Changes in stratospheric composition, chemistry, radiation and climate caused by volcanic eruptions

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Abstract: The primary effect of a volcanic eruption is to alter the composition of the stratosphere by the direct injection of ash and gases. On average, there is a stratospherically significant volcanic eruption about every 5.5 years. The principal effect of such an eruption is the enhancement of stratospheric sulphuric acid aerosol through the oxidation and condensation of the oxidation product H_2SO_4. Following the formation of the enhanced aerosol layer, observations have shown a reduction in the amount of direct radiation reaching the ground and a concomitant increase in diffuse radiation. This is associated with an increase in stratospheric temperature and a decrease in global mean surface temperature (although the spatial pattern of temperature changes is complex). In addition, the enhanced aerosol layer increases heterogeneous processing, and this reduces the levels of active nitrogen in the lower stratosphere. This in turn gives rise to either a decrease or an increase in stratospheric ozone levels, depending on the level of chlorine loading.

Introduction

This paper addresses the composition, chemistry, radiation and climate effects caused by large amounts of material injected into the stratosphere by volcanic eruptions. The primary effect of a volcanic eruption is to alter the composition of the stratosphere by the direct injection of ash and gases. The ejecta themselves have a relatively small effect on the atmospheric state, but the secondary product, stratospheric sulphate aerosol, has a major effect on stratospheric radiation, chemistry and climate. The two most recent large eruptions were those of El Chichón, Mexico in April 1982 and of Mount Pinatubo, Philippines, in June 1991. Detailed reviews of these eruptions can be found in Hofmann (1987) and McCormick *et al.* (1995). For reviews of the atmospheric effects of stratospheric aerosols, see Lamb (1970) or Pueschel (1996). An extensive review of the impact of volcanic eruptions on climate is given by Robock (2000).

In general, only eruptions that penetrate into the stratosphere produce atmospheric effects on time-scales greater than a few days, as concentrations of volcanic ejecta in the troposphere are relatively quickly depleted through precipitation, diffusion and rainout. The significant exceptions are long-lived effusive eruptions which can create a tropospheric 'steady state' of enhanced levels of volcanic debris. The eruption of Laki in Iceland in 1783 is one such example.

Indirect effects of volcanic perturbations considered elsewhere include:

- cooling of the ocean surface (Robock & Mao 1995),
- changes in cirrus microphysical properties (Minnis *et al.* 1993),
- changes in polar stratospheric cloud properties (Deshler *et al.* 1994).

Volcanic episode

Eruption

A volcanic event occurs when there is a sudden or continuing release of energy caused by near-surface or surface magma movement, and can include explosions with an eruption plume. Eruption duration can range from a few minutes to thousands of years, with the median duration being seven weeks (Simkin & Siebert 1994). Volcanic ash clouds can be produced in extremely small eruptions of duration less than one minute. Violent eruptions often occur after

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long periods of repose, so dangerous volcanoes may not currently be recognized as active. Of the 16 largest explosive eruptions in the last 200 years, 12 were the first historic eruption known from the volcano.

During a single eruption, styles of activity and types of products may change within minutes to hours, depending upon changes in magma composition, volatiles, or other magma chamber and vent conditions. The diversity of volcanoes and volcanic products is due to differences in the composition of the magma (molten or liquid rock), which control its viscosity and gas content. Gases become less soluble in magma as it approaches the surface and the pressure decreases. The greater the gas content of a magma, the more explosive the eruption. Additionally, magma water interaction can generate very explosive eruptions.

Eruptions with a Volcanic Explosivity Index (VEI) greater than 4 are likely to penetrate into the stratosphere (see Newhall & Self 1982, for definition of the VEI). Table 1, adapted from Bluth *et al.* (1997), lists such eruptions from 1979 to 1994. Although all penetrated into the stratosphere, most of these eruptions did not have a strong effect on the atmosphere. Figure 1 shows a measure of global stratospheric aerosol loading from 1850 to 2000. During this period there were 26 eruptions that produced a global stratospheric optical depth greater than 0.02. This suggests that, on average, there is a significant eruption into the stratosphere about every 5.5 years.

Volcanic plume

The most abundant gases typically released into the atmosphere from volcanic systems are water

Table 1. *Recent Eruptions with Volcanic Explosivity Index (VEI) ≥4 (from Bluth et al. 1997).*

Volcano	Latitude of volcano	Volcano height (km above sea-level)	Eruption date
St Helens	46. 2° N	3.1	18 May 1980
Pagan	18.1° N	0.6	15 May 1981
El Chichón	17.3° N	1.1	4 April 1982
Colo	0.2° S	0.5	23 July 1983
Augustine	59.4° N	1.2	27 March 1986
Kelut	7.8° S	1.7	11 February 1990
Pinatubo	15.1° N	1.7	15 June 1991
Hudson	45.9° S	2.5	12 August 1991
Rabaul	4.3° S	0.2	19 September 1994
Kliuchevskoi	56.1° N	4.8	1 October 1994

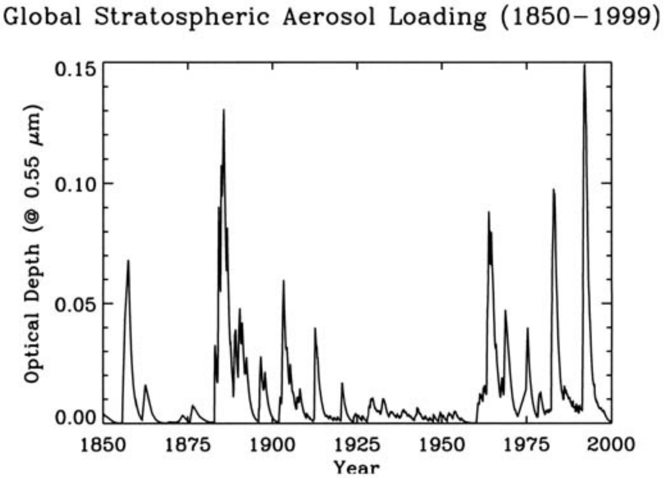


Fig. 1. Global stratospheric aerosol optical depth at 0.55 μm (from the data of Sato *et al.* 1993, including updates to 2000).

vapour (H_2O), followed by carbon dioxide (CO_2) and sulphur dioxide (SO_2). Volcanoes also release smaller amounts of other gases, including hydrogen sulphide (H_2S), hydrogen (H_2), helium (He), carbon monoxide (CO), hydrogen chloride (HCl), hydrogen fluoride (HF), nitrogen (N_2), and argon (Ar).

In addition to the release of a number of gases, an explosive eruption blasts molten and solid rock fragments (tephra) into the air. The largest fragments (bombs) fall back to the ground near the vent, usually within 3 km. The ash (rock fragments with diameter <2 mm), continues rising into the air, forming an eruption column.

Eruption columns can grow rapidly, reaching heights of more than 20 km above the volcano in less than 30 minutes. The upper surface of the eruption cloud may be tens of degrees cooler than the surrounding environment, owing to intertial overshoot of the erupted mixture above the neutral buoyancy height (Woods & Kienle 1994). This can complicate the estimation of cloud height from thermal satellite imagery.

