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Specific surface area, density and microstructure of frost flowers

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[1] Frost flowers often grow on new sea ice. They are thought to have a high specific surface area (SSA) that provides sites for heterogeneous reactions. We have measured the SSA of frost flowers using CH₄ adsorption at 77 K and obtained a value of 185 (+80 –50) cm²/g, much lower than inferred by others. Their density is 0.02 g/cm³. We calculate that the total surface area of frost flowers is 1.4 m² per m² of ice surface, so that they do not increase the ice surface area significantly. Their role as sites for enhanced heterogeneous reactions should be reconsidered. Frost flowers also commonly grow on fresh water and the saline brine seen on young sea ice is not necessary for their growth. Photo- and electro-micrographs reveal hollow and concave structures, typical of very fast growing crystals. The brine that wicks up frost flowers considerably perturbs their growth. **Citation:** Domine, F., A. S. Taillandier, W. R. Simpson, and K. Severin (2005), Specific surface area, density and microstructure of frost flowers, *Geophys. Res. Lett.*, 32, L13502, doi:10.1029/2005GL023245.

1. Introduction

[2] Frost flowers (FF) are delicate ice crystals that often form on the surface of young sea ice [Perovich and Richter-Menge, 1994]. A highly saline brine also forms on young sea ice and wicks up the FF, leading to FF salinities of up to 115 g/kg [Rankin *et al.*, 2002]. The fragile FF can be wind-blown and supply sea salt aerosol to the atmosphere and the marine and coastal snowpacks. The interest for FF has grown recently because of their possible role in supplying bromine compounds to the atmosphere, thus leading to ozone and mercury depletion events in polar regions [Kaleschke *et al.*, 2004]. Rankin *et al.* [2000, 2002, and references therein] and Wolff *et al.* [2003], based on the observation that sea salt from frost flowers was fractionated due to mirabilite precipitation, also suggested that they may be the main wintertime source of sea salt to the Antarctica. This has important implications for ice core interpretation and our understanding of past atmospheric circulation around Antarctica [Rankin *et al.*, 2002]. Finally, Rankin *et al.* [2002] estimated that FF had a total surface area (TSA,

as defined by Dominé *et al.* [2002]) in the range 50–1000 m² per m² of ice surface, “probably nearer the upper limit”, and suggested that they provide sites for enhanced exchanges and chemical reactions [Rankin *et al.*, 2002].

[3] To obtain their estimate of the TSA of FF, Rankin *et al.* inferred values of the specific surface area (SSA, i.e. the surface area per unit mass) of FF in the range 0.2 to 2 m²/g. However, a recent set of 176 measurements of the SSA of snow by Legagneux *et al.* [2002] has found a maximum value of 0.15 m²/g, observed for fresh dendritic snow. Our observations of frost flowers during several Arctic trips suggested to us that their SSA could not be greater than that of dendritic snow. We have therefore measured the SSA of FF in Alaska, using the method of Legagneux *et al.* [2002] and taken optical and electronic micrographs to observe their microstructure. We have also observed FF on lake and river ice in Alaska, which constrains their formation mechanism. Finally, we have measured the density of FF in Spitsbergen.

2. Experimental

[4] The SSA of FF was measured using CH₄ adsorption at 77 K [Legagneux *et al.*, 2002]. Briefly, the adsorption isotherm of CH₄ on the FF sample was recorded at 77 K. A B.E.T. mathematical treatment was used to extract the SSA. We looked for FF near Barrow, Alaska. Success commanded that we be at Barrow with liquid N₂ when FF formed. A lead opened in the sea ice and FF did form before the liquid N₂ arrived, but did not reform during our 18 days of presence with the liquid N₂. We therefore drilled large holes in the sea ice to expose sea water, let it freeze, and let the frost flowers grow naturally on the forming ice.

