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Author

H. J. McLellan

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Introduction

Early investigations into the effect of freezing upon the salts in sea water were carried out by Ringer (Krummel, 1907). He cooled small quantities of sea water and noted that sodium sulphate began to crystallize out at -8.2 °C. while sodium chloride did not begin to separate out until -23 °C. From the results of his experiments it was reasoned that the formation of sea ice might have a pronounced effect upon the ionic ratios in sea water. The constancy of ionic ratios had been a basic concept of oceanography since the voyage of the H.M.C.S. "Challenger" (Dittmar 1884). Ringer's work, then, since it suggested that the density chlorinity relationship might not hold for waters which had been subjected to freezing, cast doubts upon the results of classical oceanography for Northern waters.

During the Maud Expedition, Sverdrup (1929) determined the chlorinity of sea water and ice samples from the Siberian Shelf by two methods: by titration with Ag NO_3, and by hydrometer and reduction through Knudsen's hydrographic tables. He found that, relative to the chloride content, the density was consistently low for the melted ice and high for the water below the ice. This he interpreted as indicating an excess of chloride ions in the ice, and inferred a sulphate deficit since these are the only anions found in significant quantities in sea water.

The order of differences found is indicated by the results of freezing experiments carried out at the same time. These are tabulated below. The figure Δ Cl is the Chlorinity by titration less the Chlorinity as computed from the density.

Results of freezing experiments carried out during the "Maud" Expedition (Sverdrup 1929).

Air Temperature	-13° C.		-15° C.		-14° C.	
	Cl	Δ Cl	Cl	Δ Cl	Cl	Δ Cl
Water before freezing	16.92	-0.030	2.94	-0.125	14.90	-0.045
Water after	18.52	-0.045	3.63	-0.135	15.79	-0.040
Ice	7.12	0.030	1.59	-0.075	5.41	0.025

Wiese (1930), during the "Sedoff" expedition, subjected surface waters to analysis for chlorinity by titration and for sulphate content by gravimetric determination. For 12 stations in Franz Joseph Land Sound and Queen Victoria Sound, and 7 stations in the Barent Sea, he found SO_4/Cl ratios from 0.1406 to 0.1429 in the water above 25 metres. These ratios are somewhat higher than for normal sea water where the value is 0.1394 (Thompson, Johnson and Wirth 1931). These abnormalities Wiese explained by the large contribution to the surface layer from melting ice. He contended that the sea ice contained on excess of SO_4 ion as was to be expected from Ringer's observations. At the most northerly of the Sedoff stations, station 7 (Lat. 82° 14'N, Long. 52° 10'E) abnormally low ratios (0.1370 to 0.1385) were obtained. Here, explained Wiese, large quantities of ice are formed and are moved out of the area before melting. Wiese also examined the ratio in sea ice, obtaining values from 0.1405 to

0.1478 in 100 cm. of year old ice.

These conflicting results of Wiese and Sverdrup leave one in doubt as to what effect freezing does have upon the salt ratios in sea water, and present the possibility that some of the disagreement may be due to the different methods of approaching the problem. It was considered of interest to carry out freezing experiments where water and ice samples could be examined for chlorinity, sulphate and density.

Experimental

The first experimental freezings to be discussed here were carried out in a cold room at U.S. Naval Electronics Laboratory which was kindly provided by Dr. Waldo Lyon. The tank used was constructed of plywood with horizontal inside dimensions 35 inches by 35 inches and filled to a depth of 31 inches with filtered sea water from the laboratory system of Scripps Institution of Oceanography. The tank was insulated on the sides and bottom so that the greater part of the heat loss would be from the surface. Two ice covers were formed and sampled in this tank. The first, 1½ inches thick, on April 24th, 1950; the second, ¾ inches to 1 inch thick sampled May 31st, 1950, and 1 inch to 1½ inches thick sampled June 1st, 1950. It was not possible at this time to have the cold room operating at full efficiency, so freezing was carried out at room temperatures of approximately -8 °C.

