ANNUAL SEA ICE. AN AIR-SEA GAS EXCHANGE MODERATOR

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ABSTRACT

Arctic annual sea ice, particularly when it is relatively warm ($> -15^{\circ}\text{C}$) permits significant gas exchange between the sea and air throughout the entire year. Sea ice, particularly annual sea ice, differs from freshwater ice with respect to its permeability to gases. The presence of brine allows for significant air-sea-ice exchange of CO_2 throughout the winter, which may significantly affect the global carbon dioxide balance. Other trace gases are also noted to be enriched in sea ice, but less is known about their importance to air-sea-interactions at this time. Both physical and biological factors cause and modify evolution of gases from the surface of sea ice. Quantitative and qualitative descriptions of the nature and physical behavior of sea ice with respect to brine and gases are discussed.

INTRODUCTION

Freshwater ice (river, lake, glacier) differs from annual sea ice with respect to its gas permeability. Multi-year sea ice behaves much like freshwater ice as a result of melt water filling and refreezing in the brine drainage channels. Multi-year sea ice is for all practical purposes sealed against gas exchange. Hemmingsen (1959) correctly reported that freshwater ice is nearly impermeable to gases with a permeation of $D \approx 10^{-11} \text{ cm}^2 \text{ s}^{-1} \text{ atm}^{-1}$. Gosink *et al.* (1976) reported that sea ice, on the other hand, was

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10^4 to 10^5 times more permeable to gases, and that the platelet orientation of the sea ice affects the horizontal penetration of gases by a factor of about 2. Therefore, annual sea ice should play a significant role in the exchange of gases across the sea-ice-air boundary.

GRAIN BOUNDARIES, BRINE CHANNELS, AND FLUID CONTENT

The difference between fresh water formed ice and sea ice is readily seen in their microscopic structure. The normally low salt content of fresh water tends to concentrate at multi-grain boundaries. Figure 1 shows a three grain boundary system of melting freshwater ice. The width of the melt zone between the grains in this case is on the order of 10^{-2} cm. When the temperature is lowered to 0.037°C below the freezing point, the system closes substantially so that the largest feature, the point of intersection, is on the order of 10^{-5} cm radius (Langhorn, 1974). A gas molecule is about 10^{-7} cm in diameter. At -0.2°C , the radius of the three grain boundary closes to about 10^{-6} cm and continues to close with decreasing temperatures. This explains why Hemmingsen's (1959) data, collected between -0.5 and -10°C , demonstrates pure ice to be virtually impenetrable to gases and why gas bubbles in glacier ice can be used to assess ancient atmosphere composition measurements (e.g. Gow and Williamson, 1975; and Berner *et al.*, 1978). Hemmingsen's lake and river water ice data did show an order of magnitude increase in permeability over that for pure water ice because of the low salt content.

Annual sea ice, which includes a high concentration of brine, is composed of platelet boundaries and brine drainage channels. The platelets are crystals of pure ice and are readily identifiable in Figure 2. Eide

and Martin (1975) and Niedrauer and Martin (1979) described the size, frequency, and dendritic structure of brine channels in sea ice, and a pumping phenomenon that is most active in the lower portion of sea ice at the sea-ice interface. Figure 2 shows cold sea ice (ca. -20°C) with platelet separations on the order of 10^{-2} cm. The width of the platelets are about 10^{-1} cm. Channel diameter and platelet separations can be approximated from Raymond and Harrison's (1975) formula for multi-grain boundary sizes. Application of this formula indicates that sea ice platelets separations and brine channels should close by two orders of magnitude between -10° and -20°C . We did observe a 20-40 fold decrease in the flux of CO_2 across the sea ice-air interface in that temperature range (Gosink and Kelley, 1979a, 1982).

