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Ice nucleation activity of silicates and aluminosilicates in pure water and aqueous solutions – Part 2: Quartz and amorphous silica

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S1 DSC thermograms of immersion freezing with emulsions of freshly prepared SA quartz suspensions in glass vials in water or aqueous solutions

We show one set of DSC thermograms (1 K min^{-1} cooling cycle) for each solute concentration for the freshly prepared suspensions in glass vials and measured emulsions.

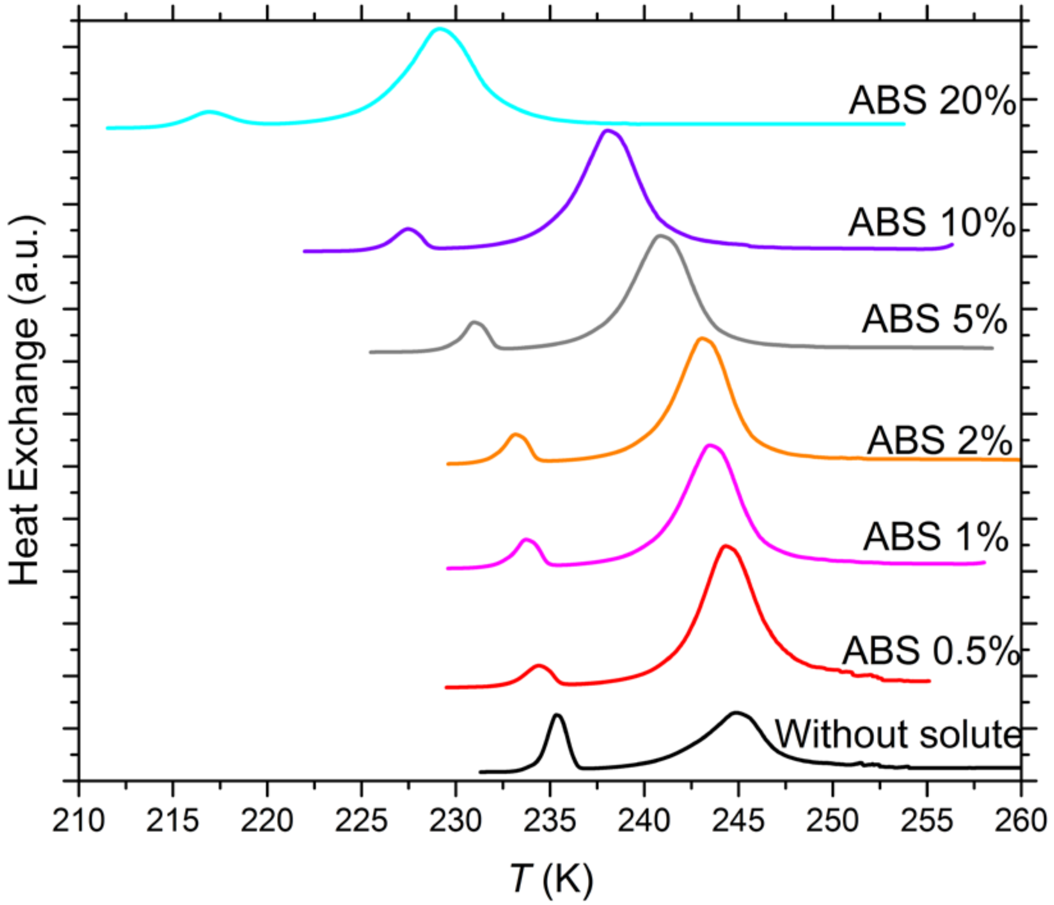


Figure S1. DSC thermograms of 5 wt% of SA quartz particles suspended in ammonium bisulfate (ABS) solution droplets of varying concentration. All curves are normalized such that the areas under the heterogeneous and homogeneous freezing curves sum up to the same value. Numbers next to each curve: Solute concentration in wt%.

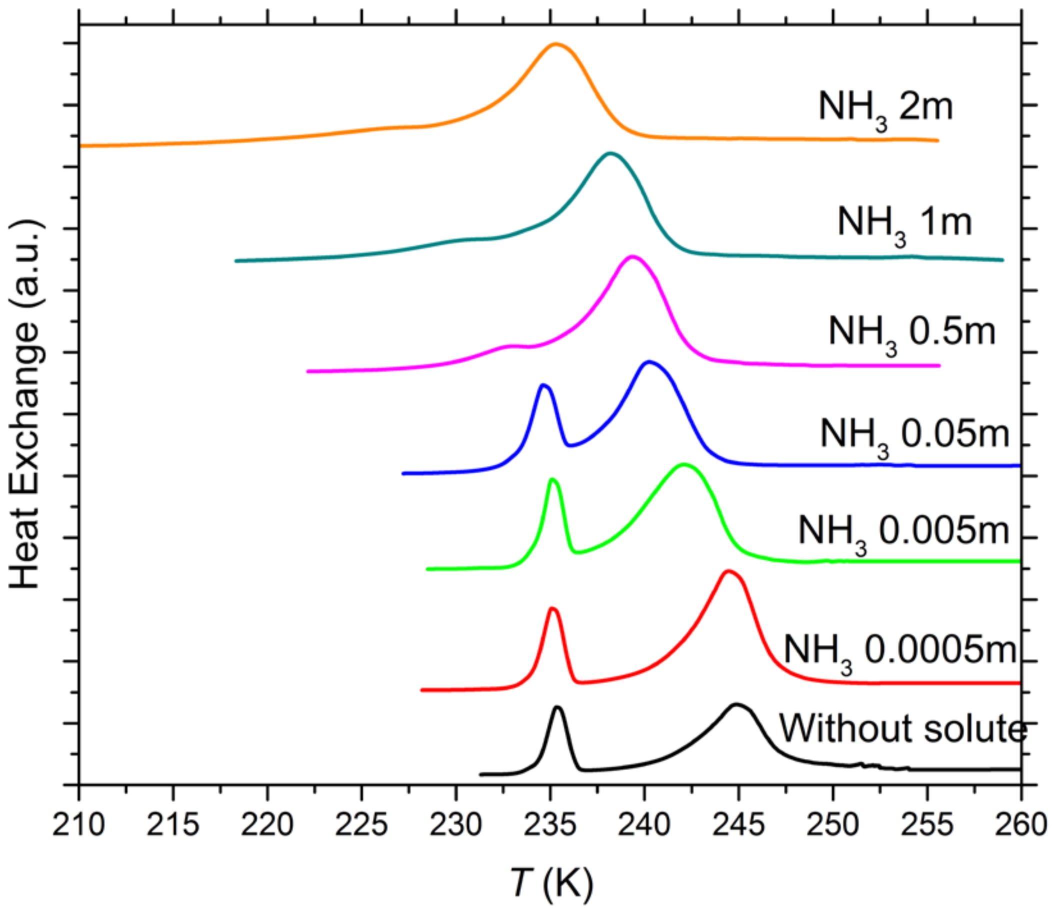


Figure S2. DSC thermograms of 5 wt% SA quartz particles suspended in ammonia (NH_3) solution droplets of varying concentration. All curves are normalized such that the areas under the heterogeneous and homogeneous freezing curves sum up to the same value. Numbers next to each curve: Solute concentration in molality.

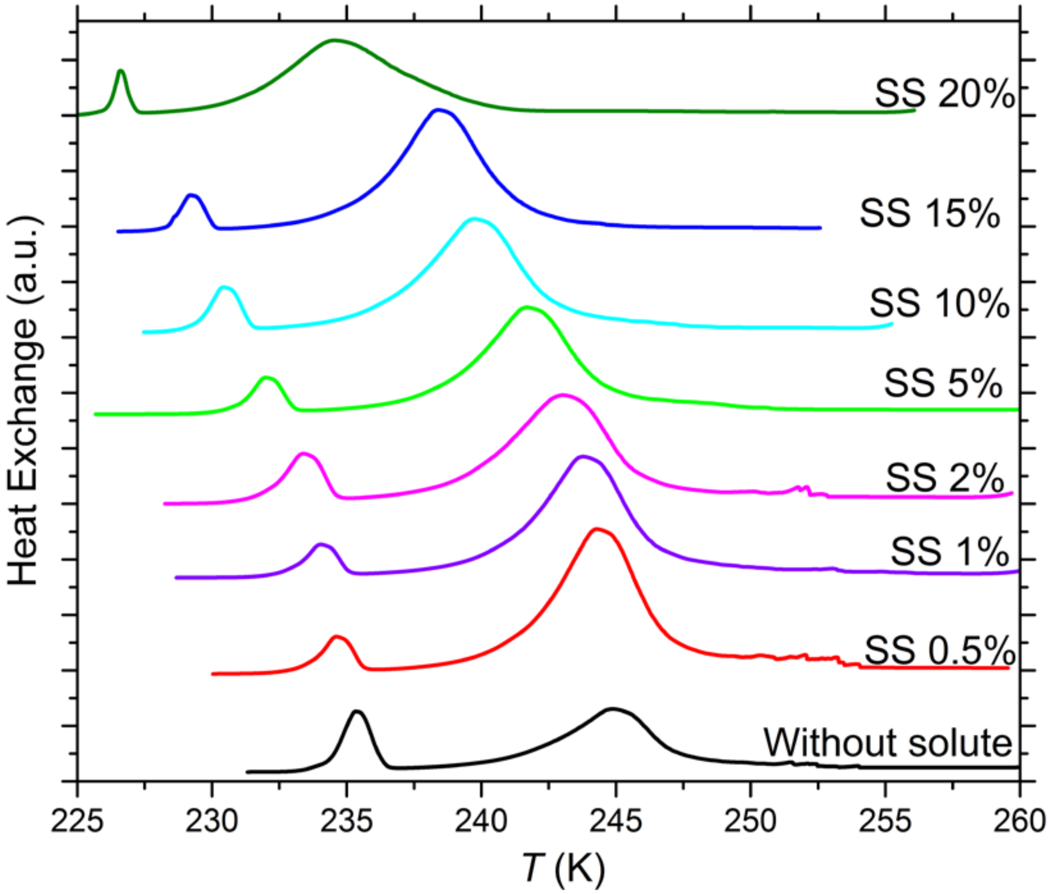


Figure S3. DSC thermograms of 5 wt% SA quartz particles suspended in sodium sulfate (SS) solution droplets of varying concentration. All curves are normalized such that the areas under the heterogeneous and homogeneous freezing curves sum up to the same value. Numbers next to each curve: Solute concentration in wt%.

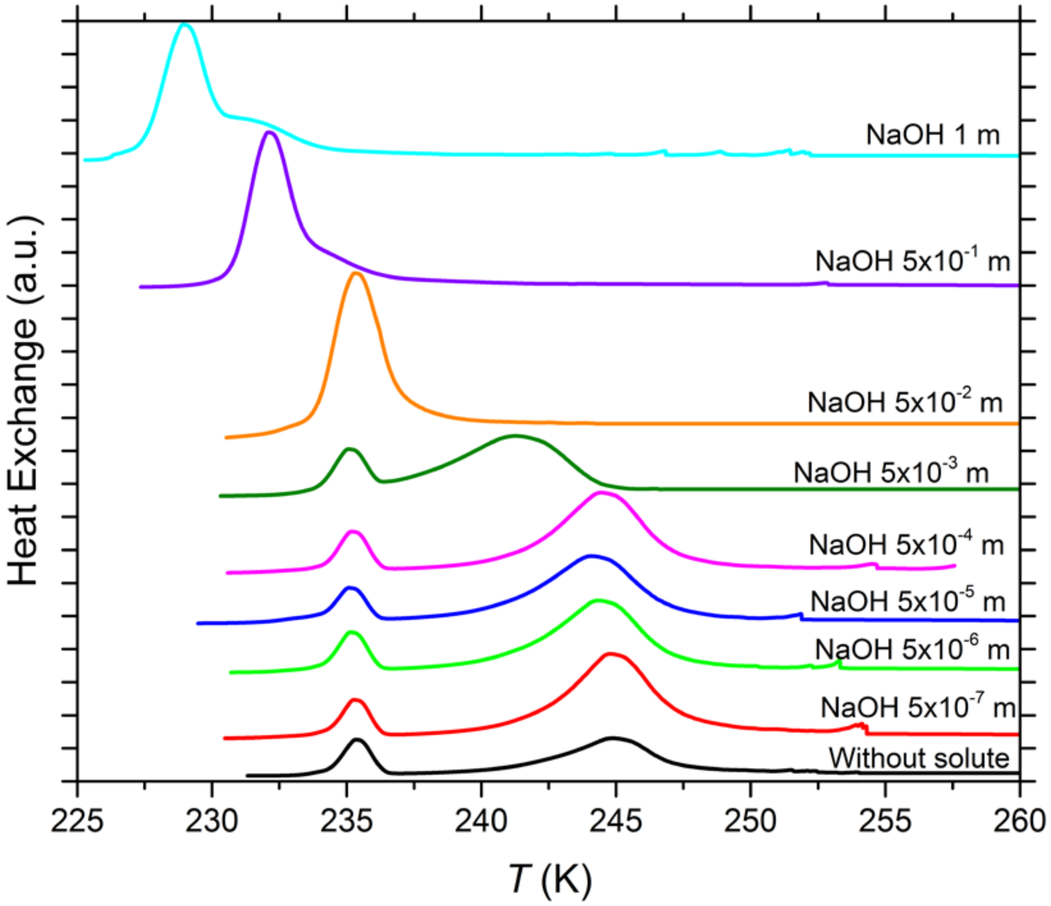


Figure S4. DSC thermograms of 5 wt% SA quartz particles suspended in sodium hydroxide (NaOH) solution droplets of varying concentration. All curves are normalized such that the areas under the heterogeneous and homogeneous freezing curves sum up to the same value. Numbers next to each curve: Solute concentration in molality.

S2 DSC thermograms of immersion freezing with emulsions of SA quartz suspensions in water or aqueous solutions prepared in glass vials and aged over a period of 5 days

At least two sets of suspensions prepared in glass vials with SA quartz (5 wt%) in pure water, NH_3 solution (0.005 molal), $(NH_4)_2SO_4$ solution (10 wt%), NH_4HSO_4 solution (2 wt%) Na_2SO_4 solution (5 wt%) and NaOH solutions ($5x10^{-3}$ and $5x10^{-6}$ molal) were aged over a period of 5 days. Immersion freezing experiments were carried out with the DSC setup on the day of preparation (fresh), then on 5 subsequent days after preparation in order to assess the long-term effect of various solutes on the IN efficiency of quartz. We show one set of DSC thermograms (1 K min^{-1} cooling cycle) containing each solute concentration once over the measured time period.

