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17. After February, only the edge of the vortex was sampled by the ER-2, so details of the recovery of air deeper within the interior are unclear. However, on the basis of observations from February and the fact that temperatures remained well above those required for PSCs for the previous month (*3*), the abundance of ClO was probably no greater than observed in February and likely decreased to more normal abundances by early March with continued release of NO_x as the solar declination increased. A recent overview of satellite observations of ClO during this same time period by J. W. Waters *et al.* [*Nature* **362**, 597 (1993)] presents a complementary view.
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21. We are indebted to the pilots of the ER-2 and the Lockheed ground crew at the National Aeronautics and Space Administration (NASA) Ames Research Center, without whom this work would not have been possible. Special thanks are due to N. Allen, J. Demusz, N. Hazen, B. Heroux, T. Martin, E. Schomp, D. Spillane, E. Thompson, and E. Weinstock for logistical and engineering support throughout the mission. We are especially grateful for various forms of support provided by P. Hathaway, S. Gaines, S. Hipskind, J. Arvesen, E. Condon, V. Eliason, A. Roberts, and S. Wegener. L.M.A. acknowledges a NASA Global Change Research Graduate Fellowship. This work was supported by the NASA Upper Atmosphere Research Program, grant number NAG-1-1305, under the direction of M. Kurylo.

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Heterogeneous Reaction Probabilities, Solubilities, and the Physical State of Cold Volcanic Aerosols

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On 19 January 1992, heterogeneous loss of HNO_3, $ClNO_3$, and HCl was observed in part of the Mount Pinatubo volcanic cloud that had cooled as a result of forced ascent. Portions of the volcanic cloud froze near 191 kelvin. The reaction probability of $ClNO_3$ and the solubility of HNO_3 were close to laboratory measurements on liquid sulfuric acid. The magnitude of the observed loss of HCl suggests that it underwent a heterogeneous reaction. Such reactions could lead to substantial loss of HCl on background sulfuric acid particles and so be important for polar ozone loss.

Chemical reactions occurring on particles set the stage for O_3 loss in the global stratosphere. At most latitudes, sulfuric acid aerosols drive heterogeneous chemistry. At high latitudes, polar stratospheric clouds (PSCs) dominate heterogeneous chemistry because of their large surface areas. Sulfuric acid aerosols may also be important in the polar regions because chlorine-containing gases react on them at temperatures higher than those at which PSCs form (*1, 2*). However, there are several difficulties in assessing the role of sulfuric acid aerosols in polar chemistry.

Laboratory studies have shown that some heterogeneous reaction rates are greatly reduced on frozen sulfuric acid (*3*). Opposing theories suggest that sulfuric acid aerosols freeze either near 205 K (*4*), before significant heterogeneous conversion of chlorine into ozone reactive forms, or at about 190 K (*5*), allowing conversions to occur in the polar stratosphere. Reaction rates and solubilities also vary significantly with particle composition (*3, 6–8*). Because the minor components of stratospheric particulates are not known, reaction rates measured on laboratory analogs have uncertain applicability to the stratosphere. Unfortunately, background sulfuric acid aerosols have a limited abundance so that heterogeneous reactions involving chlorine-containing gases occur too slowly to be observed easily in the atmosphere.

Aerosols from the Mount Pinatubo eruption have the same composition as the background sulfuric acid aerosols, which may originate from smaller volcanic eruptions. However, the Pinatubo aerosols have enough mass to impact clearly the chlorine and nitrogen chemistry of the stratosphere. Observations from the National Aeronautics and Space Administration's (NASA's) DC-8 aircraft allow us to infer the physical state, heterogeneous reaction probabilities, and solubilities of cold volcanic aerosols.

The heterogeneous reaction probability γ is the fraction of molecules hitting a particle that irreversibly react either on the surface of or within the particle. The temporally and vertically averaged γ_a equals

$$4\ln(C_o/C)/(svt) \qquad (1)$$

where C_o is the initial column concentration of the gas in the altitude region of the volcanic cloud, C is the concentration after exposure to the particle surface for a time t, and v is the thermal velocity of the gas molecules. The particle surface area per unit volume is found from $s = S/\ell$, where S is the total surface area of particles per unit area of vertical column and ℓ is the vertical thickness of the cloud. For soluble gases, the vertically averaged effective Henry's

