Project Title: Relating the Chemical and Physical Properties of Aerosols to the Water Uptake and Ice Nucleation Potential of Particles Collected During the Carbonaceous Aerosols and Radiative Effects Study (CARES)

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Period of time report covers: 09/01/2012-08/31/2016

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Award Number: DE-SC0008613

Discovering how aerosol particles, present in the atmosphere in sizes of a few nanometers to hundred micrometers, initiate ice crystal formation presents a great challenge. Atmospheric ice nucleation is important because ice crystals alter the radiative properties of clouds and thus climate, and impact precipitation and thus the hydrological cycle. The difficulty in predicting atmospheric ice formation is attributable at least in part to several factors: 1) the diversity of ice nucleation pathways, 2. the physical and chemical complexity of the diverse particles types acting as ice nucleating particles (INPs), and 3. the relatively small numbers of INPs (compared with all other aerosol particles), sometimes less than one in 100000. These factors in turn makes constraining ice nucleation parameterizations for modeling applications challenging. The majority of airborne particles are organic or contain organic biogenic material. The presence of organic material adds to the complexity of the particles and therefore the predictability of ice nucleation events since the organic species can be present in different phase states, e.g. liquid or solid, in response to temperature and humidity. The award DE-SC0008613 to PI Prof. Daniel Knopf at Stony Brook University, "Relating the Chemical and Physical Properties of Aerosols to the Water Uptake and Ice Nucleation Potential of Particles Collected During the Carbonaceous Aerosols and Radiative Effects Study (CARES)", allowed the examination of laboratory generated aerosol particles and field-collected particles for their propensity to nucleate ice under typical tropospheric conditions and to relate ice nucleation to the physicochemical properties of the particles including their morphology and chemical composition. This in turn allowed for development of ice nucleation parameterizations for implementation in cloud models.

The award resulted in 10 fully and partially funded peer-reviewed publications and more than 20 seminar and conference presentations as listed below which addressed the ice nucleation conundrum and improved our predictive capabilities of understanding atmospheric ice crystal formation. This award resulted in substantial new insights into the processes governing immersion freezing, the role of organic aerosol particles in ice cloud formation, and the importance of the ambient aerosol population for prediction of ice nucleation events in an air parcel. These findings have significant implications for modeling and field measurement strategies of atmospheric ice nucleation.

We examined the physicochemical properties and the ice nucleation potential of particles collected during CARES using a novel experimental method that allows identification of the individual INPs within a large population of particles sampled from an ambient environment. Taking advantage of a variety of micro-spectroscopic techniques, we characterized the composition and morphology of INP and non-INP particles present in the airborne population (Knopf et al., 2014). Coupling our ice nucleation experiments with state-of-the art single particle compositional analysis by using scanning transmission X-ray microscopy with near edge X-ray fine structure spectroscopy (STXM/NEXAFS), we found that the identified INPs belong to the most common particle-type classes observed in the CARES field samples and as such are not special or rare particles (Fig. 1). In other words, the INPs are not unique which contrasts with the common paradigm that the INPs are rare and exceptional particles. Either there are differences between particles acting as INPs and particles not acting as INPs which are beyond our current detection limit or nucleation occurs randomly on the surface of any one of the present and compositionally equivalent particles as classical nucleation theory (CNT) suggests. These results also indicate that total particle surface area of the different particle types present in an aerosol population is a crucial factor for prediction of ice nucleation in an air mass. Additionally, our measurements demonstrated that organic aerosol particles can initiate ice nucleation. These findings challenge future field measurement strategies and particle types to be investigated in the laboratory for their ice forming potential.

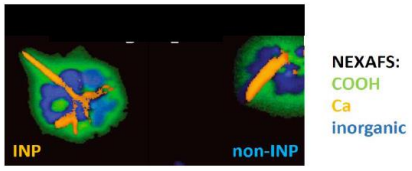

Figure 1 STXM/NEXAFS characterization of INP and non-INP as false color X-ray image [Knopf et al., 2014]. Legend gives dominant particle composition.

