View metadata, citation and similar papers at core.ac.uk

brought to you by CORE

provided by Woods Hole Open Access Server

THE OFFICIAL MAGAZINE OF THE OCEANOGRAPHY SOCIETY

Oceanography

CITATION

Loose, B., L.A. Miller, S. Elliott, and T. Papakyriakou. 2011. Sea ice biogeochemistry and material transport across the frozen interface. *Oceanography* 24(3):202–218, http://dx.doi.org/10.5670/oceanog.2011.72.

COPYRIGHT

This article has been published in *Oceanography*, Volume 24, Number 3, a quarterly journal of The Oceanography Society. Copyright 2011 by The Oceanography Society. All rights reserved.

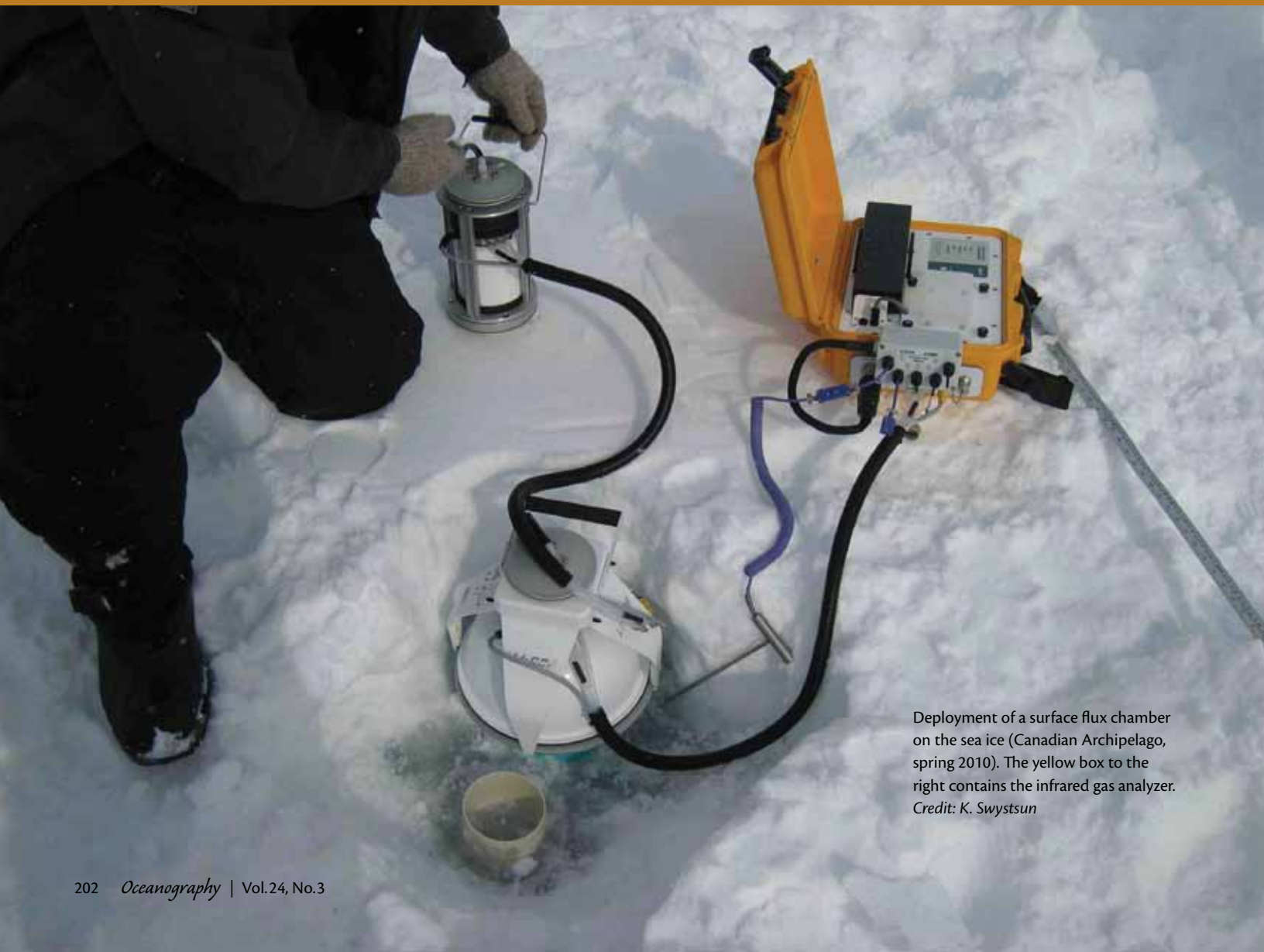
USAGE

Permission is granted to copy this article for use in teaching and research. Republication, systematic reproduction, or collective redistribution of any portion of this article by photocopy machine, reposting, or other means is permitted only with the approval of The Oceanography Society. Send all correspondence to: info@tos.org or The Oceanography Society, PO Box 1931, Rockville, MD 20849-1931, USA.

DOWNLOADED FROM WWW.TOS.ORG/OCEANOGRAPHY

Sea Ice Biogeochemistry and Material Transport Across the Frozen Interface

BY BRICE LOOSE, LISA A. MILLER,
SCOTT ELLIOTT, AND TIM PAPAKYRIAKOU



Deployment of a surface flux chamber on the sea ice (Canadian Archipelago, spring 2010). The yellow box to the right contains the infrared gas analyzer. *Credit: K. Swystsun*

ABSTRACT. The porous nature of sea ice not only provides a habitat for ice algae but also opens a pathway for exchanges of organic matter, nutrients, and gases with the seawater below and the atmosphere above. These constituents permeate the ice cover through air-ice gas exchange, brine drainage, seawater entrainment into the ice, and air-sea gas exchange within leads and polynyas. The central goal in sea ice biogeochemistry since the 1980s has been to discover the physical, biological, and chemical rates and pathways by which sea ice affects the distribution and storage of biogenic gases (namely CO_2, O_2, and dimethyl sulfide) between the ocean and the atmosphere. Historically, sea ice held the fascination of scientists for its role in the ocean heat budget, and the resulting view of sea ice as a barrier to heat and mass transport became its canonical representation. However, the recognition that sea ice contains a vibrant community of ice-tolerant organisms and strategic reserves of carbon has brought forward a more nuanced view of the "barrier" as an active participant in polar biogeochemical cycles. In this context, the organisms and their habitat of brine and salt crystals drive material fluxes into and out of the ice, regulated by liquid and gas permeability. Today, scientists who study sea ice are acutely focused on determining the flux pathways of inorganic carbon, particulate organics, climate-active gases, excess carbonate alkalinity, and ultimately, the role of all of these constituents in the climate system. Thomas and Dieckmann (2010) recently reviewed sea ice biogeochemistry, and so we do not attempt a comprehensive review here. Instead, our goal is to provide a historical perspective, along with some recent discoveries and observations to highlight the most outstanding questions and possibly useful avenues for future research.

THE IMPORTANCE OF SEA ICE IN GLOBAL BIOGEOCHEMICAL CYCLES

Sea ice biogeochemistry is still a young discipline, with relatively few studies dispersed through the last half century, increasing in numbers during the last decade. We are only now progressing from the phase of exploratory discovery into that of defining and refining the details that are ultimately necessary to understand the controlling processes. Biogeochemical cycles in sea ice occur on microscopic scales in a harsh, unstable environment that is difficult to study without disturbing and fundamentally altering the processes of interest. Laboratory experiments have been an essential substitute—but it is has not been uncommon that phenomena revealed in the laboratory had to wait 30 years or more to be substantiated by field data.

Since the 1960s, sea ice researchers have been fascinated with brine in ice and its capacity to both alter the physical properties of ice and provide a vital ecological province. Early research was concerned with determining the effect of brine and sea ice algae on both the mechanical and radiative properties of sea ice (Weller, 1968). Principal among these efforts was the determination of heat flux from the polar ocean to the atmosphere, especially during winter (Untersteiner, 1964). The exploration of sea ice algal communities in brine began in the 1960s; these communities held interest for polar biologists as both extremophiles and as potentially important elements in the polar ocean food web (Arrigo et al., 2010; Caron and Gast, 2010). By 1965, it had been established that at least two microalgal communities existed in sea ice: (1) the epontic (under ice) community found principally in the skeletal layer and bottom 20 cm of sea ice, and (2) the brown algal bands found below the ice freeboard level during the spring and summer (Burkholder and Mandelli, 1965). These organisms are able to thrive in the ambient sea ice conditions in part because of the stable light regime they experience as compared to the mixed layer. The two communities (epontic and banded algae) have proven to be photo-adapted to very different light conditions, with the epontic variety exhibiting photoinhibition at 1 kilolux (~ 14 $\mu E\ m^{-2}\ s^{-1}$) and the algae in the surface brown bands tolerating up to 18 kilolux before photoinhibition (Burkholder and Mandelli, 1965).

The global abundance of the sea ice biome has been difficult to determine because of sampling difficulties coupled with sea ice patchiness. Estimates of primary production in sea ice have been derived by estimating the standing stock of ice algae (Legendre et al., 1992), by ^{14}C incubation (Burkholder and Mandelli, 1965; Booth, 1984), and by immersion of oxygen microprobes for the measurement of net oxygen

production in artificial sea ice (Mock et al., 2002, 2003). In a review of the AMERIEZ (Antarctic Marine Ecosystem Research at the Ice Edge Zone) project, Legendre et al. (1992) estimated that ice algal primary production was between 63 and 70 Tg C yr^{-1} for the Southern Ocean seasonal ice zone (SIZ), defined by these authors as south of 65°S). They also cited similar estimates for ice algal production in the Arctic (for waters north of 65°N). Although these results for primary production in ice were originally thought to be too large, they have withstood time and bracket subsequent measurements and model estimates (e.g., Lizotte, 2001; Arrigo et al., 2010). Based on these values, primary production in ice algae would appear to represent at most 5% of water-column primary production in the Antarctic and 17% of primary production in the Arctic on an annual basis. With the development of cold-temperature microbiological methods over the last two decades, we have come to understand that, in contrast to the photosynthetic community, the heterotrophic microbial community in sea ice is distributed throughout the ice column (Mock and Thomas, 2005; Deming, 2010). In fact, bacterial respiration in sea ice may at times exceed primary production (Deming, 2010).

The strategic importance of sea ice to polar ecology and carbon cycling may be based on the role that it plays as nutrient supply and as feed stock for production in the benthos, in the water column, and along its retreating edge in spring. In the 1980s, Carey (1987) documented the steady particle flux from sea ice providing a small but significant carbon source for benthic dwellers. The importance of the ice edge to the food web was being established; stable density stratification and water-column seeding of algae and nutrients by melting ice were invoked as explanations for the observation of ice edge blooms (Smith and Nelson, 1985, 1986). By the 1990s, tests of the "seeding hypothesis" indicated that ice algae can provide a starter community for phytoplankton growth in the water column at least under some conditions (Kuosa et al., 1992). Beyond algae, melting sea ice may serve as a source of organic matter and micronutrients, such as iron (Lannuzel et al., 2007; Thomas and Dieckmann, 2010). Concrete field evidence for these processes are still few in number, and it will be a challenge to establish a connective relationship between ice algal colonies and the phytoplankton blooms that succeed them. However, advances in rapid DNA identification and quantification, such as quantitative polymerase chain reaction (QPCR) techniques, may revolutionize the field through their ability to readily establish species abundance and distribution and thereby chart the temporal and spatial evolution of these communities.