Sea ice maintains a high fluid content even at low temperatures. At -10 , -20 and -30°C it is respectively 20, 12 and 3% liquid (Richardson, 1976). The heat source of the ocean under sea ice, and the insulating property of the frost and snow cover over it, maintains a high internal ice temperature relative to the atmosphere. For example, 140-cm thick Arctic Ocean sea ice under a 50-cm snow drift was observed to have an ice surface temperature of -6°C when the air was -28°C . That was, however, an unusually thick snow cover for arctic ice; it normally ranges between 2 and 20 cm. At the other extreme, 120-cm thick sea ice deliberately swept clean of snow cover was about 6°C warmer 30 cm below the surface than the air-ice interface. The clean ice surface maintained a temperature $1-2^{\circ}\text{C}$ warmer than the air measured 10 cm above the ice (Shapiro, Geophysical Institute; personal communication, 1978).

POROSITY AND BUBBLES IN SEA ICE

A consideration of the bubbles in sea ice is in order to establish the porosity of sea ice and some of its seasonal changes. The porosity of ice by definition is not the same as permeability but has a bearing on it. Porosity is a measure of the total volume of voids (liquid or gas filled) in the sea ice. Permeability implies that there are connections between the pore structures so that diffusion through the matrix can occur.

Tsurikov (1975) has approached the question from the point of view that gases such as nitrogen and oxygen released from solution in sea water during the freezing process, and by photosynthesis during melt are mainly responsible for the porosity of sea ice. He lists seven mechanisms by which sea ice may gain its porosity. In his observations of subarctic and low latitude sea ice (White and Caspian Seas), Tsurikov (1975) found that 15-20% of the ice volume was porous.

Bubbles are common in sea ice (e.g. Fig. 2), but we have yet to find any under pressure in annual sea ice. Bubbles in tundra lake ice that we have worked with are essentially all under pressure as are those in glacier ice (e.g. Gow and Williamson, 1975). The quantity of entrained gas bubbles in annual sea ice varies with season, age, and depth of the ice sample. Multi-year sea ice elevated above the ocean surface is highly vesicular and may contain 200+ ml of air kg^{-1} ice. Annual Arctic Ocean sea ice, above the hydrostatic level, has a variable gas bubble loading of ca. 10 to >100 ml kg^{-1} . Below the hydrostatic level, the volume of the bubbles is <0.1 to ca. 5 ml kg^{-1} of sea ice, usually on the low end of the range (Kelley *et al.*, 1976; Gosink and Kelley, 1977). The entrained

gas volumes were determined in a manner similar to Langway (1963) by trapping the liberated bubbles of a weighed piece of ice allowed to melt under cold toluene.

There is a period of 4-6 weeks during the initial melt period of Arctic Ocean sea ice when bubbles form as a result of photosynthesis. The quantity escaping to the surface is unknown and variable. By early May, melt water bubbles on the surface of the sea ice are still slightly enriched in CO_2 (340-350 ppm) as compared to winter values (ca. 400 ppm) and to the ambient atmosphere (ca. 335 ppm). During June the CO_2 partial pressure in the ice and bubbles decreases due to photosynthesis, and high concentrations of CO and methane (5-20 ppm) are readily observed in the numerous bubbles trapped under the melt water skim ice (Gosink and Kelley, 1979b). Oxygen was also enriched by a few percent in those bubbles because of photosynthetic activity. All of our analyses were made by gas chromatography as described elsewhere (Gosink and Kelley, 1982). Later in July, no unusual concentrations of CO were noted in the bubbles, and the CO_2 had been decreased by photosynthesis (<300 ppm).

There is some evidence that photosynthesis may begin in the Arctic (71-74°N) as early as February to April during sunny periods (Gosink and Kelley, 1979a). Algal blooms on the underside of the ice are known to be patchy, even at 60-65°N latitude. Nevertheless, the primary food chain must be well under way by April because this coincides with the northward migration of whales past 71°N. In late February we measured light levels of 3.2 w m^{-2} in an open lead on a sunny day at 10 m depth (71.5°N). In mid-April at 71.1°N algae were observed by divers to be growing abundantly under sea ice, but in patches. Diver-held light meters on areas where no

growth was evident indicated 2.5 w m^{-2} . These areas of no growth were under snow drifts up to 0.5 m thickness. The ice was *ca.* 1.6 m thick. Light levels under heavy algal blooms were 2.7 w m^{-2} , but were 4.8 w m^{-2} when the algal layer was scraped off. It appears then that 2.7 w m^{-2} is the lower limit for algal blooms and that light levels are sufficient as early as February to initiate photosynthesis in the Arctic. In addition, the irregular thickness of the snow cover and/or pressure ridges causes variations in the light reaching the bottom of the ice, possibly contributing to the observed patchiness in the algal blooms and presumably to some of their trace gas products. In April during a period of continuous clear or light cloud covered skies, the water under the sea ice was observed to be continually at 295-300 ppm at 74°N . This suggests that some photosynthesis was underway. November to January PCO_2 data for water under sea ice was 340-400 ppm (Gosink and Kelley, 1979a; and Kelley, 1968).

