

**BALLOONBORNE PARTICLE COUNTER OBSERVATIONS OF THE  
EL CHICHÓN AEROSOL LAYERS IN THE 0.01 - 1.8  $\mu\text{m}$   
RADIUS RANGE**

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**RESUMEN**

Mediante el uso de contadores de partículas ópticas adheridos a los globos meteorológicos se obtuvieron las conclusiones siguientes, concernientes a los efectos de la erupción de El Chichón sobre el aerosol estratosférico. Inicialmente se formaron dos capas de aerosol, la mayor de ellas constituida por gotitas muy grandes (radio modal principal de  $0.3\mu\text{m}$ ) a 25 km de altura, y otra capa de casi la misma concentración, pero con gotitas de menor tamaño (radio modal principal  $\sim 0.15\mu\text{m}$  a alrededor de 18 km de altura. Ambas capas eran volátiles en  $\geq 98\%$  a  $130^\circ\text{C}$ , lo que indica una composición predominante de ácido sulfúrico. La distribución de partículas por tamaños a 25 km era al inicio marcadamente bi-modal, con modos cerca de  $0.02\mu\text{m}$  y  $0.7\mu\text{m}$ , sugiriendo la condensación de nuevas gotitas a partir de la fase gaseosa y un aumento excesivo de la distribución anterior a la erupción. La nueva condensación de aerosol pareció cesar después de unos tres meses, pero el crecimiento de las gotitas siguió ocurriendo todavía después de nueve meses. Para diciembre, las capas de aerosol se habían extendido ampliamente hasta la latitud de Laramie. Las características del crecimiento del aerosol sugieren una concentración de vapor de ácido sulfúrico de  $\sim 10^7$  moléculas  $\text{cm}^{-3}$ , alrededor de 40 días después de la erupción, y una persistencia del vapor de 22-45 días. La masa total de aerosol de ácido sulfúrico se estima en alrededor de 10 Tg unos nueve meses después de la erupción y hasta de 20 Tg al inicio del fenómeno. En enero de 1983 se descubrió una nueva y extensa nube de gotitas de ácido sulfúrico muy pequeñas ( $r \sim 0.02\mu\text{m}$ ) sobre Laramie, en la región de 30-35 km de altitud. Estas nuevas gotitas parecen haberse condensado termalmente en las regiones polares derivándose probablemente de los vapores de El Chichón y/o de vapores que emanaban de la evaporación del aerosol de ácido sulfúrico del volcán durante los episodios de calentamiento estratosférico polar.

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## ABSTRACT

Through the use of balloonborne optical particle counters, the following conclusions concerning the stratospheric aerosol effects of the eruption of El Chichón have been drawn. Initially, two aerosol layers formed with a major layer of very large droplets (main mode radius  $\sim 0.3\mu\text{m}$  at 25 km and a layer of nearly the same concentration but of lesser size (main mode radius  $\sim 0.15\mu\text{m}$ ) at about 18 km. Both layers were  $\geq 98\%$  volatile at  $130^\circ\text{C}$  indicating a predominant sulfuric acid composition. The particle size distribution at 25 km was initially highly bimodal with modes near  $0.02\mu\text{m}$  and  $0.7\mu\text{m}$  suggesting the nucleation of new droplets from the gas phase and extensive growth of the pre-eruption distribution. New aerosol nucleation appeared to cease after about 3 months but droplet growth was still present after 9 months. By December, the aerosol layers had largely spread to the latitude of Laramie. Aerosol growth characteristics suggest a sulfuric acid vapor concentration of  $\sim 10^7$  molecules  $\text{cm}^{-3}$ , about 40 days after the eruption, and a vapor lifetime of 22-45 days. The total sulfuric acid aerosol mass is estimated to have been about 10 Tg some 9 months after the eruption and as much as 20 Tg early in the event. In January 1983, a new, extensive cloud of very small ( $r \sim 0.02\mu\text{m}$ ) sulfuric acid droplets was discovered over Laramie in the 30-35 km altitude region. These new droplets appear to have been thermally nucleated in polar regions and were probably derived from El Chichón vapors and/or vapors emanating through the evaporation of El Chichón sulfuric acid aerosol during polar stratospheric warming episodes.

## INTRODUCTION

Since the series of volcanic eruptions of El Chichón (March 28, April 3 and April 4, 1982) numerous balloon soundings at Laramie, Wyoming ( $41^\circ\text{N}$ ) and soundings on four occasions in southern Texas ( $27^\circ\text{N}$  -  $32^\circ\text{N}$ ) have been conducted in a continuing effort to study the mechanisms of sulfurous gas to sulfuric acid droplet conversion in the stratosphere following volcanic eruptions. In this work, a complement of three optical particle counters has been employed. These include a CN (condensation nuclei) counter ( $r \geq 0.01\mu\text{m}$ ), a dustsonde ( $r \geq 0.15$  and  $\geq 0.25\mu\text{m}$ ) and a large aerosol counter ( $r \geq 0.25, 0.95, 1.2$  and  $1.8\mu\text{m}$ ). Air sample heaters were used to determine aerosol volatility and diffusion batteries were used to determine average CN size. Descriptions of these instruments have been given in the literature (Hofmann *et al.*, 1975; Rosen and Hofmann, 1977; Hofmann and Rosen, 1982a) and will not be repeated here. The polyethylene balloon systems normally employed, are capable of carrying the three instruments to altitudes in excess of 30 km.

In order to place the El Chichón eruption in perspective in terms of aerosol effects on the stratosphere, we show in Figure 1 the stratospheric aerosol peak mixing ratio (particles per milligram ambient air) for the two size ranges measured by the dustsonde in approximately monthly soundings from Laramie and for 4 soundings from southern Texas, versus time since measurements began in 1971. These data include the effects of at least five major eruptions, Fuego in 1974, Mt. St. Helens in 1980, Alaid in 1981, an undetected eruption early in 1982 and El Chichón also in 1982.

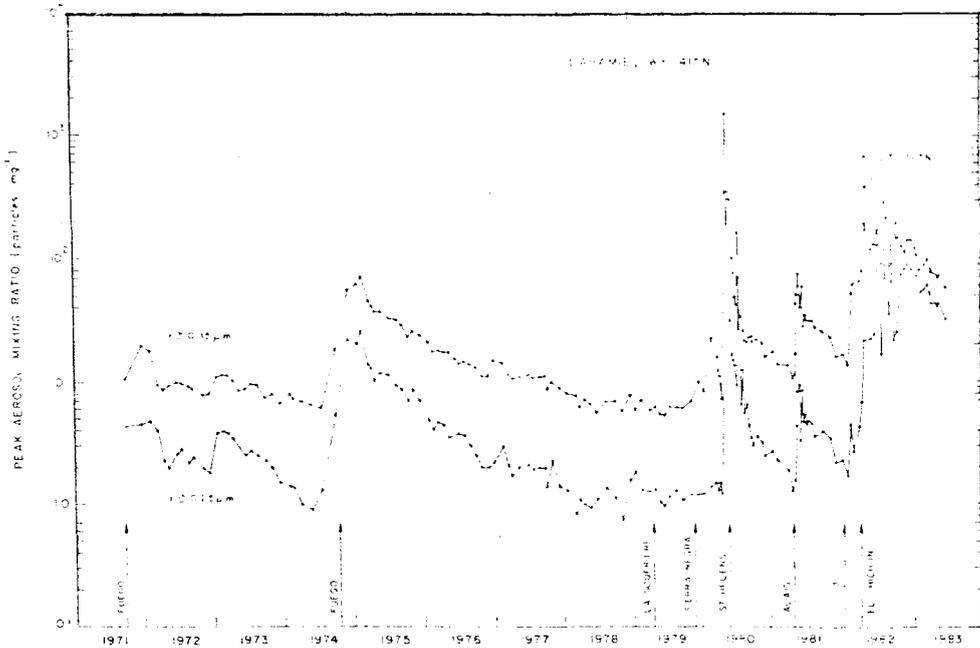


Fig. 1. Maximum stratospheric aerosol mixing ratio for two size ranges measured by the dust-sonde as a function of time at Laramie and in southern Texas. Times of volcanic eruptions which caused stratospheric aerosol perturbations at Laramie are indicated.

The feature which causes the El Chichón eruption to stand out from the others is the larger size of the aerosol, indicated by the similarity in the mixing ratio of the two sizes following that eruption, in contrast to the other eruptions. The large mixing ratios shortly after the eruption of Mt. St. Helens should be ignored as they are transient effects due to the passage of the fresh ash cloud directly over Laramie. Thus the aerosol mixing ratios observed in Texas shortly after the eruption of El Chichón are at least an order of magnitude larger than previously observed volcanic increases. This is partially due to the higher altitude of the main layer in the El Chichón eruption (~25 km) as compared to previous eruptions (18 - 20 km), but also to the higher concentrations of aerosol present.

Analyses of data obtained during 1982 have appeared in the literature (Hofmann and Rosen, 1983a, b) and will be extended and elaborated on in what follows.

## OBSERVATIONS

*Aerosol concentration time variation*

Figure 2 shows the maximum aerosol concentration above 17 km altitude observed for 3 size ranges at Laramie and in southern Texas as a function of time after the eruption of El Chichón. The  $r \geq 0.01 \mu\text{m}$  data at Laramie shows two periods of new aerosol nucleation, during the first 100 days after the eruption and in early 1983. While the first period is probably due to sulfuric acid vapor supersaturation associated with the initial phases of the eruption, the latter period appears to be a new delayed aerosol production phenomenon which will be elaborated on later. The  $r \geq 0.15 \mu\text{m}$  data suggests a general decay shortly after the eruption both at Laramie and Texas while the  $r \geq 0.25 \mu\text{m}$  data indicates this feature only in the Texas data. The Laramie  $r \geq 0.25 \mu\text{m}$  data shows a gradual buildup to a maximum in early 1983. This is most probably due to the gradual transport northward of the generally larger aerosol at higher altitudes.

