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Frost flower chemical signature in winter snow on Vestfonna ice cap (Nordaustlandet, Svalbard)

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Abstract

The chemistry of snow and ice cores from Svalbard is influenced by variations in local sea ice margin and distance to open water. Snow pits sampled at two summits of Vestfonna ice cap (Nordaustlandet, Svalbard), exhibit spatially heterogeneous soluble ions concentrations despite similar accumulation rates, reflecting the importance of small-scale weather patterns on this island ice cap. The snow pack on the western summit shows higher average values of marine species and a winter snow layer that is relatively depleted in sulphate. One part of the winter snow pack exhibits $[\text{SO}_4^{2-}/\text{Na}^+]$ ratio reduced by two thirds compared with its ratio in sea water. This low sulphate content in winter snow is interpreted as the signature of frost flowers, which are formed on young sea ice when offshore winds predominate. Frost flowers have been described as the dominant source of sea salt to aerosol and precipitation in ice cores in coastal Antarctica but this is the first time their chemical signal has been described in the Arctic. The eastern summit does not show any frost flower signature and we interpret the unusually dynamic ice transport and rapid formation of thin ice on the Hinlopen Strait as the source of the frost flowers.

1 Introduction

Investigations focussing on the glaciology of Vestfonna glacier (Nordaustlandet, Svalbard) form a part of the IPY-Kinnvika project – an International Polar Year initiative aimed at understanding the past, present and future environmental changes in the high Arctic. This study results from preliminary work carried out on Vestfonna ice cap in spring 2007.

Nordaustlandet is the northernmost island of Svalbard archipelago (Fig. 1). With an area of 2623 km^2 (Schytt, 1964) and a maximum altitude of 622 m (Palosuo, 1987), Vestfonna is the second largest ice cap on Nordaustlandet, the adjacent Austfonna being the largest one. Like all the glaciers of Svalbard and almost everywhere in the

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Arctic (except on the highest part of Greenland), Vestfonna is subject to seasonal melting during most summers (nominally from June to September), though because of its very maritime climate, sporadic warmings can occur even during winter. The summer melting generally soaks a large part of the annual snow layer even though accumulation rates in Svalbard are relatively high compared to Greenland and other Arctic sites (Koerner, 1997).

The melt water percolation affects the temperature near the surface of the glacier and plays a major role in the firn/ice transition, which in Vestfonna occurs between 5 and 10 m deep (Watanabe, 2001). At this depth, the ice temperature is -3.7°C (Kotlyakov, 2004). However, despite melt rates of 30–50% on another Svalbard glacier (Lomonosovfonna), isotopic variations (Pohjola et al., 2002) and chemical records (Moore et al., 2005) of climate are well preserved on annual or multi-year scales. Vestfonna winter surface snow contains a record of chemistry that has not been altered by melting and the ice cap has provided reliable climatic and environmental information (Watanabe, 2001; Matoba et al., 2002). Preliminary studies of snow are essential to interpret the ice core records, and snowpack stratigraphy and chemistry can provide information on the annual accumulation rate at the drilling sites, the elution rates of chemical species, the formation mechanism of superimposed ice and other post-depositional phenomena.

Svalbard snow chemistry is also affected by anthropogenic pollution (Simões, 2001). In winter, Arctic haze from industrialized areas of Eurasia and North America (Barrie, 1986) can bring significant acidic and ammonium ions to the archipelago (Kekonen et al., 2005). For example Moore (2006) calculated that the western European anthropogenic source represents 10 to 25% of the 20th century sulphate budget of Lomonosovfonna.

This article is based on the chemistry of snow pit samples from each end of the east-west summit ridge of the ice cap. Few chemical investigations have been conducted previously on Vestfonna (Schytt, 1964; Matoba et al., 2002). Earlier authors (e.g. Matoba et al., 2002) reported highly soluble ions (principally NO_3^- and non sea-salt (nss)

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SO_4^{2-}) concentrations in winter snow which they attributed to anthropogenic impurities advected with warm air masses coming from the south. This study concentrates on a particular layer of the winter snowpack with a high sea salt load that we propose to be of frost flower origin.

