

ELECTRON MICROSCOPE STUDIES OF MT. PINATUBO AEROSOL LAYERS
OVER LARAMIE, WYOMING DURING SUMMER 1991

Patrick J. Sheridan¹, Russell C. Schnell¹, David J. Hofmann²
and Terry Deshler³

Abstract. Stratospheric aerosol layers resulting from the June 1991 eruptions of Mt. Pinatubo were first observed over Laramie, Wyoming in July 1991. Atmospheric particles were collected from these layers during three balloon flights in July and August using cascade impactors. Analytical electron microscope analysis of the aerosol deposits indicated that a large majority (> 99%) of the fine particles in all three samples were collected as submicrometer aqueous H₂SO₄ droplets, which changed to (NH₄)₂SO₄ particles over time. Other particles observed in the aerosol were larger, and consisted of supermicrometer sulfate particles and composite sulfate/crustal particles which ranged up to ~10 μm in size. Peak aerosol concentrations for r > 0.15 μm diameter particles (determined by optical particle counters) in the layers were higher for the July flights than for the August sounding. This was reflected in the electron microscope results, which showed that the July impactor samples had particulate loadings on the fine particle stages which were 20-30% higher than those from the corresponding substrate from the August sample. A detailed analysis of the fine sulfate aerosol was performed to assess whether the sulfate particles contained small condensation nuclei. Nearly all analyzed sulfate particles showed no evidence of a solid or dissolved nucleus particle, which suggests that the volcanic H₂SO₄ aerosol formed through homogeneous nucleation processes. These data support heated-inlet optical particle counter data from the balloon flights which suggest that 95-98% of the volcanic particles were aqueous H₂SO₄.

Introduction

The eruption of El Chichon in 1982 injected large amounts of particles and gases into the stratosphere. The decay in the concentrations of these volcanic aerosols was monitored on a routine basis by the University of Wyoming at Laramie [Hofmann, 1987]. Using balloon-borne optical particle counters (OPC's), a continuous data record of vertical aerosol concentration profiles from near the surface up to ~10 mb has been amassed. These and other data indicate that the stratospheric aerosol burden, which was severely perturbed in the early- and mid-1980's by the El

Chichon eruption, was by 1990 approaching "background" concentrations [Hofmann, 1990].

The major eruptions of Mt. Pinatubo in the Philippines on 15-16 June 1991 were reported to have reached the 30-40 km level in the stratosphere [Smithsonian, 1991]. The volcanic cloud was observed to circle the globe in about 3 weeks, and was tracked by ground-, aircraft- and satellite-based sensors, so that its location and extent were reasonably well known at all times. Initial observations of this violent eruption indicated that the aerosol cloud injected into the stratosphere was more extensive by perhaps a factor of two than that from El Chichon [Smithsonian, 1991].

Although the major portion of the Mt. Pinatubo aerosol cloud remained over the tropics, a fragment broke away and was first observed over Laramie on 16 July 1991. The cloud was originally present as a relatively thin layer at ~16-17 km altitude. Over the next two weeks, this volcanic layer thickened, and a higher layer centered at ~23 km was detected [Deshler et al., 1991].

On several of the balloon flights during late July and early August, cascade impactors were used to sample these volcanic aerosols. In this paper, we report on electron microscope (EM) analyses of the aerosol particles, which permitted us to characterize the physical and chemical nature of the volcanic debris. Size distribution information was obtained from the microanalyses, as were discrete particle and bulk aerosol composition, and are compared with OPC measurements.

Methods

On all flights, aerosol sampling commenced on the ascent just above the tropopause and continued for approximately 65 min up to the 37.5 km level. This permitted collection of particles from the enhanced aerosol layers at 17 and 23 km altitude. Aerosol particles were size segregated in single-orifice cascade impactors and deposited onto thin (~10-20 nm thick) formvar films supported by Ni transmission electron microscope (TEM) grids. The three impactor stages used for size fractionation had aerodynamic cutoff diameters (ACD's) of 4 μm, 1 μm and 0.25 μm.