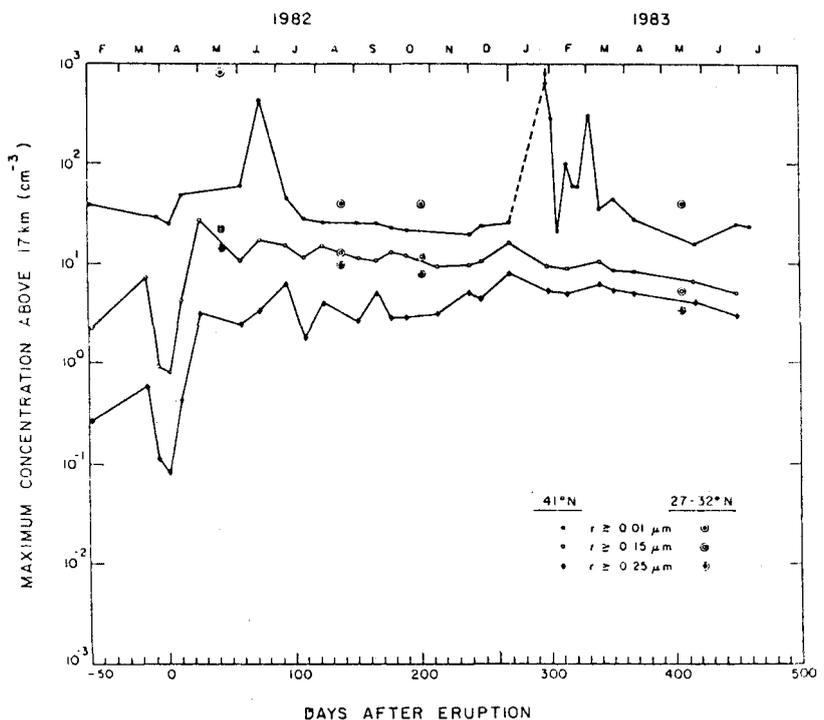


Fig. 2. Maximum aerosol concentration above 17 km for three size ranges at Laramie and in southern Texas as a function of time after the eruption of El Chichón.

That the aerosol initially appeared in two distinct layers and that larger aerosol was present at higher altitudes is clearly shown in Figure 3 where concentration profiles for  $r \geq 0.15 \mu\text{m}$  and  $r \geq 0.25 \mu\text{m}$  in Texas on August 21, 1982 are presented.

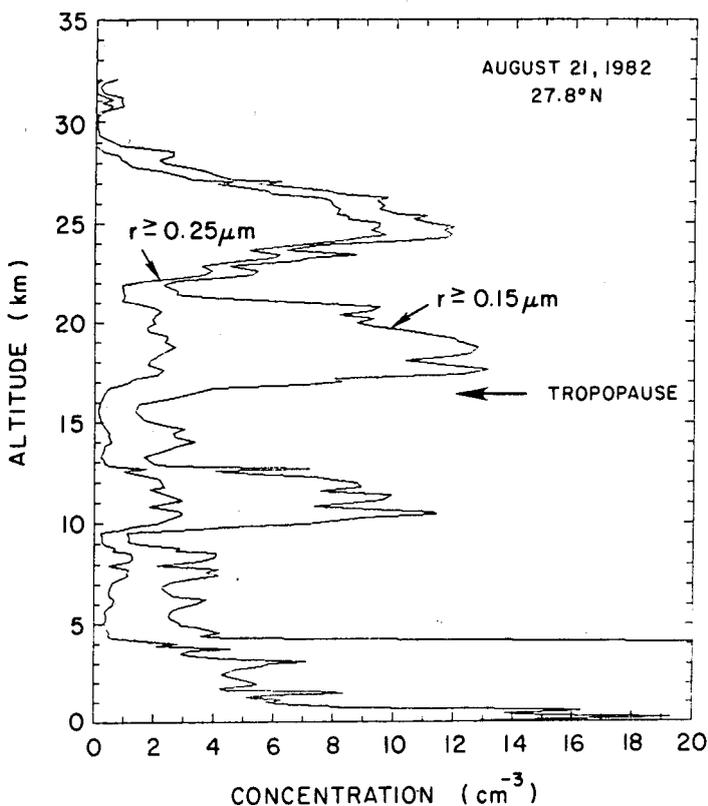


Fig. 3. Aerosol concentration profiles for two size ranges as measured at Sinton, Texas on August 21, 1982. Note the excess of larger particles in the 25 km layer compared to that at 18 km.

The ratio of these two size ranges in the 18 km layer ( $\sim 5$ ) is typical of previous volcanic aerosol in the 18 - 20 km region while the value at 25 km ( $\sim 1.25$ ) is indicative of unusually large sizes and may be associated with the height of the layer as suggestions of larger aerosol at higher altitudes, although not as obvious as in the case of El Chichón, were present following the eruption of Mt. St. Helens (Hofmann and Rosen, 1982a). This feature will be discussed in more detail later.

#### *Aerosol size distribution*

The nature of the early 25 km aerosol size distribution may be seen in Figure 4.

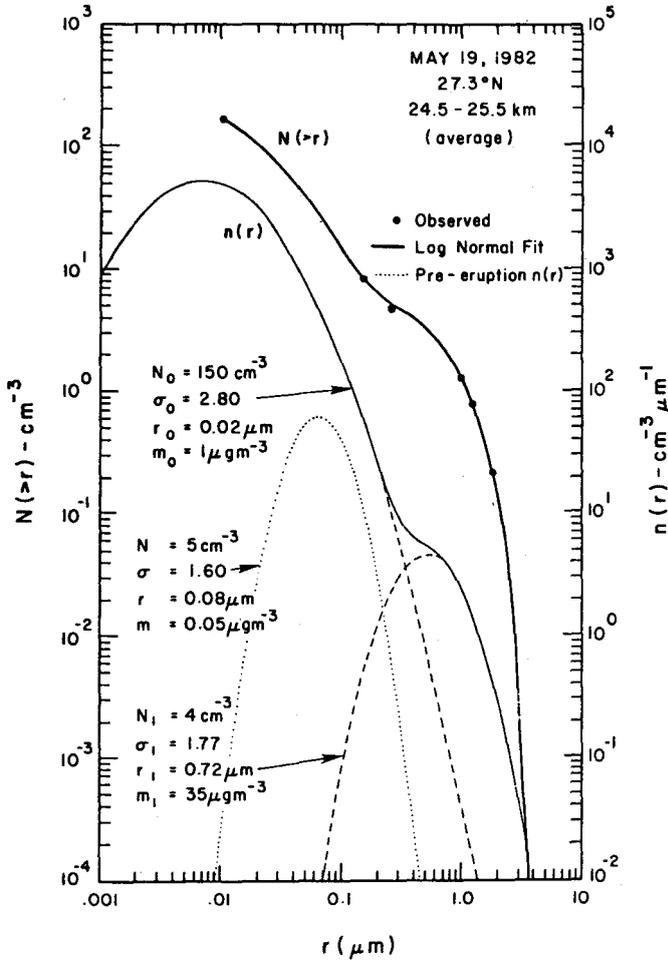


Fig. 4. The aerosol size distribution in the 25 km layer as measured in six integral size ranges. Smooth curves represent a bimodal log normal distribution fit to the data for the differential ( $n$ ) and integral ( $N$ ) size distributions. The dotted curve is the preeruption differential distribution.

These data were obtained in southern Texas on May 19, 1982 about 45 days after the eruption at the peak of the cloud on its second circumnavigation of the globe. Shown are the integral concentrations above the six sizes measured and fitted functions in the form of multi-modal normal distributions in the logarithms of the radius ( $r$ ):

$$n(r)dr = \sum_i \frac{N_i}{(2\pi)^{1/2}} \exp\left(-\frac{\alpha_i^2}{2}\right) d\alpha_i \quad (1)$$

where  $n(r)$  is the number concentration per unit radius,  $N_i$  is the total concentration of the  $i$ th mode, and

$$\alpha_i = \frac{\ln(r/r_i)}{\ln \sigma_i} \quad (2)$$

where  $r_i$  is the  $i$ th modal radius (the median radius) and  $\sigma_i$  is the  $i$ th modal width (dimensionless). The integral of  $n(r)dr$  above a radius  $r$  gives  $N(>r)$ , the measured parameter.

Also indicated in Figure 4 is the typical preeruption distribution (dotted curve) for the 25 km level. The early El Chichón aerosol distribution appears to be bimodal with mode radii at about 0.02 and 0.7  $\mu\text{m}$ . As suggested previously (Hofmann and Rosen, 1983b), the large particle mode has nearly the same total concentration as the preeruption mode indicating evolution through growth of the latter. The small particle mode, which was not present prior to the eruption, indicates new aerosol production 1½ months after the eruption. Since the coagulation time of 0.02  $\mu\text{m}$  aerosol for the observed concentrations is of the order of a few days, these droplets were being produced well after the eruption. The mass concentration, indicated for each mode in Figure 4, was concentrated in the large particle mode.

Measurements in Texas in August 1982 (see Figure 3) indicated that while the aerosol was still concentrated in two layers, nucleation had ceased and the 0.01  $\mu\text{m}$  aerosol population had been severely depleted by coagulation and growth to larger sizes. The measured integral size distributions in the two layers are shown in Figure 5. Aerosol with radii  $<0.05 \mu\text{m}$  were essentially absent in the upper layer. They had presumably coagulated and grown to form the excess of aerosol in the 0.15 - 1  $\mu\text{m}$  size range. This effect was not as severe in the lower layer where a highly bimodal size distribution is apparent. The bi-modal nature of this distribution is attributed to sedimentation of large particles from the upper layer. Thus the concentrations of  $r \geq 1 \mu\text{m}$  aerosol are very similar in the two layers whereas this is not true for the  $r \geq 0.25 \mu\text{m}$  aerosol as sedimentation effects are not as large for the latter.

By the end of 1982, the aerosol had migrated to the latitude of Laramie and the 18 and 25 km layers had mixed to form a broad layer from the tropopause to about 30 km. This can be seen in Figure 6 where aerosol profiles obtained at Laramie in late 1982 are shown. Although a relative excess of larger particles at high altitude remains evident in Figure 6, the larger particles had settled somewhat, peaking in the 18 - 20 km range. This can be seen in Figure 7 where concentration profiles of the 6 size ranges on January 28 are shown. The  $r \geq 0.01 \mu\text{m}$  data indicates the large increase at 29 km alluded to earlier. The CN counter on this sounding saturated at a concentration of about 600  $\text{cm}^{-3}$  and remained saturated to the top of the sounding at about 33 km. Data on parachute descent verified the existence of this new layer of very small droplets.

