6	39°59'51.00''	00°54'01.49'' E	4450	355.5	29/10/2010
Station 6	39°59'51.00''	00°54'01.49'' E	4850	418	29/10/2010
Station 6	39°59'51.00''	00°54'01.49'' E	4920	354	29/10/2010
Station1	34°37.28	'17°2.18'	20	591	08/11/2010
Station1	34°37.28	'17°2.18'	200	859.5	08/11/2010
Station1	34°37.11	'17°2.29'	1600	342	19/11/2010
Station1	34°37.11	'17°2.29'	-50	391	19/11/2010
Station 11	39°17.67'	7°40.224'	10	329	16/11/2010
Station 11	39°17.67'	7°40.224'	200	392	16/11/2010
Station 11	39°17.67'	7°40.224'	600	526.5	16/11/2010
Station 11	39°15.30'	7°43.42'	3241	182	15/11/2010
Station 11	39°15.30'	7°43.42'	4241	302	15/11/2010
Station 11	39°15.30'	7°43.42'	4741	286	15/11/2010
Station 11	39°15.30'	7°43.42'	5141	229	15/11/2010
Station 11	39°15.30'	7°43.42'	5211	450	15/11/2010

**Table 3:** List of radium/ actinium samples from the standalone pumping systems. Shallow samples are shown in black. 13 samples of surface and intermediate water depths were collected, each consisting of Mn-absorbers in series, in order to compensate for the effects of incomplete Ra/Ac recovery at high flow rates. All samples have been measured a first time for  $^{223,224}\text{Ra}$ , a second measurement of supported activities, to be measured in Edinburgh, still stands out. Based on these results, samples will be selected for measurement of  $^{228}\text{Ra}/^{226}\text{Ra}$  ratios. Subsamples (250 mL) for  $^{226}\text{Ra}$  analysis have been taken for all stations.  $^{227}\text{Ac}$  will be calculated from the results of the second measurement, and selected samples will be measured by established alpha-spectrometric methods (Geibert and Vöge 2008) to confirm the results of the RaDeCC system, and to achieve a higher precision.

#### 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  $\text{MnO}_2$  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  $^{227}\text{Ac}$  and  $^{228}\text{Th}$ , 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<sub>2</sub> 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 <sup>226</sup>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.

After the counting for short-lived isotopes has been finished (after all excess <sup>223</sup>Ra has decayed to levels supported by <sup>227</sup>Ac, approximately three months), the Mn fiber will be ashed, an actinium fraction separated for later analysis via alpha-spectrometry, and the <sup>228</sup>Ra/<sup>226</sup>Ra ratio will be measured by MC-ICP-MS in Oxford. Together with the absolute <sup>226</sup>Ra concentration from the subsample, the <sup>228</sup>Ra concentration can be calculated.

The methods of using MC-ICP-MS to measure <sup>226</sup>Ra concentrations and <sup>228</sup>Ra/<sup>226</sup>Ra ratios are followed by Foster et al. (2004) and the new technique developed by Hsieh and Henderson (unpublished), respectively. A <sup>228</sup>Ra spike is used to determine <sup>226</sup>Ra concentrations and chemical blanks. For <sup>226</sup>Ra samples, Ra is pre-concentrated by the precipitation of CaCO<sub>3</sub> from seawater then sequentially purified by AG1-X8, AG50-X8 and Sr-spec column chemistries. For <sup>228</sup>Ra/<sup>226</sup>Ra samples (Mn-fibers), ashed fibers are leached with 30 mL 6N HCl then centrifuged to remove Ra. The precipitation of SrSO<sub>4</sub> in the HCl solution and the following conversion of SrSO<sub>4</sub> to SrCO<sub>3</sub> are used to purify Ra before column chemistries (AG50-X8 and Sr-spec). The remaining solution after SrSO<sub>4</sub> precipitation is preserved for <sup>227</sup>Ac counting by alpha spectrometry in Edinburgh.

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

#### Preliminary results

Virtually no excess <sup>224</sup>Ra and <sup>223</sup>Ra were found in surface waters. A re-count of several samples after <sup>224</sup>Ra<sub>ex</sub> would have decayed revealed no significant decrease in activities. Therefore, I assume that <sup>223</sup>Ra is supported by <sup>227</sup>Ac (except a potential small depletion in surface waters due to the particle-reactive intermediate <sup>227</sup>Th). <sup>224</sup>Ra is essentially supported by <sup>228</sup>Th, which in turn reflects the distribution of <sup>228</sup>Ra. <sup>228</sup>Th is particle reactive, and with a comparatively long half-life of 1.8 years, it may be depleted compared to <sup>228</sup>Ra, and remineralized at greater depths. This promises an interesting comparison with the <sup>228</sup>Ra data, once they have been analysed. <sup>223</sup>Ra can be used as an indicator for <sup>227</sup>Ac, which can be used in conjunction with <sup>228</sup>Ra in surface waters to identify different water masses.

The actual target areas for the application of <sup>224</sup>Ra and <sup>223</sup>Ra in surface waters, the South American shelf and Gough Island, were not reached due to the early end of the transect.

# NEODYMIUM ISOTOPES

By Alex Thomas

Samples to be analysed by Alex Piotrowski

## Objectives

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  $^{143}\text{Nd}$  from the alpha decay of  $^{147}\text{Sm}$  (Samarium, half live =  $1.06 \times 10^{11}$  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  $^{143}\text{Nd}$  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  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio whereas the pacific which is surrounded by young volcanic rocks recently derived from the mantle has a higher  $^{143}\text{Nd}/^{144}\text{Nd}$ . 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.

## Sampling protocol

### *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 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 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.



## Samples collected

Overview of samples: A total of 103 samples were collected spanning the full water column at: Station 1 (13 samples), Station 3 (13 samples), Station 5 (11 samples) Station 6 (12 samples), Station 8 (8 samples), Station 9 (12 samples), Station 10 (12 samples), and Station 11 (22 samples). Details of samples collected are presented in Table PaTh1.

## Sample analysis

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 ( $^{143}\text{Nd}/^{144}\text{Nd}$ ) will be made using a Nu Instruments MC-ICP-MS (Piotrowski et al. 2009).

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# NOBEL GASES AND TRITIUM

By Róisín Moriarty

Samples to be analysed by Róisín Moriarty

## Introduction

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 ( $^3\text{H}$ , an isotope of hydrogen) but helium ( $^3\text{He}$  and  $^4\text{He}$ ) and, neon ( $^{20}\text{Ne}$ ) 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  $^3\text{He}$  and  $^4\text{He}$ . The isotopic ratio of  $^3\text{He}/^4\text{He}$  is  $1.4 \times 10^{-6}$  in air with  $^4\text{He}$  being one million times more prolific than  $^3\text{He}$ . 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  $^3\text{He}/^4\text{He}$  in helium that originates from mantle out gassing is between ten and thirty times greater than the atmospheric  $^3\text{He}/^4\text{He}$  ratio.  $^3\text{He}/^4\text{He}$  ratios are therefore a useful indicator of the origin of intermediate depth waters.

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

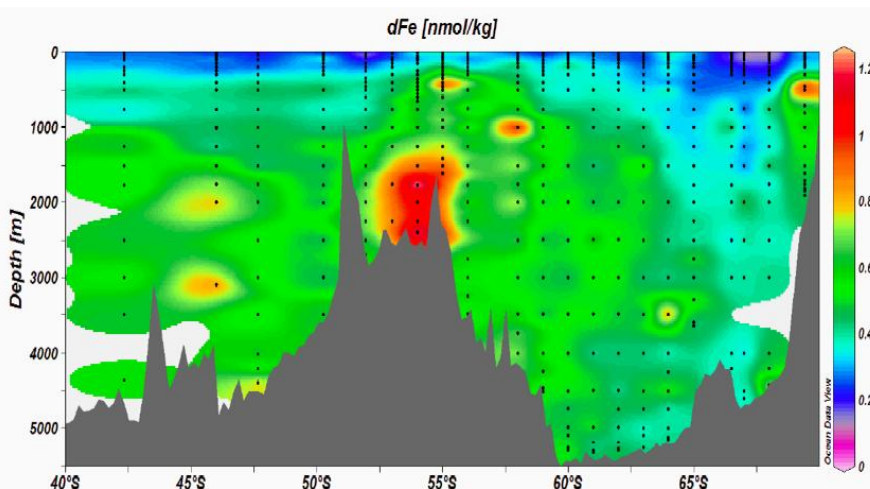
Argon will be measured as a matter of course and data supplied to Patrick Martin who will use  $\text{Ar}/\text{O}_2$  ratios to estimate net community production in the surface layer.

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 its radioactive decay product – tritogenic  $^3\text{He}$  – simultaneously we can calculate the tritium/ $^3\text{He}$  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  $^3\text{He}$  in certain water masses there is a non-negligible tritogenic  $^3\text{He}$  source that needs to be corrected for to separate large-scale background  $^3\text{He}$  from terrigenous sources.

## Scientific rationale

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. Terrigenous or volcanic  $^3\text{He}$  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 sparse micronutrient observations in intermediate and deep waters. Using a  $^3\text{He}$  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

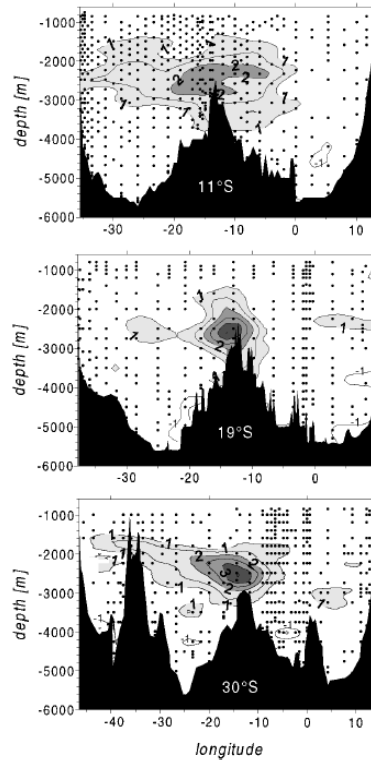
composition and origin. Noble gases (helium ratios and neon) along with tritium allow us to identify source inputs of micronutrient from the MAR and allow us to trace the scavenging of micronutrients away from the hydrothermal vent source. Understanding the distribution of terrigenic  $^3\text{He}$  can help to identify the source inputs of micronutrients along  $40^\circ\text{S}$ .



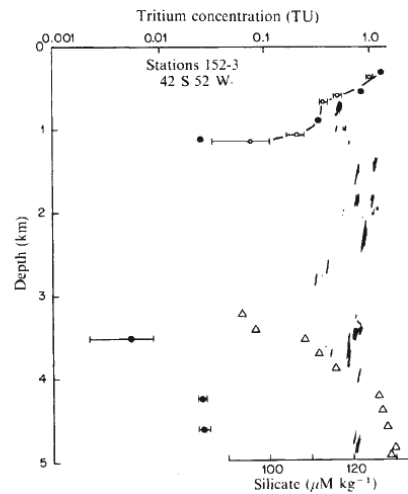
**Figure 11:** A cross-section showing the concentration of dissolved iron in seawater, with an obvious peak in concentration over the mid-ocean ridge (ref).

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  $^3\text{He}$  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  $40^\circ\text{S}$  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  $11^\circ\text{S}$ ,  $19^\circ\text{S}$  and  $30^\circ\text{S}$  (see Figure 1.2). This finding is in contrast with those of Reid (1989) who suggests eastward transport near  $30^\circ\text{S}$  and along  $11^\circ\text{S}$  and meridional transport along  $19^\circ\text{S}$ . 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 12:** Sections of terrigenous  $^3\text{He}$  from the Ruth et al. (2000) showing the hydrothermal vent plume extending to the west.



**Figure 13:** Tritium concentrations near the western section of the UK GEORACES  $40^\circ\text{S}$  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  $^3\text{He}/^3\text{H}$  will allow the calculation of water mass age. Identification of tritogenic  $^3\text{He}$  will help in separating out background  $^3\text{He}$  concentrations from the hydrothermal vent source signal.

### Samples collected

A total of 150 noble gas samples, including four from the underway fish, and 135 tritium samples, including nine duplicates, were collected across the transect. Each noble gas sample was taken in

duplicate and at every station. Apart from station 1 (CTD 003) a duplicate was taken at one depth (same Niskin bottle) for each station that tritium was sampled on.

Apart from noble gases and tritium collected on station 12 (CTD 042) (no regular rosette biological rosette only) and tritium collected on station 1 (CTD 003) samples collected spanned the full water column at all other stations (1 (CTD 003, He), 4 (CTD 015, CTD 018, regular rosette and biological), 5 (CTD 019), 7 (CTD 026), 8 (CTD 028), 9 (CTD 030), 10 (CTD 033), 11 (CTD 037). Tritium was not collected from the biological rosette on station 4 (CTD 018) whereas noble gases were.

### **Collection details:**

Noble gas/helium samples will be collected in 40cm long 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 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 directly after noble gas 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

### **Sampling issues**

Around a quarter of the noble gas samples taken had obvious leaks or failed to pass the 'click' test. This problem was noticed at station 4 (CTD 015). As all noble gas samples are taken in duplicate usually one of the samples remained intact and so this does not present such a major problem. There were a number of samples where both duplicates were compromised resulting in a loss of sample for the associated depths with station 4 (CTD 015) being particularly bad.

The crimping machine was dismantled and cleaned and the crimping faces renewed. The problems persisted. Further investigation is necessary but it seems that the copper tubing used to take the samples may be the issue. Usually the copper is crimped to a smooth clean knife-edge and duplicates break apart along the knife-edge. Copper was ordered to the same specification as normal for collecting samples of this type, however the knife-edge is consistently damaged, even after the crimping faces have been removed, cleaned and repositioned (even though originally they showed no sign of damage). The copper seems to be pulling apart before the crimper has completely sealed the ends. The quality of the copper will have to be investigated both through the supplier and further tests at the university. The integrity of the samples that have passed the 'click' test and show no visible leaks will have to be assessed when the samples are being analysed. Copper for sampling on any future cruises will have to be quality controlled to prevent similar problems.

### **Sample analysis**

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 from 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.

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# NITRATE $\delta^{15}\text{N}$ AND $\delta^{18}\text{O}$

By Robyn Tuerena

To be measured by:

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## Objectives

To understand the cycling of nitrogen isotopes in the south Atlantic, and critically observe changes in the isotopic composition of nitrate with changing water masses and oceanic processes. The coupled study of  $\text{NO}_3^-$  N and O isotopes can be used to constrain the nitrogen budget of the south Atlantic at  $40^\circ\text{S}$ . The isotopes of nitrate can help to identify inputs and losses of nitrogen as a macronutrient for biological processes.

## Sample collection

Samples have been collected from the stainless steel rosette, from every station at each depth. Seawater was filtered through an acropak ( $0.4\ \mu\text{m}$ ) into acid clean 60 ml nalgene bottles and frozen at  $-20\ ^\circ\text{C}$ . 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  $\text{d}^{18}\text{O}$  in addition to  $\text{d}^{15}\text{N}$ .

## 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) and incubate in dark for 3-4 days.
- Approximately one week prior to sample preparation, inoculate 9ml tubes in pairs. Transfer a single colony from freshly grown plate to media using a flamed loop, incubate overnight on shaker.
- Mix media from the 2 tubes into bigger tube, then use this to inoculate all media bottles. Transfer 2.7ml freshly inoculated bacterial media into each bottle by injecting through seal, put bottles on shaker table for 6-10 days.
- Divide culture evenly between autoclaved 250 ml centrifuge bottles and centrifuge for 10 minutes at 4950 rpm.
- Pink-white bacteria at bottom of bottles, pour off liquid above cells and add appropriate volume of nitrate free media (NFM) to the first centrifuge bottle (0.15 ml NFM per 1 ml original medium) pour back and forth till all cells resuspended into one centrifuge bottle, add antifoam using sterile pipette.
- Pipette 3 ml of cell concentrate into vials then insert venting needles into edge of stoppers.
- Purge vials with He gas by placing all vials on purge needles for ~45 minutes.
- Remove and place sideways on shaker table for 5 hours then return to purge system for one hour, remove and close gas cylinder and regulator, this removes all remaining  $\text{N}_2$  gas.
- Rinse syringe then inject sample (20 nmol) into vial through stopper, shake, invert and.
- Incubate at room temperature for a few hours in inverted position.
- Inject with 6M NaOH into each vial and shake to lyse the bacteria.

References:

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Correspondence with Laura Campesi and Jan Kaiser (UEA)



### 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 an *in situ* 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.

#### Samples collected

This calibration exercise will be done at each sampling station at 8 sampling depths, which will be selected based on the downward fluorescence trace measured by the CTD fluorometer. A complete list of the samples analysed on the GEOTRACES cruise can be found in Table 4.

**Figure 14:** a) Map showing locations where FISH and CTD samples were collected during the four sampling transects (Leg 1: Cape Town to Station 7, Leg 2: surface sampling from Station 7 back to Cape Town, Leg 3: Cape Town to Station 3, Leg 4 Station 3 back to Cape Town). b-d) Contour plots of the vertical distribution of chlorophyll-a measured using the fluorometric method. Note that Leg 2 is not shown since only surface samples were collected from the FISH during the transit back to Cape Town. Arrows above plots indicate the direction that samples were collected for a particular transect.

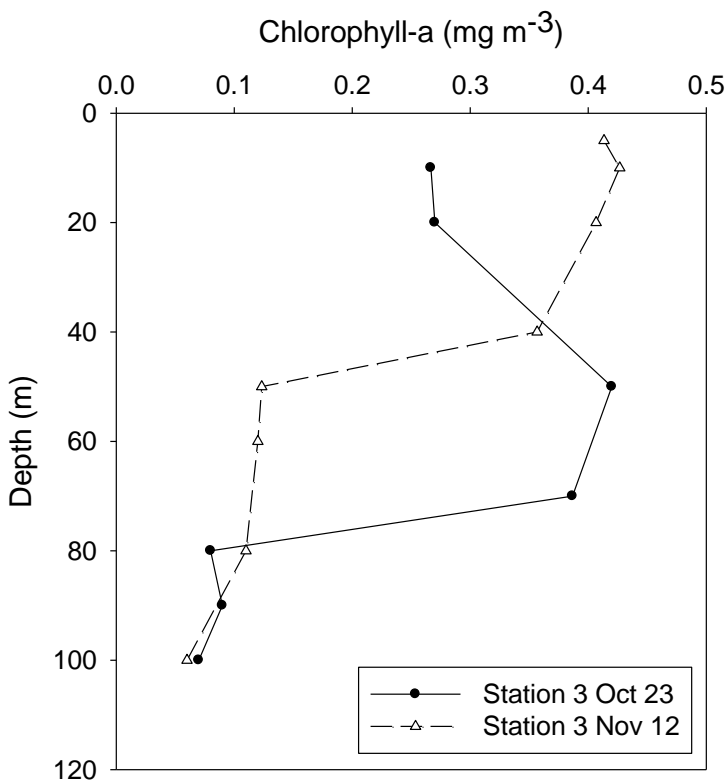
### Sample analysis

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 is measured both before and after acidification according to the method of Holm-Hansen et al. (1965).

### Preliminary results

Chlorophyll-a concentrations showed significant spatial and temporal variation. Maximum concentrations were observed in near-surface samples toward the end of the sampling period. The highest concentration ( $1.36 \text{ mg m}^{-3}$ ) was found at Station 12 on November 17. Vertical profiles also in terms of their shape, with subsurface maxima observed at the beginning of the sampling period, whereas towards the end maximum concentrations were typically found close to the sea surface.

Station 3 was sampled twice: once on Oct 23<sup>rd</sup>, and again on November 12<sup>th</sup>. We therefore used this station to assess the temporal change in the both the magnitude and shape of the vertical profile of chlorophyll-a concentration. Although the magnitude of maximum chlorophyll-a was the same for the two sampling periods, the vertical shape of the chlorophyll profiles was markedly different, with the first profile (Oct 23) having a distinct subsurface chlorophyll maximum, whereas the profile measured four weeks later has maximum chlorophyll-a concentrations near the sea surface. This change in the vertical structure of chlorophyll-a concentrations will likely have implications for rates of water-column primary productivity, since the light available for photosynthesis will be significantly greater at shallower depths.



**Figure 15:** Vertical profiles of chlorophyll-a concentration take at Station 3 on Oct 23 and Nov 12, 2010. The October 23 profile exhibits a subsurface chlorophyll-a maximum at 50m, whereas the November 12 profile shows maximum concentrations at the sea surface.

# 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 6-8 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, HPLC, fluorometric and flow cytometric analysis. In addition, surface samples were collected from the FISH in between Standard and Superstations and on a transect from station 7 to Capetown. A detailed list of samples collected may be found in Table 4.

## 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 (Hypersil 3 mm C8 MOS-2) 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).

The column is a 3 µm Shandon Hypersil MOS2 (endcapped), C-8 (6.2 to 6.8% carbon), 120 Å pore size, 100 X 4.6 mm and maintained at 30°C. Pigments will be separated at a flow rate of 1 ml min<sup>-1</sup> by a linear gradient programmed as follows (minutes; % solvent A; % solvent B): (0; 75; 25), (1; 50; 50), (20; 30; 70), (25; 0; 100), (32; 0; 100). 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.

# 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 6-8 sampling depths, The depths coincided with those selected for FRRF, HPLC, fluorometric and flow cytometric analysis. In addition, surface samples were collected from the FISH in between Standard and Superstations and on a transect from station 7 to Capetown. A detailed list of samples collected may be found in Table 4.

## 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  $\mu$ m 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  $\lambda$ , to account for pathlength amplification due to scattering by the filter. The geometric absorption pathlength 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:

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

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  $\lambda$  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):

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

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,  $a_p(\lambda)$ .

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

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

# ADSORPTION 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 refine algorithms used to detect the concentration of chlorophyll-a and the presence of algal functional types by ocean-colour remote sensing.

## 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). Unfortunately the region where the contribution of CDOM to the remote sensing signal would be most significant, the Rio del Plata plume, could not be sampled during this expedition, due to an unanticipated change in the cruise plan.

## 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  $\mu$ m nucleopore filter, pre-soaked in 10% HCl and 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 filtered 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 will be measured using a Shimadzu UV-2550 spectrophotometer, equipped with an integrating sphere. 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).

# 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 pigments over the GEOTRACES cruise transect. Samples were collected at 6-8 depths, which were 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. Duplicate 2 ml cryovials were 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 6-8 sampling depths, The depths coincided with those selected for FRRF, HPLC, fluorometric and flow cytometric analysis. In addition, surface samples were collected from the FISH in between Standard and Superstations and on a transect from station 7 to Capetown. A detailed list of samples collected may be found in Table 4.

## Sample analysis

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

# 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 Niskin 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). A detailed list of samples collected during the cruise can be found in Table 4.

## 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.

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

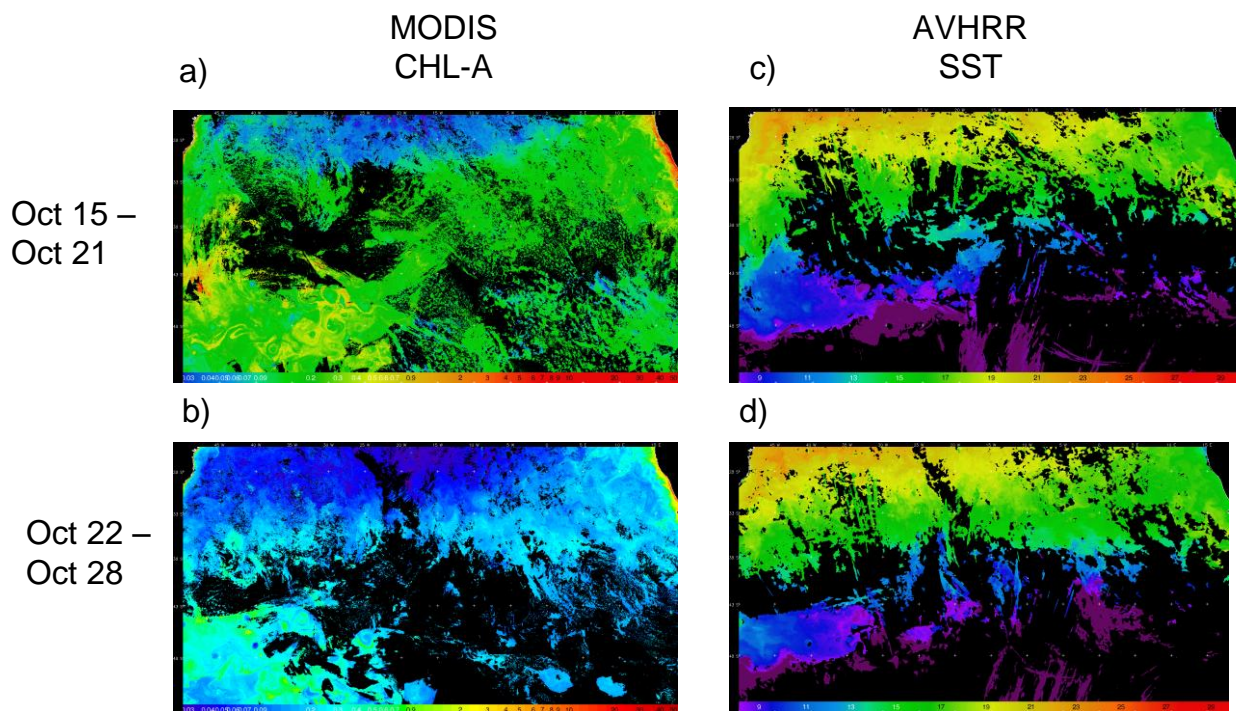
By Heather Bouman & Thomas Browning  
Department of Earth Sciences, University of Oxford

## 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 Chl and AVHRR Sea-Surface T 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 16).



**Figure 16:** 8-day composites of sea-surface chlorophyll and temperature provided by NEODAAS. Note that the colour scale of panels a) and b) are different.

## 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. The overall aim of this work will be to apply and refine satellite ocean-colour algorithms developed for open-ocean Chl retrieval and deriving maps of the large-scale distribution of phytoplankton taxonomic groups (Sathyendranath et al. 2004, Alvain et al. 2005). Additional data from both AMT cruises and a 30°S Atlantic transect will be used to validate both Chl and phytoplankton type algorithms.



# FAST REPETITION 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 phytoplankton physiology along the transect 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 a number of inter-station 5m depth fish samples. Results from this analysis are intended to be interpreted on the basis of nutrient availability, light climate, and taxonomic composition (see other relevant sections of cruise report).

## Sampling protocol

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

## Samples collected

At 13 stations 6 samples were taken from the depths of interest (Stations 1, 2, 3, 4, 5, 6, 9, 3R (R = Reoccupation), 11, 12, 10R, 1R2 (R2 = 2<sup>nd</sup> Reoccupation), and 13). 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 were always less than 120m. At 2 stations less than 6 depths were acquired: Station 7 (4 depths) and Station 8 (3 depths). This was a result of no specific biological cast being deployed. In these instances samples were taken from the main stainless steel cast for which there were limited samples taken from the depths of interest for FRR fluorometry measurements.

Fish samples were all taken from 5m depth and were taken between some stations (4 samples on first leg out from Cape Town; 9 samples on second leg out from Cape Town), at 2 to 4 hour intervals for a 26 hour period on first return to Cape Town (12 samples), at 2 to 4 hour intervals for a complete transect on final return to Cape Town (19 samples), and at 10 minute intervals for the shelf section of the transect (11 samples).

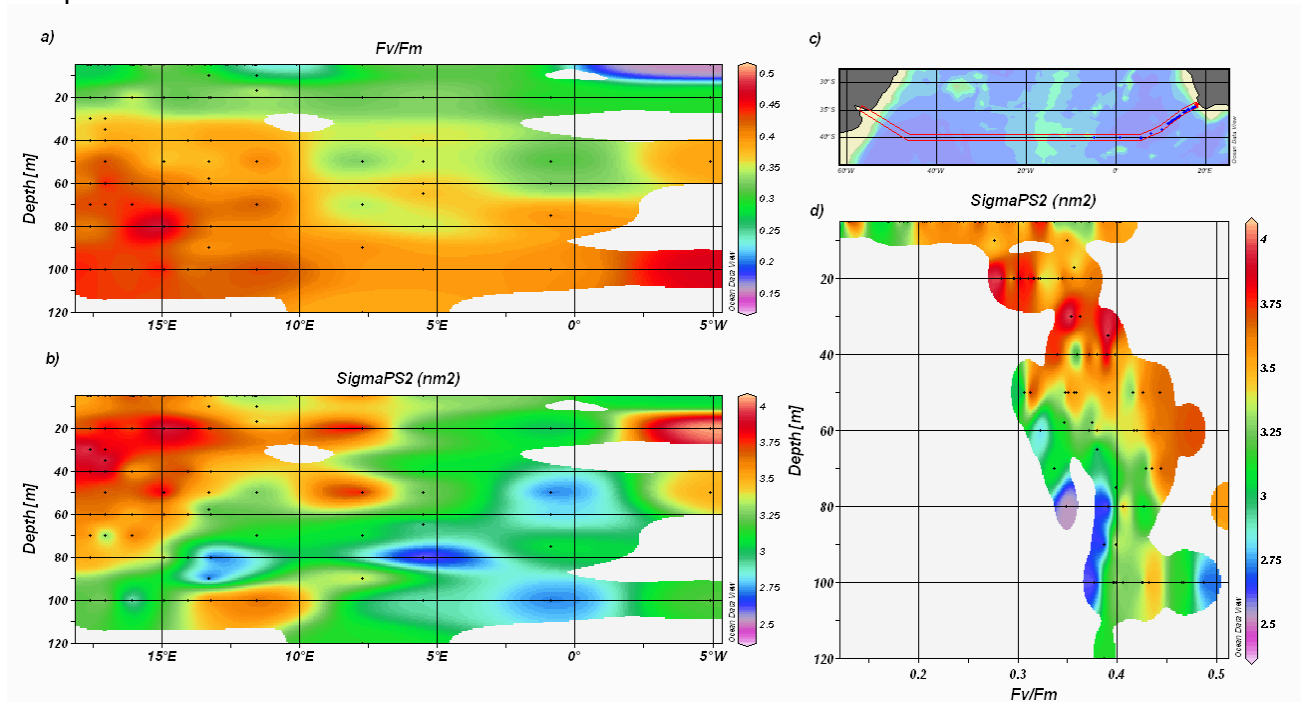
## Sample analysis

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 adapted. 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 3ml 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<sup>act</sup> sample chamber, FAST<sup>act</sup> base unit, and FAST<sup>tracka 2</sup> 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 Turnover (ST) 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  $\sigma_{PS2}$  (the functional absorption cross section of PS II, nm<sup>2</sup>). Rapid Light Curves (RLC) were obtained for samples from 2 to 3 depths at each station (in nearly all cases this included surface (5m depth) and Deep Chlorophyll Maximum (DCM)). The water jacket pump was run between samples for ST measurements and continuously at a low rate during RLC analysis to maintain sample temperature at that of the ships underway water flow. ST and RLC were taken for all fish samples except for the shelf section of the transect, where the high frequency of sample collection precluded RLC data collection. Blanks were run for nearly all samples using the following procedure: an aliquot of roughly 3ml of sample was filtered using a 0.2µm pore size filter and an ST measurement was then made using the same FRRF

settings as the unfiltered sample (N.B. The test tube used for the blank was washed 3 times with filtered water prior to the filling with 3 ml of filtered sample).

### Preliminary results

Refer to Fig. 17 below.  $F_v/F_m$  values generally show an increase with depth, together with a lower magnitude and generally inconsistent variation in profiles between stations (Fig. 1a). Values of  $\sigma_{PS2}$  show a general decrease with depth and show significant variability between stations (Fig. 1b).  $F_v/F_m$  and  $\sigma_{PS2}$  show a general inverse relationship with  $F_v/F_m$  increasing, and  $\sigma_{PS2}$  decreasing, with depth (Fig. 1c). Although there is some correlation of these parameters with nutrients (not shown), micronutrient concentrations, light climate, and taxonomic variability will also need to be consulted in order for interpretations to be made. RLC data collected are yet to be observed in any detail or interpreted.



**Figure 17:**  $F_v/F_m$  and  $\sigma_{PS2}$  for fish and station samples along transect. Cross sections of a)  $F_v/F_m$  and b)  $\sigma_{PS2}$ , for transect section until the most westerly station; c) transect with station and fish sampling locations; d) bivariate plot of  $F_v/F_m$  and  $\sigma_{PS2}$  against depth.

# ADDITIONAL MEASUREMENTS TAKE FOR BIOGEOTRACES

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

## **i) DNA / RNA analyses of marine diazotroph assemblages**

Wiebke Mohr & Rebecca Langlois Marine Biogeochemie  
Leibniz-Institut für Meereswissenschaften (IFM-GEOMAR), Kiel, Germany

### 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).

## **ii) Flow cytometry and qPCR analyses of marine picocyanobacteria**

Paul Berube & Allison Coe, Chisholm Laboratory  
Massachusetts Institute of Technology, Department of Civil and Environmental Engineering

### Objectives

Samples were collected to determine the spatial distribution of marine picocyanobacteria ecotypes along the 40°S cruise transect.

### Sampling protocol

#### *i) Flow Cytometry (FCM)*

1 ml seawater was added to 1.2 ml cryovials (use P1000 pipetman). 6 µl of 25% glutaraldehyde (Tousimis) was added to inverted caps. Caps were tightened and tubes inverted in rack to mix the preservative. Vials were then incubated for 10 minutes in the dark and then flash frozen in liquid N<sub>2</sub>. Vials were then transferred to the -80°C freezer for long-term storage.

#### *ii) qPCR*

Pre-bleached filter funnel tops and bottoms for each sample depth was rinsed with milli-Q water using a squirt bottle. 25 mm diameter 0.2 µm polycarbonate filters were loaded onto filter bases. Using 50 ml disposable pipettes, 100 ml of sample was filtered under a maximum pressure of 9 in Hg. Once the 100 ml of samples passed through the filter, it was chased with 3 ml preservation solution. Filters were folded once and placed carefully into a pre-labeled bead beater tube. Each replicate was filtered using the same filter funnel. Once all four replicates were filtered the samples were transferred to a cryobox and stored in the -80°C freezer.

#### Samples collected

Six depths were sampled within the photic zone. Sampling depths were chosen based on vertical profiles of in vivo fluorescence obtained from the Biological CTD cast. A complete list of stations and depths sampled can be found in Table 4.

#### Sample analysis

Information not available.

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**Table 4:** List of stations (Standard, Super and FISH), depths, and samples collected for biological sampling by Bouman/Browning

Stn	Date	Time In	Time Bot	Time Out	Lat (Dec)	Long (Dec)	CTD	Depth	Bottle	Oxford HPLC	Oxford ABS	Oxford FCM	Oxford TChl	Oxford CDOM	Oxford Microscopy	Kiel DNA/RNA	MIT qPCR	MIT FCM	MIT Gly1
1	10/19/10	06:27	06:47	M	-34.628	17.066	5S	5	24	1000	1000	1.875 X 2	100 x 3	250	250 x 2	800	100 x 4	1 X 2	X
1	10/19/10	06:27	06:47	M	-34.628	17.066	5S	20	23	1000	1000	1.875 X 2	100 x 3	X	X	2000	100 x 4	1 X 2	1 X 2
1	10/19/10	06:27	06:47	M	-34.628	17.066	5S	30	22	1000	1000	1.875 X 2	100 x 3	X	X	2000	100 x 4	1 X 2	X
1	10/19/10	06:27	06:47	M	-34.628	17.066	5S	40	21	1000	1000	1.875 X 2	100 x 3	X	X	2000	100 x 4	1 X 2	1 X 2
1	10/19/10	06:27	06:47	M	-34.628	17.066	5S	50	20	1000	1000	1.875 X 2	100 x 3	X	X	2000	100 x 4	1 X 2	X
1	10/19/10	06:27	06:47	M	-34.628	17.066	5S	60	14	1000	1000	1.875 X 2	100 x 3	X	X	2000	100 x 4	1 X 2	1 X 2
2	10/20/10	10:08	10:30	11:03	-35.374	14.909	8S	5	24	1000	1000	1.875 X 2	100 x 3	250	250 x 2	2000	100 x 4	1 X 2	X
2	10/20/10	10:08	10:30	11:03	-35.374	14.909	8S	20	22	1000	1000	1.875 X 2	100 x 3	X	X	2000	100 x 4	1 X 2	1 X 2
2	10/20/10	10:08	10:30	11:03	-35.374	14.909	8S	50	21	1000	1000	1.875 X 2	100 x 3	X	X	2000	100 x 4	1 X 2	X
2	10/20/10	10:08	10:30	11:03	-35.374	14.909	8S	60	15	1000	1000	1.875 X 2	100 x 3	X	X	2000	100 x 4	1 X 2	1 X 2
2	10/20/10	10:08	10:30	11:03	-35.374	14.909	8S	80	14	1000	1000	1.875 X 2	100 x 3	X	X	2000	100 x 4	1 X 2	X
2	10/20/10	10:08	10:30	11:03	-35.374	14.909	8S	100	13	1000	1000	1.875 X 2	100 x 3	X	X	2000	100 x 4	1 X 2	1 X 2
2	10/20/10	10:08	10:30	11:03	-35.374	14.909	8S	160	7	X	X	X	100 x 3	X	X	X	X	X	X
3	10/23/10	03:46	04:11	04:57	-36.487	13.274	11S	10	23	1000	1000	1.875 X 2	100 x 3	X	250 x 2	1540	100 x 4	1 X 2	X
3	10/23/10	03:46	04:11	04:57	-36.487	13.274	11S	20	20	1000	1000	1.875 X 2	100 x 3	250	X	1770	100 x 4	1 X 2	1 X 2
3	10/23/10	03:46	04:11	04:57	-36.487	13.274	11S	50	18	1000	1000	1.875 X 2	100 x 3	X	X	2000	100 x 4	1 X 2	X
3	10/23/10	03:46	04:11	04:57	-36.487	13.274	11S	70	17	1000	1000	1.875 X 2	100 x 3	X	X	1570	100 x 4	1 X 2	1 X 2
3	10/23/10	03:46	04:11	04:57	-36.487	13.274	11S	80	15	1000	1000	1.875 X 2	100 x 3	X	X	2000	100 x 4	1 X 2	X
3	10/23/10	03:46	04:11	04:57	-36.487	13.274	11S	90	12	1000	1000	1.875 X 2	100 x 3	X	X	1730	100 x 4	1 X 2	1 X 2
3	10/23/10	03:46	04:11	04:57	-36.487	13.274	11S	100	11	1000	1000	1.875 X 2	100 x 3	X	X	780	100 x 4	1 X 2	X
FISH	10/25/10	06:40	06:40	06:40	-37.561	11.398	FISH	5	FISH	1000	1000	1.875 X 2	100 x 3	X	X	2000	X	X	X
4	10/26/10	06:22	06:40	07:22	-38.426	10.090	18S	5	24	1000	1000	1.875 X 2	100 x 3	X	250 x 2	1490	100 x 4	1 X 2	X
4	10/26/10	06:22	06:40	07:22	-38.426	10.090	18S	20	22	1000	1000	1.875 X 2	100 x 3	X	X	1655	100 x 4	1 X 2	1 X 2
4	10/26/10	06:22	06:40	07:22	-38.426	10.090	18S	40	21	1000	1000	1.875 X 2	100 x 3	X	X	1615	100 x 4	1 X 2	X
4	10/26/10	06:22	06:40	07:22	-38.426	10.090	18S	50	20	1000	1000	1.875 X 2	100 x 3	X	X	X	100 x 4	1 X 2	1 X 2
4	10/26/10	06:22	06:40	07:22	-38.426	10.090	18S	60	18	1000	1000	1.875 X 2	100 x 3	X	X	1650	100 x 4	1 X 2	X
4	10/26/10	06:22	06:40	07:22	-38.426	10.090	18S	100	15	1000	1000	1.875 X 2	100 x 3	X	X	1735	100 x 4	1 X 2	1 X 2
4	10/26/10	06:22	06:40	07:22	-38.426	10.090	18S	200	11	1000	X	X	100 x 3	X	X	1865	X	X	X
FISH	10/26/10	18:57	18:57	18:57	-39.177	7.828	FISH	5	FISH	1000	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
5	10/27/10	M	M	00:00	-40.062	5.527	21S	5	23	1000	1000	1.875 X 2	100 x 3	X	X	2000	100 x 4	1 X 2	X
5	10/27/10	M	M	00:00	-40.062	5.527	21S	20	21	1000	1000	1.875 X 2	100 x 3	X	250 x 2	2000	100 x 4	1 X 2	1 X 2
5	10/27/10	M	M	00:00	-40.062	5.527	21S	30	20	1000	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
5	10/27/10	M	M	00:00	-40.062	5.527	21S	50	14	1000	1000	1.875 X 2	100 x 3	X	X	2000	100 x 4	1 X 2	X
5	10/27/10	M	M	00:00	-40.062	5.527	21S	65	13	1000	1000	1.875 X 2	100 x 3	X	X	X	100 x 4	1 X 2	1 X 2
5	10/27/10	M	M	00:00	-40.062	5.527	21S	80	11	1000	1000	1.875 X 2	100 x 3	X	X	2000	100 x 4	1 X 2	X
5	10/27/10	M	M	00:00	-40.062	5.527	21S	100	9	1000	1000	1.875 X 2	100 x 3	X	X	2000	100 x 4	1 X 2	1 X 2
5	10/27/10	M	M	00:00	-40.062	5.527	21S	150	8	1000	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
5	10/27/10	M	M	00:00	-40.062	5.527	21S	200	7	X	X	X	X	X	X	2000	X	X	X
5	10/27/10	M	M	00:00	-40.062	5.527	21S	400	1	X	X	X	X	X	X	2000	X	X	X
FISH	10/28/10	16:36	16:36	16:36	-40.001	2.510	FISH	5	FISH	1000	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
6	10/29/10	18:33	18:49	19:23	-40.020	0.886	24S	5	24	1000	1000	1.875 X 2	100 x 3	X	250 x 2	2000	100 x 4	1 X 2	X
6	10/29/10	18:33	18:49	19:23	-40.020	0.886	24S	20	22	1000	1000	1.875 X 2	100 x 3	250	X	X	100 x 4	1 X 2	1 X 2
6	10/29/10	18:33	18:49	19:23	-40.020	0.886	24S	50	20	1000	1000	1.875 X 2	100 x 3	X	X	2000	100 x 4	1 X 2	X
6	10/29/10	18:33	18:49	19:23	-40.020	0.886	24S	60	18	1000	1000	1.875 X 2	100 x 3	X	X	2000	100 x 4	1 X 2	1 X 2
6	10/29/10	18:33	18:49	19:23	-40.020	0.886	24S	75	16	1000	1000	1.875 X 2	100 x 3	X	X	X	100 x 4	1 X 2	X
6	10/29/10	18:33	18:49	19:23	-40.020	0.886	24S	85	14	1000	1000	1.875 X 2	100 x 3	X	X	2000	X	X	X
6	10/29/10	18:33	18:49	19:23	-40.020	0.886	24S	100	12	1000	1000	1.875 X 2	100 x 3	X	X	X	100 x 4	1 X 2	1 X 2
6	10/29/10	18:33	18:49	19:23	-40.020	0.886	24S	150	10	1000	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
6	10/29/10	18:33	18:49	19:23	-40.020	0.886	24S	200	6	X	X	X	X	X	X	2000	X	X	X
6	10/29/10	18:33	18:49	19:23	-40.020	0.886	24S	400	2	X	X	X	X	X	X	2000	X	X	X

