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Effect of sea ice meltwater on the alkalinity of seawater

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ABSTRACT

Alkalinity values in the top few hundred meters in Baffin Bay were about $100 \mu\text{eq kg}^{-1}$ above those expected from deeper values when the effect of salinity is removed. This "excess" alkalinity is attributed to calcium carbonate that precipitated from brines in sea ice and was subsequently reintroduced into the water column when the ice melted. The "excess" alkalinity is then used to estimate the amount of sea ice meltwater formed in Baffin Bay.

1. Introduction

The alkalinity of seawater is only very slightly affected by chemical processes in the ocean other than those involving the direct input or removal of carbonates (Brewer *et al.*, 1975). A process which might alter alkalinity in polar regions is the redistribution of calcium carbonate brought about by the formation and subsequent melting of sea ice. In this paper, alkalinity data are presented for samples from Baffin Bay where an "excess" alkalinity was observed in the upper few hundred meters. These elevated alkalinity values are attributed to calcium carbonate, which is precipitated in brines in sea ice during freezing, being reintroduced into the water column when the ice melts. We show how this effect can be used to estimate the amount of sea ice meltwater in the surface regions of the ocean which experience the effects of ice.

2. Methods

Seawater samples were collected in central Baffin Bay (Fig. 1) during August and September 1977 (CSS *Hudson* Cruise 77-024), and alkalinity was determined within a few hours of sample collection by a modification of the method described by Dyrssen and Sillén (1967). The semi-automated potentiometric titration of approximately 150 ml of seawater was carried out in a closed cell at constant temperature ($25^\circ \pm 0.1^\circ$) and pressure by adding fifty 0.1 ml increments of titrant (0.0991 N HCl + 0.53 m NaCl). The titrant was previously standardized against a CSK Stan-

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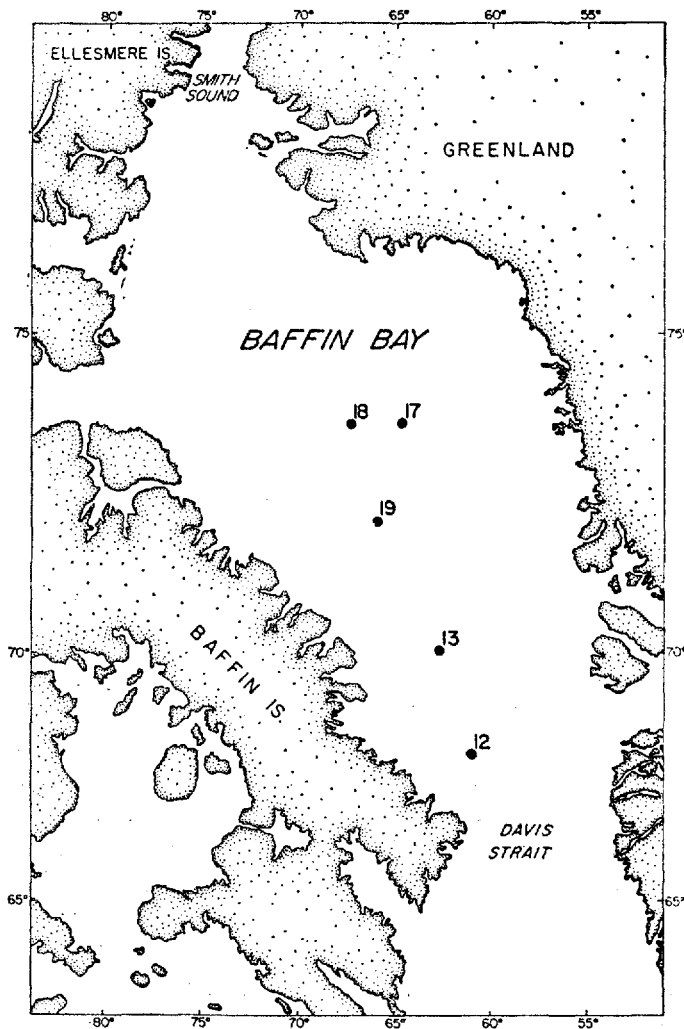


Figure 1. Station locations in Baffin Bay.

