

Chemical fractionation in sea ice and glacier ice

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(Received October 5, 1992 ; Revised manuscript received February 23, 1993)

Abstract

Analyses of SO_4^{2-} , Na^+ , Cl^- , Mg^{2+} and Ca^{2+} in ice core samples of multiyear sea ice in the Fram Strait show strong correlations between the concentrations of Mg^{2+} , Na^+ , Cl^- and Ca^{2+} ($r=0.99$) while the correlation coefficients between these ions and SO_4^{2-} were less than 0.9. Most samples had a deficit of sulfate relative to sea water of the same salinity. Excess sulfate was found in a few samples with low salinities. Chemical analyses of snow, ice and meltwater from temperate glaciers have demonstrated that sulfate is more efficiently washed out when meltwater penetrates through ice than are Cl^- , Mg^{2+} and Ca^{2+} . Washout therefore leads to deficit of sulfate in ice, whereas refreezing of meltwater creates an excess of sulfate relative to sea water with the same content of chloride.

1. Introduction

Sea ice formation, ageing and melting involve both physical and chemical processes and a number of studies on the physical processes have been carried out (Doronin and Kheisin, 1977 ; Richardson, 1976). The physical processes are at present fairly well understood. When sea water freezes a solid phase of ice crystals and a liquid phase of brine entrapped in the ice are formed. Young surface sea ice has high salinity, with 25.00 ‰ having been reported (Malmgren, 1927). As freezing continues, ice crystals orientate randomly and accumulate in platelets and brine pockets are formed when salt and water are removed from the fluid by freezing. The mechanisms of brine drainage have been discussed by several authors (Eide and Martin, 1975 ; Lake and Lewis, 1970 ; Niedrauer and Martin, 1979 ; Wakatsuchi and Kawamura, 1987). Cox and Weeks (1974) demonstrated that the mean salinity of ice with temperatures below the melting point (cold ice) decreased with ice thickness, while the

mean salinity of ice at the pressure melting point (warm ice) was independent of the ice thickness.

The chemical processes that take place during the physical processes described above are so far less well understood in spite of the fact that the chemical composition of sea ice was among the early problems considered in marine chemistry. During the Vega Expedition (1878–79), Pettersson (1883) found the sulfate/chloride ratio to be greater in sea ice than in sea water. On the Maud Expedition (1922–25), sea ice was studied by F. Malmgren and by H. U. Sverdrup. Malmgren (1927) found by chemical analyses that the sulfate/chloride ratio in sea ice was lower than in sea water while Sverdrup (1929) came to the opposite conclusion by comparing the salinity of sea ice based on chloride titration and by measuring density.

Results of more recent studies (Reeburgh and Springer-Young, 1983) show a minor deficit of sulfate in sea ice relative to sea water of the same salinity. Anderson and Jones (1985a, 1985b) however reported

on enrichment of sulfate relative to sea water of the same salinity in both first-year and multiyear ice collected in the Fram Strait. This relative enrichment varied considerably and did not correspond quantitatively with what has been observed in sea ice produced in laboratories.

Several authors (*e. g.* Assur, 1958 ; Richardson, 1976) have studied the changes of relative composition of salt and brine in sea ice formed under laboratory conditions. The concentration of salt in brine increases with decreasing temperature and at a certain temperature salts start to precipitate. According to the most recent experiment (Richardson, 1976) the total salt content in brine decreased by 20% when the temperature decreased from -1.8 to -24°C . At -36°C only 18% of the salt remained, the rest having precipitated. It is generally accepted that the solid salts that form in sea ice are hydrates. Some of the results of Richardson's experiment are illustrated in Fig. 1. $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ starts to precipitate at -2°C , $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ at -8°C , $\text{NaCl} \cdot 2\text{H}_2\text{O}$ at -22°C and $\text{MgCl}_2 \cdot 8\text{H}_2\text{O}$ starts at -34°C . According to Fig. 1, which is based on Richardson (1976), there is a deficit of SO_4^{2-} in the brine for ice temperatures lower than -8°C . Drainage of this brine from the ice layer should consequently lead to an enrichment of sulfate in the ice relative to Na^+ , Cl^- and Mg^{2+} and can not explain any relative deficits of sulfate in ice.