Tundra lakes also show the effect of light on the dissolved gases in mid-March, which is two to three months before melting starts. Oxygen concentrations increased in the lake water under ice (1.5 to 2 m thick) blown clear of snow and the CO_2 lowered from the usual 1000-3000 ppm to 480-500 ppm (this work and J. Mellor, personal communications, 1979).

BRINE AND DISSOLVED GASES IN SEA ICE

With exception of the influence of photosynthesis in the late spring, chemical factors associated with high PCO_2 partial pressure of carbon dioxide within and below the sea ice matrix govern its concentration.

Air-sea transfer processes appear to be controlled by physical stresses on the sea ice (Gosink and Kelley, 1977). It is possible that the winter transfer of other gases through annual sea ice could be restricted relative to CO_2 because of their reduced solubility in brines, even though CO and CH_4 are enriched at the air-ice interface (Gosink and Kelley, 1982). We have observed oxygen to be evolved from sea ice surfaces at a significantly slower rate than that of carbon dioxide on several occasions (Gosink and Kelley, 1982). Carbon dioxide takes part in the complex carbonate-bicarbonate chemistry of sea water and the brine in sea ice which may affect the transfer process.

The chemistry of the cations and anions in sea ice can be found elsewhere (e.g. Addison, 1977; Richardson, 1976; Cox and Weeks, 1974). We have noted that the pH of the concentrated brines is about 6.8-7.2. These pH values are uncorrected for the sodium ion effect of the brine, and probably cause the readings to be 0.1-0.3 pH units high. The relatively low pH helps to explain the observed high partial pressure of carbon dioxide associated with the brine (400-1000 ppm) (Gosink and Kelley, 1977). In June, standing salty surface Arctic Ocean melt water (0.5-3‰) still displayed a low pH (7.2) as compared to the sea water under the ice (pH 8.0).

Six to nine months old sea ice, when melted, produces a liquid of 3-4‰ salinity. On the other hand, if a hole is drilled about half way through sea ice, the surface of the hole insulated and then inspected later, brine from the sea ice matrix will have pooled in the bottom of the hole. When air temperatures are cold (ca. -25°C) an overnight period is usually required to accumulate a few cm of brine. The salinity of this

brine is about 120-150‰. If the air temperature is warmer (ca. -10°C) 10-20 cm of liquid will pool in a few hours and be of lower salinity (80-120‰). Under relatively warm air conditions (ca. -5°C) the hole will flood to the hydrostatic level with ca. 30-40‰ water in minutes.

Given a suitable pumping mechanism such as tides, changes in air pressure, ice pack pressures, etc., gases dissolved in the brines can also be moved through sea ice. Carbon dioxide is being evolved from annual sea ice throughout the winter. Rates significant to global atmospheric monitoring studies (up to $30 \times 10^6 \text{ g CO}_2 \text{ km}^{-2} \text{ mo}^{-1}$) have been observed (Gosink and Kelley, 1982). Physical disturbances to sea ice were noted to cause the largest changes of the PCO_2 in the air trapped in test holes drilled part way through annual ice (Gosink and Kelley, 1977). Walking near the test hole was sufficient to cause some fluctuations (10-40 ppm). Periods of substantial movement in the nearby ice pack caused large fluctuations (100-300 ppm). A pressure plate ($\sim 600 \text{ cm}^{-2}$) frozen into a slot within 30 cm from a test hole caused the largest change with the application of less than 50 psi. The result was that the entire 3 l volume of the test hole was immediately flooded with water.