Stn	Date	Time In	Time Bot	Time Out	Lat (Dec)	Long (Dec)	CTD	Depth	Bottle	Oxford HPLC	Oxford ABS	Oxford FCM	Oxford TChl	Oxford CDOM	Oxford Microscopy	Kiel DNA/RNA	MIT qPCR	MIT FCM	MIT Gly1
FISH	10/31/10	11:38	11:38	11:38	-40.000	-2.269	FISH	5	FISH	1000	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
7	11/01/10	12:56	12:56	12:56	-40.000	-4.892	FISH	5	FISH	1000	650	1.875 X 2	100 x 3	X	X	X	X	X	X
7	11/01/10	M	M	01:16	-40.000	-4.892	M	20	M	1000	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
7	11/01/10	M	M	01:16	-40.000	-4.892	M	50	M	1000	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
7	11/01/10	M	M	01:16	-40.000	-4.892	M	100	M	1000	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
FISH	11/02/10	10:03	10:03	10:03	-37.74286	3.68908	FISH	5	FISH	1000	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
FISH	11/02/10	12:19	12:19	12:19	-37.63335	4.12661	FISH	5	FISH	1000	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
FISH	11/02/10	14:03	14:03	14:03	-37.5466	4.47423	FISH	5	FISH	1000	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
FISH	11/02/10	16:06	16:06	16:06	-37.44927	4.86271	FISH	5	FISH	1000	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
FISH	11/02/10	18:03	18:03	18:03	-37.3515	5.25251	FISH	5	FISH	1000	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
FISH	11/02/10	20:07	20:07	20:07	-37.24781	5.66376	FISH	5	FISH	1000	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
FISH	11/02/10	22:03	22:03	22:03	-37.14692	6.06561	FISH	5	FISH	1000	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
FISH	11/03/10	02:05	02:05	02:05	-36.93413	6.90743	FISH	5	FISH	1000	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
FISH	11/03/10	05:59	05:59	05:59	-36.6823	7.90615	FISH	5	FISH	1000	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
FISH	11/03/10	08:02	08:02	08:02	-36.63002	8.11028	FISH	5	FISH	1000	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
FISH	11/03/10	10:12	10:12	10:12	-36.53401	8.49018	FISH	5	FISH	1000	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
FISH	11/03/10	12:02	12:02	12:02	-36.43397	8.8838	FISH	5	FISH	1000	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
8	11/09/10	02:24	02:57	03:49	-34.335	17.609	28S	5	FISH	1000 X 2	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
8	11/09/10	02:24	02:57	03:49	-34.335	17.609	28S	30	21	1000 X 2	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
8	11/09/10	02:24	02:57	03:49	-34.335	17.609	28S	70	19	1000 X 2	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
8	11/09/10	02:24	02:57	03:49	-34.335	17.609	28S	100	17	1000 X 2	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
FISH	11/09/10	09:03	09:03	09:03	-34.88666	16.08326	FISH	5	FISH	1000	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
FISH	11/09/10	20:09	20:09	20:09	-34.88312	15.99604	FISH	5	FISH	1000	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
9	11/10/10	12:34	12:52	13:37	-34.898	16.076	32S	5	24	1000	1000	1.875 X 2	100 x 3	X	250 x 2	2000	100 x 4	1 X 2	X
9	11/10/10	12:34	12:52	13:37	-34.898	16.076	32S	20	22	1000	1000	1.875 X 2	100 x 3	250	X	X	100 x 4	1 X 2	1 X 2
9	11/10/10	12:34	12:52	13:37	-34.898	16.076	32S	40	20	1000	1000	1.875 X 2	100 x 3	X	X	2000	100 x 4	1 X 2	X
9	11/10/10	12:34	12:52	13:37	-34.898	16.076	32S	50	18	1000	1000	X	100 x 3	X	X	X	X	X	X
9	11/10/10	12:34	12:52	13:37	-34.898	16.076	32S	60	13	1000	1000	1.875 X 2	100 x 3	X	X	X	100 x 4	1 X 2	1 X 2
9	11/10/10	12:34	12:52	13:37	-34.898	16.076	32S	70	12	1000	1000	X	100 x 3	X	X	X	X	X	X
9	11/10/10	12:34	12:52	13:37	-34.898	16.076	32S	80	10	1000	1000	1.875 X 2	100 x 3	X	X	1300	100 x 4	1 X 2	X
9	11/10/10	12:34	12:52	13:37	-34.898	16.076	32S	100	9	1000	1000	1.875 X 2	100 x 3	X	X	2000	100 x 4	1 X 2	1 X 2
9	11/10/10	12:34	12:52	13:37	-34.898	16.076	32S	200	6	X	X	X	X	X	X	2000	X	X	X
9	11/10/10	12:34	12:52	13:37	-34.898	16.076	32S	400	1	X	X	X	X	X	X	2000	X	X	X
FISH	11/11/10	00:02	00:02	00:02	-35.24979	15.44727	FISH	5	FISH	1000	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
FISH	11/11/10	04:02	04:02	04:02	-36.33205	13.43849	FISH	5	FISH	1000	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
3 Reocc	11/12/10	07:13	07:38	08:39	-36.451	13.217	35SS	5	24	1000	1000	1.875 X 2	100 x 3	X	250 x 2	2000	100 x 4	1 X 2	X
3 Reocc	11/12/10	07:13	07:38	08:39	-36.451	13.217	35SS	10	23	1000	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
3 Reocc	11/12/10	07:13	07:38	08:39	-36.451	13.217	35SS	20	22	1000	1000	1.875 X 2	100 x 3	250	X	2000	100 x 4	1 X 2	1 X 2
3 Reocc	11/12/10	07:13	07:38	08:39	-36.451	13.217	35SS	40	21	1000	1000	1.875 X 2	100 x 3	X	X	2000	100 x 4	1 X 2	X
3 Reocc	11/12/10	07:13	07:38	08:39	-36.451	13.217	35SS	50	19	1000	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
3 Reocc	11/12/10	07:13	07:38	08:39	-36.451	13.217	35SS	60	17	1000	1000	1.875 X 2	100 x 3	X	X	2000	100 x 4	1 X 2	1 X 2
3 Reocc	11/12/10	07:13	07:38	08:39	-36.451	13.217	35SS	80	16	1000	1000	1.875 X 2	100 x 3	X	X	X	100 x 4	1 X 2	X
3 Reocc	11/12/10	07:13	07:38	08:39	-36.451	13.217	35SS	100	15	1000	1000	1.875 X 2	100 x 3	X	X	X	100 x 4	1 X 2	1 X 2
3 Reocc	11/12/10	07:13	07:38	08:39	-36.451	13.217	35SS	200	10	X	X	X	X	X	X	2000	X	X	X
3 Reocc	11/12/10	07:13	07:38	08:39	-36.451	13.217	35SS	400	1	X	X	X	X	X	X	2000	X	X	X

Stn	Date	Time In	Time Bot	Time Out	Lat (Dec)	Long (Dec)	CTD	Depth	Bottle	Oxford HPLC	Oxford ABS	Oxford FCM	Oxford TChl	Oxford CDOM	Oxford Microscopy	Kiel DNA/RNA	MIT qPCR	MIT FCM	MIT Gly1
11	11/15/10	02:35	M	02:52	-39.257	7.728	39S	5	24	1000	1000	1.875 X 2	100 x 3	X	250 x 2	2000	100 x 4	1 X 2	X
11	11/15/10	02:35	M	02:52	-39.257	7.728	39S	20	23	1000	1000	1.875 X 2	100 x 3	250	X	X	100 x 4	1 X 2	1 X 2
11	11/15/10	02:35	M	02:52	-39.257	7.728	39S	40	22	1000	1000	1.875 X 2	100 x 3	X	X	2000	X	X	X
11	11/15/10	02:35	M	02:52	-39.257	7.728	39S	50	21	1000	1000	1.875 X 2	100 x 3	X	X	X	100 x 4	1 X 2	X
11	11/15/10	02:35	M	02:52	-39.257	7.728	39S	70	20	1000	1000	1.875 X 2	100 x 3	X	X	X	100 x 4	1 X 2	1 X 2
11	11/15/10	02:35	M	02:52	-39.257	7.728	39S	90	19	1000	1000	1.875 X 2	100 x 3	X	X	2000	100 x 4	1 X 2	X
11	11/15/10	02:35	M	02:52	-39.257	7.728	39S	100	18	1000	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
11	11/15/10	02:35	M	02:52	-39.257	7.728	39S	120	17	1000	1000	1.875 X 2	100 x 3	X	X	2000	100 x 4	1 X 2	1 X 2
11	11/15/10	02:35	M	02:52	-39.257	7.728	39S	200	12	X	X	X	X	X	X	2000	X	X	X
11	11/15/10	02:35	M	02:52	-39.257	7.728	39S	400	1	X	X	X	X	X	X	2000	X	X	X
FISH	11/16/10	07:00	07:00	07:00	-37.44399	11.62727	FISH	5	FISH	1000	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
FISH	11/16/10	09:00	09:00	09:00	-37.44063	11.61079	FISH	5	FISH	1000	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
FISH	11/16/10	11:00	11:00	11:00	-37.45057	11.57268	FISH	5	FISH	1000 x 2	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
FISH	11/16/10	13:00	13:00	13:00	-37.47136	11.54522	FISH	5	FISH	1000	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
FISH	11/16/10	15:00	15:00	15:00	-37.37941	11.69067	FISH	5	FISH	1000	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
FISH	11/16/10	17:00	17:00	17:00	-37.22606	11.98357	FISH	5	FISH	1000	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
FISH	11/16/10	19:00	19:00	19:00	-37.04292	12.28406	FISH	5	FISH	1000	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
FISH	11/16/10	21:00	21:00	21:00	-36.85159	12.58881	FISH	5	FISH	1000	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
12	11/17/10	11:50	12:24	13:45	-37.470	11.550	42S	5	24	1000	1000	1.875 X 2	100 x 3	X	250 x 2	2000	100 x 4	1 X 2	X
12	11/17/10	11:50	12:24	13:45	-37.470	11.550	42S	10	23	1000	400	1.875 X 2	100 x 3	X	X	X	100 x 4	1 X 2	1 X 2
12	11/17/10	11:50	12:24	13:45	-37.470	11.550	42S	17	22	1000	400	1.875 X 2	100 x 3	250	X	2000	X	X	X
12	11/17/10	11:50	12:24	13:45	-37.470	11.550	42S	30	20	1000	510	1.875 X 2	100 x 3	X	X	X	100 x 4	1 X 2	X
12	11/17/10	11:50	12:24	13:45	-37.470	11.550	42S	50	19	1000	1000	1.875 X 2	100 x 3	X	X	X	100 x 4	1 X 2	1 X 2
12	11/17/10	11:50	12:24	13:45	-37.470	11.550	42S	70	18	1000	1000	1.875 X 2	100 x 3	X	X	2000	100 x 4	1 X 2	X
12	11/17/10	11:50	12:24	13:45	-37.470	11.550	42S	80	16	1000	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
12	11/17/10	11:50	12:24	13:45	-37.470	11.550	42S	100	15	1000	X	1.875 X 2	100 x 3	X	X	2000	100 x 4	1 X 2	1 X 2
12	11/17/10	11:50	12:24	13:45	-37.470	11.550	42S	200	10	X	X	X	X	X	X	2000	X	X	X
12	11/17/10	11:50	12:24	13:45	-37.470	11.550	42S	400	8	X	X	X	X	X	X	2000	X	X	X
FISH	11/17/10	17:57	17:57	17:57	-35.34016	15.38941	FISH	5	FISH	1000	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
FISH	11/17/10	21:57	21:57	21:57	-35.02829	16.12815	FISH	5	FISH	1000	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
FISH	11/18/10	02:00	02:00	02:00	-34.69193	16.86541	FISH	5	FISH	1000	510	1.875 X 2	100 x 3	X	X	X	X	X	X
10 Reocc	11/18/10	06:31	06:54	07:53	-35.918	14.064	43S	5	24	1000	500	1.875 X 2	100 x 3	X	250 x 2	X	X	X	X
10 Reocc	11/18/10	06:31	06:54	07:53	-35.918	14.064	43S	20	22	1000	500	1.875 X 2	100 x 3	250	X	X	X	X	X
10 Reocc	11/18/10	06:31	06:54	07:53	-35.918	14.064	43S	40	21	1000	500	1.875 X 2	100 x 3	X	X	X	X	X	X
10 Reocc	11/18/10	06:31	06:54	07:53	-35.918	14.064	43S	50	20	1000	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
10 Reocc	11/18/10	06:31	06:54	07:53	-35.918	14.064	43S	60	16	1000	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
10 Reocc	11/18/10	06:31	06:54	07:53	-35.918	14.064	43S	70	15	1000	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
10 Reocc	11/18/10	06:31	06:54	07:53	-35.918	14.064	43S	80	14	1000	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
10 Reocc	11/18/10	06:31	06:54	07:53	-35.918	14.064	43S	100	12	1000	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
FISH	11/18/10	12:08	12:08	12:08	-34.53613	17.301	FISH	5	FISH	1000	500	1.875 X 2	100 x 3	X	X	X	X	X	X
FISH	11/18/10	14:01	14:01	14:01	-34.33737	17.60477	FISH	5	FISH	1000	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
FISH	11/18/10	16:01	16:01	16:01	-34.32073	17.60806	FISH	5	FISH	1000	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
FISH	11/18/10	17:59	17:59	17:59	-34.31139	17.59431	FISH	5	FISH	1000	500	1.875 X 2	100 x 3	X	X	X	X	X	X
FISH	11/18/10	19:57	19:57	19:57	-34.30281	17.57724	FISH	5	FISH	1000	500	1.875 X 2	100 x 3	X	X	X	X	X	X
FISH	11/18/10	22:15	22:15	22:15	-34.32454	17.60533	FISH	5	FISH	1000	500	1.875 X 2	100 x 3	X	X	X	X	X	X
FISH	11/19/10	02:01	02:01	02:01	-34.37169	17.55121	FISH	5	FISH	1000	1000	1.875 X 2	100 x 3	X	X	X	X	X	X

Stn	Date	Time In	Time Bot	Time Out	Lat (Dec)	Long (Dec)	CTD	Depth	Bottle	Oxford HPLC	Oxford ABS	Oxford FCM	Oxford TChl	Oxford CDOM	Oxford Microscopy	Kiel DNA/RNA	MIT qPCR	MIT FCM	MIT Gly1
2nd Reoc	11/19/10	09:02	09:17	10:16	-34.701	17.035	44S	5	24	1000	500	1.875 X 2	100 x 3	X	250 x 2	X	X	X	X
2nd Reoc	11/19/10	09:02	09:17	10:16	-34.701	17.035	44S	10	23	1000	500	1.875 X 2	100 x 3	X	X	X	X	X	X
2nd Reoc	11/19/10	09:02	09:17	10:16	-34.701	17.035	44S	20	22	1000	500	1.875 X 2	100 x 3	X	X	X	X	X	X
2nd Reoc	11/19/10	09:02	09:17	10:16	-34.701	17.035	44S	35	21	1000	500	1.875 X 2	100 x 3	X	X	X	X	X	X
2nd Reoc	11/19/10	09:02	09:17	10:16	-34.701	17.035	44S	40	20	1000	500	1.875 X 2	100 x 3	X	X	X	X	X	X
2nd Reoc	11/19/10	09:02	09:17	10:16	-34.701	17.035	44S	50	19	1000	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
2nd Reoc	11/19/10	09:02	09:17	10:16	-34.701	17.035	44S	70	18	1000	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
2nd Reoc	11/19/10	09:02	09:17	10:16	-34.701	17.035	44S	100	17	1000	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
8 Reocc	11/19/10	19:34	20:04	21:01	-34.303	17.578	46SS	5	24	1000	500	1.875 X 2	100 x 3	X	250 x 2	X	X	X	X
8 Reocc	11/19/10	19:34	20:04	21:01	-34.303	17.578	46SS	10	23	1000	500	1.875 X 2	100 x 3	250	X	X	X	X	X
8 Reocc	11/19/10	19:34	20:04	21:01	-34.303	17.578	46SS	20	21	1000	500	1.875 X 2	100 x 3	X	X	X	X	X	X
8 Reocc	11/19/10	19:34	20:04	21:01	-34.303	17.578	46SS	40	18	1000	500	1.875 X 2	100 x 3	X	X	X	X	X	X
8 Reocc	11/19/10	19:34	20:04	21:01	-34.303	17.578	46SS	50	17	1000	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
8 Reocc	11/19/10	19:34	20:04	21:01	-34.303	17.578	46SS	70	15	1000	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
8 Reocc	11/19/10	19:34	20:04	21:01	-34.303	17.578	46SS	80	14	1000	1000	1.875 X 2	100 x 3	X	X	X	X	X	X
8 Reocc	11/19/10	19:34	20:04	21:01	-34.303	17.578	46SS	100	13	1000	1000	1.875 X 2	100 x 3	X	X	X	X	X	X



# **<sup>234</sup>Th ASSESSMENT OF C AND MICRONUTRIENT FLUXES**

By Patrick Martin  
NOC Southampton, UK

All analyses are to be conducted by Patrick Martin, NOC Southampton, UK (Tel: +44 2380 596336; patrick.martin@noc.soton.ac.uk)

## **Objectives**

<sup>234</sup>Thorium (<sup>234</sup>Th) is a tracer for particle export out of the upper 100-200 m. <sup>234</sup>Th was analysed to quantify the downward particulate flux out of the upper ocean of organic carbon and nitrogen, inorganic carbon, opal, intact polar lipids (IPL), and micronutrient metals. Fluxes of micronutrient metals can then be related to their concentration profiles, and the upward flux via mixing, to construct budgets.

## **Sampling and analysis protocol**

The method follows Pike *et al.* (2005). 4 L of water per sample were collected from the stainless steel rosette into acid-cleaned polyethylene carboys, acidified with 7 mL of concentrated HNO<sub>3</sub>, spiked with 23 pg of <sup>230</sup>Th (yield tracer), and allowed to equilibrate for at least 8 h. The pH was then raised to >8 with concentrated ammonia, and KMnO<sub>4</sub> and MnCl<sub>2</sub> solutions were added to co-precipitate Th with MnO<sub>2</sub>. The precipitate was filtered onto QMA filters, rinsed with deionised water, dried, and the beta-radiation counted on a GM-25 low-level beta counter (Risø, Denmark). Repeated counting of samples confirmed that the activity was decreasing according to the half-life of <sup>234</sup>Th.

After six months (>7 half-lives of <sup>234</sup>Th), the background radiation of the samples is counted. They are then spiked with <sup>229</sup>Th and dissolved in HNO<sub>3</sub> + H<sub>2</sub>O<sub>2</sub>, and Th isotopes are then purified via anion exchange chromatography on AG1-X8 resin. The eluted fraction is converted to a 2% HNO<sub>3</sub> matrix, and the 229:230 ratio measured by multicollector inductively-coupled plasma mass spectrometry.

The <sup>238</sup>Uranium activity was calculated from salinity, following Chen *et al.* (1986).

Samples of sinking particles were collected from stand-alone pumping systems (SAPS, an *in situ* pump) to determine the ratios of elements of interest to <sup>234</sup>Th. Filter housings were cleaned with deionised water, and filters loaded in a laminar flow hood. Sinking particles were collected onto an acid-cleaned, 53 µm mesh-size Nitex mesh that was fitted as a pre-filter in the filter housing. Upon recovery, a one-quarter section of the Nitex was cut out for analysis of micronutrient metals (by Maeve Lohan), and three-quarters were used for analysis of <sup>234</sup>Th, organic carbon and nitrogen, inorganic carbon, opal, and IPL. Particles were rinsed off the Nitex using filtered (0.2 µm pore-size Durapore) seawater, divided into four equal subsamples with a Folsom splitter, and filtered onto pre-combusted QMA filters (<sup>234</sup>Th + organic carbon and nitrogen, and IPL), or onto 0.4 µm polycarbonate filters (opal, inorganic carbon). The filters for <sup>234</sup>Th + organic C and N were oven-dried at 50°C overnight, and <sup>234</sup>Th counted as for water samples. Following background counting after six months, they will be fumed for 24 h with concentrated HCl, oven dried for 24 h, and C and N analysed on a CHN analyser. Inorganic carbon is measured as calcium via inductively-coupled plasma atomic emission spectroscopy after a 24 h leach with 1 M acetic acid. Opal is measured as silicon on an autoanalyser after digestion in 0.2 M NaOH for 3 h at 90°C. The filters for IPL were frozen in liquid nitrogen, stored at -80°C, and will be analysed by high-performance liquid chromatography / electrospray ionisation mass spectrometry after Bligh & Dyer extraction in collaboration with Benjamin Van Mooy in Woods Hole (see separate IPL section for more information).

The analysis will be completed by the end of June 2011.

## **Samples collected**

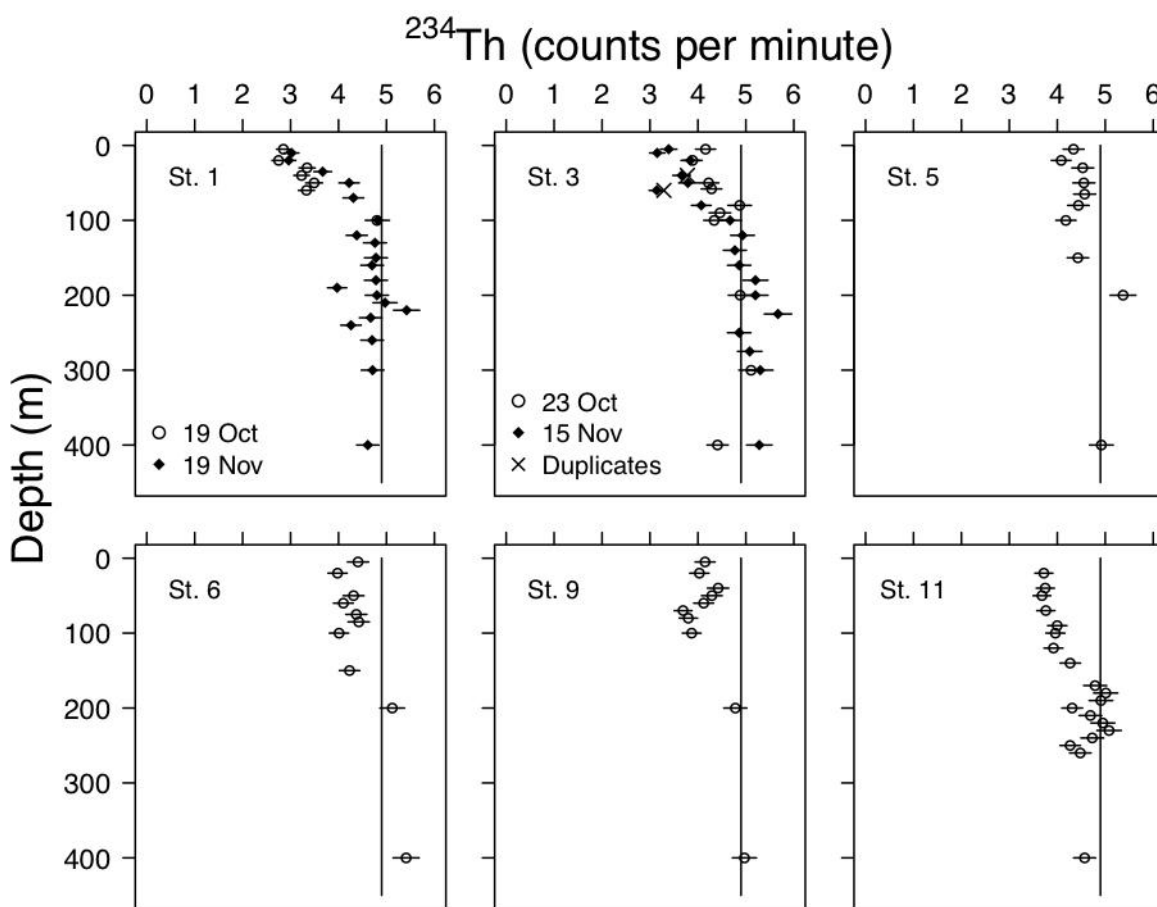
Ten samples, between 5 and 400 m, were collected at each of Stations 1, 3, 5, 6, and 9. Four samples were collected between 1000 and 3500 m at Station 10. At Stations 3 (re-occupation), 11, and 1 (2<sup>nd</sup> re-occupation), twenty samples were collected between 5 and 400 m to provide better resolution in the upper mesopelagic to examine particle remineralization. SAPS were deployed

between 70 and 220 m at Stations 3 (70 m, 120 m, and 220 m), 6 (70 m, 120 m, and 220 m), 1 re-occupation (120 m), and 11 (70 m and 120 m). Additionally, six water samples were collected from the trace-metal-clean underway supply on 2 November.

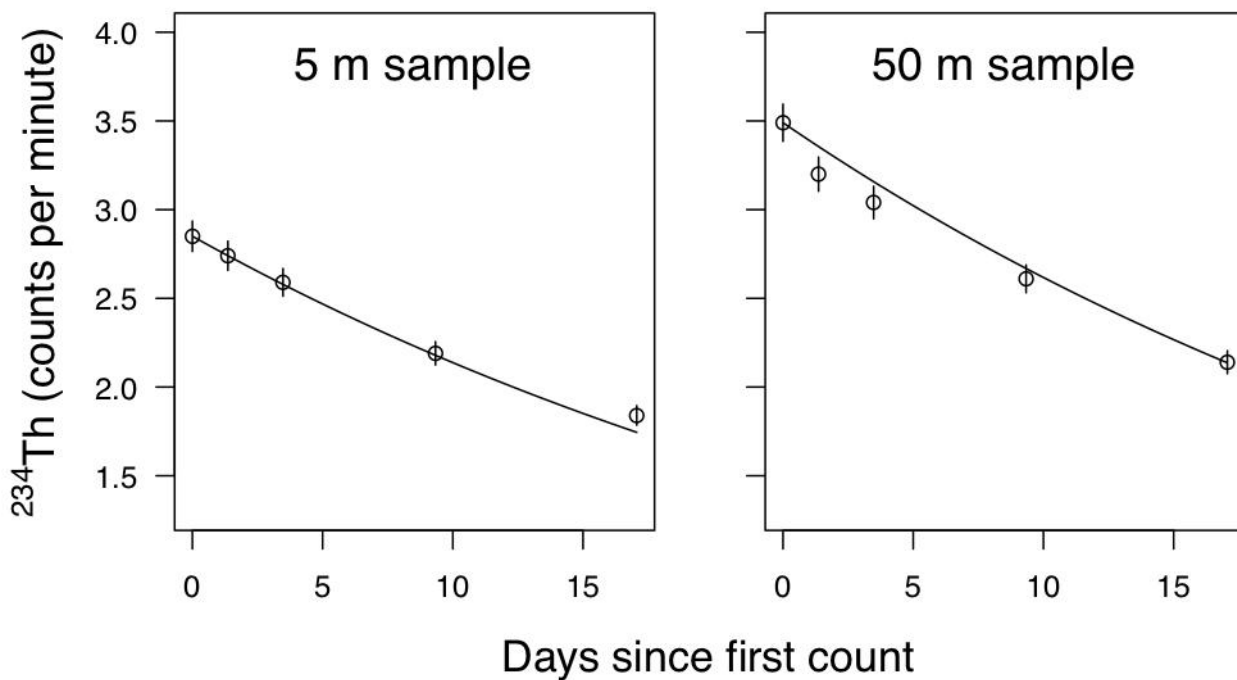
### Preliminary results

Figure 18 shows the first counts of each profile, generally taken about three days after sampling. They are uncalibrated, and have not been corrected for yield, in-growth from  $^{238}\text{U}$ , or decay of  $^{234}\text{Th}$ . However, these corrections tend to be relatively constant, and the counting efficiency is close to 50%. The error bars show a constant  $\pm 5\%$  error, which is a typical final error for  $^{234}\text{Th}$  – however, they have not been calculated from the data. The solid lines show the likely value for samples at secular equilibrium with  $^{238}\text{U}$ .

Figure 19 shows the decay of activity measured in two samples from Station 1, which very closely follows the decay predicted from the decay constant, lambda, of  $^{234}\text{Th}$  ( $0.02786\text{ d}^{-1}$ ).



**Figure 18:** Preliminary (uncorrected/uncalibrated) profiles of  $^{234}\text{Th}$  activity. The solid lines indicate the likely equilibrium activity, all error bars show  $\pm 5\%$  of the measured value.



**Figure 19:** Measured decay in activity of two samples from Station 1. Circles show the measured activity (error bars indicate the counting uncertainty), and solid lines show the predicted decay of the initial activity according to the decay constant of <sup>234</sup>Th (0.02786 d<sup>-1</sup>).

#### References

- Chen JH, Edwards RL, Wasserburg GJ (1986). <sup>238</sup>U, <sup>234</sup>U and <sup>232</sup>Th in seawater. *Earth and Planetary Science Letters* **80**:241-251.
- Pike SM, Buesseler KO, Andrews J, Savoye N (2005). Quantification of <sup>234</sup>Th recovery in small volume sea water samples by inductively coupled plasma-mass spectrometry. *Journal of Radioanalytical and Nuclear Chemistry* **236**:355-360.

# MICRONUTRIENT ISOTOPE RATIOS

By Angela Milne

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

V isotopes	Sune Nielsen, Department of Earth Sciences, University of Oxford, South Parks Road, Oxford, OX1 3AN.
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.
Ni isotopes	Chris Seibert, Department of Earth Sciences, University of Oxford, Parks Road, Oxford, OX1 3PR.
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.
Tl isotopes	Sune Nielsen, Department of Earth Sciences, University of Oxford, South Parks Road, Oxford, OX1 3AN.
Pb isotopes	Dominik Weiss, Department of Earth Science & Engineering, Imperial College, Prince Consort Road, London, SW7 5PD.

**Sampling protocol:** 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. Samples for Ni were later (after all samples were collected) acidified with 1.5 mL of concentrated HNO<sub>3</sub> per 1 L of sample. All other isotope samples collected were stored unacidified. All samples were double bagged within the clean container before storage.

Eight OTE bottles could be pressurised and sampled at one time. Filtration of all twenty-four bottles was completed in approximately six-seven hours.

**Samples collected:** Isotope samples were only collected at the four super-stations; Stations 3, 6, 8 (revisited) and 11. The number of samples collected for each element at the four stations is detailed below, it should be noted that multiple bottles filled at the same depth for the same element are classed as one sample, e.g. Pb required 2 x 1 L to be filled at each depth, therefore the whole 2 L is classed as one sample.

Isotope	Station 3	Station 6	Station 8	Station 11
V	13	13	7	14
Cr	13	13	7	13
Fe	12	12	7	13
Ni	2			1
Cu/Zn	11	10	6	12
Cd	13	12	2	13
Tl	13	13	7	14
Pb	11	11	5	12

There were three instances where there was insufficient water in the OTE bottle to collect full samples. This occurred on three different stations and affected three different isotopes;

Station 6: Insufficient volume for 433 to collect a full Cu/Zn sample.

Station 8: Insufficient volume for 884 to collect a full sample for Pb.

Station 11: Insufficient volume for 771 to collect a full sample for Cr.

In addition, there were also a couple of instances which may have resulted in sample contamination.

At Station 6, the acropak filter attached to the OTE bottle of sample 438 flew off whilst the Cd sample was being collected, this may have resulted in splashes entering the sample. Due to volume requirements (the whole 10 L from the OTE bottle was required) it was decided to continue with the collection of the sample (after reattachment of the filter capsule) rather than discard what had been collected.

At Station 8, seawater in the OTE bottle entered two sample gaslines (896 & 904) prior to the bottles being sampled. The samples for Cu/Zn and Pb collected from these bottles may therefore be contaminated.

**Sample 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.

# PARTICULATE $\delta^{15}\text{N}$ , $\delta^{13}\text{C}$ , AND POC/PON

By Robyn Tuerena

Analysed by

Robyn Tuerena, School of Geosciences, University of Edinburgh.

Email: R.E.Tuerena@sms.ed.ac.uk

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

Email: r.ganeshram@ed.ac.uk

## Objectives

To constrain the flux of POC and PON and the decrease of particles with depth below the euphotic zone. The concentrations can provide information to the extent of decomposition and recycling by zooplankton and bacteria. Although the majority of particles are broken down in surface waters, pelagic processes are also important, therefore samples at depth have also been taken to help understand the fluxes of sinking particles and the biological consumption taking place at 40°S.

## Sample collection

Particulate samples were collected onto ashed, pre weighed GF/F microfibre filters (0.7 $\mu\text{m}$  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, University of Edinburgh using a Carlo Erba NA 2500 elemental analyser. 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 chapter).

# BARIUM

By Robyn Tuerena

Contact:

Dr Raja Ganeshram

School of Geosciences, University of Edinburgh.

## Rationale

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 ( $0.4\ \mu m$ ) 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.

Occasional surface samples were collected for the measurement of particulate Barium. Sample volumes of 20 litres are required therefore this was limited to surface (fish) samples. Water was filtered through Millipore filters ( $0.8\ \mu m$  pore size, 152 mm diameter), filters were folded into quarters, dried at  $50\ ^\circ C$  and frozen.

## 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.

Prior to analysis of particulate barium samples, sequential leaching will be required using a method modified from Ganeshram et al., 2003 and Carson, 2008. Samples will be analysed by inductively coupled plasma optical emission spectroscopy (ICP-OES) at the School of Geosciences, University of Edinburgh.

## **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

### VELOCITY MICROPROFILER

By Dr. Matthew R. Palmer, National Oceanography Centre, UK

Turbulent mixing modifies water masses, controls ocean stratification, drives the vertical flux of nutrients and plays a key role in air-sea interaction of gases. A number of methods are employed in Geotraces to estimate mixing by proxy. We are able to measure ocean mixing directly however using measurements of shear microstructure. Using velocity ( $u$ ) shear microstructure we may derive the dissipation rate of turbulent kinetic energy,  $e$ , (Dewey et al, 1987)

$$e = 7.5m \left\langle \frac{\partial u}{\partial z} \right\rangle^2$$

Where  $\mu$  is the dynamic viscosity of seawater. Using  $e$  we can estimate the rate of vertical mixing  $K_z$  as,

$$K_z = G \frac{e}{N^2}$$

where the buoyancy frequency  $N^2 = g/\rho \cdot d\rho/dz$  represents the strength of local stratification and  $G$  is an efficiency factor which for the stratified ocean is estimated to be  $\sim 0.2$  (Osborn, 1980).

Microstructure measurements were made using a Rockland Scientific International manufactured **V**elocity **M**icrostructure **P**rofiler (VMP750) provided by NOC. The VMP750 (figure 1) is a free-falling instrument rated to 1000m depth that was deployed from the aft of the RRS Discovery, connected via a neutrally buoyant Kevlar tether which is fed sufficiently fast over the ship's stern to prevent any interference with the free-fall of the instrument from the surface to the seabed. During descent the instrument simultaneously measures shear microstructure, from which the dissipation rate of turbulent kinetic energy can be derived (Dewey et al, 1987), temperature and conductivity microstructure, fluorescence, optical backscatter, pressure, tri-axis acceleration and temperature and conductivity.



The VMP750 prior to deployment

At the majority of stations visited 2 single casts were made with the VMP to a depth of approximately 800m, although depth varied depending on sea state and vessel movement. When time allowed additional deployments were made. During adverse weather conditions the VMP was not always deployed due to the high risk of damage on recovery. Some damage was sustained to sensors during 2 collisions with the ship's hull in rough weather. Details are included in the attached log.

At the end of the cruise a series of measurements were made with the VMP over a single tidal cycle (12.5 hours) in 700m water depth. The aim of the experiment was to identify tidal variation and controls on mixing at the shelf break. The shallow water is within the operating range of the instrument so as to allow measurements of turbulence to the seabed.

Measurements from the VMP will provide estimates of the mixing rate in the upper ocean and help validate other methods



that will attempt to quantify mixing over the full water depth using CTD and LADCP measurements.

Data collection log:

VMP cast#	Time (UTC)	Station	Position	VMP max depth(m)	Water depth (m)	Comments
18 <sup>th</sup> October						
002	1025	On shelf		257	257	
003	1041	On shelf		260	260	
006	2349	1	Lat:34 36.77588 S Lon:17 2.59145 E	296	2620	Damage to sensors on deployment

**Damage report:**

- Fluorescence/OBS sensor damaged beyond repair. No replacement is available.

VMP cast#	Time (UTC)	Station	Position	VMP max depth(m)	Depth (m)	Comments
20 <sup>th</sup> October						
007	Start:0320 Stop:0342 Onboard:0400	2	Lat 35 26.50548 S Lon 014 59.38775E	772	4678	
008	In water:0903 Start:0909 Stop:0928 Onboard:0950	2	Lat 35 23.71945 S Lon 14 56.34373 E	781	4678	
<b>21<sup>st</sup> October: VMP cancelled due to poor weather</b>						
<b>22<sup>nd</sup> October:</b>						
010	In water:1103 Start: 1113 Stop: 1128	3		566	4906	
011	Start: 1146 Stop: 1203 Onboard:1225	3	Lat 36 29.06086 S Lon 013 9.77202 E	617	4909	Damage sustained on recovery. Tail bent, requires extensive repair. SBE equipment possible damage, requires test. Probe guard bent.
Tail repaired but not fully straightened due to concerns over strength. Seabird conductivity cell is broken. No spare available.						
25 <sup>th</sup> October						
012	In water:1931 Start: 1932 Stop:1952	4	Lat: 38 24.20697 S Lon: 010 0.46257 E	664	5075	
013	Start: 2005 Stop: 2024 Onboard:2040	4	Lat: 38 24.68361 S Lon: 010 0.73087 E	682	5094	
27 <sup>th</sup> October						
014	In water:1307 Start: 1310 Stop:1331	5	Lat:40 2.16676 S Lon:05 31.92582 E	772	5218	
015	Start: 1342 Stop: 1408 Onboard:1428	5	Lat: 40 2.40881 S Lon: 05 31.60112 E	917	5206	
29 <sup>th</sup> October						

016	In water:1704 Start: 1707 Stop:1730	6	Lat:40 0.30193 S Lon: 00 51.73288 E	748	4946	
017	Start:1744 Stop: 1805 Onboard:	6	Lat: 40 0.81429 S Lon: 00 52.68829 E	747	4933	
1 <sup>st</sup> November						
018	In water:1040 Start: 1044 Stop:1109	7	Lat: 40 0.73244 S Lon: 04 53.56153 W	874	3862	
019	Start:1120 Stop: 1122 Onboard:	7	Lat: 40 0.86082 S Lon :04 53.78374 W	975	3856	
020	Start: 1130 Stop:1158 Onboard:1215	7	Lat: 40 0.87504 S Lon: 04 53.81668 W	720	3856	

#### Shallow station.

VMP cast	Time (UTC)	Station	Position	VMP max depth(m)	Depth (m)	Comments
8 <sup>th</sup> November						
021	In water:2325 Start: 2329 Stop:2355 Onboard:0024	8	Lat:34 19.95072 S Lon: 17 36.85008 E	721	756	Didn't make bottom. Ship drifted to 800m due to strong wind. Brought VMP on board to reposition at 700m depth.
9 <sup>th</sup> November						
022	In water:0040 Start: 0045 Stop:0104 Onboard:0120	8	Lat:34 19.31300 S Lon:17 37.71436 E	724	724	Hit bottom, 731.44 dBar..
025	In water:1455 Start:1459 Stop: 1522	1	Lat:34 37.23939 S Lon:17 1.33467 E	854	2682	
026	Start:1534 Stop:1558 Onboard:1618	1	Lat:34 37.42504 S Lon:017 1.16827 E	903	2685	
10 <sup>th</sup> November						
027	In water:0603 Start:0605 Stop:0607 Onboard:0610	1.5	Lat: 34 56.64280 S Lon:16 2.19244 E	50	4312	Aborted at 50m. Water ingress to SBT plug. Cleaned and dried.
028	Test	---	---		---	SBT ok
029	In water:0616 Start:0619 Stop:0640	1.5	Lat:34 56.34336 S Lon: 16 2.51530 E	809	4319	SBT ok.
031	Start:0656 Stop:0717 Onboard:0737	1.5	Lat:34 55.39612 S Lon: 16 3.25787 E	803	4300	
14 <sup>th</sup> November						
032	In water:1247 Start:1249 Stop:1309	4.5	Lat:39 13.16123 S Lon:07 46.77096 E	748	5162	
033	Start:1326 Stop:1344	4.5	Lat:39 12.97353 S Lon:07 45.93249 E	654	5164	

	Onboard:1400					
15 <sup>th</sup> November						
034	In water:1055 Start:1058 Stop:1118	4.5	Lat:39 16.47269 S Lon:07 40.33877 E	730	5264	
035	Start:1131 Stop:1155 Onboard:1210	4.5	Lat:39 16.89741 S Lon:07 39.88133 E	870	5269	
17 <sup>th</sup> November						
036	In water:1013 Start:1016 Stop:1042	3.5	Lat:37 26.66276 S Lon:11 35.05860 E	962	5126	Made 975m!
037	Start:1055 Stop:1119 Onboard:1135	3.5	Lat:37 26.72274 S Lon: 11 34.94624 E	852	5126	
18 <sup>th</sup> November						
039	In water:0758 Start:0801 Stop:0817	2.5	Lat: 35 54.60505 S Lon: 14 4.78596 E	574	4866	576m only, winch paying out too slow.
040	Start:0831 Stop:0849	2.5	Lat: 35 54.40033 S Lon: 14 5.85147 E	692	4861	700m only.
041	Start:0907 Stop:0926 Onboard:1140	2.5	Lat:35 54.39759 S Lon: 14 6.74108 E	712	4861	Still shallow at 726m
21 <sup>st</sup> November: start of 12.5 hour tidal station at station 0.5 (~700m contour)						
VMP cast	Time (UTC)	Station	Position	VMP max depth(dBar)	Depth (m)	Comments
042	In water:1405 Start:1408 Stop:1426	0.5	Lat:34 18.62581 S Lon:17 37.58039 E	652	644	Hit bottom,.
043	Checking sensors	--	--		--	Checking sensors
044	In water:1448 Start:1453 Stop:1511	0.5	Lat: 34 19.11668 S Lon: 17 37.50409 E	740	730	All okay. Hit bottom. 740 dBar.
045	Start:1525 Stop:1543	0.5	Lat:34 19.50919 S Lon:17 37.56767 E	714	714	Hit bottom
046	Start:1557 Stop: 1614	0.5	Lat:34 20.02951 S Lon:017 37.65505 E	660	713	Problem with the sbt, suspect water ingress. Only made 660m due to line thrower slipping. Change elastic bands.
047	Test	--	--		--	Testing sbt. Sbt looks fine again, probably resealed at depth.
048	Start:1633 Stop:1651 Onboard:1702	0.5	Lat:34 20.60289 S Lon: 17 37.83608 E	745	737	Hit bottom @745 dBar. Sbt dipped out again at ~450m, returning later Recover to reseat sbt.
049	In water:1705 Start:1710 Stop:1729	0.5	Lat: 34 21.02911 S Lon: 17 38.07940 E	726	742	Possibly missed bottom. SBT is all good.
050	Start:1741 Stop: 1801	0.5	Lat: 34 21.43808 S Lon: 17 38.46258 E	756	744	Hit Bottom <b>Thin persistent warm layer near bed.</b>
051	Start:1820 Stop:1839	0.5	Lat:34 21.64469 S Lon: 17 39.08797 E	724	712	Hit bottom,
052	Start:1855	0.5	Lat 34	610	707	Not bottom

	Stop:1911		22.09910 S Lon 017 39.49270 E			
053	Start:1926 Stop:1943	0.5	Lat:34 22.74739 S Lon: 17 39.87530 E	660	715	Not bottom
054	Start:2003 Stop: 2021	0.5	Lat: 34 23.32647 S Lon: 17 40.48435 E	666	706	Not bottom
055	Start:2034 Stop: 2053	0.5	Lat:34 23.74459 S Lon:17 40.90375 E	710	700	not quite bottom.
056	Start:2104 Stop:2120	0.5	Lat: 34 24.16331 S Lon: 17 41.26855 E	640	700	Not bottom
057	Start:2134 Stop:2153	0.5	Lat:34 24.64438 S Lon:17 41.75399 E	693	694	not quite bottom
058	Start:2206 Stop:2225	0.5	Lat:34 25.18263 S Lon: 17 42.21491 E	701	693	Hit bottom, yeh! 701 dBar
059	Start:2235 Stop: 2252	0.5	Lat: 34 25.39668 S Lon:17 42.44053 E	691	691	Not bottom, but nearly!
060	Start:2306 Stop: 2322	0.5	Lat: 34 25.83826 S Lon: 17 42.68468 E	630	700	Not bottom! Only 630 dBar.
061	Start:2334 Stop:2352	0.5	Lat:34 26.36633 S Lon: 17 42.87414 E	718	719	Not bottom but nearly,
062	Start:0003 Stop:0022	0.5	Lat:34 26.69929 S Lon:17 43.12918 E	724	724	Hit bottom
063	Start:0033 Stop:0051	0.5	Lat: 34 26.94171 S Lon: 17 43.20649 E	748	734	nearly bottom.
064	Start:0104 Stop:0120	0.5	Lat: 34 26.94171 S Lon: 17 43.20649 E	618	734	Not bottom
Repositioned due to increased depth.						
065	Start:0154 Stop:0209	0.5	Lat:34 27.49987 S Lon: 17 42.99066 E	550	808	False start, jumped line thrower, remove first dip.
066	Start:0226 Stop:0232	0.5	Lat: 34 26.63973 S Lon: 17 43.16037 E	200	720	Bad cast, line thrower is playing up.
067	Start:0236 Stop:0252 On board:	0.5	Lat: 34 26.37170 S Lon: 017 43.11924 E	605	705	605 dBar. The end!
The end!						

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# ASSESSING MIXING AND CIRCULATION IN DEEP WATERS WITH $^{227}\text{Ac}$ AND $^{223,224,226,228}\text{Ra}$

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  $^{227}\text{Ac}$ , 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,  $^{227}\text{Ac}$  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  $^{231}\text{Pa}$  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 (for exact volumes see Table ), pumped over  $\text{MnO}_2$  absorbers in situ. The absorbers consisted of two 10 inch wound polypropylene filter cartridges (5  $\mu\text{m}$ , Parker) in series, each stuffed with ~25 g of  $\text{MnO}_2$  fibre inside. 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  $^{223}\text{Ra}$  or  $^{224}\text{Ra}$  excess near the sea floor, if present. The counter was calibrated regularly with two standard samples of the short-lived Ra parent nuclides  $^{227}\text{Ac}$  and  $^{228}\text{Th}$ , 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  $\text{MnO}_2$  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  $^{226}\text{Ra}$ , 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  $^{228}\text{Ra}/^{226}\text{Ra}$  in Oxford. At this stage, the fraction that is expected to contain  $^{227}\text{Ac}$  will be separated and representative samples will be analysed for  $^{227}\text{Ac}$  by alpha-spectrometry to further validate the Ac results from the RaDeCC system. The methods for measuring  $^{228}\text{Ra}/^{226}\text{Ra}$  ratios and  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  concentrations are described above (see sample analysis in WP4).

### Samples collected

An overview of the samples obtained is given in Table 5. In total, 15 deep samples, each consisting of two absorbers, were collected from four sites. One sample was lost because the sea water did not pass the absorber because of a broken connection.