BIOGENIC GASES IN SEA ICE: A BRIEF HISTORY AND THE STATE OF THE ART

The first hints that solution chemistry might be interesting in sea ice came from laboratory thermodynamic studies of salt precipitation that focused on understanding the structural properties of sea ice (Gitterman, 1937; Nelson and Thompson, 1954; Assur, 1958). These studies found that $CaCO_3$ is likely the first salt to precipitate from cooling ice brines. However, gas concentrations (N_2, O_2, Ar, and CO_2) in natural sea ice were not reported until the early 1960s (Miyake and Matsuo, 1963; Matsuo and Miyake, 1966). Although those CO_2 results may have been compromised (see section on "Measuring Gas Dynamics in Sea Ice"), they generated ideas about carbon cycling in polar waters that are still being tested. In the 1970s, a group in Fairbanks, Alaska, reported concentrations of CO_2, CO, CH_4, and N_2O in sea ice (Kelley and Gosink, 1979; Gosink, 1980) and confirmed that gases can move through sea ice, at least at temperatures above –15°C (Gosink et al., 1976).

In 2002 and 2003, three groups independently attempted to measure CO_2 fluxes in sea ice in situ: one in Alaska (Semiletov et al., 2004), one in the Weddell Sea (Delille, 2006), and one in the Canadian Archipelago (Papakyriakou and Miller, 2011). These three studies, using different methods in different places (but all on first-year ice in spring), observed surprisingly large CO_2 fluxes that contradicted expectations and challenged assumptions about the role of sea ice in biogeochemical cycles. Since then, additional data sets using increasingly refined eddy covariance methods to directly measure gas

Brice Loose *(bloose@whoi.edu) is Postdoctoral Fellow, Woods Hole Oceanographic Institution, Woods Hole, MA, USA.* **Lisa A. Miller** *is Research Scientist, Institute of Ocean Sciences, Fisheries and Oceans Canada, Sidney, BC, Canada.* **Scott Elliott** *is a scientist at Los Alamos National Laboratory, Los Alamos, NM, USA.* **Tim Papakyriakou** *is Acting Director, Centre for Earth Observation Science, Department of Environment and Geography, University of Manitoba, Winnipeg, Manitoba, Canada.*

fluxes have been published, confirming gas fluxes over multiyear ice (Zemmelink et al., 2006), showing that dimethyl sulfide (DMS) is also released from sea ice (Zemmelink et al., 2008), and finding that CO_2 fluxes through the autumn (Else et al., in press) and into winter (Miller et al., 2011). Notwithstanding these advances, the magnitude and prevalence of these fluxes have yet to be concretely established as a widespread sea ice process. In parallel to these studies of gas fluxes over sea ice, the last 10 years have also been a period of intense research into the geochemistry of the ice itself and the role it may play in gas exchange.

Carbon

The idea that sea ice might participate in the carbon cycle dates to the work of Miyake and Matsuo (1963), where they speculated that melting sea ice would release CO_2 to the atmosphere. Their back-of-the-envelope calculations concluded that while CO_2 release from sea ice would be about an order of magnitude less than that from seawater, it was still significant. Recent laboratory studies have supported the hypothesis that sea ice is not only gas permeable (Nomura et al., 2006; Loose et al., 2010) but it can also act as a direct CO_2 source to the atmosphere (Nomura et al., 2006). However, the rate of diffusive fluxes reported by Nomura et al. (2006) and Loose et al. (2010) indicate that CO_2 fluxes in winter would only be significant if pCO_2 (CO_2 partial pressure) in the ice were several orders of magnitude higher than that in the water. On the other hand, Nagurnyi (2008) found that only deformed or broken ice released CO_2, and evidence exists that sea ice can also consume atmospheric CO_2 as a result of ice algal blooms in spring (Delille et al., 2007).

Considering surface waters overlain by sea ice, Kelley (1987) concluded that the ice-covered seas may serve as a net source of atmospheric CO_2, simply because sea ice is porous and the underlying surface waters are often supersaturated in CO_2. Similarly, Bakker et al. (1997) observed CO_2 supersaturation in the Weddell Gyre even as ice cover retreated, implying a net flux of CO_2 to the atmosphere. In contrast, the "seasonal rectification (of CO_2)" hypothesis for the Arctic proposed that respired CO_2 remains trapped by sea ice until spring, when sea ice melt and stratification cause high primary production (Yager et al., 1995). In this scenario, sea ice-covered regions, like the Arctic, are a net sink for atmospheric CO_2. Several studies, including Gibson and Trull (1999) and Sweeney (2003), reported a net sink for the Southern Ocean. However, all of these studies used the wind-speed parameterization for air-sea gas exchange in the sea ice zone, and there is evidence that this scaling is not applicable (Loose et al., 2009). Furthermore, gas exchange and primary production are leading-order processes in determining net flux from the surface ocean. Collectively, these studies demonstrate that it is difficult to establish the net effect of sea ice on the carbon budget because the presence of sea ice inhibits gas exchange and supports primary production to varying degrees at different times of the year and over a range of spatial scales.

In addition to the autotrophic and heterotrophic communities found in sea ice, which may influence gas fluxes, the solution chemistry in sea ice brines may also lead to gas transport through $CaCO_3$ precipitation, leading to changes in pCO_2 and associated fluxes. Early observations that $CaCO_3$ precipitates in sea ice at relatively high temperatures (up to –2.2°C; Gitterman, 1937; Nelson and Thompson, 1954; Assur, 1958), coupled with knowledge of the marine carbonate system (Marion, 2001), implied that CO_2 partial pressures could be quite high in sea ice brines, particularly at low temperatures, a speculation that has now been supported by measurements (Figure 1; Delille et al., 2007; Miller et al., 2011; recent work of authors Miller, Papakyriakou, and colleagues).

Lyakhin (1970) was the first to discuss the geochemical implications of $CaCO_3$ precipitation in sea ice as a possible explanation for the high $CaCO_3$ saturation states that he observed in Okhotsk Sea waters. Jones and Coote (1981) next proposed that high-pCO_2 ice brines (produced by $CaCO_3$ precipitation) would effectively export inorganic carbon (TIC) into the ocean, possibly even contributing to the global solubility pump, and others developed this idea further (Alekseev and Nagurny, 2007; Delille et al., 2007; Rysgaard et al., 2007; see Figure 2 for a schematic description of the TIC pump). However, the hypothesis of the "TIC pump" has not been consistently supported by field data, which sometimes show only insignificant alkalinity fractionation in the ice (Anderson and Jones, 1985; Miller et al., 2011). Furthermore, the TIC pump requires certain physical forcing conditions that may not take place everywhere in the ice pack. Specifically, sea ice formation and convection must be strong enough to produce brine

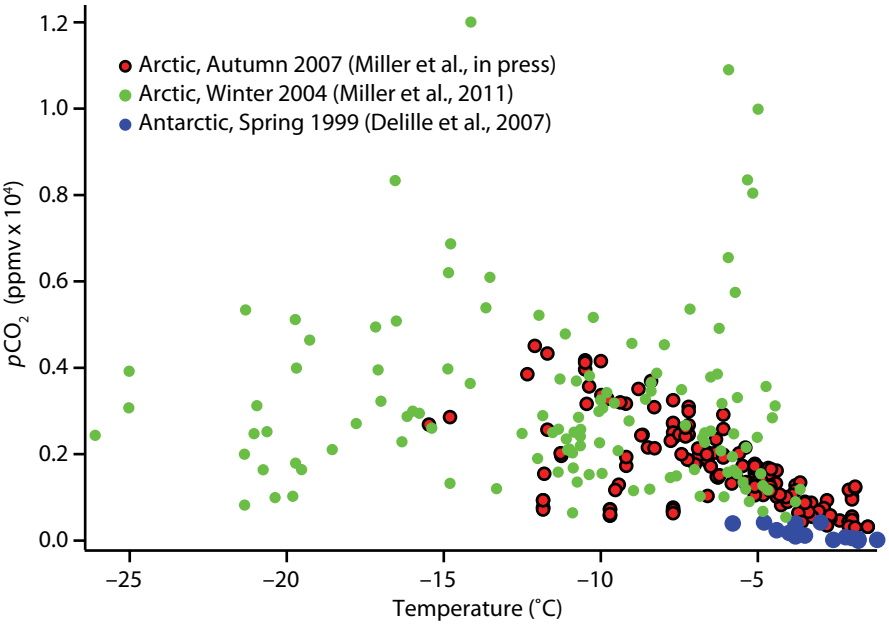


Figure 1. Carbon dioxide partial pressure (pCO_2) values from sea ice, as determined to date. The trend indicates that pCO_2 inside sea ice generally increases with decreasing temperature, which may be the result of $CaCO_3$ precipitation in ice brines and/or reduced gas solubility at high salinities. The scatter may indicate the influence of other processes, such as biological consumption, remineralization, and increased solubility with decreasing temperature.

that is dense enough to sink beneath the mixed layer and enter the abyssal current system (Figure 2). This kind of deep convection typically occurs in polynyas (Orsi et al., 1999), but is not necessarily descriptive of sea ice formation over the entire sea ice zone where sea ice and the mixed layer depth are coupled (Martinson, 1990). Proof of the TIC pump has also been substantially hampered by the fact that $CaCO_3$ precipitation had not been confirmed in natural sea ice. That is, $CaCO_3$ had only been recovered from sea ice in laboratories. Dieckmann et al.'s (2008) successful isolation and identification of $CaCO_3$ precipitates from Antarctic sea ice is an intriguing development in the sea ice TIC pump hypothesis, but it is only one component of a complicated physicochemical process, which requires a concerted research effort to build more conclusive evidence.

Anderson et al. (2004) proposed a very interesting alternative mechanism for ice-facilitated CO_2 export that does not invoke $CaCO_3$ precipitation. They suggested that the process of frazil ice formation (first stage of "new" ice when slender spikes or plates of ice are suspended in turbulent water) at the ocean surface hydrodynamically enhances air-sea gas exchange, allowing the cold surface waters to equilibrate with the atmosphere (or nearly so) before the ice completely covers the sea surface. Thus, the polar mixed layer could become saturated with CO_2 before contributing to any deep convection.

In summary, recent work has indicated that all these conjectured sea-ice CO_2 transport mechanisms may be valid, depending on time and place. During freeze-up, strong downward fluxes in the presence of at least some remaining open water punctuated by sharp, brief upward fluxes (Else et al., in press) support both the Anderson et al. (2004) hypothesis of enhanced CO_2 drawdown into open waters in which sea ice is beginning to form and the suggestion that $CaCO_3$ precipitation as ice cools increases pCO_2 within the ice, which can then outgas to the atmosphere. To date, only one investigation of CO_2 in winter sea ice has been published (Miller et al., 2011), and that study found that very small CO_2 fluxes (both upward and downward) above the ice persisted throughout the coldest part of the year. Because the ice was extremely cold and likely impermeable (Golden et al., 1998), those deep-winter fluxes were probably exchanges with the snow and brine above the ice, and possibly the top layer of the ice, but not with the ice interior. However, Miller et al. (2011) did find evidence that ice brines contribute inorganic carbon to the water under the ice. As spring approached, Miller et al. (2011) saw upward fluxes, increasing in magnitude as the temperature increased. Other springtime studies also saw upward fluxes at the beginning of their deployments, but the fluxes very quickly switched, continuing strongly downward into the ice, as primary production and melt (and therefore, possibly $CaCO_3$ dissolution) advanced (Delille, 2006; Nomura et al., 2010a; Papakyriakou and Miller, 2011).

Other Gases

After CO_2, DMS is the most extensively studied gas in sea ice (Thomas and Dieckmann, 2010). An important link in

the global sulfur cycle (Charlson et al., 1987; Ayers and Cainey, 2007), DMS is a microbial decay product of dimethylsulfoniopropionate (DMSP), which is produced by a number of algal species. Thus, DMS is one of the primary vectors (after sea salt aerosols) for transporting sulfur from the ocean to the atmosphere, where sulfur plays a significant role in cloud condensation and climate regulation. A number of studies have reported high DMS and DMSP concentrations in sea ice (e.g., Trevena et al., 2000, 2003; Trevena and Jones, 2006) and significant DMS fluxes out of sea ice (Zemmelink et al., 2008).