Analysis of the Geostationary Meteorological Satellite (GMS) and Advanced Very High Resolution Radiometer (AVHRR) images of the Mount Pinatubo eruption plume by Holasek *et al.* (1996) gave the initial plume radius as 50 km; this increased to about 275 km after about 2 hours 45 minutes. Woods & Kienle (1994) state that the 18 May 1980 Mount St Helens ash plume increased in radius from 20 km to 50 km in about 10 minutes. It also took about 10 minutes for the 21 April 1990 Redoubt volcanic plume to increase in radius from about 6 km to over 15 km.

Volcanic cloud

After its initial expansion the ash cloud drifts following the local wind patterns, becoming separated from the volcanic source. The rates of drift of ash clouds are typically in the range of 20–100 km/h. Vertical wind shear may result in the cloud moving in different directions as a function of altitude. This happened following the 28 March 1982 eruption of El Chichón, when the tropospheric component of the ash cloud spread in a northeasterly direction, whereas the stratospheric component moved to the southwest (Matson 1984).

Sawada (1994) tabulates the dimensions of the highest ash clouds for 17 volcanic eruptions detected using the GMS from December 1977 to June 1991. These clouds had a typical area equivalent radius of about 110 km, with the largest being the 14–15 June 1991 Mount Pinatubo cloud, which had an area equivalent radius of about 1230 km.

For equatorial latitudes, the typical time for the cloud of volcanic debris to circle the globe was measured as 21 days (Matson & Robock 1984) and 22 days (Bluth *et al.* 1992) for the eruptions of El Chichón and Mount Pinatubo respectively. At higher latitudes, the time is less, e.g. Schoeberl *et al.* (1993*a*) show the SO_2 plume from the Cerro Hudson (45.9° S) eruption of August 1991 circled the globe in seven days.

Volcanic ash properties

COMPOSITION

The physical properties of volcanic ashes depend mostly on their relative proportions of glass, mineral fragments and rock fragments (Heiken 1994). Volcanic ash is abrasive, mildly corrosive, and conductive (especially when wet), and may also carry a high static charge. Bayhurst *et al.* (1994) give the density of ash from the 15 December eruption of Mount Redoubt as 2.42 ± 0.79 g/cm^3. In addition, they found the average aspect ratio and surface area of an ash particle to be 3.5 and 284 μm^2 respectively.

SIZE DISTRIBUTION

The initial particle-size distribution of volcanic ejecta is poorly understood, although Sparks *et al.* (1994) note that 70% of ejecta from explosive eruptions is less than 1 mm in radius. Hobbs *et al.* (1991) measured the *in situ* particle-size distributions of ash emissions from Mount Redoubt, Mount St Helens and Mount Augustine. The size distributions were approximately multimode log-normal distributions with a nucleation mode ($r_{\mathrm{mode}} < 0.05$ μm), an accumulation mode (r_{mode} 0.05–0.5 μm), and one or more giant modes ($r_{\mathrm{mode}} > 0.5$ μm). Hobbs *et al.* (1991) considered the nucleation mode to be composed of sulphuric acid–water drops, where the H_2SO_4 was produced either in the volcanic throat or by gas to particle conversion of the SO_2 in the eruption plume. The accumulation and giant modes were thought to be composed of silicate particles.

The evolution of the ash cloud was principally a decrease in the concentration at all particle sizes. This is not surprising as the residence time of a volcanic ash particle is strongly controlled by its mass (i.e. size) and non-spherical morphology (Mackinnon *et al.* 1984). Table 2 from Bursik *et al.* (1994) shows the estimated terminal velocity and typical residence times as a function of particle size for an ash cloud with a particle density of 2 g/cm^3 at 12.9 km. Some of the smaller particles aggregate into clusters due to electrostatic attraction, giving them settling

Table 2. *Estimated particle terminal velocities and residence times. Adapted from Bursik* et al. *(1994).*

Radius (μm)	Fall speed (m/s)	Residence time
700	9	9.3 min
355	6.4	13 min
173	3.2	26 min
85	1.9	43 min
45	0.64	2.2 h
22	0.15	9.3 h
11	0.05	1.1 days
5.5	0.012	4.8 days
2.75	0.0025	23 days

velocities higher than those shown, i.e. ≈0.3–1.0 m/s (Macedonio *et al.* 1994).

It is important to realize that most of the ash mass in the early lifetime of a cloud is contained in relatively large particles (i.e. 90% of the mass of the volcanic cloud is contained in particles bigger than 2 μm) which rapidly sediment out of the atmosphere. This is consistent with the conclusion of Knollenberg & Huffman (1983) that volcanic material injected into the stratosphere by large volcanic eruptions is typically less than 1 μm in radius. From the measurements of Gooding *et al.* (1983) for the El Chichón eruption, the *e*-folding time for volcanic ash is estimated to be about 40 days (the *e*-folding time is the time it takes for an amount to decay to l/*e* of its initial value).

Although the amount of ash injected for recent eruptions is relatively well known, considerable research is still required to quantify the effect of ash on the stratosphere. The relatively minor role of the ash component in climate modification is largely due to its short residence in the atmosphere; rapid aggregation leads to the fallout of even the finest tephra within a few hundred to 1000 kilometres from the source (Sigurdsson & Laj 1992).

Development of the aerosol cloud

The flow of sulphur into the stratosphere is dominated by large explosive eruptions which account for about 60% of stratospheric sulphur budget (Sedlacek *et al.* 1983). Pyle *et al.* (1996) estimate that on average about 0.06–0.15 Mt/y of stratospheric sulphur (as SO_2) is from non-volcanic sources, while about 1 Mt/y arises from volcanic injection. Individual eruptions such as those detailed in Table 3 may increase the SO_2 loading by more than an order of magnitude. Historic eruptions such as the 1815 Tambora and the 1783 Laki eruptions are thought to have injected about 50 Mt (SO_2 equivalent) into the stratosphere (Sigurdsson & Laj 1992).

Volcanic emissions also include sulphur in the form of H_2S. This reacts to form HS which in turn forms SO_2 though reaction mechanisms involving O_2, O_3, or NO (Sigurdsson & Laj 1992). As this process is very rapid H_2S can be thought of as an additional source of SO_2.

The enhancement in gas concentrations reduces the ability of solar and terrestrial radiation to penetrate the atmosphere in the gas absorption bands. For example, increased absorption by SO_2 in the wavelength intervals 180–235 nm, 260–340 nm and 340–390 nm reduces the transmission of solar flux and so reduces the photolysis rates of key species such as ozone (Bekki *et al.* 1993). Stratospheric ozone can also be directly influenced by SO_2. Bekki *et al.* (1993) suggest that ozone production is catalysed by SO_2 above about 25 km. Below this level the absorption of radiation by SO_2 dominates.

Once in the stratosphere, SO_2 is oxidized to H_2SO_4 through:

$$SO_2+OH+M \rightarrow HSO_3+M$$
$$HSO_3+O_2 \rightarrow SO_3+HO_2$$
$$SO_3+H_2O \rightarrow H_2SO_4$$

where M is any third molecule (McKeen *et al.* 1984). The removal rate of SO_2 has an *e*-folding time of about 35 days for equatorial eruptions (Heath *et al.* 1983; Bluth *et al.* 1992; Read *et al.* 1993).