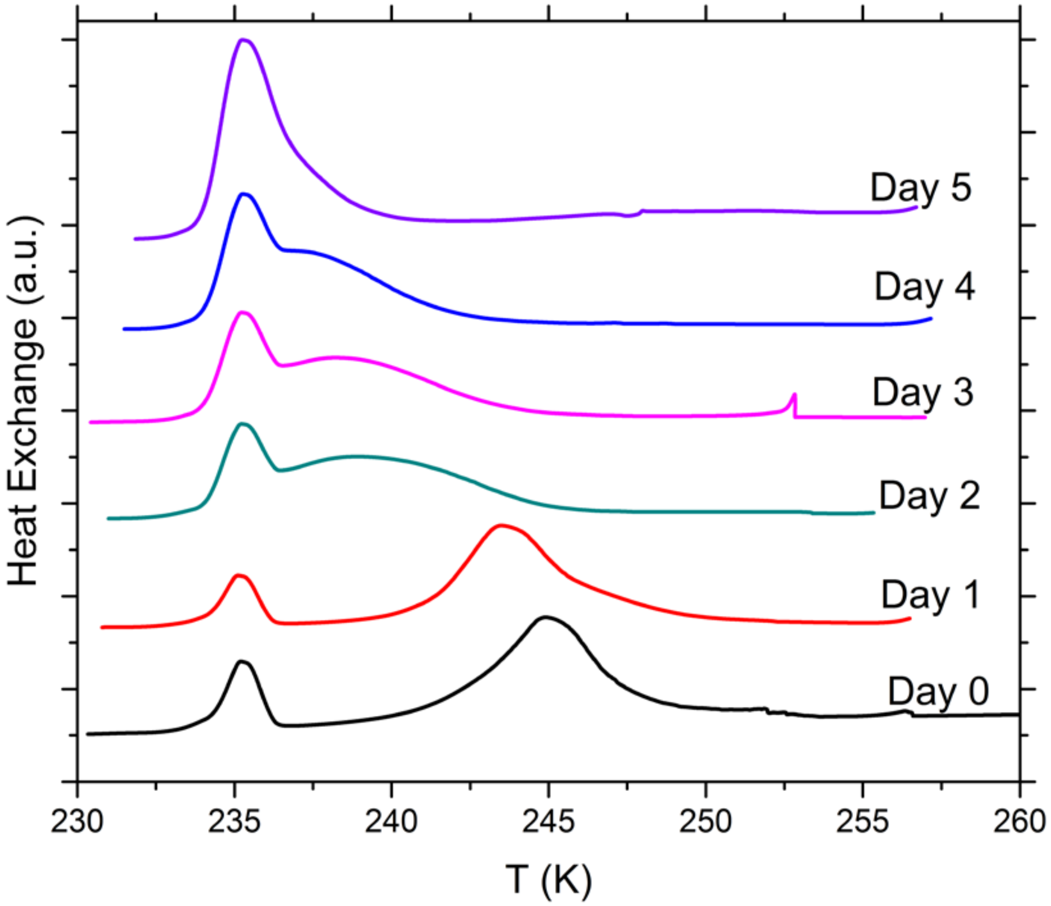


Figure S5. DSC thermograms of aging tests with 5 wt% SA quartz particles suspended in pure water droplets measured over a period of 5 days. All curves are normalized such that the areas under the heterogeneous and homogeneous freezing curves sum up to the same value.

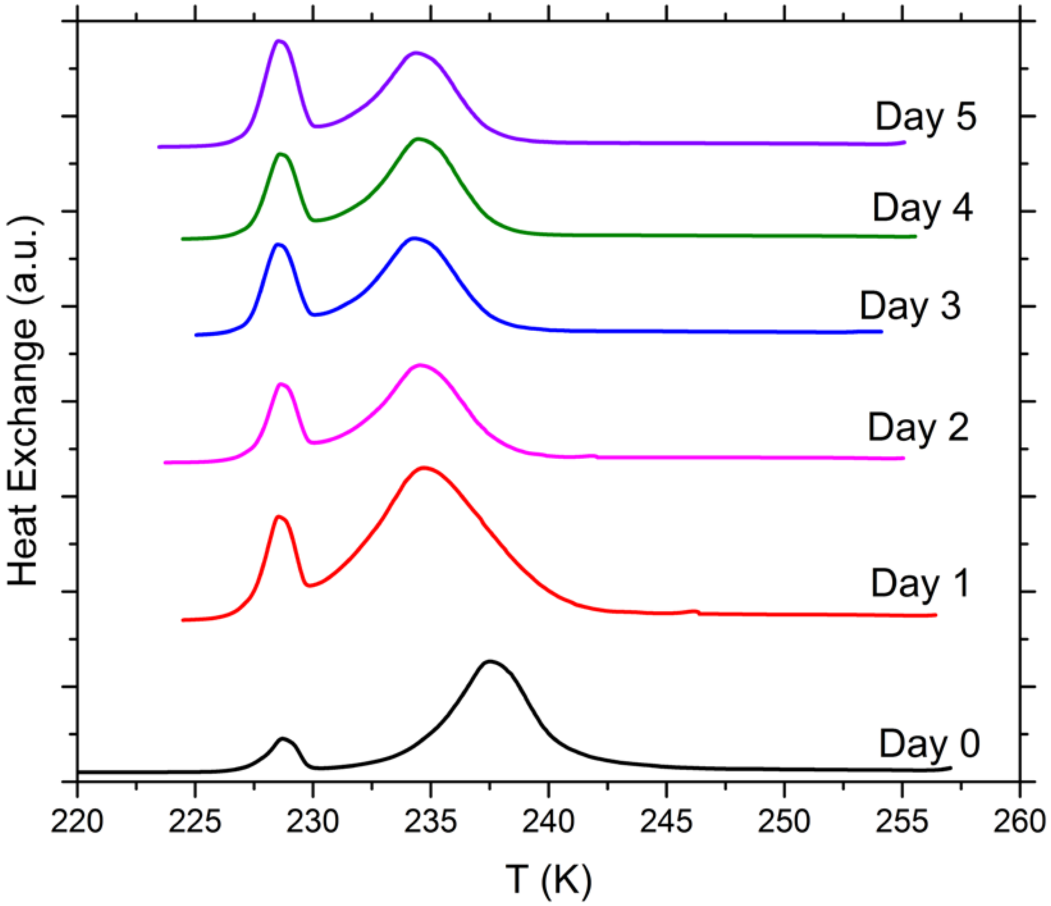


Figure S6. DSC thermograms of aging tests with 5 wt% SA quartz particles suspended in 10 wt% ammonium sulfate solution droplets measured over a period of 5 days. All curves are normalized such that the areas under the heterogeneous and homogeneous freezing curves sum up to the same value.

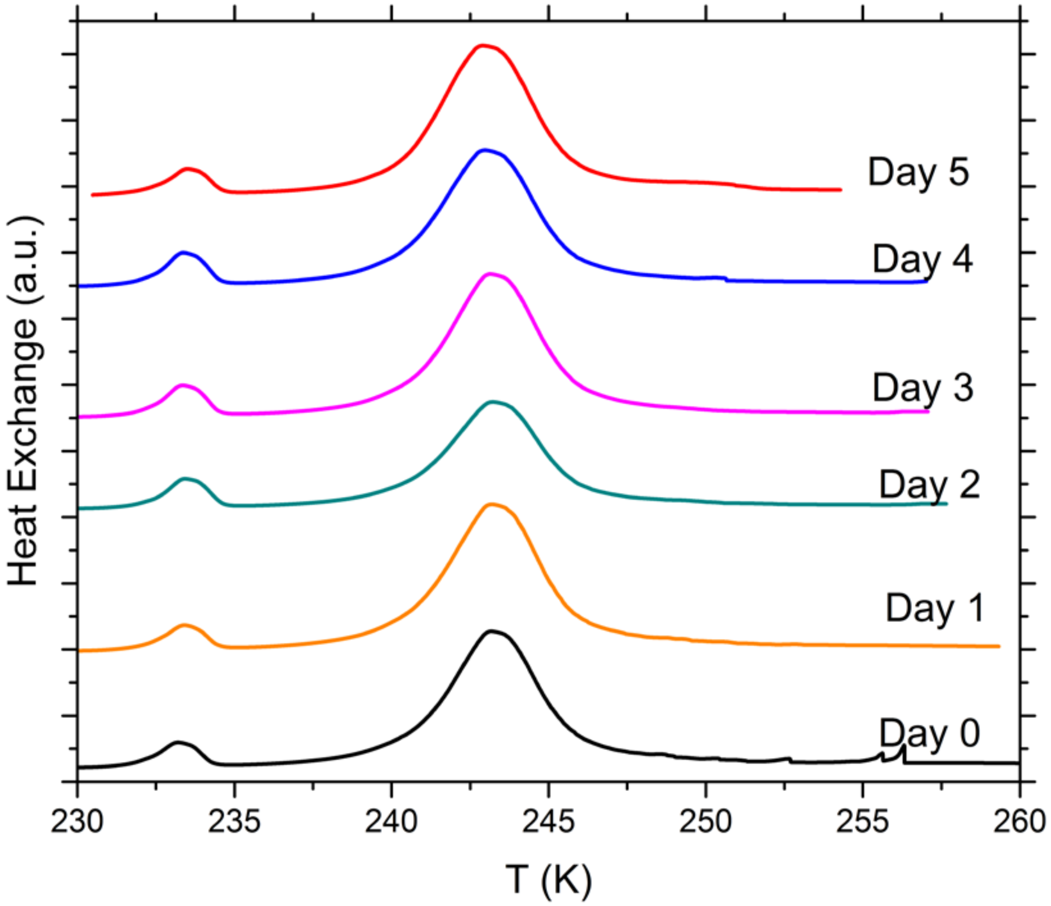


Figure S7. DSC thermograms of aging tests with 5 wt% SA quartz particles suspended in 2 wt% ammonium bisulfate solution droplets measured over a period of 5 days. All curves are normalized such that the areas under the heterogeneous and homogeneous freezing curves sum up to the same value.

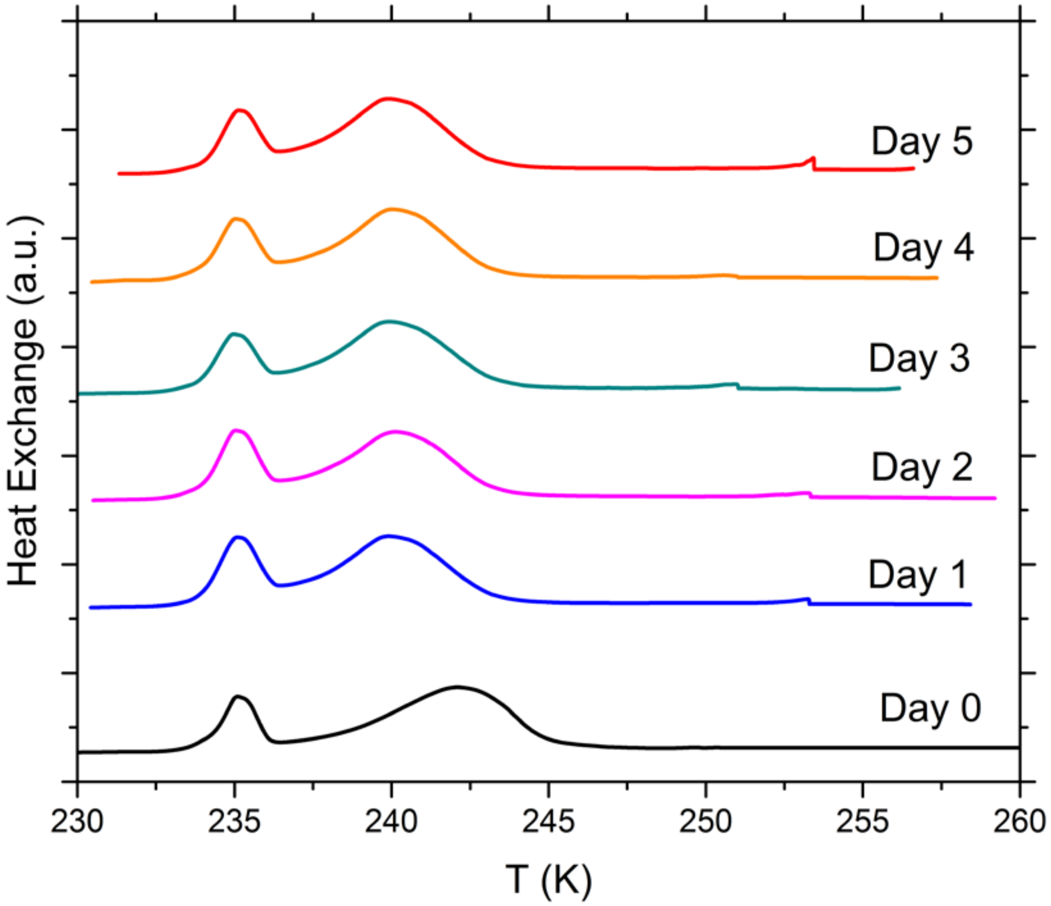


Figure S8. DSC thermograms of aging tests with 5 wt% SA quartz particles suspended in 0.005 molal ammonia solution droplets measured over a period of 5 days. All curves are normalized such that the areas under the heterogeneous and homogeneous freezing curves sum up to the same value.

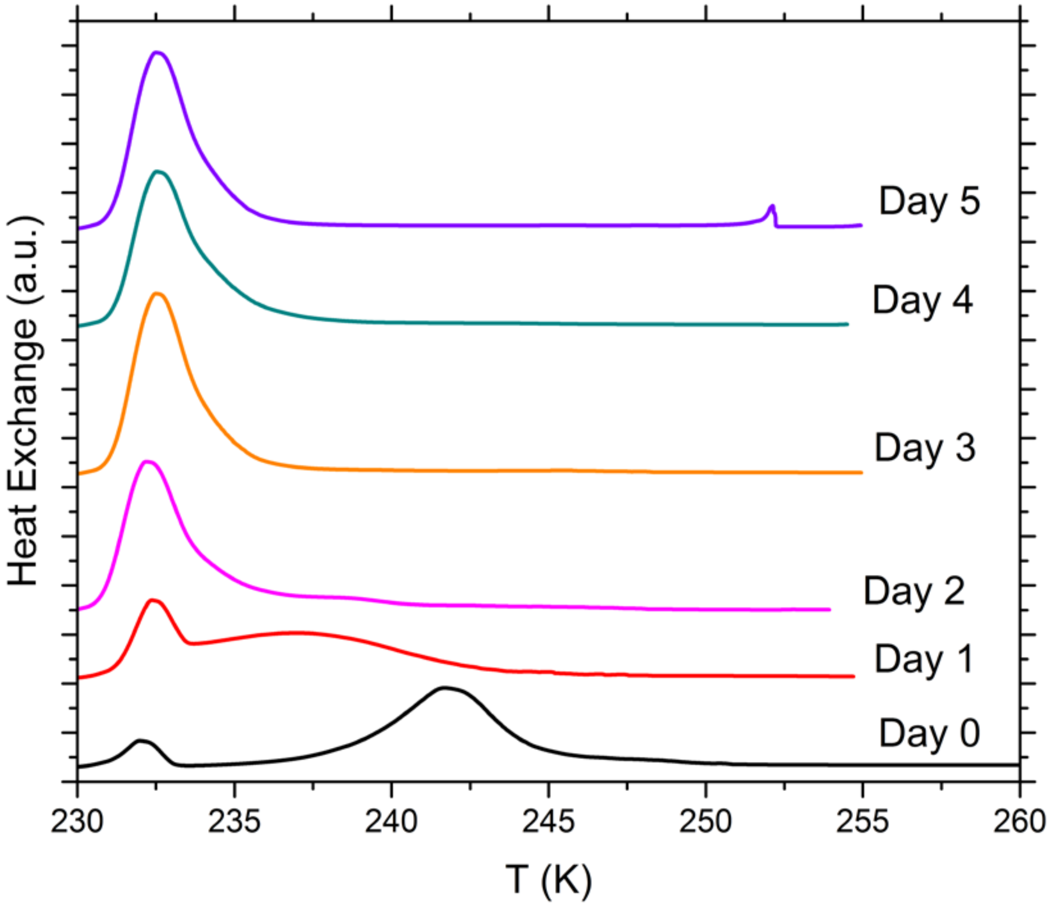


Figure S9. DSC thermograms of aging tests with 5 wt% SA quartz particles suspended in 5 wt% sodium sulfate solution droplets measured over a period of 5 days. All curves are normalized such that the areas under the heterogeneous and homogeneous freezing curves sum up to the same value.

