

*MEASUREMENT OF THE SULFURIC ACID WEIGHT PERCENT  
IN THE STRATOSPHERIC AEROSOL FROM THE  
EL CHICHÓN ERUPTION*

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### RESUMEN

Durante un descenso lento de balón desde los 30 km de altitud sobre el sureste de Texas en octubre de 1982, el tubo de entrada a un contador de partículas capaz de medir las concentraciones de aerosol de  $r \geq 0.15 \mu\text{m}$  y  $r \geq 0.25 \mu\text{m}$  fue calentado a  $150^\circ\text{C}$ , permitiendo su enfriamiento periódico para determinar la volatilidad del aerosol. Al hacerse la medición, el aerosol inyectado por El Chichón se caracterizaba por dos capas principales centradas a alrededor de 17 y 24 km. La capa superior contenía partículas más grandes (radio modal principal de  $\sim 0.3 \mu\text{m}$ , comparado con  $\sim 0.1 \mu\text{m}$  en la capa inferior). Al calentarlo, el aerosol indicaba una concentración de  $\sim 1\%$  de los valores ambientales, sugiriendo que la mayoría de las partículas eran muy volátiles o tenían cubierta muy volátil con núcleos posiblemente no volátiles, de radios  $< 0.15 \mu\text{m}$ . La distribución vertical del componente restante no volátil podía ser resuelta. Observando la temperatura a la cual podía suprimirse la mayor parte del aerosol (punto de vaporización) a varias altitudes (presiones), se construyó una curva de presión de vapor. Los resultados indican que el material volátil en la capa superior consistía en  $\sim 80\%$   $\text{H}_2\text{SO}_4$  -  $20\%$   $\text{H}_2\text{O}$  (por peso) mientras que la capa inferior consistía en un 60 - 65% de aerosol ácido. Esta diferencia es debida principalmente a las temperaturas más altas en la capa superior. Los porcentajes de ácido sulfúrico medidos en peso concuerdan bien con los valores teóricos según fueron calculados para las temperaturas observadas y las concentraciones típicas del vapor de agua.

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## ABSTRACT

During a slow balloon descent from 30 km over southern Texas on October 23, 1982, the intake tube to a particle counter capable of measuring the concentrations of  $r \geq 0.15 \mu\text{m}$  and  $r \geq 0.25 \mu\text{m}$  aerosol was heated to  $150^\circ\text{C}$  and allowed to cool periodically to determine aerosol volatility. At the time of the measurement, the El Chichón injected aerosol was characterized by two main layers centered at about 17 and 24 km. The upper layer contained the larger particles (main mode radius of  $\sim 0.3 \mu\text{m}$  as compared to  $\sim 0.1 \mu\text{m}$  in the lower layer). The aerosol, when heated, indicated a concentration of  $\sim 1\%$  of the ambient values suggesting that most of the particles were highly volatile or had a highly volatile sheath with possibly nonvolatile cores of radii  $< 0.15 \mu\text{m}$ . The vertical distribution of the remaining nonvolatile component could be resolved. By observing the temperature at which the bulk of the aerosol was removed (vaporization point) at several altitudes (pressures), a vapor pressure curve was constructed. The results indicate that the volatile material in the upper layer consisted of  $\sim 80\%$   $\text{H}_2\text{SO}_4$  -  $20\%$   $\text{H}_2\text{O}$  (by weight) while the lower layer consisted of a 60 - 65% acid aerosol. This difference is due mainly to the higher temperatures in the upper layer. The measured sulfuric acid weight percentages are in good agreement with theoretical values as calculated for observed temperatures and typical water vapor concentrations.

## INTRODUCTION

The technique of measuring the vapor pressure curve of stratospheric aerosols *in situ* utilizing a heated intake particle counter was developed in 1967 by Rosen (1971). He determined that the best fit to the observed aerosol vaporization temperature versus atmospheric pressure relation in the stratosphere was that expected for a 75%  $\text{H}_2\text{SO}_4$ , 25%  $\text{H}_2\text{O}$  solution. Subsequent theoretical studies indicated that this was a representative value for known stratospheric properties (Toon and Pollack, 1973; Hamill *et al.*, 1977) and has been used throughout the field of study since.