Properties of volcanically enhanced stratospheric aerosol

A volcanically enhanced stratospheric aerosol layer is formed as H_2SO_4 that has been produced

Table 3. *Estimates of the amount of SO_2 injected into the stratosphere from recent major eruptions.*

Volcano	Latitude	Eruption date	SO_2 emitted (Mt)	Reference
El Chichón	17.3°N	April 1982	7	Hofmann & Rosen (1983)
Mount Pinatubo	15.1°N	June 1991	12–15	McPeters (1993)
			20	McCormick *et al.* (1995)
Cerro Hudson	45.9°S	August 1991	1.5	Schoeberl *et al.* (1993*a*)

from the SO_2 condenses onto pre-existing condensation nuclei such as existing sulphuric acid particles, and perhaps ash particles, ion clusters, or trace meteoric material. It is this aerosol layer, whose mass is enhanced by several orders of magnitude following a large eruption, which gives rise to the strong perturbations to atmospheric chemistry and radiation discussed later.

There is no 'typical' volcanic aerosol during the decay of the cloud. The aerosol evolves with time through transport and through aerosol processes of evaporation, condensation, collision, coalescence, and sedimentation. As a result, estimates of the impact of such aerosol on the radiation budget of the Earth have appropriately large error estimates.

Morphology

The increase in temperature with height makes the stratosphere extremely stable, so that there is little vertical convection. The injected aerosol cloud tends to spread with the horizontal winds and to slowly descend through gravitational motion. The main removal mechanism for aerosols is gravitational settling into the troposphere, after which the particles are removed by deposition processes. Aerosols can remain in the stratosphere for up to a few years; during this time they can be transported a significant distance from the source.

The rate of descent of the core of the Mount Pinatubo volcanic cloud was about 17 m day^{-1} at 23 km (Lambert *et al.* 1993), which was consistent with particles with an aerodynamic radius of about 0.25 µm. The removal rate from the stratosphere is dependent on season and the size of the particles. Pinto *et al.* (1989) suggested that aerosol residence time in the stratosphere is self-limiting, as larger eruptions produce larger particles that precipitate out more quickly. This is consistent with data from a number of eruptions shown in Table 4, where the estimates of the stratospheric aerosol *e*-folding loss rate do not increase linearly with injected SO_2 mass.

Eruptions at tropical latitudes are particularly effective at producing global-scale perturbations to the background stratospheric aerosol amounts, since the aerosol can be transported around the equator in about 20 days, and to the poles of both hemispheres on time-scales of a few weeks. Figure 2 shows the evolution of the Mount Pinatubo aerosol cloud observed by instruments on the Upper Atmosphere Research Satellite. Evident in the images is the slow descent of the aerosol and the containment of the cloud in a tropical reservoir which is slowly eroded through transport to higher latitudes (principally the winter hemisphere). Large amounts of sulphuric acid deposition in ice cores in both the Arctic (Zielinski 1995) and Antarctic (Delmas *et al.* 1992) in the years following major eruptions also testify to the global spread of aerosols.

Composition

Because of its low vapour pressure, almost all of the H_2SO_4 vapour condenses to form liquid H_2SO_4–H_2O particles. The larger sulphuric acid particles typically contain volcanic ash particles (Pueschel *et al.* 1994). However, it is not clear if this is an indication of heterogeneous nucleation or if these are particles that have undergone coagulation. The weight fraction of sulphuric acid in the particles is determined by the temperature and humidity (Steele & Hamill 1981): the higher the humidity the lower the sulphuric acid concentration. Lambert *et al.* (1997) used satellite temperature and water vapour measurements to calculate that the Mount Pinatubo aerosol cloud had compositions typically in the range

Table 4. *Stratospheric aerosol e-folding time loss rates estimated from either point measurements or from near-global satelllite data. The SO_2 amounts are taken from Bluth et al. (1997).*

		Loss rate (months)		
Volcano	SO_2 (Mt)	Point	Near global	Reference
St Helens	1.0	3.6		Jäger & Carnuth (1987)
Alaid	1.1	6.6		Jäger & Carnuth (1987)
El Chichón	7	10.4–12.3		Hofmann & Rosen (1984)
		11.5–14.3		Jäger & Carnuth (1987)
			14	Yue *et al.* (1991)
Mount Pinatubo	20	11.3		Rosen *et al.* (1994)
			8.3–10.9	Kent & Hansen (1998)
			11.3	Lambert *et al.* (1997)

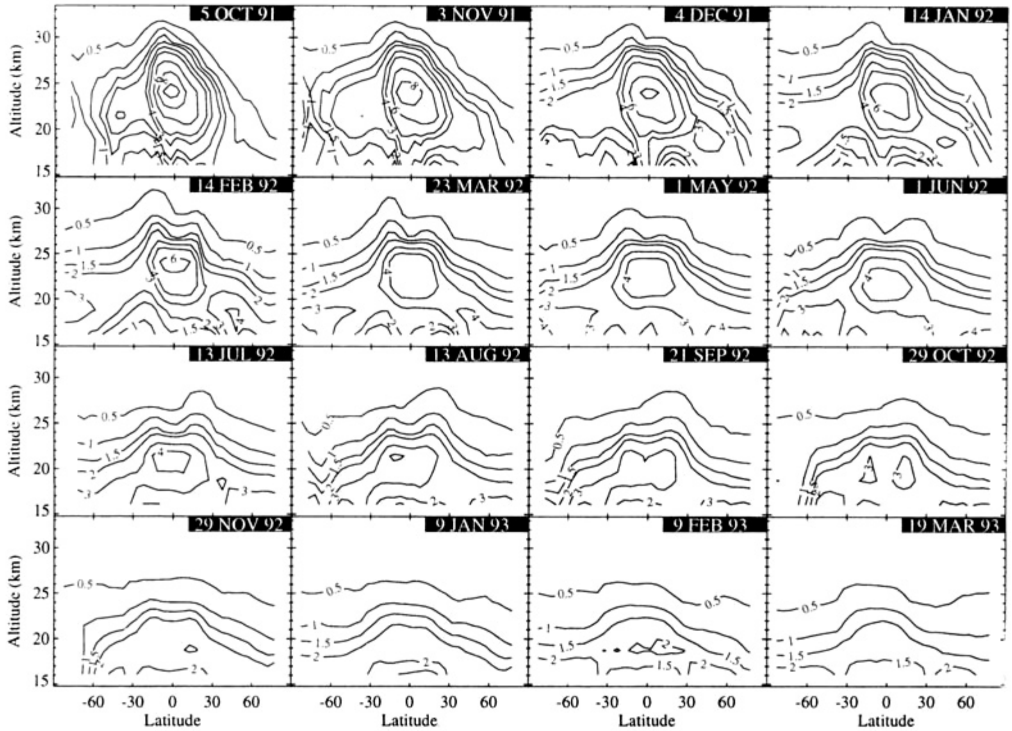


Fig. 2. Zonal mean distribution of the Pinatubo aerosol volume density. Contour levels are set at 0.5, 1, 1.5, 2, 3, 4, 6, 8, and 10 μm³/cm³ (from Lambert *et al.* 1997). Reproduced by permission of the American Geophysical Union.

55–80% sulphuric acid by weight. The core of the aerosol cloud had a composition of about 70% sulphuric acid by weight (Grainger *et al.* 1993; Rinsland *et al.* 1994*b*).

