# TEMPORAL VARIATIONS IN CHARACTERISTICS OF THE EL CHICHON STRATOSPHERIC CLOUD

R. L. CHUAN*
D. C. WOODS**

## RESUMEN

Durante el periodo comprendido desde abril hasta diciembre de 1982 se hicieron mediciones y muestreos *in situ* de la nube de la erupción de El Chichón, a 18 - 21 km de altitud, para examinar las características físicas y químicas de las partículas de aerosol, su distribución por tamaños, concentración de masa, morfología y composición elemental. Dentro del primer mes después de la erupción, en la distribución del aerosol por tamaños predominaban partículas magmáticas sólidas y líticas con diámetros aerodinámicos entre alrededor de 3 m$\mu$ y 20 m$\mu$. A principios de mayo de 1982 (un mes después de la erupción), la distribución por tamaños era trimodal, con fracciones significativas de la masa tanto en el tamaño medio (0.5 a 3 m$\mu$) como en la banda de tamaño grande ( > 3 m$\mu$). En el extremo superior de la banda de tamaño medio (alrededor de 1 a 3 m$\mu$), las partículas eran sólidas pero cubiertas de ácido sulfúrico, mientras que el extremo inferior de la banda estaba casi totalmente poblado por gotitas de ácido sulfúrico de alrededor de 0.5 a 1.0 m$\mu$ de diámetro. La banda de tamaño pequeño ( < 0.5 m$\mu$) consistía en gotitas de ácido muy fina. Hubo otros rasgos adicionales que aparecieron en varias ocasiones, que son poco usuales en aerosoles causados por erupciones. Entre ellos hay muestras colectadas en abril y mayo que presentan una banda casi monodispersa (de alrededor de 1 m$\mu$ a 3 m$\mu$), consistente en partículas halíticas, las cuales se cree que se formaron por la condensación de vapores de un domo salino abajo de El Chichón. A fines de julio de 1982, abundaron las partículas de óxido de cobre-zinc, formadas posiblemente por oxidación de vapores volatilizados del magma durante la erupción, y sus tamaños variaban desde > 20 m$\mu$ a tamaños submicrónicos. Entre julio y diciembre de 1982, en la banda de tamaños de < 0.2 m$\mu$ predominaban aglomeraciones de partículas carbonáceas, probablemente no relacionadas con la erupción sino posiblemente de origen meteorítico.

* *Brunswick Corporation, Costa Mesa, California 92626, U.S.A.*

** *NASA Langley Research Center, Hampton, Virginia 23665, U.S.A.*

## ABSTRACT

*In situ* measurements and sampling of the El Chichón eruption cloud, at 18 - 21 km altitude, were conducted over an extended period from April to December 1982, to examine the physical and chemical characteristics of the aerosol particles, their size distribution, mass concentration, morphology, and elemental composition. Within the first month after the eruption, the aerosol size distribution was dominated by solid magmatic and lithic particles, between about 3 $\mu$m and 20 $\mu$m aerodynamic diameter. In early May 1982 (1 month after the eruption), the size distribution was trimodal, with significant fractions of the mass in both the mid-size (0.5 to 3 $\mu$m) and the large-size (> 3 $\mu$m) bands. At the upper end of the mid-size band (about 1 to 3 $\mu$m), the particles were solid but mantled in sulfuric acid, while the lower end of the band was almost totally populated by sulfuric acid droplets about 0.5 to 1.0 $\mu$m diameter. The small-size band (<0.5 $\mu$m) consisted of very fine acid droplets. There were additional features appearing at various times which are unusual for eruption aerosols. Among them are samples collected in April and May which had a nearly monodisperse band (about 1 $\mu$m to 3 $\mu$m), consisting of halite particles, which are believed to have been formed by the condensation of vapors from a salt dome under El Chichón. In late July 1982, copper-zinc oxide particles, possibly formed by oxidation of vapors volatized from the magma during eruption, were abundant in sizes ranging from >20 $\mu$m to submicron sizes. Between July and December 1982, the <0.2 $\mu$m size band was dominated by clusters of carbonaceous particles, probably not related to the eruption but possibly of meteoritic origin.

## INTRODUCTION

A series of major volcanic eruptions of El Chichón (17.33$^{\circ}$N., 93.20$^{\circ}$W.), occurring on March 28, April 3, and April 4, 1982, produced large enhancements in the stratospheric aerosols by direct injection of particles and by formation of hydrated sulfuric acid droplets from sulfur dioxide injected in the gas phase. Since aerosol enhancements in the stratosphere such as these are thought to be a possible contributor to climate changes, through scattering and absorption of solar and terrestrial radiation, investigations were conducted to assess the optical and radiative properties of the aerosols. Airborne sampling experiments, using a U-2 research aircraft with a variety of sensors, were conducted to obtain data in the eruption cloud at selected times between mid-April and mid-December 1982. These experiments are described in the November 1982 issue of *Geophysical Research Letters* (vol. 10, No.11).

