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THE ROLE OF THE ARCTIC SEA ICE COVER IN CARBON DIOXIDE EXCHANGES

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1. Introduction

One of the most important processes determining the carbon dioxide content of the atmosphere is the CO_2 exchanges between the ocean and the atmosphere. In the Arctic Basin the role of sea ice in absorption or emission CO_2 must be considered in addition to open ocean exchanges. Sea ice is a complicated physical-chemical system. During freezing different chemical reactions take place in the brine that is stored between crystals of pure ice in the upper (slash) layer and the lower layers of the ice. From a physical-chemical point of view the intensity and direction of CO_2 fluxes in presence of sea ice (from or to atmosphere) can be addressed by a model of the total inorganic carbon content in sea ice and its changes during ice formation and melting. Total inorganic carbon (TC) in sea ice or water can be described as:

$$TC = [HCO_3-] + [CO3_2-] + [CO_2]$$

It is well known from laboratory experiments that at low temperatures that the following reaction results in the emission CO_2 to atmosphere and residual $CaCO_3$ in the ice as follow:

$$Ca_{2+} + 2HCO_3- = \downarrow CaCO_3 + CO_2 \uparrow + H_2O \quad (1)$$

As described by (1) calcium carbonate crystals $CaCO_3 * 6H_2O$ have been detected in sea ice in both the Arctic and Antarctic (*Dieckmann et al, 2008, 2010*) and has furthermore been associated with the emission of CO_2 from the ice to the Arctic atmosphere [*Alekseev&Nagurny, 2007*].

To study this process, special measurements have been made at the Russian drifting station "North Pole35". NP-35 drifted from November 2007 to May 2008 in the Arctic Ocean to the north of archipelagos Severnaya Zemlya and Franz Josef Land. The results of these measurements and the possible large-scale consequences of this sea-ice to atmosphere gas exchange process are discussed below.

2. Experiment Description

The study consisted of a combination of on-site laboratory experiments and field observations of in-situ sea-ice. The laboratory experiments were conducted to determine the emission rate of CO_2 during the formation of sea ice by freezing 7 samples of seawater in a fixed container at air temperatures ranging -37 C° to -27 C°. The amount of CO_2 released during the freezing process was estimated from the change in CO_2 partial pressure in the container head space measured with an automatic LI-8100 (LI-COR Inc., USA). The relative error of measurements was 2%.

Estimates of the total inorganic carbon content (TC) in the upper layer slash and first year sea ice core were made from measurements of total alkalinity (TA) and pH obtained from sea ice samples. The samples were melted without gas exchange with the atmosphere, and subsequent calculations of TC were made on the basis of seawater carbonate content theory. This procedure is described by *Nedashkovsky & Shvetsova, 2010.*

3. Results

For the laboratory experiments (*Nedashkovsky & Makshtas, 2010.*) we collected sea water from the ocean mixed layer beneath the sea ice which had CO_2 partial pressures of 280-300 ppm and which was 250-260% oversaturated with respect to calcite. Table 1 shows CO_2 emissions for each sample.

Table 1
CO_2 emissions during freezing of sea water in laboratory experiments

Date	Mass of sea water,	Freezing time	Air temperature,	Water salinity,	TC,	Emission of CO_2	
	g	hour	°C	psu	mmol/kg	mkmol/kg	mmol/м^2
13.03	1436	22	-37	34.13	2.14	45 (4,2 %)	2.0
16.03	1048	24	-32	34.13	2.14	32 (3,0 %)	3.4
17.03	1083	71	-34	34.16	2.12	58 (5,5 %)	7.3
20.03	660	54	-37	34.18	2.13	74 (7,0 %)	4.8
20.03	1039	54	-37	34.18	2.13	57 (5,4 %)	6.9
03.04	1089	71	-27	34.17	2.10	70 (6,6 %)	9.1
03.04	1620	71	-27	34.17	2.10	37 (3,5 %)	7.0

The data, presented in Table 1 show that during freezing of sea water at ambient temperatures around -30^{0}C the percentage of emitted CO_2 is only 3-7% of net content. Richardson, 1976 recorded emission rates of close to 90 % when freezing Copenhagen standard sea water at ambient temperatures of -10^{0}C with the formation of $CaCO_3$ * $6H_2O$ crystals beginning as soon as freezing commenced. In our experiments the ambient temperature was much lower which may account for difficulties in separating the reaction components described in (1) as they formed in the container.