Size distribution

If the H_2SO_4 concentration is sufficiently high, homogeneous nucleation may occur. Aerosols grow rapidly through condensation to obtain a radius of about 0.01 μm (Hofmann 1987) and additionally through coagulation to about 0.1 μm.

The size distribution, $n(r)$, is usually expressed so that $n(r)dr$ is the number of drops per unit volume having a radius between r and $r+dr$. Several mathematical functions have been used to express $n(r)$, the commonest being the sum of log-normal distributions, i.e.

$$n(r) = \sum_{i=1}^{M} \frac{N_i}{\sigma_i \sqrt{2\pi}} \frac{1}{r} \exp\left[\frac{(\ln r - \ln r_i)^2}{2\sigma_i^2} \right]$$

where M is the number of modes and N_i, r_i, and σ_i are the particle number density, the mode radius and the spread for the ith distribution. The particle-size distribution is a strong function of height, location, and time since eruption (Deshler *et al.* 1993; Lambert *et al.* 1997). In general the increase in aerosol density is associated with the size distribution having more than one mode (Thomason 1992; Pueschel 1996).

The size distribution is often characterized in terms of the effective radius, r_e, defined by

$$r_e \equiv \frac{\int_0^\infty r^3 n(r) dr}{\int_0^\infty r^2 n(r) dr}$$

Like the particle-size distribution, the effective radius varies strongly with altitude, location, and time (Grainger *et al.* 1995).

Figure 3 shows the particle-size distributions for measurements made at Laramie, Wyoming, before and after the arrival of the Mount Pinatubo aerosol cloud. Following the eruption, the number of particles was typically enhanced by two orders of magnitude (Deshler *et al.* 1993).

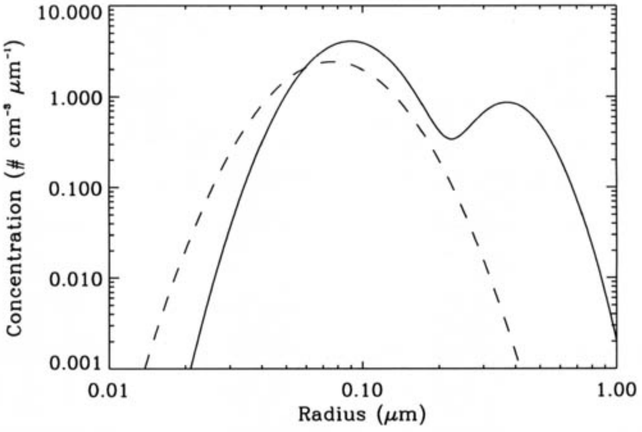


Fig. 3. Particle-size distributions measure at 41°N before (dashed line) and after (solid line) the eruption of Mount Pinatubo (Deshler *et al.* 1993).

These results are consistent with the impactor measurements of Pueschel (1996), who found the aerosol surface area and volume density increased from values of 0.48±0.12 $\mu m^2/cm^3$ and 0.04±0.02 $\mu m^3/cm^3$ in early 1989 to values of 20.4 $\mu m^2/cm^3$ and 11.5 $\mu m^3/cm^3$ about six months after the eruption.

Optical properties

The influence of stratospheric aerosol on the radiative field at a particular location can be assessed from three components:

- the volume extinction coefficient, β^{ext}, can be thought of as the cross-sectional area per unit volume that intercepts a beam of light
- the single scatter albedo, $\tilde{\omega}$, is the ratio of the scattered energy to the energy that is both scattered and absorbed, hence if $\tilde{\omega}=0$ all intercepted energy is absorbed while if $\tilde{\omega}=1$ all intercepted energy is scattered
- the asymmetry parameter, *g*, which indicates the distribution of directions of scattered light. A value of 1 indicates forward scattering, −1 backscattering and 0 isotropic scattering.

These parameters can be calculated using Mie theory given the composition of the aerosol and its particle size distribution. Figure 4 shows these parameters for a volcanically enhanced sulphuric acid cloud as a function of wavelength. The plots indicate two regimes; in the visible the extinction is about a factor of 10 higher than the infrared, the single scatter albedo is close to unity while the asymmetry parameter is about 0.8, so that almost all the intercepted radiation is scattered mostly in the forward direction. In the infrared the asymmetry parameter approaches 0 so that single scattered radiation is approximately isotropic. However, in the infrared, single scatter albedo is generally much less than 1, so that most of the intercepted radiation is absorbed rather than scattered.

Radiative changes

Stratospheric aerosols scatter incoming solar radiation and absorb outgoing terrestrial radiation. At short wavelengths the pattern of scattered light is a function of the aerosol size distribution and the composition of the particles. Generally, there is an increase in the solar radiation that is reflected back into space; also the amount of diffuse radiation incident on the Earth's surface increases, while there is a concomitant decrease in the direct solar beam. The change in the direct and diffuse ratio was noted after the eruption of Agung (Dyer & Hicks 1965) when the solar flux was reduced by 24% from the mean unperturbed level. This was concurrent with a 100% increase in the diffuse flux (De Luisi & Herman 1977). The change in the radiative field caused by volcanic aerosols also has the potential to alter the photolysis rates of key species such as O_2 and O_3 that induce chemical changes in the stratosphere (Huang & Massie 1977; Michelangeli *et al.* 1992).

A measure of the radiative effects of stratospheric aerosols is given by the stratospheric optical depth, $\tau(\lambda)$, at wavelength λ, defined by

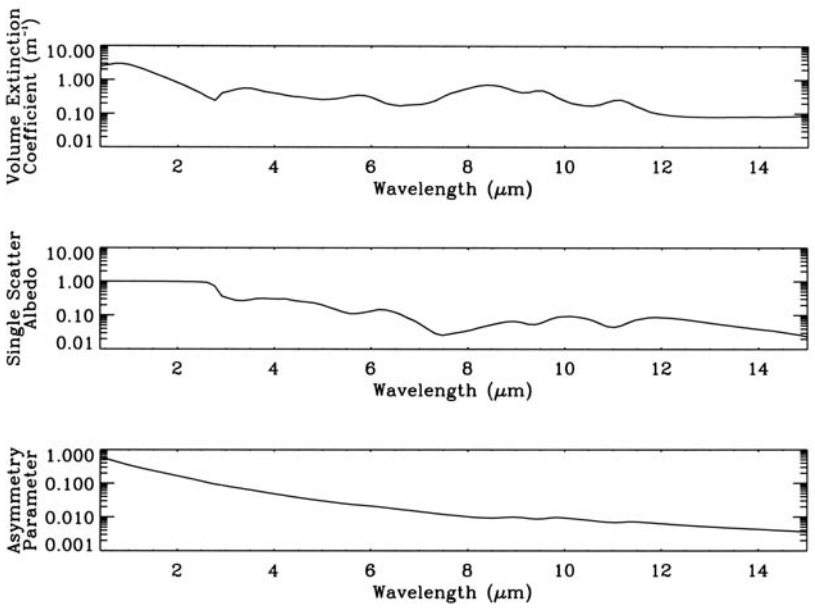


Fig. 4. Optical properties of a volcanically enhanced stratosphere aerosol for a composition of 75% H_2SO_4 by weight.

$$\tau(\lambda)=\int_{\text{tropopause}}^{\infty}\beta^{\text{ext}}(\lambda,z)dz,$$

where β^{ext}, the volume extinction coefficient, changes with height as a function of the particle composition and size distribution. The peak global loading following an eruption will occur at different times at different wavelengths as the aerosol size distribution evolves. Grant *et al* (1996) observed this effect when comparing measurements from a number of instruments following the eruption of Mount Pinatubo. Measurements made at longer wavelengths are more sensitive to larger particles (which precipitate out of the stratosphere more quickly) and so have an earlier peak aerosol loading and more rapid aerosol decay. For example, multiwavelength LIDAR observation of the same aerosol volume gave aerosol decay rates following the Mount Pinatubo eruption of 10.9 months at 335 nm and 8.3 months at 1064 nm (Kent & Hansen 1998).

