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Oceanic CO₂ increase in Baffin Bay

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ABSTRACT

Measurements of the total inorganic carbon in the water of Baffin Bay are interpreted to reflect increases in atmospheric carbon dioxide due to fossil fuel combustion. The increases are indicated by differences at various depths in the alkalinity and total inorganic carbon values after correction for calcium carbonate dissolution and decay of organic matter. These differences are comparable to the changes reported for GEOSECS Atlantic and Pacific Stations.

1. Introduction

Fossil fuel CO₂ buildup in the atmosphere has been well documented and extensively discussed by many authors (eg., Marland and Rotty, 1979). While there is some controversy regarding various aspects of the global carbon cycle, it seems evident that a considerable fraction of the fossil fuel CO₂ has entered the oceans (Broecker *et al.*, 1979). An increase in oceanic CO₂ has been very difficult to observe, however, because of the large carbon reservoir in the oceans and the relatively complicated chemistry of carbon in the oceans which involves both organic and inorganic processes. Recently, however, an increase of carbon in the ocean due to fossil fuel combustion was reported for GEOSECS stations in the Atlantic Ocean (Brewer, 1978; Chen and Millero, 1979) and the Pacific Ocean (Chen and Pytkowicz, 1979).

We report observations of a possible similar increase in oceanic CO₂ deduced from alkalinity measurements made at several locations in Baffin Bay (Fig. 1).

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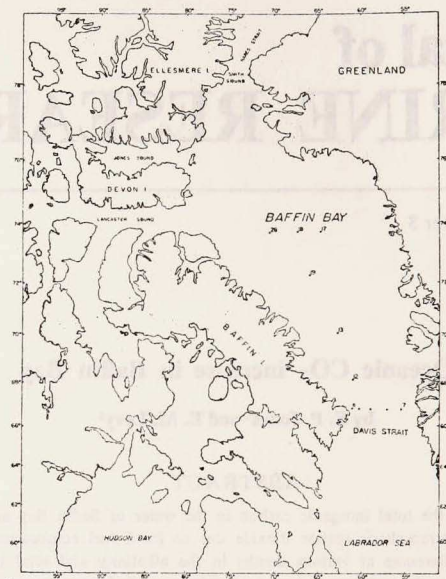


Figure 1. Station locations in Baffin Bay.

Baffin Bay is a relatively isolated body of water with a maximum depth of about 2300 m. Water flows into Baffin Bay from the Arctic Ocean over sills of about 150 m in Jones and Lancaster Sounds and 250 m in Nares Strait, and from the North Atlantic Ocean by way of the West Greenland Current over a sill of about 800 m in Davis Strait. The water within Baffin Bay has been described by Muench (1971) in terms of an upper, intermediate, and deep layer. The upper layer (salinity from less than 31‰ to about 34.5‰, temperature from 0°C to -1.8°C except at the surface during summer) extends to depths of 150 to 300 m and is comprised of Arctic Ocean Surface Layer water which has entered through the Canadian Archipelago together with Atlantic water which has entered through Davis Strait. The intermediate layer (salinity between 34.2‰ and 34.5‰, temperature from 0°C to about 2°C) extends to a depth of about 1200 m and is predominantly Atlantic Ocean water which has entered Baffin Bay through Davis Strait. The deep layer (salinity near 34.5‰, temperature from 0°C to -0.4°C) extends from about 1200 m to the bottom and includes Baffin Bay Bottom Water, water below 1800 m with very uniform salinity (near 35‰) and temperature (near -4°C). The deep layer between 1200 m and 1800 m is believed to be Arctic Ocean water of Atlantic

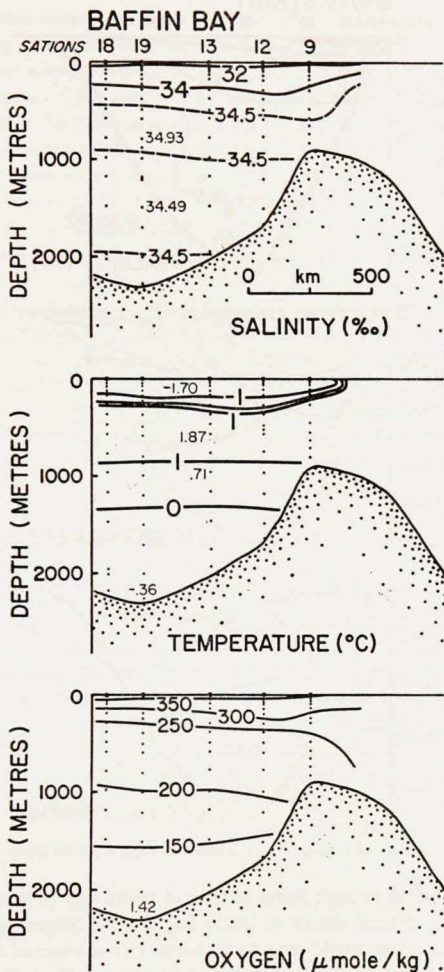


Figure 2. Longitudinal sections of salinity, temperature, and oxygen through Baffin Bay.