A quartz crystal microbalance cascade impactor (Chuan, 1975), which classifies the aerosol and measures their mass by size, and retains size-segregated samples for chemical and morphological analyses, was included among the sampling instruments on the U-2 aircraft. Results from the QCM measurements revealed that the aerosol particles in the eruption cloud were quite complex, ranging in size from larger than 20 $\mu$m to smaller than 0.05 $\mu$m, but the composition and particle type

tend to be size specific (Woods and Chuan, 1983). It was also noted that there was a possible intrusion of non-volcanic material, including very small carbonaceous particles. In this paper we present additional results from these measurements, and discuss observed changes in size distribution, chemical composition, and particle type, as they occurred over a 9-month period after the El Chichón eruptions.

*Sampling and Analysis Methods*

The measurements and sampling were obtained with a quartz-crystal microbalance (QCM) cascade impactor instrument mounted on a NASA U-2 research aircraft. The instrument samples ambient air at a rate of 3 liters per minute, and separates the aerosol particles into 10 size bands by means of aerodynamic-inertial impaction. The geometric, mean aerodynamic diameter* of particles collected on the impactor stages are approximately: >25, 20, 10, 4.5, 2.0, 0.86, 0.34, 0.14, 0.07, and 0.03 μm for stages 1 through 10, respectively. The exact values depend on altitude, which in our sampling flights varied from 18 to 21 km. The plates onto which the particles are impacted are piezoelectric quartz crystals whose resonant frequencies vary in proportion with the mass of material deposited on the surface. Thus, the mass of the aerosol particles deposited on each surface is measured directly by measuring the frequency of the collecting crystal. The 10 QCM impaction stages can thereby report, *in situ,* the aerosol mass concentration as a function of size. Furthermore, the particles collected on the crystals are retained so that post-flight analysis can be made of their morphology and elemental composition, by means of scanning electron microscopy (SEM), X-ray energy spectroscopy (XES) for identification of elements with atomic number of 11 and higher, and by Auger-electron spectroscopy (AED) for elements with atomic number lower than 11. The size of the crystal (about 1.3 cm diameter) makes it possible to place it directly in the SEM without the necessity of transferring the samples which, therefore, remain undisturbed from the time they are collected in the atmosphere.

* For purposes of describing airborne particles, the "aerodynamic diameter" is usually adopted. It is a convenient means of sizing irregularly-shaped particles of various mass-density, being defined as the diameter of an equivalent homogeneous sphere of density 1 g/cm$^3$, which experiences the same resistance moving through air as is experienced by the actual particle of interest. Thus, a highly irregularly-shaped particle with low bulk density (fluffy, spongy or flaky) would have an "aerodynamic diameter" considerably smaller than its largest geometric dimension.

The size fractionation process separates the total assembly of aerosol particles into distinct groups by aerodynamic size, which in the case of volcanic aerosols tend to relate to the chemical composition and formation processes (Woods and Chuan, 1983). Thus, solid lithic and magmatic particles tend to be found in the first four stages ($>3~\mu$m); lithic and magmatic particles, usually mantled in sulfuric acid, in stages 4 through 6 (between $\approx 0.8$ and 3 $\mu$m); most of the sulphuric acid in stages 6 and 7 (0.3 to 0.8 $\mu$m); and finally, small crystals and other particles formed by nucleation from the vapor phase, in the last three stages ($<0.2~\mu$m). Because of the high sensitivity of the QCM ($\approx 2$ ng), very little sample is needed to obtain an aerosol mass/size distribution (about 10 minutes sampling time in the background stratosphere). The total mass collected on a typical 6-hour flight is about 1 to 10 $\mu$g. It is, therefore, quite easy to analyze individual particles, since many of them are discretely dispersed over the collection surface.