Following the eruption of El Chichón in April 1982, a comparison of measurements of University of Wyoming balloonborne particle counters (Hofmann and Rosen, 1982) and the NASA airborne lidar (McCormick and Swissler, 1983) was planned for October 1982 in southern Texas. Since the lidar backscatter depends critically on particle size, shape and composition, it was crucial that a well defined size distribution be determined, which could be obtained from the six size ranges of the Wyoming particle counters, and that the particle shape and composition, for example liquid spherical droplets or silicate nonspherical particles, be ascertained. The latter could be determined, in principle, by vaporization techniques. To obtain the maximum information, the vaporization measurement should be made at as many altitudes (pressures) as possible. Since a balloon rises too rapidly ( $\sim 5 \text{ m s}^{-1}$ ), a controlled balloon descent was considered necessary. Such a flight was successfully carried out at Del Rio, Texas ( $28.5^\circ\text{N}$ ) on October 23, 1982. A summary of the results has been reported (Hofmann and Rosen, 1983) and the details of the measurement will be presented in what follows.

## OBSERVATIONS

The balloon flight on October 23, 1982 at Del Rio, Texas incorporated a set of particle counters which covered a size spectrum from radii of  $0.01 \mu\text{m}$  to  $1.8 \mu\text{m}$  in six integral ranges. Details of the particle counters have appeared in the literature (Hofmann and Rosen, 1982) and some of the results of this particular flight have been reported (Hofmann and Rosen, 1983; special issue, 1st. part.). We are concerned here with the results obtained with the heated intake dustsonde employed on the flight, which measures particles having  $r \geq 0.15 \mu\text{m}$  and  $r \geq 0.25 \mu\text{m}$ . Figure 1 shows the data obtained during the ascent portion of the flight when the particle counter was operated normally (intake at ambient temperature). As observed in southern Texas in May and August, the El Chichón aerosol was again characterized by two layers of similar concentration for  $r \geq 0.15 \mu\text{m}$  but of a distinctly different size distribution. This can be seen in Figure 1 where the profile of the ratio of  $r \geq 0.15 \mu\text{m}$  to  $r \geq 0.25 \mu\text{m}$  concentrations indicates that the upper layer centered at about 24 km contained nearly equal concentrations for these two integral size ranges which indicates that most of the aerosol had radii greater than  $0.25 \mu\text{m}$ . In contrast, the