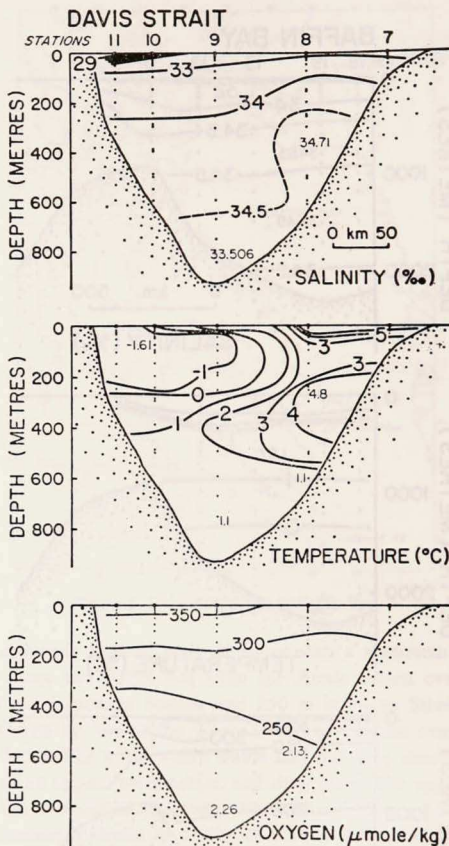


Figure 3. Sections of salinity, temperature, and oxygen across Davis Strait.

origin which has pulsed through Nares Strait into Baffin Bay at irregular intervals. There is no clearly defined source of Baffin Bay Bottom Water, though Muench (1971) argues that it, too, would seem to be Arctic Ocean water of Atlantic origin. The general characteristics of these layers and of water in Davis Strait are shown in our data (Figs. 2 and 3).

To observe an increase in oceanic CO_2 due to fossil fuel combustion, we must satisfy two conditions. We must have water old enough so that it was at the surface

before most of the increase in atmospheric CO₂ occurred, and we must be able to compare this older water to younger water which experiences the same conditions except for being in contact with an increased concentration of atmospheric CO₂. From tritium-He³ measurements, the age of Baffin Bay Bottom Water is probably a few hundred years, while that of the intermediate layer between 500 m and 600 m was indicated to be between five and ten years (Top *et al.*, 1980). No specific ages could be ascribed to water below about 600 m and above 1800 m, though clearly some of these waters must be somewhere between about ten and one hundred years old. It is more difficult to demonstrate that the second condition regarding common initial conditions for the older and younger water is fulfilled. We will assume that the water in the intermediate and deep layers of Baffin Bay was last in contact with the atmosphere in the North Atlantic Ocean and, at least with respect to carbon dioxide, it has subsequently remained isolated. As indicated earlier, the water in both the intermediate and deep layers of Baffin Bay is of Atlantic origin. Both the water in the deep layer which entered Baffin Bay by way of the Arctic Ocean and water in the intermediate layer which entered by way of Davis Strait have a common origin in the North Atlantic Current. This current divides to supply eventually both the West Spitzbergen Current which flows into the Arctic Ocean and the West Greenland Current which flows directly into Baffin Bay. Various authors have presented different aspects of water in these currents (Lazier, 1973; Lee, 1968; Dietrich, 1969). To compare the currents, we examine the salinity and temperature in the different regions at a depth of 500 m. This is a typical depth at which Atlantic water is found in Davis Strait (Fig. 3). The water in the North Atlantic Current is slightly more saline and warmer (35.1‰ and 7°C) than that in the West Greenland Current near Cape Farewell (34.9‰ and 4°C) or that in the West Spitzbergen Current (34.9‰ and 1°C) (Dietrich, 1969). The freshening and cooling which has affected both water masses about the same amount presumably occurs in both instances by mixing with Arctic Water. The Atlantic Water in Davis Strait is slightly freshened still further (Fig. 3). The tritium-He³ age of the Atlantic Water in Davis Strait at 500 m is about two years, thus indicating a substantial fraction, quite possibly almost all, of the water has been isolated from the surface for much of its journey from the North Atlantic. Although the upper layer in Baffin Bay is also primarily of Atlantic origin, this water has undergone obvious modifications such as inclusion of Bering Sea water (Coachman and Aagaard, 1974; Codispoti and Owens, 1975; Jones and Coote, 1980), and therefore we do not include it in our discussion of the increase of dissolved inorganic carbon in Baffin Bay.

