T376

Carbon System Measurements

Nick Bates Group

Bermuda Institute of Ocean Sciences (BIOS)

Group Members:

Rebecca Garley (BIOS)

Matt Enright (BIOS)

Judith Murdoch (University of Otago)

Objectives:

To undertake high quality dissolved inorganic carbon (DIC) and total alkalinity (TA) measurements throughout the cruise from both the CTD rosette and the ships underway system. Sampling especially in features with high coccolithophore biomass in order to understand the influence of these phytoplankton blooms on biogeochemistry, carbon dynamics (including biological pump of carbon) and air-sea gas exchange. Also to support other biogeochemical measurements on the cruise as a means to understand Southern Ocean ecosystem dynamics.

We will use the carbon chemistry measurements to help understand the dynamics of preconditioning of the mode waters formed in the Southern Ocean. Inputting the DIC and TA data into CO2SYS (Lewis and Wallace, 1998; using the constants from Mehrbach et al., 1973 refit by Dickson and Millero, 1987) to compute other carbonate parameters (e.g. pH, pCO2, calcium carbonate mineral saturation states) to further understand the carbonate system of these waters.

Methods and Samples:

Samples for Dissolved Inorganic Carbon (DIC) and Total Alkalinity (TA) were collected in 250ml glass bottles according to standard JGOFS methods. Milli-Q cleaned bottles were rinsed out 3 times, bottom filled using silicone tubing, allowed to overflow at least 1 times the bottle volume, ensuring no bubbles are in the sample, and sealed with a small headspace to allow for water expansion.

Water samples were collected from all depths the CTD-rosette sampled. Two samples were collected from each Niskin bottle. The first sample set was poisoned with 100µl mercuric chloride for analysis back at the BIOS lab. The second set was not spiked and stored in the dark for no longer than 12 hours (to minimise any biological activity altering the sample) before being run on board, DIC first then TA. In addition to sampling from the rosette, samples were also collected and run on board from the underway system approximately every 2 hours whilst towing the VPR or when CTD station were further part than ~24nm. Also, samples for the 4 incubation experiments were taken; 4-6 initial starting samples, then one sample from each of the 18 cubitainers for the further 3 time points of the experiment. Both the underway and carboy samples were un-spiked, stored in the dark and run on board.

Samples were run on the VINDTA 3S (Versatile Instrument for the Determination of Titration Alkalinity) and the AIRICA (Automated Infra-Red Inorganic Carbon Analyzer) (www.marianda.de).

TA is measured on the VINDTA 3S by titration with a strong acid (HCl). The titration curve shows 2 inflection points, characterising the protonation of carbonate and bicarbonate respectively, where consumption of acid at the second point is equal to the titration alkalinity.

DIC is measured on the AIRICA by the extraction of total dissolved inorganic carbon content from the sample by phosphoric acid addition. The liberated CO_2 flows with a N_2 carrier gas into a Li-Cor non-dispersive IR gas analyser where the CO_2 levels are measured.

For both instruments within bottle replicates were run consecutively on start up to check the precision, continuing once the instrument precision was ±2µmol kg^{-1} or better. These were followed by Certified Reference Materials (CRMs) produced by the Marine Physical Laboratory at UCSD, which were run every 12 hours on the VINDTA and every ~5 samples on the AIRICA, to determine the accuracy of the measurements and to correct for any discrepancies. The TA system CRM values did not vary more than 2umol within each batch of HCl acid. The AIRICA is more susceptible to drift and can be affected by the lab temperature which is why CRMs were run much more often on the AIRICA.

The values for DIC and TA were used to calculate other parameters of the carbonate system using CO2sys (Lewis and Wallace, 1998). Parameters able to be calculated are pH, fCO_2, pCO_2, $[HCO_3^-]$, $[CO_3^{2-}]$, $[CO_2]$, alkalinity from borate; hydroxide ion; phosphate and silicate, Revelle Factor, plus the saturation states of calcite and aragonite.

Sample	# of stations	# of samples	analysis
CTD DIC/TA	73	685	Future processing at BIOS
CTD DIC/TA	73	825	Analysed on board
Underway DIC/TA	127	127	Analysed on board
Incubation DIC/TA	4	238	Analysed on board

Table 1: Summary of sample collection and analysis

Initial Findings:

Figure 1 below shows surface plots of the samples collected from the underway seawater system. With higher sample density in the 2 features that were sampled more intensively. Both DIC and TA have been normalized to a salinity of 35 to remove the effects of salinity on the data. The Agulhas mender shows a higher nDIC and nTA with lower pCO2m temperature and salinity. With the opposite in the eddy feature further to the North.