Particles on the three thin film substrates in each sample were analyzed using a 200-kV analytical electron microscope (AEM). The central aerosol deposit area on each grid was analyzed under low magnifications (200-600X) and the extent and approximate particle loading of the deposit over the film was documented. This provided a rough estimate of total particulate loading for each stage. Next, a suitable area of each grid was chosen for a particle identification and classification study. All particles falling within a small rectangular analysis area at 20,000X magnification were counted and classified on each 1 μm and 0.25 μm ACD stage until 500 particles per stage were encountered. At this magnification, particles as small as

¹ Cooperative Institute for Research in Environmental Sciences, University of Colorado at Boulder

² NOAA Climate Monitoring and Diagnostics Laboratory

³ Department of Physics and Astronomy, University of Wyoming at Laramie

0.01 μm were easily observed and counted. Since the 4 μm stage substrates always collected few particles, formal 500-point counts of these films were not attempted.

The detector used for x-ray spectrometry was sensitive to x-rays from elements of $Z > 4$, which permitted direct detection of the light element x-rays of C and O in individual particles. Details of the particle counting, x-ray analysis, and particle classification procedures have been presented elsewhere [Sheridan et al., 1991].

Results and Discussion

The three stratospheric aerosol samples were collected on 26 and 30 July, and on 14 August, 1991 (hereafter referred to in this paper as Samples #1, #2 and #3, respectively), between the altitudes of ~ 15.5 and 37.5 km. This was during a period when the volcanic aerosols were consistently observed in relatively high concentrations over Laramie. Vertical aerosol profiles from the Wyoming balloon soundings between the middle of June and late August can be found in Deshler et al. [1991]. The OPC's produced aerosol soundings of $r > 0.15 \mu\text{m}$ particles during this time period that showed the aerosol layer centered at 17 km was spreading vertically. By 30 July, a second major volcanic layer was detected at 23 km altitude. The volcanic layers centered at ~ 17 and 23 km showed significantly enhanced concentrations of particles of all sizes, including supermicrometer particles. The 23 km aerosol layer was sampled in addition to the lower layer on the 30 July balloon flight, whereas the overwhelming majority of aerosols on the 26 July and 14 August flights were collected below the 20 km level.

The samples were largely composed of neutralized sulfate particles, most of which were observed on the 0.25 μm ACD impactor stages. While it is difficult to determine absolute atmospheric aerosol concentrations with this sampling method [Sheridan, 1989], relative loadings (and relative aerosol concentrations) between samples are straightforward to ascertain. Based on the extent of the heavy central aerosol deposit on all 0.25 μm ACD grids and on comparisons of point counts of particle numbers over limited grid areas, the three sample substrates showed similar (within a factor of two) loadings of fine particles. Figure 1 shows the central

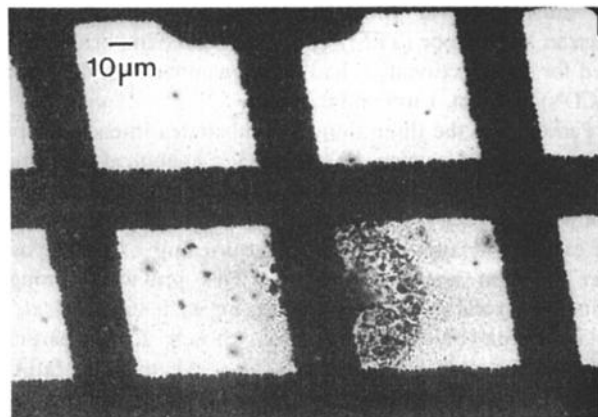


Fig. 1. Central aerosol deposit from the 0.25 μm ACD stage of Sample #2.

aerosol deposit from the 0.25 μm stage of Sample #2. Large numbers of supermicrometer H_2SO_4 -coated crustal particles were observed on the Sample #2 film (presumably from particle bounce from upstream stages), whereas the other 0.25 μm ACD substrates collected fewer large particles. Samples #1 and #2 showed submicrometer particle loadings which were only $\sim 30\%$ heavier than those for Sample #3. Since similar volumes of air were sampled, this is interpreted to mean that the average fine particle concentration during the sampling period was $\sim 30\%$ higher for Samples #1 and #2 than for Sample #3. This is consistent with OPC data which show that peak aerosol concentrations ($r > 0.15 \mu\text{m}$ particles) during collection of Samples #1 and #2 were higher by only 50-100% over those observed in Sample #3 [Deshler et al., 1991]. The increased vertical thickness of the 17 km layer in Sample #3 may have effectively decreased these differences by increasing sampling time in the aerosol-enhanced region on the 14 August flight.