The $\text{SO}_4^{2-}/\text{Na}^+$, $\text{SO}_4^{2-}/\text{Cl}^-$ and $\text{SO}_4^{2-}/\text{Mg}^{2+}$ ratios in deposited old snow in the coastal area of Antarctica are markedly lower than for sea water (Gjessing, 1989). The mean deficit with respect to sea water Na^+ for 10 samples from a 1 m snow layer close to the shelf edge was approx. 1400 ppb. On the other hand, precipitation and newly fallen snow in the same area have excess SO_4^{2-} . The most reasonable explanation for the observed SO_4^{2-} deficit in old snow that has been exposed to dry deposition, are contribution from deposition of brine from frozen sea drops. This brine, which have gone through a separation process of Na_2SO_4 and NaCl during freezing, has deficit of sulfate relative to the other main ions in sea water. As the mass of this brine is order of magnitude one percent of the total mass of the frozen sea drop, the brine will have longer residence time in the atmosphere compared to the frozen sea drops and may be transported inland. The frozen sea drops, which have excess of sulfate, will fall back into the sea.

The present work reports studies of chemical fractionation of ice during phase changes from sea ice

collected in the Fram Strait and on glaciers in Svalbard and Norway. The main purpose is to demonstrate how melting and drainage of meltwater through ice may lead to washout processes resulting in chemical fractionation in ice.

2. Sampling methods and methods of chemical analyses

The samples used in this study were collected from the following locations : 1) The Fram Strait ($79^{\circ}20'\text{N}$, $1-3^{\circ}\text{E}$) ; 2) On the top of the Jostedalbreen Glacier ($61^{\circ}41'\text{N}$, $7^{\circ}3'\text{E}$, 1950 m a. s. l.) and 3) the Austfonna Glacier, Svalbard ($79^{\circ}30'\text{N}$, 24°E , 600 m a. s. l.).

As a result of co-operation between Japanese and Norwegian glaciologists, a 46.8 m full depth ice core from Hogste Breakulen on Jostedalbreen was left in Norway for chemical analyses. These analyses were carried out on 21 samples representing the last winter precipitation, which had not been exposed to melting, and 33 samples were analysed from the layer 39–41 m depth. Samples of the water which appeared at the bottom of the borehole were also analysed. SIPRE corers were used for sampling the sea ice in location 1. On location 2 and 3 the snow samples were taken from the walls of snow pits while the ice samples were collected by electromechanical drilling. The snow and ice samples were transferred to double polyethylene bags which were sealed and kept frozen during transport to the laboratory. This type of bag has been tested at the Norwegian Institute of Water Research (NIVA) for possible extraction of metal ions in the plastic material and resistance towards acids. No detectable contribution of relevant elements from the plastic bags was found.

After melting, concentration of Ca^{2+} , Na^+ and Mg^{2+} were determined by atomic absorption spectroscopy. The SO_4^{2-} concentration was determined by the Thorin-method after passing an acid cation exchange resin. This method is not entirely specific. It suffers from interferences from phosphate, fluoride and from large excesses of chloride and nitrate. The method has been tested by analysing diluted sea water from the Weddell Sea (Gjessing 1989) and the results showed that the relative concentrations of sulfate was normal. According to Swedish Standard (1986) these interferences can be neglected for concentrations of chloride, phosphate and nitrate less than respectively 1000 ppm, 2 ppm and 50 ppm, and can consequently be

