Chapter 3B

Upper-Atmosphere Aerosols: Properties and Natural Cycles

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ABSTRACT

The middle atmosphere is rich in its variety of particulate matter, which ranges from meteoritic debris, to sulfate aerosols, to polar stratospheric ice clouds. Volcanic eruptions strongly perturb the stratospheric sulfate (Junge) layer. High-altitude "noctilucent" ice clouds condense at the summer mesopause. The properties of these particles, including their composition, sizes, and geographical distribution, are discussed, and their global effects, including chemical, radiative, and climatic roles, are reviewed. Polar stratospheric clouds (PSCs) are composed of water and nitric acid in the form of micron-sized ice crystals. These particles catalyze reactions of chlorine compounds that "activate" otherwise inert chlorine reservoirs, leading to severe ozone depletions in the southern polar stratosphere during austral spring. PSCs also modify the composition of the polar stratosphere through complex physicochemical processes, including dehydration and denitrification, and the conversion of reactive nitrogen oxides into nitric acid. If water vapor and nitric acid concentrations are enhanced by high-altitude aircraft activity, the frequency, geographical range, and duration of PSCs might increase accordingly, thus enhancing the destruction of the ozone layer (which would be naturally limited in geographical extent by the same factors that confine the ozone hole to high latitudes in winter). The stratospheric sulfate aerosol layer reflects solar radiation and increases the planetary albedo, thereby cooling the surface and possibly altering the climate. Major volcanic eruptions, which increase the sulfate aerosol burden by a factor of 100 or more, may cause significant global climatic anomalies. Sulfate aerosols might also be capable of activating stratospheric chlorine reservoirs on a global scale (unlike PSCs, which represent a localized polar winter phenomenon), although existing evidence suggests relatively minor perturbations in chlorine chemistry. Nevertheless, if atmospheric concentrations of chlorine (associated with anthropogenic use of chlorofluorocarbons) continue to increase by a factor of two or more in future decades, aircraft emissions of sulfur dioxide and water vapor may take on greater significance.

INTRODUCTION

Particles and clouds in the stratosphere and mesosphere have been under study for more than 100 years. High-altitude aerosols were the subject of scientific speculation during the 1880s, when the powerful eruption of Krakatoa caused spectacular optical displays worldwide, attracting attention to the upper atmosphere. The presence of a permanent tenuous particle layer in the lower stratosphere was postulated in the 1920s through studies of the twilight glow (1). The first in situ samples of these particles showed they are composed of sulfates, most likely concentrated sulfuric acid (2-5). Subsequent research was spurred by the realization that stratospheric particles can influence the surface climate of Earth by modifying atmospheric radiation (6). Such aerosols can also affect the trace composition of the atmosphere, ozone concentrations, and the electrical properties of air (7).

Stratospheric particulates have been sampled by balloon ascents and high-altitude aircraft to determine their properties directly (8). The aerosols have also been observed remotely from the ground and from satellites using both active (lidar) and passive (solar occultation) techniques (remote sensing instruments have been carried on aircraft platforms as well) (9,10). In connection with the experimental work, models have been developed to test theories of particle formation and evolution, to guide measurement strategies, to provide a means of integrating laboratory and field data, and to apply the diverse scientific knowledge gained to answer practical questions related to issues of global changes in climate, depletion of the ozone layer, and related environmental problems (11).

In the following sections, primarily stratospheric, but also mesospheric, particles are described, and their global effects are discussed. Figure 1 illustrates many of the species of

aerosols that have been identified in the upper atmosphere. The diagram provides information on the size dispersion and concentration of these diverse particulates (12). Table 1 provides a summary of the key characteristics of stratospheric aerosols.

Table 1. Characteristics of Stratospheric Aerosols

Particle type	Sulfate aerosol	Type-I PSC	Type-II PSC	Meteoric dust	Rocket exhaust
Physical state	Liquid or slurry with crystals	Solid nitric acid trihydrate, solid solutions	Solid crystal, hexagonal or cubic basis	Solid granular irregular or spherical	Solid spheres or irregular surface ablated debris
Particle radius (μm, 10^{-6}m)	0.01 - 0.5, Amb. 0.01 - 10, Volc.	0.3 - 3	1 - 100	1 - 100, Micro-meteorites 0.01 -0.1, smoke	0.1 - 10
Number (# cm^{-3})	~1- 10	~0.1-10	<<1	10^{-6}, 100 μm 10^{-3}, 1 μm	10^{-4}, 10 μm 10^{-2}, 1 μm
Principal composition	H_2SO_4/H_2O ~70%/30%	HNO_3/H_2O ~50%/50%	H_2O	SiO_2, Fe, Ni, Mg; C	Al_2O_3
Trace composition	NH_4^+, NO_3	HCl SO_4^{2-}	HNO_3, HCl	SO_4^{2-} (surface)	Cl$^-$, SO_4^{2-} (surface)
Physical characteristics	Dust inclusions, in solution	Equidimensional crystalline or droplets	Elongated crystals with polycrystalline structure	Irregular mineral grains, grain defects	Homogeneous composition; smooth spheres

STRATOSPHERIC SULFATE AEROSOLS

The presence of trace amounts of sulfur-bearing gases in the stratosphere favors the formation of sulfuric acid aerosols (13-18). In particular, carbonyl sulfide in the background atmosphere is largely responsible (19) for the tenuous, ubiquitous ambient sulfate haze observed in the stratosphere (20-21). The general properties of these aerosols are summarized in Table 2. The processes that control this haze also influence the formation and evolution of volcanically induced aerosols. Accordingly, investigations of the ambient stratospheric aerosol layer provide insights into the behavior of volcanic eruption clouds above the tropopause.

