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**Chemical
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C. H. Twohy and
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Chemical characteristics of ice residual nuclei in anvil cirrus clouds: evidence for homogeneous and heterogeneous ice formation

C. H. Twohy¹ and M. R. Poellot²

¹College of Oceanic and Atmospheric Sciences, Oregon State University, Corvallis, Oregon, 97331-5503, USA

²Dept. of Atmospheric Sciences, University of North Dakota, Grand Forks, North Dakota, 58202-9006, USA

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Correspondence to: C. H. Twohy (twohy@coas.oregonstate.edu)

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Abstract

A counterflow virtual impactor was used to collect and analyze residual particles from anvil cirrus clouds generated over the state of Florida in the southern United States. A wide variety of particle types were found, including salts, crustal material, industrial metals, carbonaceous particles, and sulfates. Ambient aerosol particles near the anvils were found to have similar compositions, indicating that anvils act to redistribute particles over large regions of the atmosphere. Sampling occurred at a range of altitudes spanning temperatures from -21 to -56°C . More insoluble (crustal and metallic) particles typical of heterogeneous ice nuclei were found in ice crystals at warmer temperatures, while more soluble salts and sulfates were present at cold temperatures. At temperatures below about -35 to -40°C , soluble nuclei outnumbered insoluble nuclei, reflecting the transition from primarily heterogeneous to primarily homogeneous freezing as a source of anvil ice.

1. Introduction

Ice nucleation occurs in the atmosphere in two primary ways: through homogeneous freezing of liquid solution droplets and through heterogeneous interaction on a particulate nucleus. Homogeneous nucleation, or freezing, occurs at temperatures at or below about -35 to -40°C , while heterogeneous freezing may occur at much warmer temperatures. For both these processes, nucleating efficiency varies with temperature and supersaturation with respect to ice. Ice may also be formed by secondary processes such as rime splintering (Hallett and Mossop, 1974).

Homogeneous ice nucleation can be predicted by theory (Heymsfield and Miloshevich, 1995; Tabazadeh et al., 1997), while heterogeneous ice nucleation is much more complex. There are several mechanisms by which a heterogeneous ice nucleus may initiate ice formation, including deposition, contact, immersion, and condensation. It is generally accepted that heterogeneous ice nucleation occurs at specific sites on a

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nucleating particle and that favored ice nuclei are particles that have a lattice structure similar to ice. These processes, and particle types thought to be important for cirrus cloud formation, are summarized by DeMott (2002). Modeling studies have shown that the type and quantity of atmospheric aerosol particles acting as ice nuclei can influence ice cloud microphysical and radiative properties (Jensen et al., 2001; Gierens, 2003; Haag and Kärcher, 2004).

Ice nuclei have been studied in both the laboratory and the atmosphere. We briefly summarize atmospheric measurements applicable to convective and cirrus clouds here. Heintzenberg et al. (1996) and Twohy and Gandrud (1998) measured residual nuclei from cirrus and contrail ice, respectively, and found that mineral dust elements were common. In air traffic corridors, Petzold et al. (1998) found high concentrations of black carbon particles in both cirrus and contrails. Chen et al. (1998) found that mineral, carbonaceous and metallic particles all acted as heterogeneous ice nuclei, and DeMott et al. (2003a) determined that Saharan mineral dust had strong ice-nucleating activity. Flying at altitudes as high as 15 km, Cziczo et al. (2004a) measured high concentrations of sulfates and sea-salt in ice residual nuclei, presumably from homogeneous freezing mechanisms. Sassen et al. (2003b) hypothesized that pristine crystal shapes detected in aged cirrus advected from a marine convective system may have been resulted from homogeneous freezing of sea-salt solution droplets. Cziczo et al. (2004b) and DeMott et al. (2003b) found that organic aerosols were less likely to partition to the ice phase than other particle types, and Kärcher and Koop (2005) show that differences in water uptake between organic and inorganic materials may cause this effect.

2. Experiment

The Cirrus Regional Study of Tropical Anvils and Cirrus Layers-Florida Area Cirrus Experiment (CRYSTAL-FACE; Jensen et al., 2004) was conducted in July 2002 in order to better understand anvil cirrus clouds. Several aircraft flew in anvils generated from thunderstorms that usually were located over the Florida landmass, at a latitude of

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about 26° N. The particles described here were collected using the University of North Dakota Citation aircraft, which flew at cloud levels between about six and twelve km, spanning temperatures between –8 to –56°C. Particles from ambient clear air near the convection were sampled at generally lower altitudes, at temperatures between about +7 to –32°C.

