

## Observations of organic species and atmospheric ice formation

D. J. Cziczo,<sup>1,2</sup> P. J. DeMott,<sup>3</sup> S. D. Brooks,<sup>3</sup> A. J. Prenni,<sup>3</sup> D. S. Thomson,<sup>1,2</sup>  
D. Baumgardner,<sup>4</sup> J. C. Wilson,<sup>5</sup> S. M. Kreidenweis,<sup>3</sup> and D. M. Murphy<sup>1</sup>

Received 25 February 2004; revised 26 May 2004; accepted 8 June 2004; published 30 June 2004.

[1] Aerosol particles found in the lower confines of the atmosphere are typically internal mixtures of sulfate, inorganic salts, refractory components, and organic species. The effect these complex combinations have on cloud formation processes remains largely unknown. We have conducted two complementary studies on one important process, the homogeneous formation of ice by small particles. In the first study the freezing of atmospheric aerosol was induced using controlled temperature and humidity conditions. In the second study the chemical composition of the residue from ice crystals in high altitude clouds was analyzed. Here we show that organic components do not partition equally to the ice and aqueous phases. Instead, organic-rich particles preferentially remain unfrozen. These results suggest that emissions of organic species have the potential to influence aerosol-cold cloud interactions and climate. *INDEX TERMS*: 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0320 Atmospheric Composition and Structure: Cloud physics and chemistry; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 1610 Global Change: Atmosphere (0315, 0325). *Citation*: Cziczo, D. J., P. J. DeMott, S. D. Brooks, A. J. Prenni, D. S. Thomson, D. Baumgardner, J. C. Wilson, S. M. Kreidenweis, and D. M. Murphy (2004), Observations of organic species and atmospheric ice formation, *Geophys. Res. Lett.*, 31, L12116, doi:10.1029/2004GL019822.

### 1. Introduction

[2] The term ‘indirect effect’ has been applied to the impact of particles on climate through their complex interaction with clouds. Indirect radiative forcing is subdivided into effects attributed to warm clouds, which remain entirely unfrozen, and those that contain ice crystals. Warm cloud processes are the better understood, including observed links between aerosol, cloud drop number, and precipitation [Brenquier *et al.*, 2000; Baker, 1997]. Although ice formation can be an important step in precipitation, this aspect of the indirect effect remains largely unexplored. IPCC [2001] notes that anthropogenic effects on ice and mixed-phase

clouds, and the related climatic impact, also remain unknown. A number of factors are responsible, among them the high altitude of frozen clouds, a lack of appropriate instruments, and uncertain processes such as ice multiplication and scavenging. Because of these uncertainties, atmospheric ice formation, specifically cirrus cloud formation, remains a difficult process to model. The state of knowledge of ice nucleation currently hinders our ability to understand ice cloud formation and the humidity of the upper troposphere and stratosphere.

[3] Primary ice formation proceeds via two distinct pathways, homogeneous or heterogeneous freezing. Both are climatically important. Homogeneous nucleation refers to the spontaneous formation of the ice phase within an aqueous matrix. Water droplets found in the atmosphere do not homogeneously freeze at 0°C due to a kinetic barrier to crystal formation. ‘Supercooling’ to approximately –38°C is required before the spontaneous formation of ice becomes probable [Pruppacher and Klett, 1997]. Solutes commonly associated with atmospheric aerosol have been shown to further increase the amount of supercooling [Koop *et al.*, 2000]. At temperatures warmer than about –38°C, or at relative humidities lower than a few percent below water saturation, heterogeneous ice formation is initiated by the presence of solid particles with an appropriate structure, known as ice nuclei (IN) [Roddy and O’Connor, 1981]. The majority of particles found in the troposphere do not appear to contain IN, however [Sassen and Dodd, 1988]. The semi-volatile nature of the large reservoir of particles able to undergo homogeneous freezing has precluded extensive study using traditional EM techniques that take place *in vacuo* [Heintzenberg *et al.*, 1996]. Only recently have experiments been performed to understand volatile and semi-volatile components of particles that form ice in the atmosphere [DeMott *et al.*, 2003]. The focus of this work is to describe two studies of aerosol that homogeneously freezes using a single particle laser ablation technique that is sensitive to both refractory and non-refractory aerosol components [Cziczo *et al.*, 2003].

