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ROCKET EFFLUENT: ITS ICE NUCLEATION ACTIVITY AND RELATED PROPERTIES

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ABSTRACT

To investigate the possibility of inadvertent weather modification from rocket effluent, aerosol samples were collected from an instrumented aircraft subsequent to the Voyager I and II launches. The aerosol's morphology, concentration, and size distribution were examined with an electron microscope. The elemental compositions of individual particles were analyzed with an X-ray energy spectrometer. Ice nucleus concentration was measured with a thermal diffusion chamber. The particles' physical and chemical properties were related to their ice nucleation activity. A laboratory experiment on rocket propellant exhaust was conducted under controlled conditions. Both laboratory and field experimental results indicated that rocket propellant exhaust can produce active ice nuclei and modify local weather in suitable meteorological conditions.

1. Introduction

Solid rocket propellant consists of aluminum, ammonium perchlorate, calcium phosphate, and sulfur and iron compounds as well as organic polymers. The major exhaust products are aluminum oxide, hydrogen chloride, carbon oxides, nitrogen oxides, and water. For every rocket launch, approximately 10^9 g of propellant are released and residual clouds of effluent are left suspended in the atmosphere. These are a cause of great concern because of their environmental impact. NASA has sponsored much research on this subject (e.g. Gregory et al., 1976; Hwang and Gould, 1978; Mohnen, 1976; Pellet, 1974; Pergament and Thorse, 1975; Stewart and Gomberg, 1970; Varsi, 1976; Woods, 1977). This paper will discuss the ice nucleation activity and related properties of rocket-exhaust aerosol. The knowledge are related to potential inadvertant weather modification.

The Voyager I and II payloads were launched from Kennedy Space Center (KSC) on 5 September and 20 August 1977, respectively. The solid rocket motors emitted a vast amount of effluent and kicked up considerable amounts of dust into the atmosphere to form a visible stabilized ground cloud (SGC) downwind for hours. An instrumented aircraft (NOAA C-130) was used to make multiple passes in the SGC. Because the aircraft flew at 110 m s^{-1} and was in the SGC for only 10 to 40 s, it was necessary to use a grab-sampling system. A 1-m^3 Mylar bag was rapidly filled with SGC aerosol and then immediately sampled with an ice nucleus

(IN) counter and a cloud condensation nucleus (CCN) counter (Mee instruments). The detailed sampling procedure and results of the in-situ measurements were reported by Hindman (1978). Particle samples were collected simultaneously on Nuclepore filters and Millipore filters from the bag and later sent to NOAA APCL for analysis of their chemical composition, physical properties and ice nucleus concentration.

Since the SGC aerosol was a mixture of rocket exhaust, ground dust, and natural aerosol, it is uncertain what was the contribution of the rocket aerosol to the measured properties. For a better understanding of rocket propellant aerosol, we conducted laboratory experiments to measure its ice nucleus concentration and related properties. The laboratory results will be compared with field data.

2. Analyses of rocket effluent collected at KSC

a. Ice nucleus concentration

The ice nuclei were measured with a sub-freezing thermal diffusion chamber at -20°C and 1% supersaturation (Langer and Rodgers, 1975). Sample filters were placed in the chamber to allow the active ice nuclei to initiate growth of ice crystals. The ice crystals were counted with an optical microscope. Ice nucleus activity strongly depends on the humidity in the chamber. If condensation nuclei are present on the sample filter, they can adsorb most of the moisture and

prevent ice nuclei from becoming active. Consequently, less activity was measured than would be found in the free atmosphere.

The results of Voyager II samples collected on 20 August 1977 are shown in Fig. 1. For samples pumped at one liter per minute (1 ℓpm) IN concentration increased two orders of magnitude after the launch and gradually reduced to background value after three or four hours. For the samples pumped 10 ℓpm the increase is only one order of magnitude. The difference in results between the two pumping rates is caused by the presence of CCN which numbered $>10^4 \ell^{-1}$ (Hindman, 1978). The larger the sample volume, the more CCN collected on the filters and the stronger the volume effect. For comparison, the ice nucleus concentrations of all samples were standardized to 1 ℓ and 10 ℓ. The results showed higher IN concentration for the samples collected within 3 hr after launch. However, the actual magnitude of the increase is uncertain because of the deficiency of the measuring method, i.e., a large amount of CCN caused severe interference.

The results of Voyager I samples collected on 5 September 1977 are shown in Figure 2. The samples collected at 1 ℓpm flow rate yield numbers of ice nuclei approximately one order of magnitude higher than numbers in the samples collected at 10 ℓpm as the results of Voyager II measurements. The second set of samples collected from the aged air bags (several minutes later) showed still less activity. This is due to decreasing particle concentration as a result of coagulation and loss to

the wall during storage. Again because of the presence of condensation nuclei, the results must be considered as relative values.

b. Particle concentration and size distribution

A transmission electron microscope (TEM) that has a resolution of 10 Å was used for particle analysis. Because the electron beam cannot penetrate through the filter, samples were replicated on a layer of SiO film, and the filter was dissolved away with chloroform. Electron micrographs were taken at various magnifications; particles were counted and sized manually from the micrographs. The concentration of particles per cc of air samples can be calculated on the basis of the flow rate, the length of sampling time, and the number of particles on the filter.

Figure 3 shows the particle concentration and size distribution of the aerosols collected on 20 August. It indicates that the number distributions are bimodal at 0.03 μm and 0.3 μm. The particle concentration was as high as 10^6 ℓ^{-1} at 10 minutes after launch and decreased two orders of magnitude after 90 minutes. The fast reduction of concentration is probably due to diffusion, coagulation, and sedimentation.

Voyager I sample of 5 September was pumped from the grab-sampling bags which were aged several minutes. The particle concentration

decreased with time as did the Voyager II samples. However they generally gave a lower concentration than Voyager II samples collected at similar periods. The bimodal size distribution shifted to the larger diameters and the electromicrographs of the aerosol showed many agglomerates. Because of the sampling deficiency, the data of Voyager I were less significant.

c. Elemental composition of individual particles

An X-ray energy spectrometer (XES) interfaced with a scanning electron microscope (SEM) is used for elemental analysis. Elements with an atomic number $Z > 10$ can be analyzed simultaneously in a spectrum. The horizontal axis indicates the X-ray energy in KeV which identifies the elements in the particles. The vertical axis indicates the X-ray intensities which reflect the quantities of the contained elements.