Closer inspection of these fine sulfate particles revealed that most were surrounded by one or more rings of smaller S-containing particles. Figure 2 shows a field of submicrometer particles from the 0.25 μm ACD stage of Sample #1. The "satellite" rings of particles were most likely formed upon impaction of liquid droplets onto the film, and acidic sulfate particles have been shown in previous works to be largely liquid [Frank and Lodge, 1967]. These particles were probably collected as aqueous H_2SO_4 and were subsequently neutralized by ambient NH_3 during handling. The rectangular particles at the center of the rings are most likely products of this reaction. They are unstable under the intense electron beam required for electron diffraction, so direct mineralogical information could not be obtained. Since H_2O is driven off in the vacuum, we believe that the analyzed particles are small, relatively pure $(\text{NH}_4)_2\text{SO}_4$ crystals.

The 1 μm and 4 μm ACD stages were analyzed to determine the relative fractions of coarse particles in these samples. The 4 μm ACD stages were always lightly loaded and most particles on these stages were composite sulfate/crustal particles in the 2-5 μm size range. Figure 3

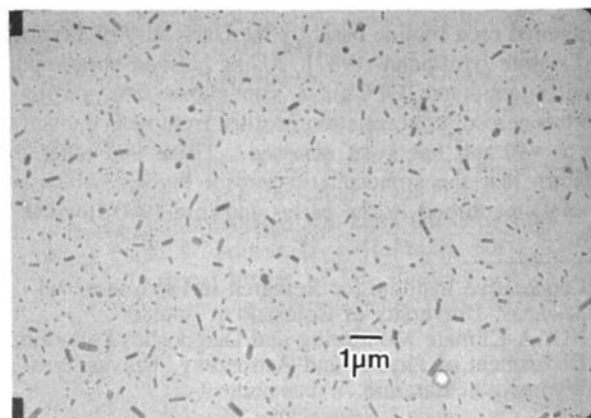


Fig. 2. Submicrometer sulfate particles from the 0.25 μm ACD stage of Sample #1. Impaction satellite morphology and S-rich composition indicate that the particles impacted as liquid H_2SO_4 droplets.

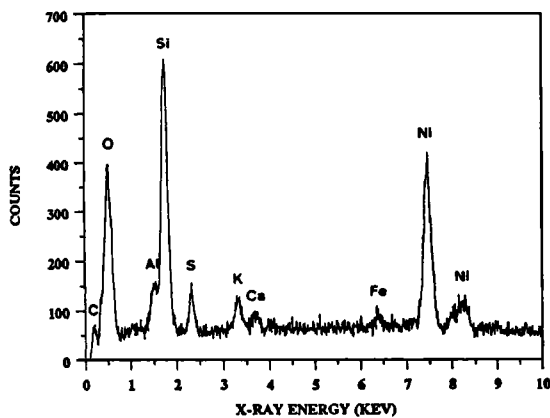
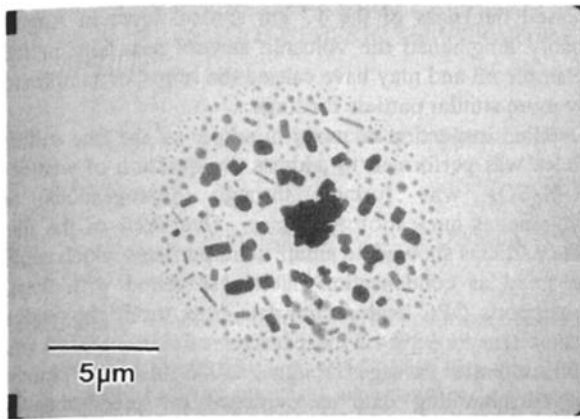


Fig. 3. Composite sulfate/crustal particle from 4 μm ACD stage of Sample #2. Satellite sulfate particles were probably formed during impaction of the H_2SO_4 -encased crustal particle. Nickel peaks in this spectrum are from the TEM grid.

shows one of these large particles from Sample #2 along with its x-ray spectrum. The solid crustal cores of these particles were observed to range up to $\sim 10 \mu\text{m}$ in size.