Background Aerosols

It is fairly well established now that the ambient stratospheric sulfate layer is formed as a result of the chemical transformation of sulfur-bearing gases (carbonyl sulfide, OCS, and sulfur dioxide, SO_2) transported into the stratosphere from the troposphere or injected there by major volcanic eruptions (19). Chemical reactions of these precursor sulfur gases lead to the produc-
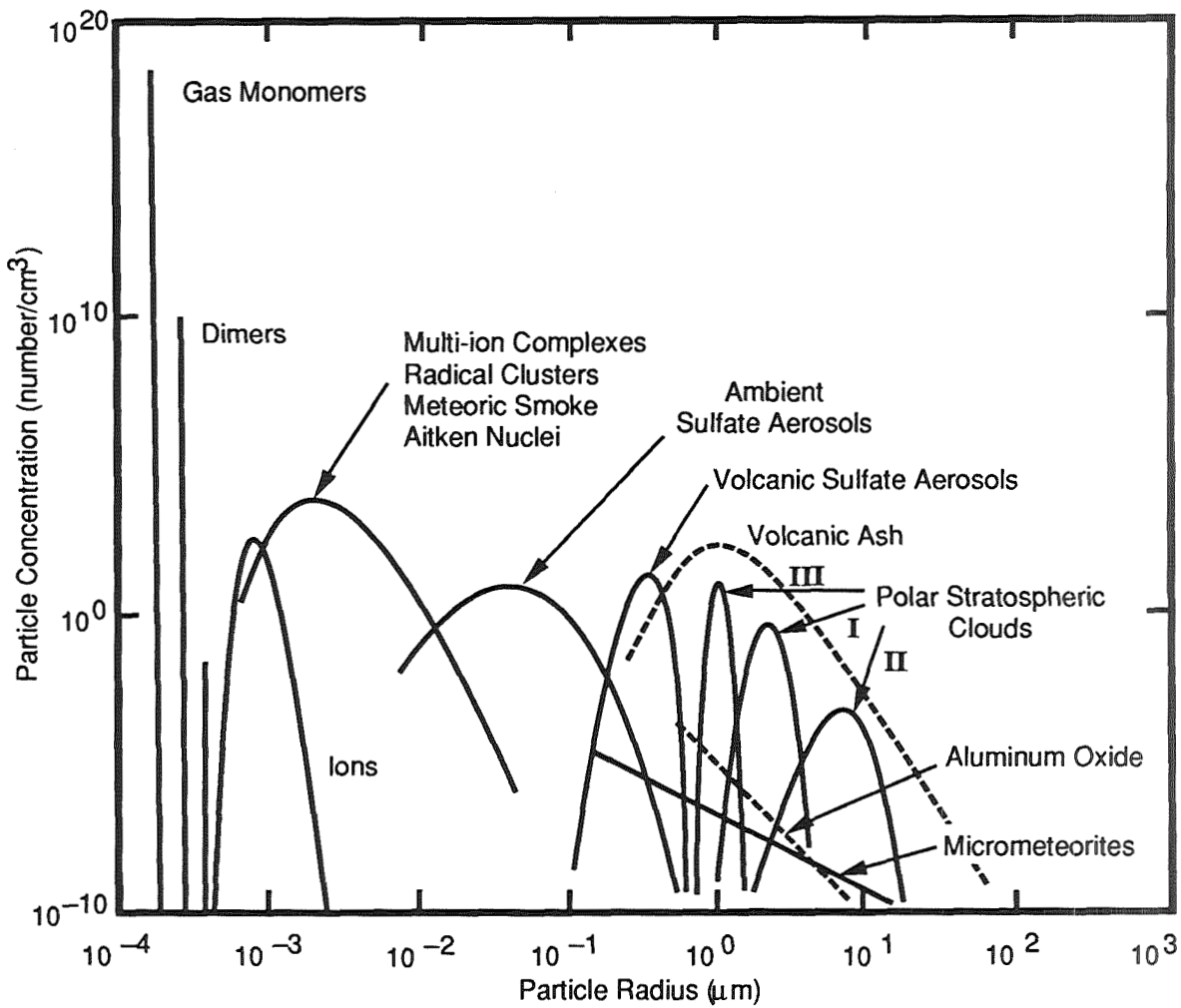
Figure 1. Spectrum of particles in the Earth's middle atmosphere. Shown are the approximate size distributions for particles with different origins. The total (number) concentration of each type of particle is roughly indicated by the peak value on the vertical scale. Some aerosols are highly variable in concentration and properties, particularly the "ash" component of volcanic eruption clouds; typically, these particles will fall out of the stratosphere within a few months following an eruption.

tion of condensible sulfur compounds — primarily H_2SO_4 [detected in situ by Arnold et al., (22)]. The sulfur conversion process is dominated by the reaction sequence: (23)

$$SO_2 + OH + M \longrightarrow HSO_3 + M \tag{1}$$

$$HSO_3 + O_2 \longrightarrow SO_3 + HO_2 \tag{2}$$

$$SO_3 + H_2O \longrightarrow H_2SO_4 \tag{3}$$

Table 2. Properties of Stratospheric Sulfate Aerosols

Composition	H_2SO_4/H_2O (~70%/30%); traces of sulfates, nitrates, nitryls, chlorides
Origin	OCS, CS_2 (also volcanic sulfur emissions); tropospheric sulfides; SO_2 photochemical oxidation to H_2SO_4 via OH; high-altitude aircraft SO_2 emissions (contribution unknown)
Properties	Liquid spheres, perhaps slurry and some solids; < 1 ppbm; ~1-10 cm^{-3} ~ 0.05 μm radius
Distribution	Global; 12 to 30 km altitude; latitudinal and seasonal variations
Mass Budget	~ 0.1 Tg-S/yr (background); ~ 1-100 Tg-S (volcanic event)
Residence Time	~ 1-2 yr (average, based on radioactive tracer studies)
Effects	Shortwave radiation scattering (τ< 0.01); longwave absorption/emission (τ<< 0.01); heterogeneous chemical conversion of NO_x to HNO_3
Influences	Natural and anthropogenic OCS sources; volcanic activity; stratospheric dynamics
Trends	Variable over 2 orders of magnitude following major volcanic eruptions (e.g., El Chichon). Possible long-term increase of ~ 6%/yr by mass

Reactions (2) and (3) are so rapid that sulfur radicals (e.g., HSO_3) never achieve a significant concentration, and thus do not play a role in the chemical evolution of the aerosol cloud (except as an intermediary sulfur species). Although reaction (3) may require the presence of surfaces to occur rapidly, it does not limit the overall oxidation rate of sulfur dioxide. Importantly, reaction sequence (1) and (2) does not consume odd-hydrogen, HO_x, as would the competing process consisting of reactions (1) and (4),

$$HSO_3 + OH ----> SO_3 + H_2O . \tag{4}$$

Hence, HO_x oxidizes SO_2 catalytically, and the rate of SO_2 conversion can remain high throughout the evolution of a volcanic cloud provided there is sufficient recycling of HO_2 to OH.

The properties of the sulfate particle layer are strongly influenced by microphysical processes, including heterogeneous nucleation, growth by condensation, evaporation of volatiles, coagulation, and gravitational sedimentation (24). Some of the complex physicochemical interactions responsible for the formation of the stratospheric aerosol layer are illustrated schematically in Figure 2; the potential contributions of naturally occurring meteoritic particles and ion clusters to sulfate aerosol formation are also indicated. Exhaust particles from Space Shuttle or high-altitude aircraft operations would enhance the condensation nuclei abundances. Detailed discussions of microphysical processes can be found in several papers, reviews, and books (25,26).

MESOSPHERE

METEOR
ABLATION

GALACTIC
COSMIC
RAYS

SMOKE
PARTICLES
(2-10Å)

UNABLATED
METEORITES
MICROMETEORITES

METEORIC
VAPORS
(METALS, SILICA,
SULFUR, etc.)