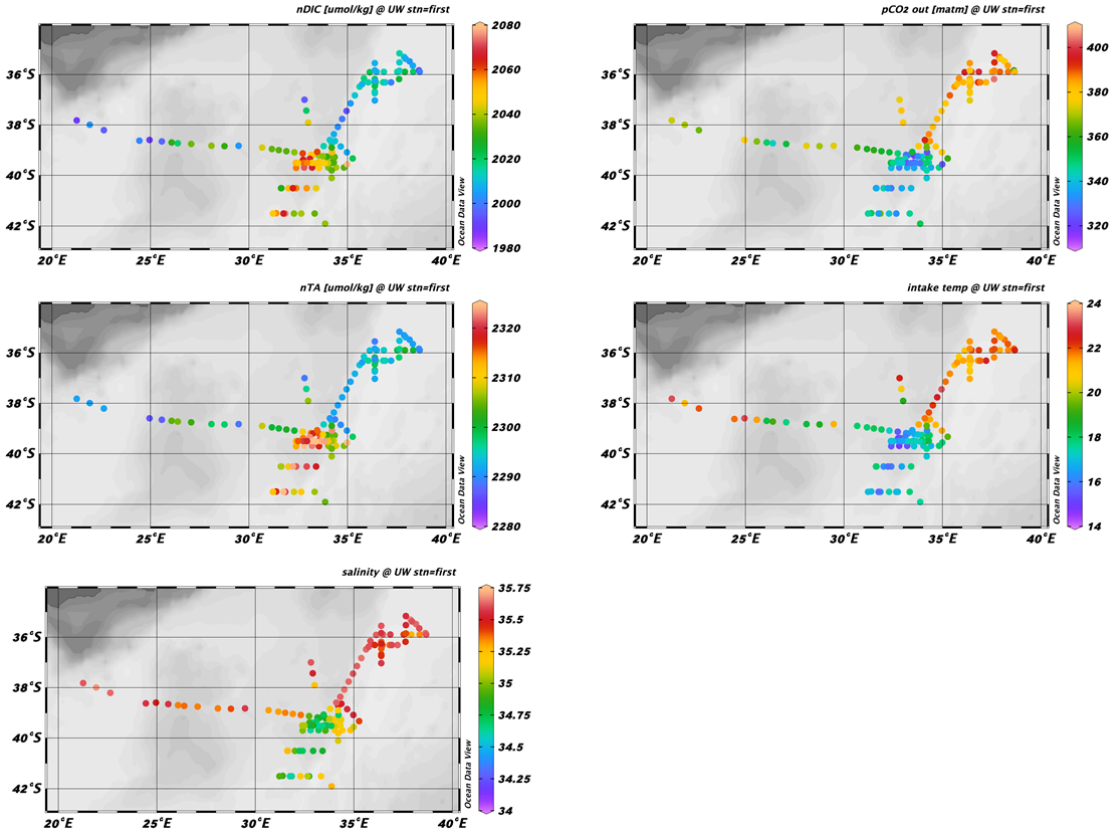

Figure 1: Underway sample data showing salinity normalized DIC (nDIC), pCO2, salinity normalized TA, sea temperature and salinity.