Station	Lat	Lon	depth	volume	Sampling Date
Station 3	36°29.73392 S	13°6.54662 E	10	460	22/10/2010
Station 3	36°29.73392 S	13°6.54662 E	50	(3771) 0	22/10/2010
Station 3	36°29.73392 S	13°6.54662 E	100	217	22/10/2010
Station 3	36°29.73392 S	13°6.54662 E	200	607	22/10/2010
Station 3	36°29.73392 S	13°6.54662 E	1410	364	22/10/2010
Station 3	36°29.73392 S	13°6.54662 E	4335	350	22/10/2010
Station 3	36°29.73392 S	13°6.54662 E	4706	169	22/10/2010
Station 3	36°29.73392 S	13°6.54662 E	4776	(3312) 0	22/10/2010
Station 6	40°00'50.90''	00°56'25.60'' E	5	306	29/10/2010
Station 6	40°00'50.90''	00°56'25.60'' E	45	301	29/10/2010
Station 6	40°00'50.90''	00°56'25.60'' E	95	409.5	29/10/2010
Station 6	40°00'50.90''	00°56'25.60'' E	195	373	29/10/2010
Station 6	39°59'51.00''	00°54'01.49'' E	1500	340	29/10/2010
Station 6	39°59'51.00''	00°54'01.49'' E	4450	355.5	29/10/2010
Station 6	39°59'51.00''	00°54'01.49'' E	4850	418	29/10/2010
Station 6	39°59'51.00''	00°54'01.49'' E	4920	354	29/10/2010
Station1	34°37.28	'17°2.18'	20	591	08/11/2010
Station1	34°37.28	'17°2.18'	200	859.5	08/11/2010
Station1	34°37.11	'17°2.29'	1600	342	19/11/2010
Station1	34°37.11	'17°2.29'	-50	391	19/11/2010
Station 11	39°17.67'	7°40.224'	10	329	16/11/2010
Station 11	39°17.67'	7°40.224'	200	392	16/11/2010
Station 11	39°17.67'	7°40.224'	600	526.5	16/11/2010
Station 11	39°15.30'	7°43.42'	3241	182	15/11/2010
Station 11	39°15.30'	7°43.42'	4241	302	15/11/2010
Station 11	39°15.30'	7°43.42'	4741	286	15/11/2010
Station 11	39°15.30'	7°43.42'	5141	229	15/11/2010
Station 11	39°15.30'	7°43.42'	5211	450	15/11/2010

**Table 5:** List of radium/ actinium samples from the standalone pumping systems. Deep samples are shown in black. 15 samples of deep and near bottom water depths were collected, each consisting of two Mn-absorbers in series, in order to compensate for the effects of incomplete Ra/Ac recovery at high flow rates. All samples have been measured a first time for  $^{223,224}\text{Ra}$ ; a second measurement of supported activities, to be measured in Edinburgh, still stands out. Based on these results, samples will be selected for measurement of  $^{228}\text{Ra}/^{226}\text{Ra}$  ratios in Oxford. Subsamples (250 mL) for  $^{226}\text{Ra}$  analysis have been taken for all stations.  $^{227}\text{Ac}$  will be calculated from the results of the second measurement, and selected samples will be measured by established alpha-spectrometric methods (Geibert and Vöge 2008) to confirm the results of the RaDeCC system, and to achieve a higher precision.

### Preliminary results

Shipboard results indicate that the deepest samples are enriched in  $^{227}\text{Ac}$ , and to a lesser extent in  $^{228}\text{Th}$ , which is a non-quantitative indicator of  $^{228}\text{Ra}$ . Some evidence of elevated  $^{223}\text{Ra}_{\text{xs}}$  and  $^{224}\text{Ra}_{\text{xs}}$  very close to the sea floor was found, which would allow an estimate of the release of substances from the benthic nepheloid layer, but the significance of these findings needs to be investigated further, after the samples have returned.

$^{227}\text{Ac}$  activity levels, estimated from  $^{223}\text{Ra}$ , turned out to be much 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  $^{223}\text{Ra}/^{224}\text{Ra}$  (total) with water depth suggests that we should still be able to constrain vertical mixing in the deep Atlantic with our approach, as anticipated. However, the low concentrations would lead to relatively large uncertainties, and a re-analysis of some samples by alpha-spectrometry is currently planned in order to minimise uncertainties.

Preliminary data have been made available to the cruise participants.

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## 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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### NUTRIENTS

By Malcolm Woodward and Susan Reynolds

#### **Objectives**

To investigate the spatial and temporal variations of the micromolar nutrient species; Nitrate, Nitrite, Silicate, Ammonium and Phosphate during the research cruise across the 40 degree south transect line between CapeTown, South Africa, and Montevideo, Uruguay. Also where necessary to deploy an innovative analytical technique for nanomolar nutrient concentrations.

Analysis was also carried out for sediment Core water samples from Will Homoky, of NOC, and Gideon Henderson of Oxford University. Underway surface water samples were analysed for the transect back to CapeTown and during the inter-stations transects on the second leg after the medi-vac.

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.

Unfortunately the original aim to complete the cruise in Montevideo was not possible due to a medical emergency and the cruise terminated instead in CapeTown with a truncated cruise track.

#### **Sampling and Analytical Methodology**

The micro-molar analyser used was a 5 channel (nitrate, nitrite, phosphate, silicate, ammonium) Bran and Luebbe AAIII segmented flow, colorimetric, autoanalyser, and classical proven analytical techniques were used. The ammonium channel was dropped once we left the waters of the continental shelf of CapeTown and the sensitivity of the colorimetric system was insufficient for the water column concentrations found.

The system then used for ammonium 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 frozen, 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.

**CTD SAMPLES ANALYSED by AAIII AUTOANALYSER.**

Date	CTD	Position	CTD or TM bottle analysed
18/10/10	Test	34 <sup>0</sup> 11.43 <sup>°</sup> S 17 <sup>0</sup> 58.47 <sup>°</sup> E	1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18, 19, 20, 21, 22, 23, 24.
19/10/10	CTD_003 (SS)	34 <sup>0</sup> 36.73 <sup>°</sup> S 17 <sup>0</sup> 02.46 <sup>°</sup> E	1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18, 19, 20, 21, 22, 23, 24.
19/10/10	CTD_004 (TiT)	34 <sup>0</sup> 36.73 <sup>°</sup> S 17 <sup>0</sup> 02.46 <sup>°</sup> E	TM:45,44,43,42,41,40,39,38,37,36,35,34,33,3 2,31,30,29,28,27,26,25
19/10/10	CTD_005 (SS-Bio)	34 <sup>0</sup> 37.67 <sup>°</sup> S 17 <sup>0</sup> 04.07 <sup>°</sup> E	24,23,22,21,20,14,13,12,6,5
20/10/10	CTD_006 (SS)	35 <sup>0</sup> 28.32 <sup>°</sup> S 14 <sup>0</sup> 59.68 <sup>°</sup> E	1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18, 19, 20, 21, 22, 23, 24.
20/10/10	CTD_007 (TiT)	35 <sup>0</sup> 26.22 <sup>°</sup> S 14 <sup>0</sup> 58.93 <sup>°</sup> E	TM:82,83,84,85,86,87,88,89,90,91,92,93,94,9 5,96,97,98,99,100,101,102,103,104,105
20/10/10	CTD_008 (SS-Bio)	35 <sup>0</sup> 22.25 <sup>°</sup> S 14 <sup>0</sup> 54.48 <sup>°</sup> E	24,22,20,15,14,13,7,6,1
21/10/10	CTD_009 (SS)	36 <sup>0</sup> 30.38 <sup>°</sup> S 13 <sup>0</sup> 06.84 <sup>°</sup> E	1,2,4,5,9,10,11,13,14,15,16,17
23/10/10	CTD_011 (SS)	36 <sup>0</sup> 29.22 <sup>°</sup> S 13 <sup>0</sup> 16.63 <sup>°</sup> E	5,6,7,8,9,11,12,13,15,16,17,18, 19, 20, 22, 23
24/10/10	CTD_013 (TiT)	36 <sup>0</sup> 27.91 <sup>°</sup> S 13 <sup>0</sup> 21.15 <sup>°</sup> E	TM:163,164,165,166,167, 168,169,170,171,172,173,174,175,176,177,17 8,179,180,181,182,183,184,186.
24/10/10	CTD_014 (TiT)	36 <sup>0</sup> 27.65 <sup>°</sup> S 13 <sup>0</sup> 12.39 <sup>°</sup> E	TM:187,188,189,190,191,192,193,194,195,19 6,197,198,199,200,201,202,203,204,205,206, 207,208,209,210
25/10/10	CTD_015 (SS)	38 <sup>0</sup> 24.13 <sup>°</sup> S 010 <sup>0</sup> 00.04 <sup>°</sup> E	1,3,4,6,7,8,10,11,13,14,16,17,18, 19, 20, 21, 22, 23, 24.
26/10/10	CTD_017 (TiT)	38 <sup>0</sup> 25.62 <sup>°</sup> S 10 <sup>0</sup> 03.14 <sup>°</sup> E	TM:235,236,237,238,239,240,241,242,243,24 4,245,246,247,248,249,250,251,252,253,254, 255,256,258
26/10/10	CTD_018 (SS-Bio)	38 <sup>0</sup> 25.46 <sup>°</sup> S 010 <sup>0</sup> 05.17 <sup>°</sup> E	1,3,4,6,7,8,9,10,11,12,13,14,15,16,18, 19, 20, 21, 22, 23, 24.
27/10/10	CTD_019 (SS)	40 <sup>0</sup> 00.58 <sup>°</sup> S 005 <sup>0</sup> 30.55 <sup>°</sup> E	2,3,4,6,7,8,9,11,12,13,14,15,16,18, 19, 21, 23, 24.
27/10/10	CTD_020 (TiT)	40 <sup>0</sup> 02.57 <sup>°</sup> S 05 <sup>0</sup> 31.48 <sup>°</sup> E	TM:307,308,309,310,311,312,313,314,315,31 6,317,318,319,320,321,322,323,325,326,327, 328,329,330
27/10/10	CTD_021 (SS-Bio)	40 <sup>0</sup> 25.52 <sup>°</sup> S 005 <sup>0</sup> 31.61 <sup>°</sup> E	1,7,8,9,10,11,12,13,14,15,20, 21, 22, 23, 24.
29/10/10	CTD_022 (SS)	39 <sup>0</sup> 59.99 <sup>°</sup> S 000 <sup>0</sup> 49.21 <sup>°</sup> E	1,2,3,5,7,8,9,10,11,12,13,14,15,16,17,18, 19, 22, 24.
29/10/10	CTD_023 (TiT)	40 <sup>0</sup> 00.86 <sup>°</sup> S 00 <sup>0</sup> 49.97 <sup>°</sup> E	TM:380,381,382,383,384,385,386,387,388,38 9,390,391,392,393,394,395,396,397,398,399, 400,401,402,403
29/10/10	CTD_024 (SS-Bio)	40 <sup>0</sup> 01.21 <sup>°</sup> S 000 <sup>0</sup> 53.16 <sup>°</sup> E	1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18, 19, 20,21,22, 23,24.
30/10/10	CTD_025 (TiT)	39 <sup>0</sup> 59.46 <sup>°</sup> S 000 <sup>0</sup> 55.21 <sup>°</sup> E	TM:428,429,430,431,432,433,434,435,436,43 7,438,439,440,441,442,443,444,445,446,447, 448,449,450,451

01/11/10	CTD_026 (SS)	40 <sup>0</sup> 00.54'S 04 <sup>0</sup> 54.30'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.
9/11/10	CTD_028 (SS)	34 <sup>0</sup> 20.08'S 17 <sup>0</sup> 36.54'E	1,2,3,4,5,6,7,8,9,11,12,14,15,16,17,18, 19, 20,21,24.
9/11/10	CTD_029 (TM)	34 <sup>0</sup> 37.35'S 17 <sup>0</sup> 00.97'E	TM:476,477,478,479,480,481,482,483,484, 485,486,487,488,489,490,491,492,493,494,49 5,496,497
10/11/10	CTD_030 (SS)	37 <sup>0</sup> 58.76'S 16 <sup>0</sup> 00.97'E	1,2,3,4,5,6,7,8,9,10,11,12,15,16,17,18, 19, 20,21,22, 23,24.
10/11/10	CTD_031 (TM)	34 <sup>0</sup> 54.27'S 16 <sup>0</sup> 04.27'E	TM:548,549,550,551,552,553,554,555,556,55 7,558,559,560,561,562,563,564,565,566,567, 568,569,570,571
10/11/10	CTD_032 (SS-Bio)	37 <sup>0</sup> 54.20'S 16 <sup>0</sup> 04.49'E	1,6,7,8,9,10,11,12,13,14,19, 20,21,22, 23,24.
11/11/10	CTD_033 (SS)	35 <sup>0</sup> 54.99'S 14 <sup>0</sup> 03.66'E	1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18, 19, 20,21,22,23,24.
11/11/10	CTD_034 (TM)	35 <sup>0</sup> 57.42'S 14 <sup>0</sup> 04.68'E	TM:620,621,623,624,625,626,627,628,629,63 0,631,632,633,634,635,636,637,638,639,640, 6421,642,643
12/11/10	CTD_035 (SS-Bio)	36 <sup>0</sup> 27.07'S 13 <sup>0</sup> 13.03'E	1,6,7,8,9,10,11,12,13,14,15,16,17,18,19, 20,21,22, 23,24.
12/11/10	CTD_036 (TM)	36 <sup>0</sup> 27.87'S 13 <sup>0</sup> 12.66'E	TM:644,645,646,647,648,649,650,651,650,65 1,652,653,654,655,656,657,658,659,660,661, 662,663,664,665,666,667
14/11/10	CTD_037 (SS)	39 <sup>0</sup> 12.83'S 07 <sup>0</sup> 48.49'E	1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18, 19, 20,22,23,24.
15/11/10	CTD_038 (TM)	39 <sup>0</sup> 14.98'S 07 <sup>0</sup> 44.71'E	TM:716,717,718,719,720,721,722,723,724,72 5,726,727,728,729,730,731,732,733,734,735, 736,737
15/11/10	CTD_039 (SS-Bio)	39 <sup>0</sup> 15.42'S 07 <sup>0</sup> 43.69'E	1,2,6,7,8,9,10,11,12,13,14,15,16,17,18,19, 20,21,22, 23,24.
15/11/10	CTD_040 (TM)	39 <sup>0</sup> 17.61'S 07 <sup>0</sup> 38.99'E	TM:764,765,766,767,768,769,770,771,772,77 3,774,775,776,777,778,779,780,781,782,783, 784,785,786,787
17/11/10	CTD_041 (TM)	37 <sup>0</sup> 26.51'S 11 <sup>0</sup> 38.70'E	TM:788,789,790,791,792,793,794,795,796,79 7,798,799,800,801,802,803,804,805,806,807, 808,809,810,811
17/11/10	CTD_042 (SS-Bio)	37 <sup>0</sup> 27.83'S 11 <sup>0</sup> 33.58'E	1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,1 9, 20,21,22, 23,24.
18/11/10	CTD_043 (SS-Bio)	35 <sup>0</sup> 55.06'S 14 <sup>0</sup> 03.83'E	1,2,6,7,8,9,10,11,12,13,14,15,16,17,18,19, 20,21,22, 23,24.
19/11/10	CTD_044 (SS-Bio)	34 <sup>0</sup> 42.07'S 17 <sup>0</sup> 02.11'E	1,2,3,4,5,6,7,8,9,10,11,13,14,15,16,17,18,19, 20,21,22, 23,24.
19/11/10	CTD_045 (TM)	34 <sup>0</sup> 18.75'S 12 <sup>0</sup> 36.06'E	TM:884,885,886,887,888,889,890,891,892,89 3,894,895,896,897,898,899,900,901,902,903, 904,905,906,907
19/11/10	CTD_046 (SS-Bio)	34 <sup>0</sup> 18.20'S 17 <sup>0</sup> 34.69'E	1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,1 9, 20,21,22, 23,24.

**CTD SAMPLES ANALYSED for NANOMOLAR AMMONIUM.**

Date	CTD	Position	CTD bottles analysed
19/10/10	CTD_003 (SS)	34 <sup>0</sup> 36.73°S 17 <sup>0</sup> 02.46°E	2,3,4,5,6,8,9,10,11,12,13,14,15,16,18, 19,21, 22, 23, 24.
19/10/10	CTD_005 (SS-Bio)	34 <sup>0</sup> 37.67°S 17 <sup>0</sup> 04.07°E	24,23,22,21,20,14,12,6,5
20/10/10	CTD_006 (SS)	35 <sup>0</sup> 28.32°S 14 <sup>0</sup> 59.68°E	1,2,3,4,5,7,9,10,12,14,16,17,18, 19, 20, 21, 22, 23, 24.
20/10/10	CTD_008 (SS-Bio)	35 <sup>0</sup> 22.25°S 14 <sup>0</sup> 54.48°E	24,22,20,15,14,13,7,6,1
21/10/10	CTD_009 (SS)	36 <sup>0</sup> 30.38°S 13 <sup>0</sup> 06.84°E	1,2,4,5,9,10,11,13,14,15,16,17
23/10/10	CTD_011 (SS)	36 <sup>0</sup> 29.22°S 13 <sup>0</sup> 16.63°E	5,6,7,8,9,11,12,15,16,17,18, 19, 20, 22, 23
25/10/10	CTD_015 (SS)	38 <sup>0</sup> 24.13°S 010 <sup>0</sup> 00.04°E	1,3,4,6,7,8,10,11,13,14,16,17,18, 19, 20, 21, 22, 23, 24.
26/10/10	CTD_018 (SS-Bio)	38 <sup>0</sup> 25.46°S 010 <sup>0</sup> 05.17°E	7,8,11,13,15,18,20, 21, 22,24.
27/10/10	CTD_019 (SS)	40 <sup>0</sup> 00.58°S 005 <sup>0</sup> 30.55°E	2,3,4,6,7,8,9,11,12,13,14,15,16,18, 19, 21, 23, 24.
27/10/10	CTD_021 (SS-Bio)	40 <sup>0</sup> 25.52°S 005 <sup>0</sup> 31.61°E	1,7,8,9,11,13,14,15,20, 21, 24.
29/10/10	CTD_022 (SS)	39 <sup>0</sup> 59.99°S 000 <sup>0</sup> 49.21°E	1,2,3,5,7,8,9,10,11,12,13,14,15,16,18, 19, 22, 24.
29/10/10	CTD_024 (SS-Bio)	40 <sup>0</sup> 01.21°S 000 <sup>0</sup> 53.16°E	2,4,6,8,10,12,14,16,18,20,22, 24.
01/11/10	CTD_026 (SS)	40 <sup>0</sup> 00.54°S 04 <sup>0</sup> 54.30°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.
10/11/10	CTD_030 (SS)	37 <sup>0</sup> 58.76°S 16 <sup>0</sup> 00.97°E	1,3,5,6,8,9,11,15,16,18, 19, 20,21,22, 23,24.
11/11/10	CTD_033 (SS)	35 <sup>0</sup> 54.99°S 14 <sup>0</sup> 03.66°E	1,2,3,4,5,6,7,8,9,10,11,12,14,15,17,19, 20,21,22,23,24.
12/11/10	CTD_035 (SS-Bio)	36 <sup>0</sup> 27.07°S 13 <sup>0</sup> 13.03°E	1,6,7,8,9,10,11,12,13,14,15,16,17,18,19,21,22 , 23,24.
14/11/10	CTD_037 (SS)	39 <sup>0</sup> 12.83°S 07 <sup>0</sup> 48.49°E	1,3,5,6,8,9,11,13,15,16,17,18, 19, 20,22,23,24.
15/11/10	CTD_039 (SS-Bio)	39 <sup>0</sup> 15.42°S 07 <sup>0</sup> 43.69°E	1,2,6,7,8,9,10,11,12,13,14,15,16,17,18,19, 20,21,22, 23,24.
17/11/10	CTD_042 (SS-Bio)	37 <sup>0</sup> 27.83°S 11 <sup>0</sup> 33.58°E	1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,1 9, 20,21,22, 23,24.
18/11/10	CTD_043 (SS-Bio)	35 <sup>0</sup> 55.06°S 14 <sup>0</sup> 03.83°E	1,2,6,7,8,9,10,11,12,14,15,16,17,21,22, 23,24.
19/11/10	CTD_044 (SS-Bio)	34 <sup>0</sup> 42.07°S 17 <sup>0</sup> 02.11°E	1,2,3,4,5,6,7,8,9,10,11,13,14,15,16,17,18,19, 20,21,22, 23,24.
19/11/10	CTD_046 (SS-Bio)	34 <sup>0</sup> 18.20°S 17 <sup>0</sup> 34.69°E	1,2,3,5,6,7,9,10,11,13,14,15,16,17,18,19, 20,22,24.

### **Coring samples for nutrients**

These samples were from Will Homoky and Gideon Henderson, so please see their cruise report for details as to how these samples were acquired. They were taken and then frozen at -20C, and then defrosted just prior to analysis.

Before analysis they were defrosted and then diluted to a volume of 30 mls total so as to allow for sufficient sample to analyse on the AAIII.

The samples were taken by the Multi-Corer on the first transect, and with a Gravity corer during the second cruise leg after the medi-vac.

The normal volume provided to us was around 2 mls, making a dilution of x15, but this did vary and corrections were applied accordingly to calculate the exact concentrations of the original samples.

**Core 1:** 13 depths analysed 22<sup>nd</sup> October, bottle numbers:

001,002,008,009,010,011,012,013,014,016,017,018,020

**Core 2:** 24 depths analysed 24<sup>th</sup> October, bottle numbers:

015,022,023,024,025,026,027,028,029,020,031,032,033,034,035,036,037,038,039,040,041,042,043,044.

**Core 3:** 15 depths analysed 31<sup>st</sup> October, bottle numbers:

045,046,047,048,049,050, 051,052,053,054,055,056,057,058,059.

**Core 4:** 12 depths analysed 17<sup>th</sup> November, bottle numbers:

060,061,062, 063, 064, 065, 066, 067, 068, 069, 070, 071.

**Gideon dSi: Station 11:** Analysed 17<sup>th</sup> November:

Surface, 0-2, 2-4, 4-6, 6-8, 8-10,10-12,12-14 cms

**Core 5:** 15 depths analysed 21<sup>st</sup> November, bottle numbers:

072,073,074,075,076,077, 078,079,080,081,082,083,084,085,086.

**Gideon dSi: Station 13:** Analysed 21<sup>st</sup> November:

0-2 cms

**Gideon dSi: Station 8:** Analysed 21<sup>st</sup> November:

0-2, 2-4, 4-6, 6-8, 8-10,10-12,12-14 cms

### **Underway sampling from Trace Metal Fish**

Samples taken for nutrients:

2/11/10 @ 1000 to 4/11/10 @0800

4/11/10@1200 to 5/11/10@1400

9/11/10@2000 to 10/11/10@0001

10/11/10@2355 to 12/11/10@0200

16/11/10@0600 to 17/11/10@0100

17/11/10@1400 to 18/11/10@0200

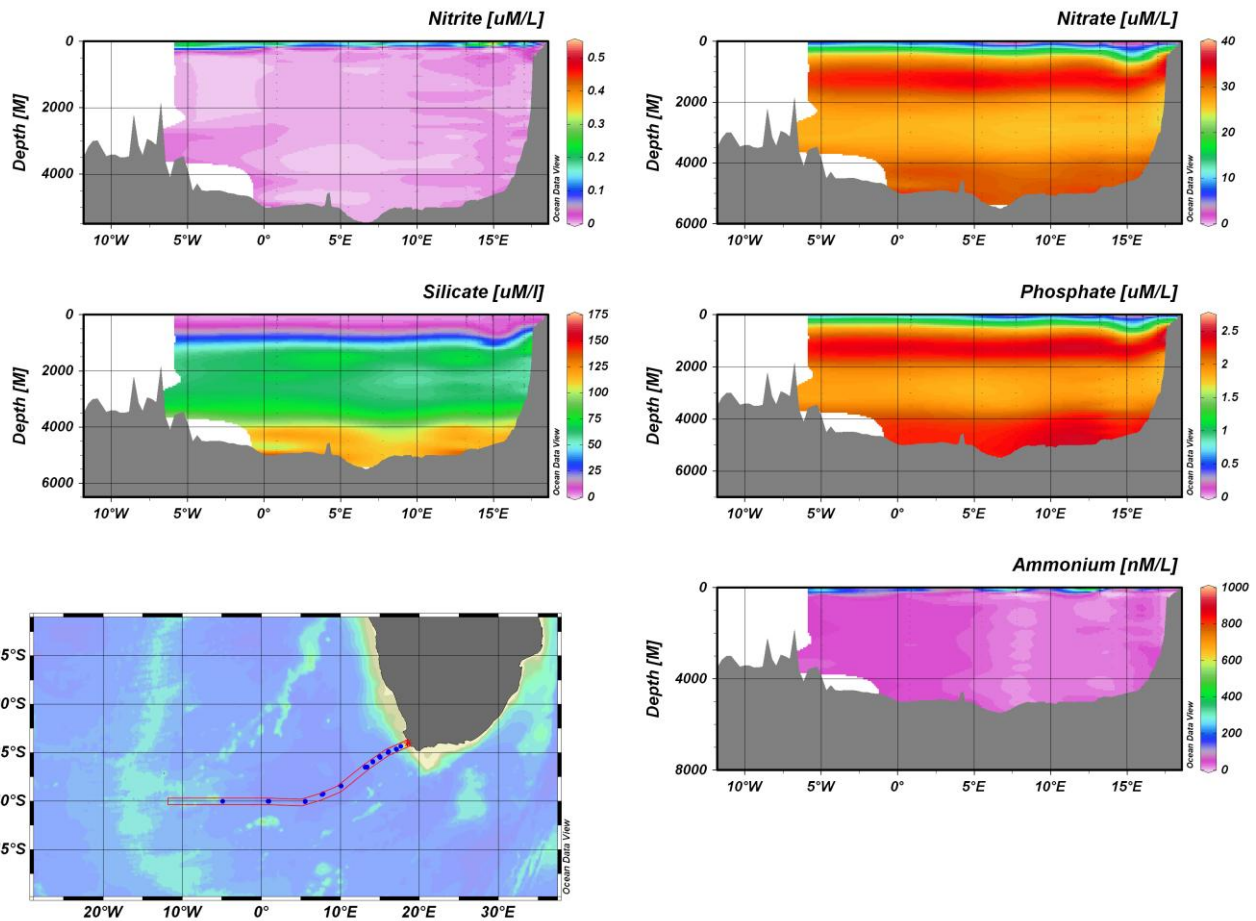
18/11/10@1200 to 19/11/10@1200

20/11/10@2120 to 21/11/10@0800

### **Cruise results and summary**

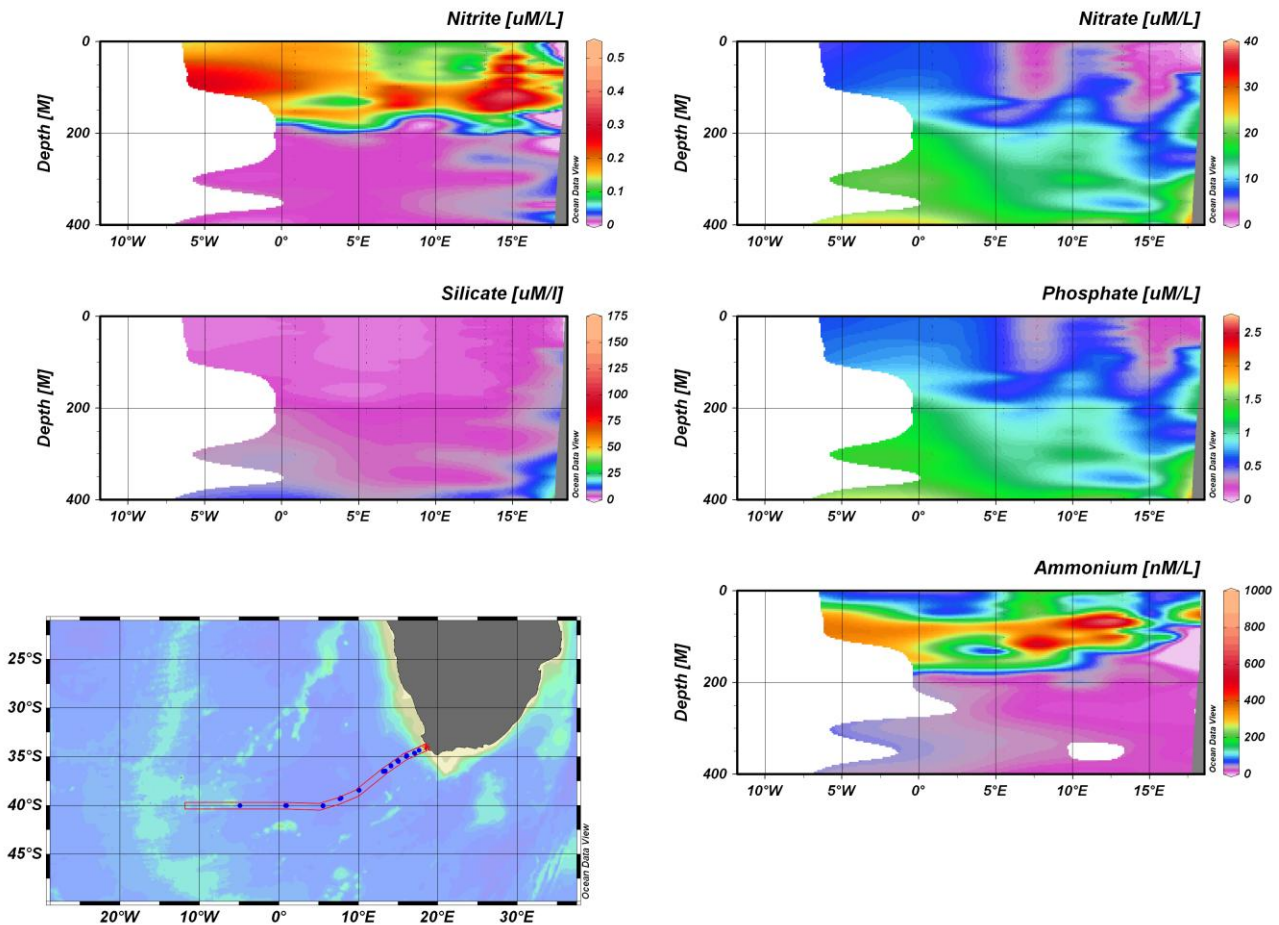
The 5-channel autoanalyser worked very well throughout the cruise, all preliminary data handling and work-up was carried out on the cruise. Likewise all the data for the nanomolar ammonium analyser was also worked up in its preliminary form.

Initial results are shown below using Ocean Data View (ODV) for the plotting.



This plot shows the nutrient results for the initial transect from CapeTown out to approximately 5 degrees West. These results are for the CTD stations and results reported from the samples to full ocean depth.

The different nutrient field concentrations show clearly the different water masses found when investigating the water column in the regions, for example the deep Antarctic bottom water can be observed with its very high silicate concentrations of over 100µM. There is finer scale detail that can be seen on the South African continental shelf.



This second diagram shows the results for just the upper 400 metres of the water column. Much finer scale detail can be seen for these surface waters and particularly visible is the ammonium maximum region between 100 and 200 metres and the linked nitrite maximum area, both are caused by the increased biological activity in that region of the water column where the chlorophyll maximum is found and where the nitrate is increasing from the more nutrient depleted surface mixed layer waters to the nutrient replete deeper colder waters. It is interesting that we can see the effect of the results of the second leg of the cruise when we carried out sampling about 3 weeks after the initial pass through the region, and areas of nutrient depletion for the phosphate and nitrate can clearly be seen. These results were mirrored in the chlorophyll results and indicated that from when the first transect was carried out it was just a pre-bloom situation whereas 3 weeks later the bloom had started to build and the nutrients were being depleted as the chlorophyll increased. A more detailed and time organised report will need to be carried out to highlight the different results and the effect of the onset of the spring bloom.

#### Thanks:

To the RRS Discovery, her officers, crew, and catering superstars for making it all possible. Thanks also to CSIRO Hobart and Dave Terhell in particular for making it possible for this collaboration to happen, and for allowing Sue to participate on this cruise and for the support of CSIRO in the form of a CDF grant. To Myriam and Cynthia who helped when asked with sampling and washing bottles, we thank you. Special thanks to all the other cruise scientists for making this cruise a pleasure to be a part of, a great team effort. See you all soon in CapeTown again ....Geotraces will be back !!!!

# DISSOLVED OXYGEN

By Susan Reynolds, CSIRO Marine and Atmospheric Research, Hobart, Tasmania

## Objectives

To measure dissolved oxygen concentrations at discreet depths in the water column as captured by the CTD/Rosette system to calibrate the CTD oxygen sensors during the research cruise across the 40 degree south transect line between CapeTown, South Africa, and Montevideo, Uruguay. However, due to an unforeseen circumstance, the ship had to turn around from this transect and covered only a section of it before returning to Cape Town. Dissolved oxygen values and temperatures measured during sampling were also useful indicators of CTD bottle misfiring.

## Sampling and Analytical Methodology

Water samples were taken from a 24 x 20 litre stainless steel CTD/Rosette system (SeaBird). Wide-mouth gravimetrically calibrated BOD bottles of 115ml nominal capacity were used to collect dissolved oxygen samples in. Samples were taken from the Rosette bottles through silicone tubing and both bottles and stoppers were rinsed thoroughly with the tubing at the bottom of the horizontally held bottle. The bottles were then turned upright and 3-4 volumes of water allowed to overflow from the bottle. While filling, the temperatures were recorded with a submersible thermometer. Then the tube was slowly withdrawn from the bottles while water was still flowing. Immediately after filling the bottles, 1ml manganous chloride followed by 1ml of sodium iodide-sodium hydroxide solution were added such that the tip of the automatic dispenser was submerged while adding both reagents. The bottle stoppers were carefully placed in the bottles to ensure no bubbles were trapped and the samples were shaken vigorously. The samples were then reshaken about 20 minutes later once the precipitate had settled to the bottom of the bottles. Clean handling techniques were employed to avoid any contamination of the samples and Dura-Touch gloves were worn at all times during sampling and analysis.

Samples were analysed at least 2 hours after, or within 24 hours of, collection by Winkler Titration using an Amperometric End Point Detection on a Metrohn Titrimo.

Standardization of the automated system was carried out using repeat aliquots of 10ml and 1ml volumes of OSIL Iodate Standard (0.01N, 1.667mM) in deionized water to produce a titre volume and reagent blank volume respectively. These were then used to determine the Thiosulphate Normality. Samples are then acidified with 1ml of diluted sulfuric acid solution and titrated with thiosulphate until the sample solutions were clear and a current was no longer flowing between the indicator electrodes

No water column water samples were frozen or stored in any way.

## CTD Samples analysed for dissolved Oxygen

Date	CTD	Position	CTD or TM bottle analysed
19/10/10	CTD_003 (SS)	34 <sup>0</sup> 36.73'S 17 <sup>0</sup> 02.46'E	1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18, 19, 20, 21, 22, 23, 24.
20/10/10	CTD_006 (SS)	35 <sup>0</sup> 28.32'S 14 <sup>0</sup> 59.68'E	1,2,4,5,6,,8,10,12,15,17,18, 20.
20/10/10	CTD_008 (SS-Bio)	35 <sup>0</sup> 22.25'S 14 <sup>0</sup> 54.48'E	1,6,7,13,14,15,20,22,24.
21/10/10	CTD_009 (SS)	36 <sup>0</sup> 30.38'S 13 <sup>0</sup> 06.84'E	1,2,4,5,9,10,11,13,14,15,16,17.
23/10/10	CTD_011 (SS)	36 <sup>0</sup> 29.22'S 13 <sup>0</sup> 16.63'E	5,7,9,12,14,16,18, 20,22,23.
25/10/10	CTD_015 (SS)	38 <sup>0</sup> 24.13'S 010 <sup>0</sup> 00.04'E	1,3,4,6,7,8,10,11,13,14,16,17,18,19,20,21,22, 23,24.
26/10/10	CTD_018 (SS-Bio)	38 <sup>0</sup> 25.46'S 010 <sup>0</sup> 05.17'E	1,8,9,10,11,12,13,14,15,16,18,19,20,21,22,23, 24.
27/10/10	CTD_019	40 <sup>0</sup> 00.58'S	2,3,4,6,7,8,9,11,12,13,14,15,16,18,19,21,23,



	(SS)	005 <sup>0</sup> 30.55°E	24.
27/10/10	CTD_021 (SS-Bio)	40 <sup>0</sup> 25.52°S 005 <sup>0</sup> 31.61°E	1,7,8,9,10,11,12,13,14,15,20,21,22,23,24.
29/10/10	CTD_022 (SS)	39 <sup>0</sup> 59.99°S 000 <sup>0</sup> 49.21°E	1,2,3,4,5,7,8,9,10,11,12,13,14,15,16,17,18,19, 22,24.
29/10/10	CTD_024 (SS-Bio)	40 <sup>0</sup> 01.21°S 000 <sup>0</sup> 53.16°E	2,4,6,8,10,12,14,16,18,20,22,24.
01/11/10	CTD_026 (SS)	40 <sup>0</sup> 00.54°S 04 <sup>0</sup> 54.30°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.
09/11/10	CTD_028 (SS)	34 <sup>0</sup> 20.08°S 017 <sup>0</sup> 36.54°E	1,2,3,4,5,6,7,8,9,11,12,14,15,16,17,18,19,20, 21,24.
10/11/10	CTD_030 (SS)	34 <sup>0</sup> 58.76°S 016 <sup>0</sup> 00.94°E	1,2,3,4,5,6,7,8,9,10,11,12,15,16,17,18, 19, 20, 21, 22, 23, 24.
10/11/10	CTD_032 (SS-Bio)	34 <sup>0</sup> 54.20°S 016 <sup>0</sup> 04.49°E	1,6,7,8,9,10,11,13,14,19, 21, 23.
11/11/10	CTD_033 (SS)	35 <sup>0</sup> 54.99°S 014 <sup>0</sup> 03.66°E	1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,1 9,20,21,22,23,24.
12/11/10	CTD_035 (SS-Bio)	36 <sup>0</sup> 27.07°S 013 <sup>0</sup> 13.03°E	1,6,7,8,9,10,11,12,13,14,15,16,17,18,19,20, 21, 22, 23, 24.
14/11/10	CTD_037 (SS)	39 <sup>0</sup> 12.83°S 007 <sup>0</sup> 48.49°E	1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18, 19, 20,22, 23,24.
15/11/10	CTD_039 (SS-Bio)	39 <sup>0</sup> 15.42°S 007 <sup>0</sup> 43.69°E	1,2,6,7,8,9,10,11,12,13,14,15,16,17,18,19,20, 21,22,23,24.
17/11/10	CTD_042 (SS-Bio)	37 <sup>0</sup> 27.83°S 011 <sup>0</sup> 33.58°E	1,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18, 19,20,21,22,23,24.
18/11/10	CTD_043 (SS-Bio)	32 <sup>0</sup> 55.06°S 014 <sup>0</sup> 03.83°E	1,2,6,7,8,9,10,11,12,13,14,15,16,17,21,22,23, 24.
19/11/10	CTD_044 (SS-Bio)	34 <sup>0</sup> 42.07°S 017 <sup>0</sup> 02.11°E	1,2,3,4,5,6,7,8,9,10,11,13,14,15,16,17,18, 19,20,21,22,23,24.
19/11/10	CTD_046 (SS-Bio)	34 <sup>0</sup> 18.20°S 017 <sup>0</sup> 34.69°E	1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,1 9,20,21,22,23,24.

### Cruise Results and Summary

The Titrino Titrator with Amperometric Detection worked very well throughout the cruise. All data handling and work-up was carried out on the cruise. Dissolved oxygen concentrations were calculated in  $\mu\text{mol/L}$  and the data values were available prior to the end of the cruise. DO values and their corresponding sampling temperatures were quite useful in indicating CTD Rosette bottle misfires. Preliminary plots by the Data Manager indicated a slight offset in dissolved oxygen data from oxygen sensor data in mainly surface bottles. There appeared to be a few dissolved oxygen outliers, but for the most part, dissolved oxygen data indicated that the CTD oxygen sensor functioned quite well and accurately.

### Thanks

To the RRS Discovery, her officers and crew for making it all possible. Special thanks to all the other cruise scientists for making this cruise a pleasure to be a part of, a great team effort.

# SALINITY

By Myriam Lambelet and Ed Mawji

Samples analysed by Myriam Lambelet

## 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 stainless steel casts and for all Ti main casts. Most biological stainless steel cast were sampled as well. However, when several OTE bottles were fired at the same water depth (e.g. during recovery of large volume samples for Ra analysis), some were sampled for salinity measurement. A total of 712 sample measurements were made during D357. All samples were analysed by Myriam Lambelet

## Sample analysis

The measurements were conducted on board with a Guildline Autosol 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 24°C, and the room temperature was about 2°C below the bath temperature.

The Autosol was standardized before each batch of samples with IAPSO Standard Seawater (SSW) provided by OSIL. All SSW were from the batch P151, the conductivity ratio of which was  $K_{15}=0.99997$  corresponding to practical salinity 34.999. After each batch of samples, a SSW was measured in order to verify the stability of the Autosol.

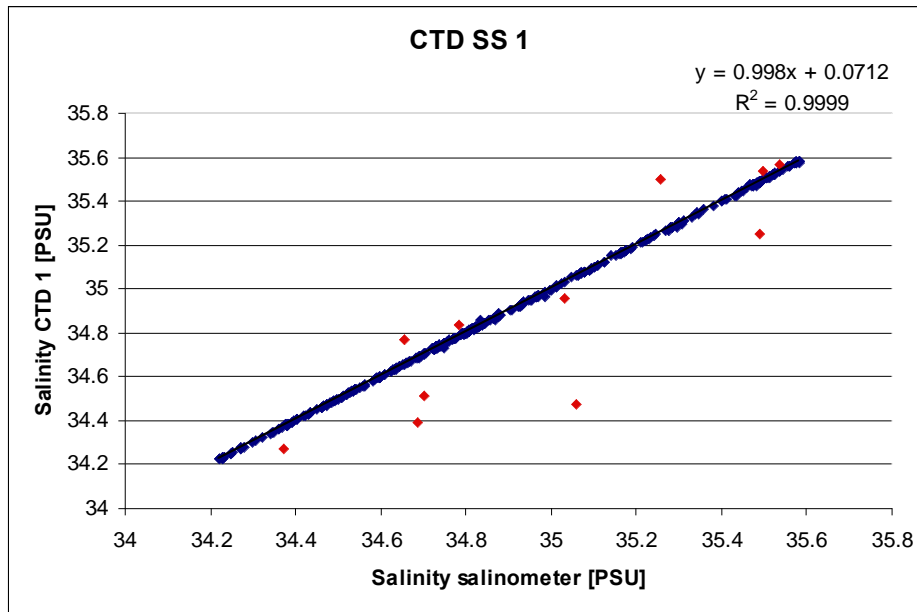
A sample measurement consisted in flushing three times the conductivity cell with sample water, then measuring three times the double conductivity ratio of the sample, the cell being flushed between each measurement. The data standard deviation was set to  $\pm 0.00005$ , and if a double conductivity ratio value was exceeding this standard deviation, another measurement was done to replace the "outlier" value.

The Autosol 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

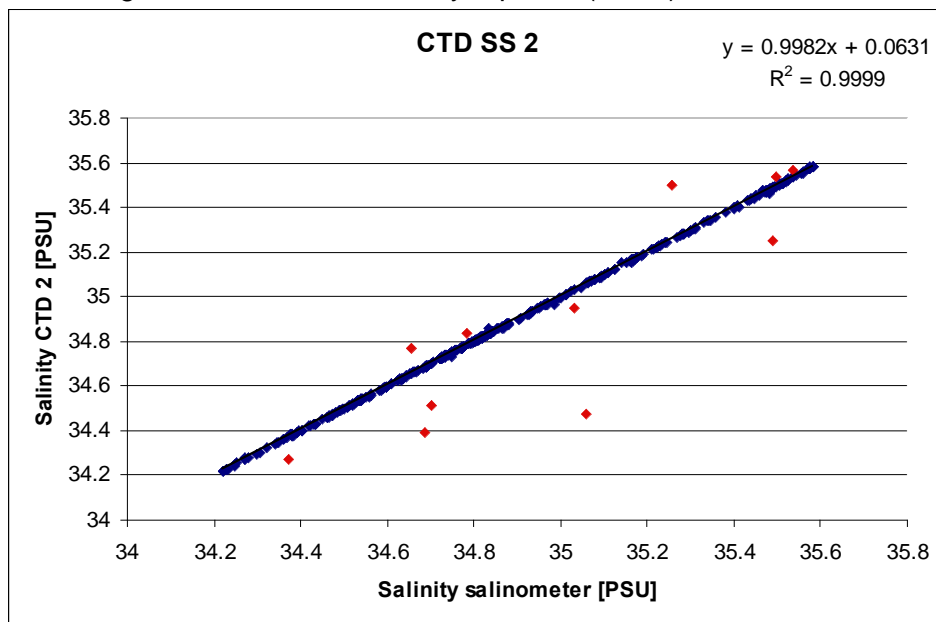
the average value for the 3 measurements and the data standard deviation. The software allowed as well the calculation of the practical salinity, which was done offline.

## Results

The graphs 1 and 2 show the correlation between the salinity measured with the salinometer and the one obtained by the CTD 1 and 2 respectively for the stainless steel (normal and biological) casts (SS).



**Graph 1:** correlation between the salinity measured by the salinometer (x-axis) and the one measured by the CTD 1 (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.