### 2. Field Studies

[4] The first set of experiments was conducted during November 2001 at Storm Peak Laboratory (SPL) in northern Colorado. SPL is equipped with extensive particle monitoring equipment. Further, the remote location and high elevation, 3200 meters above sea level, permitted sampling from the clean troposphere [Borys and Wetzel, 1997] in which the majority of ice cloud formation takes place. Aerosol was subjected to controlled temperature and saturation conditions using the Colorado State University Continuous Flow Diffusion Chamber (CFDC), described previously [DeMott *et al.*, 2003]. Briefly, the CFDC focuses aerosol between two

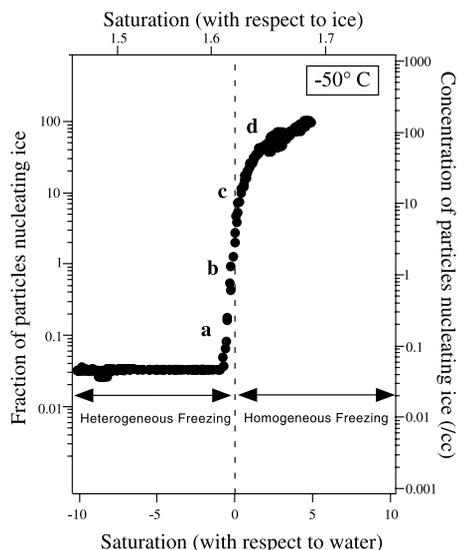
<sup>1</sup>Aeronomy Laboratory, National Oceanic and Atmospheric Administration, Boulder, Colorado, USA.

<sup>2</sup>Cooperative Institute for Research in the Environmental Sciences, University of Colorado, Boulder, Colorado, USA.

<sup>3</sup>Department of Atmospheric Science, Colorado State University, Fort Collins, Colorado, USA.

<sup>4</sup>Centro de Ciencias de la Atmósfera, Universidad Nacional Autónoma de México, Mexico City, Mexico.

<sup>5</sup>Department of Engineering, University of Denver, Denver, Colorado, USA.

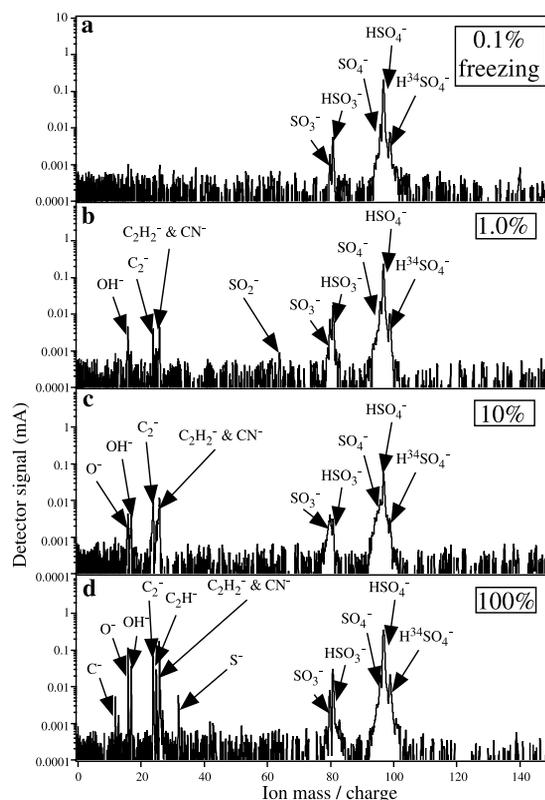


**Figure 1.** Fraction of aerosol particles in the background atmosphere that nucleated ice as a function of saturation. This figure represents a single experiment, conducted at a temperature of  $-50^{\circ}\text{C}$ , but is indicative of all data collected at Storm Peak Laboratory. The discontinuity just under water saturation, at which point the number of particles nucleating ice increased by four orders of magnitude, is due to a change from heterogeneous to predominantly homogeneous freezing. The dashed line indicates saturation, with respect to water. Points are certain to  $\pm 1\%$  relative humidity. Conditions at which single particle mass spectra are presented in Figure 2 are indicated by letters a, b, c, and d.