Other gases of biogeochemical interest that are associated with sea ice include the halogens (mainly alkyl bromides), which strongly influence polar atmospheric chemistry (Simpson et al., 2007), and methane, an ultrastrong "greenhouse" gas that is produced in anoxic sediments and is often found in bubbles trapped under sea ice (Kvenvolden et al., 1993; Shakhova et al., 2009). However, as yet, little work has been done on the behavior of these gases within sea ice.

MEASURING GAS DYNAMICS IN SEA ICE

Matsuo and Miyake's (1966) measurements of gas concentrations in sea ice were based on collecting and analyzing the gas released from ice through successive melting and refreezing cycles under a vacuum. Adapted from the field of glacial ice geochemistry, the first "modern" studies of gases in sea ice generally involved crushing the ice in a vacuum and collecting the gas released for analysis (Tison et al., 2002). This approach extracts gas from the gas pockets and from the brine, and then a correction is made to account for the gas in brine. This approach works well for nonbuffered gases such as N_2 and O_2, but it is problematic for CO_2. Exposing a sea ice sample (or seawater) to a vacuum disrupts the equilibria between the gas (CO_2) and its hydrolysis products (H_2CO_3, HCO_3^-, and CO_3^{2-}), quantitatively drawing CO_2 out of the solution and giving unrealistically high pCO_2 estimates in the ice. Therefore, further technique development has focused on crushing the ice in smaller volumes of head space so that there is no need to draw a vacuum in order to get an accurate estimate of the gas mixing

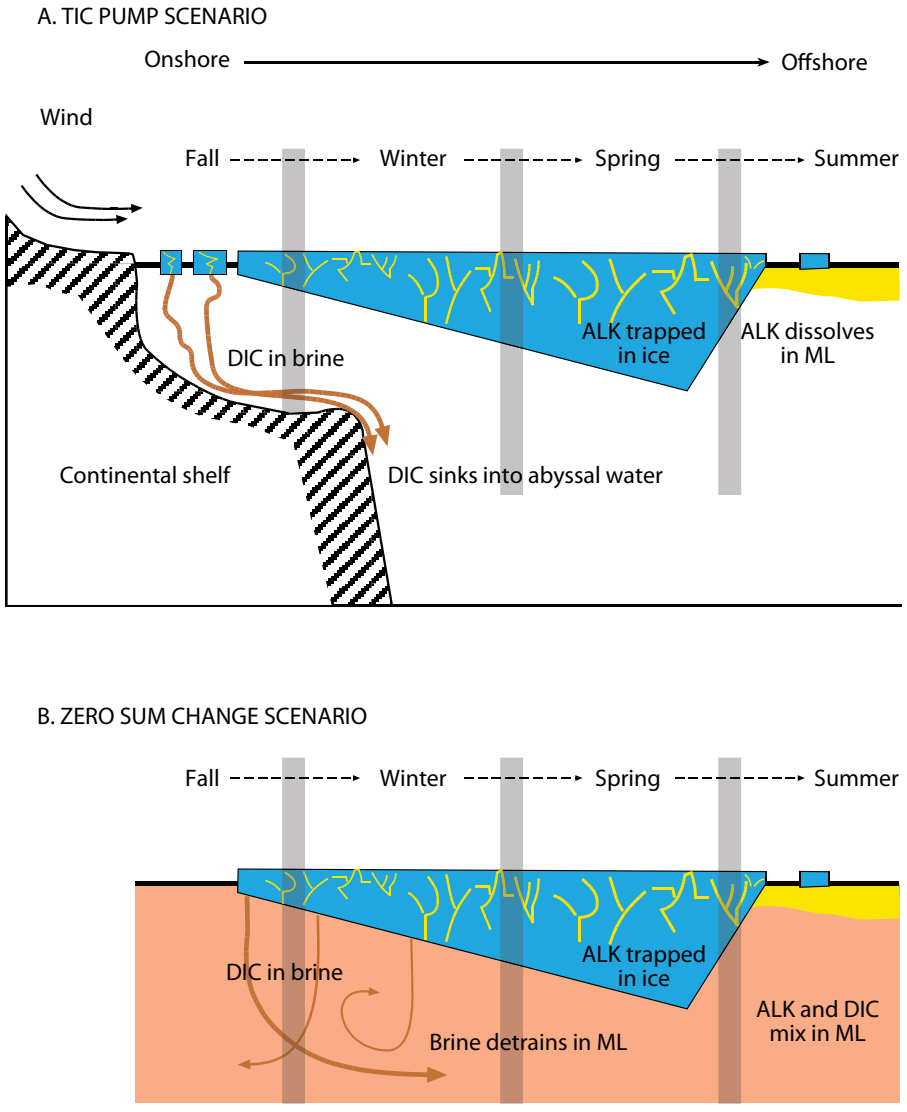


Figure 2. Schematic of the total inorganic carbon (TIC) pump. In panel A, the scenario depicts abyssal water formation in polynyas and the offshore transport of sea ice so that freeze and melt occur in different regions of the ocean. Under such a scenario, if carbonate alkalinity (ALK) remains trapped in the ice as salt crystals and dissolved inorganic carbon (DIC) drains with the brine, then a "TIC pump" might result in a net transport of inorganic carbon to the deep ocean. Panel B depicts a scenario where ice forms and melts over a water column with a homogeneous mixed layer (ML). In this case, brine from sea ice is likely to detrain in the mixed layer and subsequently recombine with carbonate alkalinity in the ice. This scenario depicts a zero-sum change in the mixed layer inorganic carbon budget.

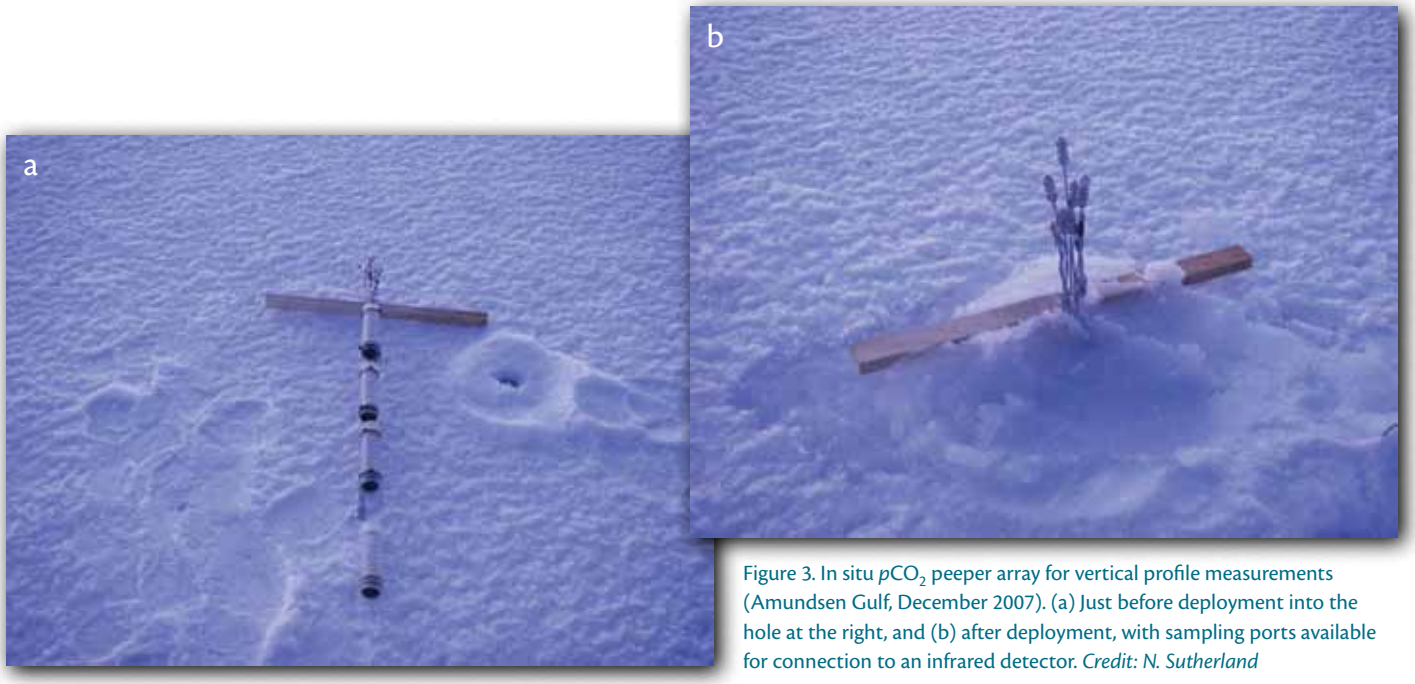


Figure 3. In situ pCO_2 peeper array for vertical profile measurements (Amundsen Gulf, December 2007). (a) Just before deployment into the hole at the right, and (b) after deployment, with sampling ports available for connection to an infrared detector. *Credit: N. Sutherland*

ratios within the ice. In contrast, recent measurements of DMS, a relatively nonbuffered gas, in sea ice have been relatively straightforward, involving melting the ice in a closed vessel that is then purged with N_2 to extract the DMS from solution (Trevena and Jones, 2006).

Destructive methods, requiring removal and melting or crushing of ice cores, are not ideal when attempting to study a natural system, and researchers have had some success freezing in situ probes into the ice to measure gases. Most notably, oxygen-sensing optodes have generated some very intriguing data, although their field deployment has been limited and not much has been published to date (Mock et al., 2002, 2003; Rysgaard et al., 2008). The one drawback to measuring oxygen in sea ice using optodes is that their response time is quite slow. Slow response times are also a problem for in situ CO_2 probes that have been used in sea ice, which can take about 24 hours to equilibrate with their surroundings at subzero temperatures. These probes, dubbed "peepers," were adapted from methods used in soil sciences (Holter, 1990; Jacinthe and Dick, 1996; Kammann et al., 2001), and are simply gas-permeable silicone chambers that are frozen into the ice. Narrow-bore tubing leads from the peepers to the surface and is connected to a portable gas analyzer (Figure 3). To date, this approach has only been used for CO_2 measurements, although results from soils studies have indicated that peepers should also be appropriate for other gases in sea ice (Jacinthe and Dick, 1996; Kammann et al., 2001). When measuring CO_2 pressures in sea ice using peepers, they must be connected to the gas analyzer (generally a nondispersive infrared detector) in a closed loop so that the gas is recycled back into the peeper, assuring that a vacuum is not drawn on the ice (see Figure 1 for a summary of pCO_2 in sea ice analyzed using peepers).