The 1 μm ACD impactor stages in all 3 samples resembled the corresponding 0.25 μm stage from the same sample in distribution of particle types, but aerosol loadings were usually lower by several orders of magnitude. The exception to this was Sample #2, where coarse particulate mass appeared to be substantially greater. Figure 4 shows the central aerosol deposit area on the 1 μm stage from Sample #2. Numerous solid, supermicrometer particles were observed, along with a considerable amount of large sulfate particles. Many of the larger particles probably came from the well-defined aerosol layer at 23 km, where concentrations of $r > 1.0 \mu\text{m}$ particles reached 0.5 cm^{-3} [Deshler et al., 1991]. This value was several orders of magnitude higher than corresponding concentrations outside of this layer. Samples #1 and #3 showed smaller fractions of large particles, and the major aerosol layers were below 20 km altitude.

The 3 stratospheric impactor samples were all very similar in composition. Approximately 98 to > 99% of all analyzed particles in all 3 samples were collected as aqueous H_2SO_4 . The absolute accuracy of this figure is questionable, due to uncertainties in the counting method caused by the

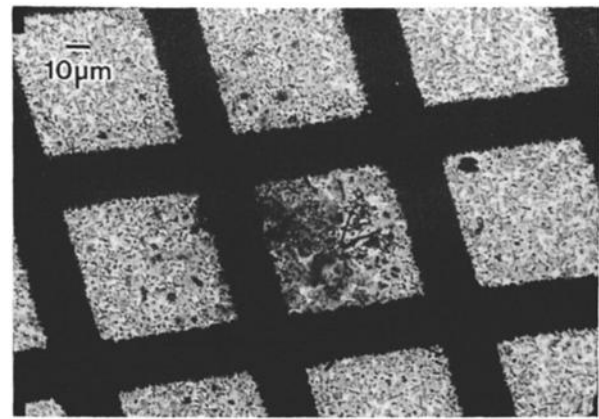


Fig. 4. Central aerosol deposit region from 1 μm stage of Sample #2. This coarse-stage particulate deposit was far more extensive than any of the 0.25 μm stage aerosol deposits.

presence of small impactation satellite particles and because of particle overlap. We do not believe this to be a major problem in this study, however, because of the predominance of the sulfate particles on the thin films, and a slightly different number for the fraction of sulfate particles in these samples would not change our assessment of a mostly H_2SO_4 aerosol. In other heavily-loaded samples that contained several major particle types, this could cause significant counting errors.

Crustal particles coated with H_2SO_4 accounted for < 1% of the particles on all of the 0.25 μm ACD stages. The 1 μm ACD stage films showed larger crustal particle number fractions, estimated to be in the 3-10% range. Of the relatively few particles collected on the 4 μm ACD stages, roughly 40-70% were composite crustal particles with sulfate coatings. The remaining coarse particles on 4 μm ACD substrates were large sulfate droplets.

One of the major questions we wanted to investigate was whether the H_2SO_4 was formed primarily through homogeneous or heterogeneous nucleation. This was accomplished by inspecting many sulfate particles at high magnification, and then increasing the power density of the electron beam until the sulfate began to volatilize. Small, solid nucleus particles, if present, would have remained after the sulfate boiled away. Figure 5 shows two photomicrographs taken of the same grid area from the 0.25 μm ACD stage of Sample #2, both before and after electron beam damage to the particles has occurred. At this magnification, solid particles down to $\sim 0.01 \mu\text{m}$ in size can be observed. For a subset of the particles, the magnification was increased by a factor of two so that particles as small as $\sim 0.005 \mu\text{m}$ could be examined. After the sulfate had largely disappeared (Figure 5B), it is evident that small solid particles were not left behind. This indicates that solid particles of $> \sim 0.01 \mu\text{m}$ diameter were not acting as condensation nuclei for the H_2SO_4 droplets, unless they were dissolved by the acid. Since the particles usually showed only S and O as major detectable elemental constituents with no trace elements, the dissolution of solid particles of other compositions is unlikely and is discounted. Our microanalytical observations agree well with the OPC heated

