

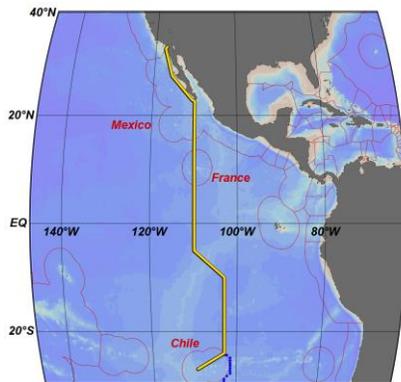


# Cruise Report of the 2016/2017 P18 US GO-SHIP Reoccupation

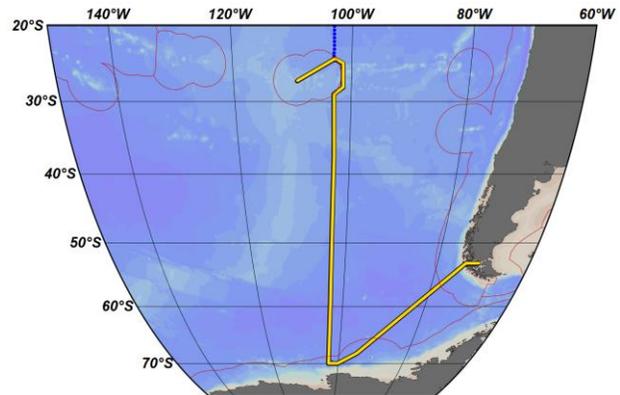
*Updated 03/16/2017*

## *Project Summary*

<i>Section Name</i>	<i>P18</i>
Expocode	33RO20161119
Chief Scientist Leg 1	Brendan Carter
Co-Chief Scientist Leg 1	Annie Bourbonnais
Chief Scientist Leg 2	Rolf Sonnerup
Co-Chief Scientist Leg 2	Sarah Purkey
Leg 1 Dates	11/19/2016 to 12/24/2016
Leg 2 Dates	12/30/2016 to 02/03/2017
Ports of call	Leg 1: San Diego, CA, USA to Hanga Roa, Chile Leg 2: Hanga Roa, Chile to Punta Arenas, Chile
Stations occupied	115 on leg 1 and 96 on leg 2 on P18 line with 2 SOCCOM float calibration stations
Equipment deployed	29 floats and 20 drifters



**P18 Leg 1**



**P18 Leg 2**

# 1 Abstract

This report details the 2016/2017 occupation of the P18 hydrographic section aboard the National Oceanic and Atmospheric Administration (NOAA) vessel the Ronald H. Brown (the Brown) acting under the auspices of the Global Ocean Ship-based Hydrographic Investigations Program (GO-SHIP).

## Table of contents

1	Abstract.....	1
2	Involvement .....	2
2.1	Participating Institutions .....	2
2.2	Leg 1 Science Party .....	3
2.3	Leg 2 Science Party .....	4
2.4	Programs and Principal Investigators (PIs).....	5
3	Program and Project Overview .....	6
4	The P18 section.....	7
4.1	The 2016/2017 P18 occupation.....	9
4.2	Leg 1 cruise narrative.....	9
4.2.1	Challenges and lessons learned on leg 1 .....	9
4.2.2	Leg 1 transit and station-work efficiency.....	12
4.3	Leg 2 cruise narrative.....	13
5	Underway Data Acquisition.....	17
5.1	M-AERI measurements.....	17
5.2	Surface Acoustic Doppler Current Profiler.....	20
5.3	Underway pCO <sub>2</sub> Analyses .....	21
6	Conductivity Temperature Depth (CTD) Stations .....	23
6.1	Underwater Electronics Package .....	23
6.2	Discrete Niskin Sampling .....	25
6.3	Bottle Data Processing .....	26
6.4	Collected Samples.....	27
7	Ship-Board Analysis Sections.....	28
7.1	Figures of ship-board analyses during P18 .....	28
7.2	Changes in Ship-Board Properties Since 2007/8 .....	35
8	Individual Sub-project reports .....	37
8.1	Deployments .....	37
8.2	Discrete Salinity Sampling.....	39
8.3	NO <sub>3</sub> <sup>-</sup> isotopes on leg 2.....	41
8.4	NO <sub>3</sub> <sup>-</sup> and NO <sub>2</sub> <sup>-</sup> isotopes leg 1, dissolved gases (O <sub>2</sub> , N <sub>2</sub> , Ar, and N <sub>2</sub> O), N <sub>2</sub> O Isotopomers .....	42
8.5	Dissolved Inorganic Carbon.....	45
8.6	Discrete pH Analyses.....	47
8.7	Total Alkalinity .....	49
8.8	Genetics and Particulate Organic Matter .....	51
8.9	Microbial Genetics and Transcriptomics (iTag™) .....	52
8.10	Total Organic Carbon (TOC) and Dissolved Nitrogen (TDN) in Seawater .....	53
8.11	Rare Earth Elements (REEs).....	53
8.12	Lowered Acoustic Doppler Current Profiler.....	55
8.13	CHIPOD.....	57

8.14	DI <sup>14</sup> C in seawater.....	61
8.15	Helium, noble gases (Ne, Ar, Kr and Xe) and Tritium.....	61
8.16	Dissolved organic matter <sup>14</sup> C, black carbon <sup>14</sup> C, biomarkers, and dissolved organics.....	63
8.17	DOM Biomarkers and Molecular Composition.....	64
8.18	Chlorofluorocarbons and Sulfur Hexafluoride (CFCs/SF <sub>6</sub> ).....	67
8.19	Dissolved Oxygen (discrete).....	71
8.20	DOC14 Pyrolysis.....	73
8.21	SOCCOM sampling/HPLC and POC.....	74
8.22	Plastics Net Deployment.....	74
9	Appendix 1: Water Sample Quality Code Summary.....	76
10	Appendix 2: Timeline, Leg 1.....	76
11	Appendix 3: Station Timing, Leg 1.....	81
12	Appendix 4: Weekly updates.....	83
12.1	Weekly report -1.....	84
12.2	Weekly report 0.....	86
12.3	Weekly report 1.....	87
12.4	Weekly report 2.....	91
12.5	Weekly report 3.....	95
12.6	Weekly report 4.....	99
12.7	Weekly Report 5.....	102
12.8	Weekly report 6.....	106
12.9	Weekly Report 7.....	107
12.10	Weekly Report 8.....	109
12.11	Weekly Report 9.....	112
13	Appendix 5: Sample cop notes.....	114

## 2 Involvement

### 2.1 Participating Institutions

#### Primary:

United States Department of Commerce  
National Oceanic and Atmospheric Administration  
Pacific Marine Environmental Laboratory (NOAA/PMEL)  
7600 Sand Point Way NE  
Seattle, WA 98115 USA  
Telephone: 206-526-4314  
Facsimile: 206-526-6744

#### *Additional (alphabetical)*

---

APL	Applied Physics Laboratory
AOML	Atlantic Ocean and Meteorological Laboratory
CCU	Coastal Carolina University
CICIMAR	Centro Interdisciplinario de Ciencias Marinas, Mexico
GIT	Georgia Institute of Technology
INU	Incheon National University, Seoul, Korea

IPN	Instituto Politécnico Nacional, Mexico
JISAO	Joint Institute for the Study of Atmosphere and Ocean, Univ. of Washington
MIT	Massachusetts Institute of Technology
MPIC	Max-Planck-Institut für Chemie, Germany
NESDIS	NOAA Satellite and Information Service
ODU	Old Dominion University
OSU	Oregon State University
Ox	Oxford University, England
PMEL	Pacific Marine Environmental Laboratory
PML	Plymouth Marine Laboratory, England
PU	Princeton University
RSMAS	Rosenstiel School of Marine and Atmospheric Science/University of Miami
SIO	Scripps Institution of Oceanography/University of California at San Diego
UAF	University of Alaska, Fairbanks
UCI	University of California, Irvine
UCSD	University of California, San Diego
UMe	University of Maine
UMi	University of Miami
UMich	University of Michigan
URI	University of Rhode Island
USM	University of Southern Mississippi
Uval	Valparaiso Universidad, Valparaiso, Chile
UW(A)	University of Washington, Seattle
UW(I)	University of Wisconsin, Madison
WHOI	Woods Hole Oceanographic Institution
Yale	Yale University

## 2.2 Leg 1 Science Party

Primary Task	Name	Affiliation	Additional Tasks
<i>Chief Scientist</i>	Brendan Carter	PMEL	<i>Deployments</i>
<i>Co-Chief Scientist</i>	Annie Bourbonnais	WHOI	<i>Deployments, lead: stable gases, shore-side N<sub>2</sub>O, He/T, NO<sub>3</sub> isotopes, NO<sub>2</sub> isotopes</i>
<i>CTD lead</i>	Kristene McTaggart	PMEL	<i>Deployments</i>
<i>Data Manager</i>	Remy Okazaki	PMEL	<i>DIC, deployments</i>
<i>Salinity/CTD</i>	James Hooper	AOML	<i>LADCP, rosette, deployments</i>
<i>Salinity/CTD</i>	Andrew Stefanick	AOML	<i>LADCP, rosette, deployments</i>
<i>CTD Watchstander</i>	Shineng Hu	Yale	<i>Chipods, LADCP, REE</i>
<i>CTD Watchstander</i>	Margot White	SIO	<i>DO<sup>14</sup>C by pyrolysis, REE</i>
<i>Dissolved O<sub>2</sub></i>	Samantha Ladewig	CCU	<i>Microplastics tows</i>
<i>Dissolved O<sub>2</sub></i>	Alexander Sidelev	UMi	<i>CTD-rosette deployments</i>
<i>Nutrients</i>	Charles Fischer	AOML	<i>CFC sampling</i>
<i>Nutrients</i>	Eric Wisegarver	PMEL	<i>CFC sampling</i>
<i>DIC lead</i>	Robert Castle	AOML	<i>Underway pCO<sub>2</sub></i>
<i>DIC</i>	Dana Greeley*	PMEL	

<i>CFCs/SF<sub>6</sub> lead</i>	Bonnie Chang	PMEL	<i>N<sub>2</sub>O lead</i>
<i>CFCs/SF<sub>6</sub></i>	Tae-Jun Choi	INU	<i>N<sub>2</sub>O</i>
<i>CFCs/SF<sub>6</sub></i>	Laura Whitmore	USM	<i>N<sub>2</sub>O, REE lead</i>
<i>TALK/pH</i>	Ryan Woosley	RSMAS	
<i>TALK/pH</i>	Fen Huang	RSMAS	
<i>TALK/pH</i>	Andrew Babbin	WHOI	<i>H<sub>2</sub>O isotopes</i>
<i>TALK/pH</i>	Alexandra Fine	RSMAS	
<i>Black carbon</i>	Brett Walker	UCI	<i>DO<sup>14</sup>C, biomarkers, organics, incubations</i>
<i>Black carbon</i>	Christian Lewis	UCI	<i>DO<sup>14</sup>C, biomarkers, organics, and He/T</i>
<i>Net Tows</i>	Javier Hernandez*	CICIMAR	
<i>Genetics</i>	Alyse Larkin	UCI	<i>NO<sub>3</sub> isotopes, NO<sub>2</sub> isotopes</i>
<i>DOC and TDN</i>	Mariana Bernardi Bif	RSMAS	<i>DI<sup>13/14</sup>C, incubations</i>
<i>LADCP</i>	Pierre Dutrieux*	LDEO	
<i>Satellite Cal/Val</i>	Charles Kovach	NESDIS	<i>HPLC, POC</i>

\*unable to participate after delays leaving San Diego

### 2.3 Leg 2 Science Party

Duties	Name	Affiliation	Additional Tasks
<i>Chief Scientist</i>	Rolf Sonnerup	JISAO	<i>Deployments, sampling, LADCP, rosette</i>
<i>Co-Chief Scientist</i>	Sarah Purkey	LDEO	<i>Deployments, sampling, LADCP, CHIPOD</i>
<i>CTD Processing</i>	Kristene McTaggart	PMEL	<i>Deployments, rosette</i>
<i>Data Manager</i>	Remy Okazaki	PMEL	<i>Deployments</i>
<i>Salinity/CTD</i>	James Hooper	AOML	<i>Deployments, LADCP, CHIPOD</i>
<i>CTD Watchstander</i>	Paige Logan	JISAO	<i>Salts, Deployments</i>
<i>CTD Watchstander</i>	Conrad Luecke	UMich	<i>CHIPOD, Deployments, sampling</i>
<i>iTag Genetics</i>	Bethany Kolody	SIO	
<i>Dissolved O<sub>2</sub></i>	Christopher Langdon	UM	
<i>Dissolved O<sub>2</sub></i>	Emma Pontes	UM	
<i>Nutrients</i>	Charles Fischer	AOML	<i>CFC sampling</i>
<i>Nutrients</i>	Eric Wisegarver	PMEL	<i>CFC sampling, Deployments</i>
<i>DIC/underway pCO<sub>2</sub></i>	Charles Featherstone	AOML	
<i>DIC</i>	Andrew Collins	PMEL	
<i>CFCs/SF<sub>6</sub></i>	Bonnie Chang	PMEL	<i>N<sub>2</sub>O lead</i>
<i>CFCs/SF<sub>6</sub></i>	Tae-Jun Choi	INU	<i>N<sub>2</sub>O</i>
<i>CFCs/SF<sub>6</sub></i>	Rachel McMahan	ODU	<i>N<sub>2</sub>O</i>
<i>TALK/pH</i>	Ryan Woosley	RSMAS	
<i>TALK/pH</i>	Fen Huang	RSMAS	
<i>TALK/pH</i>	Andrew Babbin	MIT	<i>H<sub>2</sub>O isotopes</i>
<i>TALK/pH</i>	Alexandra Fine	RSMAS	
<i>DO<sup>14</sup>C, black carbon</i>	Christian Lewis	UCI	<i>Biomarkers</i>
<i>Rare Earth Elements</i>	Yves Plancherel	Ox	<i><sup>3</sup>H-<sup>3</sup>He</i>
<i>Genetics</i>	Cathy Garcia	UCI	

<i>DOM</i>	Mariana Bif	RSMAS	<i>DI<sup>14</sup>C</i>
<i>Satellite Cal/Val</i>	Charles Kovach	NESDIS	<i>HPLC/POC</i>
<i>Observer (Chile)</i>	Javiera Veloso	U Val	<i>iTag, Genetics, and REE sampling, NH<sub>4</sub></i>

## 2.4 Programs and Principal Investigators (PIs)

Program	PI	Institution	E-mail
CTD	Greg Johnson	PMEL	<i>gregory.c.johnson@noaa.gov</i>
	Molly Baringer	AOML	<i>Molly.Baringer@noaa.gov</i>
Salinity	Molly Baringer	AOML	<i>Molly.Baringer@noaa.gov</i>
LADCP	Andreas Thurnherr	LDEO	<i>ant@ldeo.columbia.edu</i>
Dissolved Oxygen	Chris Langdon	RSMAS	<i>clangdon@rsmas.miami.edu</i>
Nutrients	Calvin Mordy	PMEL	<i>Calvin.W.Mordy@noaa.gov</i>
	Jia-Zhong Zhang	AOML	<i>Jia-Zhong.Zhang@noaa.gov</i>
CFCs/SF <sub>6</sub> /N <sub>2</sub> O by ECD	John Bullister	PMEL	<i>John.L.Bullister@noaa.gov</i>
Total CO <sub>2</sub> (DIC)	Richard Feely	PMEL	<i>richard.a.feely@noaa.gov</i>
	Rik Wanninkhof	AOML	<i>Rik.Wanninkhof@noaa.gov</i>
Total Alkalinity/pH	Frank Millero	RSMAS	<i>fmillero@rsmas.miami.edu</i>
DI <sup>14</sup> C	Ann McNichol	WHOI	<i>amcnichol@whoi.edu</i>
	Robert Key	PU	<i>key@princeton.edu</i>
DO <sup>14</sup> C	Ellen Druffel	UCI	<i>edruffel@uci.edu</i>
Dissolved Organics	Brett Walker	UCI	<i>Brett.walker@uci.edu</i>
DOC and TDN	Dennis Hansell	RSMAS	<i>dhansell@rsmas.miami.edu</i>
Helium/Tritium ( <sup>3</sup> He- <sup>3</sup> H)	Scott Doney	WHOI	<i>sdoney@whoi.edu</i>
	William Jenkins	WHOI	<i>wjenkins@whoi.edu</i>
Stable Gases, O <sub>2</sub> , N <sub>2</sub> , Ar	Annie Bourbonnais	WHOI	<i>abourbonnais@whoi.edu</i>
Floats	Greg Johnson	PMEL	<i>Gregory.C.Johnson@noaa.gov</i>
	Lynne Talley	SIO	<i>ltalley@ucsd.edu</i>
	Craig McNeil	UW	<i>cmcneil@apl.washington.edu</i>
	Steve Emerson	UW	<i>emerson@u.washington.edu</i>
	Giorgio Dall'Olmo	PML	<i>gdal@pml.ac.uk</i>
Drifters	Shaun Dolk	AOML	<i>shaun.dolk@noaa.gov</i>
HPLC	Emmanuel Boss	UMe	<i>emmanuel.boss@maine.edu</i>
Transmissometry	Wilf Gardner	TAMU	<i>wgardner@ocean.tamu.edu</i>
Fluor./backscatter	Emmanuel Boss	UMe	<i>emmanuel.boss@maine.edu</i>
Chipods	Jonathan Nash	OSU	<i>nash.coas@gmail.com</i>
Net tows*	Laura Sanchez Velasco	CICIMAR	<i>lsvelasc@gmail.com</i>
Bathymetry	Ship personnel	NOAA	<i>ops.ronald.brown@noaa.gov</i>
Underway TSG	Ship personnel	NOAA	<i>ops.ronald.brown@noaa.gov</i>
Underway pCO <sub>2</sub>	Rik Wanninkhof	AOML	<i>Rik.Wanninkhof@noaa.gov</i>
Genetics	Adam Martiny	UCI	<i>amartiny@uci.edu</i>
iTag Genetics	Eric Allen	SIO	<i>eallen@ucsd.edu</i>
	Bethany Kolody	SIO	<i>bck243@gmail.com</i>
Nitrate/nitrite isotopes	Daniel Sigman	PU	<i>sigman@princeton.edu</i>
	François Fripiat	MPIC	<i>f.fripiat@mpic.de</i>
	Annie Bourbonnais	WHOI	<i>abourbonnais@whoi.edu</i>

N <sub>2</sub> O isotopomers	Annie Bourbonnais	WHOI	<i>abourbonnais@whoi.edu</i>
Radiometry/Chlorophyll	Michael Ondrusek	NESDIS	<i>Michael.Ondrusek@noaa.gov</i>
H <sub>2</sub> O isotopes	Kim Cobb	GIT	<i>kim.cobb@eas.gatech.edu</i>
DO <sup>14</sup> C by Pyrolysis	Lihini Aluwihare	SIO	<i>laluwihare@ucsd.edu</i>
Microplastics	Shaowu Bao	CCCU	<i>sbao@coastal.edu</i>

---

\* Program cancelled after the first cast

### 3 Program and Project Overview

Hydrographic measurements were made along the P18 section in late 2016 and early 2017 under the direction of the Global Ocean Ship-Based Hydrographic Investigation Program, or GO-SHIP. This reoccupation was jointly funded by NOAA Climate Observation Division of the Climate Program Office and NSF-OCE (National Science Foundation Division of Ocean Sciences). Numerous academic institutions and NOAA research laboratories participated.

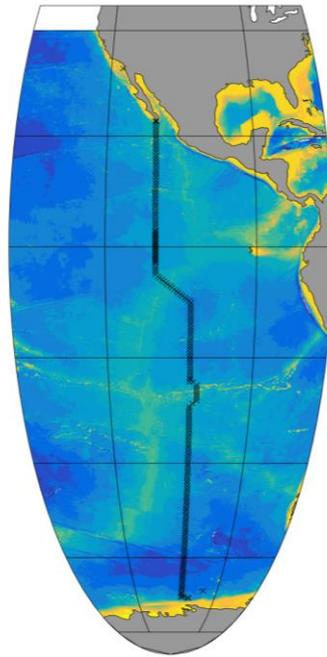
GO-SHIP aims to address the need to monitor inventories and transports of CO<sub>2</sub>, heat, and freshwater in the ocean. The program serves to measure long-term changes and variability in marine biogeochemical and physical processes in response to natural and human-induced forcing. The program provides unique high-quality measurements of key oceanographic parameters at all ocean depths. These measurements are a cornerstone of several major efforts to quantify long-term changes and decadal variability in ocean properties, and are critical for calibrating and validating other observation and modeling programs. Earlier programs under the Joint Global Ocean Flux Study (JGOFS), World Ocean Circulation Experiment (WOCE), and Climate Variability and predictability (CLIVAR) programs provided an approximately decadal set of observations on hydrographic lines, including the P18 line that GO-SHIP builds upon. Examples of critical findings made possible by decadal measurements include ongoing ocean uptake and subsurface storage of anthropogenic CO<sub>2</sub> with consequent ocean acidification, ongoing warming and freshening of the deepest bottom waters, and accelerated overturning of intermediate depth water masses in the Southern Ocean. The Repeat Hydrography Program provides a robust observational framework to monitor these long-term trends.

Continuation of these programs under GO-SHIP involves reoccupying the same set of hydrographic transects spanning the global ocean with full water column measurements. These measurements are in support of:

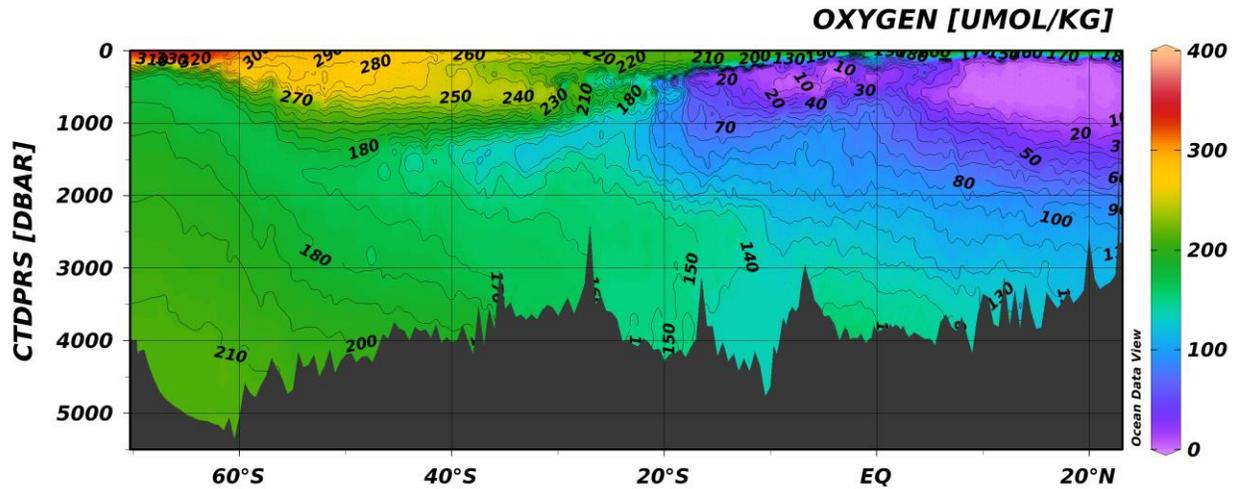
- Model calibration and validation
- Studies of ocean circulation
- Carbon system studies
- Heat and freshwater storage and flux studies
- Changes in volumes and properties of water masses
- Quantification of turnover timescales
- Calibration of autonomous sensors and satellites

In addition to its core missions, GO-SHIP secondarily provides a platform for collaborations with other ongoing and novel scientific programs. Examples include satellite algorithm calibration and validation, novel instrument and method testing and deployment, calibration and deployment of novel floats with biogeochemical sensors, and contributions to surface ocean pCO<sub>2</sub> measurement programs. Numerous discrete and underway sampling programs are supported by GO-SHIP projects on a project-by-project basis. More details on the repeat hydrography program can be found at: <http://ushydro.ucsd.edu/>.

#### 4 The P18 section



**Figure 1.** A map of the P18 section. X's indicate station locations occupied during 2016/2017. Colors indicate bathymetric depth with dark blues representing deep water and bright yellows representing shallow water.



**Figure 2.** A meridional section of oxygen along P18, highlighting the contrast between thermocline and sub-thermocline oxygen concentrations in the northern and southern portions of P18.

The P18 section runs meridionally through the Eastern Pacific. The section proceeds along 110°W from ~22.87°N (offshore Cabo San Lucas) to 5°S (Figure 1). This northern portion of the section is along 110°W to overlap with the Tropical Atmosphere Ocean (TAO) array of moored buoys along the Equator and to extend north to the tip of Cabo San Lucas. From 5°S, the section proceeds SE to 103°W and 10°S, crossing the East Pacific Rise nearly orthogonally. From 10°S, P18 extends along 103°W to nominally ~72°S, offshore Antarctica. This meridian was chosen to occupy the deeper portion of the Roggeveen, Bauer, and Southeast Pacific Basins between the Peru Chile Trench and the East Pacific Rise. Historically, the Southern terminus of the P18 section has been limited by ice cover at 66° 59.7' S in 1994 and at 69° 26.4' S in 2007/8. The P18 section is of special interest because it connects the oxygen deficient waters of the Eastern Tropical North Pacific to the high-oxygen intermediate and mode water formation region in the Southeastern Pacific. P18 crosses exclusive economic zones (EEZs) of Chile, France, and Mexico.

The previous P18 occupations were led by NOAA in 1994 aboard the Discoverer as part of WOCE, and in 2007/2008 aboard the Ronald H. Brown as part of CLIVAR. A full suite of inorganic carbon, hydrographic, and CFC measurements were performed on each of these cruises, and were measured again during this project. In this occupation, as with previous occupations, water column CTD stations were occupied at ~30 nautical mile spacings, with increased resolution near coasts and in a narrow (3°) band around the Equator. Measurements were made at each station for a variety of physical, chemical, and biological parameters. Underway sampling was conducted between stations during 2016/2017 P18, ceasing only briefly for system maintenance and occasionally due to lapses in permitting for sampling in foreign EEZs.

#### 4.1 The 2016/2017 P18 occupation

The Ronald H. Brown was initially scheduled to depart leg 1 on 11/02/2016. The Brown first left port with all leg 1 scientists aboard on 11/12/2016 after extensive mechanical difficulties. The vessel proceeded south offshore Mexico to  $\sim 28^{\circ} 36' N$  before returning to port on 11/14/2016 for continued diagnosis of engine difficulties. The vessel again departed San Diego on 11/19/2016 and began the P18 project in earnest (see Appendix 2 for a full timeline). Leg 1 was completed with the arrival of the Brown into Hanga Roa, Easter Island, Chile on the morning of 12/23/2016.

The P18 line was occupied at 30 nautical mile (nm) spacing from Cabo San Lucas to  $23^{\circ} 30' S$ . Higher resolution station work was completed offshore Cabo San Lucas and from  $3^{\circ} N$  to  $3^{\circ} S$ . While descending the continental slope off Cabo San Lucas, the intention was to do station work after every 750 m increase in the bathymetric depth. However, two such planned stations were found to be within 10 km of one another and therefore one was cut. The first station to be occupied on the P18 line (station 1) was occupied before the northernmost station on the line (Station 2) in order to more efficiently combine transit time with rosette sampling time. In total 4 stations were performed between  $22.87^{\circ} N$  and  $22.50^{\circ} N$ . While crossing the Equator, stations were performed with 15 nm resolution resulting in 12 additional stations between  $\pm 3^{\circ}$  of the Equator. This occupation also shifted the portion of the line between  $24.5^{\circ} S$  and  $28.5^{\circ} S$  up to  $1.5^{\circ}$  to the east to avoid the Chilean EEZ near Isla Sala y Gomez. The southernmost station on the line was at  $69^{\circ} 36.5' S$ , and three additional stations were performed east of the  $103^{\circ} W$  line extending to  $70^{\circ} 00.04' S$ ,  $100^{\circ} 14.4' W$ .

Due to significant early delays, the width of the Equatorial double resolution window was narrowed from the planned  $\pm 5^{\circ}$  to  $\pm 3^{\circ}$ , supplemental station work along the P17 extension connecting P18 to the Chilean coast was cancelled, and ancillary science activities designed to provide (and make use of) additional sample analysis and collection time were limited due to delays beginning station work on leg 1. These impacts on leg 1 science activities were mitigated by efficient deployments, recoveries, and transits between stations effected primarily by the Brown and her crew. Combined with fair weather and hard work, these efficiencies combined to make up  $\sim 1$  lost day.

#### 4.2 Leg 1 cruise narrative

A compilation of weekly updates on cruise life and activities is provided as Appendix 4.

##### 4.2.1 Challenges and lessons learned on leg 1

Leg 1 of the 2016/2017 P18 occupation experienced several notable challenges:

##### 1. Delays leaving port

The schedule for leaving San Diego was repeatedly delayed owing to mechanical difficulties coming out of dry dock, primarily associated with the vessel's Z-drives. A full timeline of the events surrounding these delays is included as Appendix 2. In total, these delays resulted in the project beginning 18 days after the original project start date. The delays also resulted in significant added costs for all science party

participants due to additional travel for those that returned to their jobs and additional salary and travel costs for those who remained in San Diego, and also propagated into significant problems with lapsing clearances for sampling in foreign EEZs. Ultimately, three scientists were unable to join on leg 1 due to these delays, and one scientist was unable to join on leg 2.

*Lessons learned/reaffirmed:* The impact of mechanical delays can be minimized by tempering optimism with realism when rescheduling project dates in light of vessel maintenance. As an example, the first 5 days of the P18 2016/2017 delays were planned ~4 weeks in advance and resulted in minimal added costs and difficulties. The rest of the delays included only 1-2 days of notice, making planning significantly more difficult and costly.

## **2. Foreign Clearances**

Owing to delays leaving port, the permit for research in the Mexican Exclusive Economic Zone (EEZ) expired on the same day the project entered the EEZ. Continuous efforts to seek an extension were made by scientists, Brown's leadership, laboratory administrators, and advocates at the US Department of State as soon as it was known that an extension would be required. These efforts resulted in an extension being granted after 7 business days (6 in Mexico), but not before ~1.5 days at sea were lost waiting on the first station for clearance to be granted. Later, official Chilean research approval did not arrive in time and did not cover the desired area. This resulted in moving a segment of the line 1.5°E around the Chilean EEZ surrounding Isla Sala y Gomez (Fig. 1). Debriefing suggested the difficulties were related to the changes in dates.

*Lessons learned/reaffirmed, paraphrased from our contact in Mexico City:*

- Notify the Embassy as soon as you know that a project has been cancelled or postponed.
- Consider requesting more time in the EEZ than needed.

These lessons are well taken. However, contacts at the US Department of State caution against requesting *significantly* more time than is required. Also, we ran into this problem despite having followed both suggestions (by sending a request for an extension as soon as the Brown changed heading to return to San Diego on 11/13/2016, and by requesting 17 days when we anticipated needed only 7).

## **3. The aft winch**

The aft Markey winch failed on station 18, spooling out in an uncontrolled fashion during CTD/rosette package recovery. Luck and attention to safety kept the retrieving team safe, and quick action by the winch operator in applying an emergency brake saved the package from damage. Further testing revealed the winch could no longer hold large loads without spooling out in this fashion. We therefore switched the CTD/rosette package to the forward winch, and used a pneumatic rope-spool "tugger" to deploy the package over the side from the (offset slightly aft) tracks used for conveying the package into the sampling bay. The aft winch was repaired during leg 2.

*Lessons learned/reaffirmed:* Mechanical difficulties are an inevitable part of oceanographic research. This episode served as a reminder of how valuable the Brown leadership's focus on safety practices is.

Future GO-SHIP expeditions aboard the *Brown* might consider obtaining an additional set of tracks used for sliding the CTD/Rosette into the sampling bay. An alternate set of tracks for the deck (outdoors) could be constructed that aligns with the block used for the forward winch. The existing (aligned for the aft winch) and alternate tracks could both be aboard, making CTD recoveries simpler on both winches.

#### **4. Ancillary program cuts**

Schedule pressure from challenges **1.** and **2.** led to a downscaling of planned bongo net operations and a reduction of planned hyperpro/radiometer casts. Hyperpro casts were limited to those that could be co-deployed with CTD-rosette casts (with one exception on station 117). Both operations had been planned for short pauses scheduled to allow our shipboard sample analysis teams to keep up with ongoing station work. Bongo tows were later cancelled outright after the aft winch failed (**3.**). Cancelling time dedicated for these deployments decreased the value of the records generated by these two ancillary programs and also decreased the completeness of the bottle-data records generated by our primary shipboard programs. The impacts on the primary shipboard analyses were most pronounced for the measurements with moderate throughput (*e.g.*, CFCs and carbonate parameters), especially in the Equatorial region where stations occur in rapid succession.

*Lessons learned/reaffirmed:* GO-SHIP ancillary programs that require dedicated time for deployments also allow a more complete sampling of the Niskin water brought aboard.

#### **5. CTD troubleshooting**

Significant CTD troubleshooting was required despite having brought 2 recently-serviced CTDs and the *Brown* having provided 2 additional CTDs. The first CTD furnished by the science party leaked under pressure and suffered a complete failure. The second CTD was swapped out during troubleshooting of ongoing problems (see Appendix 2). The next CTD to be used was one of the *Brown*'s, and it was found to have a miss-pinned sensor port and a pair of sensor ports that had been swapped. The other CTD provided by the *Brown* was the next to be used, which worked as intended, but had an insufficient (1 amp) current supply to power the full intended sensor package. Finally, we switched to a new CTD that had been brought as a backup for P18 or the subsequent PIRATA NE cruise. This CTD worked well for the remainder of the cruise. Spare component parts and sensors were used regularly throughout troubleshooting. Approximately one day of ship time was spent troubleshooting the CTD.

*Lessons learned/reaffirmed:* The high demands placed on CTD-sensor packages by GO-SHIP cruises require ample backup CTD units and spare components.

#### **6. Scientific staffing**

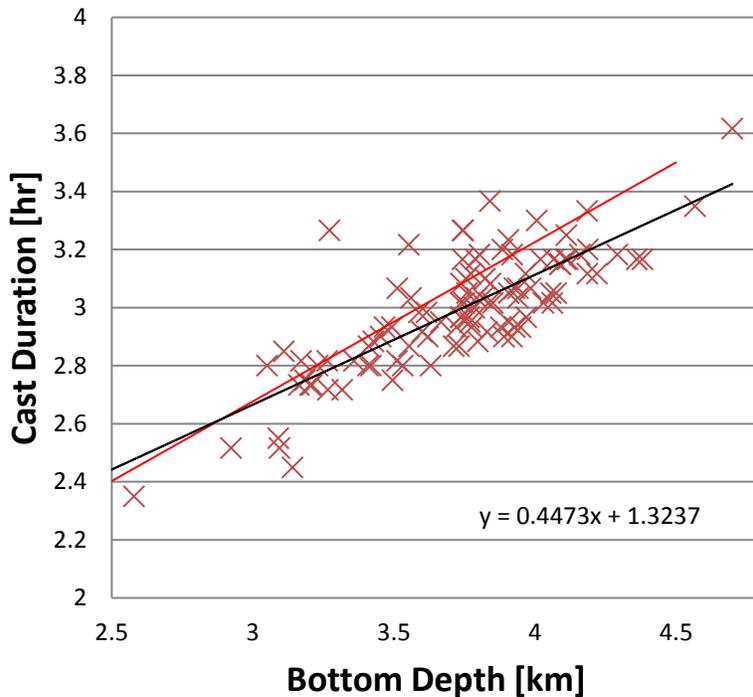
Three scientists became unable to participate before sailing on leg 1 due to challenge **1.** Also, one scientist was injured while at sea preventing him from conducting some of the volunteer work he had planned on doing. This required doubling or tripling up duties by several scientists. Finally, one console operator per watch is perhaps less than needed given the level of focus required by the position and the

number of additional jobs that tend to fall to these watchstander/students. The combined labor shortage on leg 1 was exacerbated by a number of ancillary programs that did not provide any dedicated personnel on either leg (NO<sub>3</sub> isotopes, NO<sub>2</sub> isotopes, dissolved gases, N<sub>2</sub>O analysis on land, H<sub>2</sub>O isotopes, He/T, DI<sup>14</sup>C, floats). Individually, these programs were not problematic, but collectively they created a situation in which we were weighing the value of the programs against the exhaustion levels of our scientists. The cold-welding He/T analysis specifically required an exceptional amount of work, and it is recommended that this analysis be handled by a dedicated scientist rather than a volunteer or a scientist with other responsibilities.

*Lessons learned/reaffirmed:* It is ideal to bring more scientists than the minimum necessary, perhaps by encouraging ancillary programs to sponsor additional CTD watchstanders. Also, one could prioritize ancillary analyses that provide their own personnel. Barring that, ancillary programs that have pre-identified volunteer scientists (joining for other programs) are ideal.

#### **4.2.2 Leg 1 transit and station-work efficiency**

A full schedule for station work on leg 1 is provided as Appendix 3. Excepting two troubleshooting stations, the Brown moved efficiently between stations in persistently fair weather. The vessel averaged 10.4 kts on 30 nm transits and 8.5 kts on 15 nm transits inclusive of time spent maneuvering and deploying and retrieving the package. These quick transits saved ~14 hours relative to projections. The console operators and winch drivers were also able to capitalize on the fair weather. As seen in the figure below, CTD-in-water times out-performed expectations for most stations. Excepting two troubleshooting stations, approximately 9 total hours were saved through efficient casts.



**Figure 3.** The length of time the CTD was on in the water plotted against the depth of the station for all casts on leg 1. The red x's and the black trend line and its equation reflect the actual times. The red line is the relationship expected at the outset of the project.

### 4.3 Leg 2 cruise narrative

After continuing back and forth, including a visit to the Hanga Roa Harbormaster with our Chilean observer and translator, Javiera Veloso, the Brown ultimately did not gain clearance to conduct operations within the Chilean EEZ near Easter Island. Also, our departure date from Easter Island was delayed by two days – one awaiting a 3<sup>rd</sup> engineer filling in for a crewman badly injured on Easter Island, and a second day awaiting a new motor for the ship's incinerator.

During the wait, we brainstormed a work sharing arrangement to cover, at least partially, the myriad of responsibilities handled by Andy Stefanick, who had sprained his ankle midway through Leg 1. With no signs of improvement in his ankle over the prior two weeks at sea, Andy needed to go home and look after his ankle.

We departed mid-morning the 30<sup>th</sup> of December. As the P18 line was significantly behind schedule, we elected to save ~ ten hours' time by not reoccupying station 115 from leg 1. P18 station 116, located at 23° 54' North, 103° West, was adjusted six miles north from its planned location to stay well clear of the Chilean EEZ about Easter Island and Sala Y Gomez. We occupied 116 at 7 pm local time – concurrent with the ship's new year's eve party in the library. Happy New Year, Leg 2 is underway.

To stay clear of the EEZ, and occupy a more or less meridional line, we proceeded to the Southwest to station 117 at 24° 30'S, 102° 20'W, and stations 118 through 124 from 25° to 28° S along the 101° 30'W meridian, a line as close to tangent the EEZ as comfortable. We returned to the 103°W line via stations 125 at 28° 30'S, 102° 20'W and the slightly adjusted station 126 at 29° 6'S, 103°W.

Stations 116-128 were occupied without incident, and we continued as planned (half degree spacings) along 103°W, making good time thanks to the favorable weather and seas. On Jan. 4, at stations 129 and 130, we had some issues with the CTD. Both conductivity sensors and all cabling on the lower end cap were swapped out for a total delay, including aborted (then repeated) casts, of ~five hours.

During this first week, ship's engineers continued their efforts at reviving the aft winch. Although operations were proceeding smoothly on the forward, the aft is preferable as its cable is much newer, and the CTD can be recovered with only two individuals and without coordination of the tugger, described above in the Leg 1 report. During stations 129 and 130's delays, engineers conducted yet another test of the aft winch but were frustrated again. We continued to operate with the forward winch, rehearsing our timings and roles on deck with the tugger to hasten our recoveries and assure safety in the seas to come. The winch itself worked flawlessly. The weather continued to be favorable to operations over the next few days. We had a 48 hour blow (25-30 kts) over the 8<sup>th</sup> and 9<sup>th</sup> of January that tested skills on the forward winch.

Meanwhile, the *Brown*'s engineers disassembled the aft winch's brake mechanism. They discovered that the brake assembly's friction plates were hindered from fully engaging due to a loosely mounted bracket. Once re-assembled, the rear winch passed repeated 3000# load tests in and out of the water. Emboldened, we planned a switch to the aft winch the following day.

Later that evening, the wire / termination (fwd winch) started showing signs of trouble, including alarms from the deck unit. Jeff Hill (Ship's Electronics technician) was summoned in the middle of the night to reterminate the aft winch's wire and, with Jay Hooper, set up to deploy the CTD using the aft winch. We used the aft winch for the remainder of our section.

Although we enjoyed favorable weather conditions throughout the 40s and 50s (latitude), we did have to adjust to a new normal of 25 -30 Knot South winds, seas 10-15 ft during January 14- 16<sup>th</sup>. Although our transits were slowed, sometimes drastically, we continued operations. After the 17<sup>th</sup>, we rode the Western side of a low (< 1000 mb) with very little pressure gradient. Cloudy skies, cold (2-4 °C), but with moderate winds 10-15 knots, squalls to 25.

At one station the CTD signals on the primary sensor went awry. The problem proved to be a 1.5" shrimp sucked into and jammed in the primary sensor. A similar event occurred at station #208, below, when the rosette came aboard the ctd sensors had an orange, elastic, very strong stringy gel stuck at the sensor intakes.

