

# Sea ice melt water, a source of alkalinity, calcium and sulfate?

## Results from the CESAR Ice Station

*Leif G. Anderson<sup>1)</sup> and E. Peter Jones<sup>2)</sup>*

<sup>1)</sup> Department of Analytical and Marine Chemistry, Chalmers University of Technology and University of Göteborg, S-412 96 Göteborg, Sweden.

<sup>2)</sup> Department of Fisheries and Oceans, Bedford Institute of Oceanography, P.O. Box 1006, Dartmouth, Nova Scotia, Canada B2Y 4A2.

### ABSTRACT

The objective of this work is to investigate the high surface total alkalinity and calcium concentrations found in the Arctic Ocean surface water to see if they are a result of input of sea ice melt water. The results are based on high precision determinations of chemical constituents of sea ice sampled at the CESAR Ice Camp in the western Arctic Ocean. Several samples showed relative enrichment compared to what would be observed in sea water of the same salinity. However, the enrichment was found to be much lower than expected from laboratory experiments.

It is concluded that if the sea ice samples analysed in this work are representative, sea ice melt water plays a minor role in the addition of total alkalinity and calcium to the surface waters of the Arctic Ocean.

### INTRODUCTION

The surface waters of Baffin Bay and north of Spitsbergen (Svalbard) in the Arctic Ocean have been found to contain higher total alkalinity ( $A_t$ ) than expected from the salinity (Jones et al. 1983; Anderson and Dyrssen 1980). Similar profiles for both total alkalinity and calcium were found at the CESAR Ice Station over the Alpha Ridge in the Canadian Basin of the Arctic Ocean. The salinity of the surface water is lower than that of the deeper waters, indicating that fresh water is the source of the excess alkalinity and calcium. In the Arctic Ocean there are two major fresh water inputs, runoff and sea ice melt water. The aim of this work is to investigate to what extent, if any, sea ice melt water is contributing to the above mentioned excess.

When sea water freezes, two phases are formed, a solid phase of ice crystals and a liquid phase of brine entrained in the ice. The chemical modifications that take place when sea ice is formed and aged in the laboratory have been treated in several papers (e.g. Nelson and Thompson 1954; Richardson 1976). The cause of the modifications is the formation of salts that start to precipitate in the brine at particular temperatures. Also, when sea ice is aged, the brine drains out of the ice, thereby reducing the bulk salinity of the ice. According to Richardson (1976) the first salt to precipitate as the temperature decreases is  $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$  (at  $-2.2^\circ\text{C}$ ) followed by  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  (at  $-8.2^\circ\text{C}$ ),  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (at  $-10^\circ\text{C}$ ) and  $\text{NaCl} \cdot 2\text{H}_2\text{O}$  (at  $-22^\circ\text{C}$ ). No other salts have their eutectic point above

TABLE 1

Salinity and total alkalinity of brine sampled from water drained into 10 cm deep core holes. The data are from Lyakhin (1970).  $\Delta A_t = A_t^{meas} - A_t^{calc}$ , where  $A_t^{calc}$  is based on a total alkalinity to salinity ratio of 0.0681  $mM_w / \text{‰}$ , or  $A_t / Cl = 0.123 mM_w / \text{‰}$ .

Brine temp. (°C)	Salinity $1.80655 \cdot Cl$	$A_t$ ( $mM_w$ )	$\Delta A_t$ $A_t^{meas} - A_t^{calc}$
-2.7	48.90	3.064	-0.266
-4.1	73.85	4.485	-0.544
-10.0	148.41	7.497	-2.610
-11.0	144.38	6.140	-3.692

-30°C, the lowest temperature which typically is encountered in natural sea ice. A plot drawn from the data of Richardson (1976) shows the percentage of the different ions that are precipitated in the brine at different temperatures (Fig. 2). At temperatures above -20°C the relative amount of precipitated cations is fairly low, that for calcium being highest (up to 17%). In the case of anions both sulphate and total carbonate are more than 45% precipitated at temperatures below -10°C.

There is no doubt that some salts precipitate when sea ice is forming, but are the precipitated salts trapped in the ice or are they drained out together with the brine? From publications of chemical investigations of natural sea ice one does not get a direct answer. Reeburgh and Springer-Young (1983) concluded that sulfate is both enriched and depleted in sea ice depending on its age. Overgaard et al. (1983) found excesses of sulfate and calcium plus magnesium in the top 70 cm of a core taken in an East Greenland fjord. Lyakhin (1970) reported increased relative alkalinity values for the youngest form of sea ice. He also found reduced alkalinity:chlorinity ( $A_t/Cl$ ) ratios in brine drained into core holes made in the ice, with the  $A_t/Cl$  ratio significantly lower at lower ice temperatures (Table 1).