*April-May Sampling*

On April 15, April 19, and May 5, 1982, spanning from 11 days to 1 month after the April 4 eruption, sampling flights were directed from Moffett Field, California ($\approx 37^{\circ}$N, 122$^{\circ}$W), to the vicinity of 22$^{\circ}$N, 111$^{\circ}$W off the coast of Baja California, where the edge of the eruption cloud was expected to be encountered. The U-2 aircraft's maximum ceiling of 21 km prevented sampling in the very massive aerosol layer with peak concentration near 25 km as observed by airborne lidar (Labitzke *et al.*, 1983; McCormick, EOS, 1982). Instead, *in situ* measurements were made between 18 and 21 km where lidar observations showed a much less massive layer peaking near 18 km and extending upward, and merging with the upper layer at about 21 km. The two plots in figure 1, from the April 15 and May 5, 1982 sampling flights, show the mass loadings to be substantially above background (on the order of a few tenths of 1 microgram per cubic meter), which indicates that the aircraft was indeed sampling in a heavily concentrated cloud. Also the mass loadings were higher at lower latitudes, which was generally the case for the early sampling flights. The difference between the two plots are probably due mainly to non-uniformity of the cloud, the relative positions of the aircraft in the cloud, and to some extent, the removal of large particles. The distribution of the normalized aerosol mass concentration by size, for the April 15 cloud sample in figure 2 (a), illustrates the dominance of large particles ($>3~\mu$m) 11 days after
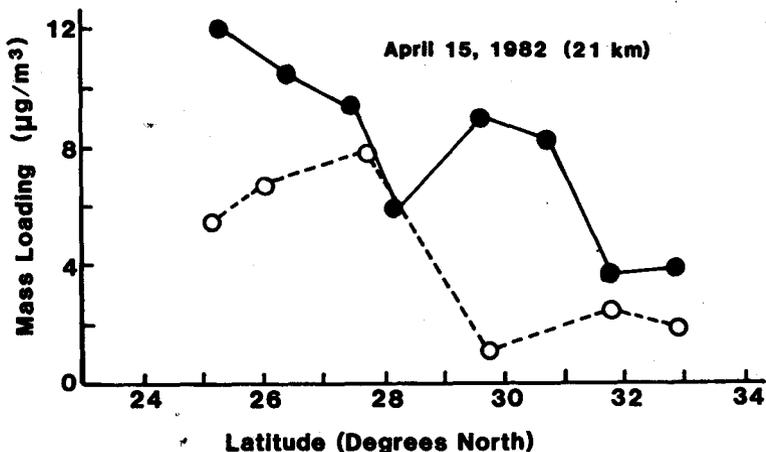
Fig. 1. Plots of aerosol mass loading as a function of latitude measured by the QCM at 21 km altitude on April 15 and May 5, 1982.
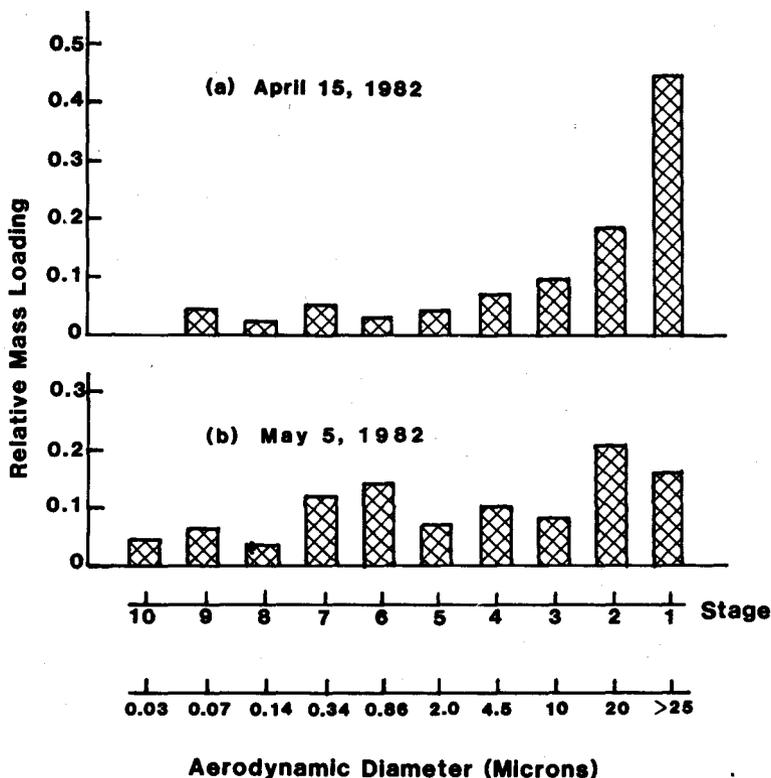


Fig. 2. Normalized size distribution histogram plots showing the mass loading in each QCM impactor stage relative to the total mass loading on (a) April 15, 1982, and (b) May 5, 1982. The bottom scale shows the geometric mean aerodynamic diameter for each impactor stage.