standard KIO_3 Solution (0.00996N) (Sagami Chemical Research Center, Japan). Analytical quality was maintained by titrating I.A.P.S.O. Standard Seawater (Batch No. P₆₄; Salinity, 35.006‰) on a regular basis. The titration data were analyzed by a curve fitting procedure (Dickson, 1981; Johansson and Wedborg, 1982) which includes corrections for nutrient concentrations. This procedure provided values for the alkalinity and total inorganic carbon with an analytical precision better than 1% as determined by replicate analyses of samples of seawater and of different batches of I.A.P.S.O. Standard Seawater. Salinity values for all samples were measured

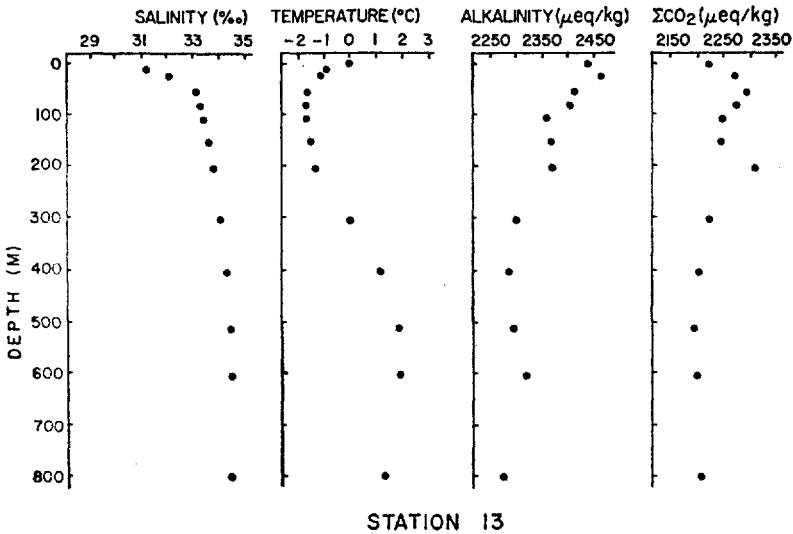


Figure 2. Salinity, temperature, normalized alkalinity, and normalized total inorganic carbon at Station 13.

with a Guildline Autosol Model 8400 salinometer, and temperatures were obtained using a Guildline Mk III analogue CTD system which was calibrated at selected depths using both protected and unprotected reversing thermometers.

3. Results

The alkalinity data for the five stations occupied in central Baffin Bay are listed in Table 1 and depth profiles for a typical station (Station 13) are presented in Figure 2. In order to compare the alkalinites of samples with different salinities, alkalinity values were normalized to a salinity of 35‰ according to the relationship, $A_n = A_m/S \times 35$, where A_n , A_m and S are the normalized alkalinity, the measured alkalinity, and the measured salinity respectively. Between about 250 m and 800 m, the normalized alkalinity was relatively uniform with an average value of 2310 $\mu\text{eq kg}^{-1}$. This value corresponds also with that measured in the Atlantic water of the West Greenland Current at Davis Strait and to values (unpublished) measured in the top few hundred meters at several locations in the Labrador Sea.

A composite plot of normalized alkalinity vs. σ_T for the five stations (Fig. 3) summarizes the alkalinity data. The highest values for normalized alkalinity, up to about 2450 $\mu\text{eq kg}^{-1}$, were found in the top 50 or so meters. Values between about 2350 $\mu\text{eq kg}^{-1}$ and 2310 $\mu\text{eq kg}^{-1}$ were found between 50 m and the bottom of the winter mixed layer (between 200 m and 300 m) at all stations.

Table 1. Station locations and data.