For investigation of CO_2 emission from ice formed in situ we measured the vertical distributions of salinity and total alkalinity in ice cores. Table 2 summarizes the characteristics of the core samples used for this study. Results are presented in Figures 1, 2, 3.

Table 2. Summary of sea ice samples, taken of on the drifting station “NP-35”

Sample number.	Date of sampling	Ice thickness, cm	thickness of slash, cm of melt water	Position of sampling	Age of ice, days
10	12/22/07	69	2.8	83°59.6' N, 98°57.4' E	30 - 40
13	01/03/08	10	1.2	84°53.4' N, 93°08.6' E.	2
15	01/06/08	33	0.8	84°50.7' N, 91°52.2' E.	4
16	01/14/08	55	1.8	85°05.5'N, 91°26.9' E.	12
18	01/25/08	53	0.6	85°19.2' N, 80°47.6' E.	11
21	02/23/08	82	2.2	85°36.4' N, 64°17.9' E.	40
25	03/22/08	122	1.0	85°14.7' N, 51°02.2' E.	120-130
32	04/17/08	4	0	84°22.3' N, 39°13.4' E.	1
36	04/28/08	7	0	84°02.9' N, 31°28.2' E.	2
39	05/07/08	144	1.8	84°44.2' N, 28°51.0' E.	165-175

Figure 1 show through most of the ice core depth that TA/Sal and TC/Sal ratios are similar to those of the sea water collected beneath the ice with the TA/TC of the ice cores equal 1.07±0.06 and TA/TC of the seawater = 1.069±0.005. The TA/TC ratios (Figure 2a) in the slash (top) layer and the thin upper (10 cm) layer of the ice are closer to 2.0. This is indicative that $CaCO_3$ is the primary from of inorganic carbon in this layer since the formation of $CaCO_3$ would decrease TC/Sal and provide evidence of the reaction releasing CO_2 to the atmosphere

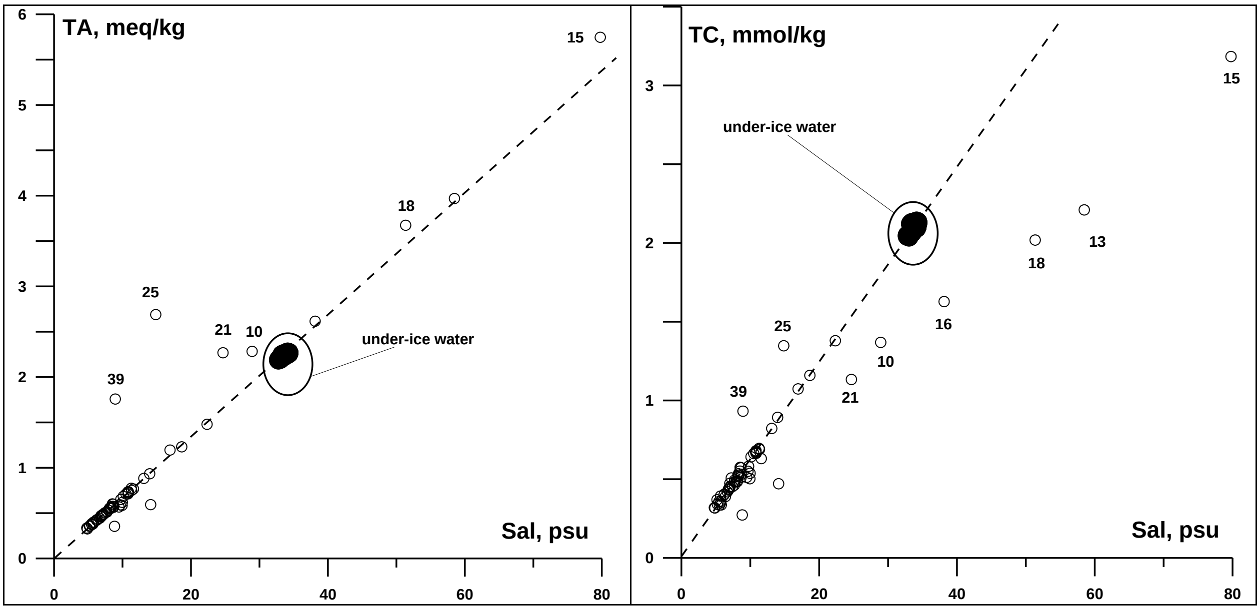

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Figure 1: (a) Correlation between total alkalinity and salinity and (b) between total inorganic carbon and salinity for sea ice core samples and sea water collected under the ice. Numbered points are results for slash and upper ice layer from samples listed in Table 2.