## METHODS

### Sampling

The samples were taken in May 1983 at the CESAR Ice Camp, located over the Alpha Ridge in the Arctic Ocean at approximately 86°N, 110°W. The water sampling was carried out using a rosette sampler with Niskin bottles attached to a CTD probe. Ice samples were taken with a corer as well as by chopping pieces out of ice flows. The samples labelled E1-E3 were taken out of the wall in a hole cut through the main camp ice flow. After sampling, the ice was cut and put in Mason glass jars, stored frozen at the camp and thereafter refrigerated until analyzed.

### Chemical analyses

The water samples were determined for total alkalinity immediately after sampling, while all other analyses were performed at the laboratory up to two months after sampling.

The alkalinities of the sea water samples were determined by potentiometric titration with a curve fitting evaluation (Johansson and Wedborg 1982). The alkalinities of the sea ice samples were determined by photometric titration with a Gran evaluation (Anderson and Wedborg 1983).

Calcium was titrated with EGTA using photometric detection (Anderson and Granéli 1982), chlorinity was titrated with silver nitrate using potentiometric detection (Jagner and Årén 1970) and sulfate was titrated in dimethylsulphoxide (DMSO) medium with hydrochloric acid using photometric detection (Jagner 1970). The calcium, chlorinity and sulfate titrations were all evaluated by the Gran function technique.

The precision of the determinations was within  $\pm 5 \mu M_w$  for alkalinity and calcium,  $\pm 25 \mu M_w$  for sulfate and  $\pm 0.01$  g/kg for chlorinity, all expressed as  $\pm \sigma$ . The accuracy was estimated by titration of standard seawater (P-88), diluted with distilled water



to cover the whole salinity range, and should be within limits not larger than twice those of the precision.

The conductivity – salinity was measured using a Guildline Autosol model 8400 salinometer (salinity precision within  $\pm 0.002$  ‰).

## RESULTS

Depth profiles for normalized total alkalinity ( $A_t-35 = A_t \cdot 35/\text{Sal.}$ ) and normalized calcium ( $\text{Ca}-35 = \text{Ca} \cdot 35/\text{Sal.}$ ) in the top 500 metres are shown in Figure 1. The normalizing was done to emphasize effects not due to changes in salinity. A distinct ex-

cess of calcium in the top 75 metres is seen. The total alkalinity shows excess down to about 130 metres. However, between 75 and 130 metres the excess is some  $25 \mu\text{M}_w$  lower than at the surface and probably of a different origin (Jones and Anderson, in prep.). The scatter in the calcium profile, which is outside the analytical precision, is most likely due to dissolution or precipitation during storage. No excess outside the analytical precision in normalized sulfate was detected in the surface waters.

The sea ice data are summarized in Table 2. The delta values tabulated are the differences between the measured concentrations and that of standard sea water diluted to the

TABLE 2

*Conductivity-salinity, chlorinity, total alkalinity, calcium and sulfate concentrations in sea ice sampled at the CESAR Ice Station in May 1983. Delta values are measured concentrations minus those expected for standard sea water of the same salinity.*