Densities were determined with a Richter and Wiese total immersion hydrometer with sufficient accuracy to give chlorinities to ±0.01 °/oo. All chlorinities were determined by the Knudsen method of titration against standard water with Ag NO_3. A number of determinations were made on each sample to determine a best value. In no case did individual determinations vary by more than 0.02 °/oo Cl.

Sulphate was determined gravimetrically by precipitation as Ba SO_4 (Thompson et al. 1931). Each test was made in triplicate in quantities to give over 0.5 gms. of precipitate. Repetition was obtained to 0.001 gms.

These determinations could be expected to yield values of ΔCl with a maximum error to ±0.03 °/oo and SO_4/Cl ratios with maximum error ±0.00035.

Only densities were determined at La Jolla for samples from the second freezing experiment. The remainder of the work was completed in the laboratory of the Atlantic Oceanographic Group at St. Andrews, New Brunswick. The densities were re-determined at St. Andrews with a set of Knudsen Hydrometers before continuing the analyses and the values obtained checked to within the accuracy of these instruments.

The results of these experiments are tabulated below.

Freezing experiment 7 April to 24 April, 1950.

	Chlorinity °/oo Titration	Chlorinity °/oo Hydrometer	ΔCl ±0.03	SO_4 °/oo	SO_4/Cl ±0.00035
Before Freezing					
Top	18.85	18.90	-0.05	2.622	0.1391
Bottom	18.85	18.99	-0.14	2.636	0.1399
<u>24 April</u>					
Ice	8.98	8.51	0.47	1.267	0.1412
Top	19.97	20.10	-0.13	2.781	0.1393
Bottom	19.98	20.15	-0.17	2.782	0.1393

Freezing experiment 22 May to 1 June, 1950.

	Chlorinity Titration	°/oo Hydrometer	ΔCl ±0.03	SO_4 °/oo	SO_4/Cl ±0.00035
Before Freezing					
Top	19.35	19.33	-0.02	2.678	0.1384
Bottom	19.31	19.32	-0.01	2.678	0.1387
31 May					
Ice	8.99	8.98	-0.01	1.255	0.1396
Water	19.94	19.95	-0.01	2.741	0.1375
1 June					
Ice	7.63	7.63	0.00	1.069	0.1401
Water	20.12	20.09	-0.03	2.781	0.1382

The variations between top and bottom in density and sulphate before the first freezing may have been due to a previous freeze that was not sampled. The mean value of the SO_4/Cl ratio was 0.1395. Anderson and Revelle (1947) give 0.1396 for the mean of five samples from the Pacific Ocean.

The first ice sample showed a very large increase in ΔCl to 0.47. This variation is in the same direction as reported by Sverdrup but of a higher order of magnitude. Coupled with this the SO_4/Cl ratio was high (0.1412) in the ice sample. That is, referred to the chloride content, the sulphate content increased and the density decreased in the melt water. To date no mechanism has been visualized which would make these two changes compatable.

The first ice cover was removed some time before the second freezing experiment and the result can be seen in the lower ratio before freezing. Both the ice samples from this experiment showed a small increase in SO_4/Cl ratio and the water below the ice cover showed a slight tendency towards a lowered ratio. In this case, there were no measurable deviations in ΔCl.

Subsequent freezing experiments were carried out at St. Andrews, New Brunswick, in a similar tank with horizontal dimensions 8 feet by 4 feet filled to a depth of 45 inches with water pumped from Passamoquoddy Bay near the mouth of the St. Croix River. The freezing in this case was carried out in the open air during January 1951. The first ice cover began to form on the morning of January 22nd, and had grown to a thickness of three and one-half inches in two days. Air temperatures over the period ranged from a maximum of 2° C. to about -20° C. Samples were taken on January 24th. Following a period of mild weather and heavy rains the remains of the ice cover were removed from the tank and a second freezing experiment begun. Ice began to form on the evening of January 26th, and was three and one-half inches thick when sampled on January 29th. This had increased to seven and one-quarter inches by February 1st, when the final samples were taken. The sample here taken from the upper four inches of the ice cover is the only one that was not subject to some contamination from the underlying water during collection.