[5] Ice chunks of about 70 × 40 cm in surface area and 70 cm deep were cut off the 1.7 m thick sea ice with a saw at 71°20.363'N, 156°40.484'W. Further drilling reached sea water, which filled the holes. Plastic pans 60 × 40 cm and 15 cm deep were also filled with sea water, and froze overnight while the air temperature dropped to –21°C. The sky was clear and the wind speed was 2.1 to 3.6 m/s. The next morning, 9 April 2004, FF had formed on the frozen sea water, mostly toward the downwind edges of the holes and pans. Two types of crystals were observed: “dry” crystals where the wicking up of brine could not be observed, and “wet” crystals, whose surface appeared to be totally covered by the brine. Three glass vials were used for sampling: N°1 contained a few wet FF for photography, N°2 a few dry ones for photography. N°3, intended for SSA measurements, contained the rest of the dry FF. Because the amount of FF was limited, all of the remaining dry FF were sampled, and a few nearby wet FF were also sampled. The vials were immediately immersed in liquid N₂ where they remained until the measurements. Photomicrographs were taken in a cold room with a 35 mm SLR camera with

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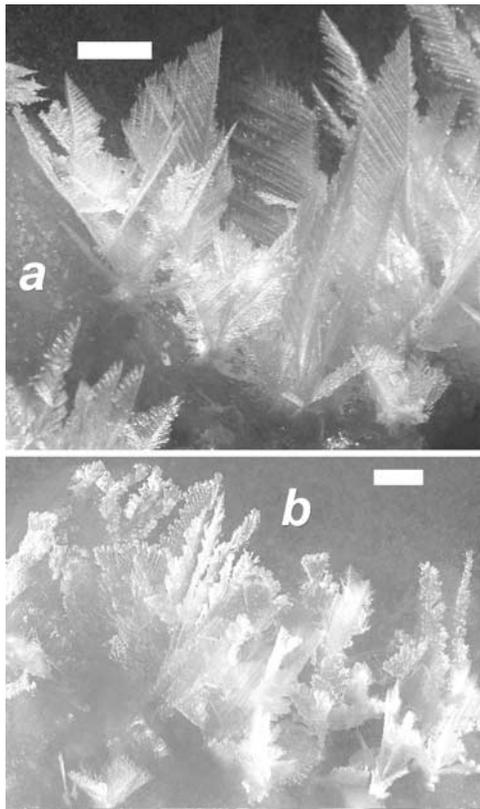


Figure 1. Frost flowers sampled for SSA measurements and photomicrographs. (a): “dry” frost flowers; (b): “wet” ones. Scale bars: 1 cm. See color version of this figure in the HTML.

bellows. An environmental scanning electron microscope (Electrosan E2020) with a cold stage maintained around -100°C was used to take electromicrographs, with O_2 as a bath gas. The density of FF that formed on the east coast of Spitsbergen ($77^{\circ}50.91'\text{N}$, $18^{\circ}27.63'\text{W}$) was measured on 27 and 28 February 2005 by delimitating an area 15×18 cm, measuring the height of the FF, and weighing them.

[6] Frost flowers were also found on lake and river ice in various places in Alaska during leisure trips and no sampling was possible. Pictures were taken with a digital camera in macro mode.

3. Results

[7] Photographs of the frost flowers just before they were sampled are shown in Figure 1. FF can grow in several crystal habits, such as stellar dendrites and needles. The crystals that formed here were the more frequent stellar dendrites, similar to those observed by others [Perovich and Richter-Menge, 1994; Martin *et al.*, 1995; Rankin *et al.*, 2002; Kaleschke *et al.*, 2004]. Some of the wet frost flowers show “fuzzy” edges (Figure 1b) whose aspect were reminiscent of riming on dendritic snow crystals [e.g., Cabanes *et al.*, 2002]. Photomicrographs of dry FF are shown in Figure 2. The structure of these frost flowers is similar to that of a dendrite of atmospheric dendritic crystals [e.g., Wergin *et al.*, 1996; Cabanes *et al.*, 2002; Libbrecht and Rasmussen, 2003], but they are about 10 times as large and