SEDIMENTATION
DIFFUSION
COAGULATION

ADSORPTION

ION-NEUTRAL
REACTIONS

METEORIC
DUST

ATTACHMENT

IONIZATION:
$NaOHH^+ \cdot (H_2O)_n$
$HSO_4^- \cdot (H_2SO_4)_n$

STRATOSPHERE

ADSORPTION

ACTIVATION

MUTUAL NEUTRALIZATION NUCLEATION

ION-NEUTRAL
REACTIONS

COAGULATION

HOMOGENEOUS
AND ION
NUCLEATION

CONDENSATION
NUCLEI

H_2SO_4
VAPOR

GROWTH COAGULATION

EVAPORATION

EVAPORATION

CLUSTERING

OXIDATION

CONDENSATION

SULFATE
AEROSOLS

ABSORPTION

SULFUR
RADICALS

COAGULATION

TROPOSPHERE

TRANSPORT
COAGULATION
NUCLEATION

DIFFUSION

AITKEN
NUCLEI

SULFUR VAPORS
(SO_2, OCS, CS_2)

SEDIMENTATION
DIFFUSION
WASHOUT

PRODUCTION
EMISSION

EMISSION

Figure 2. Diagram depicting the physical and chemical processes that affect stratospheric aerosols. Meteoritic debris, positive and negative ions, and tropospheric Aitken nuclei can serve as nucleation sources for sulfate aerosols and ice clouds. These particles can grow, evaporate, coagulate, and fall vertically. The particles are also carried in stratospheric winds and diffuse under the influence of small scale turbulent eddies.

Volcanic Aerosols

Table 3 summarizes the general properties of the aerosols generated by a modest-to-large volcanic eruptions (that is, one in which the eruption column penetrates the tropopause and deposits substantial quantities of gases and particles in the stratosphere) (27-32).

The general microphysical development and properties of volcanic eruption plumes are exemplified by the behavior of the El Chichon eruption cloud (33,34). The primary eruption of El Chichon occurred on April 4, 1982; solid debris and gases were injected to altitudes of about 30 km over the Yucatan Peninsula (35). Many observations of the clouds were made, and these data have been compared to model simulations that include the relevant physical and chemical processes (36,37). It should be noted that high-altitude sampling of the El Chichon volcanic clouds was very limited. Data collected by the Solar Mesosphere Explorer satellite suggest that the post-eruption aerosols reached altitudes of 40 km (38,39). Lidar measurements, on the other hand, indicated that the El Chichon particles remained below about 30 km for several months after the eruption.

# Table 3.   Properties of Volcanic Aerosols

Composition	Silicates; H_2SO_4/H_2O (~70%/30%); traces of sulfates, nitrates, chlorides, etc.
Origin	Terrestrial material, gaseous SO_2 with chemical oxidation to H_2SO_4 via OH
Properties	Liquid spheres; solid mineral particles dominant the first month; ~ 100-1000 ppbm; (highly variable); ~1-10 cm^{-3}; ~ 0.3 μm radius
Distribution	Regional (days); zonal (weeks); hemispheric (months); global (year); 12-35 km altitude
Mass Budget	Per event: SO_2 (~ 1-100 Tg-S); H_2O (~ 10-1000 Tg); HCl (~ 0.01-10 Tg); mineral ash (> 100–10,000 Tg)
Residence Time	~ 1-3 yr (average, based on radioactive tracer and aerosol decay studies)
Effects	Shortwave scattering of sunlight leads to surface cooling; Longwave absorption warms the stratosphere; Injection of H_2O, HCl, etc., possibly alters composition; Enhanced heterogeneous reactions on sulfate aerosol surfaces; Possible ozone perturbations; Stratospheric stability / tropospheric dynamics affected; Nuclei for upper tropospheric cirrus
Influences	Geophysical; no anthropogenic influences; geological setting determines effects; impact on ozone may be affected by chlorine levels
Trends	Random significant eruptions are ~20 years on average; major eruptions are ~100 years apart

The size distributions of volcanic aerosols (shown in Figure 3 for an El Chichon simulation) exhibit a tri-modal structure that evolves with time. The principal size modes are: a nucleation mode, which is most prominent at early times and at sizes near 0.01 μm; a sulfate accumulation mode, which evolves initially from the nucleation mode (by coagulation and condensation) and increases in size to about 0.3 μm after 1 year; and a large-particle "ash" mode (of solid mineral and salt particles) that settles out of the layer in 1 or 2 months. A primary feature of the volcanic aerosol size distribution after several months is a greatly enhanced sulfate accumulation mode. The increased aerosol size is caused by accelerated growth in the presence of enhanced sulfuric acid vapor concentrations that are maintained by continuing SO_2 chemical conversion.

Figure 4 illustrates the evolution of volcanic aerosol optical depths at mid-visible wavelengths, associated with the scattering of light by the sulfuric acid droplets. The calculations correspond to the sulfur injection scenarios used by Pinto et al. (40); i.e., SO_2 mass injections of 10 Tg (1 Tg = 1 × 10^{12} g = 10^6 metric tons) (i.e., like El Chichon), and 100 and 200 Tg (possibly similar to Tambora, 1815). At early times, and over limited geographical regions, the

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optical depths can exceed a value of 2. However, after 1 year of evolution by growth, coagulation, and fallout, the average optical depth for even the largest SO_2 injection has fallen to about 0.5. These results suggest that nonlinear physical/chemical interactions occurring in volcanic eruption clouds severely limit the aerosol optical depth that can be maintained over a period of several years (40) (i.e., the time span required to induce substantial long-term climatic impacts, see also section on Radiation and Climate Effects). Conversely, the efficiency for producing radiative effects *per unit mass of sulfur* injected is greatest for smaller injections. Accordingly, high-altitude aircraft emissions of SO_2 hold the potential for creating significant global-scale radiative effects.
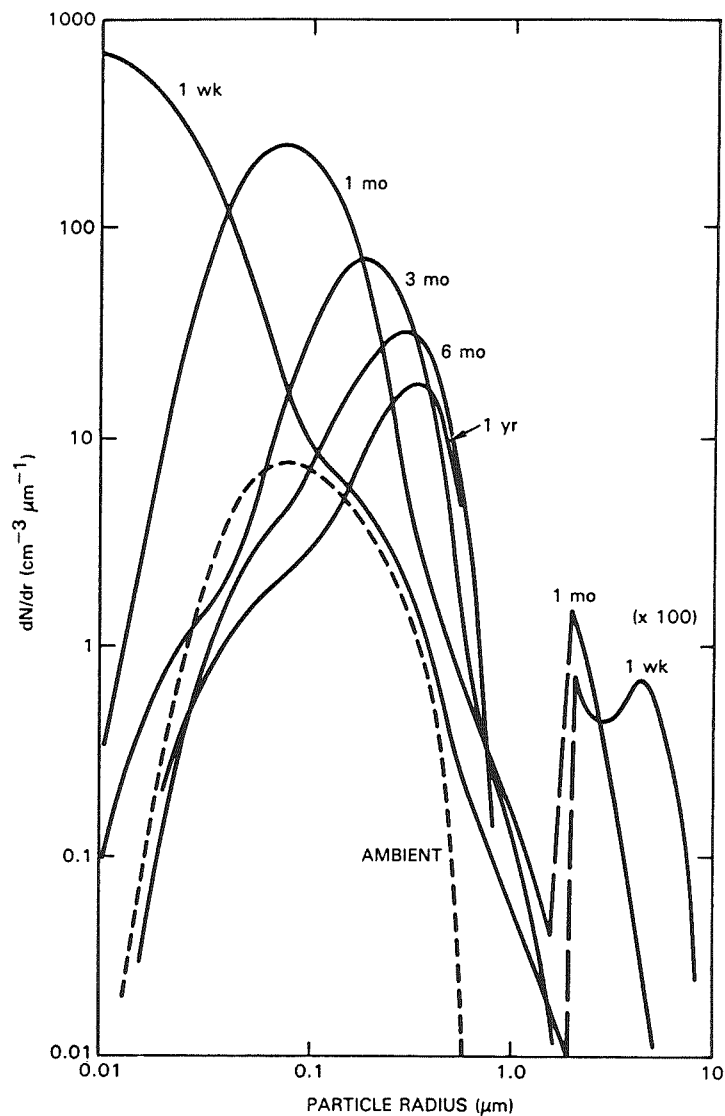
Figure 3. Evolution of the aerosol size distribution at 20 km in the simulated El Chichon eruption cloud. Size distributions are shown at various times, and are compared to the ambient size distribution (36).