Using a counterflow virtual impactor (CVI; Noone et al., 1988; Twohy et al., 1997), cirrus crystals were virtually impacted into dry nitrogen where the water was removed through drying and heating of the sample stream to 50°C. Non-volatile residual nuclei were then impacted onto carbon-coated nickel electron microscope grids using a two-stage jet impactor. The 50% cut sizes of the two impactor stages were about 0.4 and 0.07 μm diameter for 1.7 g cm⁻³ density particles at typical sampling pressures of 300 mb. Particles from these two stages will hereafter be called the “large” and “small” stage samples, respectively. (Note that we often refer to what is sampled as “residual nuclei” here, although actually material may also be incorporated from cloud processes besides nucleation, such as coagulation or chemical reactions). Several ambient aerosol samples from near and below the anvil were collected by turning off the counterflow, so that the CVI acted as a simple aerosol inlet. Samples were then sized and analyzed using a Phillips CM-12 analytical transmission electron microscope, with energy dispersive X-ray spectroscopy for information on elemental composition. The X-ray energy detector installed on the instrument has a Quantum™ thin window that allows detection of elements heavier than atomic number 5. Non-volatile particles were classified into different particle types based on the scheme shown in Table 1, using actual X-ray signatures from every particle rather than relying on morphology alone to identify particle types.

When sampling ice clouds with different inlets, Murphy et al. (2004) and Kojima et al. (2004) found high concentrations of particles containing stainless steel and zinc, respectively, that may have been produced when ice crystals abraded their inlet surfaces. Metallic particles would be included in our “industrial” category. Since the CVI inlet used in this study was composed of stainless steel, particles with this composition

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must be viewed as possible artifacts. We examined our data for particles with stainless steel composition using iron and chromium as tracers (nickel could not be positively identified since the collection grids were made of nickel). Only 1% of the small residual nuclei and 2% of the large residual nuclei were composed of just these elements.

5 These elements were sometimes mixed with substantial amounts of other metallic elements, however, with these mixtures comprising 4% of the small nuclei number and 11% of the large nuclei number. The sources of these mixed particles are unknown, but it is difficult to envision a scenario in which they could be produced from the CVI inlet itself. Since the percentage of wholly stainless steel particles was very small and
10 it is likely that the mixed metallic particles would, in fact, be good ice nuclei, we do not believe that contamination by stainless steel was significant for this study.

An additional possible sampling issue is that large ice crystals may break upon striking inlet surfaces or due to wind shear, producing multiple crystals for each original crystal (Field et al., 2003; Korolev and Isaac, 2005). Assuming that an ice crystal has
15 only one nucleus, this should not in general produce additional residual nuclei. However, material could have been added to the crystal through other processes such as scavenging. This material has the potential to produce additional small particles when crystals break up and sublimate. Apparent enhancement in fine particles larger than about 20 nm (as measured by a condensation nucleus counter; Zhang and Liu, 1991)
20 was often observed when large ice crystals are present. Seifert et al. (2003) argued, however, that the amount of material potentially added due to scavenging in cirrus is small, due to the relatively low concentrations of ice crystals and interstitial aerosol in typical cirrus. Also, the time available for large ice crystals (the ones most likely to shatter) to scavenge interstitial particles is relatively short due to their high sedimentation rates (Jensen et al., 1996).
25

In order to address the possibility that crystal breakup was affecting our electron microscope samples, the number of particles detected through collection and analysis on the microscope grids was estimated as follows. All particles in a 45 degree wedge corresponding to 1/8th of the total grid area were subjected to a visual count. This

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value was then multiplied by 8 to estimate the total number of particles on the visible area of each grid, and then corrected for the portion of each grid covered by solid grid material (on which particles cannot be observed). Finally, the sample volume and CVI enhancement factor were used to determine the effective ambient concentration of particles collected on each grid. Then, the small and large stage concentrations were totaled. We recognize that this is an imperfect method to determine particle number; the distribution of particles collected by impactors is not uniform and particles are concentrated in a region just below the jet, which may not be precisely in the center of the sampling grid. Since this is a random error, however, it should be minimized when numerous samples are analyzed. Additionally, the particle loading was light enough that particles were not piled on top of each other, so individual particles could always be discerned.

