Clarifying the dominant sources and mechanisms of cirrus cloud formation

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Abstract: Formation of cirrus clouds depends upon the availability of ice nuclei to begin condensation of atmospheric water vapor. While it is known that only a small fraction of atmospheric aerosols are efficient ice nuclei, the critical ingredients that make those aerosols so effective has not been established. We have determined in situ the composition of the residual particles within cirrus crystals after the ice was sublimated. Our results demonstrate that mineral dust and metallic particles are the dominant source of residual particles, while sulfate/organic particles are underrepresented and elemental carbon and biological material are essentially absent. Further, composition analysis combined with relative humidity measurements suggest heterogeneous freezing was the dominant formation mechanism of these clouds.

One Sentence Summary: The majority of cirrus clouds may form via heterogeneous freezing on mineral dust and metallic aerosol, not homogeneously or on elemental carbon or biological particles.

The effect of clouds on the climate system is more uncertain than the influence of heat-trapping greenhouse gases (*1*). Clouds can cool by reflection of solar radiation and warm by trapping terrestrial heat with the balance of effects depending on cloud properties such as altitude, thickness, phase and droplet or crystal size (*2*). Cirrus clouds are of particular importance because they have extensive global coverage and occur high in the atmosphere, at altitudes from 8 to 17 km (*2*). Global modeling suggests that human effects on ice clouds may rival the radiative effect of all anthropogenic aerosol particles that do not participate in cloud formation (*3*).

Due to the temperature at their altitude of formation, cirrus are composed exclusively of ice crystals *(2)*. Ice nucleation does not take place directly from water vapor, but instead requires a preexisting particle (*4*). Ice forms via two pathways, termed homogeneous and heterogeneous freezing. Homogeneous freezing, the spontaneous nucleation of ice within a sufficiently cooled solution, is better understood. A simple theoretical framework for this process has been developed for use in model studies (*5*). Because the vast majority of atmospheric aerosol particles are aqueous solutions of sulfates and organic molecules (*6*), homogeneous freezing has been assumed the dominant process (*7*). However, one drawback to homogeneous freezing is that relative humidity must be strongly supersaturated with respect to ice (RH_i 150-170%) (*4,8*). In contrast, heterogeneous freezing can start just below 0° C and at RH_i ~100% (*2,8*). Heterogeneous freezing remains poorly understood, however, because it can take several sub-pathways, among these "depositional freezing" of water vapor onto a particle surface and "immersion freezing" from within an aqueous coating (*4*). Many materials have been shown to act as ice nuclei (IN) in laboratory experiments, including mineral dust, metallic particles, some biological materials, low temperature glasses, and anhydrous salts (*4,9-11*). Despite this variety only a small fraction of atmospheric particles at ground level, as low as ~1 in 10^5, has been shown to act as IN (*4,8*).

Here, we have determined the chemical and physical properties of the particles on which cirrus ice crystals formed from measurements acquired aboard two NASA research aircraft. These data reveal which particle types are relevant for cirrus formation, from which we can infer the ice nucleation mechanism. We term the material within an ice crystal an ice residual (IR) because particles and gases may be scavenged after ice nucleation. Our data do not indicate multiple particles per IR, and the low pressure and number density of particles in the cirrus regime render it unlikely that scavenging represents a significant artifact *(12)*.

Four aircraft measurement campaigns, designed to sample within regions of high cirrus cloud abundance, were conducted between 2002 and 2011 over North and Central America and nearby ocean (Fig. 1). Data from liquid water-containing clouds are excluded. Tropical tropopause cirrus were previously considered (*13*). These clouds, which can have extensive coverage in the tropics, have been shown to consist of a low number density of relatively small ice crystals that likely formed heterogeneously on glassy aerosols or anhydrous salts (*13*). Measurements were made in air traffic corridors although contrails were not specifically targeted. Mass spectra for thousands of individual IR and near-cloud aerosol (Fig. 2) were combined into seven categories (Fig. 1). The mode of freezing is inferred from the relative composition: when the IR were predominantly sulfate/organic and similar to the near-cloud particles homogeneous freezing is inferred, whereas dissimilar IR and near-cloud particles indicate heterogeneous nucleation (*8,14*). Based on these criteria, the freezing mechanism was heterogeneous in 94% of cloud encounters.

