# Sea-ice meltwater and excess alkalinity in the East Greenland Current

Sea ice meltwater Oxygen isotopes Alkalinity East Greenland Current West Spitsbergen Current Eau de fonte de la glace Isotopes de l'oxygène Alcalinité Courant du Groënland Est

Courant du Spitsberg Ouest

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### ABSTRACT

The oxygen isotope method has been used to assess the importance of sea ice meltwater to the observed excess alkalinity in the surface waters of the Transpolar Drift Stream-East Greenland Current. Our results indicate that calcium carbonate releases due to the melting of sea ice can only contribute a maximum of 25% of the observed excess alkalinity (112  $\mu$ eq/kg). The principal source for this excess alkalinity must therefore be high alkalinity river inputs to the Arctic Ocean. In contrast, sea ice meltwater can readily account for all the observed excess alkalinity (10  $\mu$ eq/kg) in the surface waters of the West Spitsbergen Current.

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RÉSUMÉ

Eau de fonte de la glace de mer et alcalinité en excès dans le courant du Groënland Est

On a utilisé la méthode des isotopes de l'oxygène pour évaluer l'importance de l'eau de fonte de la glace de mer quant à l'alcalinité en excès observée dans les eaux de surface du courant de dérive transpolaire — courant du Groënland Est. Les résultats indiquent que le taux de dégagement de carbonate de calcium attribuable à la fonte de la glace de mer ne peut expliquer que 25% de l'alcalinité en excès observée (112 µeq/kg). La principale source de cette alcalinité en excès doit par conséquent être l'alcalinité élevée de l'eau des rivières se déversant dans l'Océan Arctique. Par contraste, l'eau de fonte de la glace de mer est facilement et à elle seule responsable de toute l'alcalinité en excès observée (10 µeq/kg) dans les eaux de surface du courant du Spitsberg Ouest.

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#### INTRODUCTION

High alkalinity in surface water in marine environments has generally been attributed to the presence of highly alkaline river water. Recently, Jones *et al.* (1982) proposed that calcium carbonate released from melting sea ice can result in high alkalinity in the surface water of Arctic or Antarctic ice-covered waters. This suggestion was based on Richardson's (1976) laboratory observation that approximately 2000  $\mu$ eq of calcium carbonate can be precipitated in 1 kg of sea ice upon freezing. The observed high alkalinity in Baffin Bay surface water was attributed to this effect (Jones *et al.*, 1982). During the Swedish Ymer 1980 expedition to the Svalbard (Fig. 1), Anderson and Dyrssen (1981) observed excess alkalinity (112  $\mu$ eq/kg) in the upper 50 m at some stations in the outflowing Transpolar Drift Stream-East Greenland Current but observed only a small excess alkalinity (10  $\mu$ eq/kg) in the inflowing Atlantic water (West Spitsbergen Current). These excess alkalinities were based on a comparison between the observed surface waters and the seawater component of North Atlantic inflowing water diluted with freshwater containing no hydrogen carbonate. Anderson and Dyrssen (1981) suggested that the excess in the outflow



Figure 1

Map of the study area showing station locations. Dashed line indicates position of surface front between the outflowing Transpolar Drift stream-East Greenland current and the inflowing West Spitsbergen current.

was due to the incorporation of highly alkaline waters from rivers of the Arctic basin in the Transpolar Drift Stream-East Greenland Current. They noted, however, that the role of sea ice meltwater must also be examined. The principles and application of stable isotope methods  $(H/D \text{ and } {}^{18}O/{}^{16}O)$  in the detection and study of sea ice meltwater have been described by Redfield and Friedman (1969) and Tan and Strain (1980). Tan and Strain (1980) have recently used <sup>18</sup>O/<sup>16</sup>O measurements to make quantitative estimates of the distribution of sea ice meltwater in surface waters of Baffin Bay and the adjoining sounds. Bédard et al. (1981) have applied the <sup>18</sup>O/<sup>16</sup>O method to coastal waters in Greenland and the Canadian Arctic. In the present paper, we use <sup>18</sup>O/<sup>16</sup>O data to assess the importance of sea ice meltwater at stations with excess alkalinity as reported by Anderson and Dyrssen (1981).

