

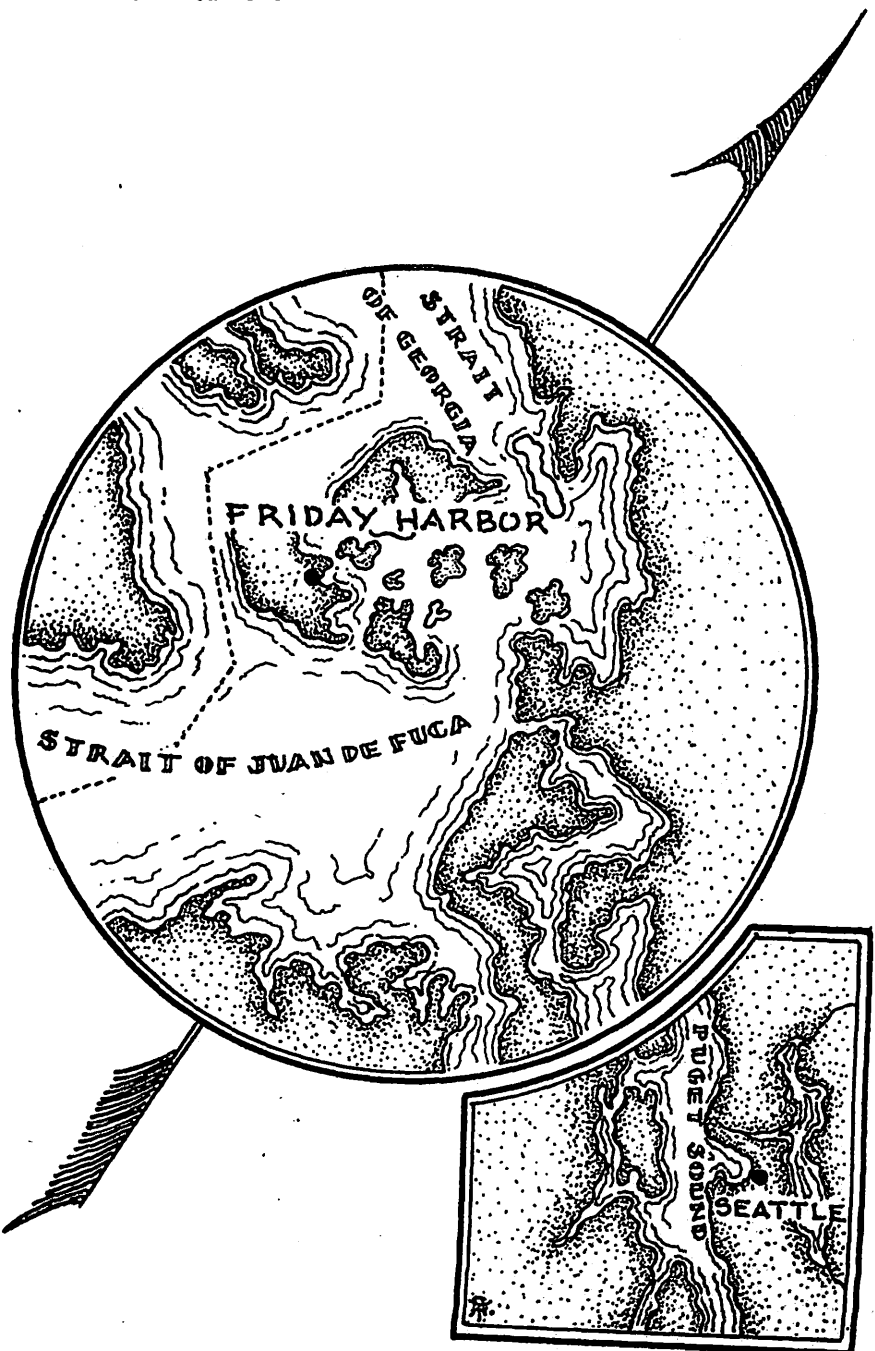
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THE EFFECT OF FREEZING UPON THE SULFATE/CHLORINITY
RATIO IN SEA WATER

Technical Report No. 1

November 1950



Office of Naval Research
Contract N8onr-520/III
Project NR 083 012

UNIVERSITY OF WASHINGTON OCEANOGRAPHIC LABORATORIES
Seattle and Friday Harbor, Washington

Reference No. 50-1 .