the eruption. By May 5, one month after the eruption, the size distribution had changed to a trimodal form (fig. 2(b)) with two submicron modes near 0.07 $\mu$m and 0.86 $\mu$m geometric mean diameter, and still a moderately strong mode near 20 $\mu$m, but representing a smaller percentage of the total aerosol mass. This decrease in the relative abundance of large particles is attributed to their removal by sedimentation.
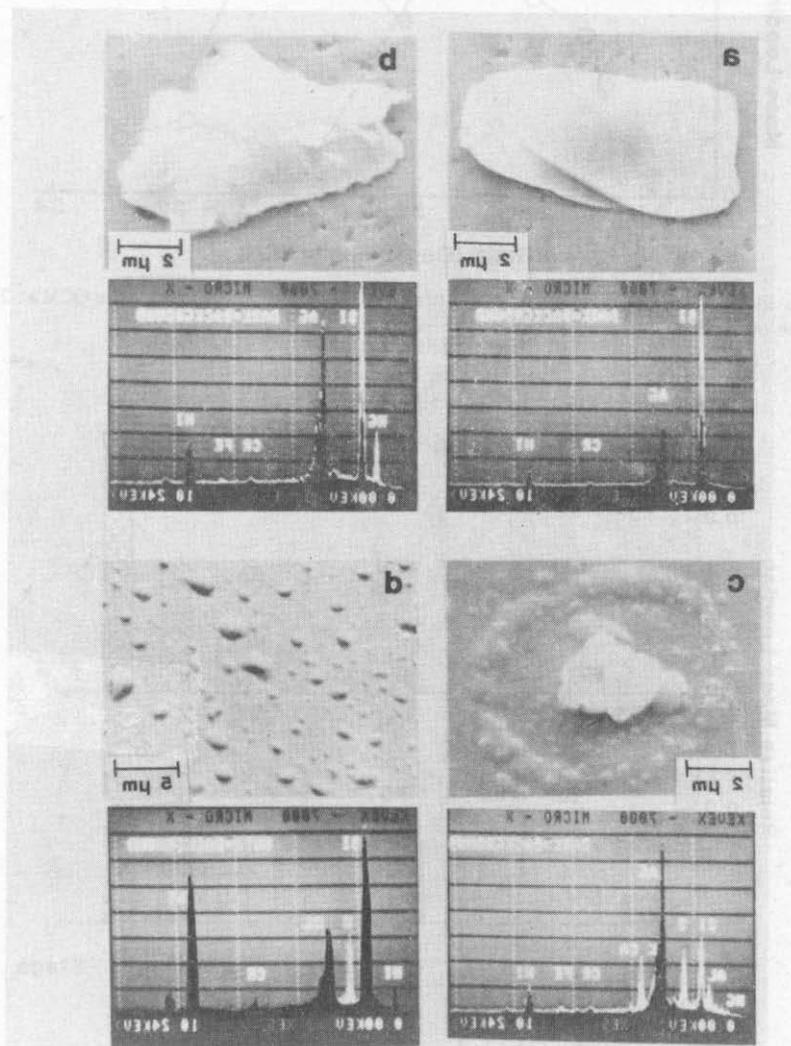


Fig. 3. SEM photographs showing examples of the various types of particles collected from El Chichón between 18 and 21 km, during the April-May 1982 period, and X-ray energy spectrum obtained from XES. (a) shows a large, glassy silicate particle collected in stage 1 on May 5, 1982, (b) a more irregular-shaped particle consisting of magnesium and silicon collected in stage 3 on May 5, 1982, (c) an acid-mantled particle consisting of magnesium, silicon, potassium, and calcium collected in stage 4 on April 15, 1982, and (d) sulfuric-acid droplets collected in stage 9 on April 15, 1982.

Examples of the different types of particles sampled during the April-May 1982 period are shown in figure 3,which includes X-ray spectra showing the elemental composition of the particles. Figure 3(a) shows a large dry silica particle measuring about 10 $\mu$m across its long dimension. Its X-ray spectrum shows only silicon.* Similarly, figure 3(b) shows a somewhat smaller dry particle with its X-ray spectrum showing magnesium and silicon (probably Mg-pyroxene). Figure 3(c) shows a typical acid-mantled, mid-size particle surrounded by a ring of acid, resulting from shedding from the particles upon impact against the collection surface. Both individual particles and larger coalesced sulfuric acid droplets resulting from multiple impactions are shown in figure 3(d). Other large, solid particles containing combinations of silicon, aluminum calcium, magnesium, and iron were also found among the samples (Woods and Chuan, 1983). Oberbeck *et al.* (1983) and Gooding *et al.* (1983), found large particles of similar composition in their samples. Oberbeck's largest particles were about 4.6 $\mu$m diameter, while Gooding found some particles as large as 40 $\mu$m. Both the solid and the acid particles had been observed in eruption plumes before, and are typical eruption products (Chuan *et al.*, 1981; Rose *et al.*, 1982).

In addition to the usual types of volcanic particles described above, the April 15 and May 5, 1982, samples had the unusual feature of a nearly mono-disperse band of halite particles, ranging between 1 and 3 $\mu$m in size. Figure 4 shows an SEM photograph of a small representative area ($\approx 4 \times 10^{-3}$ mm$^2$) of the collecting plate in impactor stage 5 ($\approx 2$ $\mu$m diameter) used on May 5. The individual halite agglomerates were uniformly spread over the impaction area in stage 5. The high magnification of one of these particles shows the cubic features of the sodium chloride particles. When these particles were analyzed by XES, their X-ray energy spectrum showed only sodium and chlorine. Their uniform size ($\approx 2$ $\mu$m mean diameter) suggests that they were formed by the nucleation of a vapor undergoing rapid cooling. The existence of a salt dome under El Chichón had been reported (SEAN Bulletin, 1982). It could well have been evaporated during the eruption.

---

* The dark area in the X-ray energy spectrum represents background from the substrate which includes silicon in the quartz crystal, the nickel electrode and small amounts of silver and chromium. Silicon in the sample is identified by the bright area above the dark area at the silicon line.