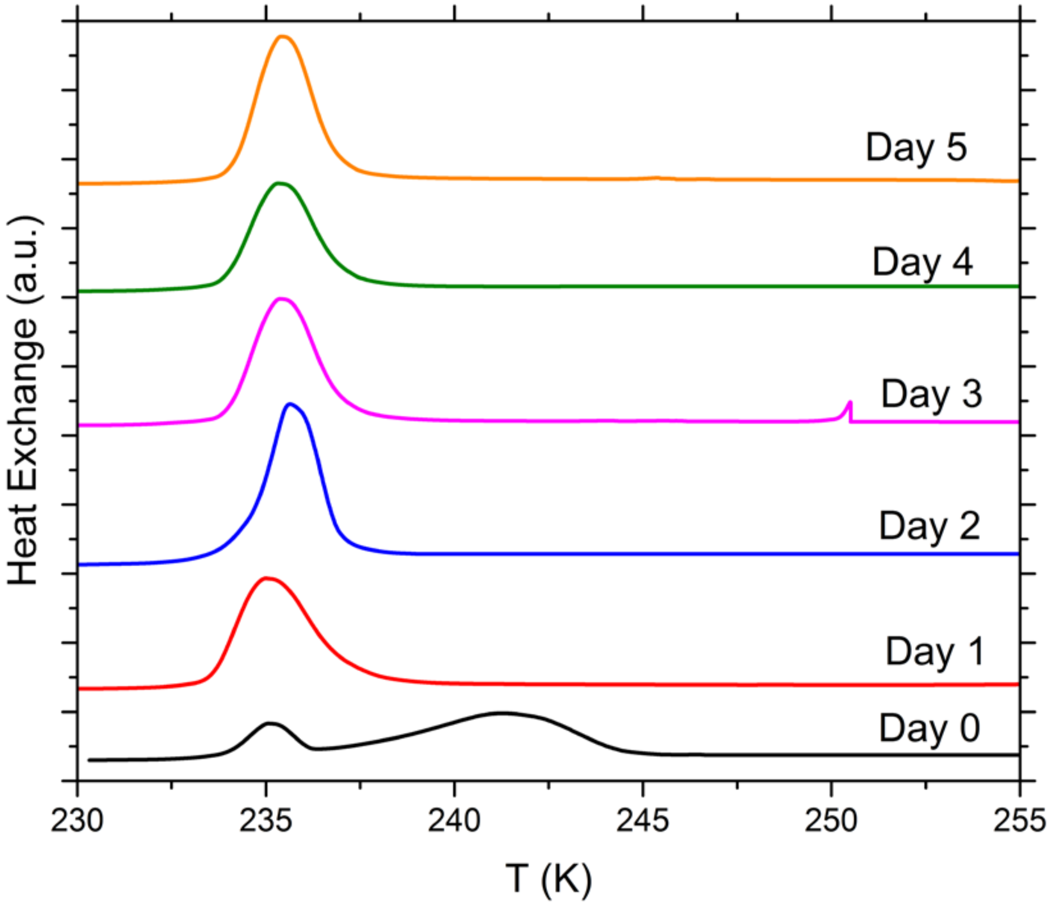


Figure S10. DSC thermograms of aging tests with 5 wt% SA quartz particles suspended in $5\text{x}10^{-3}$ molal sodium hydroxide solution droplets measured over a period of 5 days. All curves are normalized such that the areas under the heterogeneous and homogeneous freezing curves sum up to the same value.

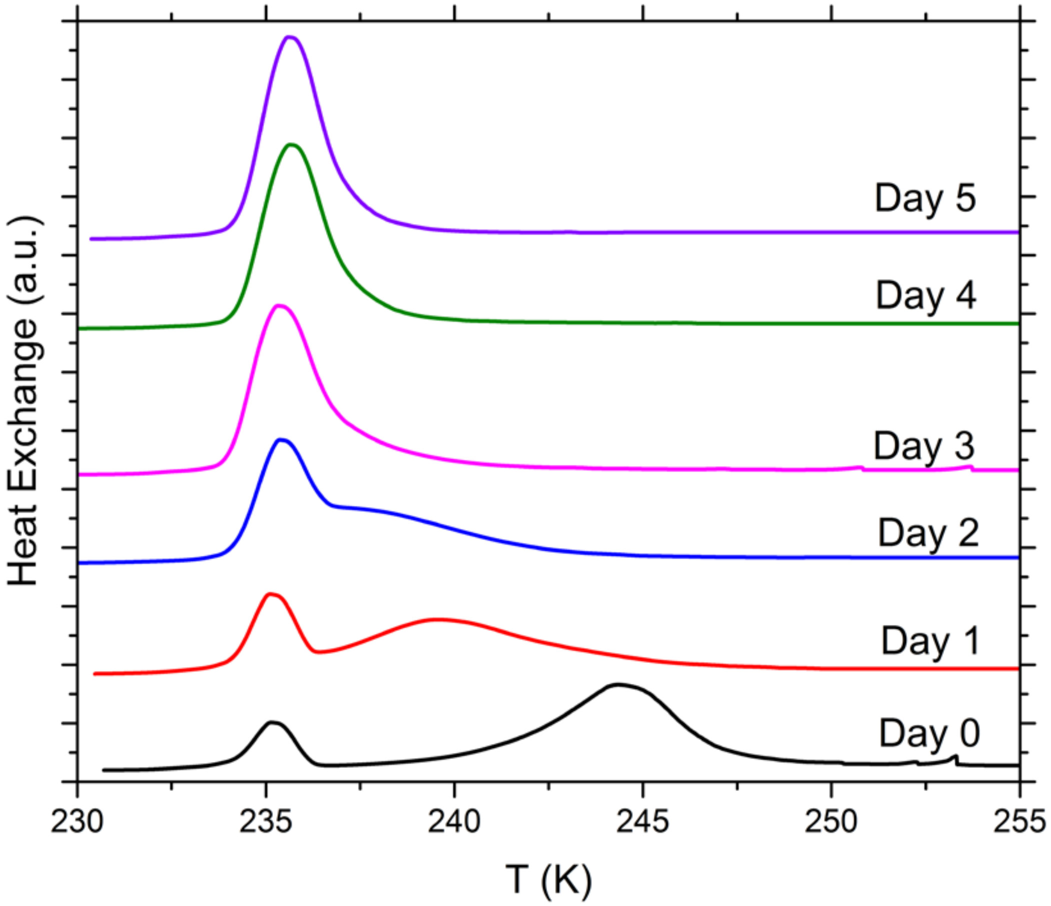


Figure S11. DSC thermograms of aging tests with 5 wt% SA quartz particles suspended in 5x10^{-6} molal sodium hydroxide solution droplets measured over a period of 5 days. All curves are normalized such that the areas under the heterogeneous and homogeneous freezing curves sum up to the same value.

S3 DSC thermograms of immersion freezing with emulsions of SA quartz suspensions prepared in glass vials in water or aqueous solutions aged over a period of 5 days and resuspended in water to assess the reversibility of the solute effect on IN efficiency

At least two sets of suspensions prepared with SA quartz (5 wt%) in pure water, NH_3 solution (0.005 molal), $(NH_4)_2SO_4$ solution (10 wt%), NH_4HSO_4 solution (2 wt%) Na_2SO_4 solution (5 wt%) and NaOH solutions ($5x10^{-3}$ and $5x10^{-6}$ molal) were aged over a period of 5 days. The aged suspensions were then centrifuged for 2 minutes at 600 rpm, the supernatant solution was removed and the settled particles were washed with pure water. This process was repeated five times and the washed particles were resuspended in pure water. Using DSC, we compared immersion freezing of emulsions containing dust treated in this manner with emulsions of the same solute concentration prepared with fresh dust. We show 2 – 4 thermograms (1 K min^{-1} cooling cycle) for each reversibility test.

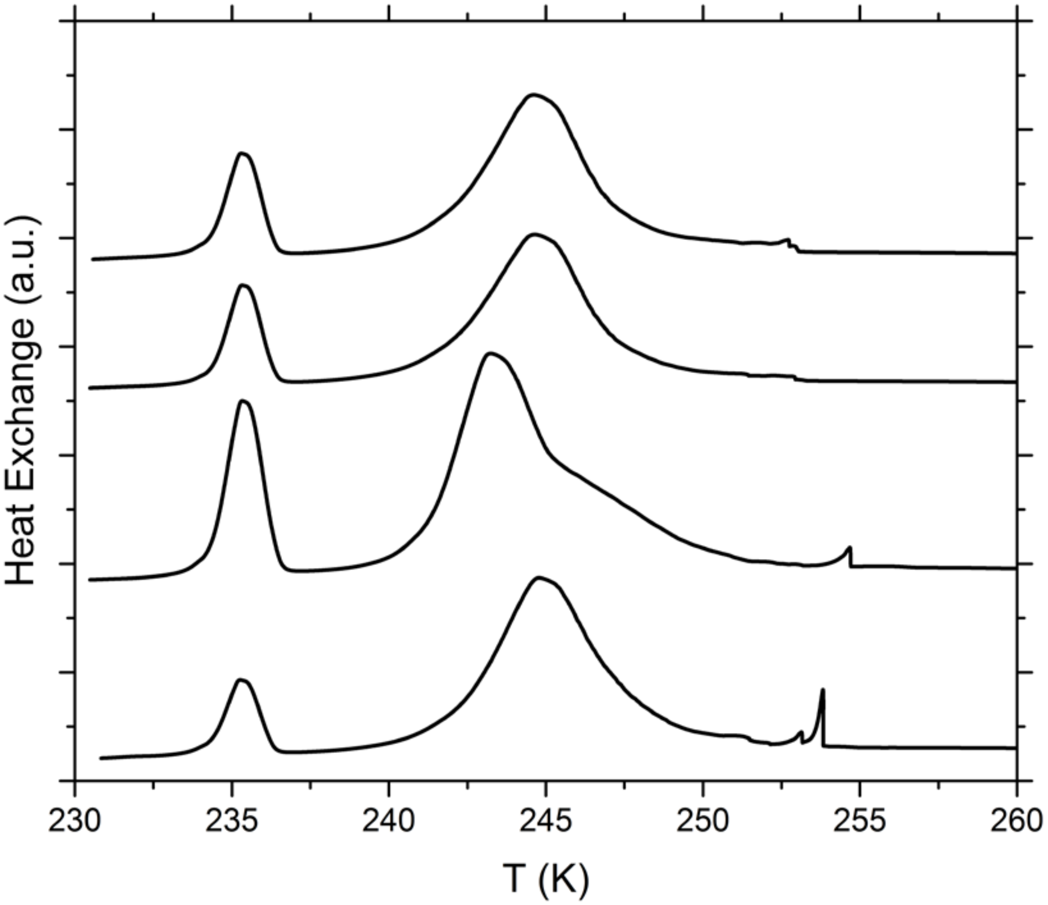


Figure S12. DSC thermograms of reversibility tests on four separate suspensions with 5 wt% SA quartz particles aged for 5 days in pure water. Aged particles were collected after aging and resuspended in pure water. All curves are normalized such that the areas under the heterogeneous and homogeneous freezing curves sum up to the same value.

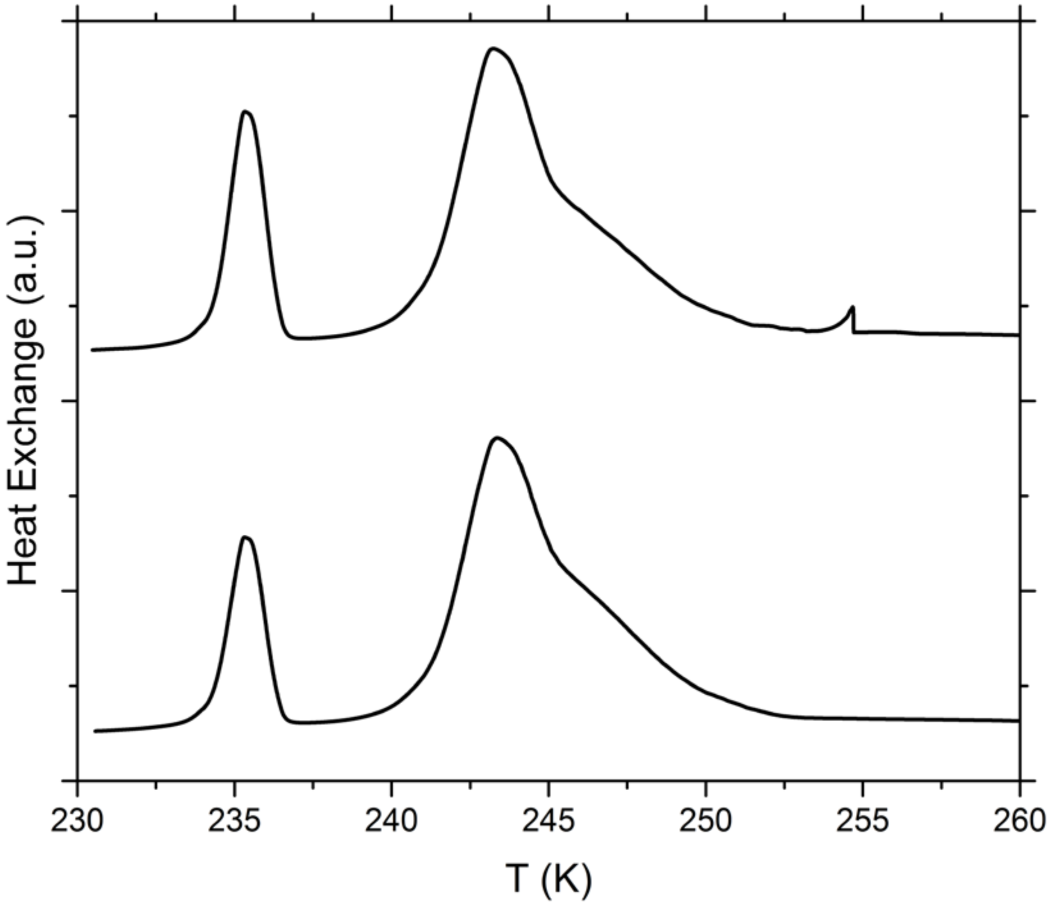


Figure S13. DSC thermograms of reversibility tests on separate suspensions with 5 wt% SA quartz particles aged for 5 days in 10 wt% ammonium sulfate solution. Aged particles were collected after aging and resuspended in pure water. All curves are normalized such that the areas under the heterogeneous and homogeneous freezing curves sum up to the same value.