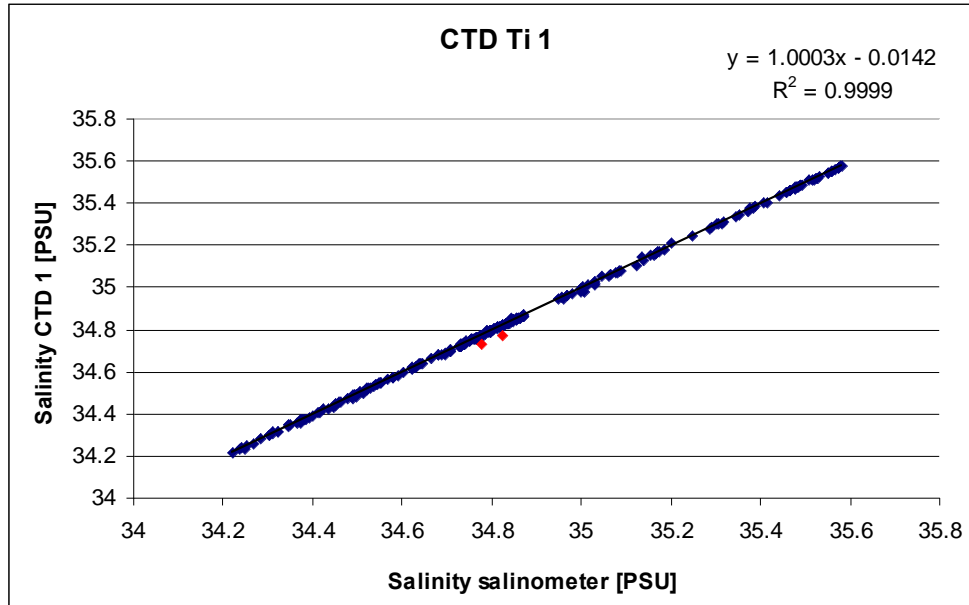
**Graph 2:** correlation between the salinity measured by the salinometer (x-axis) and the one measured by the CTD 2 (y-axis) for the stainless steel rosette. For the determination of the equation and of the regression coefficient, the flyer points (in red) were not taken in account.

For the stainless steel rosette, there are 11 flyer points (in red in graph 1 and 2). They correspond to the following Geotrace samples:

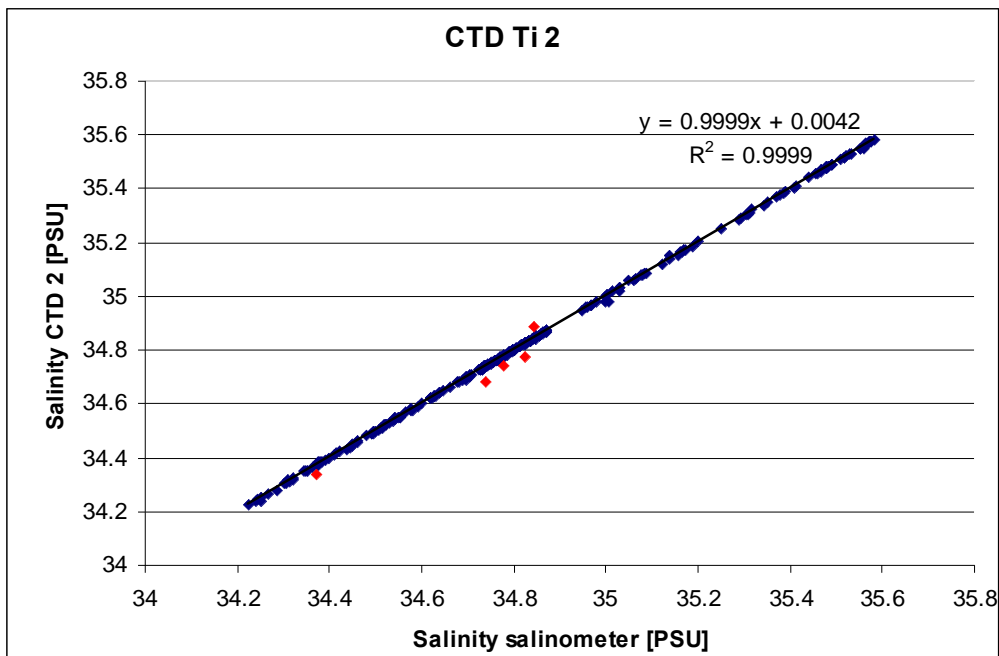
- 105, 106, 107 and 108 from CTD008\_SS
- 123, 128 and 129 from CTD009\_SS

- 288 from CTD019\_SS
- 614 from CTD033\_SS
- 912 and 916 from CTD046\_SS

The graphs 3 and 4 show the correlation between the salinity measured with the salinometer and the one obtained by the CTD 1 and 2 respectively for the Ti main casts.



**Graph 3:** correlation between the salinity measured by the salinometer (x-axis) and the one measured by the CTD 1 (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.



**Graph 4:** correlation between the salinity measured by the salinometer (x-axis) and the one measured by the CTD 2 (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.

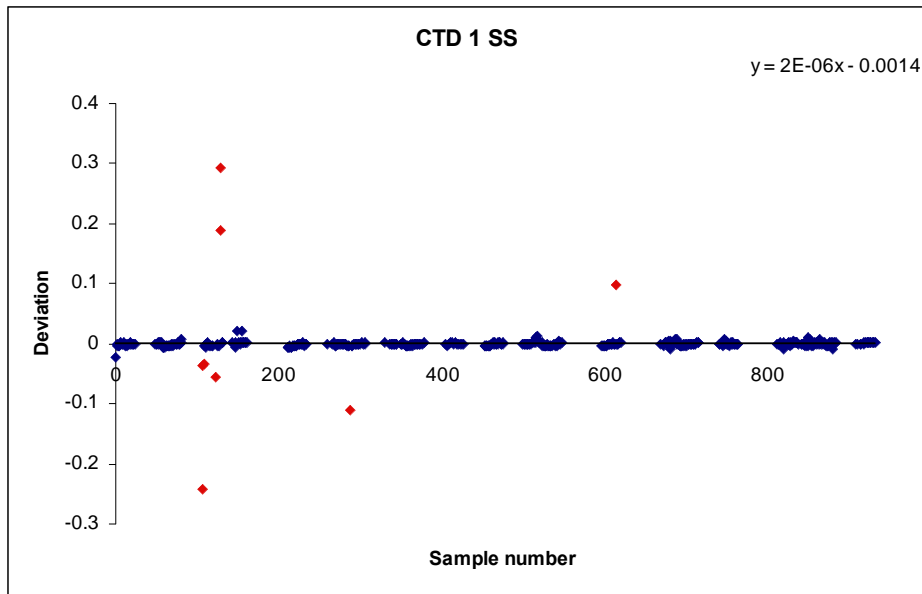
For the Ti main casts comparison with the CTD 1, there are 2 flyer points (in red in graph 3). They correspond to the following Geotraces samples:

- 481 and 482 from CTD029\_T

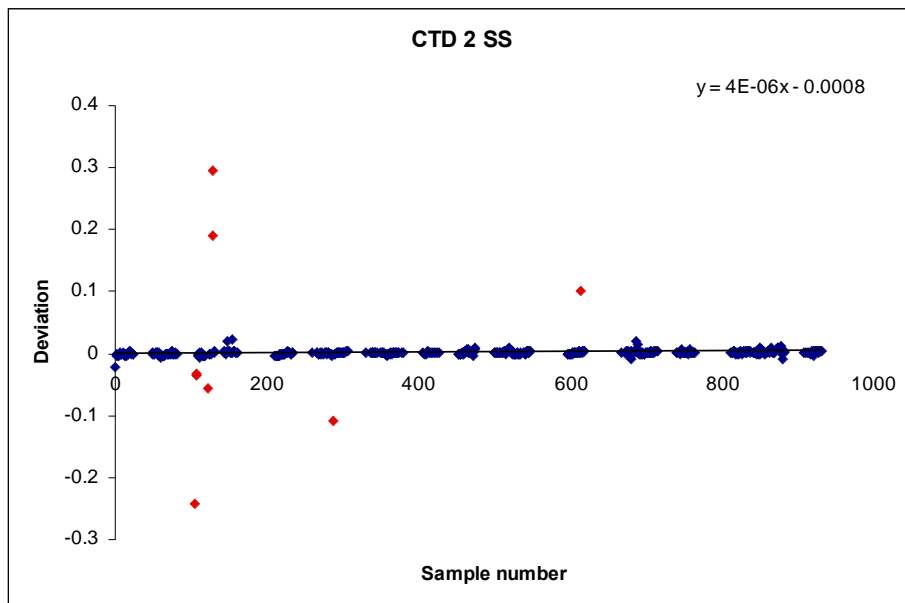
However, for the Ti main casts comparison with the CTD 2, there are 5 flyer points (in red in graph 4). They correspond to the following Geotraces samples:

- 204 and 207 from CTD014\_T
- 481 and 482 from CTD029\_T
- 559 from CTD031\_T

Graphs 5 and 6 show the deviation between the salinity measured by the salinometer and the one measured by the CTD 1 and 2 respectively for the stainless steel casts with respect to the sample number.

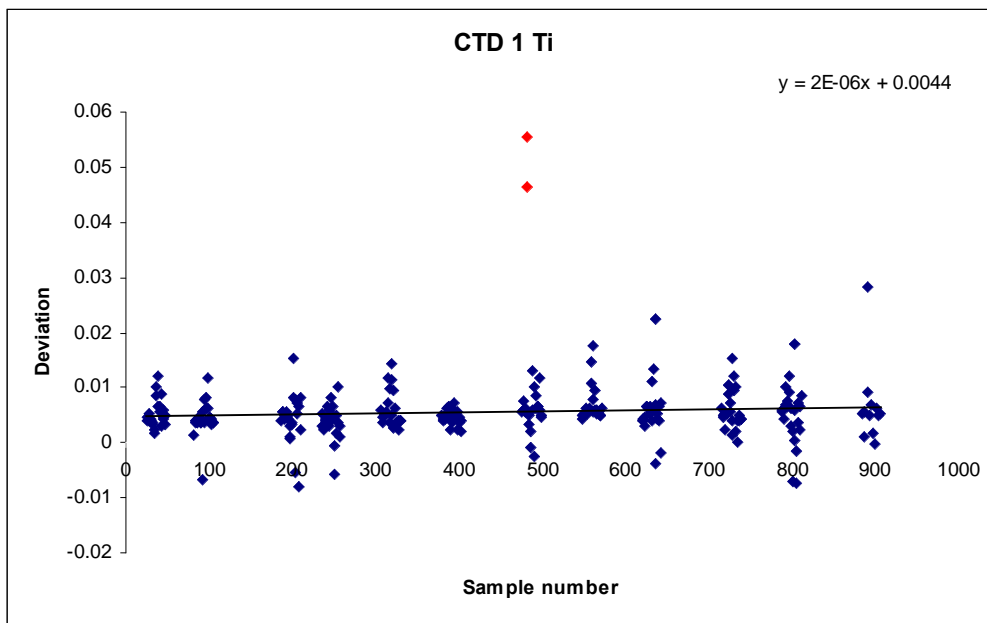


**Graph 5:** deviation between salinity measured by the salinometer and the one measured by the CTD 1 (y-axis,  $S$  (salinometer) –  $S$  (CTD1)) with respect to the sample number (x-axis) for the stainless steel casts. The flyer points (in red) were not taken in account for the calculation of the equation.

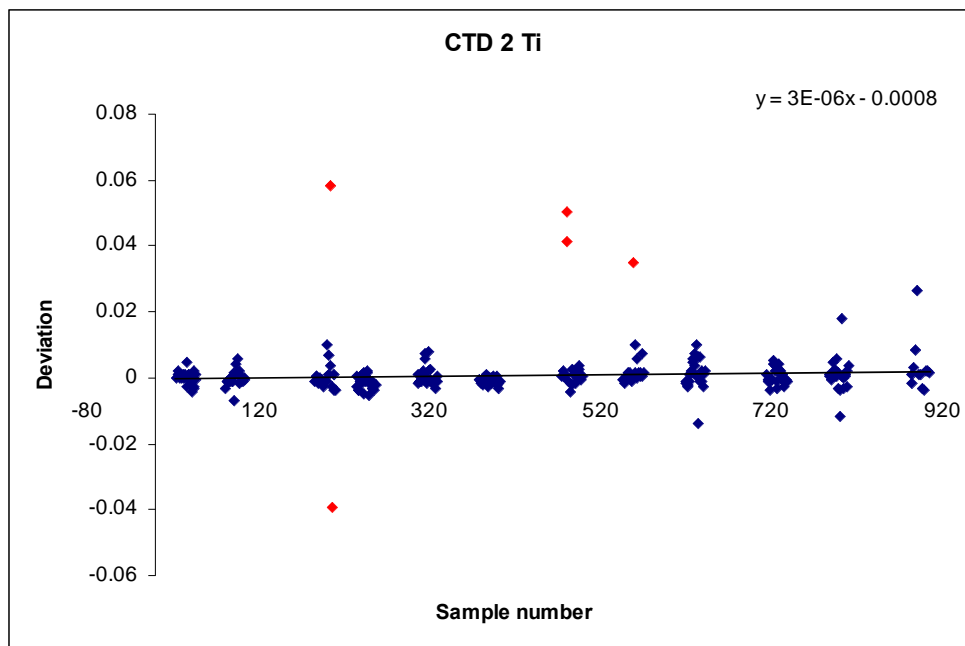


**Graph 6:** deviation between salinity measured by the salinometer and the one measured by the CTD 1 (y-axis,  $S$  (salinometer) –  $S$  (CTD2)) with respect to the sample number (x-axis) for the stainless steel casts. The flyer points (in red) were not taken in account for the calculation of the equation.

Graphs 7 and 8 show the deviation between the salinity measured by the salinometer and the one measured by the CTD 1 and 2 respectively for the main Ti casts with respect to the sample number.



**Graph 7:** deviation between salinity measured by the salinometer and the one measured by the CTD 1 (y-axis, S (salinometer) – S (CTD1)) 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.



**Graph 8:** deviation between salinity measured by the salinometer and the one measured by the CTD 1 (y-axis, S (salinometer) – S (CTD2)) 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.

# OCEAN CARBONATE SYSTEM

Report by Cynthia Dumousseaud

(School of Ocean and Earth Science, National Oceanography Centre, Southampton)

Samples analysed by Cynthia Dumousseaud

## Objectives:

The objectives on this cruise were to provide high quality carbonate system measurements. Dissolved Inorganic Carbon (DIC) and Total Alkalinity (TA) measurements were conducted to support other chemical and biological parameters collected and measured on this section. The results will be compared with existing carbonate system measurements available in this oceanic region.

## Sampling protocol:

The sampling procedure used for the determination of Dissolved Inorganic Carbon and Total Alkalinity followed Dickson et al. (2007). Samples were collected in 250 ml Schott Duran borosilicate glass bottles with glass stopper. Samples were taken as soon as possible after the Niskin bottle was opened (following trace gases, dissolved oxygen and nutrients samples). A piece of silicone tubing was used for the sampling and care was taken to prevent any air bubbles being trapped in the sample. The glass stopper was inserted in the bottle in order to remove the stopper volume and a head space of 1% (2.5 ml) was allowed for water expansion. The sample was then poisoned with a saturated solution of mercuric chloride (7 g/100 ml) in a 0.02% volume ratio (50  $\mu$ l) in order to prevent any biological activity in the stored sample. The bottle was air-tight sealed with a glass stopper and shaken to mix the mercuric chloride homogeneously. Samples were analysed within 2 days of sampling.

Seawater samples (approximately 20 ml) for DOC and TDN concentrations were filtered through combusted (450 °C, 4-6 h) glass-fibre filters (Whatman, GF/F) into combusted (450 °C, 4-6 h) glass ampoules and acidified with 30  $\mu$ l of 50 % (v/v) hydrochloric acid. After acidification, the ampoule was flame-sealed using a propane-butane burner.

## Samples collected:

Samples for DIC, TA, DOC and TDN were collected from every depth on each Regular cast (Stainless Steel CTD; see Table 6 for list of the stations and depths sampled). DIC and TA samples were collected from some of the Titanium and Biological casts when depths were missing from the Regular cast, or when no Regular cast was done.

Underway samples were also collected between stations (56 DIC/TA samples and 20 DOC/TDN samples) from the FISH underway supply in order to obtain a good surface coverage of the cruise track (Table 7).

## Sample analysis:

The instrument used for the determination of DIC and TA was the VINDTA 3C from Marianda (Kiel, Germany; Figure 20) connected with a coulometer (UIC 5011). DIC samples were analysed on board using a coulometric titration. The sample is acidified with phosphoric acid 10% which results in the conversion of total dissolved inorganic carbon ( $[\text{CO}_2^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$ ; where  $[\text{CO}_2^*] = [\text{CO}_2] + [\text{H}_2\text{CO}_3]$ ) to  $\text{CO}_2$  gas. The  $\text{CO}_2$  generated is carried into the coulometric cell using an inert gas ( $\text{N}_2$ ) and titrated coulometrically.

For the determination of TA, the sample of seawater is titrated with hydrochloric acid 0.1 M. The acid solution is added in small increments until the carbonic acid equivalence point is reached (protonation of carbonate and bicarbonate ions). The total volume added allows the calculation of total alkalinity to be undertaken. A glass electrode/reference electrode system monitors the titration (measurement of the electromotive force).

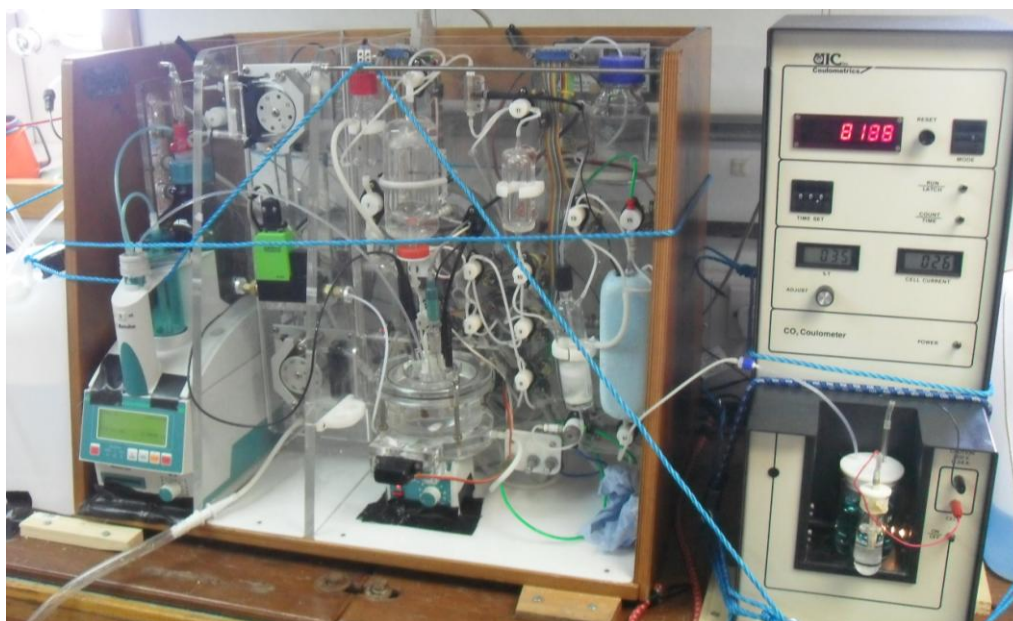


Figure 20. VINDTA 3C and UIC coulometer used for the determination of Dissolved Inorganic Carbon and Total Alkalinity.

Repeated measurements on the same batch of seawater ( $n \geq 4$ ) were run every day of analysis, prior to the samples analysis, in order to assess the precision of the method. The precision observed on average for the whole cruise was 0.12 % for DIC and 0.08 % for TA (2.4 and 1.9  $\mu\text{mol/kg}$ , respectively). Certified Reference Materials (batch 104) from A.G. Dickson (Scripps Institution of Oceanography) were used as standards to calibrate the system at the beginning of each day of analysis. A correction factor was applied to all measured values in order to normalize the measured values:

$$\begin{aligned} \text{DIC}_{\text{corr}} &= \text{DIC}_{\text{meas}} \times (\text{CRM}_{\text{cert}}/\text{CRM}_{\text{meas}}) \\ \text{TA}_{\text{corr}} &= \text{TA}_{\text{meas}} \times (\text{CRM}_{\text{cert}}/\text{CRM}_{\text{meas}}) \end{aligned}$$

where  $\text{CRM}_{\text{cert}}$  is the certified value for the specific batch of CRMs used.

Samples for the determination of Dissolved Organic Carbon (DOC) and Total Dissolved Nitrogen (TDN) will be analyzed at the National Oceanography Centre, Southampton, by HTCO (High Temperature Catalytic Oxidation) following Badr et al. (2003). Samples will be analysed within 6 months upon return.

#### Preliminary results:

All DIC and TA samples were analysed on board and no major problem was encountered with the DIC measurements. The alkalinity cell did not fill properly occasionally (30 samples) and this resulted in the alkalinity measurement being approximately  $200 \mu\text{mol.kg}^{-1}$  lower than expected. When this was the case the value was discarded and the sample replaced when possible (from the Titanium Cast or the Biology Cast).

#### **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  $\text{CO}_2$  measurements. PICES Special Publication 3, IOCCP report No. 8, 191 pp.



Station	CTD #	Depths sampled	DIC samples	DOC samples	Niskin sampled	Comments
01	003 (Reg)	21	21	x	all except 1,8,21	Bottle #1 leaker
	005 (Bio)	5	x	5	6,12,20,23,24	DOC ampoule sealing failed
02	006 (Reg)	23	23	23	all except 16	DOC ampoule from 2250 m and 50 m broken during sealing
	008 (Bio)	5	x	5	1,7,14,15,20	
03	009 (Reg)	12	12	12	all except misfired/leakers	12 bottles misfired/leakers; 14 and 15 probably leakers
	011 (Bio)	12	12	10	5-9,12,14,16-18,20,22	DOC ampoule from 300 m and 20 m broken during sealing
	014 (Ti)	4	4	x	10,12,13,14	
04	015 (Reg)	19	19	19	all except 2,5,9,12,15	
05	019 (Reg)	16	18	16	2-4,6-9,11-16,18,19,21,23,24	6 leakers; Bottle #6 looks like misfired
06	022 (Reg)	17	20	17	all except 23 and leakers	Bottles #6,20 and 21 leakers
	024 (Bio)	4	4	4	10,12,16,18	
07	026 (Reg)	18	21	18	all except 4,10 and 14	
08	028 (Reg)	13	15	13	1-3,5,7,9,11,12,14,15,17,19-20,24	Bottles #22 and 23 misfired
01b	029 (Ti)	5	5	x	7,9,10,16,19	
09	030 (Reg)	16	18	16	all except 4,7,10,13,14,18	Bottles #13 and 14 leakers
10	033 (Reg)	17	21	17	all except 4,7,17	
11	037 (Reg)	17	23	17	all except 21	Bottle #21 leaker
	039 (Bio)	4	8	x	1,12,18,24	Duplicate samples
12	042 (Bio)	21	24	21	all	DOC ampoule from 300 m broken during sealing
01c	044 (Bio)	23	23	23	all except 12	Bottle #12 leaker
8b	046 (Bio)	8	8	8	13,14,15,17,18,21,22,24	

**Table 6:** List of the stations and depths sampled for DIC/TA and DOC.

Event	Day	Time (GMT)	Sample	Event	Day	Time (GMT)	Sample
DIC1	31/10/2010	11:00	DIC/TA	DIC30	04/11/2010	14:00	DIC/TA
DIC2	31/10/2010	15:00	DIC/TA	DIC31	04/11/2010	16:00	DIC/TA
DIC3	31/10/2010	19:00	DIC/TA	DIC32	04/11/2010	18:00	DIC/TA, DOC
DIC4	02/11/2010	10:00	DIC/TA	DIC33	04/11/2010	20:00	DIC/TA, DOC
DIC5	02/11/2010	12:00	DIC/TA	DIC34	04/11/2010	22:00	DIC/TA
DIC6	02/11/2010	14:00	DIC/TA	DIC35	05/11/2010	00:00	DIC/TA
DIC7	02/11/2010	16:00	DIC/TA	DIC36	05/11/2010	02:00	DIC/TA
DIC8	02/11/2010	18:00	DIC/TA, DOC	DIC37	05/11/2010	04:00	DIC/TA
DIC9	02/11/2010	20:00	DIC/TA	DIC38	05/11/2010	06:00	DIC/TA
DIC10	02/11/2010	22:00	DIC/TA	DIC39	05/11/2010	08:00	DIC/TA, DOC
DIC11	03/11/2010	00:00	DIC/TA	DIC40	05/11/2010	10:00	DIC/TA, DOC
DIC12	03/11/2010	02:00	DIC/TA	DIC41	05/11/2010	12:00	DIC/TA, DOC
DIC13	03/11/2010	04:00	DIC/TA	DIC42	05/11/2010	14:00	DIC/TA, DOC
DIC14	03/11/2010	06:00	DIC/TA	DIC43	16/11/2010	09:00	DIC/TA, DOC
DIC15	03/11/2010	08:00	DIC/TA	DIC44	16/11/2010	11:00	DIC/TA, DOC
DIC16	03/11/2010	10:00	DIC/TA, DOC	DIC45	16/11/2010	15:00	DIC/TA, DOC
DIC17	03/11/2010	12:00	DIC/TA, DOC	DIC46	16/11/2010	17:00	DIC/TA, DOC
DIC18	03/11/2010	14:00	DIC/TA	DIC 47	17/11/2010	18:00	DIC/TA
DIC19	03/11/2010	16:00	DIC/TA, DOC	DIC 48	18/11/2010	12:00	DIC/TA
DIC20	03/11/2010	18:00	DIC/TA, DOC	DIC 49	18/11/2010	14:00	DIC/TA
DIC21	03/11/2010	20:00	DIC/TA	DIC 50	18/11/2010	16:00	DIC/TA
DIC22	03/11/2010	22:00	DIC/TA	DIC 51	18/11/2010	18:00	DIC/TA, DOC
DIC23	04/11/2010	00:00	DIC/TA	DIC 52	18/11/2010	20:00	DIC/TA, DOC
DIC24	04/11/2010	02:00	DIC/TA, DOC	DIC 53	18/11/2010	22:00	DIC/TA, DOC
DIC25	04/11/2010	04:00	DIC/TA, DOC	DIC 54	19/11/2010	00:00	DIC/TA
DIC26	04/11/2010	06:00	DIC/TA	DIC 55	19/11/2010	02:00	DIC/TA
DIC27	04/11/2010	08:00	DIC/TA	DIC 56	19/11/2010	10:30	DIC/TA
DIC28	04/11/2010	10:00	DIC/TA				
DIC29	04/11/2010	12:00	DIC/TA				

**Table 7:** Time and date of collection of the underway samples for DIC, TA and DOC/TDN samples.

# Comprehensive Calibration of Critical Paleoceanographic Proxies

(NERC Standard Grant)

# $^{231}\text{Pa}/^{230}\text{Th}$

By Alex Thomas

Samples to be analysed by Alex Thomas

## Objectives

The naturally occurring radioisotopes  $^{231}\text{Pa}$  and  $^{230}\text{Th}$  are both produced in the ocean from the decay of uranium ( $^{235}\text{U}$  and  $^{234}\text{U}$  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  $^{231}\text{Pa}$  and  $^{230}\text{Th}$  are rapidly removed from the ocean by scavenging onto particle surfaces and settling. The distribution of  $^{231}\text{Pa}$  and  $^{230}\text{Th}$  in the oceans is therefore governed by the degree of particle affinity for each  $^{231}\text{Pa}$  and  $^{230}\text{Th}$ , the flux of particles, and the advection of any  $^{231}\text{Pa}$  or  $^{230}\text{Th}$  remaining in the dissolved, or “non-sinking” fraction. Measurement of the distributions of the “non-sinking” fraction of  $^{231}\text{Pa}$  and  $^{230}\text{Th}$  will be made by using a 0.45  $\mu\text{m}$  filter cartridge during sampling. Obtaining a section of  $^{231}\text{Pa}$  and  $^{230}\text{Th}$  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  $^{231}\text{Pa}$  and  $^{230}\text{Th}$  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  $^{231}\text{Pa}$  and  $^{230}\text{Th}$  to oceanic sediments. Though coupled measurements of water column and sedimentary  $^{231}\text{Pa}$  and  $^{230}\text{Th}$  along the 40S transect at localities where the sediment is sited in different water masses with characteristic  $^{231}\text{Pa}$  and  $^{230}\text{Th}$  concentrations will enable the water depth which is most represented by the sedimentary  $^{231}\text{Pa}$  and  $^{230}\text{Th}$  to be investigated which remains controversial (Thomas et al. 2006). High resolution  $^{231}\text{Pa}$  and  $^{230}\text{Th}$  profiles through the surface sediment, coupled with the  $^{231}\text{Pa}$  and  $^{230}\text{Th}$  concentrations of bottom water, will also be informative as to the control leakage of  $^{231}\text{Pa}$  and  $^{230}\text{Th}$  from sediment has on the oceanic inventory of  $^{231}\text{Pa}$  and  $^{230}\text{Th}$ , 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 affects the oceanic  $^{231}\text{Pa}$  and  $^{230}\text{Th}$  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. 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 0.45 $\mu\text{m}$  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 ~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 filtered 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 where 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.

### 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. This was only done for the mega-corer and not the box core due to the mixing of the overlying water in the box core with the rest of the water column during retrieval from the seabed. The mega-core was sampled for water twice (stations 3 and 6), with unfiltered water taken at station 3 and water combined from two core tubes at station 6 and filtered through a 0.4µm 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 aliquots.

### Samples collected

Overview of samples: A total of 103 samples were collected spanning the full water column at: Station 1 (13 samples), Station 3 (13 samples), Station 5 (11 samples) Station 6 (12 samples), Station 8 (8 samples), Station 9 (12 samples), Station 10 (12 samples), and Station 11 (22 samples). Details of samples collected are presented in Table PaTh1.

Station	Sampler	Bottle	Target depth, m	Estimated volume, L	Box #	Comment
1	reg	0002	2600	10	ALT1	
1	reg	0003	2500	10	ALT1	
1	reg	0005	2000	10	ALT1	
1	reg	0007	1500	10	ALT1	
1	reg	0008	1500	10	ALT1	
1	reg	0010	1000	10	ALT1	
1	reg	0011	800	10	ALT26	
1	reg	0012	715	10	ALT26	
1	reg	0013	630	10	ALT26	
1	reg	0014	500	10	ALT26	
1	reg	0017	150	10	ALT26	
1	reg	0021	50	10	ALT26	
1	reg	0024	5	10	ALT12	
3	reg	0115	-30	3	ALT13	non d13C
3	reg	0116	-100	10	ALT13	
3	reg	0118		10	ALT13	
3	reg	0119	4000	10	ALT13	
3	reg	0124	2000	10	ALT13	
3	reg	0129	1000	10	ALT13	
3	reg	0131	500	10	ALT13	
3	bio	0147	100	10	ALT11	
3	bio	0157	50	10	ALT11	
3	bio	0160	10	10	ALT11	
3	tit	0192	3000	10	ALT11	no d13C
3	tit	0194	2500	10	ALT11	no d13C
3	tit	0197	1500	10	ALT11	no d13C
3	core		bottom water	0.5	ALT11	core top water from megacorer not filtered
5	reg	0284	-10	10	ALT32	

Station	Sampler	Bottle	Target depth, m	Estimated volume, L	Box #	Comment
5	reg	0285	5050	10	ALT32	
5	reg	0289	3500	10	ALT32	
5	reg	0290	3000	10	ALT32	
5	reg	0293	1750	10	ALT32	
5	reg	0294	1500	10	ALT32	
5	reg	0297	750	10	ALT12	
5	reg	0300	350	10	ALT12	
5	reg	0303	100	10	ALT12	
5	reg	0304	50	10	ALT12	
5	reg	0306	5	10	ALT12	
6	reg	0357	4894	10	ALT4	
6	reg	0358	4500	10	ALT4	
6	reg	0360	4000	10	ALT4	
6	reg	0363	3000	10	ALT4	
6	reg	0364	2500	10	ALT4	
6	reg	0366	2000	10	ALT4	
6	reg	0368	1500	10	ALT6	
6	reg	0370	1000	10	ALT6	
6	reg	0372	700	10	ALT6	
6	reg	0374	200	10	ALT6	
6	reg	0377	50	10	ALT6	
6	reg	0379	5	10	ALT6	
6	core		bottom water	5	ALT6	Water siphoned from mega-corer through 0.4um AcroPak
8	reg	0501	793	10	ALT29	
8	reg	0503	700	10	ALT21	
8	reg	0505	600			d13C only
8	reg	0507	500	10	ALT29	
8	reg	0508	380	10	ALT29	
8	reg	0511	300			d13C only
8	reg	0513	200	10	ALT29	
8	reg	0515	150			d13C only
8	reg	0517	100	10	ALT29	
8	reg	0519	50	10	ALT21	
8	reg	0521	20			d13C only
8	reg	0523	5	10	ALT29	
9	reg	0525	4354	10	ALT14	
9	reg	0527	4000	10	ALT14	
9	reg	0528	3500	10	ALT14	
9	reg	0530	3000	10	ALT14	
9	reg	0532	2500	10	ALT14	
9	reg	0535	2000	10	ALT14	
9	reg	0538	1250	10	ALT33	
9	reg	0589	1000	10	ALT33	
9	reg	0541	800	10	ALT33	
9	reg	0542	500	10	ALT33	
9	reg	0544	100	10	ALT33	
9	reg	0546	20	10	ALT33	
10	reg	0597	-10	10	ALT??	
10	reg	0599	4500	10	ALT??	
10	reg	0600	4000	10	ALT??	

Station	Sampler	Bottle	Target depth, m	Estimated volume, L	Box #	Comment
10	reg	0602	3500	10	ALT??	
10	reg	0605	2500	10	ALT??	
10	reg	0606	2000			d13C only
10	reg	0607	2000	10	ALT??	
10	reg	0609	1500	10	ALT7	
10	reg	0612	1000	10	ALT7	
10	reg	0614	750	10	ALT7	
10	reg	0615	500	10	ALT7	
10	reg	0617	100	10	ALT7	
10	reg	0619	20	10	ALT7	
11	reg	0692+0693	-10	10	ALT3	
11	reg	0694+0695	5000	10	ALT3	
11	reg	0696	4500	7	ALT3	
11	reg	0697+0698	4000	10	ALT3	
11	reg	0699	3500	7	ALT21	no d13C
11	reg	0700+0701	3000	10	ALT3	
11	reg	0702+0703	2500	10	ALT3	
11	reg	0704+0705	2000	10	ALT21	
11	reg	0706	1500	10	ALT23	
11	reg	0707	1250	5	ALT23	
11	reg	0708	1000	3	ALT23	
11	reg	0709	700	2	ALT23	
11	bio	0740+0741	400	10	ALT10	no d13C
11	bio	0745	260	10	ALT10	no d13C
11	bio	0746	240	10	ALT10	no d13C
11	bio	0749	220	10	ALT10	no d13C
11	bio	0751	200	6	ALT10	no d13C
11	bio	0753	180	10	ALT10	no d13C
11	bio	0755	140	10	ALT23	no d13C
11	bio	0759	70	4	ALT23	no d13C
11	bio	0760	50	3	ALT23	no d13C
11	bio	surface fish	5	10	ALT23	no d13C

**Table 8:** 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.

### Sample analysis

Samples will be analysed ashore at the University of Oxford, by MC-ICP-MS. Yield tracers of <sup>236</sup>U, <sup>229</sup>Th and <sup>233</sup>Pa 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 NH<sub>4</sub> 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<sub>3</sub>, HCl, HF digestion using HClO<sub>4</sub> to mitigate fluoride formation, and then spiked with the tracer isotopes and then processed as water samples.

## References:

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# SILICON ISOTOPES

By Gideon Henderson

Samples to be analysed by Kate Hendry, Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, MA 02543, USA. khendry@whoi.edu

## 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<sub>2</sub> cycles (Katsumoto et al. 2002). We have a simple understanding of the  $\delta^{30}\text{Si}$  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 $\delta^{30}\text{Si}$ of the upwelled nutrient pool?*

To use  $\delta^{30}\text{Si}$  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°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  $\delta^{30}\text{Si}$  in deep water.

### 2. *What is the natural isotope fractionation during Si uptake?*

Interpreting sedimentary  $\delta^{30}\text{Si}$  values in terms of past nutrient utilisation relies on knowledge of the fractionation factor ( $\alpha$ ) induced by biological uptake of Si. This has been constrained in the laboratory, but a values in the field and variability of  $\alpha$  have not been assessed. We will make such assessment by measuring co-existing particulate and dissolved  $\delta^{30}\text{Si}$  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  $\alpha$  with species.

### 3. *What is the impact of dissolution on $\delta^{30}\text{Si}$ ?*

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  $\delta^{30}\text{Si}$  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  $\delta^{30}\text{Si}$  equal to upwelled water.  $\delta^{30}\text{Si}$  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 three sites:

Station 3: 8x 250 ml and 3x 500 ml seawater samples, 1x 250 ml sample of water from above one of the megacores, 1x core-top sediment from megacore.

Station 8: 4x 250 ml and 6x 500 ml seawater samples, and 7 ≈150 ml pore-water samples from the box core

Station 11: 9x 250ml and 3x 500 ml seawater samples, and 8 ≈200 ml pore-water samples from box core

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 Stations 8 and 11 should they be required. Matching samples of unprocessed sediment were kept from each aliquot of sediment used for pore-water extraction, and a range of other sediment samples are available, as described in the sediment section of this report.

Portions of SAPs filters are available at all sites where SAPs work was conducted – Stations 3, 6, 8, and 11.

#### 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)<sub>2</sub>), 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 will be dissolved in 1ml 0.5 M in-house Teflon-distilled HCl and diluted five-fold with Milli-Q water.

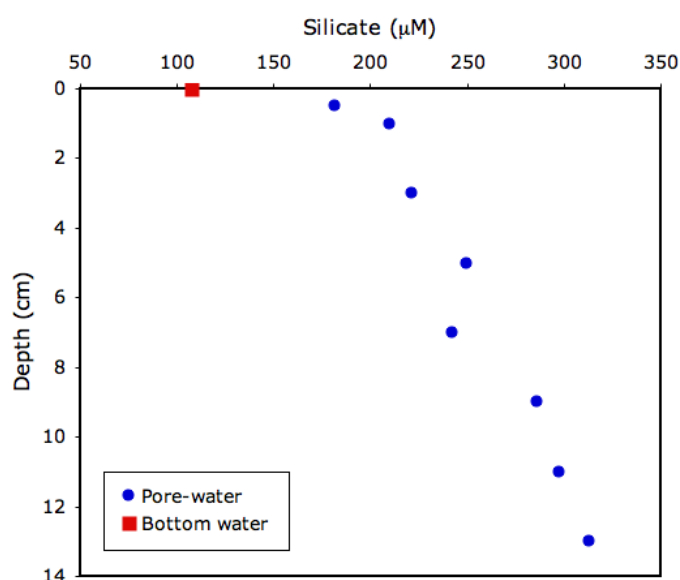
*Sediments/particulates*: Sedimentary diatoms will be separated from lithics using heavy liquid flotation. Organic matter will be removed by heating three times in H<sub>2</sub>O<sub>2</sub> (30% reagent grade) and

then three times in distilled concentrated HNO<sub>3</sub>, followed by thorough rinsing in 18 MΩ Milli-Q water. The samples will be cleaned in 50% distilled HNO<sub>3</sub>/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).

### Preliminary results

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

Analysis of silicate concentrations in the pore-waters was performed on the ship by Malcolm Woodward. Results from Station 11 are shown in the figure below and compared to the silicate concentration in bottom water at that location. Pore-waters show a clear increase in silicate concentration with depth in the sediment, due to dissolution of detrital silicates and/or biogenic opal in the sediment. The pore-waters therefore provide a good target for analysis to assess the nature of silicate diagenesis in marine sediments and of the silica isotope flux from sediments to the deep ocean. Such analysis will help to improve understanding of the uses of Si isotope for modern and paleo oceanography.



**Figure 20:** Ship-board silicate concentrations for Station 11 pore-waters recovered for analysis of Si isotopes.

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## Lipid biomarkers

By Maite Hernández, University of Bristol; [maite.hernandezsanchez@bristol.ac.uk](mailto:maite.hernandezsanchez@bristol.ac.uk)

There is a range of phytoplankton lipids (Brassicasterol, C<sub>28</sub>-alkyl-1,14-diols, dinosterol, 24-methylcholesta-5,24(28)-dien-3 $\beta$ -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.

Cast n°	Station	Date	
CTD_8_s	2	20/10/2010	
Niskin bottle	Depth (m)	IPL (vol filtered, L)	Prot/gen (vol filtered, L)
23	5	2?	5.42
22	20	1.7	0.45
20	50	1.9	3.44
15	60		3.51
14	80	1.94	4
13	100	2	4.91
7	160		5.28
6	200	1.92	5.3
Cast n°	Station	Date	
CTD_18_ss	4	26/10/2010	
Niskin bottle	Depth (m)	IPL (vol filtered, L)	Prot/gen (vol filtered, L)
23	5		5.39
24	5	1.86	
22	20	2	3.32
21	40		4.4
20	50	2	5.35
18	60	2	3
15	100	1.94	5.28
11	200	1.84	5.28
Cast n°	Station	Date	
CTD_8_s	1.5	10/11/2010	
Niskin bottle	Depth (m)	IPL (vol filtered, L)	Prot/gen (vol filtered, L)

23	5	2	2.46
21	20	2	2.43
19	40	2	2.51
11	70	2.25	
14	80	1.94	
8	100	2.29	
6	200	2.24	
<b>CTD_035_ss</b>	<b>3 revisited</b>	<b>12/11/2010</b>	
<b>Niskin bottle</b>	<b>Depth (m)</b>	<b>IPL (vol filtered, L)</b>	<b>Prot/gen (vol filtered, L)</b>
23	10	2	2.48
21	40	2	2.45
17	60	2.2	
15	100	2.3	
10	200	1.6	
<b>CTD_042_ss</b>	<b>12 (3.5)</b>	<b>17/11/2010</b>	
<b>Niskin bottle</b>	<b>Depth (m)</b>	<b>IPL (vol filtered, L)</b>	<b>Prot/gen (vol filtered, L)</b>
24	5	2.41	
23	10		3.18
21	20	1.98	
20	20		5.1
19	30		5.21
18	50	1.92	2.78
17	70		2.59
16	80	2.14	
14	120	2.15	5.22
10	200	1.94	4.26
<b>CTD_043_ss</b>	<b>10(2.5)</b>	<b>18/11/2010</b>	
<b>Niskin bottle</b>	<b>Depth (m)</b>	<b>IPL (vol filtered, L)</b>	<b>Prot/gen (vol filtered, L)</b>
24	5	3.2	5
21	40		5.21
22	20	1.92	
20	50	2	2.3
15	70		5.41
14	80	2.31	3.9
13	100	1.99	5
7	200	2.33	5.47
<b>CTD_044_ss</b>	<b>8 (0.5)</b>	<b>19/11/2010</b>	
<b>Niskin bottle</b>	<b>Depth (m)</b>	<b>IPL (vol filtered, L)</b>	<b>Prot/gen (vol filtered, L)</b>
24	5	2	2.5
21	20	2	2.3
17	50	2	2.39
14	80	2	1.4
13	100	2	1.4

**Table 9:** Samples collected from IPL and proteomic/genomics analysis from several CTDs.

## 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  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  analysis; briefly a cubic cm of sediment was sampled, stored in a ziplog bag and kept at -20 °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<sub>2</sub> 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 -80°C until analysis. IPL are quantified using high-performance liquid chromatography electrospray-ionisation mass spectrometry (HPLC ESI MS).

### *Stand Alone Pump Systems (SAPS)*

SAPS have been deployed at four stations in two separate deployments (shallow and deep), generally pumping for 2 hours and filtering hundreds to thousands of litres. 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 <sup>234</sup>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.

