Supplement of

Technical note: Sublimating frozen CsCl solutions in ESEM: the number and size of salt particles are influenced by the ice sublimation temperature, salt concentration and freezing method

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Text S1: Calculating the vapour pressure above brine at −20 °C

The saturated vapour pressure above the brine can be approximated by Raoult's law (Eq. 1):

$$p_{\mathrm{brine}} = x_{\mathrm{H_2O}} \cdot p^*_{\mathrm{H_2O}}, \tag{1}$$

where p_{brine} is the saturated vapour pressure above the brine, $p^*_{\mathrm{H_2O}}$ is the saturated vapour pressure of pure water, and $x_{\mathrm{H_2O}}$ is the mole fraction of water in the brine. At −20 °C, the saturated vapour pressure above ice is 103 Pa (Wexler, 1977), and the $p^*_{\mathrm{H_2O}}$ of supercooled water is 22 Pa higher, equalling 125 Pa (Murphy and Koop, 2005). The eutectic molality (at −23 °C) of the CsCl in the brine is 7.7485 mol kg^{-1}; at −20 °C, the equilibrium molality of the CsCl in the brine reaches about 7.2 mol kg^{-1} (Gao et al., 2017). As CsCl is an electrolyte and dissociates into Cs$^+$ and Cl$^-$ ions, there is 7.2 mol of each of the ions in a solution containing 1 kg (55.6 mol) of water. Thus,

$$x_{\mathrm{H_2O}} = \frac{n_{\mathrm{H_2O}}}{n} = \frac{n_{\mathrm{H_2O}}}{n_{\mathrm{H_2O}} + 2 \times n_{\mathrm{CsCl}}} = \frac{55.6}{55.6 + 2 \times 7.2} = 0.794. \tag{2}$$

From eq. 1 and eq. 2

$$p_{\mathrm{brine}} = 0.794 \times 125 = 99.25\ \mathrm{Pa} \tag{3}$$

This calculation is based on the assumptions of ideal behaviour of CsCl solution and full dissociation of CsCl salt in the brine, therefore, the value of 99 Pa is just an approximate estimate.

Text S2. Adhesion of the salt particles to the silicon pad of the cooling stage

The microscopic images did not allow us to determine if the salt particles were firmly affixed to the cooling stage or lay on the silicon surface freely. Therefore, we tested the adhesivity of the fine particles and larger aggregates to the silicon pad of the cooling stage in the 0.05 M non-seeded sample. After the ice sublimation was completed, we imaged the chosen spot of the sample (which contained both the fine particles and the aggregates, Figure S5a), aerated the ESEM, and opened the specimen chamber. Aerating the chamber alone sufficed for most of the aggregates to fly away. Additionally, we blew upon the sample a gentle stream of air from an air gun. Subsequently, we closed and evacuated the chamber and imaged the same spot after the aeration/air blowing (Figure S5b). By this process, most of the aggregates were removed, while the fine particles stayed almost intact; thus, the particles had probably been firmly affixed to the stage, but the salt flakes and tufts lay on it without any fixation. These results are in accordance with our inspection of the sublimation process, where the fine particles appeared from below the frozen sample (they had likely formed in its bottom part, in direct contact with the cooling stage), and the flakes and tufts surfaced on the frozen sample and fell on the ground after the ice had sublimated (they had likely formed on the surface and in the body of the ice matrix).

Although adhesion of the fine particles to the pad was detected in our experiments, the effect might be irrelevant in natural samples. In Arctic conditions, the underlying ice and snow would most probably serve as the basis for the fine particles, and these would be released by the sublimation of such a ground layer.

Text S3. Calculating the particle number density

The shape of the droplet was approximated by a spherical cap with a base diameter of 4 mm and a height of 1 mm. The maximum drop height was measured using an electron microscope, as a difference in the working distance between the plane of focus of the drop-top and the surface of the silicon pad (wafer). The droplet's base and volume were calculated to be 12.6 mm^2 and 6.81 mm^3, respectively.

The surface densities are estimated based on the image analyses of the micrographs via the Mountains® software (Digital Surf). The analyses were performed for the samples where potentially aerosolizable particles were detected: non-seeded and seeded samples (concentration of 0.005 and 0.05 M) sublimated at −25 °C. A few representative spots were analysed for each sample. In the Mountains software, a binarized (black-and-white) imaged was created; the threshold value was selected so that the white spots best represented the individual salt particles. Then the software recognized individual particles and calculated the surface number density of the analysed spot.