Figure 4 shows the electromicrograph of the particles collected after Voyager II launch and the X-ray energy spectra of the individual particles.

Figure 5 shows the percentage of the particles containing certain elements. Sample #2 is a background sample taken before launch. It shows that less than 20% of the marine aerosol contains Al. Sample #4 is a sample collected 10 minutes after launch; 20% of the particles are pure Al_2O_3, and 40% of the particles contain Al, S, Cl, Ca, Fe, etc.

These Al-containing particles are mostly spherical and in a diameter range of 1 μm ± 0.5 μm. They can be identified as a combustion product of the rocket propellant. Another 40% of the particles do not contain Al; they are probably the dust carried up by the launch or natural aerosol. Samples #7 and #14 were taken 32 and 90 minutes after launch. The Al-containing particles are present as 60% and 20% of the total, respectively, and few contain pure Al_2O_3. This indicates that diffusion, coagulation, and sedimentation occurred in these periods.

Because Voyager I samples suffered from aging effect, coagulation of the particles must have occurred inside the air bags. Most of the particles contain multi-elements and the percentage of Al-containing particles did not decrease with diffusion time as we have shown in the Voyager II sample. However, it is interesting to note that Cl-containing particles increase with time. Filters do not collect gases. It is possible that HCl gas had reacted with ambient NH_3 to form NH_4Cl which can either produce new particles or coat the existing particles. Thus, the percentages of Cl-containing particles increased in the later Voyager I samples.

3. Laboratory experiments

The laboratory experiments were conducted in the Cloud Simulation and Aerosol Laboratory of Colorado State University. The wind tunnel, the isothermal cloud chamber, and other facilities have been described

by Garvey (1975). Rocket propellant was burned at unpressurized condition to generate aerosols with three methods: 1) Propellant material (100 g) burned in the wind tunnel with fan on (wind speed 100 knots); 2) 100 g propellant burned in the wind tunnel with the fan off (natural draft); 3) 0.1 g propellant burned in a closed tank (770 ℓ). The aerosols generated were collected on Nuclepore filters and analyzed in the same way as the field samples.

a. Aerosol size distribution

Figure 6 shows the size distributions of the aerosols. For the sample generated in the wind tunnel with fan on, the maximum concentration is between 0.007 and 0.03 μm. The formation of such small particles is due to the 100-knot wind that induces quick quenching rate for vapor-to-particle conversion. All the particles are spherical. Because of the high concentration ($10^8 cm^{-3}$), some are agglomerates.

Aerosol generated in wind tunnel with fan off shows bimodal size distribution with one mode at 0.02 to 0.05 μm and another at 0.3 to 0.5 μm. The size distribution curve is similar to that of the Voyager II sample collected in the field (Fig. 3). Most of the particles are agglomerates of spheres and <1% of the particles are in orthorhombic structure with open lace-like texture. They are probably γ-Al_2O_3 which forms at low quenching rate. The solid spheres should be α-Al_2O_3 which is the most stable allotropic form.

The aerosol generated in the enclosed tank showed that most particles are agglomerates, and the size distribution has a major mode at 0.3 μm and a minor mode at 0.07 μm. No γ-Al_2O_3 was observed.

b. Elemental composition of individual particles

Although the aerosols' size distributions differ because of different generation methods, the elemental composition of the particles is almost the same by all three methods. Figure 7 shows that 89% of the particles contain only Al, presumably Al_2O_3, and 3% contain only Cl, presumably NH_4Cl or organic chloride (XES cannot detect light elements such as H, C, N, O, etc.). The remaining 7% shows Al mixed with Si, P, S, Ca, or Fe; 1% particles do not contain Al or Cl.

The elemental composition of the rocket aerosols generated in the laboratory (fig. 7) is very different from that of the rocket effluents collected in the field (fig. 5). In the field samples, even the early ones collected 10 or 32 minutes after the launch, 40% of the particles did not contain Al and less than 20% were pure Al_2O_3. The high percentage of Si-containing particles (60%) indicates that large amounts of dust were blasted from the ground and served as heterogenous nuclei for Al_2O_3 vapor to condense upon and form particles of multiple elements. Pure Al_2O_3 particles formed through homogeneous nucleation can also coagulate with natural aerosol to form mixed particles. Consequently, only 20% of the total particles were found as pure Al_2O_3 in the field

samples. As for the laboratory experiments there was little contamination of foreign particles. Almost 90% of the Al_2O_3 particles were formed by homogeneous nucleation.

c. Ice nucleus (IN) concentration

The aerosols generated in the wind tunnel were transferred with a 4-ℓ syringe to the isothermal cloud chamber (ICC) to test their ice nucleus concentration. Because the combustion time of 100 g of propellant was approximately 15 s, the grab-samples collected in the syringe may not be from the main stream. Thus, the concentration of particles in the syringe varied from one experiment to another. Consequently the results of IN concentration measurements were inconsistent. For a controlled experiment 0.1 g of the propellant was burned to generate aerosol in a 770 ℓ tank which was closed but not sealed. The aerosol sample was drawn from the tank with the syringe and introduced into the ICC which was regulated at -20°C. It yielded 7×10^6 ice crystals per liter of sample. The ice nucleation activity is calculated as $7 \times 10^6 \ell^{-1} \times 770 \ell \div 0.1 \text{ g} = 5.4 \times 10^{10} g^{-1}$. This means that every gram of propellant produced 5.4×10^{10} IN at -20°C. The result agreed with Dr. K. Odencrantz' unpublished data (Naval Weapons Center, China Lake, Ca.).

From the same tank, the aerosol was sampled on a filter and the concentration was measured with a TEM as $10^9 \ell^{-1}$. Thus the IN ability can also be expressed as 7×10^{-3} which means that 0.7% of the particles generated served as IN at -20°C.

A NASA HCl monitor (Gregory et al., 1976) and an NCAR acoustic IN counter (Langer, 1973) were connected to the tank to take measurements simultaneously. The results are shown in Figure 8. The HCl concentration rose to 3 ppm immediately after the ignition of the propellant decreased to 0.4 ppm in the first minute, and continued to decrease slowly thereafter. The NCAR IN counter regulated at -15°C did not respond until the second minute and reached the maximum of 750 ℓ^{-1} about 10 min later. The slow response of IN activity was probably due to the presence of HCl gas which could either dissolve in the cloud droplets in the IN counter to depress the water freezing point or poison the IN by coating them. Since the IN activity was alleviated as soon as HCl concentration decreased, it appeared that the former course was more important because coating on a particle, either physisorption or chemisorption, takes time to separate. On the basis of the IN measurement 750 ℓ^{-1}, the IN activity was calculated as $5.7 \times 10^{6} g^{-1}$, that is, every gram of propellant produced 5.7×10^{6} IN, or as 1.3×10^{-6}, that is, 1.3 particles out of one million acted as IN at -15°C.

