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Scientific Paper

## CARBON DIOXIDE VARIATIONS IN THE GREENLAND SEA

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**Abstract:**  $pCO_2$  in the surface layer of the Greenland Sea shows spatial and temporal variations. Lower values appear in the western and northern part of the sea in August, rising in value eastward and southward. The east-west gradient of  $pCO_2$  is larger than the north-south gradient. A positive relationship between  $pCO_2$  and sea surface temperature (SST) was observed in the open water region; the rate of change was 0.06 °C<sup>--1</sup>. This rate cannot be explained only by the temperature dependence of  $CO_2$  solubility in sea water because the observed rate is higher than that of the pure temperature effect. No relationship between  $pCO_2$  and SST was found in the pack ice region.

 $pCO_2$  in the surface layer of the Greenland Sea was higher in April, followed by a dramatic decrease in mid-May. These lower values of  $pCO_2$  were observed until the end of August.  $pCO_2$  in the ocean surface layer was always lower than that in the atmosphere from April to August. The difference of  $pCO_2$  between the atmosphere and the ocean was about 40  $\mu$ atm in April and reached a maximum of about 190  $\mu$ atm in mid-May. Therefore, the Greenland Sea seems to act as a strong sink for atmospheric  $CO_2$ , especially in summer.

 $\Sigma CO_2$  and  $\delta^{13}C$  were vertically and latitudinally uniform below 200 m depth in the Greenland Sea in August. The uniformity suggests strong vertical mixing of sea water. The mean values of  $\Sigma CO_2$  and  $\delta^{13}C$  below 200 m were 2.13 mmol kg<sup>-1</sup> and 1.2% respectively.  $\Sigma CO_2$  and  $\delta^{13}C$  above 200 m depth had a linear relationship with a coefficient of -10% (mmol kg<sup>-1</sup>)<sup>-1</sup>, suggesting  $\Sigma CO_2$  decrease caused by strong biological activity.

#### 1. Introduction

Concentration of atmospheric CO<sub>2</sub> has been increasing at an annual rate of about 1.5 ppmv yr<sup>-1</sup> (=3.4 GtC yr<sup>-1</sup>) in recent years (TANAKA *et al.*, 1987; NAKAZAWA *et al.*, 1992; AOKI *et al.*, 1992). The growth rate corresponds to about one half the annual emission of about 6 GtC from fossil fuel combustion (MARLAND *et al.*, 1994). Therefore, the other half of the emitted CO<sub>2</sub> should be absorbed by the oceans and the land biosphere. Extensive research studies have been done to obtain quantitative evaluation of CO<sub>2</sub> exchanges between the atmosphere and the oceans, and between the atmosphere and the land biosphere (KEELING and HEIMANN, 1986; SARMIENTO *et al.*, 1992; TANS *et al.*, 1990; QUAY *et al.*, 1992). Many investigators have estimated that the strength of the oceanic CO<sub>2</sub> uptake is about 2 GtC yr<sup>-1</sup>, using their models of the global carbon cycle. On the

other hand, ecologists have estimated that the land biosphere acts as a net  $CO_2$  source because of large-scale deforestation in the tropical regions (WOODWELL *et al.*, 1978; WATSON *et al.*, 1990). Therefore, with the present level of knowledge we cannot balance the global carbon cycle budget. Further investigations and reevaluations are needed for solving the global carbon cycle.

The Greenland Sea is a most important area for deep water formation among the world oceans (BROECKER *et al.*, 1985). This area is also thought to be an important place for the global CO<sub>2</sub> budget, because atmospheric CO<sub>2</sub> is directly transported to the deep ocean in this area. Therefore, we measured CO<sub>2</sub> partial pressure (pCO<sub>2</sub>) of the ocean surface layer in August 1992, August 1993 and April to May 1994. Vertical distribution of total inorganic carbon ( $\Sigma$ CO<sub>2</sub>) and its carbon isotope ratio ( $\delta$ <sup>13</sup>C) were also measured from the surface to the deep ocean in the Greenland Sea in August 1992 and August 1993. In this paper, we will present results of these measurements. The experimental procedure will be described elsewhere.

### 2. Results and Discussion

We have conducted several projects in the arctic region of the Svalbard Islands and the Greenland Sea, in cooperation with the Norwegian Polar Institute. One of the projects is reported here. We participated in summer cruises of the Norwegian research vessel "LANCE" in the Greenland Sea in August 1992 and 1993. We collected air samples which equilibrated with surface water to measure  $pCO_2$  and water samples from the surface to



Fig. 1.  $pCO_2$  (µatm) in the surface layer of the Greenland Sea observed in August 1993.

the bottom of the sea to measure  $\Sigma CO_2$  and  $\delta^{13}C$ . We also made XBT measurements during the cruises. The CTD measurements were made by Norwegian scientists on board the vessel. In April and May 1994, we went on board the Norwegian fishing ship "POLAR STAR". As the ship was not a research vessel, we only collected equilibrated air samples and surface water samples during the cruise.