Average volume densities of the salt particles (a number of particles generated from 1 mm^3 of the original frozen sample after the ice sublimation) were calculated via multiplying the average surface densities by the area of the base (12.6 mm^2), and subsequently dividing this total number of salt particles in a sample by the volume of the droplet (6.81 mm^3).

		0.005 M CsCl, non-seeded, −25 °C	**0.005 M CsCl, seeded, −25 °C**	**0.05 M CsCl, non-seeded, −25 °C**	**0.05 M CsCl, seeded, −25 °C**
Surface number density of salt particles / mm^{-2}	Spot #1	5550	7730	56900	62800
	Spot #2	1260	12000	21500	59500
	Spot #3		22900		43800
	Spot #4		8400		72400

	Mean	3405 ± 3033	12758 ± 7017	39200 ± 25032	59625 ± 11885
Volume number density of salt particles / mm^{-3}		6300 ± 5613	23604 ± 12983	72528 ± 46314	110319 ± 21989

Table S1. The calculated surface number density (mm^{-2}) and volume number density (mm^{-3}) with sample standard deviation under different conditions.

Text S4. Evaluating the particle size

The sizes of the residual salt particles are evaluated based on the image analyses of the micrographs via the Mountains® software (Digital Surf). As we focus on formation of small particles with a potential to become aerosols (those are usually smaller than 30 µm), the particles larger than 120 µm are not displayed in the analysis. The analyses were performed for the samples where potentially aerosolizable particles were detected: non-seeded and seeded samples (concentration of 0.005 and 0.05 M) sublimated at −25 °C. Each histogram embraces the particles from 3 representative images of the sublimated samples. The images were first contrasted and converted to black-and-white mode. Then the individual particles were recognized by the Mountains® software. The maximum diameter of the particle, measured from its centre of gravity, is presented in the histograms; the maximum diameter is the diameter of the minimum enclosing circle. The normal distribution curve is presented in red.