#### SAMPLING AND ANALYTICAL METHODS

The water samples analyzed for this study were collected in August and September 1980 during leg two of the Swedish Ymer 80 expedition and were generously supplied to us by Dr. Gote Ostlund of the University of Miami. The positions of the stations are shown in Figure 1. The <sup>18</sup>O/<sup>16</sup>O results that will be presented in this discussion are from stations 159, 153, 168 and 164 in the outflowing Transpolar Drift Stream-East Greenland Current and stations 102 and 105/106 in the Atlantic inflowing waters. The <sup>18</sup>O/<sup>16</sup>O ratios were determined by the CO<sub>2</sub>-H<sub>2</sub>O equilibrium technique and the isotope data reported with respect to standard mean ocean water (SMOW) in the usual  $\delta^{18}$ O notation. The precision of seawater isotope analysis is constantly monitored by analyzing a natural seawater standard with every batch of 24 water samples prepared. This internal standard, which has been in use for more than four years, has an overall single sample standard deviation of  $0.17^{\circ}/_{00}$ ,  $(\sigma_m = 0.02^{\circ}/_{00})$ , n = 62). The precision on some critical samples (notably the surface samples) was improved by duplicate analysis.

The following equation (from Tan, Strain, 1980) was used to calculate the concentrations of sea ice meltwater:

$$f_{si} = \frac{\delta - (AS + B)}{\delta' - (AS' + B)} \tag{1}$$

where  $f_{si}$  = fraction of water at a particular depth of sea ice origin;

 $\delta$ ,S = the  $\delta^{18}$ O, salinity of water at that depth;  $\delta'$ , S' = the  $\delta^{18}$ O, salinity of sea ice;

A,B = the slope, intercept of the deep water  $\delta^{18}$  O-S regression line.

#### **RESULTS AND DISCUSSION**

The <sup>18</sup>O/<sup>16</sup>O results are presented in Figures 2 to 7 and listed in the Table. Since there were no Svalbard sea ice cores available for  $\delta^{18}$ O and salinity analysis, ice core data from the area south of Davis Strait previously reported by Tan and Strain (1980) were used to calculate the concentrations of sea ice meltwater. Since  $f_{si}$  is not sensitive to the exact values of these two parameters, the use of the Davis Strait data does not significantly affect the resulting sea ice meltwater concentrations. The  $\delta^{18}$ O and salinity values are  $\delta' =$  $0.05^{\circ}/_{00}$  (1 $\sigma = 0.38^{\circ}/_{00}$ , n = 30) and S' =  $6.13^{\circ}/_{00}$  (1 $\sigma =$  $1.66^{\circ}/_{\circ\circ}, n = 104$ ).

The  $\delta^{18}O$ , S coordinates of surface samples may be offset from the deep water regression line by scatter or by a real change of slope in the  $\delta^{18}$ O-S curve. Since the question being addressed is whether calcium carbonate presence in sea ice meltwater can account for the observed excess alkalinity, we have assumed that any such small offsets in surface samples are real, and have excluded such data points from the deep water regression lines. The sea ice meltwater concentrations we report here are therefore upper limits.





 $\delta^{18}O$ -salinity data for station 159. The deep water regression line slope, intercept and correlation coefficient and  $\delta^{18}O$  precision are shown in the upper left; the maximum sea-ice meltwater concentrations are shown in the lower right.

#### Table

 $\delta^{18}O$ , alkalinity and related oceanographic data for selected stations from Ymer 80 expedition.