The analysis of the CARES aerosol population led to the development of a new parameterization for quantifying the mixing state of the entire aerosol populations in terms of the particle-specific diversity and bulk population diversity which we introduced as a mixing state index (O'Brien et al., 2015; Moffet et al., 2016). During a period of high photochemical activity and pollution buildup, we characterized the particle mixing state and morphology using STXM. Observations of compacted black carbon (BC) core

morphologies with relatively thick organic coatings at both urban and rural sites highlight the importance of highly aged particles at urban sites during periods of high photochemical activity. We observed that BC inclusions were located closer to the edge of particles when inorganic inclusions were present in the particles which can impact the radiative properties of these internally mixed particles.

To improve our predictive understanding of ice nucleation by the chemically complex ambient particles, as observed during CARES, we used a wide range of laboratory generated particles to systematically examine ice nucleation for typical tropospheric conditions. We demonstrated that the rate of immersion freezing, when a particle immersed in an aqueous droplet acts as an ice nucleus (IN), can be predicted by knowledge of the IN particle type present and the droplet's water activity which is equal to ambient relative humidity (Knopf and Alpert, 2013, Rigg et al., 2013). Our water activity based immersion freezing model can successfully predict freezing data including INPs such as mineral dusts, marine biological material, organic species, and surfactant molecules (Fig. 2). The model relates the heterogeneous ice nucleation rate coefficient to ambient temperature and relative humidity using a linear function for each IN type. Its mathematical simplicity makes it an ideal candidate for implementation in cloud and climate models.

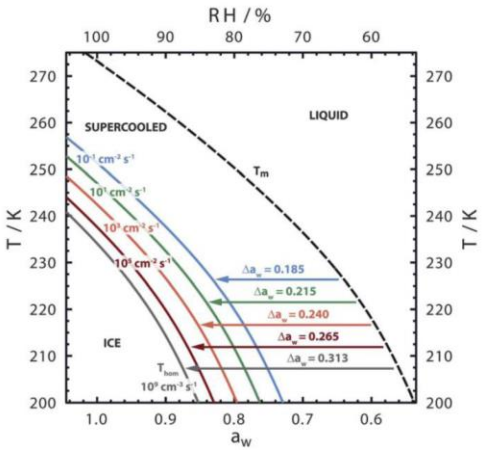

Figure 2. Concept of the water activity based immersion freezing model (Knopf and Alpert, 2013). Freezing occurs along solid lines with a constant nucleation rate coefficient. This freezing line is parameterized by the water activity criterion Δa_w.

In a follow up study we were able to demonstrate that the water activity based immersion freezing model can reproduce many past laboratory measurements which were generated using a variety of instruments to study immersion freezing (Alpert and Knopf, 2016). The CARES data demonstrated that ice nucleation likely follows stochastic behavior as expected from CNT. Results of our immersion freezing study (Alpert and Knopf,

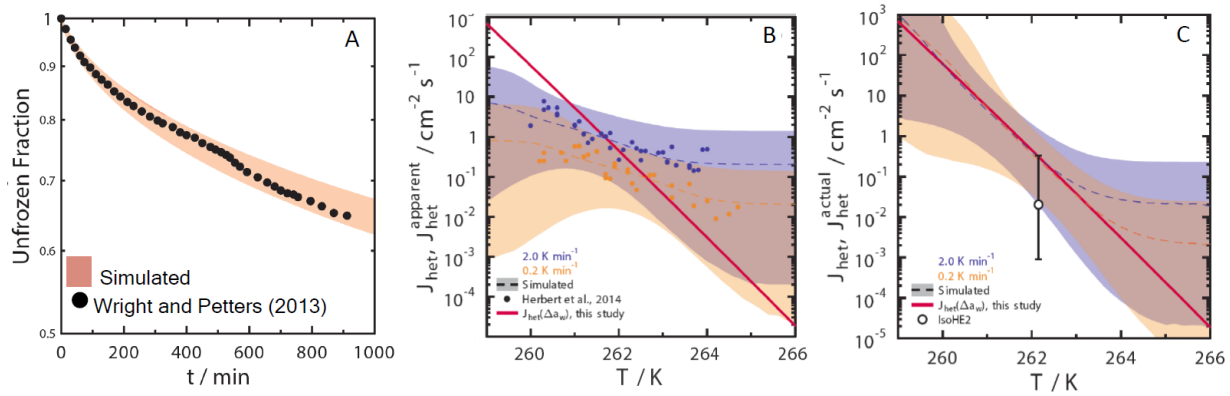

Figure 3. Application of a stochastic ice nucleation model to describe immersion freezing data. (A) The model can nicely predict the time dependent freezing of droplets observed by Wright and Petters (2013). (B) and (C) The model can explain the artifact observed by Herbert et al. (2014) that J_{het} varies with cooling rate. When accounting for actual INP surface areas the experimental data fall in line with the predictions of the water activity based immersion freezing model (red line) (C).