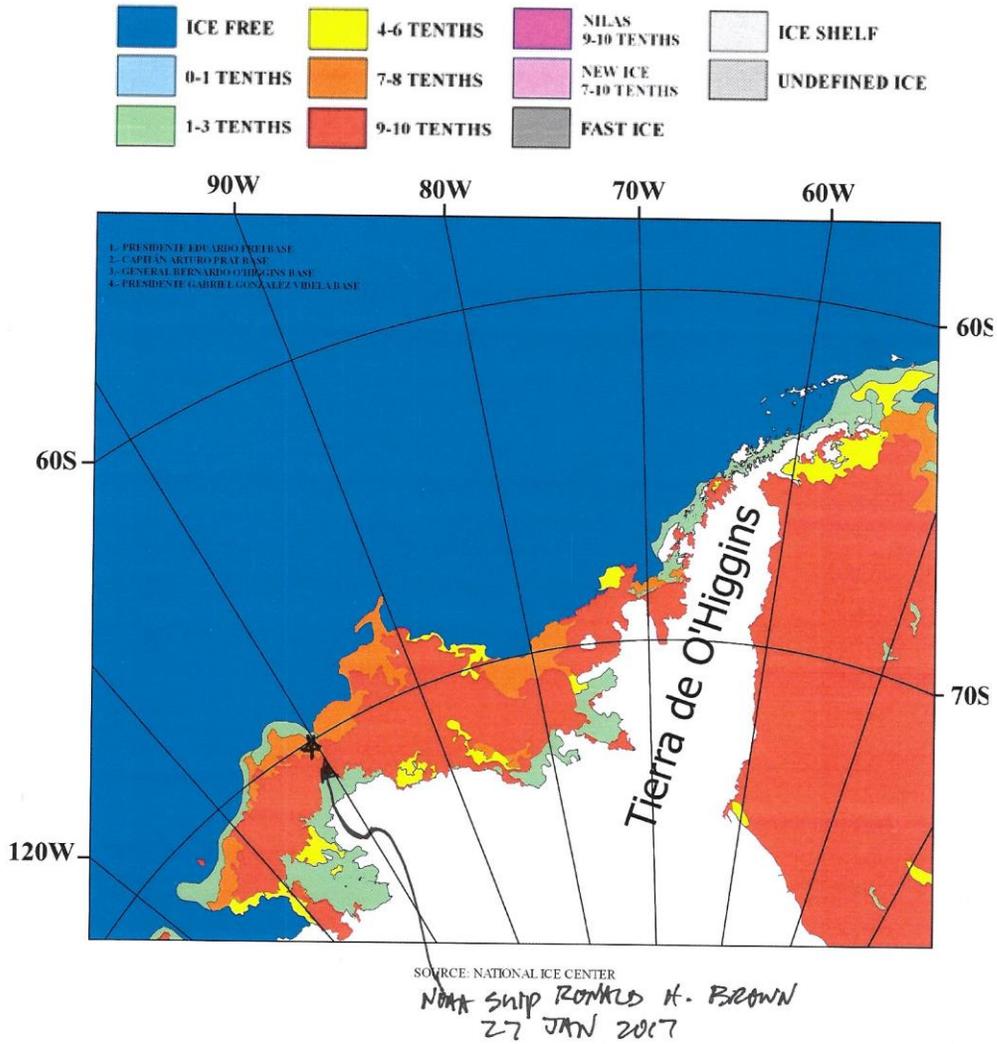
South of 60° we were enchanted by the endless supply of icebergs and by our continued good weather fortunes. After two days of spectacular scenery, sliding in amongst icebergs, we were warned: “This is probably your last station”. With so many groups requiring large volumes of water, and all wanting to characterize that southernmost station, we guessed that #206 (69°S, 103°W) would be our last. We conducted two casts, one for the usual GO-SHIP medley (CFCs,  $^3\text{H}$ - $^3\text{He}$ ,  $\text{O}_2$ , DIC, pH, ALK, nutrients and salts, with REEs and Black C, and  $\text{HH}^{18}\text{O}$  as add-ons), another (cast 2) at the same depths for the exotics, with S and  $\text{O}_2$  for CTD calibrations, like  $\text{N}_2\text{O}$  isotopes,  $\text{DI}^{14}\text{C}$ ,  $\text{DO}^{14}\text{C}$ , dissolved organics,  $\text{NO}_3$  isotopes, iTag, and Genetics. As this latter cast included  $\text{DI}^{14}\text{C}$ , DIC and ALK were sampled on niskins where the depths did not exactly replicate cast 1’s. This completed, we occupied two more 103°W stations: #207 at 69.5°S, and, our ultimate 103°W station #208 at 69°36.5’S, only 6.5 miles away, near-encircled by sea ice and bergs.

After #208, we escaped the cul-de-sac by heading north and then East, following the ice edge we had seen in reports from the National Sea Ice Center. Our plan was to follow the edge occupying stations 30 miles apart until we ran out of room. At our next station, we occupied a small void in the bergs for #209 at 69° 41.468’S, 102° 01.581’W. After 209 we retreated northwards, then proceeded again Eastward along the ice edge to # 210 69° 54.175’S, 100° 40.301’W and to our final station of P18 2016/2017, #211 completed Jan 28 at 01:28 GMT, 70° 00.04’S, 100° 14.4’W (Fig. 4).

From that turnaround point there was a recently surfaced Southern Ocean Carbon and Climate Observations and Modeling (SOCCOM) float to visit, #12559, last surfaced at 94° 59.46’ W, 68° 04.74’S on Jan 23. As a visit to that site was almost exactly on our way to Punta Arenas, we made our way past the ice to station #212, occupied at 68° 03.393’S 95° 0.043’ W for  $\text{O}_2$ , DIC, ALK, pH, Salts, REEs, iTag and of course (for SOCCOM) HPLC-pigments and POC. Our transit to the SOCCOM station had occurred at a pedestrian pace, first due to dodging icebergs, and for the latter ~ half, due to engine troubles. Looking at the weather conditions, we decided to retain our 15 remaining weather hours to ease pressure on the ship personnel (engineering and navigation) during the return to Punta Arenas.

## CONCENTRATION ICE CHART ANTARCTIC PENINSULA

UPDATED : 20170119



**Figure 4.** Ice cover map from the Chilean Navy. As a therapeutic measure, the *Brown's* location was added by Capt. Kamphaus to reassure Chief Sci. that he had indeed exhausted his options.

## 5 Underway Data Acquisition

Navigation data were acquired at 1-second intervals from the ship's Furuno GP150 P-Code GPS receiver from the start of the cruise. In addition, centerbeam depth data, with a correction for hull depth included in each data line, were acquired directly from the ship's Multibeam/Kongsberg EM122 system. These data were used to connect the timestamps for each deployment with position and ocean depth information.

The centerbeam depths were also continuously displayed, and data were manually recorded at cast start/bottom/end on CTD Cast Logs.

Various underway data were sent from the ship's computer systems, and stored at 1-second intervals:

<u>Column</u>	<u>Data Type and units</u>
1	Winch payout (uncorrected meters)
2	Winch speed (meters/minute)
3	Winch tension (pounds)
4	Multibeam Bottom Depth (meters to tenths) - corrected for Sound Velocity but not for hull depth (approx. 5.8m more)
5	UTC Julian Date (day of year in 2015)
6	UTC Time (hh:mm:ss) (hh=hours, mm=minutes, ss=seconds)
7	GPS Latitude (ddmm.mmmmH) (d=degrees, m=minutes to 4 places, H=Hemisphere)
8	GPS Longitude (dddmm.mmmmH)
9	TSG Sea Surface Temp (SST - degrees Celsius)
10	TSG Sea Surface Salinity (last calibrated 7-Jan-2015)
11	True Wind Speed (knots) - divide by 1.9438445 to get m/sec
12	True Wind Direction (compass degrees)
13	Barometer - Sea Level (millibars)
14	Relative Humidity (%)
15	Air Temperature (degrees Celsius)

### 5.1 M-AERI measurements

PI: Peter Minnett, with Miguel Angel-Izaguirre and Goshka Szczodrak, University of Miami, Rosenstiel School of Marine and Atmospheric Science

#### **Scientific goals:**

The goal of the University of Miami (UM) group was to take radiometric measurements of the sea surface skin temperature (SST) along the ship's cruise track. These measurements will be used to validate the SST derived from satellite observations, in particular for MODIS (on AQUA and TERRA satellites) and VIIRS (on the S-NPP satellite) and provide guidance for improving the algorithms for the derivation of SST from satellites.

To facilitate these goals the following instrumentation was installed by the UM group on the NOAA ship *Ronald H. Brown* in November 2016 during the ship stay in San Diego:

- 1) Atmospheric Sounder Spectrometer by Infrared Spectral Technology (ASSIST)

- infrared spectra of atmospheric emitted radiation
- infrared spectra of sea surface emitted radiation
- skin sea surface temperature
- near surface air temperature

2) Vaisala Weather Transmitter WXT 520 system

- air temperature
- air relative humidity
- barometric pressure
- wind speed
- wind direction

3) Gimbaled Eppley pyrometer and pyrgeometer

- short wave insolation (SW↓)
- incident long wave radiation (LW↓)

4) Microwave Radiometer (MWR)

- precipitable water vapor (PWV)
- cloud liquid water (CLW)

5) All sky camera

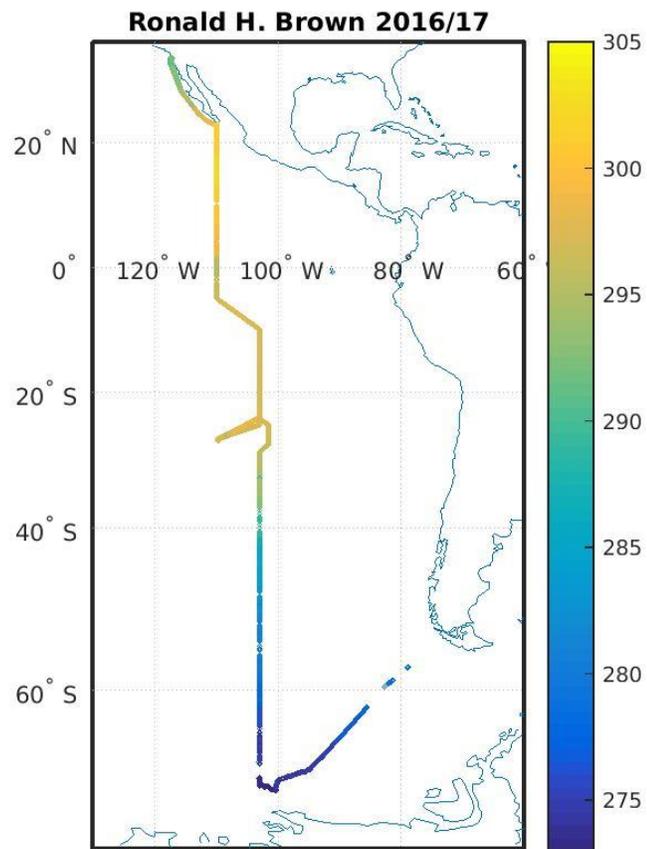
- cloud cover and cloud type
- 

The primary instrument, the ASSIST, measures spectra of infrared radiation emitted by atmosphere, and the sea surface from which the SST and other variable are derived. The UM group operated a similar instrument the Marine Atmosphere Emitted Radiance Interferometer (M-AERI) for over 15 years. The ASSIST is a new instrument that has replaced the M-AERI.

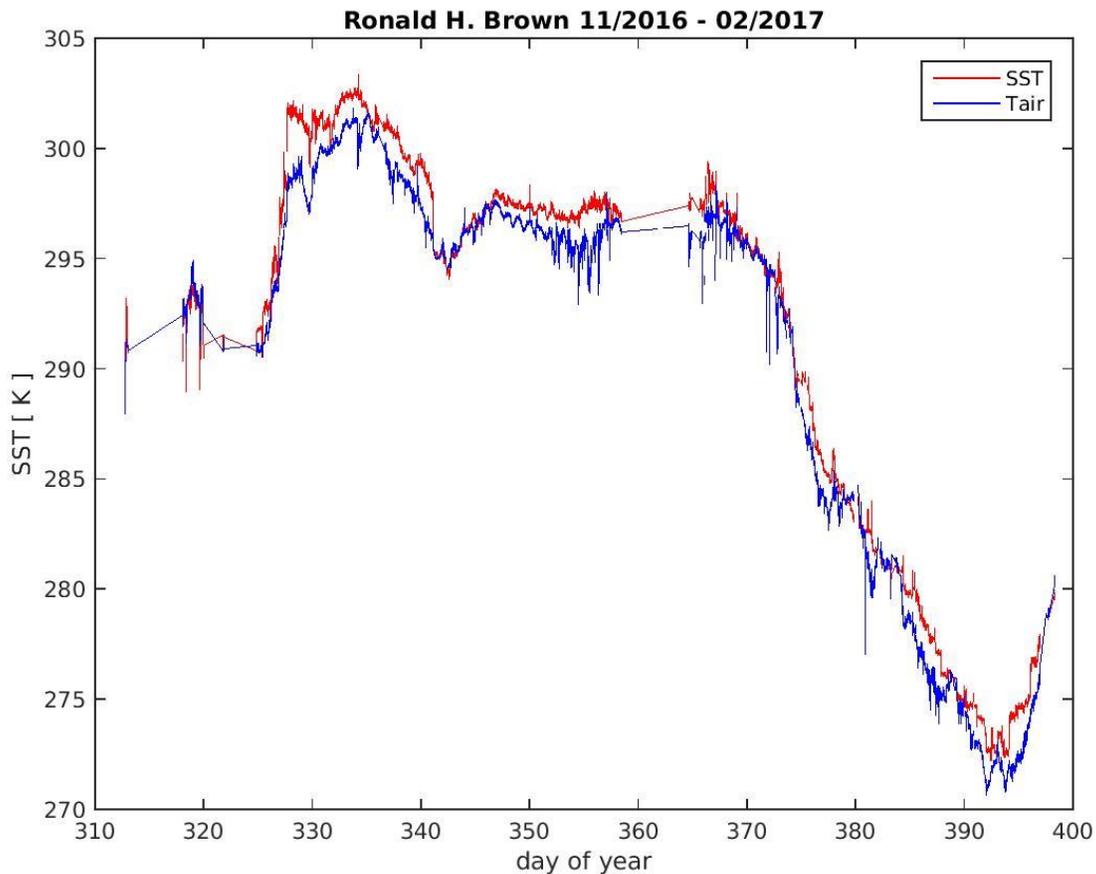
**Preliminary results:**

All instruments set up on *Ronald H. Brown* operated continuously throughout the cruise. The gaps in the ASSIST data are weather related as the instrument does not operate in rain nor while exposed to sea spray.

A number of atmospheric and oceanic variables were obtained in real time: ASSIST derived SST and air temperature, air temperature and humidity and barometric pressure from the weatherpak suite, downwelling short and long wave radiation from the Eppley radiometers, and the PWV and CLW from the microwave radiometer. The SST derived from ASSIST radiance measurements along the ship cruise track is shown in Figure 1. Figure 2 shows the time series of the SST and the air temperature derived from ASSIST during the cruise. The ASSIST SST measurements will submitted to the VIIRS (and MODIS) SST match-up database.



**Figure 5.** ASSIST measured sea surface temperature (SST) along the cruise track. The colors represent the skin SST, in K, as shown at right.



**Figure 6.** Time series of sea surface temperature (SST) and air temperature (Tair) measured by ASSIST during Ronald H. Brow cruise from San Diego, CA to Punta Arenas, Chile 2016/11/06 to 2017/02/01.

## 5.2 Surface Acoustic Doppler Current Profiler

Eric Firing (UH; PI) and Jules Hummon (UH, PI)

### Sampling

The Ronald H. Brown has a permanently mounted 75 kHz acoustic Doppler current profiler (“ADCP” Teledyne RDI) for measuring ocean velocity in the upper water column. The ADCP is a Phased Array instrument, capable of pinging in broadband mode (for higher resolution), narrowband mode (lower resolution, deeper penetration), or interleaved mode (alternating). On this cruise, data were collected with 8 m broadband pings and 16 m narrowband pings.

### Processing

Specialized software developed at the University of Hawaii has been installed on the Brown for the purpose of ADCP acquisition, preliminary processing, and figure generation during each cruise. The acquisition system ("UHDAS", University of Hawaii Data Acquisition System) acquires data from the ADCPs, gyro heading (for reliability), position and orientation systems for marine vessels (POSMV) headings (for increased accuracy), and GPS positions from various sensors. Single-ping ADCP data are automatically edited and combined with ancillary feeds, averaged, and disseminated via the ship's web, as regularly-updated figures on a web page and as Matlab and netCDF files.

## Data Quality

The POSMV on board the Ron Brown never worked very well, but in preparation for a mapping cruise in early 2016, they worked very hard to get the POSMV going. That has provided significant improvement to the ADCP data quality and we are grateful for their effort.

A glitch in the acquisition software resulted in a timestamping problem when, in leg 2, the year rolled over from 2016 to 2017. The bug resulted in data being timestamped as 2018, until (after several attempts) we figured out what the problem was. The underlying currents are not affected; the dates will be fixed in post-processing, and the segmented acquisition (multiple "cruise segments" as debugging proceeded) will be repaired at that time.

## Summary

Shipboard ADCP data were collected for the duration of P18N, Legs 1 and 2. Data range is typical, 600m-700m in general. There is some data corruption near the surface due to bubbles or ice, but that is not uncommon. The ADCP system and data were monitored remotely. There were no changes or errors noted, beyond the timestamping problem noted above. The automated at-sea product should be good enough for preliminary use, and the final dataset should be among the best to come from this ship.

## 5.3 Underway pCO<sub>2</sub> Analyses

PI's: Rik Wanninkhof (NOAA/AOML) and Denis Pierrot (UM/CIMAS)

Technicians: Robert Castle (NOAA/AOML), Charles Featherstone (NOAA/AOML), Kevin Sullivan (UM/CIMAS) and Andrew Collins (NOAA/PMEL)

An automated underway pCO<sub>2</sub> system from AOML was installed in the Hydro Lab of the RV Ronald H. Brown. The design of the instrumental system is based on Wanninkhof and Thoning (1993) and Feely et al. (1998), while the details of the instrument and of the data processing are described in Pierrot, et.al. (2009).

The repeating cycle of the system included 4 gas standards, 5 ambient air samples, and 100 headspace samples from its equilibrator every 4.5 hours. The concentrations of the standards range from 282 to 539 ppm CO<sub>2</sub> in compressed air. These field standards were calibrated with primary standards that are directly traceable to the WMO scale (Table 5.3.1). A gas cylinder of ultra-high purity air was used every 19 hours to set the zero of the analyzer.

The system included an equilibrator where approximately 0.6 liters of constantly refreshed surface seawater from the bow intake was equilibrated with 0.8 liters of gaseous headspace. The water flow rate through the equilibrator was 1.8 to 2.8 liters/min.

The equilibrator headspace was circulated through a non-dispersive infrared (IR) analyzer, a LI-COR™ 6262, at 50 to 120 ml/min and then returned to the equilibrator. When ambient air or standard gases were analyzed, the gas leaving the analyzer was vented to the lab. A KNF pump constantly pulled 6-8 liter/min of marine air through 100 m of 0.95 cm (= 3/8") OD Dekoron™ tubing from an intake on the bow mast. The intake had a rain guard and a filter of glass wool to prevent water and larger particles from contaminating the intake line and reaching the pump. The headspace gas and marine air were dried before flushing the IR analyzer.

A custom program developed using LabView™ controlled the system and graphically displayed the air and water results. The program recorded the output of the IR analyzer, the GPS position, water and gas flows, water and air temperatures, internal and external pressures, and a variety of other sensors. The program recorded all of these data for each analysis.

The automated pCO<sub>2</sub> analytical system had several issues during the cruise:

1. January 8-9 – emergency shutdown approx 11:15 local time; water in the EQU and ATM condensers; condensers along with chiller were dried out and system was restarted on January 9 at approx. 17:30 local time.
2. January 11 – cleaned filter.
3. January 19 – Error 6 occurred at approx. 7:00 local time; no communication with the wet box, one of the red cables was loose, after being tightened the system was restarted at approx. 9:00 local time.
4. January 25 – Error 6 occurred approx. 8:00 local time; no communication with the dry box, another red cable was loose, tightened cable and restarted system at approx. 10:35 local time.
5. January 26 – Air line was blocked, air line was disconnected at base of mast and the air flow was restored; the air line may have been frozen higher on the mast.

The system worked well for the remainder of the cruise. A total of 19 underway samples were collected (DIC, pH, Alkalinity, Nutrients and Oxygen) during the transit from Station 112 to Punta Arenas, Chile for comparison with the pCO<sub>2</sub> system.

**Table 5.3.1.** CO<sub>2</sub> standard cylinders used during the 2016/17 P18 cruise.

Cylinder#	ppm CO <sub>2</sub>
CA04957	282.6
CC05863	380.2
CB09696	453.0
CB09032	539.4

**References:**

Pierrot, D.; Neill, C.; Sullivan, K.; Castle, R.; Wanninkhof, R.; Luger, H.; Johannessen, T.; Olsen, A.; Feely, R.A.; and Cosca, C.E. (2009). *Recommendations for autonomous underway pCO<sub>2</sub> measuring systems and data-reduction routines*. Deep-Sea Res., II, v. 56, pp. 512-522.

Feely, R.A.; Wanninkhof, R.; Milburn, H.B.; Cosca, C.E.; Stapp, M.; and Murphy, P.P. (1998). *A new automated underway system for making high precision pCO<sub>2</sub> measurements onboard research ships*. *Analytica Chim. Acta*, v. 377, pp. 185-191.

Wanninkhof, R., and Thoning, K. (1993). *Measurement of fugacity of CO<sub>2</sub> in surface water using continuous and discrete sampling methods*. *Mar. Chem.*, v. 44, no. 2-4, pp. 189-205.

## 6 Conductivity Temperature Depth (CTD) Stations

### 6.1 Underwater Electronics Package

A Sea-Bird Electronics SBE9*plus* CTD was connected to a 24-place SBE32 carousel, providing for two-conductor sea cable operation. Two conducting wires in the 0.322 sea cable were soldered to their counterparts in the end termination: black for signal, and white for ground; the third (red) wire was cut back/unused. Power to the CTD and sensors, carousel and most instruments attached to the CTD was provided through the sea cable from an SBE11*plus* deck unit in the computer lab.

The CTD supplied a standard SBE-format data stream at a data rate of 24 Hz. The CTD provided pressure plus dual temperature, conductivity and dissolved oxygen channels. The CTD system also incorporated an altimeter, transmissometer, and fluorometer/backscatter (FLBB) sensor. A Lowered Acoustic Doppler Profiler (LADCP) and Chipods were also mounted on the rosette frame; both were powered separately and collected data internally.

The CTD system was outfitted with dual pumps. Primary temperature, conductivity and dissolved oxygen were plumbed into one pump circuit; and secondary temperature, conductivity and oxygen were plumbed into the other. The CTD and sensors were deployed vertically. The primary temperature and conductivity sensors were used for reported CTD temperatures and salinities on all casts. The secondary temperature and conductivity sensors were used as calibration checks.

**Table 6.1.1** Package component and calibration data

Manufacturer/Model	Serial No.	Calib.Date	Stations Used
Markey DESH-5 Winch	AFT	n/a	1-19,156-212
Electrical and Mechanical	FWD	n/a	20-155
Reterminations Before These Stations			116/2, 138, 156
Sea-Bird SBE11 <i>plus</i> Deck Unit	11P111660		1-212
Sea-Bird SBE32 Carousel Water Sampler	163	n/a	1-8
(24-place)	053	n/a	9-212
Sea-Bird SBE35RT Reference	0072	19-Sep-2016	1-10
Temperature	0076	28-Oct-2013	17, 27-212
Sea-Bird SBE9 <i>plus</i> CTD	0489	26-Sep-2016	1-26
Sea-Bird SBE9 <i>plus</i> CTD	1292	14-Sep-2016	27-212
<i>Primary Sea-Bird Sensors:</i>			
SBE3 <i>plus</i> Temperature (T1)	03-4569	30-Aug-2016	1-212
SBE4C Conductivity (C1)	04-3068	07-Sep-2016	1-128
	04-3157	31-Aug-2016	129-212
SBE43 Dissolved Oxygen	43-3419	02-Sep-2016	1-212
SBE5 Pump	05-8794	N/A	1-176
	05-8774	N/A	177-212
<i>Secondary Sea-Bird Sensors:</i>			
SBE3 <i>plus</i> Temperature (T2)	03P-4193	30-Aug-2016	1-10, 64-212
	03-1710	31-Aug-2016	11-63
SBE4C Conductivity Sensor (C2)	04-4600	31-Aug-2016	1-63
	04-4604	31-Aug-2016	64-128
	04-1467	07-Sep-2016	129-212
SBE43 Dissolved Oxygen	43-3420	10-Sep-2016	1-212
SBE5 Pump	05-8793	N/A	1-212
<i>Other Devices Connected to CTD:</i>			
Valeport VA500 Altimeter	56634	N/A	1-212
Manufacturer/Model	Serial No.	Calib.Date	Stations Used
WetLabs FLBBRTD	3698	23-Sep-2014	1, 27-212
WETLabs C-Star Transmissometer	CST-1803DR	16-Sep-2016	1-212
<i>Teledyne RDI WHM150-1-UG15 LADCP</i>			
150KHz Downlooker/Master	19394		1 – 204
150KHz Downlooker/Master	24544		204 - 212
300KHz Uplooker/Slave	12734		1 – 212

**Table 6.1.2** P18 Underwater Package Configuration

Chipod Serial Nos. (OSU-assembled - no fr)					
Up/Down Orientation	Logger Board	Pressure Case	Sensor	Sensor Holder	Stations Used
Up	1014	Ti44-8	14-24D	-	116-177
Up	2016	Ti44-1	14-25D	-	178-212
Up	1008	Ti44-5	14-28D	-	100-112
Up	2018	Ti44-3	11-25D	-	116-212
Down	2013	Ti44-7	14-263D	-	116-212

With the exception of 3 stations, all rosette casts were lowered to within 8-12 meters of the bottom using the altimeter on the CTD-rosette package. The three exceptions came early on leg 1 in regions of rough topography and before the altimeter and its communications were stable and trusted. These three exceptions were lowered to within 120 meters of the bottom according to the LADCP (but below the depth of read by the multibeam). Three sampling schema were used in rotation to stagger standard sampling depths for consecutive stations. There were occasional exceptions made to the order of the schema or to capture a feature in the water column. Occasionally, changing bottom depths countered the changes from the scheme rotation such that two adjacent stations had samples at similar depths over portions of the water column. Exceptions to the schema rotation were also made to prevent this from happening.

## 6.2 Discrete Niskin Sampling

At the end of each rosette deployment water samples were drawn from the bottles in the following order:

- Chlorofluorocarbons(CFCs) /N<sub>2</sub>O/SF<sub>6</sub>
- Helium isotopes and noble gases (Neon, Argon, Krypton, and Xenon)
- Dissolved O<sub>2</sub>
- Dissolved Inorganic Carbon (DIC)
- Total pH
- Total Alkalinity (TALK)
- Stable gases (N<sub>2</sub>, O<sub>2</sub>, Ar)
- N<sub>2</sub>O (measured on land)
- <sup>13</sup>C and <sup>14</sup>C of DIC
- Dissolved Organic Carbon / Total Dissolved Nitrogen (DOC/TDN)
- Tritium
- Nutrients
- Salinity
- Biomarkers
- Black Carbon/ DO<sup>14</sup>C/DO<sup>14</sup>C via pyrolysis/Incubations/HPLC/Genetics (Kolody and Martiny)/Dissolved Organics (Walker)

The sample order was not strictly enforced between DOC/TDN and Biomarkers inclusive. The items on the final bullet in this list typically used all remaining water and were never sampled from the same bottles as one another. N<sub>2</sub>O (measured on land) and dissolved gases were placed after TALK in the sampling order due to concerns over whether the sampler would be able to sample in a reasonable

timeframe given the numerous other samples this sampler was responsible for. Also there were redundancies in the N<sub>2</sub>O measurement. The order of the samples collected was verified at the time of collection by a designated "sample cop." The log kept by the sample cop noted any sampling problems, the temperature of the water as measured by the dissolved oxygen sampler, and any issues with the Niskins (e.g. leaky valves and lanyards caught in end-caps).

### 6.3 Bottle Data Processing

Water samples collected and properties analyzed shipboard were managed centrally through a new, Fortran-based bottle data management system (BDMS) developed by Dr. John Bullister at PMEL. The system was set up on a Fedora 24 Linux workstation with network access to the ship and shell scripts for pulling data and pushing summary HY1 files.

The CTDO data and bottle trip files were acquired by SBE SeaSave V7 version 7.23.0.2 on the ship's Windows 7 workstation. Pre-cruise calibration data were applied to CTD Pressure, Temperature and Conductivity sensor data acquired at full 24-Hz resolution. Bottles were closed on the upcast through the software, and were tripped 30 seconds after stopping at a bottle depth to allow the rosette wake to dissipate and the bottles to flush. The upcast continued 15 seconds after closing a bottle to ensure that stable CTD and reference temperature data were associated with the trip.

Sea-Bird Data Processing Version 7.23.0.2 software module BOTTLESUM averages burst data over an 8-second interval (+/- 4 seconds of the confirm bit) and derives both primary and secondary salinity, potential temperature ( $\theta$ ), and potential density anomaly ( $\sigma_\theta$ ). Primary and secondary oxygen (in  $\mu\text{mol/kg}$ ) were derived in DATCNV and averaged in BOTTLESUM, as recommended by Sea-Bird.

Once the rosette was sampled, sample quality flags (1 = sampled or 9 = not sampled) plus comments were recorded for every parameter from the scanned sample logsheets. Approximately daily, the BDMS was updated, combining all available CTD bottle data and analytical data (with their associated quality flags). Quality flags follow the coding scheme developed for the World Ocean Circulation Experiment (WOCE) Hydrographic Programme (WHP, Table 6.4.3).

Various consistency checks and detailed examination of the data continued throughout the cruise. A summary of Cast Log and Sample Log comments, mis-trips, bottle lanyard issues and associated quality codes can be found in Appendix 1.

## 6.4 Collected Samples

**Table 6.4.1.** P18 Samples collected and analyzed aboard, or stored for shore-based analysis

Samples analyzed on-board	Samples collected (not analyzed at sea)
Chlorofluorocarbons(CFCs)/SF <sub>6</sub> /N <sub>2</sub> O	<sup>3</sup> He / Neon / Tritium
Dissolved O <sub>2</sub>	<sup>13</sup> C / <sup>14</sup> C-DIC
Total CO <sub>2</sub> (DIC)	DOC / TDN
Total Alkalinity/pH	DO <sup>14</sup> C / Black Carbon/Biomarkers/
Nutrients	Dissolved Organics (Walker)
Salinity	HPLC / POC
	Dissolved Gases
	N <sub>2</sub> O concentrations, stable isotopes and isotopomers (shore measurement)
	NO <sub>3</sub> and NO <sub>2</sub> <sup>-</sup> stable isotopes
	H <sub>2</sub> O isotopes
	Genetics (iTag)
	Genetics (Martiny)
	DO <sup>14</sup> C via Pyrolysis

**Table 6.4.2.** Summary of samples collected, and their associated quality flags, for the suite of GO-SHIP core measurements during P18.

parameter	flag					
	1	2,6	3	4	5	9
CTDSAL	0	5147	0	0	0	0
SALNTY	0	5099	0	0	0	48
CTDOXY	0	5147	0	0	0	0
OXYGEN	36	4837	178	30	4	61
SILCAT	81	5051	2	2	0	11
NITRAT	81	5051	2	2	0	11
NITRIT	81	5051	2	2	0	11
PHSPHT	81	5051	2	2	0	11
CFC-11	16	3726	11	32	0	1362
CFC-12	16	3726	11	32	0	1362
SF6	16	3722	15	32	0	1362
CCL4	16	3725	12	32	0	1362
N2O	3746	0	0	0	0	1401
TCARBN	3	4855	13	35	1	240
ALKALI	7	4808	46	29	5	252
PH_SWS	3	4879	32	17	1	215

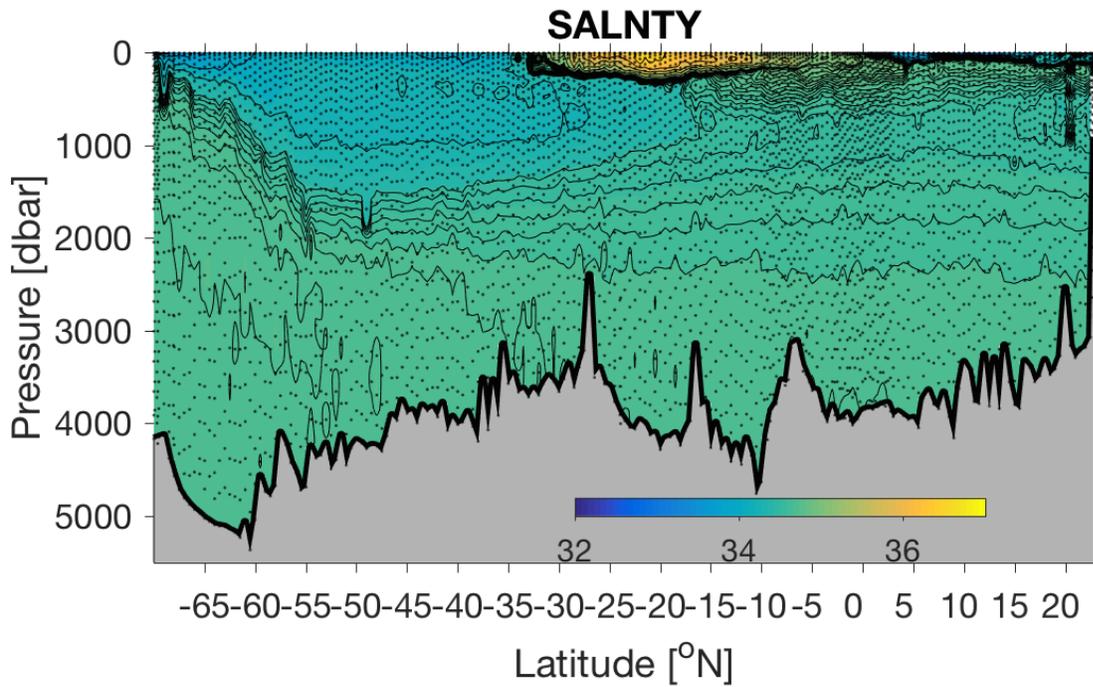
**Table 6.4.3.** GO-SHIP quality flag key.

Flag	Key
1	collected, not reported
2	good
3	questionable
4	bad analysis or sample
5	sample lost
6	average of replicate values
9	sample not collected

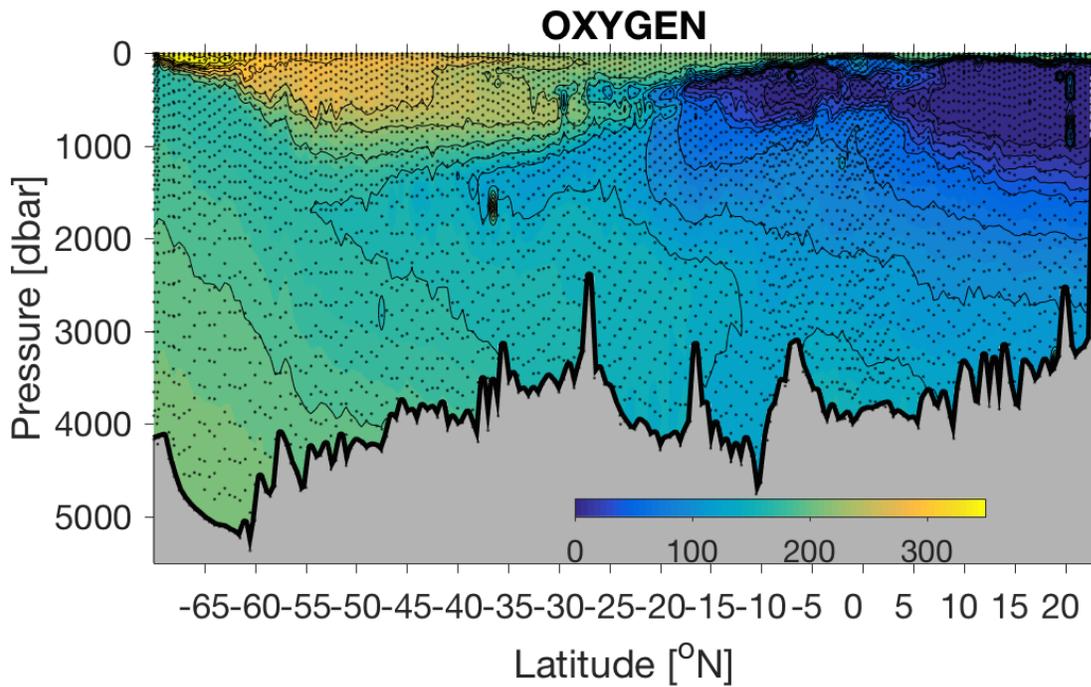
## **7 Ship-Board Analysis Sections**

### **7.1 Figures of ship-board analyses during P18**

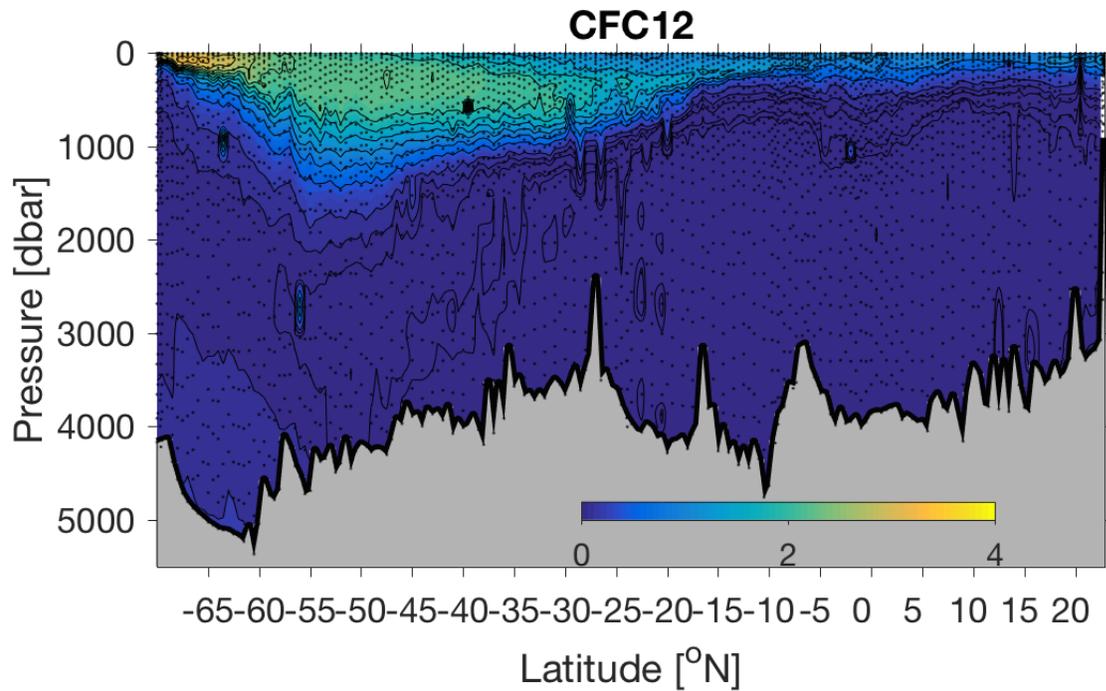
The following are gridded latitude-depth sections of bottle samples collected and analyzed during P18.



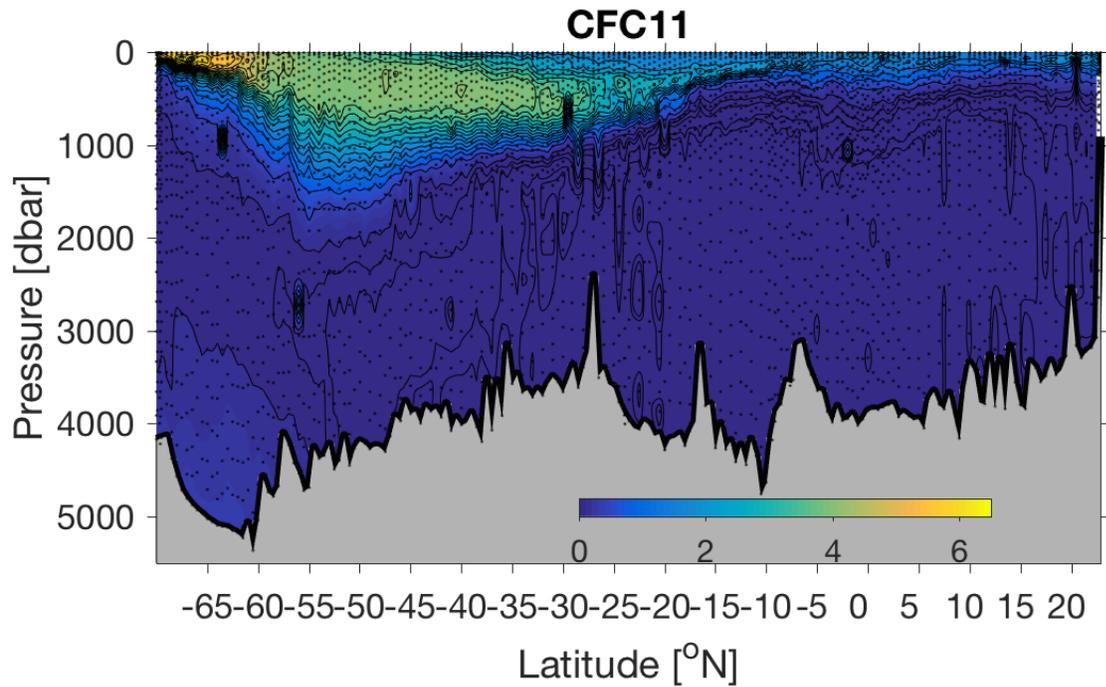
**Figure 7a.** The meridional – depth distribution of salinity along the 2016/17 P18 line in the South Pacific Ocean.



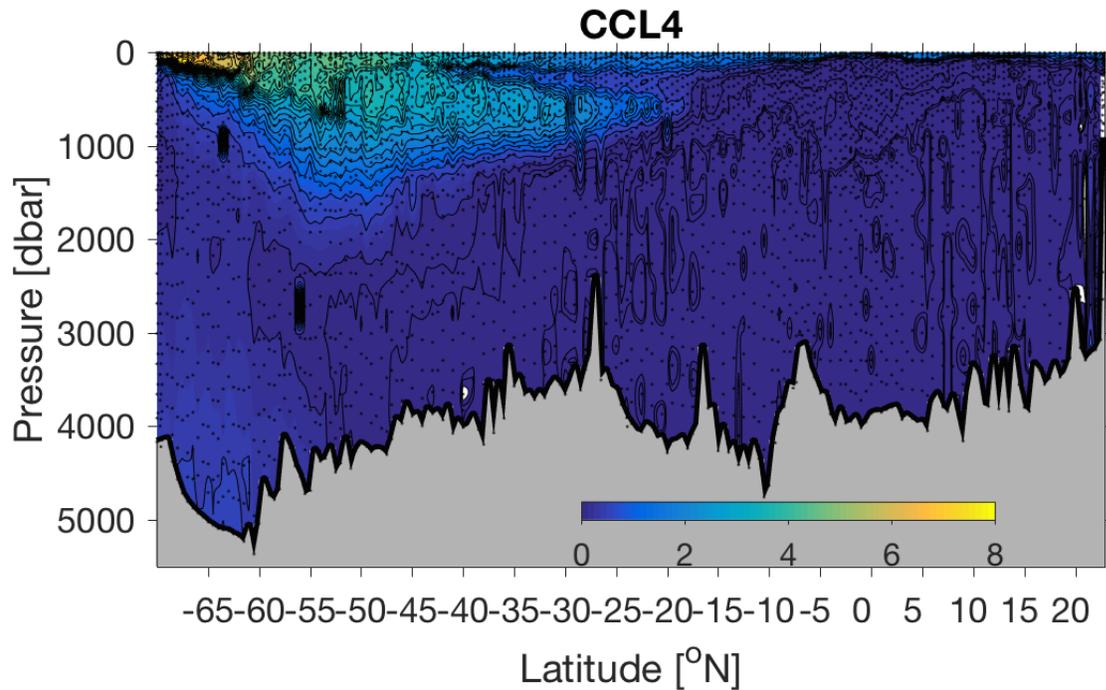
**Figure 7b.** The meridional – depth distribution of dissolved oxygen ( $\mu\text{mol kg}^{-1}$ ) along the 2016/17 P18 line.



