

Frost flowers as a source of fractionated sea salt aerosol in the polar regions

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Abstract. Frost flowers collected from the surface of new sea ice near the Brunt Ice Shelf, Antarctica, show depletion in sulphate and sodium relative to other sea water ions. This is consistent with loss of mirabilite (Na_2SO_4) during formation of the brine from which the frost flowers grow. Aerosol generated from frost flowers would have higher sodium:sulphate ratios than aerosol generated from sea water. This would explain low values of non-sea-salt sulphate encountered in winter aerosol, and winter layers in ice cores, at coastal Antarctic sites. Calculations confirm that the frost flower source should be significant compared to an open water source for coastal regions.

Introduction

As sea ice forms from open water salt is expelled from the ice crystals, forming a thin layer of highly saline brine on the surface of the ice. In low wind conditions frost flowers may form from this surface brine. The frost flowers are thought to pull brine up from the surface layer by capillary action, and measurements of the salinity of the frost flowers have shown salinities comparable to that of the brine layer from which they form [Perovich and Richter-Menge, 1994].

These frost flowers significantly alter the radiative characteristics of the sea ice surface and recently there has been much interest in the use of the characteristic remote sensing signature of frost-flower covered leads to investigate sea-ice formation (eg. [Nghiem *et al.*, 1997]). The formation of frost flowers has been investigated in Arctic leads [Perovich and Richter-Menge, 1994], and they have also been successfully grown in the laboratory [Martin *et al.*, 1995, 1996]. However, apart from typical salinities, little is known of the chemical composition of the flowers.

Laboratory work has shown that as seawater is frozen, ice forms with a low salinity, and leaves a highly saline brine behind [Richardson, 1976]. As the ice is progressively cooled below freezing the volume ratio of brine to ice decreases, the salinity of the brine increases, and salts begin to precipitate. Mirabilite (Na_2SO_4) begins to precipitate at temperatures below -8°C , the precipitate being incorporated into the sea ice matrix. This leaves a surface brine that is depleted in sodium and in sulphate. NaCl is not significantly precipitated until temperatures are below -26°C , and potassium and magnesium salts do not begin to precipitate until temperatures are below -34°C . It can therefore be predicted that frost flowers forming at temperatures below -8°C should be depleted in sodium and in sulphate relative to the other

seawater ions, and if temperatures are significantly lower other ions may also be affected.

One component of aerosol in polar regions and in ice cores that is frequently reported is non-sea-salt sulphate, which is calculated by using the sodium component of the aerosol (assumed to come entirely from sea salt), together with the ratio of sulphate to sodium in bulk seawater, to subtract the sea-salt component from the total sulphate concentration. However, the non-sea salt-sulphate concentration of aerosol collected at a number of stations in coastal Antarctica often has significantly negative values in the winter months [Wagenbach *et al.*, 1998]. Negative nss-sulphate values have also been observed in a number of snow samples and in ice cores, for example on the Antarctic Peninsula [Aristarain *et al.*, 1982; Mulvaney and Peel, 1988], and in East Antarctica [Legrand *et al.*, 1985; Ivey *et al.*, 1986; Gjessing, 1989]. Negative non-sea-salt sulphate concentrations in winter layers have been observed as far as 300 km inland on the Filchner-Ronne Ice Shelf [Minikin *et al.*, 1994]. The sulphate deficit is generally well correlated with the concentration of seasalt in the aerosol or snow [Wagenbach *et al.*, 1998].

The low or negative values observed in winter aerosol are consistent with fractionation of sea salt similar to that expected to occur during sea-ice formation, as this causes the sea-salt component of sulphate in aerosol to be overestimated. Fractionation is often apparent in aerosol containing a high sea salt loading, and local meteorological conditions during periods of high sea salt suggest they occur when the wind blows from areas of new sea ice formation [Hall, 1998].

It has been suggested that fractionation may occur during the freezing of airborne water droplets and that this may be an alternative explanation for observed negative non-sea-salt sulphate values [Gjessing, 1989]. However, experimental work found no evidence that significant fractionation could occur by this mechanism [Wagenbach *et al.*, 1998].