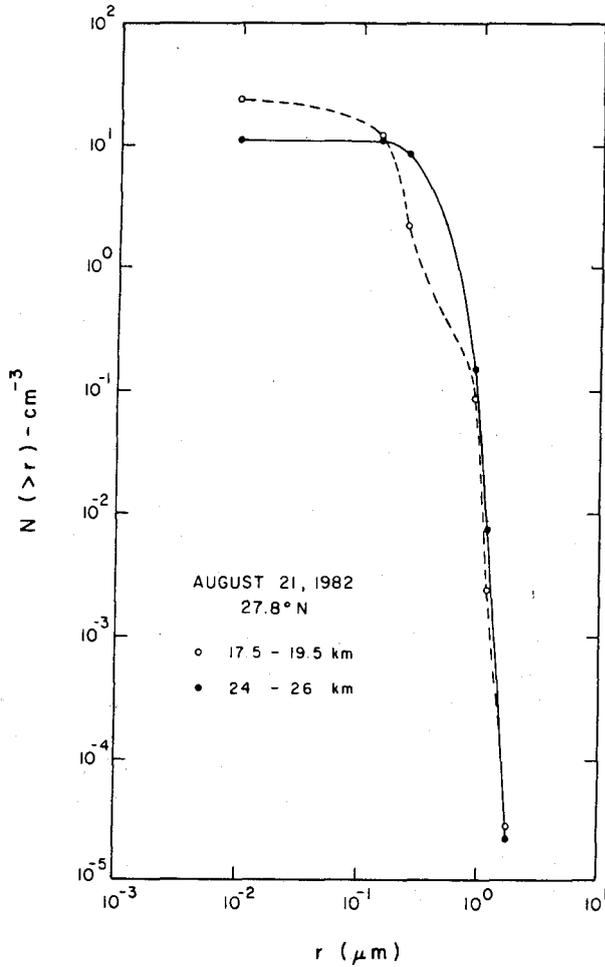


Fig. 5. The aerosol size distribution in the two main layers as measured in six integral size ranges at Sinton, Texas on August 21, 1982. Note the excess concentration in the  $0.15 \mu\text{m}$  to  $1 \mu\text{m}$  size range in the upper layer.

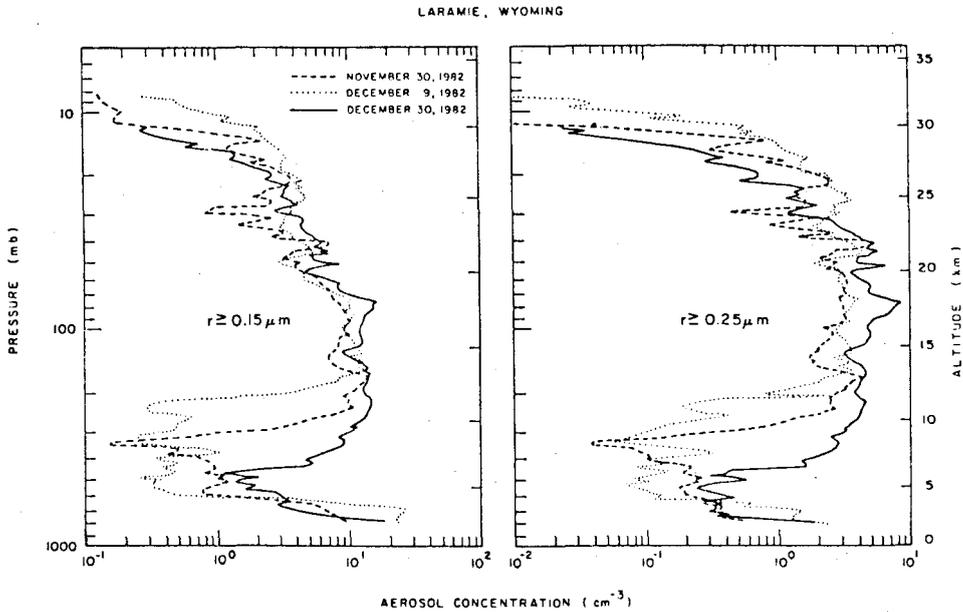


Fig. 6. Aerosol concentration profiles for the two size ranges measured by the dustsonde at Laramie in late 1982. Note the excess of the larger aerosol above about 20 km.

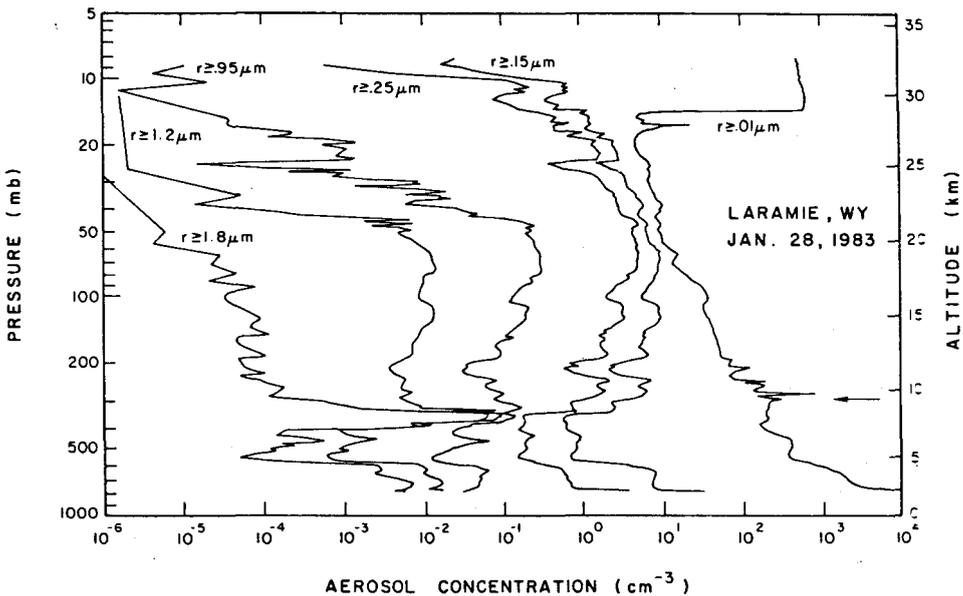


Fig. 7. Aerosol concentration profiles for six size ranges as measured at Laramie on January 28, 1983. The arrow marks the position of the tropopause. Note the large increase of the smallest size aerosol at about 29 km.

Size distributions constructed from the data in Figure 7 for the region of maximum concentration (18 - 21.5 km) are given in Figure 8. Since the measured data are integral values and the differential distribution is required for mass calculations, one needs either to fit some functional form to the data or use computer generated splines under tension (Cline, 1974). The latter appears preferable as it is the least biased with the spline tension the only adjustable parameter. It also tends to blend modes together in a perhaps more realistic manner and can fit data which has been skewed due to gravitational settling such as that for aerosol above about  $0.7 \mu\text{m}$  in Figure 8.

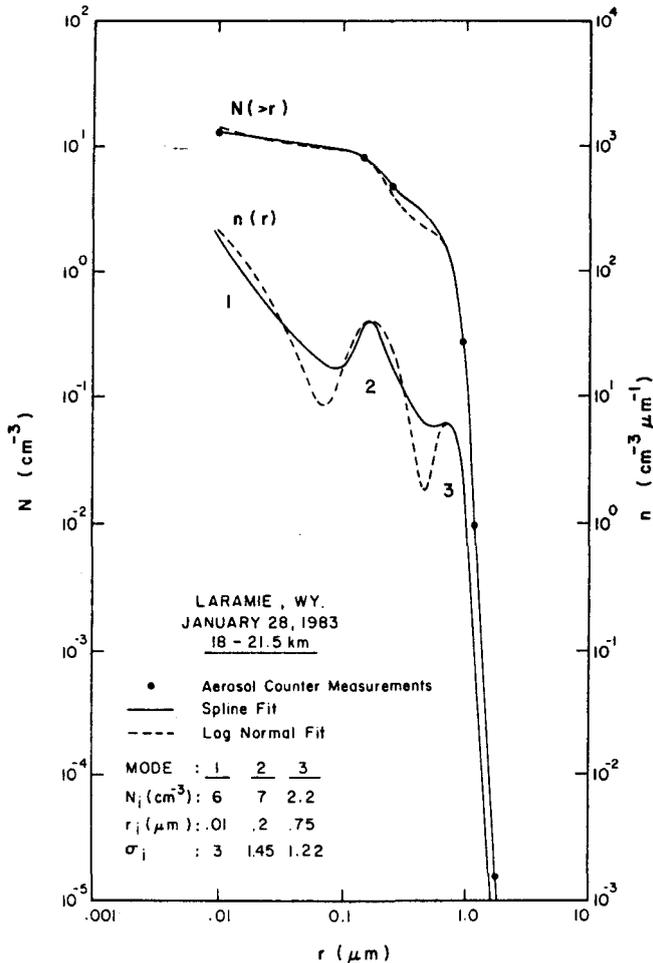


Fig. 8. The aerosol size distribution as measured in six integral size ranges at the stratospheric maximum from the data in Figure 7. Smooth curves are computer generated spline fits to the data for the integral ( $N$ ) and differential ( $n$ ) size distribution. Dashed curves are approximate fits of a tri-modal log normal distribution. Numbers along the curves refer to the mode number. Mode parameters are given in the figure.

In order to assign parameters to the distribution, for discussional purposes, a multi-modal log normal distribution which best describes the spline fit is shown in Figure 8. Three modes appear to be present. The main mode at about  $0.2 \mu\text{m}$  probably evolved through growth of the small particle mode observed in Texas shortly after the eruption (see Figure 4). The large particle mode at about  $0.7 \mu\text{m}$  is probably the remnants of the preeruption distribution which has grown considerably and settled into the region from higher altitude. There is a suggestion of a small particle mode at about  $0.01 \mu\text{m}$  indicating a weak aerosol source.

### *Aerosol composition*

In order to construct mass profiles and obtain total mass estimates, it is necessary to ascertain the composition of the aerosol. This is done by heating the intake tube of the particle counter and observing the aerosol boiling point. An example of this is shown in Figure 9 for a sounding at Laramie on May 25, 1983. During balloon ascent the counter was operated normally while during parachute descent the intake was heated to  $130^\circ\text{C}$ . The data indicate that in the main aerosol layer only

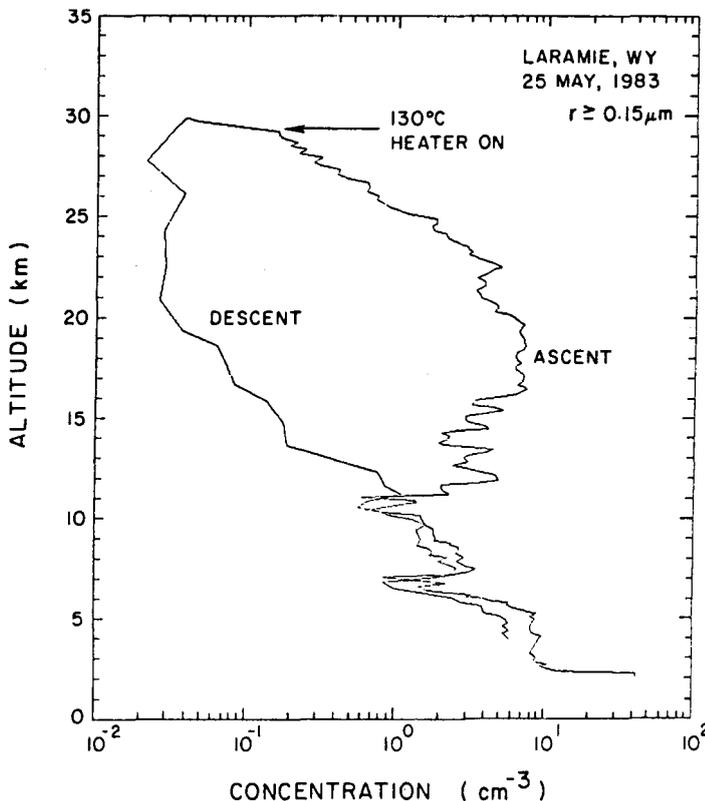


Fig. 9. A comparison of the normal (ascent)  $r \geq 0.15 \mu\text{m}$  aerosol profile and the profile on descent when the intake tube to the aerosol counter was heated to  $130^\circ\text{C}$  at Laramie on May 25, 1983.

about 1% of the aerosol survive this heating suggesting a high degree of volatility. This is consistent with previous results following volcanic eruptions (Hofmann and Rosen, 1977; 1982a). A study of the aerosol volatility versus pressure during a slow balloon descent in southern Texas on October 23, 1982 indicated that the observed boiling points were consistent with a composition of 80% sulfuric acid, 20% water at 25 km and 60% sulfuric acid, 40% water at 18 km (Hofmann and Rosen, 1983a; this issue).