Station	Julian day	Latitude	Longitude	Water depth (m)
3	295	36° 29.73´S	13° 6.5´E	4918
SAPS n°	Filter type	Sampling depth (m)	Vol filtered (L)	Comments
8	GFF/Mn	5	460	
7	PES/NITEX	25	1054	
6	GFF/Mn	45	838	Filter bursted
5	PES/Mn	65	1339	
4	GFF/Mn	95	217	
3	PES/NITEX	115	1139	
2	GFF/Mn	195	607	

1	PES/NITEX	215	2254	
<b>Station</b>	<b>Julian day</b>	<b>Latitude</b>	<b>Longitude</b>	<b>Water depth (m)</b>
3	295	36° 30.85´S	13° 10.38´E	4896
<b>SAPS n°</b>	<b>Filter type</b>	<b>Sampling depth (m)</b>	<b>Vol filtered (L)</b>	<b>Comments</b>
8	PES/NITEX	1390	1089	
7	GFF/Mn	1410	364	
6	PES/Mn	4315	1607	
5	GFF/Mn	4335	350	
4	PES/NITEX	4686	77	DID NOT START
3	GFF/Mn	4706	169	
2	PES/NITEX	4756	1525	
1	GFF/Mn	4776	736	

<b>Station</b>	<b>Julian day</b>	<b>Latitude</b>	<b>Longitude</b>	<b>Water depth (m)</b>
6	302	40° 0´ 50.90´´S	00° 56´ 25.6´´E	4915
<b>SAPS n°</b>	<b>Filter type</b>	<b>Sampling depth (m)</b>	<b>Vol filtered (L)</b>	<b>Comments</b>
8	GFF/Mn	5	306	
7	PES/NITEX	25	626	
6	GFF/Mn	45	301	
5	PES/Mn	65	1221	
4	GFF/Mn	95	409	
3	PES/NITEX	115	893	
2	GFF/Mn	195	373	
1	PES/NITEX	215	1540	

<b>Station</b>	<b>Julian day</b>	<b>Latitude</b>	<b>Longitude</b>	<b>Water depth (m)</b>
6	303	39° 59´ 51´´S	0° 54´ 1.49´´	4930
<b>SAPS n°</b>	<b>Filter type</b>	<b>Sampling depth (m)</b>	<b>Vol filtered (L)</b>	<b>Comments</b>
8	PES/NITEX	1480	997	
7	GFF/Mn	1500	340	
6	PES/Mn	4430	1573	
5	GFF/Mn	4450	355	
4	PES/NITEX	4830	1453	
3	GFF/Mn	4850	418	
2	PES/NITEX	4900	1492	
1	GFF/Mn	4920	354	

<b>Station</b>	<b>Julian day</b>	<b>Latitude</b>	<b>Longitude</b>	<b>Water depth (m)</b>
1	313	34° 37.28´S	17° 2.18´E	2630
<b>SAPS n°</b>	<b>Filter type</b>	<b>Sampling depth (m)</b>	<b>Vol filtered (L)</b>	<b>Comments</b>
3	GFF/Mn	20	544	
2	PES/NITEX	120	1507	

1	GFF/Mn	200	591	
<b>Station</b>	<b>Julian day</b>	<b>Latitude</b>	<b>Longitude</b>	<b>Water depth (m)</b>
1	323	34°37.11'S	17°2.29'E	2630
<b>SAPS n°</b>	<b>Filter type</b>	<b>Sampling depth (m)</b>	<b>Vol filtered (L)</b>	<b>Comments</b>
5	GFF/Mn	1600	342	
4	PES/NITEX	2130	1454	
3	PES/NITEX	2530	1437	
2	PES/NITEX	2560	895	
1	GFF/Mn	2580	391	

<b>Station</b>	<b>Julian day</b>	<b>Latitude</b>	<b>Longitude</b>	<b>Water depth (m)</b>
11 (4.5)	320	39° 17.67'S	7°40.22'E	5267.5
<b>SAPS n°</b>	<b>Filter type</b>	<b>Sampling depth (m)</b>	<b>Vol filtered (L)</b>	<b>Comments</b>
5	GFF/Mn	10	329	
4	PES/NITEX	70	1165	
3	PES/NITEX	120	1461	
2	GFF/Mn	200	392	
1	GFF/Mn	600	526.5	
<b>Station</b>	<b>Julian day</b>	<b>Latitude</b>	<b>Longitude</b>	<b>Water depth (m)</b>
11 (4.5)	318	39°13.16'S	7°46.91'E	5162
<b>SAPS n°</b>	<b>Filter type</b>	<b>Sampling depth (m)</b>	<b>Vol filtered (L)</b>	<b>Comments</b>
5	PES/NITEX	1500	885	
4	PES/NITEX	3500	1528	
3	PES/NITEX	4662	1416	
2	PES/NITEX	5062	821	
1	PES/NITEX	5132	1395	
<b>Station</b>	<b>Julian day</b>	<b>Latitude</b>	<b>Longitude</b>	<b>Water depth (m)</b>
11 (4.5)	319	39°15.30'S	7°43.421'E	5241
<b>SAPS n°</b>	<b>Filter type</b>	<b>Sampling depth (m)</b>	<b>Vol filtered (L)</b>	<b>Comments</b>
5	GFF/Mn	3241	182	
4	GFF/Mn	4241	302	
3	GFF/Mn	4741	286	
2	GFF/Mn	5141	229	
1	GFF/Mn	5211	450	

**Table 10:** Summary of SAPs deployments for trace metals, biomarkers and Ra.



# Other Research Objectives

# ANTHROPOGENIC RADIONUCLIDES (ARNs)

By Alex Thomas

Samples to be analysed by Tim Kenna, Lamont-Doherty Earth Observatory

## Objectives

The anthropogenic radioisotopes of plutonium ( $^{239}\text{Pu}$  and  $^{240}\text{Pu}$ ), neptunium ( $\text{Np-237}$ ) and cesium ( $\text{Cs-137}$ ) were added to the surface ocean, largely, by fallout from nuclear weapons testing in the 1960s-1970s. 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 where 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

Overview of samples: A total of 22 samples were collected spanning the full water column at: Station 4 (9 samples), Station 7 (8 samples), and Station 8-reoccupation (5 samples). A further 4 samples were collected from the surface fish on the South African Shelf during transit back to CapeTown. Details of samples collected are presented in Table 11.

Station	Sampler	Bottle	Target m	depth	Approximate volume L
4	reg	212	-10		20
4	reg	215	4500		20
4	reg	219	3000		20
4	reg	222	2000		20
4	reg	225	1250		20
4	bio	265	700		20
4	bio	267	500		20
4	bio	270	200		20
4	bio	274	100		20
7	reg	452+453	3500		20
7	reg	454+455	3250		20
7	reg	456			20

7	reg	460+461	2000	20
7	reg	464+465	1250	20
7	reg	467+468	700	20
7	reg	471	300	10
7		surface fish	5	20
8 reocc	bio	908	-10	20
8 reocc	bio	911	700	20
8 reocc	bio	915	300	20
8 reocc	bio	919	100	20
8 reocc	bio	927	20	20

**Table 11:** Details of samples taken for Pu analysis. Sampler refers to the type of rosette: reg = stainless steel - deep cast; bio = stainless steel – shallow cast. Negative depths indicate meters above the sea floor rather than below sea level.

### 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 anion chromatography, and measured by isotope dilution on an 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).

### References:

- Aoyama, M., Hirose, K., Miyao, T., and Igarashi, Y. 2000. Low level Cs-137 measurements 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 spectrometry with total sample dissolution. *Journal of Analytical Atomic Spectrometry* 17, 1471-1479.
- Livingston, H. D., Mann, D. R., Fettes, R. C., and Dempsey, B. L. 1974. Radiochemical procedures for the analysis of strontium, cesium, iron, transuranics and the rare earths in seawater samples: Laboratory Operations Protocol. Woods Hole Oceanographic Institution, Woods Hole, MA.
- Wong, K. M., Jokela, T. A., and Noshkin, V. E. 1994. Radiochemical procedures for analysis of Pu, Am, Cs, and Sr in seawater, soil, sediments, and biota samples. Technical Report, UCRL-ID-116497. Lawrence Livermore National Laboratory, Berkeley, CA.

## PLATINUM GROUP METALS

By Angela Milne

Samples will be analysed by Kevin Burton at the University of Oxford, Department of Earth Sciences, South Parks Road, Oxford, OX1 3AN.

**Sampling protocol:** Profiles were collected from varying depths through the whole water column using 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. Seawater samples from the OTE bottles were filtered under pressure through acid washed 25 mm (0.2 µm) polyethersulfone filters (PES, Supor, Pall Gellman) housed in clean filter holders (Swinnex, Millipore). The filter holders were attached to the Teflon taps of the OTE bottles using acid cleaned Bev-A-Line (Cole Parmer) tubing and luer lock fittings. Sample bottles (1 L HDPE) and caps were rinsed 3 times with filtered seawater sample before being filled. After all the OTE bottles had been sub-sampled, the samples were acidified with 1.5 mL of concentrated HNO<sub>3</sub> per 1 L of sample. Furthermore, an additional 1 L HDPE bottle (a 'blank') was opened and exposed for 1 minute to the atmosphere within the clean container. All sample bottles were sealed with parafilm and double bagged prior to storage.

Eight OTE bottles could be pressurised and sampled at one time. Filtration of all twenty-four bottles was completed in approximately nine hours.

**Samples collected:** A total of 62 samples spanning the whole water column (from 5 m to approximately 5200 m) were collected from station 1 (11 samples), station 3 (11 samples), station 6 (11 samples), station 8 re-occupied (7 samples), station 9 (11 samples) and station 11 (11 samples).

**Sample analysis:** Samples will be analysed for the full suite of PGE concentrations (and for <sup>187</sup>Os/<sup>188</sup>Os) using ICP-MS and TIMs respectively, at Oxford University.

# $\delta^{13}\text{C}$ 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 of biological activity. Biomass production in the surface ocean preferentially incorporates the lighter of the carbon isotopes ( $\text{C}^{12}$ ,  $\text{C}^{13}$ , and  $\text{C}^{14}$  –  $\text{C}^{14}$  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 of 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  $\delta^{13}\text{C}$  of DIC. The longer a water mass is isolated from the atmosphere – and re-equilibration of its carbon isotopes with atmospheric  $\text{CO}_2$  – and the greater the amount of organic carbon export the lighter the  $\delta^{13}\text{C}$  of that water mass will be. The  $\delta^{13}\text{C}$  can therefore be thought of as an integrated carbon export that a water mass has experienced since it left the surface.

The aims of the measurements made here are to use the  $\delta^{13}\text{C}$  as a productivity and watermass-history tracer to better parameterise the controls on other tracers ( $\delta^{15}\text{N}$  and  $^{231}\text{Pa}/^{230}\text{Th}$ ), which are related to water mass histories and particle scavenging.

## Sampling protocol

### *Water samples*

Samples for the measurement of the stable isotopes of carbon ( $\delta^{13}\text{C}$ ) in dissolved inorganic carbon (DIC) were collected from the regular (stainless steel) rosette's 20L OTE bottles. The  $\delta^{13}\text{C}$  samples were taken immediately after the other dissolved gaseous samples ( $\text{He}$ ,  $^3\text{H}$ ,  $\delta^{17}\text{O}$ ,  $\text{O}_2$ ), nutrients, and DIC and DOC.  $\delta^{13}\text{C}$  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 then placed in the bottle and then removed so that 2.5 mL of sample could be removed (to allow for thermal expansion) and 50  $\mu\text{L}$  of 100%  $\text{HgCl}_2$  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  $\text{HgCl}_2$ .

## Samples collected

Overview of samples: A total of 94 samples were collected spanning the full water column at: Station 1 (13 samples), Station 3 (13 samples), Station 5 (11 samples), Station 6 (12 samples), Station 8 (8 samples), Station 9 (12 samples), Station 10 (12 samples), and Station 11 (22 samples). Details of samples collected are presented in Table PaTh1.

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

Dissolved oxygen  $\Delta^{17}\text{O}$  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  $\delta^{18}\text{O}$ :* Near-shore, where riverine and submarine groundwater discharge is expected, these freshwater inputs will have distinctive  $\delta^{18}\text{O}$  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  $\delta^{18}\text{O}$  profile at the specific site where sediment components (e.g. forams, coccoliths) formed.

*Dissolved  $\text{O}_2$   $\Delta^{17}\text{O}$ :* 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  $\Delta^{17}\text{O}$  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  $\Delta^{17}\text{O}$  signal by diapycnal mixing from above, or isopycnal transport. Samples from 40oS will allow the possibility of a high  $\Delta^{17}\text{O}$  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  $\delta^{18}\text{O}$ :* 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°C on the ship.

*Dissolved  $\text{O}_2$   $\Delta^{17}\text{O}$ :* 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.  $\Delta^{17}\text{O}$  samples were either the first to be taken from the OTE, or the second, following directly after  $^3\text{He}$  sampling (see relevant log sheets for flask by flask details).

## Samples collected

*Water  $\delta^{18}\text{O}$ :* The main stainless cast was sampled at all stations and all depths to give to provide  $\approx 230$  water samples. Underway sampling from the trace-metal fish was also conducted during the medi-vac transit, and during the final approach to Cape Town to provide another  $\approx 30$  samples.

*Dissolved  $\text{O}_2$   $\Delta^{17}\text{O}$ :* 36 samples were taken in duplicate (i.e. to fill 72 flasks). Samples were taken at Stations 9 and 11. In both cases, deeper samples were collected on the main stainless cast (CTD 30, CTD 37 respectively), and shallower samples on the 400 m biological stainless cast (CTD 32, CTD 39 respectively). Minor intake of air was witnessed during sampling of two of the flasks and is noted on the log sheets.

### Sample analysis

No shipboard analysis of oxygen isotopes was performed.

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

$\Delta^{17}\text{O}$  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., Thieme, 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 Composition of Dissolved Oxygen. *Science* **288**.

# BATHYMETRY

By Mounir Lekouara

## Instrumentation

The RRS *Discovery* was equipped with a Simrad EA500 echo sounder (10.2/12.0kHz ‘fish’ and hull mounted system) to allow bathymetric profiling throughout the cruise. The estimated depth of the hull-mounted transducer was 5.3m. The Precision Echosounding (PES) transducer mounted in a ‘fish’ was towed at an estimated depth of 8.5m.

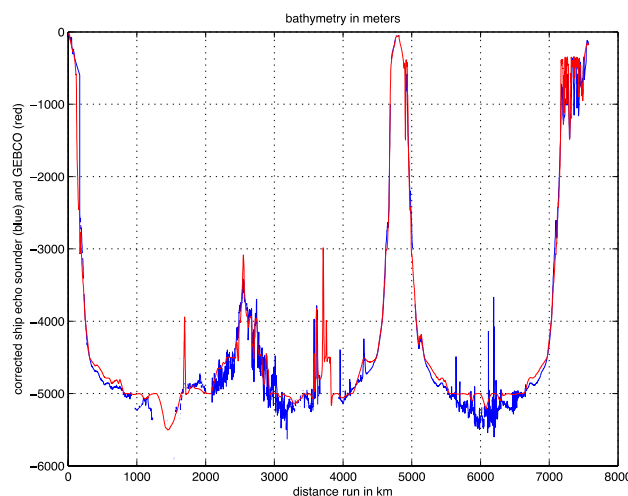
The measured depth was logged by the TECHSAS system and displayed on the Simrad visual display unit. A hardcopy of this display was also produced on a colour printout.

## Routine Processing

Following the methodology of D346, files were transferred from the onboard logging system (TECHSAS) to the UNIX system on a daily basis using the Matlab function `mday_00('sim',day#)`. The raw data files have extensions of the form `_di357_d***.nc` where \*\*\* is the number of the Julian day.

During the cruise, the echosounder often failed to detect the bottom and reported either zeros or spuriously large depths. The script `msim_01.m` was run to remove data outside a tolerated range and apply a 5-minute median despiking, outputting the file `sim_di357_d***_smooth.nc`. The script `msim_plot.m` copied the smoothed data to the file `sim_di357_d***_edited.nc` and called the function `mplxied` to allow a manual removal of the remaining spikes. The paper record was proved useful in detecting spurious depths resulting from side-echoes off steep topography and reflection off the CTD cable. However it is not available for the whole duration of the cruise, and very noisy parts of the measurements were manually discarded. Incorrect values for the bottom depth were also detected when the transmitted ping penetrated thick layers (up to ~200m) of soft sediment on the sea floor before being reflected by the underlying bedrock.

Following the manual edit of the smoothed data, the script `mapend_sim.m` was run to append all existing `sim_di357_d***_edited.nc` files to `sim_di357_01.nc`. Once a clean navigation file had been produced, `mmerge_sim_nav_di346.m` was run to merge the position and bathymetry data and correct for the variable speed of sound using Carter table climatologies. The corrected depths were saved in the file `sim_di357_nav_merged`. This data is shown in Figure 21 and compared with the depth extracted from the GEBCO dataset. The gaps are associated with discarded noisy data.



**Figure 21:** Bathymetry from the *Discovery* echo-sounder after filtering and sound-speed correction (blue) compared with the GEBCO bathymetry along the D357 track.



# VESSEL MOUNTED ADCP INSTRUMENTS

By Mounir Lekouara

## Introduction

Two vessel-mounted Acoustic Doppler Current Profilers (ADCPs) onboard *RRS Discovery* were used throughout the cruise to measure the horizontal velocity field (cross-track and along-track). The 75kHz and 150kHz Ocean Surveyor (OS) instruments are supplied by Teledyne RD Instruments, Poway, California. Unlike *RRS James Cook*, *RRS Discovery* does not have retractable keels so these instruments are fitted to the hull of the ship. The depths of the transducers are 5.3m. Both transducers are phased-array, which means that they are made up of many elements each transmitting in different phase. This is advantageous, because it means that the accuracy of the velocities, derived from the Doppler shifted return signals, is not affected by speed of sound changes throughout the water column. However, the range and accuracy of the instruments is known to be affected by exposure to bubbles.

The different frequencies of the two instruments affect both their depth range and resolution. The 150kHz allows smaller depth bins and consequently higher vertical resolution, but the signal is more rapidly attenuated and typically only penetrates to approximately 400-500m. The 75kHz lacks such good vertical resolution but penetrates to approximately 800-1000m.

## 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>\_di357<nnn>\_<filename>.<ext>*, where *<inst>* is the instrument name (75 or 150), *<nnn>* is the file sequence number, *<filename>* 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:

/ADCP150/di357 (for 150kHz transducer data)  
/ADCP75/di357 (for 75kHz transducer data)

## Sound Speed Considerations

Measurements of *x* and *y* velocities are independent of the speed of sound for phased array ADCP instruments such as those used on D357. If the speed of sound changes in the vertical water column or in front of the transducer, the angle of the beam will consequently change. This change

in beam angle change occurs in the same ratio as the Doppler shift equation, meaning that a change in the Doppler frequency shift of a particle moving parallel to the face is compensated entirely by the corresponding beam angle shift, cancelling out the change in the speed of sound. For a more in-depth account of speed of sound considerations when using ADCP units please refer to JC032 cruise report.

### 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.

CODAS was run on the *nomore* Unix station at NOCS. The raw data were copied into either the */vmadcp/di357\_os75/rawdata* directory or the */vmadcp/di357\_os150/rawdata* directory, depending on the instrument.

### Setting Up the Directories and loading the data

Once loaded into the *rawdata* directory, the following steps were followed:

1. *movescript* 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 di357<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.

### Time varying heading correction

The processing of the VMADCP requires a precise and continuous dataset of ship heading, in order to translate the measurements from ship coordinates to absolute Earth coordinates without bias. The ship's gyro offers a continuous stream of ship heading data, however it oscillates when the direction of the ship changes. This effect is corrected with the heading information provided by the four Ashtec GPS antennas. Once the daily navigation was processed for the duration of the cruise, the Ashtec heading minus the shipboard gyro heading data in the file *ash\_di357\_01.nc* was despiked with the Matlab routine *m\_median\_despike.m*. It was then manually despiked using the function *mplxeyed.m* before its missing values were interpolated with *mintrp.m*. The Matlab function *make\_g\_minus\_a.m* was executed for each instrument (75 and 150) and each data sequence to create the files (*di357<nnn>nnx.rot*) which contain the required 5-minute heading adjustment. Finally the Unix command "*quick\_adcp.py --cntfile q\_pyvrot.cnt*" was run to apply the time varying correction to the VMADCP files.

### Fixed calibration

The next step is to correct for the discrepancy between the beam coordinates and the ship heading. This difference is the angle at which the instruments are fixed under the hull. It should be constant during the cruise.

The *quick\_adcp.py* script estimates amplitude and phase corrections for each set of data. It is only by specifying a calibrated rotation in the *q\_pyrot.cnt* file that accurate velocities could be obtained. 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\_pyrot.cnt* control file.

ENX file number	phase (median)	amplitude (median)	number of pings
6	-2.852	1.004	27
12	-2.7626	1.0038	64
13	-2.8206	1.0006	53
22	-2.9483	1.0075	9
23	-2.8384	1.0051	159
D346	-2.88	1.002	
<b>D357</b>	<b>2.88</b>	<b>1.005</b>	

**Table 13:** bottom track calibration data for the OS75 instrument.

ENX file number	phase (median)	amplitude (median)	number of pings
3	-2.9409	0.9904	63
4	-	-	-
9	-0.2827	1.0045	115
10	-2.2422	1.0026	54
11	-8.5268	0.907	13
13	-1.1316	0.9332	43
20	-2.0406	0.9462	47
D346	-1.58	1.005	
<b>D357</b>	<b>-1.58</b>	<b>1.005</b>	

**Table 14:** bottom track calibration data for the OS150 instrument.

The calibrations chosen were as follows: OS75 rotation angle = -2.88, rotation amplitude = 1.005; OS150 rotation angle = -1.58, rotation amplitude = 1.005.

It should be noted that the final heading for the OS150 is much less consistent, therefore more significance should be given to the velocities derived from the OS75 instrument.

### **Manual editing**

The data were then checked in Gautoedit to ensure that any vertical striping associated with on/off station differences had been removed by application of the calibration. Any alterations that needed to be made to the files, for example due to bad profiles or bad bins were edited using 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\_di357<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\_di357<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\_di357<nnn>nnx\_spd.nc* and *os150\_di357<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\_di357nnx\_01.nc* and *os150\_di357nnx\_01.nc* which contain appended on-station and underway data.

The tables below summarize the sequence log of the OS75 and OS150 instruments.

ENX file number	start date	end date
6	18/10/2010 13:38	20/10/2010 05:20
7	20/10/2010 05:20	27/10/2010 08:53
8	27/10/2010 08:53	29/10/2010 09:06
9	29/10/2010 09:06	30/10/2010 10:13
10	30/10/2010 10:13	02/11/2010 12:48
11	02/11/2010 12:48	04/11/2010 13:41
12	04/11/2010 13:42	06/11/2010 12:30
13	08/11/2010 13:54	09/11/2010 19:35
14	09/11/2010 19:35	10/11/2010 09:26
16	10/11/2010 09:31	11/11/2010 11:07
17	11/11/2010 11:08	12/11/2010 08:21
18	12/11/2010 08:21	14/11/2010 09:01
19	14/11/2010 09:02	15/11/2010 18:19
20	15/11/2010 18:19	17/11/2010 13:07
21	17/11/2010 13:07	18/11/2010 11:41
22	18/11/2010 11:42	20/11/2010 00:57
23	20/11/2010 00:57	22/11/2010 14:57

**Table 15:** sequence log of the OS75 instrument.

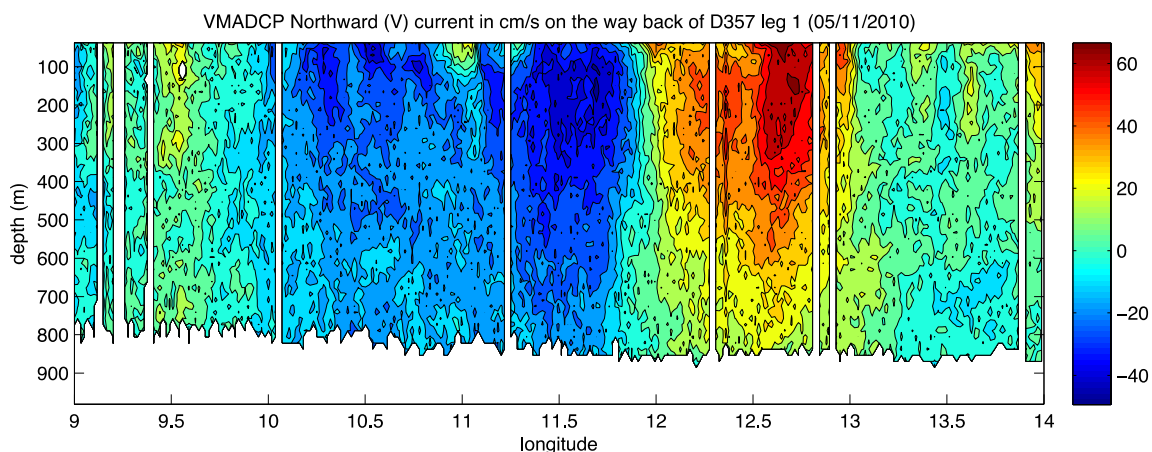
ENX file number	start date	end date
3	18/10/2010 13:37	20/10/2010 05:19
4	20/10/2010 05:20	27/10/2010 08:52
5	27/10/2010 08:53	29/10/2010 09:06
6	29/10/2010 09:06	30/10/2010 10:13
7	30/10/2010 10:13	02/11/2010 12:48
8	02/11/2010 12:48	04/11/2010 13:41
9	04/11/2010 13:42	06/11/2010 12:30
10	08/11/2010 13:54	09/11/2010 19:35
11	09/11/2010 19:35	10/11/2010 09:26
13	10/11/2010 09:30	11/11/2010 11:07
14	11/11/2010 11:08	12/11/2010 08:21
15	12/11/2010 08:21	14/11/2010 09:01
16	14/11/2010 09:01	15/11/2010 18:19
17	15/11/2010 18:19	17/11/2010 13:07
18	17/11/2010 13:07	18/11/2010 11:41
19	18/11/2010 11:42	20/11/2010 00:57
20	20/11/2010 00:57	22/11/2010 08:37

**Table 16:** sequence log of the OS150 instrument.

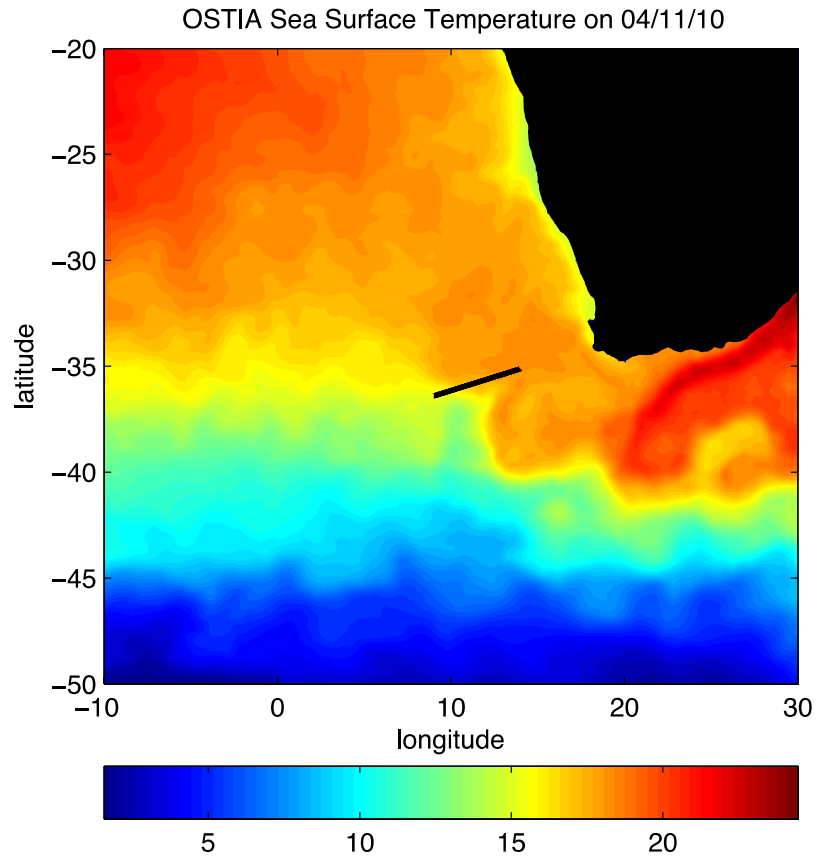
### Initial results

The instruments seem to have performed well, except for the OS150 after the 15<sup>th</sup> of November when most of the deep measurements were discarded by the CODAS post-processing. For a detailed discussion on the contamination sources of VMADCP data, please refer to the D346 cruise report. The figure XXX shows an example of measured Northward velocities on what seems to be a warm-core anti-cyclonic eddy. The figure XXX shows that it happened at the Western boundary of the Agulhas current leakage.

The files *os75\_di357nnx\_01.nc* and *os150\_di357nnx\_01.nc* contain the VMADCP data for the whole cruise. They are common Net-CDF files and can be accessed easily in Matlab or with simpler softwares such as Ferret and Ncview.



**Figure 22:** probable anti-cyclonic warm-core eddy as observed by the OS75 between 4/11/2010 12:00 and 5/11/2010 12:00.



**Figure 23:** OSTIA (UK Met Office) satellite Level-4 Sea Surface Temperature on 04/11/2010 with the track of the ship during the acquisition of Figure 22.

# LOWERED ACOUSTIC DOPPLER CURRENT PROFILER (LADCP)

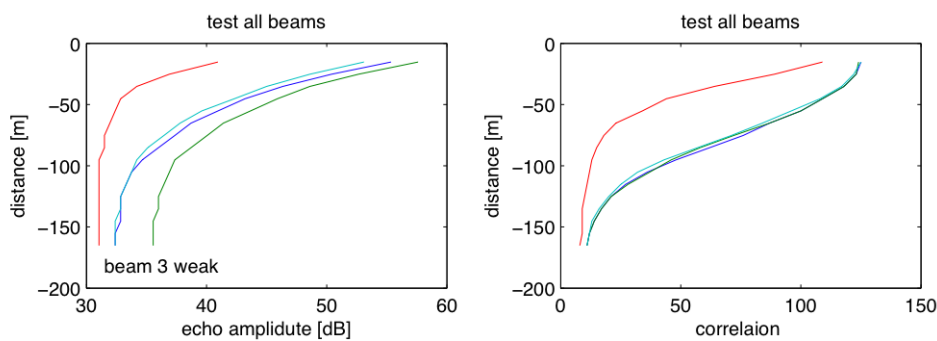
By Mounir Lekouara

## Instruments Setup and Performance

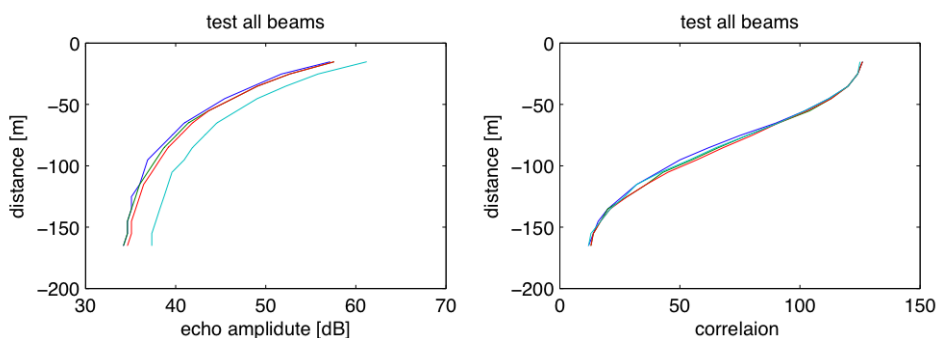
4 RDI 300kHz Workhorse LADCP units were available on D357: two aluminium-cased unit and two titanium-cased units. The LADCP was configured to have a standard 16 x 10 m bins. There was also a 5m blank below the transmitter. Data were collected in Earth co-ordinates..

The cruise began with a downward-looking titanium-cased LADCP on the trace metal CTD frame, and a downward-looking aluminium-cased LADCP on the stainless CTD frame. The beam 3 on the LADCP on the stainless rosette became weak after cast 6 and had around 25% 3 beam solutions for the rest of the cruise. The figure XXX illustrates the weakness of beam 3 and the low correlation with the other 3 beams on the aluminium-cased instrument. The titanium-cased LADCP performed well, its beams were correlated and of similar strength. Before cast 28, slave upward-looking LADCPs have been fitted on the rosettes (an aluminium-cased on the stainless rosette and a titanium-cased on the trace metal one). They both performed well and improved the quality of the current profiles.

Table 17 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. It is sometimes not achieved on titanium casts due to the low weight of the titanium rosette which means that it can be dragged by the current and lowered in an oblique trajectory. Hence the package may not be lowered all the way to the sea floor and the LADCP may not detect the bottom. The notes on the performance of the down looking LADCP are extracted from the log files of the LDEO processing (see below).



**Figure 24:** aluminum-cased LADCP performance on cast 22. The third beam (red) is weaker than the others and it has a poor correlation with the others. This leads to 44% of pings that are processed in a 3-beam solution (using the other beams) on this cast.



**Figure 25:** titanium-cased LADCP performance on cast 23. One beam is stronger than the others but retains a close correlation with them.

cas t	st n	year day	coord	dept h (m)	config	bot. trac k	notes
1	tes t	291	34° 13' S 17° 59' E	257	TI down	-	not processed
2	tes t	291	34° 12' S 17° 59' E	247	Ti down	-	not processed
3	1	291	34° 36.63' S 17° 2.48' E	2632	SS down	yes	
4	1	292	34° 36.93' S 17° 02.64' E	2620	Ti down	yes	
5	1	292	34° 37.7' S 17° 03.99' E	2639	SS down	no	bio cast
6	2	292	35° 28.32' S 14° 59.68' E	4684	SS down	yes	weak down-looking beam 3
7	2	293	35° 26.2' S 14° 58.9' E	4678	TI down	yes	no CTD processing due to corrupted data until 2000m
8	2	293	35° 22.25' S 14° 54.48' E	4678	SS down	no	bio cast, weak down-looking beam 3
9	3	294	36° 30.4' S 13° 6.84' E	4911	SS down	yes	cable damaged, no CTD processing, weak down looking beam 3 (31% 3 beam solution)
10	3	295	36° 29.37' S 13° 9.80' E	4908	SS down	-	aborted due to swell, not processed
11	3	296	26° 29.2' S 13° 16.67' E	4899	SS down	no	bio cast, weak down looking beam 3 (21% 3 beam solution)
12	3	296	36° 29.61' S 13° 16.30' E	4896	TI down	no	no CTD data
13	3	296	36° 27.91' S 13° 21.15' E	4893	TI down	no	
14	3	297	36° 27.65' S 13° 12.39' E	4903	TI down	no	
15	4	298	38° 24.13' S 10° 0.1' E	5065	SS down	yes	weak down looking beam 3 (39% 3 beam solution)
16	4	298	38° 25.3' S 10° 01.19' E	5074	TI down	yes	with CTD not processed because of uncorrect SBE CTD data because of corruption in the original CTD file



17	4	299	38° 25.6' S 10° 03.14' E	5100	TI down	yes	
18	4	299	38° 25.5' S 10° 05.17' E	5129	SS down	no	bio cast, weak down looking beam 3 (26% 3 beam solution)
19	5	300	40° 0.58' S 5° 30.55' E	5227	SS down	yes	weak down looking beam 3 (43% 3 beam solution)
20	5	300	40° 02.57' S 4° 31.48' E	5200	TI down	yes	
21	5	300	40° 03.52' S 5° 31.61' E	5175	SS down	no	bio cast, weak down looking beam 3 (20% 3 beam solution)
22	6	302	39° 59.9' S 0° 49.21' E	4902	SS down	yes	weak down looking beam 3 (44% 3 beam solution)
23	6	302	40° 0.86' S 0° 49.94' E	4896	TI down	yes	
24	6	302	40° 01.21' S 0° 53.16' E	4921	SS down	no	bio cast, weak down looking beam 3 (22% 3 beam solution)
25	6	303	39° 59.46' S 0° 55.21' E	4947	TI down	no	
26	7	305	39° 59.7' S 04° 53.63' W	3809	SS down	-	WHMD357_Palmer config for hi-res along-beam velocities for turbulence measurement experiment. Nort processed.
27	8	313	34° 19.82' S 17° 37.02' E	731	-	-	no LADCP
28	8	313	34° 20.08' S 17° 36.54' E	789	SS up and down	yes	weak down looking beam 3
29	8	313	34° 37.4' S 17° 00.97' E	2709	TI up and down	-	LADCP failure
30	9	314	34° 59.91' S 16° 0.19' E	4376	SS up and down	yes	broken down looking beam 3 (25% 3 beam solution)
31	9	314	34° 54.27' S 16° 04.27' E	4250	TI up and down	no	
32	9	314	34° 54.2' S 16° 04.55' E	4279	SS up and down	no	bio cast, weak down looking beam 3 (26% 3 beam solution)
33	10	315	35° 55.6' S 14° 3.50' E	4866	SS up and down	yes	broken down looking beam 3 (28% 3 beam solution)
34	10	315	35° 57' S 14° 05' E	4874	TI up and down	no	

35	3	316	36° 27.20' S 13° 12.93' E	4898	SS up and down	no	bio cast, broken down looking beam 3 (24% 3 beam solution)
36	3	316	36° 27.9' S 13° 12.66' E	4898	TI up and down	yes	pb with compass on slave LADCP
37	11	318	39°12.8 ' S 7° 48.49' E	5179	SS up and down	yes	broken down looking beam 3 (29% 3 beam solution)
38	11	318	39° 14.98' S 7° 44.71' E	5214	TI up and down	yes	
39	11	319	39° 15.42' S 7° 43.69' E	5241	SS up and down	no	bio cast, broken down looking beam 3 (22% 3 beam solution)
40	11	319	39° 17.6' S 7° 38.99' E	5286	TI up and down	yes	
41	12	321	37° 26.51' S 11° 38.70' E	5195	TI up and down	no	
42	12	321	37° 27.8' S 11° 33.58' E	5152	SS up and down	no	broken down looking beam 3 (22% 3 beam solution)
43	10	322	35° 55.06' S 14° 03.83' E	4868	SS up and down	no	bio cast, broken down looking beam 3 (22% 3 beam solution)
44	1	323	34° 42.07' S 17° 02.11' E	2771	SS up and down	no	bio cast, waiting for CTD data, CTD not processed, broken down looking beam 3 (20% 3 beam solution)
45	11	323	34° 18.8' S 17° 36.06' E	737	TI up and down	yes	waiting for CTD data, CTD not processed
46	8	323	34° 18.2' S 17° 34.69' E	801	SS up and down	yes	waiting for CTD data, CTD not processed, broken down looking beam 3

**Table 17:** LADCP configurations for each cast, the level of processing achieved and notes about the quality of the results

### Data Processing

The data collected by the instrument were downloaded after each cast and stored as RDI binary files and corresponding text files in the directory */Drobo/D357/* by the operators.

Following the methodology developed on D346, 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.

All the processing for the LADCP was carried out on the *brianking* Mac Mini onboard the ship and on the *nomore* Linux terminal back at NOCS.

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.

1. **source LADall** sets up the paths required for the processing.
2. **cd proc/Rlad**; Symbolic links from the binary \*.000 files to the real raw file were created. As processing was performed on the local disk of *brianking*, the raw files were copied from the network and symbolic links were created to the required filenames. The UH and LDEO softwares requires a filename of *dNNN\_LL.000*, where *NNN* is the station number. The suffix *LL* is *02* if the LADCP is down-looking and *03* if it is up-looking.
3. **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 were checked to ensure the details of the cast (i.e. depth, downcast/upcast times) agree approximately with the CTD logsheet.
4. **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
5. **perl -S load.prl NNN\_02** loads the raw data, correcting for *magvar.tab* to start processing.
6. **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.
7. **cd Rnav; matlab; make\_sm** makes a smoothed navigation file for the cast.
8. **cd proc; matlab; plist = NNN.02; do\_abs**; calculates the relative velocity profiles. These plots were checked for reasonable agreement between downcast and upcast and that the vertical velocity changes sign between downcast and upcast .

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. As opposed to previous cruises (i.e. D346) the CTD data was not processed through Mstar but with SeaBird software. The function *create\_ctd\_for\_ladcp.m* was written. It allows the creation of 1Hz *cnv* files with time, pressure, temperature and salinity from the Seabird processed *cnv* files (after align CTD and cell thermal mass corrections).

9. **ctd\_in(NNN,02)** reads the 1Hz CTD data in. **plist=NNN.02; fd** aligns the LADCP and CTD data sets in time.
10. **cd proc; perl -S add\_ctd.prl NNN\_02** adds the CTD data to the \*.*blk* LADCP files in the *sldb* directory.
11. **perl -S domerge.prl -c1 NNN\_02** merges the single pings into corrected shear profiles. The *-c1* option now states that CTD data have been included.
12. **matlab; plist=NNN.02; do\_abs**; calculates the velocities again with the merged pings.

Steps 4,6,7,8,9,10,11,12 were repeated for the up-looking LADCP data (from cast 28), replacing 02 with 03. The processing of the up-looking LADCPs with CTD data did not succeed and more work is needed to fix the UH routines.

### LDEO Processing

As with the UH processing the LDEO processing can first be carried out without the CTD data to monitor the results and performance of the beams.

1. In Matlab: **sp** to setup the station letter and the run letter (*'noctd'* for no CTD data and *'wctd'* when CTD data are included).
2. **lp** to run the processing scripts.

The steps above were then repeated to include the CTD data after it has been processed, when available (see table 17). However, the time variable of the SeaBird files is in seconds from the CTD

log in, which is different from the Mstar time variables (seconds of year). The function loadctd.m was adjusted for this discrepancy. The processing of the up-looking LADCPs with CTD data worked fine with the LDEO suite.

The LDEO processing extracts the useful bottom track velocities. These velocities were not used to constrain the full velocity profile but existed as a method of verifying the reality of the near bottom velocities calculated by the standard LDEO inverse calculation.

## **Analysis of the results**

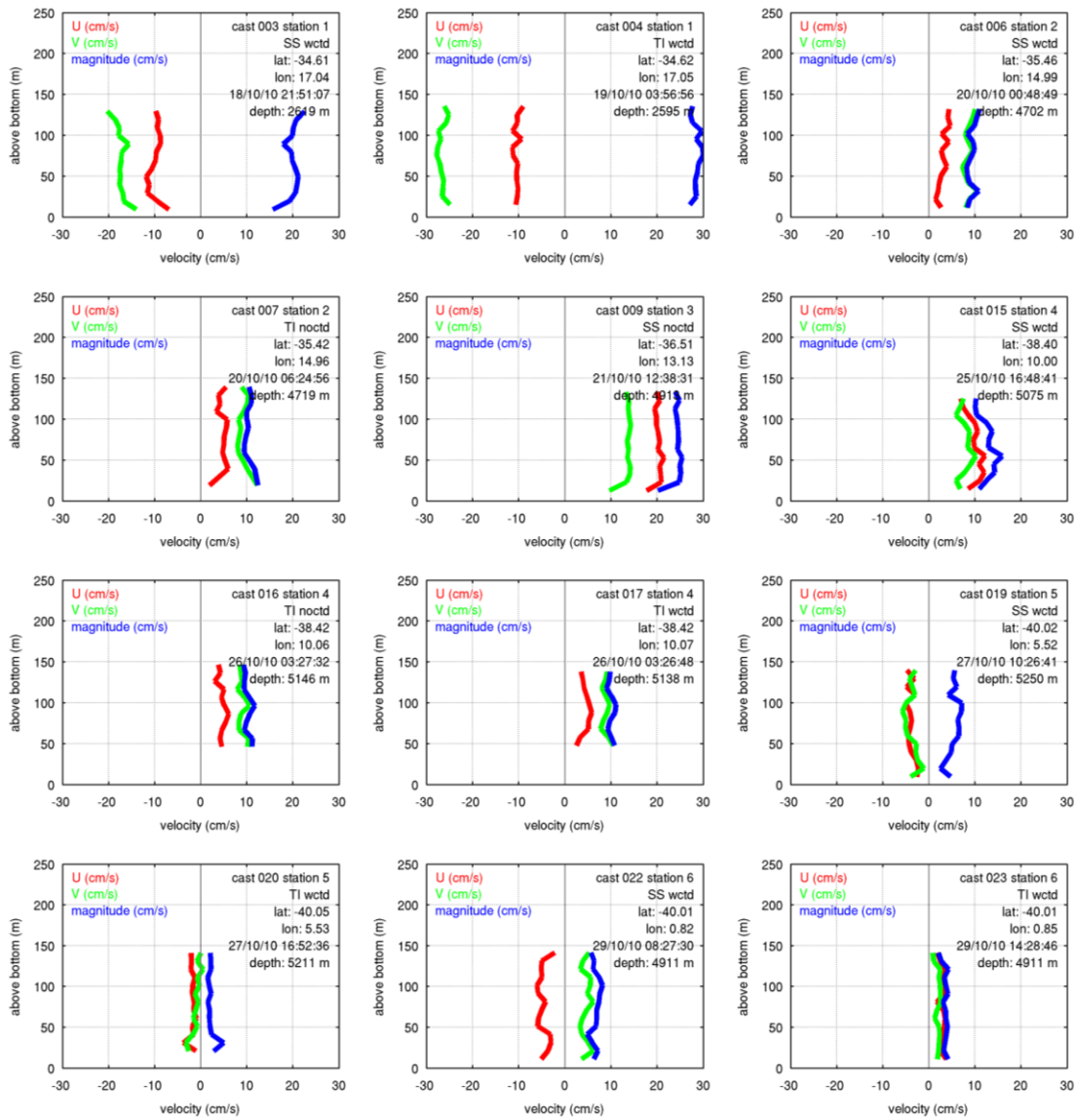
### *Needed work*

One must be careful when interpreting LADCP measurements in the Sub-Tropics. Indeed their accuracy is strongly dependent on the quantity of scattering particles present in the water column. If part of the profile is bad, the measured shear will be relatively correct but the absolute offset will be wrong. The LADCP measurements need a cautious adjustment and calibration, part of the profiles must be discarded, especially at depth. This work is what remains to be done to provide useful profiles of horizontal velocities.