Atmospheric CO<sub>2</sub> concentration has been monitored using the grab sampling method once a week at Ny-Ålesund, Svalbard (78°56'N, 11°56'E) since August 1991. Spatial variations of the atmospheric CO<sub>2</sub> concentration over the ocean are generally so small over a distance of several hundred kilometers that the same concentration of atmospheric CO<sub>2</sub> at Ny-Ålesund could be assumed over the Greenland Sea. Therefore, we could calculate differences of pCO<sub>2</sub> between atmosphere and surface water of the investigated area using the Ny-Ålesund and shipboard data.

Figure 1 shows the spatial variation of pCO<sub>2</sub> in the surface layer of the Greenland Sea in August 1993. Lower values were observed in the western and northern parts of the investigated area. The east-west gradient of pCO<sub>2</sub> was larger than the north-south gradient. The lowest and highest values were 189 and 321  $\mu$ atm, respectively. As seen in Fig. 2, mean value of the atmospheric pCO<sub>2</sub> at Ny-Ålesund, Svalbard was about 348  $\mu$ atm in August 1993. Therefore, all pCO<sub>2</sub> data obtained in the surface layer of the sea were lower than the atmospheric pCO<sub>2</sub>. Differences of pCO<sub>2</sub> between the surface layer of the sea and the atmosphere over the sea ranged widely from 27 to 159  $\mu$ atm; values larger than 100  $\mu$ atm were observed over more than 80% of the investigated area. These differences were extremely large compared with those reported in the Pacific Ocean, the Atlantic Ocean and the Indian Ocean (TAKAHASHI and AZEVEDO, 1982; TANS *et al.*, 1990). The observed spatial variation of pCO<sub>2</sub> in the Greenland Sea in August 1992 was not the same as that observed in August 1993. But the east-west gradients of pCO<sub>2</sub> resembled each other qualitatively, and the lowest and the highest values were almost the same.



Fig. 2. Atmospheric pCO<sub>2</sub> (μatm) observed by the grab sampling method at Ny-Ålesund, Svalbard (78°56'N, 11°56'E).



Fig. 3. Observed relationships between  $pCO_2$  and sea surface temperature in the surface layer of the Greenland Sea. The left panel shows the relationship observed in August 1992, and the right in August 1993. Solid and open circles represent values obtained in open water and pack ice regions, respectively.

These facts indicate that the Greenland Sea seems to act as a strong sink for atmospheric  $CO_2$  in August.

Figure 3 shows the relationship between  $pCO_2$  in the surface layer of the Greenland Sea and the sea surface temperature (SST) during August of 1992 and 1993. Solid and open circles represent the data obtained in open water and pack ice regions, respectively. A positive linear correlation between  $ln(pCO_2)$  and SST was observed for the open water region, with a rate of change of about  $0.06^{\circ}C^{-1}$  for both years. This observed rate is about 40% higher than the rate of  $0.042^{\circ}C^{-1}$  calculated from the solubility of  $CO_2$ due to temperature variation alone (TAKAHASHI *et al.*, 1993). Therefore, in addition to the mixing of sea waters of different origin, other factors such as biological activity could have contributed to the observed  $pCO_2$ -temperature relationship. No relationship between  $pCO_2$  and SST could be seen in the packed ice region. Intrusion of fresh water from melting sea ice would affect the  $CO_2$  solubility and might change the  $CO_2$  chemistry of sea water.

Figure 4 shows the time variation of pCO<sub>2</sub> in the Greenland Sea in the spring of 1994. The observations were made in the southwestern part of the Greenland Sea (*i.e.* 70–75°N and 10–17°W) where, based on the results obtained in August 1993 (see Fig. 1), spatial variation of pCO<sub>2</sub> was thought to be very small. Therefore, pCO<sub>2</sub> would have changed uniformly in the investigated area. The highest values of about 330  $\mu$ atm and the lowest value of about 160  $\mu$ atm appeared in mid-April and mid-May, respectively. Gradual decrease of pCO<sub>2</sub> continued until early May, followed by a dramatic drop until mid-May. SST of the investigated area was almost constant; *i.e.* –1.7 to –0.3°C, between 16 April and 13 May and increased +0.2 to +1.0°C at most between 15 and 17 May. Therefore, SST had little effect on the dramatic change of pCO<sub>2</sub>. A spring bloom of phytoplankton coincidently occurred at Kongsfjorden of Svalbard in mid-May 1994 (S. KUDOH, private commun.). Similar changes in pCO<sub>2</sub> and phytoplankton bloom in the



Fig. 4. Temporal variation of  $pCO_2$  in the surface layer of the Greenland Sea from April to May 1994. The observational area was within  $70-75^{\circ}N$  and  $10-17^{\circ}W$ .

surface water have also been observed in the Iceland Sea during late May through early June (TAKAHASHI *et al.*, 1993). Therefore, the spring bloom might be related to the drastic depletion of  $pCO_2$  in the Greenland Sea. Extremely low values of  $pCO_2$  below 200  $\mu$ atm were also observed in the northwestern part of the investigated area during the summer cruise, as shown in Fig. 1. Chemical and/or biological conditions at the sea surface would be maintained in such a low  $pCO_2$  area from mid-May to the end of August.