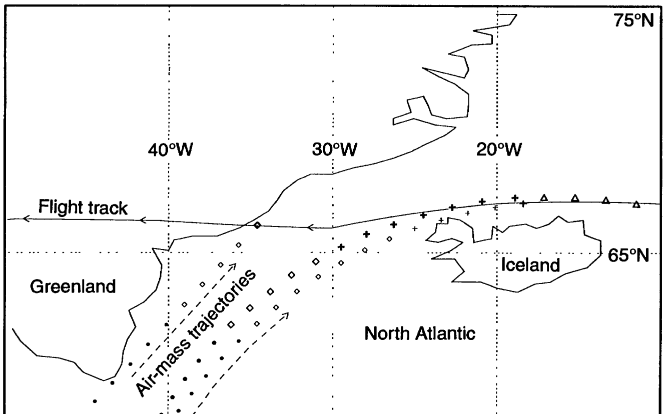

Fig. 1. Details of selected air mass trajectories ending at longitudes of 34.6°W, 18.4°W, and 11.5°W on the DC-8 flight track of 19 January 1992. The trajectories, which are on the 440 K potential temperature surface, reach a pressure of 60 mbar and a pressure altitude of 19.5 km near Iceland. Symbols show the hourly progression of the calculated W of the sulfuric acid in the volcanic cloud, which declined because of dropping temperatures: triangles, $W < 50\%$ and $T < 195$ K; crosses, $50\% < W < 55\%$ and $195\text{ K} < T < 198.5$ K; diamonds, $55\% < W < 60\%$ and $198.5\text{ K} < T < 203$ K; circles, $W > 60\%$ and $T > 203$ K.

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Law constant H_a^*, which is the ratio of the solubility of the gas to the vapor pressure of the gas, is (*7, 9*)

$$3 \ln (C_o/C)/(sRTr) \qquad (2)$$

where R is the gas constant, T is the temperature, and r is the particle radius.

Our observations are from the 19 January 1992 flight of NASA's DC-8 aircraft from Stavanger, Norway, to Bangor, Maine. At this time, an anticyclonic ridge covered the Atlantic Ocean from Norway to Iceland. The ridge forced the tropopause upward and pushed the Arctic stratospheric vortex poleward in the general vicinity of Iceland. Air mass trajectories, which we calculated from National Meteorological Center (NMC) analyses, indicate that the air above the DC-8 near Iceland had originated several days earlier in middle latitudes. This air moved northeastward between Greenland and Iceland and then eastward over Iceland as it ascended over the lifted tropopause and cooled (Fig. 1). As the DC-8 flew from 10°W to 35°W longitude, it encountered air that had spent progressively less time exposed to low temperatures. Volcanic debris was present above the aircraft between these longitudes (Fig. 2).

The volcanic cloud thickness was 8 to 9 km (Fig. 3), with the cloud top altitude measured by lidar (Fig. 2). The cloud base altitude was the tropopause altitude between 11.5°W and 18.4°W and the aircraft altitude at 34.6°W longitude where the DC-8 flew in the lower stratosphere inside the volcanic cloud (Fig. 3). The particle surface area (Fig. 3) is proportional to the aerosol optical depth. The constant of proportionality and r (Fig. 3) were obtained from the wavelength dependence of the optical depth (*10*). We find that s was 18 μm^2 cm^{-3}. The lidar backscatter (Fig. 2) suggests that s varied over altitude by a factor of about 2 from this mean value (*11*). The thermal velocity of a gas is found from its molecular weight and the temperature. For $ClNO_3$ at 195 K, v = 2.05×10^4 cm s^{-1}.

The exposure time is the most difficult parameter in Eq. 1 to specify. The trajectories (Fig. 1) show that as the aircraft flew westward, the air parcels sampled had spent progressively smaller amounts of time at low temperatures. Column abundances of HNO_3 and $ClNO_3$ (Fig. 4) at the most westward longitude (34.6°W) on 19 January were similar to values observed well outside the Arctic vortex on 14 January 1992 (*12*) (HCl at 34.6°W was different from HCl at other high-latitude, extra-vortex locations). Therefore, we adopt the conditions at 34.6°W as our starting point.