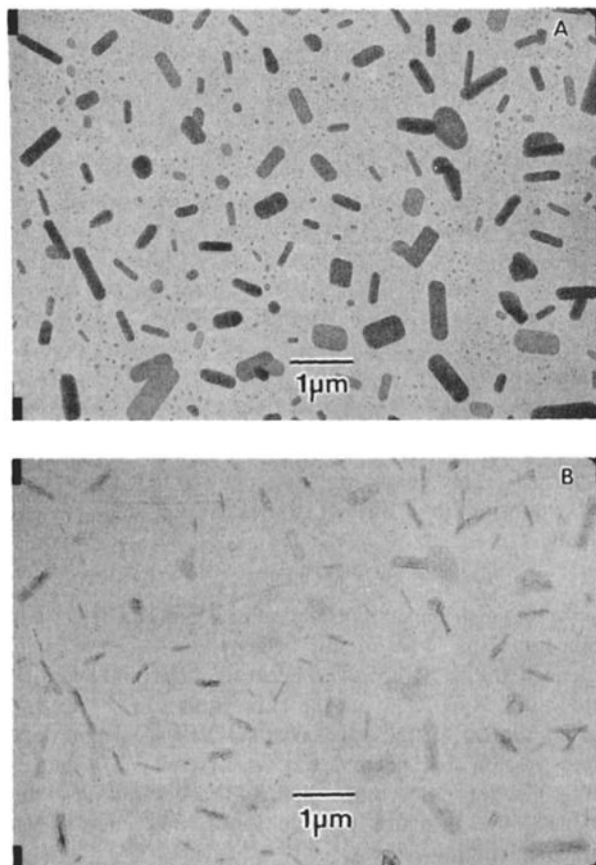


Fig. 5. Sulfate particles from the 0.25 μm ACD stage of Sample #2. (A) before electron beam damage; (B) after electron beam has vaporized most of the sulfate. No solid particles which may have acted as condensation nuclei are evident.

inlet data, which indicate that ~95-98% of particles of size $r > 0.15 \mu\text{m}$ disappeared after passage through an inlet heated to 150°C, which is hot enough to vaporize H_2SO_4 [Deshler et al., 1991]. These data suggest that the vast majority of the H_2SO_4 aerosol was formed through homogeneous nucleation processes.

Conclusions

The use of cascade impactors on several balloon flights over Laramie, Wyoming has permitted us to characterize particles in stratospheric aerosol layers which have been tracked from the eruption of Mt. Pinatubo. In all samples, the volcanic aerosol was composed predominantly ($> \sim 98\%$) of submicrometer H_2SO_4 droplets, which had subsequently changed to $(\text{NH}_4)_2\text{SO}_4$ during handling, and lesser numbers of supermicrometer crustal particles.

The relative particle concentrations determined by microanalysis of the samples were consistent with OPC aerosol concentration data. The samples collected on 26 and 30 July showed 20-30% more fine particles on the 0.25 μm ACD stages than did the 14 August sample. Peak aerosol concentrations for $r > 0.15 \mu\text{m}$ particles during the July flights were 50-100% higher than on the August profile. The

increased thickness of the 17 km aerosol layer in August probably lengthened the volcanic aerosol sampling period for Sample #3 and may have caused the impactor samples to show more similar particle loadings.

Detailed inspection of many hundreds of the fine sulfate particles was performed to address the question of whether the H_2SO_4 was formed through homogeneous or heterogeneous nucleation processes. Over 99% of the fine sulfate particles showed no small, solid particles which could have acted as condensation nuclei associated with them. This supports OPC heated inlet data from the flights which indicates that 95-98% of the particles of size $r > 0.15 \mu\text{m}$ disappeared after passage through a 150°C inlet. We present these corroborating data as evidence for predominantly homogeneous nucleation of the H_2SO_4 aerosol in the Mt. Pinatubo volcanic cloud.

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T. Deshler, Department of Physics and Astronomy, University of Wyoming, Laramie, WY 82071.

D.J. Hofmann, NOAA Climate Monitoring and Diagnostics Laboratory, Boulder, CO 80303.

R.C. Schnell and P.J. Sheridan, Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO 80303.

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