Supplementary figures

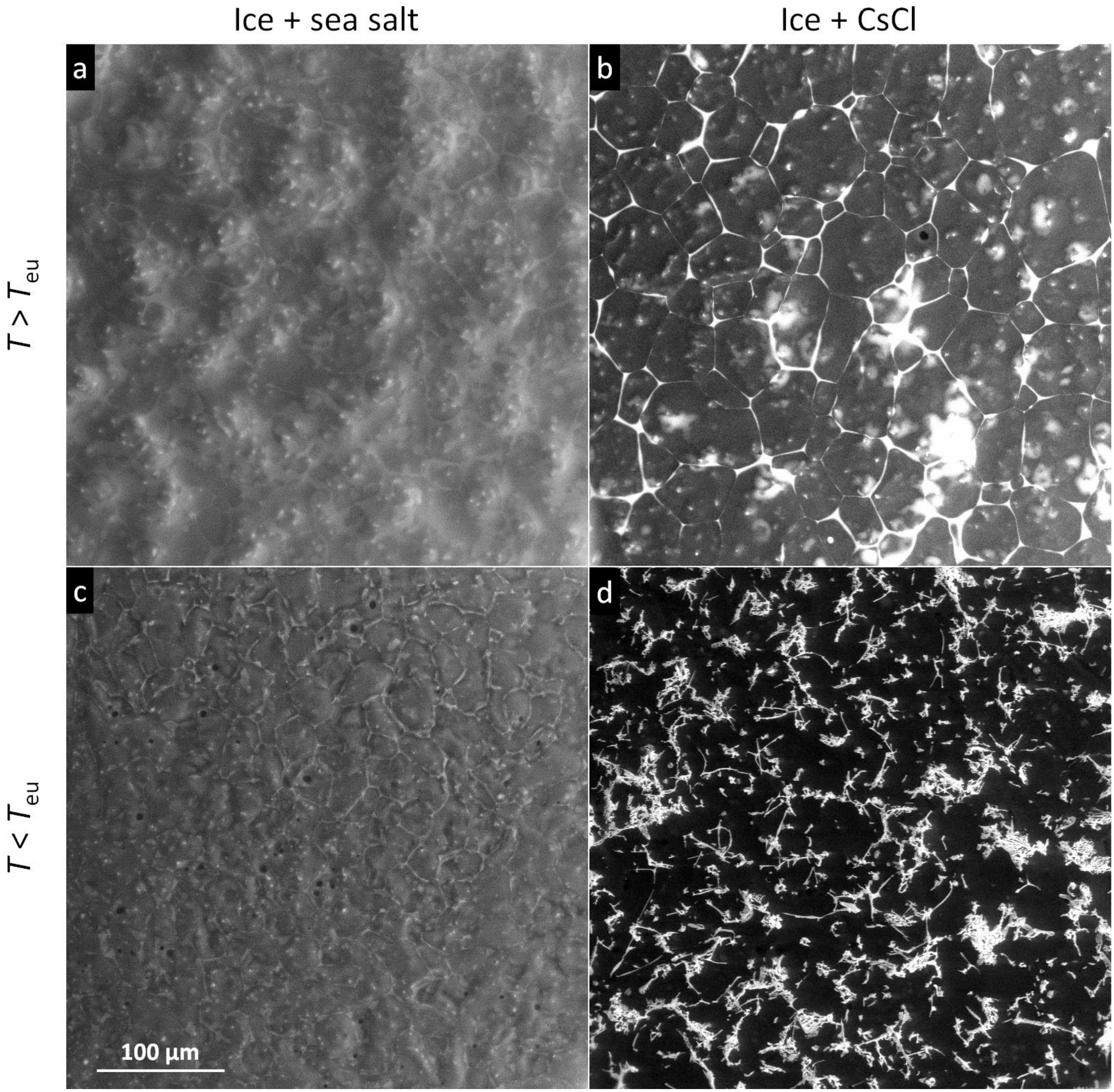

Figure S1: Comparison of the sea salt-ice (left) and CsCl-ice (right) contrast in the BSE detector under similar conditions. The concentrations/salinities and temperatures of the frozen solutions were as follows: a) 3.5 psu sea water (eq. ~0.06 M NaCl), -20°C; b) 0,05 M CsCl (~8.3 psu), -21 °C; c) 3.5 psu sea water (eq. ~0.06 M NaCl); -35 °C, d) 0,05 M CsCl (~8.3 psu), -25 °C.