	Sal cond.	Cl g/kg	$A_t$ $\mu\text{M}_w$	$\Delta A_t$ $\mu\text{M}_w$	Ca $\mu\text{M}_w$	$\Delta \text{Ca}$ $\mu\text{M}_w$	$\text{SO}_4$ mM <sub>w</sub>	$\Delta \text{SO}_4$ mM <sub>w</sub>	
A1	0–20 cm	11.329	6.39	787	13	3253	-74	8.393	-0.747
A2	20–35 cm	7.543	4.23	516	1	2164	-51	5.989	-0.097
A3	35–53 cm	6.058	3.49	416	2	1741	-38	4.670	-0.218
B1	0–10 cm	4.674	—	242	-77	1343	-30	—	—
B2	10–21 cm	6.800	—	371	-93	1949	-48	—	—
B3	21–32 cm	5.120	—	207	-143	1468	-36	—	—
B4	32–43 cm	5.847	—	225	-174	1671	-46	—	—
C1	0–12 cm	6.126	3.57	445	27	1774	-25	4.306	-0.664
C2	12–20 cm	3.956	2.31	282	12	1141	-21	2.756	-0.436
C3	20–31 cm	6.325	—	422	-10	1781	-77	6.107	1.004
D1	0–15 cm	0.087	-0.02	109	103	30	4	—	—
D2	15–30 cm	0.168	—	39	28	47	-2	—	—
D3	30–48 cm	0.497	0.20	94	60	150	4	—	—
D4	48–75 cm	0.830	—	10	-47	237	-7	—	—
D5	75–141 cm	1.541	0.84	206	101	460	7	1.042	-0.201
D6	141–172 cm	2.329	—	117	-42	684	0	—	—
E1	59 cm from surface	2.110	—	237	93	631	11	—	—
E2	110 cm from surface	3.701	—	275	22	1078	-9	—	—
E3	170 cm from surface	3.402	—	260	28	993	-6	—	—
1	Water collected under 2 cm new ice	31.946	17.84	2272	90	9411	27	25.600	-0.174
2	Water from core hole in the ice	24.558	13.86	1613	-64	7215	2	17.150	-2.663
3	Slush from on top of new ice	34.016	18.64	2354	31	9909	-81	32.663	5.219
4	Very new ice, 2 cm thick	19.915	10.95	1404	44	5710	-149	16.000	-0.067
5	Icicles from bottom of floe in pressure ridge	39	21.46	2807	143	11538	84	34.534	3.069
6	Ice from fresh water lake on top of ice	0.256	—	57	40	66	-9	—	—
7	Ice from bottom of first year ice	3.271	1.77	237	14	947	-14	2.141	-0.498
8	Ice from vertical ice floe in pressure ridge	2.174	—	192	44	630	-9	—	—
9	Ice floe	2.565	—	181	6	730	-23	—	—

salinity of the sample. The delta values for sulfate, total alkalinity and calcium versus salinity are plotted in Figure 3.

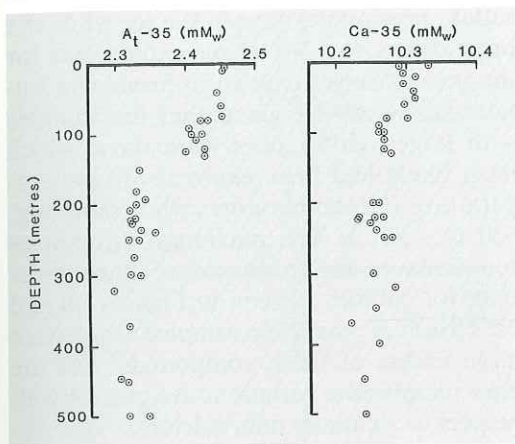


Fig. 1. a) The normalized total alkalinity and b) normalized calcium concentrations in the upper 500 metres of the western Arctic Ocean at the CESAR Ice Station, May 1983.

DISCUSSION

As the aim of this investigation was to study the effects of sea ice melt water on the chemical composition of the surrounding waters, conductivity-salinity was used as salinity reference. This will cause a slight error as the conductivity-salinity function changes slightly with changing ionic composition. For exact calculations a conservative quantity is needed, for example an ion that is not incorporated in any precipitations within the expected temperature range. Chloride does not start to precipitate until below  $-22^{\circ}\text{C}$  (see Fig. 2). Therefore the chlorinity (determined by silver nitrate titration) in some samples was used to investigate the effect of ion composition on the conductivity-salinity. The differences between  $1.80655 \cdot \text{Cl}$  and conductivity-salinity for the samples in Table 2 are within  $-0.13$  to  $+0.32$  g/kg, except for the samples

the CESAR water of the

$\Delta SO_4$   
 $M_W$   $mM_W$

393	-0.747
989	-0.097
670	-0.218
—	—
—	—
—	—
—	—
306	-0.664
756	-0.436
107	1.004
—	—
—	—
—	—
—	—
042	-0.201
—	—
—	—
—	—
600	-0.174
150	-2.663
663	5.219
000	-0.067
534	3.069
—	—
141	-0.498
—	—
—	—

