Summary

Global climatic effects brought about by volcanism are related to the impact of volcanic gases and their derivative aerosols on the atmosphere, rather than the effects of volcanic ash. Evidence from both historic eruptions and polar ice cores indicates that volcanic sulfur gases are the dominant aerosol-forming component, resulting in production of a sulfuric acid-rich stratospheric aerosol that can have profound effects on the Earth's radiation budget over periods of a few years. Due to highly variable sulfur content of different magma types, the climatic effects do not relate simply to total erupted mass. There is a close relationship between volcanic sulfur yield to the atmosphere and hemispheric surface temperature decrease following an eruption, with up to 1 °C surface temperature decrease indicated following a major volcanic event such as the 1815 Tambora eruption. While the erupted mass of HCl and HF is equal to or greater than that of sulfur gases in some
volcanic events, the halogens do not form known aerosols nor are they abundant in ice core acidity layers. The early removal of halogens from eruption columns occurs by rain flushing and adsorption onto tephra particles, but the fate of halogens in the atmosphere following very large explosive eruptions is unknown. \( \text{CO}_2 \) flux to the atmosphere from volcanic eruptions is volumetrically one of the most important of the gas species, but owing to the huge size of the atmospheric reservoir of this gas, the volcanic contribution is likely to have negligible effects.

Introduction

Due to the effects of volcanic aerosols on the Earth's radiation budget, volcanic activity is frequently cited as one of the principal forcing functions that lead to short-term climate change. Two principal types of atmospherically transported particles of volcanic origin are recognized: (a) silicate dust particles, derived from the quenching of magma to glass and its fragmentation to volcanic ash, and (b) sulfuric acid aerosols derived from the conversion of volcanic sulfur dioxide gas to sulfuric acid liquid particles. The earliest documented recognition of the effects of volcanic eruptions on climate was made in 1784 by Benjamin Franklin, who observed the cooling effects of a "dry fog" on the atmosphere over Europe following the great Laki fissure eruption in Iceland in 1783.

Initial assessment of the effects of volcanism were based on the assumption that the silicate dust particles or volcanic ash played a major role in climate change by backscattering incident solar radiation and increasing the planetary albedo, leading to a net cooling of the Earth. Direct sampling of the stratospheric volcanic aerosol following the 1963 Agung eruption showed, however, that it was composed principally of sulfuric acid. The minor role of the silicate component of the volcanic aerosol in climate modification is in large measure due to its short atmospheric half-life, because of rapid silicate ash aggregation that leads to fallout of clumps of even the finest tephra within a few hundred to one thousand km from the source.

Volcanic aerosols from explosive eruptions can have at least six important effects on the Earth's atmosphere, some of which with opposite surface temperature signal. During fallout of tephra and condensation of volcanic gases in the troposphere, volcanic activity leads to increased condensation nuclei, cloud formation and thus increased tropospheric albedo, causing local surface cooling. Secondly, a stratospheric sulfuric acid aerosol formed by \( \text{SO}_2 \) gas-to-particle conversion leads to increased backscatter of solar radiation and surface cooling. This is likely to be the most significant volcanic effect on global climate, and recent studies show that the magnitude of cooling of the Earth following major volcanic eruptions is controlled by the sulfuric acid aerosol mass. Third, enhanced stratospheric absorption of solar radiation by the volcanic aerosol can also contribute to surface cooling. Fourth, a volcanic aerosol containing large (\( \geq 1 \mu\text{m} \)) silicate particles, which cause infrared heating, can lead to surface warming which may balance the cooling effect of a sulfuric acid aerosol, but this warming is likely to be short-lived or negligible due to very rapid fallout of such coarse silicate ash.
Fifth, increase in greenhouse gases, such as CO$_2$ from a volcanic source can contribute to surface warming. As shown below, this factor is likely to be negligible due to the small mass of volcanically derived CO$_2$ emissions, compared to the large anthropogenic source of this gas. Finally, volcanic components, such as HCl and other halogen gases and magmatic water vapor, may contribute to stratospheric ozone depletion, due to reactions of volcanic odd-chlorine and hydroxyl molecules with ozone.