2. Methods

Our samples were collected during August and September 1977 from the CSS *Hudson* Cruise 77-024. The alkalinity determinations were made by a modification

of the method described by Dyrssen and Sillen (1967) from which one can obtain the alkalinity, A , and total inorganic carbon, ΣCO_2 , fairly directly. Our semi-automated titration was done within a few hours of sample collection in a closed cell at constant temperature (25°C) and pressure using 50 incremental additions of acid to cover the whole titration curve. The titration data were analyzed using a curve fitting procedure for the whole titration curve (Dickson, 1981) which includes corrections for nutrient concentrations. This procedure gives values for alkalinity and total inorganic carbon which are very similar to those given by the procedure described by Bradshaw and Brewer (1981). Our estimated analytical precision was better than 1%. Oxygen concentrations were measured using a modified Carpenter-Winkler technique (Levy *et al.*, 1977) and salinity values were measured with a Guildline Autosol Model 8400 salinometer. Continuous temperature profiles were measured with a Guildline Mk III analogue CTD system. Temperatures were also measured at selected depths using both protected and unprotected reversing thermometers to check the CTD results.

3. Results and discussion

We use the model described by Brewer (1978) but presented in a slightly different way to describe our results. Because the temperature variation among our samples is relatively small, almost all temperatures being between about -0.5°C and 2°C , we do not include any temperature effects on alkalinity or on ΣCO_2 . The procedure followed by Brewer (1978) is to determine the changes in alkalinity and ΣCO_2 brought about by changes in CaCO_3 concentrations and by the decay of organic matter. The dissolution of one mole of CaCO_3 produces an increase of one mole of ΣCO_2 and two equivalents in alkalinity. The decay of organic matter contributes to ΣCO_2 by the production of CO_2 and decreases the alkalinity by the production of HNO_3 . We thus write the change in ΣCO_2 from its value when the water was in contact with the atmosphere, ΣCO_2° , in terms of the measured alkalinity, A , and the alkalinity when the water was in contact with the atmosphere, A° , as follows:

$$\Sigma\text{CO}_2 - \Sigma\text{CO}_2^\circ = 0.5 (A + \Delta\text{NO}_3 - A^\circ) + \Delta\text{CO}_2 \quad (1)$$

The effects of the decay of organic matter on alkalinity are represented by ΔNO_3 and on ΣCO_2 by ΔCO_2 . Because it is the more reliably determined measurement, we use the oxygen utilization, ΔO_2 , to determine ΔNO_3 and ΔCO_2 . Oxygen utilization is the difference between the measured oxygen concentration and the saturated value calculated assuming the water was in equilibrium with the atmosphere. From the well known Redfield-Ketchum-Richards relationship which relates the average stoichiometric composition of organic matter to decay products (Redfield *et al.*, 1963), $\text{C}_{106} \text{H}_{263} \text{O}_{110} \text{N}_{16} \text{P}_1 + 1380_2 \rightarrow 106\text{CO}_2 + 16\text{NO}_3^- + \text{HPO}_4^{2-} + 122\text{H}_2\text{O} + 18\text{H}^+$ the amount of CO_2 due to organic decay is $0.768 \Delta\text{O}_2$. From

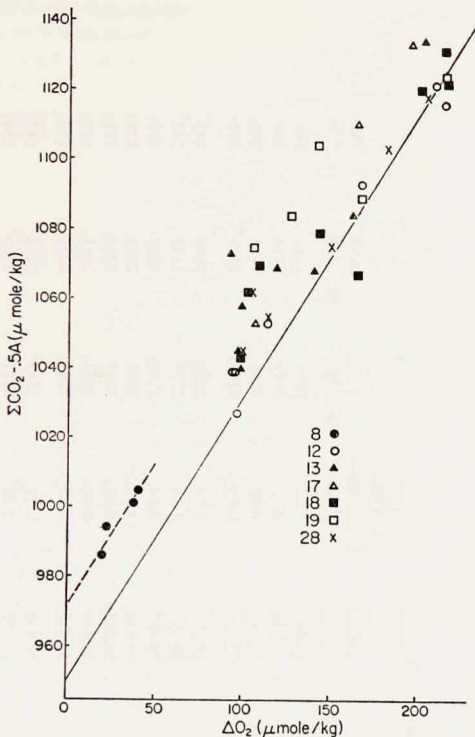


Figure 4. Plot of $\Delta\text{CO}_2 - 0.5A$ vs ΔO_2 for Stations 8, 12, 13, 17, 18, 19, and 28. The largest values of ΔO_2 correspond to the oldest water.