Figure 1 shows the result of this analysis for seven pairs of nuclei. Concentrations measured by the Forward Scattering Spectrometer Probe (FSSP-100) and Particle Measuring Systems 2D-C probe during the sampling periods are also given for comparison. The CVI values fall between the two. Since the CVI concentrations are well below those of the FSSP, there is no evidence that breakup of ice crystals produces additional residual particles in the size range collected on the impactor. In fact, if the FSSP concentrations are overestimated by about a factor of two (Field et al., 2003), the median ratio of total crystal concentration to collected residual concentration is between two and three. This indicates that one-half to two-thirds of residual nuclei may actually be missed by the impactor/electron microscope analysis, which could happen if some of the nuclei were too small and/or too volatile to be detected. This is consistent with the results of other studies (Noone et al., 1993; Ström et al., 1997; Seifert et al., 2003) that indicate that a large fraction of nuclei in in-situ generated cirrus clouds are smaller than about 0.1 microns in diameter. While we theoretically sampled particles down to 0.07 μm , only about 1% of all particles analyzed were smaller than 0.10 μm . This suggests that loss or non-detection of small volatile particles did occur during sampling and/or analysis in the vacuum environment of the electron microscope. Therefore

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the data presented here effectively apply only to residual particles about $0.10\text{ }\mu\text{m}$ and larger in diameter.

3. Results

3.1. Percentages of chemical types observed

5 Here data from eleven flights on ten different days are presented. Sampling times ranged from six to twenty-four minutes. Fourteen cloud residual samples and four ambient samples were analyzed. Of the fourteen cloud samples, both large and small stage samples were analyzed for nine of them. Fifty particles were examined from each impactor stage, except for two samples in which fewer numbers (25 and 40) were
10 analyzed due to extremely low sample loading. The total number of particles analyzed was 1,165 (cloud residuals) and 400 (ambient). In-cloud temperatures ranged from -8 to -56°C . The warmest case was a predominately liquid cloud, while the other cases at $-21 > T > -56^{\circ}\text{C}$ were anvil ice clouds.

15 Figure 2 shows the overall composition of residual nuclei for small and large stage particles and for ambient samples collected nearby. Many different particle types are present in both the anvil nuclei and the ambient aerosol particles. The most prominent feature in the data from all particle categories is that a third or more of the particles are composed of salts. Sodium, potassium, and calcium salts, most containing sulfur, were all present in substantial amounts. These particles (with the possible exception
20 of calcium sulfate) are not traditional heterogeneous ice nuclei and are expected to act as condensation nuclei for liquid droplets instead. This indicates that a large fraction of anvil ice is produced by homogeneous freezing mechanisms at the cold temperatures in the upper portions of these deep convective clouds. The sulfate category may be combined with the salt category to show that 40–44% of the non-volatile residual
25 nuclei above about $0.10\text{ }\mu\text{m}$ are composed of soluble material. Mass spectrometric techniques have revealed that many sulfate particles in the atmosphere actually are

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mixed with carbonaceous material (Murphy et al., 1998; Guazzotti et al., 2001). Small amounts of carbon are difficult to detect by the X-ray techniques employed here, but some of the salts did contain detectable amounts of carbon, particularly the potassium salts. These potassium-containing particles were likely derived from biomass burning, and were introduced into the Florida area via long-range transport at high altitude from fires in the United States and Canada (Hudson et al., 2004).

The next most prominent particle types are insoluble materials generated from soil (crustal dust) and industry. (Note that our “industrial” category includes only metals and not other substances that might be produced by industry but also have other sources, such as sulfates and organics). These insoluble materials, which are mechanically produced and more prevalent in the large particle mode, are known to be good heterogeneous ice nuclei. Saharan dust was prevalent in the Florida region during much of the CRYSTAL-FACE sampling period (Sassen et al., 2003a). Insoluble particles account for approximately 23–40% of the residual nuclei larger than $0.10\text{ }\mu\text{m}$, and they are enhanced in the large particle mode.