pCO<sub>2</sub> in the atmosphere also showed a seasonal cycle, as seen in Fig. 2. Atmospheric CO<sub>2</sub> reached a seasonal maximum of 366.8  $\mu$ atm in April 1994 and decreased with time during May through August. A seasonal minimum of 348.5  $\mu$ atm appeared in late August. Amplitude of the seasonal cycle of atmospheric CO<sub>2</sub> was about 18  $\mu$ atm which was almost a tenth of the amplitude in the surface layer of the Greenland Sea. The seasonal cycle of atmospheric CO<sub>2</sub> is produced mainly by photosynthesis and respiration of the land biota (NAKAZAWA *et al.*, 1993), but CO<sub>2</sub> uptake by the Greenland Sea in summer might also amplify the cycle in high northern latitudes. The reason is that the amplitude of the seasonal CO<sub>2</sub> cycle in the atmosphere was largest in high northern latitudes where little land biota exists.

 $pCO_2$  in the surface ocean layer was always lower than that in the atmosphere during April through August. Differences of  $pCO_2$  between the atmosphere and the sea surface were about 40  $\mu$ atm in April, reaching a maximum value of about 190  $\mu$ atm in mid-May. Therefore, the Greenland Sea act as a CO<sub>2</sub> sink during spring through summer.

Figure 5 shows vertical profiles of  $\Sigma CO_2$  along 79°N and 75°N in August 1993. Values of  $\Sigma CO_2$  were relatively constant except for the surface layer above 200 m depth. Latitudinal gradient in  $\Sigma CO_2$  was not observed, and the deviation of each value from the



Fig. 5. Vertical profiles of  $\Sigma CO_2$  (mmol kg<sup>-1</sup>) in the Greenland Sea observed in August 1993. Solid and open circles represent data obtained along 79°N and 75°N, respectively.



Fig. 6. Vertical profiles of  $\delta^{13}C$  (‰) in the Greenland Sea observed in August 1993. Solid and open circles represent data obtained along 79°N and 75°N, respectively.

mean profile was small below 200 m depth. The uniformity of  $\Sigma CO_2$  with depth is quite different from any other ocean. The mean profile of  $\Sigma CO_2$  increases with depth in the Pacific Ocean and the Indian Ocean, and has a maximum around 800 m depth in the Atlantic Ocean (BAES *et al.*, 1985). The uniformity of  $\Sigma CO_2$  in the Greenland Sea suggests strong vertical mixing of sea water. A mean value of  $\Sigma CO_2$  below 200 m was 2.13 mmol kg<sup>-1</sup> for the Greenland Sea. This value is low compared with those obtained from the deep-ocean waters of the Atlantic, Pacific and Indian Oceans. A strong gradient of  $\Sigma CO_2$  with depth was observed in the surface layer above 200 m depth.



Fig. 7. Relationship between  $n\Sigma CO_2$  and  $\delta^{13}C$  in the surface layer above 200 m depth of the Greenland Sea in August 1993.  $n\Sigma CO_2$  means that  $\Sigma CO_2$  has been normalized to a constant salinity of 35‰ so as to remove the effect of water balance on the total inorganic carbon content.

Vertical profiles of  $\delta^{13}$ C in the Greenland Sea observed in August 1993 are shown in Fig. 6. Solid and open circles represent the data obtained along 79°N and 75°N, respectively. The vertical profile of  $\delta^{13}$ C below the 200 m depth is similar to that of  $\Sigma CO_2$ ; values are almost uniform with depth with no latitudinal difference. The mean value of  $\delta^{13}$ C below 200 m depth was 1.2‰ for the Greenland Sea in August 1993. A strong gradient of  $\delta^{13}$ C with depth was also observed in the surface layer above 200 m depth. But the vertical gradients of  $\Sigma CO_2$  and  $\delta^{13}C$  were completely reversed; the lowest  $\Sigma CO_2$ and highest  $\delta^{13}$ C appeared at the top of the surface layer. Figure 7 shows the relationship between n $\Sigma CO_2$  ( $\Sigma CO_2$  normalized to a constant salinity of 35%) and  $\delta^{13}C$  in the surface layer above 200 m depth in the Greenland Sea in August 1993. These two variables had a linear relationship with a coefficient of about -12.0% (mmol kg<sup>-1</sup>)<sup>-1</sup>. Phytoplankton consumes dissolved inorganic carbon by photosynthesis in spring and summer. Strong fractionation occurs with photosynthetic activity; phytoplankton have a tendency to uptake more  ${}^{12}CO_2$  than  ${}^{13}CO_2$ . The correlation coefficient between  $\Sigma CO_2$  and  $\delta^{13}C$  is –11.2‰ (mmol kg<sup>-1</sup>)<sup>-1</sup> for pure photosynthetic activity (KROOPNICK, 1974). This value is almost equal to that obtained by our measurements. Therefore, low  $\Sigma CO_2$  in the surface layer of the Greenland Sea in summer can be explained quantitatively by biological activity.

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