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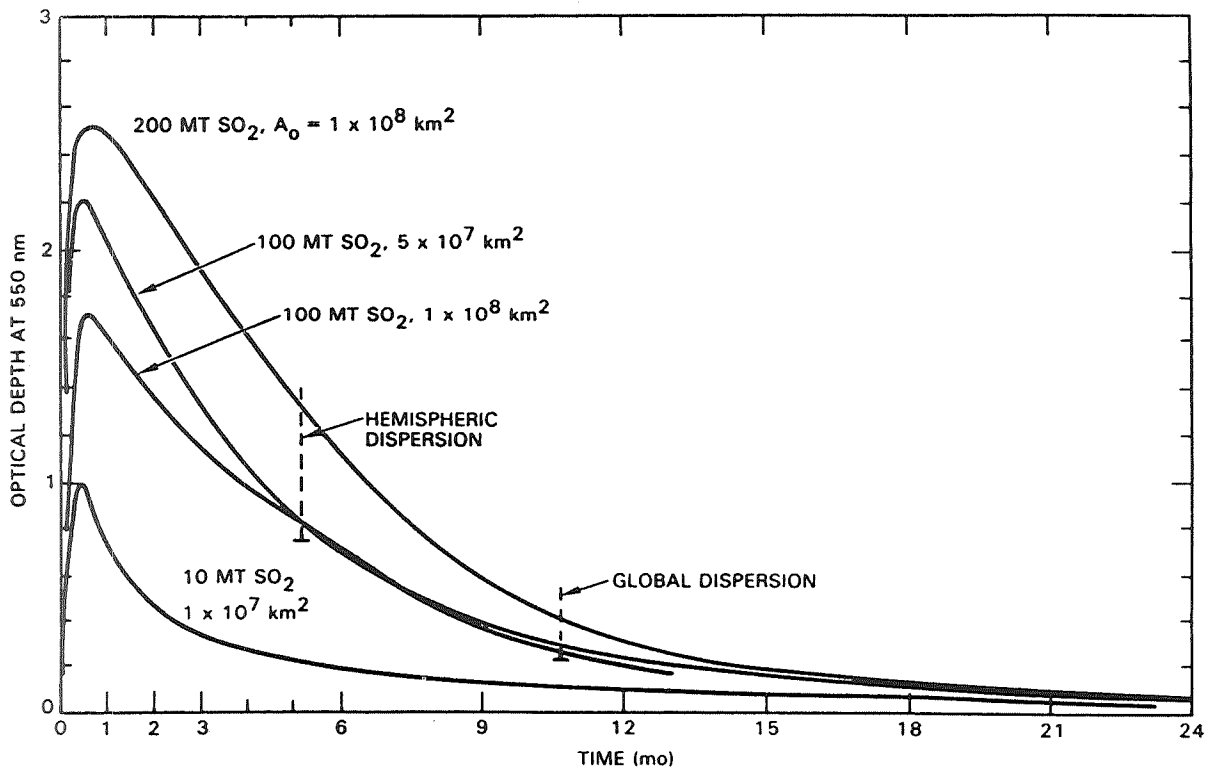
Figure 4. Volcanic aerosol optical depths (zenithal) versus time for the volcanic cloud simulations discussed by Pinto et al. (40). Indicated on the figure are the times required for the cloud to disperse over a hemisphere, or over the globe (40).

The sulfate aerosol mode radius peaks earlier with larger SO_2 injections and remains elevated throughout the history of the eruption cloud. In the simulations shown, the mode radius grows as large as 0.7 μm, which greatly exceeds the ambient sulfate mode radius, r~0.05 μm. In the instance of very large eruptions, the mode radius returns to its ambient value only after a period of several years. The mode radius is important in determining the rate at which sulfate is removed from the stratosphere. The sulfate mass flux from the stratosphere is proportional to the fallspeed, v, of the aerosols multiplied by their mass, m. Since $m \propto r^3$ and v $\propto r^{1 \to 2}$ in the regime of interest, the mass loss rate is, $m \propto r^{4 \to 5}$ The optical depth per unit mass of aerosol varies roughly as 1/r in the size range of interest. Hence, the decrease in optical depth in Figure 4 can be seen to have two causes: (1) the growth in particle size that reduces the optical efficiency; and (2) a rapid decrease in the the total sulfate mass caused by sedimentation (after a month or so). These nonlinear interactions greatly limit the potential climatic effects of explosive volcanism.

POLAR STRATOSPHERIC CLOUDS (PSCs)

The properties of stratospheric clouds in polar regions (PSCs), (41) have been defined by a decade of satellite observations (see Table 4) (42-45). Based on optical and physical evidence, PSCs fall into two broad categories, which are referred to here as Type I and Type II PSCs. Type I PSCs consist of an aerosol haze of micron-sized nitric acid ice particles composed of HNO_3 and H_2O [in roughly a 50/50 mixture by weight, similar to the trihydrate $HNO_3 \cdot 3H_2O$] (46,47). Type II PSCs are apparently composed of water-ice crystals (48). Some statistical properties of PSCs derived from satellite observations are summarized in Figure 5 (45).