have more secondary dendrites. The tips of the dendrites can form either flat faces or rounded shapes (Figure 2). Flat faces indicate rapid growth and are observed in many precipitating crystals and in crystals metamorphosing rapidly under a high temperature gradient [Wergin *et al.*, 1996; Dominé *et al.*, 2003]. Rounded shapes are seen on slow growing crystals, sublimating crystals [Dominé *et al.*, 2003], or on crystals growing extremely fast [Libbrecht, 2003]. Figure 2b shows that the primary dendrite and the first secondary ones have rounded shapes, very similar to those of large (thus fast growing) atmospheric crystals [Libbrecht and Rasmussen, 2003] while other secondary dendrites have faceted ends. The frost flowers grew by about 40 mm in about 14 h, so that their growth rate was around $0.8 \mu\text{m/s}$, close to the maximum growth rate of dendritic crystals in the atmosphere ($1 \mu\text{m/s}$) [Pruppacher and Klett, 1978]. The rounded shapes here are then due to very fast growth rates.

[8] Figure 3 shows photomicrographs of “wet” frost flowers. The brine layer that covers the crystal gives them a definitely different aspect, and smoothes out microstructures. Figure 3c also shows outgrowths at the end of brine-covered secondary dendrites. They have erratic shapes similar to rime [Dominé *et al.*, 2001] confirming the observations of Figure 1, but rime formation is not reasonable in a cold clear night. We suggest instead that the

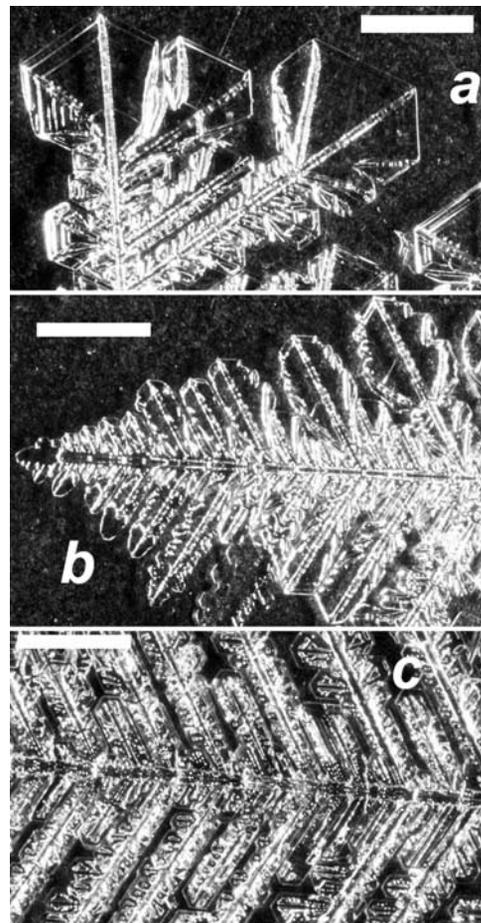


Figure 2. Photomicrographs of “dry” frost flowers. Scale bar: 1 mm.

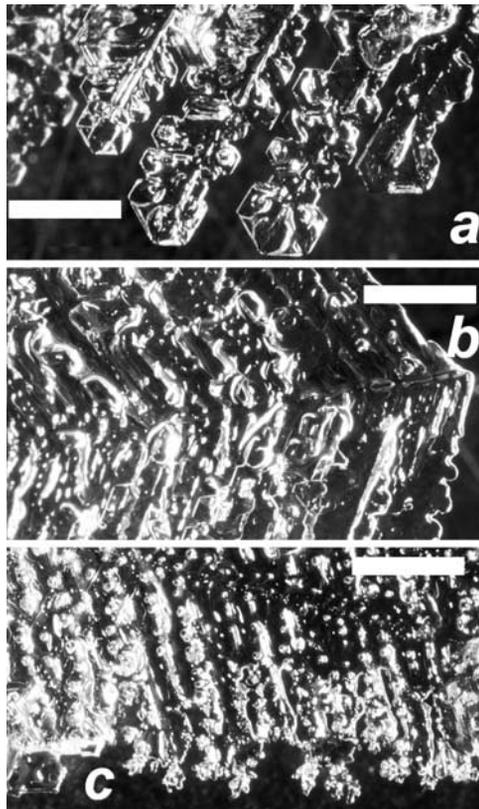


Figure 3. Photomicrographs of “wet” frost flowers. Scale bar: 1 mm.