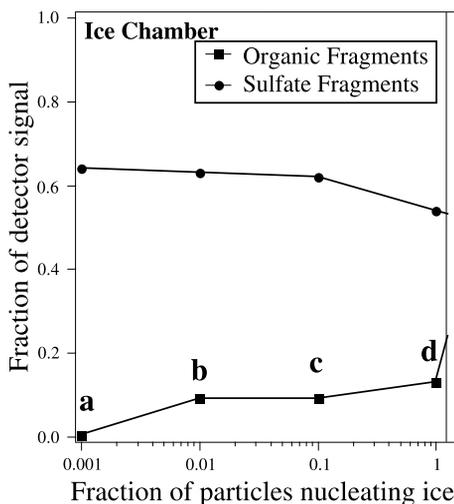
ice-coated walls held at different temperatures. The temperature gradient between the walls and a sheath flow are used to limit aerosol exposure to constant temperature ( $\pm 0.7^{\circ}\text{C}$ ) and relative humidity ( $\pm 0.7\%$  with respect to water) conditions. Particles that nucleated ice were optically counted and separated from those that did not freeze using a counterflow virtual impactor (CVI) [Cziczo *et al.*, 2003]. The fraction of aerosol nucleating ice was calculated by comparing the number of crystals formed under given CFDC conditions to the total number of atmosphere particles larger than 100 nm diameter, from which the majority of ice formation originates [Chen *et al.*, 1998], measured by scanning mobility particle sizing (SMPS-TSI). Figure 1 shows a profile of atmospheric ice formation, illustrating the dearth of IN and the switch from heterogeneous to homogeneous freezing. This signature of freezing has been previously presented [Cziczo *et al.*, 2003; DeMott *et al.*, 2003] with an emphasis on particle composition changes between the two modes of freezing and the effect of large-scale meteorology. It is used here to examine compositional differences throughout the entire homogeneous freezing regime. The onset of homogenous freezing was observed to occur a few percent sub-saturated with respect to water, consistent with laboratory studies of sulfate aerosol [Chen *et al.*, 2000]. The fraction of particles nucleating ice increased by several orders of magnitude as the humidity was raised past water saturation.

[5] Chemical composition, after evaporation of condensed-phase water, was determined using the NOAA

Aeronomy Lab Particle Analysis by Laser Mass Spectrometry (PALMS) instrument [Cziczo *et al.*, 2003]. Aerosol particles are drawn into PALMS using a vacuum. Particles are detected using a YAG laser ( $\lambda = 532\text{ nm}$ ) with scattered light used to trigger an excimer laser ( $\lambda = 193\text{ nm}$ ) that both ablates and ionizes components. A complete positive or negative mass spectrum is obtained on a particle-by-particle basis using a time-of-flight mass spectrometer. The lower particle diameter for which mass spectra were resolved for these studies was between 0.15 and 0.3  $\mu\text{m}$ . Negative polarity single particle mass spectra acquired at increasing saturation, and therefore fraction of particles freezing, are presented in Figure 2. Nearly all particles contained sulfate and/or organic material, consistent with the composition of the majority of free tropospheric aerosol [Murphy *et al.*, 1998]. The signal attributed to sulfate and organic species did not remain constant as the fraction of particles nucleating ice increased, however (Figure 3). Those particles that froze most readily (i.e., at the lowest saturation for a given temperature) exhibited minimal or no signal attributed to organic components whereas particles with large organic signal required higher saturation conditions.



**Figure 2.** Negative ion mass spectra of single particles that froze in four homogeneous freezing regimes described in Figure 1. Panels a through d correspond to particles that froze when progressively larger fractions of the background aerosol was nucleating ice. Spectra contain fragments of sulfate and organic species, components of the majority of free tropospheric particles, but the relative presence of organics was observed to decline as the fraction of particles nucleating ice decreased. Notice that no organic components were detected in the particle that froze at the lowest saturation condition.