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**Table 4.** Properties of Polar Stratospheric Clouds

Composition	Type I: HNO_3/H_2O (~50%/50%); Type-II: water ice; possibly traces of HCl, HNO_3, etc.
Origin	Type I: nucleation on sulfate, T<195 K; Type II: ice nucleation on Type I, T<189 K
Properties	Type I: ~1-10 ppbm; <1 cm^{-3}; 0.3 μm; Type II: ~1 ppmm; <<1 cm^{-3}; 3 μm radius; solid crystalline structures
Distribution	Polar winter stratospheres (>60° latitude); 14-24 km altitude; winter and early spring; S. H., June-October, widespread Type I and II; N. H., December-March, sporadic I, occasional II
Mass Budget	Type I: ~ 1-10 ppbm HNO_3 per winter season; Type II: ~ 1-5 ppmm H_2O per winter
Residence Time	Type I: ~ 1 day, to weeks (temperature control, to sedimentation control); Type II: ~ hours (condensation/sedimentation/evaporation control)
Effects	Activation of chlorine reservoirs (Type I and II); conversion of NO_x into HNO_3 (Type I); dehydration of the polar stratosphere (Type II); denitrification of the polar vortex (Type I and II)
Influences	Stratospheric polar meteorology; tropospherically driven wave events; vortex stability and temperature; springtime warming events; possible role of changes in CH_4, H_2O and NO_y
Trends	Tied to trends in polar meteorology, especially temperature

The Type I PSCs are considered the most common form, accounting for perhaps 80 to 90% of all cloud sightings. These PSCs exhibit an onset at temperatures near 195 K, whereas the more massive Type II PSCs appear to condense at colder temperatures (<187 K) consistent with the measured frost point of water vapor in the polar stratosphere (48,49). It should be expected, therefore, that Type I haze would predominate the totality of cloud observations in the earliest part of the Antarctic winter season, and that the frequency of Type II clouds would increase with the progression of winter and cooling of upper air layers. On the other hand, the observed dehydration and denitrification of the Antarctic winter stratosphere would, over the course of time, reduce the frequency of cloud formation at specific temperature thresholds (50). In the late winter and early spring, predictions and observations indicate that PSCs will dissipate abruptly when the upper strato-sphere warms (51).

Most likely, the nuclei for nitric acid ice deposition are the background sulfuric acid aerosols (46). Observational evidence on the extent to which sulfate particles are nucleated in PSCs is mixed. Aircraft measurements taken in the Antarctic ozone hole in September 1987 suggest that many, if not most, of the sulfate particles may be activated into nitric acid haze particles (52,53). On the other hand, balloon-borne aerosol measurements taken at McMurdo Station during the same period, and more recent data from the Arctic winter stratosphere, indicate that, although layers of ~1 micron-size haze particles are frequently present, on occasion the

fraction of the sulfate particles activated into haze is quite small, roughly 1 in 10^3 (54,55). If sulfate particle nucleation is limited to a small fraction of the total number of particles, the resulting large sizes of haze particles will have important implications for stratospheric denitrification (56-58).
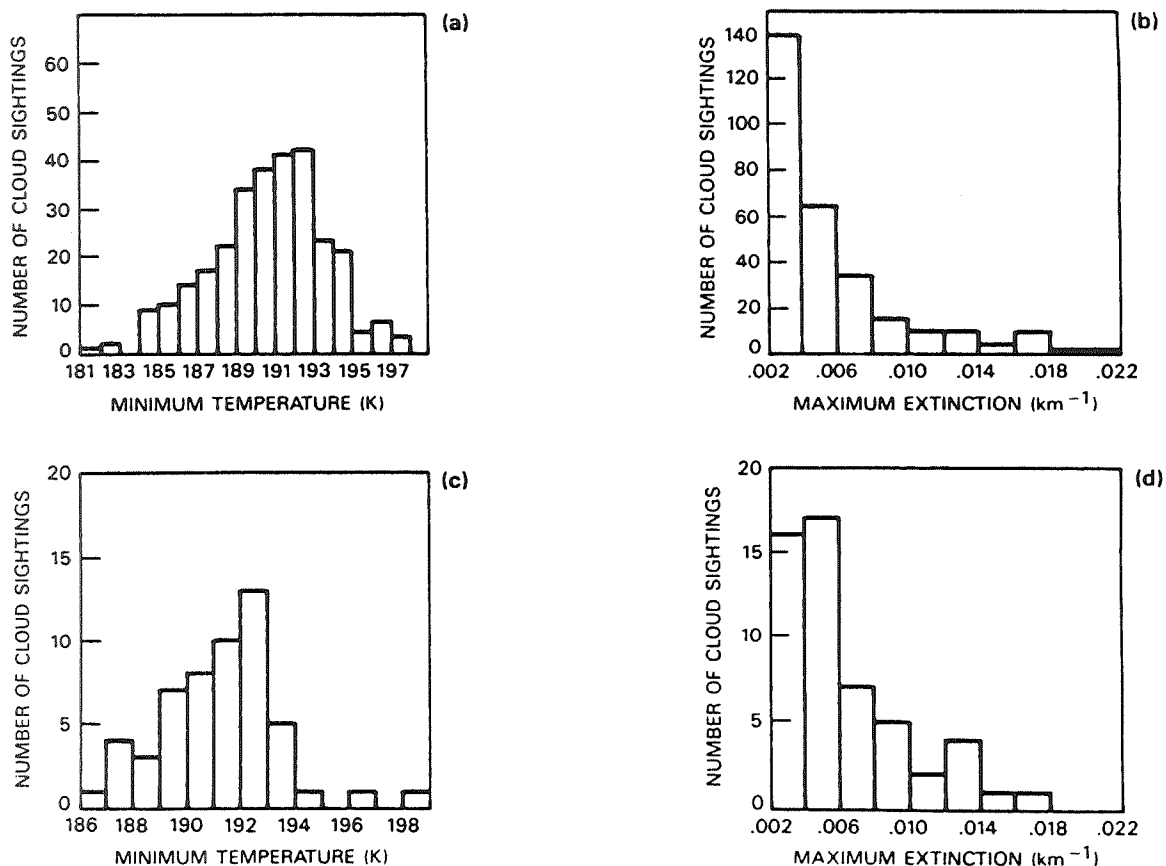
Figure 5. Statistics of polar stratospheric clouds. Panels (a) and (b) refer to the Southern Hemisphere, panels (c) and (d) to the Northern Hemisphere. The histograms represent the total ensemble of cloud sightings by the SAM-II satellite in 1986. Panels (a) and (c) show the number of cloud observations as a function of the minimum temperature in the vertical temperature profile estimated for each satellite observation. A PSC "sighting" is defined by an extinction greater than 1 x 10^{-3} km^{-1} at 3 km or more above the local tropopause. Panels (b) and (d) show the number of clouds with maximum extinctions within specific intervals. The data indicate an onset of PSC formation at approximately 195 K, with a predominance of clouds at the low extinction end of the spectrum (i.e., Type-I PSCs) (45).