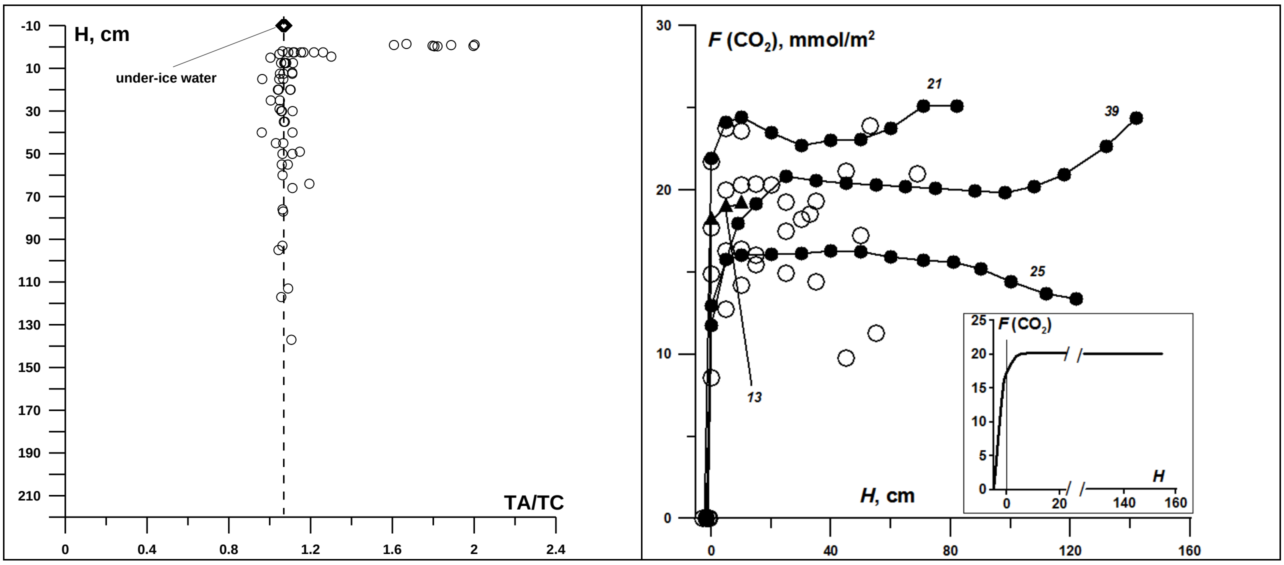

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Figure 2: (a) Vertical distribution of ratio between total alkalinity and total inorganic carbon in sea ice and slash layer and (b) integral curves of CO_2 loss as a function of sea ice core thickness.

The loss of CO_2 from a sea ice layer with thickness H (ΔCO_2, mmol/m^2) can be estimated as:

$$\Delta CO_2 = (TC1 - TC_{meas}) \times d \times H \qquad (2)$$

where TC1 is total inorganic carbon in the ice sample layer under conditions where no CO_2 emission occurs; TC_{meas} is the measured total inorganic carbon in the same layer and d is the sea ice density. For the slash on the ice surface d is the density of melt water.

From Figure 2a, TC1 = $TA_{meas}/1.07$, where TA_{meas} measured is the total alkalinity in the relevant layer of the ice sample. Then the total CO_2 emission $\uparrow F(CO_2)$ is estimated as:

$$\uparrow F(CO_2) = \sum_{i=1}^{n} \Delta(CO_2)_i \qquad (3)$$

Values of ΔCO_2, as function of depth calculated with (2) are presented in Fig. 2b.

It is evident that the main CO_2 loss occurs in slash and upper part of sea ice cover and is independent of ice thickness. This is in agreement with results of the laboratory experiments, presented in Table 1. The experimental data suggests that during January – May emission of CO_2 from first year ice, calculated with formula (3), could be estimated to be 20 ± 4 mmol/m^2 (as generalized in the inset in Figure 2b).