Frost flowers grow on a thin layer of supersaturated brine expelled from the refrozen surface of open leads (Rankin et al., 2002). Brine is drawn onto to the surface of frost crystals by capillary action, leading to large salinities in the frost flower. When sea ice surface temperatures are below -8°C , mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) starts to precipitate from the brine and is incorporated into the sea ice matrix. Because of this fractionation, the brine and, thus, the frost flowers are depleted in sodium and sulphate. Due to their fragile structure, frost flowers are easily windblown and redistributed to the snow surface. From Antarctic observations, Wolff et al. (2003) and Rankin et al. (2002) hypothesized that frost flowers constituted a significant source of sea-salt to the atmosphere and snow in winter. However, to our knowledge, the frost flower signature in the winter snow layer has never been described on an Arctic ice cap.

2 Study site and methods

Sampling locations were selected as part of a “pre-site” survey for a future deep drilling campaign. Therefore, preferences were given to flat and high elevated areas subject to minimal melting. Snow samples were collected from two pits located on the main summit ridge of Vestfonna ice cap in April–May 2007. Pit 1 ($79^\circ 59' \text{N}$, $20^\circ 07' \text{E}$, 622 m a.s.l.) is close to the western summit which we term “Ahlmann” where snow studies and meteorological measurements were carried out during the IGY 1957. Pit 2 is close to the Japanese drilling site of 1995 ($79^\circ 58' \text{N}$, $21^\circ 01' \text{E}$, 600 m a.s.l.). Figure 1 shows the locations of the sampling sites.

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2.1 Sampling

The samples were taken in accordance with the ITASE (International Trans-Antarctic Scientific Expedition) protocol (Twickler and Whitlow, 1997). The sampling equipment was cleaned in the laboratory with ethanol and packed in polyethylene (PE) sealed bags prior to the fieldwork using a technique described by Kekonen et al. (2004). Disposable face masks, powder-free vinyl gloves and full-body clean suits were worn throughout on-site and off-site activities in order to minimize contamination during sampling, manipulations and analyses. The pits were dug as small trenches in the snowpack down to the visually located hard and icy layers of firn corresponding to the previous summer or warm autumn surface. Snow samples from Pit 1 were taken continuously in 5 cm increments down to a depth of 220 cm by pushing clean plastic cups into the side-wall of the trench. In Pit 2 (180 cm deep), 20 cm vertical snow cores were retrieved using a clean metallic cylinder and placed into double PE bags. In the presence of ice layers, a sharp clean stainless-steel knife was used to cut the samples. The snow cores were also weighed for density measurements. After retrieval, the samples were stored and transported in insulated boxes to the laboratory where they were kept frozen until analyses.

2.2 Analyses

Ten major water-soluble ions were measured with a Dionex DX-120 suppressed ion chromatograph, at the Finnish Forest Research Institute (Rovaniemi Unit). The anions (methanesulfonate acid MSA, Cl^- , SO_4^{2-} , NO_3^-) were determined using Dionex Ionpack AS15 columns. The cations (Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+}) were determined using Dionex Ionpack CS12 columns. To minimize the effect of any systematic errors, samples were analyzed in a random depth order. The analytical method is described in detail by Virkkunen (2004). The non sea-salt sulphate (nssSO_4^{2-}) and non sea-salt calcium (nssCa^{2+}) fraction have been calculated using sodium as the reference species

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assuming that all observed sodium originates from sea-salt: $[nssX]=[X]-a[Na]$ (where X is the fractionated species and $a=[X]/[Na^+]$ in sea water).

3 Results

The samples of surface snow, i.e. the snow above the last summer layer, span the time period between the sampling time (April 2007) and the autumn of the previous year (2006). For each of the pits, Fig. 2 shows the stratigraphy and the vertical variance of snow density. Log $[Na^+]/[Mg^{2+}]$ ratio has been shown to be a good indicator of summer melting in Svalbard snow by Iizuka et al. (2002) and Grinsted et al. (2006).