Finally, many of the scientists working on the problem of CO_2 cycling in sea ice are oceanographers and, therefore, have naturally attempted to calculate pCO_2 from total inorganic carbon (TIC), total alkalinity (A_T), and/or pH in bulk sea ice or brines (Delille et al., 2007; Nomura et al., 2009, 2010a; Miller et al., 2011). Ice cores are collected, sectioned, and melted, then the melts are analyzed for TIC and A_T (Rysgaard et al., 2007; Miller et al., 2011). Those values are then corrected to brine salinity from the in situ temperature (Petrich and Eicken, 2010), and pCO_2 is calculated from those extrapolated "brine" TIC and A_T concentrations. This approach requires the assumption that all the TIC and A_T measured in the bulk ice melt initially resided in the brines and that the carbonate equilibrium equations for seawater are applicable to sea ice brines, which may not be the case due to ion-ion interactions that take place in such concentrated solutions (Marion, 2001). Collecting and analyzing the brines allows pH to be analyzed, as well as TIC and A_T, but collecting a sufficient quantity of brine for such analyses requires allowing brines to drain either into sackholes drilled into the ice (Delille et al., 2007) or from cores extracted from the ice (Nomura et al., 2009). The brine drainage process can take some time, particularly at low

temperatures, during which it is difficult to limit CO_2 exchange with the atmosphere, which affects both the TIC and pH measurements, and again, pCO_2 is underestimated. This problem of gas exchange during brine collection also applies to the measurement of any gas, including O_2 and DMS (Delille et al., 2007), although Papadimitriou et al. (2007) calculated that when sufficient brine can be collected quickly (i.e., in about 10 minutes), the sheltered conditions and low temperatures of a capped sackhole limit gas exchange, and the analyses should not be significantly impacted. Regardless of whether data are from melted ice cores or brines, calculating pCO_2 from the other parameters is also fundamentally dubious for sea ice because the available stability constants have only been defined for conditions of low salinity and high temperature (i.e., seawater). The one published study that collected the data necessary to overdetermine the system found that calculated and measured pCO_2 in ice brines agreed well, at least in spring ice (Delille et al., 2007), indicating that the constants can be applied at least a bit beyond their empirical range.

The Ins and Outs of Flux Measurements

To date, three different methods have been employed to measure gas flux in and out of sea ice. The first to make such measurements were Gosink et al. (1976), who charged boreholes with gases, sealed the boreholes, then measured the gas concentrations in cores taken from the surrounding ice over the subsequent hours. This approach generated extremely interesting results, but most efforts since have focused on less-destructive measurements employing some variation on either eddy covariance or bell-jar chambers.

Enclosures (or chambers) act to control the volume of air available for exchange across a covered surface so that emission or uptake can be measured as a concentration change (see photo of surface flux chamber on article title page). The validity of the flux measurement depends on the extent to which the enclosure impacts gas transport, production, or consumption in the snow or upper sea ice. Further, enclosures sample over only a very small area, which substantially limits the utility of the data in a heterogeneous environment. Enclosures modify the surface's thermal regime by affecting energy exchange via radiation and convection, possibly affecting carbon equilibrium relations and restricting measurement to a diffusive flux. Other problems relate to pressure changes in the enclosure associated with wind fluctuations and modified gas concentration in the closed head space, which impact the surface-to-chamber concentration gradient and hence the diffusive flux (Nomura et al., 2010b). Benefits of the technique are that enclosures are inexpensive and relatively simple to operate, allowing for frequent deployments in numerous locations. Results provide, if not an accurate measure of the flux, a feature-driven indication of relative uptake and emission activity. Valuable insight on the CO_2 source-sink character of sea ice has been acquired through the use of enclosures in the Arctic (Semiletov et al., 2004; Nomura et al., 2006, 2010b; Miller et al., in press) and in the Antarctic (Delille, 2006; Delille et al., 2007).

Eddy covariance (EC) is a micrometeorological tower-based technique that relates a flux (e.g., heat, trace gas) to the time-averaged covariance between high-frequency fluctuations of vertical wind velocity and a scalar (e.g., temperature or gas concentration; see Figure 4; Bakan, 1978; Edson et al., 1998). Typically, measurements are made with fast-response sensors at a frequency between 10 Hz and 20 Hz over a period of approximately 30 to 60 minutes. Like the enclosure method, the EC technique also has limitations, being most applicable over flat and homogeneous surfaces under steady or slowly changing atmospheric conditions (Baldochi, 2003). A suite of corrections is also required to account for, among other things, the separation distance between the measurement of vertical wind velocity and the scalar, and to compensate for our inability to sample all significant scales of turbulence contributing to the turbulent transfer of CO_2. Further details on the technique are available from numerous sources (e.g., Massman and Lee, 2002; Baldochi, 2003).

The technique for trace gas studies over sea ice has thus far been limited to fluxes of H_2O and CO_2 (Semiletov et al., 2004; Miller et al., 2011; Papakyriakou and Miller, 2011), and these studies use fast-response nondispersive infrared analyzers (NDIR) of open-type (OP) architecture, meaning the sensor's optical path is in the free atmosphere. Alternatively, measurements can be made within a confined cell using a closed-path NDIR (CP). The OP system has the advantages of the optical path being very near to the vertical wind velocity measurement, sampling air with minimal aerodynamic disturbances, and of having modest power requirements.

The CP NDIR, on the other hand, is typically located several meters from the vertical wind velocity measurement, requiring that air be drawn through a tube to the sensor using a high-capacity pump (McGillis et al., 2001). Cold-region measurements of the CO_2 flux using a CP EC system do not contain biases that have been recently reported for open-path EC systems (Amiro, 2010; Prytherch et al., 2010). Although corrections are available (Webb et al., 1980; Burba et al., 2008) to OP data sets, and have been used in CO_2 flux studies over sea ice (Papakyriakou and Miller, 2011), they can be large in relation to the observed fluxes, and some are empirically based (Burba et al., 2008) and untested over polar snow and sea ice surfaces. Further work is required to confirm the results of previous studies.

Fast-response detectors have not been incorporated in EC systems for DMS over sea ice; rather, existing measurements of DMS emission are based on a modification of the EC method, in which the average gas concentration over the period required for the detector response is compared to the average air movement over the same period (relaxed eddy accumulation; Zemmelink et al., 2008). In many ways, sea ice is an ideal environment for EC measurements because the surface can be relatively smooth and uniform (at least for first-year ice) and the platform is stable. On the other hand, sea ice is an extremely variable environment on the mesoscale, with cores collected only a couple of meters apart often displaying quite different characteristics (Miller et al., 2011) that result in spatial variations at a scale not resolved by eddy covariance measurements.

Figure 4. Eddy covariance system for measurements of CO_2 fluxes deployed over the sea ice (Franklin Bay, winter 2004). The sonic anemometer and open-path CO_2 detector are at the top of the picture. *Credit: T. Papakyriakou*

SEA ICE MICROSTRUCTURE: A TRANSPORT PATHWAY AND A HOME AWAY FROM HOME

One of the remarkable capacities of sympagic (ice-associated) organisms is to maintain viability inside the porous microstructure of the ice throughout the winter and subsequently to multiply in spring. These organisms inhabit the interstitial spaces (brine channels and gas pockets) within the ice crystal structure (Burkholder and Mandelli, 1965; Arrigo et al., 2010; Deming, 2010). Diatoms comprise an important part of the ice algal community and appear to have the capacity not only to adapt from surface ocean to interstitial ice conditions but also to modify the physical structure of the ice to suit their needs (Krembs et al., 2002, 2011). Here, we discuss what is known about the rates of material fluxes through the ice microstructure and their mechanisms.

The porous microstructure of sea ice is the central factor controlling biogeochemical cycling and fluxes in the ice. The fluid phase of sea ice is composed of brine inclusions that range from 0.1 to 10 mm in length (Light et al., 2003) and air inclusions spanning sizes of 0.01 to 1 mm in first-year sea ice (Light et al., 2003), to tens of millimeters in multiyear hummock ice (Perovich and Gow, 1996). Porosity, defined as the volume of the voids divided by the total volume of ice, can range from 2 to 40% (Perovich and Gow, 1996). Much of this internal volume is filled with brine, but in first-year ice, some 1 to 5% is filled with gas, and the gas-filled voids are known to increase significantly in multiyear, as well as springtime, ice. The connectivity of these individual inclusions is difficult to measure, although

computed tomography scans and network algorithms have made some progress in quantifying this connectivity (Golden et al., 2007). Pore connectivity is certainly the controlling factor determining transport within the sea ice microstructure; however, transport is usually related to porosity as that is easier to quantify.

Brine drainage from sea ice is by far the best-studied result of solute segregation and internal sea ice microstructure (Cox and Weeks, 1988; Golden et al., 1998, 2007; Freitag and Eicken, 2003; Oertling and Watts, 2004). Brine drainage plays a role in forming deep-water masses throughout the global ocean and establishing the high salinities required for deep convection (Steele and Morison, 1995; Orsi et al., 1999; Tamura et al., 2008). As discussed above, several hypotheses exist for sea ice enhancement of the CO_2 solubility pump in these deep- and intermediate-water formation regions.

The liquid permeability of sea ice is well established and is similar to fine-grain sand (on the order of 10^{-13} m^2; Golden et al., 2007). Below 5% porosity, brine drainage is thought to virtually cease (Cox and Weeks, 1988). Golden et al. (2006) established a theoretical upper bound for liquid permeability that reproduces this behavior using cylindrical capillaries whose internal radii are representative of brine porosity. However, some debate exists on precisely what stage of ice growth leads to brine drainage and what processes are responsible for transporting brine out of the ice. Solute segregation during ice growth leads to solute accumulation at the freezing interface. The canonical view has been that this brine subsequently convects away from the freezing interface and into the water column. However, new studies using the "mushy layer" theory indicate that brine drainage requires a critical ice thickness and that drainage by gravity alone is the primary process leading to bulk desalination (Feltham et al., 2006; Notz and Worster, 2009).

In comparison to the permeation of brine, there has been relatively little consideration given to the process of gas permeation through sea ice, but it is conceptually similar to gas diffusion through the unsaturated (vadose) zone in soils. From those empirical relationships, we can infer that sea ice permeability would range from about 10^{-7} to 10^{-4} cm^2 s^{-1} in first-year sea ice with 1 to 5% gas porosity, based on the Penman-Millington Quirk soil gas diffusion model (Moldrup et al., 2004; Kawamoto et al., 2006). The few laboratory and field estimates that have been made of gas diffusion through sea ice fall within this range, exhibiting large differences in magnitude, depending on the specific gas. For CO_2, gas diffusivity ranges from 18 to 90 x 10^{-5} cm^2 s^{-1} (Gosink et al., 1976; Nomura et al., 2006). Diffusion ranges from 3 to 6 x 10^{-5} cm^2 s^{-1} for O_2 (Loose et al., 2010) and from 0.4 to 20 x 10^{-5} cm^2 s^{-1} for SF_6 (Gosink et al., 1976; Loose et al., 2010). Much of this variability can probably be attributed to differences in sea ice porosity, and/or gas permeation through sea ice may be fundamentally different from liquid permeation. However, we lack sufficient research to link porosity and gas diffusivity in sea ice in a quantitative fashion.

It is important to point out that all studies of gas diffusion have been conducted in cold, columnar first-year sea ice where porosity was low, especially near the ice surface, as a result of cold temperatures. To date, the rate of gas diffusion in warm, springtime ice has not been documented in the field or the laboratory. The progressive freshening and drainage of springtime sea ice will likely yield much larger gas diffusion rates, although gas transport by brine convection will complicate this picture.

INSIGHTS FROM THEORY AND EXPERIMENTATION

Sea Ice and the Mushy Layer

To determine the physical properties of sea ice, all models, including those based on first physical principles, require, at minimum, profiles of either temperature or salinity through the ice (Feltham et al., 2006). Beyond this constraint, models based on sea ice thermodynamics require nothing else. The greatest recent theoretical advance in sea ice simulations has come from the recognition that sea ice can be treated as a "mushy layer" (Worster, 1991). This constitutive formulation describes the evolution of a pure crystalline phase bathed within its impure fluid. The advantage of mushy layer theory is that it presents the most elegant, and in some cases analytical, solutions to the equations describing the physical evolution of sea ice and, therefore, represents a principal tool in describing the behavior of growing sea ice and associated brine drainage.