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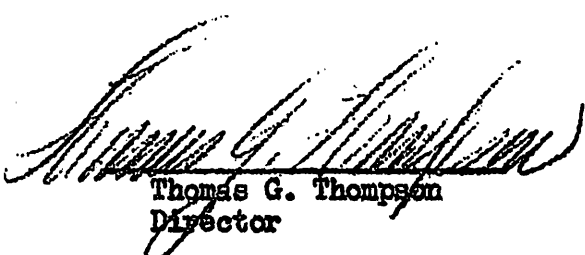
by

George J. Lewis, Jr. and Thomas G. Thompson

Technical Report No. 1

Office of Naval Research
Contract N6onr-520/III
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Thomas G. Thompson
Director

ABSTRACT

A special refrigeration apparatus was constructed to simulate freezing of sea water under natural conditions. Ice thus obtained, as well as the residual waters, were studied to ascertain the effect of freezing upon the sulfate/chlorinity ratio. This ratio was found to be greater for salts retained by the ice than for the original water. An equivalent decrease in the ratio occurred for the residual water. The ratio in the ices varied considerably and was a function of the rate of formation of ice and the temperatures of exposure. Maximum ratios were obtained at -8°C and -45°C . Minimum ratios were obtained at about -25°C .

INTRODUCTION

The alteration of the ratios of the major constituents in sea water, particularly the ratio sulfate/chlorinity, as a result of freezing and aging processes, has been a subject of considerable controversy. Its importance lies in the fact that any measurable alteration might be used in studying the transport of sea ice as well as determining its age.

In view of the conflicting reports outlined in the following section, the present laboratory investigation was undertaken.

PREVIOUS INVESTIGATIONS

The ratio, sulfate/chlorinity, was investigated extensively by one of the authors (7). An average value of 0.1395 was obtained when the concentrations of the sulfate ions were calculated as grams per kilogram of sea water. The values secured on most of the samples were within ± 0.0004 of the average but a few showed deviations greater than the experimental errors of the methods used for analysis. Data reported by some investigators (8) give varying ratios, which in many cases, may be attributed to differences in the methods employed. However, a few of the deviations of the ratio indicate that conditions do exist which may tend to affect the constancy of the sulfate/chlorinity ratio.

The work of Ringer (4,6) indicated that a considerable increase in the sulfate/chlorinity ratio might occur in sea ice as the result of freezing. He noted that sea water first began to freeze at about -1.8°C and that further cooling resulted in the initial precipitation of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ at -8°C . This decahydrate continued to crystallize with decreasing temperature until at -20°C less than one-tenth of the original sulfate remained in solution. At -23°C $\text{NaCl} \cdot 2\text{H}_2\text{O}$ began to crystallize and continued to form with decreasing temperature to -53°C . The laboratory conditions of Ringer were decidedly different from those occurring naturally and thus his results are not generally accepted as indicative of sea ice (6).

Wiese (9), of the Russian SEDOFF Expedition to Franz Joseph's Land in 1929, found an increase in the ratio with thickness for ice formed the previous winter; and reported a maximum increase of 7% at 97 cm. Six samples of ice which had aged for several years gave a mean value for the ratio nearly four times as great as the normal value for sea water. However this ice was nearly free of salt, the salinity being only $0.15 \text{ }^{\circ}/\text{oo}$.

Repa (3) reported a selective adsorption of sulfate ions by ice from solutions containing both sulfate and chloride ions. He exposed distilled water ice to solutions containing known amounts of sulfate and chloride.

Pettersson (2) reported an increase in the sulfate/chlorinity ratio in natural sea ice.

The data of Sverdrup (5) and Malmgren (1) appear to contradict the results cited above. Their conclusions, based on investigations of natural ice were made during the MAUD Expedition. However, no direct determinations of the sulfate ions were made (6).

The studies reported in the present paper were made under laboratory conditions using especially constructed apparatus so that the formation of ice approached more nearly natural conditions.

