

Frost flowers and sea-salt aerosols over seasonal sea-ice areas in north-western Greenland

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Sea-salts and halogens in aerosols, frost flowers and brine play an important role in atmospheric chemistry in polar regions. Sea-salt fractionation proceeds gradually on new and young sea ice with decrease of temperature (e.g., Hara et al., 2004, 2012). Thus, sea-salt ratios in sea-salt aerosols (SSA) released from sea-ice areas differ from those of bulk seawater ratio, because of sea-salt fractionation on frost flower and in brine. Sea-salt fractionation can engender modification of aerosol hygroscopicity, which is closely related to phase transformation, heterogeneous reactions, and abilities of cloud condensation nuclei and ice nuclei. Furthermore, enrichment of halogens such as Br⁻ and iodine in SSA and frost flowers can be associated with atmospheric halogen cycles in polar regions, which engender surface O₃ and Hg depletion during polar sunrise (Barrie et al., 1988; Ebinghaus et al., 2002). To elucidate the atmospheric impact of fractionated sea-salt particles, and their relation between sea-salt particles in the atmosphere and frost flowers on sea ice, one must ascertain their (1) chemical properties (e.g., concentrations, ratios, and pH) of frost flowers and brine, and (2) the physical and chemical properties of aerosols (e.g., size distribution, constituents, and mixing states) above seasonal sea ice with frost flowers. In spite of the importance, simultaneous observations and measurements of aerosols and frost flowers over seasonal ice areas with frost flower appearance have not been reported for polar regions.

Simultaneous sampling and observations of frost flowers, brine, and aerosol particles were conducted on several types (fresh - aged) of sea-ice and frost flowers around Siorapaluk in north-western Greenland during December 2013 – March 2014. Sea-salt constituents in frost flowers were determined with ion chromatograph (IC). Br⁻ and iodine (I⁻ + IO₃⁻) were analyzed with IC-MS and ICP-MS, respectively. Individual aerosol particles were observed and analyzed using SEM-EDX.

Results show that water-soluble frost flower and brine constituents were sea salt constituents (e.g., Na⁺, Cl⁻, Mg²⁺, and Br⁻). Concentration factors of sea-salt constituents of frost flowers and brine relative to seawater were 1.14–3.67. Sea-salt enrichments of Mg²⁺, K⁺, Ca²⁺, and halogens (Cl⁻, Br⁻, and I) relative to Na⁺ in frost flowers were associated with sea-salt fractionation by precipitation of mirabilite (Na₂SO₄ 10H₂O) and hydrohalite (NaCl 2H₂O). Particularly, mirabilite precipitation contributed remarkably to sea-salt fractionation in frost flowers. In spite of clear change of sea-salt ratios of frost flowers, sea-salt ratios in brine were resemble bulk seawater ratios. We took slush layer on sea-ice as “brine samples” in this study. Therefore, our brine samples may contain both sea-salts precipitated on sea-ice (slush layer) and the concentrated seawater (residual brine). Consequently, significant difference of seawater ratios was not observed in brine samples. Comparison between sea-salt ratios in brine and frost flower implied that precipitation of mirabilite and hydrohalite proceed in slush layer and then the residual brine were migrated vertically onto frost flowers in our research conditions. Molar ratios of sea-salts (Mg²⁺/Cl⁻, K⁺/Cl⁻, Ca²⁺/Cl⁻, and Br⁻/Cl⁻) changed gradually with aging and growth of frost flowers and sea-salt fractionation under colder conditions. Furthermore, sea-salt fractionation was associated with not only surface air temperature but also sea-ice thickness which related to heat conduction from seawater. In contrast to Br⁻ enrichment in frost flower with the aging, changes of I/Cl⁻ ratio in frost flowers, however, were not clear.

Aerosol number concentrations, particularly in coarse mode, were increased considerably by release from the sea-ice surface under strong wind conditions. Sulphate depletion by sea-salt fractionation was found to be slight in sea-salt aerosols because of heterogeneous SO₄²⁻ formation from anthropogenic SO₂ on SSA. Mg was enriched in coarse and fine SSA under colder conditions, although Mg/Na ratios in SSA collected near sea-ice margin were similar to bulk seawater ratio. Mg in SSA was in the form of MgCl₂ and MgSO₄ in this study. Strong Mg enrichment might be more likely to proceed in fine SSA. Although Mg-rich SSA was present in all samples, higher Mg/Na ratios in SSA were observed under not strong winds but calm winds without blowing snow. Therefore, release of highly Mg-rich SSA from sea-ice surface might depend on wind speed and surface conditions. In addition, ikaite-like and mirabilite-like particles were identified in the atmosphere only near new sea ice close to the sea-ice margin. Thus, ikaite-like and mirabilite-like particles might be released from initial sea-ice before freezing over.