In addition to decay times changing with observing wavelength, Kent & Hansen (1998) show that the decay rate changed as a function of time since eruption, and as a function of location. Point measurements are unable to differentiate between the decay of the cloud through dilution and decay through precipitation.

Figure 5 shows the SAGE II optical depth at 1.02 μm from 1984 to 1998. The extreme left of the plot shows the decay of the El Chichón aerosol as a function of time. The increase in optical depth from about 0.002 to 0.04 following the Mount Pinatubo eruption is the most striking feature of the image. Also apparent is the dispersal of the cloud to high latitudes and its gradual decay with time.

Chemical and ozone changes

The odd-chlorine species (Cl, ClO, HCl, HOCl, and $ClONO_2$) are important to stratospheric chemistry because of the potential of Cl and ClO to catalyse the removal of O_3. Additionally the heavy halogens, bromine and iodine, are also efficient in destroying stratospheric ozone (Bureau *et al.* 2000). Up to a 40% enhancement in the abundance of HCl was observed after the El Chichón eruption by Mankin & Coffey (1984). Not all of this change was due to the volcanic injection of HCl gas, as halite particles were also observed in the stratosphere and these are thought to form HCl through the reaction (Woods *et al.* 1985):

$$2NaCl+H_2SO_4\rightarrow Na_2SO_4+2HCl \qquad (1)$$

Following collision with an aerosol, a gas molecule may briefly stick to the aerosol surface or be

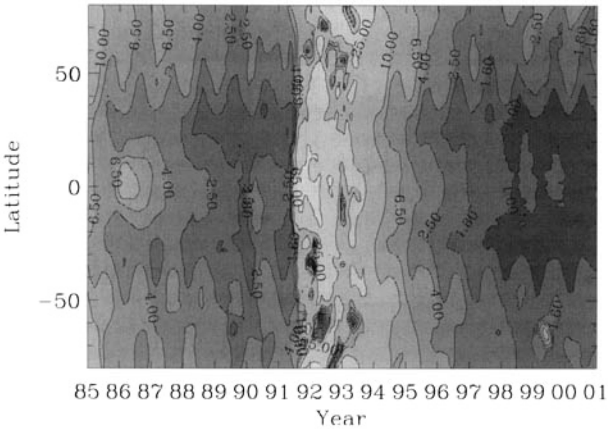


Fig. 5. SAGE II measurements of stratospheric optical depth (1000x) at 1.02 μm.

temporarily absorbed into the aerosol volume. In this way the aerosols can promote reactions between species whose reactions are much slower in the gas phase. The reactions between species that involve an aerosol particle in this way are called heterogeneous reactions.

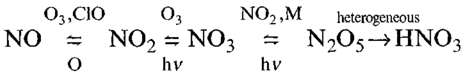
Laboratory studies have shown that:

$$N_2O_5+H_2O \rightarrow 2HNO_3 \qquad (2)$$

proceeds rapidly in the presence of H_2SO_4 aerosol (Mozurkewich & Calvert 1988). The background level of sulphuric acid aerosol in the high-latitude winter stratosphere is required to explain the low values of N_2O_5 and NO_2 (Evans *et al.* 1985) and the high values of HNO_3 (Austin *et al.* 1986).

If the reaction in solution is very fast, then the surface area of the drop is the rate-controlling aerosol parameter. If the reaction is slow compared with the rate at which the reactants diffuse into the aerosol, then the aerosol volume is the limiting parameter (Hanson *et al.* 1994). The heterogeneous reaction (2) is sufficiently fast that it effectively occurs on the surface of the aerosol and is limited by the amount of available aerosol surface area. The volcanically enhanced stratospheric aerosol perturbs stratospheric chemistry by providing additional surface area and volume for heterogeneous reaction to occur.

Reaction (2) can have a significant impact on the ratio of reactive nitrogen NO_x ($NO+NO_2+NO_3$) to its reservoir species, HNO_3, in the lower stratosphere. At low aerosol loadings an increase in aerosol surface area decreases NO_x. The system can be summarized (Seinfeld & Pandis 1998) as



$$NO \underset{O}{\overset{O_3,ClO}{\rightleftharpoons}} NO_2 \underset{h\nu}{\overset{O_3}{\rightleftharpoons}} NO_3 \underset{h\nu}{\overset{NO_2,M}{\rightleftharpoons}} N_2O_5 \xrightarrow{\text{heterogeneous}} HNO_3$$

where the additional reactants are shown above or below the reaction symbol and hv represents photolysis. As the aerosol area increases there is a point reached where the rate of removal of N_2O_5 exceeds the rate of formation, in which case the rate-limiting step for the $NO_x \rightarrow HNO_3$ conversion is the

$$NO_2+O_3 \rightarrow NO_3+O_2 \qquad (3)$$

reaction. This point occurs for surface area concentrations greater than 0.5 $\mu m^2/cm^3$ near altitudes of 20 km, and for concentrations greater than about 3 $\mu m^2/cm^3$ at about 30 km (Mills *et al.* 1993).

The removal of NO_2 reduces the active catalytic destruction of O_3 (see Dessler 2000). The reduction of NO_x levels additionally increases the amount of ClO as the scavenging of ClO through

$$ClO+NO_2 \rightarrow ClONO_2$$

is reduced. Hence increases in aerosol surface area increase the amount of reactive Cl.

Under colder conditions the heterogeneous reaction

$$ClONO_2+H_2O \rightarrow HNO_3+HOCl \qquad (4)$$

can become significant (Tie & Brasseur 1995). Importantly, Reaction (4) does not saturate as the aerosol loading increases.

Additional heterogeneous reactions that are included in modelling studies are (Hendricks *et al.* 1999).

$$ClONO_2+HCl \rightarrow Cl_2+HNO_3$$

$$BrONO_2+H_2O \rightarrow HOBr+HNO_3$$

$$HOBr+HCl \rightarrow BrCl+H_2O$$

$$HOBr+HBr \rightarrow Br_2+H_2O$$

These reactions effectively release chlorine or bromine from their relatively inactive state and in some cases move nitrogen from a more to a less reactive state.

Observational evidence consistent with heterogeneous processing on aerosols is very strong. Observed changes following the El Chichón and Mount Pinatubo eruptions include:

- decreases in stratospheric NO_2 (Johnson *et al.* 1993; Koike *et al.* 1993),
- enhanced levels of HNO_3 (Spreng & Arnold 1994; Rinsland *et al.* 1994*a*),
- enhanced levels of ClO (Avallone *et al.* 1993).