Station (position)	Depth* (m)	Salinity* (g/kg)	δ <sup>18</sup> Ο (SMOW)	A <sub>i</sub> * (µeq/kg)
159	15	32.09	-2.81	
(80°16.4'N 15°14'W)	25	32.44	2.62	2 2 6 4
	50 75	32.00	-2.38 -2.48	2 283
	100	33.42	-1.54	2 283
	125	33.93	-0.82	
	150	34.33	-0.12	2 296
	200	34.60	0.02	2317
	230	34.75	0.19	2 3 3 8
153	25	32.07	-2.82	2 2 3 9
(79°34'N 4°43'W)	50	32.97	-2.04	2 308
	75	33.38	-0.92	2 293
	100	33.97	-0.62	2 302
	200	34.40	-0.20	2 3 0 9
	300	34.87	0.10	2318
	500	34.92	0.22	2 3 1 8
	1 000	34.92	0.13	2 3 3 0
	1350	34.94	0.19	2351
164 (01041)NI 0006/WD	15	30.43	- 3.48	2159
(81 41 N 9 00 W)	20	31.67	-3.49	2 2 3 0
	30	31.75	-2.36	2250
	40	32.39	-2.42	
	50	32.59	-2.16	2 268
	60 70	32.83	- 2.19	
	75	33.40	-1.40	2 285
	80	33.27	-1.29	
	90	33.37	-1.07	
	100	34.05	-0.42	2 287
	200	34.51	-0.08	2312
	350	34.90	0.06	2335
	500	34.90	0.20	2 3 4 1
	750	34.91	0.17	2312
	1 380	34.91 34.93	-0.02	2319
168	5	30.02	-3.57	2545
(81°43'N 3°31'W)	10	31.28	-3.26	
````	20	31.39	- 3.40	
	25	31.88	-2.95	2 2 4 5
	40 50	32.73	- 2.08	2 277
	50 70	33.71	-0.80	2211
	100	34.08	-0.57	2 301
	150	34.39	-0.15	2 306
	300	34.88	0.29	
102 (91925) N 22920/E)	10	33.03	0.13	2215
(01 33 N 22 39 E)	50 50	34.13	0.00	2337
	100	34.80	0.14	2337
	150	34.94	0.10	2 3 4 4
	200	34.56	0.23	2340
	300	34.95	0.22	2340
	500	34.93	0.21	2 348
	750	34.93	0.46	2351
	1 000	34.92	0.17	2351
105/106	10	34.10	-0.29	
(82°30'N 18°41'E)	20	33.85	-0.24	2 2 6 5
	40 50	34.22 34.27	0.12 0.01	2 290 2 293
	100	34.33	-0.09	2316
	150	34.55	0.39	2312
	200	34.75	0.28	2 326
	- 300	34.90	0.28	2336
	1000	34.94	0.14	2 303
	2 000	34.93	0.23	2337
	3 1 2 5	34.95	0.24	2335

## Outflowing Transpolar Drift Stream-East Greenland Current

The results for the four stations (159, 153, 164, 168) located within the outflowing Transpolar Drift Stream-East Greenland Current are shown in Figures 2 to 5.

#### Station 159

There is no unequivocal evidence for the presence of sea ice meltwater at station 159 (Fig. 2). An inspection of the  $\delta^{18}$ O-S plot for this station suggests the presence of sea ice meltwater in the 15, 25 and 50 m samples. Samples from depths greater than or equal to 75 m are used to calculate the deep water parameters: A = 1.357, B = -46.98, correlation coefficient r = 0.982. The meltwater concentrations at 15, 25 and 50 m are 1.6, 0.9 and 0.2% respectively.

#### Station 153

There is not even a suggestion of sea ice meltwater in the surface samples at this station (Fig. 3) but this lack of evidence may simply reflect the small number of surface layer samples available.





#### Station 164

This station (Fig. 4) shows potential low surface concentrations of sea ice meltwater similar to station 159. Both stations are quite close to the east Greenland coast. Maximum meltwater concentrations are 2.9, 1.8, -0.2 and 2.2% at 15, 20, 25 and 30 m respectively. The negative meltwater concentration is an artifact of the scatter in the data.

\* From Anderson and Dyrssen (1980)





#### Station 168

This offshore station (Fig. 5) also shows the potential presence of meltwater. Surface meltwater concentrations are 1.4, 1.2, 0.3 and 0.1% at 5, 10, 20 and 25 m respectively.

#### Atlantic inflowing water (West Spitsbergen Current)

Surface waters at stations 102 and 105/106 north of Svalbard are more saline than waters in the Transpolar Drift Stream-East Greenland Current. The resulting narrow range of  $\delta^{18}$ O and salinity values through the water column makes the interpretation of these data



much more difficult. As Figures 6 and 7 show, the scatter in these closely packed data make it impossible to obtain a meaningful deep water regression line from the data at these stations alone. Another possible approach, which has been used in the interpretation of tritium data in this context (Ostlund, 1982), is to assign average values to the precipitation derived inputs, which can then be used to calculate the amount of sea ice meltwater present. However, evaluating the available oxygen isotope data from precipitation samples to yield an average precipitation value for a given ocean area is both difficult and subject to a large number of uncertainties. The alternative adopted here has been to calculate the sea ice meltwater concentrations using the deep water regression lines from stations 159, 153, 164 and 168. The ranges of sea ice meltwater concentrations in Figures 6 and 7 are the ranges of results obtained with the different regression lines. The slope and intercept of the straight lines drawn on these figures are average values for the four lines. Although the validity of applying deep water data from stations located in the surface outflow to surface water calculations at stations in the surface inflow might be questioned, three considerations suggest that this approach is a useful first approximation: 1) most of the deep water data at stations 102 and 105/106 fall on the average line within the  $\delta^{18}$ O measurement error; 2) the range of  $\delta^{18}$ O values for deep water masses of the world oceans is very small  $(<0.3^{\circ}/_{00})$ ; and 3) the estimated sea ice meltwater concentrations show only small variations with the regression lines used.