	Depth (m)	Salinity (‰)	Temperature (°C)	A ($\mu\text{eq kg}^{-1}$)	ΣCO_2 ($\mu\text{mol kg}^{-1}$)
Station 12 68°09'N, 61°21'W	1	29.331	-0.73	2052	1840
	14	32.568	-1.21	2219	2079
	34	32.919	-1.59	2225	2092
	55	33.048	-1.63	2226	2100
	83	33.227	-1.56	2254	2131
	105	33.400	-1.65	2237	2112
	156	33.550	-1.75	2232	2111
	208	33.598	-1.76	2249	2133
	401	34.321	1.36	2260	2149
	509	34.475	1.74	2259	2153
	611	34.517	1.67	2228	2127
	786	34.517	1.21	2273	2175
Station 13 70°02'N, 62°46'W	1	28.093	-0.24	1955	1781
	12	31.191	-0.91	2375	2160
	23	32.534	-1.41	2289	2108
	54	33.103	-1.70	2281	2168
	80	33.265	-1.72	2282	2161
	105	33.370	-1.72	2248	2141
	150	33.611	-1.55	2269	2159
	200	33.768	-1.39	2285	2227
	302	34.076	-0.01	2240	2165
	398	34.330	1.14	2243	2160
	509	34.492	1.83	2261	2160
	600	34.547	1.87	2288	2169
795	34.532	1.28	2247	2178	
Station 17 73°42'N, 64°35'W	1	29.641	2.20	2011	1831
	14	32.838	-0.14	2251	2051
	24	32.524	-0.56	2228	2009
	33	33.309	-1.53	2271	2151
	54	33.488	-1.74	2293	2160
	76	33.567	-1.71	2249	2132
	91	33.626	-1.71	2271	2157
	153	33.753	-1.46	2273	2202
	205	33.879	-1.03	2273	2187
	308	34.232	0.94	2260	2179
	405	34.420	1.60	2394	2286
	490	34.519	1.93	2268	2182
	596	34.549	1.82	2268	2173
	811	34.521	1.12	2283	2207

Table 1. (continued)

	Depth (m)	Salinity (‰)	Temperature (°C)	A ($\mu\text{eq kg}^{-1}$)	ΣCO_2 ($\mu\text{mol kg}^{-1}$)
Station 18 73°40'N, 67°17'W	1	30.223	2.79	2093	1920
	12	32.475	0.86	2253	2006
	33	33.110	-1.66	2255	2113
	81	33.572	-1.62	2256	2134
	153	33.782	-1.49	2278	2151
	206	33.905	-0.84	2258	2142
	300	34.255	1.14	2272	2152
	396	34.452	1.76	2257	2156
	502	34.548	1.99	2279	2187
	599	34.556	1.77	2317	2210
Station 19 72°14'N, 65°57'W	1	28.388	2.91	1980	1812
	15	32.116	-0.85	2216	2035
	26	32.381	-1.49	2256	2057
	34	32.835	-1.63	2278	2152
	54	33.020	-1.68	2217	2010
	205	33.812	-1.20	2249	2151
	262	33.962	-0.43	2262	2163
	310	34.167	0.50	2309	2223
	514	34.520	1.82	2258	2114
	616	34.556	1.79	2300	2211
	822	34.531	1.16	2318	2228

4. Discussion

Sea ice formation and aging involve several physical and chemical processes. The physical aspects such as freezing-temperature and brine drainage are fairly well understood (eg, Niedrauer and Martin, 1979; Doronin and Kheisin, 1977; Lake and Lewis, 1970; Groen, 1967). Briefly, as seawater freezes, most brine is rejected from the ice, but some is physically entrained within the ice. As freezing progresses brine drainage begins to occur, and after one year the bulk salinity of sea ice is reduced from about 20‰ to about 5-6‰. The chemical changes that take place within the ice and brine are not very well known, although it is clear that changes occur in the concentration and composition of the salts both in the brine and in the ice and that these changes are temperature dependent (Richardson, 1976; Tsurikov and Tsurikova, 1972; Blinov, 1965; Assur, 1958; Thompson and Nelson, 1956; Nelson and Thompson, 1954).