The NCAR counter was also regulated at -20°C to measure IN concentration. Again it did not respond in the first minute and went off the scale of $10^{4}\ell^{-1}$ after 5 min. No exact value of IN could be estimated.

The IN activity of pure Al_2O_3 reported in the literature is either uncertain or unclear. Mason (1971) indicated that "a small fraction of the particles became effective IN between -6 and -12°C, the activity

increased only very slowly with falling temperatures, and only a very small fraction of the particles were activated even at -30°C". Rocket aerosol contains not only Al_2O_3 but also compounds of Cl, S, Ca, etc. To find out what were the IN among all the particles, ice crystals formed in the ICC were replicated on a Formvar coated film. The ice nuclei at the center of the ice crystals were analyzed with SEM-XES according to the procedure described previously (Parungo et al., 1976). Fig. 9 shows two examples of ice crystals and X-ray spectra of their ice nuclei (arrowed). The left IN contains Al, S, and Ca: the right one contains Al and Ca. Because Cl and P are contained in the Formvar film, their presence should be discounted.

The analysis of 100 IN is summarized in Fig. 10. It shows that 85% of the IN contained Al, but only 2% were pure Al_2O_3. S and Ca appeared in 80% and 60% of the total IN respectively. The result indicates that the mixed particles of Al, S, and Ca were the active IN. Comparing with Fig. 7, where pure Al_2O_3 was 89% of the total particles and S and Ca were only 3% and 1% respectively, one would doubt that pure Al_2O_3 has much ice nucleation ability.

4. Conclusion

Investigations of the ice nucleation ability of rocket aerosol were conducted with both field and laboratory samples. The conclusions are as follows:

1) Both field and laboratory results indicated that rocket aerosol can serve as ice nuclei. Laboratory test showed the ice nucleation activity was $5.4 \times 10^{10} g^{-1}$ at -20°C and $5.7 \times 10^{6} g^{-1}$ at -15°C. Since a rocket launch consumes 10^{9} g of propellant, the ice nuclei released into the atmosphere could be sufficient for inadvertant cloud seeding in suitable meteorological conditions.

2) The aerosol concentration was measured as $10^{6} cm^{-3}$ 10 min after launch, and decreased to $10^{4} cm^{-3}$ 90 min after launch. The rapid reduction rate was due to coagulation, sedimentation, and diffusion. Consequently the potential for long range effect on weather modification is not great. However, monitoring of ice nucleus concentration and other properties for a long period after launch would clarify the duration effect.

3) X-ray analysis of active ice nuclei which were found at the center of the rocket-aerosol seeded ice crystals showed most of them contained Al, S, and Ca, indicating that mixed particles were more active ice nuclei than pure Al_2O_3.

4) HCl gas deactivated the particles' ice nucleation ability. Effects of other co-released gases, e.g. nitrogen oxides and carbon oxides, are unknown. For a better understanding of ice nucleus activation or de-activation, more laboratory research is needed.

5) The aerosol generated in the laboratory showed that approximately 90% of the particles were Al_2O_3, and rest were Al_2O_3 mixed with other propellant components. The aerosol collected after launch was a mixture of rocket aerosol, ground dust, and natural aerosol. Twenty percent of the particles were Al_2O_3; 40% contained Al and other elements, and 40% did not contain Al at all. Therefore the behavior of rocket aerosol in the atmosphere cannot be predicted on the basis of on laboratory results. More in-situ measurements are needed.

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LEGENDS

Figure 1. Ice nucleus concentration of Voyager II SGC aerosols collected on 20 Aug. 1977.

Figure 2. Ice nucleus concentration of Voyager I SGC aerosols collected on 5 Sept. 1977.

Figure 3. Particle concentrations and size distributions of Voyager II SGC aerosols.

Figure 4. An electron micrograph of the particles on filter and the X-ray energy spectra of the individual particles.

Figure 5. Frequency of elements present in the particles collected before and after the Voyager II launch.

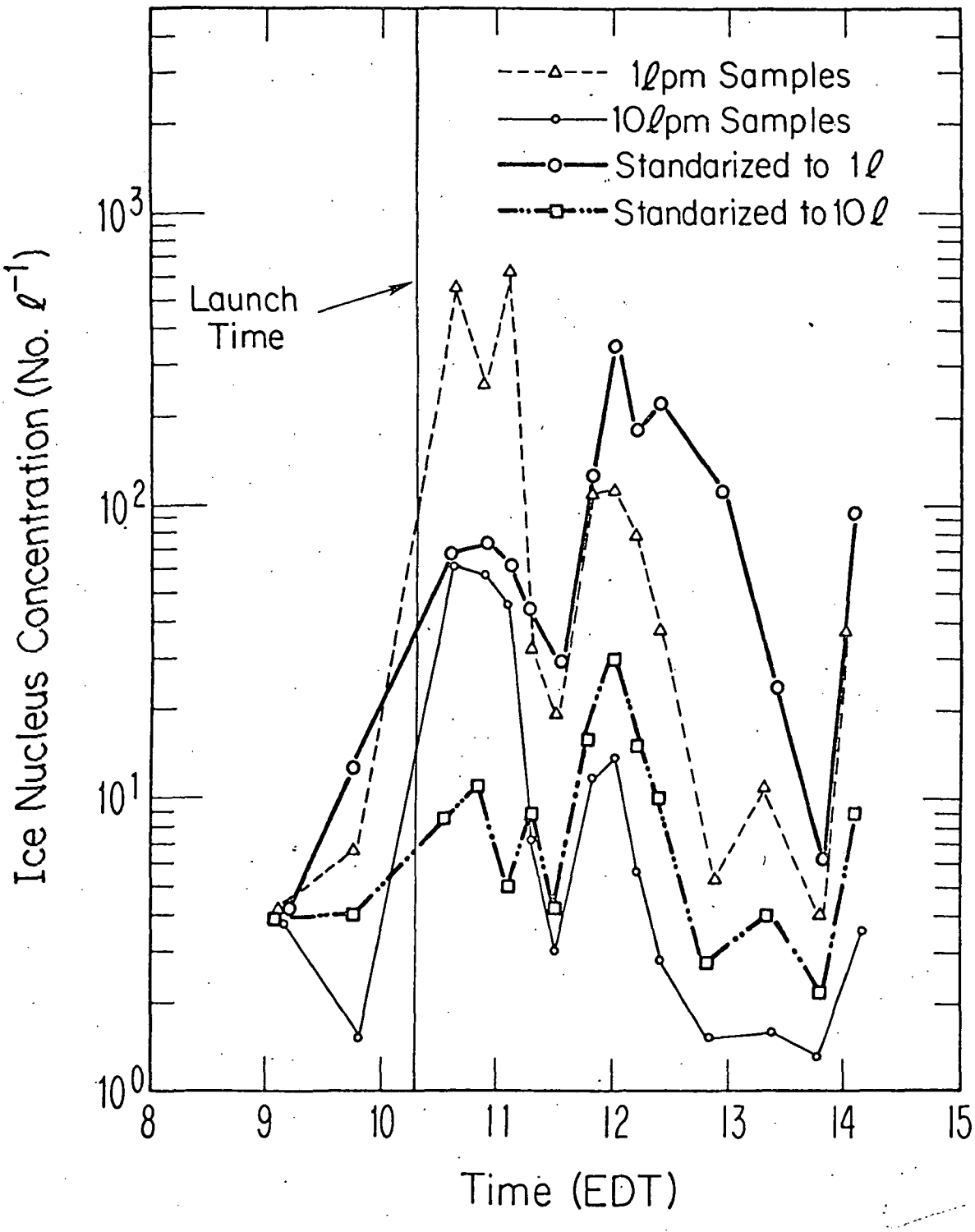
Figure 6. Particle concentrations and size distributions of propellant aerosols generated at unpressurized conditions.