Laboratory data show that the reaction rate of $ClNO_3$ on sulfuric acid, as well as the solubilities of HCl and HNO_3 in sulfuric acid, increases rapidly with declining weight percentage concentration of the sulfuric acid, W (*3, 6–8*). Calculations (*13*) using a water vapor mixing ratio of 5 parts per million by volume (ppmv) from our column water vapor measurements and temperatures from the NMC data set show that the vertical average W above the aircraft was about 60% (Fig. 3) at 34.6°W. At the altitudes with lowest temperatures, W had been below 60% for only a few hours (Fig. 1). We calculated W along a set of trajectories ending at the times of the DC-8 passage and at the locations where column chemistry measurements were made (*14*). We defined t as the time during which W was less than 60% along these trajectories (Fig. 3).

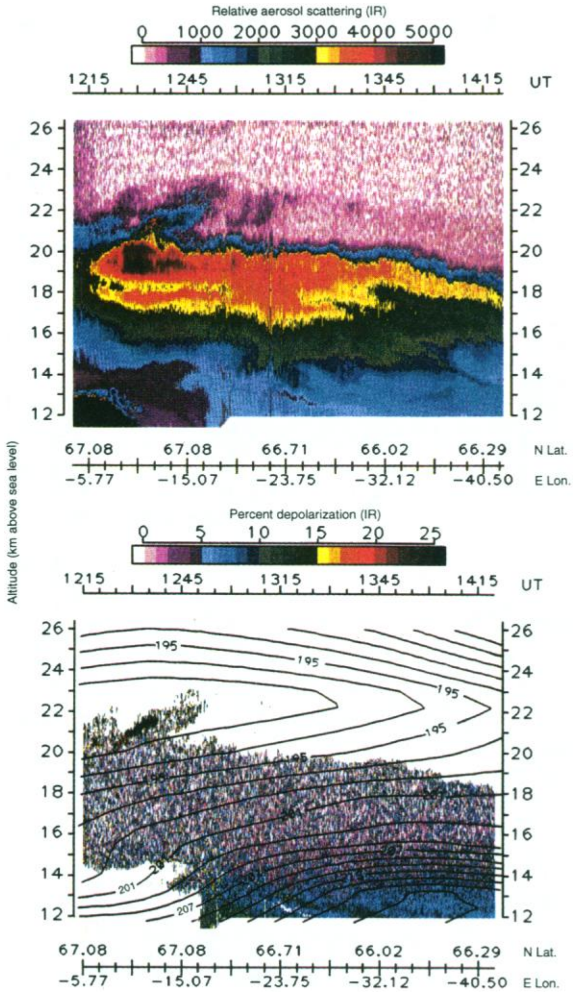

Fig. 2. (**Top**) The lidar backscatter, which is roughly proportional to the surface area of the particles. Volcanic material is present in significant quantities at relative scattering values greater than 1000. The time (universal time) of the observations is given along the top of the figure. (**Bottom**) The aerosol lidar depolarization ratio with superimposed temperature contours from the NMC data set. Significant lidar depolarization occurs below about 14 km because of volcanic ash particles and near 21 km at temperatures below about 191 K. Latitude (Lat.) and longitude (Lon.) of the aircraft are given in degrees along the bottom of the figure.

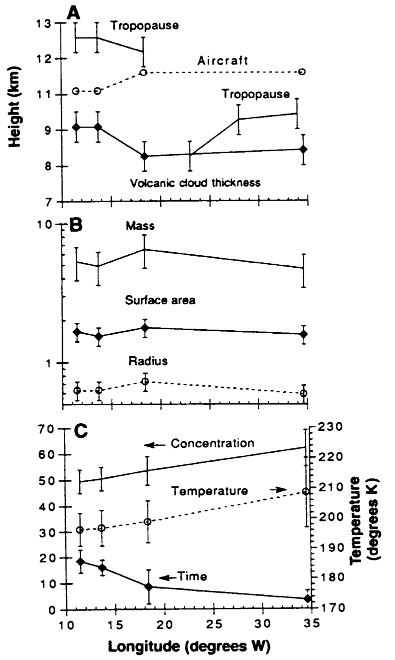

Fig. 3. (**A**) The aircraft altitude, tropopause altitude, and thickness of the volcanic cloud. (**B**) The aerosol column mass (micrograms per square centimeter), column surface area (square micrometers per square centimeter × 10^7), and particle radius (micrometers). (**C**) The concentration (percent by weight) and temperature (degrees kelvin) vertical average above the aircraft as well as the time (hours) spent on trajectories with W < 60%. Error bars denote extreme values over the altitude region of the volcanic cloud.