Analyses were carried out on the samples from these experiments in the same manner as those already mentioned. In this case, however, density was determined by means of a set of Knudsen hydrometers and the same accuracy can not be claimed. A good estimate of the maximum error seems to be ± 0.03 ‰ in chlorinity. This given a maximum error in Δ Cl of ± 0.05 ‰. The results obtained are tabulated below.

Freezing experiment 16 January to 24 January, 1951.

	Chlorinity Titration	°/oo Hydrometer	Δ Cl °/oo (±0.05)	SO_4 °/oo	SO_4/Cl (±0.00035)
Before Freezing					
Top	16.43	16.33	+0.10	2.275	0.1385
Bottom	16.42	16.38	+ 0.04	2.273	0.1384
24 January					
Ice	7.17	7.01	+0.16	1.013	0.1413
Top	20.18	20.13	+0.05	2.798	0.1386
Bottom	17.39	17.33	-0.06	2.395	0.1378

Freezing experiment 26 January to 1 February, 1951.

	Chlorinity Titration	°/oo Hydrometer	Δ Cl °/oo (±0.05)	SO_4 °/oo	SO_4/Cl (±0.00035)
Before Freezing					
Top	16.65	16.52	+0.13	2.315	0.1390
Bottom	18.62	18.49	+0.13	2.581	0.1386
29 January					
Ice	8.68	8.24	+0.44	1.220	0.1406
Top	17.89	17.80	+0.09	2.484	0.1388
Bottom	18.01	17.94	+0.07	2.507	0.1392
1 February					
Ice (Top 4")	5.09	5.14	-0.05	0.782	0.1477
Ice (bottom 4")	7.78	7.85	-0.07	1.093	0.1406
Water (top)	19.35	19.33	+0.02	2.680	0.1385
Water (bottom)	21.37	21.41	-0.04	2.964	0.1387

Again, in all cases, there was observed a definite increase in SO_4/Cl ratio in the ice samples. The sample taken from the top 4" on February 1st, the only completely dry sample taken, showed a ratio of 0.1477, as high as any observed by Wiese.

As in previous observations, there was no consistency in the observed Δ Cl. The ice of January 24 showed an increase to

+ 0.16 with no measurable change in the water. In the second experiment the ice sample of January 29th had a Δ Cl of +0.44, of the same order as that observed April 24th, 1950. At this time there was an apparent drop in ΔCl for the water, though not beyond the limits of maximum error (±0.05). The same ice, sampled two days later, showed values of Δ Cl -0.05 and -0.07 while the water below showed +0.02 and -0.04. These values are all lower than that for the original water (+0.13).

One may conclude from the above experiment that when sea water freezes, there is a selective retention of sulphate in the ice, with a resulting increase in the SO_4/Cl ratio for the melt water. A corresponding decrease in this ratio takes place in the water below the ice.

Further experimentation, with the observation of more variables, is required before anything definite can be said regarding variations in Δ Cl.

Observations on the SO_4/Cl ratio of Coastal Waters

Following the experiments detailed above a number of samples from Canadian Atlantic Coastal waters were analysed for SO_4/Cl ratio in an attempt to determine whether the ice formation and melting that takes place here has any measurable effect on this parameter.

These waters, for most of the year are characterized by very high stabilities and a marked layer of minimum temperature at mid-depths. Stretching along the Nova Scotia coast, where it roughly follows the edge of the continental slope, and cutting eastward south of the Grand Banks, is a region of strong horizontal gradients both of temperature and salinity which delimits the outer boundary of the coastal waters (Sandstrom, 1919, Smith, Soule and Mosby, 1937).

The cold water layer has a minimum temperature as low as -1.85° C. on the outer coast of Newfoundland and Labrador. Here it may extend to depths greater than 200 metres and is associated with the Labrador current. In the Gulf of St. Lawrence, the minimum temperature is as low as -1.5° C. in the Spring and is modified throughout the year in temperature and thickness. The core of this layer has a depth of about 75 to 100 metres and it overlies modified Atlantic water of higher salinity and temperature. The well mixed surface layer is subject to extreme fluctuations in temperature and salinity and varies in thickness from 5 to over 60 metres (Lauzier, Trites and Hachey, 1951).

