do not, however, uniquely determine crystallization mechanisms (*3*).

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14. For details of the implementation of these tests, consult (*3*), in which identical procedures were followed.
15. These simulations use the same simple model for crystallization described in (*4*) but explore a wider range of possible cluster geometries.
16. Because marked inhomogeneity in the distribution of aluminous minerals is evident in Fig. 1C, this factor probably accounts for the relatively large scatter for sample MD.
17. See (*4*) for discussion of the relation between Voronoi polyhedra and the actual diffusional domains.

18. This work was supported by National Science Foundation grant EAR-9118338 and by grants 003658-147 and 003658-157 from the Texas Advanced Research Program. We thank S. Jones, L. Eclarinal, M. Guckeyson, and S. Dholakia for their efforts in data collection; R. Ketcham for invaluable programming assistance; and D. Cunningham for collecting sample MD. Informal reviews by L. Land, S. Mosher, J. Rosenfeld, T. Rowe, and D. Smith are gratefully acknowledged. The Geology Foundation (University of Texas) helped to defray publication costs.

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Mount Pinatubo Aerosols, Chlorofluorocarbons, and Ozone Depletion

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The injection into the stratosphere of large quantities of sulfur during the June 1991 eruption of Mount Pinatubo (Philippines) and the subsequent formation of sulfate aerosol particles have generated a number of perturbations in the atmosphere with potential effects on the Earth's climate. Changes in the solar and infrared radiation budget caused by the eruption should produce a cooling of the troposphere and a warming of the lower stratosphere. These changes could affect atmospheric circulation. In addition, heterogeneous chemical reactions on the surface of sulfate aerosol particles render the ozone molecules more vulnerable to atmospheric chlorine and hence to man-made chlorofluorocarbons.

After having been inactive for 635 years, Mount Pinatubo in the Philippines (15.1°N, 120.4°E) injected 15 to 30 MT of sulfur dioxide (SO_2) into the stratosphere in mid-June 1991 (*1–3*). In about a month the SO_2 was converted into sulfuric acid (H_2SO_4), which in the stratosphere condenses into small particles (called aerosols) (*4*). The aerosol load after this volcanic eruption was one or two orders of magnitude larger than that produced by biological and anthropogenic sources (*5*). These small droplets are expected to remain in the atmosphere for 1 to 3 years (*6*).

In 1982, another volcano, El Chichón, located in Mexico (17.3°N, 92.3°W) at approximately the same latitude as Mount Pinatubo, injected 7 to 20 MT of SO_2 into the stratosphere (*7*). Several perturbations resulting from this eruption were reported (*8*), including an increase in the temperature of the lower stratosphere (*9*), probably a slight cooling of the surface (*10*), and a reduction in the concentration of stratospheric ozone (O_3) (*11*). The observed O_3 depletion is believed to be associated with heterogeneous chemical reactions involving nitrogen and chlorine compounds on the surface of the aerosols. Similar processes on the surfaces of ice particles in polar stratospheric clouds have led to the formation of the O_3 hole over Antarctica. Volcanoes also release chlorine compounds but, after the eruption of Mount Pinatubo, the input of chlorine to the stratosphere was probably small (*12*).

Although both eruptions share several common features (for example, SO_2-rich plumes) (*13*), there were several differences in the fate and impact of the clouds [different phases in the quasi-biennial oscillation (QBO) of winds in the atmosphere and different atmospheric concentrations of anthropogenic chlorine and bromine] (*14*).

The gas-phase destruction of O_3 by chlorine in the lower stratosphere is relatively inefficient because the reactive Cl and ClO radicals are rapidly converted into less reactive compounds such as HCl and $ClONO_2$ (*15*). Because $ClONO_2$ is formed by the reaction of ClO with NO_2, the oxides of nitrogen are sometimes referred to as the "immune system" of the lower stratosphere.