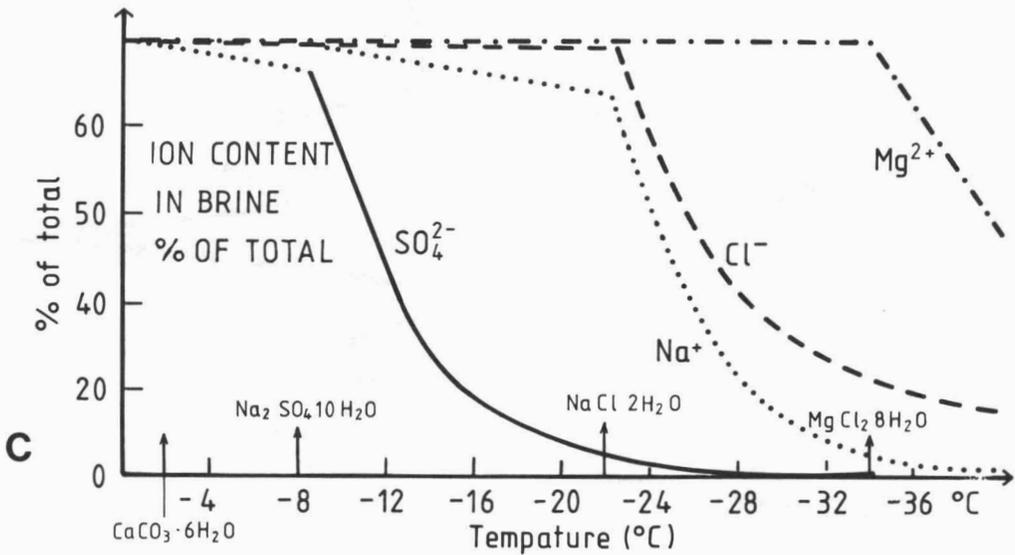
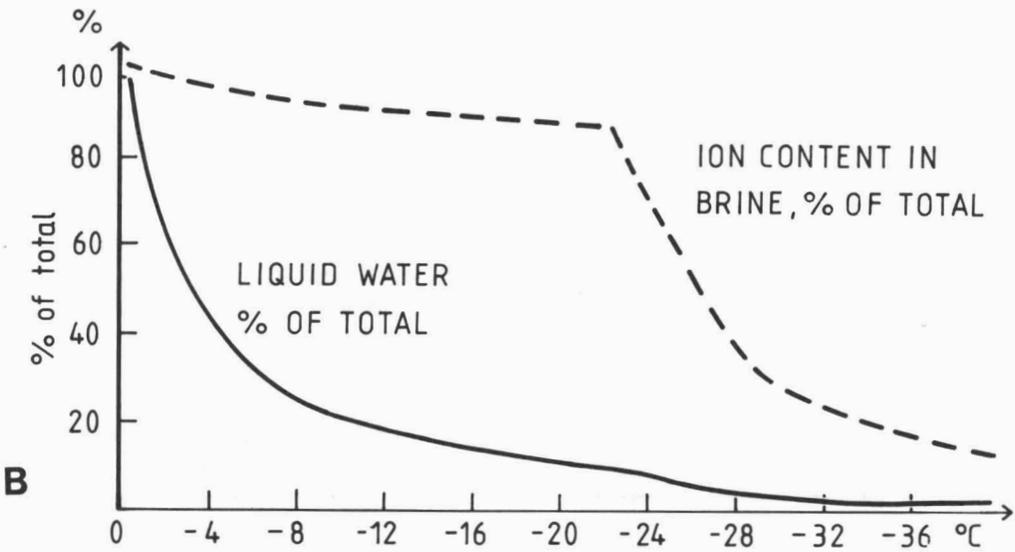
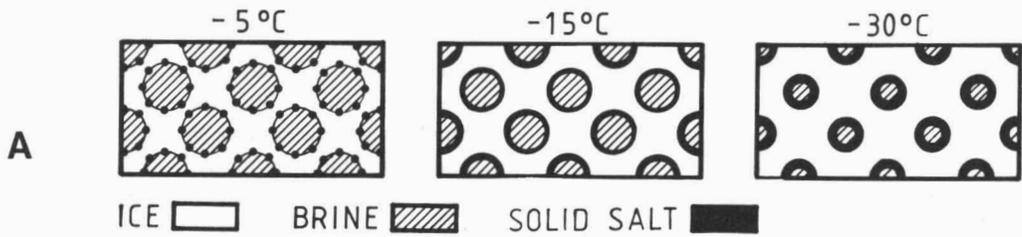


Fig. 1. Phase relation of freezing standard sea water based on laboratory experiments (Richardson 1976).

neglected in the present studies. Cl^- concentration was determined colometrically. The laboratory utilized participates in an intercalibration routine with other laboratories in Norway and Europe. The precision of the chemical analyses are better than 5ppb for Mg^{2+} and SO_4^{2-} and better than 15 ppb for Cl^- and Na^+ .