In addition, modelled mid-latitude and polar ozone values are in much better agreement if heterogeneous reactions on aerosols are included (Portman *et al.* 1996; Solomon *et al.* 1996).

In the absence of enhanced chlorine loading of the stratosphere, a Mount Pinatubo-like volcanic eruption would be expected to enhance ozone levels by about 3%, as the loss of ozone in the middle stratosphere is dominated by NO_x (Tie Brasseur 1995). However, the high levels of stratospheric chlorine from anthropogenic sources allow a decrease in ozone through the catalytic cycle

$$ClO+O \rightarrow Cl+O_2$$

$$Cl+O_3 \rightarrow ClO+O_2$$

$$\text{Net: } O_3+O \rightarrow O_2+O_2$$

Typically, reported ozone reductions of up to 15% were observed in the tropics following the Mount Pinatubo eruption (Schoeberl *et al.* 1993*b*; Weaver *et al.* 1993; Hofmann *et al.* 1994; McGee *et al.* 1994; Grant *et al.* 1994; Randel & Wu 1995). Figure 6 shows the ozone loss measured by the Total Ozone Mapping Spectrometer after the Mount Pinatubo eruption. The ozone changes observed at mid-latitudes after the Pinatubo eruption may not be entirely caused by heterogeneous chemistry, because some of the changes were due to changes in the stratospheric general circulation.

By about 2015 the Cl loading should have dropped so that the response of the stratosphere to an increase in aerosols will be ozone enhancement rather than depletion (Tie & Brasseur 1995).

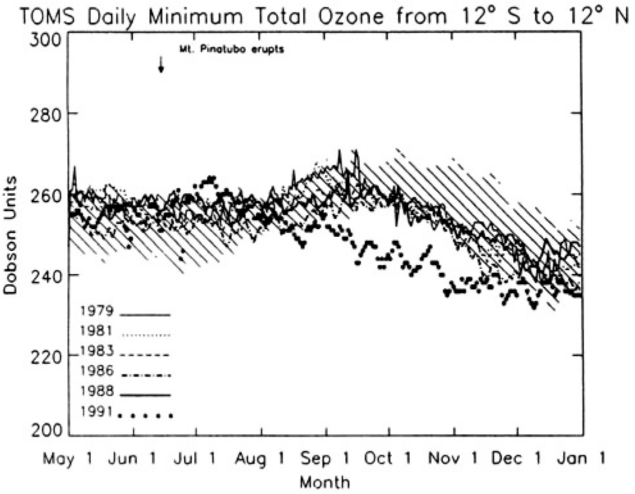


Fig. 6. Minimum total ozone amounts recorded by the Total Ozone Mapping Spectrometer in the region 12°S to 12°N. The dotted line shows the anomalously low ozone measurements made after the eruption of Mount Pinatubo (from Schoeberl *et al.* 1993*b*). Reproduced by permission of the American Geophysical Union.

Radiative forcing

Radiative forcing is a useful measure of the perturbation to the Earth's energy budget that occurs due to an external influence. It is easier to calculate than the full climate response (i.e. changes in temperature, precipitation, etc.), since knowledge of the complex feedbacks between different components of the climate system is not required. Radiative forcing is defined as the change in net irradiance at the tropopause as a result of, for example, changes in the atmospheric composition (after the stratosphere has been allowed to return to radiative equilibrium). A negative radiative forcing implies a net loss of energy to the coupled surface–troposphere system, while a positive radiative forcing implies a net gain of energy. Thus negative radiative forcing will tend to lead to a cooling of the surface, while a positive forcing leads to warming. Global and annual mean radiative forcing due to changes in external influences since 1750 have been used by Houghton *et al.* (2001) to compare the effect of different anthropogenic and natural influences. The spatial distribution is also crucial, especially for short-lived species such as aerosols or ozone.

In the case of volcanoes, the main source of radiative forcing is the large increase in stratospheric sulphuric acid aerosols. Such sulphate aerosols mainly scatter solar radiation back to space, with the immediate effect of reducing the solar irradiance at the ground and causing a negative radiative forcing. Additionally, the relatively large stratographic aerosol also interacts with absorbing long-wave radiation that would otherwise be emitted to space from the surface and lower atmosphere, and re-emits less radiation (since the stratosphere is at a lower temperature). Some of this radiation is re-emitted back towards the Earth's surface. Thus the system loses less long-wave radiation to space and this results in a small positive radiative forcing. Since the aerosol tends to be largest immediately following the eruption (Lacis *et al.* 1998), this 'greenhouse effect' will be largest then. Generally, however, this effect is overwhelmed by the negative radiative forcing (Stenchikov *et al.* 1998). The global mean radiative forcing due to Mount Pinatubo peaked at -3 W/m^2 and persisted for approximately two years (Stenchikov *et al.* 1998).

A small amount of absorption of solar and terrestrial radiation occurs in the aerosol layer, and this, accompanied by an increase in absorption of the reflected short-wave radiation above the aerosol layer by ozone and SO_2, tends to lead to heating in the stratosphere, in turn leading to an increase in long-wave radiation emitted downwards to the troposphere. Again, this contribution to radiative forcing is generally small (although the effect of the heating of this layer is an important part of the climate response to volcanic aerosol, as will be discussed in the next section).

As discussed earlier, the other particulate material ejected by the eruption includes dust and volcanic ash. These larger, heavier particles tend to have an impact on the radiation budget on smaller spatial and temporal scales than the stratospheric sulphate aerosol, as they are much more quickly removed from the atmosphere. However, locally these effects can be very large. There are large uncertainties in some of the critical properties of volcanic ash, in particular the refractive index, meaning that reliable modelling of these effects is still some way in the future.

Sulphur dioxide gas itself is a greenhouse gas. Bekki *et al.* (1996) showed that the lifetime of SO_2 was considerably extended after the large Toba eruption. Stevenson *et al.* (2003) also simulated an increase in the lifetime of tropospheric SO_2 following the effusive eruption of Laki in 1783. Such changes in SO_2 can affect the concentration of OH in the atmosphere (Bekki 1995). In addition, ozone depletion occurs in the stratosphere when chlorine loading is high and ozone production when Cl loading is low (see previous section for more details of the chemistry involved). The former case (as in Pinatubo) would lead to an additional negative radiative forcing, while the latter (as in Toba) would lead to a small positive radiative forcing. However, even for the large Toba eruption, the positive radiative forcing due to these changes only slightly moderated the negative forcing due to the aerosols (Bekki *et al.* 1996). Dehydration of the stratosphere is thought to occur following eruptions, due to the conversion of SO_2 to sulphuric acid aerosol. This effect potentially results in a positive radiative forcing. The relative length of these effects compared with that of the direct forcing from stratospheric sulphate aerosol may have implications for the time-scale on which the atmosphere returns to radiative equilibrium following an eruption. Radiative forcing calculations (and climate simulations) including all these effects have yet to be investigated, although Zhong *et al.* (1996) demonstrated that the long-wave heating rates in the stratosphere due to volcanic sulphur dioxide can be comparable with those due to heating by the absorption of UV by SO_2. Kirchner *et al.* (1999) demonstrated that stratospheric heating in a GCM due to the Pinatubo eruption was reduced by including the radiative effect of decreasing ozone.