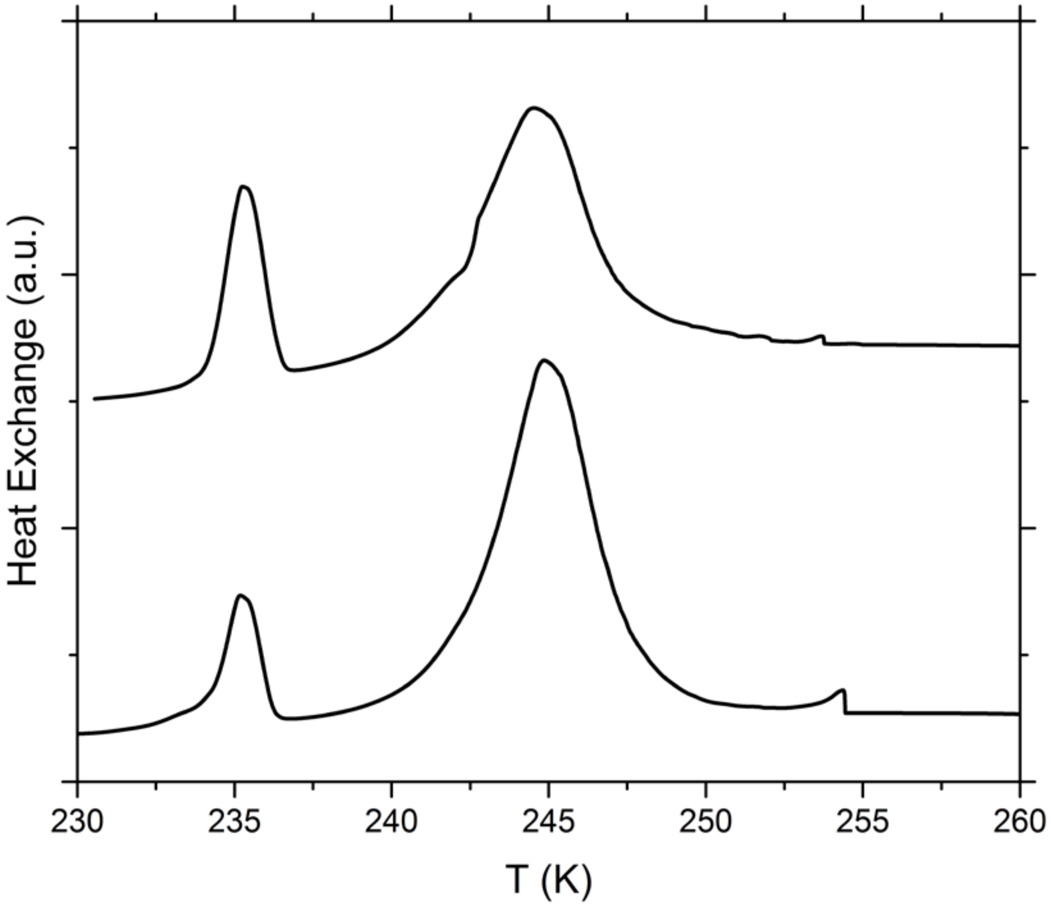


Figure S14. DSC thermograms of reversibility tests on separate suspensions with 5 wt% SA quartz particles aged for 5 days in 2 wt% ammonium bisulfate solution. Aged particles were collected after aging and resuspended in pure water. All curves are normalized such that the areas under the heterogeneous and homogeneous freezing curves sum up to the same value.

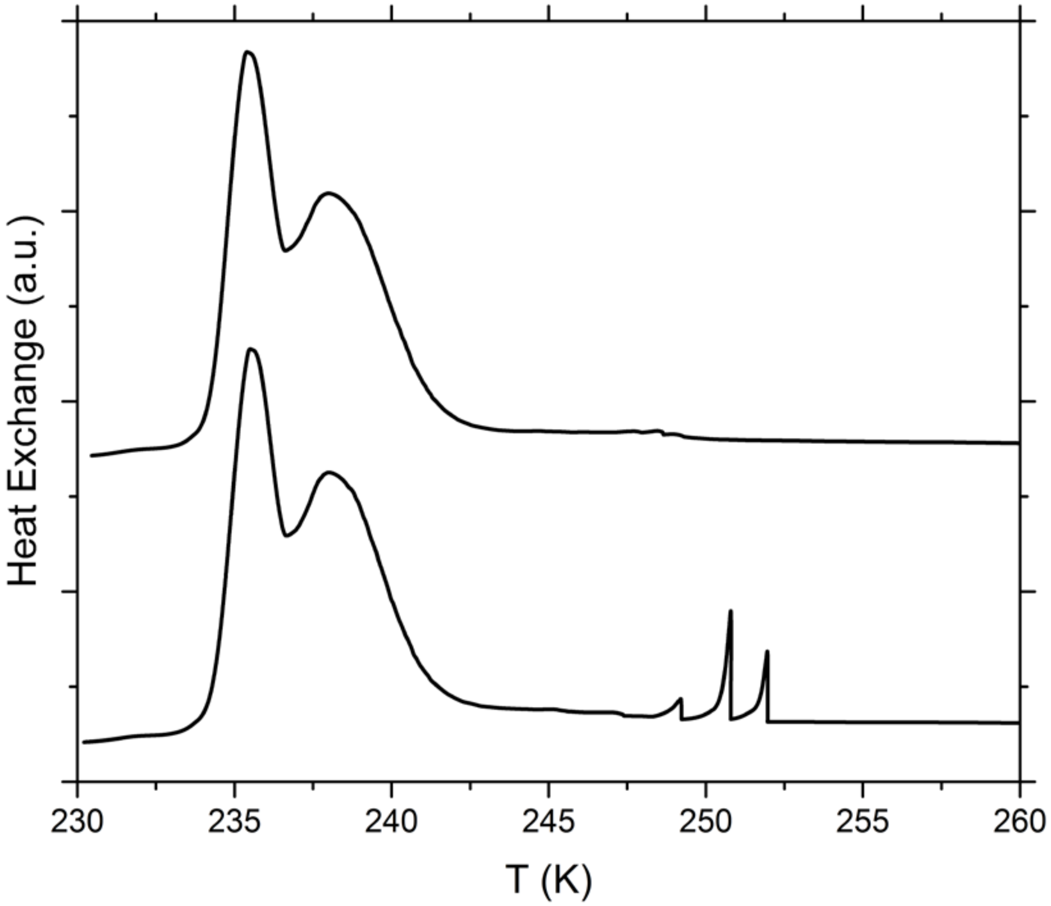


Figure S15. DSC thermograms of reversibility tests on separate suspensions with 5 wt% SA quartz particles aged for 5 days in 0.005 molal ammonia solution. Aged particles were collected after aging and resuspended in pure water. All curves are normalized such that the areas under the heterogeneous and homogeneous freezing curves sum up to the same value.

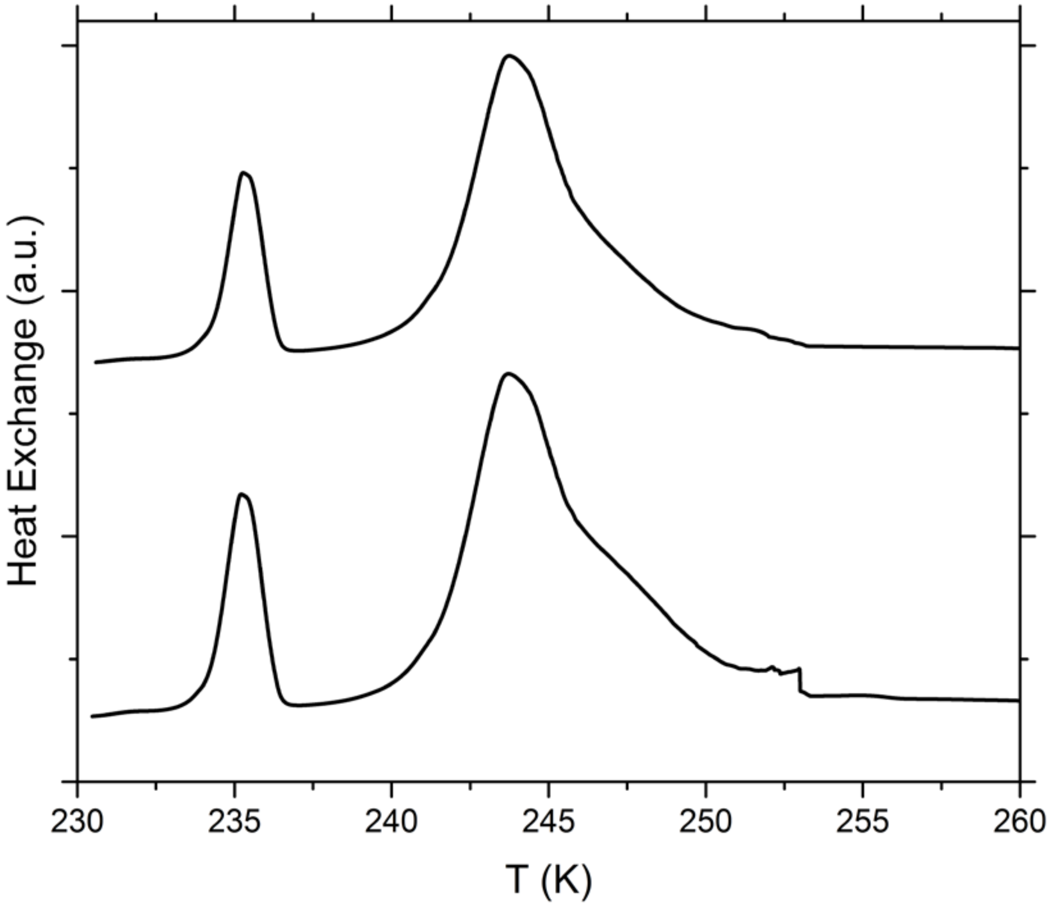


Figure S16. DSC thermograms of reversibility tests on separate suspensions with 5 wt% SA quartz particles aged for 5 days in 5 wt% sodium sulfate solution. Aged particles were collected after aging and resuspended in pure water. All curves are normalized such that the areas under the heterogeneous and homogeneous freezing curves sum up to the same value.

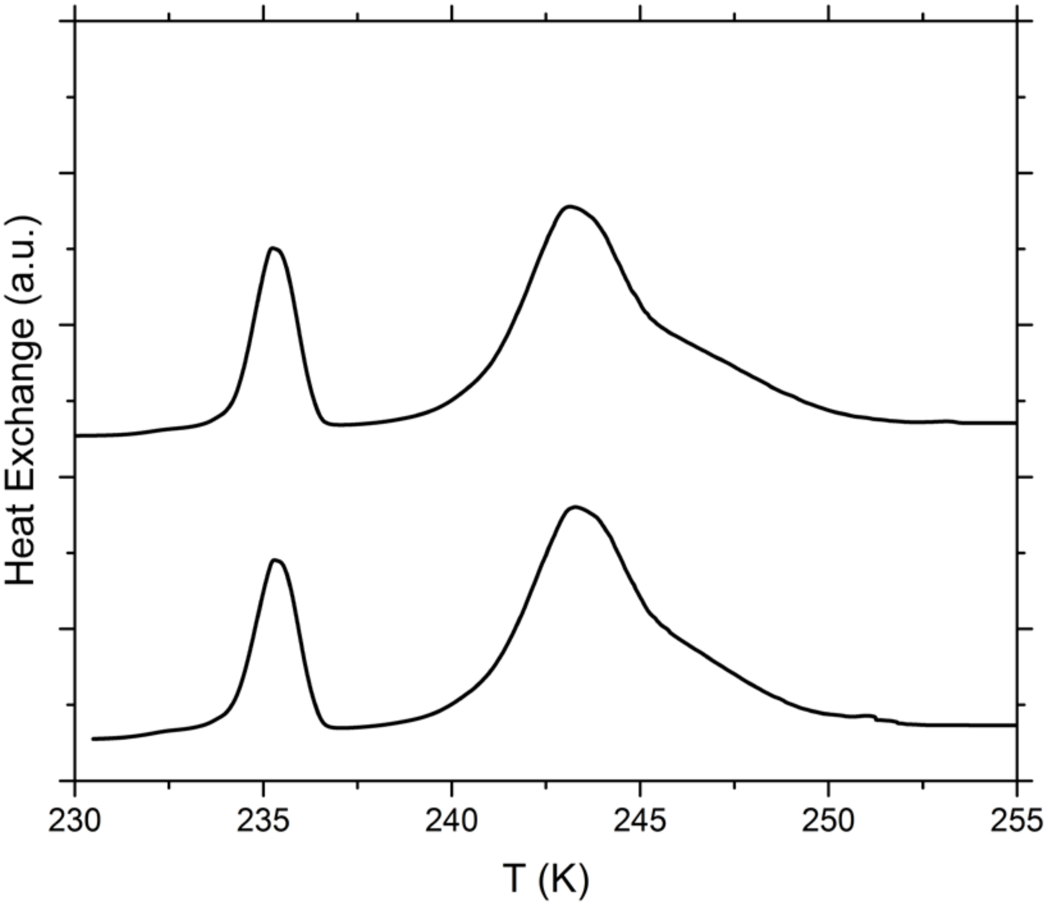


Figure S17. DSC thermograms of reversibility tests on separate suspensions with 5 wt% SA quartz particles aged for 5 days in $5x10^{-6}$ molal sodium hydroxide solution. Aged particles were collected after aging and resuspended in pure water. All curves are normalized such that the areas under the heterogeneous and homogeneous freezing curves sum up to the same value.

