

Science sub-report for SIMBA
IOS Carbonate Chemistry
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NBP07-09
SIMBA
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The SIMBA expedition has allowed us the opportunity to look at the four parameters of the carbonate system in the ice, brines and waters of the Antarctic and to directly intercalibrate some of our sampling and analytical methods with those of our Belgian colleagues. The extreme conditions challenge our normal methods of sampling and novel ways are being implemented to overcome this. Samples have been collected for total dissolved inorganic carbon (C_T), total alkalinity (A_T), and pH in the open seawater as well as insitu analysis of pCO_2 in ice and CO_2 fluxes from the ice into the atmosphere.

pH Analysis

Samples for pH were collected at 3 “Way IN” stations, 6 Ice drift stations and one deep station near Peter 1st Island. Samples were collected for the entire depth range from the hydro casts and analyzed within 12 hours. Samples for pH were collected immediately after DMS and oxygen. pH was measured using the method of Clayton and Byrne (1993). It is a spectrophotometric using meta cresol purple dye measured at 3 wavelengths at 25 °C. The challenge was to keep the cells at 25 °C in a lab with temperatures below 20°. A temperature regulated Aluminum block coupled with Neslab constant temperature bath (precision of 0.01 °C) was used to stabilize cells and seawater at 25 °C. A local small heater was also used to keep cell area within one degree of 25 °C.

Samples for pH were also collected from Ice stations using a peristaltic pump for 0, 1 and 27m below the ice and two depths in brine holes (site 1 – 15cm and 40cm; site 2 15cm and 60cm). Two profiles of ice cores were also measured for pH using melted aliquots from 5 and 6 selected 5-6cm segments melted in Tedlar bags that had the excess air removed immediately after collection.

Data still require post analysis correction for pressure, temperature and dye perturbation. The values will increase by approximately 0.3 to 0.4 pH units for insitu pH values.

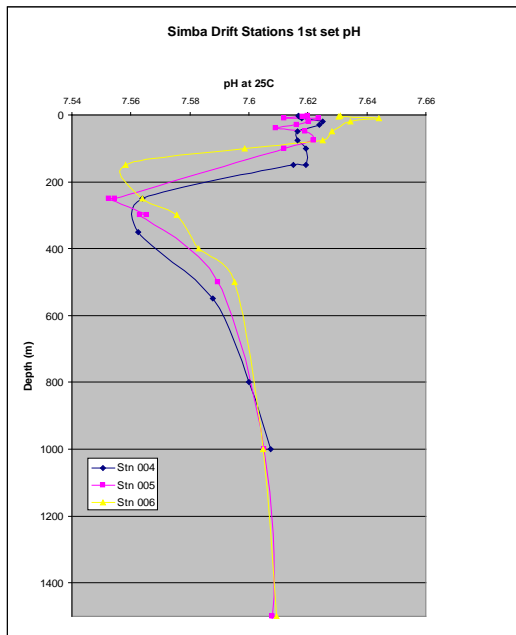


Figure 1 pH (at 25⁰ C) of first three drift stations at Ice Station Belgica

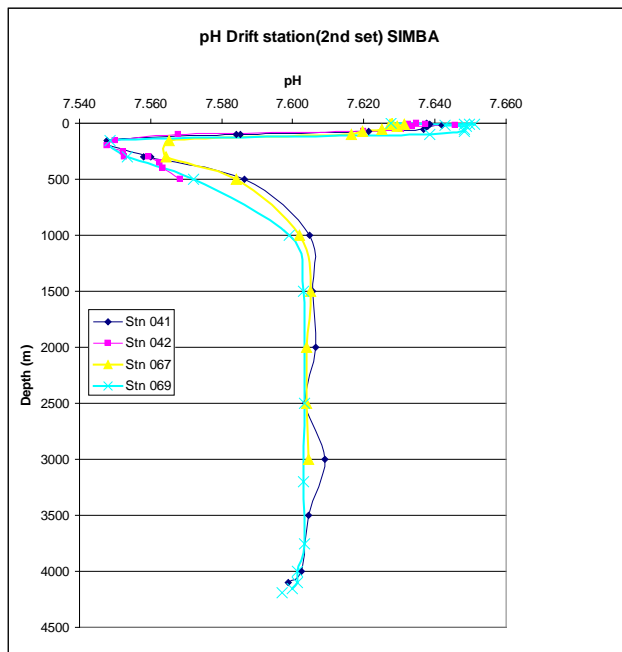


Fig. 2 pH (25⁰ C) of second three drift station analyzed at Ice Station Belgica Also added is the deep station (#069) sampled near Peter 1st Island.

