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# The Chemical Composition of Particles of $d < 0.20 \mu\text{m}$ in the Lower Stratospheric Aerosol, Spring 1993

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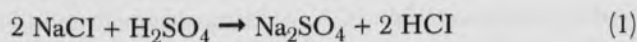
## Abstract

The majority of the mass of stratospheric aerosol collected during the spring of 1993 consisted principally of particles of  $d > 0.20 \mu\text{m}$  containing a mixture of  $\text{H}_2\text{SO}_4$  and  $(\text{NaK})_2\text{SO}_4$ . However, the composition of the more numerous particles with  $d < 0.2 \mu\text{m}$  was very different. X-ray emission spectra (EDS) of individual particles indicated that there were three different chemical populations of small particles. The most numerous population was almost all C with only traces of S and Na. The second population contained metal sulfates and chlorides, possibly accreted to a C-containing matrix. The third population consisted of S- and Cl- containing species and trace amounts of Na and K ions. The number of equivalents of metal ion was much less than that of S and Cl species, indicating that most of the S and Cl was not ionic, but was covalently bonded, perhaps to a C matrix.

## Introduction

The chemical composition and the phase of the stratospheric  $\text{H}_2\text{SO}_4$  aerosol affect the rates of heterogeneous reactions involving  $\text{N}_2\text{O}_5$ ,  $\text{HNO}_3$ , and Cl-containing species. It is possible that the reaction rates are affected by trace constituents in the aerosol. Direct injection of particulate matter and  $\text{SO}_2$  influence the particle surface area at which heterogeneous reactions are catalyzed. The normal stratospheric aerosol particle is composed of  $\text{H}_2\text{SO}_4$  and, occasionally,  $(\text{NH}_4)_2\text{SO}_4$  which results from neutralization of the acid by trace  $\text{NH}_3$  carried up from the troposphere (Junge and Manson, 1961; Bigg, 1975; Mossop, 1963, 1965). Two processes have had a significant effect on the stratospheric aerosol during the last quarter of the 20th century, injection of S and Cl species by violent volcanic eruptions and the injection of C particles by high flying jet aircraft.

The eruptions of El Chichón in March-April, 1982 injected S and Cl species into the stratosphere. Between April and December, 1982, Woods et al. (1985) sampled by impactor the cloud generated by these eruptions. In April and May, particles containing halite crystals were collected along with the majority sulfuric acid particles. The halite containing particles were irregular in shape while the sulfuric acid particles were spherical. In samples collected later in the year, no halite crystals were observed. The samples of April and May which had contained halite were reexamined to find that the  $\text{NaCl}$  had, in the interim, been converted to  $\text{Na}_2\text{SO}_4$  by reaction with  $\text{H}_2\text{SO}_4$ :



The 1991 Mount Pinatubo eruption injected 30 MT of  $\text{SO}_2$  into the stratosphere (McCormick et al., 1995) and, possibly, hydrothermal fluids and silicates. This eruption caused the greatest perturbation of the stratospheric aerosol in this century. Chittenden and Scott (unpubl.) analyzed six samples of stratospheric aerosol particles collected at altitudes of 19 - 21 km during April and May of 1993, 21 months after the eruption. The particles were neutralized by ammonia immediately after collection. The majority of the neutralized particles of  $d > 0.20 \mu\text{m}$  were composed of  $(\text{NH}_4, \text{Na}, \text{K})_2\text{SO}_4$  while a small minority of those from 21 km contained only  $(\text{NH}_4)_2\text{SO}_4$ . Most or all of the ammonium ion arises from the ammonia neutralization of  $\text{H}_2\text{SO}_4$  originally in the collected particles.