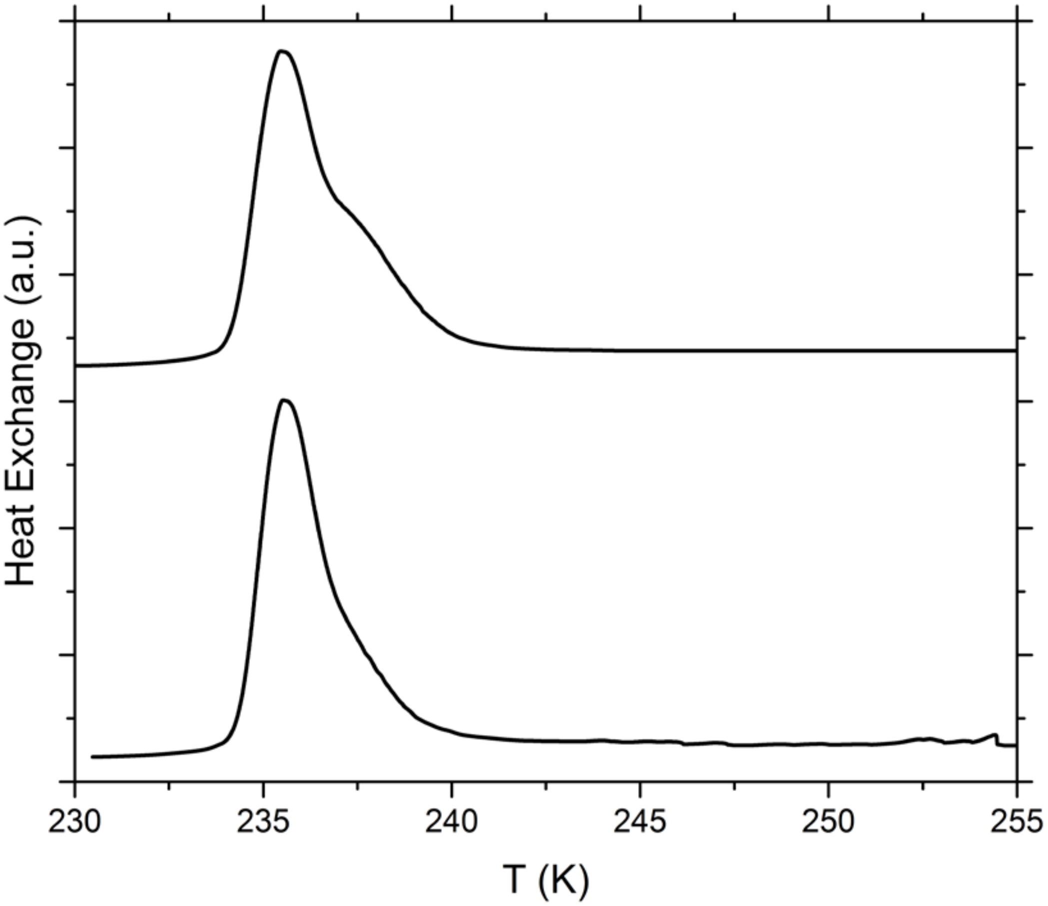


Figure S18. DSC thermograms of reversibility tests on separate suspensions with 5 wt% SA quartz particles aged for 5 days in $5x10^{-3}$ molal sodium hydroxide solution. Aged particles were collected after aging and resuspended in pure water. All curves are normalized such that the areas under the heterogeneous and homogeneous freezing curves sum up to the same value.

S4 DSC Thermograms of immersion freezing experiments with emulsions of SA quartz suspensions prepared in polypropylene falcon tubes in water or aqueous solutions aged over a period of 5 days and resuspended in water to assess the reversibility of the solute effect on IN efficiency

At least two sets of suspensions prepared with quartz (5 wt%) in pure water, NH_3 solution (0.005 molal), and NaOH solutions ($5x10^{-3}$ molal) were prepared in polypropylene falcon tubes and aged over a period of 5 days. The aged suspensions were then centrifuged for 2 minutes at 600 rpm, the supernatant solution was removed and the settled particles were washed with pure water. This process was repeated five times and the washed particles were resuspended in pure water. Using DSC, we compared immersion freezing of emulsions containing dust treated in this manner with emulsions of the same solute concentration prepared with fresh dust. We show one set of DSC thermograms (1 K min^{-1} cooling cycle) during 5-day aging and reversibility containing each solute concentration once.

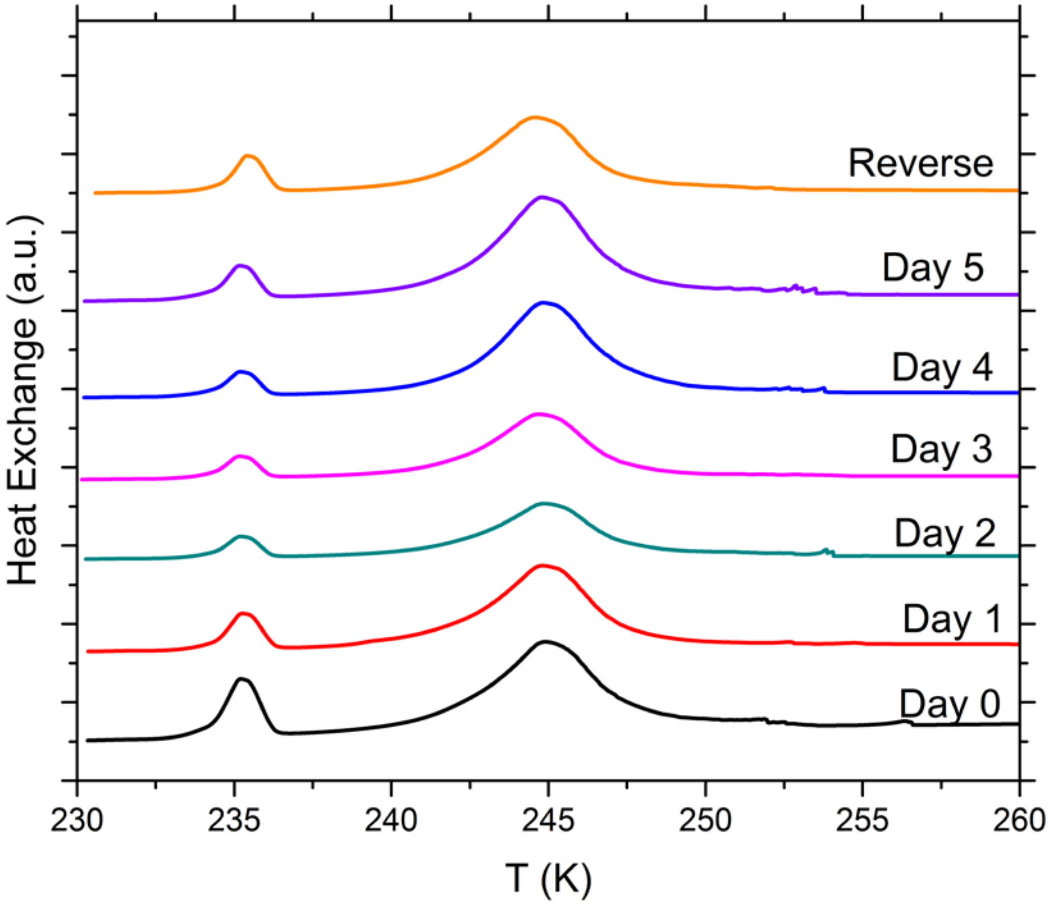


Figure S19. DSC thermograms of aging and reversibility tests on suspensions with 5 wt% SA quartz particles prepared in polypropylene vials and aged for 5 days in pure water. Aged particles were collected after aging and resuspended in pure water. All curves are normalized such that the areas under the heterogeneous and homogeneous freezing curves sum up to the same value.

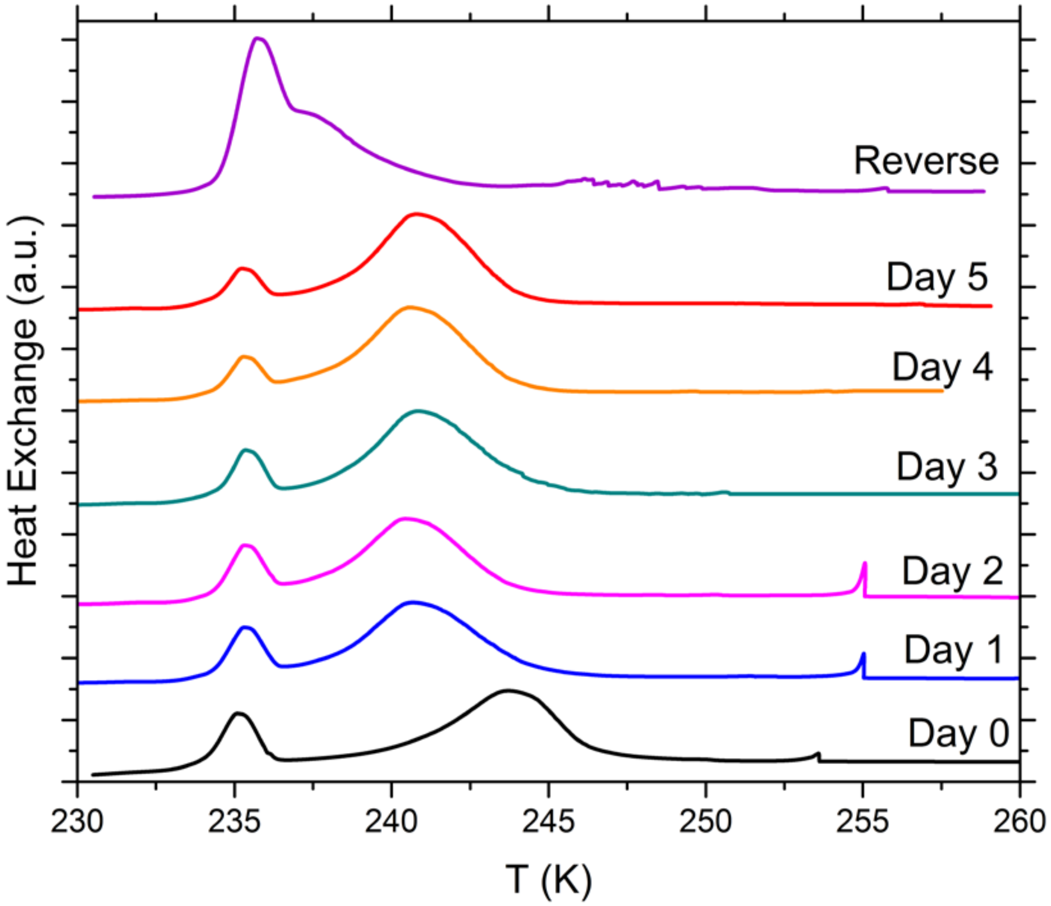


Figure S20. DSC thermograms of aging and reversibility tests on suspensions with 5 wt% SA quartz particles prepared in polypropylene tubes and aged for 5 days in ammonia solution (0.005 molal). Aged particles were collected after aging and resuspended in pure water. All curves are normalized such that the areas under the heterogeneous and homogeneous freezing curves sum up to the same value.

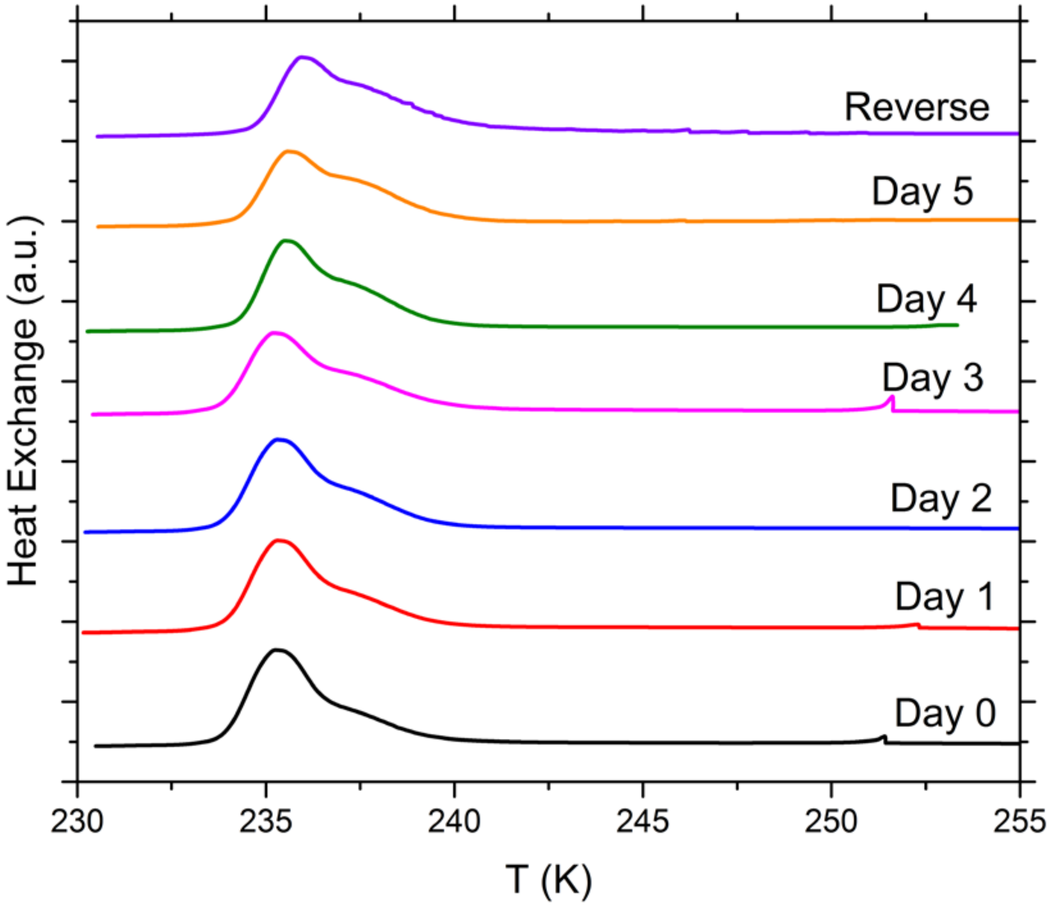


Figure S21. DSC thermograms of aging and reversibility tests on suspensions with 5 wt% SA quartz particles prepared in polypropylene vials and aged for 5 days in sodium hydroxide solution (0.005 molal). Aged particles were collected after aging and resuspended in pure water. All curves are normalized such that the areas under the heterogeneous and homogeneous freezing curves sum up to the same value.

S5 DSC Thermograms of immersion freezing experiments with emulsions of additionally milled SA quartz suspensions in water

We milled the SA quartz sample and ran emulsion freezing experiments on 1 wt % and 5wt % milled SA quartz in pure water to assess the effect of additional milling on its IN efficiency.