The same type of three layer stratification occurs on the Scotian Shelf although the minimum temperature here seldom falls below 0° C. (Hachey, 1942).

Each year large quantities of sea ice are formed along the Labrador and Newfoundland coasts, over much of the Gulf of St. Lawrence and in sheltered waters on the Nova Scotia Coast. (U.S. Hydrographic Office Ice Atlas 1946). In Spring this ice moves out as a pack and may extend as far as Sable Island where it presumably dissipates itself in contact with the warm slope waters. The observable effect upon the SO_4/Cl ratio will be determined by what portion of the ice melts in the region of formation, the depth of vertical circulation during ice formation, and the rate of replacement of surface waters.

Samples were available from a number of stations about the area which had been occupied in 1950 by the Hydrographic Service of Canada and the Atlantic Oceanographic Group. The samples were collected for chlorinity titrations and it was necessary to lump several samples in order to obtain large enough quantities for sulphate analyses. It was not possible to run check determinations on many of the samples so the results may contain accidental errors which can not be determined.

Data for five of the stations examined are tabulated below.

C.G.S. Acadia Station 10
2 June 1950
Lat. 46°46.3'N., Long. 52° 43.3'W.

Depth (metres)	T °C.	S °/oo	SO_4/Cl
0	2.8	32.36)	
10	2.64	32.38)	0.1392
25	2.10	32.43)	
50	0.32	32.81 -	0.1383
100	-1.40	33.12)	
150	-1.60	33.30)	0.1388
200	-1.58	33.28)	

C.G.S. Acadia Station 14
18 July 1950
Lat. 49°01.5'N., Long. 52° 04.2'W.

Depth (metres)	T °C.	S °/oo	SO_4/Cl
0	10.4	31.17)	
10	10.08	31.27)	0.1386
25	1.47	31.89 -	0.1388
50	-1.30	32.50	
100	-1.60	32.90)	
150	-1.60	33.06)	0.1390
200	-1.45	33.19)	
250	-1.25	33.30	
300	-0.78	33.51	0.1397

C.G.S. Acadia Station 18
August 1950
Lat. 51°54.8'N., Long. 55°41.0'W.

Depth (metres)	T °C.	S °/oo	SO_4/Cl
0	2.5	32.14)	0.1393
10	1.52	32.32)	
25	-1.30	32.63	0.1395
50	-1.60	32.84)	
100	-1.57	32.94)	0.1393
150	-1.55	33.04)	

C.N.A.V. Whitethroat Station 2 - 27
25 August 1950
Lat. 45°29'N., Long. 59°31'W.

Depth (metres)	T °C.	S °/oo	SO_4/Cl
0	15.6	30.99)	0.1395
10	13.5	30.97)	
20	12.4	31.18)	0.1385
30	11.2	31.18)	
50	1.1	32.21	0.1395
75	0.7	32.54)	
100	1.0	32.83)	0.1386
130	1.1	32.90)	

C.N.A.V. Whitethroat Stations 5 - 37
9 November 1950
Lat. 47°26'N., Long. 59°33'W.

Depth (metres)	T °C.	S °/oo	SO_4/Cl
0	5.5	31.85	
10	5.5	31.91)	
20	5.4	31.92)	0.1380
30	5.2	32.10)	
50	1.1	32.59	
75	0.5	32.77)	0.1382
100	0.4	32.88)	

At Acadia Station 10, off the South East corner of Newfoundland, the surface layer showed a somewhat higher ratio than the deeper waters. This could be due to the effect of ice melting at the surface, or due to a mixture of oceanic waters. Acadia Station 14, southeast of Funk Island on the east coast of Newfoundland, showed a ratio between 0.1386 and 0.1390 down to below the core of the cold water. The deepest sample (300 metres) had a ratio of 0.1397, close to the normal for oceanic waters. This is to be expected, as surface phenomena will have very little effect on waters below the cold layer. Acadia Station 18, at the entrance to the Strait of Belle Isle, showed no anomaly from zero to 150 metres, the ratio being essentially that for ocean water.