There are at least two important implications of mushy layer theory for biogeochemical processes. First, desalination of sea ice does not occur by solute segregation at the freezing interface (Notz and Worster, 2009). Instead, gravity-driven brine drainage is the principal drainage mechanism in young

sea ice, and this process begins only after the ice has reached a certain thickness (Notz and Worster, 2009). This outcome is supported by the results of Wettlaufer et al. (1997), but it is seemingly at odds with experimental evidence that has been used to construct empirical equations for sea ice growth, including those of Cox and Weeks (1983, 1988), as well as the results of Loose et al. (2009), who show a nearly instantaneous response in both oxygen and salt during the first stages of ice crystal nucleation. However, the apparent discrepancies may be a function of the water conditions beneath the ice during formation. In mushy layer theory, the solute boundary layer governs the transition region from ice crystal lattice to pure liquid, and transport is assumed to proceed at the rate of molecular diffusion, therefore permitting a continuous salinity gradient from the water into the ice (Notz and Worster, 2009). However, turbulence beneath the ice is a critical control on solute boundary layer thickness and, hence, on the transport of solutes away from that interface (Killawee et al., 1998). The experiments of Loose et al. (2009) involved a water bath that was mixed using submersible pumps, potentially disrupting the boundary dictated by mushy layer theory. In the polar ocean, sea ice formation occurs under a variety of turbulence conditions, but the solute boundary layer beneath natural sea ice may still be governed by molecular rates, as indicated by mushy layer theory. These phenomena may only be valid for the bottom centimeters of the ice and/or for quiescent waters, but if they prove to be more pervasive, they have tremendous implications for our understanding of the strength and timing of water column convection beneath sea ice, the processes that take place in polynyas, and even the carbonate composition of brine as it drains.

The second important implication from mushy layer theory is that gravity-driven brine drainage is accompanied by a return flow of seawater that penetrates into the ice matrix to occupy the volume recently vacated by the brine. This seawater pumping mechanism might be an important source of nutrients to the algal community living near the bottom of the ice. Indeed, the high concentrations of iron observed in sea ice (an order of magnitude higher than in the underlying water) have been explained as resulting from effective "filtering" of particle-reactive iron from seawater onto the solid ice surfaces, as large volumes of surface seawater are flushed through Antarctic sea ice, particularly as spring melt advances (Lannuzel et al., 2010). However, mushy layer theory does not account for gas processes in sea ice, as gas is actually a third phase—neither pure solid nor impure liquid. The addition of a third phase may effectively remove the seawater infiltration mechanism by allowing drained brine channels to become gas-filled void spaces that draw gas into the ice from the atmosphere, or from the brine solution. The subject of brine drainage mechanisms (solute segregation versus gravity drainage), the range of applicability of mushy layer theory, and the mechanisms that lead to seawater infiltration are all topics that remain to be conclusively resolved by theoretical and data-based representations of sea ice.

PROGRESS TOWARD SEA ICE BIOGEOCHEMISTRY IN MODELS OF THE POLAR OCEAN

Climate system models[1] to date treat sea ice in a unimodal fashion; heat, radiation, and gas fluxes are all influenced by sea ice cover, but the biogeochemistry of ice itself is only beginning to take shape within "system" codes. A Web of Science search of the terms "carbon dioxide, sea ice, model" will yield dozens of results related to climate simulations that focus on the loss of ice coverage. Carbonate chemistry within the sea ice matrix, however, is difficult to find.

Representing Organic and Inorganic Gas Production in System Models

The cycling of climate-active gases is distinct within different sea ice types, and, in turn, sea ice types are a function of age and their formation conditions (Petrich and Eicken, 2010). One strategy for representing overall biogeochemical cycling in sea ice has been to incorporate source, sink, and transport terms directly into dynamic pack models themselves (Elliot et al., 2010; Vancoppenolle et al., 2010). The vertical transport of solutes is thus handled as either simple eddy diffusion, or through mixing length theory coupled to multiphase porous flow through the evolving brine. In either case, thresholds such as "the rule of fives" (Golden et al., 1998) and pulse freezing enhancements (Fritsen et al., 1998; Vancoppenolle et al., 2010) can be represented as an easy means to parameterize more complex porous microstructure dynamics.

As in the open ocean (contrast Moore

[1] System models are defined as the class of codes that explicitly represent ecosystem dynamics and all the principal biogeochemical cycles as well as the dynamics that determine transport.

et al. [2002] with Moore et al. [2004]), modeling groups have used community ecosystem codes as a starting point for sea ice biogeochemistry. Nutrient simulations in the ice column began as box or layered models of photosynthetic uptake (Arrigo et al., 1993). Scales then expanded to the pan-polar, with heavy reliance on data assimilation to represent processes such as phytoplankton abundance and distributed sea ice plus snow cover (Arrigo et al., 1997). Early algorithms for biogeochemical cycling were then adapted to the Arctic bottom layer, usually for landfast ice (Lavoie et al., 2005; Jin et al., 2006). In a few cases, transition to full pack dynamics has been accomplished (Deal et al., 2011). Real connections to the climate system have lagged, however. Solutes are converted to phytoplankton and particulates with some fidelity, but dissolved gas chemistry is not explicitly represented in these models. For example, Redfield ratios are generally used to couple individual elements, a highly dubious approach in the extreme environment of sea ice. Meanwhile, production of O_2 and consumption of CO_2 by photosynthesis are not simulated.

The field evidence of precipitating $CaCO_3$ polymorphs from natural sea ice cores (Dieckmann et al., 2008) and the elaboration of the carbonate pump hypothesis (Alekseev and Nagurny, 2007; Delille et al., 2007; Rysgaard et al., 2007) provide strong motivation to include carbonate mineral processes into sea ice models (see above for more detail). The situation has been modeled several times at the analytical and box levels (Jones and Coote, 1981; Rysgaard et al., 2009), and the connections to ecosystem dynamics will be straightforward. In any detailed representation of the biogeochemical system, TIC must be realistically fractionated, with some portion precipitated as $CaCO_3$ and some transported along with other brine solutes, as discussed above. The eddy mixing concepts should be directly applicable (Vancoppenolle et al., 2010; Jeffrey et al., in press). But, models for thermodynamic salt effects on solubility, and acid-base and mineral equilibria all need to be extrapolated to ice temperature and salinity conditions. In an additional complication, gravity drainage leaves air-filled channels above the freeboard level (Light et al., 2003), and laminar layer models for vertical transfer can be applied inside brine tubes at the internal liquid-gas interface. One challenge will then be parameterization of gas diffusion rates through upper-level networks and snow. Another will be to account for structural effects of the carbonate solids.

All gases are subject to excess saturation as ionic strength (salinity) increases. Bubble formation is well known in sea ice (Weeks and Ackley, 1982; Light et al., 2003), but the volumes are small, and micrographs are only sometimes able to identify gas bubbles as brine channel inclusions. Nevertheless, rich headspace and surface chemistries likely occur within the ice matrix. Most current ice geochemical cycling models ignore these as secondary effects (Vancoppenolle et al., 2010; Jeffrey et al., in press), but the bubble situation may deserve closer examination.

Simulating Volatile Gas Production

In Arctic ice, algae residing primarily in the bottom layer produce and/or support locally high levels of DMS (Levasseur et al., 1994; Stefels et al., 2007). In a dynamic ice code, excess DMS emanating from the matrix must be permitted to exchange with surface waters by spilling into leads or marginal waters. There, it will concentrate in thin, freshened layers near the surface (Matrai et al., 2008), and interaction with mixed layer physics becomes critical. In the Southern Ocean, strong DMS producers such as *Phaeocystis* populate the pack surface (Stefels et al., 2007). If the increasing dominance of first-year ice in the Arctic Ocean over the coming decades creates a marine ecosystem more like that in the Antarctic, analogous phenomena may become important in the north. Ultimately, both upper-ice habitats and brine channel sulfur migration must be simulated (Arrigo et al., 1997; Stefels et al., 2007). Volatile halogens of the hypersaline regime, extending up to the sea ice-snow interface, are often present as alkylated organic molecules, but elemental iodine gas is also included. These compounds are transported into the polar troposphere where they catalyze ozone photochemistry (Saiz-Lopez et al., 2007; Simpson et al., 2007; Freiss et al., 2010). But, they are yet to be dealt with in the models.

The ultrastrong greenhouse forcing agent methane may present special difficulties. Bubble seeps or flares constitute well-known features of the natural cycle at the global scale. Moreover, large releases have recently been connected with global warming induced degradation of submarine permafrost and clathrates (frozen methane hydrates). Such structures are predominantly found in the Arctic (Kvenvolden et al. 1993; Shakhova et al. 2009). The molecule can move rapidly upward from sediments

in the bubble phase (Obzhirov et al., 2004; Shakhova et al. 2009). Therefore, concentrations build up beneath the ice pack, both in solution and as trapped pockets of vapor. It may be necessary to add yet another phase to gas mixing inside the sea ice matrix, and numerical approaches to brine transport already constitute multiphase porous flow (Jeffrey et al., in press).

Recent general evolution of the sea ice biogeochemistry models are characterized through a set of examples in Table 1. Approaches being pursued around the community tend to be ecodynamically well developed, but much hard work remains before gases will be adequately represented. This statement applies whether the compounds involved are major or trace, simple or complex, dissolved or otherwise. For example, extant codes treat the Monod equation for organism growth, as well as light limitation, in much the same fashion within their ecosystems, except for Vancoppenolle et al. (2010) who reverse engineer primary production from observed rates. Lavoie et al. (2005) include an additional, hypothetical ice growth rate restriction on the phytoplankton. But, the gases remain explicitly unincorporated across this suite of major efforts. The Deal et al. (2011) model is now being extended with bottom layer sulfur dynamics so that it will encompass ice-sourced DMSP and DMS. Dissolved inorganic carbon, alkalinity, solid precipitation, and photosynthetic conversion of carbonate to organics/molecular oxygen should be expected to make their appearance soon in at least some of these systems. Investigators in the Deal group further intend to consider methane bubbles arriving from below the ice pack (Shakhova et al., 2009).

Table 1. A survey of simulations that resolve biogeochemical cycles within sea ice. Box models may be considered zero dimensional. Note that only a few groups have ventured into the realm of horizontal distribution, and that gases are in general yet to be included. An interesting exception is ammonia/um, but this is due to its role in nitrogen remineralization.

Reference	Biological Dimensions	Physical Domain	Ice Dynamics	Elements and Cycles	Optics	Validation
Arrigo et al. (1993)	Vertical	Landfast at McMurdo Sound	Heat transfer through 10 mm layers	N, P, Si, and Redfield to chlorophyll*, recycle NH_4	Snow, ice attenuation, and self-shading	Local ice, nutrient, and chlorophyll data
Arrigo et al. (1997)	Coarse 3D	Southern Ocean	Remotely sensed ice, snow extent	N, P, Si, and Redfield to chlorophyll*, recycle NH_4	Snow, ice attenuation, and self-shading	Multiple ice cores
Lavoie et al. (2005)	Box model	Landfast at Resolute	Heat transfer through one snow, two ice layers	Si and Redfield to chlorophyll*	Snow/ice attenuation, biological heating	Local light, nutrient, and chlorophyll data
Jin et al. (2006)	Box model	Landfast at Barrow	Fixed empirical	N, Si, and Redfield to chlorophyll*, recycle NH_4	Snow, ice attenuation	Local ice column chlorophyll
Vancoppenolle et al. (2010)	Vertical	Weddell Sea	Vertical brine plus eddy drain, data flush	Si, from C rates based on empirical chlorophyll	Hard switch as short-wave diode	Drift station cores at sites Ice Station Polarstern (ISPOL) and Liège
Deal et al. (2011)	2D bottom layer	Pan-Arctic (global but Antarctic unvalidated)	Multiple layers and thicknesses	N, Si, C, and Redfield to chlorophyll*, recycle NH_4	Snow, ice attenuation, and self-shading	Multiple chlorophyll bottom data

*Ecodynamics are estimated using empirical relationships based on in situ chlorophyll concentrations and the Redfield ratios for sea ice.