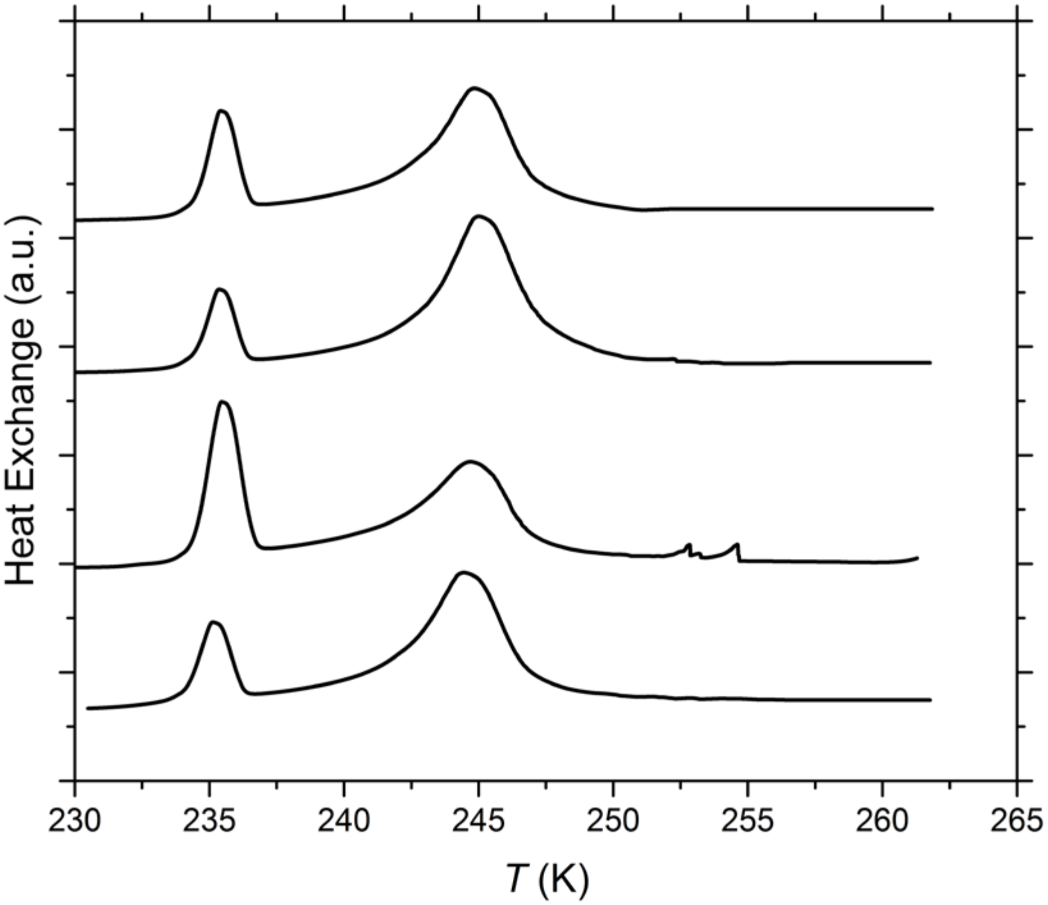


Figure S22. DSC thermograms of freezing experiments on separate suspensions with 1 wt% milled SA quartz particles in pure water. All curves are normalized such that the areas under the heterogeneous and homogeneous freezing curves sum up to the same value.

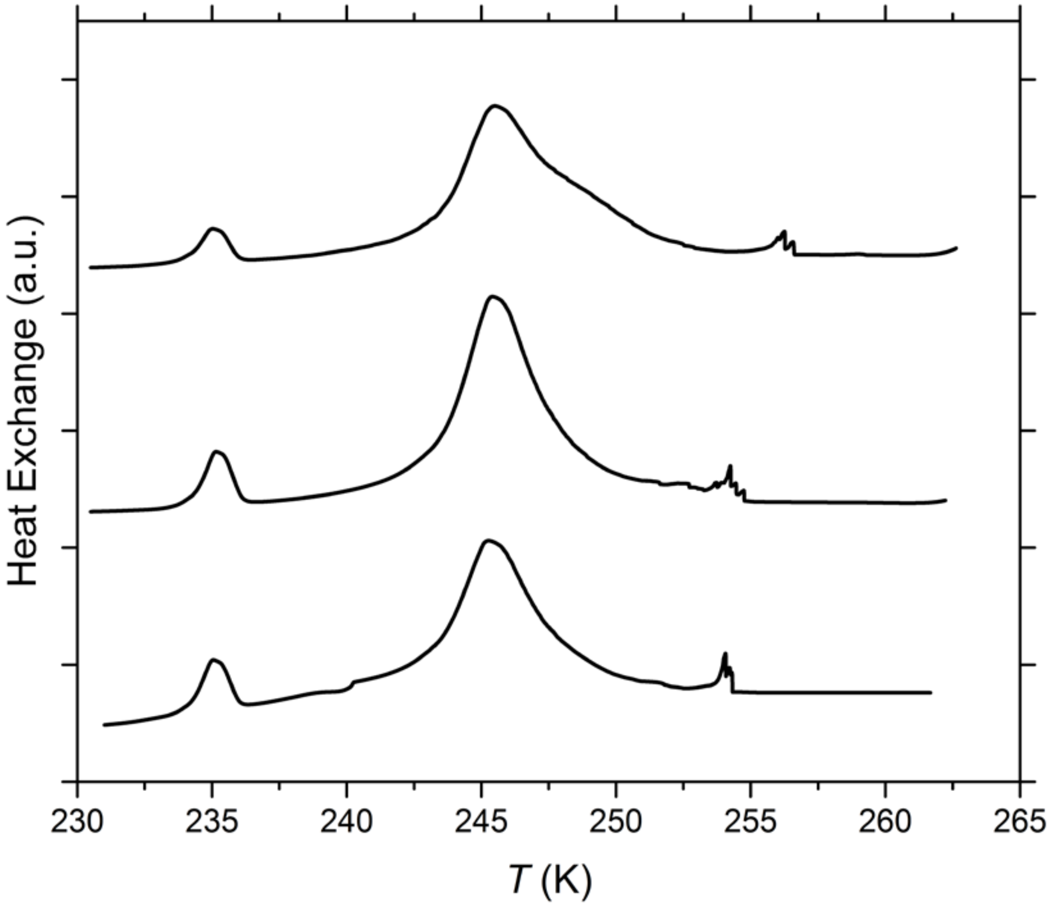


Figure S23. DSC thermograms of freezing experiments on separate suspensions with 5 wt% milled SA quartz particles in pure water. All curves are normalized such that the areas under the heterogeneous and homogeneous freezing curves sum up to the same value.

S6 Evaluation of presence of semivolatile organic species on quartz

In order to evaluate the presence of semivolatile species, if any, we ran thermogravimetric tests on Sigma Aldrich quartz, TU Vienna quartz and the quartz sample from Kaufmann et al. (2016), with a Thermogravimetric Analyzer (TGA) (Perkin Elmer Pyris 1), which has a weight sensitivity of 0.1 μg and 2 ºC temperature precision.

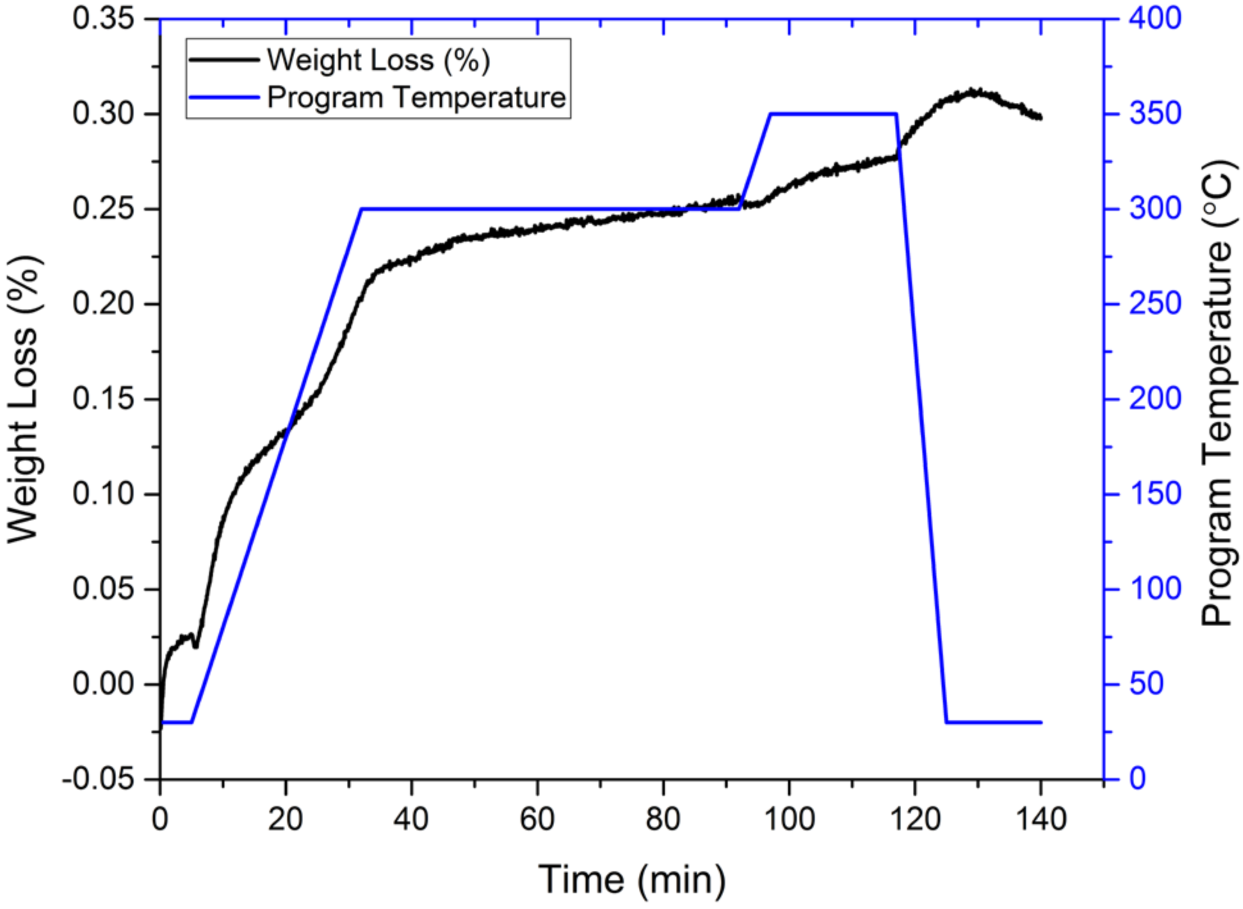


Figure S24. Mass loss of the SA quartz sample measured by thermogravimetric analysis. Blue line: temperature (ºC); black line: sample weight loss (in %). A minor loss of up to 0.30% in weight was observed.

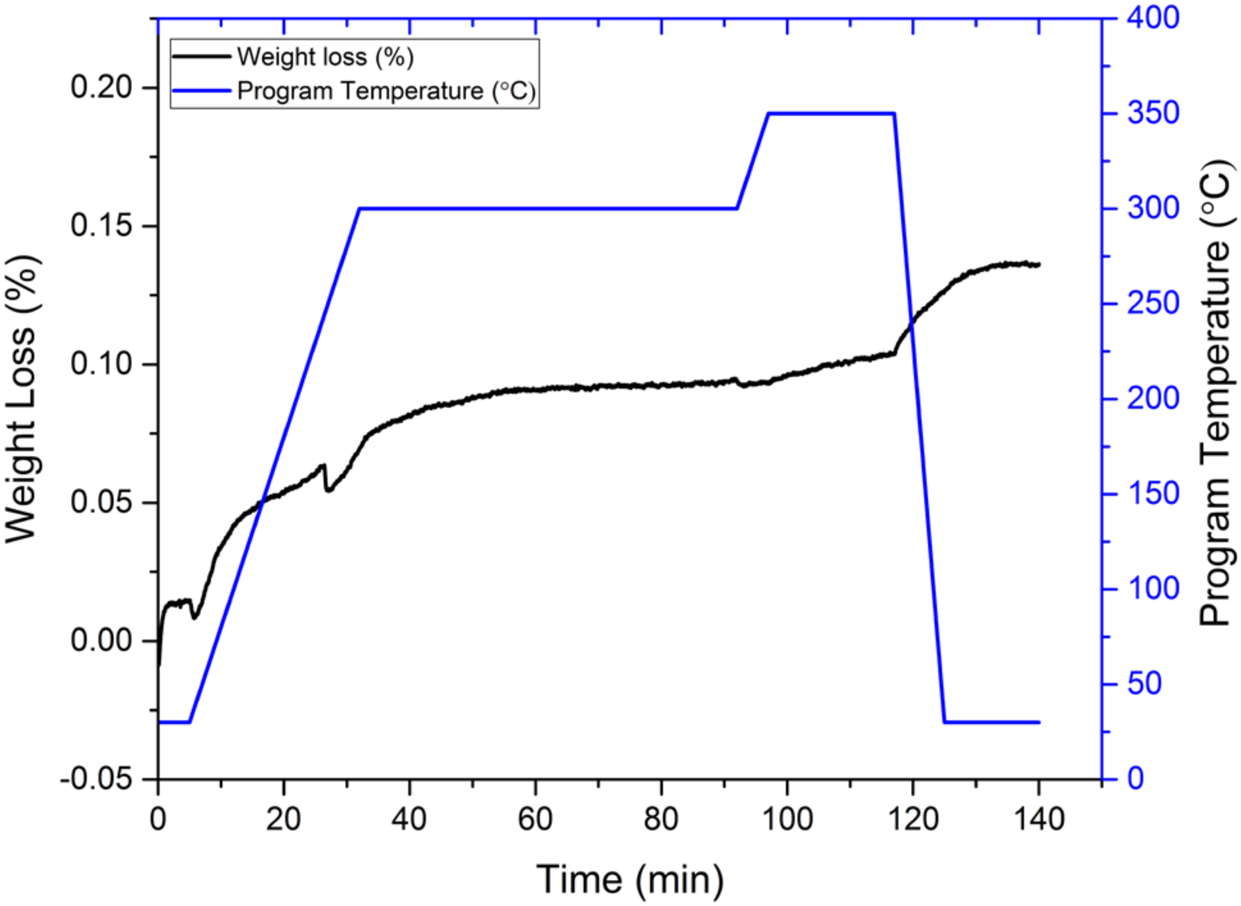


Figure S25. Mass loss of the Kaufmann quartz sample measured by thermogravimetric analysis. Blue line: temperature (ºC); black line: sample weight loss (in %). A minor loss of up to 0.14% in weight was observed.