In situ measurements of odd-nitrogen species provide direct evidence for the existence of nitric acid particles in the antarctic winter stratosphere (52,53,59). That evidence is supported by infrared spectroscopic measurements of condensed HNO_3 (60) and column measurements of depletion of the HNO_3 vapor column amount (61,62). In addition, Hanson and Mauersberger (63,64), in a series of detailed laboratory studies, have quantified the compositions and vapor pressures of the nitric acid ices under the conditions of interest, and they concluded that the nitric acid trihydrate is probably the stable form in the stratosphere.

OTHER STRATOSPHERIC AEROSOLS

Only brief mention has been made of the other types of particulates shown in Figure 1. The properties of two important varieties of these particles — spacecraft alumina debris and meteoritic dust — are summarized in Table 5 (65-67). Data collected by Zolensky et al. (68) reveal a 10-fold increase in the stratospheric burden of alumina particles and other debris associated with space activities during the decade, 1976-1986.

SOOT

Because aircraft engines also generate soot (graphitic carbon, elemental carbon, or black carbon), the presence of soot in the ambient stratosphere is of interest. To date, there have been no definitive measurements of soot aerosol in the stratosphere. Observations of light absorption (single-scatter albedo) by stratospheric aerosols show a very small residual absorption that has not been assigned to any particular species (69). Several impactor samples taken in the stratosphere have revealed soot or soot-like particles (70,71). One suggested source for these particles is fragments of carbonaceous chondrites of extraterrestrial origin (70). Large forest fires have also been observed to deposit smoke near the tropopause, and some of this aerosol would consist of soot. Deep convective storms may lift polluted air containing soot into the lower stratosphere. Substantial concentrations of soot aerosol, comprising Arctic haze, are found in the Arctic polar winter troposphere up to the height of the tropopause (72,73).

Because of a lack of data, the morphology and global budget of soot particles in the upper atmosphere remain uncertain. Nonetheless, only a very small input of soot to the stratosphere — less than 0.001 Tg-C/yr — might be expected.

NOCTILUCENT CLOUDS

Noctilucent (night-luminous) clouds (NLCs) have been under continuous investigation since the late 1800s (74-76). NLCs are the extreme manifestation of terrestrial water clouds, residing more than 80 km above the ground and lending a spectacular appearance to the nighttime sky. Yet, despite decades of remote observation, and occasional in situ probing, the physics of noctilucent clouds has not been entirely quantified. Reasons include the remoteness of the clouds, which makes observation difficult, and the complexity of the cloud processes, which involve particle microphysics, atmospheric dynamics, photochemistry and ionization processes (77-80). Table 6 summarizes our current understanding of noctilucent cloud properties, based on a number of studies and reviews (81-86); see also *Journal of Geophysical Research*, volume 94, number D12, 1989.

Table 5. Properties of Alumina Particles and Meteoritic Dust

Alumina Particles

Composition	Al_2O_3; surface traces of Cl, S, etc.
Origin	Ablated space debris; solid-fueled rocket exhaust
Properties	Solid spheres; $<< 0.1$ ppbm; >1 μm radius; $\sim 1 \times 10^{-6}$ cm^{-3}
Distribution	Globally distributed above 12 km; observations lacking, concentrated in flight corridors?
Mass Budget	~ 0.001 Tg-Al_2O_3 per year
Residence Time	< 1 yr (average, based on particle size distribution)
Effects	Provide ready nuclei for aerosols/clouds; surfaces for chemical processing
Influences	Space activity; re-entry and burn-up of old spacecraft and launch vehicles; vehicle launch rates
Trends	Apparent tenfold increase from 1976-1986

Meteoritic Dust

Composition	SiO_2, Fe, Ni, C, etc.; trace of Cl, S
Origin	Interplanetary dust; ablation debris
Properties	Solid particles, some spheres; micrometeorites; $<< 0.1$ ppbm; >1 μm radius; $<1 \times 10^{-7}$ cm^{-3}; smoke particles: ~ 0.01 μm; <100 cm^{-3}
Distribution	Distributed more-or-less globally above 12 km (observations lacking)
Mass Budget	~ 0.02 Tg/yr (global influx, meteoroid events, distribution undetermined)
Residence Time	< 1 mo (micrometeorites); 1-10 yr (meteoritic "smoke")
Effects	Provide ready nuclei for aerosols and clouds; surfaces for chemical processing
Influences	Meteor showers, cometary encounters
Trends	None are obvious

Table 6. Properties of Noctilucent Clouds

Composition	Principally water ice; some meteoritic debris
Origin	Water vapor nucleation onto ions or meteoritic dust particles
Properties	Ice crystals, likely cubic; < 1 ppmm; < 0.05-μm radius; ~ 10 cm^{-3}; optical depths, typically 10^{-4} to 10^{-5}, maximum $\sim 10^{-3}$
Distribution	Mesopause region (~ 82 km) at high latitudes ($>45°$) in the summer hemisphere; temperature of formation, ~ 130 K
Mass Budget	~ 1 ppmm H_2O at 80 km
Residence Time	Minutes to hours (sedimentation/evaporation control)
Effects	Ionization depletion; minor effects on solar or terrestrial radiation
Influences	Water vapor accumulation in the upper atmosphere; possibly release of water by rocket engines
Trends	Significant increase over last century concurrent with buildup of atmospheric methane

Sunlight scattered from noctilucent clouds has a very minor effect on the radiation balance at high latitudes. NLC particles can scavenge electrons and ions and thus alter the local charge balance. Noctilucent clouds may also control the water vapor abundance in the thermosphere by providing a "cold trap" near the mesopause. As space missions and rocket launches become more frequent, more water vapor will be deposited in the mesosphere, so noctilucent clouds may become more common (87). Besides the vehicles launched for space exploration, more rockets may be launched to exploit the solar system for energy and mineral resources. High-altitude aircraft flights may lead to further increases in the amount of water vapor in the upper atmosphere. Thomas et al. (88) have proposed that the apparent increase in NLC frequency over the last century is associated with the observed increase in the concentration of methane (and, hence, water vapor) in the upper atmosphere.

A semi-stationary summertime layer of noctilucent clouds — referred to as polar mesospheric clouds, or PMCs — has been detected and characterized by the Solar Mesosphere Explorer satellite (89). The PMCs and NLCs have similar microphysical and chemical origins: NLCs represent the weak, equator-ward manifestation of PMCs. The clouds, at their densest, have vertical optical depths of $\sim 10^{-3}$, with typical optical depths one to two orders of magnitude smaller.
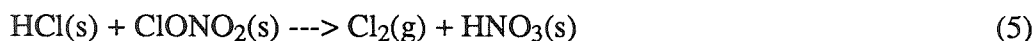
HETEROGENEOUS CHEMICAL PROCESSES AND OZONE DEPLETION

The recent discovery of an ozone "hole" over Antarctica in late austral winter and early spring (90) has led to considerable research on the causative processes (e.g., seminal discussions are given by Solomon et al. (91); Crutzen and Arnold (47); McElroy et al. (92,93). Much of the subsequent research is collected in special journal issues, including *Geophysical*

Research Letters, volume 13, number 12, 1986; and volume 15, number 8, 1988; *Journal of Geophysical Research,* volume 94, numbers D9 and D14, 1989; *Geophysical Research Letters,* volume 17, number 4, 1990; see also Solomon (94).

