

**Cruise Report: HLY1002**

**USGS research on ocean acidification**

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### ***Background on Ocean Acidification:***

The ocean has absorbed approximately one-third of the total carbon dioxide (CO<sub>2</sub>) emissions from fossil fuel combustion, cement production, and land use change during the past 200 yrs (Sabine and others, 2004). While this uptake may have moderated the rate of climate change, the uptake of CO<sub>2</sub> has also caused unprecedented changes to ocean chemistry, decreasing pH of the water and leading to a suite of chemical changes collectively known as ocean acidification. As another aspect of climate change, ocean acidification is an emerging global problem that will intensify with continued CO<sub>2</sub> emissions and will likely significantly impact marine ecosystems.

The average pH of ocean surface waters has decreased by about 0.1 unit—from about 8.2 to 8.1—since the beginning of the industrial revolution, with model projections showing an additional decrease of 0.2-0.3 by the end of the century, even under optimistic scenarios (Caldeira and Wickett, 2005; NRC report, 2010). This change exceeds any known change in ocean chemistry for at least 800,000 years (Ridgwell and Zeebe, 2005).

While ocean chemistry and the changes caused by increasing atmospheric CO<sub>2</sub> are well understood and can be precisely calculated, the direct biological effects of ocean acidification are less certain and will vary among organisms, with some adapting well and others not at all (i.e., so called winners and losers). Within the next 100 years, it is likely that society will see significant changes in marine ecosystems and their services, based on the long term effects of ocean acidification (Raven and others, 2005).

### ***Arctic Science***

The Arctic Ocean covers an area of 14,056,000 km<sup>2</sup>, has a fairly constant temperature near 0° C, and has some of the most and least productive waters in the world. Its cold waters absorb more carbon dioxide than warmer seawater. Meanwhile, increasing mean annual temperature in the region (1.8 degrees Fahrenheit over the past 150 years) has increased melting of Arctic ice. Until recently, the perennial ice cover has prohibited significant equilibration with the post-industrial atmosphere, creating a polar mixed layer that is under-saturated with respect to atmospheric CO<sub>2</sub>. Over the last three decades, retreat of summer-time sea ice cover has increasingly exposed shelf and slope waters to the atmosphere and has allowed additional absorption of atmospheric CO<sub>2</sub>. The combination of these processes accelerates the rate at which pH and carbonate mineral saturation state decrease. Models have projected that the Arctic Ocean will become under-saturated with respect to carbonate minerals in the next decade. However, some recent field results indicate that parts of the Arctic Ocean may already be under-saturated in the late summer months when ice melt is at its largest extent. The uncertainty of the models is based on lack of data. The USGS Ocean Acidification Team initiated establishing baselines to gauge future change as a response to the recognition by Department of Interior of this vulnerable ecosystem (Robbins and others, 2010a).

## Cruise Details

### Sampling water

During August 4 - September 6, 2010 a joint operation between the United States and the Canadian government occurred to collect seismic-reflection, multibeam bathymetric and high-resolution chirp data aboard the icebreakers Canadian Coast Guard Ship *Louis S. St-Laurent* and U.S. Coast Guard Cutter (USCGC) *Healy*. These operations were part of the U.S.'s interagency [Extended Continental Shelf Project](#) to determine the limits of the continental shelf in the Arctic. The Chief Scientist aboard the USCGC *Healy* was USGS scientist Brian Edwards. On a non-interference basis, a USGS Ocean Acidification team participated on the *Healy* to collect baseline water data in the Arctic. The Ocean acidification team, lead by Lisa Robbins included both shipboard and home based team members. A number of hypotheses were tested and questions asked associated with ocean acidification, including:

- How do pCO<sub>2</sub> fluxes compare within the Canada Basin?
- What is the saturation state for different parts of the Basin?
- How does saturation state compare to other regions? And if temperature was not a factor, how is the saturation state of Arctic Ocean responding to increased atmospheric CO<sub>2</sub>?
- What is the buffering capacity of the water (Revelle Factor)?
- What kind of variability does the carbon demonstrate in the Arctic (near shore vs. offshore)?