**Figure 3.** Average fraction of signal attributed to sulfate and organic fragments in mass spectra as a function of the fraction of the background aerosol that was nucleating ice. This plot incorporates data from spectra a, b, c, and d from Figure 2, as well as all other data acquired during homogenous ice nucleation studies at Storm Peak Laboratory. When only a small fraction of the background aerosol was nucleating ice those particles had negligible signal attributed to organic fragments. Only when a significant fraction of the aerosol was nucleating ice was organic material found in those particles.

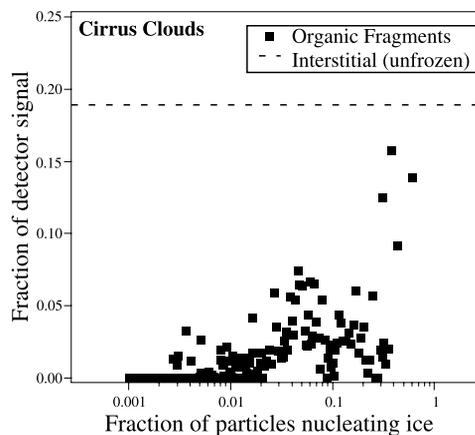
Previous studies using PALMS show that the negative ion organic signal typically represents a lower limit for the concentration of organic material in the particle [Middlebrook *et al.*, 1997].

[6] A second set of experiments was conducted by flying the same mass spectrometer aboard a NASA WB-57F aircraft. The study occurred during July 2002 as part of the Cirrus Regional Study of Tropical Anvils and Cirrus Layers - Florida Area Cirrus Experiment (CRYSTAL-FACE) [Jensen *et al.*, 2004]. Unlike the ground-based SPL mission the aircraft flights penetrated ice clouds that had resulted from atmospheric freezing. Unlike the CFDC experiments parameters such as initial saturation, temperature, cloud heterogeneity, and size-dependant sedimentation of ice crystals have an unknown impact on the data. A CVI inlet was used to separate cloud elements from  $\sim 5$ – $22$  micrometers diameter from larger crystals and unfrozen particles [Cziczo *et al.*, 2004]. Mass spectra of ice residue were taken on a crystal-by-crystal basis after condensed-phase water was evaporated. Ice crystals were sampled  $\sim 80\%$  of the in-cloud period with the inlet switched to a mode that retained small unfrozen particles within clouds, termed ‘interstitial aerosol’, for the remaining time. This allowed organic signal from the ice residue to be compared to the average value for the interstitial aerosol as a function of the fraction of the total aerosol that froze (Figure 4). The later quantity was derived by comparing the number density of unfrozen ambient particles, using the FCAS instrument [Jonsson *et al.*, 1995], to the concentration of ice crystals, using the CAPS instrument [Baumgardner *et al.*, 2002]. Consistent with the ground-based SPL study, minimal organic signal was detected when less than 1% of particles

nucleated ice. The organic signal of the unfrozen interstitial particles remained higher than the ice residue regardless of the fraction of particles freezing.

### 3. Discussion and Conclusions

[7] These data do not allow us to definitively state that organics cause a suppression of ice formation. Instead, we conclude that particles with high organic signal are not efficient at ice nucleation. We note that these complementary studies, one using controlled temperature and saturation conditions and the other from within atmospheric ice clouds, both exhibit the same behavior. Since it has been shown that single particle mass spectrometry can detect a wide range of species and abundances [Murphy *et al.*, 1998], and we find no quantity other than organic signal that co-varies in the same manner to offer an alternative explanation, we consider this association important. Furthermore, although we have not attempted to observe a direct link between organics and a perturbation of ice cloud properties, we believe it is important to note that parameters such as cloud density and dissipation may be affected by these species. It follows that aerosol particles, for which precipitation is the major removal mechanism, may have a composition-dependent lifetime. Related parameters, such as upper tropospheric humidity and precipitation, could also be modified by the presence of organic species and any changes induced in their abundance or distribution by anthropogenic activities.