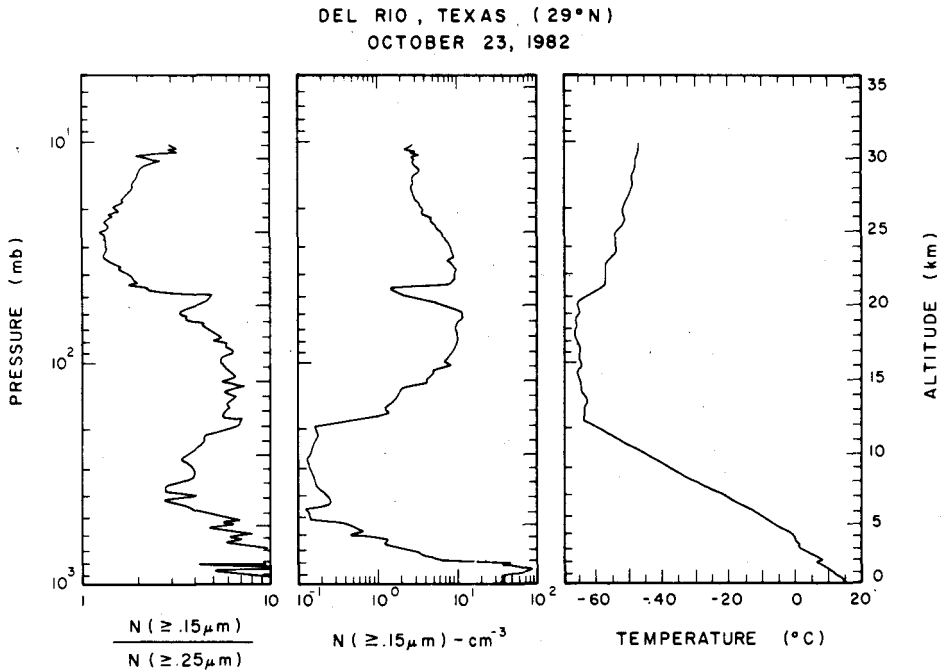


Fig. 1. Profiles of the ratio of concentrations of aerosol with  $r \geq 0.15 \mu\text{m}$  to those with  $r \geq 0.25 \mu\text{m}$ , the concentration of aerosol with  $r \geq 0.15 \mu\text{m}$ , and the temperature as measured at Del Rio, Texas on October 23, 1982. Note the large difference in the size ratio above and below about 20 km.

lower layer centered at about 17 km indicated a ratio of the two size ranges of about 6, similar to aerosol observed in previous volcanic eruptions (Hofmann and Rosen, 1982) and suggesting an average size of about  $0.1 \mu\text{m}$ .

The temperature profile in Figure 1 indicates that the lower layer was considerably colder than the upper layer. The prolonged separation of the two layers (they apparently did not coalesce until late 1982) is thought to be due to the different wind regimes which operated throughout the summer of 1982. Winds in the lower stratosphere carried particles in the lower layer to the east while upper winds carried the upper layer to the west. The lower temperatures in the lower aerosol layer are thought to be associated with the origin of the air in this region which was generally from the northwest. Aerosol heating in the region of the upper large particle layer may have contributed slightly to higher temperatures; however, most of these effects were confined to latitudes of  $10^{\circ}$  -  $20^{\circ}\text{N}$  (Labitzke *et al.*, 1983).

In Figure 2 we show the ambient  $r \geq 0.15 \mu\text{m}$  concentration profile between 10 and 100 mb during ascent and as observed on descent during the first five heating -

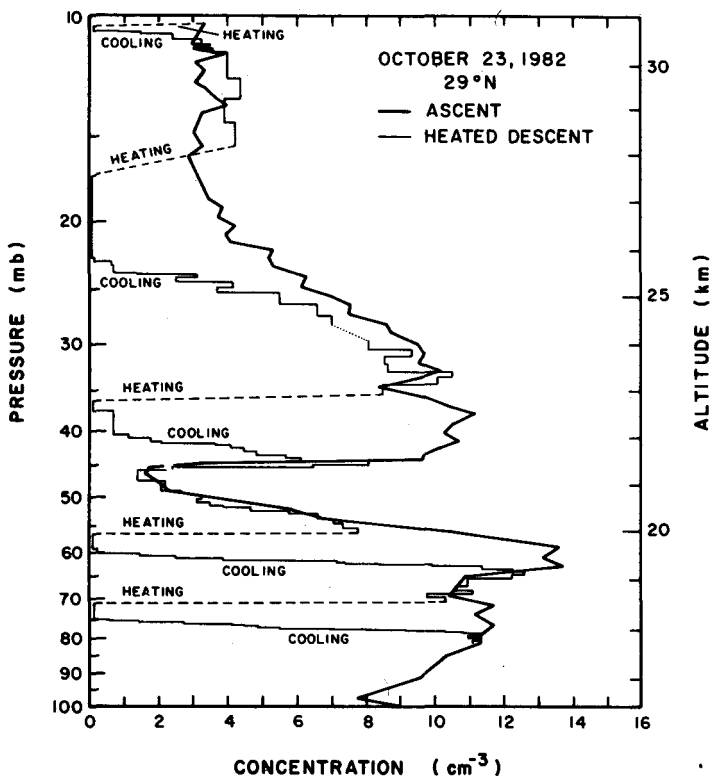


Fig. 2. The ambient  $r \geq 0.15 \mu\text{m}$  aerosol concentration on ascent and the concentration during the descent when the intake to the particle counter was heated to  $150^{\circ}\text{C}$  and allowed to cool periodically. Only the first five of nine such cycles are shown.

cooling cycles indicating very low concentrations during the heated portion of the cycle. This is typical behavior for an aerosol containing sulfuric acid. Since the wind velocity and direction varies somewhat with altitude, the balloon does not pass through the same air mass on ascent and descent. This accounts for the slight differences in aerosol concentration on ascent and during some of the portions of the descent when the heater temperature was below the aerosol vaporization point.