In this paper, we measure for the first time the ion ratios in frost flowers from Antarctica, and show that they are fractionated to a very similar extent to the aerosol and snow samples that have been investigated. We then estimate the potential size of the frost flower source to show why it is important relative to the open water sea salt source in coastal regions.

Methods

Frost flowers were collected on the 2nd October 1998 from a site near the British Antarctic Survey station at Halley, on the Brunt Ice Shelf. The monthly mean surface air temperature near Halley is around -5°C in January and drops to -30°C in August, and thus fractionation may be expected during the winter months [Richardson, 1976]. The site chosen was an extensive area of fairly new sea ice, 90% covered

Table 1. Concentrations (in ppm) of Ions in Frost Flowers (FF) and Sea Water (S1, S2) from the area of Halley Station, Antarctica. SMOW is Standard Mean Ocean Water.

	Na	K	Mg	Ca	Cl	SO ₄
FF	3531	138	493	156	7230	301
S1	10344	367	1279	385	21290	2760
S2	10976	372	1312	391	21010	2886
SMOW	10775	399	1295	412	19350	2712

with frost flowers. The ice was approximately 15 cm thick and uniform, and a lead of open water was present 20 m to the north of the sample site. The flowers were approximately 3 cm tall, on a base of almost 1 cm square, and appeared similar to thick rime. A metal spatula was used to push a number of flowers into a plastic sample tube. The sample tube was kept frozen at -20°C until analysis in Cambridge around one year later. Figure 1 shows the typical appearance of frost flower fields in the vicinity of Halley.

For comparison with the frost flowers, two samples of surface seawater collected from RRS Bransfield in the Weddell Sea, approximately 250 km from Halley, were also analysed.

The melted frost flowers and seawater samples were diluted by a factor of 10000 with ultra-high purity water and analysed for anions on a Dionex 2000 series ion chromatograph, using a sample loop injection and gradient elution with sodium hydroxide eluent. Cations were analysed with a Dionex DX500 chromatograph using isocratic methanesulphonic acid eluent. The concentrations measured are shown in Table 1, and weight ratios of ions are shown in Table 2. Weight ratios of sulphate to sodium (expected to show fractionation at the temperatures experienced at Halley during the winter) and magnesium to sodium (expected to behave conservatively) are shown graphically in Figure 2 for seawater, winter aerosol at Halley, and frost flowers.

Discussion

The seawater samples have concentrations and ratios close (within measurement accuracies around 5%) to those of standard mean ocean water. The concentrations of sea salt ions in the frost flowers analysed show significant fractionation. Sulphate is depleted by around a factor three relative to the other sea salt ions, and sodium is also depleted in comparison to other cations, by around 10%. This is consistent with loss of mirabilite from the brine from which the frost flowers grow. The ratio of sulphate:sodium we find in frost flowers of 0.0853 (Figure 2) is close to the ratios found in winter aerosol at Halley (0.107 [Hall, 1998]), and Neumayer (0.075 [Wagenbach *et al.*, 1998]), supporting the hypothesis that frost flowers and/or the brine on the sea ice surface are the source of fractionated winter sea salt aerosol. In laboratory measurements, the sulphate:sodium ratio that remains in solution continues to decrease from -8°C downwards [Richardson, 1976], reaching 0.085 at around -13°C .

The salinity of the frost flowers we analysed (around 13PSU) was considerably less than that of sea water, although previously reported values have been more saline than sea water (eg. [Martin *et al.*, 1995]). It has been shown that the salinity of a patch of frost flowers evolves with

time: In one study [Perovich and Richter-Menge, 1994] an initially fresh patch became more saline as brine was transported up the crystals by capillary action, but the salinity began to decrease after around two days as snow accumulated and the brine forming the surface skim was drawn into the snowpack. However, only the salinity of the samples should be affected by such dilution effects; the ratios of the sea water ions should depend only on the temperature at which the flowers were formed.