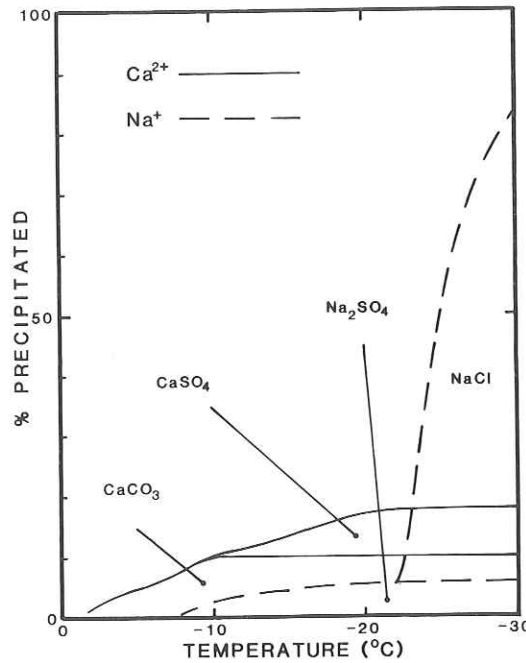
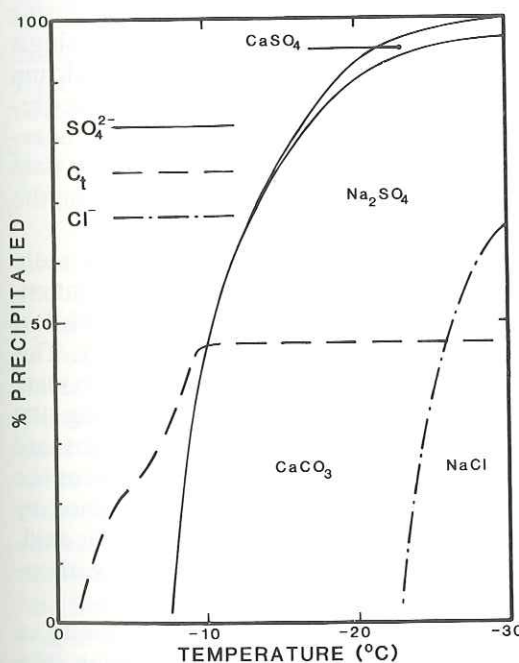


Fig. 2. The relative amounts of precipitation for a) anions and b) cations in standard sea water at sub-freezing temperatures. Redrawn from Richardson (1976).



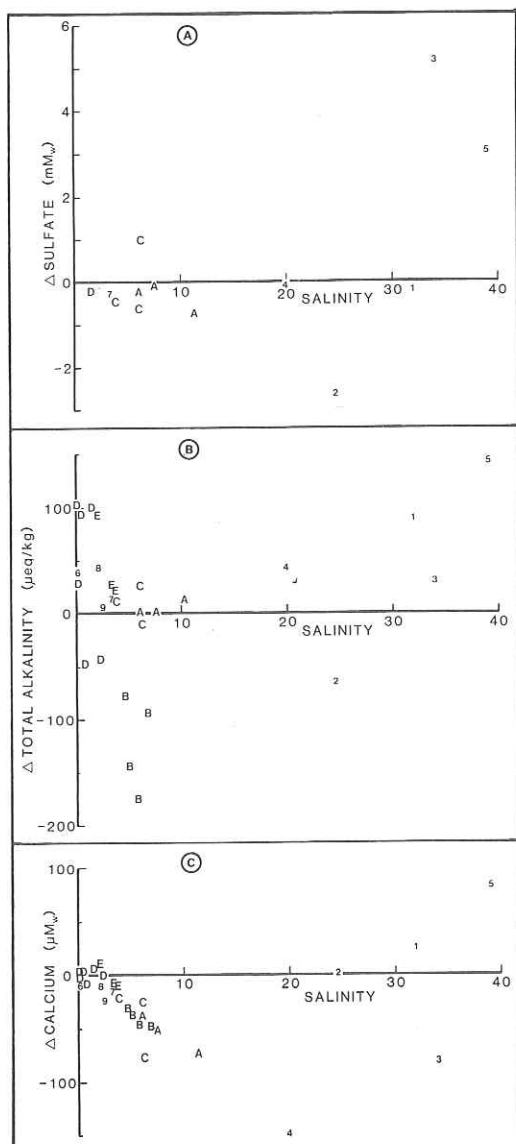


Fig. 3. a) Delta sulfate, b) delta total alkalinity and c) delta calcium versus salinity for different types of sea ice. Symbols from Table 2.