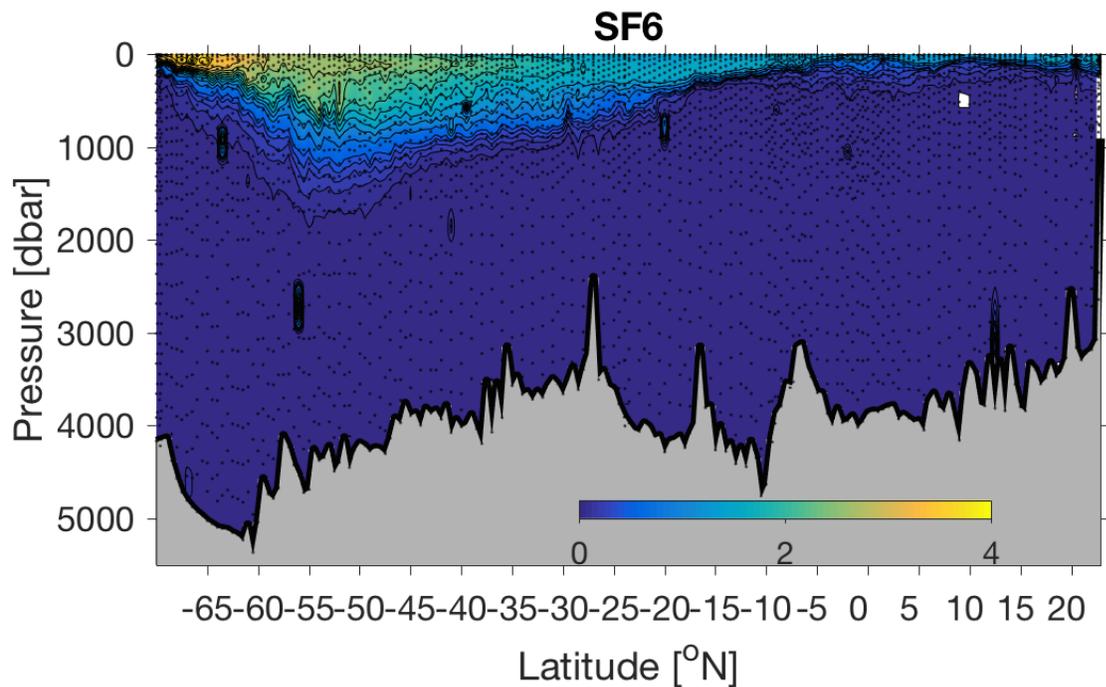
**Figure 7c.** The meridional – depth distribution of dissolved CFC-12 ( $\text{pmol kg}^{-1}$ ) along the 2016/17 P18 line in the South Pacific Ocean.



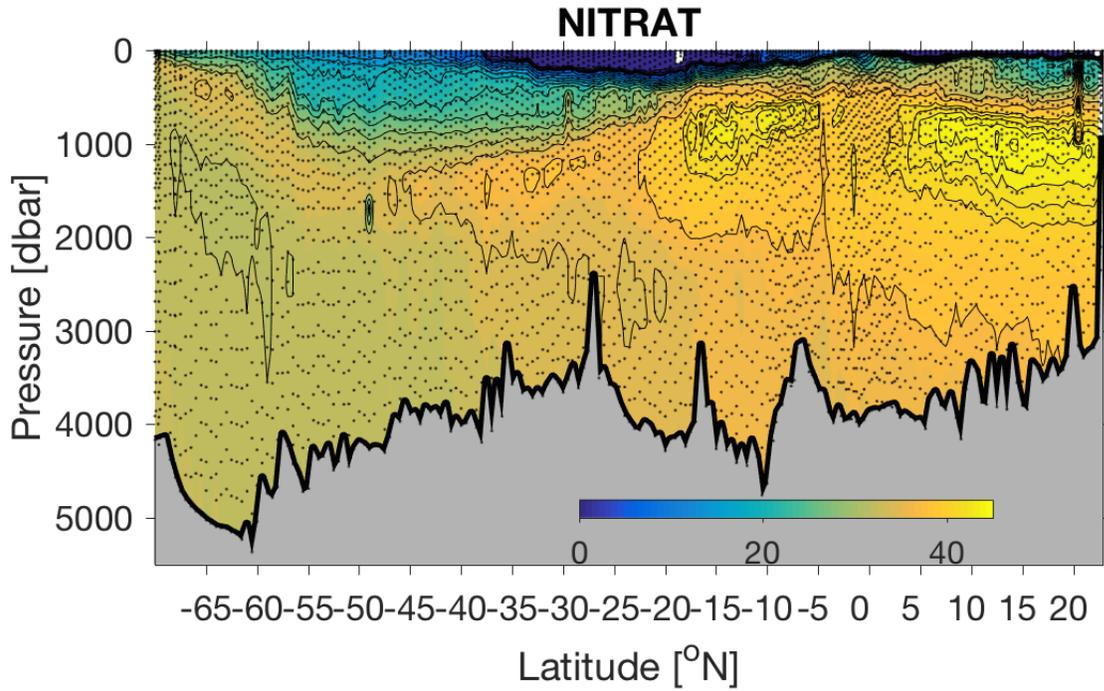
**Figure 7d.** The meridional – depth distribution of dissolved CFC-11 ( $\text{pmol kg}^{-1}$ ) along the 2016/17 P18 line in the South Pacific Ocean.



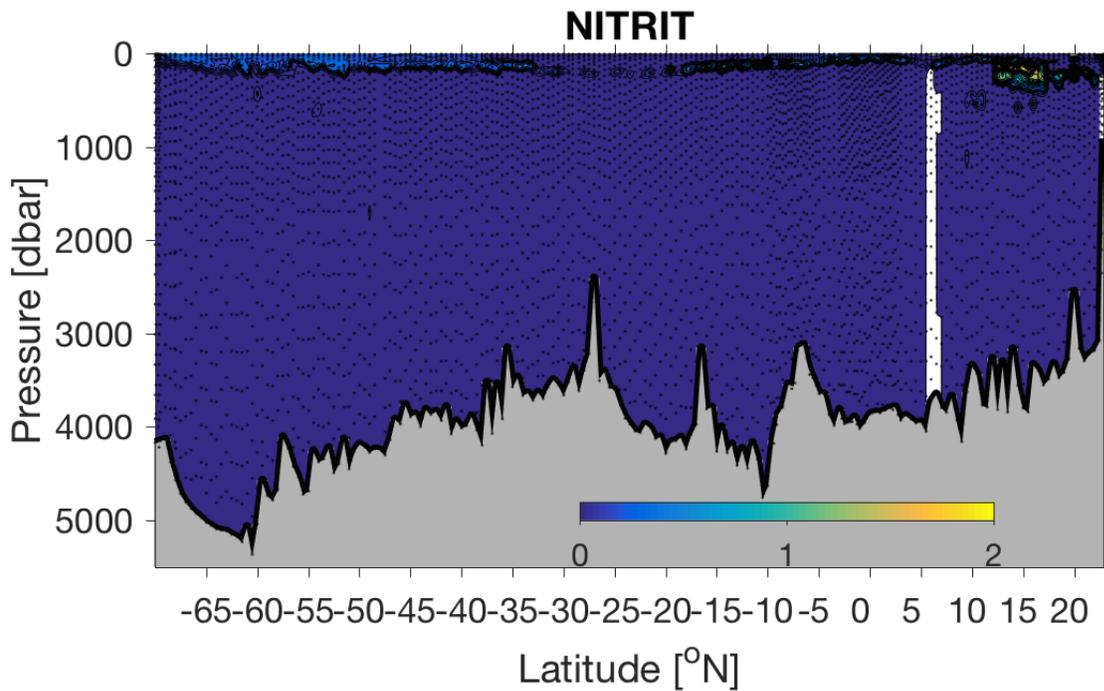
**Figure 7e.** The meridional – depth distribution of dissolved CCL<sub>4</sub> (pmol kg<sup>-1</sup>) along the 2016/17 P18 line in the South Pacific Ocean.



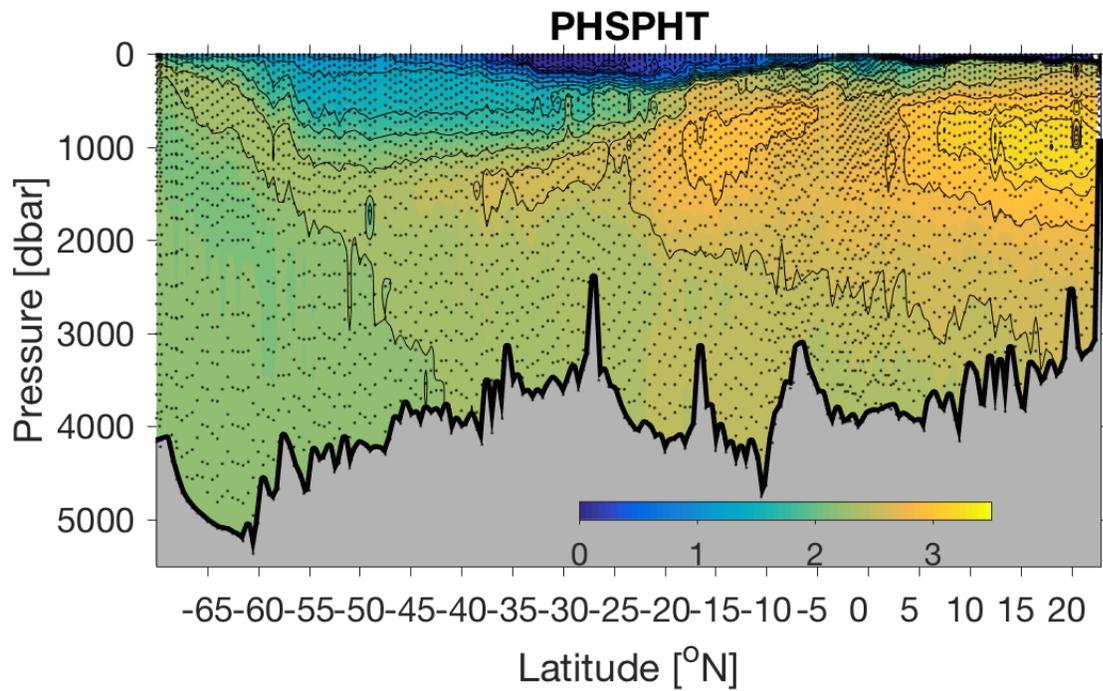
**Figure 7f.** The meridional – depth distribution of dissolved sulfur hexafluoride (fmol kg<sup>-1</sup>) along the 2016/17 P18 line in the South Pacific Ocean.



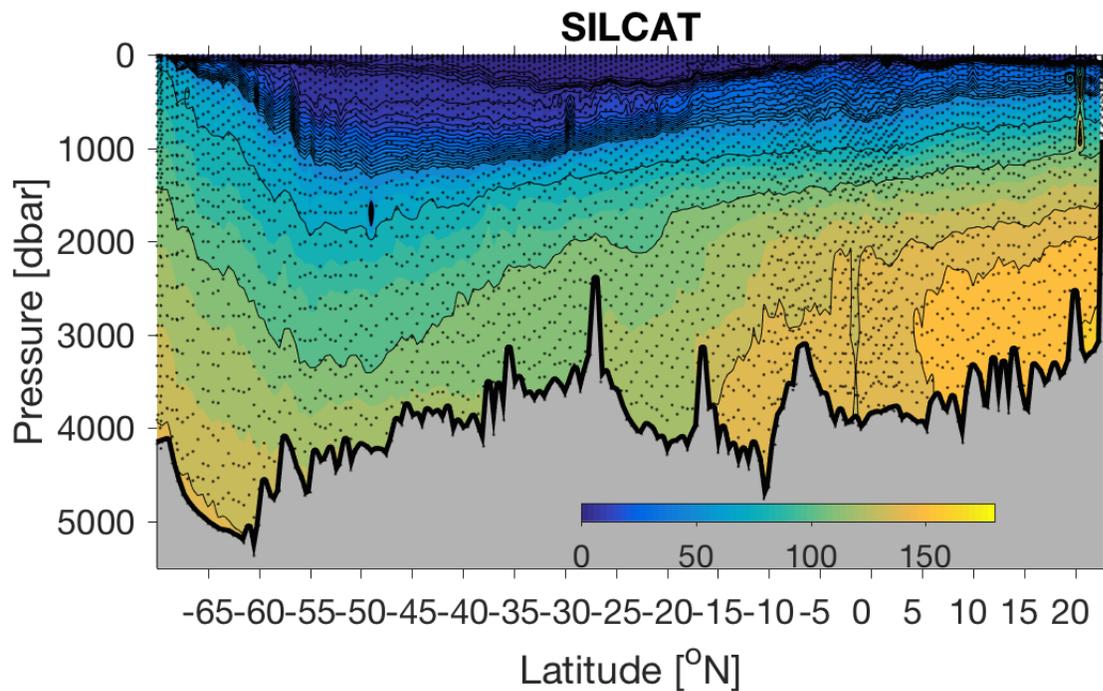
**Figure 7g.** The meridional – depth distribution of dissolved nitrate ( $\mu\text{mol kg}^{-1}$ ) along the 2016/17 P18 line in the South Pacific Ocean.



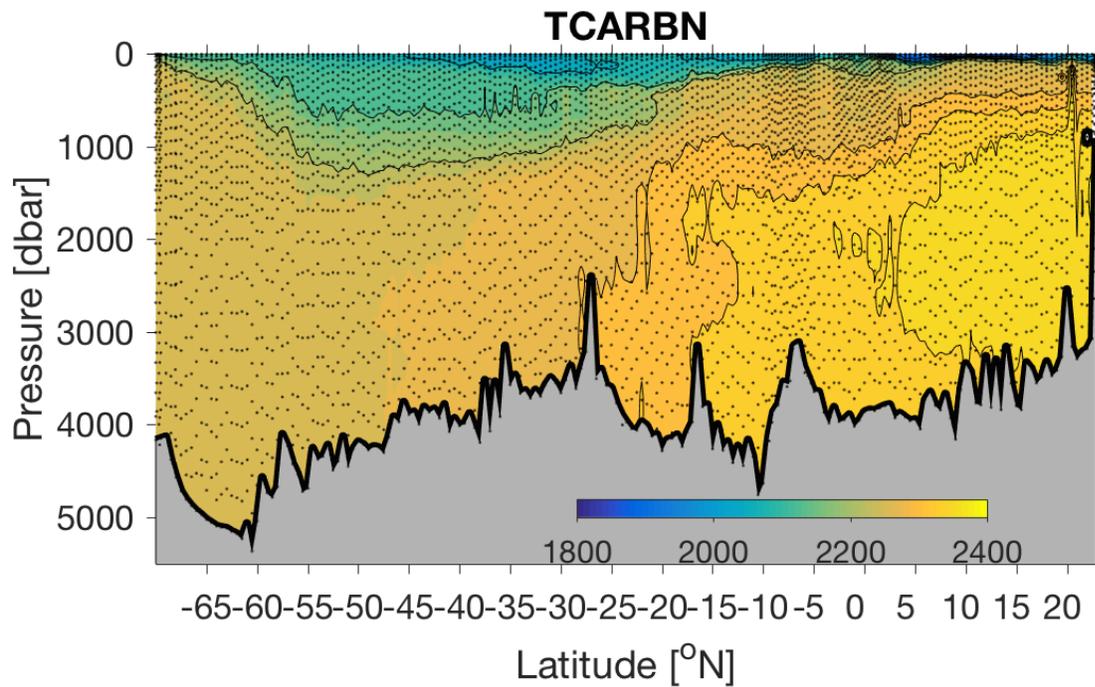
**Figure 7h.** The meridional – depth distribution of dissolved nitrite ( $\mu\text{mol kg}^{-1}$ ) along the 2016/17 P18 line in the South Pacific Ocean.



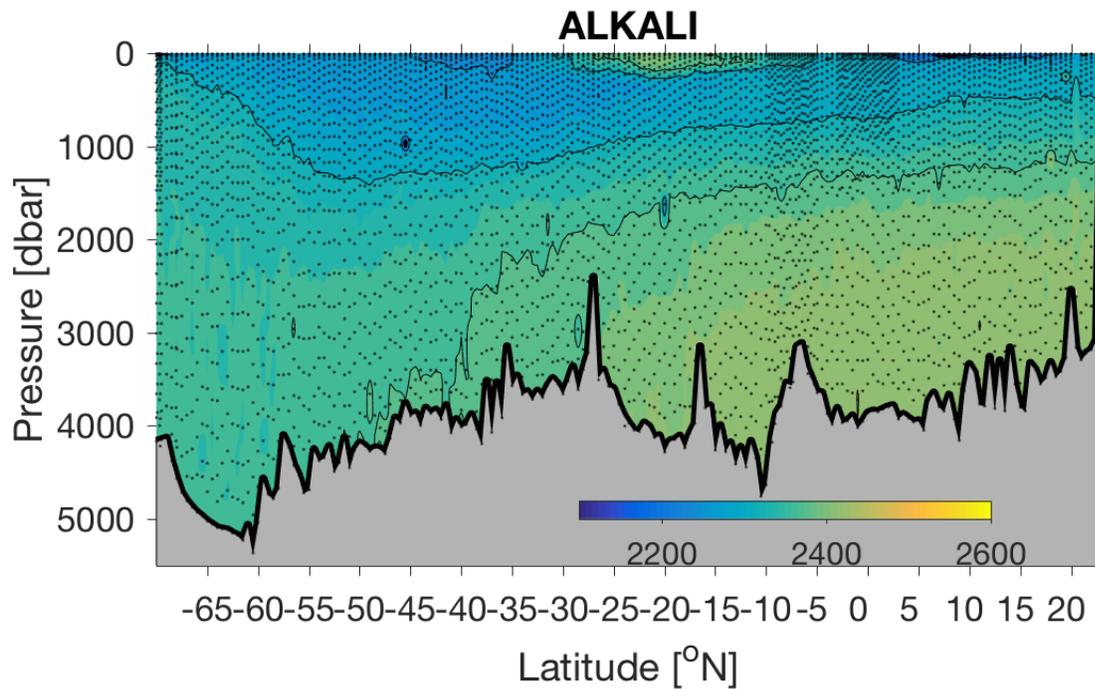
**Figure 7i.** The meridional – depth distribution of dissolved phosphate ( $\mu\text{mol kg}^{-1}$ ) along the 2016/17 P18 line in the South Pacific Ocean.



**Figure 7j.** The meridional – depth distribution of dissolved silicate ( $\mu\text{mol kg}^{-1}$ ) along the 2016/17 P18 line in the South Pacific Ocean.



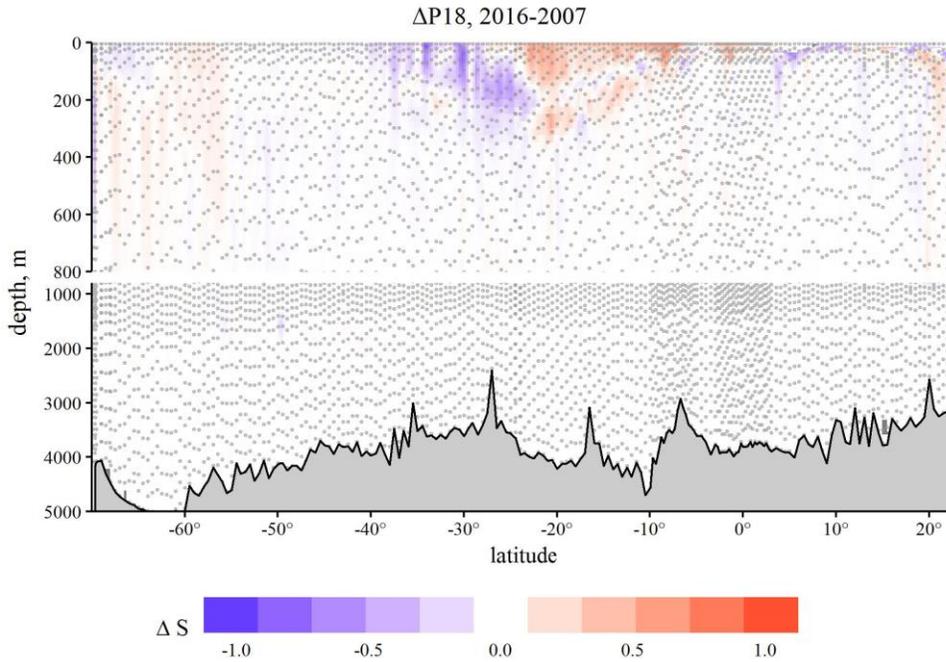
**Figure 7k.** The meridional – depth distribution of dissolved inorganic carbon ( $\mu\text{mol kg}^{-1}$ ) along the 2016/17 P18 line in the South Pacific Ocean.



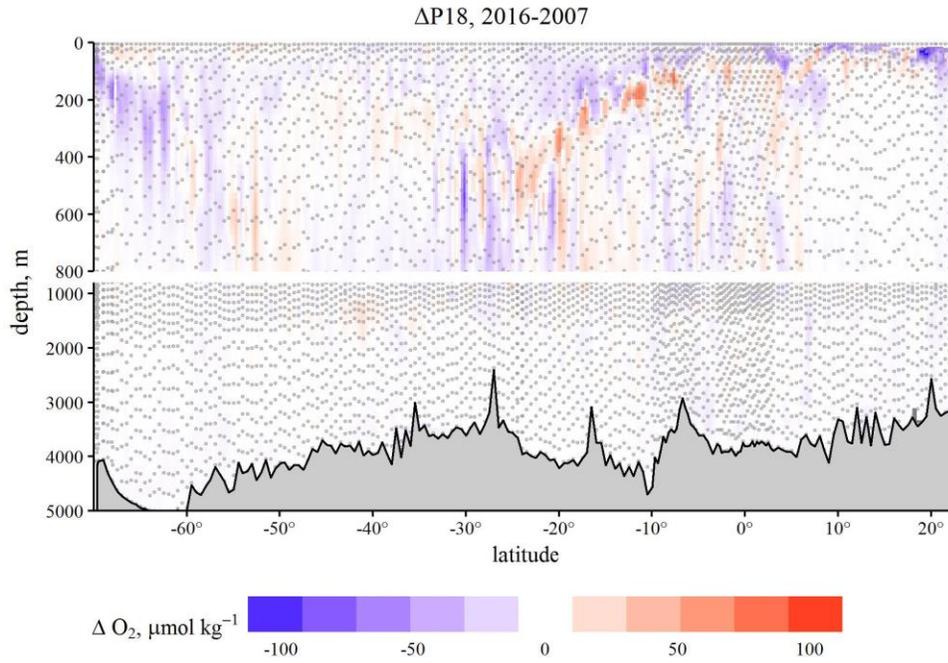
**Figure 7l.** The meridional – depth distribution of alkalinity ( $\mu\text{mol kg}^{-1}$ ) along the 2016/17 P18 line in the South Pacific Ocean.

## 7.2 Changes in Ship-Board Properties Since 2007/8

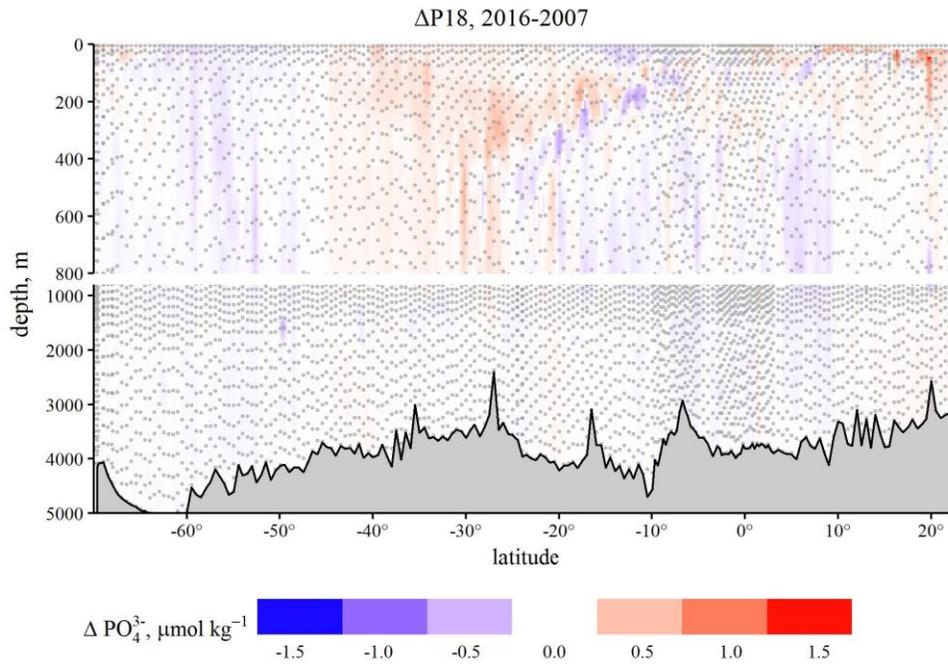
Section difference plots between the current and previous 2007 P18 occupation were created for each variable by a series of 1-dimensional interpolations. First, data from both cruises were linearly interpolated across density by station, then interpolated across latitude by density, resulting in an evenly-spaced grid of interpolated values. The density and latitude data for each cruise were inner-joined in succession on the two datasets, retaining the interpolated density x latitude grid values common between both cruises. After subtracting the older 2007 occupation from the current 2016 one, the difference grid was then interpolated back to depth based on the 2016 occupation's density-depth-latitude values. Data were processed and visualized in R v3.3.2 with the data.table v1.10.0, marelac v2.1.6, seacarb v3.1.1, and ggplot2 v2.2.1 packages.



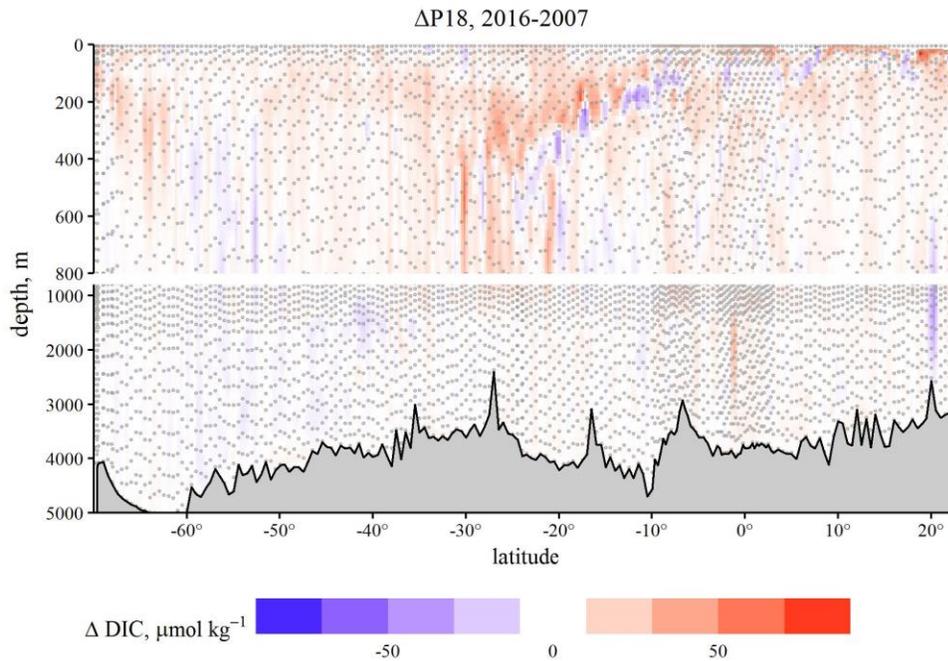
**Figure 8a.** The 2007/8 to 2016/17 change in Salinity along the P18 line.



**Figure 8b.** The 2007/8 to 2016/17 change in dissolved oxygen ( $\mu\text{mol kg}^{-1}$ ) along the P18 line.



**Figure 8c.** The 2007/8 to 2016/17 change in dissolved Phosphate ( $\mu\text{mol kg}^{-1}$ ) along the P18 line.



**Figure 8e.** The 2007/8 to 2016/17 change in dissolved inorganic carbon ( $\mu\text{mol kg}^{-1}$ ) along the P18 line.

## Collected Samples

# 8 Individual Sub-project reports

## 8.1 Deployments

**Table 8.1.1.** Summary of floats deployed during P18 2016/2017.

Floats Type	Serial #	Station	Lat °N	Lat 'N	Lon °W	Lon 'W GMT	Date and Time	Deployers
1 McNeil		15	16	59.987	110	0.057	11/27/2016 18:22	AbBcb
2 PROVOR	OIN14ENS409	19	14	59.826	110	0.0204	11/28/2016 19:20	AbBcb
3 PROVOR	OIN14ENS410	23	13	0.135	109	59.971	11/29/2016 23:41	BcBcb
4 SOS	12384	39	4	59.487	110	0	12/03/2016 23:11	BeApBc
5 SOS	12365	71	-5	-0.138	109	59.934	12/10/2016 15:43	JgAp
6 PMEL	711	88	-9	-59.96	102	59.88	12/14/2016 15:14	KmJhJg
7 PMEL	717	93	-12	-30.1965	103	0.0215	12/15/2016 22:25	KmJhAp
8 PMEL	722	98	-15	-0.1487	103	0.0251	12/17/2016 04:13	KmJhAp

9 PMEL	723	103	-17	-30.31	103	0.018	12/18/2016 07:23	KmJhJg
10 PMEL	724	108	-20	-0.3005	102	59.9667	12/19/2016 15:01	KmBcApJg
11 PMEL	725	113	-22	-30.0591	103	0.0019	12/20/2016 20:43	KmJhAp
12 SOS	12385	118	-25	-00.7025	101	29.991	01/01/2017 18:40	PlJhSpKm
13 PMEL	726	123	-27	-29.99	101	30.058	01/02/2017 22:12	PlRoKm
14 APEX SOCCOM	9766	128	-30	-00.822	102	59.959	01/04/2017 05:43	JhRsKmSp
15 PMEL	727	132	-32	-00.0969	103	00.0066	01/05/2017 07:36	SpJh
16 PMEL	733	135	-33	-30.149	102	59.965	01/05/2017 20:09	KmPlRo
17 APEX SOCCOM	9659	138	-35	-00.622	103	00.004	01/06/2017 19:40	KmRsRoPl
18 SOS	12383	143	-37	-30.509	102	59.902	01/08/2017 00:48	KmPlRo
19 APEX SOCCOM	9642	146	-39	-00.555	103	00.063	01/08/2017 19:41	KmPlRoRs
20 PMEL	737	154	-43	-00.10	103	00.05	01/10/2017 23:56	KmPlRo
21 APEX SOCCOM	12382	158	-45	-00.540	103	00.033	02/12/2017 02:04	KmPlRo
22 SOS	32173	163	-47	-30.537	102	59.938	01/13/2017 09:40	JhSpEw
23 PMEL	742	165	-48	-29.810	103	00.092	01/13/2017 22:36	KmPlRs
24 PMEL	740	168	-50	-00.019	103	00.366	01/14/2017 23:25	PlKmRo
25 APEX SOCCOM	12552	170	-51	-00.578	103	00.004	01/15/2017 09:30	JhSpEw
26 PMEL	739	174	-53	-00.0345	103	00.282	01/16/2017 14:28	SpJh
27 SOS	12395	181	-56	-30.6305	102	59.889	01/18/2017 13:26	SpJhEw
28 APEX SOCCOM	9750	186	-59	-08.844	102	59.922	01/20/2017 02:20	PlKmRo
29 APEX SOCCOM	8501	202	-67	-00.545	103	00.285	01/25/2017 17:30	PlKmRo

Deployers: Ab=Annie Bourbonnais, Bcb=Bruce Cowden (Bosun), Bc=Brendan Carter, Ap=Alyssa Pourmonir(Survey), Jg=Josh Gunter(Survey), Km=Kristy McTaggart, Jh=James Hooper, Be=Brian Elliott(Ops), Rs=Rolf Sonnerup, Sp = Sarah Purkey, Ro = Remy Okazaki, Pl=Paige Logan, Ew=Eric Wisegarver

SOS float #12365 was deployed by dropping the float overboard.

**Table 8.1.2.** Summary of Drifters deployed during P18 2016/17.

Drifters	SN	Station	Lat °N	Lat 'N	Lon °E	Lon 'E	Date and Time GMT
1	300234064706600	11	18	59.64	-109	-59.98	11/26/2016 18:53
2	300234064704760	21	13	59.863	-110	-00.059	11/29/2016 11:29
3	300234064705600	43	2	59.5645	-109	-59.991	12/04/2016 22:13
4	300234064704680	51	0	59.843	-110	-00.03	12/06/2016 11:33
5	300234064705660*	63	-2	-59.984	-109	-59.984	12/08/2016 22:21
6	300234064705690	74	-5	-00.138	-109	-59.934	12/10/2016 15:37
7	300234064706580	82	-8	-14.0553	-105	-28.09	12/13/2016 04:40
8	300234064705700	90	-11	-00.012	-102	-59.998	12/15/2016 04:11
9	300234064705740	94	-13	-00.158	-103	-00.022	12/16/2016 04:49
10	300234064705650	98	-15	-00.1071	-103	-00.0067	12/17/2016 04:11
11	300234064706750	122	-27	00.000	-101	-05.00	01/02/2017 16:38

12	300234064706690	128	-30	-00.0440	-103	-00.008	01/04/2017 05:28
13	300234064706700	138	-35	-00.0895	-102	-59.999	01/06/2017 19:31
14	300234064708590	144	-38	-00.0290	-103	-00.013	01/08/2017 06:59
15	300234064706740	158	-45	-00.3500	-103	-00.036	01/12/2017 01:56
16	300234064707590	162	-47	-00.1570	-103	-00.052	01/13/2017 03:21
17	300234064707610	174	-53	-00.2300	-103	-00.26	01/16/2017 14:33
18	300234064706630	178	-55	-00.0000	-102	59.965	01/17/2017 12:35
19	300234064707630	182	-57	-00.0450	-103	-00.121	01/18/2017 19:48
20	300234064707730	186	-58	-59.9820	-102	-59.028	01/20/2017 01:15

Drifter 300234064705660 was deployed with the protective cardboard removed.

## 8.2 Discrete Salinity Sampling

James Hooper, University of Miami

Andy Stefanick, AOML

Paige Logan, University of Washington

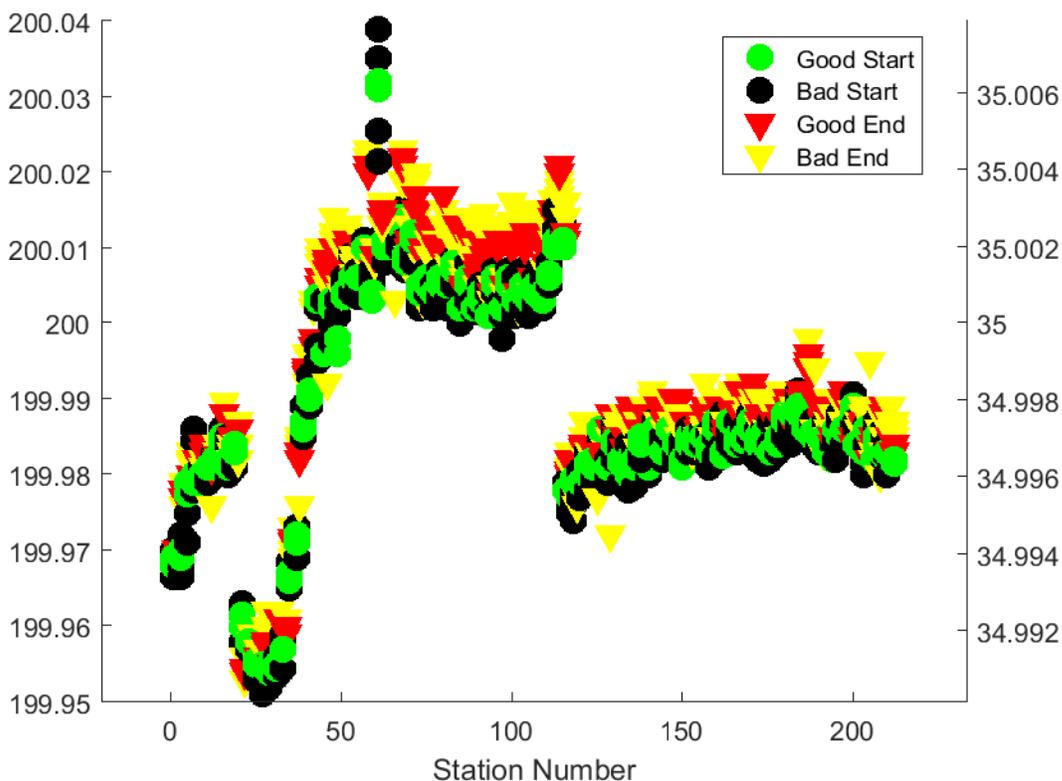
A single Guildline Autosol, model 8400B salinometers (S/N 60843, nicknamed Joysey and S/N 61664, nicknamed Miller Freeman), located in the Brown's temperature-controlled salinity analysis room, were used for all salinity measurements. The autosals were recently calibrated (9/2016) before the P18 cruise. The salinometer readings were logged on a computer using Ocean Scientific International's logging hardware and software. The Autosol's water bath temperature was set to 24°C, which the Autosol is designed to automatically maintain. The laboratory's temperature was also set and maintained to just below 24°C, to help further stabilize reading values and improve accuracy. Salinity analyses were performed after samples had equilibrated to laboratory temperature at least 12 hours after collection and at least 18 hours in colder waters. The salinometer was standardized for each group of samples analyzed (usually 2 casts and up to 52 samples) using two bottles of standard seawater: one at the beginning and end of each set of measurements. The salinometer output was logged to a computer file. The software prompted the analyst to flush the instrument's cell and change samples when appropriate. Prior to each run a sub-standard flush, approximately 200 ml, of the conductivity cell was conducted to flush out the DI water used in between runs. For each calibration standard, the salinometer cell was initially flushed 6 times before a set of conductivity ratio readings were taken. For each sample, the salinometer cell was initially flushed at least 3 times before a set of conductivity ratio readings were taken. After each run the autosal conductivity cell was flushed with approximately 200 ml of a triton-DI water solution and then rinsed and stored with DI water until the net run.

IAPSO Standard Seawater Batch P-159 was used to standardize all casts.

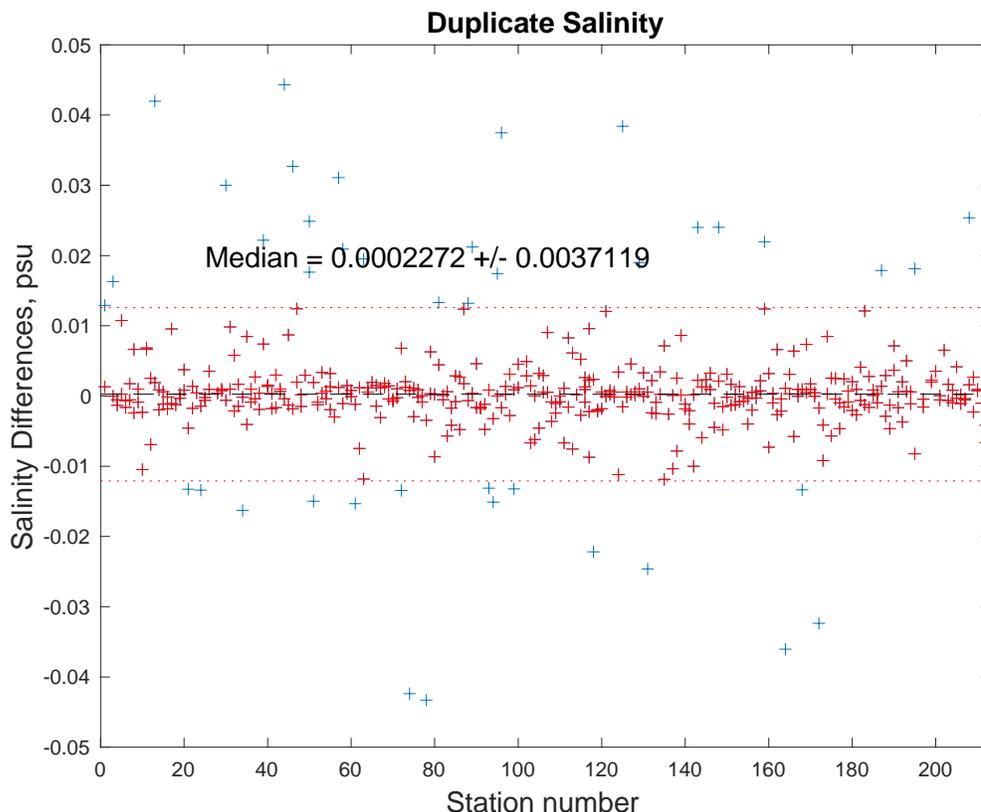
The salinity samples were collected in 200 ml Kimax high-alumina borosilicate bottles that had been rinsed at least three times with sample water prior to filling. The bottles were sealed with custom-made plastic insert thimbles and Nalgene screw caps. This assembly provides very low container dissolution and sample evaporation. Prior to sample collection, inserts were inspected for proper fit and loose inserts replaced to insure an airtight seal. PSS-78 salinity [UNES81] was calculated for each sample from the measured conductivity ratios. The offset between the initial standard seawater value and its reference value was applied to each sample. Then the difference (if any) between the initial and final vials of standard seawater was applied to each sample as a linear function of elapsed run time. The corrected

salinity data were then incorporated into the cruise database. When duplicate measurements were deemed to have been collected and run properly, they were averaged and submitted with a quality flag of 6. On P18, 5508 salinity measurements were taken, including 409 duplicates, and approximately 220 vials of standard seawater (SSW) were used. Up to two duplicate samples, one for shallow casts, were drawn from each cast to determine total analytical precision.

Joysey was used for stations 1-4 and 35-115. Miller Freeman was used for stations 5-34 and all of leg 2, stations 116-212. The Miller Freeman was set up as the primary autosal. However, during leg 1, troubleshooting issues required switching to Joysey to continue salinity sample runs. There were bad seals around the tubing connections of the conductivity cells of the Miller Freeman that required the initial switch to Joysey for stations 1-4. A shift in the standard water readings on the Miller Freeman from stations 25-34 resulted in finishing the rest of leg 1 on Joysey. It was determined that the standardization dial on the Miller Freeman had accidentally been turned causing the low readings. It was re-standardized before use on leg 2. The standard calibration values and duplicates are below in Figure 9 and Figure 10. The duplicates taken during the cruise showed a median precision of 0.0002 +/- 0.003 psu.



**Figure 9.** Standard vial calibrations during the P18 cruise.



**Figure 10.** Salinity duplicates during the P18 cruise.

### 8.3 $\text{NO}_3^-$ isotopes on leg 2

*François Fripiat and Gerald Haug, Max Planck Institute for Chemistry, Germany, f.fripiat@mpic.de*

Samples for N and O isotopes in nitrate ( $\text{NO}_3^-$ ) and nitrate+nitrite ( $\text{NO}_3^- + \text{NO}_2^-$ ) analysis were collected at 47 stations during leg 2, roughly evenly distributed along the transect (every 1-degree latitude). We collected the full water column profiles. In total, approximately 1128 samples were collected for N and O isotopes analysis. Our main interest will be in the calibration of this proxy for paleoceanographic purposes and to better understand what are the processes controlling the partitioning of nitrogen along with the meridional overturning circulation.

Unfiltered samples for N and O isotopic composition of  $\text{NO}_3^-$  were collected in 60 mL plastic bottles and stored frozen ( $-20^\circ\text{C}$ ) until analysis.