Twelve to 25% of the residual nuclei are composed of carbonaceous material, both soot (black carbon) and organic carbon. These particles are more numerous in the small particle size range. Whether these particles entered the clouds through nucleation scavenging or through in-cloud scavenging and whether they encourage or inhibit ice crystal formation is an open area of research. As discussed earlier, some organic species inhibit ice formation, while others can act as cloud condensation nuclei (Novakov and Corrigan, 1996; Raymond and Pandis, 2002) and form droplets that would later freeze. Soot has been shown to be involved in ice nucleation (DeMott, 1990), but its behavior is more complex than that of other heterogeneous ice nuclei. It is not surprising that many different particle types serve as sites for condensation at the high supersaturations (Heymsfield et al., 2005) produced in these vigorous convective clouds.

The remaining 8–9% of residual nuclei are composed of mixed particles (often crustal or industrial with salts) or particles that could not be categorized. The mixed

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category could be caused by in-cloud coagulation or aggregation, while the unknown category is most likely comprised of carbonaceous material. Carbon sometimes cannot be detected from particles too close to sample grid edges or from those that volatilize rapidly under the electron beam. Our results for residual nuclei are qualitatively similar to those of Cziczo et al. (2004a) for the Florida area, although they analyzed fewer residual nuclei and those from primarily the small ice crystals.

The relatively small difference between ambient and cloud nuclei composition shown in Fig. 2 is somewhat surprising. Ambient measurements made by the Citation were typically very near the convective cells or under the anvil itself. The composition of the ambient samples in this region is quite different from that of ambient upper tropospheric particles well removed from convection (Chen et al., 1998; Twohy et al., 2002; Cziczo et al. 2004a), which are primarily sulfates and organics. This indicates that clouds are not only particle sinks at low altitude, but can act as significant sources of particles at mid and high altitudes as well. This is probably especially important in the case of deep convective clouds, which carry particles to high altitudes and which have large anvils. In the anvil, particles are spread out over an extensive horizontal range and can be efficiently redistributed vertically through sedimentation. Particles generated at the surface such as sea-salt, soil-dust and industrial emissions are physically and chemically different from the sulfates and organics typically found in the upper troposphere. This infusion of nucleating agents of different types into the upper troposphere is expected to influence ice crystal number, size and shape (Sassen et al., 2003b) and therefore the radiative properties of clouds formed subsequently. This redistribution of low and mid-level particles is different from another important role of convection, the transport of low-level gaseous species to the upper troposphere where they can transform and create new ultrafine particles (e.g., Clarke, 1993; Twohy et al., 2002).

Fridland et al. (2004) used a large-eddy simulation model of one of the CRYSTAL-FACE cases to predict that most of the ice produced in the thunderstorm convective core nucleates not on below-cloud aerosol particles, but on particles entrained from the side of the clouds in the mid-troposphere. In their simulation, only about 1/8 of

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particles originating at 2 km and lower and about 1/3 of particles from 6 km and lower formed ice that survived to reach the anvil. We estimate that about 2/3 of the salts measured with the CVI were either sodium or calcium salts originating at low altitudes. Assuming that all the industrial particles also had surface sources, about 36% of the small residual nuclei and 47% of the large nuclei sampled in this study were from low altitudes. Crustal material (Saharan dust), potassium salts and soot from aircraft or long-range transport are expected to enter the clouds at higher levels, and these categories comprise about 30% of both the small and the large nuclei. (The remaining major categories, sulfates and organics, could come from a variety of altitudes, as they were present both in boundary layer sampling (Conant et al., 2004) and at high altitudes (Cziczo et al., 2004a)). These results suggest a higher dependence of anvil ice formation on boundary layer aerosol particles than predicted by Fridlind et al. (2004). However, many of the particles entrained at higher altitudes may have been smaller than $0.1\text{ }\mu\text{m}$ and so not included in this analysis. If up to two-thirds of anvil residuals are missed by this analysis and they were all entrained from the upper troposphere, then the model would be consistent with the measurements. Additionally, the data are averaged over a wide variety of anvil altitudes and lifetime stages, unlike the modeling study, which gives results for a fresh anvil near the convective core.

3.2. Temperature dependence and freezing mechanism

Samples were collected in anvils at a range of temperatures and altitudes. Anvil ice may be produced through heterogeneous nucleation on solid nuclei (crustal or industrial/metallic particles) or through homogeneous freezing of dilute solutions (salt or sulfate droplets). Since these nucleation processes are expected to occur at different temperatures, a dependence of nuclei composition on temperature would be expected. This dependence may be complicated by sedimentation of large ice crystals to lower altitudes and warmer temperatures in aged anvils. Here the data are used to see if such a temperature dependence can still be detected. For this analysis, the crustal and industrial particles were grouped together and the salts and sulfates were grouped

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together, since these groups are expected to have very different freezing mechanisms. Particle types whose nucleating tendencies are less clear (organics, soot, mixed, and unknown) were excluded from the analysis.