2016) demonstrated that when accounting for a stochastic and time dependence freezing process with a realistic estimate of the uncertainty in the INP surface area, discrepancies and interpretation differences among previous literature freezing data sets can be explained. Figure 3 shows that application of a stochastic immersion freezing model using the water activity based immersion freezing parameterization can resolve time dependent (Fig. 3A) and cooling rate dependent (Fig. 3B,C) immersion freezing experimental data. Application of this physical ice nucleation model allowed us to determine typical experimental uncertainties when measuring INPs in the laboratory or field. Most importantly, we emphasized the importance of accurate knowledge of the applied particle surface areas when predicting ice nucleation rates. Lastly, we

demonstrated that a water activity based immersion freezing model can also be derived for field collected particles providing an ice nucleation parameterization for implementation in cloud and climate models (China et al., 2017). In a collaborative effort, we are currently working to implement this novel parameterization of immersion freezing into a global model to estimate ice crystal number concentrations.

The CARES particle samples showed us that secondary organic aerosol (SOA) is ubiquitous and can participate in ice nucleation. To further our understanding how SOA particles can induce ice nucleation, we conducted ice nucleation experiments applying SOA particles generated from the OH oxidation of naphthalene, α-pinene, longifolene, or isoprene, with or without presence of sulfate or soot particles. This collaborative effort included colleagues from Boston College (Prof. P. Davidovits) Aerodyne Res. Inc. (Prof. D. R. Worsnop), and Dr. M. Shiraiwa (Univ. of California Irvine). Application of a suite of ice nucleation experiments in combination with a numerical diffusion model, we could show that changes in SOA particle phase state impact the ice nucleation pathway. For example, although a SOA particle can be solid (glassy) under room conditions and one would expect it to serve as IN, upon increasing humidity, this particle can deliquesce, i.e. becoming liquid, before heterogeneous ice nucleation occurs (dotted, dash-dotted, and dashed lines in Fig. 4). As a consequence, such a particle will not take part in cloud glaciation under mixed-phase cloud conditions and may only form ice homogeneously at lower temperatures. However, the phase state of the SOA particle in turn depends on current updraft velocities as shown in Fig. 4. Overall, our results suggest that biogenic SOA does not play a significant role in mixed-phase cloud formation and the presence of sulfate further renders this even less likely. However, anthropogenic SOA may have enhance cloud glaciation under mixed-phase and cirrus cloud conditions compared with biogenic SOA that dominated during preindustrial times or dominates in pristine areas. Inspired by the actual particle complexity observed during the CARES campaign, this study emphasizes the competing effects of changes in organic phase state and propensity for ice nucleation. These findings provide important information regarding how organic particles for ice nucleation studies need to be sampled.

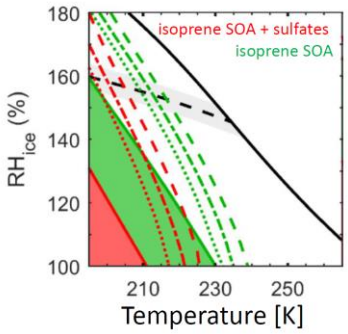

Figure 4. Full deliquescence of isoprene SOA with or without sulfates as a function of different updraft velocities (dotted, dash-dotted, and dashed lines represent updrafts of 0.03, 0.3, and 3 m s^{-1}, respectively). Solid green and red lines represent glass transition. Solid black line indicates water saturation. Black dashed line gives homogeneous freezing limit.