RESEARCH FOR THE FUTURE

This article emphasizes the role of sea ice processes in the context of polar ocean and global-scale biogeochemical cycles, with particular attention given to biogenic gas fluxes. The retreat of summer sea ice in the Arctic has brought urgency to the search for a first-order understanding of carbon, oxygen, and carbonate cycling in seasonal sea ice. In the past 50 years, ice algae cryoadaptations, mineral precipitation, and the permeability of sea ice have all been revealed as processes that may impact the polar ocean carbon cycle. Whereas these processes are now well documented—a major step forward—their net effect is far from clear. Many of the studies that we highlighted here have yielded conflicting results—often because these studies are scattered throughout the seasonal ice cycle and because of the inherent spatial variability in sea ice. Previously oversimplified processes, such as air-sea gas exchange in sea ice-covered waters, have proven important to elemental budgets in simple calculations, but remain unconstrained by direct measurement. The community awaits emerging results from the recent International Polar Year, and from future field and laboratory studies, as there is a pressing need to develop predictive scaling laws that capture the cycling of algae/phytoplankton, nutrients, and, ultimately, carbon between the water column, the ice, and the atmosphere. These microscale processes have little hope of being represented directly within Earth system models, at any dimension. Therefore, simulations will rely on approximation of these processes, and those approximations must be grounded in a robust understanding of the net balance among biological, physical, and chemical processes in the sea ice. The interplay among these processes can be revealed through laboratory and theoretical study. Ultimately, the impact of each process must be validated with field studies. Here is a list of critical topics that we hope the future of sea ice sciences will address to push our understanding to the level of prediction:

- In situ sensor development for measuring and monitoring gases in sea ice (laboratory, field)
- Validation of the timing and the processes (solute segregation vs. gravity drainage) that lead to desalination of sea ice and water column convection under ice
- Determination of the conditions under which $CaCO_3$ polymorphs are found in natural sea ice
- Determination of empirical scaling laws for the rate of bulk gas permeability in all sea ice types, including columnar, granular, multiyear, and especially springtime or melting ice (laboratory, field)
- Determination of the veracity of mushy layer theory in the study of real sea ice
  - Quantification of seawater infiltration as a return flow caused by the brine drainage process
  - Correction for the effects of gas as a third phase in ice that is not explicitly accounted for in mushy layer theory
- Exploration of the effect of organic material on the physical properties of ice: porosity, permeability, and the radiative balance
- Development of seasonally varying nutrient budgets for the seasonal sea ice zone that account for (1) sediment transport from the continental shelves to offshore melting sites, (2) aeolian deposition, and (3) water-column recycling
- Incorporation of all of the above processes into models of sea ice at the ocean basin scale and in the climate system

REFERENCES

Alekseev, G.V., and A.P. Nagurny. 2007. Role of sea ice in the formation of annual carbon dioxide cycle in the Arctic. *Doklady Earth Sciences* 417A:1,398–1,401.

Amiro, B. 2010. Estimating annual carbon dioxide eddy fluxes using open-path analysers for cold forest sites. *Agricultural and Forest Meteorology* 150:1,366–1,372.

Anderson, L.G., and E.P. Jones. 1985. Measurements of total alkalinity, calcium, and sulfate in natural sea ice. *Journal of Geophysical Research* 90:9,194–9,198, http://dx.doi.org/10.1029/JC090iC05p09194.

Anderson, L.G., E. Falck, E.P. Jones, S. Jutterström, and J.H. Swift. 2004. Enhanced uptake of atmospheric CO_2 during freezing of seawater: A field study in Storfjorden, Svalbard. *Journal of Geophysical Research* 109, C06004, http://dx.doi.org/10.1029/2003JC002120.

Arrigo, K.R., J. Kremer, and C.W. Sullivan. 1993. A simulated Antarctic fast ice ecosystem. *Journal of Geophysical Research* 98:6,929–6,946, http://dx.doi.org/10.1029/93JC00141.

Arrigo, K., T. Mock, and M. Lizotte. 2010. Primary producers and sea ice. Pp. 282–325 in *Sea Ice*. D.N. Thomas and G.S. Dieckmann, eds, Wiley-Blackwell, Oxford, UK.

Arrigo, K.R., D.L. Worthen, M.P. Lizotte, P. Dixon, and G. Dieckmann. 1997. Primary production in Antarctic sea ice. *Science* 276:394–398, http://dx.doi.org/10.1126/science.276.5311.394.

Assur, A. 1958. Composition of sea ice and its tensile strength. Pp. 106–138 in *Arctic Sea Ice*. Conference held at Easton, Maryland, February 24–27, 1958, National Academy of Sciences-National Academy of Engineering, Washington, DC, Research Publication 598.

Ayers, G.P., and J.M. Cainey. 2007. The CLAW hypothesis: A review of the major developments. *Environmental Chemistry* 4:366–374, http://dx.doi.org/10.1071/EN07080.

Bakan, S. 1978. Note on the eddy correlation method for CO_2 flux measurements. *Boundary-Layer Meterology* 14:597–600, http://dx.doi.org/10.1007/BF00121898.

Bakker, D.C.E., H.J.W. DeBaar, and U.V. Bathmann. 1997. Changes of carbon dioxide in surface waters during spring in the Southern Ocean. *Deep-Sea Research Part II* 44:91–127, http://dx.doi.org/10.1016/S0967-0645(96)00075-6.

Baldochi, D. 2003. Assessing the eddy covariance technique for evaluating carbon dioxide exchange rates of ecosystems: Past, present and future. *Global Change Biology* 9:479–492, http://dx.doi.org/10.1046/j.1365-2486.2003.00629.x.

Booth, J.A. 1984. The epontic algal community of the ice edge zone and its significance to the Davis Strait ecosystem. *Arctic* 37:234–243.

Burba, G.G., D.K. McDermitt, A. Grelle, D.J. Anderson, and L. Xu. 2008. Addressing the influence of instrument surface heat exchange on the measurements of CO_2 flux from open-path gas analyzers. *Global Change Biology* 14:1,854–1,876.

Burkholder, P.R., and E.F. Mandelli. 1965. Productivity of microalgae in Antarctic Sea Ice. *Science* 149:872–874, http://dx.doi.org/10.1126/science.149.3686.872.

Carey, A.G. Jr. 1987. Particle flux beneath fast ice in the shallow southwestern Beaufort Sea, Arctic Ocean. *Marine Ecology Progress Series* 40:247–257, http://dx.doi.org/10.3354/meps040247.

Caron, D.A., and R.J. Gast. 2010. Heterotrophic protists associated with sea ice. Chapter 9 in *Sea Ice,* 2nd ed. D.N. Thomas and G.S. Dieckmann, eds, Wiley-Blackwell, Oxford, UK, http://dx.doi.org/10.1002/9781444317145.ch9.

Charlson, R.J., J.E. Lovelock, M.O. Andreae, and S.G. Warren. 1987. Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate. *Nature* 326:655–661, http://dx.doi.org/10.1038/326655a0.

Cox, G.F.N., and W.F. Weeks. 1983. Equations for determining the gas and brine volumes in sea-ice samples. *Journal of Glaciology* 29:306–316.

Cox, G.F.N., and W.F. Weeks. 1988. Numerical simulations of the profile properties of undeformed first-year sea ice during the growth season. *Journal of Geophysical Research* 93:12,449–12,460, http://dx.doi.org/10.1029/JC093iC10p12449.

Deal, C., M. Jin, S. Elliot, E.C. Hunke, M. Maltrud, and N. Jeffrey. 2011. Large-scale modeling of primary production and ice algal biomass within arctic sea ice in 1992. *Journal of Geophysical Research* 116, C07004, http://dx.doi.org/10.1029/2010JC006409.

Delille, B. 2006. *Inorganic Carbon Dynamics and Air-Ice-Sea CO_2 Fluxes in the Open and Coastal Waters of the Southern Ocean*. Docteur en Sciences thesis, Université de Liège, Liège, France.

Delille, B., B. Jourdain, A.V. Borges, J.-L. Tison, and D. Delille. 2007. Biogas (CO_2, O_2, dimethylsulfide) dynamics in spring Antarctic fast ice. *Limnology and Oceanography* 52:1,367–1,379, http://dx.doi.org/10.4319/lo.2007.52.4.1367.

Deming, J.W. 2010. Sea ice bacteria and viruses. Chapter 7 in *Sea Ice,* 2nd ed. D.N. Thomas and G.S. Dieckmann, eds, Wiley-Blackwell, Oxford, UK.

Dieckmann, G.S., G. Nehrke, S. Papadimitriou, J. Göttlicher, R. Steninger, H. Kennedy, D. Wolf-Gladrow, and D.N. Thomas. 2008. Calcium carbonate as ikaite crystals in Antarctic sea ice. *Geophysical Research Letters* 35, L08501, http://dx.doi.org/10.1029/2008GL033540.

Edson, J.B., A.A. Hinton, K.E. Prada, J.E. Hare, and C.W. Fairall. 1998. Direct covariance flux estimates from mobile platforms at sea. *Journal of Atmospheric and Oceanic Technology* 15:547–562, http://dx.doi.org/10.1175/1520-0426(1998)015<0547:DCFEFM>2.0.CO;2.

Elliot, S., E.C. Hunke, N. Jeffrey, A. Turner, M. Maltrud, C. Deal, and M. Jin. 2010. Systems level simulation of sea ice-atmosphere biogeochemistry connections. *SOLAS News* 11:14–18.

Else, B.G.T., T.N. Papakyriakou, R.J. Galley, W.M. Drennan, L.A. Miller, and H. Thomas. In press. Eddy covariance measurements of wintertime CO_2 fluxes in an arctic polynya: Evidence for enhanced gas transfer during ice formation. *Journal of Geophysical Research*, http://dx.doi.org/10.1029/2010JC006760.

Feltham, D.L., N. Untersteiner, and J.S. Wettlaufer. 2006. Sea ice is a mushy layer. *Geophysical Research Letters* 33, L14501, http://dx.doi.org/10.1029/2006GL026290.

Freiss, U., T. Deutschmann, B. Gilfedder, R. Weller, and U. Platt. 2010. Iodine monoxide in the Antarctic snowpack. *Atmospheric Chemistry and Physics* 10:2,439–2,456.

Freitag, J., and H. Eicken. 2003. Meltwater circulation and permeability of Arctic summer sea ice derived from hydrological field experiments. *Journal of Glaciology* 49:349–358, http://dx.doi.org/10.3189/172756503781830601.

Fritsen, C., S.F. Ackley, J. Kremer, and C.W. Sullivan. 1998. Flood-freeze cycles and microalgal dynamics in Antarctic pack ice. Pp. 1–22 in *Antarctic Sea Ice: Biological Processes, Interactions and Variability*. Antarctic Research Series, vol. 73, M. Lizotte and K.R. Arrigo, eds, American Geophysical Union, Washington, DC.

Gibson, J.A.E., and T.W. Trull. 1999. Annual cycle of fCO_2 under sea-ice and in open water in Prydz Bay, East Antarctica. *Marine Chemistry* 66:187–200, http://dx.doi.org/10.1016/S0304-4203(99)00040-7.

Gitterman, K.E. 1937. Thermal analysis of sea water. *Trudy Solyanoy Laboratorii (Transactions of Saline Laboratory)* 15:5–23.

Golden, K.M., S.F. Ackley, and V.I. Lytle. 1998. The percolation phase transition in sea ice. *Science* 282:2,238–2,241, http://dx.doi.org/10.1126/science.282.5397.2238.

Golden, K.M., H. Eicken, A.L. Heaton, J. Miner, D.J. Pringle, and J. Zhu. 2007. Thermal evolution of permeability and microstructure in sea ice. *Geophysical Research Letters* 34, L16501, http://dx.doi.org/10.1029/2007GL030447.