3. Results and discussion

3.1. Chemical fractionation in sea ice

Ice cores from 5 different locations with multiyear ice were collected in the Fram Strait. The profile of the different ions from two locations are given in Fig. 2. The concentrations, given as percent of the content in normal sea water, varied from 1%–12%. Each sample represents the mean value of a 0.2 m layer and the variations with depth will probably be more extreme for thinner samples. As can be seen from Fig. 2, there is a close correlation between Mg^{2+} , Na^+ , Cl^- and Ca^{2+} . For all the 60 samples from the Fram Strait the correlation coefficients for Mg^{2+} , Na^+ , Cl^- and Ca^{2+} were 0.99 while the corresponding

correlation coefficients between SO_4^{2-} and the other ions analysed were less than 0.90.

Fig. 3 shows the relationship between chloride and sulfate concentrations for all samples. It appears that most of the samples had a deficit of sulfate relative to sea water of the same salinity, but a few samples with low salinity showed an excess of sulfate relative to chloride. Groups of 7 samples of respectively maximum excess of sulfate and maximum deficit of sulfate were compared. Table 1 gives the mean relative concentrations of the main ions in sea ice relative to the concentration in sea water for each group and for all samples. An excess of sulfate appears for samples with low salinity while the salinity of the samples showing maximum deficit of sulfate is about 10 times higher. The mean relative concentration of the other main ions is almost identical within each group. This indicates that the processes leading to both excesses and deficits of sulfate in ice, also lead to the same ionic ratios between the other major ions, and thus demonstrate that both excesses and deficits of sulfate in ice may be a result of the same chemical processes.