Biogenic material including proteins are known to efficiently nucleate ice. The PI joined a collaborative effort using sum frequency based interfacial analytical methods and molecular dynamic simulations to better understand why proteins in *P. syringae* favorably nucleate ice (Pandey et al., 2016). This study demonstrated that ice active sites within *P. syringae* feature unique hydrophilic-hydrophobic patterns to enhance ice nucleation. Furthermore, the freezing transition is facilitated by the highly effective removal of latent heat from the nucleation site, as apparent from time-resolved SFG spectroscopy. These insights help to formulate improved ice nucleation parameterizations for such biogenic/biological particles acting as INPs.

This funded project made use of state-of-the-art and novel single particle spectroscopic analytical techniques to analyze the ambient particle population but also the individual INPs. Because of our findings, the PI was invited to contribute to a review article about current progress in the analysis of complex atmospheric particles (Laskin et al., 2016).

Published Peer-Reviewed Articles:

1. Charnawskas, J. C., Alpert, P. A., Lambe, A. T., Berkemeier, T., O'Brien, R. E., Massoli, P., Onasch, T. B., Shiraiwa, M., Moffet, R. C., Gilles, M. K., Davidovits, P., Worsnop, D. R., Knopf, D. A., Condensed-phase biogenic-anthropogenic interactions with implications for cold cloud formation, *Farad. Disc.*, 2017, *accepted*.
2. China, S., Alpert, P. A., Zhang, B., Schum, S., Dzepina, K., Wright, K., Owen, R. C., Fialho, P., Mazzoleni, L. R., Mazzoleni, C., Knopf, D. A., Ice cloud formation potential by free tropospheric particles from long-range transport over the Northern Atlantic Ocean, *J. Geophys. Res.*, 122, 2017.
3. Laskin, A., Gilles, M. K., Knopf, D. A., Wang, B., China, S., Progress in the Analysis of Complex Atmospheric Particles, *Annu. Rev. Anal. Chem.*, 9, 117-143, 2016.
4. Pandey, R., Usui, K., Livingstone, R. A., Fischer, S. A., Pfaendtner, J., Backus, E. H. G., Nagata, Y., Fröhlich-Nowoisky, J., Schmüser, L., Mauri, S., Scheel, J. F., Knopf, D. A., Pöschl, U., Bonn, M., Weidner, T., Ice-nucleating bacteria control the order and dynamics of interfacial water, *Sci. Adv.*, 2:e1501630, 2016.
5. Moffet, R. C., O'Brien, R. E., Alpert, P. A., Kelly, S. T., Pham, D. Q., Gilles, M. K., Knopf, D. A., Laskin, A., Morphology and mixing of black carbon particles collected in central California during the CARES field study, *Atmos. Chem. Phys.*, 16, 14515-14525, 2016.
6. Alpert, P. A., Knopf, D. A., Analysis of isothermal and cooling-rate-dependent immersion freezing by a unifying stochastic ice nucleation model, *Atmos. Chem. Phys.*, 16, 2083-2107, 2016.
7. O'Brien, R. E., Wang, B., Laskin, A., Riemer, N., West, M., Zhang, Q., Sun, Y., Yu, X.-Y., Alpert, P., Knopf, D. A., Gilles, M. K., Moffet, R. C., Chemical imaging of ambient aerosol particles: Observational constraints on mixing state parameterization, *J. Geophys. Res.*, 120, 18, 9591–9605, 2015.
8. Knopf, D. A., Alpert, P. A., Wang, B., O'Brien, R. E., Kelly, S. T., Laskin, A., Gilles, M. K., Moffet, R. C., Micro-Spectroscopic Imaging and Characterization of Individually Identified Ice Nucleating Particles from a Case Field Study, *J. Geophys. Res.*, 119, 17, 10365–10381, 2014.
9. Knopf, D. A., Alpert, P. A., A Water Activity Based Model of Heterogeneous Ice Nucleation Kinetics for Freezing of Water and Aqueous Solution Droplets, *Farad. Disc.*, 165, 513-534, 2013.
10. Rigg, Y. J., Alpert, P. A., Knopf, D. A., Immersion freezing of water and aqueous ammonium sulphate droplets initiated by Humic Like Substances as a function of water activity, *Atmos. Chem. Phys.*, 13, 6603–6622, 2013.