In order to determine the vapor pressure curve of the aerosol, the temperature at which the aerosol begins boiling at its surface must be determined. Since in this experiment the temperature was allowed to rise rapidly above the boiling point, the vaporization point was determined on the slower cooling portion of the cycle, i.e. when the aerosol again appeared to be back to nearly its ambient concentration

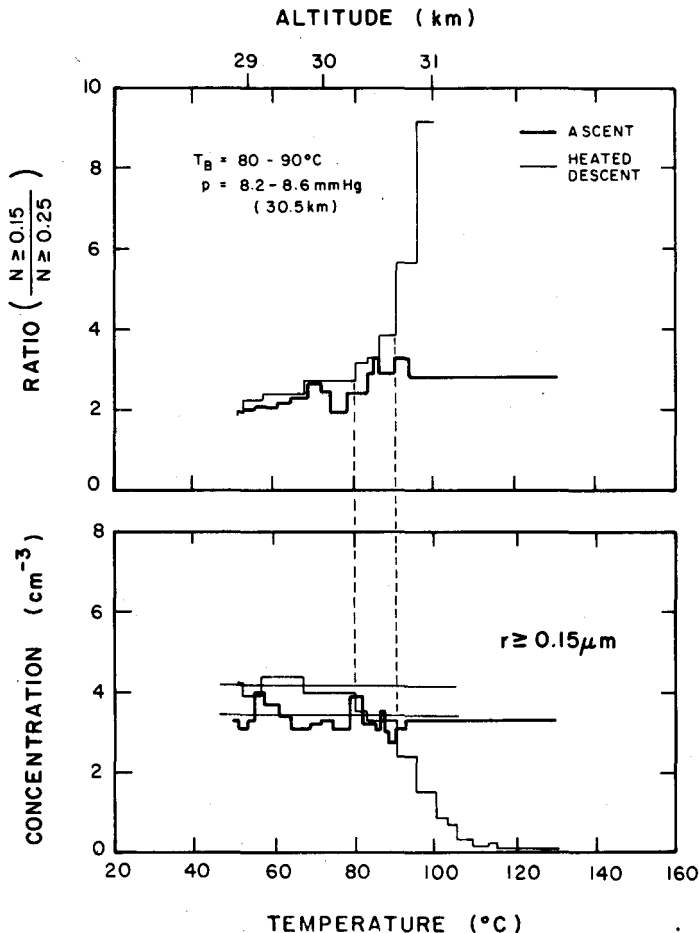


Fig. 3. The ambient  $r \geq 0.15 \mu\text{m}$  aerosol concentration and the aerosol size ratio on ascent and during the cooling portion of a heating cycle on descent at an altitude of about 30 km. The dashed lines indicate the chosen boiling point temperature range.

and, more importantly, when the size distribution, as inferred from the ratio of  $r \geq 0.15 \mu\text{m}$  to  $r \geq 0.25 \mu\text{m}$  concentrations, returned to normal. The latter indicator provides a better measurement of the vaporization point because it is independent of aerosol concentration which may be slightly different on ascent and descent.

Figures 3, 4, 5, and 6 show examples of concentration and size ratio versus temperature for several altitudes. In Figure 3 and 4, at about 30 km and 25 km altitude, respectively, the ascent and descent concentrations were slightly different so that the size ratio is a better indicator of the point when the aerosol has returned to its normal configuration. We note that the size ratio during the time when the aerosol sheath is boiled off (temperatures  $> 120^\circ\text{C}$ ) is very large indicating that the nonvolatile remnants are very small in size. This effect changed somewhat with altitude as can be seen in Figures 5 and 6, at about 19 km and 16 km, respectively.