In both sites, fresh snow, and wind packed snow layers, composed the upper parts of the sampling wall. Below 120 cm in Pit 1 and below 130 cm in Pit 2 snow grains were coarser and depth-hoar layers were interleaved with thin ice layers (0.5 to 1 cm thick). In Pit 2, at the depth of these thin ice layers the value of the melt index (Log $[Na^+]/[Mg^{2+}]$) doubles. Below this section, a firn horizon with more frequently occurring melt ice layers was found from 160 cm to the bottom of the pits. The change in snow properties at 160 cm is accompanied by a rapid decline in density in both profiles. In Pit 1 the density drop is coupled with a doubling of the melt indicator Log $[Na^+]/[Mg^{2+}]$ (Fig. 2). We assume that this transition at the depth of 160 cm is the top of the 2006 summer layer. Based on the mean density of snow between 0–160 cm, we found that the accumulation rate was approximately 0.62 mweqyr^{-1} at Pit 1 and 0.64 mweqyr^{-1} at Pit 2. These estimates are similar to the $0.595 \text{ mweqyr}^{-1}$ found during the IGY expeditions (Schytt, 1964).

Mean concentrations of the ionic species and the calculated $nssCa^{2+}$ and $nssSO_4^{2-}$, standard deviations (σ) and the coefficient of variation ($CV=\sigma/\bar{x}$) are presented in Table 1 for both pits. The concentrations of major ions (Cl^- , SO_4^{2-} , Na^+ , Ca^{2+} , Mg^{2+} , K^+) range from 1.84 to $84 \mu\text{Eq l}^{-1}$ in Pit 1 and from 0.37 to $17.3 \mu\text{Eq l}^{-1}$ in Pit 2.

The concentration profiles for the cations and anions in the two pits are shown in Fig. 3. In the case of Pit 1, there is a concentration peak present at about 100 cm for

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Na⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻ and SO₄²⁻. This snow layer between 95 cm and 115 cm presents ionic concentrations from 4 to 6 times higher than the mean concentration for the snowpack above and below (excluding the firn layer starting at 160 cm). Furthermore, the calculated concentration of nssSO₄²⁻ (Fig. 3) in this layer was found to be clearly negative. This means that in this layer sulphate ions do not have an anthropogenic or terrestrial source, but must be marine in origin. Pit 2 displays a regular decrease in ionic concentrations from the surface of the pit to the summer snow surface with the exception of a small peak between 85 cm and 105 cm.

4 Discussion

A comparison of the snowpack ionic budgets between the sites (Table 1) reveals that Pit 1 has systematically higher concentrations than Pit 2 which probably represents a geographical trend across the ice cap. The major sources of these ions are marine (Matoba et al., 2002) and there is no topographical divide between the two sites. This indicates a variable geographical distribution of major marine species on Vestfonna, with summit Ahlmann under stronger marine influence. In addition, the lower nssSO₄²⁻ and nssCa²⁺ contents observed in Pit 1 also point towards higher oceanic inputs at Pit 1 compared to Pit 2. The snow stratigraphy and densities also support the chemical melt indicator in suggesting that the snow layer at the depth of 1 m in Pit 1 has not experienced melting.

4.1 Frost flowers as a source of fractionated sea-salt in winter

At Antarctic coastal sites, high sea-salt concentrations and strong nssSO₄²⁻ depletion found in winter snow have been described as evidence of an important sea ice surface source (Rankin et al., 2002). Other studies of Antarctic winter snow (e.g. Hall and Wolff, 1998) confirm that air coming from fresh sea ice covered with frost flowers has a high salinity and a negative nss-SO₄²⁻ signal. Based on the similar chemical charac-

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teristics found in the highly saline layer in Pit 1 winter snow, we propose these features represent a frost flower chemical fingerprint. Additionally, the sulphate to sodium ratio ($\text{SO}_4^{2-}/\text{Na}^+$) in this particular layer of the winter snowpack, 0.092, is about 1/3 that of sea water (0.25) and very close to the $\text{SO}_4^{2-}/\text{Na}^+$ ratio measured by Rankin et al. (2002) in Antarctic frost flowers (0.085) and winter aerosols (0.1).