Laboratory studies show that a fast surface-catalyzed reaction of HCl with chlorine nitrate ($ClONO_2$) can occur on PSC particles to produce "active" chlorine (Cl_2, HOCl, and $ClNO_2$) (95-101). Through known homogeneous photochemical processes (102), this enhanced activated chlorine may explain most, if not all, of measured ozone deficits (103,104). The intense interest in PSCs has led to a new focus on the possible role of other stratospheric aerosols in heterogeneous chemical reactions that might affect stratospheric composition and ozone depletion (105).

The key heterogeneous chemical processes that occur on PSC particles are:

$$HCl(s) + ClONO_2(s) \longrightarrow Cl_2(g) + HNO_3(s) \tag{5}$$

$$HCl(s) + N_2O_5(s) \longrightarrow ClNO_2(g) + HNO_3(s) \tag{6}$$

$$ClONO_2(s) + H_2O(s) \longrightarrow HOCl(g) + HNO_3(s) \tag{7}$$

$$N_2O_5(s) + H_2O(s) \longrightarrow 2\ HNO_3(s) \tag{8}$$

In these chemical equations, "s" indicates that the species is likely to be adsorbed on the particle surface prior to reaction, and "g" indicates that the species rapidly desorbs from ice surfaces and is likely to be found in the gas phase (106). Chlorine activation via reactions 5 through 7 is very likely to proceed to completion on PSCs, with or without occasional solar illumination, in the early part of polar winter. This conclusion was recently confirmed by laboratory studies (107). Chlorine activation — in combination with denitrification, which is caused by PSC particle sedimentation, and de-NO_x-ification, which is the conversion of NO_x to nitric acid as in reaction (8) — results in a perturbed stratospheric composition that is extremely destructive to ozone. If the stratospheric abundances of water vapor and/or nitric acid vapor were to increase substantially in the future, PSCs could appear more widely and cause chemical perturbations over much larger regions. Similarly, continued cooling of the stratosphere caused by increasing burdens of carbon dioxide might enhance PSC formation and chemical activity.

It has been suggested chlorine activation and other heterogeneous chemical processes may occur on background sulfate aerosols (105). The significance of such reactions is that the resulting perturbation could be global in scale, and not confined to the polar winter as as they are in the ozone hole. Modeling studies support the possibility of large, widespread ozone depletions associated with heterogeneous chemistry, if the rates of one or more of reactions (5) through (7) — particularly reaction (5) — are rapid (108). In these scenarios, increasing stratospheric concentrations of background HCl and $ClONO_2$, derived from chlorofluorocarbons could be activated over global scales if sulfate levels were enhanced by anthropogenic activity (109) or by a future major volcanic eruption.

Laboratory measurements show that the reaction of N_2O_5 with H_2O (reaction 8) occurs efficiently on sulfuric acid surfaces (110,111) [this reaction also occurs on PSCs, but is quite sensitive to the fractional composition of water in the ice particles (97)]. There is, however, little evidence for the rapid reactions of chlorine gases (i.e., reactions 5 through 7) on sulfate particles, either in laboratory studies (101,112) or atmospheric analyses (113). On the other hand, accelerating ozone depletions measured in the Northern Hemisphere (114) suggest a possible increase in the activity of chlorine that may be associated with heterogeneous chemical pro-

cesses. Accordingly, global-scale chemical perturbations connected with sulfate aerosol enhancements remain uncertain.

RADIATION AND CLIMATE EFFECTS

Many scientists, beginning with Benjamin Franklin (115), have studied the relation between volcanic explosions and climate/weather change (116-121). Existing research indicates that, in the years after a major volcanic eruption, anomalous weather patterns and regional- to global-scale cooling is likely (122-127). The connection between volcanoes and climate is most directly made through the radiative effect of volcanically induced sulfate aerosols on the global radiation budget (122,128). The volcanic aerosols, when formed in the stratosphere where they can be rapidly dispersed around the Earth, increase the reflectivity of the atmosphere and reduce incoming solar energy (129). The aerosols also produce a modest infrared-trapping effect, which is not sufficient to reverse the cooling caused by the increased reflectivity (122). The net effect of a major volcanic eruption sending sulfur gases into the stratosphere is an average global cooling of perhaps ~ 0.5°C for 1 year or more; this effect is limited, to a great extent, by the thermal inertia of the oceans and the relatively short residence time of volcanic aerosols in the atmosphere (130). Many statistical correlations have linked volcanic eruptions in one year with global cooling in the following years. For example, records of tree rings (131) and other climate proxies (117) support the volcanic cooling hypothesis.

The explosive energy of a volcanic eruption may not be an accurate indicator of its climatic impact. More important is the quantity of sulfur gases (particularly SO_2) injected into the stratosphere. However, the average climate effect of an explosive eruption appears to be limited to a maximum temperature decrease of ~1°C, even for the largest eruptions. This fundamental limitation may be the result of highly nonlinear physical processes that restrict the buildup and persistence of the aerosol optical depth (40).

After a major volcanic eruption, the stratospheric aerosols settle into the upper troposphere over a period of several years. These sulfate particles are highly soluble and thus enhance the cloud condensation nuclei (CCN) population of the upper troposphere (26). Similarly, high-altitude aircraft operations might increase the CCN abundance in the upper troposphere and alter cloud properties and the radiative balance of the troposphere.

Human activities can also affect stratospheric aerosol properties. Direct emissions of SO_2 and soot from high-flying aircraft contaminate the natural sulfate layer. Rocket exhaust particles released into the stratosphere, and an increasing rate of ablation of debris from orbiting platforms (68), further enhance the concentration of stratospheric aerosols. Comprehensive studies have been carried out to estimate the potential climatic impacts of proposed fleets of high-altitude aircraft (the "supersonic transport", or SST, proposed in the early 1970s) (132), while other studies have focused specifically on the possible climatic effects of aerosols generated by SST operations and Space Shuttle launches (133). In each case, only minor global-scale effects have been predicted.