The predominant particle category on which freezing took place was mineral dust and metallic particles, 61% by number (Fig. 1). This category was also the most enhanced in cloud ice with respect to its near-cloud abundance, 5%. The overwhelming majority, ~90%, exhibit no apparent sulfate or organic coating. Mixtures of sulfate and organic carbon, in all cases the largest near-cloud category at 55%, were the principal IR in only two distinct cloud encounters for which homogeneous freezing is inferred. In all other cirrus sulfate/organic particles were 14% of IR. Sulfate and organic material can act as IN when present as glasses or anhydrous salts *(10,11)*. Therefore, some of these particles may have entered the ice phase heterogeneously, implying the 94% value of heterogeneous freezing may be a lower limit. Sea salt was abundant as IR during flights that took place over open ocean, 25% by number, but only 3% during other flights. Biomass burning was in all cases the second most abundant particle type near-cloud, 36%, but was depleted in the IR, representing <5%. These quantities represent composite averages for each of the four campaigns. Single flights within campaigns were analyzed individually with the only differences from the campaign averages being the homogeneous freezing cases *(12)*. Representative spectra are shown for four IR types in Fig. 2.

The cirrus encounters presented here include both convective outflow and synoptically formed clouds. Because of the updrafts in convection, the aerosols immediately next to these clouds may not be representative of those within. Analyzed separately, we find that mineral dust and metallic particles are the dominant IR regardless of cirrus type when heterogeneous freezing was inferred, 56% in clouds associated with convection and 63% in those without. We therefore believe this result is consistent across cirrus development scenarios. Individual field study values are provided in Fig. 1 *(12)*.

Relative humidity measurements also can be used to constrain cirrus formation mechanisms (*15,16*). Clear sky (cloud free) RH_i measurements made during the flights on which IR data were collected are shown as a function of temperature in Fig. 3, along with measurements from three campaigns spanning a larger geographic area *(17,18)*. Sampling locations include North and Central America, the western Atlantic, and from the central Pacific to the Arctic. At cirrus temperatures <3% of the clear sky RH_i data exceed ~140%, a humidity consistent with heterogeneous freezing of mineral dust (2,*4*). Less than 0.5% of the RH_i data surpass the threshold for homogeneous freezing, also suggesting that heterogeneous freezing is the dominant formation mechanism.

Since ice crystal number densities from 1's to 100's per liter are consistent with heterogeneous freezing, whereas larger abundances are indicative of homogeneous nucleation (*19*), these measurements offers a third constraint on ice formation mechanisms. Recently realized artifacts associated with ice crystal shattering and consequent over-counting of number render many previous conclusions uncertain. Higher confidence data from the most recent set of flights indicate only a few percent of clouds have numbers greater than a few hundred per liter (*19*). The combination of in situ determination of IR composition, relative humidity measurements and ice crystal number densities from multiple field campaigns in different regions present a compelling case to consider heterogeneous freezing the dominant mechanism of cirrus formation throughout the study regions. These data stand in contrast to recent model studies which suggest the opposite (*7*).

Mineral dust is ubiquitous in the atmosphere (*20*). In agreement with the data presented here, collections of snow and cloud samples have shown mineral dust to be the predominant atmospheric IN (*4,8,14,21,22*), Ground based and laboratory studies which nucleate ice under

controlled conditions also show mineral dust to be an effective IN at <-10° C and RH_i from 110 to 140% (*3*). Laboratory studies show that sulfate and organic surface coatings 'deactivate' mineral dust, rendering them less effective IN (*23*), consistent with our results. Analysis of mineral dust particles collected in the free troposphere show that uncoated particles are present thousands of kilometers from their source *(24)*. Our data show that the uncoated subset of mineral dust is the most important, likely particles which have not undergone significant aging or a cloud processing event. The climatological importance of mineral dust is consistently demonstrated by laboratory studies characterizing it as an effective IN, field studies that observe its presence in the free troposphere, and IR analyses that show it dominates within ice crystals. In regions where the concentration of mineral dust and metallic aerosol is low, such as the high latitudes of the southern hemisphere, homogeneous freezing or ice nucleation by glassy particles and anhydrous salts *(10,11)* may be of greater importance than observed in these studies.

