Probing atmospheric ice nucleation using field-collected and laboratory generated aerosol particles and global model evaluation

J. C. Charnawskas, W. P. Kilthau, D. W. Bothe, S. China, A. Laskin, M. K. Gilles, **J. P. Perlwitz**,
A. M. Fridlind, R. L. Miller, C. Pérez García-Pando, **D. A. Knopf** e-mail: Daniel.Knopf@stonybrook.edu (Stony Brook, NY 11794-5000)

Motivation

Despite much research effort, accurate prediction of atmospheric ice nucleation still remains a grand challenge. Reasons for this are manifold and include cloud dynamics as well as aerosol microphyiscal processes. Our research focuses on the physicochemical characterization of ice nucleating particles (INPs) and how different particle types impact ice nucleation. We approach this challenge employing modeling studies and laboratory experiments using field-collected and laboratory generated aerosol particles. Currently we are working on the following tasks:

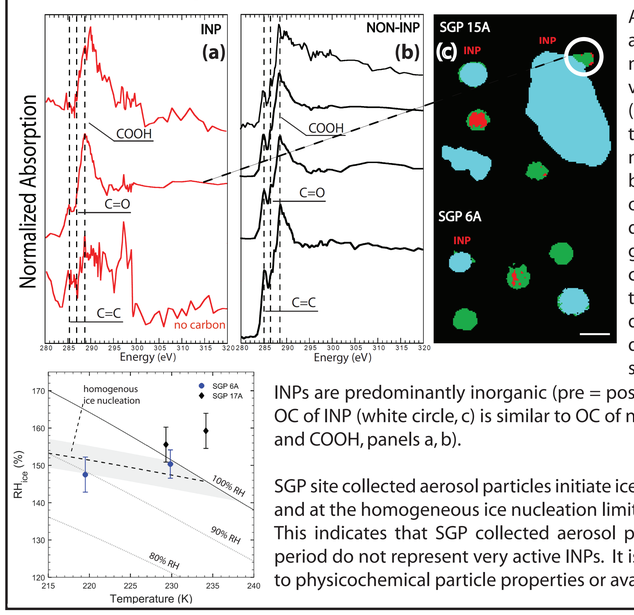
1. Use Southern Great Plains ARM site collected ambient aerosol particles for identification of INPs, evaluation of the particles' propensity for nucleating ice, and contrast physicochemical properties of INPs with the ambient particle population. Particular focus is placed on the role of airborne soil organic particles (ASOPs) that may act as INPs.

2. Physicochemically characterize ambient aerosol particles collected in the Amazon and examine the particles' ice nucleation properties. We focus on supermicron-sized particles, potentially reflecting biological particles. The analyses include particles collected above and below the forest canopy.

3. Conduct immersion freezing experiments employing mineral dust particles. Investigate how sample treatment impacts INP surface area and thus interpretation of ice nucleation kinetics. Perform ice nucleation experiments with mixed mineral dust samples to better mimic atmospheric aerosol populations (i.e. competitive immersion freezing experiments).

4. Apply an Earth System Model with an improved aerosol mineral fraction method to evaluate the atmospheric mineral dust aerosol population. The new approach is based on brittle fragmentation theory which considers re-aggregation and partial fragmentation at emission. We examine the importance of dust source distribution, dust size distribution and particle mixing state, and air temperature for simulating immersion freezing by mineral dust particles.