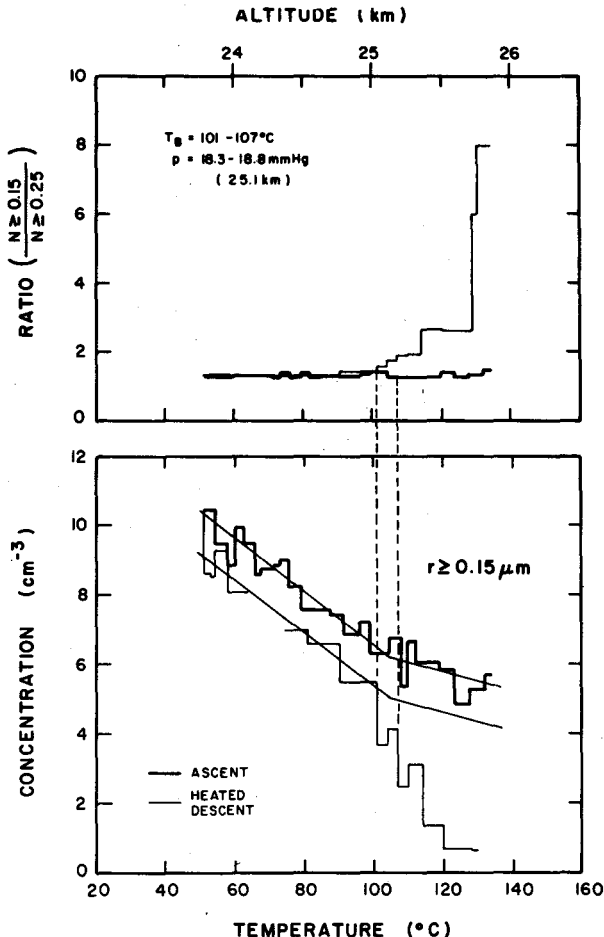


Fig. 4. Same as Figure 3 except for an altitude of about 25 km.

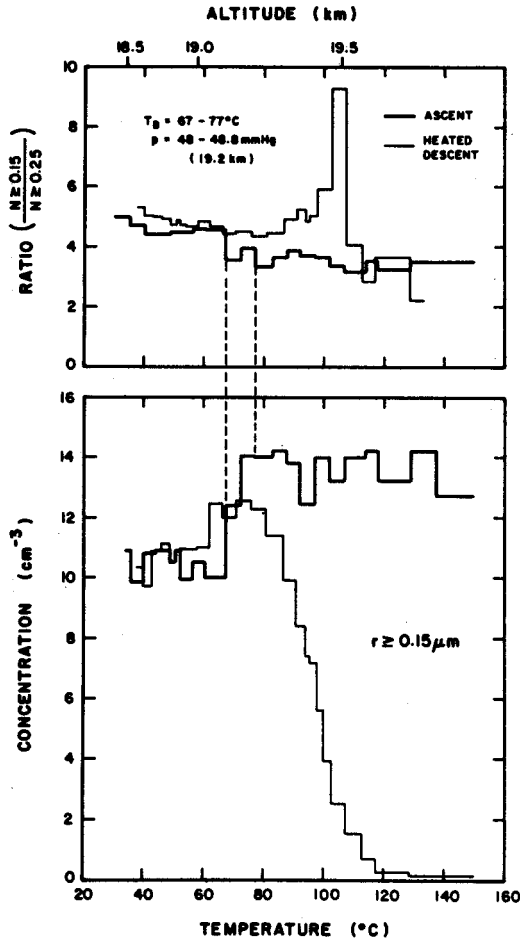


Fig. 5. Same as Figure 3 except for an altitude of about 19 km.

The nonvolatile size ratio decreases to values similar to that for the ambient aerosol at 19 km and even smaller at 16 km, indicating an increase in the size of the nonvolatile aerosol (or the nonvolatile cores) as altitude decreases.