The lack of elemental carbon (EC) and biological particles is notable. Neither was abundant in the near-cloud particles or the ice phase, representing <1% in all cases. The in situ results are supported by IR collection for off-line electron microscopy (EM) compositional analysis *(12*,*21,22*) during the most recent set of flights. Only a single possible biological and two EC ice residual particles were observed during these flights, representing <<1%.

With few exceptions, laboratory studies of EC have shown this particle type to be an inefficient IN with nucleation only at temperatures and supersaturations close to homogeneous freezing (*9,25*). We conclude that effective ice nucleating EC particles are of low abundance in the cirrus regime. This may not be valid in contrails which were not studied. Noteworthy are the 2002 and 2011 measurements where wildfires injected EC and biomass burning particles into the upper tropospheric study region, yet these particles were not abundant as IR. We suggest models ignore EC as an ice forming particle type for cirrus clouds.

The case of biological particles is more complex than those of mineral dust and EC. Laboratory studies have shown that a few types of bacteria and fungal spores act as effective IN (*9,26*). Field results, which include collections of ice-phase precipitation and residues from one orographic cloud sometimes show the presence of biological material (*27*). Particle phase scavenging is a greater concern in precipitation studies than in cirrus, but these results nonetheless suggest that a subset of biological particles are effective IN. The upper tropospheric dataset reported here does not support an abundance of biological material as IR, widespread internal mixing with mineral dust, or the simple identification suggested in other studies (*12,27*). This dataset suggests most biological particles generated at the Earth's surface are removed via dry or wet deposition due to their large size and water or ice nucleating potential before they are transported to cirrus altitude. We recommend models ignore biological material as a cirrus forming particle type. The discrepancy between this and lower altitude studies suggests a fundamental difference between measurements made within or coupled to the boundary layer and those made in the mid- to upper troposphere. Furthermore, the lower altitude IR data were obtained in a cloud with ice crystals significantly larger than those we have been able to sample without impaction artifacts *(12),* although even in that study, mineral dust residuals dominated over biological particles (*27*).

Metallic particles represent an IR particle type that has not been extensively studied in the laboratory. Our data include a diversity of species including Pb, Zn, Sn, Cu, Ag, Mo and other heavy metals which have low abundance in mineral dust (Fig. 2). These metals were present in elemental, oxide and sulfate forms. During the most recent set of flights, metallic particles

represented 9-26% of the IR. A few previous field studies have noted metal-rich 'industrial' IN (*4,8,28,29*). Lead, present in ~5% of ambient particles *(30),* has been shown to be a particularly efficient IN in the field and laboratory (*21,29*). Laboratory studies and improved emission inventories coupled to cloud formation models are needed to elucidate the global effect of anthropogenic particles on cirrus.

Both the number and activity of heterogeneous IN control the formation of cirrus clouds. A global simulation of upper tropospheric aerosol particle concentrations combined with laboratory measurements of IN was used to predict cirrus formation. Independent of the IR composition measurements, this analysis also asserts the dominance of mineral dust among cirrus IN (*9,12,31,32*) (Fig. 4). In both deposition and immersion freezing modes mineral dust contributes the largest number of free tropospheric IN. Laboratory studies of EC suggest a wide range of IN efficiencies. In only the extreme case where all EC is assumed to have the highest efficiency does this species rival mineral dust. Biological particles are shown to be extremely rare in the upper troposphere, rendering them unable to compete with mineral dust in the cirrus temperature range (< -30 °C). Although many air parcels originating from mineral dust emission areas undergo cloud processing before reaching cirrus altitudes (*20*), resulting in depletion and/or coating of these particles, no comprehensive global data measurements of aerosol coating state exist and is not included in this model. The scarcity of laboratory experiments on biomass burning and metallic particles render us unable to provide separate estimates for these species.