The majority of the particles had been originally either a slurry of  $(\text{Na}, \text{K})_2\text{SO}_4$  in  $\text{H}_2\text{SO}_4$  or particles composed of a  $(\text{Na}, \text{K})_2\text{SO}_4$  core surrounded by  $\text{H}_2\text{SO}_4$ . The  $(\text{Na}, \text{K})_2\text{SO}_4$  was not simply the small core of a predominantly  $\text{H}_2\text{SO}_4$  particle but the principle component of these particles. The particles from 19 km had a mean chemical equivalent ratio  $(\text{Na}, \text{K})_2\text{SO}_4/\text{H}_2\text{SO}_4$  of 1.70 while those from 21 km had a ratio of 1.08 (see Table 1). It was assumed that the Mount Pinatubo eruption contributed the metal ions. Only a minority of particles collected from 21 km contained only  $\text{H}_2\text{SO}_4$ .

Pueschel et al. (1992) and Blake and Kato (1995) have documented the increase in submicron graphite particles in the lower stratosphere since the introduction of high altitude supersonic aircraft with the greatest increase at the latitudes of the most heavily traveled airlines.

The present study describes the search for submicron particles collected at an altitude of 20 km whose X-ray

Table 1. Chemistry of two groups of small ( $d < 0.20 \mu\text{m}$ ) particles compared to two groups of large particles ( $d \geq 0.20 \mu\text{m}$ ).

Group	Low metal with $d < 0.20 \mu\text{m}$	High metal with $d < 0.20 \mu\text{m}$	$d \geq 0.20 \mu\text{m}$	$d \geq 0.20 \mu\text{m}$
Altitude (km)	20	20	19	21
Sample Population, N	32	20	391	178
Mean equivalent ratios				
(Na+K)/(S+Cl)	$0.28 \pm 0.16$	$1.15 \pm 0.65$	$0.66 \pm 0.29^*$	$0.52 \pm 0.33^*$
(Na+K)/Cl	$0.35 \pm 0.18$	$7.65 \pm 6.66$		

\* - no Cl detected

spectra exhibited relatively prominent peaks for C, Cl, or S that remained in the stratosphere 21 months after the Mt. Pinatubo explosion.

### Experimental Methods

For each sampling in this study the collector assembly, a modification of that used by Snetsinger, et al. (1987), consisted of a metal ring across which were stretched three  $75 \mu\text{m}$  Pd wires and two  $500 \mu\text{m}$  Pd wires. A  $3000 \mu\text{m}$  diameter transmission electron microscope (TEM) grid with a carbon coated thin polymer backing was attached to the  $75 \mu\text{m}$  wire impactors at two points. The assemblies were flown on NASA ER-2 aircraft for inertial sampling of aerosols. Aircraft speed at collection was  $200 \text{ m/s}$ . During collection, the rings were extended outside the aircraft boundary layer for 2 minutes. Collections were made during April and May 1993 at  $37^\circ - 38^\circ \text{ N}$  latitude,  $121 - 122^\circ \text{ W}$  longitude, and altitudes of  $18.8 \text{ km} - 21.3 \text{ km}$ . Immediately after collection, the samples were returned to and sealed inside modules which contained ammonia vapor. The sulfuric acid component was neutralized to form ammonium sulfate crystal(s) of density little different from the droplet from which it was formed.

**Elemental Analysis.**--Quantitative elemental analyses of several hundred spheroidal particles with  $0.20 \mu\text{m} > d \geq 0.10 \mu\text{m}$  were performed using the energy dispersive X-ray spectra (EDS) generated by irradiating individual particles with the electron beam of a JEOL JEM-100CX scanning transmission electron microscope (STEM) in the SEM mode at Arkansas State University (ASU). The areas under the X-ray peaks for the elements of interest ( $A_i$ , where  $i = \text{Na, K, S, or Cl}$ ) were calculated using the MicroEDS