The diffusion constant for SF_6 and CO_2 through annual sea ice is on the order to $10^{-7} \text{ cm}^2 \text{ s}^{-1} \text{ atm}^{-1}$ (Gosink *et al.*, 1975). It has recently been determined that deuterium oxide, which can be thought to behave either as a liquid or a gas, has diffusion constants of 6×10^{-7} to $1.2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ through ice formed from 32‰ sea water between -15° and -5°C (Gosink, 1982).

The concentration of several trace gases observed under the snow (subnivean) at the air-ice interface and in the sea ice matrix were found

to be significantly enriched over the concentration found in the air 2 meters above the ice. This indicates that throughout the winter in the arctic, the sea ice is a source of these gases to the troposphere. Carbon dioxide is enriched in the subnivean layers by 0-80 ppm, and is inversely proportional to the wind speed (Gosink and Kelley, 1979a, 1982). Carbon monoxide is frequently enriched by *ca.* 0.1 ppm and methane by 2-4 ppm in the subnivean over ambient atmospheric concentrations. During the winter, we did not observe concentrations of carbon monoxide and methane within the ice matrix greater than those reported by Lamontagne *et al.* (1976) or by Swinnerton and Lamontagne (1976). On the other hand, the carbon monoxide and methane concentrations rose substantially during the period of thaw of sea ice in June, and were on the order of $> 10^{-4}$ ml l⁻¹ in the liquid phase. Based on air samples gathered by use of aircraft during the thaw of sea ice and tundra indicates that these surface sources are of importance to temporary regional tropospheric loading of CO (Gosink and Kelley, 1979b).

Some other interesting observations were made on air from holes bored in arctic sea ice. Air sampled in the holes before the drill was removed was found to be irregularly enriched in nitrous oxide over the atmospheric concentration by 5-300%. A very brief opportunity was afforded to perform similar experiments in Antarctica (Gosink, 1980). Nitrous oxide was the only trace gas to be found regularly enriched in the subnivean environment. Another gas, presumed to be methyl chloride, is also detected in concentrations greater than ambient air on occasion. Both of these gases are biologically produced, and the irregularity of the observation possibly is related to the patchiness of the microbiota in and under the sea ice.

MISCELLANEOUS OBSERVATIONS

The permeability of annual sea ice is further substantiated by the following casual observations. A gas leak was heard during the course of flushing a surface-sealed hole in annual sea ice with a low pressure gas (< 2 psi) (Gosink and Kelley, 1977). The pressure was increased to about 10 psi and some water was thrown onto the surface in an attempt to locate the leak. Active bubbling was observed in many places as much as a meter away from the hole.

There are the observations by several persons working at various locations on the sea ice near Barrow, Alaska, who verbally reported active bubbling of scuba diver's air up through *ca.* 1.3 m of ice in the month of May 1977 and again in 1978.

Finally, a block of freshly quarried annual sea ice was laid on the surface when the air temperature was about -7°C . Ink was mixed with brine and poured into a groove scraped on the top of the ice block. Within a half hour, the ink passed completely through the interior of the 30-cm block and made a stain on the snow under it (Gosink and Kelley, 1977).

CONCLUSIONS

The concept of the Arctic as an ice-sealed passive region in the winter with respect to trace atmospheric gas exchange must be modified at least for carbon dioxide. Saline or annual ice, particularly when it is relatively warm ($> -15^{\circ}\text{C}$) permits significant gas exchange. Other trace gases such as carbon monoxide, methane, nitrous oxide, and perhaps methyl chloride also are observed to be evolved from sea ice. Biological factors,

which may commence as early as mid-February, affect the concentrations of these gases and physical factors appear to control their transfer through the sea ice.

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FIGURE CAPTIONS

- Figure 1. Fresh water ice at its melting point. Magnification 10x.
Grain boundaries are less than 10^{-2} cm. (Photo courtesy of
Dr. Tom Osterkamp, Geophysical Institute, University of
Alaska, Fairbanks).
- Figure 2. Sea ice at about -20°C . Magnification 10x. Width of brine
areas between ice platelets are on the order of 10^{-2} cm.
Note also the bubble and brine pockets and channels.
(Photo courtesy of Dr. Tom Osterkamp).