Laboratory investigations have shown that heterogeneous chemical processes on the surface of aerosol particles convert nitrogen oxides (NO_x represents NO, NO_2, NO_3, and N_2O_5) into nitric acid (HNO_3) and hence weaken the "immune system" against chlorine in the atmosphere. The reaction involved is

$$N_2O_5\ (\text{gas}) + H_2O\ (\text{aerosols}) \rightarrow 2\ HNO_3\ (\text{gas}) \qquad (1)$$

The probability that a collision of N_2O_5 with an aerosol particle results in the above reaction is of the order of 10 to 18% (*16, 17*). For background aerosol loads, the time required for this conversion is of the order of 1 day, so that, even during periods not perturbed by volcanic eruptions, reaction 1 is efficient and indirectly enhances the sensitivity of O_3 to chlorine in the lower stratosphere. The direct heterogeneous destruction of $ClONO_2$,

$$ClONO_2\ (\text{gas}) + H_2O\ (\text{aerosols}) \rightarrow HNO_3\ (\text{gas}) + HOCl\ (\text{gas}) \qquad (2)$$

also contributes to the conversion of nitrogen oxides into HNO_3 but, in addition, converts $ClONO_2$ into HOCl. This latter molecule is rapidly photolyzed into reactive chlorine (Cl, ClO). The probability for reaction 2 to occur is significantly lower than that of reaction 1 and is further dependent on the chemical composition (for example, the H_2SO_4 percentage by weight) of the aerosol (*18*). This reaction, however, becomes efficient in very cold air masses (for example, at high latitudes in winter and spring).

After large volcanic eruptions, the surface area available for these heterogeneous reactions is increased by a factor of 10 to 100 (*11*), and substantial perturbations could occur. The concentration of nitrogen oxides is expected to be reduced while the concentrations of HNO_3 and ClO should be enhanced (*19*). At the same time, the concentration of hydroxyl (OH) and hydroperoxyl (HO_2) radicals should increase. Thus, after a large volcanic eruption, the atmosphere shifts from a situation in which O_3 is primarily controlled by nitrogen oxides to one in which the O_3 loss becomes largely controlled by chlorine compounds and HO_x radicals.

In order to assess the impact of the Mount Pinatubo eruption on the O_3 layer, we used a two-dimensional (latitude-altitude) model describing chemical, radiative, and dynamical processes in the middle atmosphere (*20*). The model extends from pole to pole and from the surface to an altitude of 85 km with a resolution of 5° in latitude and 1 km in altitude. Approximately 60 species and 115 chemical and photochemical reactions are included in the chemical scheme, including heterogeneous reactions 1 and 2. For reaction 1, the reaction probability is assumed to be 0.14 for all temperatures and aerosol compositions (*16, 17*), whereas for reaction 2 values of 3×10^{-2}, 1×10^{-2}, 5×10^{-3}, and 5×10^{4} are adopted for H_2SO_4 percentages by weight of 40, 50, 60, and 70%, respectively (*18*). A simplified parameterization of heterogeneous reactions in polar stratospheric clouds is also included.

Because the dispersion of the volcanic cloud and the microphysical transformation involved (nucleation, condensation, evap-

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oration, sedimentation, and so forth) are difficult to simulate, especially in the absence of available observational constraints, we chose to specify in the model the spatial distribution of the surface area density provided by the aerosols. Furthermore, rather than simulating the evolution of the perturbation during several months after the June eruption, we examined specific situations during the dispersion phase of the volcanic material.

We first considered the relatively early time period (September) during which the cloud was confined in the tropics between 15°S and 15°N; we assumed that material was completely mixed in the zonal direction. The cloud was assumed to extend from 16 to 18 km with a peak surface area density of 100 μm^2 cm^{-3} at an altitude of 23 km above the equator. Two types of perturbations were then distinguished. In the first, where the effect of heterogeneous chemistry is ignored, we assumed that the volcanic aerosol, by absorbing the ultraviolet, visible, and near-infrared radiation of the sun and the terrestrial infrared radiation, produces a local heating of the tropical lower stratosphere. Under the assumption of a net heating rate that reaches a maximum value of 0.4 K per day in the center of the cloud, the calculated temperature increase (2 to 6 K between 16 and 25 km, see Fig. 1A) was in good agreement with the perturbation observed at 20°N and 30 mbar (2.6 K) (*21*). A direct consequence of the aerosol heating was a strengthening of the mean meridional circulation by approximately 10% (Fig. 1B); stronger upward motions were predicted in the tropics, and downward transport occurred in the model at higher latitudes. The result was a reduction of approximately 6% in the concentration of O_3 in the lower stratosphere (25 km) over the equator and a comparable increase in its density at 30°N (Fig. 1C). With the adopted aerosol heating rate, the overall reduction in the O_3 column over the tropics was less than 3%. We assumed that the cloud was symmetric about the equator (*22*); a larger response in the mean circulation would have been obtained with asymmetric aerosol heating (*23*). These changes in temperature and circulation led to perturbations in the concentration of several species; in the case of the OH and ClO radicals, for example, the density at 20 km (equator) was enhanced by 25 and 50%, respectively.