The aerosol vaporization temperatures as determined at nine different altitudes (pressures) on descent are plotted versus pressure in Figure 7 along with vapor pressure curves for a range of  $\text{H}_2\text{SO}_4$  weight percentages where the remaining material is water. The ambient temperature, as measured during the flight, is also given in the figure, indicating the higher temperatures in the region of the upper aerosol

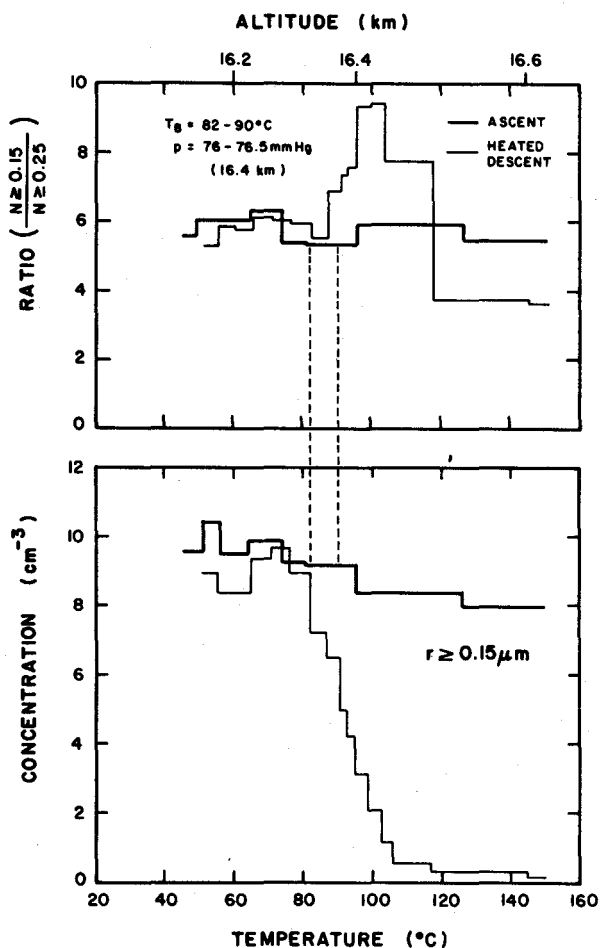


Fig. 6. Same as Figure 3 except for an altitude of about 16 km.

layer (21 - 25 km). Also shown, as dashed lines in Figure 7, are theoretical  $\text{H}_2\text{SO}_4$  weight percentages for several ambient water vapor mixing ratios as determined from the work of Steele and Hamill (1981). We see that in the colder lower stratosphere, the acid percentage is only about 60% whereas in the warmer upper regions it is as high as 80%. Comparing the observed vaporization points with theo-