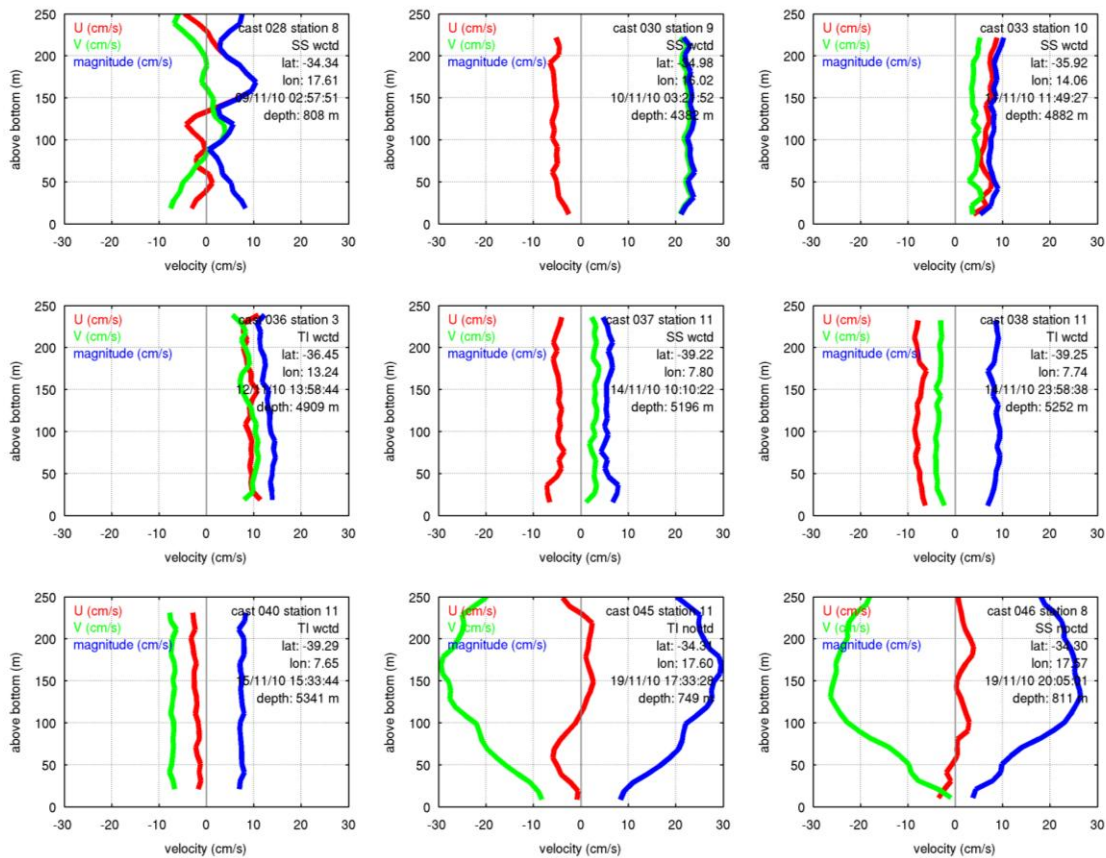
The next task would be to estimate the mixing from the combination of the LADCP shear with the CTD vertical strain. The methodology is detailed by Kunze et al. (2006). However the method needs to be adapted to each dataset, which requires both expertise and a substantial amount of dedicated time.

### *Near-bottom velocities*

In 21 casts, the CTD package was lowered enough for the LADCP to detect the sea floor. When this happens the water data can be navigated relatively to the bottom and hence is more precise. This is because the package velocities is determined accurately by the bottom tracking (BT), which is more reliable than integrating the shear throughout the water column. When part of the LADCP profile is bad (in general due to a low level of scattering particles) the absolute velocity of the package becomes unknown. The BT mode does not suffer from this limitation. The figure XXX shows the measured horizontal currents in bottom tracking mode when available. Apart from a possible tide correction, no additional adjustment is needed for this data. It should be noted however that the plots labelled as 'wctd' (when CTD data have been used in the LADCP processing) are slightly more reliable than the 'no\_ctd' plots. Finally, one should be cautious about the interpretation of the current very close to the sea bed (last 20 meters) because of the contamination of the side lobes of the LADCP beams by the sea floor.



**Figure 26:** Near-bottom horizontal currents velocity in bottom-tracking mode for the casts where it was possible. U is eastward and V is northward. SS is for the aluminum-cased LADCPs and TI is for the titanium-cased ones. 'wctd' indicates that the CTD data have been used in the LADCP processing, contrary to 'noctd'.



**Figure 27:** Near-bottom horizontal currents in bottom-tracking mode for the casts where it was possible. U is eastward and V is northward. SS is for the aluminum-cased LADCPs and TI is for the titanium-cased ones. 'wctd' indicates that the CTD data have been used in the LADCP processing, contrary to 'noctd'.

**References:**

Kunze, Eric, Eric Firing, Julia M. Hummon, Teresa K. Chereskin, Andreas M. Thurnherr, 2006: Global Abyssal Mixing Inferred from Lowered ADCP Shear and CTD Strain Profiles. *J. Phys. Oceanogr.*, **36**, 1553–1576.

# Appendices

- A: Event Log
- B: Underway Data
- C: Computing and Ship Systems Report
- D: NMF-SS Technical Report
- E: CTD log sheets
- F: Underway sampling log sheet
- G: Clean Underway sampling log sheet
- H: Core log sheet
- I: Core summary and photos

# Appendix A

## Event Log



## Cruise D357 Event Log

Event No.	Date	Station	Latitude (S)	Longitude (E)	Depth (m)	Time IN (GMT)	Time BOTTOM (GMT)	Time OUT (GMT)	Activity	Comments
357_001	18/10/10	Test	34 13.194	17 58.589	257	10.25	-	10.41	VMP#2	VMP#1 Bench test
357_002	18/10/10	Test	34 13.198	17 58.364	260	10.43		11.02	VMP#3	
357_003	18/10/10	Test	34 13.175	17 58.014	255	11.15	11.24	11.33	CTD001_T	Test TM CTD only 1 bottle fired
357_004	18/10/10	Test	34 12.724	17 58.168	255	12.12	-	-	TMFISH	Deployed TM FISH
357_005	18/10/10	Test	34 12.015	17 58.473	247	13.08	13.14	13.27	CTD002_T	Second test of TM CTD all bottles fired
357_006	18/10/10	Test	34 11.182	17 58.413	246	14.05		14.30	Megacore # 1	2 good cores
357_007	18/10/10	-	34 20.40	17 38.45	n/a	16.55	-	21/10/10 10.30	Aerosol_MI #2	Aerosol sample collected from the monkey island start of event
357_008	18/10/10	-	34 20.40	17 38.45	n/a	16.55	-	21/10/10 10.30	Aerosol_TM #2	Aerosol sample collected from the monkey island start of event
357_009	18/10/10	-	34 20.40	17 38.45	n/a	16.55		22/10/10 17.45	Aerosol_ISO #2	Aerosol sample collected from the monkey island start of event
357_010	18/10/10	Station 1	34 36.77	17 02.59	2620	23.49		12.10	VMP#6	VMP #4,5 Bench test. Flooded nose cone. This event is out of order
357_011	18/10/10	Station 1	34 36.63	17 02.50	2620	20.49	21.51	23.27	CTD003_S	Standard main CTD
357_012	19/10/10	Station 1	34 36.97	17 02.63	2615	02.52	03.53	05.30	CTD004_T	TM CTD
357_013	19/10/10	Station 1	34 37.66	17 03.98	2639	06.27	06.47	07.19	CTD005_S	Bio Cast
357_014	19/10/10	Station 1	34 38.09	17 05.04	2609	08.00		10.30	Megacore # 2	8 successful cores
357_015	19/10/10	Station 2	35 27.68	14 59.69	4681	23.13	00.48	02.53	CTD006_S	Standard main CTD
357_016	20/10/10	Station 2	35 26.51	14 59.39	4678	03.20	03.42	04.00	VMP#7	
357_017	20/10/10	Station 2	35 26.23	14 58.93	4677	04.38	06.21	08.49	CTD007_T	TM CTD
357_018	20/10/10	Station 2	35 23.48	14 56.014	4678	09.03	-	09.50	VMP#8	VMP hit ship
357_019	20/10/10	Station 2	35 22.415	14 54.556	4678	10.08	10.30	11.03	CTD008_S	Biological CTD

Appendix A: Event Log

Event No.	Date	Station	Latitude (S)	Longitude (E)	Depth (m)	Time IN (GMT)	Time BOTTOM (GMT)	Time OUT (GMT)	Activity	Comments
357_020	21/10/10	Station 3_SS	36 20.38	13 06.84	4912	9.44	12.47	15.47	CTD009_S	Main CTD at first superstition. Cross over with French IPY Bonus good hope cruise
357_021	22/10/10	Station 3_SS	36 29.733	13 06.546	4918	5.56	-	10.45	SAPS #1	8 SAPS deployed
357_022	22/10/10	Station 3_SS	36 29.24	13 09.24	4906	11.03	-	11.05	VMP#9	Failed start
357_023	22/10/10	Station 3_SS	36 29.24	13 09.24	4906	11.13	-	11.28	VMP#10	Good profile
357_024	22/10/10	Station 3_SS	36 29.24	13 09.24	4909	11.46	-	12.03	VMP#11	Good profile
357_025	22/10/10	Station 3_SS	36 29.37	13 09.80	4908	12.55		13.05	CTD010_S	Aborted due to swell
357_026	22/10/10	Station 3_SS	36 30.895	13 10.386	4896	18.00	-	02.50	SAPS #2	Last timer started at 18.15
357_027	23/10/10	Station 3_SS	36 29.22	13 16.41	4894	3.46	4.11	4.57	CTD011_S	Bio Cast
357_028	23/10/10	Station 3_SS	36 29.33	13 17.828	4895	7.02	10.24	12.40	CTD012_T	No bottles fired
357_029	23/10/10	Station 3_SS	36 29.02	13 18.67	-15	11.33	-	25/10/10 11.33	Aerosol_TM	TM#5
357_030	23/10/10	Station 3_SS	36 29.02	13 18.67	-15	11.33	-	25/10/10 11.33	Aerosol_MI	MI#5
357_031	23/10/10	Station 3_SS	36 28.19	13 18.44	4887	13.33	18.11	20.12	Megacore # 3	6 good cores
357_032	23/10/10	Station 3_SS	36 27.88	13 20.78	4894	21.57	00.48	03.27	CTD013_T	Super station Isotopes
357_033	24/10/10	Station 3_SS	36 27.65	13 12.30	4903	11.06	14.47	16.59	CTD014_T	Super station TM
357_034	25/10/10	-	36 09.60	10 24.08	-15	12.37	-	27/10/10 11.40	Aerosol_TM	TM#6
357_035	25/10/10	-	36 09.60	10 24.08	-15	12.37	-	27/10/10 11.40	Aerosol_MI	MI#6
357_036	25/10/10	Station 4	38 24.13	10 24.13	5065	15.07	16.46	19.21	CTD015_SS	
357_037	25/10/10	Station 4	38 24.21	10 0.46	5075	19.31	-	19.52	VMP#12	
357_038	25/10/10	Station 4	38 24.68	10 0.73	5094	20.05	-	20.40	VMP#13	
357_039	25/10/10	Station 4	38 25.26	10 04.23	5083	20.56	23.09	01.17	CTD016_T	CTD failed no bottles fired
357_040	26/10/10	Station 4	38 25.62	10 03.14	5100	01.52	03.24	05.33	CTD017_T	TM CTD

Appendix A: Event Log

Event No.	Date	Station	Latitude (S)	Longitude (E)	Depth (m)	Time IN (GMT)	Time BOTTOM (GMT)	Time OUT (GMT)	Activity	Comments
357_041	26/10/10	Station 4	38 25.46	10 05.17	5129	06.22	06.40	07.22	CTD018_SS	Bio Cast
357_042	27/10/10	Station 5	40 00.587	5 30.551	5200	08.43	10.25	12.58	CTD19_SS	5 LEAKERS 1 NO FIRE
357_043	27/10/10	Station 5	40 02.02	5 31.69	-15	12.45	-	13.13 29/10/10	Aerosol_TM	TM#7
357_044	27/10/10	Station 5	40 02.02	5 31.69	-15	12.45	-	13.13 29/10/10	Aerosol_MI	MI#7
357_045	27/10/10	Station 5	40 02.02	5 31.69	-15	12.45	-	12.50 31/10/10	Aerosol_ISO	ISO #7
357_046	27/10/10	Station 5	40 02.167	5 31.926	5218	13.07	-	13.31	VMP#14	
357_047	27/10/10	Station 5	40 02.409	5 31.601	5206	13.42	-	14.28	VMP#15	
357_048	27/10/10	Station 5	40 02.572	5 31.482	5219	14.42	16.57	19.10	CTD020_T	TM CTD
357_049	27/10/10	Station 5	40 03.52	5 31.482	5175	19.28	19.47	20.28	CTD021_SS	Bio Cast
357_050	29/10/10	Station 6	40 00.236	00 49.320	4900	06.41	08.19	10.40	CTD022_SS	
357_051	29/10/10	Station 6	40 00.86	00 49.94	4896	11.32	14.38	16.50	CTD023_T	TM CTD
357_052	29/10/10	Station 6	40 00.73	00 51.07	-15	14.38	-	12.53 31/10/10	Aerosol_TM#8	
357_053	29/10/10	Station 6	40 00.73	00 51.07	-15	14.38	-	12.53 31/10/10	Aerosol_MI#8	
357_054	29/10/10	Station 6	40 0.302	00 51.733	4945	17.04	-	17.30	VMP#16	
357_055	29/10/10	Station 6	40 0.3019	00 51.733	4933	17.44	-	18.23	VMP#17	
357_056	29/10/10	Station 6	40 01.21	00 53.16	5012	18.33	18.49	19.23	CTD024_SS	Bio Cast
357_057	29/10/10	Station 6	40 00.59	00 53.501	4915	19.17	-	22.55	SAPs shallow	
357_058	29/10/10	Station 6	40 00.19	00 54.415	4928	23.53	-	~4.10	Mega Core	6 cores
357_059	30/10/10	Station 6	39 59.51	00 54.01	4930	04.50	07.45	13.20	SAPs deep	
357_060	30/10/10	Station 6	39 59.49	00 55.21	4947	14.06	16.08	18.00	CTD025_T	Clean isotope
357_061	30/10/10	Station 6	39 59.66	00 51.25	-15	17.15	-	18.25	Rain	RTM#2, RMI#2
357_062	31/10/10	-	40 00.00	02 51.26	-15	14.30	-	08.56 31/11/10	Aerosol_TM#9	

Appendix A: Event Log

Event No.	Date	Station	Latitude (S)	Longitude (E)	Depth (m)	Time IN (GMT)	Time BOTTOM (GMT)	Time OUT (GMT)	Activity	Comments
357_063	31/10/10	-	40 00.00	02 51.26	-15	14.30	-	08.56 31/11/10	Aerosol MI#9	
357_064	31/10/10	-	39 59.99	2 54.84	-15	14.50	-	08.56 31/11/10	Aerosol ISO#9	
357_065	1/11/10	Station 7	39 59.69	4 53.53	3809	01.16	06.43	09.50	CTD026_SS	Winch problems
357_066	1/11/10	Station 7	40 0.73244	04 53.56153	3862	10.44	-	11.09	VMP#18	
357_067	1/11/10	Station 7	40 0.86082	04 53.78374	3856	11.20	-	11.22	VMP#19	Stopped due to high noise
357_068	1/11/10	Station 7	40 0.87504	04 53.81668	3856	11.30	-	12.15	VMP#20	
357_069	3/11/10	-	37 47.59	3 45.29	-15	10.23	-	9.04 6/11/10	Aerosol TM#10	
357_070	3/11/10	-	37 47.59	3 45.29	-15	10.23	-	9.04 6/11/10	Aerosol MI#10	
357_071	3/11/10	-	37 47.59	3 45.29	-15	10.23	-	9.04 6/11/10	Aerosol ISO#10	
357_072	8/11/10	-	34 01.96	18 09.55	-15	15.19	-	16.15	Rain	TM#3. Very small rain sample
357_073	8/11/10	Station 8	34 19.95	17 36.85	756	23.29	-	0024	VMP#21	
357_074		Station 8	34 19.313	17 37.71	724	00.40	-	01.04	VMP#22	
357_075	9/11/10	Station 8	34 19.82	17 37.02	735	01.38	01.42	01.49	CTD027_T	Used to wash bottles-all fired at the same depth
357_076	9/11/10	Station 8	34 20.09	17 36.51	805	02.24	02.57	03.49	CTD028_SS	Force 6 wind
357_077	9/11/10	Station 8	34 25.01	17 30.21	-15	07.12	-	9.19 11/11/10	Aerosol TM#11	
357_078	9/11/10	Station 8	34 25.01	17 30.21	-15	07.12	-	9.19 11/11/10	Aerosol MI#11	
357_079	9/11/10	Station 8	34 25.01	17 30.21	-15	07.12	-	9.20 13/11/10	Aerosol ISO#11	
357_080	9/11/10	Station 1 reoccupied	34 37.307	17 02.02	2637	10.57	-	14.45	Shallow SAPs	3 SAPs deployed
357_081	9/11/10	Station 1 reoccupied	34 37.24	17 01.34	2662	14.55	-	15.22	VMP#25	23, 24 bench test –not events
357_082	9/11/10	Station 1 reoccupied	34 37.42	17 01.17	2685	15.34	-	16.24	VMP#26	
357_083	9/11/10	Station 1 reoccupied	34 37.40	17 01.01	2702	16.35	17.55	19.35	CTD029_T	

## Appendix A: Event Log

Event No.	Date	Station	Latitude (S)	Longitude (E)	Depth (m)	Time IN (GMT)	Time BOTTOM (GMT)	Time OUT (GMT)	Activity	Comments
357_084	10/11/10	Station 9	34 58.78	16 00.94	4365	01.41	03.20	05.35	CTD030_SS	
357_085	10/11/10	Station 9	34 56.64	16 02.19	4312	06.03	-	06.10	VMP#27	Aborted at 50M. VMP 28 test only
357_086	10/11/10	Station 9	34 56.34	16 02.52	4319	06.16	-	06.40	VMP#29	VMP 30 deck test
357_087	10/11/10	Station 9	34 55.39	16 03.26	4300	06.56	-	07.17	VMP#31	
357_088	10/11/10	Station 9	34 54.27	16 04.29	4281	07.47	09.20	11.17	CTD031_T	TM CTD
357_089	10/11/10	Station 9	34 54.21	16 04.49	4279	12.34	12.52	13.37	CTD032_SS	Bio Cast
357_090	10/11/10	Station 9	34 52.48	16 05.22	4249	14.44	17.08	18.29	Boxcore	Trigger did not fire no core collected
357_091	11/11/10	Station 10	35 55.00	14 03.50	4866	09.53	11.50	14.14	CTD033_SS	No leakers
357_092	11/11/10	Station 10	35 57.42	14 04.68	4874	15.54	19.42	21.55	CTD034_T	TM Cast
357_093	12/11/10	Station 3 reoccupied	36 27.07	13 13.03	4898	07.13	07.38	08.39	CTD035_SS	Bio Cast
357_094	12/11/10	Station 3 reoccupied	36 27.87	13 12.67	4898	10.38	14.09	16.16	CTD036_T	Isotope cast
357_095	13/11/10	-	37 43.54	10 45.17	-15	13.40	-	08.25 17/11/10	Aerosol TM#13	
357_096	13/11/10	-	37 43.54	10 45.17	-15	13.40	-	08.25 17/11/10	Aerosol MI#13	
357_097	13/11/10	-	37 43.54	10 45.17	-15	13.40	-	08.25 17/11/10	Aerosol ISO#13	
357_098	14/11/10	Station 11	39 12.87	7 48.48	5177	08.24	10.08	12.33	CTD037_SS	
357_099	14/11/10	Station 11	39 13.16	7 46.77	5162	12.47	-	13.26	VMP#32	
357_100	14/11/10	Station 11	39 12.97	7 45.93	5164	13.26	-	14.00	VMP#33	
357_101	14/11/10	Station 11	39 12.84	7 44.90	5208	14.24	-	21.13	Deep SAPS	5 trace metal SAPS
357_102	14/11/10	Station 11	39 14.99	7 44.70	5216	21.46	00.06	02.20	CTD038_T	Main Ti Cast
357_103	15/11/10	Station 11	39 15.42	7 43.69	5241	02.36	02.52	03.50	CTD039_SS	Bio cast
357_104	15/11/10	Station 11	39 15.30	7 43.42	5241	04.05	-	10.51	Deep SAPS	Organics + Ac/Mn

Appendix A: Event Log

Event No.	Date	Station	Latitude (S)	Longitude (E)	Depth (m)	Time IN (GMT)	Time BOTTOM (GMT)	Time OUT (GMT)	Activity	Comments
357_105	15/11/10	Station 11	39 16.47	7 40.34	5264	10.55	-	11.18	VMP#34	
357_106	15/11/10	Station 11	39 16.90	7 39.88	5269	11.31	-	12.10	VMP#35	
357_107	15/11/10	Station 11	39 17.61	7 38.99	5286	13.07	15.36	17.47	CTD040_T	Isotope cast
357_108	15/11/10	Station 11	39 17.47	7 40.09	5269	19.10	-	23.15	Boxcore	Boxcore sub sampled
357_109	16/11/10	Station 11	39 17.67	7 40.229	5267	01.19	-	04.53	Shallow SAPs	
357_110	17/11/10	Station 12	37 26.51	11 38.70	5195	05.49	07.38	10.05	CTD041_T	Ti Cast
357_111	17/11/10	Station 12	37 26.66	11 35.06	5126	10.13	-	10.42	VMP#36	
357_112	17/11/10	Station 12	37 26.72	11 34.95	5126	10.55		11.35	VMP#37	
357_113	17/11/10	Station 12	37 27.83	11 33.58	5152	11.50	12.24	13.45	CTD042_SS	Bio/regular combined cast
357_114	18/11/10	Station 10 reoccupied	35 55.06	14 03.83	4867	06.31	06.54	07.53	CTD043_SS	Bio cast
357_115	18/11/10	Station 10 reoccupied	35 54.60	14 4.785	4866	07.58	-	08.17	VMP#39	VMP#38 deck test
357_116	18/11/10	Station 10 reoccupied	35 54.40	14 5.8514	4861	08.31	-	08.49	VMP#40	
357_117	18/11/10	Station 10 reoccupied	35 54.39	14 06.74	4861	09.07	-	11.40	VMP#41	
357_118	19/11/10	Station 1 2nd reoccupation	34 37.115	17 02.29	2630	03.40	-	08.40	SAPs	All ok
357_119	19/11/10	Station 1 2nd reoccupation	34 40.78	17 02.19	-15	07.45	-	09.00 21/11/10	Aerosol TM#15	Aerosol 14 blank
357_120	19/11/10	Station 1 2nd reoccupation	34 40.78	17 02.19	-15	07.45	-	09.00 21/11/10	Aerosol MI#15	
357_121	19/11/10	Station 1 2nd reoccupation	34 42.07	17 02.11	2811	09.02	09.17	10.16	CTD044_SS	Bio cast
357_122	19/11/10	Station 8 reoccupied	34 19.56	17 36.73	735	14.45	15.13	15.34	Boxcore	Boxcore sub sampled
357_123	19/11/10	Station 8 reoccupied	34 18.75	17 36.06	737	16.58	17.20	18.20	CTD045_T	Ti / isotopes combined cast
357_124	19/11/10	Station 8 reoccupied	34 18.20	17 34.69	799	19.34	20.08	21.01	CTD046_SS	Bio cast
357_125	19/11/10	Station 13	34 21.8	17 33.0	1124	11.10	-	11.21	Boxcore	Aborted at ~100M due to engine failure

Appendix A: Event Log

Event No.	Date	Station	Latitude (S)	Longitude (E)	Depth (m)	Time IN (GMT)	Time BOTTOM (GMT)	Time OUT (GMT)	Activity	Comments
357_126	20/11/10	Station 13	34 22.7	17 33.1	1120	01.30	02.08	02.37	Boxcore	Did not close
357_127	20/11/10	Station 13	34 22.4	17 33.2	1130	03.01		03.30	Boxcore	Aborted due to engine failure
357_128	20/11/10	Station 13	34 23.27	17 34.17	1168	17.35	18.18	18.53	Boxcore	Good core from O2 min
357_129	21/11/10	Station 8 reoccupied	34 18.62	17 37.58	644	14.05	-	14.26	VMP#42	
357_130	21/11/10	Station 8 reoccupied	34 19.11	17 37.50	730	14.48	-	15.11	VMP#44	VMP#43 deck test
357_131	21/11/10	Station 8 reoccupied	34 19.51	17 37.56	714	15.25	-	15.43	VMP#45	
357_132	21/11/10	Station 8 reoccupied	34 20.02	017 37.65	713	15.57	-	16.14	VMP#46	
357_133	21/11/10	Station 8 reoccupied	34 20.60	17 37.83	737	16.33	-	17.02	VMP#48	VMP#47-test
357_134	21/11/10	Station 8 reoccupied	34 21.02	17 38.07	742	17.05	-	17.29	VMP#49	
357_135	21/11/10	Station 8 reoccupied	34 21.43	17 38.46	744	17.41	-	18.01	VMP#50	
357_136	21/11/10	Station 8 reoccupied	34 21.64	17 39.08	712	18.20	-	18.39	VMP#51	
357_137	21/11/10	Station 8 reoccupied	34 22.09	17 39.49	707	18.55	-	19.11	VMP#52	
357_138	21/11/10	Station 8 reoccupied	34 22.74	17 39.87	715	19.26	-	19.43	VMP#53	
357_139	21/11/10	Station 8 reoccupied	34 23.32	17 40.48	706	20.03	-	20.21	VMP#54	
357_140	21/11/10	Station 8 reoccupied	34 23.74	17 40.90	700	20.34	-	20.53	VMP#55	
357_141	21/11/10	Station 8 reoccupied	34 24.16	17 41.26	700	21.04	-	21.20	VMP#56	
357_142	21/11/10	Station 8 reoccupied	34 24.64	17 41.75	694	21.34	-	21.53	VMP#57	
357_143	21/11/10	Station 8 reoccupied	34 25.18	17 42.21	693	22.06	-	22.25	VMP#58	
357_144	21/11/10	Station 8 reoccupied	34 25.39	17 42.44	691	22.35	-	22.52	VMP#59	
357_145	21/11/10	Station 8 reoccupied	34 25.83	17 42.68	700	23.06	-	23.22	VMP#60	
357_146	21/11/10	Station 8 reoccupied	34 26.36	17 42.87	719	23.34	-	23.52	VMP#61	

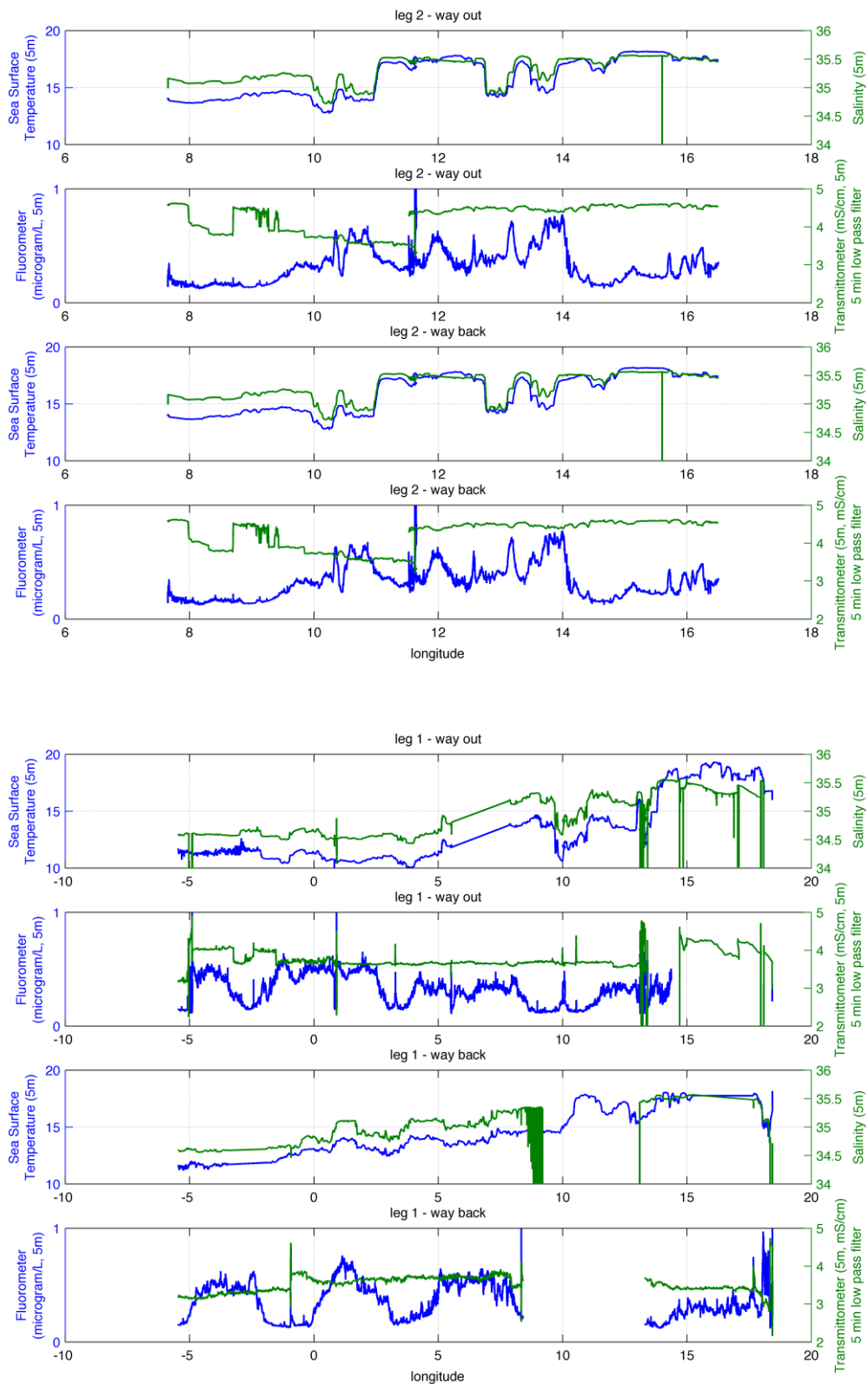
Appendix A: Event Log

Event No.	Date	Station	Latitude (S)	Longitude (E)	Depth (m)	Time IN (GMT)	Time BOTTOM (GMT)	Time OUT (GMT)	Activity	Comments
357_147	22/11/10	Station 8 reoccupied	34 26.69	17 43.12	724	00.03	-	00.22	VMP#62	
357_148	22/11/10	Station 8 reoccupied	34 26.94	17 43.20	734	00.33	-	00.51	VMP#63	
357_149	22/11/10	Station 8 reoccupied	34 26.94	17 43.20	734	01.04	-	01.20	VMP#64	
357_150	22/11/10	Station 8 reoccupied	34 27.49	17 42.99	808	01.54	-	02.09	VMP#65	
357_151	22/11/10	Station 8 reoccupied	34 26.63	17 43.16	720	02.26	-	02.32	VMP#66	
357_152	22/11/10	Station 8 reoccupied	34 26.37	17 43.11	705	02.36	-	02.52	VMP#67	

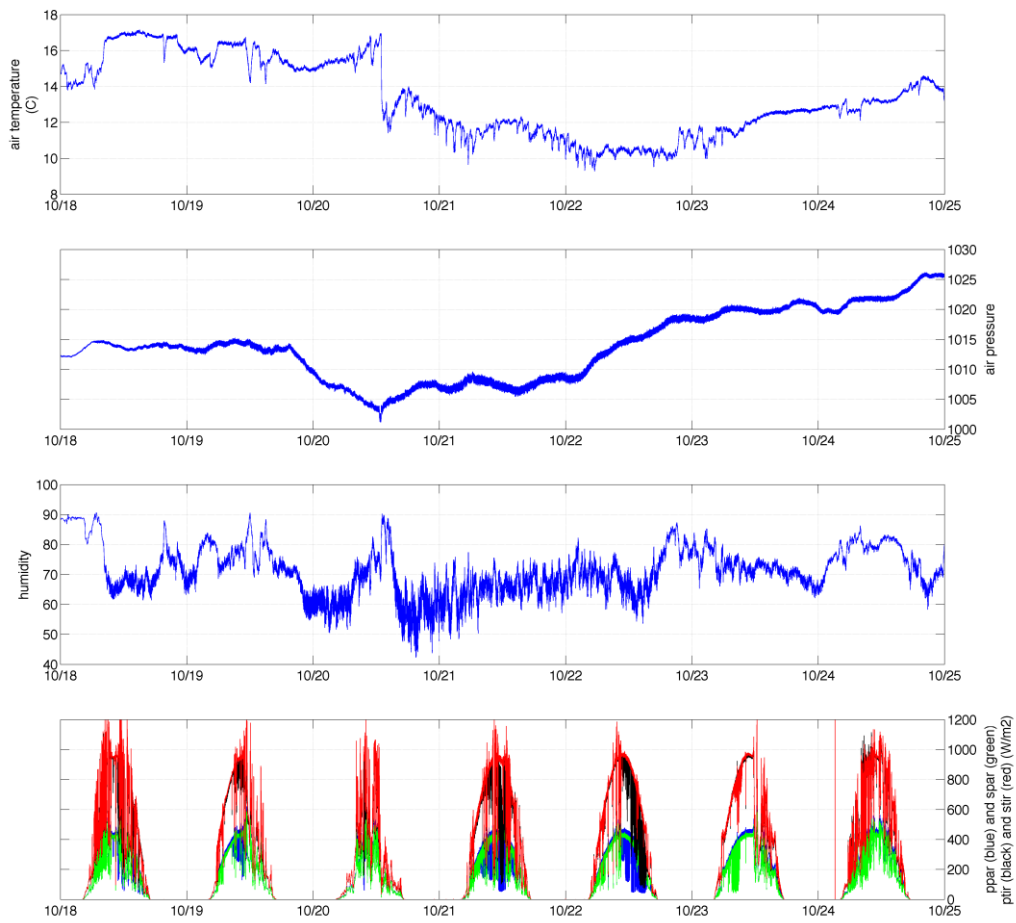


# Appendix B

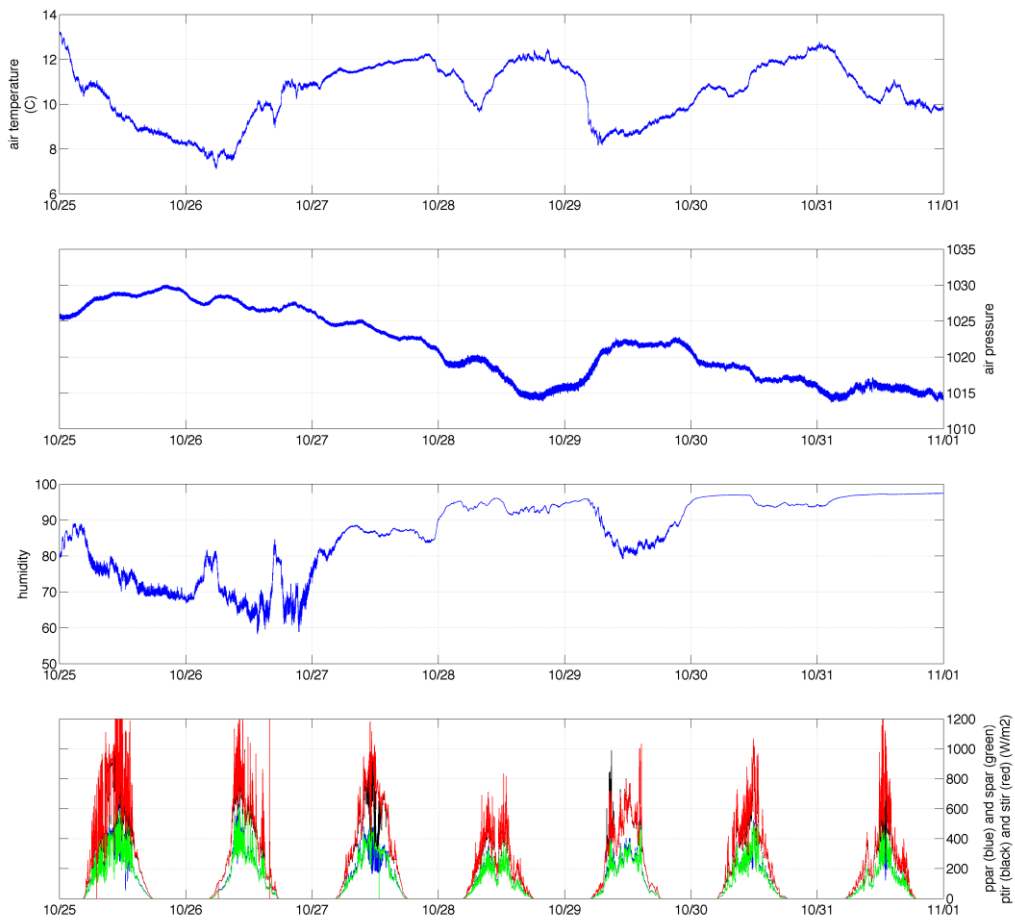
## Underway Data



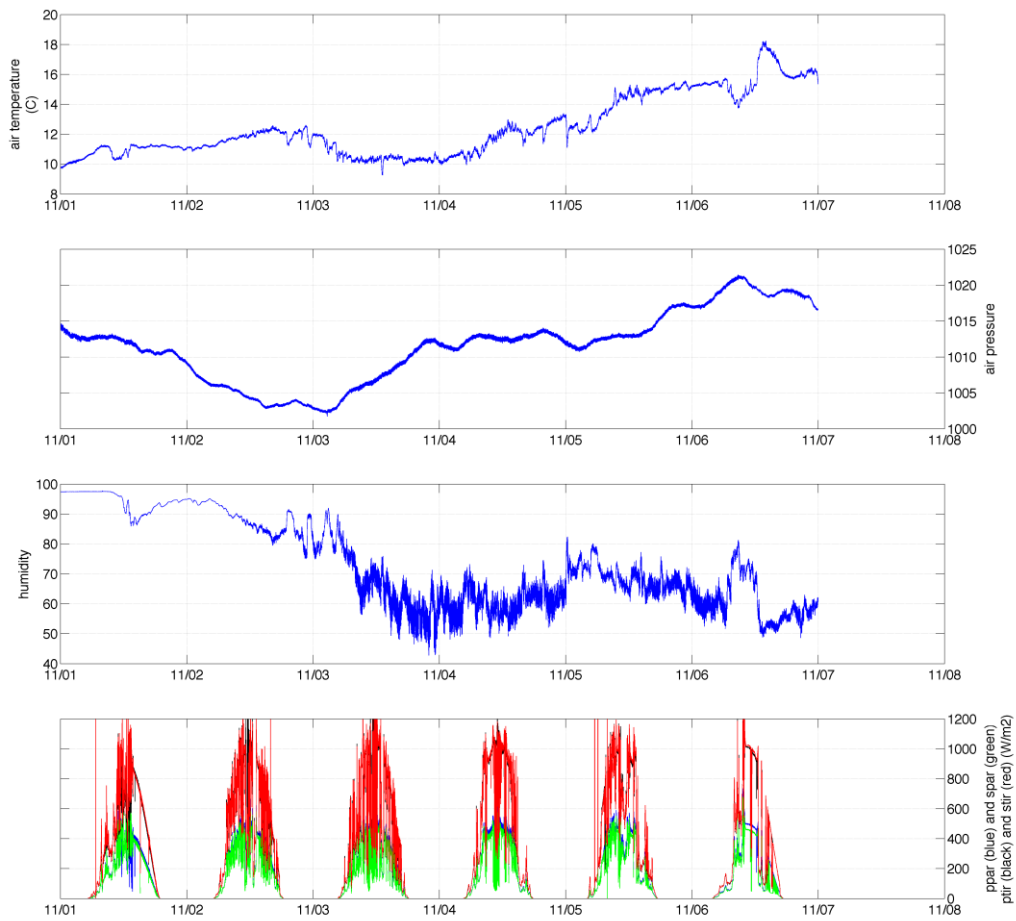
**Figure B1:** Seabird underway near-surface temperature, salinity, fluorescence and transmittance (5 minutes low pass filtered) plotted as a function of longitude for the way out and the way back of legs 1 and 2. The inlet is situated on the underside of the hull, close to the bow, at 5-6 meters depth.



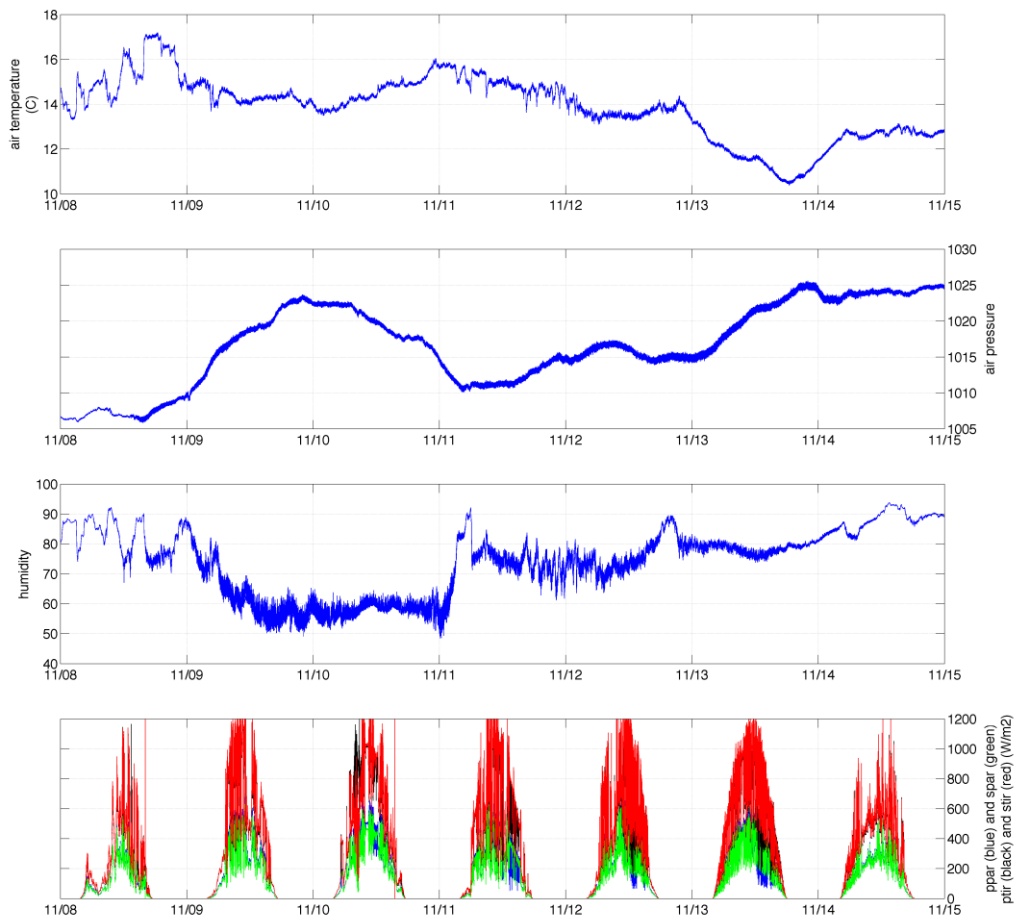
**Figure B2 (Week 1):** Underway air temperature, air pressure, humidity and light data (ppar: port photosynthetically active radiation, spar: starboard photosynthetically active radiation, ptir: port total irradiance, stir: starboard total irradiance). Dates are Midnight start of day.



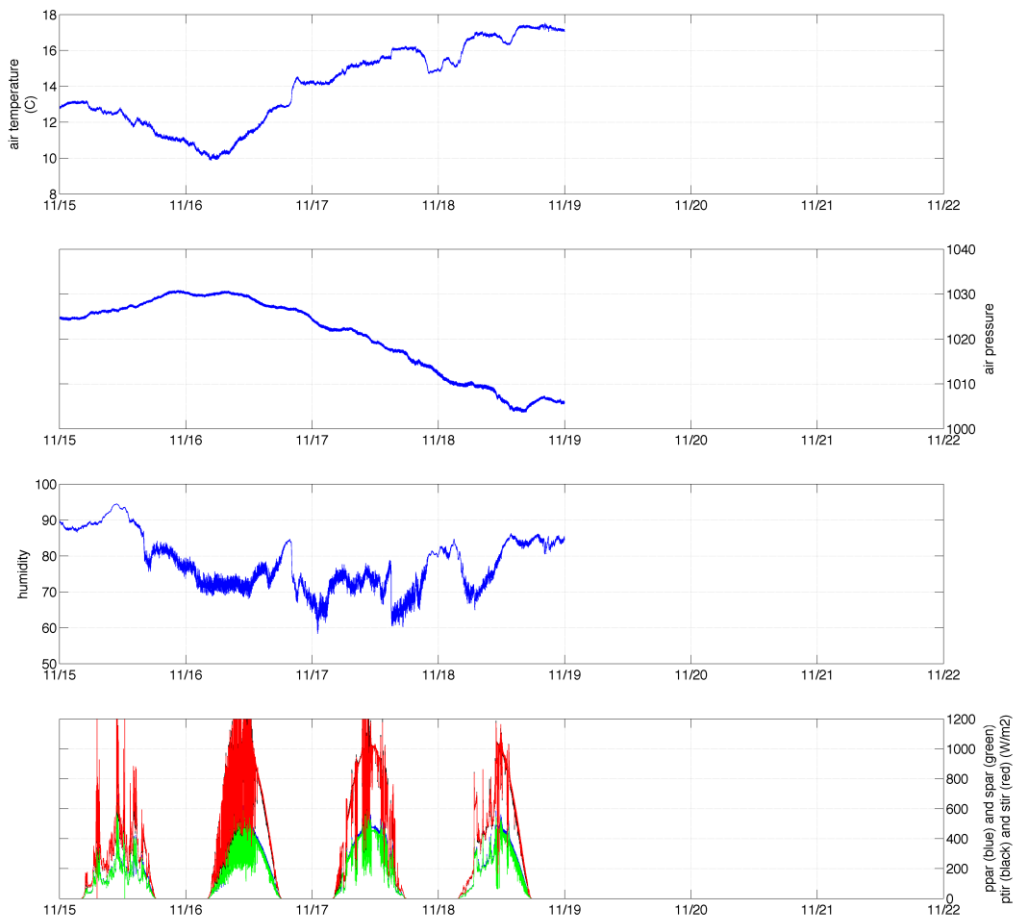
**Figure B2 (Week 2):** Underway air temperature, air pressure, humidity and light data (ppar: port photosynthetically active radiation, spar: starboard photosynthetically active radiation, ptir: port total irradiance, stir: starboard total irradiance). Dates are Midnight start of day.