presence of the brine perturbed crystal growth in a major manner. Indeed, gaseous impurities significantly modify ice habit [e.g., *Anderson et al.*, 1969], so it is reasonable to expect major modifications in the growth of crystals entirely coated with brine as growth perturbations are usually due to impurities sticking to the ice surface. The crystals showing these outgrowths were all smaller than the dry crystals, suggesting that growth of brine-covered crystals is very slow, so that to a first approximation, FF crystals stop growing when they become brine-covered.

[9] Electromicrographs of details of dry FF are shown in Figure 4. Grooves, hollows and holes are often observed. Some of the hollows (Figures 4c and 4d) are similar to those seen in depth hoar and surface hoar crystals [*Dominé et al.*, 2003]. Such concave shapes are seen when fast crystal growth is limited by the gas phase diffusion of water molecules [e.g., *Dominé et al.*, 2003, and references there-

in]. Stronger depletion of molecules near the center of the faces promotes hole formation. Larger sizes increase this effect, which is expected to be often observed on FF crystals.

[10] FF were observed frequently on fresh water in Alaska. The pictures in Figure 5 were taken on Fossil creek (65°34.0'N, 147°26.9'W) on 15 March 2004. Overflow water froze overnight and FF had grown on the newly formed ice during the clear and cold ($T < -15^{\circ}\text{C}$) night. These dendritic FF are identical to those observed on sea ice by us and others. FF of the needle type were seen on Smith Lake (64°51.9'N, 147°52.1'W) on 25 October 2003. *Perovich and Richter-Menge* [1994] observed that on forming sea ice, after a brine had appeared on the surface, small ice bumps a few mm in size formed on the surface. They deduced that both the surface brine and the ice bumps were critical to FF growth, with the brine acting as a source of additional water vapor and the bumps as nucleation site. The frequent observation of FF on fresh water show that the brine is not necessary for their formation. The bumps are needed because FF cannot nucleate on the liquid brine.

[11] The SSA of the FF in vial N°3 was measured twice, with values of 166 and 203 cm^2/g . *Legagneux et al.* [2002] mention that the reproducibility of the method is 6%. This is not verified here because there were only 6.3 g of FF, and the surface area of the sample was thus about 0.1 m^2 , while typical samples have 1 m^2 of surface area. This accounts for the lower reproducibility. Furthermore, the brine on the few wet FF in the sample added mass and reduced the SSA, and this produced a negative systematic error, leading to an asymmetric error bar. We thus conclude that the SSA of our FF was 185 (+80, -50) cm^2/g .

[12] FF in Spitsbergen were seen at least 24 hours after their formation. They were all brine-covered (“wet”) and formed discontinuous patches 10 to 30 cm in diameter, about 2 cm thick, that covered about 25% of the ice surface. The 4 density measurements yielded values of 0.012, 0.018, 0.021 and 0.028 g/cm^3 . These measurements have an accuracy better than 20%, and the variability is ascribed to the variability in sample structure, readily visible on the site. The density for these “wet” FF is then taken as 0.02. Dry FF are necessarily lighter, probably in the range 0.01 to 0.015, as frequently seen for fresh dendritic snow [*Cabanes et al.*, 2002, and unpublished results].