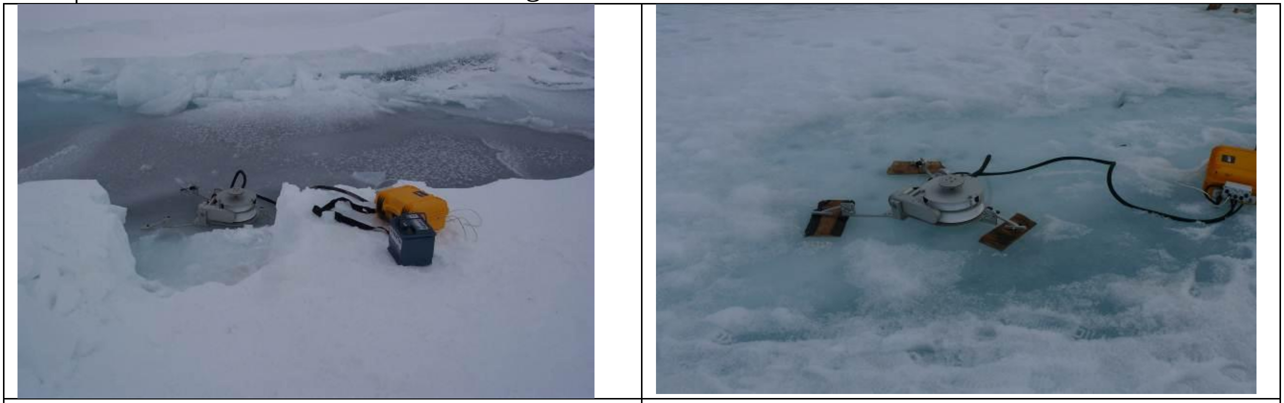
In summer, *Nedashkovsky and Shvetsova, 2010* demonstrated that the partial pressure of CO_2 over water from melted sea ice samples is much smaller then partial pressure of CO_2 in atmosphere. This implies that means that during melting the sea ice cover absorbs CO_2 from atmosphere. The potential amount of CO_2, that could be absorbed during melting ($\downarrow F(CO_2)$) is estimated as:

$$\downarrow F(CO_2) = (TC_{equlibr} - TC_{meas}) \times H \times d \qquad (4)$$

where d is ice density, H is ice thickness, $TC_{equlibr}$ is content of the total inorganic carbon in melt water when it is in equilibrium with the CO_2 concentration in atmosphere (380 ppm) which is calculated on the theoretical seawater carbonate dioxide ($TC_{equlibr} = f\{Sal, TA, t, P(CO_2)\}$). For ice sample 39 (Table 2) $\downarrow F(CO_2)$ is ~ 70 mmol/m^2.

The resulting effect of the sea ice formation (CO_2 emmitted ~20 mmol/m^2) and subsequent melting (CO_2 absorption ~70 mmol/m^2) results in a net sink of carbon dioxide from atmosphere to the ice of ~50 mmol/m^2.

This result has been obtained by through a geochemical analysis of sea ice samples. To further support these results, direct measurements were made of CO_2 fluxes on frozen leads and melt ponds (Fig.3) with a LiCor-8100. These measurements supported our main conclusions regarding carbon dioxide exchange between ocean and atmosphere in presence of sea ice.



Frozen lead, F = 0.44 µmmol/m2s

Melt pond, F = -0.43 µmmol/m2s

Figure 3 Direct measurements CO2 flux with automatic chamber LiCor-8100

4. Discussion

Semiletov et al (2004) used routine climatic measurements of carbon dioxide concentrations at Barrow, Alaska and satellite data on ice extent in the Arctic Ocean to hypothesize that ice conditions in the Arctic Basin influence the long-term and seasonal variability of atmospheric CO_2. Summer-time CO_2 concentrations were expected to decrease due to increases in the biological uptake of atmospheric CO_2 in the ice-free parts Arctic Ocean and in the fall CO_2 concentrations expected to increase due to the upwelling of bottom water enriched in CO_2. We wrote also that possible summer increases of melt ponds and lead concentration also could cause increased absorption of atmospheric CO_2 by ice algae and sub-ice water in open brine channels. In this scenario, decreases in sea ice extent would contribute to enhanced emission of CO_2 from sub-ice waters enriched by CO_2 in autumn before and during freeze-up due to convective mixing and possible additional emissions due to gas transfer through leads and the relatively “warm” ice cover.