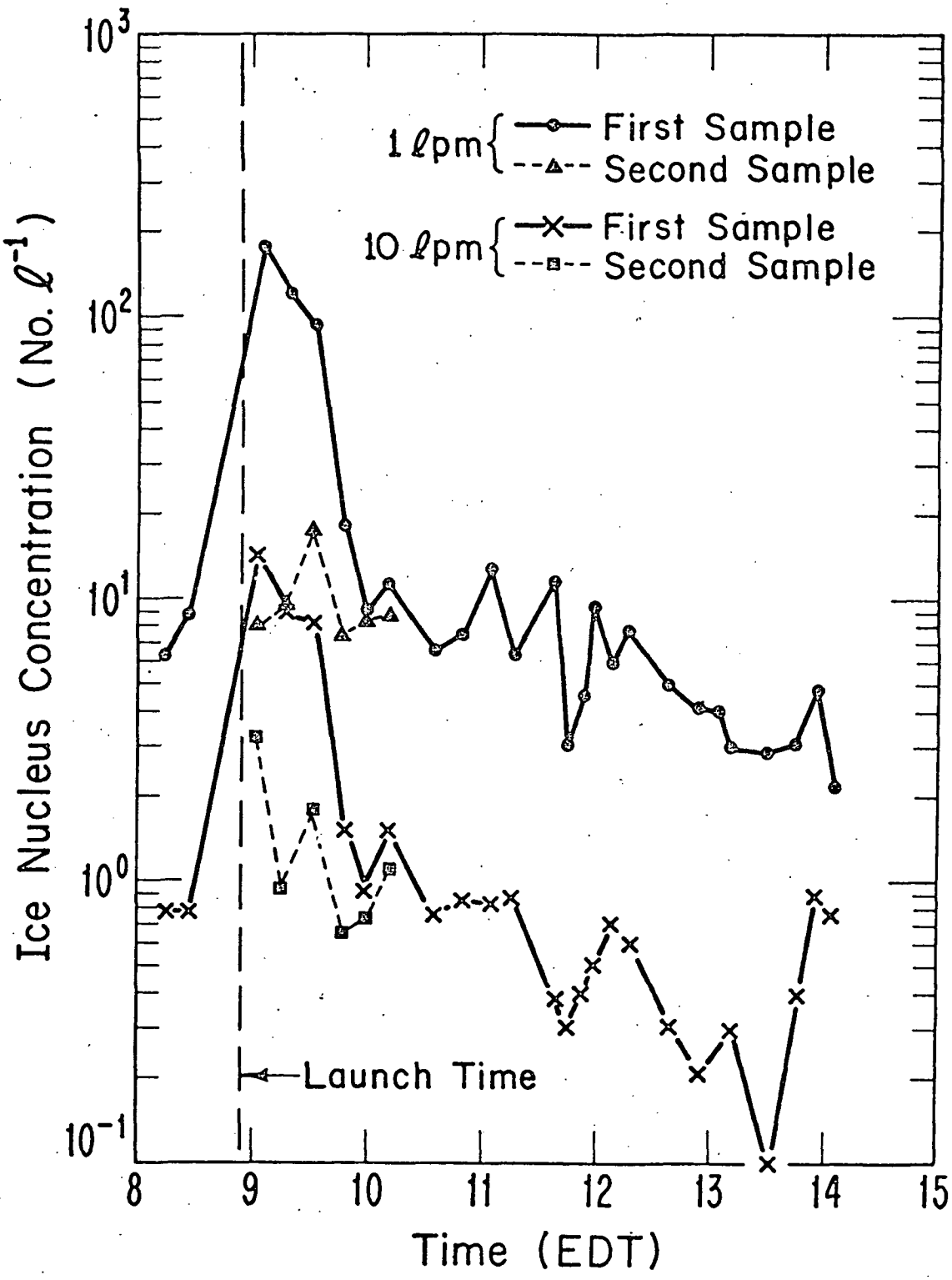
Figure 7. Frequency of elements present in propellant particles generated in the laboratory.