having delta sulfate larger than  $\pm 1 \text{ mM}_w$ . These have differences up to  $0.48 \text{ g/kg}$  with, as expected, the conductivity-salinity higher than the chlorinity-salinity for samples having excess sulfate. The maximum sulfate excess is, as seen in Figure 3a, for the high sal-

inity samples (icicle and ice slush), while the only significant deficit is for the sample taken from the water drained into a core hole. The latter result indicates that the sulfate precipitate stays in the ice while the brine drains out. No simple explanation for the mechanisms involved in producing sulfate excess can be given, but the samples with largest differences were those which most likely had been exposed to low temperatures (air temperatures while sampling,  $-20$  to  $-30^\circ\text{C}$ ). The maximum differences for alkalinity and calcium were much lower than for sulfate, as seen in Figures 3b and 3c. However, the icicle samples also have a large excess of these compounds. For the core samples the variations are greater with respect to alkalinity than calcium.

The low delta values in Figures 3b and 3c are most likely the result of either addition of brine having a deficit or, especially in the case of calcium, of calcium carbonate having precipitated in the sample (before or after sampling) and not dissolving during the titration. The latter is examined using a delta total alkalinity versus delta calcium plot (Fig. 4). When calcium carbonate precipitation or dissolution in the ice is responsible for the excess or deficit, the data points should fall close to a line having the slope 2:1.

As can be seen in Figure 4 there is a tendency for the values to follow this relation, but there are a couple of points with low calcium content but not low alkalinity. This could be explained by calcium carbonate particles not being measured during the calcium titration, since the titrations are done in a near neutral solution whereas the total alkalinity values were determined by titrating the samples with hydrochloric acid, most likely dissolving any calcium carbonate particles present.

The maximum excess total alkalinity in Figure 4 is about  $100 \mu\text{M}_w$  resulting in a calcium carbonate excess of  $50 \mu\text{M}_w$ . The surface water excess shown in Figure 1 is

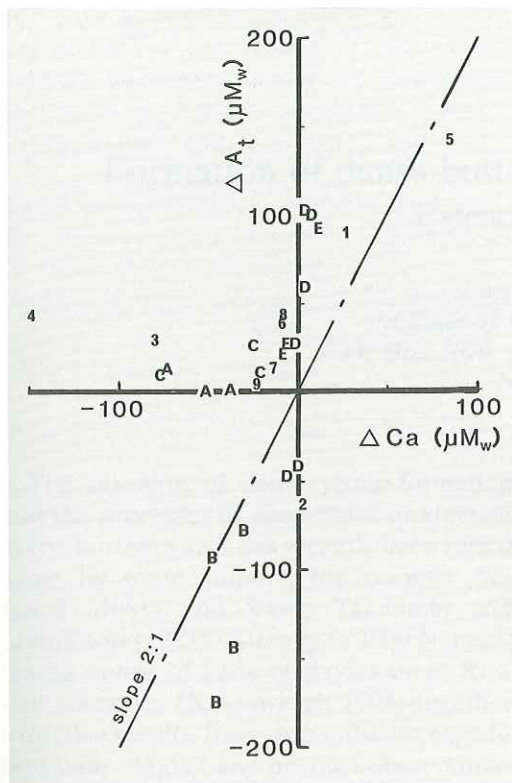


Fig. 4. Delta total alkalinity versus delta calcium. The numbers and letters correspond to the samples described in Table 2. A line with a slope of 2:1, representing precipitation or dissolution of calcium carbonate, is drawn for comparison.

close to  $120 \mu\text{M}_w$  for total alkalinity and about half of that for calcium. With a salinity at the surface of about 31 compared to 35 for the deeper waters, there is a fresh water content of around 10% at the surface. This means that the fresh water component must have a total alkalinity and calcium concentration of  $1200 \mu\text{M}_w$  and  $600 \mu\text{M}_w$  respectively, in order to account for the surface concentrations. However, the maximum excesses measured in the sea ice are less than one tenth of these values making sea ice melt water a highly unlikely source. To explain the high surface concentrations we instead have to look at the runoff from large rivers, especially from Siberia, which

have a mean total alkalinity of over  $1000 \mu\text{M}_w$  (Anderson et al. 1983).

## CONCLUSIONS

1) The excess of total alkalinity and calcium in the ice is not great enough to give measurable effects to account for the sea water composition in the Arctic Ocean surface water.

2) There are modifications of total alkalinity, calcium and sulfate in sea ice but it is not clear how much precipitate remains in the ice and how much may be removed by the brine as it drains from the ice.

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