The halite vapor, rising rapidly with the eruption column, would be cooled by the mixing with ambient air, culminating in nucleation and the formation of nearly uniform crystals such as seen in figure 4. A rough estimate of the halite mass loading over a limited segment of the cloud, on May 5, is about 0.5 $\mu m/m^3$, or roughly 7 percent of the total aerosol mass loading.
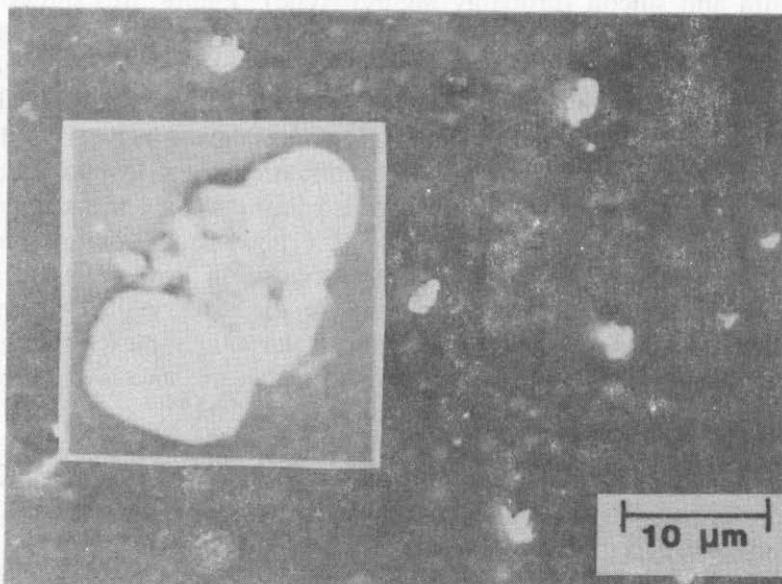


Fig. 4. SEM photographs with high and low magnification of halite particles collected on stages from the El Chichón stratospheric cloud on May 5, 1982.

Halite particles were not observed in samples obtained in July, November, and December 1982. One possible reason for this is that, by this time, the halite in the cloud had reacted with the ever-present sulfuric acid, forming sodium sulfate and releasing hydrogen chloride gas. This argument is supported by laboratory experiments in which sodium chloride aerosol was mixed with sulfuric acid aerosol collected on a plate, and observed by SEM and XES. The sample converted to sodium sulfate after about one month. In addition, when the April and May samples, which were first observed by SEM within a few days after collection, were reexamined in nearly November 1982, no halite was found. The particles had changed from the cubic shapes to a more crystalline-like appearance, showing sodium and sulfur but no chlorine in the XES. The halite samples are discussed in more detail in a separate report (in preparation).

*July Sampling*

The size distribution of the aerosol measured in July ($\approx$107 days after the April 4 eruption) was quite similar to that found in April, as may be seen by comparing the July 20 size distribution in figure 5 with the one for April 15 in figure 2. The heavy concentration of large particles in July cannot be explained by simple sedimentation from the upper layer centered near 25 km, since removal by sedimentation should have been completed in much less than 107 days. However, the residence times of these particles in the stratosphere may have been prolonged by their irregular shapes. Although the size distributions were similar, some new types of particles not seen in the earlier samples began to appear. One type, ranging in size from about 1 to 4 $\mu$m, con-
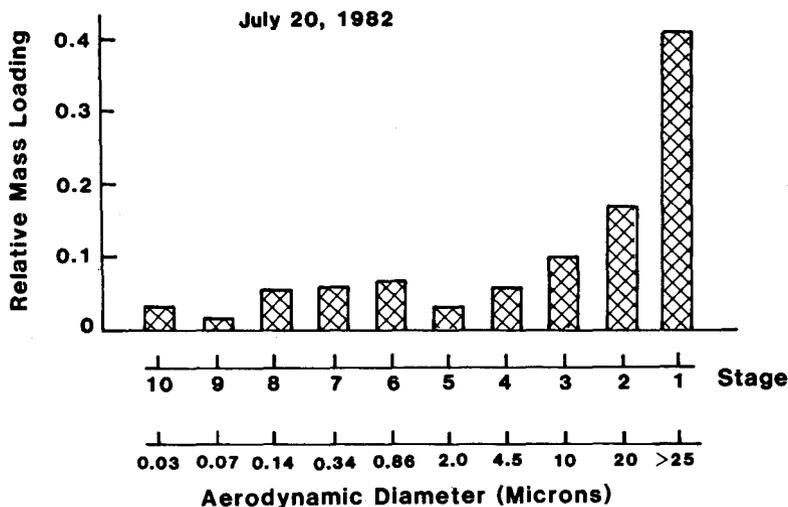


Fig. 5. Normalized size distribution histogram plot showing mass loading in each QCM impactor stage relative to the total mass loading on July 20, 1982.