In a second model calculation of the early period following the eruption, we examined the effects of heterogeneous reactions 1 and 2 while aerosol heating was ignored. With the assumptions made, the concentration of NO_2 in the cloud (Fig. 2A) was reduced by as much as 40% while that of ClO (Fig. 2B) was increased by more than a factor of 2.3. The mixing ratio of HNO_3 increased up to 50% and that of OH by 60% (not shown). The reduction in the O_3 density, in a region of the atmosphere where O3 is rapidly replenished by photolysis of molecular oxygen, did not exceed 1% (Fig. 2C). The reduction in the net heating rate associated with this small O_3 depletion is less than 0.003 K per day; consequently, no significant change occurred in the stratospheric circulation. Potential changes in the O_3 density in the tropics, several months after the eruption of Mount Pinatubo, are thus more likely due to changes in the circulation of the atmosphere than to direct chemical processes.

Finally, we considered the later period of the cloud dispersion (7 months after the eruption) and assumed that the volcanic aerosol was now relatively well mixed over the entire Earth. The distribution of the

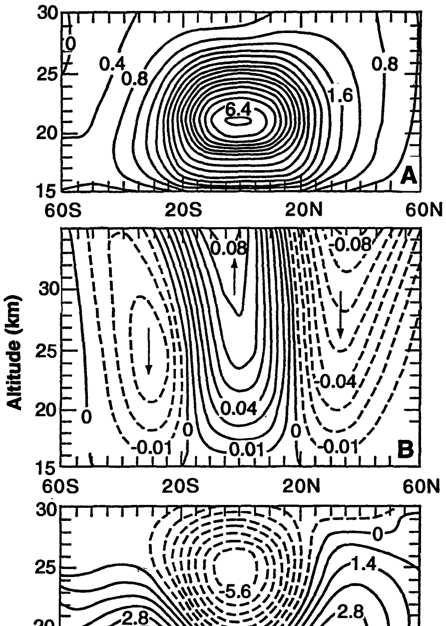

Fig. 1. Perturbations in the tropical lower stratosphere in response to prescribed heating caused by the Mount Pinatubo aerosol cloud. The cloud in September 1991 is assumed to be located between 15°S and 15°N and at an altitude of 16 to 28 km. The maximum net heating rate (at 23 km over the equator) was 0.4 K per day. (**A**) Change in temperature (in kelvins); (**B**) change in vertical wind velocity (in millimeters per second); (**C**) change in the O_3 concentration (in percent).