**Figure 4.** Average fraction of signal attributed to organic fragments as a function of the fraction of the background aerosol that was nucleating ice. Data are from all cirrus ice clouds investigated during the CRYSTAL-FACE mission except those that formed during a mineral dust transport event [Cziczo *et al.*, 2004]. Data span cirrus clouds in an altitude range from 11 to 15 km, a temperature from  $-48^{\circ}$  to  $-77^{\circ}\text{C}$ , and crystal densities from 0.001 to  $>300$  per  $\text{cm}^3$ . This plot is analogous to Figure 3 but with atmospheric conditions dictating the fraction of particles freezing. Particle composition is observed to change in that when fewer than 1% of the background aerosol was nucleating ice almost no organic fragments were observed in the ice residue. Only when almost all particles were nucleating ice were organics observed at levels approaching the average for those particles that remained unfrozen within clouds, shown as a dashed line.

[8] The unequal partitioning of organics to the ice and aqueous phases draws forth two resulting questions that require further study. First, it is uncertain by what process (es) organic components may affect ice formation. *Koop et al.* [2000] have proposed that nucleation per unit volume is solely a function of water activity. It is plausible that this theory is correct but that organic components create hygroscopicity differences between particles that affect water uptake [Rudich, 2003]. Disparate water uptake between pristine sulfate and internally mixed organic/sulfate aerosols would lead to differences in particle dilution, volume, and, ultimately, freezing point. Alternately, organics may induce kinetic effects, as would be the case with a surface coating, which are not accounted for by *Koop et al.* [2000]. *Tabazadeh et al.* [2002] have theorized that homogeneous ice nucleation does not occur within the bulk but rather at a particle surface. An organic surface component would thus affect surface nucleation, but it remains uncertain how prevalent such coatings are in the atmosphere [Intergovernmental Panel on Climate Change, 2001]. Lastly, organics may act in a manner not previously considered important for the atmosphere. *Yeh and Feeney* [1996] have suggested several mechanisms by which antifreeze proteins (AFPs), such as those found in polar fish that survive freezing conditions, inhibit bulk ice formation. For example, AFPs have been shown to bind to and inhibit ice crystal growth. It is plausible that atmospheric aerosols contain organic molecules with similar properties and similar results. Laboratory studies are required to elucidate the correct mechanism. Second, the speciation of the organics involved remains unknown. Laser ablation mass spectrometry causes extensive fragmentation of organic components making identification of precursor species difficult [Middlebrook et al., 1997]. Laboratory studies have not shown significant supercooling effects for sulfate/dicarboxylic acid mixes (S. D. Brooks, personal communication, 2004). This is significant because it indicates that some organic components can be emitted to the atmosphere with little or no effect while other species may have a substantial impact.

[9] **Acknowledgments.** The authors would like to thank D. Rogers, R. Borys, the air and ground crews of the NASA WB-57F, and the Desert Research Institute's Storm Peak Laboratory for facilities, data, and support in the field. This work was supported by NASA, NSF (awards ATM-0124927 and 0334228), and NOAA Base Funding.