Because of the observational constraints, γ_a is defined to be the average value during the time since W dropped below 60%. Therefore, γ_a varies with the trajectory. To compare γ_a with laboratory values of γ measured with temperature and W held constant, we averaged the laboratory data along the trajectories. Although H_a^* does not depend on t, allowance must still be made in comparisons with laboratory data for the vertical gradients of T and W that occurred in our observations.

The fractions of HNO_3, HCl, and $ClNO_3$ remaining in the air parcels after t are given by $C/C_o = 1 - N/fM_o$, on the assumption that concentrations changed only within the volcanic cloud. We used standard mid-latitude vertical profiles to determine f (Fig. 4), the portion of the unperturbed column that was within the altitude range covered by the cloud (*15*). The relation $N = M_o - M(HF_o/HF)$ is the difference between the unperturbed, M_o, and perturbed, M, column concentrations obtained with a mid-infrared spectrometer (*15*). We identified the column measurements at 34.6°W as M_o, except for HCl. The value of M is the column concentration measured at the other longitudes (Fig. 4). The HF column content at the two locations is used to scale M to compensate approximately for the effects of vertical motions on the column concentrations.

The HF column content, usually a good indicator of vertical motion (*15*), was typical of air outside the vortex or near its edge throughout the region between 11°W and 35°W longitude, increasing by 16% over this range (Fig. 4). The impact of vertical motions on the column concentrations depends on the vertical distribution of the species being considered. The HF scaling cannot exactly compensate for the effects of vertical motions on all of the species concentrations. For example, the O_3 column increased by about 20% between 11.5°W and 34.6°W, as opposed to 16% for HF. Nevertheless, the HF scaling should provide a good first-order estimate for the dynamical contribution to the column concentration changes.

In Fig. 4, $x = Nm/AM_a$, the possible vertical average mass mixing ratio of condensed gases in the column of aerosol above the aircraft is illustrated. Here A is Avagadro's number, and m is the molecular weight of the gas. The aerosol mass M_a was determined from the optical depth measurements for a density of 1.5 g cm^{-3} (Fig. 3). The observed loss of 50% of the HNO_3 between 34°W and 11.5°W, for instance, indicates that 13% of the aerosol column mass is composed of HNO_3 at 11.5°W.

We have assumed that the cloud above the DC-8 was composed of volcanic sulfuric acid particles. However, at low temperatures ice clouds or nitric acid trihydrate clouds (NATs) can form. The optical depth along the DC-8 route between Iceland and Greenland did not change substantially, suggesting that significant condensation of ice did not occur. At no time did NMC temperatures along the trajectories, temperatures determined to altitudes of 18 km with the DC-8 microwave temperature profiler, or temperatures measured from a sonde launched from Keflavik, Iceland, within the time period of our passage reach the ice frost point for 5 ppmv of water. It was not cold enough at 34°W or 18°W for NAT to form if the HNO_3 mixing ratio had been 10 parts per billion by volume. At 11.5°W and 13.7°W, the NAT existence region extends into the volcanic cloud but also reaches higher altitudes where only the scattering due to background sulfuric acid particles was observed. The condensed HNO_3 is at most 13% of the aerosol mass, and the amount of volcanic material present is simply too great for NAT to form. For these reasons, we believe the observed clouds are cold sulfuric acid solutions but contain significant amounts of dissolved HNO_3 at the lowest temperatures. In the frozen portion of the cloud the crystalline material may consist of intermixed grains of NAT and sulfuric acid hydrates.

The physical state of the particles was determined from lidar depolarization observations (Fig. 2). Below about 14 km, depolarization of about 10% or less was observed throughout the Northern Hemisphere in January because a small number of volcanic ash particles lingered at these altitudes. On 19 January a region of high depolarization occurred between 20 and 22 km over Iceland at temperatures of about 190 K (Fig. 2). Because frozen volcanic aerosols are large enough to depolarize the lidar beam (*16*), we conclude that the freezing of these particles, which contained significant amounts of HNO_3, occurred near 190 K. This conclusion is in agreement with theories that address the freezing of sulfuric acid in a dilute water solution (*5*). Air with temperatures between 193 and 205 K and with synoptic-scale cooling rates of about 1 to 2 K per hour was not observed to have