5 In Fig. 3, the percentages of residual nuclei types in the soluble and insoluble groups are shown as a function of average ambient temperature during each sampling period. The smaller residual nuclei, for which more samples were available, are shown. A very interesting pattern emerges moving from the coldest temperatures at the top of the plot, where soluble particle types dominate, to warmer temperatures, where insoluble ones dominate. At the warmest temperature, however, the trend seems to reverse. The
10 sample at -8°C can be explained, since this was a predominately liquid (supercooled) cloud with only small amounts of ice. Water droplets in a liquid cloud will form preferentially on soluble particle types. Another low-altitude sample that was primarily fall-out ice below the anvil was excluded from this analysis, since nuclei from these very large crystals are not thought to be efficiently collected by the CVI.

15 Note that the percentages in Fig. 3 don't add to 100, as only a subset of all particle types shown in Fig. 2 are included. The relationship between soluble and insoluble nuclei can be more clearly examined by plotting their ratio. This effectively normalizes the soluble and insoluble values and eliminates the effect of the other, less well understood, particle types on the comparison. In Fig. 4 this ratio, R , is plotted as a function
20 of temperature for both the large and small residual nuclei.

For the large residual nuclei (left pane of Fig. 4), R is only about 0.05 at the warmest temperature, indicating that nearly all large nuclei involved in heterogeneous ice formation are insoluble. At temperatures below about -35°C , R is near one. This indicates that soluble nuclei become increasingly important in ice formation at this temperature.
25 Using microphysical data, Heymsfield et al. (2005) discuss the importance of this -35 to -40°C temperature range, where homogeneous freezing of cloud droplets a few microns in size begins to occur. Using a continuous flow diffusion chamber, DeMott et al. (2003b) showed that large amounts of ice are nucleated homogeneously at these temperatures. To our knowledge this study is the first time that this transition between

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the heterogeneous and homogeneous freezing regime has been demonstrated with in-situ nuclei data in anvil cirrus clouds.

5 The reason the soluble/insoluble ratio is not larger at low temperatures for large nuclei is probably the lack of large soluble particles at these altitudes. Few soluble particles from the surface are expected to reach and survive at the highest altitudes, since they are the best cloud condensation nuclei, form the largest droplets, and are most likely to be removed from the clouds in precipitation from deep convection (Ekman et al., 2004). Any preexisting soluble particles in the mid and upper troposphere are thought to be the result of advection or in-situ production by gas-to-particle conversion and are expected to be relatively small.

10 For small nuclei (right pane of Fig. 4), R is less than one for temperatures warmer than about -35°C (with the exception of the outlying cases discussed earlier) and larger than one for temperatures colder than about -35°C . In fact, R increases with decreasing temperature up to a ratio as high as ten at the coldest temperatures. There are two possible explanations for this phenomenon. First, below -40°C , even small haze droplets ($<1\ \mu\text{m}$) will freeze. If these particles are entrained into the cloud at high altitudes, additional small ice crystals will be produced on soluble nuclei. However, Fridland et al. (2004) and Heymsfield et al. (2005) argue that most of the entrainment occurs at mid-cloud levels and that most of the ice crystal number are produced between about -35°C and -40°C , and then lofted to higher altitudes. If this is the case, the ratio of soluble to insoluble nuclei is expected to be quite large at all temperatures colder than -40°C in the convective core. Once the anvil forms, however, several processes can act to reduce R . First, dilution and evaporation in the anvil region will preferentially remove the smallest ice crystals, which nucleate on the smallest soluble nuclei. This will reduce R values. Second, aggregation will combine a few large ice crystals with many small ones. The largest crystals will be those that nucleated heterogeneously on insoluble nuclei. This process will deplete soluble nuclei and will further reduce R values. Finally, sedimentation will preferentially move large ice crystals with insoluble nuclei to lower altitudes and warmer temperatures, while the surviving small

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crystals with soluble nuclei will remain near cloud top. This could produce the trend of increasing R with decreasing temperature exhibited in the right pane of Fig. 4.