Collaborating with the University of South Florida (USF), the U.S. Geological Survey used a state of the art flow-through Multiparameter Inorganic Carbon Analyzer (MICA) ([Liu and others, 2009](#)). The MICA collected continuous measurements every two minutes of partial pressure of carbon dioxide (pCO<sub>2</sub>), pH, and total carbon (TCO<sub>2</sub>) in seawater. In addition, discrete samples were collected for on-board measurement of pH, total alkalinity (TA), and carbonate ion concentration [CO<sub>3</sub><sup>2-</sup>]. Water was also collected for TA and TCO<sub>2</sub> analyses to be performed land-side. During the cruise, instrumentation on the *Healy* continuously recorded temperature, salinity, dissolved oxygen, and fluorescence of surface water and during vertical casts of a Niskin Rosette. Discrete surface and depth-profile water samples were taken for nutrient, isotope, and elemental analyses in order to supplement our understanding of the Arctic carbonate system. During one Niskin cast, water was filtered onboard to obtain micro-organismal and microbiological community data, plus particulate organic carbon and particulate inorganic carbon data. These data are not reported here.

## ***Discrete water samples***

Discrete water samples were collected while underway following protocols outlined in Dickson and others (2007). More than 327 surface water samples were collected for measurement of pH, alkalinity and  $\text{CO}_3^{2-}$ . A smaller subset was taken for total alkalinity/total carbon, and nutrients ( $\text{NH}_4$ , Silica,  $\text{PO}_4$ , and  $\text{NO}_2+\text{N}$ ). Discrete water samples were removed from the sampling port of the vessel's flow-through seawater system in the main laboratory. Ninety nine samples were taken for nutrient analyses.

Table 1 lists the discrete samples that were collected aboard the Healy and those that were either analyzed or were stored for analyses back onshore. These include: pH, alkalinity,  $\text{CO}_3^{2-}$ , nutrients,  $\delta^{18}\text{O}$  isotope, and DIC/Alkalinity.

## **Shipboard pH and $[\text{CO}_3^{2-}]$ Analyses**

Approximately 30 mL of seawater were collected directly into cylindrical optical glass cells for  $\text{pH}_T$  measurements on the total hydrogen ion scale following the procedure of SOP6b (Dickson and others, 2007). Cuvettes were then placed into an aluminum cell warmer attached to a water bath at  $25^\circ\text{C}$  for approximately 20-30 minutes. Shipboard pH measurements were performed using an Agilent 8453 spectrophotometer, purified metacresol purple indicator dye, and equations modified by Liu and Byrne (in press). Measurement of carbonate ion concentration was performed using an Agilent 8453 spectrophotometer, and methods of Byrne and Yao (2008).

## **Underway Continuous Measurements**

Approximately 24650 continuous measurements of pH,  $\text{pCO}_2$ , and  $\text{TCO}_2$  were performed between August 4, 2012 to Sept 3, 2012 using a flow-through Multiparameter Inorganic Carbon Analyzer (MICA) and Seabird SBE49 CTD attached to the flow-through system of the *Healy*. Geographic, salinity, temperature, and fluorometric data were also collected using a shipboard Ashtech ADU5 GPS system, a SeaBird SBE45 Thermosalinograph, and a Seapoint SCF Fluorometer. A complete description of these can be found in Chayes et al. (2010). The intake of the shipboard flow-through system was located approximately 8 m below the sea surface on the port side of the vessel. Water entered the sampling baffles at depth, was pumped to a sea chest for separation of ice, and was then pumped to a multi-port sampling manifold located in the ship's main laboratory. Seawater was then fed to a custom made PVC de-bubbler containing a Seabird SBE49, prior to being transported to the intake port of the MICA. Measurements were taken and logged approximately every 2-3 minute except for during a MICA flushing cycle that occurred for approximately 10 minutes each hour. The MICA was calibrated using Certified Reference Material from Professor Andrew Dickson of the University of California at San Diego. Precision and accuracy for each channel 0.002 for pH, 2 ppm  $\text{pCO}_2$ , and 2  $\mu\text{mol}/\text{kg}$  for  $\text{TCO}_2$ .

## CTD Stations

### Discrete Vertical Profile Samples

Discrete samples from vertical profile (CTD Stations) casts were collected at 8 locations (see map and table in Main Report). For these casts, a 24-bottle Niskin rosette (12 L bottle volume) with an electronic trigger was fitted with a Seabird SBE 911plus CTD and altimeter. The CTD provided salinity, temperature, depth, fluorescence, and dissolved oxygen data. The rosette was lowered to determined depth and bottles were tripped at select depths as the rosette was brought to the surface. Water samples were collected from the Niskin bottles for the full suite of discrete analyses and included pH, CO<sub>3</sub><sup>2-</sup>, alkalinity, δ<sup>18</sup>O isotope, nutrients, total dissolved inorganic carbon/alkalinity.

### Data Analyses

Discrete data and MICA data were merged with ship's sensor data for further analyses and to provide a format for cross validating of carbon data using CO2calc (Robbins and others, 2010).

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### Disclaimer

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