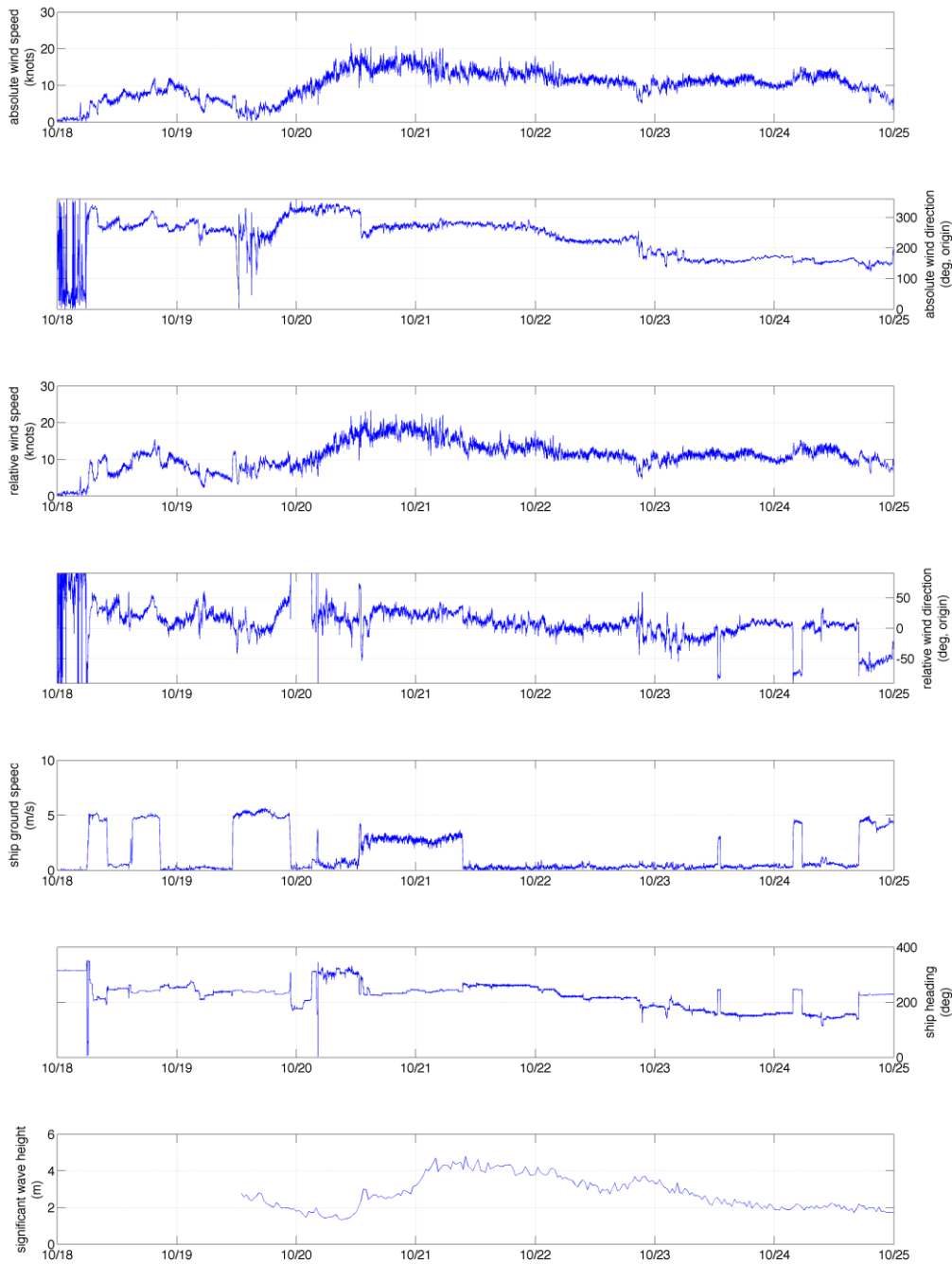
**Figure B2 (Week 3):** Underway air temperature, air pressure, humidity and light data (ppar: port photosynthetically active radiation, spar: starboard photosynthetically active radiation, ptir: port total irradiance, stir: starboard total irradiance). Dates are Midnight start of day.



**Figure B2 (Week 4):** Underway air temperature, air pressure, humidity and light data (ppar: port photosynthetically active radiation, spar: starboard photosynthetically active radiation, ptir: port total irradiance, stir: starboard total irradiance). Dates are Midnight start of day.

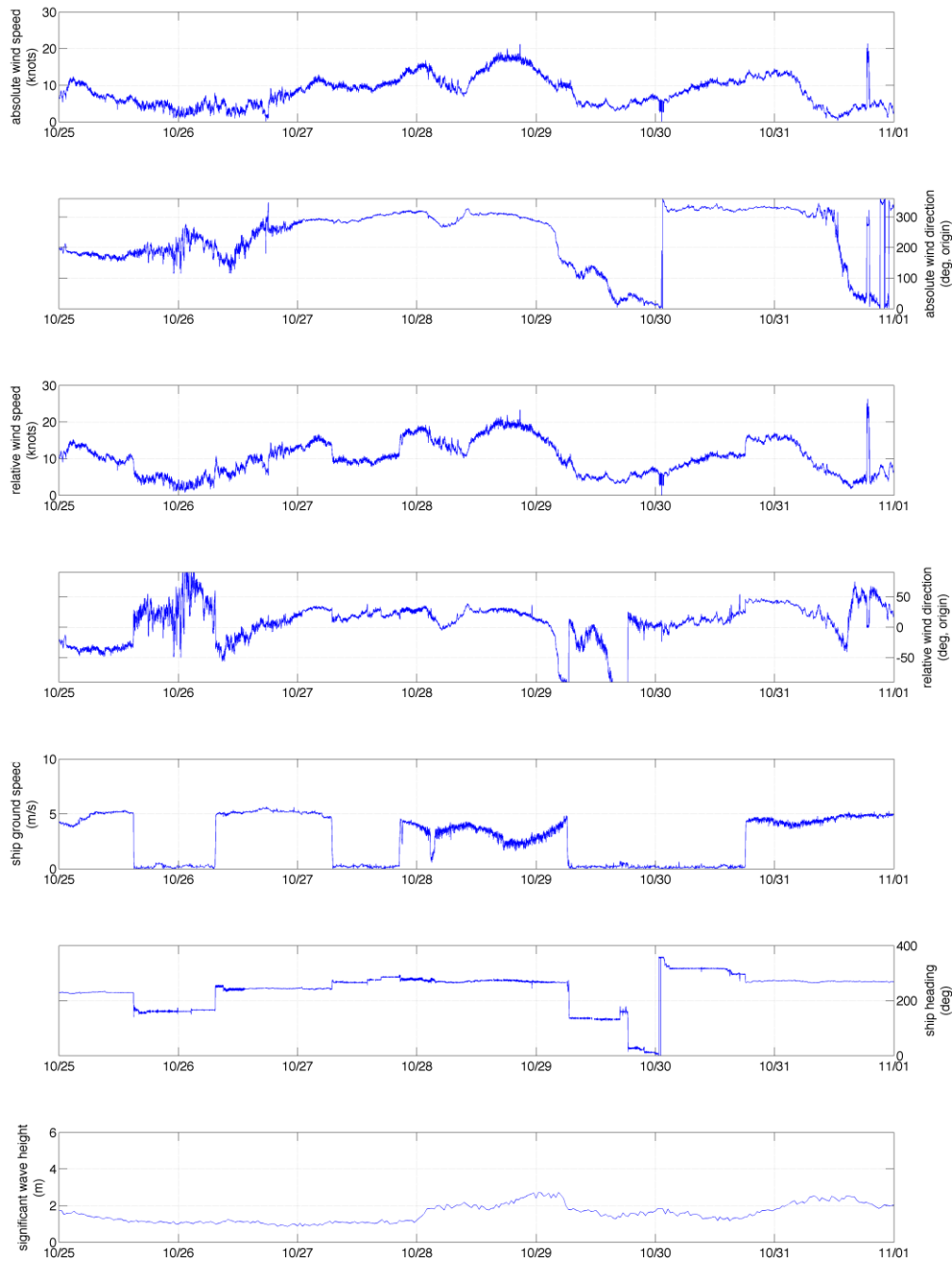


**Figure B2 (Week 5):** Underway air temperature, air pressure, humidity and light data (ppar: port photosynthetically active radiation, spar: starboard photosynthetically active radiation, ptir: port total irradiance, stir: starboard total irradiance). Dates are Midnight start of day.

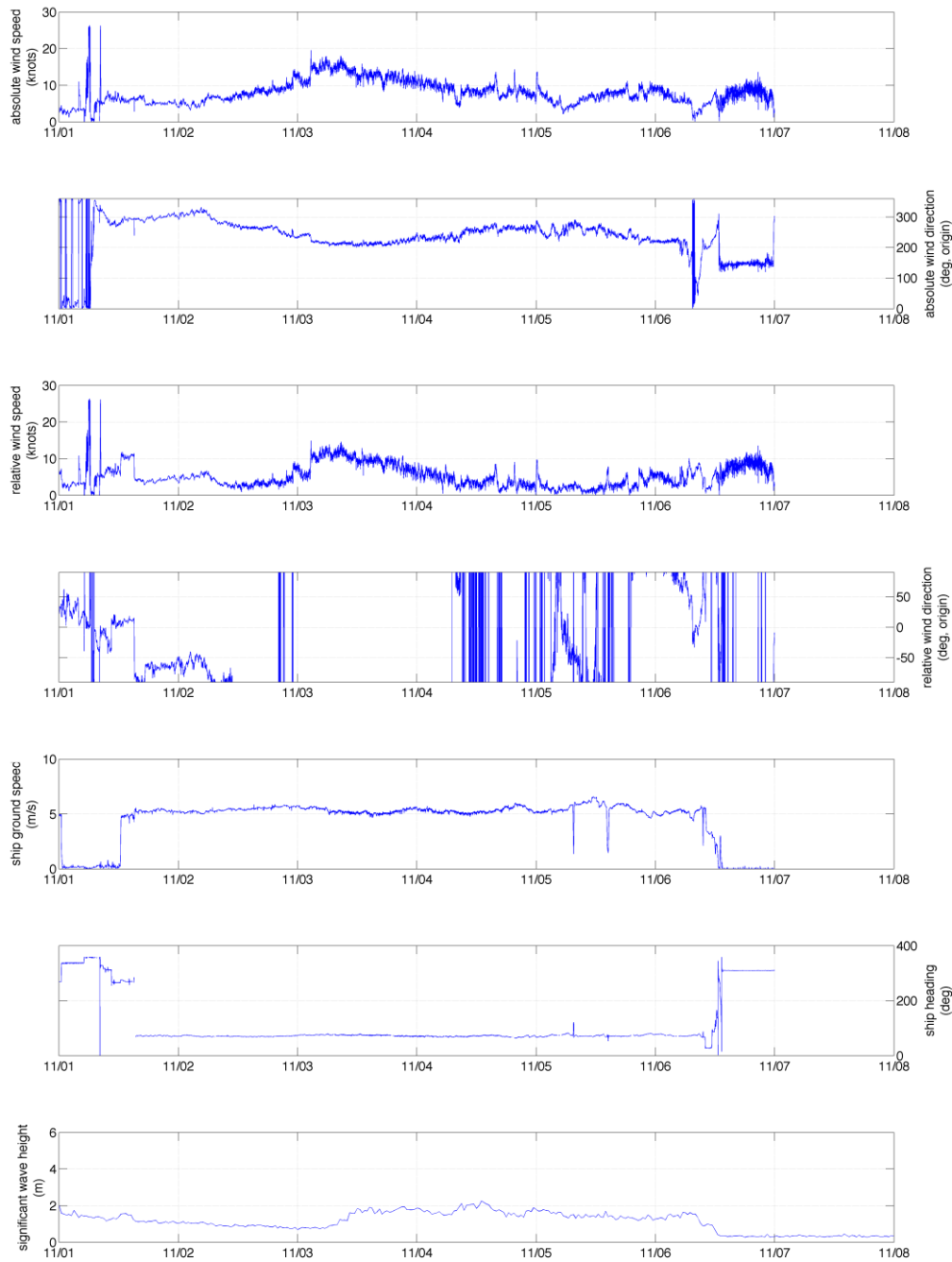


**Figure B3 (Week 1):** Underway wind (absolute and relative to the ship, speed and direction), ship ground speed and direction and significant wave height (from the Mk. IV Shipborne Wave Recorder, calculated as the RMS wave height multiplied by 4). Dates are Midnight start of day.

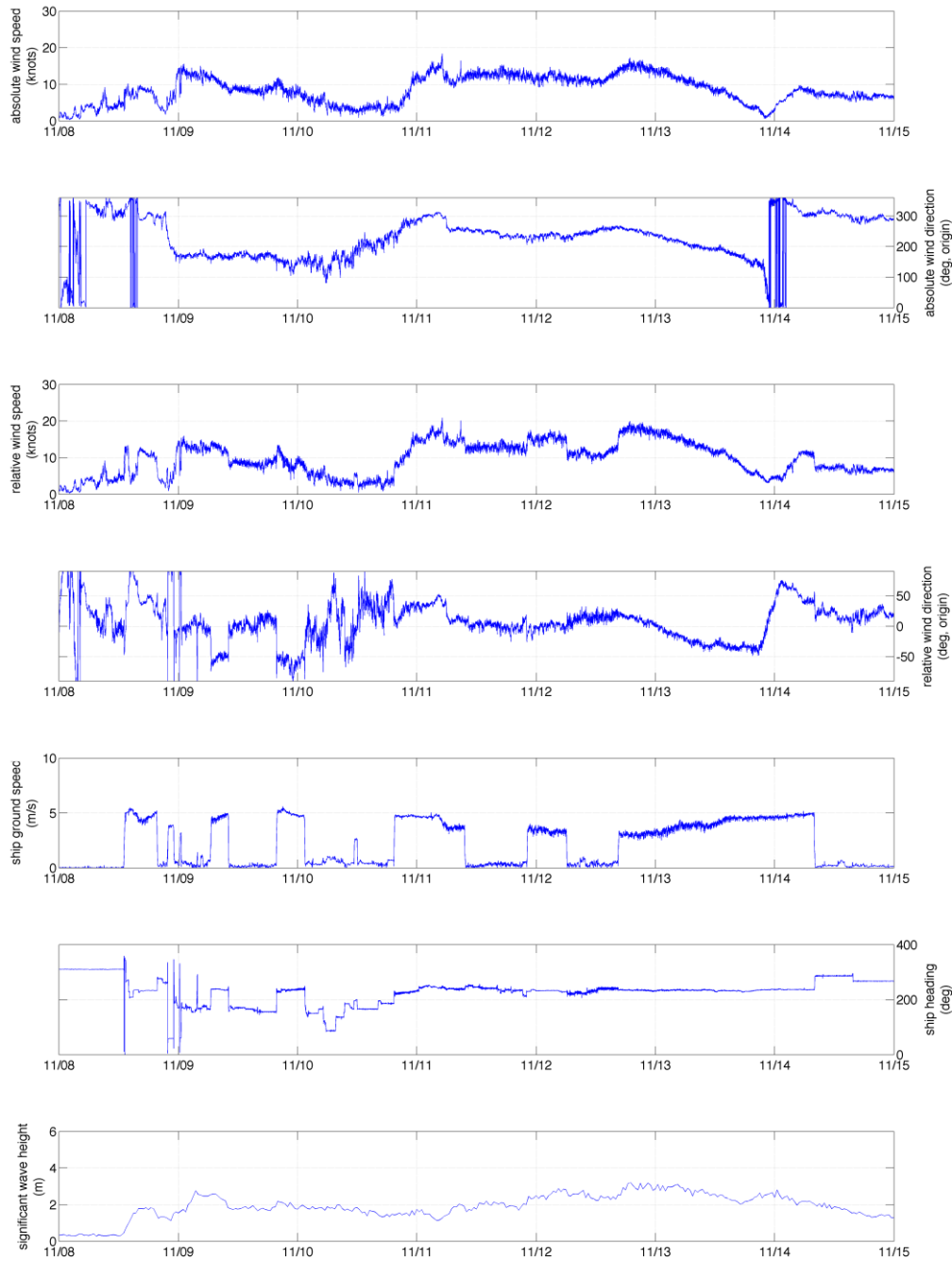




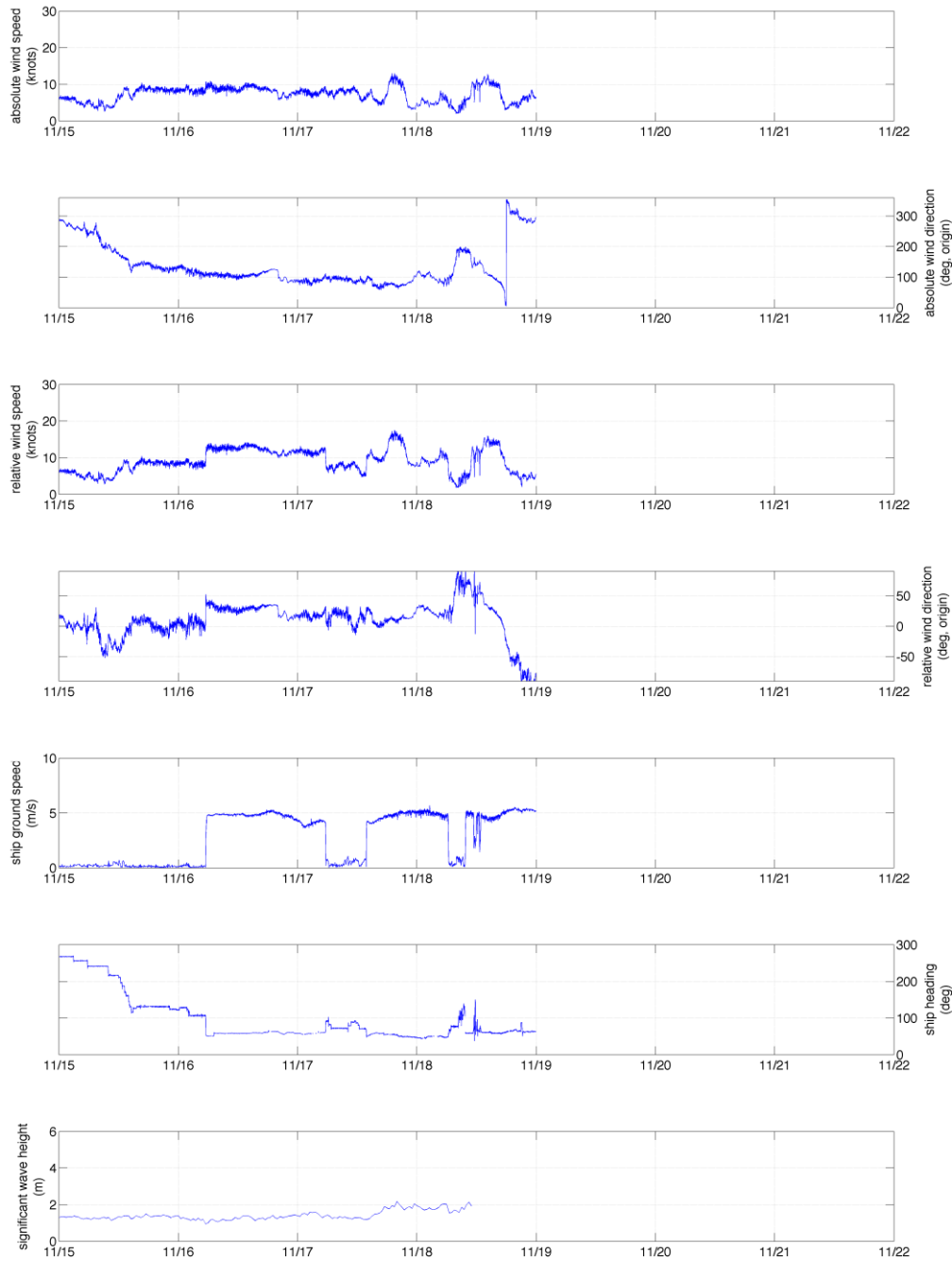
**Figure B3 (Week 2):** Underway wind (absolute and relative to the ship, speed and direction), ship ground speed and direction and significant wave height (from the Mk. IV Shipborne Wave Recorder, calculated as the RMS wave height multiplied by 4). Dates are Midnight start of day.



**Figure B3 (Week 3):** Underway wind (absolute and relative to the ship, speed and direction), ship ground speed and direction and significant wave height (from the Mk. IV Shipborne Wave Recorder, calculated as the RMS wave height multiplied by 4). Dates are Midnight start of day.



**Figure B3 (Week 4):** Underway wind (absolute and relative to the ship, speed and direction), ship ground speed and direction and significant wave height (from the Mk. IV Shipborne Wave Recorder, calculated as the RMS wave height multiplied by 4). Dates are Midnight start of day.



**Figure B3 (Week 5):** Underway wind (absolute and relative to the ship, speed and direction), ship ground speed and direction and significant wave height (from the Mk. IV Shipborne Wave Recorder, calculated as the RMS wave height multiplied by 4). Dates are Midnight start of day.



# Computing and Ship Systems Report

## Cruise: Discovery 357

Principal Scientist: Gideon Henderson

This report template based on original by Chris Barnard

## **RVS LEVEL C System**

Level C - The level C system is a Sun Solaris 10 UNIX Workstation discovery1 also known as ABCGATE. The RVS software suite is available on this machine. This suite of software allows the processing, editing and viewing of all data within the RVS data files. This system also has monitors that allow us to ensure that the level C is receiving data from the level B.

## **Ifremer Techsas System**

The Ifremer data logging system is the system that will inevitably replace the existing Level A + B system while for the most part the Level C will remain as the main system for outputting, viewing and editing the acquired data.

The Techsas software is installed on an industrial based system with a high level of redundancy. The operating system is Red Hat Enterprise Linux Edition Release 3. The system itself logs data on to a RAID 0 disk mirror and is also backed up from the Level C using a 200GB / 400GB LTO 2 Tape Drive. The Techsas interface displays the status of all incoming data streams and provides alerts if the incoming data is lost. The ability exists to broadcast live data across the network via NMEA.

The storage method used for data storage is NetCDF (binary) and also pseudo-NMEA (ASCII). At present there are some issues on some data streams with file consistency between the local and network data sets for the ASCII files. NetCDF is used as the preferred data type as it does not suffer from this issue.

The Techsas data logging system was used to log the following instruments:

- 1) Trimble GPS 4000 DS Surveyor (converted to RVS format as gps\_4000)
- 2) Chernikeef EM speed log (converted to RVS format as log\_chf)
- 3) Ships Gyrocompass (converted to RVS format as gyro)
- 4) Simrad EA500 Precision Echo Sounder (ea500)
- 5) NMFD Surface-water and Meteorology (surfmet) instrument suite
- 6) ASHTECH ADU-2 Altitude Detection Unit (gps\_ash)
- 7) NMFD Winch Cable Logging And Monitoring CLAM (winch)
- 8) Fugro Seastar 9200 G2 XP Differential (gps\_g2)
- 9) Seabird SBE45 MicroTSG (seabird)

## **Fugro Seastar DGPS Receiver**

The Fugro Seastar G2 is a Glonass and GPS receiver that is used to provide 10CM accuracy and also receives differential from the Fugro differential system. This signal

is then buffered out to multiple systems including the Trimble 4000 DS. The Seastar was purchased as an upgrade to the old Seastar and G12 combination. The system is designed to cope with the future expected solar activity that is expected to disable part of the existing GPS network. The system is also capable of receiving corrections via Internet if necessary.

NetCDF files for this system s9200G2s-FUGRO.gps  
RVS Stream gps\_g2  
Forms part of the bestnav stream

### **Trimble 4000 DS Surveyor**

The Trimble 4000DS is a single antenna survey-quality advanced GPS receiver with a main-masthead antenna. It uses differential corrections from the Fugro Seastar unit to produce high quality differential GPS (DGPS) fixes. It is the prime source of scientific navigation data aboard RRS Discovery and is used as the data source for Navigation on the ships display system (SSDS). This antenna is directly on top of the mast and suffers from negligible interference from other items on the mast. It is also almost directly at the centre point of the ship making it an ideal navigation system.

The Techsas NetCDF File ends with the following extensions :  
Position-4000.gps  
Satelliteinfo-4000.hps  
RVS Stream gps\_4000  
Forms part of the bestnav stream

### **Ashtec ADU-2**

This is a four antenna GPS system that can produce attitude data from the relative positions of each antenna and is used to correct the VMADCP for ship motion. Two antennae are on the Bridge Top and two on the boat deck.

The Ashtec system worked reliably throughout the cruise with some gaps that are quite usual with this system due to the amount of calculations necessary. No Large data gaps are present. The ADU-2 forms part of the bestnav system which is an assembly of multiple GPS signals including the gyronmea and emlog stream in order to calculate the best possible position, speed heading pitch and roll of the ship. The Ashtec is not as reliable as the Fugro Seastar G2 and the 4000DS mainly due to its low position on the ship it is hard for this system to maintain locks on satellites when the ship is maneuvering and the bridge and main mast come into its direct line of sight with the satellites.

The Techsas NetCDF File ends with the following extensions :  
ADUPOS-PAPOS.gps  
gppat-GPPAT.att

RVS Stream gps\_ash  
Forms part of the bestnav stream

### **Gyronmea**

The Gyronmea is a file that receives its data from the Ships gyro compass located on the bridge. There are two such Gyros on the bridge and we are able to use either one of them as a source of heading. The selected Gyro is logged by the TECHSAS system and is used as part of the bestnav calculation.

The NetCDF File for Techsas ends with gyro-GYRO.gyr  
RVS data stream gyro

### **RDI Ocean Surveyor 75KHz Vessel Mounted ADCP (VMADCP)**

The RDI Ocean Surveyor was setup by the science party at the start of the cruise with a bottom track and water track file that is included with the dataset. The configuration was changed when we left the shelf and went to deeper water. The Ocean surveyors are fed with data from the ships GPS, Gyro and ADU systems in order so that the system can calculate true speeds and direction of the currents below the ship.

60 Bins  
16 Meter Bin Size  
16 meter Blank  
5.3 Meter Transducer Depth  
Hi Resolution (short Range)  
Ping as fast as possible.

### **RDI 150KHz Vessel Mounted ADCP (VMADCP)**

The RDI Ocean Surveyor was setup by the science party at the start of the cruise with a bottom track and water track file that is included with the dataset. The configuration was changed when we left the shelf and went to deeper water. The Ocean surveyors are fed with data from the ships GPS, Gyro and ADU systems in order so that the system can calculate true speeds and direction of the currents below the ship.

100 Bins  
4 Meter Bin Size  
4 meter Blank  
5.3 Meter Transducer Depth  
Hi Resolution (short Range)  
Ping as fast as possible.

### **Chernikeef EM log**

The Chernikeef EM log is a 2-axis electromagnetic water speed log. It measures both longitudinal (forward-aft) and transverse (port – starboard) ships water sped.

The EM log was not calibrated prior to the cruise and was reading at 0.0 knots when alongside.

The system was logged by the TECHSAS logging system.

**DYLog-LOGCHF-DYLog**  
**RVS Stream chernikeef**



### **Simrad EA500 Precision Echo Sounder (PES)**

The PES system was used throughout the cruise, with a variation between use of the Fish and use of the hull transducer. The fish is more accurate than the hull transducer as it is capable of being deployed deeper and is also decoupled from the noise of the ship.

The PES outputs its data to a stream called ea500 on the Level C System.

### **Surfmet System**

This is the NMFD surface water and meteorology instrument suite. The surface water component consists of a flow through system with a pumped pickup at approx 5m depth. TSG flow is approx 25 litres per minute whilst fluorometer and transmissometer flow is approx 3 l/min. Flow to instruments is degassed using a debubbler with 40 l/min inflow and 10/l min waste flow.

The meteorology component consists of a suite of sensors mounted on the foremast at a height of approx 10m above the waterline. Parameters measured are wind speed and direction, air temperature, humidity and atmospheric pressure. There is also a pair of optical sensors mounted on gimbals on each side of the ship. These measure total irradiance (TIR) and photo-synthetically active radiation (PAR).

The Non Toxic system was enabled as soon as we were far enough away from land.

The port TIR sensor was changed prior to sailing as it was giving incorrect readings compared to the starboard and spare sensors.

The SBE45 unit was changed cleaned to sailing. Techsas NetCDF Files for Surfmet

Surf-SURFMET.SURFMETv2  
MET-SURFMET.SURFMETv2  
Light-SURFMET.SURFMETv2  
SBE45-SBE45.TSG

Surfmet rvs stream is the raw data captured from the TECHSAS System

The temp\_h temp\_m and cond data in the surfmet file is a direct copy of the seabird data however it can be delayed in time. For that reason, always use the data from the seabird instead of the surfmet for salinity calibrations.

These files contain

Temp\_h (Housing Temperature from the SBE45 in the wetlab)

Temp\_m (Marine Temperature from the Hull intake)

Cond (Conductivity from the SBE45 in the wet lab)

Trans (Raw Voltage from Transmissometer)

Fluo (Raw Voltage from Fluorometer)

Speed (Wind Speed from Gill Windsonic Anemometer)

Direct (Wind Direction from Gill Windsonic Anemometer)  
Airtemp (Air Temperature from Vaisala HMP45A)  
Humid (Air Temperature from Vaisala HMP45A)

Pressure (Air Pressure from Vaisala PTB100)  
PPAR (Photosynthetic Active Radiation from SKE510 PAR Sensor on PORT Gimbal)  
SPAR (Photosynthetic Active Radiation from SKE510 PAR Sensor on STBD Gimbal)  
PTIR (Total Incidental Radiation from CM6B TIR Sensor on PORT Gimbal)  
STIR (Total Incidental Radiation from CM6B TIR Sensor on STBD Gimbal)

Seabird is the raw log of the SBE45 and SBE38 through the SBE45 Junction Box.  
Temp\_h (Housing Temperature of SBE45 TSG)  
Temp\_m (Remote or Marine Temperature from Inlet pipe)  
Cond (Conductivity in SBE45 TSG)  
Salin (Calculated Salinity from Instrument)  
Sndspeed (Calculated Sound Velocity from Instrument)

SBE45 data file is the Seabird 45 data logged via the spare Techsas logger. The code is has been slightly modified to cope with spurious data from the SBE45 instrument. Where there are gaps in the SEABIRD stream, these are filled in with data from the SBE45 stream, and combined to produce a new file SEABIRDC.

### **3.5kHz Sub bottom profiler**

The sub bottom profiler consists of a transducer array in a fish housing which is dragged through the water on the end of a faired submarine cable, an amplifier rack, and a CodaOctopus Octopus 360+ Geophysical Acquisition System. Data is collected and stored on the Octopus 360+ then transferred over the network to the Drobo-FS.

During the unscheduled return trip to Cape Town, the 3.5kHz fish became detached during the hours of darkness, and was lost in the ocean. A spare fish was fitted in its place, but it was decided not to use it unless it was critical to the cruise.

## Surfmet : The Sensor List

### Met Platform Sensors

#### Wind Speed and Direction

Manufacturer : Gill  
 Model : Windsonic (Option 3)

Ultrasonic Output Rate	1, 2, 4Hz
Wind Speed	Range 0-60 m/s
Wind Direction Range	0-359 no dead band
Operating Temp Range	-35 °C to +70 °C
Moisture Protection	IP65
External Construction	Luran
Digital O/P Options	RS232 / 422 / 485 / SDI-12
NMEA O/P	Yes
Analogue Outputs	2 (optional)
Calibration	Generic



#### Total Incidental Radiation

Manufacturer : Kipp and Zonen  
 Model Number : CM6B

Spectral range (50%points)	305...2800 nm
Sensitivity	9...15 $\mu\text{V}/\text{Wm}^{-2}$
Impedance	70...100 Ohm
Response time	1/e 5 s, 99 % 55 s
Non-linearity	<1.5 % (<1000 $\text{W}/\text{m}^2$ )
Tilt error	<1.5 % at 1000 $\text{W}/\text{m}^2$
Operating temperature	-40...+90 °C
Temperature dependence of sensitivity	$\pm 2$ % (-10...+40 °C)
Maximum irradiance	2000 $\text{W}/\text{m}^2$
Directional error	< $\pm 20$ $\text{W}/\text{m}^2$ at 1000 $\text{W}/\text{m}^2$
Weight	0.85 kg
Cable length	10 m



## Temperature and Humidity

Manufacturer : Vaisala  
Model Number : HMP45A



### Relative humidity measurement

HMP45A

Measurement range	0.8 ... 100 % RH
Accuracy at +20 °C (+68 °F) % RH)	± 2 % RH (0 ... 90 ± 3 % RH (90 ... 100 % RH)
Sensor	Vaisala HUMICAP® 180

### Temperature measurement

HMP45A

Measurement range	-39.2 ... +60 °C (-38.6 ... +140 °F)
Accuracy +20 °C (+68 °F)	± 0.2 °C (± 0.36 °F)
Sensor	Pt 1000 IEC 751

### Operating environment

Temperature	
operation	-40 ... +60 °C (-40 ... +140 °F)
storage	-40 ... +80 °C (-40 ... +176 °F)

### Inputs and outputs

Operating Voltage	7 ... 35 VDC
Power consumption	< 4 mA
Output load	> 10 kohm (to ground)
Output scale	-40 ... +60 °C (-40 ... +140 °F) equals to
0...1V	
Output signal	resistive 4-wire connection

## Photosynthetic Active Radiation

Manufacturer : Skye Instruments  
Model Number : SKE 510



Spectral Range	400-700nm
Sensitivity Current	3.5 $\mu$ A/100Wm <sup>2</sup>
Sensitivity Voltage	1mV/100Wm <sup>2</sup>
Working Range	0 – 5000Wm <sup>2</sup>
Linear Error	<0.2%
Absolute Calibration Error	typ <3% max 5%
Cosine Error	3%
Azimuth Error	<1%
Temperature coefficient	+/-0.1%/°C
Longterm Stability	+/-2%
Response Time	10ns
Internal Resistance	300Ohms
Temperature Range	-35°C ... +70°C
Humidity Range	0 – 100% RH

## Barometric Pressure

### Barometric pressure measurement

Pressure range	800 ... 1100 hPa
Accuracy at +20 °C (+68 °F)	±0.3 hPa
Sensor	Vaisala

### Operating environment

Temperature range	-5 ... +45 °C (+23 ... +113 °F)
Humidity range	<80 % RH

### Inputs and outputs

Operating voltage	9 ... 16 VDC
Power consumption:	
operation mode	2 mA (typical)
shutdown mode	150 $\mu$ A (typical)
Output voltage	0 ... 2.5 VDC



## Sea Surface Instruments

### Fluorometer

Manufacturer : WetLabs  
 Model Number : WetStar

Temperature Range	0-30 C
-------------------	--------



Depth Rating	600m
Response time	0.17s
Input Voltage	7-15vdc
Current Draw	< 40 mA
Output	0-5VDC

## Transmissometer

**Manufacturer :** WetLabs

**Model Number :** CStar

Pathlength	25cm
Wavelength	660nm
Bandwidth	~ 20nm
Rated Depth	600m
Temperature	0-30°C
Power Input	7-15VDC
Current Draw	< 40mA
Data Output	0-5Volts
Time Constant	0.167 sec
Temperature Error	0.02 percent F.S./deg C



## Seabird Micro TSG SBE45

### Measurement Range

*Conductivity:* 0-7 S/m (0-70 mS/cm)

*Temperature* \*: -5 to 35 °C

### Initial Accuracy

*Conductivity:* 0.0003 S/m (0.003 mS/cm)

*Temperature* \*: 0.002 °C

*Salinity:* 0.005 PSU, typical

### Typical Stability (per month)

*Conductivity:* 0.0003 S/m (0.003 mS/cm)

*Temperature* \*: 0.0002 °C

*Salinity:* 0.003 PSU, typical

### Resolution

*Conductivity:* 0.00001 S/m (0.0001 mS/cm)

*Temperature* \*: 0.0001 °C

*Salinity:* 0.0002 PSU, typical

### Calibration Range

*Conductivity:* 0-6 S/m (60 mS/cm); physical calibration 2.6-6 S/m (26-60 mS/cm), plus zero conductivity (air)

*Temperature* \*: +1 to +32 °C

<b>Time Resolution</b>	1 second
<b>Clock Stability</b>	13 seconds/month
<b>Input Power</b>	8-30 VDC
<b>Acquisition Current</b>	34 mA at 8 VDC; 30 mA at 12-30 VDC
<b>Quiescent Current</b>	10 microamps
<b>Acquisition Rate</b>	1 Hz maximum
<b>Operating Pressure</b>	34.5 decibars (50 psi) maximum
<b>Flow Rate</b>	10 to 30 ml/sec (0.16 to 0.48 gal/min)
<b>Materials</b>	PVC housing
<b>Weight</b>	4.6 kg (10.2 lbs)



## Seabird SBE 38 Digital Oceanographic Thermometer

<b>Measurement Range</b>	-5 to +35 °C
<b>Initial Accuracy</b>	± 0.001 °C (1 mK)
<b>Typical Stability</b> certified	0.001 °C (1 mK) in 6 months,
<b>Resolution</b>	0.00025 °C (0.25 mK)
<b>Calibration</b>	-1 to +32 °C
<b>Response Time</b>	500 milliseconds
<b>Self-Heating Error</b>	less than 200 µK

**RMS Noise**  
(at temperature  
equivalent of 8.5 °C)

<b>NAvg</b>	<b>Noise (°C)</b>
1	0.000673
2	0.000408
4	0.000191
8	0.000133
16	0.000081
32	0.000052

*Note:*

**NAvg** = number of A/D cycles per sample.

Interval between samples (seconds)

$$= (0.133 * \mathbf{NAvg}) + 0.339$$

<b>External Power</b>	<i>RS-232 (standard):</i> 8 – 15 VDC at 10 milliamps average
	<i>RS-485 half-duplex (optional):</i> 8 – 15 VDC at 6 milliamps average

**Materials** Titanium pressure case rated  
at 10,500 meters (34,400 feet)

**Weight** In water: 0.5 kg (1.2 lbs)  
In air: 0.9 kg (2.0 lbs)





## Processed Data files

**Relmov** – Relmov is the relative motion file for this cruise. This is generated using the ships gyro and ships Chernikeef Log data to extract a movement in a given direction. This is then used by bestnav when and where necessary to calculate fixes if GPS fixes were not available.

**Bestnav** – Bestnav uses all 3 GPS Systems logged, gps\_4000, gps\_g2, gps\_ash and creates a best suite stream by providing an as complete account of the ships track as possible. This is done by reading all 3 GPS streams with gps\_4000 being primary, gps\_g2 as secondary and gps\_ash as tertiary. The system looks for gaps of a certain length in the primary and when it finds those gaps it requests that the next gps down fill in the gaps. If no GPS data is available it asks RELMOV to fill in until data is available again. Then the system calculates back over itself to ensure that the extrapolated positions are correct using the GPS data available around the gap.

**Bestdrf** – Bestdrf is a product of bestnav. When run bestnav uses the relmov data which contains a predicted vn and ve based upon direction and speed through the water. The Bestdrf file is the accurate drift velocity of what actually occurred based on the GPS changes between each record.

**Pro\_wind** – This program is designed to remove the relative variables from the wind data logged by surfmet. By removing any fixed offsets in the system and removing the affect of ship motion pro\_wind is a true representation of ships wind data.

**Intdep** – Intdep is a Interpolated data set that extrapolates data where none was logged based on a 2min band pass filter. Intdep is then passed to which takes Carters tables into account.

**Prodep** – Prodep is an automated process that access the bestnav position fix data and then uses a pre programmed Carters table of corrections and corrects the echo sounder data for that given time.

## Network Services

Networking worked well throughout the cruise despite a few hiccups with one of the wireless access points on the Forecastle Deck. A wireless access point was installed in the comms rooms to give network access to the port container slots.

## Data Storage

Drobo-FS is an advanced Network Attached Storage device. All scientific cruise data was stored on this device under the D357 folder.

All cruise data except for the /rvs path were stored on this storage area.

All CTD, ADCP and LADCP data was backed up to Drobo-FS on acquisition.

## Data Backups

Backups of the Level C data were done twice daily as a tar file to LTO tape. Alternating between the standard backup below and a full /rvs backup. The following paths were included in the tar file:

/rvs/raw\_data  
/rvs/pro\_data  
/rvs/def7/control  
/rvs/users

The LTO2 system was backed up on a daily basis in a rolling 2 tape system.

#### Data Archiving

The Data archive will be provided on 320GB USB Hard Drives

1 x HDD to BODC, disk to be returned once data extracted.

2 x HDD to PSO

1 x HDD to NOCS held by NMFSS for 6 Months

## Appendix 1 Surfmet Sensor Information

**Surfmet Sensor Information**

Ship	RRS Discovery
Cruise	D357
Technician	Martin Bridger
Date	19/11/10

Manufacturer	Sensor	Serial no	Comments	Calibration Expires
Seabird	SBE45	229	TSG	29/03/11
Seabird	SBE38	475	Remote Temperature	14/03/11
Wetlabs	fluorometer	117		24/05/11
Seatech	transmissometer	CST-112R		24/05/11
Vaisala	Barometer PTB100A	S3610008		15/04/11
Vaisala	Temp/humidity HMP45A	B4950010		05/04/11
SKYE	PAR SKE510	28557	PORT	11/02/11
SKYE	PAR SKE510	28556	STBD	11/02/11
Kipp and Zonen	TIR CMB6		PORT	
Kipp and Zonen	TIR CMB6	962301	STBD	19/02/11
Sensors without cal				
Seabird	P/N 90402 SBE45 JB	63	Junction Box	
Gill	Windsonic Option 3	071123		

**SPARES**

Manufacturer	Sensor	Serial no	Comments	Calibration Expires
Seabird	SBE45	NO SPARE		
Seabird	SBE38	476,490	Remote Temperature	14/03/11, 17/11/10
Wetlabs	fluorometer	WS3S-246		24/05/11
Wetlabs	transmissometer	CST-113R		24/05/11
Vaisala	Barometer PTB100A	S3440012		
Vaisala	Temp/humidity HMP45A	NO SPARE		
SKYE	PAR SKE510			
SKYE	PAR SKE510	NO SPARE		
Kipp and Zonen	TIR CMB6			
Kipp and Zonen	TIR CMB6	NO SPARE		
Sensors without cal				
Seabird	P/N 90402 SBE45 JB	65	Junction Box	
Gill	Windsonic Option 3	071121		

## D357 NMFSS Technical Cruise Report

### CRUISE OVERVIEW

D357 Pr. G. Henderson (GEOTRACES) South Atlantic 18th October – 25th November 2010	Dave Turner (STO)                      (dart) Dougal Mountifield                      (dm1) John Wynar                                      (jbwy) Martin Bridger                                (mart)
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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 40oS. This to include determination of the variations in physical and chemical speciation of these micronutrients.

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).

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.

Explore the relationship between phytoplankton ecosystem structure and functioning, and the supply of macro- and micro-nutrient concentrations and fluxes.

Use numerical models to gain a comprehensive understanding of micronutrient cycling at 40oS 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 40oS 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.

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## EQUIPMENT SUMMARY

### Clean chemistry laboratory container (NMFU 200 206-2)

Container worked well for the duration of the cruise.

The gas distribution board leaked significantly at the beginning of the cruise. It would appear that all the push fit connectors had not been pushed together properly.

During the cruise wash up meeting it was reported that this container was a little rusty on the outside, with traces of rust in the lobby area. This is far from ideal when working with trace metals. It was also suggested that this be looked into prior to the next trace cruise in Feb 2011. It was pointed out that these containers would not be returning to the UK prior to this.!!

#### *Maintenance work required.*

- Gas distribution board needs to be re-built with correct length pipes so that the valves can be correctly clamped to the board.
- Exterior of the container needs rust removal and painting. Lobby are to be looked into.

### RN laboratory container (NMFU 200 224-7)

Container worked well for the duration of the cruise.

The milli Q system from this container is currently in the Clean Chemistry Container

The A/C struggled to keep the container cool. Cooling was checked and appeared to be flowing ok.

#### *Maintenance work required.*

- None
- A/C needs checking to see if it is working to its full capacity.
- Exterior needs rust removal and re-paint.

### General Purpose laboratory container (NMFU 200 223-1)

Container worked well for the duration of the cruise.

The air conditioning cooling water was originally plumbed in the wrong way round. Hoses were connected to the correct labeled barbs on the outside of the container, but these were connected the wrong way round to the cooling unit.

The A/C in this container also struggled to keep the container cool. Cooling was checked and appeared ok.

#### *Maintenance work required.*

- Swap over A/C cooling pipes inside the container.
- A/C needs checking to see if it is running at its full capacity.

### Laboratory fume hood. (Monair Plus 1250)

Worked well for the duration of the cruise

#### *Maintenance work required.*

- None

### Main Laboratory laminar flow hood. (ser No.003)

Worked well for the duration of cruise.