CO₂ in Ice

For this variable IOS has been experimenting with the use of “peepers”. Peepers are essentially silicone chambers (1.7 in. diameter) that are positioned at various depths in the ice with stainless steel tubing and connectors that come up to the surface for sampling. They have been successfully used in soil science for a number of years to measure gases in the soils. We are attempting to use a modified version to measure carbon dioxide (CO₂) in the ice. The principle is that the silicone tubing is permeable to gas exchange but will keep water out so the gas can be run through a gas analyzer. In this case Bruno Delille’s Licor 6262 which measures CO₂ and H₂O. This is part our intercalibration of methods with Bruno Delille and Jean Louis Tison.

Twelve Peepers were installed at site 1 (Brussels), 5 surface ice installations (holes through to seawater) for spatial distribution along with one 20cm sac hole, and two profiles of three depths each comparing holes drilled through the ice and filled with seawater to holes partially down in the ice and filled with brine.

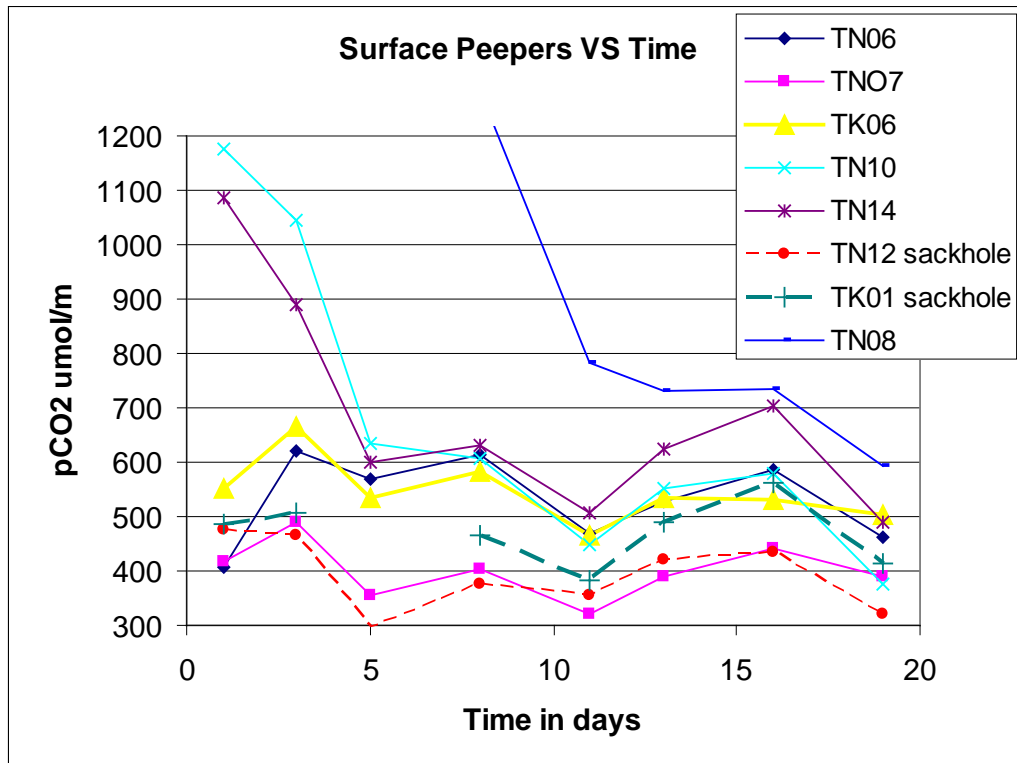


Fig. 3 Surface Peepers at Site 1 (Brussels). Six peepers were in seawater holes and two in brine holes from within a 4 square meter area.

Results still need to be corrected for drift over the 3 week time period but calibrations of the Licor were performed every day with usually less than 1% deviation so values will have only a small correction in relation to their change between sampling periods. The most notable difference between the seawater medium peepers and the brine peepers is the very high values observed initially for half the seawater peepers. These high values may be due complex chemical processes resulting from the exclusions of salts as the water freezes. Carbonate precipitation can occur at this time resulting in CO₂

generation (Rysgaard et al. 2007, Delille et al. 2007) which may be what we are seeing. The other 3 seawater peepers were similar to the brine peepers although there is a considerable range in values on a daily bases indicating that spatial variability is high. All peepers at site 1 started off with an oversaturation of CO₂ which could again be a result of the freezing process as mentioned earlier. This is in contrast to the undersaturation that Bruno Delille found for the brines during the same period. It should be noted that although data not shown the deepest peeper installed at site 1 (60-70cm depth) was found to be below the ice when recovered 3 weeks after installation. It started with oversaturated CO₂ levels but five days after installation to sixteen days it was very similar to the pCO₂ levels of the loop seawater being measure on the ship.