tained iron and some traces of nickel (fig. 6(a) and 6(b)). These were not recognized as being of volcanic origin. Also not recognized as volcanic were much smaller carbonaceous particles collected in stages 9 and 10. These particles, which seem to coagulate into clusters (fig. 7) with the constituent particles being smaller than 0.1 $\mu$m, have been identified as elemental carbon by use of Auger spectroscopy (Woods and Chuan, 1983). The appearance of the iron, nickel, and carbon par-
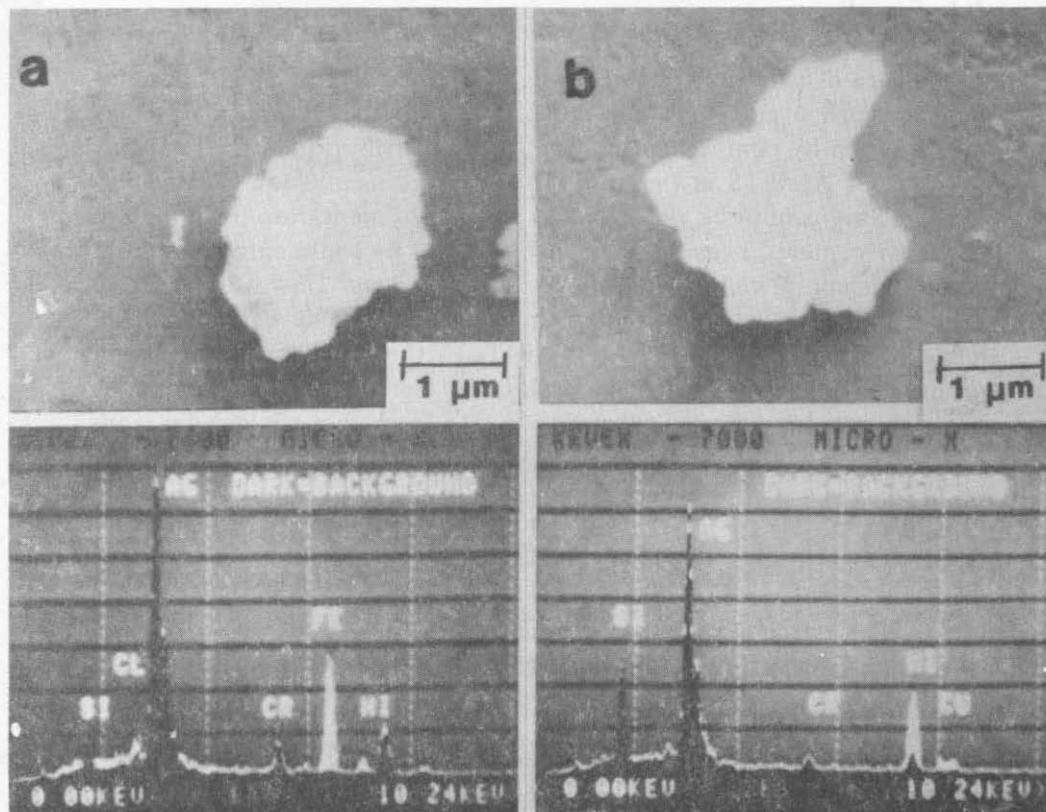
Fig. 6. SEM photographs of particles containing (a) iron on stage 1 and (b) nickel collected on stage 4 in the El Chichón cloud on July 20, 1982.

ticles are speculated to represent a possible intrusion of meteoritic debris into the lower stratosphere, which apparently persisted through the end of 1982, since similar particles were also observed in November and December.

Another unusual type of particle was observed in the July 23, 1982, samples, which consisted of Cu and Zn, with a Cu to Zn atomic abundance ratio of 2. These particles span a wide range of sizes, from agglomerates as large as 20 μm, to mid sizes and submicron sizes with acid coatings. Figure 8 shows one collected on stage 5 with an acid coating.
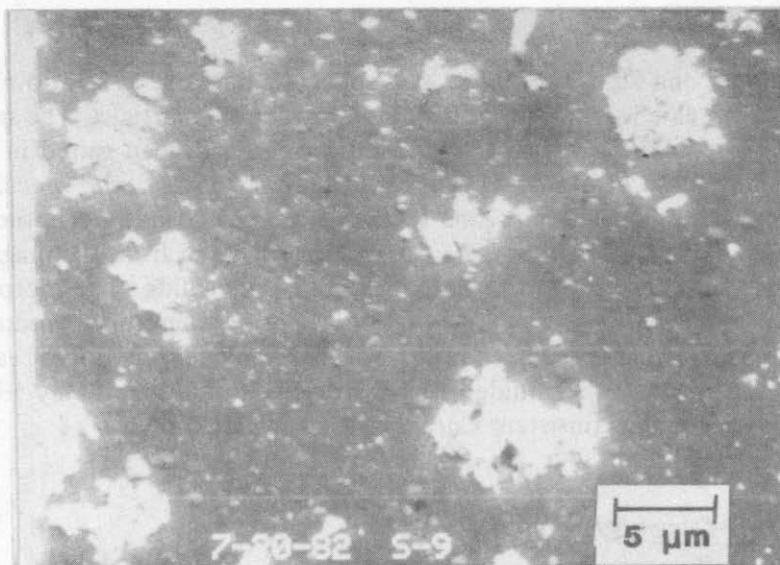
Fig. 7. SEM photographs showing clusters of carbonaceous particles on stage 9 collected between 18 and 21 km on July 20, 1982.
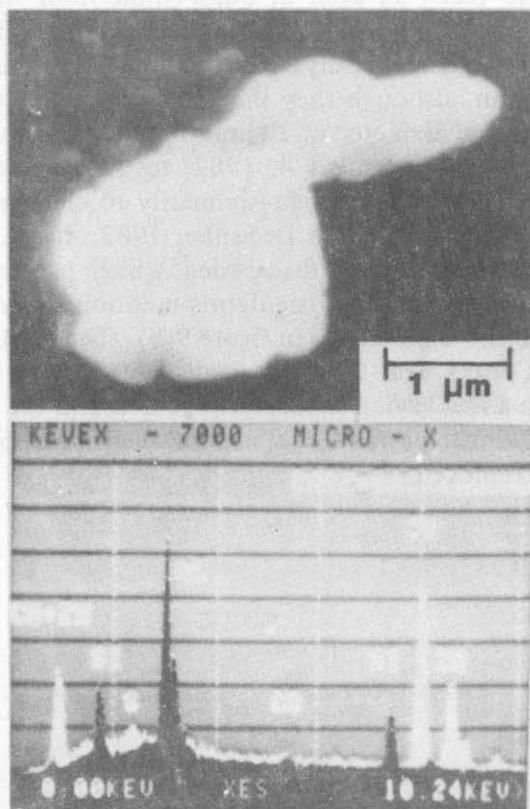