Presentations:

1. Knopf, D. A., "The Role of Solution Water Activity in Describing Ice Nucleation from Laboratory Generated and Ambient Particles", University of the Pacific, Department of Chemistry, February 26, 2013.
2. Laskin, A., Knopf, D. A., Wang, B., Alpert, P. A., Roedel, T., Gilles, M. K., Moffet, R., Tivanski, A. "Applying Chemical Imaging Analysis to Improve Our Understanding of Cold Cloud Formation".Presented at the American Geophysical Union Fall Meeting, San Francisco, December 3, 2012.
3. D. A. Knopf, "The Grand Challenge of Atmospheric Ice Nucleation: What Can Be Learned from Particle Freezing Studies and How" Invited EMSL Director's Distinguished Lecture, Richland, WA, March 17, 2014.
4. Alpert, P. A., Lambe, A. T., Massoli, P., Onasch, T. B., Davidovits, P., Worsnop, D. R, Knopf, D. A., "The Ice Nucleation Pathway of Different Amorphous Secondary Organic Aerosol – the Role of Oxidation Level and Sulfate Content". Presented at the Atmospheric System Research – PI Meeting, Potomac, Maryland, USA, March 12, 2014.
5. Knopf, D. A., Alpert, P. A., Wang, B., O'Brien, R. E., Kelly, S. T., Laskin, A., Gilles, M. K., Moffet, R. C., "What Individual Identified Ice Nuclei Tell Us About the Atmospheric Glaciation Process". Presented at the Atmospheric System Research – PI Meeting, Potomac, Maryland, USA, March 10, 2014.
6. D. A. Knopf, "Laboratory Studies on Immersion Freezing and Deposition Ice Nucleation Relevant for Atmospheric Glaciation Processes", Dept. of Atmospheric Science, Yonsei University, Seoul, January 20, 2014. (invited)