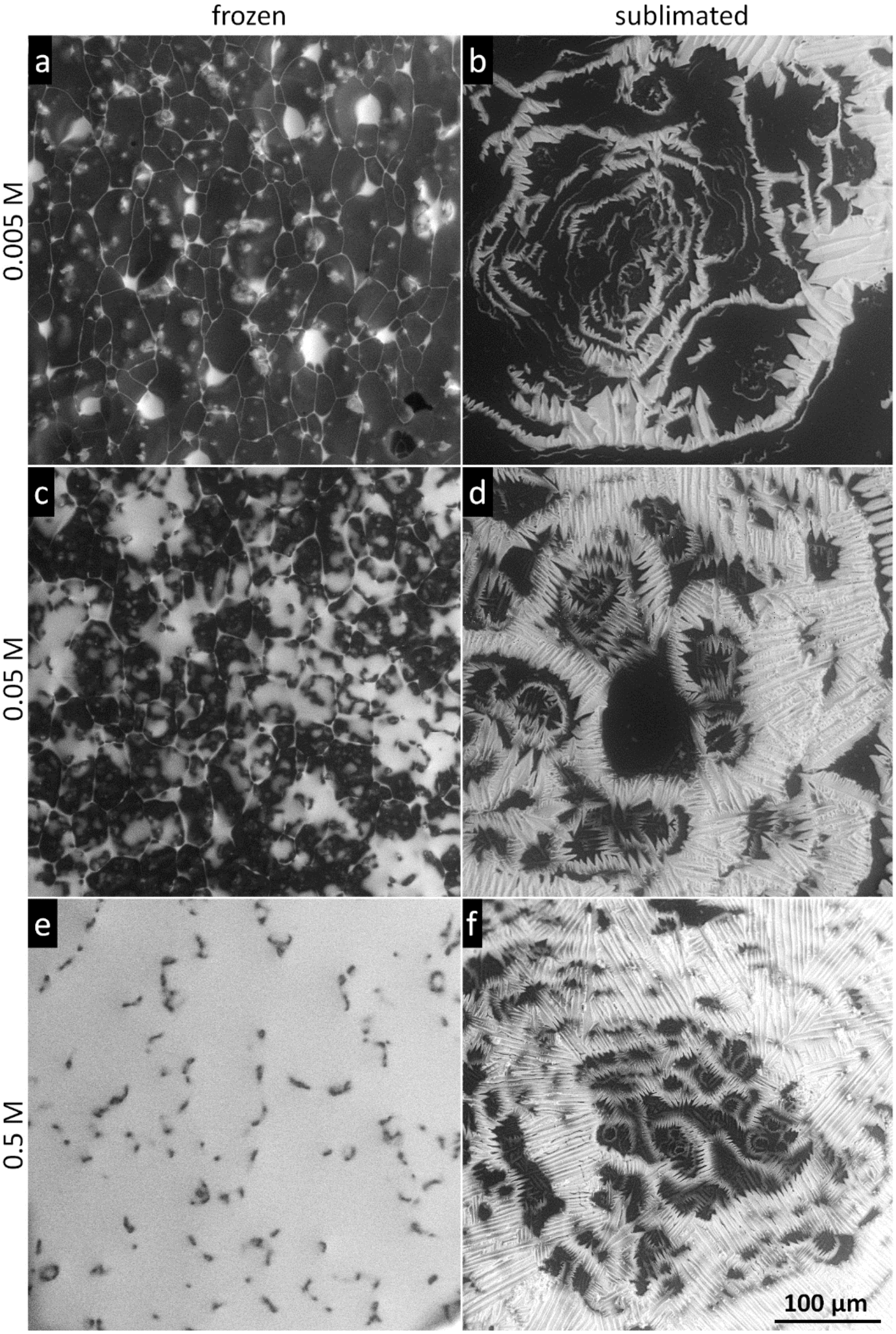

Figure S2: The structure of the frozen samples (before the sublimation) and the CsCl salt residua after the sublimation of the 0.005, 0.05, and 0.5 M non-seeded frozen samples at −20 °C, i.e., above the T_{eu}. In the frozen samples (panels a, c, and e), the white and dark areas represent liquid brine and the ice, respectively. In the sublimated samples (panels b, d, and f), the white and dark areas represent crystallized CsCl salt and the silicon pad, respectively.

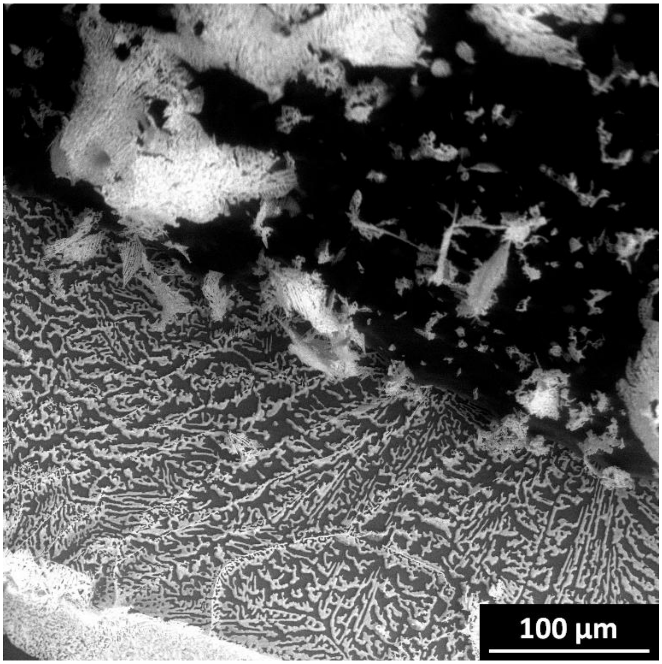

Figure S3: Partially sublimated 0.05 M seeded sample. Prior to sublimation, the frozen sample was cooled down to -25 °C, then heated up to -20 °C, then cooled down to -25 °C again. When heated to −20 °C, the brine at the surface became liquid and leaked to the edge of the sample where it solidified after further cooling. Left-down corner displays a broader salt rim of the drop caused by the liquefaction of the brine above its T_{eu}.