Peepers were installed at a second site (Liege) two days after site 1 installations. At first only 5 peepers were installed in sack holes at 5 different depths to study vertical variability. Unlike site1 initial values at this site were under saturated in pCO₂ and increased with time. This may be due to the high brine levels at site 2 which filled the Auger holes immediately. The Liege brines were even more under saturated in pCO₂ than site 1 (See Bruno Delille's data). Over time there was a general increase in pCO₂

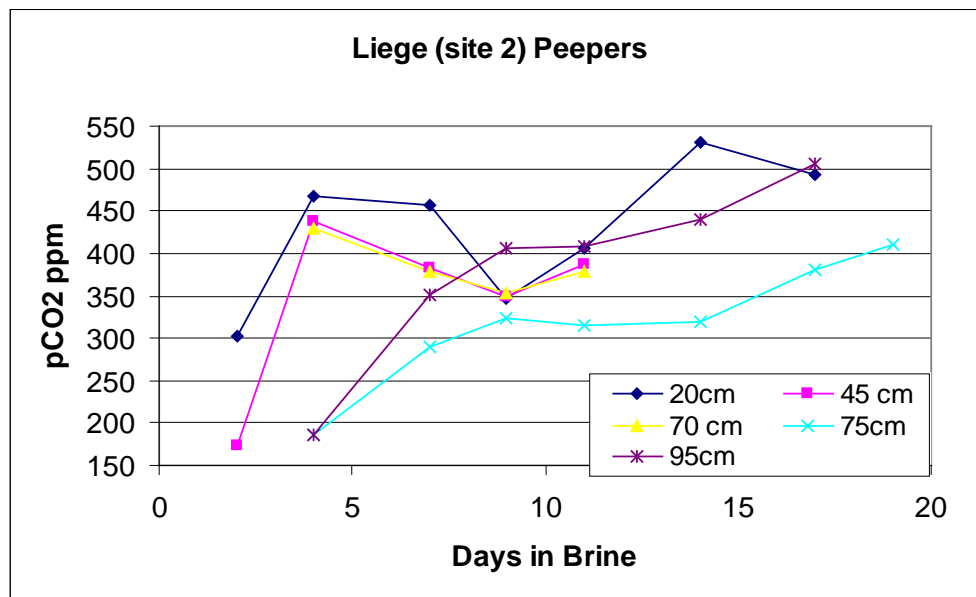


Fig. 4 Peepers placed in sack holes at various depths

with the shallow peepers very quickly indicating over saturated ice conditions. It took the 2 deepest peepers longer to become oversaturated with the 75cm peeper only reaching atmospheric levels after 17 days and then at seawater levels on it final sampling. These peepers were not recovered so we are not sure if they were in seawater or ice at the end. Core lengths showed considerable variability but the last C_T/A_T core was still 104 cm long. Two of the peepers stopped working after day 11 (Julian 287) and were thought to have ice in their stainless steel tubes.

pCO₂ fluxes

Another Ice station project was to make measurements of pCO₂ fluxes into or out of the ice. This was also part of the Belgian-Canadian intercalaboration of methodologies. For this we installed a 2 meter Eddy Covariance mast at site one on the afternoon of October 2nd. The primary instrumentation on the mast is a Licor 7500 open path infra red gas analyzer and a 3-D sonic anemometer along with accompanying humidity, temperature and Young wind monitor. The Licor 7500 measures CO₂ and H₂O, while the 3-D anemometer measures wind flow vertically as well as horizontally. Together they are used to calculate the vertical flux of CO₂ above the ice. The location chosen was a large flat area with low snow coverage (5-10cm) approximately one kilometer from the ship. The instrument samples once per second and stored data on a 2GB flash drive. The equipment is powered by four 12V automotive batteries in parallel. These were usually charged daily or at least every second day. Data is not available until post cruise processing at the University of Manitoba by Dr. Tim Papakyriakou.