4. Summary and conclusions

Non-volatile residual particles ($>$ about $0.10\text{ }\mu\text{m}$) from ice crystals in fourteen Florida anvil samples were shown to be composed of a variety of particle types, including salts, metals (industrial), crustal dust, soot, sulfate and organics. In general, larger nuclei had more industrial and crustal material, while smaller nuclei had more organics and soot. The composition of ambient aerosol near and below the anvils was similar to that in the anvil, but was very different from that in the upper troposphere in other regions not influenced by convection. In particular, large numbers of salt particles were present in the near-convective region. This indicates that convection can add to the variability and diversity of aerosol composition in the upper troposphere and possibly influence subsequent cloud formation.

Convection subjects particles to a wide variety of temperatures within a single cloud system, and the type and frequency of ice crystal nucleation is strongly influenced by temperature. Our data, taken at a range of temperatures, shows the influence of these different nucleation mechanisms. In particular, -35 to -40°C is a transition region between heterogeneous freezing processes on solid nuclei and homogeneous freezing on solution droplets. The ratio of soluble (salts and sulfates) to insoluble (metals and crustal) nuclei increases from low values to more than one at temperatures below -35 to -40°C . At the coldest temperatures, small soluble nuclei were up to ten times more numerous than insoluble ones, similar to the characteristics of a predominately liquid cloud sampled at much warmer temperatures. The variation in R with height at cold temperatures probably reflects the evaporation, aggregation, and sedimentation processes that occur in the anvil.

Deep convection and associated anvils influence large regions of the upper troposphere and stratosphere in much of the tropics and mid-latitudes. Anvils are important

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not only due to their influence on the radiative properties of the atmosphere, but for their role in distributing particles and gases from narrow regions of the lower troposphere to wide regions of the upper troposphere. As modeling studies have shown, the type and location of available ice nuclei will influence the amount and size of ice crystals formed. This, in turn, influences the evaporation and sedimentation rate and thus the vertical and horizontal distance over which nuclei are redistributed upon evaporation. Both measurements and modeling studies are needed to fully describe these processes. In addition, continuing laboratory studies are required to further understand the ice nucleating properties of organic and soot carbon, which are prevalent in most parts of the atmosphere.

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Table 1. Particle classification scheme.

Category	Compositional Signature
Crustal dust	Silicates (rich in Si, variable Na, Mg, Al, K, Ca, and Fe), carbonates (Mg and/or Ca with large C peak), phosphates (rare)
Soot	Carbon only. Characteristic morphology (chain aggregates)
Organic	Amorphous or irregular and may contain O, N, and S, and K other than C
Sulfates	Sulfuric acid and ammonium sulfate/bisulfate. S, O only
Industrial	Metals such as Al, Fe, Cr, Ti, Mn, Co, Zn, Cu
Salts	Chlorides and sulfates of Na, K, Ca and Mg

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Crystal Number Measured and Particle Number Impacted