$\text{NO}_3^- + \text{NO}_2^-$   $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  will be measured at the Max Planck Institute using the denitrifier method (Sigman et al., 2001; Casciotti et al., 2002). Briefly, 10-20 nmol of  $\text{NO}_3^- + \text{NO}_2^-$  is quantitatively converted to  $\text{N}_2\text{O}$  gas by denitrifying bacteria (*Pseudomonas Aureofaciens*) that lack an active  $\text{N}_2\text{O}$  reductase. The  $\text{N}_2\text{O}$  is then analysed by gas chromatography-isotope ratio mass spectrometer (GC-IRMS; MAT253, Thermo) with on-line cryo-trapping (Weigand et al., 2016). Measurements were referenced to air  $\text{N}_2$  for

$\delta^{15}\text{N}$  and VSMOW for  $\delta^{18}\text{O}$  using the nitrate reference materials IAEA-NO<sub>3</sub> and USGS-34. For NO<sub>3</sub><sup>-</sup>  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  analysis, NO<sub>2</sub><sup>-</sup> is removed with the sulfamic acid method prior to the isotopic analysis (Granger and Sigman, 2009). The reproducibility is generally better than 0.1 and 0.2‰ for  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$ , respectively.

## References:

- Casciotti, K.L., D.M. Sigman, M. Galanter Hastings, J.K. Böhlke, and A. Hilkert. 2002. Measurement of the oxygen isotopic composition of nitrate in seawater and freshwater using the denitrifier method. *Anal. Chem.* 74: 4905-4912.
- Granger, J., and D.M. Sigman. 2009. Removal of nitrite with sulfamic acid for nitrate N and O isotope analysis with the denitrifier method. *Rapid Commun. Mass Spectrom.* 23: 3753-3762, doi:10.1002/rcm.4307.
- Sigman, D.M., K.L. Casciotti, M. Andreani, C. Barford, M. Galanter, and J.K. Böhlke. 2001. A bacterial method for the nitrogen isotopic analysis of nitrate in seawater and freshwater. *Anal. Chem.* 73: 4145-4153.
- Weigand, M.A., J. Foriel, B. Barnett, S. Oleynik, and D.M. Sigman. 2016. Updates to instrumentation and protocols for isotopic analysis of nitrate by the denitrifier method. *Rapid Commun. Mass Spectrom.* 30: 1365-1383.

## 8.4 NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> isotopes leg 1, dissolved gases (O<sub>2</sub>, N<sub>2</sub>, Ar, and N<sub>2</sub>O), N<sub>2</sub>O Isotopomers

PI: Annie Bourbonnais

Samplers: Annie Bourbonnais (leg 1), Alexander Sidelev and Sarah Purkey (leg 2, N<sub>2</sub>O isotopomers only)

### NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> isotopes

Samples for dissolved nitrogen isotope (NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup>) analysis were collected at 51 stations during leg 1 roughly evenly distributed along the transects (every ~2 degrees latitude), except near the equator between 3°N and 3°S where the resolution was increased to ~1 degree. On leg 1, we collected water column profiles (maximum 2000 m depth) at every other station and full profiles at all other stations for NO<sub>3</sub><sup>-</sup> isotope samples. NO<sub>2</sub><sup>-</sup> isotope samples were collected between 100 and 500 m depth from 22.7°N and 8.5°N, where NO<sub>2</sub><sup>-</sup> significantly accumulated in the Mexican oxygen deficient zone and between 0 and 150 m depth from 8.5°N and 19°S based on its distribution during the previous P18 2007/2008 occupation. Full profiles were also collected at shallow stations. In total, approximately 1100 and 300 samples have been collected for NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> isotope analysis, respectively, during leg 1.

Samples for N and O isotopic composition of NO<sub>3</sub><sup>-</sup> were collected in 60 mL plastic bottles and acidified for preservation (0.5 mL of 2.5 mM sulfamic acid in 25% HCl) which also served to remove NO<sub>2</sub><sup>-</sup> at the time of sample collection. For NO<sub>2</sub><sup>-</sup> isotopic analysis, samples were collected and preserved with NaOH (1 mL of 6M NaOH, pH=12.5) to prevent oxygen isotope exchange with water during storage.

The stable isotopic compositions ( $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$ ) of NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> will be analyzed onshore in Dr. Altabet's laboratory at the University of Massachusetts (UMass) Dartmouth using the "bacteria method" (Sigman et al., 2001; Casciotti et al., 2002) and the "azide method" (McIlvin and Altabet, 2005). For NO<sub>3</sub><sup>-</sup> isotopic analysis, NO<sub>3</sub><sup>-</sup> will be quantitatively converted to N<sub>2</sub>O by cultured denitrifying bacteria that lack the active N<sub>2</sub>O-reductase enzyme (*Pseudomonas chlororaphis*, ATCC #13985) (Casciotti et al., 2002).

For  $\text{NO}_2^-$  isotopic analysis,  $\text{NO}_2^-$  will be converted to nitrous oxide ( $\text{N}_2\text{O}$ ) using sodium azide in acetic acid.  $\text{N}_2\text{O}$  gas will be automatically extracted, purified, and analyzed on-line using a purge-trap preparation system coupled to an IsoPrime CF-IRMS. Standard sample size is generally 20 nmol  $\text{N}_2\text{O}$  for  $\text{NO}_3^-$  isotope analysis and 15 nmol  $\text{N}_2\text{O}$  for  $\text{NO}_2^-$  isotope analysis. N and O isotope ratios are reported in per mil (‰), relative to AIR- $\text{N}_2$  for  $\delta^{15}\text{N}$  and to V-SMOW for  $\delta^{18}\text{O}$ .  $\text{NO}_3^-$  and  $\text{NO}_2^-$  isotope data will be calibrated using the publicly and certified reference materials (e.g. USGS32, USGS34, and USGSM35) and other in-house standards; see Casciotti and McIlvin, (2007). The reproducibility is generally better than 0.2‰ for  $\delta^{15}\text{N}$  and 0.5‰ for  $\delta^{18}\text{O}$  in  $\text{NO}_3^-$  and  $\text{NO}_2^-$ .

## References:

- Casciotti, K. L., and M. R. McIlvin (2007), Isotopic analyses of nitrate and nitrite from reference mixtures and application to Eastern Tropical North Pacific waters, *Mar. Chem.*, 107(2), 184–201.
- Casciotti, K. L., D. M. Sigman, M. G. Hastings, J. K. Böhlke, and A. Hilkert (2002), Measurement of the Oxygen Isotopic Composition of Nitrate in Seawater and Freshwater Using the Denitrifier Method, *Anal. Chem.*, 74(19), 4905–4912.
- McIlvin, M. R., and M. A. Altabet (2005), Chemical conversion of nitrate and nitrite to nitrous oxide for nitrogen and oxygen isotopic analysis in freshwater and seawater, *Anal. Chem.*, 77(17), 5589–5595.
- Sigman, D. M., K. L. Casciotti, M. Andreani, C. Barford, M. Galanter, and J. K. Böhlke (2001), A bacterial method for the nitrogen isotopic analysis of nitrate in seawater and freshwater, *Anal. Chem.*, 73(17), 4145–4153.

## Dissolved gases

Samples for  $\text{N}_2/\text{Ar}$  analysis were collected at 28 stations during leg 1 roughly evenly distributed along the transects (every ~2 degrees latitude), except near the equator between 3°N and 3°S where the resolution was increased to ~1 degree. We collected water column profiles for a maximum of 2000 m depth at every other stations and full profiles at all other stations north of 3.5°S. South of 3.5°S, samples were generally collected at maximum of 2000 m depth. In total, approximately 600 samples for  $\text{N}_2/\text{Ar}$  were collected in 60 mL serum glass bottles and preserved with 500  $\mu\text{L}$  HCl 25%.

$\text{N}_2/\text{Ar}$  and  $\delta^{15}\text{N}_2$  analyses will be made onshore in Dr Altabet's laboratory at UMass Dartmouth. Water samples will be pumped, at 5 to 10  $\text{ml min}^{-1}$ , through a continuous sparger which transfers dissolved gases quantitatively to a continuous flow of He carrier gas. Dissolved gas samples require no preparation in the lab and analysis time is about 10 min. Carrier gas is passed through water,  $\text{CO}_2$ , and software selectable hot-Cu  $\text{O}_2$  traps before admittance via an open split to an IRMS.  $\text{O}_2$  removal improves the precision of the  $\text{N}_2/\text{Ar}$  and  $\delta^{15}\text{N}_2$  measurements and eliminates analytical bias associated with changing sample  $\text{O}_2/\text{N}_2$ . Our GV IsoPrime IRMS is fitted with sufficient collectors for simultaneous measurement of  $\text{N}_2$  (masses 28 and 29),  $\text{O}_2$  (masses 32, 33, and 34), and Ar (mass 40). Gas and isotopic ratios are measured against artificial compressed gas mixtures of  $\text{N}_2$ ,  $\text{O}_2$ , and Ar close to expected dissolved gas ratios. These reference mixtures are in turn calibrated against compressed air cylinders provided and certified by Ralf Keeling (Script Institution of Oceanography). Reproducibility of  $\text{N}_2/\text{Ar}$  and  $\delta^{15}\text{N}-\text{N}_2$  is better than 0.5 ‰ and 0.05 ‰, respectively. Daily calibration is against water equilibrated with air at precisely controlled temperatures of 10.0 and 20.0 °C. Excess (biogenic)  $\text{N}_2$  will be initially calculated against equilibrium values expected from *in situ* temperature and salinity (see Charoenpong et al., 2014 for more methodological detail).

## Reference:

Charoenpong, C. N., L. A. Bristow, and M. A. Altabet (2014), A continuous flow isotope ratio mass spectrometry method for high precision determination of dissolved gas ratios and isotopic composition, *Limnol. Oceanogr.: Methods*, 12, 323–337.

## N<sub>2</sub>O isotopomer

Samples for N<sub>2</sub>O isotopomer analysis were collected at 29 stations during leg 1 roughly evenly distributed along the transects (every ~2 degrees latitude), except near the equator between 3°N and 3°S where the resolution was increased to ~1 degree. See Table 8.4.1 for stations sampled for N<sub>2</sub>O during leg 2. We generally collected water column profiles for a maximum of 2000 m depth, with deeper profiles at few stations (stn 8, which unfortunately mostly consisted of mistrip bottles, 15 and 24), and no duplicates. In total, approximately 770 samples were collected.

Samples for dissolved N<sub>2</sub>O were collected in a similar fashion as for dissolved O<sub>2</sub>/N<sub>2</sub>/Ar samples. Tygon tubing was attached to the Niskin bottle and a 165 mL serum glass bottle was filled and overflowed with seawater at least 2 times before capping with a butyl stopper and crimp sealed with aluminum seal. This procedure was executed underwater in a plastic container to avoid air bubbles. After collection, 0.2 mL of a saturated HgCl<sub>2</sub> solution was injected to prevent biological activity.

Samples will be analyzed at UMass Dartmouth using a GV IsoPrime Continuous Flow, MultiCollector, Isotope-Ratio Mass Spectrometer (CF-MC-IRMS) coupled to an automated gas extraction system similar to what is used for O<sub>2</sub>/N<sub>2</sub>/Ar samples (Charoenpong et al., 2014, as described above). For N<sub>2</sub>O isotopomer samples, additional time will be needed for sample gas extraction from the larger volume. Our IRMS has the necessary collector configuration for simultaneous determination of masses 30, 31 (for SP) and 44, 45, and 46 (bulk δ<sup>15</sup>N and δ<sup>18</sup>O). A multiple point calibration of several N<sub>2</sub>O gases of known <sup>15</sup>Nα-<sup>15</sup>Nβ (as well as bulk δ<sup>15</sup>N and δ<sup>18</sup>O) will be applied (see Mohn and al., 2014). Standard deviations for triplicate measurements of our N<sub>2</sub>O standards are typically below 0.1‰ for δ<sup>15</sup>N<sup>bulk</sup>-N<sub>2</sub>O, 0.1‰ for δ<sup>18</sup>O-N<sub>2</sub>O and 1.0‰ for SP.

N<sub>2</sub>O concentrations in our samples will be calculated from relative peak heights between the samples and a seawater standard of known N<sub>2</sub>O concentration equilibrated with seawater at 5°C (12.5 nmol L<sup>-1</sup> at salinity 34 as calculated using the Weiss and Price (1980) equation). Equilibrium N<sub>2</sub>O concentrations will be estimated using the global mean contemporary atmospheric N<sub>2</sub>O dry mole fraction at the time of sampling (<http://agage.mit.edu/data/agage-data>).

**Table 8.4.1.** Summary of stations and number of bottles sampled for N<sub>2</sub>O isotopomers during P18, leg 2.

Station	# of bottles
118	19
124	17
130	17
137	20
144	17
150	18
158	13

166	15
172	15
180	17
184	14
192	17
200	14
206	13

---

## References:

- Charoenpong, C. N., L. A. Bristow, and M. A. Altabet (2014), A continuous flow isotope ratio mass spectrometry method for high precision determination of dissolved gas ratios and isotopic composition, *Limnol. Oceanogr.: Methods*, 12, 323–337.
- Mohn, J. et al. (2014), Inter-laboratory assessment of nitrous oxide isotopomer analysis by isotope ratio mass spectrometry and laser spectroscopy: current status and perspectives, *Rapid Commun. Mass Spectrom.*, 28(18), 1995–2007.

## 8.5 Dissolved Inorganic Carbon

PI: Richard A. Feely (NOAA/PMEL) and Rik Wanninkhof (NOAA/AOML)

Technicians: Robert Castle (NOAA/AOML), Remy Okazaki (JISAO/PMEL), Charles Featherstone (NOAA/AOML) and Andrew Collins (NOAA/PMEL)

### Sample Collection

Samples for DIC measurements were drawn (according to procedures outlined in the PICES Publication, Guide to Best Practices for Ocean CO<sub>2</sub> Measurements) from Niskin bottles into 310 ml borosilicate glass flasks using silicone tubing. The flasks were rinsed twice and filled from the bottom with care not to entrain any bubbles, overflowing by at least one-half volume. The sample tube was pinched off and withdrawn, creating a 6 ml headspace, followed by the addition of 0.12 ml of saturated HgCl<sub>2</sub> solution, which was added as a preservative. The sample bottles were then sealed with glass stoppers lightly covered with Apiezon-L grease.

### Equipment

The analysis was done by coulometry with two analytical systems (PMEL1 and PMEL2) used simultaneously on the cruise. Each system consisted of a coulometer (CM5015 UIC mc) coupled with a Dissolved Inorganic Carbon Extractor (DICE). The DICE system was developed by Esa Peltola and Denis Pierrot of NOAA/AOML and Dana Greeley of NOAA/PMEL to modernize a carbon extractor called SOMMA (Johnson et al. 1985, 1987, 1993, and 1999; Johnson 1992).

The two DICE systems (PMEL1 and PMEL2) were set up in a seagoing container modified for use as a shipboard laboratory on the aft main working deck of the R/V Ronald H. Brown.

### Calibration Accuracy and Precision

The stability of each coulometer cell solution was confirmed three different ways.

1. Two gas loops were run at the beginning of cell;
2. CRM's supplied by Dr. A. Dickson of SIO, were measured at the beginning, and
3. Samples from the same Niskin were run throughout the life of the cell solution.

Each coulometer was calibrated by injecting aliquots of pure CO<sub>2</sub> (99.999%) by means of an 8-port valve (Wilke et al., 1993) outfitted with two calibrated sample loops of different sizes (1ml and 2ml). The instruments were each separately calibrated at the beginning of each cell with a minimum of two sets of gas loop injections.

The accuracy of the DICE measurement is determined with the use of standards (Certified Reference Materials (CRMs), consisting of filtered and UV irradiated seawater) supplied by Dr. A. Dickson of Scripps Institution of Oceanography (SIO). The CRM accuracy is determined manometrically on land in San Diego and the DIC data reported to the database have been corrected to this batch 159 CRM value. The CRM certified value for this batch is 2027.14 μmol/kg (1).

The precision of the two DICE systems can be demonstrated via the replicate samples. A total of 591 duplicates were collected during the cruise accounting for 10.7% of the Niskins sampled. These duplicates were collected as a check of our precision.

These replicate samples were interspersed throughout the station analysis for quality assurance and integrity of the coulometer cell solutions. The average absolute difference from the mean of these replicates is 0.66 μmol/kg for PMEL 1 and 0.83 μmol/kg for PMEL 2. No major systematic differences between the replicates were observed (2).

### Summary

The overall performance of the analytical equipment was good during the cruise. During leg 1 the coulometer bulb for PMEL 2 was replaced along with some biochem tubing. The coulometer bulbs for both systems were replaced during Leg 2 along with valve 6 on PMEL 1 and the acid pump (8) on PMEL 2.

Including the duplicates, 5507 samples were analyzed for dissolved inorganic carbon (DIC). There is a DIC value for approximately 95% of the Niskins tripped. The DIC data reported to the database directly from the ship are to be considered preliminary until a more thorough quality assurance can be completed shore side.

**Table 8.5.1.** Calibration data during this cruise:

Unit	L Loop	S Loop	Pipette	Ave CRM <sup>(1)</sup>	Std Dev	Dupes <sup>(2)</sup>
<b>LEG 1</b>						
PMEL 1	1.9842 ml	1.0006 ml	27.571 ml	2027.53	N=58, 1.61	0.66
PMEL 2	1.9885 ml	0.9857 ml	26.363 ml	2029.80	N=58, 1.68	0.83
<b>LEG 2</b>						
PMEL 1	1.9842 ml	1.0006 ml	27.571 ml	2026.38	N=50, 1.09	0.65

### References:

- Dickson, A.G., Sabine, C.L. and Christian, J.R. (Eds.), (2007): Guide to Best Practices for Ocean CO<sub>2</sub> Measurements. PICES Special Publication 3, 191 pp.
- Feely, R.A., R. Wanninkhof, H.B. Milburn, C.E. Cosca, M. Stapp, and P.P. Murphy (1998): "A new automated underway system for making high precision pCO<sub>2</sub> measurements aboard research ships." *Anal. Chim. Acta*, 377, 185-191.
- Johnson, K.M., A.E. King, and J. McN. Sieburth (1985): "Coulometric DIC analyses for marine studies: An introduction." *Mar. Chem.*, 16, 61-82.
- Johnson, K.M., P.J. Williams, L. Brandstrom, and J. McN. Sieburth (1987): "Coulometric total carbon analysis for marine studies: Automation and calibration." *Mar. Chem.*, 21, 117-133.
- Johnson, K.M. (1992): Operator's manual: "Single operator multiparameter metabolic analyzer (SOMMA) for total carbon dioxide (CT) with coulometric detection." Brookhaven National Laboratory, Brookhaven, N.Y., 70 pp.
- Johnson, K.M., K.D. Wills, D.B. Butler, W.K. Johnson, and C.S. Wong (1993): "Coulometric total carbon dioxide analysis for marine studies: Maximizing the performance of an automated continuous gas extraction system and coulometric detector." *Mar. Chem.*, 44, 167-189.
- Lewis, E. and D. W. R. Wallace (1998) Program developed for CO<sub>2</sub> system calculations. Oak Ridge, Oak Ridge National Laboratory. <http://cdiac.ornl.gov/oceans/co2rprt.html>
- Wilke, R.J., D.W.R. Wallace, and K.M. Johnson (1993): "Water-based gravimetric method for the determination of gas loop volume." *Anal. Chem.* 65, 2403-2406

## 8.6 Discrete pH Analyses

### PI: Frank Millero

Samplers and Analysts: Fen Huang, Alexandra Fine, Ryan Woosley, Andrew Babbitt

#### Sampling

Samples were collected in 50ml borosilicate glass syringes rinsing a minimum of 2 times and thermostated to 25°C before analysis. Two duplicates were collected from each station. One sample per station was collected and analyzed with double the amount of indicator in order to correct for pH changes as a result of adding the indicator, this correction has not been applied to the preliminary data. All data should be considered preliminary.

#### Analysis

pH on the seawater scale was measured using an Agilent 8453 spectrophotometer according to the methods outlined by Clayton and Byrne (1993). An RTE10 water bath maintained spectrophotometric cell temperature at 25°C. A 10 cm micro-flow through cell (Sterna, Inc) was filled automatically using a Kloehn 6v syringe pump. The purified sulfonephthalein indicator m-cresol purple (mCP) was also injected automatically by the Kloehn 6v syringe pump into the spectrophotometric cells, and the absorbance of light was measured at four different wavelengths (434 nm, 578 nm, 730 nm, and 488 nm). The ratios of absorbances at the different wavelengths were used to calculate pH on the total and seawater scales using the equations of Liu et al (2011). The equations of Dickson and Millero (1987), Dickson and Riley (1979), and Dickson (1990) were used to convert pH from the total to seawater scale. The isobestic point (488nm) will be used for the indicator correction. Salinity data were obtained from the conductivity

sensor on the CTD. These data were later corroborated by shipboard measurements. Temperature of the samples was measured immediately after spectrophotometric measurements using a Fluke Hart 1523 digital platinum resistance thermometer. All samples were analyzed within 8 hours of collection.

### Reagents

The mCP indicator dye was a concentrated solution of ~2.0 mM. Purified indicator provided by Dr. Robert Byrne, University of South Florida.

### Standardization

The precision of the data can be accessed from measurements of duplicate samples, certified reference material (CRM) Batch 146 and 129 (Dr. Andrew Dickson, UCSD) and TRIS buffers (Ramette et al. 1977). The measurement of CRM and TRIS was alternated at each station. The mean and standard deviation for the CRMs was  $7.8904 \pm 0.0040$  (N = 96) for Batch 146 and  $7.8803 \pm 0.0047$  (N = 6) for Batch 129. For TRIS buffer the mean and standard deviation was  $80920 \pm 0.0028$  (N = 98). The mean and absolute standard deviation of the duplicate samples was  $0.0002 \pm 0.0011$  (N = 378).

### Data Processing

Addition of the indicator affects the pH of the sample, and the degree to which pH is affected is a function of the pH difference between the seawater and indicator. Therefore, a correction is applied for each batch of dye. One sample from each station was measured twice, once normally and a second time with double the amount of indicator. The change in the ratio is then plotted versus the change in the isosbestic point to develop an empirical relationship for the effect of the indicator on the pH. This correction has not yet been applied to the preliminary data. A summary of the preliminary quality control of the data is given in Table 8.6.1. Underway samples were collected approximately every 4 hours after completion of the last station up through Feb. 1, but are not included in Table 8.6.1.

**Table 8.6.1.** Discrete pH preliminary Quality Control code summary.

<b>Number of Samples</b>	<b>5361</b>
<b>Good (flag=2)</b>	<b>4476</b>
<b>Dup (flag=6)</b>	<b>788</b>
<b>questionable (flag = 3)</b>	<b>43</b>
<b>bad (flag=4)</b>	<b>51</b>
<b>lost (flag = 5)</b>	<b>3</b>

### Problems

No major problems occurred during the cruise. On station 69 the lamps in the spec were replaced because they had reached the manufacturer stated lifetime usage.

### References

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

- Dickson, A. G. and Millero, F. J., "A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media," *Deep-Sea Res., Part A*, 34, 10, pp. 1733-1743 (1987).
- Dickson, A. G. and Riley, J. P., "The estimation of acid dissociation constants in seawater media from potentiometric titration with strong base, 1: The ionic product of water-K<sub>SW</sub>-w," *Mar. Chem.*, 7, 2, pp. 89-99 (1979).
- Dickson, A. G., "Thermodynamics of the dissociation of boric acid in synthetic seawater from 273.15 to 318.15 K," *Deep-Sea Res., Part A*, 37, 5, pp. 755-766 (1990).
- Liu, X, Patsavas, M. C., and Byrne, R. H., "Purification and characterization of meta-cresol purple for spectrophotometric seawater pH measurements," *Environ. Sci. and Tech.* 45, pp 4862-4868 (2011).
- Millero, F.J., The Marine Inorganic Carbon Cycle, *Chemical Reviews*, 107(2) 308-341 (2007).
- Ramette, R. W., Culberson, C. H., and Bates, R. G., "Acid-base properties of Tris(hydroxymethyl)aminomethane (Tris) buffers in seawater from 5 to 40°C," *Anal. Chem.*, 49, pp. 867-870 (1977).

## 8.7 Total Alkalinity

### PI: Frank Millero

Samplers and Analysts: Fen Huang, Alexandra Fine, Ryan Woosley, Andrew Babbitt

### Sampling

At each station total alkalinity (TA) samples were drawn from Niskin bottles into 500 ml borosilicate flasks using silicone tubing fit over the petcock. Bottles were rinsed with a small volume, then filled from the bottom and allowed to overflow half of the bottle volume. The sampler was careful not to entrain any bubbles during the filling procedure. Approximately 15 ml of water is withdrawn from the bottle by halting the sample flow and removing the sampling tube, thus creating a reproducible headspace for expansion during thermal equilibration. The sample bottles were sealed at a ground glass joint with a glass stopper. The samples were then thermostated at 25°C before analysis. Three duplicates were collected at each station.

### Analyzer Description

The sample TA was evaluated from the proton balance at the alkalinity equivalence point, pH  $\approx$  4.5 at 25°C and zero ionic strength using a closed cell HCl titration. This method utilizes a multi-point hydrochloric acid titration of seawater (Dickson 1981). The instrument program uses a Levenberg-Marquardt nonlinear least-squares algorithm to calculate the TA and DIC from the potentiometric titration data. The program is patterned after those developed by Dickson (1981), Johansson and Wedborg (1982), and U.S. Department of Energy (DOE) (1994). The least-squares algorithm of the potentiometric titrations not only give values of TA but also those of DIC, initial pH as calculated from the initial EMF, the standard potential of the electrode system (E<sub>0</sub>), and the first dissociation constant of CO<sub>2</sub> at the given temperature and ionic strength (pK<sub>1</sub>). Two titration systems, A and B were used for TA analysis. Each of them consists of a Metrohm 765 Dosimat titrator, an Orion 720A, or 720A+, pH meter and a custom designed plexiglass water-jacketed titration cell (Millero et al, 1993). The titration cell allows for the titration to be conducted in a closed system by incorporating a 5mL ground glass syringe to allow for volume expansion during the acid addition. The seawater samples were temperature equilibrated to a constant temperature of 25  $\pm$  0.1°C with a water bath (Thermo, HAAKE A10). The electrodes used to measure the EMF of the sample during a titration were a ROSS glass pH electrode (Orion, model 810100)

and a double junction Ag, AgCl reference electrode (Orion, model 900200). The water-jacketed cell is similar to the cells used by Bradshaw and Brewer (1988) except a larger volume (~200 ml) is employed to increase the precision. Each cell has a solenoid fill and drain valve which increases the reproducibility of the volume of sample contained in the cell. A typical titration records the stable solution EMF (deviation less than 0.09 mV) and adds enough acid to change the voltage a pre-assigned increment (~13 mV). A full titration (~25 points) takes about 20 minutes. A 6 port valve (VICI, Valco EMTCA-CE) allows 6 samples to be loaded into the instrument and successively measured.

## Reagents

A single 50-L batch of ~0.25 M HCl acid was prepared in 0.45 M NaCl by dilution of concentrated HCl (AR Select, Mallinckrodt), to yield a total ionic strength similar to seawater of salinity 35.0 ( $I = 0.7$  M). The acid is standardized with alkalinity titrations on seawater of known alkalinity (certified reference material, CRM, provided by Dr. Andrew Dickson, Marine Physical Laboratory, La Jolla, California). The calibrated normality of the acid used was  $0.24494 \pm 0.0001$  N HCl. The acid is stored in 500-ml glass bottles sealed with Apiezon® M grease for use at sea.

## Standardization

The reproducibility and precision of measurements are checked using low nutrient surface seawater collected from the ship's underway seawater system, used as a substandard, and Certified Reference Material (Dr. Andrew Dickson, Marine Physical Laboratory, La Jolla, California). The CRM was utilized to account for instrument drift over the duration of the cruise and to maintain measurement precision. A CRM was measured on each system on all odd numbered stations and a low nutrient surface water sample was measured on each even numbered station. Duplicate analyses provide additional quality assurance, and three duplicates, 2 samples taken from the same Niskin bottle, were collected and analyzed at each station. The duplicates are then analyzed both on system A, both on system B, or split between systems A and B. This provides a measure of the precision on both the same system and between systems. Laboratory calibrations of the Dosimat burette system with water indicate the systems deliver 3.000 ml of acid (the approximate value for a titration of 200 ml of seawater) to a precision of  $\pm 0.0004$  ml, resulting in an error of  $\pm 0.3$   $\mu\text{mol/kg}$  in TA. All samples were analyzed less than 12 hours after collection.

## Data Processing:

Measurements were made on CRM bath 129, 146, and 159. The difference between the measured and certified values on system A is  $-0.72 \pm 2.79$  (N=109) and on B is  $0.15 \pm 2.56$  (N=104). No correction to the CRM has been made on the preliminary data. Seven different batches of low nutrient surface water were used. They all had standard deviations of  $<3$   $\mu\text{mol/kg}$ , and were generally less than 2  $\mu\text{mol/kg}$ . The mean and absolute standard deviations of the duplicates were  $0.54 \pm 1.26$  (N=195),  $-0.20 \pm 1.26$  (N=176), and  $0.25 \pm 1.68$  (N=198) on system A, system B, and one on each system respectively (A-B). The preliminary quality control results are shown in Table 8.7.1. Underway samples were collected after the last station every 4 hours up through Feb. 1 and are not included in Table 8.7.1.

**Table 8.7.1:** Preliminary quality control code summary for P18 Alkalinity analyses.

Total Samples	5482
Good (flag=2)	4219
Duplicate (flag=6)	1152

questionable (flag=3)	58
Bad (flag=4)	48
lost (flag=5)	5

---

### Problems:

No major problems occurred during the cruise.

### References

- Bradshaw, A. L. and Brewer, P. G., High precision measurements of alkalinity and total carbon dioxide in seawater by potentiometric titration, *Mar. Chem.*, 23, pp. 69-86 (1988).
- DOE, (U.S. Department of Energy), *Handbook of Methods for the Analysis of the Various Parameters of the Carbon Dioxide System in Seawater. Version 2.0. ORNL/CDIAC-74*, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, Oak Ridge, Tenn. (1994).
- Dickson, A. G., An exact definition of total alkalinity and a procedure for the estimation of alkalinity and total  $CO_2$  from titration data, *Deep-Sea Res., Part A*, 28, pp. 609-623 (1981).
- Johansson, O. and Wedborg, M., "On the evaluation of potentiometric titrations of seawater with hydrochloric acid," *Oceanologica Acta*, 5, pp. 209-218 (1982).
- Millero, F. J., Zhang, J-Z., Lee, K., and Campbell, D. M., Titration alkalinity of seawater, *Mar. Chem.*, 44, pp. 153-165 (1993b).

## 8.8 Genetics and Particulate Organic Matter

PI: Adam Martiny

Samplers: Alyse Larkin (Leg 1), Catherine Garcia (Leg 2), and Javiera Veloso (Leg 2 - Genetics)

### Genetics

Genetics samples were collected approximately every degree of latitude from the surface Niskin bottle (~5m deep). In total, 105 samples were collected. Water was also collected from the uncontaminated underway seawater system and pre-filtered (30  $\mu$ m mesh) when station water budget was limited (GO-SHIP stations 19, 69, 71, 100, 150, 186, 202). Up to 4L of seawater was collected into a plastic cubitainer and filtered immediately after collection (+2 hours for stations 17 and 100). Water was filtered through a Sterivex 0.22 $\mu$ m filter using a peristaltic pump at a low speed. Once all water is pumped through the Sterivex cartridge, one end is sealed with Crito-seal putty. 1620 $\mu$ L of sterile lysis buffer is pipetted into the filter cartridge and the other end is sealed with a luer-lok cap. The filter is placed in a separate Ziplok bag and preserved frozen at -20°C until shipment to the Adam Martiny lab at UC Irvine for further analysis. Final filtration volume was recorded for all samples. Gloves were worn during all steps, and were also used by all samplers at the rosette for the surface bottle 24.

Prior to the cruise, all silicone tubing, Omnifit caps and cubitainers were cleaned in soapy water, 10% HCL, and Milli-Q water. Weekly, the tubing and Omnifit caps were soaked in a 10% bleach solution overnight and rinsed with Milli-Q water. Between sample collections, the tubing and sample container were rinsed 2x with 0.22 $\mu$ m filtered seawater and 1x with Milli-Q water.

Problems: If the water budget did not allow for a Genetics collection every degree, supplementary samples were collected from the underway seawater system. On the first leg small black metallic specks were observed from the underway system, so genetics samples were pre-filtered with a 30 $\mu$ m mesh only when collected from the underway system. Several comparison samples of underway and station Niskin water were collected to assess potential contamination problems.

#### *Particulate Organic Matter*

Particulate organic matter (POM) samples were collected for particulate organic carbon (POC), nitrogen (PON), phosphorous (POP) and biological oxygen demand (BOD). The underway seawater system was chosen to increase water volumes and replication. In total, 198 underway stations were sampled. Each sample was pre-filtered through a 30 $\mu$ m nylon mesh and passed through a GF/F filter (nominal pore size 0.7 $\mu$ m). An aspirator pump was used to pull water through the filters at a vacuum setting of -0.06 to -0.08 MPa. South of 54°S an additional set of samples was collected without a pre-filter. Twelve carboys were filled with 3-8L of water (volume biomass-dependent) and designated as follows: 3x POP, 3x POC/PON, 3x BOD method 1, 3x BOD method 2. Two triplicate sets of BOD were collected for method development and comparison. POP filters were rinsed with 5mL of 0.017M Na<sub>2</sub>SO<sub>4</sub> to remove traces of dissolved organic phosphorous at the end of filtration. Filters were folded and stored frozen at -20°C in pre-combusted foil squares.

All carboys were rinsed 1x with sample water before collection. GF/F filters and foil squares were pre-combusted at 500°C for 4.5 hours. Prior to the cruise, all silicone tubing, filter holders, and carboys were cleaned in soapy water, 10% HCL, and Milli-Q water. The 30 $\mu$ m nylon mesh was rinsed with filtered seawater between sample collections. All filters will be shipped frozen and analyzed by the Martiny lab at UC Irvine. Gloves were used for all steps mentioned above.

Problems: As in situ biomass increased around the equator and in the Southern Ocean, sample volumes were decreased from 8L to as little as 3L. A mesh pre-filter was used to remove larger zooplankton. At ~53°S, a larger portion of biomass was observed on the pre-filter. From 54°S onwards, a full set of samples was taken for a small fraction (<30 $\mu$ m) and total fraction.

### 8.9 Microbial Genetics and Transcriptomics (iTag™)

Bethany Kolody – U. C. San Diego, and Javiera Veloso, Valparaiso University

The goal of the iTAG project is to characterize the microbial species composition, via barcode sequencing, and their activity, via transcriptomics, of the water masses along the P18 transect.

iTAG samples were taken approximately every 4<sup>th</sup> station (24hrs) along the 103°W line (P18 leg 2) from 26° 29.995' S to 69° 0.014' S. Samples deviated from the 103°W line to avoid sampling in Chilean waters around Easter Island and eventually to avoid sea ice. A total of 302 samples were taken over 25 stations. Most stations were sampled at 12 depths, spread across the water column. Niskins were chosen to cover as wide a range of depths as possible, target the major water mass features predicted by the previous P18 occupation, and maximize available water. Four of the 12 samples were collected and processed expediently for transcriptomics, each one targeting a major water mass feature (chlorophyll max, oxygen minimum, deep water, bottom water).

Samples ranged from 3-8 liters in volume depending on water availability. Processing entailed filtering water sequentially through 5 $\mu$ m and .22 $\mu$ m filters to capture particle associated and free-living microbes, respectively. Filters were submersed in RNeasy™ and immediately stored in liquid nitrogen. Samples

were kept on ice throughout filtration. One mL of sample was preserved in 1% (final concentration) paraformaldehyde for flow cytometry, and one mL of water was preserved in glycerol-TE buffer for single-cell genomics. These samples were also preserved in liquid nitrogen.

## 8.10 Total Organic Carbon (TOC) and Dissolved Nitrogen (TDN) in Seawater

PI: Dennis Hansell and Lilian Custals

Sampler: Mariana Bernardi Bif – University of Miami (Rosenstiel School of Marine and Atmospheric Sciences), mbif@rsmas.miami.edu

Along the P18 line, approximately 2326 samples for TOC and TDN were collected from full profiles (24 Niskin bottles) at every odd station, except station 3 and when Niskin bottles were leaking. Gloves were used during sample collection, handling and storage in order to avoid organic contamination.

Before each station, the filter holders and silicon tubes were soaked in 10% hydrochloric acid (provided by the nutrients group) for at least 12h inside a plastic container, and stored in Milli-Q water from a second container prior to use. Briefly, using 60 mL polycarbonate bottles, 40-50 mL of water was taken directly from the Niskin after rinsing the bottle twice. Samples collected above 250 m were filtered using a silicone tube in line with the Niskin and a filter holder containing a pre-combusted 47 mm glass fiber filter. The filter holders were flushed with the Niskin water prior to sampling. After all samples were collected and placed in a rack, they were frozen upright, stored in plastic bags and placed inside coolers at the ship's walk-in freezer. The samples will be analyzed by a Shimadzu TOC-L analyzer with ASI-L auto sampler and TNM-L total nitrogen detector located in the Hansell Laboratory at RSMAS.

## 8.11 Rare Earth Elements (REEs)

PI: Yves Plancherel

**Samplers:** Laura Whitmore, Margot White, Shineng Hu (leg 1), Yves Plancherel and Javiera Veloso (leg 2)

A total of ~1200 REEs samples were taken during P18, ~500 during leg 1 (stations 1 to 115) and ~700 during leg 2 (stations 116 to 212), making P18 the most heavily sampled REEs section ever and constituting the first meridional transect in the Southeast Pacific. This is 200 more samples than originally planned for leg 2; given cancellation of the P17E segment, the bottles reserved for that segment were repurposed to leg 2 to achieve increased vertical and horizontal sampling resolution. A total of 65 stations (31 in leg 1 and 34 in leg 2) were sampled, spaced approximately 2 degrees apart, except around the equator and south of 55°S. South of that latitude (station 181 onwards), the station resolution was increased to 1 degree to capture gradients across Southern Ocean fronts. The southernmost station occupied was at 70°S (211) and the last station sampled was the SOCCOM station, #212. Vertical resolution ranged from 6 to 24 samples per cast. Duplicates were taken at station 163 (9 bottles) and 201 (6 bottles). Unfiltered samples were also drawn for comparison with filtered samples at stations 181, 185, 189, 193, 195, 197, 201, 205, 211 (~6 bottles each).

Samples were drawn from Niskins with acid-cleaned (3M HCl) 60ml PP syringes and ¼" acid-cleaned silicone tubing connected to a Luer slip syringe fitting. New tubes were used for every station and new syringes and filters were used for every 3 samples to reduce cross-contamination. After letting water through the tubing for a few seconds, a ~30ml aliquot was taken into the syringe. The plunger was then fully opened and the syringe was vigorously shaken before ejecting 25ml from the syringe. An acid-cleaned 0.45um PP Whatman Puradisc filter was connected to the syringe and the remaining 5ml were

used to sample-rinse the filter. After this systematic sample rinse, 60ml were drawn into the syringe and syringe-filtered into prelabelled acid-cleaned 60ml LDPE bottles. Back in the lab, bottles were dried with a Kimwipe and the stopper was sealed with Parafilm. All samples were then stored in Ziploc bags and put in dark plastic bags inside opaque plastic shipping crates, which were kept in the lab or in the forward science hold until the end of the cruise.

To minimize contamination, all sampling material was kept in plastic bags until sampling and nitrile gloves were worn at all times when manipulating REE equipment. The lab workbench was covered in plastic, which was cleaned regularly with DI water and a Kimwipe. Anything left on the counter was stored in a large plastic bag, which was taped to the wall and tied shut, opened only to access content.

Before sampling, the required number of bottles, tubing and syringes were placed into a clear plastic box (the sampling box), which was itself placed in a large plastic bag into a plastic shipping crate closed with a lid. All of this was taken to the sampling bay. The sampling box was taken out of the crate and bag, placed above the lid of the plastic crate and opened at the last minute before sampling. When sampling was completed, the sampling box was closed and again packed in the bag and in the crate to be carried back to the lab.

P18 represents the first attempt at REEs sampling on a GOSHIP cruise. Many valuable lessons were learned from this experience. One issue is the fact that the REE sampling station (together with other ancillary projects) was set right next to the helium station in the Biolab. Helium sampling requires substantial use and cutting of copper tubing. This was surely a significant source of metal contamination for the entire lab, but it is unclear if it was a source of REEs. Nonetheless, placing a metal-using station next to a trace metal-sampling station was a very poor choice, but any effect, if any, will only become clear once samples will have been analysed on shore. In hindsight, a better location for the REEs station would be together with the pH and alkalinity stations as these programmes strive to maintain a relatively clean analytical environment.

For added protection, future attempts at measuring REEs from GOSHIP cruises should consider bringing a portable bench-top laminar flow hood system, or at least a sealable plastic hood of sorts to further protect sampling equipment against accidental contamination. For example, as the engineers turned on the heater in the venting system of the Biolab when nearing Antarctica, this released clouds of black particles and smoke into the lab, enough to trigger a fire alarm. Smoking in and around the sampling bay by crew and scientists and the sending of coloured styrofoam objects with the CTD to shrink them at depth by some without consulting other scientists involved in the cast are two other potential sources of contamination which could be avoided. The effect of these events and practices on REEs measurements, if any, is not known at present.

There are also many positive lessons to take from this experience. First, syringe filtration aided with a modified caulking gun worked well. REE sampling can be performed sufficiently fast to keep up with other “core group” samplers as they progress around the rosette. Given GOSHIP’s priorities, the best time to sample REEs in the future would be right after alkalinity – the sampling pace of the “core group” is largely controlled by CFCs. Second, the sampling volume being small, the effect of REE sampling on the water budget is negligible. Third, going through this experience demonstrated that, from a workload perspective, it is possible to sample REEs with full depth resolution and a horizontal resolution of at least 1 degree. Fourth, aside from working cleanly (which takes awareness and care), the sampling procedure for REEs is easy and lightweight compared to the sampling procedure of other tracers (i.e. helium, CFCs, oxygen), suggesting that REEs could in principle be sampled systematically on future GOSHIP

expedition at very little cost to the programme, and maybe even simply with the help from available volunteer personnel, such as CTD watchstanders (as was done in leg 1).

## 8.12 Lowered Acoustic Doppler Current Profiler

S.Purkey (LDEO), J. Hooper (AOML), and, A.M. Thurnherr (LDEO; PI)

### Introduction

LADCP data were collected during the full-depth CTD cast at all stations. Preliminary processing and QC was performed onboard by Jay Hooper during leg 1 and Sarah Purkey during leg 2. Casts were sent to Thurnherr for shore-based processing as internet access allowed. A full QC was carried out after the cruise by Thurnherr

### LADCP System Configuration

An AOML custom 48V lead acid rechargeable battery pack was used for all deployments. Instruments and battery pack were interfaced using a standard RDI star cable. Custom AOML deck leads were used for communications and charging between casts. The battery pack was periodically vented manually to prevent pressure build up. Battery power was periodically checked to ensure proper charge level of 52V was being maintained before deployments. Both the battery pack and the ADCP's were affixed to the CTD package using custom tabbed brackets aligned on horizontal cross-members of the package. The upward ADCP was positioned between niskin bottles 1 and 24 towards the outer ring, while the downward ADCP was affixed in the middle of the package about 4 inches from the bottom ring. The configuration is shown in photo 01.