Fig. 8. SEM photograph showing copper-zinc particles collected on stage 5 in the El Chichón cloud on July 23, 1982.

The copper and zinc lines in the XES spectrum have a 2 to 1 ratio. The weak sulfur line is from the sulfuric acid coating the particle. The same type of particles, also with a Cu/Zn ratio of 2, had been found in the fumarolic plume of Mt. St. Helens by Rose *et al.* (1982), who speculate that they may be CuO and ZnO formed from the oxidation (in the atmosphere) of chloride vapors of Cu and Zn volatized from the magma, and subsequently condensing into CuO and ZnO solids. The morphology of these particles suggests that they are condensation products. These particles have also been observed in the "mystery cloud" of early 1982, and in one other unidentified volcanic cloud in April-May 1983. The reason for the consistent Cu/Zn ratio of 2 is unknown.

*November-December Sampling*

By the end of 1982, the El Chichón cloud at 18 - 20 km had apparently begun to reach an aged or quasi-equilibrium state in which the size distribution was no longer dominated by large solid particles. The largest particles (geometrically) collected in November and December were about 4 $\mu$m, although they impacted in stage 2 with a geometric, mean-aerodynamic diameter of 20 $\mu$m. Figure 9(a) shows a size distribution measured on November 4, 1982, to be trimodal, but the very small size mode at 0.03 $\mu$m is due primarily to clusters of carbon particles, which persisted through December 1982. If the contribution of these small carbon particles is disregarded, which, in effect, removes the presumed intrusion of meteoritic debris mentioned earlier, the size distribution becomes bimodal, as in figure 9(b). The dominant submicron mode, which peaks near 0.86 $\mu$m, is due, mainly, to the sulfuric acid droplets, with a few having solid, silicate cores, and the larger size mode is due to the silicate particles that are still suspended, but which should eventually be removed.
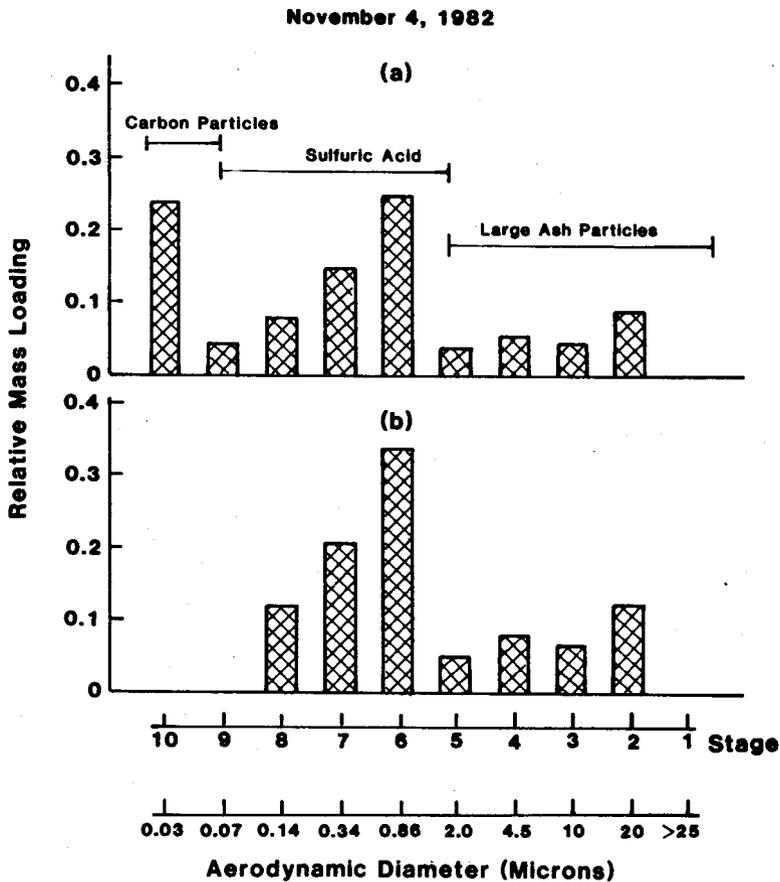
**November 4, 1982**