APPARATUS

A refrigerator was constructed which permitted freezing of samples of sea water from the surface downward. This effect was obtained by building cylindrically shaped wells in the freezing compartment into which the containers of sea water could be placed. The space between the inner wall of the well and the outside of the container was insulated with tinsel to prevent freezing around the walls of the container. The freezing compartment is shown in diagram I.

Glass battery jars of four liter capacity were used as freezing containers and were of sufficient strength to withstand the pressure of the sea ice formed. A Frigidaire Meter Miser MM-3 compressor unit, employing F-12 and capable of maintaining temperatures from -5°C to -45°C , with a variation of $\pm 3^{\circ}\text{C}$ was incorporated into the apparatus. The entire unit was portable with exterior dimensions of 76x76x170 cm. Air temp-

eratures of the freezing compartment were taken with a liquid in glass thermometer having a range from $+20^{\circ}\text{C}$ to -60°C .

EXPERIMENTAL PROCEDURE

Sea water samples, taken at various times and locations in the Puget Sound region were filtered, thoroughly mixed, and about three liters were placed in the battery jar containers. Simultaneously, a sample of the same water was taken and analyzed to determine the sulfate/chlorinity ratio of the original water.

Each sample was exposed to freezing conditions until approximately one-third of the original volume had frozen. The container was then removed from the refrigerator and the ice and solution separated and analyzed.

Air temperature readings were taken several times daily to determine the constancy of temperature within the refrigerator. These readings varied within $\pm 3^{\circ}\text{C}$ of the temperature setting on the refrigerator's thermo-regulator.

ANALYSIS OF SAMPLES

The chlorinity and sulfate content of the original water, ice, and unfrozen solution were determined. Duplicate analyses were made for each sample. The chlorinity was obtained by the Mohr method, using silver nitrate solutions standardized against "normal water" from the Laboratoire Hydrographique in

Copenhagen and against recrystallized sodium chloride. Sulfate values were determined by the method used by Thompson, Johnston and Wirth (7). Because of its low salinity content, larger samples of the melted ice were used. Samples taken from the concentrated unfrozen solution were correspondingly smaller. In this way conditions for the precipitation of barium sulfate were made more nearly the same for the original water, unfrozen solution and the melted ice.

The precision of the sulfate analysis of the original waters and unfrozen solutions was the same as that previously reported (7) or an average deviation of ± 0.002 ‰ SO_4 . The relative precision for ice samples was slightly less, and experimentally found to be one part in 500.

EXPERIMENTAL RESULTS AND DISCUSSION

Fourteen samples of sea water were frozen and analyzed for chlorinity and sulfate. The results are tabulated in Table I, and a summary of the data given are shown in Table II. The sulfate/chlorinity ratios are given for the original sea water samples, the ices and the resulting unfrozen solutions. The absolute increases in the ratios in the ices over those in the original water have been calculated and tabulated in the column under the heading $\Delta(\text{SO}_4/\text{Cl})$. The temperature at which each sample was frozen is given, as well as the time of exposure to freezing

conditions.

In Table III are tabulated $\Delta(\text{SO}_4/\text{Cl})$, ΔSO_4 ‰, and per cent SO_4 increase. These values were averaged from Table I. The difference between the experimentally determined value for sulfate in the ice and the value which would obtain if the sulfate/chlorinity ratio were the same in the ice as in the original water is designated by ΔSO_4 ‰. The value for SO_4 ‰ which would have occurred if there had been no selective retention of sulfate, was obtained by multiplying the chlorinity of the ice by the sulfate/chlorinity ratio of the original water. Per cent SO_4 increase was secured by dividing ΔSO_4 ‰ by the experimental SO_4 ‰ for the ice. $\Delta(\text{SO}_4/\text{Cl})$ versus temperature is plotted in Figure I.