During the shakedown profiles an external magnetometer/accelerometer package (independent measurement package – IMP) was installed on the rosette to collect better pitch, roll and heading data. Due to cable problems, the IMP was removed from the rosette after station 3 to simplify LADCP operations.

The power supply and data transfer were handled independently from any CTD connections. While on deck, a communications and power cable was connected to a cable in the staging bay that ran into the wet lab. This cable connected to a battery charger located in the wet lab for power and to an acquisitions computer via USB connection for data download. The LADCP acquisitions computer clock was synced to the master clock in the computer lab via network.

**Table 8.12.1:** LADCP Instruments used on cruise. DL = downloader UL = uplooker.

Model	Serial Number	Stations used
Teledyne RDI WHM150	19394	1- 204 (DL)
Teledyne RDI WHM150	24544	205 - 211(DL)
Teledyne RDI WHM300	12734	1-211 (UL)

Three different ADCP instruments were used during this cruise (Table 8.12.1). Initial configuration consisted of the WHM150 #19394 as downloader and the WHM300 #12734 as uplooker. WHM150 #19394 had not performed well during P16, but was repaired by TRDI immediately prior to the P18 cruise. On or after station 201, one of the beams of the DL failed, and the spare WHM150 #24544, a brand new unit, was installed on the rosette as a replacement. The UL performed well throughout the

entire cruise. All ADCPs were set up to record velocity data with 8m pulses/bins and zero blanking. Staggered pinging was used to avoid previous ping interference, which is particularly important for 150kHz instruments.

#### Problems/Setup Changes:

Station 1, cast1: MASTER.cmd changed from LN25 (used for the shakedown cast) to LN40

Station 1, cast 3: Errors during download at the end of cast. Generated 3 files in DL. Unplugged IMP and charged battery before trying to download again.

Station 3, cast 1: Problem with T-cable. Removed IMP and set up with single star cable.

Station 18, cast 1: On recovery, winch failed and CTD free fell ~10 m.

Station 20, cast 1: Switched to aft winch.

Station 139, cast 1: Cast aborted because of CTD cable issues. Re-done as 139, cast 2.

Station 141, cast1: Cast aborted due to CTD temperature sensor.

Station 159, cast 1: Deployment issues. CTD dropped in water. Did not hit boat and no visual issues. Re-deployed as cast 2. LADCP was not restarted but ran the whole time.

Station 168: cast 1: Data was not downloaded between casts. Data lost.

Station 187, cast 1: Cast stayed 100m off the bottom because of possible altimeter communication issues.

Station 190, cast 1: LADCP not turned on. No LADCP data for station 190.

Station 202-204: Beam 1 of the DL sn # 19394 was bad.

Station 205. Replaced DL WHM150 downlooker SN #19394 with WHM150 downlooker SN # 24544.

#### LADCP Operation

ADCP programming and data acquisition were carried out using the LDEO Acquire software running on a Mac computer. Communications between the acquisitions computer and the ADCPs took place across two parallel R5232 connections via a Keyspan USA-49WG 4-port USB-to-R5232 adapter. After station 3 no further significant communications issues were encountered. After sending the corresponding command files to the instruments prior to each cast, communication between the computer and the instrument was terminated, the deck cables were disconnected, and all connections were sealed with dummy plugs and secured. After the CTD was brought back on deck following a cast, the data and the power supply cable were reconnected to the computer and battery charger via the deck cables. Data acquisition was terminated and the data were downloaded using the Acquire software. The battery charger remained on from the time of data download until the time the instrument was prepared for the next cast. Log files were kept for each cast to ensure that all these steps were completed.

#### Data Processing and Quality Control

The LADCP data were processed by Hooper/Purkey at least once per day using the Matlab-based LDEO IX\_10 processing software(1), as well as by Thurnherr in his lab during times of good internet connection (essentially the first leg). Processing warnings and diagnostic figures created during processing were reviewed for anomalies, which included checking the realism of final profile values, checking for any biased shear, examining the agreement between aligned CTD/LADCP time series, and monitoring beam strength and range. Thurnherr was either sent data or consulted when questionable profiles were observed.

The cruise-processed profiles of LADCP-derived horizontal velocity are shown in Figure 9. Comparison of the LADCP velocities in the upper ocean with the corresponding on-station SADC velocities (not

shown) indicates that the quality of these data is high. Data quality will be assessed more quantitatively during additional post-cruise QC and re-processing by Thurnherr at LDEO.



Photo 1: Instruments and battery pack on rosette. UVP is not mounted in this photo.

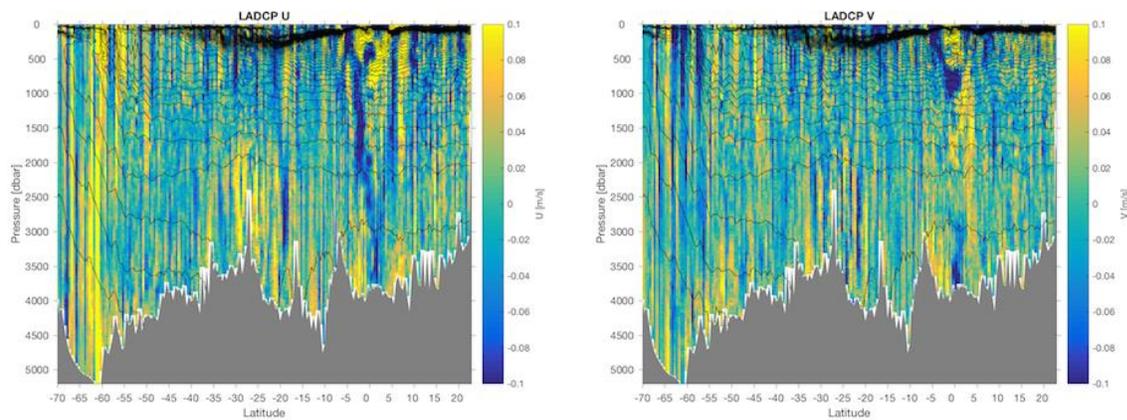


Figure 11: LADCP-derived velocities observed during P18 from preliminary processing. Left panel: Zonal velocity component. Right panel: Meridional velocity component. Available for download at <http://www.ldeo.columbia.edu/LADCP>

### 8.13 CHIPOD

PI: Jonathan Nash

Samplers: Conrad Luecke and Shineng Hu

Ocean turbulence and mixing is typically quantified through the dissipation rates of temperature variance

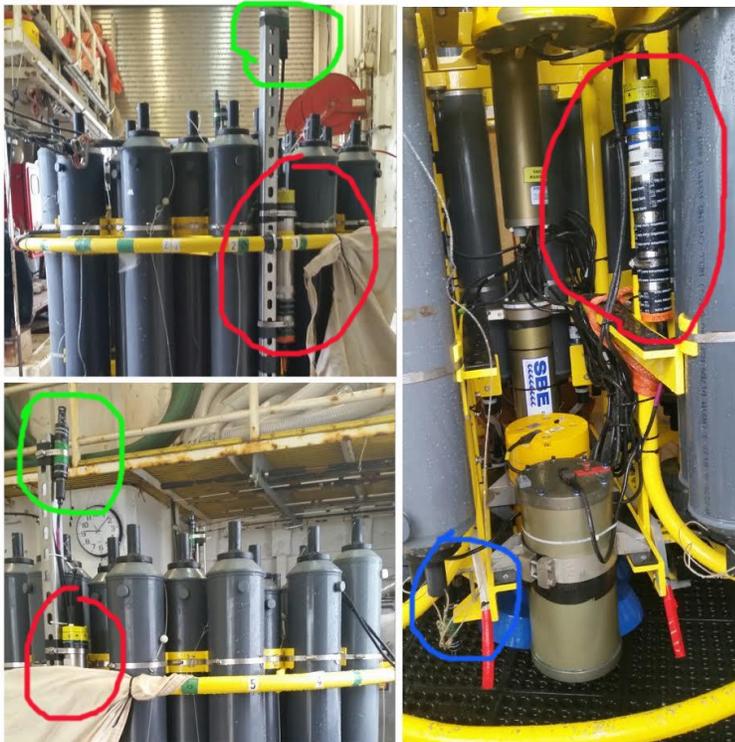
(chi) by measuring small scale temperature gradients or the dissipation rate (epsilon) of turbulent kinetic energy (TKE) by measuring small scale velocity shear. Because turbulent velocity shear is difficult to measure from a CTD rosette, OSU's chipod-CTD program relies on measuring microscale temperature variance, from which chi and epsilon are inferred.

Unlike the measurement of epsilon, chi is not particularly sensitive to platform acceleration. Chipods are self-contained mixing meters, devices that are robust and are able to record temperature and derivative signals from 2 thermistors at 100 Hz for more than a year on a single battery pack; they also record sensor motion at the same sampling rate. Measurements rely on using FP07 microbead thermistors, which are low noise and suitable for determining mixing in all but the weakest stratification.

### System Configuration and Sampling

Three Chipods were mounted on the rosette to measure temperature (T), its time derivative (dT/dt), and x and z (horizontal and vertical) accelerations at a sampling rate of 50 Hz. Two chipods were oriented such that their sensors pointed upward (circled in green in the figure below), and are referred to as uplookers. The other chipod pointed downwards and is referred to as a downlooker (circled in blue at the bottom of the rosette in the figure below).

The chipod pressure case, containing the logger board and batteries, is circled in red in the figure below.



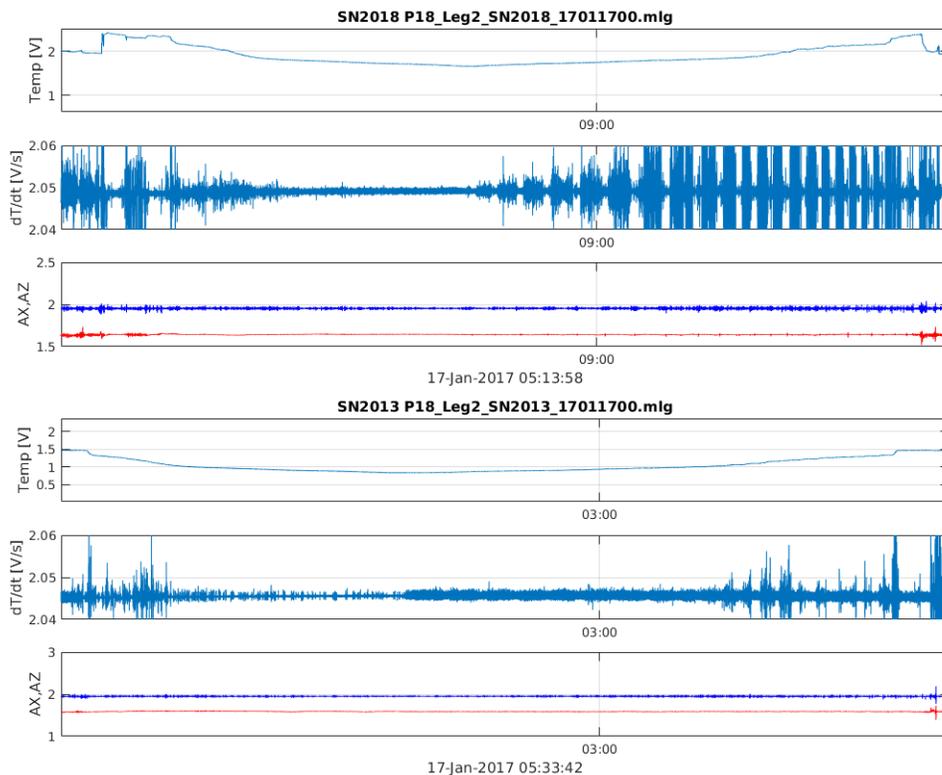
The uplooking sensors were positioned higher than the Niskin bottles on the rosette in order to avoid measuring turbulence generated by the firing of Niskin bottles. The downlooking sensors were positioned an inch above the base of the rosette at a distance of about six inches away from the frame. This ensured

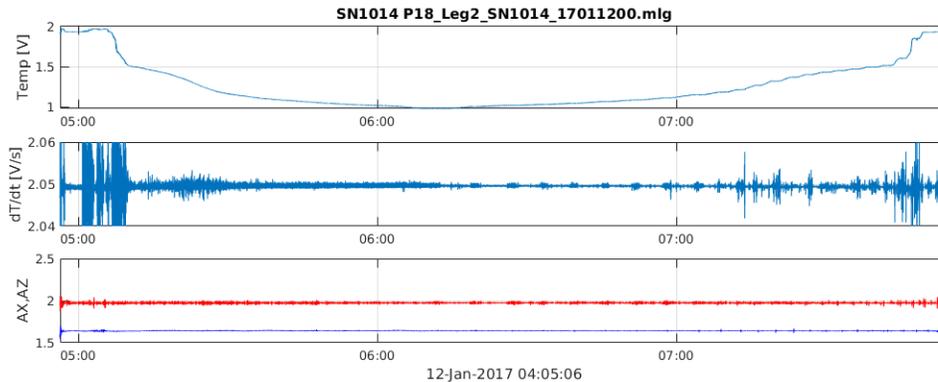
that the rosette could rest on its frame (and not on the downlooking sensors) and ensured that the downlooking sensors were as far from the frame as possible and as close to the leading edge of the rosette during descent as possible to avoid measuring turbulence generated by the rosette frame.

### Data processing

To plot vertical profiles of turbulent kinetic energy dissipation (epsilon) and dissipation of thermal variance (chi), Chipod temperature and temperature derivatives measurements must be collocated with pressure profiles. The chipods do not have a pressure sensors so vectors of doubly-integrated vertical acceleration (i.e. displacement) are fit to the pressure profiles from the CTD. Epsilon and chi as a function of pressure can be estimated by fitting the vertical temperature gradient ( $dT/dz$ ) spectrum, computed using the temperature time derivative ( $dT/dt$ ), and chipod descent rate to the theoretical temperature gradient spectrum using an iterative procedure described in Moum and Nash (2009).

Figure 12 shows typical cast measurements from the three chipods. The center plot is from a downlooker. The high signal on the temperature derivative ( $dT/dt$ ) record during the upcast is produced by the wake turbulence behind the rosette. The time record for the uplooker is similar: wake turbulence is recorded by the uplooker measurements as the rosette descends. However, there is a stronger wake turbulence signal for the uplooker because the uplooker sensors protrude beyond the top of the rosette frame. In addition, uplooker measurements on the upcast may be affected by turbulence associated with the stops to fire the Niskin bottles.





**Figure 12.** Representative cast measurements from the three chipods.

### Known Problems

Chipods proved to be quite independent, and easy to manage during the cruise. There were, however, a couple of issues encountered. These will be described in order of frequency below, starting with the most common problem. Some issues were related to equipment. The length of the USB connection cable (the long one did not function) made pulling data needlessly hard, and exposed the computer to the outside environment. More long USB spare cables are recommended. Also, the laptop computer used in conjunction with the Mini-logger program did not have a working keyboard, and an external one had to be used. This made both connecting to the Chipod and logging information while sampling difficult, especially in the sampling bay.

Mini-logger freezing when downloading data:

A very common issue when working with Chipods came from the mini-logger while recording data. Sometimes simply quitting mini logger and unplugging- the replugging the Chipod in to the data cable solved the problem, however in the worst case scenario, Mini logger (program on laptop) would freeze. One would then force quit the program. A couple of times, the Chipod would stop recording/ and or responding. The first time that this happened was before casting for leg 2 began, with the downloading Chipod #1008. This unit was replaced by #2013. 2 out of 3 Chipods did this during the cruise, and, after cast 177, uplooking chipod #1014 was replaced by #2016. Attempts at cycling the power by disconnecting the sensor did not work. Removal and replacement of the memory card on these units was not attempted.

**Table 8.13.1.** Summary of Chipod configurations used during P18.

Logger Board SN	Pressure Case SN	Sensor SN	Sensor Holder SN	Up/Down looker	Casts used
2013	Ti44-7	14-26d	-	Down	116-212
1014	Ti44-8	14-24d*	-	Up	116-177
2016	Ti44-1	14-25d*	-	Up	178-212
2018	Ti44-3	11-25d*	-	Up	116-212
1008	Ti44-5	14-28d	-	Up	100-112

Several replacements were made during the cruise, as outlined above. Sensor serial numbers are omitted as the clamps on the CTD frame obscure them. All items on the CTD except what is in the pressure case remained the same during switches between 1014-2016 and 1008-2013.

#### 8.14 $DI^{14}C$ in seawater

##### DISSOLVED INORGANIC CARBON ISOTOPES IN SEAWATER ( $DI^{14/13}C$ )

PI: Ann McNichol

Sampler: Mariana Bernardi Bif – University of Miami (Rosenstiel School of Marine and Atmospheric Sciences), mbif@rsmas.miami.edu

Along the P18 line, a total of 549 samples were collected from 26 stations using airtight 0.5L glass bottles. From the total of samples, 16 were duplicates randomly sampled from deep water Niskins (typically from bottles 1, 2 or 3). Full profiles were sampled from 15 stations (24 Niskins) and, at 11 stations, samples were collected from 16 Niskins with higher resolution at lower depths. More details about each station can be found in the deck log.

Briefly, using silicone tubing, the flasks were overflowed 1.5 times the fill time with seawater from the Niskin bottle while keeping the tubing at the bottom of the flask. Once the sample was taken, 5-10 ml of water was poured off to create a headspace and 120  $\mu$ L saturated mercuric chloride solution (provided by the DIC group) was added in the sampling bay. In order to avoid contamination, gloves were used during all collection, handling, and storage processes. Sample handling was done on a clean table covered with plastic. After all samples were collected from a station, the glass stoppers were dried and greased with Apiezon-M grease to ensure an airtight seal. The stoppers were secured with a rubber band. The samples were stored in AMS boxes inside the ship's bio-analytical laboratory and science storage room during the cruise, then transferred to the WHOI shipping container at the end of the leg to be shipped to WHOI for analysis.

The radiocarbon DIC content of seawater ( $DI^{14}C$ ) is measured by extracting the inorganic carbon as  $CO_2$  gas, converting the gas to graphite, then counting the number of  $^{14}C$  atoms in the sample directly using an accelerator mass spectrometer (AMS). Radiocarbon values will be reported as  $^{14}C$  using established conventions modified for AMS applications. The  $^{13}C/^{12}C$  of the  $CO_2$  extracted from seawater is measured relative to the  $^{13}C/^{12}C$ , a  $CO_2$  gas standard calibrated to the PDB standard using an isotope ratio mass spectrometer (IRMS) at NOSAMS.

For more information: <http://www.whoi.edu/nosams/page.do?pid=43516#3>

#### 8.15 Helium, noble gases (Ne, Ar, Kr and Xe) and Tritium

PI: William Jenkins, Scott Doney

Samplers: Annie Bourbonnais and Christian Lewis (leg 1), Yves Plancherel, Alexander Sidelev and Sarah Purkey (leg 2)

##### **He and Noble Gas Sampling**

He samples were collected at a total of 29 stations (~600 samples total) for leg 1 and 23 stations (~516 samples total) during leg 2 of the P18 cruise (52 stations in total) roughly evenly distributed along the transects (every ~2 degrees). We sampled approximately 18 to 24 depths at each station. We collected

water column profiles at maximum 3000 m depth at most of the stations, except at 13 stations (leg 1) and 17 stations (leg 2), where we collected full depth water column profiles. One duplicate sample at a randomly selected depth was collected at few stations during leg 1 (stn 27, 71, 83, 115) and leg 2 (131, 135, 147).

The copper tube used was 5/8" dehydrated refrigeration copper tube manufactured by Mueller Industries Inc. (Fulton, MS) or Cerro Flow Products USA and supplied in 50ft rolls. These rolls were stored in the air-conditioned and low humidity bio-analytical lab in order to limit corrosion and exposure risk. Poor quality copper can result in seal failure so great care is necessary in the handling of the copper in all stages of preparation, sampling, storage, and transport.

Approximately 1.5 hours before sampling a cast, the copper tubes were rolled out and cut into 30" sections. These sections were then flattened slightly so that after sampling and sealing of the copper tube samples, they could be re-rounded in order to create a small headspace allowing for expansion of the seawater when warming.

In order to sample from the rosette with the copper tubes, they were attached to the Niskins using Tygon tubing with a small silicon tubing adaptor at the nipple end. Tubing is attached to both ends of the copper tube, with the inlet tube coming in the bottom of the copper tube. Both pieces of Tygon tubing had plastic tubing clamps on them.

Water was drawn through the copper tube while gently knocking the tube with a thumper in order to remove any and all bubbles along the inside of the tubes. When all bubbles had been cleared, and at least 2 volumes of water had flushed through, the sample was ready for sealing. The 2 plastic clamps were closed and the Tygon removed from the Niskin for transport to the hydraulic sealing jaws. The jaws operate at 9000 psi on the hydraulic side when supplied with 80 psi of compressed air, press the copper together and cut it, creating a knife-edge seal and a gas tight sample chamber. Immediately after sealing, the tubes were re-rounded to create expansion space. After all samples were taken they were rinsed thoroughly with fresh water and dried before storing into a suitable green box in the Bio-Analytical Lab. Samples from both leg 1 and 2 will be stored in the Bio-Analytical Lab, which has good air conditioning, until the Brown's return to Charleston (USA) in March of 2017. As already emphasized before, a temperature controlled environment is critical to preserve the rolls of copper tubing and He/noble gas samples, which should remain moisture-free.

During leg 1, we experienced difficulties as most samples leaked at the jaws during sampling at station 7. We first switched the foot pump and then the jaws (at the end of station 11) and it seemed to resolve the problem. We think that there might have been a problem with the quality of the copper used at station 40, as most of the samples leaked at the jaws.

During leg 2, the rate of leaky samples increased when "Mueller" copper was used (stations 171, 175, 179, 183, 203, 206) relative to the fail rate of "Cerro" copper.

All samples will be analyzed onshore in Dr. Jenkins's lab at WHOI. Nobles gases analysis (Ne, Ar, Kr and Xe) are concurrently done with He analysis and do not require additional sample/water.

### **Tritium sampling**

A total of approximately 500 tritium samples were taken during leg 1 of P18 and 461 during leg 2. Tritium samples were generally drawn from the same stations and bottles as those sampled for He.

Samples were collected at maximum depth of ~1500 m during leg 1 and ~2000 m during leg 2 with full profiles collected at every 4 stations.

Tritium samples were taken using Tygon tubing to fill 1 liter glass jugs. Prior to the cruise, the jugs were baked in an oven, and backfilled with argon, then the caps were taped shut. While filling, the jugs were placed on deck and filled to about 2 inches from the top of the bottle, taking care to not spill the argon gas out. Caps were replaced and taped shut with electrical tape before being packed for shipment back to WHOI. Tritium samples will be degassed in the lab at WHOI and stored for a minimum of 6 months before mass spectrometer analysis.

#### 8.16 Dissolved organic matter $^{14}\text{C}$ , black carbon $^{14}\text{C}$ , biomarkers, and dissolved organics

PI: Ellen R.M. Druffel, Earth System Science, University of California, Irvine

Sample Collection: Brett D. Walker, Earth System Science, University of California, Irvine  
Christian Lewis, Earth System Science, University of California, Irvine

DOC is the largest pool of organic carbon in the ocean, comparable to the total carbon content in the atmosphere. Knowing the carbon isotopic signatures of DOC is important for understanding the biogeochemistry and dynamics of DOC cycling, and is essential for the C cycle modeling community. This study addresses fundamental gaps in our knowledge of the global carbon cycle and the dynamic nature of DOC in the ocean. These results will provide much needed, quantitative information on the timescale of DOC cycling in the ocean. These results will also help to determine the amount of terrestrially-derived organic carbon (*e.g.*, black carbon, BC) in the open ocean. DOC may serve as a sink for excess carbon dioxide produced from fossil fuel and biomass burning. Most of this excess carbon will end up in the ocean, and it is critical to improve our understanding of the processes that are important for its long-term storage. Results of this research will be made available for use in models that assess present and future concentrations of atmospheric  $\text{CO}_2$ .

The average radiocarbon ( $^{14}\text{C}$ ) age of dissolved organic carbon (DOC) in the deep ocean ranges from 4000 – 6500  $^{14}\text{C}$  years. However, the data set used to estimate this range is based on only a few sites in the world ocean. The main objective of this research is to determine the  $^{14}\text{C}$  signatures of DOC in seawater from low and high latitude regions of the Pacific for which there is no data. High-precision  $\Delta^{14}\text{C}$  measurements will be performed on samples using AMS (accelerator mass spectrometry) of DOC in water samples. Another objective is to isolate black carbon from DOC and determine the  $\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$  signatures of this recalcitrant DOC fraction. We are testing the following hypotheses:

(1)  $^{14}\text{C}$  of bulk DOC in the low latitude regions of the Pacific Ocean are similar to those in the south and north Pacific.

(2) Black carbon constitutes a significant amount of DOC in open ocean water, and its  $^{14}\text{C}$  age is greater than 20,000  $^{14}\text{C}$  years in the deep ocean.

*A summary of stations and number of depths sampled for  $\text{DO}^{14}\text{C}$  and Black Carbon on P18 are provided in Table 8.17.1 below.*

#### **Dissolved Organic Carbon-14 Sampling and Analysis**

Dissolved organic carbon-14 (as  $\Delta^{14}\text{C}$ ) samples were sampled in pre-combusted (540°C/2 hours) 1L borosilicate bottles (amber boston rounds). We collected 7x DOC samples below 1000m and 7x samples above 1000m at each station plus one duplicate. Samples above 400m depth were filtered using pre-combusted 70mm GF/F filters, acid cleaned silicone tubing and a stainless steel filter manifold. Samples were immediately frozen after collection and stored at -20°C for analysis at UCI. Once in the lab, samples will be acidified and sparged of dissolved inorganic carbon, and  $\text{CO}_2$  will be produced from DOC via UV oxidation and vacuum line extraction. This  $\text{CO}_2$  will then be graphitized and its radiocarbon content measured via AMS at the Keck Carbon Cycle AMS laboratory at UCI. DOC  $\delta^{13}\text{C}$  will also be measured in a split of the  $\text{CO}_2$  from each sample using light isotope mass spectrometry.

#### Black Carbon-14 Sampling

Due to extremely low concentrations of Black carbon in seawater ( $\sim <5\%$  of the DOC pool), 1x 4 gallon filtered surface (0-200m) samples and 1x8 gallon deep ( $\sim 2000\text{m}$ ) samples were collected. Surface samples were filtered using pre-combusted 150mm GF/F filters, acid-cleaned silicone tubing and a PVC filter manifold. The concentration and carbon isotopes ( $^{14}\text{C}$  and  $^{13}\text{C}$ ) of black carbon in these samples will be measured using the benzene polycarboxylic acid (BPCA) method. These data will be used to estimate the abundance and source of black carbon in oceanic DOC. Individual BPCAs will be isolated using a preparative capillary gas chromatograph (PCGC). These fractions will be combusted to  $\text{CO}_2$  gas, graphitized and radiocarbon content measured by AMS.

#### 8.17 DOM Biomarkers and Molecular Composition

PI: Dr. Brett Walker, Earth System Science, University of California, Irvine  
Co-PI: Dr. Karl Kaiser, Department of Marine Sciences and Oceanography, Texas A&M University Galveston Campus  
Co-PI: Dr. Hussain Abdulla, Department of Physical & Environmental Sciences, Texas A&M University, Corpus Christi

Sample Collection: Brett D. Walker, Earth System Science, University of California, Irvine  
Christian Lewis, Earth System Science, University of California, Irvine

Dissolved organic matter (DOM) represents the largest reservoir of organic carbon in the ocean, comparable to the total carbon content in the atmosphere. Marine DOM fuels microbial food webs, and has also been implicated to modulate transient warming events in Earth's history. Fundamental to the role of DOM in ocean biogeochemical cycles is its ability to control, store and release energy. Hence, fluxes of biologically labile DOM constituents between carbon reservoirs are arguably more important than net fluxes of total DOM. Thus, DOM cycling is largely determined by selective source and removal mechanisms. This study addresses fundamental gaps in our knowledge of DOM sources, molecular structures and removal of DOM in several unique ocean environments. Coupled with radiocarbon dating of dissolved inorganic and dissolved organic carbon (DIC, DOC), knowledge of DOM sources and composition provide much needed, quantitative information on the timescale and magnitude of DOM cycling in the largest global oxygen deficient zone (ODZ) the Eastern Tropical Pacific (ETP), the Equatorial Upwelling zone, the deep ocean and the Southern Ocean.

The main objectives of this research are 1) to investigate the formation of recalcitrant DOM by microbial processes, and 2) to identify mechanisms that remove recalcitrant DOM from the water column. Our approach relies on a comprehensive analysis of the chemical composition of DOM including organic

biomarkers (carbohydrates, DL-amino acids, lignin phenols), Proton Nuclear Magnetic Resonance ( $^1\text{H-NMR}$ ) and Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR-MS). These measurements will be integrated with existing GO-SHIP measurements (DOC and DIC  $^{14}\text{C}/^{13}\text{C}$ , Black Carbon,  $\text{O}_2$ , Nutrients, CFCs, etc.) and will provide an unprecedented analysis of DOM chemical composition in a major ocean basin. In addition, our analysis of DOM composition will evaluate the biogeochemistry of ODZs, which are predicted to expand in a warming ocean.

We will test the following hypotheses:

(1) The combination of biomarker analysis with high-resolution spectroscopic techniques (NMR, FT-ICR-MS) will reveal origins, structures and removal mechanisms of recalcitrant DOM (RDOM) molecules in the deep ocean. RDOM dynamics will be compared with the radiocarbon age of DOM (determined by Druffel Group) and thus help constrain processes responsible for DOM cycling on millennial timescales. We hypothesize that both carboxyl-rich alicyclic molecules (CRAM) and a specific dissolved organic nitrogen (DON) component will accumulate in the deep ocean, and that D-amino acids will indicate this to be the result of microbial degradation processes.

(2) Distinct DOM molecular compositions will be observed in the ODZ in the ETP/ETSP reflecting intense microbial cycling of DOM. We expect to find high bacterial contributions to DOM due to the importance of bacterial chemoautotrophy, and likely differences that can be attributed to specific chemoautotrophic metabolism (i.e. denitrification vs. anaerobic ammonium oxidation).

A summary of stations and number of depths sampled for dissolved biomarkers and molecular-level composition on P18 are provided in Table 8.17.1 below.

#### **Dissolved Organic Matter Biomarker Sampling and Analysis:**

Dissolved organic matter (DOM) biomarker samples were collected into 60 mL acid-soaked (10% HCl) and rinsed (18.2 M $\Omega$  Milli-Q water) high density polyethylene (HDPE) bottles. Sample depths shallower than 400m were filtered through a pre-combusted (540°C/2hr) GF/F filter and clean stainless steel manifold. On biomarker stations, all niskins were sampled. All samples were frozen immediately at -20°C and will be stored frozen until they can be shipped overnight and analyzed at Texas A&M Galveston (Co-PI Kaiser). Biomarker samples will be analyzed for many individual biomolecules including a suite of: total dissolved amino acids (including D-enantiomeric forms), amino sugars and neutral sugars. These will be measured via high performance liquid chromatography and ion chromatography by PI Kaiser at Texas A&M Galveston.

#### **Dissolved Organic Matter Molecular Composition Sampling and Analysis:**

Samples were taken for characterization of DOM composition at molecular level. As per all sample types, depths shallower than 400m were filtered through pre-combusted (540°C/2hrs) GF/F filter manifolds. We collected 6x DOC samples below 1000m and 8x samples above 1000m at each station and often one duplicate. First, samples were collected into pre-combusted (540°C/2hrs) 10 mL glass ampoules in triplicate, and subsequently poisoned with 1 drop saturated mercuric chloride ( $\text{HgCl}_2$ ) or 1 drop 12N hydrochloric acid. These ampoules were flame sealed and will be stored at room temperature in the dark until analysis via Proton Nuclear Magnetic Resonance Spectroscopy ( $^1\text{H-NMR}$ ) at the University of California, Irvine (PI Walker). This analysis will allow for the “bulk” molecular characterization of DOM at the functional group level. In addition, 1000 mL samples were collected into acid-soaked (10% HCl) and rinsed (18.2 M $\Omega$  Milli-Q water) polycarbonate bottles. These samples were immediately frozen at -

20°C and stored until further sample processing at Texas A&M Corpus Christi (Co-PI Abdulla). At Texas A&M, 1L samples be split for biomarker analysis (Texas A&M, Galveston) and the remaining 600ml of DOM isolated by solid phase extraction (SPE) and analyzed via either an Orbit Trap MS (Texas A&M Corpus Christi), or via Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR-MS). These latter two analyses will allow for the characterization of several thousand individual DOM molecules and fragments.

**Table 8.17.1.** Summary of stations sampled for PI Walker and Druffel parameters on GOSHIP P18N Legs 1 and 2. (*n*) indicates the number of Niskin bottles sampled from each station depth profile for each measurement parameter. A total of 36 stations were sampled on leg 1 and 27 stations on leg 2.

P18N Station #	Latitude	Longitude	DO <sup>14</sup> C ( <i>n</i> )	Black Carbon ( <i>n</i> )	Biomarkers ( <i>n</i> )	NMR ( <i>n</i> )	Biomarker + Molecular ( <i>n</i> )
5	22° 0.115'N	109° 59.992'W			24		
8	20° 30.050'N	109° 59.939'W		7			
9	20° 0.012'N	109° 59.999'W	16	5		18	14
10	19° 30.010'N	110° 0.007'W		1			
13	18° 0.012'N	110° 0.022'W				14	14
18	15° 30.043'N	110° 0.010'W			24		
22	13° 29.983'N	110° 0.008'W				14	14
23	13° 0.002'N	110° 0.017'W					
26	11° 30.007'N	109° 59.993'W			24		
30	9° 30.005'N	109° 59.988'W				14	14
34	7° 30.024'N	110° 0.066'W			24		
38	5° 29.996'N	109° 59.988'W		7			
39	4° 59.989'N	110° 0.031'W	14	3		15	14
43	2° 59.998'N	110° 0.004'W			24		
51	1° 0.000'N	110° 0.001'W				14	14
55	0° 0.226'N	110° 0.020'W			24		
59	0° 59.981'S	110° 0.010'W			24		
69	3° 59.990'S	110° 0.011'W				14	14
73	5° 35.404'S	109° 10.794'W			24		
77	6° 45.606'S	107° 31.760'W		8			
78	7° 3.599'S	107° 7.216'W	15	4		15	14
79	7° 21.001'S	106° 42.601'W		4			
82	8° 14.399'S	105° 28.188'W			24		
85	9° 7.199'S	104° 14.400'W				14	14
88	10° 0.000'S	102° 59.994'W			24		
92	12° 0.012'S	103° 0.025'W				14	14
96	14° 0.008'S	103° 0.008'W			24		
98	15° 0.005'S	102° 59.990'W		8			
99	15° 30.020'S	103° 0.000'W	14			16	14
104	17° 59.587'S	102° 59.987'W			24		
108	19° 59.995'N	102° 59.996'W				14	14

112	21° 59.995'S	103° 0.024'W			24		
116	24° 0.000'S	103° 0.002'W		8			
117	24° 30.000'S	103° 0.006'W	14			14	14
121	26°30.005'S	101°29.996'W			24		
126	29°5.738'S	103°0.380'W				14	14
130	31°0.060'S	102°59.978'W			24		
134	33°0.064'S	102°59.926'W				15	15
138	34°59.999'S	103°0.006'W			24		
142	37°0.041'S	102°59.903'W				14	14
147	39°30.031'S	103°0.265'W			24		
150	40°59.978'S	103°0.036'W		11			
151	41°30.040'S	103°0.036'W	14			15	14
155	43°30.018'S	102°59.995'W			24		
159	46°30.801'S	102°59.966'W				14	14
163	47°30.016'S	102°59.945'W			24		
168	50°0.002'S	102°59.966'W		9			
169	50°29.940'S	103°0.011'W	14			15	14
174	53°0.010'S	103°0.007'W			24		
178	55°0.005'S	102°59.470'W				14	14
182	57°0.006'S	102°59.981'W			24		
186	58°59.968'S	102°69.945'W		9			
187	59°30.000'S	103°0.000'W	16			17	16
188	60°0.034'S	103°0.013'W		2			
191	61°29.985'S	102°59.959'W			24		
197	64°30.099'S	103°0.058'W				15	15
203	67°30.025'S	103°1.378'W			24		
205	68°30.006'S	103°0.012'W		7			
206-1	68°59.905'S	103°0.041'W		6			
206-2	69°0.009'S	102°59.947'W	16			19	18
210	60°54.058'S	100°40.188'W			24		

## 8.18 Chlorofluorocarbons and Sulfur Hexafluoride (CFCs/SF<sub>6</sub>)

PI: John Bullister, NOAA/PMEL

Lead Analyst: Bonnie Chang, NOAA/PMEL and UW (Leg 1 and Leg 2)

CFC analysts: Tae-Jun Choi (Leg 1 and Leg 2), Laura Whitmore (Leg 1) and Rachel McMahon (Leg 2)

### Chlorofluorocarbons (CFCs) and Sulfur Hexafluoride (SF<sub>6</sub>)

The PMEL analytical system (Bullister and Wisegarver, 2008) was used for CFC-11, CFC-12, sulfur hexafluoride (SF<sub>6</sub>) and nitrous oxide (N<sub>2</sub>O) analyses on the GOSHIP P18 expedition. Greater than 4000 samples of dissolved CFC-11, CFC-12 and SF<sub>6</sub> ('CFC/SF<sub>6</sub>') were analyzed.

In general, the analytical system performed well for CFCs, SF<sub>6</sub> and N<sub>2</sub>O during the cruise. Typical dissolved SF<sub>6</sub> concentrations in modern surface water are ~1-2 fmol kg<sup>-1</sup> seawater (1 fmol= femtomole = 10<sup>-15</sup> moles), approximately 1000 times lower than dissolved CFC-11 and CFC-12 concentrations. The limits of detection for SF<sub>6</sub> were approximately 0.03 fmol kg<sup>-1</sup> on this cruise. SF<sub>6</sub> measurements in seawater remain extremely challenging.

Water samples were collected in bottles designed with a modified end-cap to minimize the contact of the water sample with the end-cap O-rings after closing. Stainless steel springs covered with a nylon powder coat were substituted for the internal elastic tubing provided with standard Niskin bottles. When taken, water samples collected for dissolved CFC-11, CFC-12 and SF<sub>6</sub> analysis were the first samples drawn from the bottles. Care was taken to coordinate the sampling of CFC/SF<sub>6</sub> with other samples to minimize the time between the initial opening of each bottle and the completion of sample drawing. Samples easily impacted by gas exchange (dissolved oxygen, <sup>3</sup>He, DIC and pH) were collected within several minutes of the initial opening of each bottle. To minimize contact with air, the CFC/SF<sub>6</sub> samples were drawn directly through the stopcocks of the bottles into 250 ml precision glass syringes equipped with three-way plastic stopcocks. The syringes were immersed in a holding tank of clean surface seawater held at ~10°C until 20 minutes before being analyzed. At that time, the syringe was placed in a bath of surface seawater heated to 32°C.

For atmospheric sampling, a 75 m length of 3/8" OD Dekaron tubing was run from the CFC van, located on the fantail, to the bow of the ship. A flow of air was drawn through this line into the main laboratory using an Air Cadet pump. The air was compressed in the pump, with the downstream pressure held at ~1.5 atm, using a backpressure regulator. A tee allowed a flow of ~100 ml min<sup>-1</sup> of the compressed air to be directed to the gas sample valves of the CFC/SF<sub>6</sub> analytical systems, while the bulk flow of the air (>7 L min<sup>-1</sup>) was vented through the back-pressure regulator. Air samples were analyzed only when the relative wind direction was within 60 degrees of the bow of the ship to reduce the possibility of shipboard contamination. Analysis of bow air was performed at ~15 locations along the cruise track. At each location, at least five air measurements were made to improve the precision of the measurements.

Concentrations of CFC-11, CFC-12 and SF<sub>6</sub> in air samples, seawater, and gas standards were measured by shipboard electron capture gas chromatography (EC-GC) using techniques modified from those described by Bullister and Weiss (1988) and Bullister and Wisegarver (2008), as outlined below. For seawater analyses, water was transferred from a glass syringe to a glass-sparging chamber (volume 200 ml). The dissolved gases in the seawater sample were extracted by passing a supply of CFC/SF<sub>6</sub>-free N<sub>2</sub> through the sparging chamber for a period of 6 minutes at 150 ml min<sup>-1</sup>. Water vapor was removed from the purge gas during passage through a Nafion drier. Carbon dioxide was removed with an 18 cm long, 3/8" diameter glass tube packed with Ascarite and a small amount of magnesium perchlorate desiccant. The sample gases were concentrated on a cold-trap consisting of a 1/16" OD stainless steel tube with a 2.5 cm section packed tightly with Porapak Q, a 15 cm section packed with Carboxen 1000 and a 2.5 cm section packed with MS5A. A Neslab Cryocool CC-100 was used to cool the trap to -65°C. After 6 minutes of purging, the trap was isolated, and it was heated electrically to 170°C. The sample gases held in the trap were then injected onto a pre-column (~61 cm of 1/8" O.D. stainless steel tubing packed with 80-100 mesh Porasil B, held at 80°C) for the initial separation of CFC-12, CFC-11, SF<sub>6</sub> from later eluting peaks.

After the SF<sub>6</sub> and CFC-12 had passed from the pre-column and into the second pre-column (26 cm of 1/8" O.D. stainless steel tubing packed with MS5A, 160°C) and into the analytical column #1(174 cm of 1/8"

OD stainless steel tubing packed with MS5A + 60 cm Porasil C held at 80°C), the outflow from the first pre-column was diverted to the second analytical column (180 cm 1/8" OD stainless steel tubing packed with Porasil B, 80-100 mesh, held at 80°C). The gases remaining after CFC- 11 had passed through the first pre-column, were backflushed from the precolumn and vented. After CFC-12 had passed through the second pre-column, a flow of Argon:Methane (95:5) was used to divert the N<sub>2</sub>O to a third analytical column (30 cm of MS5A, 150°C). Column #3 and the second pre-column were held in a Shimadzu GC8AIE gas chromatograph with an electron capture detector (ECD) held at 330°C. Columns #1, and the first pre-column were in another Shimadzu GC8AIE gas chromatograph with ECD. The column #2 was also in a Shimadzu GC8AIE gas chromatograph with the ECD held at 330°C.

