Ice nucleating properties of uncoated and coated mineral dust particles

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INTRODUCTION

Mineral dust particles contribute to a major component of global aerosol fraction, and substantial evidence indicates that dust particles are most effective ice nuclei (IN). However, the ice nucleating ability of mineral dust particles could be altered if they are coated with soluble materials such as sulfates. We report ice nucleation laboratory experiments showing that IN properties of coated dust particles depends upon the mineralogy of the dust particles. The ice nucleation ability of uncoated and coated dust particles was investigated at three temperatures: -25, -30, and -35 degC. Particles were size-selected and coated with sulfuric acid, and coating thickness was estimated by measuring the hygroscopicity properties of dust coated particles. Only coated Arizona test dust particles showed suppression of IN ability, the ice nucleating ability of other particles such as illite, kaolinite, montomorillonite, and quartz was not altered. This suggests mineralogical compositions dictate the chemical reactions with sulfuric acid that affect the ice nucleating abilities.

PAST STUDIES

Recent studies investigated ice nucleating properties of various mineral dust species that are bare and coated with sulfuric acid (Table 1), and a majority of the studies conclude that surface processing leads to surface modifications and thus reduction in the heterogeneous ice nucleation ability.

Table 1: Summary of past studies that investigated the influence of sulfuric acid coating on IN activation ability of mineral dust particles above -38 degC.

Reference	*IN investigation technique*	*Mode of ice nucleation or freezing*	*Temperature (degC)*	*Mineral dust*		*Particle generation technique*	*Coating confirmation technique*	*Coating reduces IN activation efficiency?*
				Type	*Diameter (μm)*			
Cziczo et al. (2009)	Expansion type cloud chamber	Deposition, immersion, condensation	-20 to -45	ATD, Illite	< ~ 1	Dry particle suspension/ generation	Single particle mass spectroscopy	Depends upon the mineralogy
Neidermeier et al. (2010)	Continuous flow cooling chamber	Immersion	-34 to -40	ATD	0.3	Dry particle suspension/ generation	CCN activation, aerosol mass spectrometry	Depends upon the coating thickness
Neidermeier et al. (2011)	Continuous flow cooling chamber	Immersion	-28 to -40	ATD	0.3	Dry particle suspension/ generation	CCN activation, aerosol mass spectrometry	Yes
Salam et al. (2007)	Continuous flow diffusion chamber	Deposition, condensation	-5 to -45	Montmorillonite	< ~ 5	Dry particle suspension/ generation	Transmission Electron Microscopy	No
Sullivan et al. (2010)	Continuous flow diffusion chamber	Deposition, immersion/ condensation	-25 and -30	ATD	0.3	Dry particle suspension/ generation	CCN activation, aerosol mass spectrometry	Yes
Tobo et al. (2012)	Continuous flow diffusion chamber	Deposition, immersion/ Condensation	-26, -30 and -34	Kaolinite	0.3 and 0.7	Dry particle suspension/ generation	CCN activation, aerosol mass spectrometry	Yes
Knopf and Koop (2006)	Optical microscope with a flow cell	Deposition	-13 to -76	ATD	0.7 to 10	Wet atomization	Assumption of spherical core shell model	No
Eastwood et al. (2009)	Optical microscope with a flow cell	Deposition	-27 to -40	Kaolinite	5 to 15	Wet atomization	Assumption of spherical core shell model	Yes
Chernoff and Bertram (2010)	Optical microscope with a flow cell	Deposition	-26 to -39	Kaolinite, Illite, Quartz, Montmorillonite	~ 7 to 10	Wet atomization	Assumption of spherical core shell model	Yes
Present study	Continuous flow diffusion chamber	Deposition	-25, -30 and -35	ATD, Kaolinite, Illite, Quartz, Montmorillonite	0.15	Dry particle suspension/ generation	CCN activation	Depends upon the mineralogy

EXPERIMENTAL METHOD

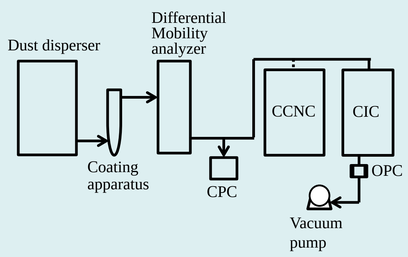


Figure shows the schematic of the experimental setup. Dust particles were generated in a dust disperser and passed through a coating apparatus that had a reservoir of sulfuric acid heated to 75 degC. Particles of mobility diameter 150 nm were transported to the condensation particle counter (CPC), cloud condensation nuclei counter (CCNC) and compact ice chamber (CIC). Dashed line indicates CCNC was used during initial experiments to estimate the mass fraction of sulfuric acid condensed per particle. CIC was connected to the optical particle counter (OPC) and further to the vacuum pump. Fraction of dust particles that nucleated ice were calculated using CPC and OPC measurements, see text for details.