#### *Aerosol mass distributions and total mass burden*

Assuming an average composition of 75% sulfuric acid, 25% water (specific gravity of  $1.65 \text{ g cm}^{-3}$ ), the aerosol mass profiles have been calculated for each sounding using the computer spline fits for the size distributions. Mass mixing ratio profiles calculated in this manner are given in Figure 10 for soundings during the first

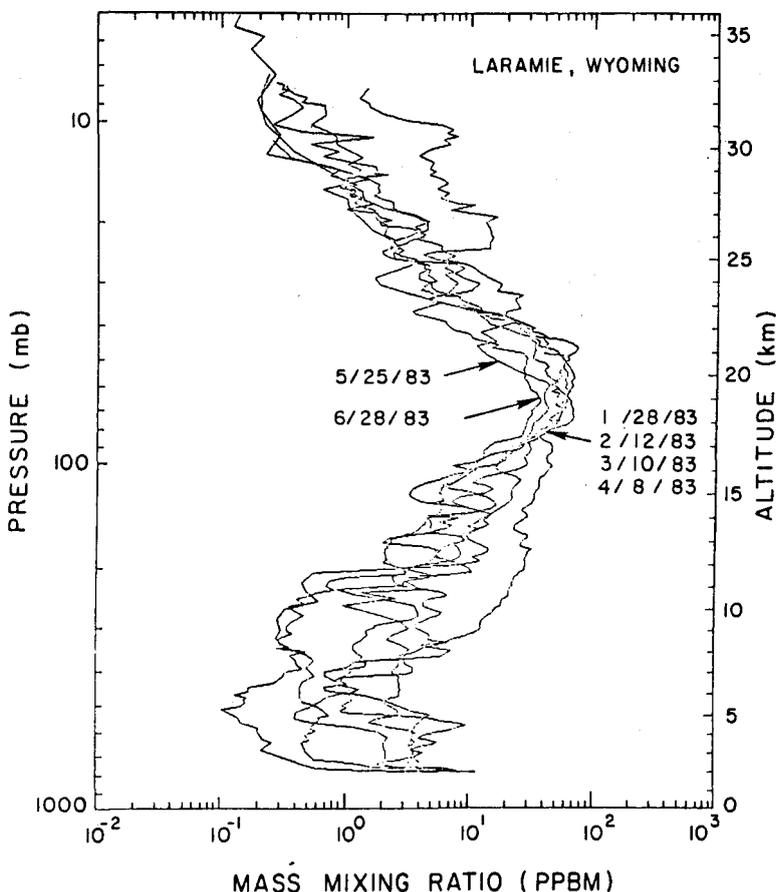


Fig. 10. Aerosol mass mixing ratio profiles as calculated from spline size distribution fits to the six integral size ranges measured at Laramie during the first 6 months of 1983. The sounding with the excess mass at high altitude occurred on January 28, 1983 while that with the excess mass at low altitude occurred on April 8, 1983. The peak mixing ratio in the 20 km region was nearly constant during the first four months but began to decay in May and June.

6 months of 1983 at Laramie when the aerosol layer was at its peak concentration. Profiles of mass concentration before the eruption and at Laramie and in Texas during August - September 1982 are compared in Figure 11. The increase at 25 km amounted to approximately two orders of magnitude. Profiles such as those in Figure 11 may be vertically integrated above a given height to obtain the total aerosol mass burden above that height. The resulting mass burden in grams per square meter column above several altitudes versus time after the eruption is shown in Figure 12 for the Laramie and Texas data. While the total mass appears to have undergone a continual decline at lower latitudes, a gradual buildup owing to meridional transport is apparent in the Laramie data. Times of penetration of the high altitude cloud to midlatitudes is evident in the  $>25$  km data.

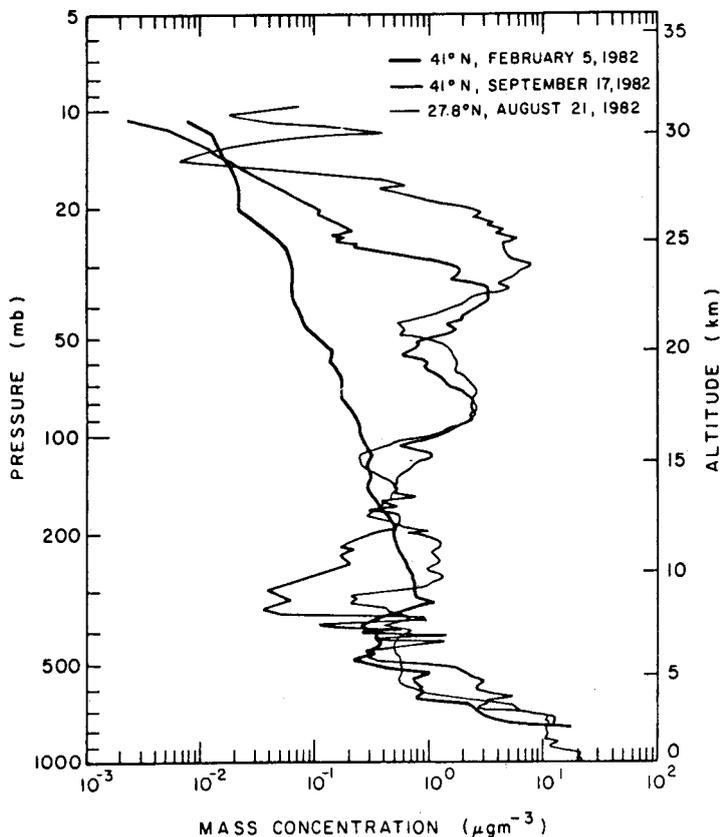


Fig. 11. Aerosol mass concentration profiles before the eruption of El Chichón and in September 1982 at Laramie. Also shown is the mass concentration profile in Texas a month earlier.

Also indicated in Figure 12 is a total mass scale which may be used to estimate the global mass burden assuming longitudinal homogeneity and various latitudinal extents. From these data, a total mass of about 10 Tg (1 Tg =  $10^6$  metric tons) is estimated to have been present in the stratosphere in early 1983 with as much as 20 Tg present early in the event. Assuming the aforementioned sulfuric acid - water composition and assuming the precursor gas to have been sulfur dioxide, these numbers translate into about 5 and 10 Tg of  $\text{SO}_2$ , respectively.

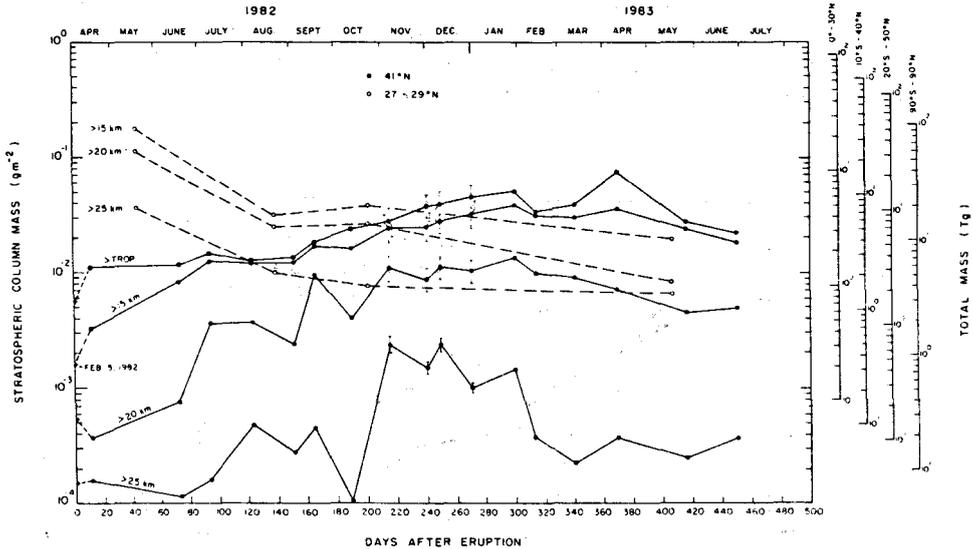


Fig. 12. Vertically integrated mass above several altitudes at Laramie and in southern Texas as a function of time after the eruption of El Chichón. The total mass scale on the right, for several assumed latitudinal bands, assumes longitudinal homogeneity of the aerosol layers and is only applicable after the first two months or so.

Decay of the event is evident following April 1983. Due to the generally larger size of the post-El Chichón droplets, as compared to previous eruptions, one may expect the aerosol decay to be somewhat faster than for other eruptions such as that of Fuego in 1974 which had an e-folding decay time of about 10-11 months for the  $r \geq 0.15 \mu\text{m}$  mixing ratio (Hofmann and Rosen, 1981) and the total sulfate mixing ratio (Sedlacek *et al.*, 1983). Although it is too early for accurate estimates, the El Chichón aerosol  $e^{-1}$  decay time after April 1983 appears to have been about 8.5 months for the  $r \geq 0.15 \mu\text{m}$  mixing ratio and about 7.5 months for both the  $r \geq 0.25 \mu\text{m}$  mixing ratio and the total mass burden above 15 km.

#### *Time variation of aerosol size*

By studying the time variation of the aerosol size, one may obtain quantitative information on the sulfuric acid source. Theoretical studies which include coagula-

tion, growth and diffusion (Kiernan, 1983) indicate that while coagulation is important in determining aerosol number, growth by condensation is the important process which determines eventual aerosol size. In particular,  $10^3 \text{ cm}^{-3}$  of  $0.01 \mu\text{m}$  radius aerosol undergoing coagulation, will have their radius doubled in a time period of 40 days. Thus, neglecting coagulation processes following the initial high concentration (nucleation) period appears valid and is useful in simplifying the discussion.