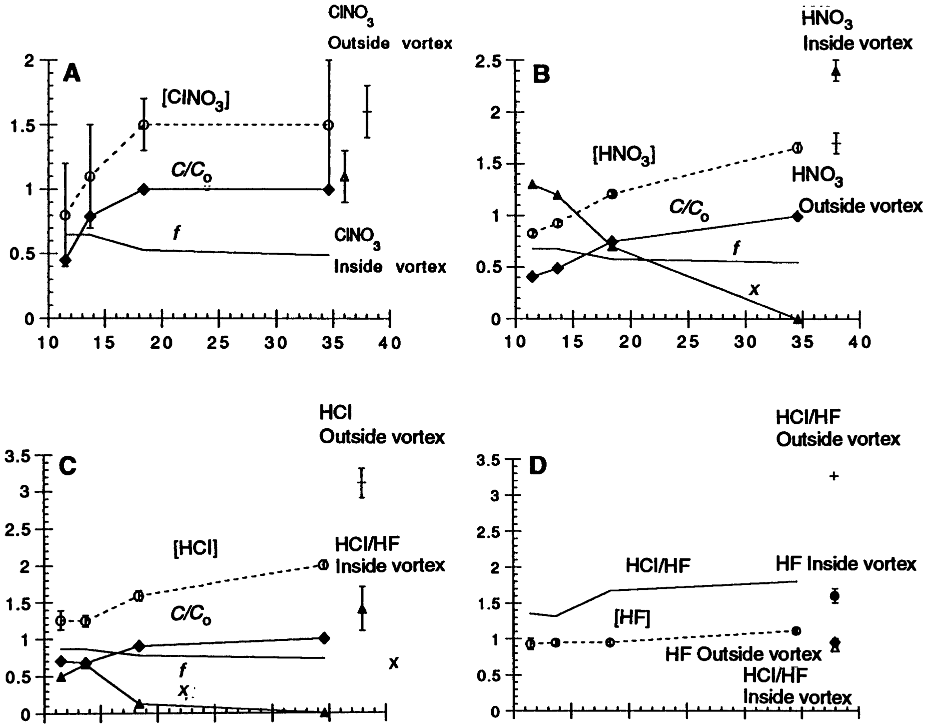

Fig. 4. (**A**) The column concentrations of $ClNO_3$ ($\times 10^{15}$ per square centimeter) on 19 January, C/C_o, the ratio of the concentration within the altitude range of the volcanic cloud at the longitude plotted to that at 34.6°W, and the fraction f that lies within the altitude range of the volcanic cloud. Also shown are typical concentrations inside and outside of the vortex determined from observations on other days. (**B** and **C**) Similar information for HNO_3 and HCl, as well as the mass fraction of gas that could be dissolved in the particles [x, percent × 0.1 in (B) and percent in (C)]. Column concentrations are $\times 10^{16}$ per square centimeter in (B) and $\times 10^{15}$ per square centimeter in (C). For HCl, the values of f, x, and C/C_o apply to case 2. (**D**) The ratio of HCl/HF and the column concentration of HF ($\times 10^{15}$ per square centimeter). Also shown are typical values of these quantities inside and outside of the vortex.

depolarization in excess of that seen in warmer air, in conflict with other theories of sulfuric acid freezing (*3*).

Using Eq. 1, we find the averaged heterogeneous reaction efficiency of $ClNO_3$ along our trajectories (Table 1). The uncertainty in our results is at least a factor of 2 because of possible errors in the surface area, the amount of $ClNO_3$ present at the altitudes of the volcanic cloud, and the time during which the reactions occurred. Only about 25% of the $ClNO_3$ loss at 11.5°W could have occurred in the frozen portion of the volcanic cloud because of its small vertical extent. The volcanic cloud contained an appreciable amount of HNO_3, and no laboratory measurements of the $ClNO_3$ reaction efficiencies are available on ternary solutions. However, our data are similar in magnitude to laboratory data for the reaction of $ClNO_3$ with water on pure sulfuric acid solutions (Table 1). To compare our values with laboratory data, we averaged the laboratory values of γ along the trajectories using the relation observed in the laboratory between W and γ (*3*).

Nitric acid is soluble in sulfuric acid. No change in HNO_3 was observed at 34.6°W relative to typical mid-latitude values, consistent with laboratory measurements of low solubility of HNO_3 in 58% sulfuric acid (*8*). At other longitudes, HNO_3 concentrations were lower than typical mid-latitude values, presumably because the HNO_3 had dissolved in the cold sulfuric acid. Only about 13% of the HNO_3 lost at 11.5°W could have been in the frozen portion of the volcanic cloud because of its limited vertical extent. We used Eq. 2 to determine values of H_a^* for HNO_3 (Table 1), which are a factor of 3 to 5 higher than laboratory data, a difference that may be close to the uncertainty of our data set (*17*). The uncertainty in our H_a^* is at least a factor of 2 because of possible errors in the surface area, r, and amount of HNO_3 in the altitude range of the volcanic cloud. An increase in H^* by a factor of 3 occurs for a 2 K temperature decline (*17*). Such a temperature difference between actual and NMC temperatures is possible and may account for much of the difference between the observed and laboratory values of H^*.