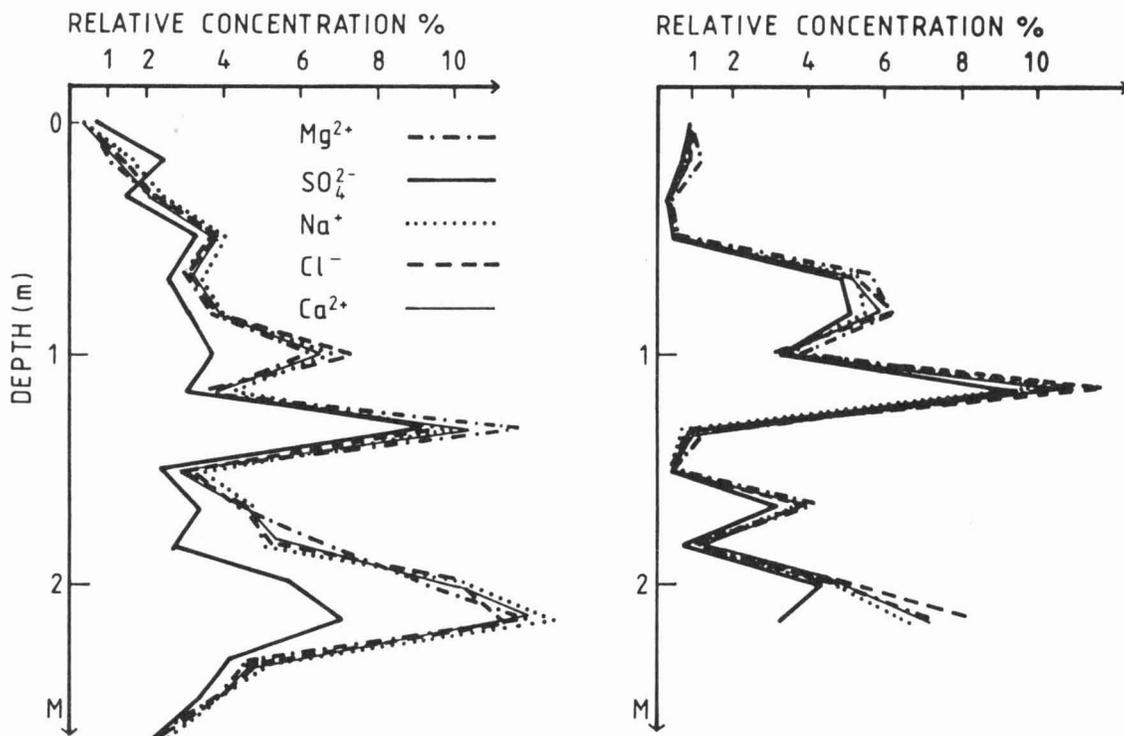


Fig. 2. Ion concentration as a function of depth for two selected ice floes in the Fram Strait.

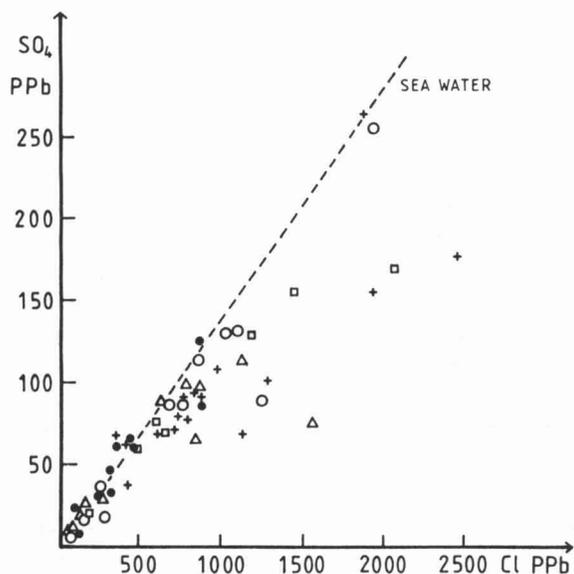


Fig. 3. The relation between concentrations of SO_4^{2-} and Cl^- for all samples. The different symbols represent the different ice floes.

Table 1. Relative concentrations of the major ions in sea ice compared to sea water in the Fram Strait.

Relative concentration = $100 \frac{\text{Ion concentration in sea ice}}{\text{Ion concentration normal sea water}}$		SO_4^{2-}	Mg^{2+}	Ca^{2+}	Cl^-	Na^+
All samples	n=60	2.59	3.51	3.49	3.54	3.42
Max excess	n=7	1.65	0.74	0.79	0.86	0.77
Max deficit	n=7	3.62	6.54	6.49	6.47	6.56

3.2. Washout processes on temperate glaciers

The melting process of sea ice and of temperate glaciers have many similarities. Except for some melting at glacier base due to frictional heat and geothermal heat, the main energy sources for glacier melting are heat fluxes from the atmosphere.

In Table 2 is given mean ion concentration of the main ions in snow, ice and meltwater from glaciers. Relative to the ionic ratios in sea water, there is an excess of sulfate of more than 50% relative to sodium and chloride in snow, ice and in meltwater. This indicates that most of the sulfate is of nonmarine origin. It appears from Table 2 that SO_4^{2-} and Mg^{2+} are the most mobile ions while Na^+ and Cl^- are the most retained ions. The high enrichments of Ca^{2+} and Mg^{2+} in meltwater at Jostedalbreen is due to

Table 2. Chemical composition ($\mu\text{eq l}^{-1}$) of snow, ice and meltwater on glaciers. The numbers in brackets are washout or enrichments given as percent of the content in surface snow.