Golden, K.M., A.L. Heaton, H. Eicken, and V.I. Lytle. 2006. Void bounds for fluid transport in sea ice. *Mechanics of Materials* 38:801–817, http://dx.doi.org/10.1016/j.mechmat.2005.06.015.

Gosink, T.A. 1980. Atmospheric trace gases in association with sea ice. *Antarctic Journal of the United States* 15:82–83.

Gosink, T.A., J.G. Pearson, and J.J. Kelly. 1976. Gas movement through sea-ice. *Nature* 263:41–42, http://dx.doi.org/10.1038/263041a0.

Holter, P. 1990. Sampling air from dung pats by silicone rubber diffusion chambers. *Soil Biology & Biochemistry* 22:995–997, http://dx.doi.org/10.1016/0038-0717(90)90143-N.

Jacinthe, P.-A., and W.A. Dick. 1996. Use of silicone tubing to sample nitrous oxide in the soil atmosphere. *Soil Biology & Biochemistry* 28:721–726, http://dx.doi.org/10.1016/0038-0717(95)00176-X.

Jeffrey, N., E.C. Hunke, and S. Elliot. In press. Modeling the transport of passive tracers in sea ice. *Journal of Geophysical Research,* http://dx.doi.org/10.1029/2010JC006527.

Jin, M., C. Deal, J. Wang, K. Shin, N. Tanaka, T. Whitledge, S. Lee, and R. Gradinger. 2006. Controls of the landfast ice-ocean ecosystem offshore Barrow, Alaska. *Annals of Glaciology* 44:63–72, http://dx.doi.org/10.3189/172756406781811709.

Jones, E.P., and A.R. Coote. 1981. Oceanic CO_2 produced by the precipitation of $CaCO_3$ from brines in sea ice. *Journal of Geophysical Research* 86:11,041–11,043, http://dx.doi.org/10.1029/JC086iC11p11041.

Kammann, C., L. Grünhage, and H.-J. Jäger. 2001. A new sampling technique to monitor concentrations of CH_4, N_2O and CO_2 in air at well-defined depths in soils with varied water potential. *European Journal of Soil Science* 52:297–303, http://dx.doi.org/10.1046/j.1365-2389.2001.00380.x.

Kawamoto, K., P. Moldrup, P. Schjonning, B.V. Iversen, D.E. Rolston, and T. Komatsu. 2006. Gas transport parameters in the vadose zone: Gas diffusivity in field and lysimeter soil profiles. *Vadose Zone Journal* 5:1,194–1,204.

Kelley, J.J. 1987. Carbon dioxide in the Arctic environment. *The Journal of Earth Sciences* 35:341–354.

Kelley, J.J., and T.A. Gosink. 1979. *Gases in Sea Ice: 1975–1979*. University of Alaska Fairbanks, Fairbanks, AK.

Killawee, J.A., I.J. Fairchild, J.-L. Tison, L. Janssens, and R. Lorrain. 1998. Segregation of solutes and gases in experimental freezing of dilute solutions: Implications for natural glacial systems. *Geochimica et Cosmochimica Acta* 62:3,637–3,655, http://dx.doi.org/10.1016/S0016-7037(98)00268-3.

Krembs, C., H. Eicken, and J.W. Deming. 2011. Exopolymer alteration of physical properties of sea ice and implications for ice habitability and biogeochemistry in a warmer Arctic. *Proceedings of the National Academy Sciences of the United States of America* 108:3,653–3,658, http://dx.doi.org/10.1073/pnas.1100701108.

Krembs, C., H. Eicken, K. Junge, and J.W. Deming. 2002. High concentrations of exopolymeric substances in Arctic winter sea ice: Implications for the polar ocean carbon cycle

and cryoprotection of diatoms. *Deep-Sea Research Part I* 49:2,163–2,181, http://dx.doi.org/10.1016/S0967-0637(02)00122-X.

Kuosa, H., B. Norrman, K. Kivi, and F. Brandini. 1992. Effects of Antarctic sea ice biota on seeding as studied in aquarium experiments. *Polar Biology* 12:333–339, http://dx.doi.org/10.1007/BF00243104.

Kvenvolden, K.A., M.D. Lilley, T.D. Lorenson, P.W. Barnes, and E. McLaughlin. 1993. The Beaufort Sea continental shelf as a seasonal source of atmospheric methane. *Geophysical Research Letters* 20:2,459–2,462, http://dx.doi.org/10.1029/93GL02727.

Lannuzel, D., V. Schoemann, J. de Jong, B. Pasquer, P. van der Merwe, F. Masson, J.-L. Tison, and A. Bowie. 2010. Distribution of dissolved iron in Antarctic sea ice: Spatial, seasonal, and inter-annual variability. *Journal of Geophysical Research* 115, G03022, http://dx.doi.org/10.1029/2009JG001031.

Lannuzel, D., V. Schoemann, J. de Jong, J.-L. Tison, and L. Chou. 2007. Distribution and biogeochemical behaviour of iron in the East Antarctic sea ice. *Marine Chemistry* 106:18–32, http://dx.doi.org/10.1016/j.marchem.2006.06.010.

Lavoie, D., K. Denman, and C. Michel. 2005. Modeling ice algal growth and decline in a seasonally ice-covered region of the Arctic. *Journal of Geophysical Research* 110, C11009, http://dx.doi.org/10.1029/2005JC002922.

Legendre, L., S.F. Ackley, G.S. Dieckmann, B. Gulliksen, R. Horner, T. Hoshiai, I.A. Melnikov, W.S. Reeburgh, M. Spindler, and C.W. Sullivan. 1992. Ecology of sea ice biota. 2. Global significance. *Polar Biology* 12:429–444, http://dx.doi.org/10.1007/BF00243114.

Levasseur, M., M. Gosselin, and S. Michaud. 1994. A new source of dimethylsulfide (DMS) for the arctic atmosphere: Ice diatoms. *Marine Biology* 121:381–387, http://dx.doi.org/10.1007/BF00346748.

Light, B., G.A. Maykut, and T.C. Grenfell. 2003. Effects of temperature on the microstructure of first-year Arctic sea ice. *Journal of Geophysical Research* 108, 3051, http://dx.doi.org/10.1029/2001JC000887.

Lizotte, M.P. 2001. The contributions of sea ice algae to Antarctic marine primary production. *American Zoology* 41:57–73, http://dx.doi.org/10.1668/0003-1569(2001)041[0057:TCOSIA]2.0.CO;2.

Loose, B., W.R. McGillis, P. Schlosser, D. Perovich, and T. Takahashi. 2009. The effects of freezing, growth and ice cover on gas transport processes in laboratory seawater experiments. *Geophysical Research Letters* 36, L05603, http://dx.doi.org/10.1029/2008GL036318.

Loose, B., P. Schlosser, D. Perovich, D. Ringelberg, D.T. Ho, T. Takahashi, J. Richter-Menge, C.M. Reynolds, W.R. McGillis, and J.-L. Tison. 2010. Gas diffusion through columnar laboratory sea ice: Implications for mixed-layer ventilation of CO_2 in the seasonal ice zone. *Tellus B*, http://dx.doi.org/10.1111/j.1600-0889.2010.00506.x.

Lyakhin, Y.I. 1970. Saturation of water of the Sea of Okhotsk with calcium carbonate. *Oceanology* 10:789–795.

Marion, G.M. 2001. Carbonate mineral solubility at low temperatures in the Na-K-Mg-Ca-H-Cl-SO_4-OH-HCO_3-CO_3-CO_2-H_2O system. *Geochimica et Cosmochimica Acta* 65:1,883–1,896.

Martinson, D.G. 1990. Evolution of the Southern Ocean winter mixed layer and sea ice: Open ocean deep-water formation and ventilation. *Journal of Geophysical Research* 95:11,641–11,654, http://dx.doi.org/10.1029/JC095iC07p11641.

Massman, W.J., and X. Lee. 2002. Eddy covariance flux corrections and uncertainties in long-term studies of carbon and energy exchanges. *Agricultural and Forest Meteorology* 113:121–144, http://dx.doi.org/10.1016/S0168-1923(02)00105-3.

Matrai, P., L. Tranvik, C. Leck, and J. Knulst. 2008. Are high arctic surface microlayers a potential source of aerosol organic precursors? *Marine Chemistry* 108:109–122, http://dx.doi.org/10.1016/j.marchem.2007.11.001.

Matsuo, S., and Y. Miyake. 1966. Gas composition in ice samples from Antarctica. *Journal of Geophysical Research* 71:5,235–5,241.

McGillis, W.R., J.B. Edson, J.E. Hare, and C.W. Fairall. 2001. Direct covariance air-sea CO_2 fluxes. *Journal of Geophysical Research* 106:16,729–16,745, http://dx.doi.org/10.1029/2000JC000506.

Miller, L.A., G. Carnat, B.G.T. Else, N. Sutherland, and T.N. Papakyriakou. In press. Carbonate system evolution at the Arctic Ocean surface during autumn freeze-up. *Journal of Geophysical Research*, http://dx.doi.org/10.1029/2011JC007143.

Miller, L.A., R.E. Collins, J.W. Deming, J.K. Ehn, R.W. Macdonald, A. Mucci, O. Owens, M. Raudsepp, and N. Sutherland. 2011. Carbon dynamics in Sea Ice: A winter flux time series. *Journal of Geophysical Research* 116, C02028, http://dx.doi.org/10.1029/2009JC006058.

Miyake, Y., and S. Matsuo. 1963. A role of sea ice and sea water in the Antarctic on the carbon dioxide cycle in the atmosphere. *Papers in Meteorology and Geophysics* 14:120–125.

Mock, T., and D.N. Thomas. 2005. Recent advances in sea-ice microbiology. *Environmental Microbiology* 7:605–619, http://dx.doi.org/10.1111/j.1462-2920.2005.00781.x.

Mock, T., G.S. Dieckmann, C. Haas, A. Krell, J.-L. Tison, A.L. Belem, S. Papadimitriou, and D.N. Thomas. 2002. Micro-optodes in sea ice: A new approach to investigate oxygen dynamics during sea ice formation. *Aquatic Microbial Ecology* 29:297–306, http://dx.doi.org/10.3354/ame029297.

Mock, T., M. Kruse, and G.S. Dieckmann. 2003. A new microcosm to investigate oxygen dynamics at the sea ice water interface. *Aquatic Microbial Ecology* 30:197–205, http://dx.doi.org/10.3354/ame030197.

Moldrup, P., T. Olesen, S. Yoshikawa, T. Komatsu, and D.E. Rolston. 2004. Three-porosity model for predicting the gas diffusion coefficient in undisturbed soil. *Soil Science Society of America Journal* 68:750–759, http://dx.doi.org/10.2136/sssaj2004.0750.

Moore, J., S. Doney, J. Kleypas, D. Glover, and I. Fung. 2002. An intermediate complexity marine ecosystem model for the global domain. *Deep-Sea Research Part II* 49:403–462, http://dx.doi.org/10.1016/S0967-0645(01)00108-4.

Moore, J., S. Doney, and K. Lindsay. 2004. Upper ocean ecosystem dynamics and iron cycling in a global three dimensional model. *Global Biogeochemical Cycles* 18, GB4028, http://dx.doi.org/10.1029/2004GB002220.

Nagurnyi, A.P. 2008. On the role of the Arctic sea ice in seasonal variability of carbon dioxide concentration in northern latitudes. *Russian Meteorology and Hydrology* 33:43–47.

Nelson, K.H., and T.G. Thompson. 1954. Deposition of salts from sea water by frigid concentration. *Journal of Marine Research* 13:166–182.