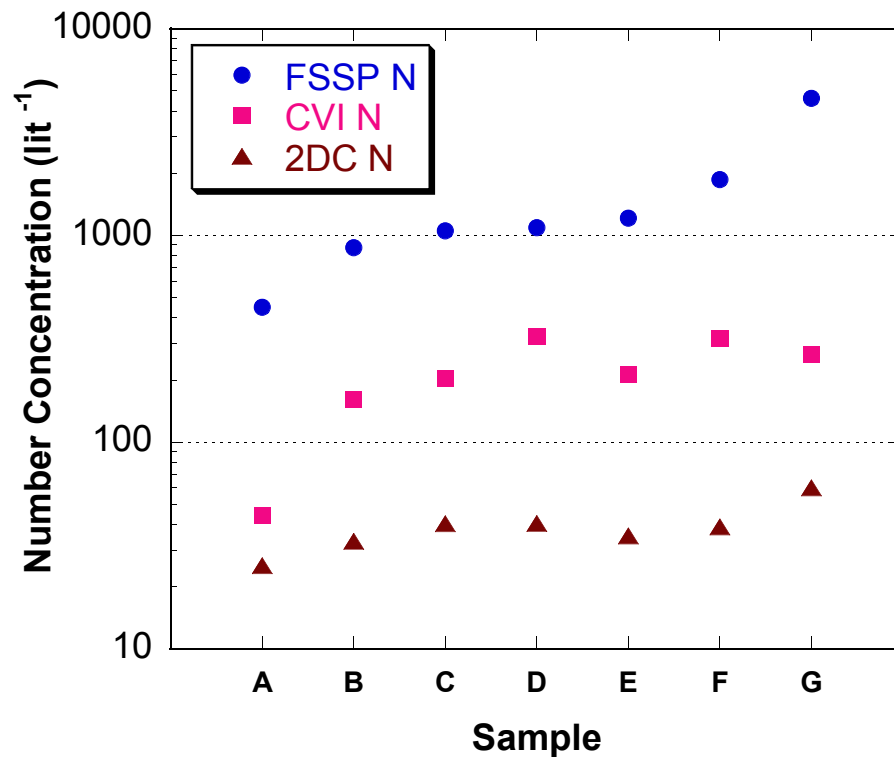


Fig. 1. Equivalent number concentration of particles collected on CVI electron microscope grids compared to number measured by the FSSP-100 and 2D-C probes for seven different samples.

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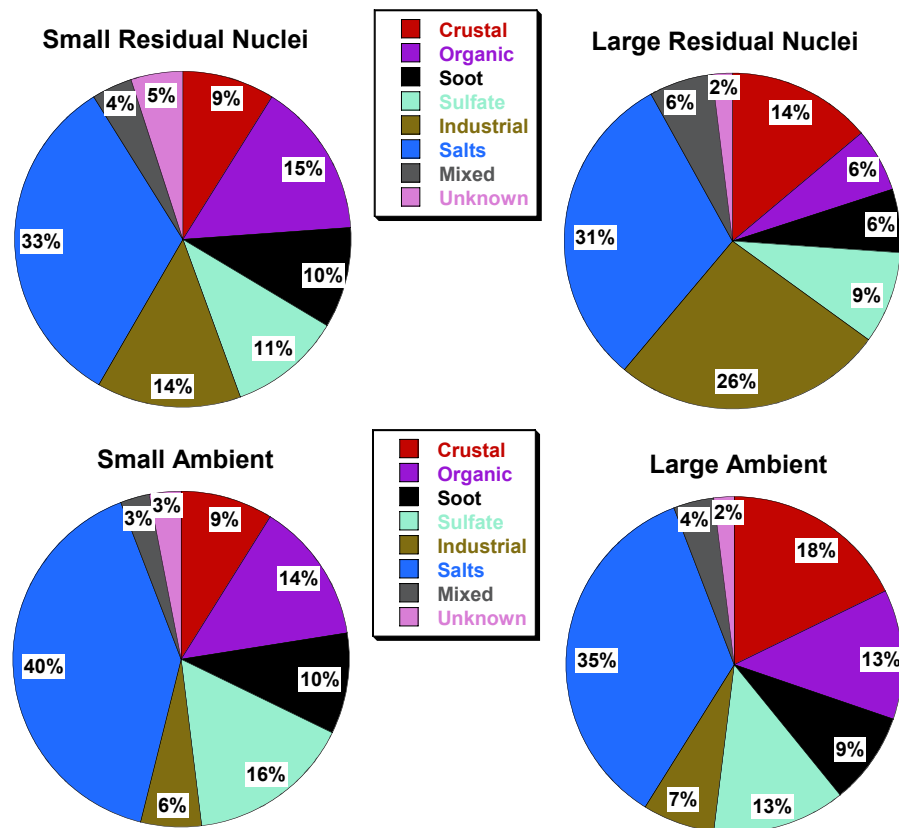


Fig. 2. The composition of small and large residual ice nuclei (top left and right) and small and large ambient particles (bottom left and right) collected during CRYSTAL-FACE. Values are percent by number of each composition as determined by X-ray analysis and the categorization scheme in Table 1.