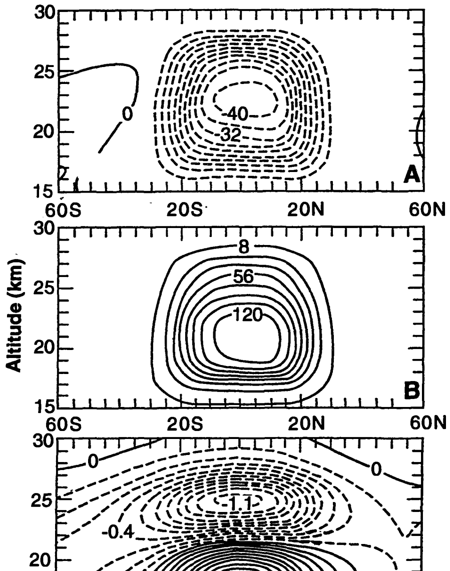

Fig. 2. Perturbations in the tropical lower stratosphere due to heterogeneous chemical reactions on the surface of sulfate particles after the eruption of Mount Pinatubo. The volcanic cloud in September 1991 is assumed to be located as in Fig. 1. The reference case for the nonvolcanic situation includes background aerosols. Maximum surface area density at 23 km over the equator is 100 μm^2 cm^{-3}. (**A**) Change in the NO_2 concentration (in percent); (**B**) change in the ClO concentration (in percent); (**C**) change in the O_3 concentration (in percent).

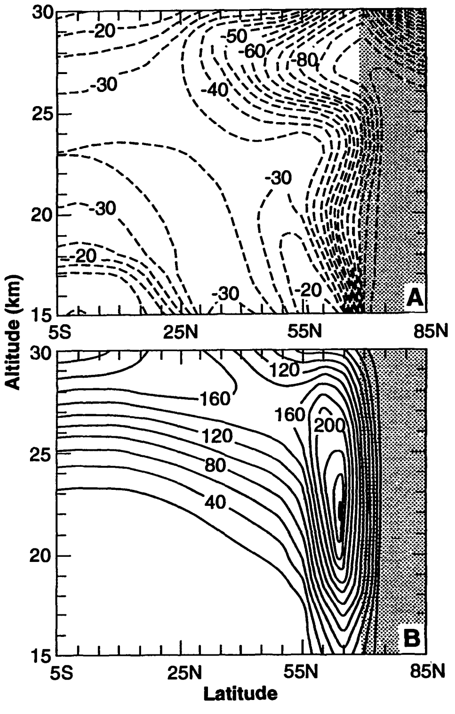

Fig. 3. Change in the chemical composition of the stratosphere in January 1992 after dispersion on the global scale of the Mount Pinatubo volcanic cloud. (**A**) Change in the NO_2 concentration as a function of latitude and altitude (in percent); (**B**) ClO mixing ratio (parts per trillion by volume). Shaded areas represent polar night zones. The reference case for the nonvolcanic situation includes background aerosols and polar stratospheric clouds.

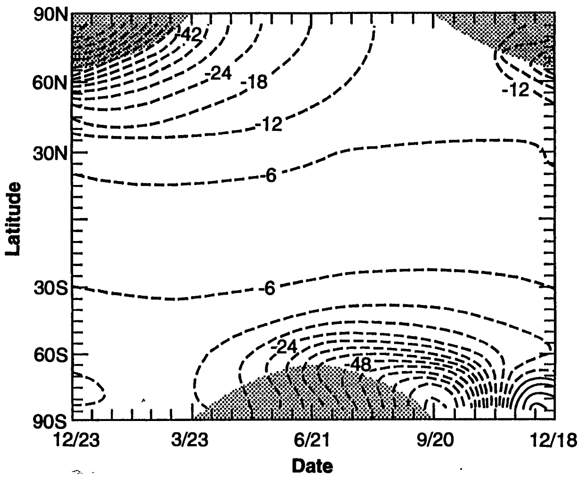

Fig. 4. Relative change in the O_3 density (in percent) at an altitude of 20 km, as a function of latitude and season. The reference case includes polar stratospheric clouds and background sulfate aerosols. Shaded areas represent polar night zones.

surface area density is specified on the basis of observations made after the eruption of El Chichón (*11*), but it accounts for the observation that the Mount Pinatubo volcanic material has been transported rather evenly in both hemispheres and that the amount of sulfur injected was at least twice that released by El Chichón. The maximum surface area density is equal to 16 μm^2 cm^{-3} at an altitude of 23 km over the tropics and values reaching 8 μm cm^{-3} are prescribed at high latitudes. These values are consistent with those derived by microphysical models (*24*) with differences, however, in the degree of large-scale horizontal mixing of the volcanic material.