Carbonate sampling Ice stations

The two major ice station sites (process stations) were visited 5 times each over the 23 day period. However for day 1 at site 1 we were installing peepers and setting up the Eddy correlation tower so did not sample that day. At all other times we sampled the two ice stations for ice cores, brines and seawater under the ice in conjunction with Bruno Delille and Jean-Louis Tison. During the 9 visits we collected 9 ice cores (46 ice melts segments for C_T and A_T and 11 for pH), 25 under the ice seawater samples and 19 brines samples also for C_T, A_T and pH. The pH were measured at sea and the C_T and A_T will be analyzes back at IOS as part of our further intercalibration of analytical methodologies with the Belgian group. The ice cores were collected and cut into 5-6cm segments by Jean Louis Tison in the field where they were then placed in Tedlar gas sampling bags, sealed with subsequent removal of excess air using a hand vacuum pump. They were then transported back to ship and allowed to melt. The melted ice was then transferred to glass bottles using similar technique for collection from Niskin bottles. After preservation with 100ul of mercuric chloride the bottles were sealed and stored at 4⁰ C for subsequent transport back to IOS. For the last sampling day from each station I also collected pH samples from the Tedlar bags to get an idea of the pH in the ice. Below is a plot of the uncorrected pH data for these two cores.

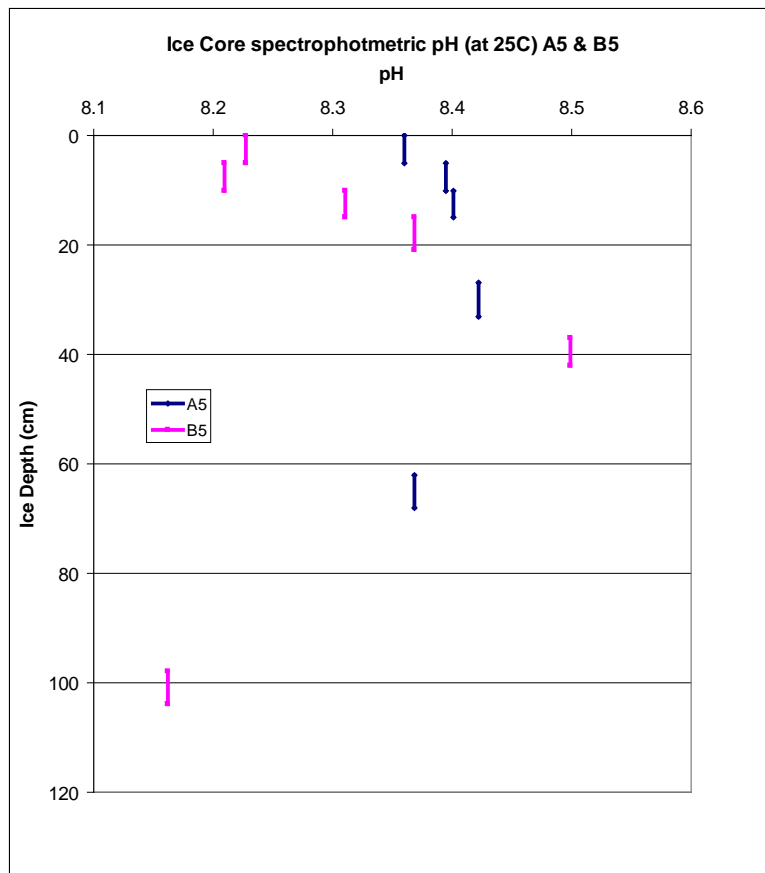


Fig. 5 Spectrometric pH (25C uncorrected) of Ice core samples from the last visits to both drift sites 1 and 2 process stations.

Carbonate sampling in seawater column

To complete our intercalibration Bruno Delille and I both collected a full profile of seawater samples for C_T , A_T and pH to allow us to compare all three parameters on a good sized data set. This was carried out at station #069 after we left the drift ice station. We concentrated on the bottom waters of this 4200 m deep area to see if we can detect any new water formation in this area. Twenty-two depths were sampled. The pH can be seen in Fig. 2.

Summary of samples collected:

SW pH ~160

Ice Cores 10

Ice melt segments

51 for C_T/A_T

11 for pH

Brines

19 for C_T/A_T

17 for pH

Under Ice SW

25 for C_T/A_T

22 for pH

Peepers

~150 measurements

EC Tower

23 days of data with a sampling rate of 20Hz (20 times per second).

I would like to thank Chief scientist Steve Ackley, and Jean Louis Tison for allowing me to participate in this expedition. I would also like to thank Bruno Delille for all his help and advice, to Captain Mike Watson his officers and crew for guiding us safely in and out of the ice and during our stay. Also to Stian Alesandrini, the MSTs, ETs, Its and especially the MTs for all their help in making this a successful expedition.