We thus assume the following concerning aerosol growth processes: (i) subsequent to an aerosol nucleation period (denoted by  $t_0$  in what follows), growth takes place by kinetic accretion of sulfuric acid molecules on the surface of the aerosol with 100% efficiency, (ii) after the time  $t_0$ , the concentration of newly nucleated droplets has decreased through coagulation to the point where only growth by molecular accretion is important in determining the size of the aerosol, (iii) the sulfuric acid vapor pressure is considerably greater than the saturation vapor pressure, (iv) the aerosol radius is much smaller than the effective mean free path of sulfuric acid molecules in the ambient air (the latter is about  $1 \mu\text{m}$  at 15 km, increasing to about  $10 \mu\text{m}$  at 30 km), and (v) the sulfuric acid vapor, although being continually produced through the oxidation of volcanic sulfurous gases, undergoes a net decay (assumed exponential with a time constant  $\tau$  in what follows) due mainly to the rapid aerosol accretion process. The latter had a lifetime of only about 15 minutes (Hofmann and Rosen, 1983b), while the observed lifetime for  $\text{SO}_2$ , following El Chichón, was about 35 days as determined from satellite observations (Heath *et al.*, 1983). Horizontal dispersion will also contribute to the sulfuric acid vapor decay.

With the foregoing assumptions, the aerosol radius as a function of time is given by (Hofmann and Rosen, 1983c):

$$r(t) = r_0 + \tau \left. \frac{dr}{dt} \right|_{t_0} \left( 1 - e^{-\frac{(t-t_0)}{\tau}} \right) \quad (3)$$

where  $r_0$  is the initial radius following nucleation (at  $t = t_0$ ),  $\tau$  is the net sulfuric acid vapor decay time and the initial growth rate is given by:

$$\left. \frac{dr}{dt} \right|_{t_0} = \frac{1}{4} \left( \frac{8kTm_a}{\pi} \right)^{1/2} \frac{n_0}{W\rho} \quad (4)$$

where  $k$  is the Boltzmann constant,  $T$  is the temperature,  $m_a$  is the mass of a sulfuric acid molecule,  $W$  is the weight fraction of sulfuric acid in the aerosol,  $\rho$  is the aerosol specific gravity and  $n_0$  is the sulfuric acid molecular concentration at  $t = t_0$ . The observed initial growth rate may be used to determine  $n_0$  and the final radius achieved,  $r_\infty$ , may be used to obtain the sulfuric acid decay constant,  $\tau$ , from the expression for  $r(t)$  as  $t$  gets large:

$$r_\infty = r_0 + \tau \left. \frac{dr}{dt} \right|_{t_0} \quad (5)$$

Figure 13 shows the main mode radius, as obtained from log normal distribution fits to the data, versus time after the eruption for the two layers observed. As pointed out earlier, the aerosol grew to larger sizes in the upper layer. The gradual merging of the two curves in Figure 13 is due to the larger aerosol in the upper layer settling and mixing with the lower layer; thus the average size in the upper layer decreases while that in the lower layer increases.

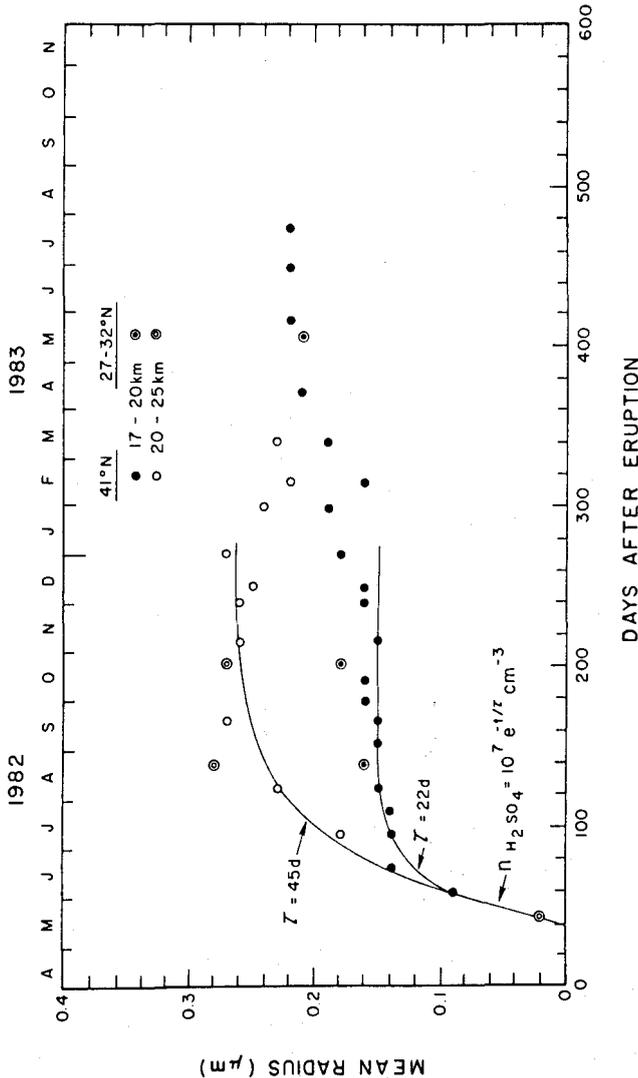


Fig. 13. Aerosol mean radius versus time in two altitude regions as obtained from log normal fits to the  $r \geq 0.01, 0.15,$  and  $0.25 \mu\text{m}$  concentration data at Laramie and in southern Texas. Smooth curves are theoretical growth curves for an initial sulfuric acid vapor concentration of  $10^7$  molecules  $\text{cm}^{-3}$  and e-folding decay times  $\tau$ .

The smooth curves in Figure 13 are theoretical fits of radius versus time according to the foregoing discussion. An  $r_0$  value of 0, a  $t_0$  value of 40 days, an  $n_0$  value of  $10^7 \text{ cm}^{-3}$ , and  $\tau$  values of 22 and 45 days for the lower and upper layers, respectively, gave the best fit to the data. Since the lifetime of the vapor to aerosol accretion is much shorter than the chemical production lifetime (which is approximately equal to the  $\text{SO}_2$  oxidation time of about 35 days), it follows that a sulfuric acid molecule produced chemically will rapidly be absorbed by a growing droplet. Thus the rate of droplet growth is rigidly controlled by the chemical vapor production rate so that the vapor lifetime, as derived here from the droplet growth rate, should reflect the chemical production lifetime, which it apparently does.

Chemical modeling of the  $\text{SO}_2$  oxidation process indicates a lifetime for  $\text{SO}_2$  of 38 days at 25 km for a series of reactions that conserve OH radicals and much longer for chains of reactions which consume OH (McKeen *et al.*, 1983). The results reported here are thus in agreement with OH serving as a catalyst in the oxidation process rather than being lost as assumed in previous aerosol chemical models (Turco *et al.*, 1979). Chemical modeling, however, does not predict a substantial difference in the  $\text{SO}_2$  lifetime at 18 and 25 km, as suggested by the results reported here. It is quite likely that dispersive effects, which were more pronounced at the lower altitude at least during the first 7 months, resulted in the smaller apparent vapor lifetime at these altitudes, so that the implied 18 km sulfuric acid vapor lifetime is not due to chemistry alone.

#### *Delayed nucleation of aerosol at high altitude*

As indicated in Figure 7, a large increase of newly nucleated aerosol was observed above 29 km on January 28, 1983. Although the condensation nuclei counter used was saturated at a concentration of about  $600 \text{ cm}^{-3}$ , a coincident reduction in electrical conductivity of about 50% (Gringel *et al.*, 1983), as measured on the same flight in the event layer, suggested that concentrations as large as  $1200 \text{ cm}^{-3}$ , for  $r \geq 0.01 \mu\text{m}$ , were present. From the coagulation lifetime at these elevated concentrations, it is estimated that the new aerosol was produced only a day or two before the observation. Figure 14 shows profiles of  $r \geq 0.01 \mu\text{m}$  aerosol from soundings between December 1982 (pre-event) through June 1983. Coagulative decay and dispersion results in the rapid decline of the concentration of these small particles so that CN counter saturation did not occur after initial detection on January 28, 1983.

A diffusion battery was used on several of the soundings in Figure 14 to obtain information on average aerosol size. It was determined that the effective diffusion radius was only about  $0.015 \mu\text{m}$  in the event layer initially. These data are shown in Figure 15 and suggest growth of aerosol in the event layer and considerable mixing by the end of June. Heating the aerosol sample verified that the new-droplets were a sulfuric acid - water mixture similar to other stratospheric aerosol.

## GEOFISICA INTERNACIONAL

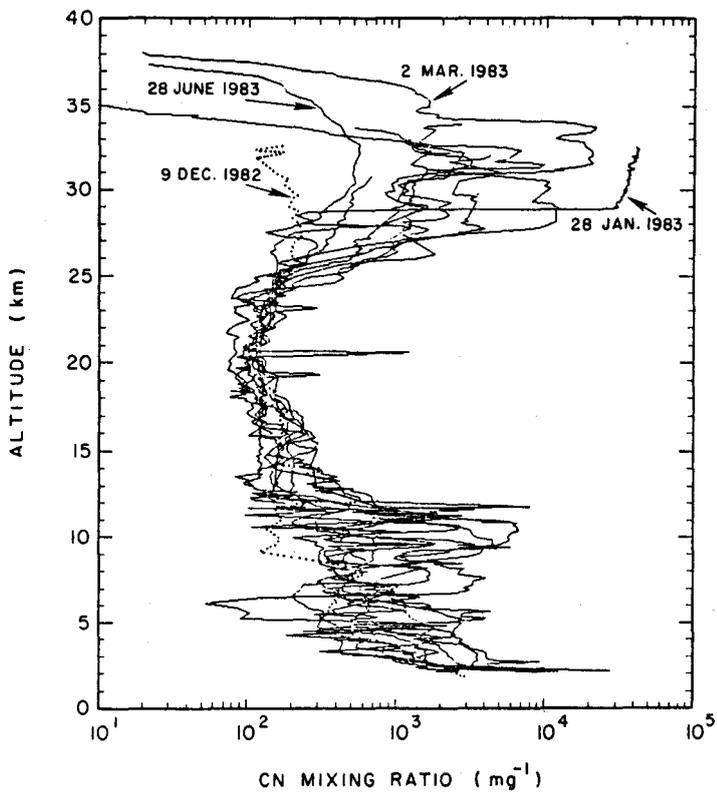


Fig. 14. Profiles of condensation nuclei ( $r \geq 0.01 \mu\text{m}$ ) at Laramie before (December 1982) and after the CN event of 1983 that began on January 28.