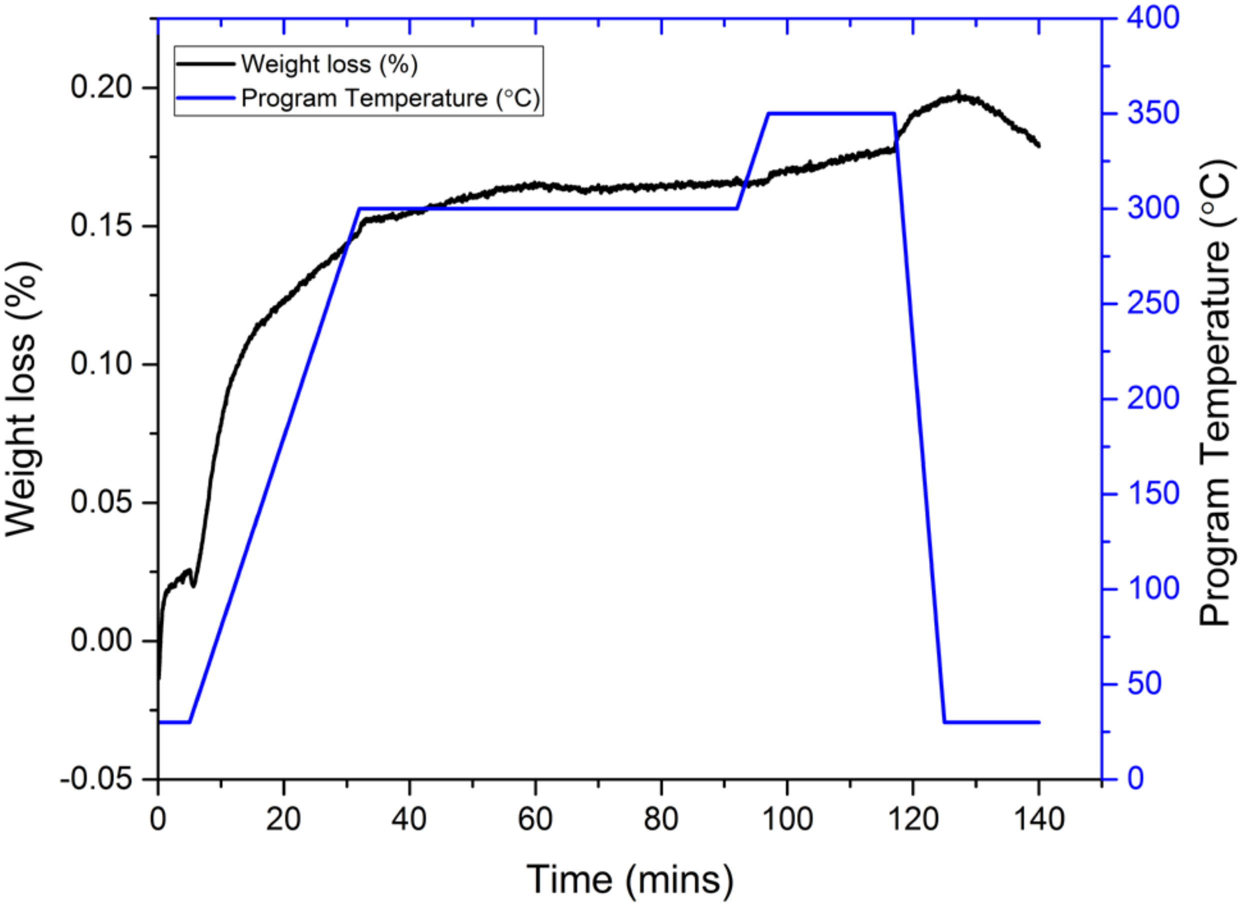


Figure S26. Mass loss of the TU Vienna sample measured by thermogravimetric analysis.. Blue line: temperature (ºC); black line: sample weight loss (in %). A minor loss of up to 0.2% in weight was observed.

S7 Silica particles

S6.1 Synthesis of submicron nonporous Stöber silica particles

Ammonia (66 ml, 28 %), deionized water (133 ml) and ethanol (217 ml, 99.8 %) were stirred at 25 °C for 10 min. Then tetraethyl orthosilicate (TEOS) (20 ml, 44.8 mmol, 99 %) was added within 20 s under vigorous stirring. After a few minutes, silica particles started to precipitate. After 4 h of reaction, the suspension was centrifuged. The precipitate was then washed with deionized water (350 ml) twice and once with ethanol (100 ml). The particles were dried (80 °C, ≥ 2 h) before they were ground in methanol (99 %) and dried (80 ° C, ≥ 1 h) again. Then they were calcined at 550 °C. A white powder was obtained with a yield of 80 % (≈ 6.5 g).

S6.2 Particle functionalization: Stöber silica particles

Stöber particles were in addition hydroxylated: A calcined sample (1.0 g) was suspended in toluene (200 mL) and heated to 60 °C. A calculated amount of water was added according to Eq. S1 with vigorous stirring, and occasional sonication, the particles were suspended during 60 min, before they were filtered off, washed with deionized water (80 mL) and dried (120 °C, 20 mbar) overnight.

$$V_w = \frac{M_w \sigma_{SiOH} A_s m_{SiO_2}}{\rho_w N_A} \tag{S1}$$

In this equation, m_{SiO_2} is the weight of the particles, A_s the specific surface area, concentration of surface silanol groups σ_{SiOH} = 4.6 nm^{-2}, M_w is the molar mass of water, ρ_w the density of water and N_A the Avogadro constant.

S8 Scanning electron microscopy images of quartz samples

S8.1 Sigma Aldrich quartz

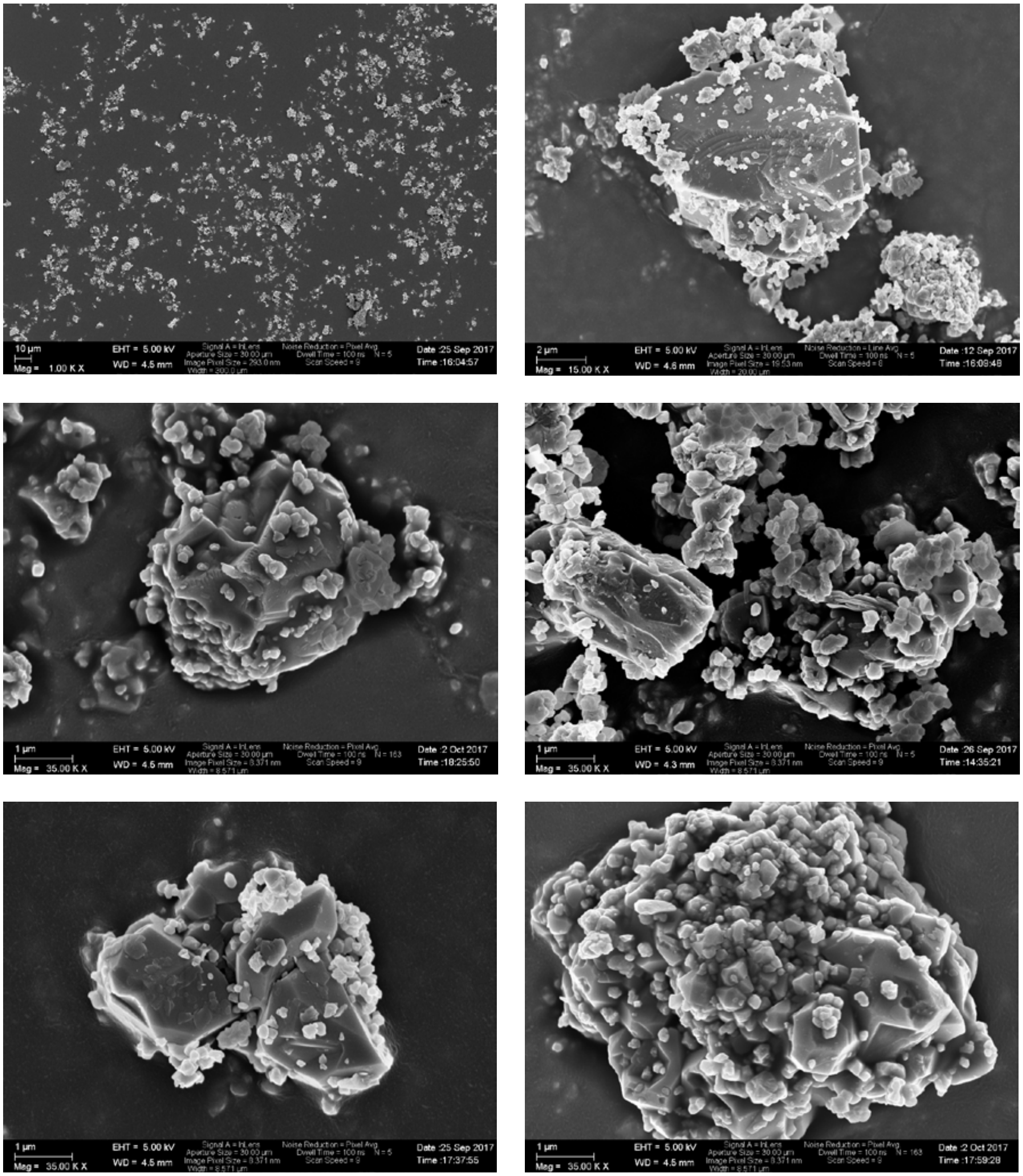


Figure S27. SEM images of SA quartz at various magnifications.

S8.2 Quartz sample from Kaufmann et al. (2016)

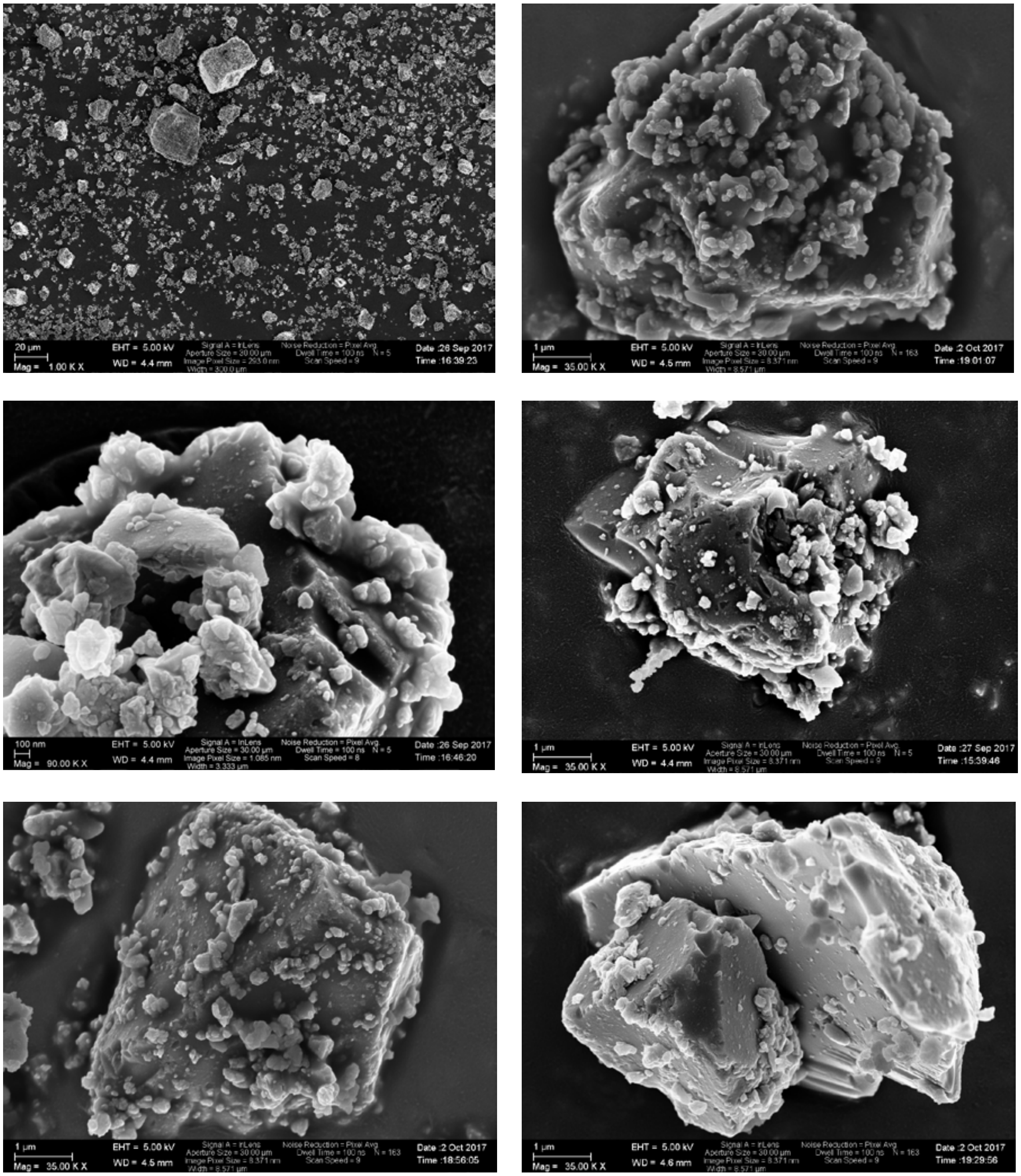
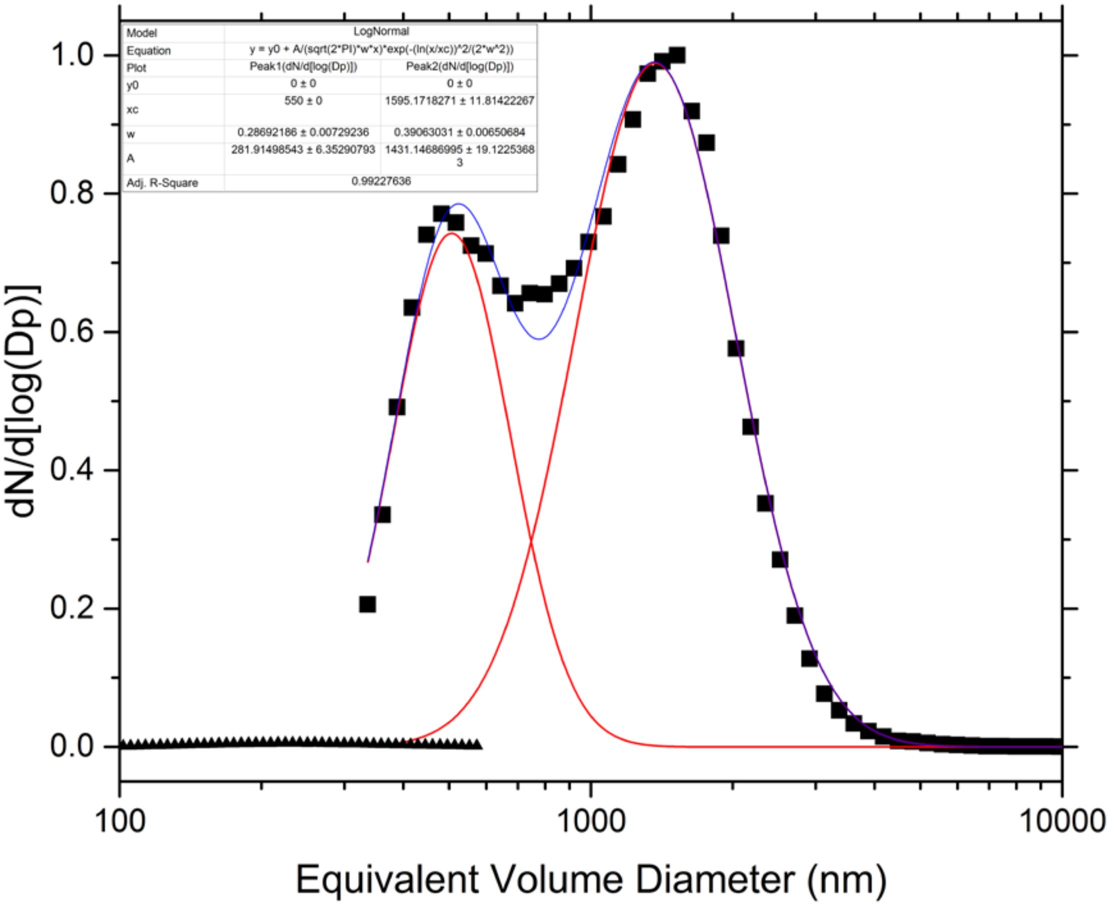


Figure S28. SEM images of Kaufmann quartz at various magnifications.