program of Dapple Systems, Inc. on the ASU system. The atomic ratios  $\text{Na/S}$  and  $\text{Na/Cl}$  are functions of the ratios of areas,  $A_{\text{Na}}/A_{\text{S}}$  and  $A_{\text{Na}}/A_{\text{Cl}}$ , respectively. The ratios  $\text{K/S}$  and  $\text{K/Cl}$  are calculated in a similar fashion. The areas must be corrected for absorption of X-rays by the particle and the detector window. Since the two standard correction models (Goldstein et al., 1992) for quantitative analysis from X-ray spectra are designed for samples with a flat surface, they were incapable of yielding usable absorption correction factors for a spheroidal particle because they over-correct for the lighter elements. To determine a correction algorithm standard aerosol samples of pure  $\text{Na}_2\text{SO}_4$  and pure  $\text{K}_2\text{SO}_4$  were prepared by atomizing saturated aqueous solutions at  $\sim 50^\circ\text{C}$ . A TEM grid was passed through the suspended cloud of droplets. The grids were stored in a desiccator and later examined in the same manner as the sample grids. From the EDS of the standard particles, the correction factors,  $f_i$ , for the area ratios as a function of mean particle cross sectional diameter were determined. The correction factors were applied to EDS peak area ratios for each particle to calculate the atomic ratios of metal ( $M = \text{Na or K}$ ):  $M/S = (A_M/A_S) f_{M,S}$ . The same factor can be used for both the S and Cl ratios since their K X-ray energies are so close that their attenuation as they pass through the particle is essentially the same, so  $M/Cl = (A_M/A_{Cl}) f_{M,S}$ .

The composition of particles of  $d < 0.20 \mu\text{m}$  collected from  $20 \text{ km}$  was more difficult to determine than that of larger particles because the sample-to-background signal ratio of their electron induced X-ray emission spectra was usually very low. The Hitachi S-4000 SEM and its associated EDS system at the NASA Ames Research Center (ARC), Mountain View, CA, yields spectra with sample-to-background signal ratios for low Z elements far superior to

the ASU system. Qualitative chemical analysis was performed at ARC on 12 particles of diameters from 0.12  $\mu\text{m}$  to 0.17  $\mu\text{m}$ , which had exhibited no detectable concentration of elements of  $Z > 10$  when analyzed in the ASU system. In all analyses, a background spectrum was taken by moving the electron beam to a vacant area of the backing lying within 2  $\mu\text{m}$  of the particle and recording the spectrum from that area.

**Measurement of Particle Size.**--The diameters of particles were obtained either by measuring the size of the particle's image directly from the CRT display of the SEM's secondary electron image (SEI) at magnifications of up to 100,000 X or by measuring the image on a magnified scan of a Polaroid photograph of the SEL. The lengths of the major axis,  $a$ , and minor axis,  $b$ , of particles were measured to the nearest 10 nanometers. The uncertainty in measured  $d [(a+b)/2]$  values was  $< 10\%$  for particles with  $d > 0.10 \mu\text{m}$ .

## Results

The 20 km sample was unusual in that particles of  $d < 0.20 \mu\text{m}$  were far more numerous than the sample's larger particles and more numerous than all particles collected at 19 km and 21 km. The majority of these particles contained no detectable quantity of elements with  $Z > 10$  but a small fraction of these particles contained detectable Cl. Of the hundreds of particles analyzed, 54 yielded X-ray spectra with at least one peak well above background level (Fig. 1) as well as an indication of the presence of C. Average analyses, in ratios of chemical equivalents of metals (Na and

K) to chemical equivalents of nonmetals (S and Cl) for two differing populations of particles, those with low metal contents and those with high metal contents, are presented in Table 1. The 12 particles which were analyzed qualitatively at ARC contain only C in appreciable concentration, although there is some indication of the presence of a small amount of S in most of these particles (Fig. 2).

## Conclusions

The particles of  $d < 0.20 \mu\text{m}$  collected at 20 km were different from the larger particles in their chemical makeup, in that they contained little or no  $\text{H}_2\text{SO}_4$ . There were three different chemical populations among these small particles, two very unlike the larger particles, one similar to them.

