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TO:  
Dr. Edward Cook, Chair  
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Dear Dr. Cook,

Please find attached our proposal to the Climate Center, entitled '*Laboratory measurement of gas transport through sea ice, with application to the Southern Ocean inorganic carbon budget*,' by Brice Loose, David Ho, Peter Schlosser and Taro Takahashi. We appreciate the opportunity to apply.

Sincerely,

Brice Loose

## Laboratory measurement of gas transport through sea ice, with application to the Southern Ocean inorganic carbon budget

Brice Loose, David Ho, Peter Schlosser and Taro Takahashi

The most recent global CO<sub>2</sub> climatology, by Takahashi et al. (in review) includes data which indicate a dramatic buildup of CO<sub>2</sub> beneath the seasonal ice zone, South of 62°S (~ 40 μatm above atmospheric concentration). This increase can be attributed to winter convection and upward distribution of deep water, rich in organic carbon. However, the high CO<sub>2</sub> may also reflect processes, which occur within the sea ice during freezing and brine rejection. These data emphasize the importance of properly estimating the effects of sea ice on gas transport, however studies of air-sea CO<sub>2</sub> flux treat sea ice as a chemically neutral, impermeable barrier, whose composition does not participate in the inorganic carbon cycle. Takahashi et al. (in review) estimate that the seasonal ice zone is a weak atmospheric source (+0.01 Pg C yr<sup>-1</sup>). Considering that seasonal sea ice cover occupies ca. 30% of the ocean surface, South of 50°S, how would this estimate change if (1) the gas permeability, and (2) the carbonate chemistry of sea ice were included? Is it possible that the Southern Ocean would become a net source to the atmosphere? The formation of sea ice concentrates solutes, both ions and dissolved gases, in the liquid phase, producing a hypersaline brine which drains through capillary structures, called brine channels. Sea ice permeability is similar to fine grained sand (10<sup>-11</sup>–10<sup>-15</sup> m<sup>2</sup>) and considerable effort has been invested in properly determining the pore structure and the dynamics of brine drainage (COX and WEEKS, 1988; FRIETAG and EICKEN, 2003; GOLDEN et al., 1998; GOLDEN et al., 2007; OERTLING and WATTS, 2004). In comparison, there is very little documentation of gas transport in sea ice; until recently, there was little motive.

During sea ice growth, the concentration of solutes increases both the alkalinity and total dissolved inorganic carbon (TCO<sub>2</sub>), just as with salinity, in the brine. As the brine becomes more concentrated and the temperature decreases, the precipitation of CaCO<sub>3</sub> and CaSO<sub>4</sub>, (HE and MORSE, 1993) may liberate CO<sub>2</sub> gas from the brine. Several authors have recently posed the idea that solute rejection makes sea ice an important chemical participant in the global carbon cycle, however they reach different conclusions about its net effect on carbon transport. When Papadimitriou et al. (2003) examined the carbonate chemistry of sea ice in the lab, they inferred the degassing of dissolved CO<sub>2</sub> from the temporal evolution of pH and the ratio of TCO<sub>2</sub> to salinity in the bulk composition. Nomura et al. (2006), went further and quantified the CO<sub>2</sub> flux into a closed headspace during sea ice growth. During 8 experiments, sea ice growth producing an increase in the headspace CO<sub>2</sub> concentration of 45% on average. Using the gas exchange model of Liss (1973), Nomura et al. (2006) estimates an ocean-atmosphere transfer coefficient (k<sub>L</sub>) of 0.14 cm hr<sup>-1</sup>. Rysgaard et al. (2007) used ice core measurements of total alkalinity (TA) to TCO<sub>2</sub> from Franklin Bay, Canada and NE Greenland to confirm the export of inorganic carbon from the ice matrix in real sea ice. Upon melting, they found that the bulk TA:TCO<sub>2</sub> ratio in sea ice samples was greater than in the water under the ice, which could indicate precipitation of alkali salts in the ice pore structure, CO<sub>2</sub> evasion from the brine or both. Using the mass balance of salinity and TCO<sub>2</sub> during a growth experiment, similar to that of Nomura et al. (2006), Rysgaard et al. (2007) reports a negligible transport of gas through the sea ice, but does not provide data to demonstrate it.