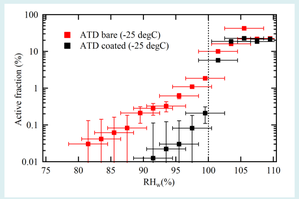
ATD (A1 Ultrafine Test Dust), illite, montmorillonite, quartz, and kaolinite mineral dust particles were dry-dispersed by means of a dust disperser. Two dust samples were purchased from Powder Technology Inc., while others were from Sigma-Aldrich Co. LLC. Their chemical compositions, obtained from the vendor, are presented in right Table.

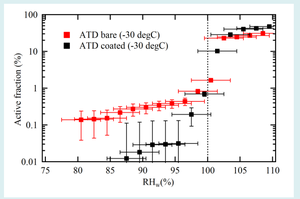
Dust	*Chemical formula*	*Supplier*
Arizona test dust	SiO_2, CaO, Al_2O_3, MgO, Fe_2O_3, TiO_2, Na_2O, K_2O	Powder Tech. Inc.
Illite	$K_{1.5}Al_4(Si,Al)_8O_{20}(OH)_4$	Powder Tech. Inc.
Montomorillonite	$(Na,Ca)_{0.7}(Al,Mg)_4(Si_8O_{20})(OH)_4 \cdot n(H_2O)$	Sigma-Aldrich
Quartz	SiO_4	Sigma-Aldrich
Kaolinite	$Al_2Si_4O_{10}(OH)_4$	Sigma-Aldrich

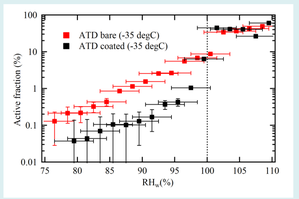
ICE NUCLEATION RESULTS

The ice nucleation properties of size-selected mineral dust particles were obtained using the CIC. Figures below present F_{ice} of bare and coated ATD and other dust particles, respectively, as a function of RH_w at different temperatures:-25, -30 and -35 degC. The results show that dust particles can nucleate ice in deposition mode of ice nucleation (water sub-saturation; < 100 RH_w) and activate to form droplets in condensation freezing mode of ice nucleation (above water saturation; ≥ 100 RH_w). In discussing these results we assume that coating mechanism (involving exposing the particles to hot vapors of sulfuric acid) does not alter the particles' original ability to nucleate ice.

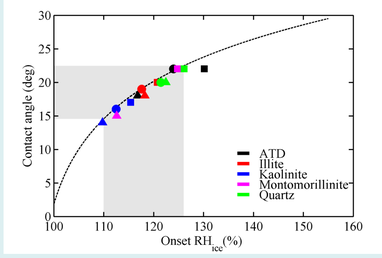
The F_{ice} spectra showed different behaviors in the water sub-saturated regime depending on temperature and dust particle type. All dust types were observed to initiate ice phase at RH_w ~ 80%, at both -25 and -30 degC. At lower temperature (-35 degC), however, the ice nucleation onset was observed at RH_w ~ 75%. Efficient ice nucleation occurring at lower temperatures implied that low equilibrium ice vapor pressures assist in forming the ice embryo, such that water vapor molecules have low mobility that increases the probability of ice formation. Different dust species exhibited different F_{ice} spectra, see below (legends). These discrepancies among the dust types to induce ice nucleation could be attributed to the variability in the efficiency of active sites present on the surface that promote ice embryo formation.

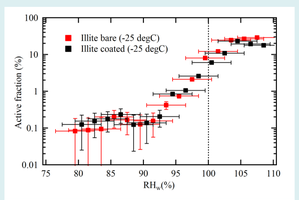


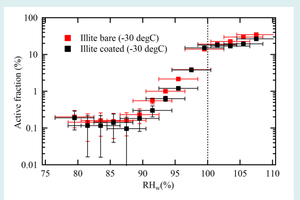


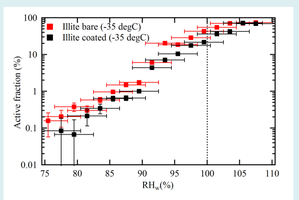


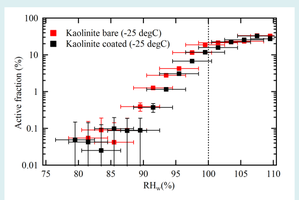
Ice nucleation properties of the different mineral dust species were also compared by calculating the onset contact angles. Contact angles were calculated at 1% nucleated fraction following Kulkarni *et al.*, (2010, 2012) formulations and assuming curvature adjustments are negligible (Fletcher, 1962) and all dust particles have the equal probabilities to nucleate ice. Contact angles illustrate (Fig. 3) good agreement with the previous studies (Wang and Knopf, 2011 and references therein) showing little temperature dependence and distribution over a range of ~ 14 to 22 degrees. Contact angles for kaolinite particles varied from 14 to 17 degrees and for ATD particles, from 18 to 22 degrees, showing kaolinite particles are effective in nucleating ice compared to ATD particles.