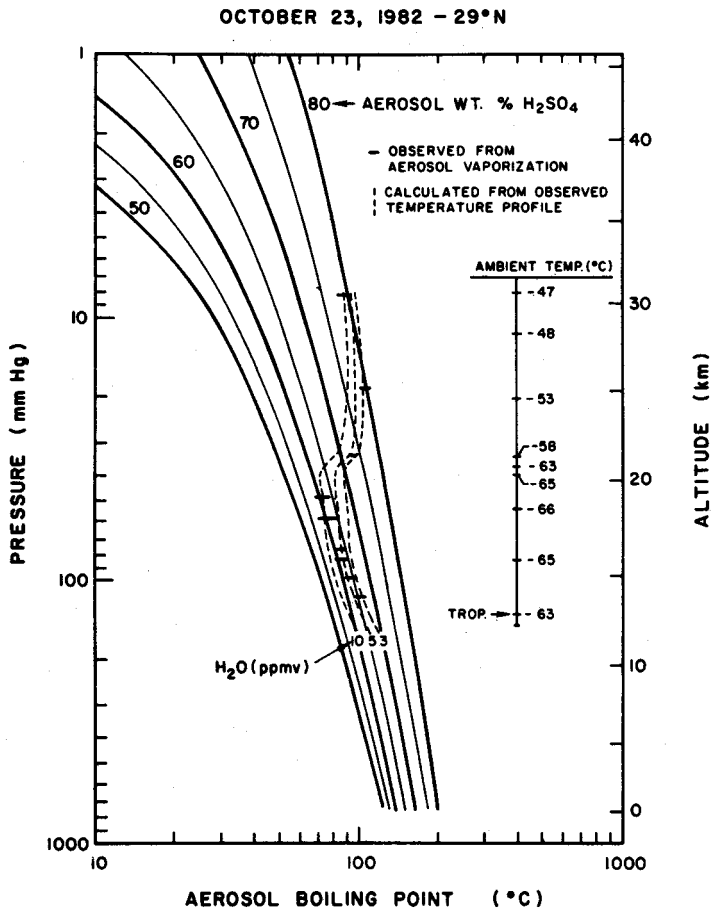


Fig. 7. Observed aerosol boiling point temperature ranges (horizontal bars) as a function of altitude (pressure). The smooth curves are vapor pressure curves for various weight percentages of  $\text{H}_2\text{SO}_4$  with water comprising the remaining fraction. The ambient temperature, as measured on the balloon flight, is given and the theoretical weight percentages of  $\text{H}_2\text{SO}_4$ , as dictated by the temperatures and by several representative ambient water vapor mixing ratios, are indicated by dashed lines.

retical predictions, we see that within experimental errors, the data are consistent with what one would expect for water vapor mixing ratios between 3 and 10 ppmv. The results for the weight percent of  $\text{H}_2\text{SO}_4$  as a function of altitude and temperature are summarized in Table 1.

Table 1  
Aerosol acid fraction  
October 23, 1982 - 28.5°N

Altitude (km)	Temperature (°C)	H <sub>2</sub> SO <sub>4</sub> (%)
30.5	-47	78.8 ± 1.2
25.1	-53	79.5 ± 1.0
21.5	-58	73.5 ± 1.0
19.2	-65	60.5 ± 2.5
18.0	-65	60.5 ± 4.5
16.4	-65	62.7 ± 1.7
15.9	-65	61.0 ± 2.0
14.8	-64	61.5 ± 2.5
13.8	-63	64.5 ± 2.5

Tropopause: 13 km, -63°C

The nonvolatile component, i.e. that which remains after heating, is shown in Figure 8 where the profiles of concentration for  $r \geq 0.15 \mu\text{m}$  and size ratio are given. The data indicate a very small concentration of about  $0.02 \text{ cm}^{-3}$  ( $< 1\%$  of the ambient concentration) of very small particles in the 30 km region. This may in fact be the meteoritic component at these altitudes. The bulk of the nonvolatile component, with a concentration of only about  $0.2 \text{ cm}^{-3}$  (about 2% of the ambient concentration), is located just above the tropopause in the 15 km region. An observed size ratio of about 3 suggests an average radius of about  $0.13 \mu\text{m}$  and a total concentration of about  $0.5 \text{ cm}^{-3}$  for an assumed log normal distribution with a width parameter  $\sigma$  (Hofmann and Rosen, 1982) of about 1.8, a value typical of the ambient aerosol. If, however, the observed distribution is the large particle tail of a wide size distribution with a  $\sigma$  of say 3, then the average radius would have been about  $0.02 \mu\text{m}$  and the total concentration about  $5 \text{ cm}^{-3}$ . While the latter distribution has 10 times the concentration, it only has about 50% more mass.

Some information on the average size of the nonvolatile or aerosol core component can be obtained from the condensation nuclei ( $r \geq 0.01 \mu\text{m}$ ) counter employing an air sample heater followed by a diffusion battery. The latter removes the smallest particles by diffusion to the walls of the battery allowing the larger particles, after being stripped of their volatile sheath by the heater, to be counted by a growth chamber - optical particle counter combination (Hofmann and Rosen, 1982). The fraction which penetrates the diffusion battery is related to the average particle size.