Eruptions that do not penetrate the stratosphere are usually regarded as being unimportant for longer-term or global climate impacts as the aerosol is removed quickly from the troposphere. However, if such an effusive eruption persists with any strength for an extended period of time, it can at least produce a large radiative forcing over local or regional scales. This would have a large impact on the surface fluxes of radiation, and therefore on evaporation, soil moisture, etc., as well as on surface temperature. The eruption of Laki in Iceland in 1783 is one such example. There is still much controversy over the extent to which material was injected into the stratosphere by this eruption. Although some sources suggest there is little evidence for stratospheric injection (e.g. Grattan & Pyatt 1999) and therefore we would not expect a prolonged climatic impact, Franklin (1785) suggested that subsequent cold winters in Europe were a direct result of aerosol from this eruption. Wood (1992) and Briffa *et al* (1998) found cold anomalies in the Northern Hemisphere mean temperature records, but the attribution of these anomalies to the Laki eruption is difficult. It is known that significant amounts of SO_2 gas were emitted to the troposphere on and off during the period June 1783 to February 1784 (Thordarson *et al.* 1996). A recent simulation of these injections and the resulting effect on atmospheric chemistry found that a tropospheric aerosol veil extended across much of the Northern Hemisphere (Stevenson *et al.* 2003). This is consistent with Europe-wide observations of a ‘dry fog’ (Stothers 1996). Subsequent simulations using the resulting sulphate aerosol distributions demonstrated that the negative radiative forcing caused by this aerosol reached – 4.5 W/m^2 over much of the Northern Hemisphere during the month following the start of the eruption, and peaked at –20 W/m^2 over small regions. A significant Northern Hemisphere mean forcing persisted until March 1784 (Figure 7 and Highwood & Stevenson 2003).

Time series of radiative forcing due to volcanic eruptions have been produced, relying on proxy data such as tree rings and ice cores, as well as on geological evidence of the type of eruption, to determine the likely impact (e.g. Sato *et al.* 1993). These can then be used in climate models. A recent attempt by Andronova *et al.* (1999) assumes that the radiative forcing generated by each eruption is similar to that of

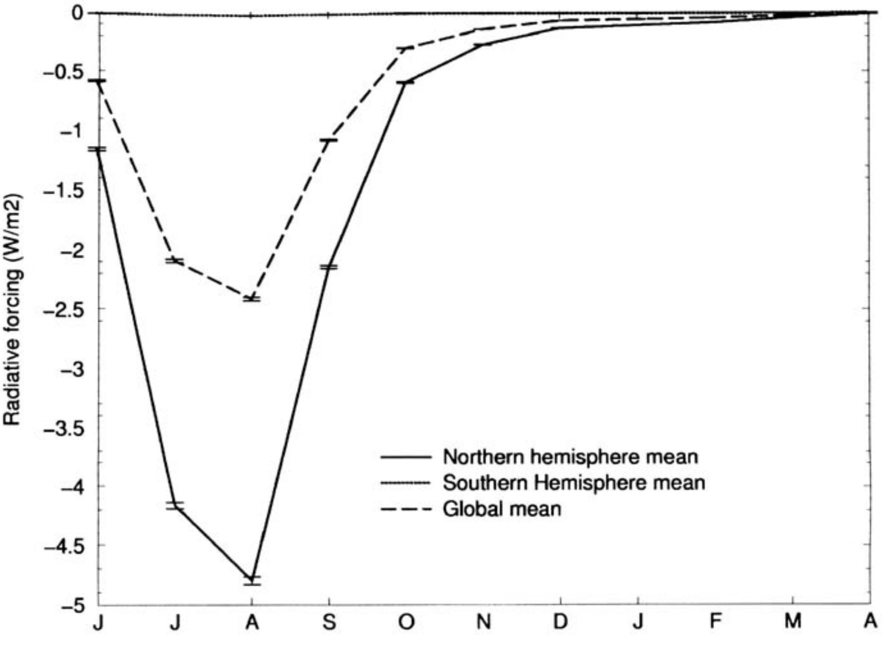


Fig. 7. Global and hemispheric mean radiative forcing due to sulphate aerosols from the eruption of Laki in 1783. The aerosol distribution has been simulated using the chemical transport model STOCHEM as in Stevenson *et al.* (2003), and the radiative forcing calculated using the Reading Intermediate General Circulation Model as in Highwood & Stevenson (2003).

Pinatubo, depending only on the distribution of the optical depth from each eruption. That study found that the radiative forcing can vary widely due to the atmospheric circulation and the geographical location and strength of the eruption. For eruptions more distant in time, and those in the data-sparse Southern Hemisphere, the estimates of radiative forcing become increasingly uncertain. It is difficult to compare volcanic radiative forcing with other forcings such as greenhouse gases, because they are discrete events. However, Shine & Forster (1999) include volcanic forcings by considering the difference between 'active' and 'quiescent' decades, considering a forcing of –0.8 W/m^2 to be appropriate when comparing the effect in an active decade to that in an inactive decade.

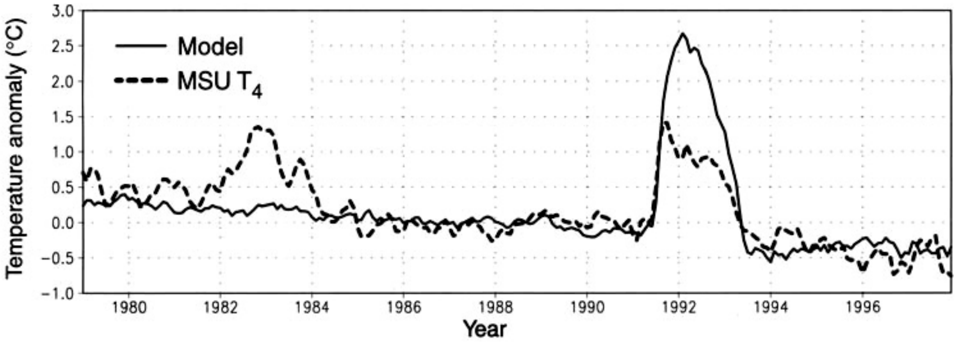
In summary, the main effect of volcanic eruptions is to produce a negative radiative forcing due to the reflection of solar radiation by extra stratospheric sulphate aerosol. The next part of the puzzle is to determine the effect on climate of this radiative forcing.

Climate response

Climate response to volcanic eruptions is much more complex than a negative radiative forcing leading to a surface cooling. In general this is true: a global mean temperature decrease of around 0.2 K was observed at the surface following the Pinatubo eruption, while the stratosphere warmed by 1 K (Houghton *et al.* 2001, and Figure 8). These temperature changes have been successfully simulated by a number of climate models (e.g. Kirchner *et al.* 1999). Angell & Korshover (1985) studied temperature records after six major eruptions and concluded that the average temperature at the surface was statistically significantly colder during the five years after each eruption than during the five years preceding the eruption.