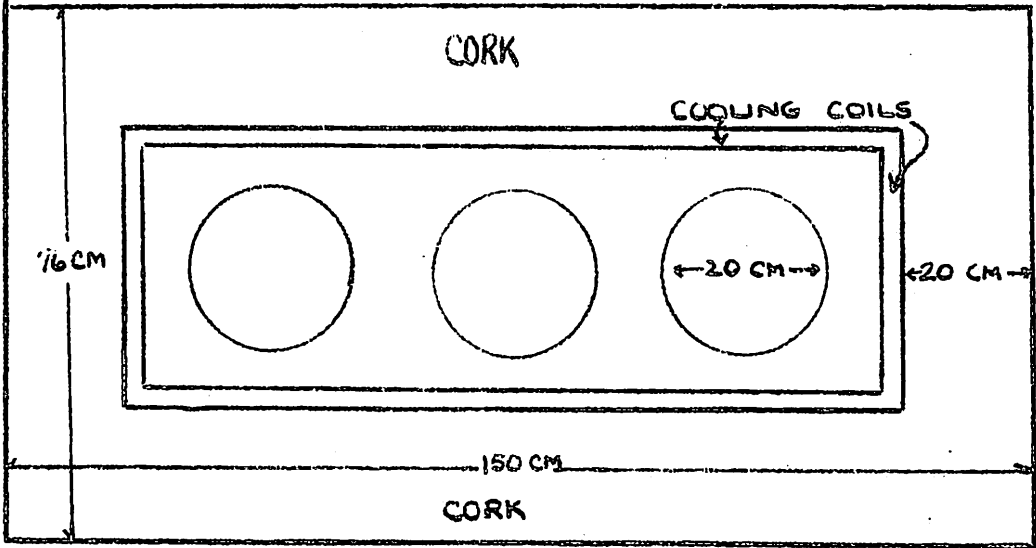
Figure I shows that the greatest increases in the sulfate/chlorinity ratio occurred in samples frozen at -8°C and at -45°C . The large increase at -8°C might be attributed to selective adsorption of sulfate ions as suggested by Repa who has reported an increase in adsorbed sulfate with time. Thus for slowly frozen samples a greater adsorption of sulfate might be expected than for more rapidly frozen samples.

In samples frozen at -45°C , the marked selective retention of sulfate by the ice was probably due to precipitation of sodium sulfate from pockets of concentrated brine which were temporarily retained by the loose network of ice crystals at the

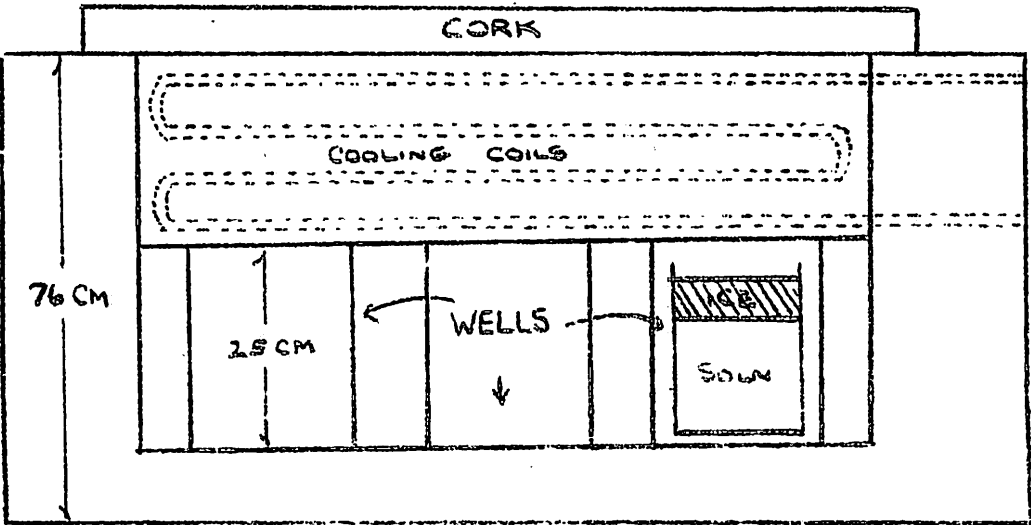
interface between solid and solution. The fact that Ringer found a maximum sulfate/chlorinity ratio in the ice at -20°C is not contradicted by a maximum with an air temperature of -45°C , because a large thermal gradient occurred in the ice (the solution never became concentrated enough to be more than about -2°C), and consequently the brine pockets were probably never much colder than -20° even in the ice which formed at the surface.