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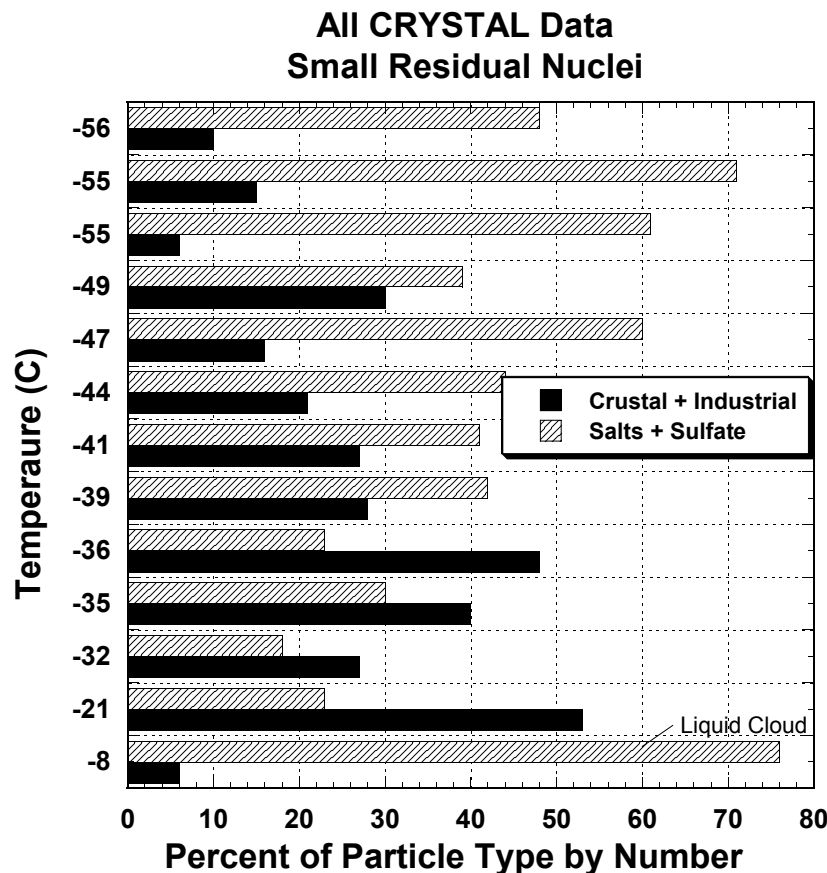


Fig. 3. Percentages of [crustal + industrial] and [salts + sulfate] particles relative to total number of residual nuclei collected in anvil cirrus as a function of temperature. The cloud at -8°C was predominately liquid, while the -22°C sample was at the base of a deep anvil where sedimentation likely had occurred.

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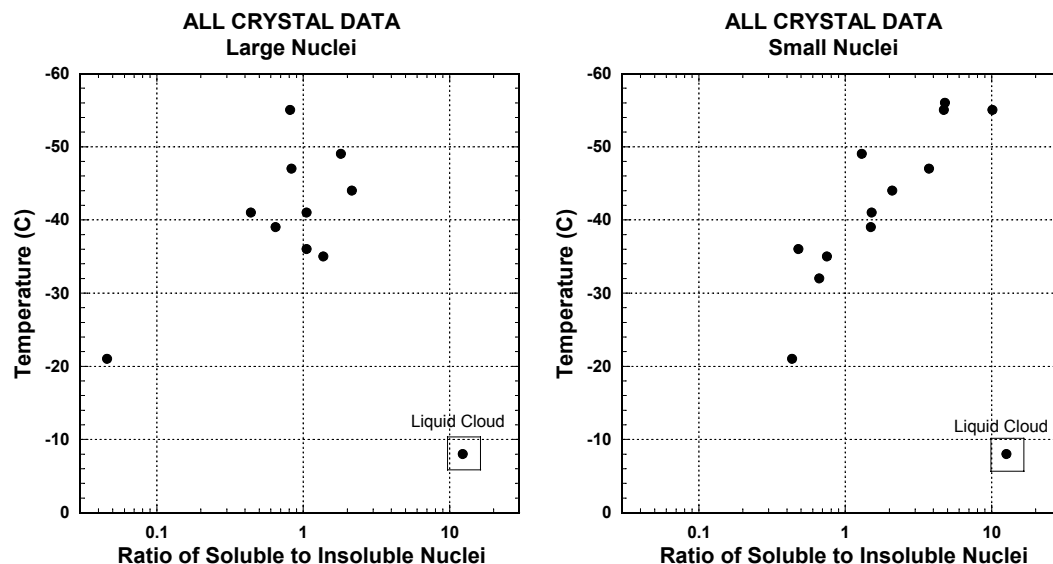


Fig. 4. Ratio, R , of soluble (salts and sulfates) to insoluble (crustal and industrial) residual nuclei as a function of anvil temperature for all CRYSTAL-FACE CVI samples. Left plot shows results for large nuclei and right plot for smaller nuclei.

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