Ice Nucleating Particles ARM SGP Site

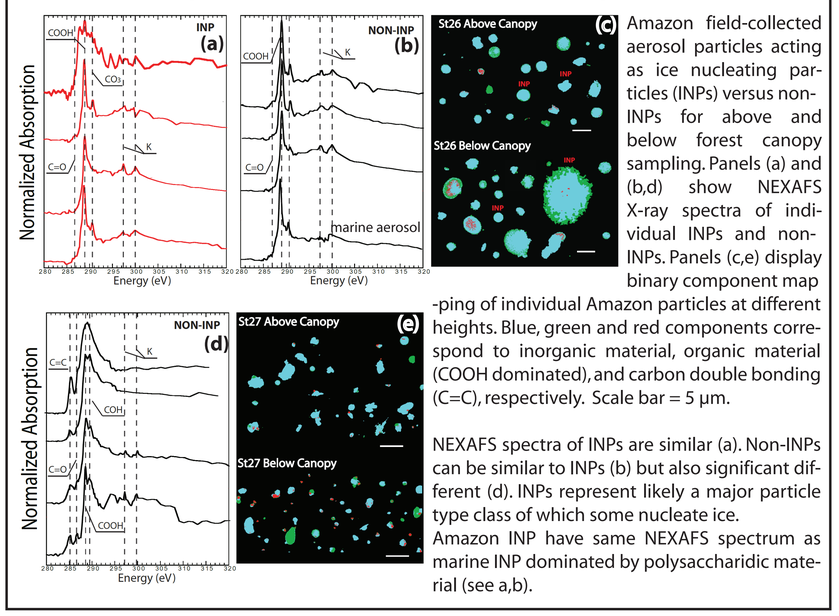


ARM SGP site field-collected aerosol particles acting as ice nucleating particles (INPs) versus non-INPs. Panel (a) and (b) show NEXAFS X-ray spectra of individual INPs and non-INPs. Panel (c) displays binary component mapping of individual SGP particles during 2 sampling times. Blue, green and red components correspond to inorganic material, organic material (COOH dominated), and carbon double bonding (C=C), respectively. Scale bar = 1 µm.

INPs are predominantly inorganic (pre = post-edge of K carbon edge). The OC of INP (white circle, c) is similar to OC of non-INP (see signatures of C=C and COOH, panels a, b).

SGP site collected aerosol particles initiate ice formation at water saturation and at the homogeneous ice nucleation limit.
This indicates that SGP collected aerosol particles for that specific time period do not represent very active INPs. It is not clear if this is due mainly to physicochemical particle properties or available particle surface areas.

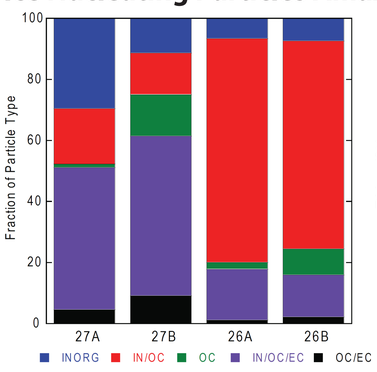
Ice Nucleating Particles From the Amazon Region



Amazon field-collected aerosol particles acting as ice nucleating particles (INPs) versus non-INPs for above and below forest canopy sampling. Panels (a) and (b,d) show NEXAFS X-ray spectra of individual INPs and non-INPs. Panels (c,e) display binary component map-ping of individual Amazon particles at different heights. Blue, green and red components correspond to inorganic material, organic material (COOH dominated), and carbon double bonding (C=C), respectively. Scale bar = 5 µm.

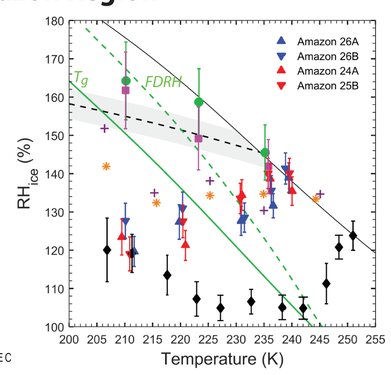
NEXAFS spectra of INPs are similar (a). Non-INPs can be similar to INPs (b) but also significant different (d). INPs represent likely a major particle type class of which some nucleate ice.
Amazon INP have same NEXAFS spectrum as marine INP dominated by polysaccharidic material (see a,b).

Ice Nucleating Particles Amazon Region



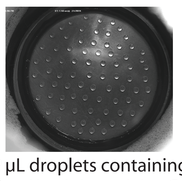
27A n=88, 27B n=88, 26A n=94, 26B n=90
IN=inorganic, OC=organic, EC=elemental carbon.

Summary of particles analyzed from Amazon sites above (A) and below (B) canopy. For both sampling times more purely organic particles are found below the canopy. However, the overall particle population differs significantly between different sampling times.