The analytical system was calibrated frequently using a standard gas of known CFC/SF<sub>6</sub> composition (PMEL-WRS-72611). Gas sample loops of known volume were thoroughly flushed with standard gas and injected into the system. The temperature and pressure was recorded so that the amount of gas injected could be calculated. The procedures used to transfer the standard gas to the trap, pre-columns, main chromatographic column, and ECD were similar to those used for analyzing water samples. Four sizes of gas sample loops were used. Multiple injections of these loop volumes could be made to allow the system to be calibrated over a relatively wide range of concentrations. Air samples and system blanks (injections of loops of CFC/SF<sub>6</sub> free gas) were injected and analyzed in a similar manner. The typical analysis time for seawater, air, standard or blank samples was ~12 minutes. Concentrations of the CFC-11 and CFC-12 in air, seawater samples, and gas standards are reported relative to the SIO98 calibration scale (Bullister and Tanhua, 2010). Concentrations of SF<sub>6</sub> in air, seawater samples, and gas standards are reported relative to the SIO-2005 calibration scale (Bullister and Tanhua, 2010). Concentrations in air and standard gas are reported in units of mole fraction CFC in dry gas, and are typically in the parts per trillion (ppt) range. Dissolved CFC concentrations are given in units of picomoles per kilogram seawater (pmol kg<sup>-1</sup>) and SF<sub>6</sub> concentrations in fmol kg<sup>-1</sup>. CFC/SF<sub>6</sub> concentrations in air and seawater samples were determined by fitting their chromatographic peak areas to multi-point calibration curves, generated by injecting multiple sample loops of gas from a working standard (PMEL cylinder WRS72611) into the analytical instrument. The response of the detector to the range of moles of CFC/SF<sub>6</sub> passing through the detector remained relatively constant during the cruise. Full-range calibration curves were run at several times during the cruise and partial curves were run as frequently as possible, usually while sampling. Single injections of a fixed volume of standard gas at one atmosphere were run much more frequently (at intervals of 90 minutes) to monitor short-term changes in detector sensitivity.

The purging efficiency was estimated by re-purging a high-concentration water sample and measuring the residual signal. At a flow rate of 150 ml min<sup>-1</sup> for 6 minutes, the purging efficiency for SF<sub>6</sub> and both CFC gases was > 99%. The efficiency for N<sub>2</sub>O was typically about 97%.

On this expedition, based on the analysis of more than 300 pairs of duplicate samples, we estimate precisions (1 standard deviation) of about 0.5% or 0.003 pmol kg<sup>-1</sup> (whichever is greater) for dissolved CFC-12 and 1% or 0.005 pmol kg<sup>-1</sup> for CFC-11 measurements. The estimated precision for SF<sub>6</sub> was 3% or 0.04 fmol kg<sup>-1</sup>, (whichever is greater). The estimated precision for N<sub>2</sub>O was 3% or 0.2 nmol kg<sup>-1</sup>, (whichever is greater). Overall accuracy of the measurements (a function of the absolute accuracy of the calibration gases, volumetric calibrations of the sample gas loops and purge chamber, errors in fits to the calibration curves and other factors) is estimated to be about 2% or 0.004 pmol kg<sup>-1</sup> for CFC-11 and CFC-12 and 4% or 0.04 fmol kg<sup>-1</sup> for SF<sub>6</sub>.

A small number of water samples had anomalously high CFC-12 and/or SF<sub>6</sub> concentrations relative to adjacent samples. These samples occurred sporadically during the cruise and were not clearly associated with other features in the water column (e.g., anomalous dissolved oxygen, salinity, or temperature features). This suggests that these samples were probably contaminated with CFCs/SF<sub>6</sub> during the sampling or analysis processes.

Measured concentrations for these anomalous samples are included in the data file, but are given a quality flag value of either 3 (questionable measurement) or 4 (bad measurement). Less than 1% of samples were flagged as bad or questionable during this voyage. A quality flag of 5 was assigned to samples which were drawn from the rosette but never analyzed due to a variety of reasons (e.g., leaking stopcock, plunger jammed in syringe barrel, etc).

Radio frequency interference (RFI) occasionally occurred and was manifested as negative excursions in the signal acquired from the CFC-11 channel. Once RFI was identified as the cause of this interference, testing was carried out to locate the source. The built-in radio in the winch house of the R/V Ronald H. Brown was identified as contributing most to the observed RFI. Handheld radios were a problem when transmitting within ~10-15 ft of the CFC-11 GC. Neither shielding the signal cable from the CFC-11 detector nor changing the frequency at which a given radio was transmitting alleviated the problem. The solution was to switch the winch house radio (broadcasting at a fixed 45W) to a lower power hand-held radio (<5W) and restrict hand-held radio transmissions to >15ft from the CFC lab van. At the start of Leg 2 the RFI problems returned. It was found that the ship had begun using new hand-held radios that broadcast at a higher power than the old hand-held radios. The solution was to restrict hand-held radio transmissions to their low power setting (<0.5W) at a distance >15ft from the CFC lab van.

A number of peaks (n= 4) on the CFC-11 channel were lost due to RF interference and were flagged as bad (4).

Some N<sub>2</sub>O samples had elevated re-strip and stripper blank values which is due to biological growth on the glass frit or walls of the stripper. These were not used in the determination of the stripper efficiency corrections. During the purging process with nitrogen gas, the seawater samples and interior of the stripping chamber become anoxic, which may lead to in-situ production of N<sub>2</sub>O in the stripping chamber. The stripping chamber remains anoxic during subsequent 12 minute stripper blank and re-strip analyses, and any in-situ N<sub>2</sub>O production during this period would increase the N<sub>2</sub>O values of the re-strip or stripper blank measurements. Washing the stripper frit and walls with 10% HCl immediately reduced the stripper blank and re-strip values. However, these values often significantly increased within a day or so after the acid rinses. During the cruise the stripper frit was washed with 10% HCl at 24-48hr intervals to maintain a stripper efficiency of approximately 97%.

#### **References:**

- Bullister, J.L., and T. Tanhua (2010): Sampling and measurement of chlorofluorocarbons and sulfur hexafluoride in seawater. In *The GO-SHIP Repeat Hydrography Manual: A Collection of Expert Reports and Guidelines*. E.M. Hood, C.L. Sabine, and B.M. Sloyan (eds.), IOCCP Report Number 14, ICPO Publication Series Number 134. Available online at <http://www.go-ship.org/HydroMan.html>
- Bullister, J.L., and R.F. Weiss, 1988: Determination of CC13F and CC12F2 in seawater and air. *Deep-Sea Res.*, y. 25, pp. 839-853.

Bullister, J.L., and D.P. Wisegarver (2008): The shipboard analysis of trace levels of sulfur hexafluoride, chlorofluorocarbon-11 and chlorofluorocarbon-12 in seawater. *Deep-Sea Res. I*, 55, 1063-1074.

Prinn, R.G., R.F. Weiss, P.J. Fraser, P.G. Simmonds, D.M. Cunnold, F.N. Alyea, S. O'Doherty, P. Salameh, B.R. Miller, J. Huang, R.H.J. Wang, D.E. Hartley, C. Harth, L.P. Steele, G. Stunock, P.M. Midgley, and A. McCulloch, 2000: A history of chemically and radiatively important gases in air deduced from ALE/GAGE/AGAGE. *J. Geophys. Res.*, y. 105, pp. 17,751- 17,792.

## 8.19 Dissolved Oxygen (discrete)

**Analysts Leg1: Samantha Ladewig and Alexander Sidelev**

**Analysts Leg2: Emma Pontes and Chris Langdon**

**(PIs: Chris Langdon, RSMAS, Molly Baringer, AOML)**

### **Equipment and Techniques**

Dissolved oxygen analyses were performed with an automated titrator using amperometric end-point detection [Langdon, 2012]. Sample titration, data logging, and graphical display were performed with a PC running a LabView program written by Ulises Rivero of AOML. The temperature-corrected molarity of the thiosulfate titrant was determined as given by Dickson [1994]. Thiosulfate was dispensed by a 2 ml Gilmont syringe driven with a stepper motor controlled by the titrator. The whole-bottle titration technique of Carpenter [1965], with modifications by Culberson et al. [1991], was used. Three to four replicate 10 ml iodate standards were run every 3-4 days ( $SD < 1$  uL). The reagent blank was determined as the difference between V1 and V2, the volumes of thiosulfate required to titrate 1-ml aliquots of the iodate standard, at the beginning and end of the cruise.

### **Sampling and Data Processing**

Dissolved oxygen samples were drawn from Niskin bottles into calibrated 125-150 ml iodine titration flasks using silicon tubing to avoid contamination of DOC and CDOM samples. Samples were drawn by counting while the flask was allowed to fill at full flow from the Niskin. This count was then doubled and repeated thereby allowing the flask to be overflowed by two flask volumes. At this point the silicone tubing was pinched to reduce the flow to a trickle. This was continued until a stable draw temperature was obtained on the Oakton meter. These temperatures were used to calculate  $\mu\text{mol/kg}$  concentrations, and provide a diagnostic check of Niskin bottle integrity. 1 ml of  $\text{MnCl}_2$  and 1 ml of  $\text{NaOH/NaI}$  were added immediately after drawing the sample using a Re-pipetor bottle-top dispenser. The flasks were then stoppered and shaken well. DIW was added to the neck of each flask to create a water seal. 24 samples plus two duplicates were drawn at each station. The total number of samples collected from the rosette was 5490.

The samples were stored in the lab in plastic totes at room temperature for 30-40 minutes before analysis. The data were incorporated into the cruise database shortly after analysis.

Thiosulfate normality was calculated for each standardization and corrected to the laboratory temperature. This temperature ranged between 15.1 and 23.1 C.

A total of 32 standardizations were performed during the legs 1 and 2 (mean=707.0,  $SD=3.6$  uL). Reagent blanks were run at the beginning ( $1.7 \pm 0.8$  uL), middle ( $0.4 \pm 0.7$  uL) and end of the cruise ( $1.2 \pm 0.6$  uL).

## Volumetric Calibration

The dispenser used for the standard solution (SOCOREX Calibrex 520) and the burette used to dispense the thiosulfate titrant were calibrated gravimetrically just before the cruise. Oxygen flask volumes were determined gravimetrically with degassed deionized water at AOML. The correction for buoyancy was applied. Flask volumes were corrected to the draw temperature.

## Duplicate Samples

Duplicate samples were drawn at two depths on every cast. The Niskins selected for the duplicates and hence the oxygen flasks were changed for each cast. A total of 419 sets of duplicates were run. The average standard deviation of all sets was  $0.36 \text{ umol kg}^{-1}$ . Fifty percent of the duplicates had a SD of  $<0.20 \text{ umol kg}^{-1}$  (Figure 10).

## Quality Coding

Based on preliminary quality control performed during the cruise the following quality flags were assigned.

**Table 8.19.1.** Analytical problems with O<sub>2</sub> during P18.

Quality flag	Number	Note
2	5257	Good
3	190	Sample value low or high for profile and adjoining casts. Questionable
4	35	Stopper loose or bubbles noted in the flask prior to titration.
5	5	Sample value not reported due to a problem occurring during the titration (spilled, overshoot endpoint).

## Problems

On station 7 burette #1 was broken and replaced with burette #2. On station 25 the platinum detector was broken and replaced with a spare. On station 70 tubing and pinch valve were replaced due to a valve failure. The consistency of standards indicate that these changes did not result in any significant bias in the results.

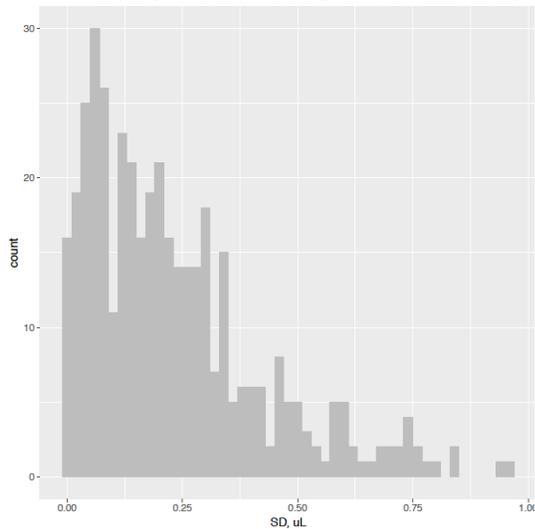
## Cross-over comparisons

None this cruise.

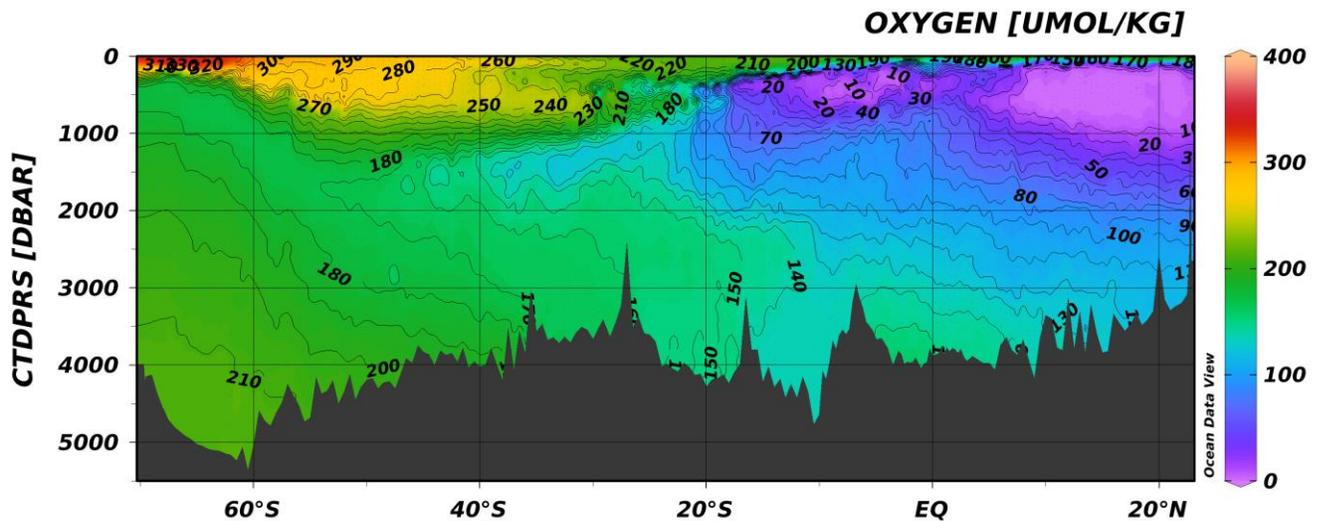
## References:

- Carpenter, J. H., "The Chesapeake Bay Institute technique for the Winkler dissolved oxygen method," *Limnology and Oceanography*, 10, pp. 141-143 (1965).
- Culberson, C. H., Knapp, G., Stalcup, M., Williams, R. T., and Zemlyak, F., "A comparison of methods for the determination of dissolved oxygen in seawater," Report WHPO 91-2, WOCE Hydrographic Programme Office (Aug. 1991).
- Dickson, A. G., "Determination of dissolved oxygen in seawater by Winkler titration," WHP Operations and Methods (1994a).

Langdon, C. (2010). Determination of dissolved oxygen in seawater by Winkler titration using the amperometric technique. The GO-SHIP Repeat Hydrography Manual: A Collection of Expert Reports and Guidelines. E. M. Hood, C. L. Sabine and B. M. Sloyan, IOCCP Report Number 14, ICPO Publication Series Number 134.



**Figure 13.** Histogram of the duplicate Standard Deviations.



**Figure 14.** Full depth vertical section of dissolved oxygen structure along 103°W (P18 line).

## 8.20 DOC14 Pyrolysis

PI: Margot White      mew070@ucsd.edu

Remaining water was collected from eight niskins at each of three stations (28, 58, and 94) along Leg 1 of the P18 line. 9L carboys were rinsed once with water from the niskin, then filled and acidified to pH 2

using concentrated hydrochloric acid. Between 5 and 9 liters were collected from each niskin. Initial samples for DOC were collected in 40mL vials from each carboy. The seawater then gravity flowed through 1g PPL cartridges. DOC samples were collected from flowthrough and the remainder of the waste collected in buckets. Cartridges were then rinsed three times with pH2 milliQ water and frozen to be sent back to Scripps Institution of Oceanography for elution in methanol. Samples will be subjected to ramped oxidation according to previously established methods and analyzed for radiocarbon content at Woods Hole Institution of Oceanography's NOSAMS facility<sup>1,2</sup>. This technique allows us to fractionate the radiocarbon pool based on thermal lability, providing more information than a single mean  $\Delta^{14}\text{C}$  measurement.

Sources:

1. Plante, Alain F., et al. "Distribution of Radiocarbon Ages in Soil Organic Matter by Thermal Fractionation." *Radiocarbon* 55.2 (2013): 1077-1083.
2. Williams, Elizabeth K., et al. "Charring and non-additive chemical reactions during ramped pyrolysis: Applications to the characterization of sedimentary and soil organic material." *Organic Geochemistry* 77 (2014): 106-114.

## 8.21 SOCCOM sampling/HPLC and POC

C. Kovach, NOAA/NESDIS/STAR

When weather and sea were conducive to sampling, HyperPro II profiling spectro-radiometer casts were performed while a CTD station was underway. Over the course of Legs 1 and 2 these casts occurred 161 times, typically in sets of 3 sets of 5 drops to ten meters depth. Deep casts up to 100 meters were performed in the South Pacific Gyre. Microtops reading for Aerosol Optical Depth were also made when sun conditions allowed, and these data can be found at:

[https://aeronet.gsfc.nasa.gov/new\\_web/cruises\\_new/Ron\\_Brown\\_16\\_1.html](https://aeronet.gsfc.nasa.gov/new_web/cruises_new/Ron_Brown_16_1.html)

At stations where HyperPro II or SOCCOM float deployments/visitations were conducted, seawater remaining in Niskins at the Chlorophyll max (and occasionally mid-way between surface and chl max) was collected for phytoplankton pigments by HPLC, and Ap (pad absorption) analyses. Surface samples were collected over the side with a bucket. These samples were filtered by vacuum pump through 25 mm GFF filters that were preserved in liquid N<sub>2</sub> and will be shipped to (UMass Boston) for analyses.

Sampling: The NESDIS group collected samples for POC/DOC and HPLC phytoplankton pigment analysis on stations where SOCCOM bio-optical floats were deployed. NESDIS used our large volume HPLC/POC/DOC filtration rig to filter the samples and the samples were stored in our liquid nitrogen Dewar during the cruise. We collected 1-2 L samples into polyethylene sample bottles from the surface and chlorophyll maximum depths at each cast.

Preparation: Samples were filtered onto pre-combusted 25 mm GF/F glass fiber filters at <-0.05 MPa vacuum pressure. The filters were folded into foil packets and immediately frozen in liquid nitrogen. The samples were returned to UMass Boston via liquid nitrogen dry shipper.

## 8.22 Plastics Net Deployment

Sampler Leg 1: Samantha Ladewig

Sampler Leg 2: Alex Sidelev

(PI: Shaowu Bao, CCU)

## **Net Deployment**

Before deployment, the inside of the plankton net and cod end were rinsed separately with a pressurized seawater hose to dislodge any remaining materials from the previous cast or from storage. After rinsing, the plankton net and cod end were attached. The plankton net was connected to a line attached to the ship's starboard side, with the flow-meter hanging in the center of the net's opening and two buoys attached, one on the net's opening and the other on the cod end. The flow-meter's reading was annotated and the "event" (which recorded weather parameters during the cast) was activated before the cast. The net was deployed three stations in a row with one station skipped in between, for a total of 67 casts and plus 1 test cast. The timing of the cast varied depending on arrival times at stations and timing with other deployments, but was always performed on an official P18 station before the CTD surfaced.

With the permission of the bridge, the net was lowered into the water and cast for 20 minutes. The amount of line let out in the beginning varied on how the net maneuvered in the water. The time the net entered the water was noted in the plastic's field log book. As the current began to take the net, the line was let out to about 50 meters and left to collect while drifting in the current. If the net's mouth was not facing into the current, the net was pulled back toward the ship and let go to drift again. The net's opening was at best kept below the water's surface to ensure an accurate flow-meter reading. Often the net's position varied from cast to cast and even during individual cast depending on current movement and strength and also the ship's maneuvers to keep the CTD package safe while deployed.

At net recover, the net was slowly pulled in without fighting the current. Once aboard, the flow-meter's reading was annotated and the net was disconnected from the line. While still connected, the outside of the net and cod end were washed top-down with a pressurized seawater hose to wash materials downwards into the cod end. The cod end was disconnected from the net and brought to the lab for storage.

The net was stowed outside to dry and the line was coiled up. The weather recording event was stopped in the computer room. Swell and wind-wave data were collected from the bridge and current velocity and direction were collected from the ship's ADCP. At the end of the cruise, all data was collected from the weather recording event on to a USB drive.

## **Sample Preservation**

The sample was poured from the cod end into a sample container. The cod end was rinsed out with Milli-Q water and into the sample container. Rinses consisted of completely cleaning the inside of the cod end with a squirt bottle full of Milli-Q water while also draining excess water that builds up inside the cod end through the slots. Draining through the cod end slots is important so that little water as possible is stored in the sample container which reduces the amount of ethanol used for sample preservation. When the sample was stuck on the sides of the cod end, the cod end was set in a small bucket half full of Milli-Q water and flushed from the outside in by pushing and pulling the cod end in and out of the bucket repeatedly, but not forcefully. When the cod end looked completely clean, three additional rinses were performed to obtain microplastic particles invisible to the eye.

After all rinses were completed, ethanol was dispensed into the sample container in an approximate volume ratio of ~1:1 ethanol: Milli-Q. The container was labeled with the official P18 station number and the word "tow." After storing the sample, the cod end was rinsed out with the ship's sink water to rinse off salts which may corrode the metal weight on the cod end. The number of jars collected from a given station was usually one, but more were used where needed. Samples were stored at room temperature in

the wet lab and remained there until arrival (~March 2017) in Charleston, SC for pickup. Sample analysis and data processing will take place at CCU's Environmental Quality Laboratory.

## 9 Appendix 1: Water Sample Quality Code Summary

This section contains WOCE quality codes [Joyc94] used during this cruise, and remarks regarding bottle data.

**Table 9.1.** P18 Water Sample Quality Code Summary

parameter	Flag					
	1	2,6	3	4	5	9
CTDSAL	0	5147	0	0	0	0
SALNTY	0	5099	0	0	0	48
CTDOXY	0	5147	0	0	0	0
OXYGEN	36	4837	178	30	4	61
SILCAT	81	5051	2	2	0	11
NITRAT	81	5051	2	2	0	11
NITRIT	81	5051	2	2	0	11
PHSPHT	81	5051	2	2	0	11
CFC-11	16	3726	11	32	0	1362
CFC-12	16	3726	11	32	0	1362
SF6	16	3722	15	32	0	1362
CCL4	16	3725	12	32	0	1362
N2O	3746	0	0	0	0	1401
TCARBN	3	4855	13	35	1	240
ALKALI	7	4808	46	29	5	252
PH_SWS	3	4879	32	17	1	215

Quality evaluation of data included comparison of bottle salinity and bottle oxygen data with CTDO data using plots of differences; and review of various property plots and vertical sections of the station profiles and adjoining stations. Comments from the Sample Logs and the results of investigations into bottle problems and anomalous sample values are included in this report. Sample number in this table is the cast number times 100 plus the bottle position number.

## 10 Appendix 2: Timeline, Leg 1

10/04/2016 Scheduled completion of dry dock repair period is delayed from 10/16/2016 to 10/20/2016:

Two significant items were discovered during the drydocking which caused the delays: (1) the #2 main propulsion diesel generator (MPDG) had mechanical damage where the rotor had touched the windings = rewinding the generator which took 30 days and (2) the thrust collars

- where the z-drives insert into the ship were worn and out of round. These required machining of the hull and fabrication of the new collars.
- 10/07/2016 Leg 1 of the P18 GO-SHIP project is delayed by 5 days in light of the shifting schedule. Leg 2 is delayed by 4 days.
- 10/20/2016 Brown completes the dry dock repair period. Many repairs were completed. Notable repairs for GO-SHIP work include: (1)overhaul of both Markey winches, and (2)replacement of the aft winch wire with new 0.322” wire. The forward wire is “gently used.”
- 10/22/2016 Brown completes sea trials (1 of 5) in the San Francisco Bay. This trial is considered a success.
- 10/24/2016 A previously unsolved intermittent issue with the GE propulsion motor drive cabinets (automation that runs the propulsion motors) re-surfaces on the transit from San Francisco to San Diego.
- 10/26/2016 A second sea trial (2 of 5) is conducted with the goal of resolving the drive cabinet issue that resurfaced on the transit, but work done on the sea trial does not identify the cause.
- ~10/27/2016 An issue is communicated regarding the aft winch’s ability to spool.
- ~10/28/2016 A Markey representative identifies a wiring error on the aft winch. Fixing it addresses the winch issue.
- 11/01/2016 A third (3 of 5) sea trial is scheduled for Monday 11/07 with representatives from the company that creates the drive cabinets on board.
- 11/04/2016 Overtightened screws on an engine part (the aluminum rocker arm baseplate) are reported to have caused damage. This damage was first apparent at the end of the second sea trial and manifested with oil leaking onto the engine. The report comes near the end of the business day, so no parts are scheduled to be ordered on 11/07. That evening the cruise is delayed to 11/09 or 11/10 on a TBD basis.
- 11/07/2016 Sea trials (3 of 5) are conducted and the drive cabinet issue is identified, a fix is made, and the issue is declared resolved. Replacement parts are considered ordered for the damaged engine part (first business day since discovery). The expected sailing date is pushed to 11/10 at 1000.
- 11/09/2016 Delays getting the part order completed and a longer estimated delivery timeframe pushes back the sailing date to 11/12/2016 at 1700.
- 11/11/2016 Parts arrive and CAT technicians work alongside engineers to get the parts installed quickly. The departure time is pushed up 2 hours to 1500. The ship is deemed ready to go in the late evening.
- 11/12/2016 Departed San Diego at 1500. Fuel redistribution operations result in loss of fuel from a small holding tank. The vessel stops for ~1-2 hours while this tank is being refilled. Separately, high temperatures are noted in two areas of the engine. Engineers work to identify the cause of the elevated temperatures.
- 11/13/2016 Troubleshooting for elevated engine temperatures is ongoing until 1700. Engine RPM slowed to 660 during troubleshooting, but speed over ground remains consistent at ~11.5 kts. At 1700, ~250 km from San Diego, it is announced that the troubleshooting has been unable to identify the root cause. Given the inability to operate the engine safely at full capacity, the Brown is turned around to return to San Diego for shore-side diagnosis and repairs by engineers working alongside Wärtsilä (the company that makes the engine) representatives. Turnaround at ~28° 36’ N.
- 11/14/2016 We return to San Diego at 11.5 to 12 kts SOG. The transit is halted at 31° 46.07’ N 117° 6.31’W for an impromptu test cast to ~1300 m. The Markey winch requires 1 adjustment at ~200 m wire out, but the winch otherwise is not a major concern. Several sensors experience

problems that are thought to be quickly resolved. The CTD pump shuts off intermittently on the return cast and is swapped out after the cast.

- 11/15/2016 A potential fix (a replaced pump) is identified and implemented. A sea trial (4 of 5) is planned for 11/16/2016.
- 11/16/2016 The sea trial (4 of 5) is conducted, and the potential engine fix is determined to have not resolved the elevated temperature issue. A representative from Wärtsilä is scheduled to join the ship on 11/17/2016 for troubleshooting. A second test cast is conducted at 32° 37.64' N 117° 26.55' W in ~280 m of water, but the CTD pump begins continuously restarting at the surface and the cast is aborted. Troubleshooting resumes.
- 11/17/2016 Sea trial (5 of 5) is conducted with the Wärtsilä rep on board. An oil pump is determined to have been in a bypass mode, restricting oil flow. The mode is switched and engine temperatures remain stable for several hours of travel at ~12.5 kts. Confirmation of this diagnosis is planned for 11/18/2016. Scientists are recalled with ~36 hours' notice to return to the vessel.
- 11/18/2016 The engine temperature problem diagnosis is confirmed while scientists return to the vessel. The Mexican offices close without having renewed the permissions to conduct work in the Mexican EEZ. The offices are closed for the next 3 days for a weekend and a Mexican Holiday.
- 11/19/2016 The Brown sets sail without three scientific personnel due to schedule conflicts that became more acute during the delays. The responsibilities of these three individuals are planned to be shared among the scientists remaining.

A test cast is conducted to ~1300 m after drills at the edge of US waters. The profile looks excellent until ~80 meters above bottom (by altimeter and consistent with the multibeam). At this point the altimeter reading abruptly decreases by 10-20 m before returning to the original reading. This process occurs too quickly to reflect a real movement of the package. At this point, the primary and secondary salinity, temperature, and O<sub>2</sub> sensor readings become unusably irregular. The primary sensors recover quickly, but the secondary sensors do not. The package is returned to the deck after finishing the cast. The bottles are sampled while a practice net tow and hyperpro are conducted. Sampling continues for 1 hour beyond the conclusion of these procedures while the Brown waits on station. We do not proceed with the transit because we intend to conduct further deployments to resolve the CTD issues, and we cannot yet (legally) do so in the Mexican EEZ. Suspecting an obstruction has been sucked into the plumbing, the first attempted fix is a flush of the sensor plumbing. Another test cast is conducted to 200 m, revealing that the primary sensor issues have been resolved while the secondary sensor issues remain. Next, it is found that the outflow to one of the plumbing ports is bent, also possibly obstructing outflow. A third test cast to 200 m reveals that fixing this has not resolved the issue. Finally, the pump is replaced and the sensor readings return to normal on a 4th cast to 200 m. Five bottles are tripped at 200 m to provide seawater for practice collecting samples during the long transit ahead.

We resume the transit to the first planned station offshore Cabo San Lucas. We arrive 11/21 at ~10:00 and begin waiting on station.

- 11/22/2016 The change in project dates is communicated to the US State Department by this time, via a vis the Chilean clearance application.
- 11/23/2016 Mexican clearance is granted at 20:00 and we begin CTD work.

Station 1: The CTD has similar problems (modulo errors, and at one point a modem disconnects before re-establishing communications) to those that were exhibited on the first test cast. The CTD is replaced with the RHB CTD 1 of 2. This recently-serviced CTD has two incorrectly swapped ports and one of the swapped ports has pins in the incorrect sequence. This CTD is replaced with the RHB CTD 2 of 2. This has functional ports, but exhibits similar problems with communication errors. It is found that the RHB CTDs have a lower maximum current draw allocated to sensors. With all sensors attached, the current draw is greater than this threshold for the P18 package. The FLBB is removed, dropping the budgeted current draw below the threshold, and the problems disappear for 2 casts. Upon taking the package deeper than ~3000 m, the problems return with sensor spikes and frequent modulo errors.

The winch wire is caked in bluish grease after this first deep cast. This grease gathers in formations on the block and periodically pops onto the deck and into the water. Some gets on the package (primarily the frame and the outside of the bottles), though the sensors and the Niskin bottles are not known to be affected. The extruding grease is later identified on ~12/5/2016 as Dynagard Blue.

11/24/2016 Station work continues while watchstanders formulate a plan. During this process, modulo errors slowly become less frequent.

11/25/2016 Several cables are swapped out and the wiring on the junction box is redone. Concurrently, efforts are taken to remove excessive grease from the winch wire (hosing down the block and wiping the wire as it spools out). This grease becomes somewhat worse after each cast that is deeper than previous casts. Modulo error counts continue to diminish in frequency as these changes are made. The forward wire is reterminated in anticipation of switching to that winch, if necessary.

On occasional stations, the surface bottle fails to report a trip event even though it comes up closed. On station 8, the shallowest two bottles are colder than anticipated by the O2<sub>1</sub> sampler. They are quickly measured for pH and found to have a pH consistent with deeper very high CT water. The carousel is swapped out for station 9. Subsequent testing reveals that bottles 7 through 24 were also likely miss-trips on station 8.

CFC lead Bonnie Chang gathers evidence demonstrating that the electron-capture detector the CFC group uses is negatively impacted by the ship communications. It is tested whether the effect is frequency specific (it is not).

11/26/2016 The changed carousel does not completely fix the problem on station 9, and there is another miss-trip on bottle 19. A cable connecting the carousel and to the CTD and the reference temperature sensor is replaced, also to little effect. Removing the reference temperature sensor and replacing the connector with a straight connector results in no further miss-trips with this CTD package.

Further testing confirms that the CFC ECD is only affected by the winch-house communications, and that the winch house operates with a 45 watt transmitter. This is replaced by a 1 watt handheld radio and the problem abates.

11/27/2016 The reference temperature sensor and the connection cable to the carousel are re-introduced and some of the communication problems return. Bottles 23 and 24 do not report having

fired, modulo errors return, and the secondary temperature sensor drifts considerably on station 17. The reference temperature sensor is removed.

11/28/2016 On station 18, the winch begins to spool-out without control during recovery. Engineers look at the winch and it is deemed likely okay to proceed. On station 19 the package begins to spool out uncontrolled after every bottle stop, with the emergency stop button being hit each time. Fortunately, the bottom depth was set to 20 m off the bottom, and no contact is made. The package is retrieved with some difficulty and without taglines.

The package is switched to the forward winch. There are strong communications problems with the package on the forward winch and the pumps appear to turn off independently. The forward winch is rewired and the package resumes normal operation. The forward winch requires use of the "tugger" to land the package on the tracks used to bring the package into the staging bay.

11/30/2016 A fix for the aft winch is tested over ~1.5 hours by repeatedly lifting a several ton weight on deck. The fix is unsuccessful, but the delay allows the CTD-sensor team to swap out the CTD and restore the package to full functionality with the FLBB, the reference temperature sensor, and the transmissometer all attached. This package is first used on station 27. This delay is more than offset by faster-than-budgeted steaming between several stations with multiple generators operated at high output.

12/1/2016 B. Carter is advised directly by Chilean authorities that a Chilean foreign observer will be joining leg 2. The dates on this communication suggest the Chilean authorities are using the original (pre-delay) project dates.

At this point contacts within the state department suggest Chilean consent is likely.

12/2/2016 A response is sent to Chilean Authorities directly by B. Carter (henceforth SHOA) accepting the observer and unofficially advising of the change in project dates.

12/4/2016 A second test of the aft winch allows the engineers to identify parts to order for Easter Island. This test takes less than 30 minutes. This delay is also more than offset by faster-than-budgeted steaming between several stations with generators operated at high output.

12/8/2016 The US Department of State contact formally communicates the change in the project dates to contacts in the Chilean Government.

12/14/2016 The forward wire is lubricated using (green) StranCore Industrial starting at ~4700 m wire out and ending at ~120 m wire out. No analyses focusing on dissolved organics are planned for this station (Station 89) or the subsequent one.

Without having yet received word of Chilean project approval, administrators and scientists begin routine follow ups with the State Department to resolve Chilean clearance prior to anticipated entry on 12/20/2016.

12/16/2016 A request is received to grant an internship to the Chilean observer. This request is accepted. Travel and lodging is being arranged for the observer in the days surrounding this one.

12/19/2016 Scientists are advised that approval from Chile is expected later this same day.

12/20/2016 Scientists are advised by the State Department that approval has been granted. The hard copy of the approval is said to be delayed, but is expected by COB on 12/20.

12/21/2016 The EEZ is entered on the morning of 12/21 and station work begins based previously received communications indicating approval.

The formal approval is sent to B. Carter in the afternoon. The approval dates begin on 12/23, and the approval only covers the minimal station work originally planned for the P17 extension and the underway measurements while transiting into Punta Arenas. Station work ceases in the Chilean EEZ. It is decided that returning to port early and adding the unused time to leg 2 is preferable to immediately occupying stations on the Eastern end of the EEZ. Clarification is sought from the issuing authority. After 3 hours on station, the Brown begins transit to Easter Island.

12/22/2016 The Brown is advised that the 103°W line is international waters and does not require Chilean authorization. It is requested that this claim be verified. Separately, the authorization documents are rescinded. The Chilean Authorities respond that the work in the Easter Island EEZ was not included in the application they received.

## 11 Appendix 3: Station Timing, Leg 1

Stn.	Lat.	GMT Start Date/Time	GMT End Date/Time
999	32.63	11/19/2016 21:20	11/19/2016 23:23
1	22.69	11/24/2016 04:28	11/24/2016 15:41
2	22	11/24/2016 18:36	11/24/2016 19:18
3	22.78	11/24/2016 20:57	11/24/2016 22:52
4	22.5	11/25/2016 00:49	11/25/2016 03:37
5	22	11/25/2016 06:30	11/25/2016 09:14
6	21.5	11/25/2016 11:58	11/25/2016 14:42
7	21	11/25/2016 17:33	11/25/2016 20:21
8	20.5	11/25/2016 23:03	11/26/2016 01:54
9	20	11/26/2016 05:03	11/26/2016 07:24
10	19.5	11/26/2016 10:19	11/26/2016 13:02
11	19	11/26/2016 15:53	11/26/2016 18:42
12	18.5	11/26/2016 21:31	11/27/2016 00:25
13	18	11/27/2016 03:12	11/27/2016 06:28
14	17.5	11/27/2016 09:22	11/27/2016 12:10
15	17	11/27/2016 15:07	11/27/2016 18:11
16	16.5	11/27/2016 21:06	11/27/2016 23:58
17	16	11/28/2016 02:56	11/28/2016 06:12
18	15.5	11/28/2016 09:10	11/28/2016 12:20
19	15	11/28/2016 15:11	11/28/2016 19:11
20	14.5	11/29/2016 02:27	11/29/2016 05:40
21	14	11/29/2016 08:31	11/29/2016 11:16
22	13.5	11/29/2016 14:14	11/29/2016 17:16
23	13	11/29/2016 20:35	11/29/2016 23:24
24	12.5	11/30/2016 02:32	11/30/2016 05:48
25	12	11/30/2016 08:49	11/30/2016 11:38
26	11.5	11/30/2016 14:43	11/30/2016 17:53
27	11	11/30/2016 21:53	12/1/2016 00:58
28	10.5	12/1/2016 03:40	12/1/2016 06:36
29	10	12/1/2016 09:18	12/1/2016 12:01

30	9.5	12/1/2016 14:49	12/1/2016 17:48
31	9	12/1/2016 20:45	12/2/2016 00:00
32	8.5	12/2/2016 02:54	12/2/2016 06:06
33	8	12/2/2016 09:08	12/2/2016 12:02
34	7.5	12/2/2016 15:07	12/2/2016 18:18
35	7	12/2/2016 20:56	12/3/2016 00:02
36	6.5	12/3/2016 02:37	12/3/2016 05:39
37	6	12/3/2016 08:11	12/3/2016 11:08
38	5.5	12/3/2016 13:46	12/3/2016 17:04
39	5	12/3/2016 19:55	12/3/2016 22:52
40	4.5	12/4/2016 01:47	12/4/2016 04:58
41	4	12/4/2016 07:30	12/4/2016 10:26
42	3.5	12/4/2016 13:06	12/4/2016 16:01
43	3	12/4/2016 18:38	12/4/2016 21:32
44	2.75	12/4/2016 23:42	12/5/2016 02:43
45	2.5	12/5/2016 04:20	12/5/2016 07:18
46	2.25	12/5/2016 08:52	12/5/2016 11:52
47	2	12/5/2016 13:25	12/5/2016 16:28
48	1.75	12/5/2016 18:12	12/5/2016 21:04
49	1.5	12/5/2016 22:52	12/6/2016 01:48
50	1.25	12/6/2016 03:33	12/6/2016 06:29
51	1	12/6/2016 08:23	12/6/2016 11:25
52	0.75	12/6/2016 13:18	12/6/2016 16:10
53	0.5	12/6/2016 18:08	12/6/2016 21:01
54	0.25	12/6/2016 22:46	12/7/2016 01:43
55	0	12/7/2016 03:32	12/7/2016 06:38
56	-0.25	12/7/2016 08:33	12/7/2016 11:49
57	-0.5	12/7/2016 13:41	12/7/2016 17:03
58	-0.75	12/7/2016 18:48	12/7/2016 21:50
59	-1	12/7/2016 23:42	12/8/2016 02:46
60	-1.25	12/8/2016 04:34	12/8/2016 07:28
61	-1.5	12/8/2016 09:22	12/8/2016 12:23
62	-1.75	12/8/2016 14:13	12/8/2016 17:27
63	-2	12/8/2016 19:09	12/8/2016 22:12
64	-2.25	12/8/2016 23:58	12/9/2016 03:02
65	-2.5	12/9/2016 04:40	12/9/2016 07:44
66	-2.75	12/9/2016 09:19	12/9/2016 12:24
67	-3	12/9/2016 13:56	12/9/2016 17:03
68	-3.5	12/9/2016 19:42	12/9/2016 22:38
69	-4	12/10/2016 01:30	12/10/2016 04:31
70	-4.5	12/10/2016 06:58	12/10/2016 09:53
71	-5	12/10/2016 12:30	12/10/2016 15:29
72	-5.29	12/10/2016 18:31	12/10/2016 21:20
73	-5.59	12/11/2016 00:15	12/11/2016 03:08
74	-5.88	12/11/2016 06:02	12/11/2016 08:50

75	-6.18	12/11/2016 11:38	12/11/2016 14:22
76	-6.47	12/11/2016 17:11	12/11/2016 19:42
77	-6.76	12/11/2016 22:24	12/12/2016 00:55
78	-7.06	12/12/2016 03:44	12/12/2016 06:11
79	-7.35	12/12/2016 08:50	12/12/2016 11:46
80	-7.65	12/12/2016 14:31	12/12/2016 17:23
81	-7.94	12/12/2016 20:13	12/12/2016 22:58
82	-8.24	12/13/2016 01:45	12/13/2016 04:33
83	-8.53	12/13/2016 07:14	12/13/2016 10:15
84	-8.82	12/13/2016 12:53	12/13/2016 15:41
85	-9.12	12/13/2016 18:25	12/13/2016 21:32
86	-9.41	12/14/2016 00:18	12/14/2016 03:28
87	-9.71	12/14/2016 06:12	12/14/2016 09:22
88	-10	12/14/2016 12:07	12/14/2016 15:28
89	-10.5	12/14/2016 18:30	12/14/2016 22:07
90	-11	12/15/2016 00:56	12/15/2016 04:07
91	-11.5	12/15/2016 07:03	12/15/2016 10:12
92	-12	12/15/2016 13:08	12/15/2016 16:18
93	-12.5	12/15/2016 19:07	12/15/2016 22:14
94	-13	12/16/2016 01:12	12/16/2016 04:22
95	-13.5	12/16/2016 07:13	12/16/2016 10:23
96	-14	12/16/2016 13:16	12/16/2016 16:23
97	-14.5	12/16/2016 19:07	12/16/2016 22:05
98	-15	12/17/2016 00:54	12/17/2016 04:05
99	-15.5	12/17/2016 06:52	12/17/2016 09:50
100	-16	12/17/2016 12:37	12/17/2016 15:35
101	-16.5	12/17/2016 18:20	12/17/2016 20:53
102	-17	12/17/2016 23:40	12/18/2016 02:36
103	-17.5	12/18/2016 05:30	12/18/2016 08:31
104	-18	12/18/2016 11:32	12/18/2016 14:44
105	-18.5	12/18/2016 17:33	12/18/2016 20:34
106	-19	12/18/2016 23:28	12/19/2016 02:37
107	-19.5	12/19/2016 05:29	12/19/2016 08:39
108	-20	12/19/2016 11:31	12/19/2016 14:51
109	-20.5	12/19/2016 17:50	12/19/2016 20:53
110	-21	12/19/2016 23:47	12/20/2016 02:50

---

## 12 Appendix 4: Weekly updates



## 12.1 Weekly report -1

### Port Repairs

Prepared by Brendan Carter

The first leg of the P18 GO-SHIP project was scheduled to begin Monday Nov. 7th, so I owe an update. However, “Report 0” is being saved for the day we depart from San Diego, CA for the first station on the P18 line at 110°W. Hence “Report -1.” The delay of our start date owes to lingering mechanical issues on the NOAA Vessel Ronald H. Brown (henceforth the “Brown”) that were identified after a dry dock period in San Francisco, CA. A timeline of the repairs and discoveries can be found at the end of this update. Our working departure date estimate is now Thursday Nov. 10<sup>th</sup>.