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Fig. 1. Flight tracks of ice cloud residual measurements for four aircraft campaigns spanning a range of geographic regions and seasons. The composition of cirrus ice residuals and near-cloud aerosol, on a number basis, are summarized for each campaign. Ice crystal separation was accomplished with a counterflow virtual impactor inlet and composition was determined using single particle mass spectrometry where individual particles were desorbed and ionized with a 193 nm wavelength excimer laser and ion abundance measured with time of flight mass spectrometry (*13,14*). This technique is sensitive to all atmospheric aerosol particle components in a range from ~0.2 – 3 μm aerodynamic diameter (*13,14*). Ice residual particles were also collected and analyzed with electron microscopy coupled to energy dispersive X-ray microanalysis (*21*). Homogeneous freezing appeared to initiate cloud formation for only two individual cirrus clouds with composition shown in two insets (*). Mineral dust is the most dominant heterogeneous ice nucleus in all other cirrus encounters despite the geographic separation between the study areas and major global dust sources, colored brown (NASA Land Processes Distributed Active Archive Center, https://lpdaac.usgs.gov/get_data).

Fig. 2. Single particle mass spectra (MS) and electron microscope images (EM; inset) of ice residual particles analyzed during MACPEX corresponding to the categories presented in Fig. 1. (**A**) MS: The most common residual, mineral dust with minimal surface coating. EM: An aluminosilicate particle, also without apparent surface coating. (**B**) MS: Metallic particle with sodium, potassium, nickel, copper, iron and lead. EM: Metallic particle with tin, carbon and silicon. (**C**) MS: One of six particles of possible biological origin suggested by a composition including carbon, nitrogen, oxygen and phosphorous *(12)*. EM: The only particle of possible biological origin found on the electron microscope grids suggested by a composition including carbon, hydrogen, oxygen and phosphorous. (**D**) MS: An EC particle. EM: One of two EC particles, identified by both composition and fractal spherule aggregate structure. Note that the spectra and images do not correspond to the same particles.

Fig. 3. The distribution of upper tropospheric clear air relative humidity with respect to ice (RH_i) as a function of temperature. The color-coding corresponds to the number of events observed in each 5% RH_i and 1° C bin. The dashed and solid black lines indicate ice and liquid water saturation, respectively. (**A**) Composite of data collected in conjunction with the ice residual data shown in Fig. 1 and 2. Inset panel displays a histogram of these data for temperatures warmer than −70°C. Greater than 99% of the RH_i data in this temperature range fall significantly below the threshold for homogeneous nucleation, denoted by the black dotted lines. (**B**) Composite of data collected over a larger geographical area onboard the NSF G-V aircraft. The RH_i data utilize water vapor mixing ratios measured by the Harvard Water Vapor instrument (*17*) and Vertical Cavity Surface Emitting Laser hygrometer (*18*).

Fig. 4. Estimates of upper tropospheric IN concentration versus relative humidity with respect to ice (RH_i) and temperature from global simulations of aerosol surface area concentration and ice nucleation active site (INAS) densities derived from various laboratory experiments *(12)*. Estimates of upper tropospheric IN concentrations and annual average aerosol particle concentration from two versions of the CAM-Oslo model (*31,32*) were used. These estimates are derived independently from the in-situ data. Deposition (between -35 and -57°C) and immersion nucleation modes are considered separately. The onset of homogeneous freezing is indicated by the red dashed lines for an approximate freezing rate coefficient of $5x10^{14}$ m^{-3} s^{-1}. The shaded areas represent the range of measured INAS densities.

Supplementary Materials

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Materials and Methods

Figures S1, S2, S3, S4

Tables S1, S2, S3, S4

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