	SO_4^{2-}	Cl^-	Mg^{2+}	Na^+	Ca^{2+}	
Jostedalbreen (61°41'N, 7°3'E, 1950 m a. s. l.) (Gjessing 1988)						
A : Snow 1986–87	n=21	7.1	25.4	2.6	24.1	3.7
B : Ice 39–41 m	n=33	2.4	11.8	0.8	11.2	2.9
C : Water in bore hole		6.7	17.1	3.2	17.8	27.5
Washout : 100 (A–B)/A	(66)	(52)	(71)	(54)	(20)	
Enrichment of meltwater : 100 C/A	(94)	(74)	(125)	(67)	(753)	
Austfonna, Svalbard (79°30'N, 24°E, 600 m a. s. l.) (Gjessing, 1977)						
A : Snow 1974–75	n : 40	7.7		6.4	31.3	1.8
B : Ice 3–4 m depth		0.6		1.2	6.3	0.5
Washout : 100 (A–B)/A	(92)		(80)	(61)	(74)	

Field experiments

(Johannessen and Henriksen, 1978)

Washout from melting snow (76) (53) (58) (57) (55)

contribution of mineral dust from the surrounding mountains and from interaction with rock in the bottom of the bore hole. The sums of cations and anions in snow at Jostedalbreen were respectively $32.5 \mu\text{eq l}^{-1}$ and $30.4 \mu\text{eq l}^{-1}$ while the corresponding values for the ice were $14.2 \mu\text{eq l}^{-1}$ and $14.9 \mu\text{eq l}^{-1}$. In the meltwater however there was a anion deficit of $25 \mu\text{eq l}^{-1}$, most probably due to interaction with the rock in the bottom of the bore hole.

Brimblecombe *et al.* (1987) showed from laboratory experiments which involved recently collected snow and artificial ices of known composition that sulfate and nitrate ions are preferentially lost with respect to chloride during melting. Of the cations, sodium appears to be removed least readily. Fractionation by melting processes has also been studied in snow lysimeters in the field (Johannessen and Henriksen, 1978). These studies (Table 2) demonstrated that the percent of total amount of compounds in snow released with the first 30% of the meltwater was 76% for SO_4^{2-} and only 53–58% for Cl^- , Na^+ , Mg^{2+} and Ca^{2+} . This process consequently leads to a

lower sulfate/chloride ratio in snow exposed to melting than in the original snow. Thodal (1986) reports that in a field experiment including nine snow lysimeters the $\text{SO}_4^{2-}/\text{Cl}^-$ ratios for the first 10 percent meltwater from a snow pack were 2–4 times higher than for the melt water when 90 percent of the snow had melted.

3.3. Processes leading to chemical fractionation

The physical processes which take place in sea ice and glacier ice and that may lead to chemical fractionation are temperature variations, freezing/melting processes and drainage of meltwater and brine.

Reeburgh and Springer-Young (1983) studied the sulfate and chloride in natural sea ice and concluded that fractionation in sea ice appears to occur during the freezing process and that further enrichment does not take place with aging. Laboratory experiments (Lewis and Thompson, 1950) showed that the sulfate/chloride ratio for salt retained by the ice was greater than for the original water. The ratio in the ices varied with the temperature at which the water was frozen. Maximum increases of 0.0032 and 0.0029 in the sulfate/chlorinity ratio relative to sea water (0.1400) were obtained at -8°C and -45°C respectively. The processes that may lead to chemical fractionation during freezing, however, were not described. These studies do not report any deficits of sulfate in ice.

According to a laboratory experiment (Richardson, 1976), the $\text{SO}_4^{2-}/\text{Cl}^-$ ratio in brine at least down to -36°C , is lower than in sea water. Any drainage of brine should therefore lead to an excess of sulfate relative to chloride in ice compared to sea water. Holmgren et al (1993) studied the chemical composition of drainage from ice formed by freezing a water solution of NaCl and Na_2SO_4 in the same relative concentrations as in sea water. The solutions were allowed to freeze at ambient temperatures of -15°C to -18°C . The ice block was then transferred to a mesh at the same ambient temperatures. The sulfate chloride ratio in the brine that drained from the ice composed only 75%–80% of the original solution.