From the evidence and results from this work and earlier works, we propose the following as hypotheses for the sea-salt fractionation processes on sea ice and the release of seasalt particles into the atmosphere.

Initial stage – open sea surface: Before sea-ice formation, SSA are released from the sea surface through bubble bursting and breaking waves. Sea-salt ratios in SSA released by bubble bursting are similar to the seawater ratio.

First stage – seawater freezing: Seawater starts freezing at lower air temperatures. In this stage, sea ice was likely present in conditions of grease ice, frazil ice, and sludge. Considering that SSA with ratios similar to seawater were found to be present only near sea ice margin, these particles must be released from the sea surface in the initial stage and first stage. Depending on the temperature at the sea-ice surface, ikaite can start precipitation at temperatures lower than $-2\text{ }^{\circ}\text{C}$.

Second stage – sea-ice formation and sea-salt fractionation: Then, the sea-surface was covered with thin sea ice (i.e., nilas). The presence of sea ice prevents the release of sea-salt particles from the sea surface into the atmosphere. A strong vertical gradient of air temperature near the sea-ice surface might cause frost flower formation on sea ice. Some brine can be migrated vertically on frost flowers. Cooling of surface of the frost flowers and brine on sea ice can engender precipitation of ikaite and mirabilite. The presence of ikaite-like particles and mirabilite-like particles in the atmosphere suggests that these particles are released into the atmosphere through physical processes. Mirabilite-like and ikaite-like particles were identified in aerosols collected only over new sea ice areas. Therefore, these particles might be released from fresh sea-ice areas. However, specific release processes remain unclear.

Third stage – frost flower growth and sea-salt fractionation: With sea-ice growth, the temperature on sea ice might decrease gradually by reduction of heat conduction from seawater to the sea-ice surface. Lower temperatures on and in the slush layer can induce sea-salt fractionation by precipitation of mirabilite and hydrohalite. Precipitation of mirabilite and hydrohalite can engender sea-salt enrichment (e.g., Mg^{2+} , K^{+} , and Ca^{2+}) in frost flowers and the residual brine. The residual brine having Mg enrichment is migrated vertically on frost flowers.

Fourth stage – strong winds and snowfall on frost flowers: Under conditions with strong winds, snowfall, and blowing snow, snow particles were attached on frost flowers and slush layers. As suggested by laboratory experiments (Roscoe et al., 2010), no aerosol particles are released from frost flowers. However, Mg-rich sea-salt particles and Mg salts might be released from the slush layer and surface snow on sea ice.

Fifth stage – frost flower and slush layer covered with snow: When snowfall and blowing snow are sufficient to cover frost flowers and the slush layer on new–young sea ice, frost flowers and slush layer are buried completely in snow after the storm. After snow deposition onto new–young sea ice, the residual brine with Mg^{2+} enrichment might be migrated vertically and gradually into the snow layer. As a result, the snow layer on new–young sea ice was wet, as observed in this study. Sea-salts in the migrated brine, frost flowers and snow can be redistributed through snow metamorphosis, although distributions of sea salts might be heterogeneous in the snow layer. Mg-rich SSA and Mg-salt particles might be released from the surface snow on sea ice because of limited loss of Mg^{2+} in the aged surface snow on sea ice. Therefore, we speculate that splash and erosion of the residual brine on snow and frost flowers by winds are plausible release processes of Mg-rich SSA and Mg-salt particles.

Sixth stage – snow erosion by strong winds: With sea-ice growth, snow and slush layers can be frozen gradually. Then, strong winds (i.e., storm condition) engender erosion of aged surface snow on sea ice and release of Mg-rich SSA into the atmosphere. A dry and hard surface of sea ice appears after snow layers are removed from old and very old sea ice. Because of wet conditions in the snow and slush layer, a large amount of surface snow remained on the young sea ice.

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