#### Alkalinity and sea ice meltwater

If it is assumed that sea ice accounts for all of the excess alkalinity observed in the Transpolar Drift Stream-East Greenland Current, the required sea ice alkalinity can be calculated from the simple relationship:

$$A_{si} = \frac{\Delta A}{f_{si}},\tag{2}$$

where  $\Delta A =$  excess alkalinity;

 $f_{st}$  = sea ice meltwater concentration;

 $A_{st}$  = sea ice alkalinity.

The term "sea ice alkalinity" may require some clarification, it is meant to represent the total alkalinity component due to sea ice melting. In the sea ice, the salts responsible may exist either as precipitates in the ice matrix or in solution in brine pockets. The latter however, cannot contribute to an excess in specific alkalinity except to the extent that carbonates are preferentially retained in the brines. Since Richardson (1976) has shown that calcium carbonate precipitates rapidly near the freezing point of seawater, we will assume that most of the carbonates in sea ice are in the solid phase and can affect the specific alkalinity.

For an excess alkalinity of  $110 \mu eq/kg$ , the sea ice alkalinity ranges from 5500 to 22,000  $\mu eq/kg$ , for a sea ice meltwater concentration range of 2.0 to 0.5%. This is substantially more than the sea ice alkalinity (2000  $\mu eq/kg$ ) observed by Richardson (1976) in the laboratory.

An alternative calculation of the sea ice alkalinity using field data yields an even lower value which implies an even smaller fraction of the excess alkalinity is due to sea ice. The following two assumptions can be used to calculate the maximum sea ice alkalinity contribution: 1) sea ice is assumed to retain all the carbonate salts trapped in the ice during initial formation, despite the reduction in salinity as the ice ages; and 2) carbonate



#### Figure 6

 $\delta^{18}$ O-salinity data for station 102. Estimated sea ice meltwater concentration ranges shown are the extreme values obtained by calculating concentrations using the deep water regression lines from the four stations in the outflowing water (Fig. 2-5). The straight line is the average of the four regression lines.



salts precipitated during freezing either redissolve when the ice melts or travel as suspended material with the meltwater and are redissolved during the laboratory acid alkalinity titration procedure. With these assumptions, it is possible to estimate the alkalinity in sea ice from the specific alkalinity for this area:

$$\frac{A_t}{S} = 0.0667$$

where  $A_t = \text{total alkalinity}$ , S = salinity (Dyrssen, unpublished data). Using a salinity value of  $20^{0}/_{00}$  for very young sea ice from Weeks and Lee (1962), the maximum sea ice alkalinity is 1334 µeq/kg, a value four times lower than that required to explain all the excess alkalinity for a sea ice meltwater concentration of 2%. In other words, sea ice meltwater can account for a maximum of 25% of the excess alkalinity in the outflowing Transpolar Drift Stream-East Greenland Current. This maximum value has been obtained with the following biases in the data analysis:

1) a high average value for the sea ice meltwater concentration (2%);

2) interpretation of the  $\delta^{18}$ O-S data to maximize  $f_{si}$ ;

3) the assumption that all of the available carbonate is converted to solid calcium carbonate during ice growth. The conclusion from this analysis is that sea ice contributes at most a relatively small fraction of the excess alkalinity in the surface water of the Transpolar Drift Stream-East Greenland Current. The principal source for this excess alkalinity must therefore be high alkalinity river inputs to the Arctic Ocean.

Equation (2) can also be used to assess the importance of sea ice meltwater as a source of excess alkalinity in the inflowing Atlantic water. Because of the very approximate nature of the meltwater contributions in this area, the sea ice alkalinity estimate of 1330 or 2000  $\mu$ eq/kg reported by Richardson (1976) and the excess alkalinity (10  $\mu$ eq/kg) will be used to derive the amount of meltwater required. The calculated  $f_{st}$  is 0.75 (1334  $\mu$ eq/kg) or 0.5% (2000  $\mu$ eq/kg) which is lower than all of the estimated surface sea ice meltwater concentrations in the Atlantic inflowing water (Fig. 6 and Fig. 7). It is quite possible then that sea ice accounts for all of the excess alkalinity found in the Atlantic inflowing water (West Spitsbergen Current).

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