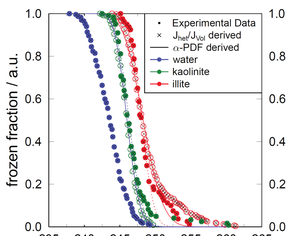


Ice nucleation of Amazon particles below (B) and above (A) forest canopy.
For comparison additional data sets:
i) pinene SOA (green circle) and T_g and FDRH lines; longifolene SOA (magenta square), both Charnawskas et al., Farad. Disc., 2017.
ii) kaolinite (black diamond), Wang et al. (2011).
iii) *N. atomus* (orange asterisk); *E. huxleyi* (purple plus), both Alpert et al. (2011).

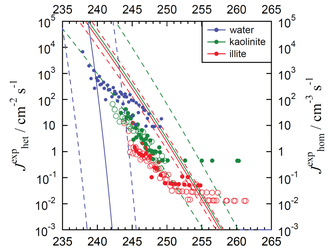
Competitive Immersion Freezing - Kaolinite vs. Illite



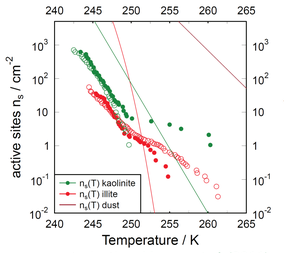
0.2 µL droplets containing either Kaolinite or Illite. Competitive experiments: Illite and Kaolinite droplets present at same time on substrate. Dust filtered: 0.8 µm - 11 µm.



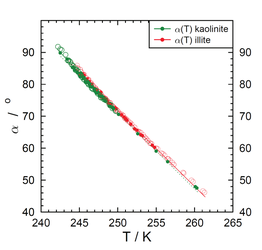
Solid symbols: competitive 2-dust species experiments. Open: 1 dust.



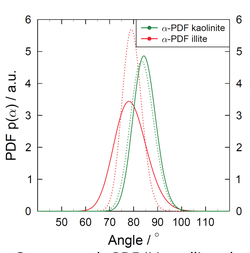
Lines: Water activity models - Koop et al. (2000); Knopf and Alpert (2013).



n_S parameterization: Murray et al. (2011), Broadley et al. (2012), Niemand et al. (2012).



Contact angle as a function of temperature: Zobrist et al. (2007).



Contact angle PDF (Marcolli et al., 2007). Dotted: comp. 2-dust exp.

Mixed droplet population behaves as expected from single droplet experiments.
Difference to parameterizations: explainable by uncertainty in particle surface area.

Earth System Model Study: INP Dependence on Feldspar Size Distribution and Mixing State for Active Site Parameterization

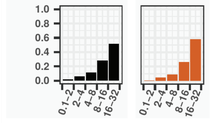


Figure 1. Volume size distributions at emission for total dust and Feldspar in the experiments (see text).

- We apply a new version of the dust module in a global model (GISS ModelE) with prognostic mineral composition of dust aerosols (8 minerals and mixtures with iron oxides, Perlwitz et al., 2015).
- The INP concentrations were calculated using the active size parameterization for different activation temperatures, following Atkinson et al. (2013).

Testing different assumptions on size distribution of the minerals:

i) 1-to-1 translation of the mineral fractions in soil to mineral fractions in dust aerosol and AeroCom-GOCART model size distribution (Fig. 1, upper row) as applied in previous studies (e.g., Atkinson et al., 2013).

ii) The size distributions are derived from combining brittle fragmentation for the emission of smaller particles (Kok, 2011) and empirically derived data (Kandler et al., 2009) for the emission of larger particles (Fig. 1, medium and lower row). Lower row: Feldspar is modified to have the same size distribution as quartz.

- External vs. internal mixture of Feldspar for calculating INP.
- Testing AeroCom-GOCART model vs. ModelE geographical source distribution.