Whether excess CO<sub>2</sub> is driven into the atmosphere by gas transfer, or conveyed into the mixed layer by brine drainage depends on the liquid and gas permeability of sea ice, which in turn depends on permeability and porosity. To date we have found only two studies that attempt to infer the transport of gas through sea ice, neither of which relates the transport to intrinsic ice properties (permeability, porosity). Fanning and Torres (1991) used profile of <sup>222</sup>Rn and <sup>226</sup>Ra; their results yielded piston velocities of 4 – 20 cm h<sup>-1</sup>; however, this may be more reflective of partial ice cover with a freshwater lens. In the Arctic, Gosink et al. (1976) measured the penetration rate of CO<sub>2</sub>, ranging from 30 – 60 cm h<sup>-1</sup>, but they make no clear distinction between aqueous gas transport and gas phase transport. These results are not conclusive, but they indicate that gas transfer through sea ice is orders of magnitude greater than gas transfer through freshwater ice.

### Research Question:

The potential for the supersaturated pCO<sub>2</sub> in sea ice brine and the uncertainty of gas transport processes in sea ice raises several questions: (1) what is the rate of gas transport through sea ice, and what

are the primary controls on that rate, (e.g temperature, salinity, porosity), (2) over what range does the magnitude of gas transport vary, and (3) how does gas exchange scale with the percent of ice cover?

### **Experiment Description:**

We propose a laboratory study of gas transport in sea ice that can act as a basis to answer these questions. We will use a chemically inert gas to focus on the rate of gas transport during three separate regimes; (1) sea ice formation and build up during a cooling regime, (2) gas transport during a warming regime without melting or loss of ice thickness, and (3) variation in percent cover of sea ice during a stable temperature regime. We will use temperature, salinity and ice porosity as the dominant control variables on gas transport and brine drainage. Having obtained a time-series of gas exchange and brine concentration in sea ice, we can explore the importance of the competing effects of decreasing permeability on gas exchange and the coincident increase in brine residence time within the ice.

The US Army Corps of Engineers, Cold Regions Research and Engineering Lab (CRREL) operates cold room facilities in Hanover, NH. One room is equipped with a 37 x 10 x 2 m sea ice test basin. In September we visited the CRREL facility and spoke with Leonard Zabilansky, the manager of the test basin. CRREL has offered to let us conduct our experiment in a portion of the test basin. CRREL, as a facility offers technical expertise on the growth and formation of sea ice as well as measurements of sea ice volume, salinity, porosity and thin section imaging. The test basin is equipped with an instrument gondola, which can be positioned directly over an experiment so that electronics and people can operate at room temperature in proximity to the experiment despite the ambient temperature in the test basin (Figure 1)

The experimental apparatus for gas exchange through sea ice consists of a tank with artificial seawater, insulated and wrapped with heat tape, to avoid ice formation on the sides of the tank (Figure 2). The tank is open at the surface, and cooling the ambient air, in combination with seeding, forms sea ice. Water is kept well mixed using a submersible pump to circulate the fluid and minimize thermal and solute gradients. The rate of gas exchange can be inferred from the time rate of change of  $N_2O$  gas in the tank. The diffusivity and solubility of  $N_2O$  are similar to  $CO_2$ , and  $N_2O$  can be measured using a gas chromatograph (GC) equipped with an electron capture detector (ECD).  $N_2O$  is much less reactive than  $CO_2$ ; the transport parameters of  $N_2O$  can be related to those of  $CO_2$  using the ratio of their molecular weights. Sampling for dissolved gas is achieved by equilibration between the water in the tank and a small gas volume connected to the water bath through a microporous membrane diffuser. Sample gas is isolated in a calibrated volume and periodically conveyed to the GC-ECD via carrier gas ( $N_2$ ). This method of sampling has a response time that is proportional to the mixing rate in the tank; using a submersible bilge pump we can exchange the entire volume of the tank in 8 minutes. Sections of sea ice are removed from the tank surface at the end of each phase to determine ice volume, bulk salinity and porosity. The removal of sea ice enhances gas exchange, and allows us to evaluate the scaling between percent sea ice cover and gas exchange under windless conditions. Sea ice sections are collected in accordance with the methods outlined by Tison et al. (2002) in order to minimize brine drainage and preserve the dissolved gas properties. Sea ice sections are sliced into multiple sections for which the volume ( $V_i$ ), salinity ( $S_{s,i}$ ) and volume upon melting ( $V_m$ ) can be determined. From these parameters, the brine fraction, bulk density and porosity in each section can be estimated using the empirical relations of Cox and Weeks (1988).