S9 Particle size distribution of Sigma-Aldrich quartz

Number size distribution of the SA quartz sample was obtained with a TSI 3080 scanning mobility particle sizer (SMPS) and a TSI 3321 aerodynamic particle sizer (APS). The dry particles were dispersed using a fluidized bed. The sample shows a strong bimodal particle size distribution with mode diameters of 481 nm and 1.5 µm. There is a third, yet extremely weak, mode around 201 nm particle diameter.



Model	LogNormal	
Equation	y = y0 + A/(sqrt(2*PI)*w*x)*exp(-(ln(x/xc))^2/(2*w^2))	
Plot	Peak1(dN/d[log(Dp)])	Peak2(dN/d[log(Dp)])
y0	0 ± 0	0 ± 0
xc	550 ± 0	1595.1718271 ± 11.81422267
w	0.28692186 ± 0.00729236	0.39063031 ± 0.00650684
A	281.91498543 ± 6.35290793	1431.14686995 ± 19.1225368 3
Adj. R-Square	0.99227636	

Figure S29. Particle size distribution of SA quartz sample. Solid black squares: APS; solid black triangles: SMPS; red lines: two lognormal fits to data obtained from APS and SMPS; blue line: resultant bimodal lognormal fit to the observed dataset.

S10 ICP-MS measurement on supernatant of SA and Kaufmann quartz suspensions

In order to assess the leaching of contaminants from quartz and the glass vial walls, suspensions of quartz were prepared in pure water in both borosilicate glass vials and polypropylene falcon tubes and aged for 72 hours. The freshly prepared and aged suspensions were centrifuged to remove the particles. The supernatant liquid in each case was collected and tested for the concentration of leached elements via inductively coupled plasma mass spectroscopy (ICP-MS). Tables S1 and S2 shows the concentration of various elements measured in the ICP-MS tests.

Table S1. ICP-MS measurement of supernatant from SA quartz sample fresh (0.5 h) and aged (72 h) in an aqueous suspension (0.5 wt %) in a glass vial. Element concentrations from pure water reference are subtracted

Element	Concentration of leached elements in pure water and in the supernatant (ppb)					
	Pure water in glass vial		**SA quartz suspension in water (0.5 wt%)**		**Release from SA quartz only**	
	fresh	**aged**	**fresh**	**aged**	**fresh**	**aged**
Li	0.2529	0.8250	0.3902	1.0830	0.1374	0.2581
Be	0.0000	0.0000	0.0016	0.0062	0.0016	0.0062
Na	764.94	2121.77	1153.09	2825.74	388.154	704.007
Mg	1.8608	0.8039	7.4628	24.2016	5.6019	23.3977
Al	0.8997	1.2930	61.2125	270.4301	60.3127	269.1372
Si	203.568	4476.53	1558.39	11910.063	1354.8169	7433.5304
K	12.5988	11.1557	82.8685	143.0657	70.2697	131.9099
Ca	2.9858	2.1018	3.2150	3.9564	0.2292	1.8546
Cr	0.2336	0.3716	0.4002	0.7795	0.1666	0.4080
Mn	0.0385	0.0149	0.0675	0.1235	0.0290	0.1086
Fe	0.0440	0.1643	6.1151	20.2883	6.0711	20.1241
Ni	0.0800	0.0281	0.0615	0.1658	-0.0185	0.1377
Co	0.0114	0.0032	0.0051	0.0130	-0.0064	0.0098
Cu	0.2046	0.2847	0.0688	0.1856	-0.1358	-0.0991
Zn	0.0007	0.0000	0.0000	0.0000	-0.0007	0.0000
Ga	0.4642	0.5297	0.9478	0.8716	0.4836	0.3419
Se	0.0064	0.0058	0.0100	0.0097	0.0036	0.0039
Sr	0.0701	0.0337	0.2470	0.5777	0.1769	0.5439
Ba	1.9989	2.0659	4.1506	3.7032	2.1517	1.6373
Tl	0.0009	0.0000	0.0011	0.0034	0.0002	0.0034

Pb	0.0122	0.0022	0.0164	0.0428	0.0042	0.0406
Bi	0.0007	0.0002	0.0000	0.0002	-0.0007	0.0000

Table S2. ICP-MS measurement of supernatant from SA quartz and Kaufmann quartz suspensions (0.7 wt%) fresh (0.5 h) and aged (72 h) in pure water in polypropylene vials. Concentrations of elements are determined from subtracting pure water blank (possibly responsible for some of the negative numbers). Average and standard deviations of two independent aging experiments are given

	Concentration of leached elements in the supernatant (ppb)			
Element	**SA quartz suspension in water (0.7 wt%)**		**Kaufmann quartz suspension in water (0.7 wt%)**	
	fresh	**aged**	**fresh**	**aged**
Li	0.063 ± 0.009	0.102 ± 0.006	1.429 ± 0.141	2.180 ± 0.090
Be	0.0062 ± 0.0002	0.0093 ± 00014	0.0001 ± 0.0005	-0.0001 ± 0.0002
Na	372.62 ± 50.33	383.07 ± 31.34	384.05 ± 48.73	402.32 ± 100.69
Mg	32.779 ± 1.269	41.827 ± 0.625	6.626 ± 0.647	7.918 ± 0.384
Al	130.99 ± 16.52	159.39 ± 23.14	1.312 ± 0.885	0.104 ± 0.384
Si	6068.1 ± 1405.1	4945.0 ± 198.92	3955.2 ± 113.8	3761.8 ± 439.5
K	139.35 ± 9.23	139.88 ± 3.375	58.608 ± 28.880	52.365 ± 30.785
Ca	92.702 ± 11.237	92.649 ± 1.570	62.162 ± 6.744	44.560 ± 4.535
Cr	0.365 ± 0.053	0.213 ± 0.017	1.365 ± 0.039	1.061 ± 0.037
Mn	0.516 ± 0.019	0.746 ± 0.030	0.315 ± 0.016	0.334 ± 0.005
Fe	14.36 ± 2.774	15.478 ± 1.697	3.643 ± 0.143	1.881 ± 0.158
Ni	0.652 ± 0.056	0.153 ± 0.057	4.579 ± 0.439	5.990 ± 0.248
Co	0.126 ± 0.075	0.044 ± 0.007	312.92 ± 31.77	536.42 ± 10.98
Cu	-0.025 ± 0.034	-0.472 ± 0.125	0.161 ± 0.033	-0.434 ± 0.073
Zn	0.150 ± 0.580	-2.207 ± 0.091	2.024 ± 0.141	0.098 ± 0.092
Ga	0.035 ± 0.004	0.047 ± 0.002	0.0010 ± 0.0000	-0.0009 ± 0.0012
As	0.059 ± 0.004	0.088 ± 0.033	0.435 ± 0.419	0.690 ± 0.417
Br	1.165 ± 0.148	0.504 ± 0.146	1.240 ± 0.161	0.871 ± 0.168
Se	0.0044 ± 0.0063	-0.005 ± 0.009	0.0087 ± 0.0077	-0.0068 ± 0.0089

Rb	0.345 ± 0.005	0.371 ± 0.008	0.717 ± 0.093	1.068 ± 0.070
Sr	2.653 ± 0.181	3.734 ± 0.306	0.306 ± 0.072	0.327 ± 0.068
Mo	0.165 ± 0.002	0.181 ± 0.019	0.152 ± 0.049	0.220 ± 0.061
Ru	-0.0003 ± 0.0000	0.0000 ± 0.0000	0.0000 ± 0.0000	0.0008 ± 0.0000
Rh	0.0000 ± 0.0000	-0.0010 ± 0.0000	0.0001 ± 0.0000	-0.0010 ± 0.0000
Pd	0.0012 ± 0.0030	0.0024 ± 0.0026	-0.0020 ± 0.0032	-0.0022 ± 0.0030
Ag	0.0034 ± 0.0006	-0.0048 ± 0.0041	0.0010 ± 0.0026	-0.0071 ± 0.0043
Cd	-0.0025 ± 0.0079	-0.034 ± 0.011	0.018 ± 0.009	-0.019 ± 0.011
I	1.113 ± 0.037	0.018 ± 0.124	1.145 ± 0.022	-0.002 ± 0.081
Cs	0.012 ± 0.003	0.014 ± 0.002	0.105 ± 0.009	0.163 ± 0.006
Ba	4.347 ± 0.158	4.518 ± 0.163	3.518 ± 0.818	3.548 ± 1.006
La	0.085 ± 0.002	0.117 ± 0.036	0.0002 ± 0.0009	0.0006 ± 0.0009
Ce	0.114 ± 0.059	0.134 ± 0.031	-0.0007 ± 0.0010	-0.0008 ± 0.0013
Gd	0.025 ± 0.010	0.021 ± 0.004	-0.0075 ± 0.0099	-0.0060 ± 00024
W	3.130 ± 1.753	0.406 ± 0.125	815.61 ± 58.96	1619.7 ± 64.62
Tl	0.0020 ± 0.0012	0.0029 ± 0.0009	0.0035 ± 0.0007	0.0041 ± 0.0004
Pb	0.0939 ± 0.1006	-0.108 ± 0.027	0.0134 ± 0.0172	-0.1252 ± 0.0278
Bi	0.0005 ± 0.0000	-0.0009 ± 0.0002	0.0017 ± 0.0002	-0.0003 ± 0.0003
Th	0.0123 ± 0.0023	0.016 ± 0.002	0.0016 ± 0.0007	0.0037 ± 0.0005

S11 DSC Thermograms of ice melting

Here we show DSC thermograms of melting cycle (1 K min^{-1}) for pure water and 10 wt% ammonium sulfate solution cases. While melting of ice occurs at one temperature, ice within a freeze concentrated solution shows eutectic melting yielding a melting peak with no well-defined onset (in form of an extended shoulder). Since ice remains all the time in thermodynamic equilibrium with the freeze concentrated solution, it melts gradually, such that the melting signal constantly increases until it peaks when ice completely melts. Therefore, the peak of the melting curve can be used to evaluate the water activity of the solution.

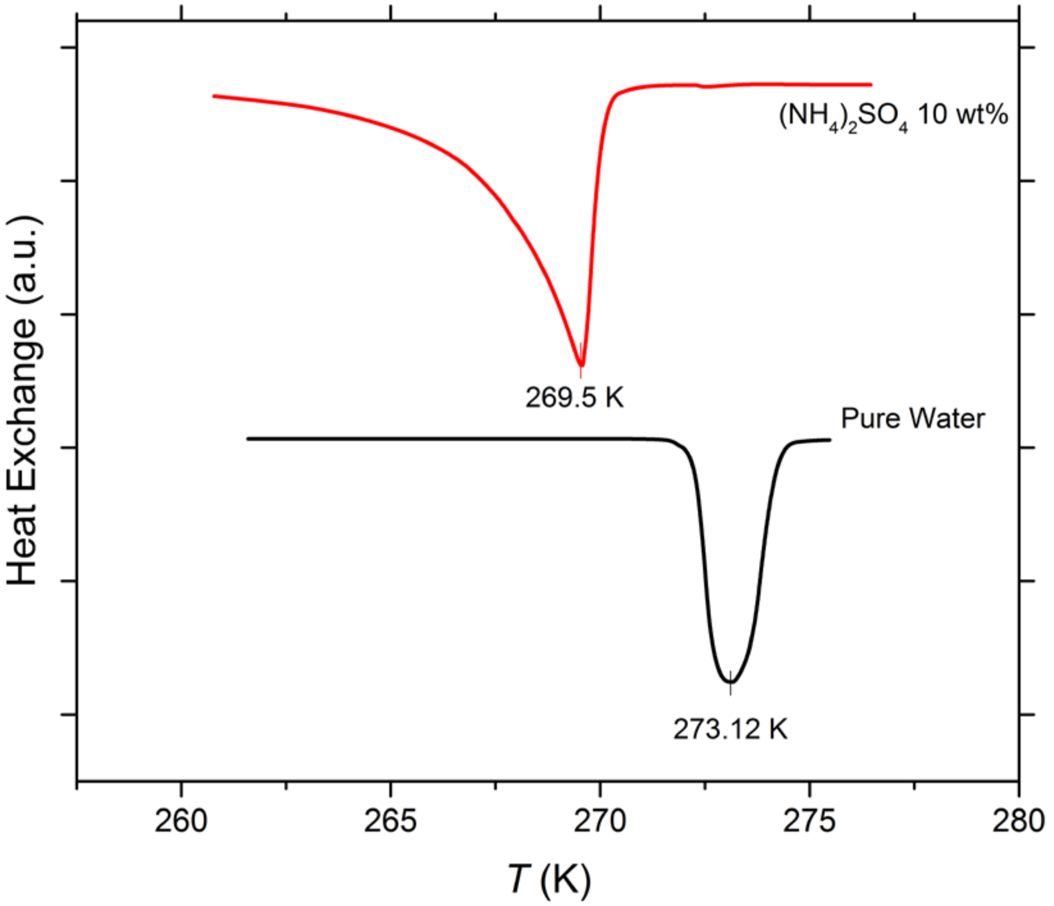


Figure S30. DSC thermograms of melting cycle (1 K min^{-1}) for pure water and 10 wt% ammonium sulfate solution cases.