Unlike the other gases we studied, about 30% of the HCl column had been removed at 34.6°W, relative to typical mid-latitude values. The HCl/HF ratio, an indicator of the chemical removal of HCl, was much lower between 11°W and 34°W than is typical outside the vortex (Fig. 4). There are two possible explanations for the behavior of HCl. Essentially all of the HCl in the altitude region of the volcanic cloud may have been lost during the event observed on 19 January 1992 before the air parcel's arrival at 34°W. We refer to this possibility as case 1, for which M_o is taken to be the typical mid-latitude value for the column concentration of HCl. Alternatively, in case 2 about 30% of the HCl was lost in events occurring before 19 January, but continuing losses occurred on that day. In case 2, we assume that M_o is the column concentration of HCl at 34.6°W. It is unlikely that an earlier processing event occurred in the altitude region of the volcanic cloud because the trajectories in that altitude region diverge. The air at 34°W originated a few days before 19 January over northern Alaska, but the air at the other longitudes originated over the middle latitudes of the continental United States. Heterogeneous processing in the volcanic cloud region would have to have been widespread over the Northern Hemisphere to account for the 19 January observations, but such widespread processing was not observed on numerous flights of the DC-8 in January, February, and March of 1992. In contrast, trajectories at altitudes above the volcanic cloud suggest a common origin for that air, namely the edge of the Arctic vortex, where processing is plausible. We derived a value of f for case 2 on the assumption that the previous processing occurred above the volcanic cloud.

Table 1. Inferred reaction probabilities and solubilities.

Parameter	Location		
	67°N 11.5°W	67.1°N 13.7°W	67°N 18.4°W
$ClNO_3$			
γ_a	10^{-2}	4×10^{-3}	
Lab. γ†	7×10^{-3} (4, 14)	6×10^{-3} (3, 12)	
Lab. conc.†	54% (49, 57)	55% (49, 58)	
HNO_3			
H_a^*	14×10^9	11×10^9	4×10^9
Lab. H^*‡	3×10^9 (0.4, 9)	2×10^9 (0.2, 8)	1.2×10^9 (0.07, 4)
Lab. conc.‡	46%	47%	48%
HCl (case 2)			
H_a^*	5×10^9	6×10^9	1.5×10^9
γ	3×10^{-3}	4×10^{-3}	2×10^{-3}

†Vertical average along trajectories, with extreme values over altitude given in parentheses (*3*). Laboratory (Lab.) concentrations (conc.) of sulfuric acid were averaged with Lab. γ as the weighting factor. ‡Vertical average, with extreme values over altitude given in parentheses (*17*). Laboratory concentrations were averaged with H^* as the weighting factor. Values for H^* and H_a^* are in moles per liter·atmosphere.

Henry's law coefficients for HCl in sulfuric acid for case 2 (Table 1) are three to five orders of magnitude higher than those found in the laboratory studies (*17*). We cannot derive an H^* for case 1 because all of the HCl in the volcanic cloud has been removed from the gas phase in that case. However, the mass of HCl potentially dissolved in the volcanic aerosol is even larger in case 1 than in case 2, indicating a larger value of H^* for case 1. The most likely explanation of the vast difference between the values from our observations and the laboratory solubility data is that HCl undergoes heterogeneous reactions on volcanic particles.

For case 2, it is possible that HCl reacted with $ClNO_3$ on volcanic aerosols because nearly equal numbers of HCl and $ClNO_3$ molecules were lost. At most about 30% of the HCl might have been lost on the frozen portions of the volcanic cloud at 11.5°W. Laboratory data show that the reaction of HCl and $ClNO_3$ on sulfuric acid solutions is not important (*3*), but cold volcanic aerosols are not pure sulfuric acid solutions and do contain dissolved HNO_3.