Previous research on gas transport in the vadose zone provides a theoretical framework for the estimation of transport parameters from the time-varying gas concentration. The vertical gradient in kinetic energy (temperature) is approximately canceled by the potential energy gradient so that advective transport can be neglected. Estimates of the gas diffusion coefficient ( $D$ ) in sea ice can be determined using the one-dimensional diffusion equation, for which there is an analytical solution, given both constant and time-varying boundary conditions. Self-similar models for gas diffusion in soils relate the ratio of porous media to free air diffusivity ( $D/D_0$ ) to the air-filled porosity ( $\phi$ ) and total porosity ( $\epsilon$ ) (KAWAMOTO and KOMATSU, 2006).

### **Summary:**

The processes that regulate  $CO_2$  in sea ice are exceedingly complex. We propose a laboratory experiment to quantify the rate of gas transport through sea ice during stages of growth, variable temperature and variable lead fraction. This experiment can begin to address one component of sea ice

carbon cycle, which is not well understood. The parameterization of gas transport will yield an indication of the importance of CO<sub>2</sub> evasion as compared to TCO<sub>2</sub> drainage with the brine, and can help guide the design of future field studies focused on the seasonal ice zone. These results will also be incorporated into our existing simulations of carbonate chemistry in sea ice, and yield an initial estimate of the net CO<sub>2</sub> transport between the sea ice and the atmosphere during a typical season.

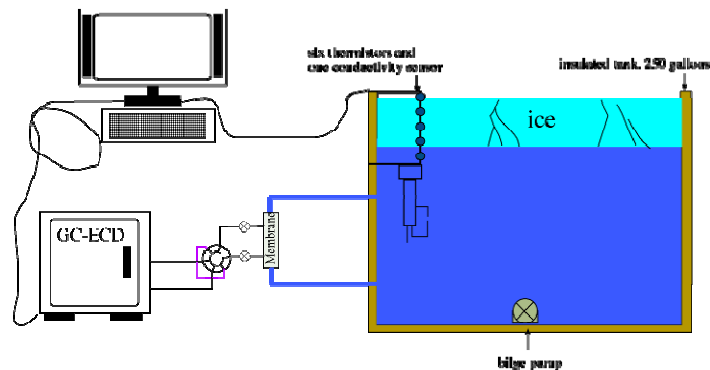
We have secured access to most of the equipment necessary to execute this experiment, including a GC-ECD, microporous membrane contactor, computer, and liquid/gas routing system. The budget for this experiment is as follows:

U-Haul rental to and from Hanover, NH	1200.00
Housing in Hanover, NH	800.00
Car rental	1175.00
Gas	363.00
250 gallon tank	1130.00
6 Hobo water temperature loggers	750.00
Bilge pump	142.00
Campbell conductivity sensor	350.00
Sea Salt	90.00
Total	<u>\$6000.00</u>

We ask for Climate Center funding.



**Figure 1.** Images of the CRREL test basin from September, 2007. The 37 m sea ice tank is pictured on the left. Guides on both sides of the basin allow for the lateral placement of the instrument gondola whose exterior and interior are pictured on the lower and upper right, respectively.



**Figure 2:** The experiment design involves a sea ice tank equipped for semi-continuous sampling of dissolved tracer gas. The Submersible pump ensures a homogeneous mixture inside the insulated walls of the tank. Vertically-oriented thermistors are used to establish the temperature distribution in the ice for calculation of phase separation between ice, brine and precipitated salts. Submerged temperature and conductivity sensors establish the temperature and salinity of the bath.

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