As fractionation significantly alters the relative concentrations of the sea salt ions in aerosol and hence, after deposition, snow and ice, the possibility of fractionation must be taken into account when ice core records are interpreted. In the past, nss-sulphate data may have been erroneously interpreted because this factor was not taken into account, for example in time trends of aerosol species at Mawson, Palmer and Marsh stations [Savoie *et al.*, 1993], and in profiles of non-sea-salt sulphate and sea salt ions in an ice core from Doleman Island [Peel and Mulvaney, 1992]. In particular, MSA to non-sea-salt sulphate ratios, which have in the past been used to try to quantify the biogenic component of non-sea-salt sulphate, need to be corrected in the winter months to allow for fractionation [Hall, 1998].

Although frost flower formation can cause significant perturbation of the composition of sea salt aerosol, the effect may be both localised and seasonal. Appropriate meteorological conditions in terms of wind speed and direction are necessary to create leads of open water in which new sea ice may form, and these must be combined with sufficiently low temperatures to allow fractionation to occur. Even when conditions are suitable for frost flowers to form, low wind speeds will not generate aerosol from the flowers, while high wind speeds will rapidly destroy the flowers, or bury them with blowing snow. However, when conditions are suitable, the combination of the high concentrations of salt within the flowers, and their fragility, may lead to very high loads of aerosol being generated. Therefore, although conditions suitable for fractionation may only occur a small percentage of the time, fractionated aerosol may dominate the sea salt budget in some coastal Antarctic locations.



Figure 1. A typical field of frost flowers forming over new sea ice near Halley, Antarctica. The individual frost flowers are around 2-3 cm high.

Table 2. Weight Ratios of Ions in Frost Flowers and Sea Water from the area of Halley Station, Antarctica

	K/Na	Mg/Na	Ca/Na	Cl/Na	SO ₄ /Na
FF	0.0389	0.140	0.0441	2.04	0.0853
S1	0.0355	0.124	0.0372	2.04	0.267
S2	0.0339	0.119	0.0356	1.92	0.263
SMOW	0.0370	0.120	0.0382	1.79	0.252

Importance of frost flower source

In this paper, we have confirmed that fractionation does occur in frost flowers, and that it is similar to that occurring in coastal Antarctic aerosol and snowfall. This makes it highly probable that the sea ice surface, and frost flowers in particular, are the source of fractionated sea salt aerosol. We now estimate the likely importance of a frost flower source.

We can attempt to estimate the annual source of salt to the atmosphere from frost flowers in various ways. The majority of Antarctic sea ice melts and re-forms each year; wherever there is new ice, we can expect fractionation to occur provided the temperature is below -8°C (which is normally true). Although frost flowers are only observed when wind conditions are light [Perovich and Richter-Menge, 1994], we can assume that fractionation does occur at all times, but during windy conditions the frost flowers are blown away as they form. The flowers will be mobilised into the atmosphere unless they become covered in snowfall before that can occur, although the size of particles formed as they disintegrate is of some importance as only small particles will be exported from the sea-ice zone.

It has been found that, under laboratory conditions, the slush and flowers are equivalent to a 2 mm water column, and have a maximum salinity of around 100PSU [Martin *et al.*, 1996; Perovich and Richter-Menge, 1994]. Therefore the total salt content available to be mobilised is $0.2 \text{ kg m}^{-2} \text{ yr}^{-1}$ for the entire sea ice area. This is of course an upper limit to the amount actually produced which might be an order of magnitude or more lower. In one case the mass of frost flowers per unit area of sea ice was estimated to be $0.025\text{--}0.05 \text{ g cm}^{-2}$ [Perovich and Richter-Menge, 1994], or $250\text{--}500 \text{ g m}^{-2}$, which at a salinity between 10 and 100 PSU gives a range for salt production of $0.0025\text{--}0.050 \text{ kg m}^{-2} \text{ yr}^{-1}$.