It is yet to be determined how the 3 days lost with our new departure date will be made up. The delays could make us somewhat more efficient as leg 1 originally planned to go beyond Easter Island (backtracking from 32°S to 27.15°S). Ending leg 1 further north could save up to ~0.9 days at sea (DAS) from decreased transit times. The question of whether and how time will be restored to leg 1 or added to leg 2 will be resolved once we are underway.

### Science readiness

The scientific parties are now ready to sail. The 6+ month trail of paperwork leading up to this point concluded on the morning of 11/7 with the last Mexican Visa being issued to a scientist. All permits to conduct research in foreign EEZs have been secured. Most groups have reported successful tests of their equipment. Most equipment is already secured from being sent on a sea trial on 11/7. All scientists are have checked in on the boat at least once. We are not aware of any major unresolved issues.

Staging was complicated but successful, and is now complete aside from tidying up. We simultaneously staged for both legs of the P18 project and the subsequent PNE project. In addition to the full complement of analytical gear, we have 41 floats, ~30 drifters, 5 vans, and ~20 tons of mooring equipment aboard. Accessing the Navy Base pier proved challenging for our personnel and deliveries. However, most problems were anticipated and all were overcome by some combination of extra paperwork, extra money (higher prices for cranes delayed in security), extra effort (notably from the

federal employees able to escort scientists on base), and a great deal of help from Brown's crew. The boat is nearly full with respect to lab and berthing space. Lab space is currently especially tight, but room will be freed up in the coming days as we move empty boxes into empty shipping vans. The space vacated by drifter deployments will be filled in with filled sample containers that need to be kept temperature controlled. We anticipate the heavy load-out will ultimately save considerable taxpayer money and scientist time that would otherwise have been spent shipping to remote foreign ports.

Stay tuned for report 0 for an overview of the scientific programs aboard.

#### Other notes

Captain Kamphaus and his crew have been communicative, responsive, supportive, and welcoming throughout the process of planning, staging, and dealing with the Brown's mechanical issues. We have relied heavily on his team for navigating Navy Base security measures and getting equipment aboard and stowed.

#### Summary

In short, the science complement seems ready and eager to depart from port. Hopefully the mechanical issues will be addressed on schedule soon, and I can start sending you cruise reports with positive integers.



(Timeline omitted)

## 12.2 Weekly report 0



*The science team with a few of the crew.*

Prepared 11/20/2016

*“After one more delay that pushed our sailing date back to 1500 on Saturday, Nov. 12<sup>th</sup>, we are excited and relieved to be underway.”*

This was the original start of this report written on Nov. 13th. Unfortunately, we since returned to San Diego for diagnosis and repairs to the port Z drive. It was an approximately 48 hour round trip followed by an additional 5 days in port with 2 sea trials. We are pleased to again be about a day from port and heading to the P18 line. The modified schedule has us getting to Easter Island around Christmas. The date of the Punta Arenas arrival at the end of leg 2 is less certain. This report contains an updated timeline of issues affecting the P18 schedule at the bottom (dates of new updates are in bold).

We went through the flurry of activity that usually marks the beginnings of a cruise on our first round trip: We had a brief all-science meeting to share a broad overview of the many critical questions about Earth’s climate that the P18 GO-SHIP data will help to address. We had several meetings to square away aspects of our planned ship operations and to train newer watch-standers in laboratory and GO-SHIP protocols. These meetings covered console watching protocols, CTD-rosette and bongo net deployment protocols, and data management plans. We completed emergency drills and took group pictures. Instruments were unpacked, tested, and secured.

The major concern is currently renewing our clearance to conduct research in the Mexican Exclusive Economic Zone (EEZ). Our permit was approved for the window of Nov. 1<sup>st</sup> through 18<sup>th</sup>, with only 7 days of planned work in the EEZ. Unfortunately, this means the Brown has re-entered the EEZ on the same day the permit expired. We are allowed to transit through, just not conduct science. We’ve

therefore shut down all underway scientific instrumentation until we can extend our clearance. The application to extend clearance was originally submitted to US authorities once the Brown turned back to San Diego, i.e. as soon as it became clear that an extension would be needed. We are currently transiting and expect to arrive on our first station at approximately noon on Tuesday in the Mexico City time zone, so we are hopeful we will be able to begin station work soon thereafter. We understand we have many people pushing for this clearance to be granted at various levels of the US and Mexican State Departments. However, we are naturally working on contingency plans in case it is not granted in time. In total, 18 stations over ~7 degrees are in jeopardy. These are important stations in the oxygen deficient zones of the Eastern Tropical North Pacific.

Two CTD-rosette issues arose on test casts and were troubleshot by our experts: one was a CTD with damaged electronics from seawater intrusion on an early test cast and the second was a compromised CTD pump from a suspected biofouling incident on the second test cast. Otherwise, the sensors are responding and agreeing well, though we will not have had a test cast to deeper than 1300 m prior to beginning station work. This is an unfortunate byproduct of our schedule deadlines and our lack of an extension for our Mexican clearance.

Schedule changes and mechanical issues are an inevitable aspect of oceanographic science, but knowing to expect them doesn't always make them easy to adjust to. The Mexican clearance took 6 months to secure, and we have unfortunately now missed our window. We are also short 3 scientists who could not join Leg 1 after the delays were incurred. Their work has been absorbed by the remaining scientists, many of whom already had a full plate. We are tentatively continuing as planned for now. If workload issues become problematic then we may later need to reevaluate that plan.

I am glad and grateful for the patience, commitment, volunteerism, and good humor that the scientists and crew have already demonstrated. I look forward to having our plates full again, and to getting into the swing of our important work. I will remain committed to listening to the needs of the many parties that have come together for this project as we plan our path forward, and to communicating the certainties and the uncertainties involved in any plans we make.

#### List of science and PIs on P18

I foolishly said I'd give an overview of the science going on this cruise in this update. When I wrote that I'd momentarily forgotten the tremendous volume and diversity of the science efforts on this cruise. So, in this update I'm going to cheat and just provide a list of the programs. Subsequent reports will provide some details on these projects. Many of these programs are core Global Ocean Ship-based Hydrographic Investigations Program (GO-SHIP) projects that are detailed in [this report](#).

List omitted here because it is given earlier in this report.

In addition, we have a number of individual projects being conducted by our graduate and postdoctoral students aboard. These include two types of incubations, additional genetics work, micro-plastics analysis, and an analysis of the natural radiocarbon concentration of a component of dissolved organic carbon.

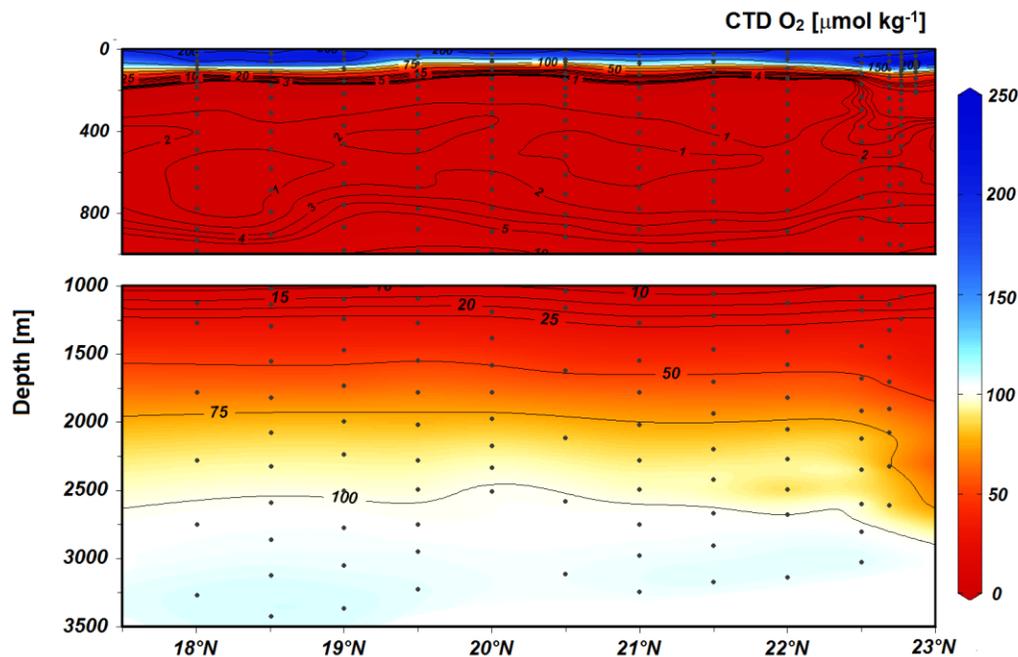
(Timeline omitted for full timeline provided in this report)

12.3 Weekly report 1  
Clearance extended!

Prepared by Brendan Carter 11/27/2016

We are pleased to report that we are making our way south out of the Mexican EEZ and doing station work as we go. We were briefly faced with the difficult decision between waiting on station and abandoning the work in the Mexican EEZ. Some offshore islands make the Mexican EEZ more than twice as thick as the default 200 nautical mile (nm) limit along our track. This meant that going south to accomplish work outside of the EEZ while we waited was not a good solution, and also that an unusually large amount of station work (~15% of leg 1) would have been lost if we had given up on the EEZ. Ultimately, we spent nearly a day and a half waiting on station. We are now slightly behind our ambitious schedule, but relieved to be able to fill in these important measurements of the oxygen deficient zone (ODZ) off Mexico.

Measuring the ODZ is critical for the GO-SHIP goal of monitoring the ocean's response to climate change. It has been hypothesized that the ocean will lose oxygen over time and ODZs will expand under global warming, consistent with many—but not all—simulations of Earth's future climate. A portion of our cruise track has been [recently identified](#) as a region where the impacts of climate change on interior oxygen may already be detectable. Deploying instruments to monitor this region and testing this hypothesis with another decade of high-quality GO-SHIP measurements were key objectives for this project. Several of our instruments and personnel were sent with us specifically in order to capture the unique biogeochemistry in the ODZs.



*We have (preliminary) data! This is a section of dissolved O<sub>2</sub> concentrations as measured by the CTD-rossette sensor package. Black dots are where we have collected seawater for discrete measurements. The blue band at the top is well-ventilated surface water. About one hundred meters below are the (deep red) very low oxygen waters of the ODZ.*

### Path and station work

As noted in the report 0, we initially transited from San Diego to our test station in US waters, and from there headed to the first station offshore Cabo San Lucas at 22.69°N and 110°W. That first station had an intended depth of 2500 meters. We waited there for clearance, moving offshore after business hours in Mexico City to take care of ship functions (e.g. making freshwater from seawater). We quickly began station work after receiving clearance, though we stayed on station for some hours to troubleshoot the CTD-rosette sensor package (see below). We then moved onshore to collect measurements at a 220 m depth station at 22.87°N and 110°W. Since then, we have been moving south along the 110°W meridian. We made the brief northward trip instead of starting at our northernmost station to save a few hours that would otherwise have been spent waiting on station for samplers to finish collecting seawater from the CTD-rosette. After turning south, we had one more nearshore station in 1250 m of water at 22.78°N. Our fourth station was at 22.5°N. Since occupying this station we've been transiting south for 0.5° (30 nm) between each station, as we intend to continue to do for most of the P18 line. We deployed floats on stations 15 and 19 and one drifter on station 13. We are currently on station 20 at 14.5°N.

This [first float](#) we deployed is specially designed to collect data from the ODZs with a gas tension device. The device will be calibrated using measurements of stable gases being made by Co-Chief Annie Bourbonnais.

Profiles of temperature, salinity, beam transmittance, and oxygen were collected at every station. Profiles of fluorescence and backscatter were also collected at the earlier stations. More than 2000 seawater samples have been collected by our analysts for discrete analyses on the boat and back on land. Data from discrete shipboard analyses are beginning to trickle in to our central repository from our shipboard analysts. We expect the floodgates will open soon as our analysts catch up from the abrupt change of pace from prolonged waiting to nearly constantly working.

### Troubleshooting

Unfortunately, the ban on research activities in the Mexican EEZ prevented us from more thoroughly testing the CTD-rosette package while we waited. We therefore spent some additional time on the first station resolving problems with the electronics that manifested on our first cast below 1300 m. Less than a day of troubleshooting time was required for this and all subsequent package troubleshooting, and the delay allowed time for a bongo tow for coastal organisms and micro-plastics sampling. After many sensors, cables, and parts were replaced by our experts on board—and after some clean-up of the winch electronics by our shipboard electronics technician—we now seem to have a functional package to at least 3500 m depth.

One concerning issue has resulted from the new aft winch wire having come from the manufacturer pre-lubricated, contrary to the expectations of the ship personnel when they placed the order. The wire began to extrude the lubricant during the casts, and did so increasingly as the package got deeper and the wire tension increased. This resulted in gooey blue lubricant cakes forming up on the block (pulley) that the winch wire spools over. This lubricant then began to slough off onto the deck and, until we developed means to prevent this, onto the rosette frame. It is not believed that this lubricant has affected the package in a meaningful way yet, though there is concern over whether it could and whether we would know if it had. The ship's crew has gone to lengths to keep this lubricant from affecting the CTD rosette package since it emerged as an issue. Looking forward, it seems most of the lubricant on the first ~3000 m of cable has already been removed since the caking has significantly abated on recent casts. However, we fear this problem will return as we begin doing deeper casts.

\*A quick update on this before I send this out. We've switched to the forward winch since the aft winch began spooling out in an uncontrolled fashion during a recovery on station 18. Everyone is safe, the rosette package is intact, and we're now close to finishing a successful cast on the forward winch. There will probably be more on this in the next weekly update, so stay tuned.

#### A storm dodged?

We've been watching the track of Hurricane Otto as it bee-lined for us from the Atlantic. Luckily, it seems to have slowed considerably, and weakened into an extra-tropical depression on its way over.

#### Summary

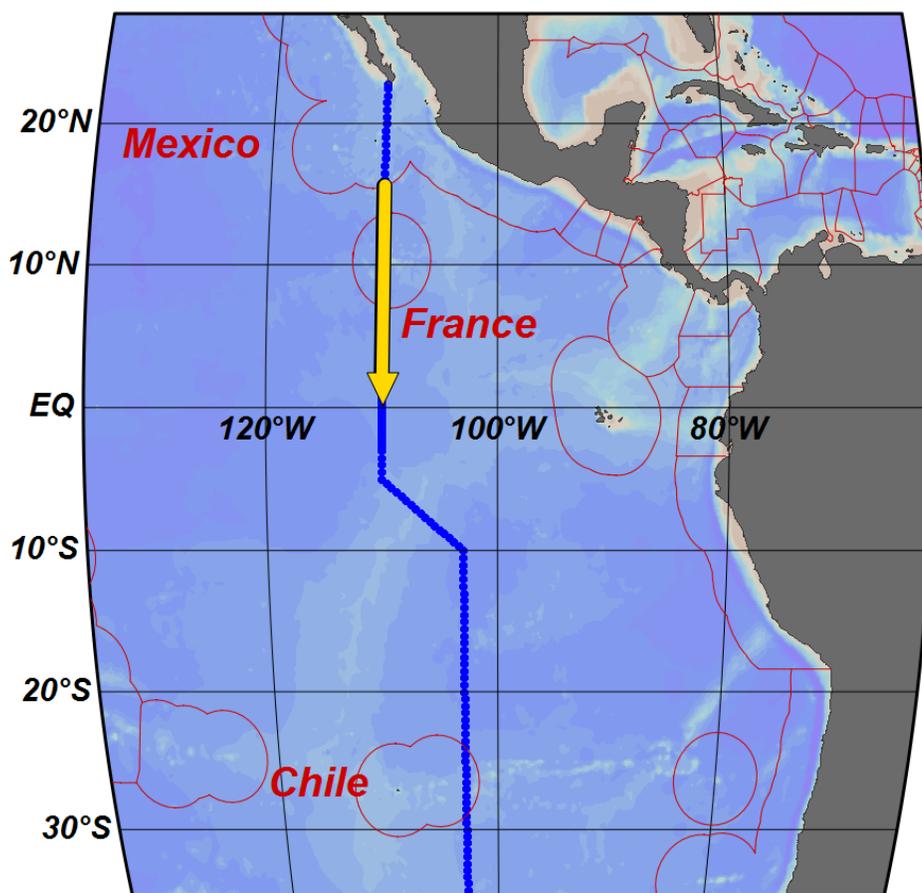
We're pleased to be doing work again, and I look forward to providing updates on the measurements as we continue south along the P18 section. We have some concerns for our schedule and some work to do optimizing our CTD/rosette/winch setup. However, it is refreshing to be facing these more-typical oceanographic hurdles instead of waiting on station 1.



*Annie, Mike, Brian, Josh, and Sean, working together to deploy the APL/UW Gasfloat by crane over the Mexican ODZ. Photo credit: Christian Lewis.*

(Timeline omitted)

12.4 Weekly report 2  
Down the line.



*A map of our section, with the yellow arrow highlighting what we've done this week. We have now emerged from the French and Mexican EEZs (red circles) with a complete set of measurements from each region. French? In the middle of that circle we passed through is a small island claimed by France named Clipperton. It is still the closest land to us.*

Prepared 12/05/2016

It has been a pretty good week. We've hit our stride, and have begun completing our station work quickly and efficiently. We did 29 stations across 13.5° between Nov 28<sup>th</sup> and Dec 5<sup>th</sup>. The Brown has been averaging more than 10.5 kts between stations, our team is sending the CTD-sensor rosette package down to 10 meters off the ocean floor and bringing it back filled with water as quickly as we'd hoped, and we've had calm weather and no additional major delays. Our quick pace perhaps feels faster still due to the ~3700 m average depth of the stations, which is a bit shallower than many of our veteran repeat

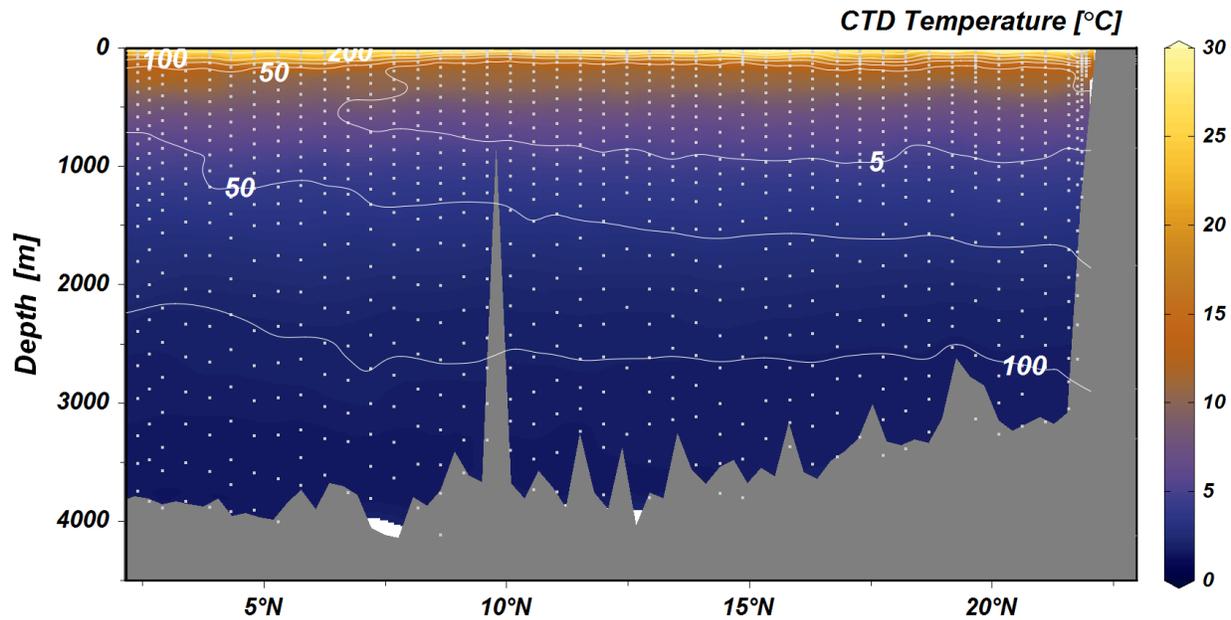
hydrographers are used to. We are testing the throughput of our teams various analytical systems despite using a 24 position rosette (vs. the 36 position rosettes that bring back 150% as much seawater).

Our pace southward has slowed somewhat in the last day as we've hit the high-resolution equatorial stations. We've doubled the resolution from one station per 30 nautical miles to one per 15 nautical miles within a  $\pm 3^\circ$  window of the equator. This is to capture the unique mixing, currents, and upwelling found in this narrow band where the influence of the Coriolis force—one of the major factors that governs the movement of water throughout the ocean—effectively vanishes. The Brown has slowed, but samples are coming aboard more quickly than ever. This is crunch time for samplers on leg 1, and we're looking forward to a return to normalcy in 4° south/3 days. We'll cross the equator Tuesday around dinner.

#### Impacts of delays

Our schedule for this cruise has been in flux since early October due to our various delays, but we've finally settled on port dates for arriving in Easter Island: Dec. 24<sup>th</sup>, Christmas Eve. Leg 2 will depart on the 28<sup>th</sup>. We are glad to be able to begin booking flights and planning our time on Easter Island. Leg 2 should arrive back in Punta Arenas within the first two days in February, 2017.

In light of the delays, we have opted to reduce our double resolution equatorial stations from a  $\pm 5^\circ$  to a  $\pm 3^\circ$  band around the equator. Also, we are no longer planning any station work on the P17 extension that connects the P18 line to Chile. The increased need for efficiency has decreased our tolerance for delays. Typically, infrequent short delays can provide the valuable service of allowing our analysts time to collect and analyze more samples per station, especially in high-resolution sampling regions like the equator. An increased need for efficient progress south may therefore translate into a less-complete record of the seawater brought aboard. Bongo net casts had been planned to take place during such brief delays, but with the need for efficiency the bongo net program was planned to be scaled back. (Later the bongo tows were cancelled entirely, see below.) Similarly, Charles Kovach—our scientist making measurements of the optical properties of seawater who is constrained as to when he can do his measurements by cloud-cover and the timing of satellite overpasses—is now also limited to conducting his work when we are already on station. In short, the delays have made things harder for most scientists and forced us to be slightly less ambitious.



*A section of temperature against depth with contours for dissolved  $O_2$  in  $\mu\text{mol kg}^{-1}$ . Profiles go to the ocean floor. Dots indicate where seawater samples were collected for discrete analyses. Grey areas represent the ocean floor as it is represented in a low resolution data set.*

#### Continued science

Aside from fallout from the delays our scientific programs are going as planned. Our teams are still building up and combing through a wealth of calibration and assessment data. Samples are piling up for shore-side analysis, and data is beginning to pour into our data files through the hard work of our shipboard analysts and our data manager, Remy Okazaki. The new (or rather updated) data submission and management software developed by John Bullister is working well for us, which is wonderful because Remy has also absorbed much of the work of the scientists we lost to the delays leaving port (e.g. see the picture below).

#### The aft winch

As mentioned in the previous report, the aft winch began spooling out in an uncontrolled fashion toward the end of last week. Our quick-thinking winch drivers saved the package by applying a failsafe break, and our team was able to retrieve the CTD-sensor package intact. Troubleshooting is ongoing and the Brown's engineers have ordered several parts for Easter Island that we hope will make the aft winch whole again in time for leg 2. In the meantime, we've been using the forward winch. While fully functional, the forward winch comes with the added difficulty that it is situated a bit further forward of the tracks we use to move the package in and out of the staging bay. We're therefore using a "tugger" or a pneumatic rope-winch, to reposition the package before landing it on the platform. This is adding a bit more work and a lot more excitement to retrievals. This strategy is working great for now, but we hope to have a better way of doing retrievals before the project moves into the nearly-permanent winds and high seas of the Southern Ocean (i.e. before leg 2).



*Jay Hooper (left) and Remy Okazaki (middle) using the “tugger” to get the package safely onto the rails from the forward winch.*

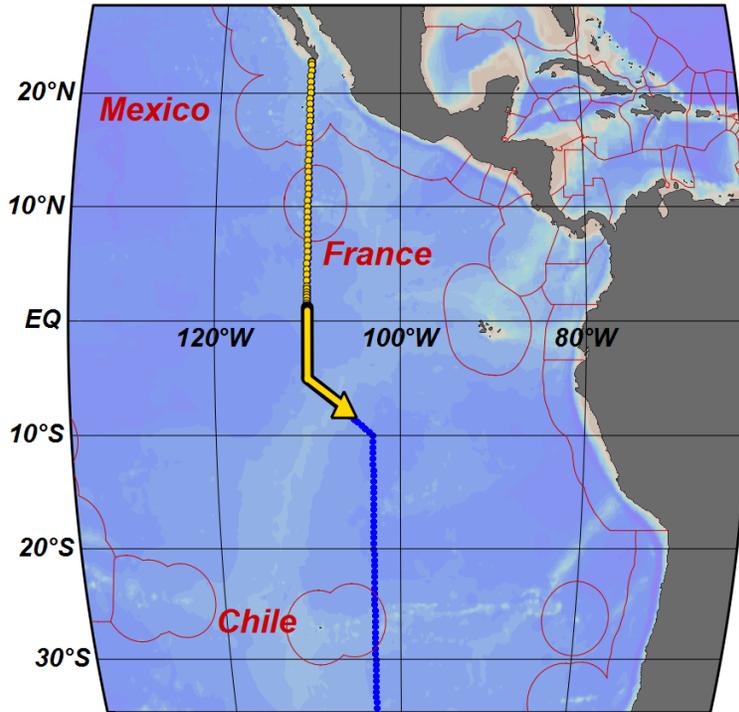
The bongo nets need to be deployed on a different wire than the CTD-sensor package. They had previously been deployed off the forward winch. However, with the aft winch not working and the CTD having been moved to the forward winch, the bongo tows have now been put on hold entirely. In retrospect, it is perhaps fortunate for Javier (our sole bongo specialist) that the delays prevented him from joining us.

#### Aft winch silver lining: a complete sensor package

During a brief downtime while the aft winch was being actively troubleshot, our CTD team swapped out the CTD for a spare, and we now have a fully functional package with primary and secondary sensors for conductivity, temperature, pressure, and dissolved oxygen, as well as a reference temperature sensor and sensors measuring optical transmittance, backscatter, and fluorescence.

#### Summary

We’re making good time and assessing the impact of the many delays to date. We’re digging in for a long cruise, and we are hoping for continued efficient southward progress toward Easter Island. That port date remains distant, but at least it is now solid.



*A map of our section, with the yellow arrow highlighting what we've done this week.*

### 12.5 Weekly report 3

Across the Equator.

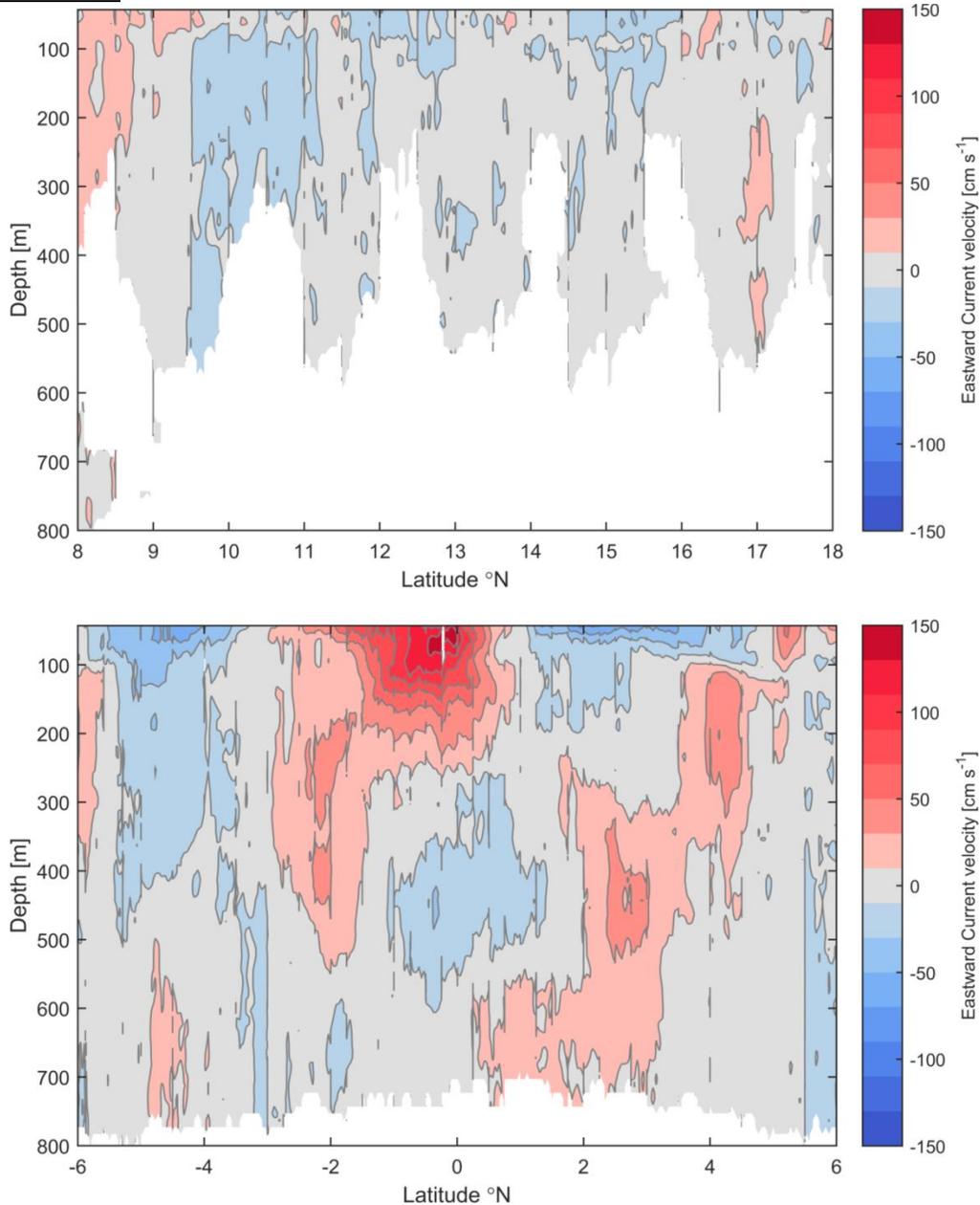
Prepared 12/12/2016

We have had another productive week. We crossed the Equator and started our journey across the Southern Hemisphere, completing 33 stations and the rest of our high-resolution Equatorial work in the process. We've had very few delays this week, and no significant ones. We are making good time, and are on track to make it far enough South to have a short and efficient transit to our end-of-leg-1 port call on Easter Island.

We are now on the diagonal that takes us from the 110°W meridian to the 103°W meridian. As I write this we are on one of the pair of shallower (~3000 m) stations directly over the East Pacific Rise. The East Pacific Rise is a mid-ocean spreading ridge, a massive underwater feature of the Earth's crust that has fascinating physical and geochemical interactions with the ocean above it (it can be seen as a lighter blue band in the map above). Some of our analysts are specifically aiming to measure the signatures of these interactions. The P18 line angles NW/SE between 5° and 10° S to capture this feature while still resolving the deeper ocean basin between the East Pacific Rise and the Peru-Chile Trench. There will be a long set of deeper stations as we come down off the Rise and continue South into that basin in the remaining two weeks of leg 1.

One exciting bit of news is that we will have a Chilean observer joining us in Easter Island. The observer is trained as a marine biologist at the Universidad de Valparaíso, and we look forward to having her input and company.

### Equatorial Currents



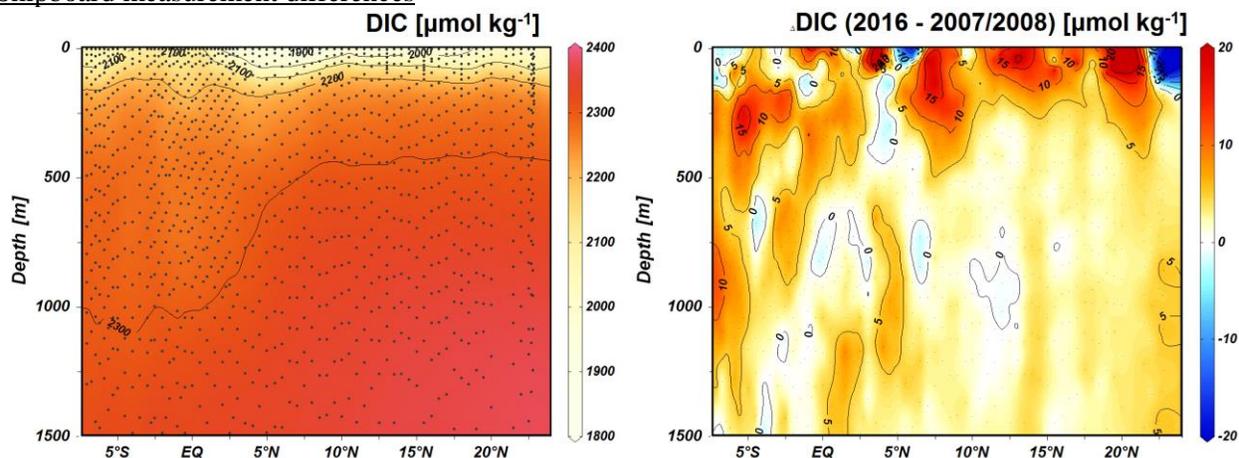
*SADCp measurements of the eastward current velocities (top) between 8° and 18°N and (bottom) around the equator. The white areas are where there weren't strong enough echoes to make a reliable measurement. The alternating deep and shallow readings on the top plot hint at what time of day it was when the boat was making the measurements. The deeper measurements are from the day when many small organisms go down to the darker depths to hide from predators. At night, the critters return to the surface to feed on even smaller organisms, so the SADCp doesn't have anything good to bounce sound*

waves off of at depth. Credit for this data belongs primarily to Jules Hummon who leads the SADC data collection effort.

As mentioned in the last update, the narrow band around the Equator has strong and unique currents that are possible due to the disappearance of the Coriolis force at the boundary between the Northern and Southern Hemispheres. Our shipboard Acoustic Doppler Current Profiler (or SADC) can measure these currents directly by pinging the ocean with sound waves and measuring the frequency (pitch) of the echoes. The echoes bounce off of things caught up in the currents (mostly small plankton). Two plots are provided for comparison, both showing the eastward current versus depth across a range of latitudes. The top one is from further north and shows a typical current structure. The second plot shows the much stronger and more confused current structure expected across the Equator (0°N on the figure).

Staying on station while also keeping the CTD rosette package more-or-less directly below the boat as the package sank through the strong and variable Equatorial currents provided an extra challenge for the Brown's crew. However, they were successful, and we completed all of our Equatorial work without any significant problems. The Brown's crew should also be commended on having recently repaired the ship's POSMV system in January of 2016. This system provides accurate position, heading, and velocity information that the SADC needs to make accurate measurements of the currents.

#### Shipboard measurement differences



*Preliminary measured distributions of total dissolved inorganic carbon (DIC: left panel), and the increases (red) in DIC relative to concentrations measured during the previous P18 occupation in 2007/2008 (right panel). The concentration changes shown are relative to the measured DIC in the earlier occupation interpolated onto the same neutral density surface that the water was on when we measured it on this occupation. These data are brought to you through hard work from analysts Bob Castle and Remy Okazaki.*

We've begun plotting many of the properties we're measuring on board and mapping the differences between our measurements and the measurements from decades past. This is primarily a quality control exercise. Very large differences between the decades can be a sign of problems with the analysis or data entry, especially when only a single measurement shows the large difference. Fortunately, the data appear to be quite clean so far.

Of course the other reason to make difference plots is that we are all very eager to see how the seawater properties have changed since the last time scientists measured the P18 section (even though we recognize the data we are producing are still too preliminary to do solid research with). As an example, the plot above shows the increase in total dissolved inorganic carbon (DIC) over the last decade on surfaces of constant density mapped back onto a depth section. We expect to see increases in DIC as the ocean continues to absorb the CO<sub>2</sub> that humans are emitting into the atmosphere. This plot shows the expected increases have continued over this last decade, especially near the ocean surface. However, finalized fully-calibrated data and a more thorough analysis will be required to accurately quantify how much of this increase is attributable to human CO<sub>2</sub> emissions.

### Life at sea

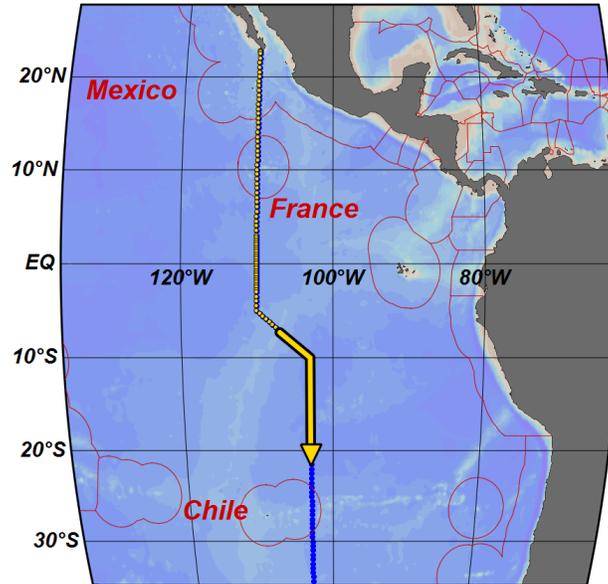


*Pictures of Mari (our dissolved organic matter and radiocarbon sampler) enjoying the sunset (left), and Christian (who is currently involved in too many measurements to easily list) making sure none of our hard-earned seawater is going to waste (right). Brett Walker kindly supplied both pictures.*

We've been working long days without weekends or vacations for several weeks, and many of us spent weeks more in port in San Diego. I won't presume to speak for everyone, but I know I am missing the people, pets, and places that make up my life on land. Fortunately, we have a brilliant, joyful, and hardworking team of scientists and crew aboard making the long days and nights go quickly and with no small amount of fun. It also helps that the persistent beauty of the sea, the sky, the sun, and the stars are always just beyond the nearest bulkhead. For a more about how (and why) we are spending our days at sea, consider checking out the [P18 blog](#).

### Summary

It has been a good week for most aboard, and the science and crew team should feel proud of hard work they did through the Equator crossing. Nevertheless, we are steeling ourselves for another two weeks of focused work and trying not to daydream too much about the island that awaits us at the end of this first leg of P18.



*A map of our section, with the yellow arrow highlighting what we've done this week.*

## 12.6 Weekly report 4

Onward!

Prepared 12/18/2016

We're on fire! (Figuratively, of course.)

We are at the tail end of a third week in a row of efficient southward progress with data from another 29 stations to show for our hard work. These were somewhat deeper (i.e. longer) stations with an average depth >4000 m crossing the Bauer and Roggeveen Basins. We owe our solid progress to continued laudable efforts from the scientists and crew, fair weather, and no small amount of luck. We are still on pace to have an efficient transit to Easter Island. If all goes to plan, next week's update will have pictures of stoic stone Moai statues and leg 2 folks getting settled. That will be my last update, and Rolf Sonnerup will take over from there.

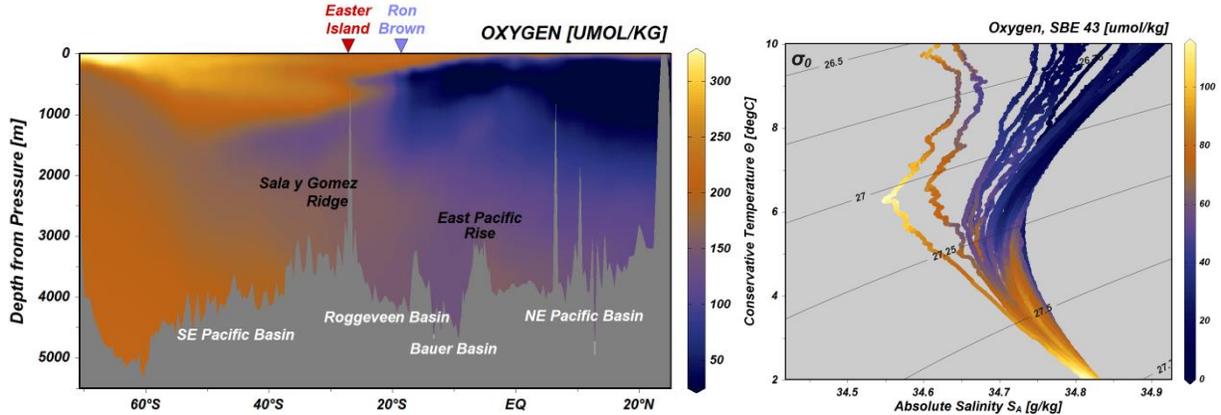
In addition to our normal duties, we are busy documenting the analyses and troubleshooting that went on during leg 1. While this information will ultimately be included in the P18 project report compiled at the end of leg 2, our goal is to gather as much of this information as possible now while all of the leg 1 participants are still on hand.

We are also excited and gratified to be receiving data from the scientists operating the floats we deployed several weeks ago. It sounds like those measurement programs are off to a good start.

### Ocean ventilation on leg 1 vs. leg 2

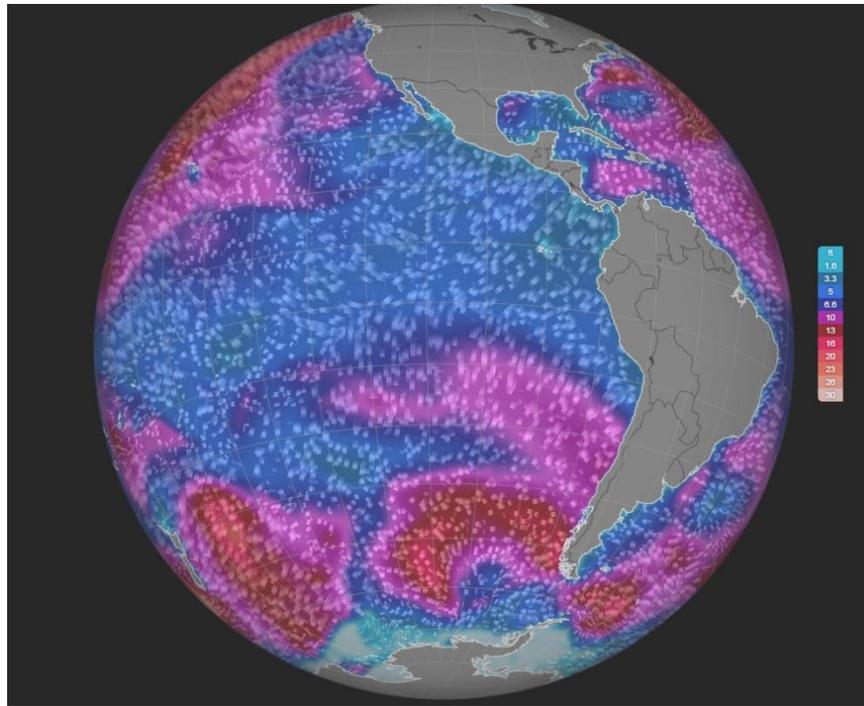
P18 connects the oxygen deficient zones of the Eastern Tropical North Pacific with the formation region for Antarctic Intermediate Water (AAIW) and Subantarctic Mode Water (SAMW) in the Southeastern

Pacific sector of the Southern Ocean. AAIW sits at the base of the thermoclines of the Southern Hemisphere and is noted for being unusually fresh (i.e. a salinity minimum). SAMW is found above AAIW in a portion of the ocean that is weakly stratified (i.e. low potential vorticity). Both water masses are noted for their comparatively high oxygen concentrations, and the two water masses have similar densities to the oxygen deficient waters on the north end of P18. The juxtaposition of these high oxygen water masses to the south next to low oxygen water masses to the north makes for a dramatic transition at about the latitudes we are currently crossing. The two plots below—highlighting this transition—jumped out at us while we were comparing CTD data against the measurements from decades past.