Results – Testing Size Distribution and Source Distribution

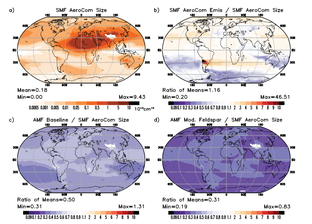


Fig. 2. INP concentration at 600 hPa for 253 K

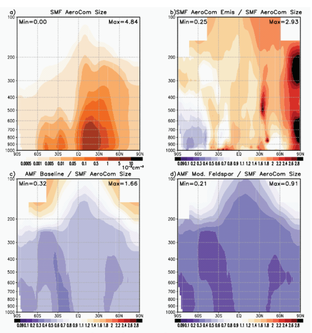


Fig. 3. Vertical and zonal-mean INP concentration.

- Figure 2a displays the geographical distribution of INP for 1-to-1 translation of soil mineral fractions to dust mineral fractions, AeroCom size distribution, and ModelE sources (reference experiment). Figure 3a shows the vertical and zonal-mean distribution for the same experiment. The INP concentrations are shown for an activation temperature of 253 K.
- Using the same size distribution, but the AeroCom-GOCART source distribution instead leads both to modifications in the geographical (Fig. 2b) and vertical (Fig. 3b) distribution of the INP concentration: Different source distributions can obscure the effect by different size distributions.
- Using the new version of the dust module for the prognostic minerals with size distributions based on brittle fragmentation theory and empirical data (Figs. 2c, 3c), reduces the calculated INP concentration by 50% for the same source distribution. The decrease is not geographically uniform, but depends on the mineral composition of the soils.
- Assuming the same size distribution for Feldspar as for quartz, where the size distribution is shifted to larger particle sizes, decreases the INP concentration even more (Figs. 2d, 3d).

Different source size distributions result in significant changes of INP number concentrations

Mineral Dust Mixing State Effect in Global Model

INP conc. for different activation T and for external and internal mixtures of Feldspar. SMF Aerocom Size: 1-to-1 soil to air mineral fractions, AeroCom Size distribution, ModelE sources; SMF AeroCom Emis: 1-to-1 soil to air mineral fractions, AeroCom Size distribution, AeroCom-GOCART sources; AMF Baseline: New prognostic mineral dust module, ModelE sources; AMF Mod. Feldspar: New dust module with modified Feldspar, ModelE sources.

- In all experiments, fine silt Feldspar is most active of all sizes to serve as INP.
- Activation is strongly reduced with the new version of the dust module due to the shift of the size distribution to larger particle sizes.
- The INP concentration shows little dependence on the mixing state of Feldspar for warmer activation temperatures.
- In contrast, for the lowest activation temperature, the INP concentration is an order of magnitude larger for internal mixing than for external mixing of Feldspar.
- When saturation of active sites is reached for low temperatures, the difference between external and internal mixture is solely determined by the number of dust particles available for activation as INP.

Summary and Conclusions

- Preliminary results suggest that SGP site collected aerosol contains inorganic and organic dominated particles. The ice active particles are dominated by inorganic material with potentially incomplete organic coatings. These particles do not represent very efficient INPs forming ice at the homogeneous ice nucleation limit.
- The populations of supermicron Amazon particles show distinctive compositional differences between above and below forest canopy but also during sampling periods. Below the canopy the occurrence of purely organic particles is enhanced. The INPs share spectral features of non-INPs but also show distinguished chemical differences to other non-INPs. Interestingly, the Amazon INPs show a similar spectral feature as organic sea spray aerosol acting as INP. The INPs initiate ice formation before reaching the homogeneous freezing limit. For cirrus temperatures, these INPs show similar efficiency nucleating ice as Kaolinite dust particles.
- Immersion freezing experiments that apply droplets that contain either Kaolinite or Illite dust can be explained by nucleation kinetics derived from droplets containing only one dust species. Different sample preparation results in different particle surface areas present in droplets and likley explains differences to previous parameterizations.
- An Earth System Modeling study reveals the importance of mineral dust source size distribution for prediction of atmopheric INPs on the example of Feldspar. An improved dust module reduces INP concentrations by 50% compared to more simplified assumptions. Presence of larger Felspar particles does not necessarily result in more INP numbers. At lower temperatures, INP concentrations are sensitive to the mixing state. INP numbers increase with internally mixed dust particles present.

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