Earlier investigations on Vestfonna snow (Matoba et al., 2002) showed that peaks of $\delta^{18}\text{O}$, Na^+ , Cl^- in winter snow were caused by advection of warm air masses with a high content of sea-salt. These winter warm events were also associated with high NO_3^- , NH_4^+ and nssSO_4^{2-} peaks and the authors concluded in favor of both anthropogenic and sea water sources. The concentrations of NO_3^- and NH_4^+ do not exhibit peaks and nssSO_4 is clearly negative (Fig. 3) in the frost flower layer. We can therefore exclude anthropogenic contribution to the sulphate. In addition, the Mg/Na (0.236) and Ca/Na (0.045) weight ratios in the frost flower layer are slightly higher than those in bulk sea water (SMOW, Standard Mean Ocean Water) (0.12 and 0.038, respectively, Table 2), implying that sea-salt aerosols incorporated into the winter snow are depleted also in sodium. This is to be expected if we assume that the depletion of both sodium and sulphate is due to crystallization of mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) from sea water at temperatures below -8.2°C . Simulations of sea water freezing along the Gitterman pathway by Marion et al. (1999) reveal that mirabilite is the only salt to precipitate out when sea ice is formed between -8.2°C and -22°C . Colder ice surfaces are generally associated with multiyear ice on which frost flowers do not form. The ions deposited in the frost flower layer clearly display a fractionated sea-salt signature and we can conclude that sodium is the cation depleted with sulphate.

According to Rankin et al. (2002) sodium and sulphate depletion due to mirabilite precipitation are expected in glacier snow if this snow has been affected by a frost flower wind deposition. Frost flowers grow on patches of thin slush layers on young sea-ice formed in leads of open water. To create these leads, appropriate meteorological conditions in terms of wind speed and direction are necessary and must be combined with sufficiently low temperatures (below -8°C) to allow fractionation to occur. Such

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cold temperatures are frequently reached during the winter in Nordaustlandet (Fig. 4). Once offshore winds open up a coastal lead, new sea ice is produced. Then, the wind direction must change to blow onshore in order to carry the aerosols derived from the frost flowers inland. Hall and Wolff (1998) show that strong winds are not associated with frost flower signatures perhaps because strong winds destroy the flower's fragile crystals and the thin surface skim of brine on which they form. So moderate winds and low temperatures are needed.

Patches of enriched brine on solid ice create an irregular surface with a greater roughness and backscatter coefficient at radar frequencies than ice without flowers. A synthetic aperture radar (SAR, carried by the ERS-1 satellite), which is sensitive to the nature of sea ice surface, has been used to identify leads covered by frost flowers in the Arctic (Melling, 1998; Ulander et al., 1995). In addition, a radar study conducted in Svalbard archipelago using the ERS-2 satellite in March–April 1998 (Augstein, 2000) registered strong reflectance of a $15 \times 15 \text{ km}^2$ area of the Arctic Ocean west of Nordaustlandet ($80^\circ 42' \text{ N}$, 8° E), which was interpreted as frost flowers by Kaleschke et al. (2004). These observations support our assumption that frost flowers can form around Nordaustlandet and constitute a potential source of fractionated aerosols for Svalbard winter snow.

Moreover, the snow layer affected by the frost flower peak is too thick (20 cm) to be formed by fog, which is also unsupported by the stratigraphy (Fig. 2). The importance of fog deposits (rime, hoar frost) has been overestimated in Nordaustlandet during the past; Schytt (1964) observed that the snow mass contributed by fog deposits amounts to roughly 3 percent of the total accumulation.

4.2 Hinlopen Strait: newly formed sea ice in winter

To locate the young winter sea ice formation area, we used the records from the weather station installed on the eastern coast of Ripfjorden ($80^\circ 13' \text{ N}$, $22^\circ 31' \text{ E}$) (see Fig. 1 for location). The wind data for the period 2007–2008 are plotted in Fig. 5. Two predominant wind directions are observed: one is 290 to 340° (from the Arctic Ocean,

NW) and the other is 110 to 135° (from Austfonna ice cap, SE). These wind directions recorded in Ripfjorden are consistent with our field observations in spring 2007 and 2008 at summit Ahlmann where strong winds came most of the time from the Arctic Ocean channeled by Lady Franklinfjorden (Fig. 1). This suggests that the Arctic Ocean is not the frost flowers source area, since the frost flower signature is not a continuous signal in the snow pack, but an infrequent event. The only plausible source is Hinlopen Strait (SSW).