For comparison, the production flux for sea salt aerosol from open water is of order $10^{-9} \text{ kg m}^{-2} \text{ s}^{-1}$, which is $0.03 \text{ kg m}^{-2} \text{ yr}^{-1}$ [Gong *et al.*, 1997a, b]. However, this is controlled by the state of the sea surface. In the sea ice zone, the sea surface is generally very calm, and the open water percentage in winter is of order 10% at most. Thus we would expect the sea salt production from the sea ice zone itself to be well below $0.001 \text{ kg m}^{-2} \text{ yr}^{-1}$ (based on the area of the sea ice zone, not of the open water leads). This is lower even than our lowest estimate of the production from frost flowers. For the open water zone around the sea ice zone, production will again be at open water levels, but model calculations suggest that only 1–2% is exported beyond an individual 300 km grid box [Gong *et al.*, 1997b]. Thus the import to the sea ice zone is again likely to be much smaller than the frost flower production. We can therefore tentatively estimate that frost flower production should always

dominate over open water production at any coastal location where there is at least 300 km of sea ice.

It is less easy to estimate the relative importance of the two sources further inland, because this depends on the ability of salt to take part in long-range transport. Only a small proportion of the particles produced by open water is sub-micron, and can be transported long distance [Gong *et al.*, 1997a]. We can speculate that frost flower salt will also be on large particles, but no data exists as yet. Observations of fractionation in different size ranges in sea salt aerosol, and more knowledge of frost flower distribution and production will be needed to improve these estimates.

Satellite imagery of sea ice may well prove a useful tool in the future for improving our knowledge of the distribution and rate of production of frost flowers. Synthetic Aperture Radar, such as that carried by the ERS-1 satellite, is sensitive to the nature of the sea ice surface and has been used to identify frost-flower covered leads in the Arctic [Melling, 1998; Ulander *et al.*, 1995]. However, little quantitative data exists as yet for the Antarctic.

Conclusions

Frost flowers are considerably depleted in sulphate, and to a lesser extent sodium, compared to the bulk seawater ratio. This is consistent with precipitation of mirabilite during sea ice formation below -8°C .

Aerosol generated from frost flowers would have high sodium:sulphate ratios. This would cause nss sulphate values calculated using the ratio of sodium:sulphate in bulk seawater to be unrealistically low or even negative in winter aerosol, and in ice cores at coastal sites.

Aerosol generation from frost flowers, or the brine from which they are formed, would also explain events of high salt loading in winter months, owing to the high concentrations of salt in the flowers and the fragility of the flowers.

The production of sea salt aerosol from frost flowers in the sea ice zone is likely to exceed the production of aerosol from open water during the winter months when sea ice is abundant. We should therefore expect winter snow and aerosol at coastal Antarctic sites to contain fractionated sea salt,

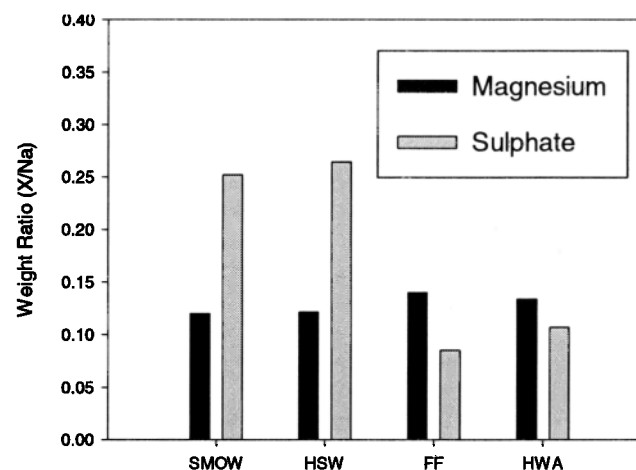


Figure 2. Ratios of sulphate and magnesium to sodium in various samples. SMOW is standard mean ocean water; HSW is sea water from near Halley; FF is frost flowers; HWA is Halley winter aerosol [Hall, 1998]

but further data is needed to estimate the likely importance of this source further inland.

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