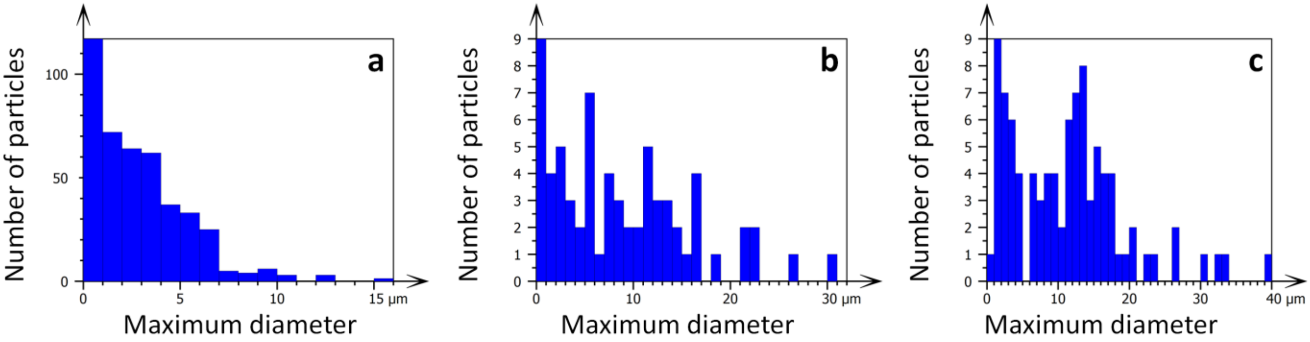

Figure S4: The histograms showing the distribution of the maximum particle diameters of the salt particles found beyond the perimeter of original frozen samples: a) 0.005 M seeded sample, −25 °C; b) 0.05 M seeded sample, −20 °C; 0.05 M non-seeded sample, −25 °C. The smallest applied interval is 1 µm. The data were recorded with the instrumental resolution of 0.5 µm.

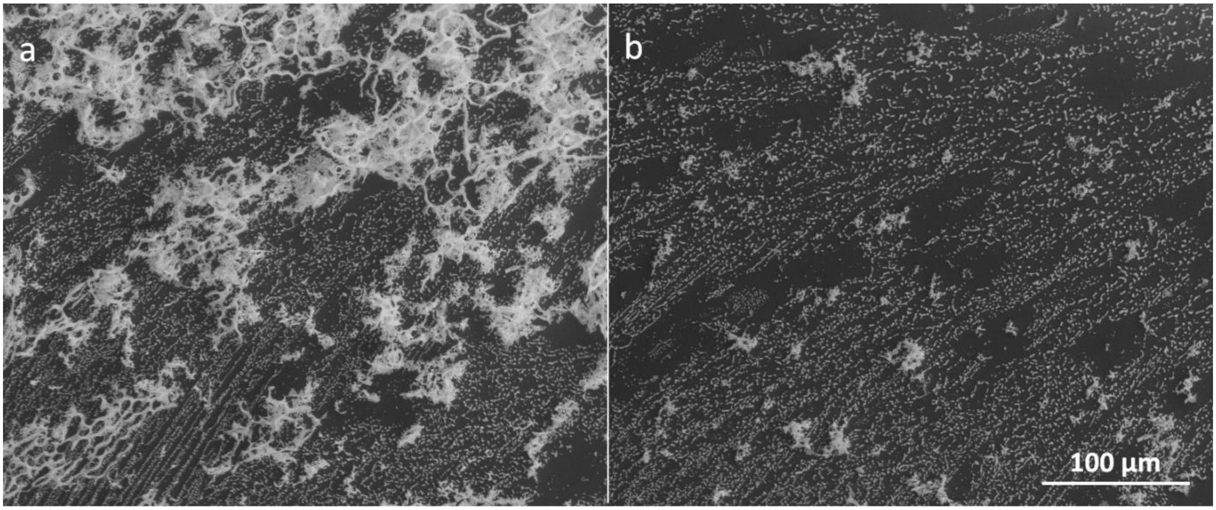

Figure S5: The salt residues in 0.05 M non-seeded sample just after the sublimation process at −25 °C (a) and after venting the chamber, blowing the sample with air gun, and evacuation procedure (b). A same spot is imaged in both panels. The scale in panel b is valid for both the images.