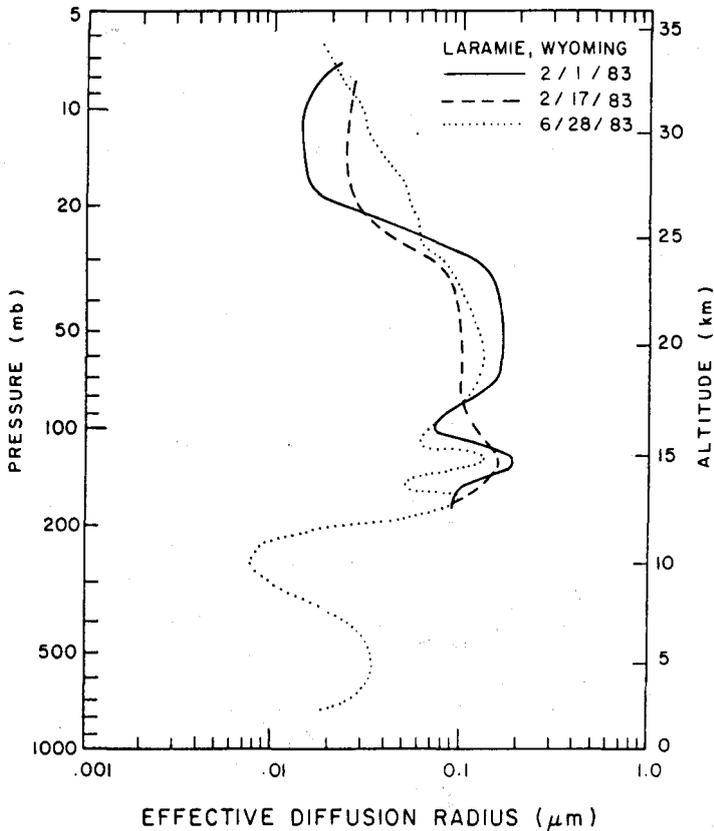


Fig. 15. Average aerosol radius profiles as determined by diffusion batteries for three soundings at Laramie following the CN event of 1983.

Observations of late winter increases in condensation nuclei at high altitude are not new. We have detected these CN events every year since 1979 and have reported them and their possible causes in the literature (Hofmann and Rosen, 1982b; Rosen and Hofmann, 1983; Hofmann and Rosen, 1983d). What is remarkable about the 1983 event is its magnitude; however, we had predicted a larger than normal event on the basis of a theory involving the thermal nucleation of aerosol from volcanically derived sulfuric acid vapor in polar regions (Rosen and Hofmann, 1983). Briefly, this mechanism involves the sufficiently rapid cooling of air supersaturated with sulfuric acid vapor and is thus more favorable following large volcanic eruptions. The mechanism may be clarified by examining the relationship of the sulfuric acid vapor saturation curve and the ambient sulfuric acid vapor concentration in the stratosphere.

Figure 16 shows the mass mixing ratio of sulfuric acid vapor, as reported by Arnold and Bührke (1983), and as estimated from the aerosol growth rate discussed earlier. Also shown is the saturation mixing ratio for nominal mid-latitude stratospheric temperatures and an indication of the reduction due to a  $-10^{\circ}\text{C}$  temperature variation. In addition, aerosol mass mixing ratios are given, showing the increase of about a factor of 100 at 25 km, as compared to 1980, due to the eruption of El Chichón. Of importance here is the effect of the saturation mixing ratio curve

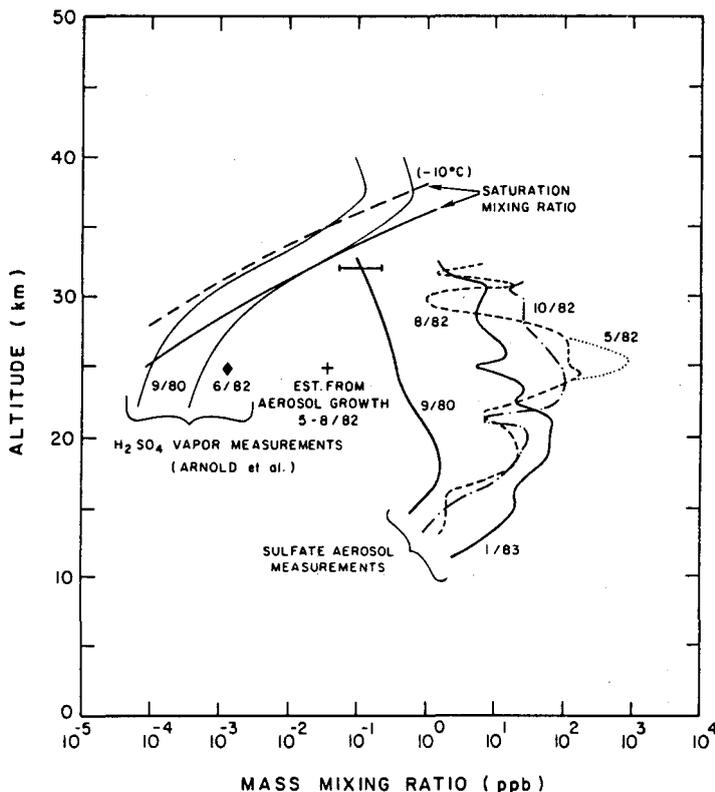


Fig. 16. Mass mixing ratio (parts per billion) profiles of aerosol and sulfuric acid vapor. The sulfuric acid saturation mixing ratio is also shown for standard midlatitude temperatures and for a reduction of  $10^{\circ}\text{C}$ .

as it is displaced due to large temperature variations. For example, a warming of about  $20^{\circ}\text{C}$  above normal could result in the evaporation of aerosol above about 30 km. Subsequent cooling would then result in recondensation in the 30 - 35 km region. The necessary temperature variations probably only occur in polar regions where stratospheric warming events occur in late winter which are occasionally sufficient to vaporize existing sulfuric acid aerosol with subsequent recondensation when the air parcel is transported to lower latitudes and cooled. The process is also aided by the natural transport of stratospheric gases and aerosol to polar regions during the winter.

Stratospheric warming episodes in the northern hemisphere are occasionally accompanied by a high pressure system pushing in over the Aleutian Islands, attempting to replace the winter polar low pressure system. This occurrence sets up a fortuitous situation for stratospheric observations within the United States as very high wind speeds result between the two systems bringing polar air rapidly down to our site of observation ( $41^{\circ}\text{N}$ ). An example of this is shown in Figure 17 where the U. S. Weather Service 10 mb pressure height contours of 1200Z, 27 January, 1983 are shown. This time corresponds approximately with the time when air sampled over Laramie on the morning of January 28 left the polar region. We note that the sampled event air originated in a very warm region ( $-15^{\circ}\text{C}$  at 10 mb,  $-30^{\circ}\text{C}$  at 30 mb) but ended up at about  $-51^{\circ}\text{C}$  at 14 mb (base of the event layer) over Laramie.

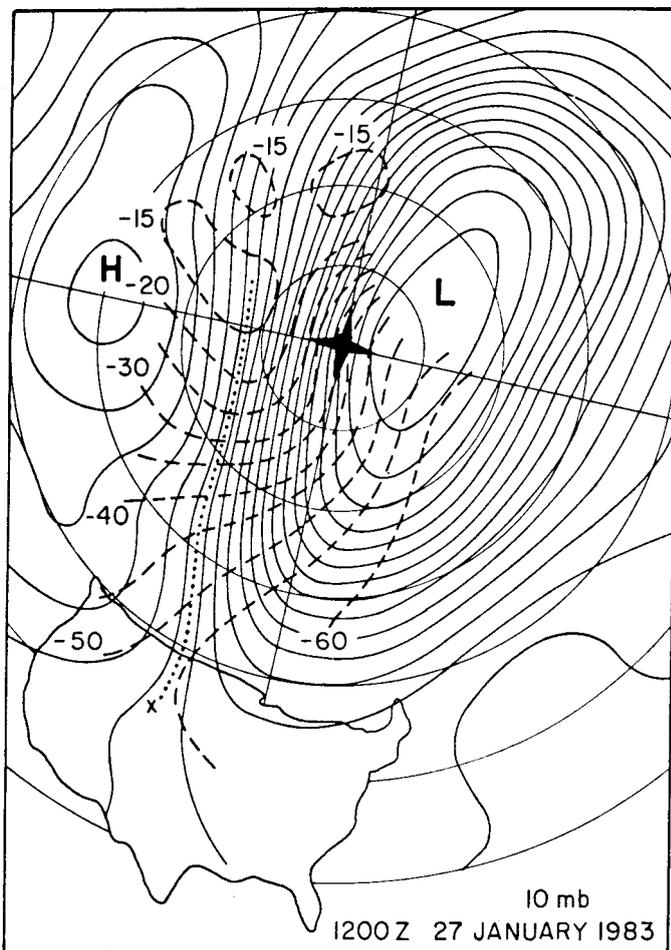


Fig. 17. The 10 mb pressure height map for 1200Z 27 January 1983. The dotted curve is the estimated trajectory of the air sample measured at Laramie on the morning of January 28.