Volcanic eruptions of sufficient magnitude to have significant climatological effects occur about once a century. Recent and frequent minor events such as the 1963 Agung eruption in Indonesia, whose atmospheric effects have been well monitored, are two orders of magnitude smaller than the great eruptions, such as Tambora in 1815. Such large-magnitude events are capable of producing short-term climate change and may thus severely impact the biosphere and influence the future of mankind. The study of past events of this type has been hampered by paucity of observations, but the recent development of techniques to extract data on past eruptions of this magnitude, both from their volcanic deposits and from ice cores, has resulted in the development of a database on source parameters of major explosive volcanic eruptions. Results of these studies show that the magnitude of observed surface cooling after large volcanic events correlates with the mass of sulfur degassing during the eruption.

Source Parameters

A volcanic eruption represents rapid transfer of matter and energy from the Earth's interior to the surface and to the atmosphere. The critical source parameters for evaluation of the atmospheric and global effects of an eruption include the mass eruption rate (intensity), total erupted mass (magnitude), eruption column height, and the type and mass of volcanic aerosols (principally sulfuric acid and water vapor) and other but non-condensible volatile components released to the atmosphere, principally CO$_2$, HCl and HF.

The first three source parameters can be determined from characteristics of the proximal volcanic deposit from an eruption. Figure 1 shows that a typical range of column height of fifty recent explosive eruptions is 10 to 50 km, corresponding to magma discharge rate or intensity of $10^6$ to $10^9$ kg s$^{-1}$. The range in magnitude or total erupted mass may reach values as high as $10^{15}$ kg, or of the order 400 km$^3$ of magma. Rare high-magnitude events with $10^{16}$ kg total erupted mass (~4000 km$^3$) are present in the geologic record when one considers volcanic activity during the past one hundred thousand years, such as the great Toba eruption in Indonesia about 75,000 years before present. At present, magma eruption rate estimates are only available for peak rates of plinian explosive eruptions; rates during ignimbrite phases of explosive eruptions are unknown but significantly higher.
Ash Fallout

Fallout from major explosive eruptions can blanket vast areas of the Earth's surface with a layer of volcanic ash. Very large explosive eruptions have produced ash fallout blankets that cover over $10^4 \text{ km}^2$ with 1 m of ash, and up to $10^5 \text{ km}^2$ with 10 cm thick ash. The environmental effects of volcanic ash blankets of this magnitude include increase in the Earth's albedo and possibly consequent surface cooling. Effects of ash fall on agriculture can also be very severe, both in terms of crop damage and also because of the harmful effects of ash ingested by grazing livestock. Fallout from some volcanoes is often high in fluorine, due to adsorption of fluorine from the eruption plume on ash particles, thus leading to poisoning of livestock by fluorosis.

Volcanic eruption plumes which reach levels of the upper troposphere and lower stratosphere down-wind from active volcanoes can be very hazardous to aircraft. Serious incidents occurred in Indonesia in 1982, when two large commercial jet aircraft flew through the eruptive plume of Galunggung volcano at 11 km altitude and suffered severe engine damage that resulted in emergency landings. Volcanic ash and sulfur-rich volcanic aerosol clouds in the stratosphere are also known to cause severe windshield damage to commercial aircraft, such as after the 1982 El Chichon eruption in Mexico. The eruption columns reached heights of 21 to 25 km, but the stratospheric plumes gradually subsided due to sedimentation and conversion of SO$_2$ gas to sulfuric acid aerosol particles, until the widespread aerosol plume enveloped the flight paths of intercontinental jets at 8 to 12 km altitude, about nine months after the eruption. The windshields of commercial aircraft flying at this altitude suffered deterioration due to corrosion and abrasion by the volcanic aerosol, leading to over fifty times higher rate of windshield replacement during 1983 and 1984 than in non-volcanic periods.