Laboratory results (Thompson and Nelson, 1956) show that at a temperature just below the freezing point calcium carbonate begins to precipitate from the entrained brines in sea ice and remains in the ice. Other salts precipitate as the temperature of the ice lowers, but, except for carbonate salts, these will not alter the

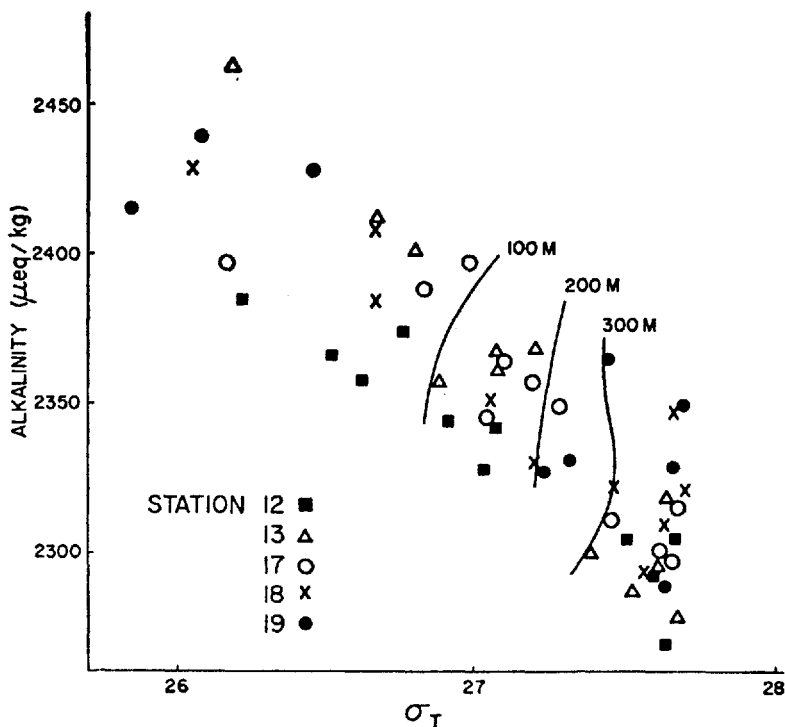


Figure 3. Composite plot of normalized alkalinity vs. σ_T for Stations 12, 13, 17, 18 and 19.

alkalinity. Thus, the alkalinity of the brines remaining in the ice and those rejected from the ice will decrease because of calcium carbonate precipitation in the ice. This effect may not be easily observable in the water column, however, because the brines rejected from the ice on freezing and those draining from the ice as the ice grows older are more dense than the seawater under the ice and, as they sink, mix with a volume of water considerably greater than that of the sea ice itself (Weber, 1977; Foster, 1972). When the weather warms and the ice melts, the precipitated calcium carbonate is released with the meltwater. Because of the increased stability of the water column resulting from the release of meltwater and subsequent increase in temperature of the surface water as the season turns warmer, this calcium carbonate is constrained to relatively near the surface and its effect on alkalinity can be observed because mixing processes that had obscured the reverse effect during the cold season are inhibited. Our analytical procedure would detect the increase in alkalinity resulting from this calcium carbonate whether it dissolves or remains as a precipitated solid suspended in the water column.

At the time this study was done, summer conditions were well established with a warmer, lower salinity region above a cold (-1.8°C) core, a remnant of the previous

winter mixed layer (Fig. 2). In the "upper layer," above about 300 m, which is comprised of Arctic Ocean Surface Layer water (Muench, 1971), the generally higher normalized alkalinity may be due partly to a higher alkalinity of the Arctic Ocean Surface Layer water.

Above about 50 m, the region of excess alkalinity ($\approx 100 \mu\text{eq kg}^{-1}$) corresponds reasonably well to the region of higher temperature and lower salinity associated with summer heating and melting of sea ice. This region also corresponds well with the penetration depth of sea ice meltwater as shown by measurements of oxygen isotope ratios in the same samples (Tan and Strain, 1980). Below about 300 m in the "intermediate" layer which is Atlantic water that has entered Baffin Bay via Davis Strait (Muench, 1971), the normalized alkalinity was almost constant.