During the field campaigns we noted that Hinlopen Strait was partially covered with a thin slick of ice and partially ice free, whereas Lady Franklinfjorden was completely frozen. Strong currents in the Hinlopen Strait continuously create exposed areas of sea water which freeze rapidly in the winter and create areas of local, freshly formed ice with a surface cover of concentrated brine. Moreover, the decrease in sea-salt concentrations with distance across the ice cap (at Pit 2), indicates that the sea-salt source is closer to Pit 1 than to Pit 2. Unlike in Pit 1, melting layers are present in the winter snowpack of Pit 2 while the frost flower chemical signature is absent in the pack. This shows evidence of locally variable atmospheric conditions at the two summits which are 20 km apart. From these observations we can speculate that the principal source of saline air masses is most likely Hinlopen Strait (about 45 km from Pit 1 and about 60 km from Pit 2).

4.3 Fractionated salt as a new sea ice production proxy

Wolff et al. (2003) have suggested that sea-salt concentrations in ice cores can be used to infer aspects of the marine environment in the past. Generally, such studies have assumed that the atmospheric sea-salt concentrations are related to a combination of sea ice extent and wind speed. Although Svalbard ice cores suffer from postdepositional percolation they have been proven to give reliable paleo-information (Kekonen, 2005; Moore, 2009; and Grinsted, 2006). Iizuka et al. (2002) successfully extracted information on environmental changes from chemical signals in a Nordaustlandet ice core. Also, Watanabe et al. (2001) reported that most of the chemical features contained in

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the initial snow of Austfonna still remained in the ice core. We could therefore expect that the preservation of the frost flower chemical signature in Vestfonna ice is possible. If the signal described in this paper is not disrupted by melt percolation, it might serve as a potential proxy for sea ice production (extent) in winter via the reconstruction of past atmospheric conditions. Additionally, if higher sea-salt levels measured in winter snow are systematically associated with moderate winds (and not strong winds), we could attribute high sea-salt concentrations (Table 3) seen in cold periods, such as the Little Ice Age, in coastal or maritime ice cores to changes in sea ice production, rather than increased storminess and more efficient transport.

The apparent rarity of the frost flower signature in Arctic regions may be related to the quite different sea ice conditions in the Arctic Ocean compared with the seas surrounding Antarctica. Multi-year floes tend to be much more common in the Arctic basin, while in the Southern Ocean the pack ice reforms each year, so there is much more young and thin ice that provides suitable frost flower sites around Antarctica than in much of the Arctic. The Arctic is also much more affected by anthropogenic and terrestrial SO_4^{2-} input than Antarctica and large SO_4^{2-} are typical. This would tend to disguise the characteristic ($\text{SO}_4^{2-}/\text{Na}^+$) frost flower signature.

5 Conclusions

By comparing chemical analyses of the snowpack from two snow pits in Vestfonna ice cap, we show that the western side of Vestfonna receives a greater marine ionic contribution than the eastern edge, and that the winter snowpack at the western end (summit Ahlmann) is enriched in sea-salt fractionated in sodium and sulphate. As the particular nature of this saline content corresponds to a typical frost flower signature described in aerosols and snow from Antarctic coastal regions, we hypothesize that frost flowers, possibly formed in Hinlopen Strait, could form a significant source of sea-salt in winter snow in Vestfonna. We therefore suggest that sea-salt records retrieved from ice cores from Ahlmann summit may give us information on the past extent of

new sea ice. However, to rigorously assess the reliability of the frost flower chemical signature as a proxy for winter sea ice production around Nordaustlandet, the annual snowpack needs to be analyzed at different locations on Vestfonna glacier; more snow pit studies carried out along with continuous meteorological measurements should be performed. Studies of shallow ice cores drilled at the two summits and new snow analyses are currently underway.

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Table 1. Mean concentrations (\bar{x}), standard deviations (σ) in μEqL^{-1} and coefficients of variation, CV, in the entire surface snowpack of Pit 1 and Pit 2.