To account for removal processes resulting from transport by the atmospheric circulation and gravitational sedimentation, we assumed that the surface area density decreased uniformly as a function of time with an *e*-folding time of 15 months. With the adopted aerosol surface area density, the concentration of NO_2 at low and mid-latitudes for January 1992 is reduced by approximately 30 to 35% for altitudes of 20 to 25 km (Fig. 3A). Near the terminator, where N_2O_5 becomes the dominant form of nitrogen oxides, the rate of transformation of NO_x into HNO_3 by reaction 1 was high and the partitioning of the chlorine family was modified in favor of ClO, at the expense of $ClONO_2$. In addition, at these latitudes where the temperature is low the direct conversion of $ClONO_2$ by heterogeneous reaction 2 is significant. As a consequence, near 60°N where solar radiation is present at this time of the year, the level of ClO is enhanced (Fig. 3B) and large amounts of O_3 are destroyed.

The most pronounced O_3 depletion in the lower stratosphere (20 km) was found near the terminator (Fig. 4). Reductions in the O_3 column abundance at mid-latitudes in the Northern Hemisphere (not shown) are of the order of 10% in January to March and 6% during the following summer. Recent reports (*25*) suggest that O_3 abundances in the winter of 1991–1992 have been abnormally low in several regions of the northern mid-latitudes. Concentration changes inside the polar vortex in response to the volcanic eruption are expected to be small because the air contained in the vortex is largely isolated from the rest of the atmosphere. The presence of polar stratospheric clouds in these cold air masses, however, provides surfaces on which reactions similar to reactions 1 and 2 can occur, and thus there is the potential for large O_3 depletion.

Ozone monitoring should provide the information needed to validate these model predictions. The chemical perturbations in the tropics appear to be relatively limited, but heating due to the cloud produced by volcanic eruptions in the tropics could enhance the strength of vertical motions in this region and hence reduce the O_3 column abundance. This latter dynamical effect is entirely natural, whereas the chemical effect results from a combination of natural and anthropogenic perturbations.

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masses contained in the polar vortex have been displaced from the pole toward the European continents during most of January 1992. The monthly mean January 1992 temperature at 30 mbar over the North Sea was 10 K lower than the 20-year (1965 to 1984) mean January values (K. Labitzke and B. Naujokat, *Beil. Berl. Wetterkarte* KNH1/1992). It remains to be established to what extent the low O_3 values observed over Europe are associated with this wave number 1 event or result from chemical destruction.

26. Discussions with J. Calvert, M. Coffey, and R. Garcia are gratefully acknowledged. The National Center for Atmospheric Research is sponsored by the National Science Foundation. C.G. is supported in part by the Gas Research Institute (contract 5090-254-1993) and by the Commission of the European Communities (Step Program).

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Manganese Flux from Continental Margin Sediments in a Transect Through the Oxygen Minimum

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The flux of manganese from continental margin sediments to the ocean was measured with a free-vehicle, benthic flux chamber in a transect across the continental shelf and upper slope of the California margin. The highest fluxes were observed on the shallow continental shelf. Manganese flux decreased linearly with bottom water oxygen concentration, and the lowest fluxes occurred in the oxygen minimum zone (at a depth of 600 to 1000 meters). Although the flux of manganese from continental shelf sediments can account for the elevated concentrations observed in shallow, coastal waters, the flux from sediments that intersect the oxygen minimum cannot produce the subsurface concentration maximum of dissolved manganese that is observed in the Pacific Ocean.

Manganese is widely used as a model element for studies of redox chemical cycles in the sea. Insoluble manganese oxides are readily reduced to soluble Mn^{2+} by bacteria, photochemical reactions, and hydrothermal processes (*1*). Elevated concentrations of dissolved Mn are often evidence of active redox cycling. The processes controlling the oxidation states of a variety of other metals (for example, Ce, Co, and Cr) are interpreted by comparing their distributions with that of Mn (*2*).

Dissolved Mn profiles in the Pacific Ocean are characterized by maxima in the upper 100 m and wherever O_2 concentrations drop below 100 μM (*3*). The subsurface maximum is believed to be produced by the flux of dissolved Mn^{2+} from reducing sediments that intersect the O_2 minimum zone (*4–7*). However, there have been no direct measurements of the Mn flux from sediments along the continental margin, except in waters shallow enough to be reached by divers (*8*, *9*). To test this hypothesis, we have directly measured the flux of Mn from sediments of the continental shelf and slope of the central California coastline using benthic chambers.