Likewise, the minimum between -8°C and -45°C may be attributed to conditions which were conducive to neither appreciable precipitation of Na_2SO_4 nor selective adsorption of sulfate.

DIAGRAM I



TOP VIEW



SIDE VIEW

REFRIGERATOR BOX

TABLE I

Experimental Results

Sample	Cl ^o /oo	SO ₄ ^o /oo	SO ₄ /Cl	Δ(SO ₄ /Cl)	Temp. °C	Freezing Period (hrs)
Y Orig	16.48	2.307	0.1400		-8	158
Ice	4.47 ₃	0.640 ₇	0.1432	0.0032		
Soln	21.16	2.952	0.1395			
Z Orig	16.46	2.301	0.1398		-8	193
Ice	4.30 ₆	0.614 ₇	0.1430	0.0032		
Soln	20.20	2.816	0.1394			
P Orig	18.05	2.516	0.1394		-16	42
Ice	7.23 ₃	1.019	0.1408	0.0014		
Soln	19.67	2.740	0.1393			
G Orig	17.10	2.387	0.1396		-25	19
Ice	7.76 ₄	1.087	0.1400	0.0004		
Soln	19.97	2.776	0.1390			
I Orig	17.11	2.386	0.1395			24
Ice	7.06 ₇	0.989 ₆	0.1400	0.0005	-25	
Soln	20.34	2.818	0.1385			
R Orig	16.64	2.325	0.1397		-25	41
Ice	6.28 ₃	0.882 ₀	0.1403	0.0006		
Soln	21.95	3.053	0.1391			
U Orig	15.81	2.205	0.1395		-25	32
Ice	6.36 ₁	0.888 ₃	0.1397	0.0002		
Soln	20.53	2.870	0.1398			
T Orig	17.67	2.475	0.1401		-27	41
Ice	7.59 ₁	1.068	0.1407	0.0006		
Soln	-	-	-			
W Orig	16.44	2.305	0.1402		-28	24
Ice	6.84 ₄	0.963 ₀	0.1407	0.0005		
Soln	24.60	3.440	0.1398			
V Orig	18.16	2.540	0.1399		-40	20
Ice	6.66 ₇	0.939 ₃	0.1410	0.0011		
Soln	22.33	3.114	0.1395			
X Orig	16.43	2.306	0.1404		-40	18
Ice	6.82 ₃	0.960 ₀	0.1406	0.0002		
Soln	21.56	3.010	0.1396			
J Orig	16.87	2.353	0.1395		-45	19
Ice	8.64 ₂	1.251	0.1424	0.0029		
Soln	21.60	2.994	0.1386			
L Orig	16.03	2.227	0.1389		-45	16
Ice	8.47 ₄	1.206	0.1423	0.0034		
Soln	20.66	2.850	0.1380			
M Orig	15.96	2.229	0.1397		-45	16
Ice	7.04 ₂	1.001	0.1422	0.0025		
Soln	20.39	2.814	0.1380			