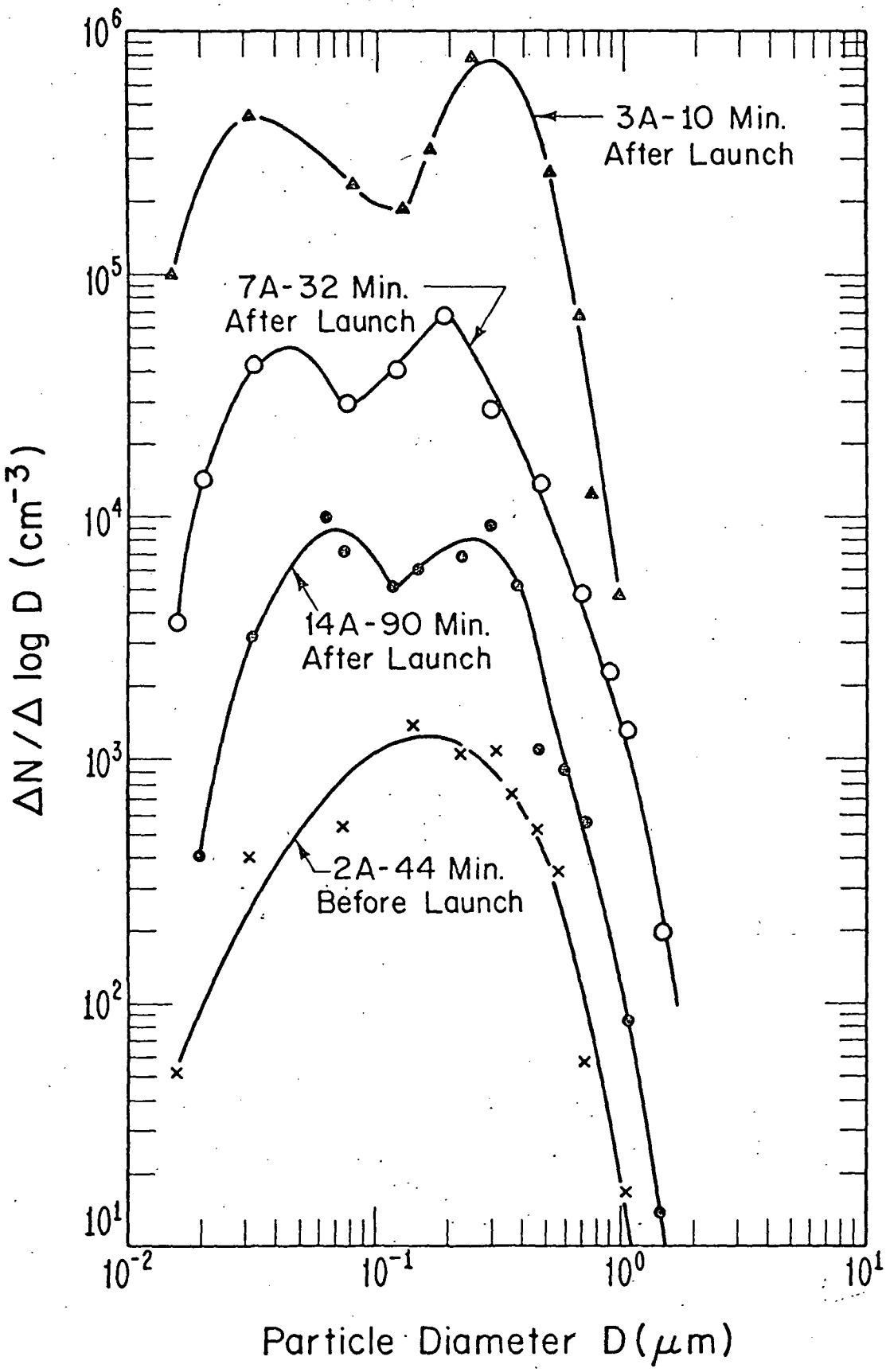
Figure 8. Concentrations of HCl gas and ice nuclei measured after ignition of propellant in a closed tank.

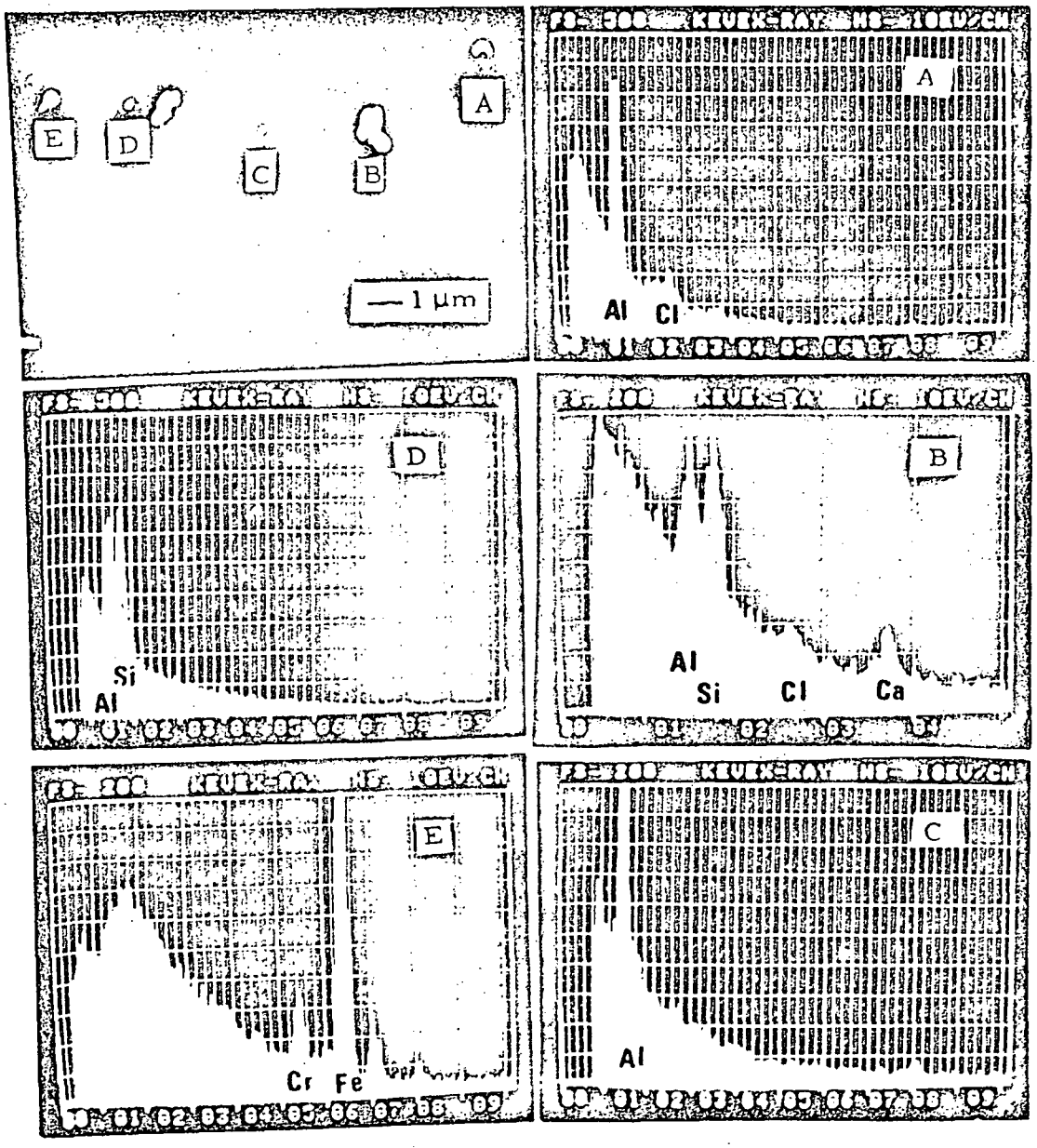
Figure 9. Electron micrographs of ice crystals nucleated by rocket aerosol and the X-ray energy spectra of their nuclei.