Figure 6 presents calculations of the sulfate aerosol size distribution and optical depth that result from an order-of-magnitude increase in either the OCS or SO_2 concentration in the upper troposphere. The modified size distribution contains significantly larger particles, which increase in the optical depth of the aerosol layer. For an OCS enhancement by a factor of 10, the optical depth is increased by a factor of almost 5 (134). Such increases, while smaller than those observed after major volcanic explosions (i.e., factors of 10-100), approach the threshold for climatic significance.
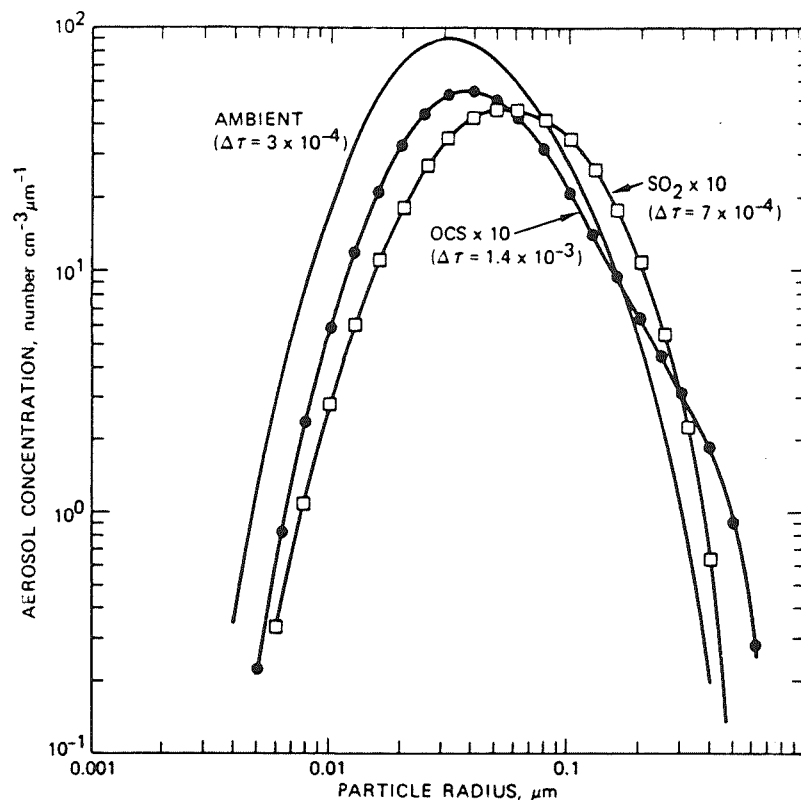
Figure 6. Calculated aerosol size distributions at 20 km for background stratospheric sulfur gas abundances, and for an increase by a factor of 10 in either the OCS or SO_2 abundance in the upper troposphere. Also indicated in each case is the aerosol optical depth corresponding to a layer 1-km thick centered at a height of 20 km (134).

OUTSTANDING SCIENTIFIC ISSUES

Some of the questions about the role of aerosols in upper-atmosphere chemistry and in climate change are summarized in Table 7. Because aerosols in the upper atmosphere can affect the state of the troposphere and biosphere, it will be important to establish baseline properties for these particles and monitor any changes in these properties. Among other signals of aerosol activity are variations in solar radiation reaching the lower atmosphere and surface and alterations in the chemistry of the ozone layer (38). Upper-atmospheric particles are subject to modification by many human activities, including high-altitude commercial and military flight. It remains to be determined whether such activities — at projected levels — can lead to climatic and other environmental changes. Specific scientific studies include:

1) Heterogeneous chemistry studies: Accurate laboratory studies on the reactivity of sulfate (sulfuric acid) aerosols should be carried out under realistic stratospheric conditions; as opportunities arise, in situ chemical perturbations associated with enhanced sulfate aerosols might be studied directly (e.g., after a volcanic eruption, or in a planned sulfur release).

2) Predictive model development: Forecasting the effects of natural events, such as volcanic eruptions and of various human activities on middle-atmosphere aerosols, upper-tropospheric aerosols, the global radiation budget, and climate, requires sophisticated models, which should be global in scale — optimally three-dimensional — and include accurate treatments of the appropriate dynamical, photochemical, microphysical and radiative processes.

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Table 7. Questions and Uncertainties

Sulfate Aerosols
- Is the background sulfate mass increasing, and if so, why?
- Will proposed high-altitude aircraft traffic increase the mass and/or chemical activity of the global background sulfate aerosol layer?
- Is increased sulfate aerosol reactivity possible with increasing water vapor, among other factors?
- Are stratospheric particles a significant component of the global radiative energy balance under normal conditions, and thus of global climate change?

Volcanic Particulates
- Is there a measurable effect of volcanic eruptions on climate, or is the effect illusory?
- Are volcanic aerosols important for heterogeneous chemistry?
- What are the types and frequencies of volcanic eruptions that produce global effects?
- What are the injection efficiencies of SO_2, HCl, H_2O, and other gases?
- Are there strong nonlinear limits to the global effects of very large volcanic injections?

Polar Stratospheric Clouds
- Will high-altitude flight enhance water vapor concentrations, leading to a greater frequency, range and duration of PSCs?
- Will high-flying aircraft create long-lived contrails in the polar stratosphere and modify stratospheric chemistry and ozone?
- Are there other species/reactions (e.g., of NO_x), which might be important, on stratospheric ice particles?
- What is the precise composition and morphology of Type I and Type II ice particles?
- How does denitrification occur on Type I and Type II particles?
- Can we directly observe chlorine activation on Type I PSCs?

Soot
- What are the ambient sources and concentrations of soot particles in the stratosphere?
- Can the morphology or trace chemistry of soot be used to identify and quantify uniquely its sources?
- Can soot particles catalyze heterogeneous chemical processes under stratospheric conditions?
- Is soot absorption of shortwave radiation in the stratosphere dynamically or climatically significant?

Alumina Particles
- What increase in stratospheric alumina debris can we expect from future aerospace fleets, including rockets and aircraft?
- What is the reactivity of alumina particles coated with sulfates?
- Can the total surface area of alumina particles in the stratosphere be determined? Is it significant?
- Are these particles an important sink for sulfate, chloride, or other stratospheric materials?

Meteoritic Dust
- Are claims of potential significant chemical impacts in the stratosphere reasonable?
- What are the effects of meteoritic material on stratospheric composition above ~30 km, due to neutralization reactions, etc.?

Noctilucent Clouds
- Will water vapor emissions by high-altitude aircraft increase the frequency and range of NLCs?
- Are the frequency and density of NLCs increasing in pace with methane or other gases?

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3) Global aerosol monitoring program: A global monitoring program for middle atmosphere aerosol trends — particularly trends that may be associated with anthropogenic emissions but also transients associated with volcanic eruptions — could be built on existing and planned satellite and lidar measurement projects; in situ measurements would be necessary for calibration and detailed microphysical/radiative/chemical definition of the aerosols over time. The mesosphere could also be monitored for changes in key parameters, such as water vapor content and the occurrence of clouds.

ACKNOWLEDGMENTS

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