TABLE II

Average of All Results Shown in Table I

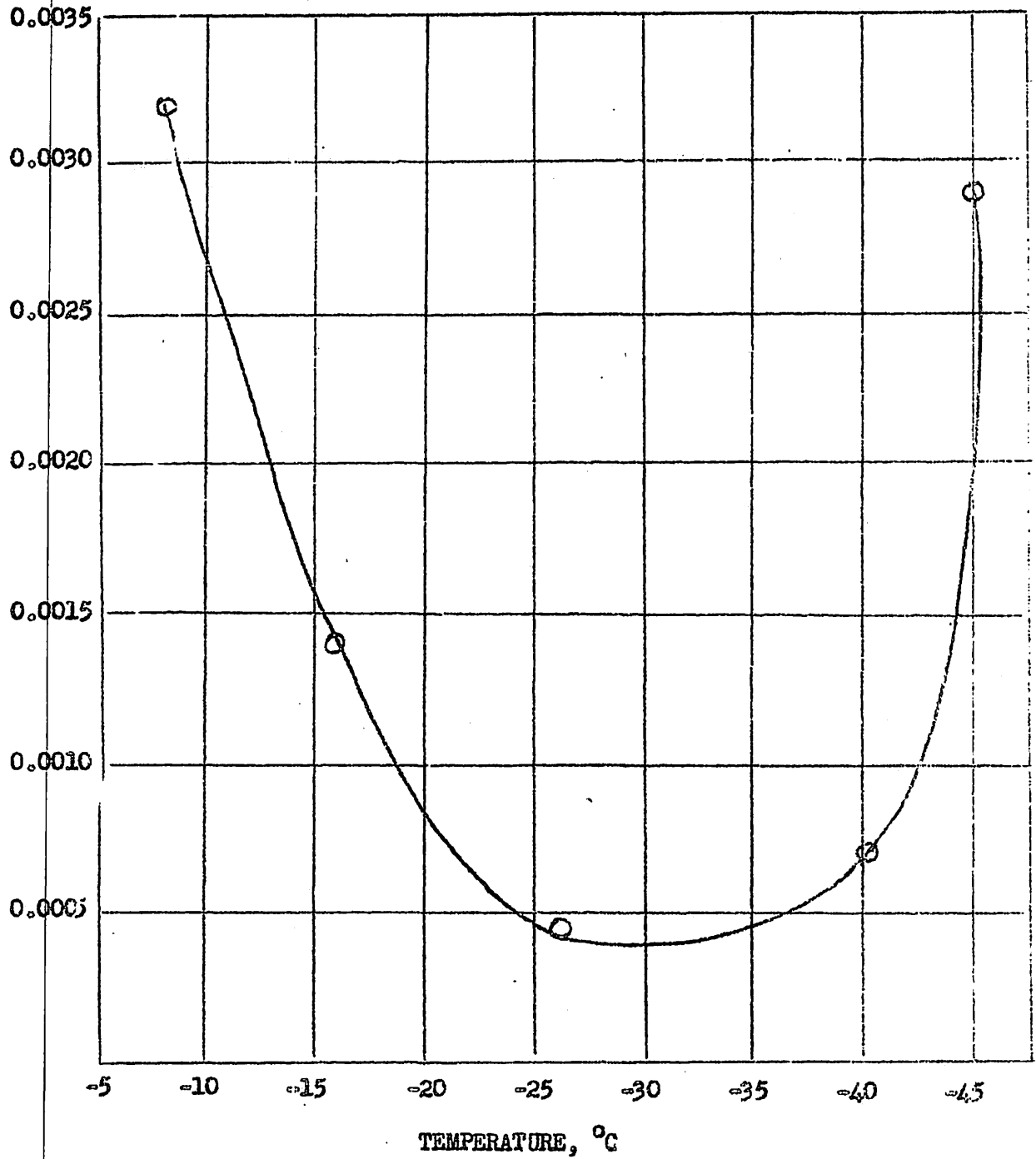
	Cl ^o /oo	SO ₄ ^o /oo	SO ₄ /Cl	Δ(SO ₄ /Cl)
Orig	16.80	2.347	0.1397	
Ice	6.82 ₇	0.963 ₈	0.1412	0.0015
Soln	21.15	2.942	0.1391	

TABLE III

Increases in SO_4/Cl and $\text{SO}_4^{\circ}/\text{oo}$, and per cent increase in Concentration of Sulfate Ion In Ice Frozen at Various Temperatures. (Mean Values taken from Table I)

Temperature °C	$\Delta(\text{SO}_4/\text{Cl})$	$\Delta\text{SO}_4^{\circ}/\text{oo}$	Per Cent SO_4 Increase
-8°	0.0032	0.015	2.39
-16°	0.0014	0.010	0.98
-26°	0.0005	0.004	0.36
-40°	0.0007	0.004	0.42
-45°	0.0029	0.024	2.04

FIGURE I



Increase in SO_4/Cl in Ice Versus Temperature
(Data from Table II)

CONCLUSIONS

1. An increase in the sulfate/chlorinity ratio occurred in the salts retained by ice as the result of the freezing of sea water.
2. The increase in this ratio varied with the temperature at which the water was frozen.
3. Maximum increases in the sulfate/chlorinity ratio of 0.0032 and 0.0029 were obtained at -8°C and -45°C respectively.
4. A minimum increase in the sulfate/chlorinity ratio of 0.0004 was obtained for samples frozen at temperatures -25°C to -28°C .

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