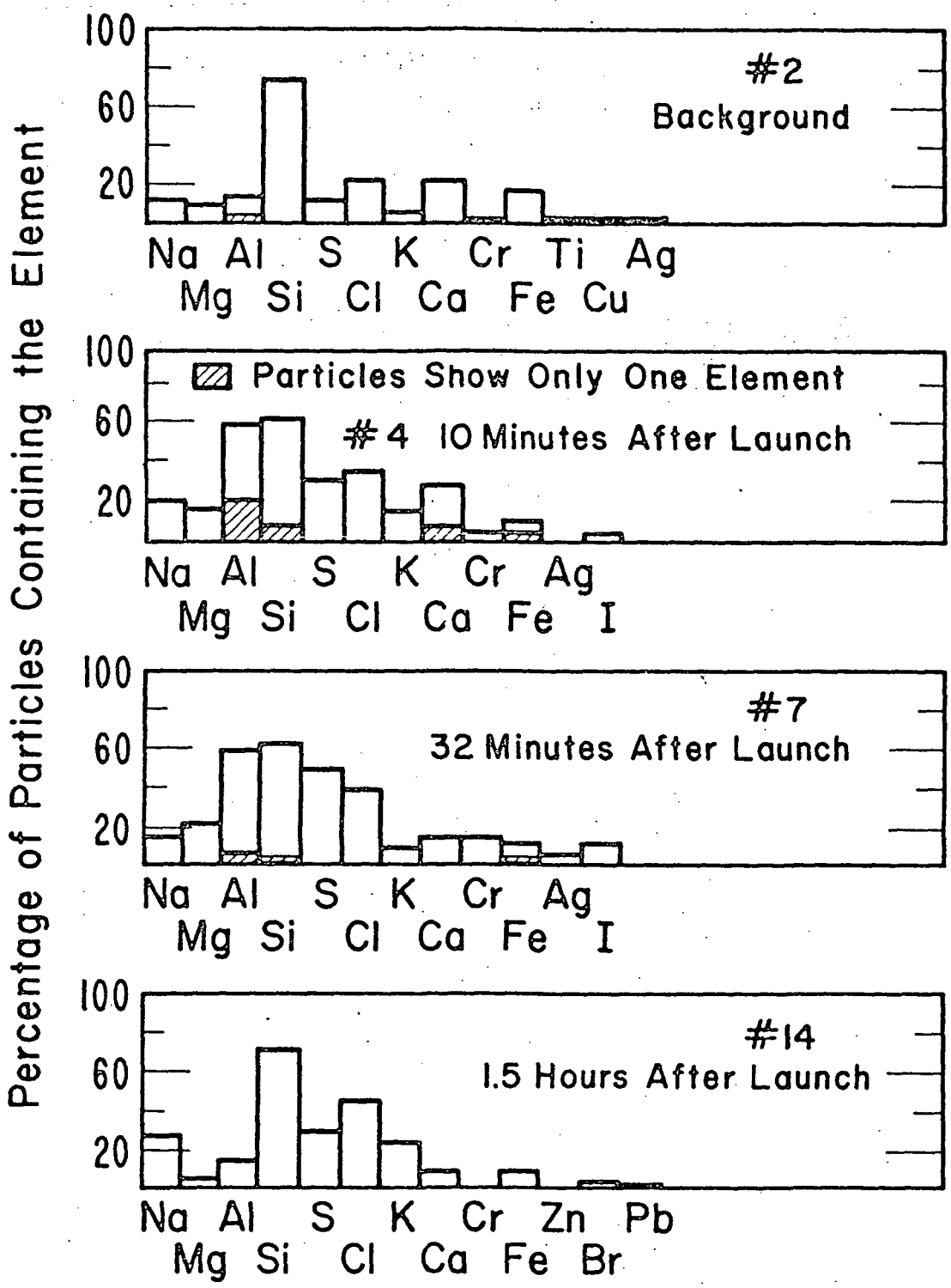
Figure 10. Frequency of elements present in ice nuclei.