In Figure 18 the temperature profile, as observed in the event layer at Laramie, and an estimated profile in the region of origin at 70 - 75°N 24 hours earlier are shown. The air parcel in question has been traced back in an approximate fashion using constant potential temperature in Figure 18. We find that the observed event layer, between 8 and 14 mb with a temperature between -49 and -51°C, had been in

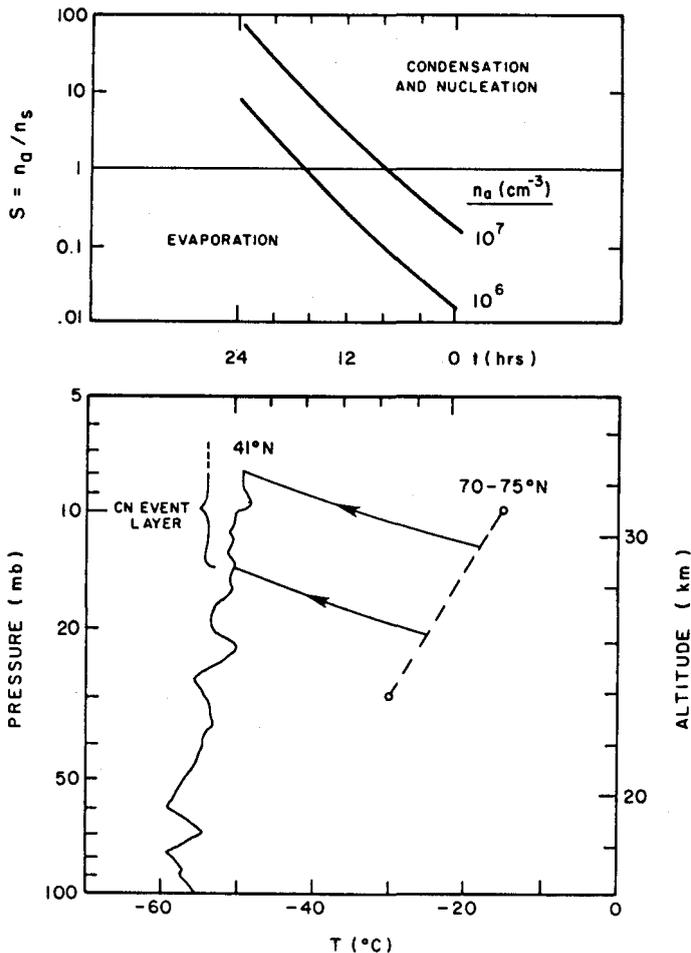


Fig. 18. The temperature profile as measured at Laramie on January 28, 1983, when the large increase of condensation nuclei was observed, and as estimated in the region of origin of the event layer 24 hours earlier. The smooth curves with arrows are constant potential temperature curves indicating the vertical trajectory and temperature history of the event air parcel for an isentropic displacement. The estimated sulfuric acid vapor saturation ratio ( $S$ ) for two assumed ambient vapor concentrations, as a function of time along the estimated trajectory, is also shown.

the polar region between 12.5 and 21 mb with a temperature between  $-18$  and  $-25^{\circ}\text{C}$  about 24 hours earlier. The latter temperatures are sufficiently high to have evaporated sulfuric acid aerosol which may have been in the region. During the subsequent transport to the latitude of Laramie, the air parcel underwent a cooling of about  $30^{\circ}\text{C}$  in about 24 hours. Rosen and Hofmann (1983) showed that vapor pressure equilibrium cannot be maintained by condensation on the aerosol which is normally present at 30 km for cooling rates faster than about  $0.5^{\circ}\text{C}$  per day. While the complete aerosol history (origin, etc.) of this air parcel is not known, this condition would have been met in this case even with 10 times as much aerosol as is normally present. Under such circumstances a very high degree of supersaturation may develop which could result in the nucleation of new droplets.

Also shown in Figure 18 is the estimated supersaturation ratio ( $S$  = the ratio of actual sulfuric acid vapor pressure to the saturation vapor pressure) versus time during the approximate transit from the polar region to the latitude of Laramie for sulfuric acid vapor concentrations of  $10^6$  and  $10^7$  molecules  $\text{cm}^{-3}$ , a likely range of values. Evaporation occurs for  $S < 1$  and condensation and/or nucleation occurs for  $S > 1$ . We see that initial evaporation followed by nucleation and condensation could have occurred to account for the new aerosol observed in the layer.

Whether the sulfuric acid vapor was derived from poleward transport of remnant El Chichón vapors or from the evaporation of El Chichón aerosol which had been transported into the polar region during the winter is difficult to determine. The 1982 event (Rosen and Hofmann, 1983) was about 50 times less intense compared to the 1983 event. The former, however, indicated a decrease in concentration of  $r \geq 0.15 \mu\text{m}$  aerosol coincident with the increase of  $r \geq 0.01 \mu\text{m}$  aerosol suggesting that the evaporation process had been operative. This was not the case for the 1983 event as can be seen in Figure 7. Although both the  $r \geq 0.15 \mu\text{m}$  and  $r \geq 0.25 \mu\text{m}$  data show a drop at the lower boundary of the  $r \geq 0.01 \mu\text{m}$  event layer, they show enhancements above this level in the event layer. The  $1 \mu\text{m}$  data showed a substantial reduction in aerosol concentration coincident with the event layer and it is possible that partial evaporation of these larger droplets was primarily responsible for the sulfuric acid vapor necessary for the nucleation of the new droplets. The  $1 \mu\text{m}$  aerosol concentration was about  $10^{-3} \text{cm}^{-3}$  just below the event layer and dropped to about  $10^{-5} \text{cm}^{-3}$  in the layer. A concentration of  $10^{-3} \text{cm}^{-3}$  of  $1 \mu\text{m}$  aerosol corresponds to a concentration of  $10^3 \text{cm}^{-3}$  of  $0.01 \mu\text{m}$  aerosol in terms of aerosol volume. Thus the observed concentration of  $r \geq 0.01 \mu\text{m}$  aerosol in the event layer probably can be accounted for through evaporation of existing aerosol. However, since prior history of the air parcel involved is not known, its original aerosol content cannot be accurately ascertained.

In terms of accounting for the new aerosol mass by preexisting vapor, an average aerosol radius of  $0.015 \mu\text{m}$  at a concentration of  $300 \text{cm}^{-3}$ , as observed in the event layer on February 1, 1983, amounts to a mass concentration of  $6.7 \times 10^{-3} \mu\text{g m}^{-3}$

or about  $3 \times 10^7$  sulfuric acid molecules  $\text{cm}^{-3}$  for a 75% sulfuric acid composition. Considering that dispersion as well as coagulation may have reduced the mass concentration from its initial value, this must be considered a lower limit so that a sulfuric acid vapor concentration as large as  $10^8 \text{ cm}^{-3}$  may be necessary to account for the event solely through the nucleation of preexisting vapor. It thus seems likely that aerosol evaporation played a major role.

On March 2, 1983 a second CN event was observed superimposed on the remnants of the January event. These data are shown in Figure 19. The new aerosol was observed in a layer between the altitudes of 31 and 34 km. Positive and negative ion density were also measured during this sounding and both indicated reductions of about 20% due to attachment to the excess aerosol in the region of the new layer. The latter observations are shown in Figure 20.

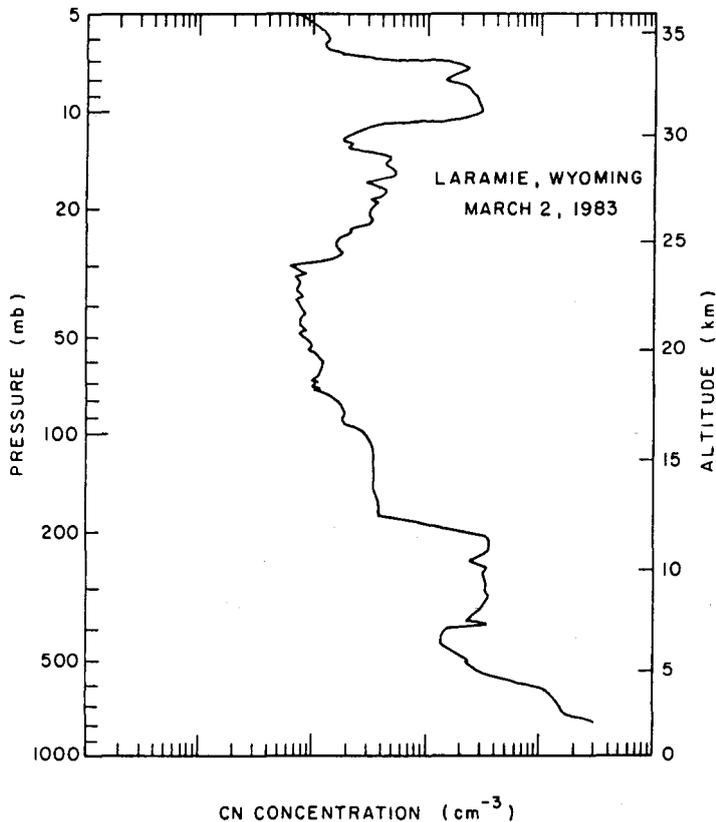


Fig. 19. CN ( $r \geq 0.01 \mu\text{m}$ ) profile measured at Laramie on March 2, 1983. Note the increase between about 31 and 34 km.

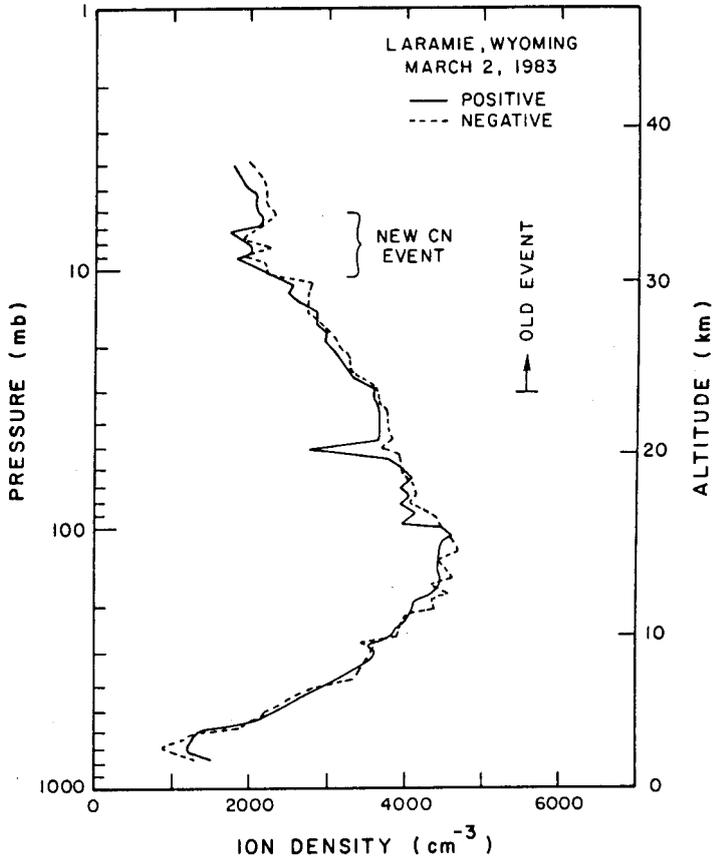


Fig. 20. Positive and negative ion density profiles measured on the same sounding as in Figure 19. Note the ion decrease due to aerosol attachment in the new layer.