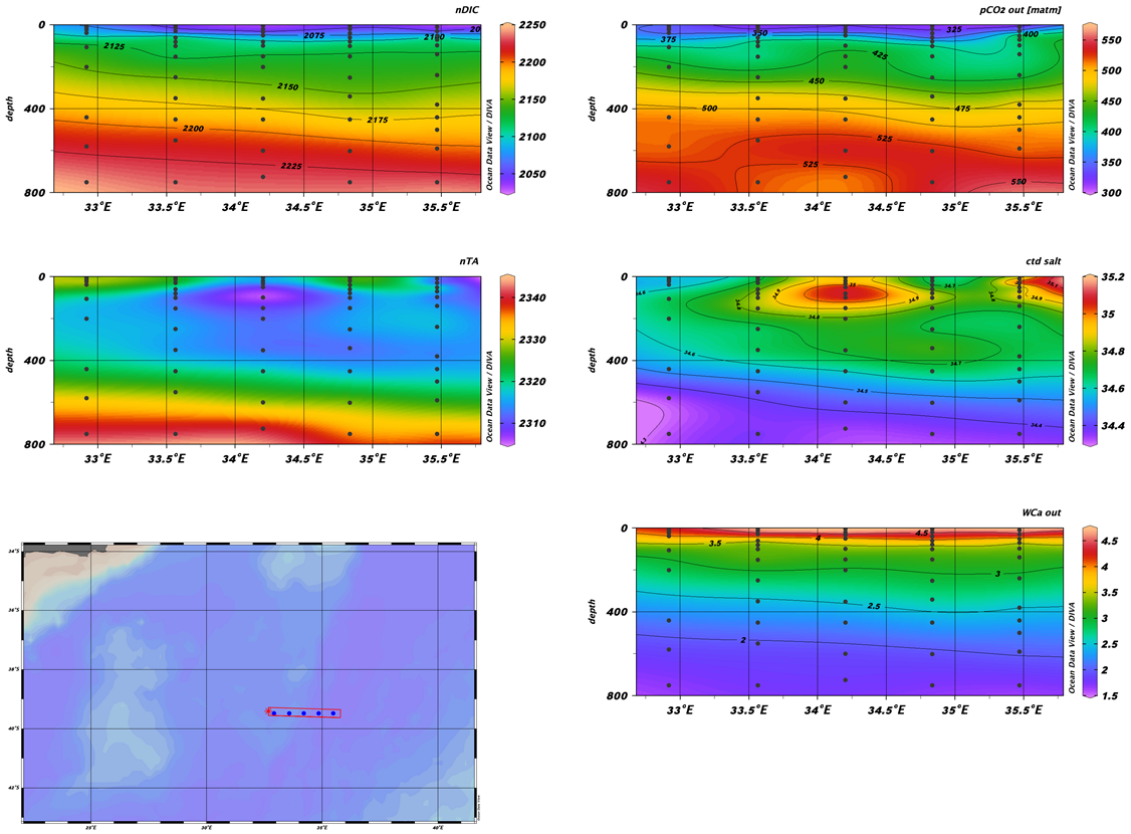

Figure 2: CTD profiles of stations 13-17 at the first sampling of the Agulhas meander. Plots of depth against longitude for nDIC, nTA, pCO2, salinity and calcite saturation state.

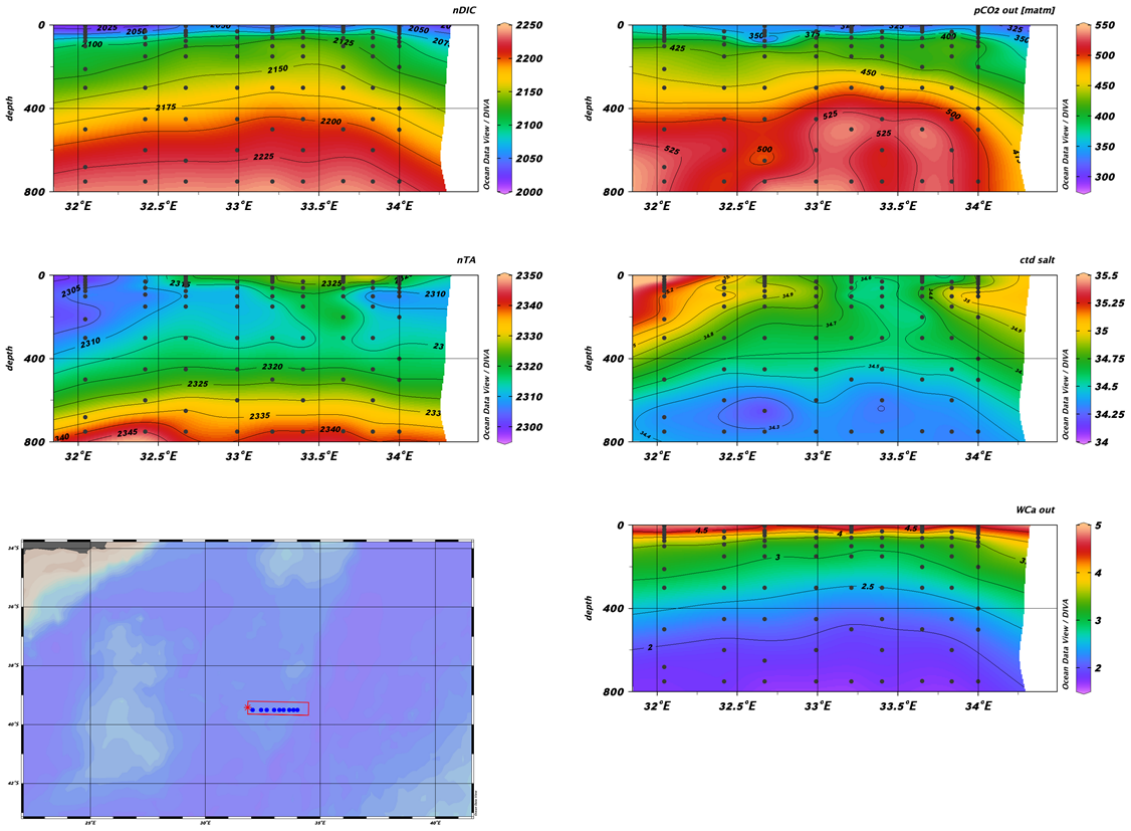

Figure 3: CTD profiles of stations 44-52 at the second sampling of the Agulhas meander. Plots of depth against longitude with nDIC, nTA, pCO2, salinity and calcite saturation state.

The CTD profiles show the temporal changes, particularly in nTA, between the 2 visits to the Agulhas meander, with CTD station 13 on 3rd February and CTD station 44 on 20th February.

Further comparisons between the surveys will be made within the carbonate chemistry data and with rest of the cruise data. Also comparisons between DIC and TA sample analysis on board and back at the lab in Bermuda.

References:

Lewis, E., and D. W. R. Wallace. 1998. Program Developed for CO2 System Calculations. ORNL/CDIAC-105. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tennessee.

Robbins, L.L., Hansen, M.E., Kleypas, J.A., and Meylan, S.C., 2010, CO2calc—A user-friendly seawater carbon calculator for Windows, Max OS X, and iOS (iPhone): U.S. Geological Survey Open-File Report 2010–1280, 17 p.