	Pit 1 ($n=39$)			Pit 2 ($n=12$)		
	\bar{x}	σ	CV	\bar{x}	σ	CV
MSA	0.03	0.06	1.87	0.01	0.02	2.04
Cl^-	64.68	66.32	1.03	16.72	18.51	1.11
SO_4^{2-}	8.59	7.92	0.92	2.44	2.47	1.01
NO_3^-	0.61	0.53	0.88	0.27	0.29	1.08
Na^+	75.15	85.83	1.14	17.30	18.94	1.09
NH_4^+	0.75	0.42	0.56	1.14	0.56	0.49
K^+	1.65	1.94	1.17	0.38	0.40	1.08
Mg^{2+}	17.46	20.25	1.16	4.15	4.81	1.16
Ca^{2+}	3.56	3.82	1.07	2.55	1.76	0.69
nssCa^{2+}	0.25	0.43	1.69	1.79	1.33	0.74
nssSO_4^{2-}	-0.46	3.33	-7.20	0.36	0.51	1.42

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Table 2. Weight ratios of ions in Halley station Frost Flowers, Antarctica (HFF), Frost Flowers Layer (FFL) and bulk sea water (SMOW).

	K/Na	Mg/Na	Ca/Na	Cl/Na	SO ₄ /Na
HFF	0.0389	0.14	0.0441	2.04	0.0853
FFL	0.022	0.236	0.0452	0.812	0.092
SMOW	0.037	0.12	0.0382	1.79	0.252

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Table 3. Concentration ($\mu\text{Eq l}^{-1}$) of ions in Halley station Frost Flowers, Antarctica (HFF), Frost Flowers Layer (FFL) and Bulk Sea water (SMOW).

	Na	K	Mg	Ca	Cl	SO ₄
HFF	154	4	41	8	207	6
FFL	263	6	62	12	208	25
SMOW	468	10	107	21	553	56

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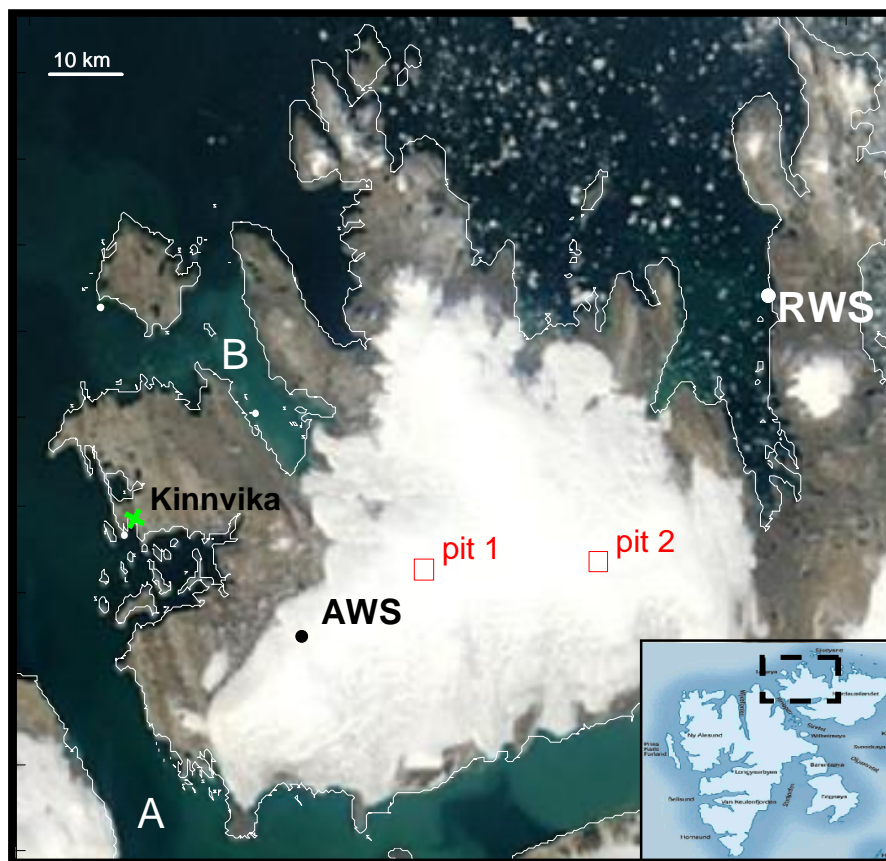


Fig. 1. Satellite image (image from NASA) of western Nordaustlandet with location of Kinnvika station, snow-pit sampling sites (Pit 1 and Pit 2), Automatic Weather Station (AWS), Ripfjorden Weather Station (RWS), Hinlopen straight (A) and Lady Franklinfjorden (B).