A well-developed O_2 minimum zone impinges on the continental margin between 600 and 1000 m along the central California coastline. Water column Mn concentrations in this zone are elevated twofold over background concentrations (Fig. 1). The flux of Mn from sediments that intersect this O_2 minimum was measured with a free-vehicle, benthic chamber (*10*) at depths from 95 to 1010 m along a transect near Point Piedras Blancas (35°40′N, 121°17′W). Similar benthic chambers have been used for studies of C and nutrient cycling in the deep sea (*11*, *12*).

Manganese concentrations measured in benthic chambers deployed at all depths changed linearly with time (Fig. 2). Initial Mn concentrations in the chambers, determined from a straight line fitted to the data by least squares, were not significantly different ($P < 0.05$) from the corresponding ambient bottom water concentrations, which varied from 0.6 to 10 nM. There is no evidence of a change in the slope of a plot of Mn concentration versus time that would indicate enhanced release of the metal as O_2 concentrations decreased in the chambers (*13*). The benthic Mn flux calculated from these data is greatest at the shallowest sites, where O_2 levels in the overlying water are the highest, and the smallest Mn fluxes occurred in the O_2 minimum zone (Fig. 3A). The benthic Mn flux was proportional to the rate of O_2 consumption in the flux chambers (Fig. 3B).

A relation between benthic Mn and O_2 fluxes could be the result of several processes. Remineralization of organic C and release of bound metals could be limited by the flux of O_2 through a diffusive, benthic-boundary layer (*14*). To test this hypothesis, we performed an experiment at a site near the Los Angeles County sewage outfall at Whites Point where the rate of O_2 consumption was high and there was little sediment irrigation. Stirring rates in the benthic flux chambers were varied from 1.5 to 12 rpm, and no significant change was seen in the flux of O_2 or metals (*15*). Chambers were stirred at 6 rpm in the experiments shown here. Thus, we do not believe that benthic-boundary-layer hydrodynamics are responsible for the observed relation in metal and O_2 flux.

Changes in the rate of input of organic carbon to the sediments along the transect could link benthic Mn and O_2 fluxes. A positive relation between benthic Mn flux and primary production has been seen in experimental mesocosms (*16*). One hypothesis to account for this observation is that O_2 depletion and manganese oxide reduction occur in the near-surface sediments that receive the largest carbon input (*3*). Alternatively, trace metal fluxes could be controlled by release of bound metals, perhaps from particulate organic carbon (*17*) or calcium carbonate ($CaCO_3$) (*18*),

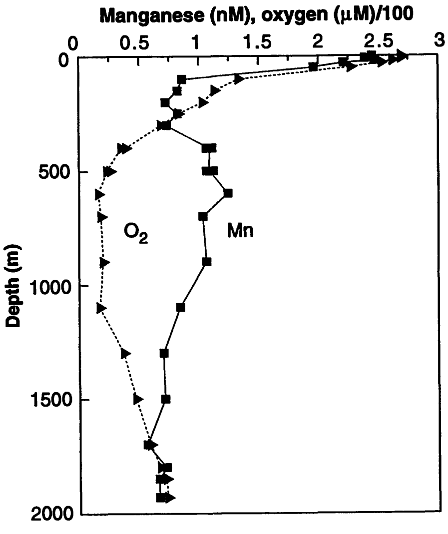

Fig. 1. Vertical profiles of dissolved Mn and O_2 from a hydrocast at 35°15′N, 121°52′W on 11 June 1991. Samples were collected with a General Oceanics Rosette sampler and 10-liter Niskin bottles. Manganese in each sample was determined at sea by flow injection analysis with chemiluminescence detection (FIA-CL) (*37*). The precision for replicate analyses was ±0.2 nM (90% confidence interval). Oxygen was determined by Winkler titration. Bottom depth is 2000 m.

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