## References

- Baker, M. B. (1997), Cloud microphysics and climate, *Science*, *276*, 1072–1078.
- Baumgardner, D., H. Jonsson, W. Dawson, D. O. Connor, and R. Newton (2002), The cloud, aerosol and precipitation spectrometer (CAPS): A new instrument for cloud investigation, *Atmos. Res.*, *59–60*, 251–264.
- Borys, R. D., and M. A. Wetzell (1997), Storm Peak Laboratory: A research, teaching, and service facility for the atmospheric sciences, *Bull. Am. Meteorol. Soc.*, *78*, 2115–2123.
- Brenguier, J. L., H. Pawlowska, L. Schüller, R. Preusker, J. Fischer, and Y. Fouquart (2000), Radiative properties of boundary layer clouds: Droplet effective radius versus number concentration, *J. Atmos. Sci.*, *57*, 803–821.
- Chen, Y., S. M. Kreidenweis, L. M. McInnes, D. C. Rogers, and P. J. DeMott (1998), Single particle analyses of ice nucleating aerosols in the upper troposphere and lower stratosphere, *Geophys. Res. Lett.*, *25*, 1391–1394.
- Chen, Y., P. J. DeMott, S. M. Kreidenweis, D. C. Rogers, and D. E. Sherman (2000), Ice formation in sulfate and sulfuric acid aerosol particles under upper tropospheric conditions, *J. Atmos. Sci.*, *57*, 3752–3766.
- Cziczo, D. J., et al. (2003), A method for single particle mass spectrometry of ice nuclei, *Aerosol Sci. Technol.*, *37*, 460–469.
- Cziczo, D. J., D. M. Murphy, P. K. Hudson, and D. S. Thomson (2004), Single particle measurements of the chemical composition of cirrus ice residue during CRYSTAL-FACE, *J. Geophys. Res.*, *109*, D04201, doi:10.1029/2003JD004032.
- DeMott, P. J., et al. (2003), Measurements of the concentration and composition of nuclei for cirrus formation, *Proc. Natl. Acad. Sci. U. S. A.*, *100*, 14,655–14,660.
- Heintzenberg, J., K. Okada, and J. Strom (1996), On the composition of non-volatile material in upper tropospheric aerosols and cirrus crystals, *Atmos. Res.*, *41*, 81–88.
- Intergovernmental Panel on Climate Change (2001), *Climate Change 2001: The Scientific Basis*, edited by J. T. Houghton et al., pp. 291–335, Cambridge Univ. Press, New York.
- Jensen, E., D. O. C. Starr, and O. B. Toon (2004), Mission investigates tropical cirrus clouds, *Eos Trans. AGU*, *84*(5), 45–50.
- Jonsson, H. H., et al. (1995), Performance of a focused cavity aerosol spectrometer for measurements in the stratosphere of particle size in the 0.06–2.0 micrometer diameter range, *J. Atmos. Oceanic Technol.*, *12*, 115–129.
- Koop, T., B. Luo, A. Tsias, and T. Peter (2000), Water activity as the determinant for homogeneous ice nucleation in aqueous solutions, *Nature*, *406*, 611–614.
- Middlebrook, A. M., D. S. Thomson, and D. M. Murphy (1997), On the purity of laboratory-generated sulfuric acid droplets and ambient particles studied by laser mass spectrometry, *Aerosol Sci. Technol.*, *27*, 293–307.
- Murphy, D. M., D. S. Thomson, and M. J. Mahoney (1998), In situ measurements of organics, meteoritic material, mercury, and other elements in aerosols at 5 to 19 kilometers, *Science*, *282*, 1664–1669.
- Pruppacher, H. R., and J. D. Klett (1997), *Microphysics of Clouds and Precipitation*, D. Reidel, Norwell, Mass.
- Roddy, A. F., and T. C. O'Connor (Eds.) (1981), *Atmospheric Aerosols and Nuclei*, pp. 333–387, Galway Univ. Press, Galway, Ireland.
- Rudich, Y. (2003), Laboratory perspectives on the chemical transformations of organic matter in atmospheric particles, *Chem. Rev.*, *103*, doi:10.1021/cr020508f.
- Sassen, K., and G. C. Dodd (1988), Homogeneous nucleation rate for highly supercooled cirrus cloud droplets, *J. Atmos. Sci.*, *45*, 1357–1369.
- Tabazadeh, A., Y. S. Djikaev, and H. Reiss (2002), Surface crystallization of supercooled water in clouds, *Proc. Natl. Acad. Sci. U. S. A.*, *99*, 15,873–15,878.
- Yeh, Y., and R. E. Feeney (1996), Antifreeze proteins: Structures and mechanisms of function, *Chem. Rev.*, *96*, 601–617.

D. Baumgardner, Centro de Ciencias de la Atmósfera, Universidad Nacional Autónoma de México, Mexico City, Mexico.

S. D. Brooks, P. J. DeMott, S. M. Kreidenweis, and A. J. Prenni, Department of Atmospheric Science, Colorado State University, Fort Collins, CO, USA.

D. J. Cziczo, D. M. Murphy, and D. S. Thomson, Aeronomy Laboratory, National Oceanic and Atmospheric Administration, 325 Broadway, R/AL6, Boulder, CO, USA. (djciczo@al.noaa.gov)

J. C. Wilson, Department of Engineering, University of Denver, Denver, CO, USA.