This paper further indicates that an additional important mechanism in controlling the recent increase of Arctic atmospheric CO_2 (Fig.4a) is the complicated physical-chemical sea-ice system. The influence of the sea ice chemistry may be evident in the differences in the concentration CO_2 observed at (Barrow – Mauna Loa) and (Alert – Mauna Loa) (Figure 4b). In spite of the fact that Barrow and Alert are situated in different parts of the Arctic Ocean, and the ocean near Barrow is characterized by seasonal open water and the ocean near Alert is characterized by permanent ice cover, the seasonal variability of ΔCO_2 is almost the same. Positive ΔCO_2 takes place during cold months (October – May) and negative ΔCO_2 occurs in the relatively warm months (June–October). The pronounced decrease of ΔCO_2 that takes place during June–August may be due in part to the mechanism suggested by our results showing that the melting sea ice is a strong absorber of atmospheric CO_2 that the increases observed in the September–November period is influences by the freezing of open water, melt ponds, leads and the upper sea ice surface. This would explain the smaller seasonal amplitude and ΔCO_2 at Alert whereas the larger Barrow seasonal amplitudes and ΔCO_2 would be due to the extensive areas of open water close to Barrow in summer and the larger area of young ice formation in the fall.

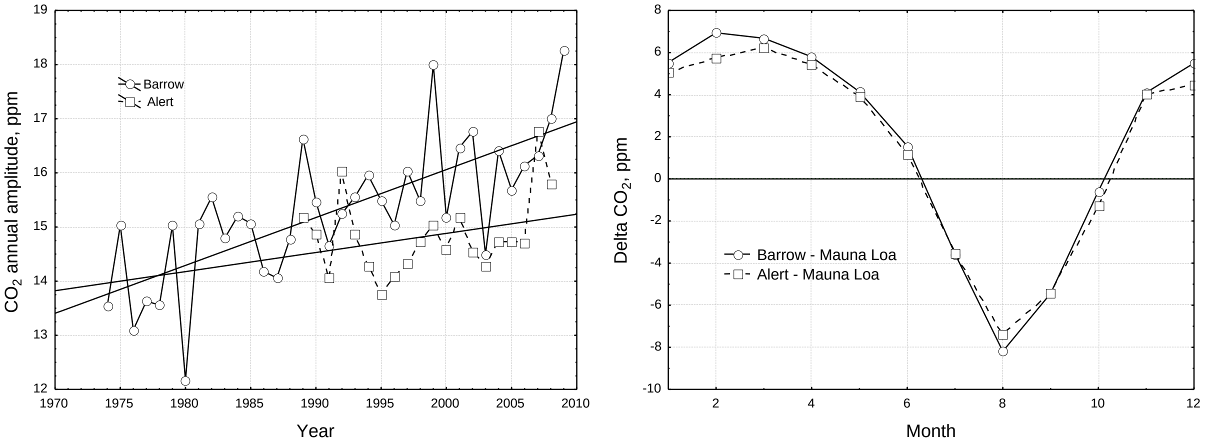


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Figure 4. (a) Time series of the variability of CO_2 annual amplitudes in Barrow and Alert and (b) and the differences between monthly mean concentrations of CO_2, measured at Barrow and Alert with respect to those measured at Mauna Loa.

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5. Conclusions

Observations at the drifting station “North Pole-35” showed that total inorganic carbon stores in the main part of sea ice cores maintain the same ratios of total alkalinity and salinity as the under-ice water. In cold seasons the slash layer and upper levels of the sea ice lose carbon dioxide to atmosphere due to the reaction of bicarbonate calcium decomposition and formation of $CaCO_3$ and CO_2. The value of CO_2 emission to the atmosphere from beginning of freeze up to start of melting is estimated as 20±4 mmol/m^2. It is approximately 10% of maximum possible value of CO_2 emission under conditions of total bicarbonate calcium decomposition in the sea ice with a thickness of 1 m. The water that results from the melting of first year ice is strongly under saturated with respect to CO_2. This leads to absorption of carbon dioxide from atmosphere. The total absorption of CO_2 by first year ice is equal to approximately 50 mmol/m^2 resulting from the net effect of the freezing and melting processes.

The contribution of pCO_2 from the physical chemical processes in ice over the seasonal cycle could be equivalent to 10 ppm for an atmospheric layer of 50 meters. Furthermore, the total sink of CO_2 in the Arctic basin due to chemical physical processes in sea ice could be estimated as $3x10^{12}$ gC/year.

Based on the routine measurements of carbon dioxide concentration at Barrow, Alert, and Mauna Loa we hypothesize that decreases in sea ice concentration and thickness in the Arctic Ocean will significantly influence the long-term balances in the Arctic region.

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Data in Figure 4b from
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