Nomura, D., H. Eicken, R. Gradinger, and K. Shirasawa. 2010a. Rapid physically driven inversion of the air-sea ice CO_2 flux in the seasonal landfast ice off Barrow, Alaska after onset of surface melt. *Continental Shelf Research* 30:1,998–2,004, http://www.sciencedirect.com/science/article/pii/S0278434310003067.

Nomura, D., T. Takatsuka, M. Ishikawa, T. Kawamura, K. Shirasawa, and H. Yoshikawa-Inoue. 2009. Transport of chemical components in sea ice and under-ice water during melting in the seasonally ice-covered Saroma-ko Lagoon, Hokkaido, Japan. *Estuarine, Coastal and Shelf Science* 81:201–209, http://dx.doi.org/10.1016/j.ecss.2008.10.012.

Nomura, D., H. Yoshikawa-Inoue, and T. Toyota. 2006. The effect of sea-ice growth on air-sea CO_2 flux in a tank experiment. *Tellus* 58B:418–426, http://dx.doi.org/10.1111/j.1600-0889.2006.00204.x.

Nomura, D., H. Yoshikawa-Inoue, T. Toyota, and K. Shirasawa. 2010b. Effects of snow, snow-melting and refreezing processes on air-sea-ice CO_2 flux. *Journal of Glaciology* 56:262–270, http://dx.doi.org/10.3189/002214310791968548.

Notz, D., and M.G. Worster. 2009. Desalination processes of sea ice revisited. *Journal of Geophysical Research* 114, C05006, http://dx.doi.org/10.1029/2008JC004885.

Obzhirov, A., R. Shakirov, A. Salyuk, E. Suess, N. Biebow, and A. Salomatin. 2004. Relations between methane venting, geological structure and seismo-tectonics in the Okhotsk Sea. *Geo-Maring Letters* 24:135–139, http://dx.doi.org/10.1007/s00367-004-0175-0.

Oertling, A.B., and R.G. Watts. 2004. Growth of and brine drainage from NaCl-H_2O freezing: A simulation of young sea ice. *Journal of Geophysical Research* 109, C04013, http://dx.doi.org/10.1029/2001JC001109.

Orsi, A.H., G.C. Johnson, and J.L. Bullister. 1999. Circulation, mixing and production of Antarctic Bottom Water. *Progress in Oceanography* 43:55–109, http://dx.doi.org/10.1016/S0079-6611(99)00004-X.

Papadimitriou, S., D.N. Thomas, H. Kennedy, C. Haas, H. Kuosa, A. Krell, and G.S. Dieckmann. 2007. Biogeochemical composition of natural sea ice brines from the Weddell Sea during early austral summer. *Limnology and Oceanography* 52:1,809–1,823, http://dx.doi.org/10.4319/lo.2007.52.5.1809.

Papakyriakou, T., and L. Miller. 2011. Springtime CO_2 exchange over seasonal sea ice in the Canadian Arctic Archipelago. *Annals of Glaciology* 52:215–224, http://dx.doi.org/10.3189/172756411795931534.

Perovich, D.K., and A.J. Gow. 1996. A quantitative description of sea ice inclusions. *Journal of Geophysical Research* 101:18,327–18,343, http://dx.doi.org/10.1029/96JC01688.

Petrich, C., and H. Eicken. 2010. Growth, structure and properties of sea ice. Chapter 2 in *Sea Ice,* 2nd ed. D.N. Thomas and G.S. Dieckmann, eds, Wiley-Blackwell, Oxford, UK, http://dx.doi.org/10.1002/9781444317145.ch2.

Prytherch, J., M.J. Yelland, R.W. Pascal, B.I. Moat, I. Skjelvan, and C.C. Neill. 2010. Direct measurements of the CO_2 flux over the ocean: Development of a novel method. *Journal of Geophysical Research* 37, L03607, http://dx.doi.org/10.1029/2009GL041482.

Rysgaard, S., J. Bendtsen, L.T. Pedersen, H. Ramlov, and R.N. Glud. 2009. Increased CO_2 uptake due to sea ice growth and decay in the Nordic Seas. *Journal of Geophysical Research* 114, C09011, http://dx.doi.org/10.1029/2008JC005088.

Rysgaard, S., R.N. Glud, M.K. Sejr, J. Bendtsen, and P.B. Christensen. 2007. Inorganic carbon transport during sea ice growth and decay: A carbon pump in polar seas. *Journal of Geophysical Research* 112, C03016, http://dx.doi.org/10.1029/2006JC003572.

Rysgaard, S., R.N. Glud, M.K. Sejr, M.E. Blicher, and H.J. Stahl. 2008. Denitrification activity and oxygen dynamics in Arctic sea ice. *Polar Biology* 31:527–537, http://dx.doi.org/10.1007/s00300-007-0384-x.

Saiz-Lopez, A., A. Mahajan, R. Salmon, S. Bauguitte, A. Jones, H. Roscoe, and J. Plane. 2007. Boundary layer halogens in coastal Antarctica. *Science* 317:348–351, http://dx.doi.org/10.1126/science.1141408.

Semiletov, I., A. Makshtas, S.-I. Akasofu, and E.L. Andreas. 2004. Atmospheric CO_2 balance: The role of Arctic sea ice. *Geophysical Research Letters* 31, L05121, http://dx.doi.org/10.1029/2003GL017996.

Shakhova, N., V. Sergienko, and I. Semiletov. 2009. The contribution of the East Siberian Shelf to the modern methane cycle. *Herald of the Russian Academy of Science* 79:237–246, http://dx.doi.org/10.1134/S101933160903006X.

Simpson, W.R., R. von Glasow, R. Riedel, K. Anderson, P. Ariya, J. Bottenheim, J. Burrows, L.J. Carpenter, U. Frieß, M.E. Goodsite, and others. 2007. Halogens and their role in polar boundary-layer ozone depletion. *Atmospheric Chemistry and Physics* 7:4,375–4,418, http://dx.doi.org/10.5194/acp-7-4375-2007.

Smith, W.O., and D.M. Nelson. 1985. Phytoplankton bloom produced by a receding ice edge in the Ross Sea: Spatial coherence with the density field. *Science* 227:163–166, http://dx.doi.org/10.1126/science.227.4683.163.

Smith, W.O., and D.M. Nelson. 1986. Importance of ice edge phytoplankton production. *Bioscience* 36:251–257, http://dx.doi.org/10.2307/1310215.

Steele, M., and J.H. Morison. 1995. Halocline water formation in the Barents Sea. *Journal of Geophysical Research* 100:881–894, http://dx.doi.org/10.1029/94JC02310.

Stefels, J., M. Steinke, S. Turner, G. Malin, and S. Belviso. 2007. Environmental constraints on the production and removal of dimethylsulphide and implications for ecosystem modeling. *Biogeochemistry* 83:245–275, http://dx.doi.org/10.1007/s10533-007-9091-5.

Sweeney, C. 2003. The annual cycle of surface CO_2 and O_2 in the Ross Sea: A model for gas exchange on the continental shelves of Antarctica. Pp. 295–312 in *Biogeochemistry of the Ross Sea*. G.R. DiTullio and R.B. Dunbar, eds, Antarctic Research Series, American Geophysical Union, Washington, DC.

Tamura, T., K. Ohshima, and S. Nihashi. 2008. Mapping of sea ice production for Antarctic coastal polynyas. *Geophysical Research Letters* 35, L07606, http://dx.doi.org/10.1029/2007GL032903.

Thomas, D.N., and G.S. Dieckmann, eds. 2010. *Sea Ice*, 2nd ed. Wiley-Blackwell, Oxford, UK, 640 pp.

Tison, J.-L., C. Haas, M.M. Gowing, S. Sleewaegen, and A. Bernard. 2002. Tank study of physico-chemical controls on gas content and composition during growth of young sea ice. *Journal of Glaciology* 48:177–191, http://dx.doi.org/10.3189/172756502781831377.

Trevena, A.J., and G.B. Jones. 2006. Dimethylsulphide and dimethylsulphoniopropionate in Antarctic sea ice and their release during sea ice melting. *Marine Chemistry* 98:210–222, http://dx.doi.org/10.1016/j.marchem.2005.09.005.

Trevena, A.J., G.B. Jones, S.W. Wright, and R.L. van den Enden. 2000. Profiles of DMSP, algal pigments, nutrients and salinity in pack ice from eastern Antarctica. *Journal of Sea Research* 43:265–273, http://dx.doi.org/10.1016/S1385-1101(00)00012-5.

Trevena, A.J., G.B. Jones, S.W. Wright, and R.L. van den Enden. 2003. Profiles of dimethylsulphoniopropionate (DMSP), algal pigments, nutrients, and salinity in the fast ice of Prydz Bay, Antarctica. *Journal of Geophysical Research* 108(C5), 3145, http://dx.doi.org/10.1029/2002JC001369.

Untersteiner, N. 1964. Calculations of temperature regime and heat budget of sea ice in the Central Arctic. *Journal of Geophysical Research* 69:4,755–4,766, http://dx.doi.org/10.1029/JZ069i022p04755.

Vancoppenolle, M., H. Goosse, A. de Montety, T. Fichefet, B. Tremblay, and J.-L. Tison. 2010. Modeling brine and nutrient dynamics in Antarctic sea ice: The case of dissolved silica. *Journal of Geophysical Research* 115, C02005, http://dx.doi.org/10.1029/2009JC005369.

Webb, E.K., G.I. Pearman, and R. Leuning. 1980. Correction of flux measurements for density effects due to heat and water vapour transfer. *Quarterly Journal of the Royal Meteorological Society* 106:85–100, http://dx.doi.org/10.1002/qj.49710644707.

Weeks, W., and S.F. Ackley. 1982. *The Growth, Structure and Properties of Sea Ice*. Cold Regions Research and Engineering Laboratory, ERDC, Hanover, NH, 140 pp.

Weller, G. 1968. Heat-energy transfer through a four-layer system: Air, snow, sea ice, sea water. *Journal of Geophysical Research* 73:1,209–1,220, http://dx.doi.org/10.1029/JB073i004p01209.

Wettlaufer, J.S., M.G. Worster, and H.E. Hupper. 1997. Natural convection during solidification of an alloy from above with application to the evolution of sea ice. *Journal of Fluid Mechanics* 344:291–316, http://dx.doi.org/10.1017/S0022112097006022.

Worster, M.G. 1991. Natural convection in a mushy layer. *Journal of Fluid Mechanics* 224:335–359, http://dx.doi.org/10.1017/S0022112091001787.

Yager, P.L., D.W.R. Wallace, K. Johnson, W.O. Smith, P.J. Minnett, and J.W. Deming. 1995. The northeast water polynya as an atmospheric CO_2 sink: A seasonal rectification hypothesis. *Journal of Geophysical Research* 100:4,389–4,398, http://dx.doi.org/10.1029/94JC01962.

Zappa, C.J., W.R. McGillis, P.A. Raymond, J.B. Edson, E.J. Hintsa, H.J. Zemmelink, J.W.H. Dacey, and D.T. Ho. 2007. Environmental turbulent mixing controls on air-water gas exchange in marine and aquatic systems. *Geophysical Research Letters* 34, L10601, http://dx.doi.org/10.1029/2006GL028790.

Zemmelink, H.J., B. Delille, J.L. Tison, E.J. Hintsa, L. Houghton, and J.W.H. Dacey. 2006. CO_2 deposition over multi-year ice of the western Weddell Sea. *Geophysical Research Letters* 33, L13606, http://dx.doi.org/10.1029/2006GL026320.

Zemmelink, H.J., J.W.H. Dacey, L. Houghton, E.J. Hintsa, and P.S. Liss. 2008. Dimethylsulfide emissions over the multi-year ice of the western Weddell Sea. *Geophysical Research Letters* 35, L06603, http://dx.doi.org/10.1029/2007GL031847.