Case 1 is not easily explained by a reaction between HCl and $ClNO_3$ because we observed no measurable loss of $ClNO_3$ at 34.6°W or at 18.4°W. If $ClNO_3$ reacted with HCl in case 1, $ClNO_3$ must have been regenerated so rapidly that its loss was not apparent. However, simulations of similar events on PSCs show that the recovery of $ClNO_3$ requires days, not a few hours as would be needed to explain our observations (*18*). Hydrochloric acid could react with several other substances on sulfuric acid surfaces including N_2O_5, HOCl, nitrosyl sulfuric acid formed in sulfuric acid, or odd hydrogen since OH, HO_2, and CH_2O are all taken up by sulfuric acid solutions (*19*).

Case 1 suggests that HCl is converted into more reactive forms of chlorine on sulfuric acid surfaces at temperatures above 200 K. Unfortunately, we cannot obtain a γ for this case because the conversion is already complete at 34°W. A rapid conversion at these high temperatures could allow a substantial loss of HCl before the formation of the first polar stratospheric clouds. If future laboratory studies confirm that HCl reactions occur with high efficiency, then sulfuric acid aerosols will have to be considered as potential major contributors to polar ozone loss even in years without significant volcanic eruptions.

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12. The eruption of Pinatubo occurred about 7 months before our observations. However, the column concentrations of HCl, HNO_3, and $ClNO_3$ that we observed outside the Arctic vortex in 1992 were similar to those observed in earlier nonvolcanic years, when the steadily rising amount of chlorine in the stratosphere is taken into account (*15*). Thus, the volcanic cloud had not measurably altered the concentrations of these species in extra-vortex air before the event of 19 January 1992.
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In Situ Observations of Aerosol and Chlorine Monoxide After the 1991 Eruption of Mount Pinatubo: Effect of Reactions on Sulfate Aerosol

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Highly resolved aerosol size distributions measured from high-altitude aircraft can be used to describe the effect of the 1991 eruption of Mount Pinatubo on the stratospheric aerosol. In some air masses, aerosol mass mixing ratios increased by factors exceeding 100 and aerosol surface area concentrations increased by factors of 30 or more. Increases in aerosol surface area concentration were accompanied by increases in chlorine monoxide at mid-latitudes when confounding factors were controlled. This observation supports the assertion that reactions occurring on the aerosol can increase the fraction of stratospheric chlorine that occurs in ozone-destroying forms.

We have made in situ observations of changes in the size distribution of stratospheric aerosols after the 15 June 1991 eruption of Mount Pinatubo. We compared these measurements with satellite and lidar measurements, which served to locate the in situ observations with respect to the vertical extent of the volcanic cloud and to demonstrate the consistency of the in situ and remote measurements. The spatial and temporal distributions of the aerosol properties are described. Relations between the aerosol surface area concentration S (in square micrometers per cubic centimeter) and chlorine monoxide (ClO) concentrations (in parts per trillion by volume) are described for mid-latitude measurements.

The aerosol properties reported here were determined from the output of three instruments flown on the National Aeronautics and Space Administration (NASA) ER-2 high-altitude aircraft in the Airborne Arctic Stratospheric Expedition II (AASE II). The ER-2 Condensation Nucleus Counter (ER-2 CNC) (*1*) measures the concentration of particles in the diameter range from ~0.02 to ~2 μm. The size distributions measured with the focused cavity aerosol spectrometer (FCAS) (Particle Measuring Systems Inc., Boulder, Colorado) typically extend from 0.068 to 3.3 μm (*2*). These highly resolved size spectra extend to the smallest diameters accurately measured in the stratosphere. The forward scattering spectrometer probe (FSSP-300) covers the diameter range from ~0.4 to 20 μm (*3*). The measurements reported here were made between 20 August 1991 (910820) and 26 March 1992 (920326) (Table 1).

Balloon soundings, lidar measurements, and data from the Stratospheric Aerosol and Gas Experiment II (SAGE II) aboard the Earth Radiation Budget Satellite (*4*) show that much of the cloud was above the ER-2 ceiling in August and September 1991. Most of the cloud was within reach of the ER-2 during the high-latitude flights made in October. During the winter of 1991–1992, we made in situ measurements in portions of the mid-latitude cloud having the greatest optical extinctions (Fig. 1) and maximum values of S. The fraction of the

Table 1. Analyzed flights from AASE II.

Dates	Latitude range	Number of flights
910820–910917	22°N to 51°N	3
911004–911014	37°N to 90°N	5
911208–920326	22°N to 70°N	15

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