Whitethroat Stations 2-27, well in on the Scotian Shelf southeast of Cape Breton Island, showed an alternation from high to medium values. One or more of these values may have been the result of accidental errors. No samples were available for checking the sulphate determinations.

Whitethroat Station 5-37, in Cabot Strait, showed in the surface and cold water layers, a ratio which is markedly low (0.1380 and 0.1382). This corresponds to observations within the Gulf as detailed below.

Composite samples were made from three stations in a crossing from Gaspe to Anticosti on the 1st of September, 1950 (Whitethroat 2-46, 2-47, 2-48). Figure 1 shows the location of samples, temperature and salinity, the composition of the composite samples and their SO_4/Cl ratios. The core of the cold water layer and the waters below showed values of 0.1390 and greater. The marked tendency towards lowered values in the surface layers (0.1381 to 0.1387), together with similarily low values observed in Cabot Strait (Whitethroat Station 5-37), may be interpreted as the effect of the formation of large quantities of ice which subsequently drift out of the area and melt elsewhere.

The fact that this ratio variation is observable in September is suggestive of a long term internal circulation of the surface layers in the Gulf with no large replacement.

Figure I.

Gaspe Section — 1 September 1950

Station	2 - 46		2 - 47		2 - 48	
Lat. N.	49° 30'		49° 36'		49° 43'	
Long. W.	64° 34'		64° 30'		64° 25'	
Depth (metres)	T °C.	S °/oo	T °C.	S °/oo	T °C.	S °/oo
0	13.5	29.3	12.9	29.7	12.4	29.5
10	13.3	29.3	13.0	29.8	12.1	29.5
	SO_4/Cl = 0.1381		SO_4/Cl = 0.1381			
20	5.5	31.2	3.3	30.6	4.1	30.1
30	1.4	31.6	2.7	31.3	3.3	30.9
					SO_4/Cl = 0.1387	
50	-0.3	32.4	1.0	32.1	1.6	31.8
			SO_4/Cl = 0.1384			
75	-0.5	32.6	0.0	32.5	0.1	32.4
100	0.5	33.0	-0.1	32.6	0.0	32.8
				SO_4/Cl = 0.1390		
150	2.4	33.6	2.0	33.4	1.5	33.2
200	3.7	34.0	3.7	33.9	3.2	33.7
			SO_4/Cl = 0.1393			
300	4.8	34.5	4.9	34.5	4.7	34.5
350			5.0	34.7		
			SO_4/Cl = 0.1390			

Discussion

The experimental work herein described confirms the idea of selective retention of sulphate in sea ice and the implication regarding the constancy of ionic ratios in ice areas is obvious. A recent work by Lewis and Thompson (1950) shows similar results and attributes the effect to crystallization of sodium sulphate at the lowest experimental temperatures and to absorption of SO_4 ions at the higher temperatures (Repa 1938). The variations in density observed, together with the observations of Sverdrup (1929), point to the existence of some other transformation associated with the freezing process, whose nature is not evident from these results.

The field observations from the Canadian Atlantic indicate that ice formation and melting do indeed have their effect upon the ionic ratios in these waters. This is particularly true of the Gulf of St. Lawrence. Here it might have been expected that the accumulation of land drainage with its very high sulphate-chlorinity ratio would establish a regime of high sulphate content. That the ratio was found to be low in the surface layers indicates that the reduction has been brought about by repeated freezing of ice which melts elsewhere. It also points to the existence of a long term internal circulation of these waters.

Summary

1. Experimental freezings show a selective retention of sulphate ions in sea ice with consequent abnormal SO_4/Cl ratios in melt water and water left behind on freezing.
2. Density variations which were not consistent but usually

of opposite sign to those expected from sulphate variation were observed.

3. Field observations from the Canadian Atlantic indicate that the ratios may often be abnormal. In particular the surface layer of the Gulf of St. Lawrence shows depletion of sulphate due to formation of ice which melts elsewhere.

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