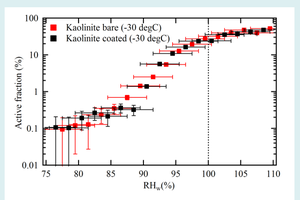


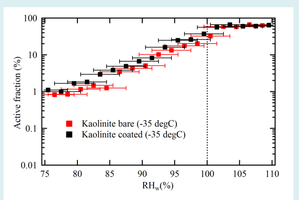


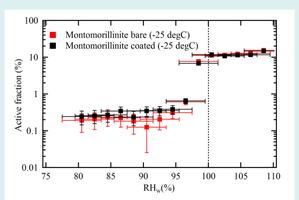


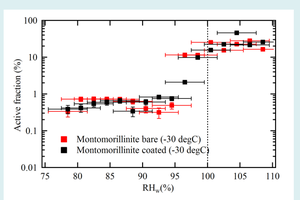


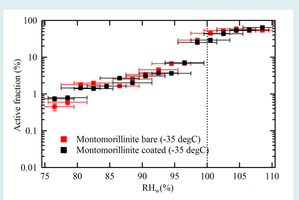


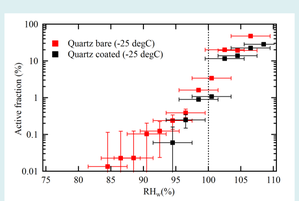


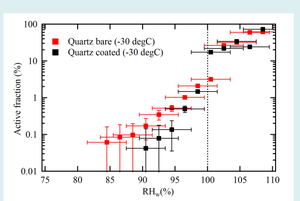


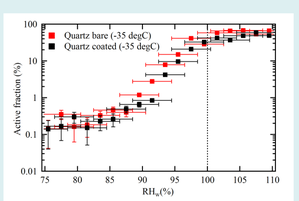






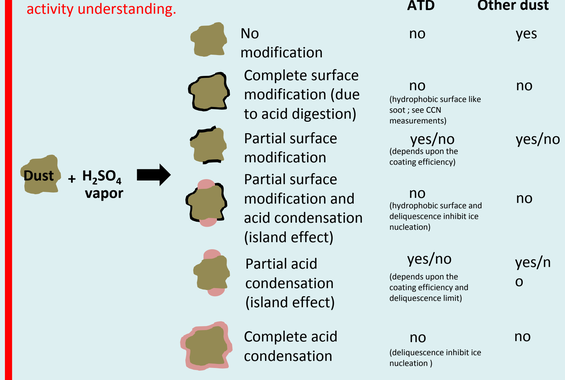






INTERPRETATION OF RESULTS

Hypothetical scenarios of interactions between dust and sulfuric acid vapor, and possibility of such interactions deduced from their deposition IN activity understanding.



Adding sulfuric acid to the ATD particles reduced their ability to nucleate ice, but for the other four dust species we did not observe this reduction. This demonstrates that sulfuric acid reactivity depends upon the mineralogy of the dust species. We think sulfuric acid cannot react with certain dust species effectively to displace the ordered water structures at the mineral-aqueous acid interface (Yang *et al.*, 2011), resulting in no/slight surface modifications even after the treatment, and therefore the ice nucleation properties of certain dust species may still be retained.

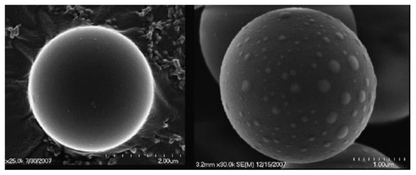


Fig. 1 SEM images of polystyrene latex spheres uncoated (left) and coated with oleic acid (right).

Garland et al., *PCCP*, 2008

Also, it is possible that ice nucleation properties remained because some dust particles did not contain sulfuric acid or were partially coated with sulfuric acid. This could be caused when acid condenses into the form of islands rather than depositing uniformly over the surfaces (Garland *et al.* 2008).

SUMMARY

The ice nucleation properties of bare and coated dust particles were investigated experimentally in the deposition ice nucleation mode. ATD, illite, kaolinite, montomorillonite and quartz dust species of mobility diameter 150 nm were used as a surrogate for natural mineral dust. The particles were coated after passing through coating apparatus where the sulfuric acid bath was maintained at 75 degC. The total sulfuric acid mass condensed upon the particles was estimated by determining the hygroscopicity with a CCNC, and we estimate ~ 2.7e-18 kg of mass was condensed per particle.

Our results indicate that different dust species act efficiently as IN for the temperature range from -25 to -35 degC. A trend of increase in the F_{ice} of dust particles with increasing RH_w was observed. It was also observed that ice nucleation properties depend upon the dust composition and temperature. Adding sulfuric acid onto the ATD particles reduced their ice nucleation ability compared to bare particles; however, for other dust species we did not find this effect.

In addition to deposition ice nucleation experiments, keeping similar experimental conditions (coating technique, temperature and size-selected dust species), we investigated the droplet activation efficiency of bare and coated particles. This was carried out to measure the maximum fraction of particles that can activate into droplets under given experimental conditions. Results indicate that the fraction varied from ~20 to 80%, depending on the temperature and composition of dust species, but never reached 100%.

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