*Left: a section of  $O_2$  concentrations as measured during the 2007/2008 occupation about a decade ago. The low oxygen water masses to the north abruptly transition to higher oxygen water masses to the south near where we presently are (the blue arrow labeled "Ron Brown"). Right: this transition can be seen in our CTD data as well as intrusions of high-oxygen (brightly colored) fresh (low-salinity) waters in the most recent casts (notably the most recent two stations with lines on the left side of this plot).*

### Looking ahead



*A map of wave heights along our section (from windytv.com). Notice the placid blues across leg 1 and the band of red across the southern end of the P18 line.*

We have had a good set of weeks, but, as ever, we are anticipating challenges as we look ahead. Here are a few things on our radar:

1. Whether leg 2 will have enough time to cross the Southern Ocean: these last three weeks have helped us to recover from the delays of the first week. However, it is difficult to predict how much time leg 2 will require crossing the Southern Ocean. The only surety in that region is that there will be bad weather at some point. The question is how bad it will be and for how long. The map above of wave heights might give a sense for why I am concerned. This forecast has been similarly calm on the north end of P18 and restless on the south for at least the last month. It is impossible to safely deploy our equipment and collect seawater when winds and waves get strong enough.
2. The aft winch: we've put an additional 80+ casts on the forward winch, and the wire on that winch has been used on previous projects as well. This leaves leg 2 with one winch in need of repairs and one with a wire that has been extensively used. We are hoping the repair efforts go well in Easter Island, and that the parts being flown in allow the aft winch to be used (thereby avoiding relying on the tugger in rough seas).
3. ~~Chilean clearance:~~ We had been assured our research in the Chilean EEZ would be approved, but we didn't get confirmation that we were good to go until very recently. We were understandably concerned given our experiences off Mexico. However, we are now cleared to continue our leg 1 work into the EEZ, which we'll enter late on Tuesday December 20th. Kudos again to our contacts in the State Department for helping us to push this issue forward. **EDIT, this was written on assurances that the approval had been issued and was making its way to the Brown. The clearance documents arrived shortly after this was sent, but did not include the Isla Sala y Gomez region or the timespan needed for this work. We therefore ended the leg early and returned to Easter Island.**

### Summary

It has been another great week. We're beginning to wrap up leg 1 activities and working to lay the groundwork for leg 2. A lot of work remains between us and port, but the end is in sight, and just in time... we've run out of milk and we're down to our last jelly beans.



*Sampling at sunset... photo from DOM analyst Mari.*

## 12.7 Weekly Report 5

Jan 5, 2017 - Rolf Sonnerup

We are now one week into Leg 2 of GO-SHIP P18 2016/17. About half of the scientific staff have changed hands. Sarah Purkey and I thank Brendan Carter and Annie Bourbonnais for remaining aboard to ease our transition, and in particular for leaving us with a crew of scientists in excellent spirits. Weather must've been great. One person who is sorely missed is Andy Stefanick, Jedi Master of the CTD and salt analysis, who returned home from Easter Island with a sprained ankle.

After a bit of back and forth, including a visit to the Hanga Roa Harbormaster with our Chilean observer and translator, we did not gain clearance to conduct operations within the Chilean EEZ near Easter Island. Also, our departure date from Easter Island was delayed by two days - one awaiting a 3<sup>rd</sup> engineer filling in for a badly injured crewman, and a second day awaiting a new motor for the ship's incinerator. Basics before science. During the wait, Sarah, Jay Hooper and Kristy McTaggart brainstormed a worksharing arrangement to cover, at least partially, the myriad of responsibilities handled by Andy Stefanick.

We departed mid-morning the 30<sup>th</sup> of December, Destination: P18 station 116, located at 23° 54' North, 103° West, adjusted six miles north from its planned location to stay well clear of the Chilean EEZ about

Easter Island and Sala Y Gomez. We occupied 116 at 7 pm local time - concurrent with the ship's new year's eve party in the library. Happy New Year, we're underway.

To stay clear of the EEZ, and occupy a more or less meridional line, we proceeded to the Southwest to station 117 at 24° 30'S, 102° 20'W, and stations 118 through 124 from 25° to 28° S along the 101° 30' W meridian, a line as close to tangent the EEZ as comfortable. We returned to the 103° W line via stations 125 at 28° 30'S, 102° 20'W and the slightly adjusted station 126 at 29° 6'S, 103° W.

These stations were occupied without incident, and we continued as planned (half degree spacings) along 103° W, making up time due to the favorable weather and seas. We had some issues on Jan. 4 at stations 129 and 130. Both conductivity sensors and all cabling on the lower end cap were swapped out for a total delay, including aborted (then repeated) casts, of ~five hours, before we were back in business.

This delay was opportune for the ship's engineers, who conducted yet another test of the aft winch. They had been troubleshooting this winch nigh-daily in Easter Island and, sadly, were frustrated again. We continue to operate with the forward winch and are rehearsing our timings and roles on deck with the tugger (for centering the CTD/rosette on the Brown's sliding platform) to hasten our recoveries and assure safety in the seas to come. Thankfully, the forward winch is working flawlessly.

Our current station timings provide for half-degree spacings to 72° S, but with only just under four weather days' cushion.

Depending on ice and weather conditions, an XCS section has been proposed from 103°W to Thurston Island (72°S, 101°36'W, so 24 mi. to the East), to capture boundary flow from the East. To conserve fuel and time, the XCS section will be conducted via small boat by Dr. Sonnerup and may, at the discretion of the co-chief, be limited to one-way.

Welcome aboard to new scientists for Leg 2  
Cathy Garcia (Genetics)  
Yves Plancherel (<sup>3</sup>H-<sup>3</sup>He and Rare Earth Elements)  
Bethany Kolody (iTag genetics)  
Myself (Chief Sci.)  
Sarah Purkey (Co-Chief Sci.)  
Emma Pontes (O<sub>2</sub>)  
Chris Langdon (O<sub>2</sub>)  
Conrad Luecke (CTD watchstander)  
Paige Logan (CTD watchstander)  
Rachel McMahon (CFC/SF<sub>6</sub> analysis)  
Andrew Collins (dissolved inorganic carbon)  
Charles Featherstone (dissolved inorganic carbon)

And a special welcome to our Chilean observer and sample cop/genetic sampler extraordinaire: Javiera Veloso, who is assisting our Genetics programs as part of the requirements for her undergraduate degree in marine biology at Valparaiso University.

For Leg 2 we have one new project aboard - iTag® - genetic fingerprinting of South Pacific water masses as part of Bethany Kolody's PhD dissertation.

In all, during week one we transited to the 103° W Meridian, occupied 20 full-depth CTD stations, deployed four ARGO floats, two SOCCOM floats, and three drifters. The weather continues to be very nice with (mostly) calm seas so we're keeping our fingers crossed for, ahem, a peaceful occupation of the 40s and 50s on the P18 line, and a full two-way section to Thurston Island.

As a follow up to Weekly Rept. #4, our primary concerns going forward are the weather, the continued viability of using the forward winch under adverse conditions, ice cover South of 68° S, and the limited zone within the Chilean EEZ where we do have clearance (Fig. 1). The zone permitted, part of earlier plans to occupy the P17E section, involves either a substantially longer transit into the Straits of Magellan, or conclusion of all underway measurements just beyond the Chilean EEZ.

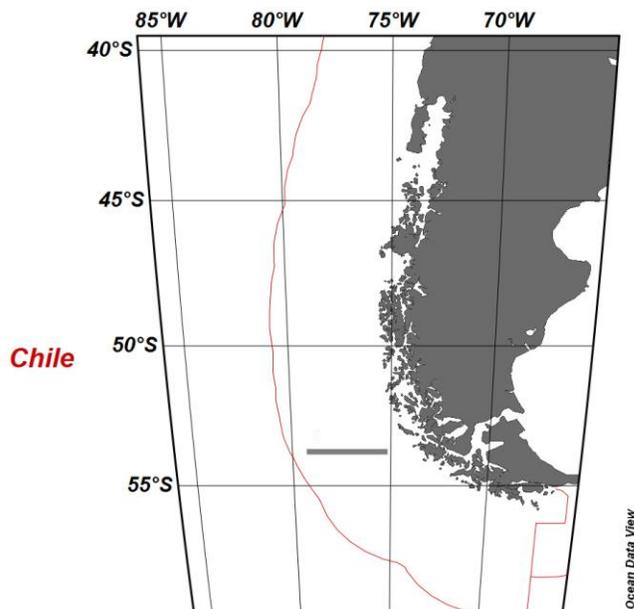


Figure 1. Map of the Chilean EEZ in the South Pacific Ocean. The grey rectangle near 53.5° is the region within the EEZ where we have clearance to conduct measurements.

Twitter.com/thesciencepaige

## 12.8 Weekly report 6

Jan 12, 2017 - Rolf Sonnerup

Two weeks into Leg 2 of GO-SHIP P18 2016/17, we're at 47° 30'S, and the weather is ... NICE! Sun rises at 6:20, and sets at 9:45.

Not that we haven't seen some weather. We had a 48 hour blow (25-30 kts) over the 8<sup>th</sup> and 9<sup>th</sup> that tested our deploy / recover skills on the forward winch.

We have been occupying stations more or less on schedule, losing time in poor weather, clawing it back in good. In the meantime, ship's engineers disassembled the aft winch's brake mechanism. They discovered a flaw similar to your throwout bearing failing to fully re-engage your clutch. Once re-assembled, the rear winch passed repeated 3000# load tests in and out of the water. Emboldened, we planned a switch to the aft winch the following day.

It was not to be. Later that evening, the wire / termination (fwd winch) started showing signs of trouble, including alarms from the deck unit. While we puzzled over this one, a water supply line ruptured in survey tech Alyssa Pourmonir's stateroom, flooding her belongings. Next, a fire alarm. Not a drill. The CTD was at 3000 m, with orders to bring it aboard immediately. While we assembled at our muster station, Commando K. McTaggart tripped bottles on the ascent. Nothing else matters.

In the end, the source of the fire alarm was discovered: water tripped the smoke detector in Alyssa's room. Commando, ahem, Commander McTaggart seized the opportunity: ``Jeff (ship electronics tech) is awake now anyway, he may as well stay up and reterminate this thing''. And so it was. Special thanks to Jeff Hill, and to operations officer Brian Elliot, who, on 6 minutes' sleep, was confronted with lively, if not hysterical, accounts of submerged laptops and personal effects, a real fire alarm, and a surprise request for a midnight winch swap. He handled these with aplomb, and in pajamas, no less.

We have been using the aft winch now for three days. We've been advised against throwing a retirement party for the tugger. No need to tempt the winch gods.

Our schedule provides for half-degree spacings to 70°, or maybe even 72°S (depending on topography) with just under four weather days' cushion. Ice conditions are improving. Our official arrival date in Punta Arenas has now been posted - Afternoon of the 4<sup>th</sup> of February.

Having verified that somebody actually reads these, we clarify: XCS is shorthand for ``eXpendable Chief Scientist''. Although one XCS deployment per cruise would do wonders for morale, and may improve the job market, I wonder if it's really true that ``The chief scientist goes down with the ship''. We learned this at drills today.

For the weekly ``We miss Andy, and how'' column, a special congratulations and thanks to Paige 'Float Lady' Logan. Paige is doing a great job at the very important task of running salts during

part of her watch. We promise to come get her next time there's a fire alarm.

Box score: P18 Leg 2, Week 2  
26 CTD stations occupied  
6 Argo/SOCCOM floats deployed  
4 drifters deployed  
Currently at 47°30'S  
Ice cream still in good supply

## 12.9 Weekly Report 7

1/20/2017 - Rolf Sonnerup

60°S!

After we gloated about our good weather fortunes last week, King Neptune returned the favor with a weekend blow: 25 -30 Knot South winds, seas 10-15 ft were our new normal during the 14- 16<sup>th</sup>. Although our transits were slowed, sometimes drastically, we continued operations. Since the 17<sup>th</sup>, however, we've been riding the Western side of a low (< 1000 mb) with very little pressure gradient. Cloudy skies, cold (2-4 °C), but with moderate winds 10-15 knots, squalls to 25.

It snowed today. We're not missing winter after all, with the added bonus that the sun keeps summer hours: rising a little after 5, setting around 11.

We continue to operate on the aft winch with very few problems with the wire or the CTD. We had a problem on the downcast at one station. Jay Hooper enthusiastically stayed up past bedtime for a mid-afternoon sensor swap. When the CTD came on deck, a 1.5'' shrimp was discovered jammed in the primary sensor. Problem solved. Bedtime.

This week marked an important, and sad milestone: We deployed our last drifter at 59°S. The instructions are designed with modelers in mind: Unwrap, then toss the thing overboard. For a time, Chief Sci. was trusted with this task. He should not have bragged about how fun it is.

Our schedule still provides for half-degree spacings to 70°S with a healthy (now that the 40s and 50s are behind us) weather / mechanical cushion of ~ two days remaining. However, ice conditions may limit our Antarctic approach to ~68°S. Our weather cushion is not enough to pursue reoccupation of P17E, so we are eyeing instead the option of straying a few degrees West of the 103°W meridian, where ice conditions may be more favorable. There is a Soccom float approx. On our return, we'll chase floats for calibration/validation as part of SOCCOM.

Box score: P18 Leg 2, Week 3  
23 Full depth CTD stations occupied, 46°S to 57°30'S, 103°W  
7 Floats deployed  
Our final (sniff) four drifters deployed  
Yves Plancherel still free to saunter about  
Ice Cream still in good supply



## 12.10 Weekly Report 8

1/26/2017 - Rolf Sonnerup

We continue to operate on the aft winch with very few problems with the wire or the CTD. We continue to have excellent, if cold, weather. We have continued, until very recently, to occupy stations at half-degree spacings. This report would end there if it weren't for some deception and sandbagging that warrant attention. Also, we reached the end of the 103°W P18 line, and conducted an XCS section.

It all started with that float. Out on the fantail, ready to deploy, it was noted that the float had been scratched in transit. Although slight, fouling of the exposed metal could affect the float's buoyancy. In the heat of the moment, a stroke of genius: Touch it up with the strongest sealant known, fingernail polish. K. McTaggart was dispatched, to return with the first of the week's many alternative facts: "There's no fingernail polish on this ship". McTaggart produced some Seabird approved enamel that dried in about twelve minutes. Although the float was touched up and deployed without incident, we can't go to Punta Arenas with our nails like this.



Float 9750, post makeover at Kristy's Spa [*Paige Float Lady Logan, 2017*].

It's been easy to adopt a laissez-faire attitude. Why plan when so much is to be determined by weather and ice anyway? This week brought three full days of Co-Chiefly admonishments: "We have to start thinking ahead", she scolded. "We need to think about how to end this section", she chided. "YOU need to make some decisions". My reveries interrupted, I spent two days with Brian Elliot, agonizing over spreadsheets, charts, and strategies, dashing to and from the bridge. At our meeting with the Captain, Co-Chief wondered: "Why be so worried about all that? We're just gonna go in and get really far south, do some stations, and let the weather decide". On the bridge, this strategy is known as "Purkey's Plan". There can only be one cool Chief Scientist, I get that, but it would be nice to be cited from time to time.

After two days of spectacular scenery, sliding in amongst icebergs, we were warned: "This is probably your last station". With so many groups requiring large volumes of water, and all wanting to characterize that southernmost station, a decision had to be made. Guessing that #206 (69°S, 103°W) would be our last, we planned two casts, one for the usual GO-SHIP medley, another at the same depths for the exotics (with S and O<sub>2</sub> for CTD calibrations). This completed, we occupied two more stations: #207 at 69.5°S, and, following Purkey's Plan, our ultimate 103°W station #208 at 69°36.5'S, only 6.5 miles away.



Playing Space Invaders on the bridge [*Float Lady*, 2017].

Beautiful Spot, but not the continent. Being drill day, it was time to test small boat operations. As always, a ranking member of the science team was required, for safety's sake. As Co-Chief offered: "You're on watch. You need to sample cop, but I don't mind staying up." The long-awaited XCS section was completed. It was a two-way occupation, this time.



GOSHIP XCS section P1 underway [*Float Lady*, 2017].

Our plan going forward: We are steaming to the East, occupying stations at 30 mi. spacings, hoping to proceed farther South along  $\sim 101^{\circ}\text{W}$ . From there a SOCCOM float at  $\sim 68^{\circ}\text{S}$ ,  $95^{\circ}\text{E}$  interrupts our path to Punta Arenas. Factoring in a 2000m CTD to calibrate/validate this float, our break off point should be  $\sim 1$  AM on the 29<sup>th</sup> of January.

Snowing regularly, yet the sun keeps summer hours: rising a little after 4, setting around 2.

Box score: P18 Leg 2, Week 4  
23 Full depth stations,  $58^{\circ}\text{S}$  to  $69^{\circ}36.5'\text{S}$ , along  $103^{\circ}\text{W}$   
1 XCS section  
2 SOCCOM Floats deployed  
Ice Cream still in good supply

## 12.11 Weekly Report 9

2/1/2017 - Rolf Sonnerup

Greetings from the *Brown*. We are steaming towards Punta Arenas, making reasonable time (7-8 knots) in 12'-15' seas with steady 20-25 knot Northwest winds. This report comes one day early, as a little bird tells me I'll be very busy over the next few days. We arrive Punta Arenas during the afternoon of Feb. 3<sup>rd</sup>. Friday night in Punta Arenas.

70°S.

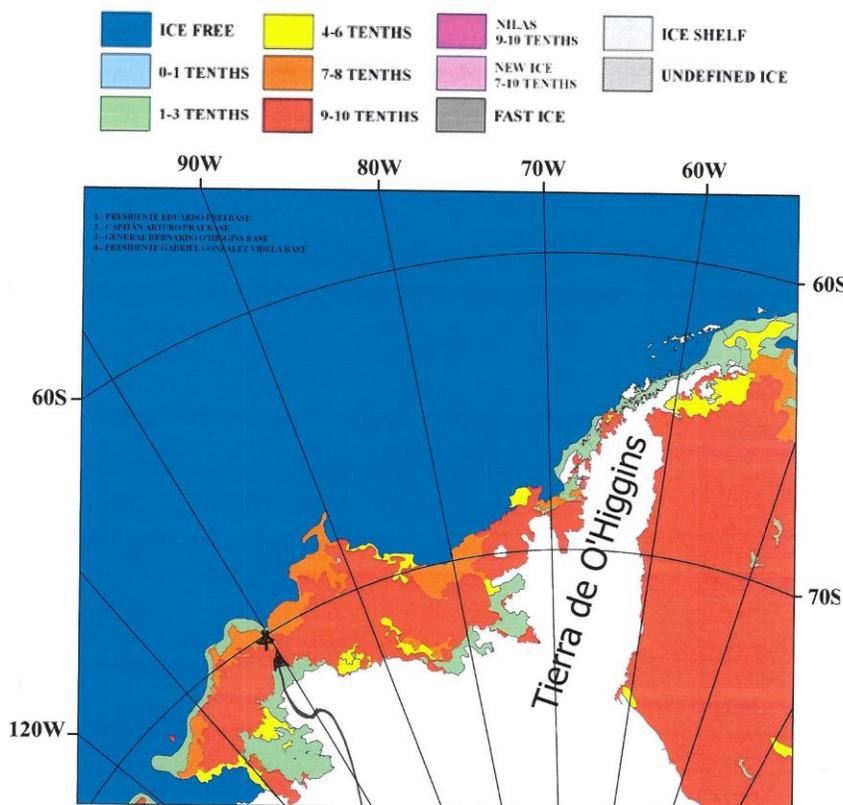
After our expendable Chief Scientist section (last week's report) at 69° 36.5'S 103°W, we escaped the cul-de-sac by heading north and then east, following the ice edge we had inferred from satellite images from the National Sea Ice Center. Our plan was to follow the ice edge occupying stations 30 miles apart until we ran out of room. At our next station, we found a small void in the bergs for #209 at 69° 41.468'S, 102° 01.581'W. After 209 we retreated northwards, then proceeded Eastward again along the ice edge to # 210 at 69° 54.175'S, 100° 40.301'W and to our final station of the P18 line in 2016/2017: Station #211 completed Jan 28 at 01:28 GMT, 70° 00.04'S, 100° 14.4'W.

From that point a Soccom float, #12559, had recently surfaced at 94° 59.46' W, 68° 04.74'S on Jan 23. A visit to that site was almost exactly on our way to Punta Arenas, so we picked our way back out of the ice to our truly final station, #212, at 68° 03.393'S 95° 0.043'W, sampling for O<sub>2</sub>, DIC, ALK, pH, Salts, REEs, iTag genetics and, for SOCCOM calibration, HPLC-pigments and POC.

Our transit to the Soccom station had occurred at a pedestrian pace, first because we were dodging icebergs, and for the latter half, due to engine troubles. Considering the weather to come, we elected to retain our 15 remaining weather hours to ease pressure on the ship personnel (engineering and navigation) during the return to Punta Arenas. Our final routefinding and deliberations were not taken lightly. After that final station, when I arrived at my desk I saw that the captain had kindly left me some reassurance: An image from the Chilean Navy indicating that we had, indeed, come to the end of the road on our journey Southward.

## CONCENTRATION ICE CHART ANTARCTIC PENINSULA

UPDATED : 20170119



Ice cover map from the Chilean Navy. The *Brown's* location was

added by Capt. Kamphaus as a therapeutic measure.

We are busy stowing away eleven weeks' worth of samples, reagents, instruments, supplies, gear and ... clutter. Our goal over the next 36 hours is to clear out the laboratory spaces and staterooms so that the next expedition aboard the *Brown*, the 2017 Atlantic PNE cruise headed by one Dr. Renellys Perez, will be as trouble free and enjoyable as ours was. A hearty thank you to the officers, crew, and scientists aboard the *Brown* for a job well done!

- Rolf Sonnerup and Sarah Purkey, Feb 1, 2017

## 13 Appendix 5: Sample cop notes

Note: #x = Niskin x (where x = position 1-24, not serial number)

[RO after station 146: I'm no longer going to be recording if sample sheets say: "no dups", "wear gloves", or any of that stuff. Just Niskin and sampling issues.]

Station 1, Cast 3:

Waypoint 3, Water Budget 4

Use data from secondary sensors!

#20 leaking/open.

#23 ran out pre salt.

#24 did not fire.

Station 2, Cast 2:

#11 (5 m): sampled for HPLC only.

Station 3, Cast 1:

#14 leaking (deluging). Held a seal after un/rescrewing.

#18 same problem [as #14].

#19 drippy nipple.

#23 leaking from the base.

Station 4, Cast 1:

#23 had pinched #22's lanyard.

#20 had a leaky vent (3rd strike) still works when really creanked down.

Station 5, Cast 1:

Biomarker Station please wear nitrile gloves.

#19 \*blue grease on top of bottle #19 [difficult to read handwriting from scan.].

Station 6, Cast 1:

#8 O2 was repeated - first T was 8.1 degC.

Station 7, Cast 1:

#6-14 sampled out of order, He after TA.

#? 10/12 CFC, order reconstructed.

Station 8, Cast 1:

\*OMZ.

Please wear gloves this station + use silicone tubes.

#15 DIC glove may have touched nipple. It was kim-wiped.

#24 No confirmation on #24 fire.

#23,24 Misfires based on teams' measurements.

Station 9, Cast 1:

DO14C Station, please wear gloves.

TA -> please sample same Niskins as DO14C/DI14C.

Station 10, Cast 1:

#19 I think bottle #19 was tripped at wrong depth! [O2 draw T and DIC confirm this.]

Station 11, Cast 1:  
#24 He tube lost during cold welding.

Station 12, Cast 1:  
[no comments]

Station 13, Cast 1:  
#6,8,18,20,22 skip these if you're behind and not ODZ-focused.  
This is biomarker station. Please wear gloves.

Station 14, Cast 1:  
#3 (Annie) valve was not closed all the way... dripping out the nozzle.  
O2 145 --> there was a bubble (after taking).  
#4 Switching thermometer at Niskin #4 (#1 to #2).  
#4 is leaking => small(?) leak(?) (same as #3).  
#16 O2 was redone. Original T degC was 16.2.

Station 15, Cast 1:  
#1 2nd reading on Niskin 1, O2 draw temp.

Station 16, Cast 1:  
\*No dups on 24, please. [for HPLC/POC, but these samples were scrapped and DIC took dups on 24].  
#20 He 21 may be on Niskin 20.

Station 17, Cast 1:  
Jelly-like guts all over rosette, removed by Jay.

Station 18, Cast 1:  
No duplicates on starred bottles please (#21).  
Please wear gloves.

Station 19, Cast 1: [no comments]

Station 20, Cast 2: [no comments]

Station 21, Cast 1:  
#24 Wear gloves bottle 24.  
O2 #209 --> flask is leaking.

Station 22, Cast 1:  
Please wear gloves + use SiO2 tubes.

Station 23, Cast 1:  
#1 Helium sampled tube #2 on Niskin 1. 2B is leaky.  
Helium sample 11 may leak, 12 is lost, 16 leaked, 24A leaked.  
#17 [CFC] \*283 came out of 17 (we think)

Station 24, Cast 1:  
#5 vent was open.

Station 25, Cast 1:

#24 No duplicates on 24 please! Wear gloves on 24!

Station 26, Cast 1:

Please wear gloves - biomarkers.

#1 Internal linyards [sic] replaced Bottle #1 before cast.

#17 bad reading from thermometer!

Station 27, Cast 1:

#1 Bottle 1 leaking from the bottom.

#9 Bottle 9 is a leaker (needed more tightening).

He 8b failed (leaked).

Station 28, Cast 1:

Avoid \* for duplicates please (1,2,5,10,11,15,16).

[illegible:] 6 resample.

#1 Bottle 1 is leaking from the bottom.

Station 29, Cast 1:

#24 Avoid duplicates on the surface bottle, please.

#9 Niskin 9 is leaking from vent.

Station 30, Cast 1:

Please wear gloves.

#9 slight leak.

#7 O2 redone (2nd temp. 7.3 degC).

Station 31, Cast 1:

He: 2b is lost, 23b is a leaker.

Station 32, Cast 1: [no comments]

Station 33, Cast 1: [no comments]

Station 34, Cast 1:

Please wear gloves!

#7 small leak.

#9 small leak from nozzle.

#24 small leak from nozzle.

Station 35, Cast 1:

He: 5 leaked, 10A leaked, 17B leaked, 19A lost, 23A leaker.

Station 36, Cast 1:

#24 minorly drippy.

Station 37, Cast 1:

#9 small leak from vent!

#24 small leak from vent!

Station 38, Cast 1:

Please wear gloves.

#9 small leak at nozzle!

Station 39, Cast 1:  
Please wear gloves & use tubes.

Station 40, Cast 1:  
He: 4A, 5B, 6B 11B, 19A, 20A, 21B, 22A leaked. 15 lost. 23B.  
#17 was almost empty when sampled for gas + N<sub>2</sub>O.

Station 41, Cast 1:  
#24 small leak from vent.

Station 42, Cast 1:  
#9 small leak from valve.

Station 43, Cast 1:  
Please wear gloves + use tubes.  
O<sub>2</sub>: #6 might be okay on O<sub>2</sub> draw temp inversion: 6.2 degC was after 3 prior samples, 5.7 was after 1.  
#7 leaky nipple even with cranked down vent.  
#9 leaky until vent cranked down.

Station 44, Cast 1:  
#5 did not fire.

Station 45, Cast 1:  
#24 has full-blown leak (after new [illegible] o-ring). Remade seal at top and held a vacuum afterwards.

Station 46, Cast 1:  
Alex's time 56 min.

Station 47, Cast 1: [no comments]  
Station 48, Cast 1: [no comments]

Station 49, Cast 1:  
#22 probable mis-trip based on O<sub>2</sub> temp.

Station 50, Cast 1: [no comments]  
Station 51, Cast 1:  
#12,24 No duplicates please.  
Please wear gloves.

Station 52, Cast 1:  
#18 375 m in depth scheme; 405 is the O<sub>2</sub> min.  
He: 2A last tube slipped off, 8A leaked at jaws! 16A tube slipped off.

Station 53, Cast 1: [no comments]  
Station 54, Cast 1: [no comments]  
Station 55, Cast 1:  
Please wear gloves.  
#11 has a bubble on stable gases.  
He: lost 23.  
#17 almost empty. NO<sub>3</sub> isotopes didn't rinse tubing.  
#23 totally mtfon [?] salinity.

Station 56, Cast 1: [no comments]

Station 57, Cast 1: [no comments]

Station 58, Cast 1:

Please use gloves and try to avoid duplicates on starred bottles (#1,2,6,7,11,17,18,23).

O2: 113 "NaI dispenser stuck."

Station 59, Cast 1:

Please wear gloves.

Station 60, Cast 1: [no comments]

Station 61, Cast 1: [no comments]

Station 62, Cast 1:

#16 original depth 530 m (modified to include O2 min).

Station 63, Cast 1:

#1,2,23,24 No duplicates here!

Station 64, Cast 1:

O2 dispenser sticky on these bottles (182, 233 on Niskins 23, 24).

Station 65, Cast 1: [no comments]

Station 66, Cast 1:

O2 troubleshooting their instrument. No more bottles left. Skip this station.

Station 67, Cast 1: [no comments]

Station 68, Cast 1:

#22 No duplicates on 22, please.

Station 69, Cast 1:

Please wear gloves.

#16 Niskin was unsealed (vent not screwed down enough).

Station 70, Cast 1: [no comments]

Station 71, Cast 1:

Trit #18 fell on ground.

[illegible:] 11 capa[?]

[Box around values. Not sure to which parameter they belong.]

Bottle 15, 16, 17, 18 --> 16, 17, 18, 15, respectively.

He: 12A lost (tube slipped off), 13B is leaking, 18A is leaking, 19.

Station 72, Cast 1:

#22,24 No duplicates please and wear gloves.

Station 73, Cast 1:

Please wear gloves.

Station 74, Cast 1: [no comments]

Station 75, Cast 1:

#24 wear gloves, no duplicates.

#17 He: resampled hole in.

Station 76, Cast 1: [no comments]

Station 77, Cast 1:

#1,2,3,4,5,19,20,21,22,23,24 No duplicates on these bottles, please.

Wear gloves.

Station 78, Cast 1:

#8,14 No duplicates & please wear gloves.

O2: both dispensers are sticky.

\* Salinity and Nuts 1 big rinse only on bottles ~ 12 --> 21.

#23 not poisoned for stable gas.

Station 79, Cast 1: [no comments]

Station 80, Cast 1: [no comments]

Station 81, Cast 1: [no comments]

Station 82, Cast 1:

#24 No duplicates & please wear gloves. Thanks!

Station 83, Cast 1:

He: 4A and 8A lost.

Station 84, Cast 1: [no comments]

Station 85, Cast 1:

#21-24 No duplicates, please wear gloves!

Station 86, Cast 1:

#22 No duplicates, please.

Station 87, Cast 1:

#7 is leaking.

He: 13A on Helium was leaking.

Station 88, Cast 1:

Wear gloves (all bottles).

No duplicates on bottle 24.

Station 89, Cast 1:

No duplicates, por favor (#22,23).

O2: #14 sampled twice, still odd temperature.

#4 Vent left open.

Station 90, Cast 1:

First cast after wire lubrication.

No duplicates on bottle #24 and wear gloves, please.

Station 91, Cast 1: [no comments]

Station 92, Cast 1:

Wear gloves (all bottles).

No duplicates on bottle #24 please.

O2 draw temp estimated by Alex: Subtracting 2 degC. Thermometer is malfunctioning below 10 degC.

Station 93, Cast 1:

No duplicates on #22-23.

O2: Bottle 100 on #20 got a bubble in it from the dispenser.  
CFC: #23, #24 endless bubbles. [Sampler gave up.]

Station 94, Cast 1:  
Wear gloves and no duplicates on bottles 1,2,7,8,12,17,18,23,24.

Station 95, Cast 1:  
Helium: 14A is broken.

Station 96, Cast 1:  
Wear gloves (all bottles!) and no duplicates on bottle 24 please.

Station 97, Cast 1:  
No duplicates [on #22, 23].

Station 98, Cast 1:  
Wear gloves [all bottles] and no duplicates on starred bottles please.

Station 99, Cast 1:  
Please wear gloves and use tubes.

Station 100, Cast 1:  
Wear gloves and no duplicates on #24.  
#24 Not enough water left (~1 L).

Station 101, Cast 1: [no comments]  
Station 102, Cast 1:  
Wear gloves and no duplicates on #24 please.

Station 103, Cast 1: [no comments]  
Station 104, Cast 1:  
Wear gloves and no duplicates on #24.

Station 105, Cast 1:  
No duplicates on #22, 23, please!

Station 106, Cast 1:  
Wear gloves and no duplicates on #24 please.

Station 107, Cast 1:  
Christmas Week! Semana de navidad! Semana de natal!

Station 108, Cast 1:  
Wear gloves (all bottles) and no duplicates on bottle 24.

Station 109, Cast 1:  
#6 O2 temp? [7.5 written on log sheet]

Station 110, Cast 1:  
Wear gloves and no duplicates on bottle 24 please.

Station 111, Cast 1: [no comments]

Station 112, Cast 1:  
Wear gloves (biomarker bottles) and no duplicates on #24.  
#7 leaking from vent (small leak).

Station 113, Cast 1:  
#21-23 Avoid duplicates here, please.  
O2 dispensers are being proper jerks.

Station 114, Cast 1:  
Wear gloves and no duplicates on bottle 24 please.

Station 115, Cast 1: [no comments]  
Station 116, Cast 1:  
Wear gloves and no duplicates on bottle 24.

Station 117, Cast 1:  
Please wear gloves and no duplicates (dissolved organics bottles).  
#14 Outer o-ring broken (replaced after sampling).

Leg 2:  
Station 116, Cast 2:  
#23 bottom seal leaks very slowly.

Station 117, Cast 2:  
Please wear gloves.

Station 118, Cast 1:  
Wear gloves and no duplicates on bottle 24.  
#23 bottom o-ring leaks.  
Argo deployment.

Station 119, Cast 1:  
#23 slow leak.  
#24 not enough water for REE and tritium.

Station 120, Cast 1:  
Wear gloves and no duplicates on bottle 24 please.  
#23 leaking!

Station 121, Cast 1:  
Wear gloves!  
No dups on iTag bottles.  
Please use provided and cleaned tubing.  
iTag or #1: did not use clean tubing.

Station 122, Cast 1:  
Drifter deployment.  
Wear gloves and no duplicates on bottle 24.  
#20 leaking.

Station 123, Cast 1:  
Argo float deployment. PMEL Navis 726.

He: 13a and 19b failed to seal.  
#20 okay.

Station 124, Cast 1:  
Wear gloves and no duplicates on bottle 24.

Station 125, Cast 1:  
gloves.

Station 126, Cast 1:  
Wear gloves and no duplicates on bottle 24.  
[no idea if this is in reference to niskins in general or dissolved organics] #12,13,19 Rotate to align.

Station 127, Cast 1:  
He: 2b is lost.  
O2: #5 O2 temp 6.0.  
Tritium: #8 cap fell on the floor; still took sample.

Station 128, Cast 1:  
No duplicates at Chl max and at surface, please (#20, 24).

Station 129, Cast 2:  
Gloves on all.  
No dups on iTag or genetics.

Station 130, Cast 2:  
Wear gloves and no duplicates on bottle 24.  
Biomarkers - gloves on all.  
N2O: 21- [ $\Delta$ ]pi compromised[?]

Station 131, Cast 1:  
O2: #9 108/129.  
He: 21a is lost.  
REE: 21 possible filter contamination.

Station 132, Cast 1:  
Wear gloves and no duplicates on bottle 24.  
#7 leaking - slow drip.  
#23 leak out bottom - stream.  
Float PNMEL Navis 727.

Station 133, Cast 1:  
Gloves, please! No dups on iTag.  
#23 slow leak.

Station 134, Cast 1:  
Wear gloves for all Niskins please & use cleaned silicone tubing.  
#21 chl max.

Station 135, Cast 1:  
Please recover rinse water on #s 22, 23.  
He: 19 lost, 6a - lost.

#22 chl max.  
#7 sticky stopcock.

Station 136, Cast 1:  
Wear gloves and no duplicates on bottle 24.

Station 137, Cast 1:  
Wear gloves and no duplicates on bottle 24 or iTag bottles.  
#7 leak.

Station 138, Cast 1:  
No duplicates at 22-24 please.  
Gloves on all.  
#7 slow leak bottom seal.  
Salt bottle 812 chipped at lip.  
Soccom float #9659. Drifter 300234064706700.

Station 139, Cast 1:  
#7 loose cap.  
#19 Nipple imploded after He. (RS: repaired)  
Fix nip. #7, #19 done RS.  
He: 8a lost.

Station 140, Cast 1:  
Wear gloves on 14 and no duplicates on 24.

Station 141, Cast 1:  
Gloves, no dupes on iTag.  
#7 leaking.

Station 142, Cast 1:  
Wear gloves on all bottles, and no duplicates on bottle 24.  
Collect rinses on 22 & 23.  
#7 slow air leak.

Station 143, Cast 1:  
#23 Lanyard caught on bottom cap.  
He: 1b lost.  
Salt 1401 chipped @ seal.  
Tritium: #16 cap loose.  
REE: filter bag fell on floor before Niskin 4 (also used for 5).  
Float 505 12383.

Station 144, Cast 1:  
Wear gloves and no duplicates on bottle 24 (only).  
Raining.  
Drifter 300234064708590 (in sampling bay).

Station 145, Cast 1:  
Wear gloves (all bottles), no duplicates on #24 & iTag.

Station 146, Cast 1:

No duplicates and recover rinse waters at 22 and 23 please.  
#5 leaking from bottom slow.  
#12 Rotate, Rolf.  
#15 Remount.  
SOCCOM float # 9642.

[RO: I'm no longer going to be recording if sample sheets say: "no dups", "wear gloves", or any of that stuff. Just Niskin and sampling issues.]

Station 147, Cast 1:  
#5 bottom seal slow leak.

Station 148, Cast 1: [no bottle comments]  
Station 149, Cast 1:  
#5 leaking.

Station 150, Cast 1: [no bottle comments]  
Station 151, Cast 1: [no bottle comments]  
Station 152, Cast 1:  
#7 leaking.  
He: 11b, 15b, 17A failed.

Station 153, Cast 1:  
#7 drip leak from nipple.

Station 154, Cast 1:  
#7 1/10 New o-ring air valve.  
#13 vent loose; tiny tiny [leak]

Station 155, Cast 1:  
#11,12 fired on the fly with no pre/post soak.  
He: 6B failed.  
Tritium 23: cap fell off.

Station 156, Cast 1:  
#23 leak, closed on lanyard.

Station 157, Cast 2: [no bottle comments]  
Station 158, Cast 1:  
N2O: Switch [sample numbers] @ Niskins 15 & 16.

Station 159, Cast 1: [no bottle comments]  
Station 160, Cast 1:  
He: 3A,4B failed.  
Tritium: 10 on Niskin #11 and 11 on Niskin #10.

Station 161, Cast 1:  
#24 no fire.  
carousal released.

Station 162, Cast 1: [no bottle comments]  
Station 163, Cast 1:

He: 13A dup failed. 17A failed.

Station 164, Cast 1: [no bottle comments]

Station 165, Cast 1: [no bottle comments]

Station 166, Cast 1:

#9 leak lanyard.

N2O: #11 splash [fon] over bottles. Sample 1667 air bubble.

Station 167, Cast 1:

He: 19A, 24A failed.

Station 168, Cast 1:

CFC: #12 bubbles CFC sample.

Station 169, Cast 1:

#9 bottle nipple open.

Station 170, Cast 1:

NO3 not sampled.

Station 171, Cast 1:

He: 6a, 6b, 11a, 11b lost. 14a,b lost, leaking.

Cathy says genetics was sampled on this cast.

Station 172, Cast 1: [no bottle comments]

Station 173, Cast 1: [no bottle comments]

Station 174, Cast 1: [no bottle comments]

Station 175, Cast 1:

He- 8b, 9b, 11b, 15a [lost?]. Need to replace 1 ziptie.

Station 176, Cast 1: [no bottle comments]

Station 177, Cast 1: [no bottle comments]

Station 178, Cast 1:

#7 Very slow drip. Air seal too tight.

Station 179, Cast 1:

He: 13b, 16b,a, 17a, 21b,a, 23b lost.

Station 180, Cast 1: [no bottle comments]

Station 181, Cast 1: [no bottle comments]

Station 182, Cast 1: [no bottle comments]

Station 183, Cast 1:

He: 2b, 4b, 8b, 9a, 18a.

Station 184, Cast 1: [no bottle comments]

Station 185, Cast 1: [no bottle comments]

Station 186, Cast 1:

#24 vent not closed.

Station 187, Cast 1:

#24 [water drains from stopcock even while vent is closed (Actual comment says "runs closed")]- top o-ring?

He: 14A lost.

Station 188, Cast 1:  
#12 vent open.

Station 189, Cast 1: [no bottle comments]  
Station 190, Cast 1:  
#18 opened on [illegible].

Station 191, Cast 1:  
#24 leaking.

Station 192, Cast 1:  
N2O: 1734 not sampled.

Station 193, Cast 1:  
#24 leaked. o-ring.  
NO 3200 ever again.  
[illegible scrawl] 19-21?

Station 194, Cast 1:  
He lost: 14A, 21A, 15 st, 18A dropped.

Station 195, Cast 1:  
REE: 1 filtered. 2 unfiltered.

Station 196, Cast 1:  
CFC: swap [syringes so that] 277 on 8 and 294 on 9

Station 197, Cast 1: [no bottle comments]  
Station 198, Cast 1: [no bottle comments]  
Station 199, Cast 1:  
#5 bottom open.  
#8 bottom open.  
#8 spigot pushed out but not leaking.  
He: 4b, 10b, 23a lost.

Station 200, Cast 1: [no bottle comments]  
Station 201, Cast 1: [no bottle comments]  
Station 202, Cast 1: [no bottle comments]  
Station 203, Cast 1:  
He 7a, 8b, 10a. Sampled 17 on Niskin 18. 18b [failed?], 21A, 24A, 24B.

Station 204, Cast 1: [no bottle comments]  
Station 205, Cast 1: [no bottle comments]  
Station 206, Cast 1:  
He: 1A, 4A, 8A, 16B, 18b, 20a [lost?].  
Black carbon: actually sampled Niskins 2,5,21-24.

Station 206, Cast 2:  
#5 leak at bottom o-ring.

Station 207, Cast 1:

#5 leaking from bottom.  
#7 leaking from nipple.

Station 208, Cast 1:  
#5 is still leaking. :( Bottom o-ring swapped out by KMeT + old man.

Station 209, Cast 1: [no bottle comments]  
Station 210, Cast 1:  
CFC: 277 small bubble in sample.  
Fast 1,7,20. [Niskins?]

Station 211, Cast 1: [no bottle comments]