Sulfur Sources

Because of the predominant role of volcanic sulfur in atmospheric impact, it is essential to evaluate the origin of this element and the factors that control its output from volcanic sources. The behaviour of sulfur in magmas is complex, as it occurs in four oxidation states and in different physical states, as solid, liquid or in gaseous form. The four oxidation states of sulfur in geological environments are S$^{2-}$ (in sulfides and H$_2$S volcanic gas), as S (elemental sulfur), as S$^{4+}$ (in SO$_2$ volcanic gases) and as S$^{6+}$ (in SO$_3$ volcanic gases and sulfates). While sulfur is relatively abundant in our planet, or about 2.7 wt.% of the bulk Earth composition, its distribution is rather uneven due to its complex chemical and physical behaviour. Thus sulfur is highly concentrated in the deep Earth as dense sulfides, while it is also enriched in the oceans as the sulfate anion (0.265 wt.% of sea water).

The yield of sulfur to the atmosphere during volcanic eruptions depends on a number of factors, such as the total erupted mass of magma, its pre-eruption sulfur solubility, the efficiency of sulfur exsolution before quenching of the erupted magma, the presence of sulfur-rich mineral phases that may break down
and release a sulfur-dominated gas during eruption, and the presence of a sulfur-dominated volatile phase in the magma reservoir.

The evolution of sulfur in magmas is intimately linked with the \( fO_2 \), \( fSO_2 \) and activity of iron in the melt. Thus basaltic magmas, characterized by high temperature (1200°C) and low fugacity of oxygen (10^{-10}) are generally saturated with a sulfide phase, which occurs as immiscible droplets in equilibrium with the silicate melt, which may crystallize upon cooling (pyrrhotite; FeS). An understanding of the behaviour of sulfur in immiscible systems is important not only for sulfur volatile emissions from major volcanic eruptions, but also because of the partitioning of so-called chalcophile elements into the immiscible sulfide phase, leading to the concentration of such metals in the Earth as Fe, Ni, Pd, Ir, Pt and other platinum group elements, and formation of economically important magmatic sulfide mineral deposits. As sulfide minerals are present in a wide variety of volcanic rocks, it is likely that the majority of magmas that have evolved at low \( fO_2 \) are sulfide saturated. The sulfides in the erupted magmas are, however, in extremely low abundance, probably largely due to their high density and tendency to sink and accumulate at the base of magma bodies. Sulfur may also occur as a free fluid phase in magmas, but direct evidence for such discrete vapor (fluid) sulfur phase is as yet lacking.

In a melt with a separate sulfide phase, the sulfur dissolved in the silicate melt decreases with increasing O content of the melt, due to the fact that sulfur dissolves by displacing oxygen bonded to Fe^{++} and the increasing oxygen results in an increase in Fe^{+++} at the expense of Fe^{++} in the melt. In natural magmas which contain a free immiscible sulfide phase, there is a strong positive correlation between the sulfur dissolved in the silicate melt and the FeO and to lesser extent TiO_2 content of the melt, and the sulfur content increases with decreasing \( fO_2 \) at constant FeO. A typical range of sulfur dissolved in natural basaltic magmas is from about 1000 ppm at 9 wt. % FeO, to 2000 ppm at 15 wt% FeO, but sulfur content of silicic and other Fe-poor magmas is significantly lower, as shown in Figure 3.

Sulfur solubility is also sensitive to temperature at constant \( fO_2 \) and FeO content; thus the dissolved sulfur increases by factor of three to eight per 100°C temperature increase in the range 1000 to 1400°C. Sulfur solubility in magmas is also sensitive to pressure. In the pressure range from 15 to 30 kb, which is approximately equivalent to depths of 45 to 100 km in the Earth's mantle, the solubility increases with decreasing pressure at a rate of about 50 ppm/kb. On the other hand, at pressures lower than 15 kb, i.e. in the Earth's crust, the sulfur solubility decreases with decreasing pressure, at a rate of about 70 ppm/kb. Because of these solubility relations, magmas ascending in the crust are likely to reach sulfide saturation and experience some sulfur loss due to precipitation of sulfides and their removal by settling to deeper levels of the magmatic system.