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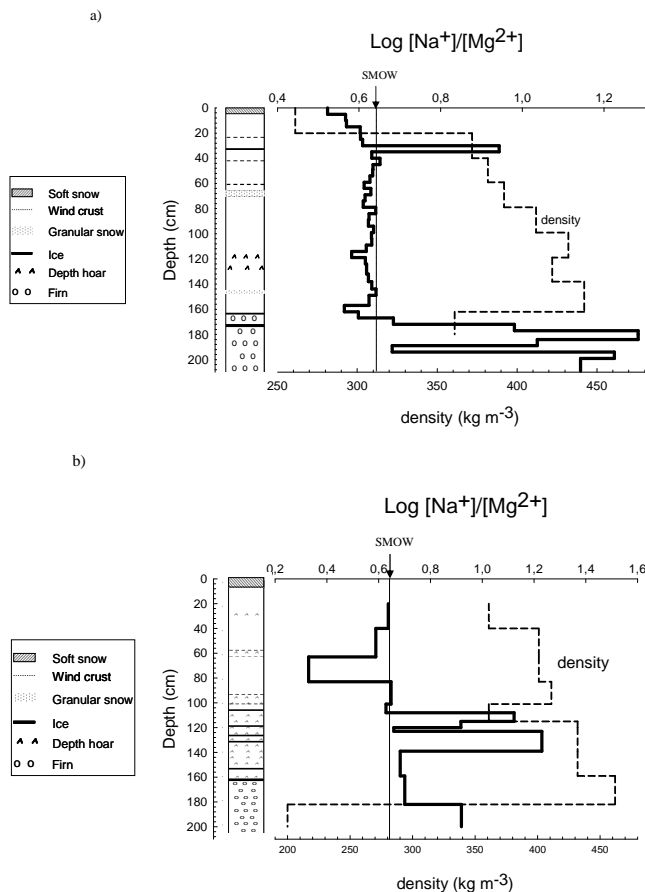


Fig. 2. Stratigraphy and depth profile of the melting indicator $\text{Log} [\text{Na}^+]/[\text{Mg}^{2+}]$ in $\mu\text{Eq l}^{-1}$ (solid line) and density (dashed line) for (a) Pit 1 and (b) Pit 2. The black arrow points the melting indicator value for Standard Mean Ocean (SMOW).

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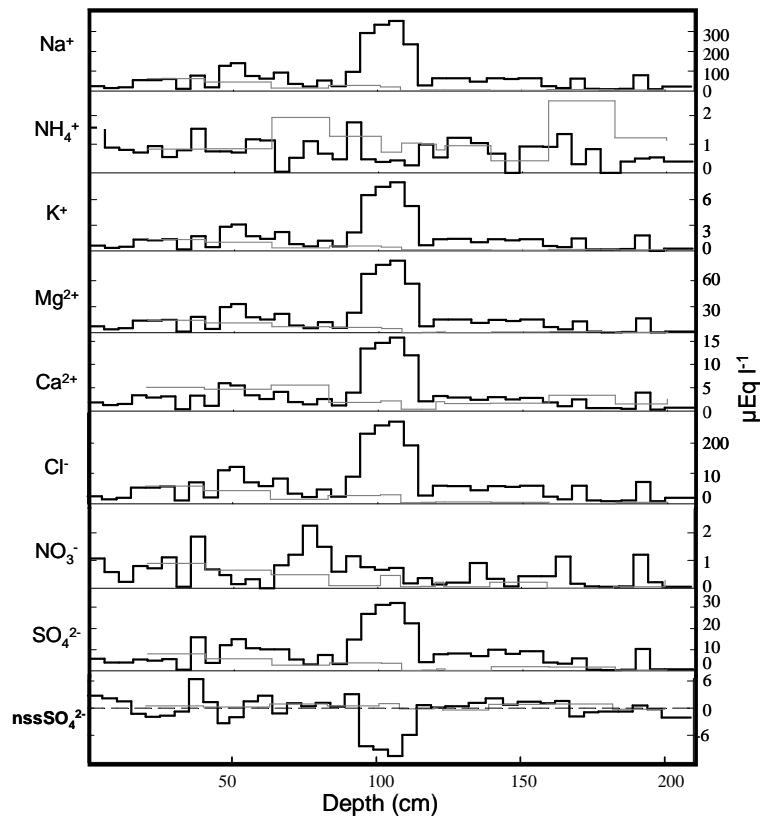


Fig. 3. Ion concentration (in $\mu\text{Eq l}^{-1}$) in Pit 1 (black histogram) and Pit 2 (grey histogram).