4. Discussion

[13] The SSA measured is much lower than the estimate of *Rankin et al.* [2002], 2000 to 20000 cm^2/g . The FF used

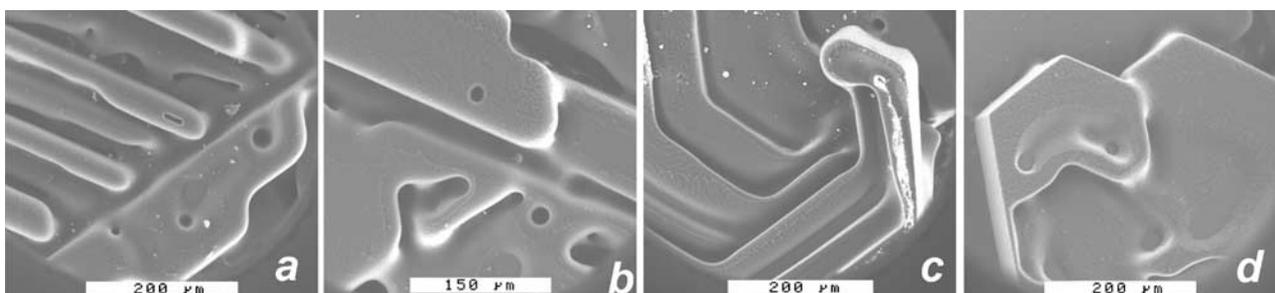


Figure 4. ESEM images of details of frost flowers.

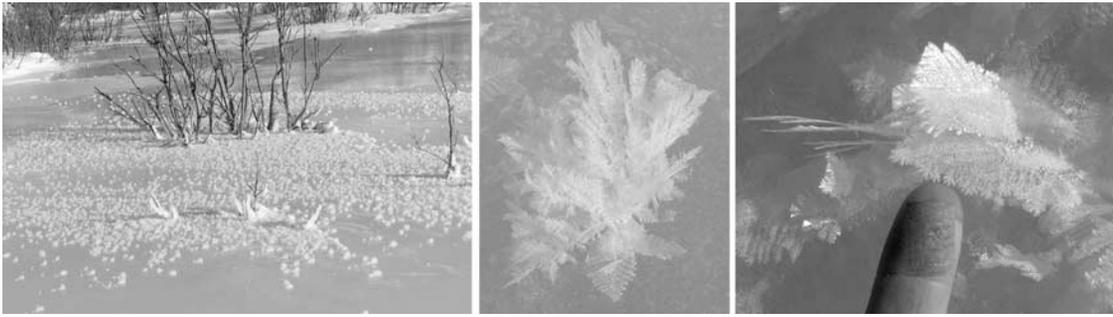


Figure 5. Photographs of frost flowers on rivers in Alaska. Width of finger: 19 mm. See color version of this figure in the HTML.

had a microstructure similar to those of dendritic snow crystals, that have a SSA in the range 800–1500 cm²/g [Legagneux *et al.*, 2002]. Since for a given shape, SSA is inversely proportional to size and FF are about 10 times larger than dendritic crystals, we expect that of FF to be 80–150 cm²/g, consistent with our measurements of 185 cm²/g. This value can be used to estimate the TSA of FF, which is the dimensionless product of SSA (cm²/g), density (g/cm³) and height of the FF layer (cm). Since the FF in Spitsbergen covered $\frac{1}{4}$ of the surface, our estimate of the TSA of dry FF is $185 \times 0.015 \times 2/4 = 1.4$ m² per m² of sea ice. For wet FF, Figure 4 suggests that a brine would smooth out microstructures and reduce this TSA to less than 1 m² per m² of sea ice. Additional measurements of SSA and density are needed to confirm this value, but it seems unlikely that FF can provide much additional surface area relative to the ice surface itself and thus have limited potential to serve as sites of enhanced exchanges and chemical reactions. With regards to the activation of Br⁻ contained in sea salt into forms that destroy tropospheric ozone, this result supports the conclusion of Simpson *et al.* [2005] that this process is not likely to take place on frost flowers themselves, but may rather be faster on surfaces where sea salt coming from FF has been deposited. FF, because they are highly saline and are easily windblown, can be considered as a source of sea salt and Br⁻ to the snowpack, but probably not as sites for enhanced chemical reactions.

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