the concept of 'NO' (Broecker, 1974), $9 \Delta\text{NO}_3 = \Delta\text{O}_2$, the change in alkalinity resulting from the change in nitrate concentration due to organic decay is $0.111\Delta\text{O}_2$. We thus can write Eq. 1 as

$$\Sigma\text{CO}_2 - \Sigma\text{CO}_2^\circ = 0.5(A + 0.111\Delta\text{O}_2) + 0.768\Delta\text{O}_2 - 0.5A^\circ$$

or

$$\Sigma\text{CO}_2 - 0.5A = 0.82\Delta\text{O}_2 + \Sigma\text{CO}_2^\circ - 0.5A^\circ \quad (2)$$

The values of ΣCO_2° and A° are taken to be constant.

Our data for Baffin Bay (Table 1) is plotted in this way (Fig. 4). The values

Table 1. Baffin Bay station locations and data.

| | Depth (m) | Salinity (‰) | Potential Temperature (°C) | <i>A</i> ($\mu\text{eq kg}^{-1}$) | ΣCO_2 ($\mu\text{mol kg}^{-1}$) | O_2 (mol kg^{-1}) |
|--------------------------------|--------------|-----------------|----------------------------------|--|--|--|
| Station 8 66°45'N, 57°06'W | 205 | 34.447 | 3.08 | 2251 | 2110 | 286 |
| | 256 | 34.726 | 4.75 | 2279 | 2118 | 290 |
| | 403 | 34.719 | 4.02 | 2271 | 2125 | 293 |
| | 509 | 34.750 | 3.66 | 2284 | 2139 | 278 |
| Station 12 68°09'N, 61°21'W | 401 | 34.321 | 1.34 | 2260 | 2149 | 244 |
| | 509 | 34.475 | 1.70 | 2259 | 2153 | 242 |
| | 611 | 34.517 | 1.64 | 2228 | 2127 | 240 |
| | 786 | 34.517 | 1.17 | 2273 | 2175 | 226 |
| | 1224 | 34.485 | 0.20 | 2269 | 2212 | 182 |
| | 1531 | 34.489 | -0.24 | 2272 | 2241 | 143 |
| 1689 | 34.491 | -0.29 | 2265 | 2232 | 140 | |
| Station 13 70°02'N, 62°46'W | 398 | 34.330 | 1.12 | 2243 | 2160 | 242 |
| | 509 | 34.492 | 1.80 | 2261 | 2160 | 238 |
| | 600 | 34.547 | 1.84 | 2288 | 2169 | 236 |
| | 795 | 34.532 | 1.24 | 2247 | 2178 | 221 |
| | 1005 | 34.501 | 0.66 | 2323 | 2215 | 204 |
| | 1195 | 34.486 | 0.22 | 2250 | 2194 | 186 |
| | 1504 | 34.488 | -0.23 | 2289 | 2261 | 151 |

| | | | | | | |
|------------------|------|--------|-------|------|------|-----|
| Station 17 | 596 | 34.549 | 1.79 | 2268 | 2173 | 228 |
| 73°42'N, 64°35'W | 1002 | 34.552 | 0.62 | 2303 | 2205 | 204 |
| | 1186 | 34.483 | 0.19 | 2432 | 2310 | 185 |
| | 1429 | 34.487 | -0.16 | 2348 | 2291 | 157 |
| Station 18 | 396 | 34.452 | 1.74 | 2257 | 2156 | 237 |
| 73°40'N, 67°17'W | 502 | 34.548 | 1.96 | 2279 | 2187 | 230 |
| | 599 | 34.556 | 1.74 | 2317 | 2210 | 226 |
| | 996 | 34.493 | 0.52 | 2287 | 2207 | 203 |
| | 1201 | 34.483 | -0.24 | 2294 | 2213 | 184 |
| | 1500 | 34.488 | -0.25 | 2281 | 2249 | 153 |
| | 2044 | 34.502 | -0.44 | 2293 | 2253 | 140 |
| | 2214 | 34.501 | -0.44 | 2288 | 2259 | 141 |
| Station 19 | 616 | 34.556 | 1.76 | 2300 | 2211 | 229 |
| 72°14'N, 65°57'W | 822 | 34.531 | 1.12 | 2318 | 2228 | 213 |
| | 1025 | 34.495 | 0.51 | 2360 | 2268 | 204 |
| | 1229 | 34.486 | 0.13 | 2321 | 2233 | 183 |
| | 2046 | 34.506 | -0.46 | 2282 | 2249 | 141 |
| Station 28 | 311 | 34.330 | 1.24 | 2276 | 2163 | 240 |
| 73°42'N, 70°29'W | 516 | 34.538 | 1.75 | 2287 | 2191 | 231 |
| | 618 | 34.519 | 1.59 | 2272 | 2176 | 223 |
| | 1027 | 34.490 | 0.44 | 2273 | 2196 | 197 |
| | 1229 | 34.484 | 0.85 | 2286 | 2230 | 168 |