Fig. 9. Normalized size distribution histogram plots show the mass loading in each QCM impactor stage relative to the total mass loading on November 4, 1982. (a) shows the complete size spectrum and (b) shows the spectrum with stage 9 and 10 (where the carbon particles dominate) deleted.

## CONCLUSIONS

The large, solid, magmatic and lithic particles observed between 18 and 21 km accounted for a substantial fraction (60 to 80 percent) of the aerosol mass, during the first several months after the eruption. These large particles are likely to have contributed to the very high, lidar-backscatter values observed early after the El Chichon eruption. Since their residence time in the stratosphere is relatively short (particles > 4 $\mu$m were removed by November 1983), it is unlikely that they will

13

have any significant long-term effects on the radiation balance. However, since they were collected in the eruption cloud, their chemical composition and morphology may reveal information of geological significance that may not be obtained from ground tephra. In contrast to the large particles, the submicron-size sulfuric-acid droplets are expected to remain in the stratosphere for a much longer time ($>10^3$ days) before they are removed by sedimentation. They showed a relatively strong mode (well above background level) in the size distribution (similar to that observed in the 1980 Mt. St. Helens stratospheric plume), after most of the large solid particles had been removed. Their mean diameter of $\approx 0.86$ um suggests that they are efficient in scattering visible and near-infrared radiation. These acid particles, therefore, have the potential of playing an active role in climate perturbations. The intrusion of the presumably nonvolcanic carbon and iron particles, although small in quantity, adds additional potential for climate effects. Because of their small aerodynamic size ($<0.2$ $\mu$m), they should be expected to reside in the stratosphere at least as long as the sulfuric acid droplets. Since most forms of carbon and iron are highly absorbing, they are also likely to have some effect on the radiation balance. There tends to be a correlation between the appearance of these particles and the high absorption coefficients measured from samples collected by Clarke *et al.* (1983). However, since the source of these particles have not been defined, it is not known if they are widely distributed (horizontally or vertically) as the volcanic cloud. The magnitude of their effects would, therefore, depend on how localized they are.

Finally, the halite particles observed in the stratospheric cloud were apparently present for only a short time after the eruption (they were not observed after May 5, 1982), and, therefore, should not have a significant role in scattering and absorption of radiation. However, their presence should not go unnoticed, since they may serve as a source of C$\ell$ in the stratosphere.

## *BIBLIOGRAPHY*

CHUAN, R. L., 1975. Fine particles, aerosol generation, measurement, sampling, and analysis, B. Y. H. Liu, Ed. Academic Press, New York, 763.

CHUAN, R. L., D. C. WOODS, and M. P. McCORMICK, 1981. Characterization of aerosols from eruptions of Mt. St. Helens, *Science, 211,* 830-832.

CLARKE, A. D., R. J. CHARLSON, and J. A. OGREN, 1983. Stratospheric aerosol light absorption before and after El Chichón, *Geophys. Res. Lett., 10,* 1017-1020.

GOODING, J. L., U. S. CLANTON, E. M. GABEL, and J. L. WARREN, 1983. El Chichón volcanic ash in the stratosphere: particle abundances and size distributions after the 1982 eruption, *Geophys. Res. Lett., 10,* 1033-1036.

KNOLLENBERG, R. G., and D. HUFFMAN, 1983. Measurement of the aerosol size distributions in the El Chichón cloud, *Geophys. Res. Lett., 10,* 1025-1028.

LABITZKE, K. B., NAUJOKAT, and M. P. McCORMICK, 1983. Temperature effects on the stratosphere of the April 4, 1982 eruption of El Chichón, México, *Geophys. Res. Lett., 10,* 24-26.

McCORMICK, M. P., 1982. Ground-based and aircraft Lidar measurements and initial results from the SAM II Satellite, *EOS 63, 900,* (Abstr.).

OBERBECK, V. R., E. F. DANIELSEN, K. G. SNETSINGER, G. V. FERRY, W. FONG, and D. M. HAYNES, 1983. Effect of the eruption of El Chichón on stratospheric aerosol size and composition. *Geophys. Res. Lett., 10,* 1021-1024.

ROSE, W. I., Jr., R. L. CHUAN, and D. C. WOODS, 1982. Small particles in plumes of Mount St. Helens, *J. Geophys. Res., 87,* 4956-4962.

WOODS, D. C. and R. L. CHUAN, 1983. Size-specific composition of aerosols in the El Chichón volcanic cloud. *Geophys. Res. Lett., 10,* 1041-1044.