Relatively simple energy-balance models can be of great use in understanding the influence of individual eruptions on the global mean climate. Lindzen & Ginnitsis (1998) modelled the impact of the 1883 Krakatau eruption in this way. The

(a) Global lower stratospheric temperature anomalies



(b) Global lower tropospheric temperature anomalies

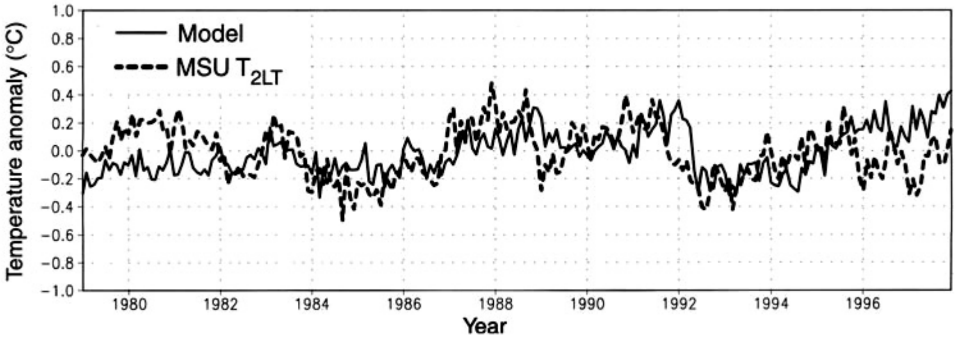


Fig. 8. Satellite observations and model predictions of lower-stratospheric and tropospheric temperature anomalies after the eruptions of El Chichón and Pinatubo (from Houghton *et al.* 2001).

importance of frequent volcanic eruptions for the global annual mean temperature over the past 150 years, using the time series of forcing of Sato *et al.* (1993) and the associated uncertainties, has been demonstrated in Shine & Highwood (2002). The importance of the cumulative effect of periods of several eruptions can clearly be seen in Figure 9. There is certainly justification for including volcanic forcings in climate simulations; however, the impact on climate in that model is necessarily simplified. The magnitude of the results is also sensitive to the value of 'climate sensitivity' that is used. Observations of lower-stratospheric temperature changes over the past 30 years have led to speculation that trends have not been linear, and there is an apparent step change to cooler temperatures after each large eruption; however, the shortest length of the data-set prevents any more concrete conclusions from being drawn.

As well as reducing the solar radiation reaching the ground, the after-effects of an eruption can alter the large-scale circulation of the atmosphere, producing complex spatial patterns of change. Robock (2000), and references therein, highlight the importance of dynamical changes brought about as a result of the changing aerosol. In particular, for a tropical eruption the heating of the tropical lower stratosphere by aerosol increases the meridional temperature gradient, which can affect the strength of the polar vortex and therefore the strength of the zonal flow in mid-latitudes. Dynamical coupling of the stratosphere and troposphere through the interaction of large-scale planetary waves with the mean flow modulates tropospheric temperatures. This type of extended influence in the Northern Hemisphere has been used to explain the frequent observations of warm European temperatures following large tropical eruptions, despite a global mean surface cooling. Such a pattern was seen after Mount Pinatubo and has been successfully simulated using climate models (e.g. Kirchner *et al.* 1999; Graf *et al.* 1993). After other eruptions, including that of Laki in 1783 (Stothers 1999), a warm summer is experienced in Europe and it is suggested that this too is the result of complex dynamical changes brought about by the different distribution of heating, although the precise mechanism by which this occurs is still the subject of much research. In the study by Highwood & Stevenson (2003), the climate response to the radiative forcing due to sulphate aerosols alone produced a cold Northern Hemisphere mean temperature over the summer of the eruption, rather than a warming; however, the response had a complex spatial structure.

Further changes to the climate response could be due to the indirect effect of tropospheric aerosols, whereby they could act as cloud condensation nuclei and thus alter the microphysics of clouds (Jensen & Toon 1992). After eruptions such as Laki there could also be substantial modification of the vegetation as a result of the deposition of fluorinated gases and sulphuric acid. This might also introduce unexpected feedbacks to amplify or reduce the climatic impact of volcanic eruptions. To date there have been few attempts to quantify these effects.

It is worth remembering that even if an eruption does not penetrate the stratosphere directly, the impact on local climate can be large immediately following the eruption. This was

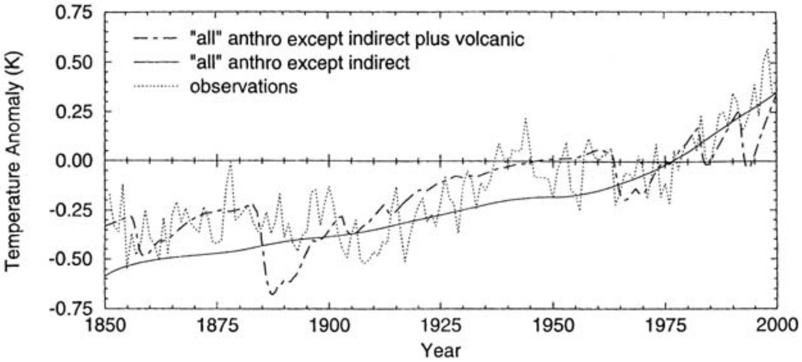


Fig. 9. Evolution of global mean surface temperature derived using a simple climate model, radiative forcings from Myhre *et al.* (2001), and a climate sensitivity of 0.67 K $(W/m^2)^{-1}$ for all anthropogenic forcings except the indirect aerosol effect, with and without volcanic aerosol forcing. The observations are from Parker *et al.* (2000) and all temperatures are shown as anomalies from the 1960–1990 mean of each series. Adapted from Shine & Highwood (2002).

particularly apparent after the Mount St Helens eruption in 1980. This eruption did not produce much enhancement of stratospheric aerosol since it emitted mainly into the upper troposhere and lower stratosphere and did not release much sulphur. Hence no prolonged or global signal was observed in temperature records at this time. However, Mass & Robock (1982) demonstrated that local surface temperatures were up to 8 K cooler during the daytime immediately after the eruption. Night-time temperatures over a considerable region were up to 8 K warmer as a result of the greenhouse effect of the low-level volcanic dust.

There have been several very large volcanic eruptions during Earth's history (e.g. Toba, 71 000 years ago). There is great interest in these mega-eruptions, not least from the media and the general public; however, it is extremely difficult to extrapolate results on climate impact from known/observed eruptions. There is little evidence that aerosol production, and certainly not the climate response to those aerosols, would be at all linear with eruption strength. However, recent advances in observations (particularly the advent of satellite remote sensing of emissions and climate response) and modelling studies suggest that we are at a point where we can begin to gain a much improved understanding of climate response to volcanic eruptions.

Summary

On average there is a stratospherically significant volcanic eruption about every 5.5 years. The principal effects of large volcanic injection of material into the stratosphere are:

- the injection of a large amount of volcanic ash, which precipitates out with an *e*-folding time of about 40 days
- the injection of a large amount of sulphur, principally in the form of SO_2, which converts into H_2SO_4 and condenses, enhancing the stratospheric aerosol loading
- a reduction in the amount of direct radiation reaching the ground and a concomitant increase in diffuse radiation
- an increase in heterogeneous processing, mostly of active nitrogen into less reactive forms
- either a decrease or an increase in stratospheric ozone levels, depending on the level of chlorine loading
- an increase in stratospheric temperature
- a decrease in global mean surface temperature, although the spatial pattern of temperature changes is complex.

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