The total inorganic carbon, ΣCO_2 , should also reflect the addition of calcium carbonate from sea ice meltwater to the surface region of the ocean. The expected change in ΣCO_2 would be one-half the corresponding change in alkalinity, or about $50 \mu\text{mol kg}^{-1}$. Although there is not clear evidence for these changes in profiles of normalized values for ΣCO_2 (Fig. 2), there is some indication of increases in the normalized ΣCO_2 values in the surface region. This increase, however, is not as large as expected from the alkalinity results. A plausible explanation for this may lie in the fact that ΣCO_2 is decreased by biological processes which fix carbon. Alkalinity is also very slightly affected by biological processes through the change in nutrient concentration, primarily nitrates, but this effect is an order of magnitude smaller. Biological uptake of carbon in the surface region could lower ΣCO_2 by very nearly the same amount as calcium carbonate from sea ice meltwater would increase it. For example, at Station 18, the near surface nitrate concentration is about $10 \mu\text{g-at kg}^{-1}$ lower than at a depth of 200 m (Jones and Coote, 1980). The Redfield-Ketchum-Richards relationship (Redfield *et al.*, 1963) predicts a decrease of 16 moles in nitrate concentration for a decrease of 106 mol in ΣCO_2 . Thus the decrease of $10 \mu\text{g-at kg}^{-1}$ in nitrate concentration corresponds to $65 \mu\text{mol kg}^{-1} \Sigma\text{CO}_2$, almost exactly compensating for the increase in ΣCO_2 expected from the observed excess alkalinity values of about $100 \mu\text{mol kg}^{-1}$ at Station 18.

One application of the effect of sea ice meltwater on alkalinity is to estimate the amount of sea ice meltwater present in the upper region of the ocean. The excess alkalinity from melting sea ice can be related to the amount of sea ice which has melted during the summer if the amount of calcium carbonate initially present in the sea ice is known. As no such data are available, it is assumed, following Richardson (1976), that $1000 \mu\text{mol kg}^{-1}$ or 10% of the total calcium initially present in the seawater was retained in the sea ice as calcium carbonate. The excess alkalinity, ΔA , in the surface region due to the release of calcium carbonate by melting sea ice is given by

$$\Delta A = A_m - A^n \frac{S}{35}$$

where A_n is the normalized alkalinity which is assumed to be unaffected by sea ice meltwater, and S is the salinity (‰) of the sample. Since a change of one mole of calcium carbonate produces a change of two equivalents alkalinity, the fraction of sea ice meltwater, f_{st} , at a particular depth can be related to the excess alkalinity as follows:

$$f_{st} = \frac{.5}{1000} \Delta A$$

where we assume $1000 \mu\text{mol kg}^{-1}$ calcium carbonate is released by melting sea ice. A typical near surface value for ΔA in central Baffin Bay is $100 \mu\text{eq kg}^{-1}$ which results in a typical value for f_{st} of 5%. This value is similar to those reported by Tan and Strain (1980). A typical depth to which we observe excess alkalinity is 50 m, corresponding to an original ice cover of 2.5 m. This value for ice thickness also is similar to previous estimates (Redfield and Friedman, 1969).

5. Concluding remarks

Data from Baffin Bay demonstrate the presence of seawater having an excess alkalinity near the surface during the summer season which we attribute to calcium carbonate from sea ice meltwater. Higher near surface alkalinity values have been reported for other areas. For example, in the Weddell Sea, Weiss *et al.* (1979) report excess alkalinity values of about $28 \mu\text{eq kg}^{-1}$ in Summer Surface Water compared to Winter Water. They explain their high alkalinity values in terms of upwelled Warm Deep Water because they knew of no mechanism which would otherwise explain this rather large difference. Since there is a considerable amount of sea ice meltwater in the Summer Surface Water, we suggest that sea ice meltwater should be contributing to the excess alkalinity and could help account for the high values that Weiss *et al.* observed. High alkalinity values were also observed in near surface water in the Greenland Sea (Anderson and Dyrssen, 1981). These were subsequently ascribed to calcium carbonate from river input because, in contrast with our work, oxygen isotope ratios did not indicate the presence of any substantial amount of sea ice meltwater in this region (Tan *et al.*, 1982). Excess alkalinity in the West Spitzbergen Current on the other hand, can be accounted for by sea ice meltwater (Tan *et al.*, 1982).

For Baffin Bay we conclude, based on the close relationship between excess alkalinity and stable isotope measurements indicating the presence of sea ice meltwater and on determination of the composition of sea ice produced in the laboratory, that sea ice meltwater can increase the alkalinity of the surface seawater. Before quantitative conclusions can be drawn relating the amount of sea ice meltwater to the excess alkalinity, however, a much better knowledge is needed of the chemical composition of sea ice formed under natural conditions.

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