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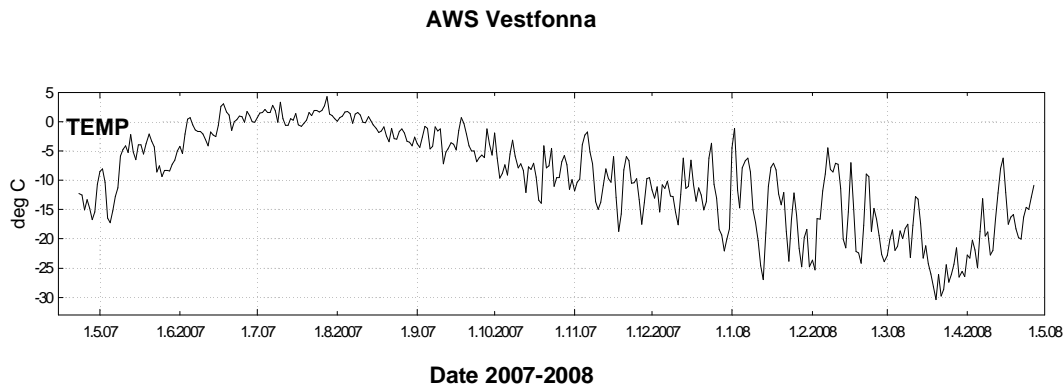


Fig. 4. Temperature ($^{\circ}\text{C}$) plotted from AWS (R. Hock and U. Jonsell, personal communication, 2008).

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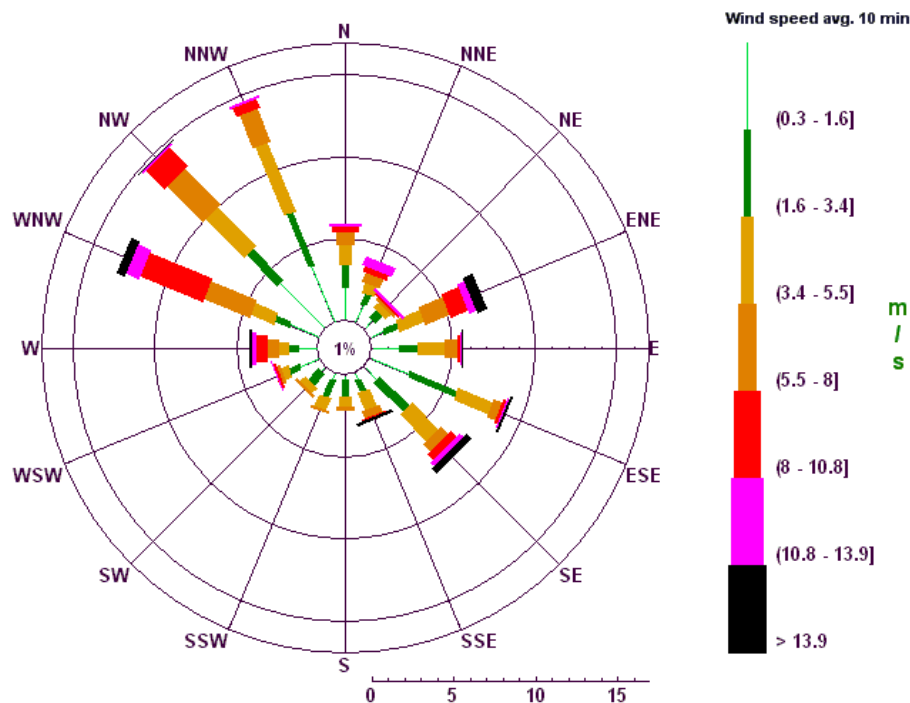


Fig. 5. Rose diagram showing wind direction (deg.) and speed (m/s) from August 2007 to August 2008 at Ripfjorden Weather Station (source: <http://158.39.11.101/command=RTMC&screen=WindYear%20%20>).

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