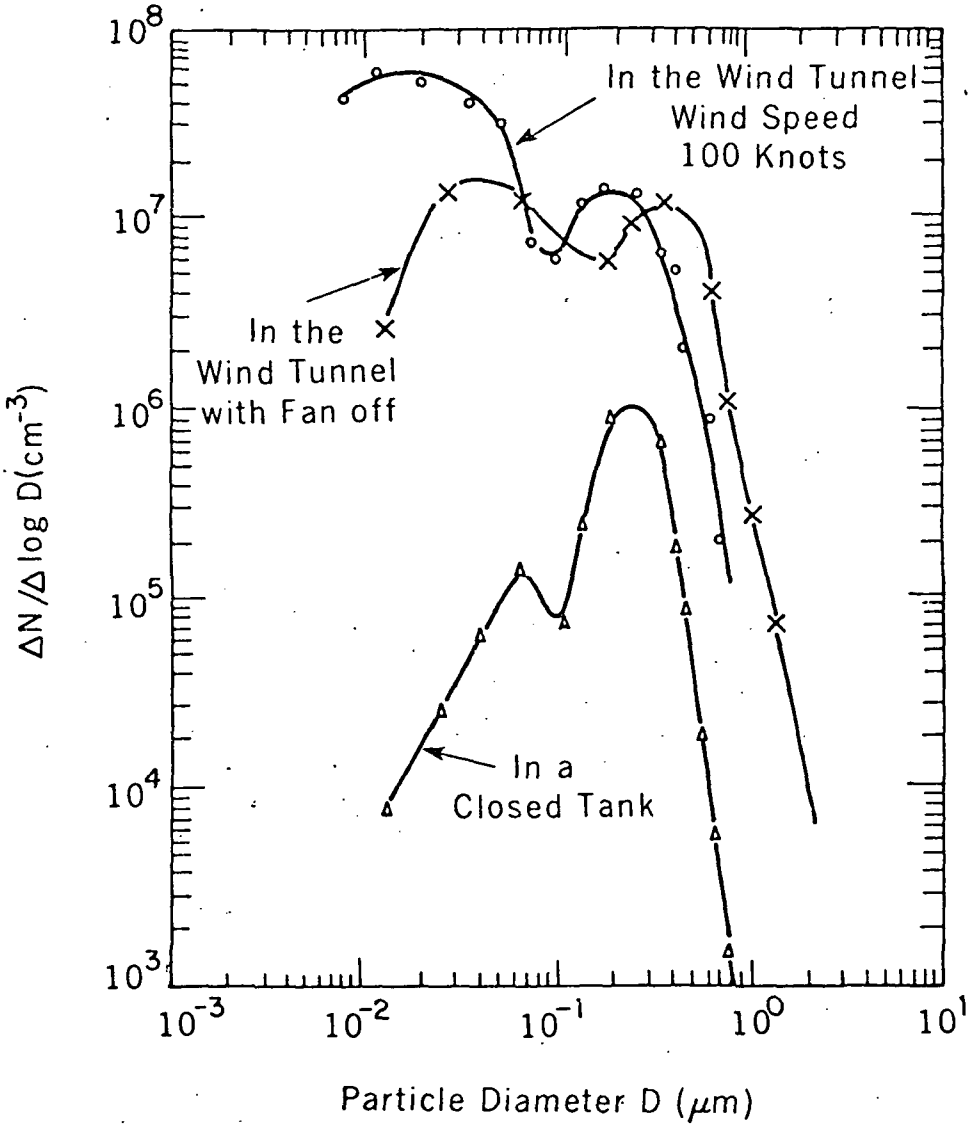

1ℓpm Samples
10ℓpm Samples
Standarized to 1ℓ
Standarized to 10ℓ
Launch Time
Ice Nucleus Concentration (No. ℓ⁻¹)
10³
10²
10¹
10⁰
8
9
10
11
12
13
14
15
Time (EDT)

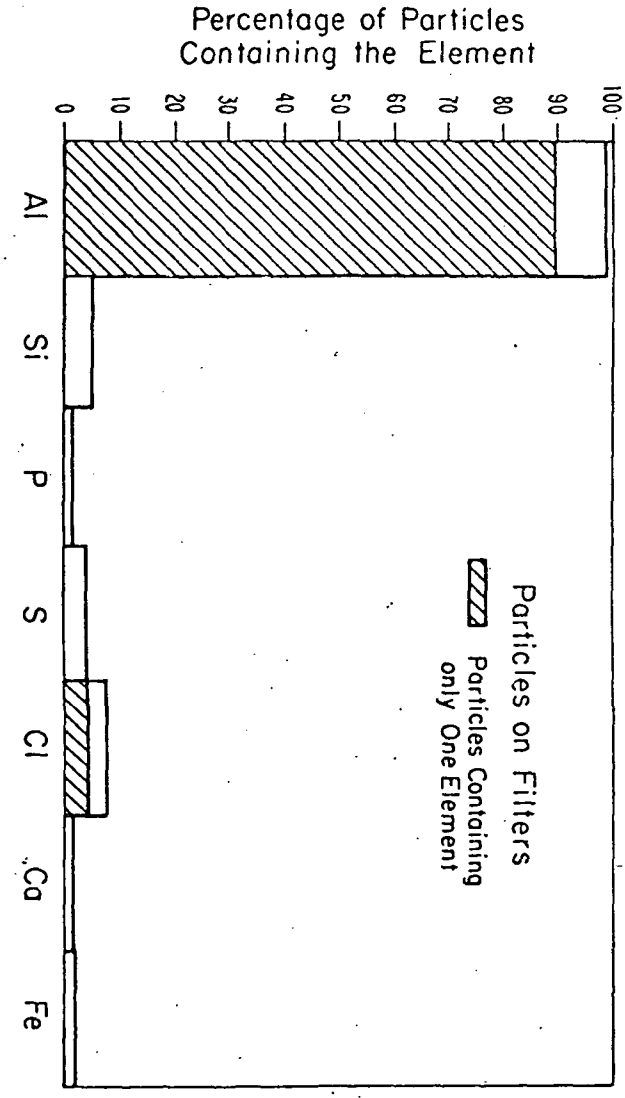

10^3
10^2
10^1
10^0
10^{-1}
Ice Nucleus Concentration (No. ℓ^{-1})
1 ℓpm
First Sample
Second Sample
10 ℓpm
First Sample
Second Sample
Launch Time
8
9
10
11
12
13
14
15
Time (EDT)