Most of the smaller particles analyzed contained only C in detectable quantities. It is possible that the matrix of all smaller particles is graphite. The other two populations contain detectable quantities of S and/or Cl.

The high metal particle population exhibits some similarity to the larger particles, having a mean chemical equivalent ratio  $(\text{Na}+\text{K})/(\text{S}+\text{Cl}) \sim 1$ , leading to the conclusion that they are essentially alkali metal sulfates and chlorides. They may be simply salt crystals or, perhaps, ions adsorbed on or mixed in with a carbon matrix. Since  $(\text{Na}+\text{K})/(\text{Cl}) \gg (\text{Na}+\text{K})/(\text{S}+\text{Cl})$ , the sulfate is the dominant anion. They differ from the larger particles in that they lacked  $\text{H}_2\text{SO}_4$ . The presence of  $\text{H}_2\text{SO}_4$  would result in the equivalent ratio being  $< 1$  and the chloride ion being converted to volatile HCl.

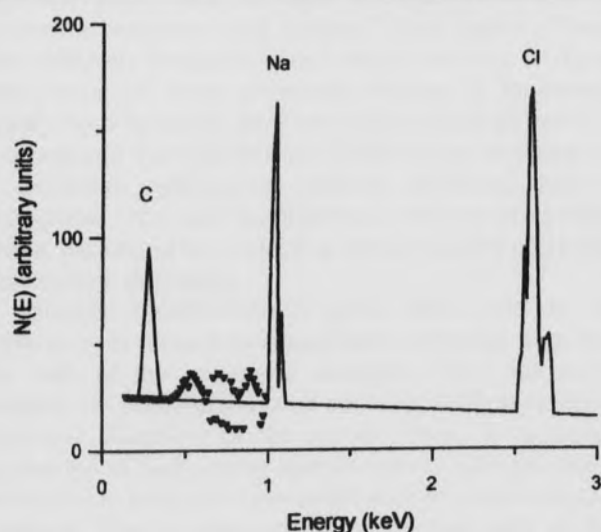


Fig. 1. EDS spectrum of Cl-containing particle. Background, containing the Si and Cu-L peak from X-ray detector and TEM grid, has been subtracted and the baseline has been smoothed.

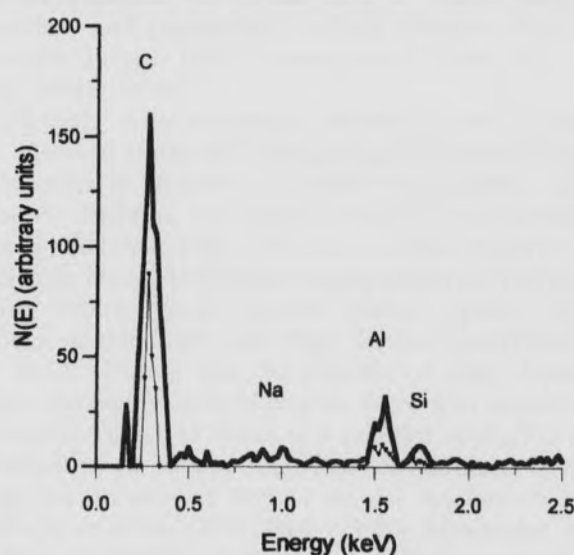


Fig. 2. EDS spectrum of carbon particle. The darker line is the sample spectrum; the lighter line is the background spectrum.

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The low metal particles are even more interesting. The  $(\text{Na}+\text{K})/(\text{S}+\text{Cl}) \ll 1$  and since  $(\text{Na}+\text{K})/(\text{S}+\text{Cl}) \sim (\text{Na}+\text{K})/\text{Cl}$ , Cl is the dominant nonmetallic species. This leads to the conclusion that the majority of the Cl is not ionic. It is possible that Cl atoms produced by photochemical decomposition of the HCl produced by reaction (1) reacted with the C containing particle matrix to form covalently bonded Cl species.

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