for ΣCO_2 and A were normalized to a salinity of 35‰, the alkalinity because it is directly proportional to salinity in almost every oceanic condition and ΣCO_2 because we believe there would be little change in the preformed ΣCO_2 by the addition of fresh water during the course of the Atlantic water to Baffin Bay. The contribution to ΣCO_2 from decay of organic matter within Baffin Bay is small enough so that a change in this correction due to normalization to constant salinity is negligible. As indicated earlier, only samples from the intermediate and deep layers are included. The relative age of the water should be reflected by oxygen utilization, the older water having larger values of ΔO_2 . This is supported by helium-tritium measurements (Top *et al.*, 1980). We have drawn a line on the plot whose equation is of the form of Eq. 2 and which was chosen to represent the average value of the three deepest and oldest samples. The equation for this line is

$$\Sigma\text{CO}_2 - 0.5A = 0.82\Delta\text{O}_2 + 950 \quad (3)$$

If as the water ages it is not subjected to processes other than those included in deriving Eq. 2, this line should also represent the less deep, younger samples. The observed deviations from Eq. 3 (Fig. 4) imply other processes are important; the most likely is an increase in ΣCO_2 in younger waters relative to older waters due to an increased atmospheric CO_2 concentration from fossil fuel combustion. At depths less than about 1000 m, all points lie above the line drawn through the deep points. The youngest water tends to show the greatest deviation from the plotted line, and, as a general rule, the older, deeper points show smaller deviations.

An estimate of the total increase in dissolved inorganic carbon in the ocean since the onset of the industrial revolution can be obtained from our results as follows. From the equation of the line plotted in Figure 4 and Eq. 2, we get, at $\Delta\text{O}_2 = 0$,

$$\Sigma\text{CO}_2^\circ = 950 + 0.5A^\circ \quad (4)$$

We obtain the present surface value of ΣCO_2 by fitting Eq. 2 to the young water of the four points plotted in Figure 4 for Station 8 in Davis Strait. For these points, we get a line with the equation,

$$(\Sigma\text{CO}_2 - 0.5A) = 0.82\Delta\text{O}_2 + 971 \quad (5)$$

At the surface, we take $\Delta\text{O}_2 = 0$ and $A = A^\circ$. Thus from Eq. 4 and 5, $\Sigma\text{CO}_2 - \Sigma\text{CO}_2^\circ = 21 \mu\text{mol kg}^{-1}$. If we take the average value of A for the four points of Station 8 to represent A° , we get $A^\circ = 2271 \mu\text{eq kg}^{-1}$, and from Eq. 5 we get $\Sigma\text{CO}_2 = 2106 \mu\text{mol kg}^{-1}$. The total relative increase in dissolved inorganic carbon is thus $21/2106 = 1.0\%$. Within the limitations of the model used to analyze our results, this is in excellent agreement with the value of 1.3% given by Broecker *et al.* (1979).

For the purpose of comparison we have plotted the data presented by Brewer (1978) in the same way as our own. We find the equation fitted to his oldest samples gives an intercept of 960 compared to our value of 950 and the relative increase in dissolved inorganic carbon is 1.4% compared to our value of 1.0%. This rather good agreement between the two sets of data from quite different regions represents encouraging support to the basic concepts of the model, although there are questions which could arise such as effects from mixing different water masses. We believe, however, that the data are abundant enough and the interpretation compelling enough to give considerable credibility to the qualitative observation and probably to a semi-quantitative assessment of fossil fuel CO₂ buildup in the ocean.

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