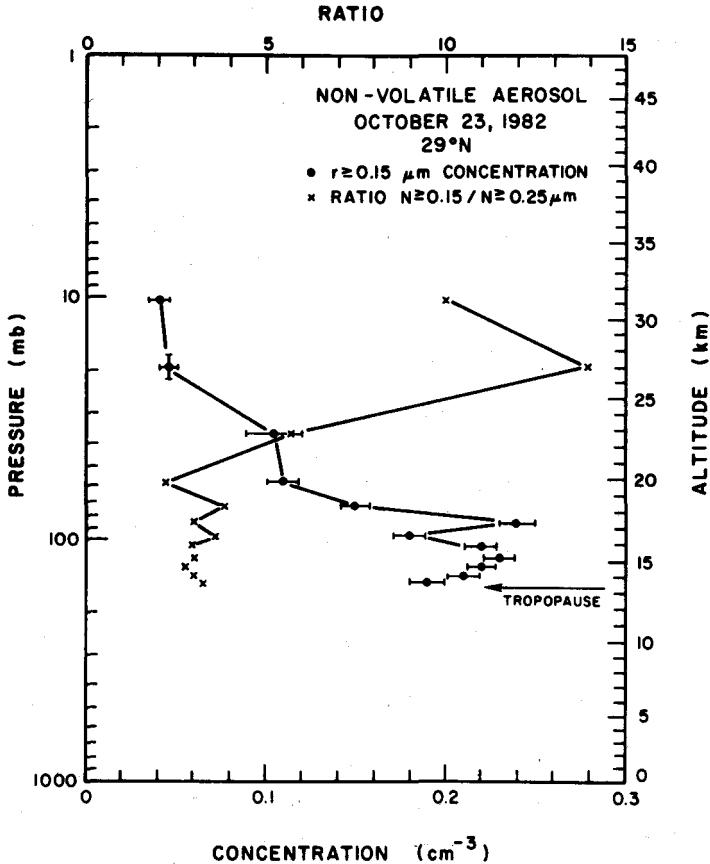


Fig. 8. Profiles of the  $r \geq 0.15 \mu\text{m}$  concentration and size ratio for the nonvolatile (at a temperature of  $150^\circ\text{C}$ ) particles as measured during a balloon descent at Del Rio, Texas on October 23, 1982. A large size ratio indicates small particles.

Measurements which utilized this scheme were made in February and July 1983. They indicated that in the main El Chichón layer at 17 - 21 km, 20 - 50% of the ambient aerosol with  $r \geq 0.01 \mu\text{m}$  contained an apparent core particle (concentration of 3 - 8  $\text{cm}^{-3}$ ) which survived the  $150^\circ\text{C}$  heating and that the average core radius was about  $0.02 \mu\text{m}$ . This would suggest that the nonvolatile distribution in Figure 8 could be the large particle tail of a rather broad distribution and that a fraction of one fifth to one half of the sulfuric acid droplets have small nonvolatile cores. There is a possibility however that the heater employed did not completely volatilize the relatively large El Chichón droplets down to  $0.01 \mu\text{m}$  and that the surviving concentration and size is indicative of this. This problem would not arise for the instrument used to obtain the data in Figure 8 as it only requires volatilization

down to a radius of  $0.15 \mu\text{m}$ . Further research, for example using a higher temperature to assure complete evaporation of the volatile component, should be conducted to conclusively determine the existence of a small nonvolatile core in the El Chichón droplets.

In summary, the technique of *in situ* aerosol vaporization using particle counters on a slowly descending balloon is capable of providing data which may be used to determine the weight percent of sulfuric acid in the stratospheric aerosol. The percentages so determined ranged from about 60 to 80%  $\text{H}_2\text{SO}_4$  and were in reasonable agreement with what is expected from theory. The nonvolatile aerosol component was resolved for  $r \geq 0.15 \mu\text{m}$  but the total distribution of this component, possibly the aerosol core component, could not be conclusively distinguished.

#### ACKNOWLEDGEMENTS

We are indebted for the assistance in the field of N. Kjome, D. Martell and G. Olson, and for the computational work of J. Kiernan and J. Vali. This research was supported by the U. S. National Aeronautics and Space Administration and the U. S. National Science Foundation.

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(Accepted: February 20, 1984)