Tube light played up a couple of times, possible replacement required.

*Maintenance work required.*

- Replacement of the lighting tube.

**Hanger liquid nitrogen generator. (Inv no. 2509006330)**

Worked well for the duration of the cruise.

The low oxygen alarm went off on the last day of science. With the hanger door open and good ventilation, it is unlikely that it was due to low oxygen. To silence the alarm the battery was disconnected.

Low oxygen sensor has been returned to the UK.

*Maintenance work required.*

- Low oxygen sensor needs looking at, and possible calibration. Battery is disconnected and unit not operational.
- Compressor condensate drain quarter turn valve, is very stiff and needs servicing or replacing.

**oil less air comp. (Ident oac2)**

Worked well for the duration of the cruise.

*Maintenance work required.*

- Test expired 08/08/2002

**UMFS Air Dryer. (Ident umfs)**

Worked well for the duration of the cruise.

*Maintenance work required.*

- Power lead cable gland in the back of the unit needs replacing with a more substantial (st steel) type.

**UMFS comp/receiver. (Ident umfs)**

Worked well for the duration of the cruise.

*Maintenance work required.*

- Power lead cable gland needs replacing with a more substantial (st steel) type.

**Scotsman Icemaker. (Ident icem-02)**

Worked well for the duration of the cruise.

*Maintenance work required.*

- None

**Liquid scintillation counter.**

Not used for the duration of the cruise

*Maintenance work required.*

- None

**Deck Laboratory pure water system (Millipore system -07).**



Slight problem with this Milli Q system, in that we could not turn off the flow of water from the trigger dispenser. This was gotten around this by getting the scientists to operate the water flow from the Milli Q unit push buttons. For this to work we had to turn off the safeguard of the timer activation. With the timer activation on, we could not get the unit to produce water.

Following a bit of an investigation, some fuses were checked that previously had been related to water flow problems from the Q Pod in the past, these checked out ok.

A replacement Q pod was then put into place, and appears to be working fine. The timer activation was then turned on and set to 20mins, this also appears to be working well.

#### **Maintenance work required.**

- Broken Q Pod returned to the UK for repair.
- Send out new Q pod as a spare replacement.

#### **Containerised Pure Water System (Millipore)**

This unit was removed from the Clean Chemi container and used in the RN Container. Worked well for the duration of the cruise.

#### **Maintenance work required.**

- None

#### **Echo sounder 10kHz.**

Echo Sounder system worked well throughout cruise.

The PES fish suffered a split in the outer casting during one recovery; the wire jumping the sheave caused this. The damage was repaired with self-amalgamating tape. The damaged section will not be submerged, as it is too high up the cable.

#### **Maintenance work required.**

- Refer to lost equipment report D357-02

#### **Echo sounder 3.5Khz.**

Prior to the cruise commencing the 3.5kHz system was set up and tested while in port. The fish was lowered into the water, and attempts were made to fire the system up. Initially it failed to ping, and this was eventually tracked down to a failed power supply in the amplifier rack. The -15V side of the power supply was not working. The power supply was removed and examined, but a clear diagnosis was not possible without circuit diagrams. The power supply was fitted back into the rack, and a standalone 15V power supply was connected into the rear of the rack with +15V being connected to the 0V rail, to give -15V.

The Octopus screen just flickered with random noise when first powering on. An external screen was connected to prove the system was powering up. Hitting the Octopus screen with a fist, brought the screen to life, so there may be something loose inside.

Once the system was powered up, the test was carried out and the system deemed fit for purpose.

During the night of Thursday 4th Nov the cable of the fish parted approximately 1 to 2 meters from the fish. This was during a steam back to port for a medical emergency at approximately 9.5 knots.

This was noted first thing the following morning.

The remains of the cable were recovered. (See lost equipment report D357-01)

The spare 3.5kHz was put into place and not wired up. The cable was noted as being a little tired, and due to the non-essential use of the fish for the remainder of the cruise, it was decided not to deploy.

However, the cable was inspected and repaired where necessary. But at the end of the day the cable still pretty worn, and would have only been used if totally essential to the cruise work.

*Maintenance work required.*

- Refer to lost equipment report D357-01
- The replacement fish needs to be wired up electrically into the junction box.
- In the light of the recent loss, the cable for the replacement fish, needs to be fully assessed, and possibly replaced.

**CTD/rosette sampler systems (Stainless Steel).**

~23 casts completed, deepest cast ~5500m, most casts deeper than 4000m.

Severe damage incurred to CTD wire in very marginal conditions early in the cruise. A cluster of cats paws and one broken strand. Lack of package rotation confirmed by LADCP compass heading.

Outer armour of CTD wire still suspect with single strand displaced as seen earlier this year. This strand eventually stood quite proud and in places became a loose bight. 720m of wire removed to reduce risk of this strand parting and collecting. Wire condition has not since deteriorated (with close inspection during last deep SAPs deployment).

No instrument problems apart from failure of transmissometer cable late in the cruise. Cable replaced with spare.

Three pingers were available for use onboard (B6, B8 and B9) all three have exhibited a similar intermittent double pinging with significantly reduced intensity. Repeated attempts to resolve the problem (lightly twisting the chassis exhibits the problem) failed. One unit only showed this on the last deployment and is still useable (though weaker). All batteries are new. The two worst units will be returned for service. These ageing units (~30yrs?? Old) require replacement with a bought in alternative. The use of lower accuracy and resolution, but longer range (3-400m) altimeters is suggested on CTDs in conjunction with the existing 100m range units.

System stripped down at end of cruise, leaving 9+, altimeter, and carousel fitted for use on RAPID with 10l Niskins already onboard.

*Maintenance work required.*

- Temperature and Conductivity sensors s/n's: 3p-4782, 3p-4116, 4c-2580, and 4c-2841 returned to Seabird for calibration on RMA number 62214R.
- No replacement transmissometer cable required as adequate stock onboard.
- Send two-three replacement pingers. Investigate commercially available pingers and long-range altimeters and cost.

**CTD/rosette sampler systems (Titanium).**

~23 casts completed, deepest cast ~5500m, most casts deeper than 4000m. System deployed on 22mm plasma rope reeved through coring block. The use of the buoyant plasma rope was often not practical in marginal conditions where the CTD could be used. However in good conditions these CTD were faster than the CTD wire (50m/min veer, 60m/min haul) as no bottle stops are required. Even when slowing to 10m/min 20m either side of 4-5 bottle stops and maintaining 10m/min for the last 200m the cast duration was still quicker than a normal CTD in good conditions.

Seabird 17plus Searam problems:

Used with new Seabird 17plus Searam units for power, data acquisition and bottle firing. Searam s/n 0326 has suspect flash memory, with problem now acknowledged by Seabird. Both Searam units have poor surface quality on piston seal 'o' ring

surfaces at battery compartment end. NimH battery packs do not fit inside pressure case (1mm interference) without modification. The clear plastic guard plate requires removal (four screws) to gain 2mm, yielding 1mm clearance. Screws on inside of battery end-cap insulated with insulation tape. One new Seabird NimH battery charger that was supplied with the two Searam units fails to charge either battery with either cable. The other charger worked well. The 25-way D connector on one of the Searam interface boxes has same gender as the supplied cable. No dummy plugs were supplied with the Searam deck cables. The 4 pin dummy plugs for the Searam comms connector fit poorly. Problems were encountered with the battery type panel not showing in SeatermAF. This problem was resolved by copying all exe, dll, and ini files from a machine where it worked to the one that didn't. Numerous re-installations were attempted prior to this to no avail. Unit s/n 0327 was eventually used for the majority of the cruise with no problems. Both units will remain onboard pending discussions with Seabird to yield a backup for D361 (Achterberg). Both NimH batteries fully discharged, then full recharged prior to stowage onboard out of pressure cases in Searam kit box.

Transmissometer failure:

Transmissometer s/n 09-7107-001 failed repeatedly below 100-200m, then recovered during the upcast. First the instrument cable, then the y-cable were replaced but the problem remained. Eventually the unit was replaced with s/n 161-2642-002 which resolved the problem. The failed unit is less than two years old and has only been used on one cruise prior to D357. We suspect the bulkhead connector requires replacement, and the unit will be returned post-cruise for service by CTG.

Instrument guard on fin damaged after two glancing blows against the ship's side. Welds have failed, and close inspection indicates poor weld quality. It is recommended that due to the closer proximity of the CTD to the ship's side on deployment and recovery using the core block, that the fin is not used when using the plasma rope.

System stripped down but remains onboard for D361.

*Maintenance work required.*

- Temperature and Conductivity sensors s/n's: 3p-4381, 3p-4380, 4c-2164, and 4c-2165 returned to Seabird for calibration on RMA number 62214R.
- Seabird to supply prior to D361:
- 2 off 4 pin male dummies for deck cable (and perhaps 2 off 4 pin female to replace ill-fitting comms connector dummies).
- 1 off NimH battery charger to replace failed unit.
- 1 off Aluminium cased Searam on loan either to be used as is, or its internals used within Ti pressure case of unit s/n 0326.
- After D361 both units along with loaner Al case unit to be returned to Seabird for modification of pressure cases to fit batteries correctly and remanufacture of o-ring surfaces. Electronics of unit s/n 0326 to be repaired/replaced.
- Transmissometer s/n 09-7107-001 to be returned to CTG for replacement of bulkhead connector.
- Fin sensor guard returned to NOC for repair. (Investigate a better arrangement for welding the plates to the bar stock).

**LADCP RDI WH monitor 300kHz.**

Al cased units 12919 and 13329 used on S/S frame. Unit s/n 12919 developed a weak beam 3 very early in the cruise, but this did not deteriorate. Due to the general shortage of LADCPs, as this unit is still serviceable (though for how long we are not

sure) it was not returned to RDI, but remains onboard. Both units have firmware 50.36 but we are certain that we witnessed the same battery discharge problem that RDI claim only affects 50.38. Problems experienced later in the cruise with the master unit crashing during deployment. Visual damage found on star cable. Cable to be returned to NOC for repair by PDM.

Ti cased units 13399 and 10607 used on Ti frame. Unit s/n 10607 firmware updated to 50.38 onboard to resolve synchronization problems (using 16.30 with 50.38).

Repeated problems with units waking up on their own and discharging the battery (RDI FSB exists for this problem and they are working on a fix).

Both Aluminum and Titanium cased batteries were fully charged and vented at the end of the cruise. The ti battery remains on the Ti frame for storage, the Al battery is in its storage box.

*Maintenance work required.*

- Repair of damaged LADCP star cable by PDM.
- Upgrade firmware of all units once RDI release update to cure battery depletion issue.

**Salinometer.**

Unit s/n 68958 used in Stable lab at 24 degrees C bath temperature. A large number of salts were run (~1000 samples). No problems were encountered and the machine was very stable.

Unit s/n 60839 was available but not used.

*Maintenance work required.*

- None

**Stand alone pumps (SAP).**

10 SAPS used (entire NMEP pool) for first part of cruise before detour back to Cape Town for Med-evac.

Subsequently 5 units discharged (2 to JC, 3 to JCR) leaving 5 remaining onboard.

After a lot of preparation work by Dave Teare at NOC, all units used performed very well with no major problems.

There are a few missing parts on some units, Dave already has this in hand.

Two toolkits have a few missing parts (inventoried onboard).

The old Farnell battery chargers are starting to fail and two units (sent to the JC) have no chargers (one down at start of cruise, one failed during). Two remaining Farnell chargers require replacement as well (handle fell off one, current meter unreliable on other). There are no spare chargers available.

Two SAPs weights used onboard, initially 160kg one on its own, but eventually this banded to the lighter one after use for box-coring.

*Maintenance work required.*

- Purchase at least 4 30V 5A bench PSU's for SAPS charging and consider purchasing spares too (one per ship, 3 ships??) Yielding 7 bench PSU's required??
- Nylon CSK screws around rim of pancake filter housing severely damaged by ham-fisted scientists. All screws on all pancake filter housing require replacement.

**NMF Megacorer**

Worked well for the duration of the cruise.

The use of the Plasma Core Rope meant that this package became fairly light the deeper it went, with the decent rates having to be adjusted accordingly, with the max wire out speed being 15 to

20m/min, having to slow right down to 5 to 10m/min when zero tension is observed. 4 to 5 hrs to reach the seabed in 5000m of water. Deep water operations are more limited due to ships motion and weather than would normally be the case using the Core Wire.

Adding additional weight to the Corer was considered, but this meant that the Corer would penetrate the sediment further. This was not required as the samples achieved were just right. The addition of planks to the base was also considered to reduce the penetration, but then this would possibly increase resistance through the water and counteract the effect of adding extra weight. Due to good weather opportunities and careful winch driving we were able to operate safely, and achieve good cores.

Due to a medical emergency, and the change to the cruise plan, the ship was no longer going to S. America. This meant the Megacorer had to be taken off the ship in Cape Town and sent by sea freight to Puntarenas, to be able to be there in time for JC055 cruise in January 2011.

*Maintenance work required.*

- None to the MegaCore.
- Look into the manufacture of a custom weight that can be added to the Plasma Rope, as described for the Box Core, to compensate for the buoyancy, and help increase decent speeds.

### **NMF Gravity Corer**

Not used for the duration of the cruise.

*Maintenance work required.*

- None

### **SMBA Box Corer**

This was first deployed using the Plasma Core Rope in approx 4300m. Unfortunately this triggered but failed to let the pin release that allows the spade to be pulled under the bucket, and therefore no sample was taken. This was later determined to be attributed to the buoyancy in the Plasma Rope, applying an upward force to the release mechanism on the Box Core. For 4300m of Rope the buoyancy equates to approx 140kg of upwards force. By applying an upward load to this mechanism whilst on deck it was quiet clear that this was the problem, not allowing the pin to release.

To overcome this buoyancy a method to attach 150kg of weight to the Plasma Rope was devised. Two SAPS weights were strapped together, these were then suspended from a short strop. The Plasma rope was then wrapped in an anti slip (bandage) tape approx 1m in length where the weights were to be attached. A Siemens stopper was used to grip the Plasma Rope where the tape had been applied, and the weights were then suspended from the stopper on the short strop. This procedure was tested on deck and an amendment to the Risk assessment was put in place.

The first and only deployment using this weight addition, was to be for a 5000m Box Core. The strapped together weights were first lifted and lowered over the side of the ship on a secondary short strop, connected to their underside, they were then secured to an eye bolt on the bulwark and left to hang. The Box Core was then deployed in the normal fashion and lowered to 30m below the surface. The Plasma Rope was then brought to the side of the ship where the tape and Siemens stopper, and short strop was applied, along with a split rubber hose, to prevent the weights from chaffing the rope. The weights were then attached to the Siemens stopper and short strop assembly. The Plasma Rope was then hauled in until the SAPS weights were lifted, allowing them to be disconnected from the bulwark. They were then lashed to the Plasma Rope and the rubber protection. The system was then deployed as normal.

(See Pic)



The addition of the weight to counteract the ropes buoyancy allowed the Coring system to work as normal, achieving a good mud sample. However, this method does add some extra time to the deployment and recovery, but after a couple of deployments, and getting a system together, it was a pretty smooth straightforward operation.

A further deployment of the Box Core was carried out in 750m of water, without the use of the additional weights. (approx 20kg of upward force/buoyancy) This worked well. At 1000m (approx 30kg of upward force/ buoyancy) the Box Core failed to trigger. The weight was then attached to the Plasma Rope, as detailed above, but due to ships propulsion problems was not completed and the core cancelled.

This was again attempted later in the cruise, producing a good core.

*Maintenance work required.*

- None to the Box Core
- Should this rope be used with this Box Core again a 150-200kg weight needs to be custom built so that it can be easily attached to the rope, as detailed above. If the weight were to have a slot taken out of one side, so that the Plasma could pass down the side more easily, without any nasty angles or edges to rub against. A similar weight should also be considered for attachment above the trace metal CTD, so that the deployment speeds can be increased, and the weather windows opened.

**-20 degree centigrade freezer.**

Two new units fitted at the start of D350.

Both units have been lashed to the vessel by ratchet strap. The ratchet strap on one unit has intersected with the screen, which has now been damaged. The screen does not visibly display the temperature without pressing on it.

*Maintenance work required.*

- New Screen fitted if possible.

**-80 degree centigrade freezer.**

Worked well for the duration of the cruise.

*Maintenance work required.*

- None

**Refrigerators.**

No Problems.

*Maintenance work required.*

- None.

**150 kHz hull mounted ADCP system.**

150Khz ADCP worked well for the entire cruise.

*Maintenance work required.*

- None

**75 kHz hull mounted ADCP system.**

75Khz ADCP worked well for the entire cruise.

*Maintenance work required.*

- None

**Pumped sea water sampling system [hull bottom intake].**

Worked well for the duration of the cruise.

*Maintenance work required.*

- None.

**Sea surface monitoring system/ Meteorology monitoring package.**

Worked well for the duration of the cruise. It was necessary to ensure the flow of water through the TSG section was maintained. If the flow gets too low, air can become trapped and cause noise in the transmissometer.

The port TIR sensor (sn 047462) was replaced prior to the cruise, as it was shown to be reading too high compared to the starboard TIR sensor and the spares.

*Maintenance work required.*

- None.

**CLAM System**

Worked well for the duration of the cruise.

*Maintenance work required.*

- None.

**Ship scientific computing systems.**

Worked well for the duration of the cruise.

*Maintenance work required.*

- None.

**Ship Communications Cruise IP and associated equipment**

A new version of AMS was installed on the ship prior to the cruise. The system transfers email to and from NOCS/NERC mail servers and synchronises mailboxes using IMAP. AMS3 can connect through either cruise-ip or FleetBroadband 500.

Issues resolved during the cruise:

- Incorrect passwords for the glne-sci-xx accounts

- Non-working glne-sci-xx accounts

Issues that still exist:

- AMS3 not working well with Apple Mail (AMS3 can't handle all the tags)

- Transfers are not automated (unless using CRON)

No Webmail client (squirrelmail?)

The AMS3 Administrator interface status page is incomplete

The IMAPSYNC is gets many failures, and doesn't provide much feedback to say what is going on. It times out a lot and fails to connect for some users in a seemingly random fashion.

The EXIM send mail command also doesn't show much feedback also, and times out a lot.

The glne-sci-xx accounts are administered at NERC Keyworth, thus any problems with the accounts are out of our hands, as are the NOCS accounts.

For future cruises, those users wishing to use their NOC accounts with the system should empty their inbox and all folders before joining the vessel, otherwise all the mail sitting on the server will be downloaded onto the ship server.

The Cruise-IP worked until we left the known coverage area. After this, AMS3 was the only means of electronic communication to and from the ship for scientists and technicians. After many teething problems most users were satisfied with the service.

*Maintenance work required.*

- None at present.

#### **LEBUS Portable HYDROGRAPHIC Winch (PHW)**

Wound on 6000m of Phyllistran 9.4mm 12-strand Technora Non-Conducting Synthetic Rope during mobilisation after removal of grooved shells.

Hard eye spliced on.

Cooling hoses run.

Not used for the duration of the cruise.

*Maintenance work required.*

- When possible investigate whether this winch will scroll this rope under working tension.

#### **5T Lebus GP Deck Winch**

Not used for the duration of the cruise.

*Maintenance work required.*

- None.

#### **1.6T lebus gp Deck Winch (trace metal fish)**

- Worked well for the duration of the cruise.

*Maintenance work required.*

None.



## APPENDIX I NMF-SS SENSORS & MOORINGS CRUISE REPORT

D357 (GEOTRACES) – Gideon Henderson, Oxford  
17 October – 22 November 2010  
NMF – Sea Systems  
CTD, LADCP, Autosal & SAPs Operations

Dougal Mountifield & John Wynar

Sensors & Moorings Group  
National Marine Facilities  
National Oceanography Centre, Southampton

### 1. CTD Operations

A total of 46 CTD casts were completed during the cruise.

Both a stainless steel and a titanium CTD system were used. CTD cast numbers were of the form CTDxxxxs for SS casts and CTDxxxxt for titanium, where xxx was the cast number.

A total of 22 titanium and 24 stainless steel profiles were completed. There were no major operational issues with the CTD suites during the cruise. However the transmissometer on the Titanium frame had a pressure related problem with the output saturating at 5V below 100-200m. The problem persisted after the replacement of the instrument cable, and later the Y-cable to the 9+. Eventually the instrument was replaced and the problem was resolved. The failed transmissometer will be returned to the manufacturer for the replacement of the bulkhead connector post-cruise.

An LADCP profile was obtained from each of the CTD casts. From cast CTD001t to CTD026s there was a single Workhorse 300kHz LADCP on each CTD frame, in a downward looking master configuration. From cast CTD028s onwards, two LADCP's were fitted to each frame in a master-slave configuration, the master looking downwards and the slave upwards. All LADCP's were Workhorse 300kHz units. The LADCP's were not run on CTD002t and 027t because this cast was only to 50m to clean the trace-metal free samplers.

#### 24-way Stainless Steel CTD Frame

The stainless steel frame configuration was as follows:

- Sea-Bird 9/11 plus CTD system with fin-mounted secondary sensors
- Sea-Bird SBE-32 24 way rosette pylon on NMF 24 way frame
- 24 by 20L custom OTE external spring water samplers
- Sea-Bird SBE-43 oxygen Sensor
- Chelsea MKIII Aquatracka fluorometer
- Chelsea MKII Alphatracka 25cm path transmissometer
- Wetlabs BBRTD 660nm backscatter sensor
- PML 2PI PAR sensors (UWIRR and DWIRR)

- NMF LADCP pressure-case battery pack
- RD Instruments Workhorse 300 KHz lowered ADCP (downward-looking master configuration)
- RD Instruments Workhorse 300 KHz lowered ADCP (upward-looking slave configuration)
- Tritech PA200 200kHz altimeter
- Sonardyne Deep HF Marker Beacon

For the 20l bottles, the pressure sensor was located 20cm below the bottom of the water samplers, and 131cm below the top of the water samplers. The 20l niskins are 111cm in height between end-cap seals.

#### 24-way Stainless Steel CTD Frame Instrument Configuration

The Sea-Bird CTD configuration for the stainless steel frame was as follows:

- SBE 9 plus Underwater unit s/n 09P-46253-0869
- Frequency 0—SBE 3P Temperature Sensor s/n 03P-4782 (primary – 9+ mounted)
- Frequency 1—SBE 4C Conductivity Sensor s/n 04C-2580 (primary – 9+ mounted)
- Frequency 2—Digiquartz Temperature Compensated Pressure Sensor s/n 100898
- Frequency 3—SBE 3P Temperature Sensor s/n 03P-4116 (secondary – fin mounted)
- Frequency 4—SBE 4C Conductivity Sensor s/n 04C-2841 (secondary – fin mounted)
- SBE 5T Submersible Pump s/n 05T-2279 (primary)
- SBE 5T Submersible Pump s/n 05T-3002 (secondary – fin mounted)
- SBE 32 Carousel 24 Position Pylon s/n 32-37898-0518
- SBE 11 plus Deck Unit s/n 11P-24680-0587 Main Unit with BestPower UPS s/n ET62010000110004
- SBE 11 plus Deck Unit s/n 11P-19817-0495 Spare Unit

The auxiliary A/D output channels were configured as below:

- V0 --- SBE 43 Oxygen s/n 43-0709 (primary duct - 9+ mounted)
- V1 --- Unused – obsolete oxygen temperature
- V2 --- Chelsea MKIII Aquatracka Fluorometer s/n 088-2050-095
- V3 --- Tritech PA-200 Altimeter s/n 6196.118171
- V4 --- 2PI PAR (DWIRR) s/n PML9
- V5 --- 2PI PAR (UWIRR) s/n PML10
- V6 --- Wetlabs BBRTD backscatter s/n 167
- V7 --- Chelsea MKII Alphatracka 25cm path Transmissometer s/n 161047

The additional self-logging instruments were configured as follows:

- RDI Workhorse 300 KHz Lowered ADCP (down-looking master configuration) s/n 12919
- RDI Workhorse 300 KHz Lowered ADCP (upward-looking slave configuration) s/n 13329

The LADCP's were powered by the NMF battery pack WH007. Battery pack WH001 was also available as a spare, but was not used.

To provide a means of location in the event of total loss, the frame was fitted with a 12,000m rated Sonardyne Deep HF Marker Beacon s/n 245116-001 / ID=19 (A13-1).

#### Stainless Steel CTD Seasave Configuration

Date: 11/18/2010

Instrument configuration file: C:\Program Files\Sea-Bird\SeasaveV7\D357\SBEcon\D357\_st\_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 : 4782  
Calibrated on : 12 February 2010  
G : 4.34994325e-003  
H : 6.36521273e-004  
I : 2.09171407e-005  
J : 1.77111645e-006  
F0 : 1000.000  
Slope : 1.00000000  
Offset : 0.0000

#### 2) Frequency 1, Conductivity

Serial number : 2580  
Calibrated on : 18 June 2010  
G : -1.04717968e+001  
H : 1.53925719e+000  
I : 4.91756755e-004  
J : 4.24840415e-005  
CTcor : 3.2500e-006  
CPcor : -9.57000000e-008  
Slope : 1.00000000  
Offset : 0.00000

3) Frequency 2, Pressure, Digiquartz with TC

Serial number : 100898  
Calibrated on : 31 July 2009  
C1 : -4.405863e+004  
C2 : -6.206030e-002  
C3 : 1.337540e-002  
D1 : 3.669100e-002  
D2 : 0.000000e+000  
T1 : 2.990734e+001  
T2 : -3.493620e-004  
T3 : 4.061200e-006  
T4 : 3.043880e-009  
T5 : 0.000000e+000  
Slope : 0.99994000  
Offset : -1.08250  
AD590M : 1.288520e-002  
AD590B : -8.271930e+000

4) Frequency 3, Temperature, 2

Serial number : 4116  
Calibrated on : 20 May 2010  
G : 4.42666651e-003  
H : 6.85870735e-004  
I : 2.54542765e-005  
J : 2.24277925e-006  
F0 : 1000.000  
Slope : 1.00000000  
Offset : 0.0000

5) Frequency 4, Conductivity, 2

Serial number : 2841  
Calibrated on : 30 June 2010  
G : -1.03615643e+001  
H : 1.42702878e+000  
I : 8.51837737e-004  
J : 2.66486564e-006  
CTcor : 3.2500e-006  
CPcor : -9.57000000e-008  
Slope : 1.00000000  
Offset : 0.00000

6) A/D voltage 0, Oxygen, SBE 43

Serial number : 0709  
Calibrated on : 28 May 2008  
Equation : Sea-Bird  
Soc : 4.29400e-001

Offset : -4.95700e-001  
A : -1.33110e-003  
B : 1.51160e-004  
C : -3.22560e-006  
E : 3.60000e-002  
Tau20 : 1.58000e+000  
D1 : 1.92630e-004  
D2 : -4.64800e-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 : 6196.118171  
Calibrated on :  
Scale factor : 15.000  
Offset : 0.000

9) A/D voltage 3, Fluorometer, Chelsea Aqua 3

Serial number : 88-2050-095  
Calibrated on : 19 January 2009  
VB : 0.205600  
V1 : 2.178000  
Vacetone : 0.480100  
Scale factor : 1.000000  
Slope : 1.000000  
Offset : 0.000000

10) A/D voltage 4, PAR/Irradiance, Biospherical/Licor

Serial number : 09  
Calibrated on : 21 June 2008  
M : 0.49602600  
B : 1.03304500  
Calibration constant : 100000000000.00000000  
Multiplier : 0.99990000  
Offset : 0.00000000

11) A/D voltage 5, PAR/Irradiance, Biospherical/Licor, 2

Serial number : 10  
Calibrated on : 14 April 2008  
M : 0.49292500  
B : 1.01139400  
Calibration constant : 100000000000.00000000  
Multiplier : 0.99990000

Offset : 0.00000000

12) A/D voltage 6, Turbidity Meter, WET Labs, ECO-BB

Serial number : 167  
Calibrated on : 13 May 2008  
ScaleFactor : 0.003380  
DarkVoltage : 0.119000

13) A/D voltage 7, Transmissometer, Chelsea/Seatech/WET Lab CStar

Serial number : 161047  
Calibrated on : 18 March 2008  
M : 23.5882  
B : -0.4954  
Path length : 0.250

Scan length : 37  
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24-way Titanium CTD Frame

The titanium frame configuration was as follows:

- Sea-Bird 9/11 plus Titanium CTD system with fin-mounted secondary sensors
- Sea-Bird SBE-32 Titanium 24 way rosette pylon on NMF 24 way Titanium frame
- Sea-Bird 17 plus SeaRAM Titanium battery powered datalogger and interface
- 24 by 10L custom OTE trace-metal free external spring water samplers
- Sea-Bird SBE-43 oxygen Sensor
- Chelsea MKIII Aquatracka fluorometer
- Chelsea MKII Alphatracka 25cm path transmissometer
- Wetlabs BBRTD 660nm backscatter sensor
- PML Titanium 2PI PAR sensors (UWIRR and DWIRR)
- NMF Titanium LADCP pressure-case battery pack
- RD Instruments Titanium Workhorse 300 KHz lowered ADCP (downward-looking master configuration)
- RD Instruments Titanium Workhorse 300 KHz lowered ADCP (upward-looking slave configuration)
- Benthos PSA-916T Altimeter
- Sonardyne Deep HF Marker Beacon

For the 10l Trace-Metal Free bottles, the pressure sensor was located 34cm below the bottom of the water samplers, and 121cm below the top of the water samplers. The 10l niskins are 87cm in height between end-cap seals.

24-way Titanium CTD Frame Instrument Configuration

The Sea-Bird CTD configuration for the titanium frame was as follows:

- SBE 9 plus Underwater unit s/n 09P-34173-0758(T)

- Frequency 0—SBE 3P Temperature Sensor s/n 03P-4381(T) (primary)
- Frequency 1—SBE 4C Conductivity Sensor s/n 04C-2164(T) (primary)
- Frequency 2—Digiquartz Temperature Compensated Pressure Sensor s/n 90074
- Frequency 3—SBE 3P Temperature Sensor s/n 03P-4380 (T) (secondary – fin mounted)
- Frequency 4—SBE 4C Conductivity Sensor s/n 04C-2165(T) (secondary – fin mounted)
- SBE 5T Submersible Pump s/n 05T-3085 (primary)
- SBE 5T Submersible Pump s/n 05T-3086 (secondary – fin mounted)
- SBE 32 Carousel 24 Position Pylon s/n 32-34173-0493(T)
- SBE 17 plus SeaRAM s/n's 17p-59976-0326(T) and 17p-59976-0327(T)
- SBE 11 plus Deck Unit s/n 11P-24680-0587 Main Unit with BestPower UPS s/n ET62010000110004
- SBE 11 plus Deck Unit s/n 11P-19817-0495 Spare Unit

The auxiliary A/D output channels were configured as below:

- V0 --- SBE 43 Oxygen s/n 43-0619 (primary duct - 9+ mounted)
- V1 --- Unused – obsolete oxygen temperature
- V2 --- Chelsea MKIII Aquatracka Fluorometer s/n 088244
- V3 --- Benthos PSA-916T Altimeter s/n 874
- V4 --- 2PI PAR Titanium (DWIRR) s/n 02
- V5 --- 2PI PAR Titanium (UWIRR) s/n 03
- V6 --- Chelsea MKII Alphatracka 25cm path Transmissometer s/n 09-7107-001
- V7 --- Wetlabs BBRTD backscatter s/n 168

The additional self-logging instruments were configured as follows:

- RDI Workhorse 300 KHz Lowered ADCP (down-looking master configuration) s/n 13399(T)
- RDI Workhorse 300 KHz Lowered ADCP (upward-looking slave configuration) s/n 10607(T)

The LADCP's were powered by the NMF titanium battery pack WH008T.

To provide a means of location in the event of total loss, the frame was fitted with a 12,000m rated Sonardyne Deep HF Marker Beacon s/n 234002-002 / ID=18 (A12-1).

#### Titanium CTD Seasave Configuration

Date: 11/18/2010

Instrument configuration file: \\drobo-fs\Science\D357\CTD data\Ti\_SeaRAM data\D357\_ti\_SEARAM\_8Hz.con

Configuration report for SBE 911plus/917plus CTD

-----  
Frequency channels suppressed : 0

Voltage words suppressed : 0  
Computer interface : RS-232C  
Scans to average : 3  
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 : 4381  
Calibrated on : 25 March 2010  
G : 4.42342032e-003  
H : 6.44571572e-004  
I : 2.24453967e-005  
J : 1.92899395e-006  
F0 : 1000.000  
Slope : 1.00000000  
Offset : 0.0000

2) Frequency 1, Conductivity

Serial number : 2164  
Calibrated on : 18 June 2010  
G : -1.02203864e+001  
H : 1.40879771e+000  
I : -2.48732230e-003  
J : 2.38515145e-004  
CTcor : 3.2500e-006  
CPcor : -9.57000000e-008  
Slope : 1.00000000  
Offset : 0.00000

3) Frequency 2, Pressure, Digiquartz with TC

Serial number : 90074  
Calibrated on : 17 November 2008  
C1 : -6.571123e+004  
C2 : 2.050504e-001  
C3 : 1.612220e-002  
D1 : 2.883800e-002  
D2 : 0.000000e+000  
T1 : 2.986693e+001  
T2 : -2.678465e-004  
T3 : 3.986390e-006  
T4 : 7.472100e-010  
T5 : 0.000000e+000  
Slope : 0.99995000  
Offset : -0.04600



AD590M : 1.283700e-002  
AD590B : -8.642460e+000

4) Frequency 3, Temperature, 2

Serial number : 4380  
Calibrated on : 20 May 2010  
G : 4.37235062e-003  
H : 6.55530501e-004  
I : 2.41332113e-005  
J : 1.95364223e-006  
F0 : 1000.000  
Slope : 1.00000000  
Offset : 0.0000

5) Frequency 4, Conductivity, 2

Serial number : 2165  
Calibrated on : 18 June 2010  
G : -9.76358270e+000  
H : 1.34235737e+000  
I : -2.14009249e-003  
J : 2.06407043e-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 : 0619  
Calibrated on : 27 October 2009  
Equation : Sea-Bird  
Soc : 5.07300e-001  
Offset : -4.90700e-001  
A : -2.78180e-003  
B : 1.64750e-004  
C : -3.37680e-006  
E : 3.60000e-002  
Tau20 : 2.24000e+000  
D1 : 1.92630e-004  
D2 : -4.64800e-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 : 874  
Calibrated on :  
Scale factor : 15.000  
Offset : 0.000

9) A/D voltage 3, Fluorometer, Chelsea Aqua 3

Serial number : 088244  
Calibrated on : 11 February 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, PAR/Irradiance, Biospherical/Licor

Serial number : 02  
Calibrated on : 29 January 2010  
M : 0.48485000  
B : 1.04840900  
Calibration constant : 100000000000.00000000  
Multiplier : 0.99990000  
Offset : 0.00000000

11) A/D voltage 5, PAR/Irradiance, Biospherical/Licor, 2

Serial number : 03  
Calibrated on : 14 March 2008  
M : 0.49395100  
B : 1.07795600  
Calibration constant : 100000000000.00000000  
Multiplier : 0.99990000  
Offset : 0.00000000

12) A/D voltage 6, Transmissometer, Chelsea/Seatech/WET Lab CStar

Serial number : 09-7107-001  
Calibrated on : 9 June 2009  
M : 23.8478  
B : -0.2862  
Path length : 0.250

13) A/D voltage 7, User Polynomial

Serial number : 168  
Calibrated on : 19 October 2009  
Sensor name : Wetlabs BBRTD  
A0 : -0.00025772

A1 : 0.00303560  
A2 : 0.00000000  
A3 : 0.00000000

Scan length : 30  
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## 24-way CTD Frame Deployment Notes

### Sensor changes

Problems with the transmissometer on the Ti frame prompted the original unit to be changed to s/n: 161/2642/002 from cast CTD034t onwards. Hence a change in the configuration file (with suffix `_new_trans`) as follows:

### 12) A/D voltage 6, Transmissometer, Chelsea/Seatech/WET Lab CStar

Serial number : 161-2642-002  
Calibrated on : 4 September 1996  
M : 23.1791  
B : -0.6722  
Path length : 0.250

PAR sensors were only employed on casts with a maximum depth of 500m on the s.s. frame i.e. casts 005s, 008s, 010s, 011s, 024s, 032s, 035s, 039s, 043s, 044s. PARs were not fitted on cast CTD021s as it was dark. Titanium cased PARs were available for the Titanium frame and calibrations for them were entered in the con file, however they were not deployed during the cruise.

The fin on the titanium frame was removed prior to cast 041t following damage sustained to the sensor guard by contact with the ship's side. Hence from cast 041t onwards the secondary temperature and conductivity sensors were mounted to the 9+ within the CTD frame. It is recommended that future deployments of CTD frames using the core block should have the fin removed to prevent damage. The fin on the stainless steel frame was used throughout the cruise with the secondary sensors mounted on it.

### Deployment Comments

The Stainless Steel CTD system was deployed using the 11.43mm double armoured conducting galvanised steel CTD wire. This CTD suite was run in real time at 24Hz using an 11 plus deck unit.

The Titanium CTD system was deployed using the 22mm plasma synthetic deep-coring warp reeved through the coring block.

Due to the characteristics of the buoyant plasma rope, often the CTD was not brought to the surface after the approx 2 min soak. Instead the downcast was often started immediately from the 10m depth. Also the veer speeds were often slower than using the CTD wire. In good conditions it was possible to veer at 50m/min and haul at

60m/min. Due to the absence of bottle stops, in good conditions the titanium casts on the plasma rope were quicker than the stainless steel casts on the CTD wire. However the titanium system could not be deployed in some conditions that were ok for the stainless steel suite.

#### Seabird 17plus Searams

This suite was fitted with a newly acquired Seabird 17 plus SeaRAM unit to power the system, log the data and fire the bottles. Bottle stops were programmed into the SeaRAM using SeaterMAF software prior to each cast, and data downloaded afterwards. To reduce the redeployment time for the Titanium CTD system, two SeaRAMs (s/n: 0326 & 0327) were used in rotation, one being deployed whilst the second was being charged and downloaded. Both units were initially problematical and gave mixed results. SeaRAM s/n:0327 eventually proved to be the more reliable and was solely used from cast CTD017t onwards. Due to the difference in measurement of wire out and CTD pressure (used by the SeaRAM for bottle stops), the winch hauled continually without stopping for bottle closures, data “smearing” not being considered a significant problem at depths greater than 1000m. At depths less than 1000m the winch slowed to approximately 10m/min 20m either side of the bottle stop depth.

The pressure change to start upcast setting must be larger (20m used) than the ascent from soak depth or bottles will be fired prematurely (cast CTD001t suffered this problem). It is recommended to use the bottom bottle logic and set the enable pressure to at least the pressure of the second-deepest bottle. The bottom bottle window was set to 10m and the time in window to 2 minutes.

The number of averaged scans (i.e. the sample frequency) of the Searams was initially varied before final use of 3 scans averaged (8Hz) logging. Cast CTD001t and CTD007t were at 24Hz, CTD002t and 004t were at 1Hz, from cast CTD013t onwards 8Hz was used.

Both conductivity channels were advanced by two scans in the Searam and none of the auxiliary channels were suppressed.

There were numerous issues with the Searams:

The finish on the piston seal o-ring surface of the battery compartment end cap was very poor on both units. There is machining scoring and it seems as though the finishing cut was missed. This makes the battery compartment end cap hard to fit and will eventually damage the o-ring.

There were no dummy plugs available for the deck cables.

The 25-way D connector on one deck interface box was the same gender as the supplied cable.

The dummy connector for the 4 pin comms cable fits poorly on both units

Seabird have acknowledged that there is a flash memory problem with unit s/n 0326. This was shown using the testee command followed by the flashmap command. The data on cast CTD012t only had one sample and was hence not included in the data archive. This may be caused by the memory fault with unit 0326.

One of the NimH battery chargers failed to charge either battery.

The NimH batteries were too long to fit the end-cap on the pressure case (1mm interference). Seabird have since acknowledged that they have changed the thickness of the battery PCB that is mounted midway through the pressure case without changing its location. The pressure cases will be re-machined by Seabird when existing cruise obligations for them have been completed. The workaround is to remove the 4 screws that secure the clear plastic protective guard on the pack and remove the guard. Insulation tape was fitted over the endcap screws, and 1mm clearance was obtained. Care must be taken when plugging and unplugging the charger cable with the guard absent.

There is no record in the instrument header displayed by the ds command of the unit's serial number. Seabird have acknowledged this and will include this in future firmware.

The used memory is displayed in scans, but free memory in bytes, this can be confusing. It has been suggested to Seabird that used memory be displayed in scans and bytes in future firmware versions.

The 1.1ft cable to interface the 17plus to the 9plus is too short for our application. Hence 2m long cables from the 32 plus were used. There was some concern about interference coupled to this cable from the 3p and 4c sensors nearby, hence the orientation of the Searam was changed and the cable re-routed. More suitable cables have been requested from Seabird.

#### Further Documentation

A sensor information sheet 'D357 Sensor Information.doc' and calibration & instrument history sheets were included in the main cruise archive in electronic format (Adobe Acrobat & Microsoft Word). Original copies of all log sheets were supplied to the PSO in addition to the scanned electronic copies that NMF will retain and also supply to BODC.

#### Salinometry

Two Guildline Autosal 8400B salinometers were available for use having serial numbers 68958 and 60839. Unit s/n 68958 was used for all samples with unit s/n 60839 being reserved as a spare.

The main salinometer was located in the stable lab and operated at 24°C bath temperature in 22-23.5°C ambient lab temperature.

The CTD and underway samples were taken by the science party and run using the OSIL PC by scientists.

RDI Workhorse LADCP Configuration

The same command file was used for both pairs of CTD frame-mounted LADCPs:

Downward-looking Master WH300kHz WH300kHz WHMD357.TXT	Upward-looking Slave WHSD357.TXT
PS0	PS0
CR1	CR1
CF11101	CF11101
EA00000	EA00000
EB00000	EB00000
ED00000	ED00000
ES35	ES35
EX11111	EX11111
EZ0011101	EZ0011101
WM15	WM15
LW1	LW1
LD111100000	LD111100000
LF0500	LF0500
LN016	LN016
LP00001	LP00001
LS1000	LS1000
LV250	LV250
SM1	SM2
SA001	SA001
SW5000	ST0
TE00:00:01.00	TE00:00:01.00
TP00:00.00	TP00:00.00
CK	CK
CS	CS

Note: Only the downward-looking (master) LADCP was used until CTD028s but the same Master command script was sent.

For cast CTD026s the following command script was used to obtain high resolution along-beam velocities for turbulence measurements:

Downward-looking WH300kHz  
WHMD357\_Palmer.txt

PS0  
CR1  
CF11101  
EA00000  
EB00000  
ED00000  
ES35

EX00000  
EZ0011101  
WM15  
LW1  
LD111100000  
LF0191  
LN64  
LP00001  
LS50  
LV250  
SM0  
TE00:00:01.00  
TP00:00.00  
CK  
CS

From cast CTD037s onwards the following commands were added to the scripts after CR1 in the light of RDI notice ICN-118 (March 2009) and were designated WHMD357\_new.txt and WHSD357\_new.txt respectively:

CL0  
SB0

#### Deployment Comments

The LADCP's were operated by NMF technicians.

Prior to each deployment the BBtalk terminal session was logged to a file named with the format CTDxxxsm.txt for the down-looking master, CTDxxxss.txt for the up-looking slave (both for the stainless steel frame) and CTDxxxsm/s.txt for the down-looking titanium CTD, where xxx was the CTD cast number.

Then the following commands were sent:

CB411 – to change baud rate to 9600 for sending the command file  
PS0 – to provide an additional check of serial number (also in the command file)  
TS? – time set, offset from GPS clock noted and time reset if greater than a few seconds.  
RS? – to check flashcard space and re ErAse if necessary  
PA and PT200 – pre-deployment and built in self tests  
PC2 – to check for the NaN compass bug (ref :RDI FSB-181 Feb 2009)

About 10 minutes before the CTD was deployed the command files were sent and BBtalk file logging stopped. Deployment and end of pinging times were recorded on the rough log sheets.

After pinging was stopped, the number of deployments in the recorder was queried with RA? And the most recent file downloaded in the default RDI-xxx.000 name format. The file was then renamed to the form CTDxxxs/tm/s.000. All filenames were noted on the rough log sheets.

The battery was fully charged at 58V until it was drawing 100mA between each cast. Every 5-10 casts the battery was vented.

#### Stand Alone Pumps (SAPs)

10 SAPs were available for use during the cruise. Planned use was for 8 units at a time with a further 2 available as spares. There were 3 off MkII and 7 off MkIII units with serial numbers:

02-002, 02-003, 02-004, 03-01, 03-02, 03-03, 03-04, 03-05, 03-06 and 03-07. After the mid-cruise port call however, five of the SAPs were offloaded leaving units: 02-002, 02-003, 02-004, 03-02 and 03-07. The SAPs were deployed on the galvanised steel CTD wire.

#### Deployment Comments

There was some difficulty in hearing the sounders when starting the SAPs with the end caps screwed on, even using the stethoscopes. To get round this problem the end caps were screwed on first and a slightly longer delay employed to account for preparation work prior to attachment to the CTD wire. For stations with the deepest SAP only a few tens of metres above the sea floor, a pinger was attached and height above the sea-bed monitored on the echo-sounder. Poor bottom reflectivity and deep water often made this quite difficult. After deployment the SAP batteries were immediately re-charged at 20V and 4A until the current drawn fell below 0.5A, the units then being trickle-charged at approximately 19V.