7. Knopf, D. A., Alpert, P. A., Wang, B., Obrien, R. E., Moffet, R. C., Aller, J. Y., Laskin, A., Gilles, M. K., "Micro-Spectroscopic Chemical Imaging of Individual Identified Marine Biogenic and Ambient Organic Ice Nuclei". Presented at the AGU Fall Meeting 2013, San Francisco, December 13, 2013. (invited)
8. Knopf, D. A., "Parameterizations for immersion and deposition ice nucleation based on laboratory studies". Presented at the Atmospheric System Research Fall Working Group Meeting, Rockville, Maryland, USA, November 5, 2013.
9. Knopf, D. A., "The Physical and Chemical Transformation of Atmospheric Aerosol – Ice Nucleation and Heterogeneous Kinetics", New Jersey Institute of Technology, Department of Chemistry, September 25, 2013. (invited)
10. Knopf, D. A., Alpert, P. A., Kilthau, W., Radway, J., Aller, J. Y., "The effect of marine biological activity on aerosol generation and cold cloud formation". Presented at the Goldschmidt Conference, Florence, Italy, August 27, 2013. (invited)
11. Knopf, D. A., Alpert, P. A., Wang, B., O'Brien, R., Moffet, R. C., Laskin, A., Gilles, M. K., "Chemical Imaging of Individual Ice Nuclei and a New Physical Model of Immersion Freezing". Presented at Gordon Research Conference, Mt. Snow, Vermont, August 1, 2013.
12. Knopf, D. A., Alpert, P. A., "A Water Activity Based Model of Heterogeneous Ice Nucleation Kinetics for Freezing of Water and Aqueous Solution Droplets". Presented at Faraday Discussions 165, Leeds, UK, July 24, 2013. (invited)
13. Knopf, D. A., Alpert, P. A., Wang, B., O'Brien, R. E, Laskin, A., Gilles, M. K., Moffet, R., "Characterization of Individually Identified Ice Nucleating Particles within an Ambient Particle Population: Implications for Ice Nucleation Description". Presented at the AGU Fall Meeting 2014, San Francisco, December 16, 2014.
14. Fridlind, A. M., Avramov, A., Ackerman, A. S., Alpert, P. A., Knopf, D. A., " Response of Simulated Mixed-Phase Arctic Stratus Clouds to Slowly Activated Ice Nuclei". Presented at the AGU Fall Meeting 2014, San Francisco, December 16, 2014.
15. D. A. Knopf, "Heterogeneous Processes of Atmospheric Particles: Ice Nucleation and OH Oxidation Kinetics", Swiss Federal Institute of Technology (ETH), Zürich, IACETH Colloquium, November 17, 2014.
16. D. A. Knopf, "Atmospheric Ice Formation: The Role of Water Activity & Identification of Ambient Ice Nucleating Particles", The Weizmann Institute, Rehovot, October 21, 2014.
17. D. A. Knopf, "Micro-Spectroscopic Chemical Imaging of Individual Identified Ice Nuclei From an Ambient Particle Population", Max Planck Institute for Chemistry, Mainz, October 8, 2014.
18. D. A. Knopf, "A Physical Description of Immersion Freezing of Water and Aqueous Solution Droplets Using a Water Activity Based Model", Max Planck Institute for Chemistry, Mainz, October 7, 2014.
19. D. A. Knopf, "The Role of Interfaces in Ice Nucleation and Multiphase Chemical Kinetics", Institute of Organic Chemistry and Biochemistry, Academy of Sciences Czech Republic, Prague, May 5, 2014.
20. D. A. Knopf, "The role of Phase State and Interface in Ice Nucleation and Multiphase Chemical Kinetics", University of California at Irvine, Chemistry Department, January 26, 2015.
21. Knopf, D. A., "The Role of Mixing State in Atmospheric Ice Nucleation". Presented at the DOE ASR Joint User Facility and PI Science Team Meeting, Vienna, Virginia, March 19, 2015.
22. Knopf, D. A., Alpert, P. A., Wang, B., Kilthau, W. P., Bothe, D., O'Brien, R. E, Kelly, S. T., Aller, J. Y., Laskin, A., Gilles, M. K., Moffet, R., "Atmospheric Ice Nucleation: Micro-Spectroscopic Imaging and Characterization of Individually Identified Ice Nucleating Particles". Presented at the ACS Spring Meeting, Denver, March 22, 2015.
23. Moffet, R. C., O'Brien, R. E., Pham, D., Knopf, D. A., Laskin, A., Gilles, M. K., "Single particle measurements of atmospheric aerosol chemistry: Past, present and future". Presented at the Goldschmidt Conference, Prague, August 18, 2015.
24. Moffet, R. C., O'Brien, R. E., Wang, B., Laskin, A., Alpert, P., Riemer, N., West, M., Qi, Z., Sun, Y., Yu, X.-Y., Knopf, D. A., Gilles, M. K., "Towards quantitative mixing state measurements: The Sacramento case study". Presented at the Goldschmidt Conference, Prague, August 19, 2015.

25. D. A. Knopf, “The Role of Organic and Biogenic Material in Atmospheric Ice Nucleation and Multiphase Chemical Kinetics”. Stony Brook University, Chemistry Department, November 12, 2015.
26. Knopf, D. A., Alpert, P. A., Bothe, D., Charnawskas, J. C., Kilthau, W., Wang, B., O’Brien, R. E., Moffet, R. C. Laskin, A., Gilles, M. K., Aller, J. Y., “Microspectroscopic Examination of Atmospheric Ice Nucleating Particles”. Presented at Pacifichem, Honolulu, December 18, 2015.
27. Fridlind, A., Avramov, A., Ackerman, A., Alpert, P., Knopf, D., DeMott, P., Brooks, S., “Response of mixed-phase boundary layer clouds with rapid and slow ice nucleation processes to cloud-top temperature trend”. Presented at the American Geophysical Union Fall Meeting, San Francisco, December 16, 2015.
28. Alpert, P. A., Knopf, D. A., “Application of a New Unifying Stochastic Ice Nucleation Model to Examine Isothermal and Cooling Rate Dependent Immersion Freezing”. Presented at the DOE ASR PI Science Team Meeting, Vienna, Virginia, May 4, 2016.
29. Moffet, R., China, S., Wang, B., Tristan, H., Alpert, P., Knopf, D., Gilles, M., Laskin, A., “Characterization of the Mixing State of Aerosols in the Amazon Basin” Presented at the DOE ASR PI Science Team Meeting, Vienna, Virginia, May 4, 2016.