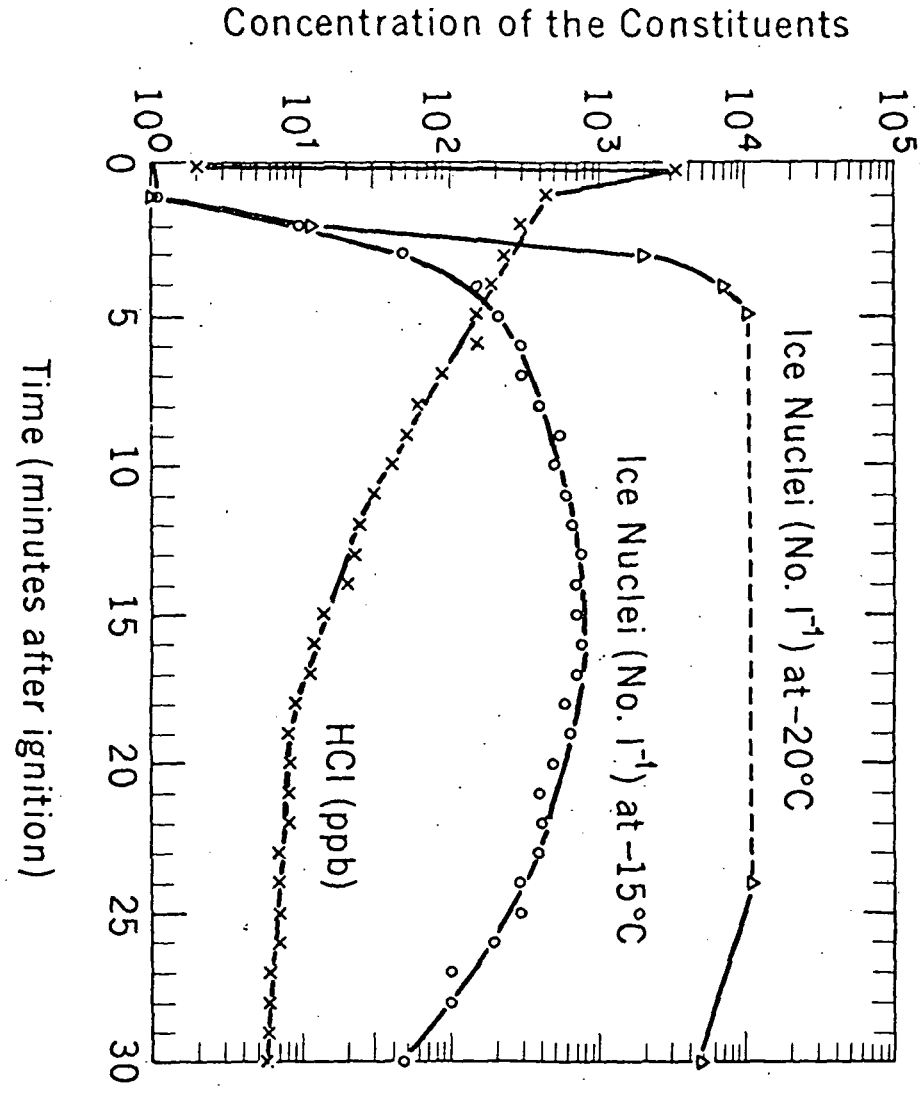

3A-10 Min.
After Launch
7A-32 Min.
After Launch
14A-90 Min.
After Launch
2A-44 Min.
Before Launch
ΔN/Δ log D (cm⁻³)
Particle Diameter D(μm)
10⁶
10⁵
10⁴
10³
10²
10¹
10⁻²
10⁻¹
10⁰
10¹


A
B
C
D
E
1 µm
Al Cl
Si
Al
Al
Si Cl Ca
Cr Fe
Al

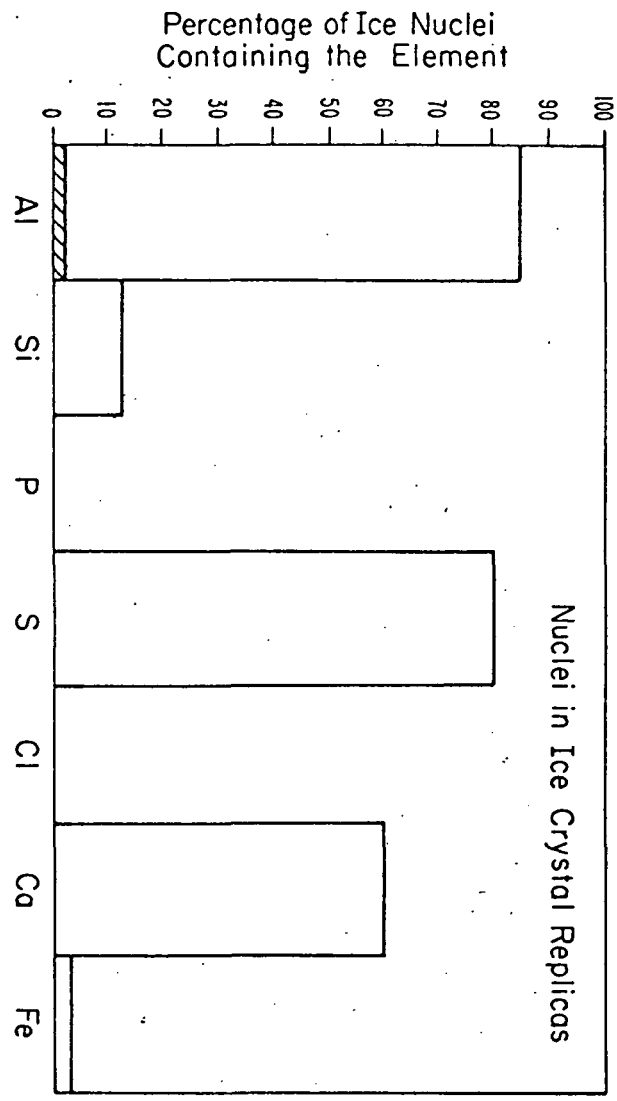

Percentage of Particles Containing the Element
100
60
20
#2
Background
Na Al S K Cr Ti Ag
Mg Si Cl Ca Fe Cu
Particles Show Only One Element
#4 10 Minutes After Launch
Na Al S K Cr Ag
Mg Si Cl Ca Fe I
#7
32 Minutes After Launch
Na Al S K Cr Ag
Mg Si Cl Ca Fe I
#14
1.5 Hours After Launch
Na Al S K Cr Zn Pb
Mg Si Cl Ca Fe Br


In the Wind Tunnel
Wind Speed
100 Knots
In the
Wind Tunnel
with Fan off
In a
Closed Tank
10^8
10^7
10^6
10^5
10^4
10^3
10^{-3}
10^{-2}
10^{-1}
10^0
10^1
$\Delta N/\Delta \log D(cm^{-3})$
Particle Diameter D (μm)


Percentage of Particles
Containing the Element
0
10
20
30
40
50
60
70
80
90
100
Al
Si
P
S
Cl
Ca
Fe
Particles on Filters
Particles Containing
only One Element


Concentration of the Constituents
10^0
10^1
10^2
10^3
10^4
10^5
0
5
10
15
20
25
30
Time (minutes after ignition)
Ice Nuclei (No. l^{-1}) at −20°C
Ice Nuclei (No. l^{-1}) at −15°C
HCl (ppb)

20 μm
Al PSCl
Ca
Al
Cl
Ca


Percentage of Ice Nuclei
Containing the Element
0
10
20
30
40
50
60
70
80
90
100
Al
Si
P
S
Cl
Ca
Fe
Nuclei in Ice Crystal Replicas