The peak aerosol concentration of about  $300 \text{ cm}^{-3}$ , observed in the new event layer, suggested that it was probably about 5 days old, based on the coagulative time variations of the aerosol observed following the January event. Inspection of pressure height data revealed that a warm region was again present ( $-15^{\circ}\text{C}$  at 10 mb,  $-35^{\circ}\text{C}$  at 30 mb) approximately over the north pole 5 days earlier, and that crude trajectory estimates indicated that this air could have been over Laramie on March 2. The 1200Z 25 February, 1983 10 mb map is reproduced with an estimated trajectory in Figure 21. No similar warming events occurred in the intervening time between these events and there is no evidence for other CN increases. Thus it appears likely that the events are intimately associated with stratospheric warmings which are capable of evaporating existing aerosol thereby creating a high degree of sulfuric acid vapor supersaturation resulting in the subsequent recondensation of

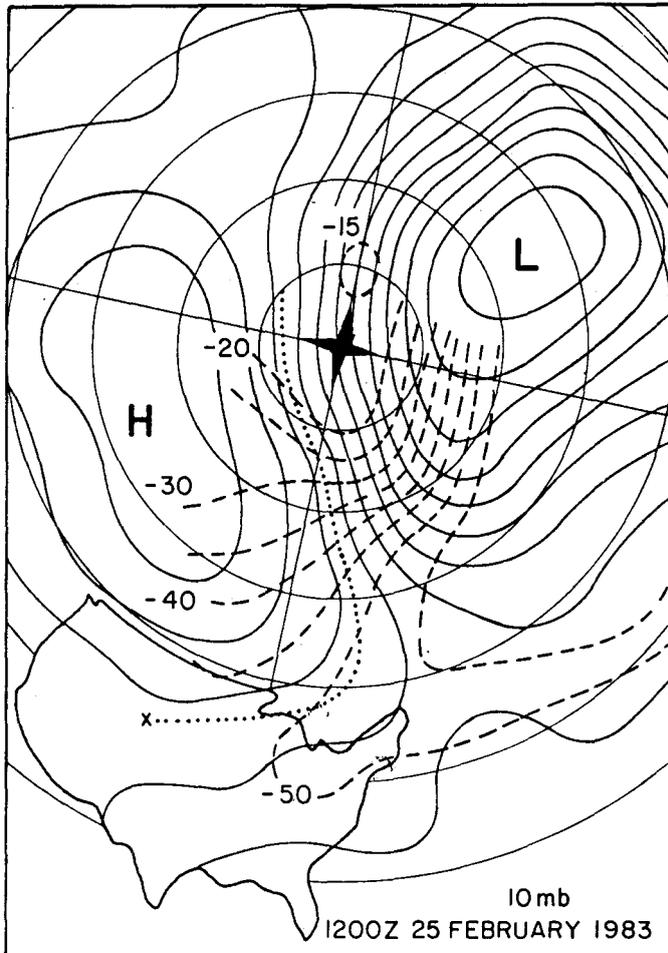


Fig. 21. The 10 mb pressure height map for 1200Z 25 February 1983. The dotted curve is the estimated trajectory of the air sample measured at Laramie on March 2.

small droplets. This in effect extends the lifetime of aerosol in this region of the atmosphere as gravitational sedimentation is essentially negligible for these small particles whereas a  $1 \mu\text{m}$  droplet will fall 1 km every 10 days at 25 km.

Figure 22 shows the  $r \geq 0.01 \mu\text{m}$  concentration in the event layers versus time. Also shown is the approximate expected temporal behavior for self coagulation of the new droplets and coagulation with the existing aerosol distribution. The initial time variation appears to resemble the expected coagulative reduction closely. At later times, a more complete analysis which takes into account the growing size distribution properly would be necessary.

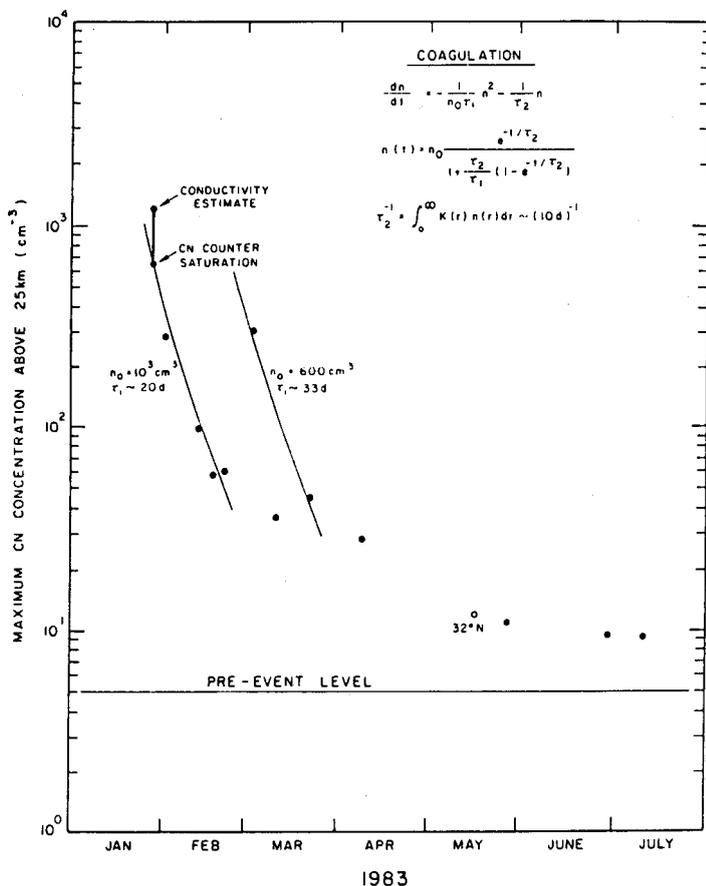


Fig. 22. Maximum CN ( $r \geq 0.01 \mu\text{m}$ ) concentration in the event layer at Laramie (solid circles) and in Texas (open circles) versus time. The smooth curves are approximate theoretical coagulation curves.

A measurement in Palestine, Texas ( $32^{\circ}\text{N}$ ) on May 16, 1983 (open circle in Figure 22) indicated results similar to the Laramie data so that the event remnants appear to have spread at least to this latitude. Thus, during volcanically active periods, these events apparently create a near global layer of small droplets at 30 km as a similar phenomenon is expected to occur during warmings in the Antarctic stratosphere during the corresponding season (August - October). Measurements in the Antarctic, to test this hypothesis, will be conducted in October 1983.

Figure 23 shows the  $r \geq 0.01 \mu\text{m}$  mixing ratio in the event layers (25 - 35 km) and at about 20 km as measured at Laramie since 1978. The latter region, except for the major aerosol nucleation episode that took place following the eruption of

El Chichón in 1982, is normally the point of minimum  $r \geq 0.01 \mu\text{m}$  aerosol concentration (see Figure 14) and is generally very stable. The annual occurrence of an enhancement in the 25 - 35 km region during the early portion of a year is evident. The increasing magnitude of the enhancements is probably associated with the increase in volcanic eruptions which caused measurable aerosol perturbations in the stratosphere (indicated in Figure 23). However, the event in 1979 occurred prior

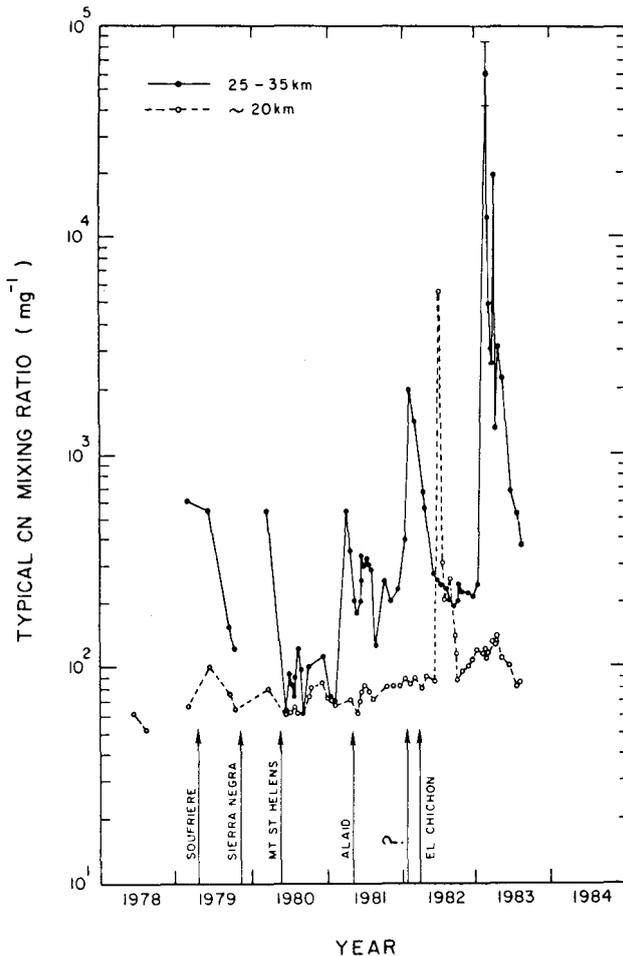


Fig. 23. CN ( $r \geq 0.01 \mu\text{m}$ ) mixing ratios versus time in the region of the events (25 - 35 km) and at 20 km as measured at Laramie. Times of major volcanic eruptions which perturbed the larger aerosol concentrations are indicated. An unidentified eruption in early 1982 is indicated by a question mark.

to the eruption of La Soufrière and after a period of about two years when stratospheric aerosol levels appeared to be at low background concentrations (Hofmann and Rosen, 1981). It thus appears that even under the latter conditions, sufficient aerosol is present at 30 km to provide condensable vapors during stratospheric

warming episodes. As has been indicated earlier, very little aerosol is necessary to account for the new, smaller aerosol associated with the events.

Of considerable interest in Figure 23 is the observation that the level of  $r \geq 0.01$   $\mu\text{m}$  aerosol present at 25 - 35 km following the initial rapid reduction due to coagulation (i.e., during the latter portion of the year), has increased by a factor of about 3 since 1980. Thus the event remnants appear to have created a pseudo-permanent layer of small aerosol in the 30 km region. These droplets, while unimportant in the total stratospheric aerosol mass distribution, could be important as they may serve as sites for further aerosol growth to larger, optically active aerosol under suitable conditions. In particular, a subsequent injection of sulfurous vapors to these altitudes by a large volcanic eruption would probably result in more numerous optically active aerosol at the present time as compared to several years ago. In addition, eruptions which occur early in the year may have a larger aerosol effect than those that occur later in the year because of the larger number of condensation nuclei present at that time.

In summary, very much has been learned about the effects of volcanic eruptions on the stratosphere in the last three years. The eruption of El Chichón played a major role by providing the opportunity to study a truly massive event. The large amount of material deposited in the stratosphere made the effects of this eruption quite obvious even to the untrained eye and especially to numerous remote sensing experiments which were not designed with the detection of volcanic effluents in mind. This has been very good for the science as many new techniques have been brought to bear and a number of very illuminating comparisons of different techniques have been possible. The unquestionable importance of such research, which has a direct bearing on climatic perturbations, cannot be overstressed. In the case of the authors' research program, and similarly with many others, if we had not been actively conducting the measurements before El Chichón and thus able to intensify study without serious perturbation following the eruption, little of the results reported here could have been obtained. The applicable time constant in the stratosphere is measured in years; thus, so also must the time constant of research programs involved in stratospheric phenomena be measured if they are to be successful.

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