Temperatures encountered in natural sea ice are never lower than -20°C to -30°C (Untersteiner, 1964). At low temperatures (-10°C – -20°C) very strong temperature gradients exist in the lower part of a layer of sea ice. As the chemical fractionation in ice depends on the temperature, the chemical composition of the brine that drains through ice will be strongly affected

by the temperature of the lower part of the layer of sea ice which is close to the freezing point of sea water.

Mulvaney *et al.* (1988) used scanning electron microscope to determine the location of S in ice from the Antarctic Peninsula. The ice samples had a concentration of excess $\text{SO}_4^{2-}=719$ ppb. The S was undetectable in the bulk of the ice. However at the triple junctions S was found in concentrations > 1 M. Calculations showed that between 40 and 100% of the H_2SO_4 present in this ice was found at the triple junctions and would have been liquid at ice sheet temperatures. Analysis of an ice sample with an estimated age of 125 years from the Antarctic Peninsula (Wolff et al. 1988) showed also that H_2SO_4 occurs mainly at the triple junction while the sea salt showed no such localization. They concluded that the different behaviour may be due to the freezing-point behaviour of each chemical substance and to the effect this has both in the atmosphere and during the recrystallization in the ice sheet.

In ice with a high ion content such as in sea ice and glaciers close to the sea, the ions are present in the form of concentrated brine solution which are located in brine pockets and, most probably also at the triple junctions. During melting, the aqueous phase increases in volume, giving rise to strong ionic concentration differences. This leads to diffusion of ions from the highly concentrated trapped brine solutions to diluted meltwater. In this situation separation effects may be due to differences in ion mobilities and conductance which are given in Table 3 for some relevant ions.

These are equivalent conductances and in an electric field the effect of the double charge on the sulfate ion will be important, leading to a preferential enrichment of H^+ and SO_4^{2-} ions.

As the drainage capacity in ice is low, the residence time of meltwater in ice is an order of magnitude longer than in snow. As meltwater accordingly

Table 3. Ion mobilities and conductance for some relevant ions. (Weast R. C. ed., 1981)

	SO_4^{2-}	Cl^-	Na^+	Mg^{2+}	Ca^{2+}
Ion mobilities (10^4 cm sec^{-1})	8.27	7.51	5.19	5.42	5.91
Equivalent Cond. 0°C ($\Omega^{-1}\text{cm}^{-1}$)	41.0	41.1	26.0	27.0	30.0

is enriched with sulfate relative to chloride, refreezing of meltwater in the ice will produce ice layers with an excess of sulfate. Consequently, the enrichment of sulfate in meltwater is a process that may explain the sulfate deficit as well as the sulfate excess in ice. According to Table 1 the relative concentrations of Na^+ , Cl^- , Mg^{2+} and Ca^{2+} are almost identical for groups of 7 samples of maximum excess of sulfate (0.74–0.86) and for maximum deficit of sulfate (6.47–6.56). This indicates that the processes leading to excesses or deficits of sulfate in ice lead to the same ratios between the other major ions in ice. This supports the argument that the same chemical processes may lead to an excess of sulfate as well as to a deficit of sulfate in ice.

4. Concluding remarks

The chemical processes leading to chemical fractionation in ice are extremely complex and not well understood. There is strong evidence that both relative enrichment and relative loss of sulfate occur in sea ice. The results of field studies however are not in good accordance with what is expected from laboratory studies. (*e. g.* Richardson, 1976). These laboratory studies demonstrated that drainage of brine led to a relative enrichment of sulfate in ice.

The main purpose of this study is to demonstrate how melting and drainage of meltwater through ice may lead to washout processes resulting in chemical fractionation in ice. During melting, the aqueous phase increases in volume, giving rise to strong ionic concentration differences. This in turn, leads to diffusion of ions from the highly concentrated trapped brine solutions to diluted meltwater. In this situation separation effects may be due to differences in ion mobilities and conductance. This process will lead to a preferential depletion in meltwater of H^+ and SO_4^{2-} ions. Refreezing of meltwater may lead to an enrichment of sulfate. However other processes than these may also disturb the ion ratios in sea ice.

Acknowledgment

We want to thank B. Halsvik and her staff for careful chemical analyses and Dr. H. Parker for improving the English.

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