Solubility of sulfur in melt with 5.72% FeO coexisting with immiscible sulfide melt (1 to 5% pyrrhotite) at 10 kbar at 1200 to 1400°C...
ranges from 285 ppm S at 1200 °C to 753 ppm S at 1400 °C for 1 % pyrrhotite runs. The general equation for sulfur solubility at 10 kbar and 1 % pyrrhotite is:

\[ S \text{ (ppm)} = 1.34(°C) - 1209 \] (1)

In magmas characterized by high oxygen fugacity (\( \log f_{O_2} > -10 \)), the stable sulfur phase in the melt is the sulfate mineral anhydrite (CaSO\(_4\)), as shown in Figure 2. Although anhydrite is not a common mineral in magmas, it has been observed e.g. in the erupted products of El Chichon in Mexico, Nevado del Ruiz in Colombia and Mt. Lamington, Papua New Guinea. The high sulfur content of these oxidizing and anhydrite-bearing silicic magmas is of great interest to the study of volcanic sulfur emission, and stands in contrast to the relatively low sulfur content typical of most silicic magmas. Breakdown of anhydrite to yield sulfur-bearing gases during eruption of oxidized silicic magmas may contribute significantly to the volcanic aerosol.

Magmas rising in the Earth’s crust generally reach saturation in one or more volatile species before eruption, because of the decreasing solubility of H\(_2\)O and CO\(_2\) with decreasing pressure. In basaltic magmas, carbon dioxide is the dominant volatile component, whereas in silicic magmas, such as rhyolites and dacites, water is dominant. Nucleation and growth of vapor bubbles will occur at some depth in the magma conduit and sulfur is likely to be partitioned from the silicate melt into this volatile phase, either as H\(_2\)S or SO\(_2\), depending on f\(_{O_2}\). Volatile exsolution of these main volatile phases in magmas and bubble expansion play a crucial role in the loss of sulfur during volcanic eruptions, as the process increases the magma surface area and facilitates sulfur degassing.

Sulfur Output

The emission of sulfur and other volatiles to the atmosphere through volcanic activity occurs primarily in two ways. On one hand there is the steady-state or rather continuous volatile emission to the troposphere from fumarolic and low-level eruptive activity, which for sulfur is estimated 12x10\(^9\) kg yr\(^{-1}\) globally. This volcanic sulfur emission is dominantly from weak eruptions or fumaroles, and therefore little or none of this output is injected into the stratosphere. It is therefore removed rapidly by normal precipitation processes in the troposphere, where it has no global environmental impact and is minor in comparison to the 65x10\(^9\) kg yr\(^{-1}\) global emission rate of anthropogenic sulfur. Annual sulfur output to the troposphere from individual and frequently active volcanoes such as Kilauea and Etna is in the range 0.17 to 1.1x10\(^9\) kg yr\(^{-1}\). Locally, the emission of sulfurous gases combines with atmospheric moisture and produces acid rain that severely affects vegetation around the volcano, such as during emission of sulfur from the hot crater lake of Poas volcano in Costa Rica.

Of much greater significance than these low-level tropospheric emissions is
the highly episodic but nearly instantaneous emission of sulfur during large volcanic events, which generate high (20 to 50 km) eruption columns and stratospheric injection. Thus events such as the 1815 Tambora eruption and the Laki 1783 eruption injected 24 to 26x10^9 kg sulfur to the stratosphere, or factor of three to four larger than the annual steady-state tropospheric volcanic background value. Owing to the great height attained by large explosive eruption columns, their sulfur output may have a long residence time in the stratosphere and consequently significantly impact the Earth's radiation budget.

Measurements of the stratospheric volcanic aerosol mass have been made following some recent eruptions, by use of the SO2-sensitive Total Ozone Mapping Spectrometer on the Nimbus-7 satellite due to absorption by volcanic gases at the wavelengths of 312.5 and 317.5 nanometers, by airborne and ground-based Lidar and by balloon-borne sensors. Thus a notable stratospheric input of a volcanic aerosol was observed following the 1985 eruption of Nevado del Ruiz volcano in Colombia, appearing first as a plume over the Pacific at 24 to 27 km elevation. The stratospheric sulfur dioxide plume was detected and tracked for about seven days, indicating mass output of 6.6x10^8 kg SO2. This is a relatively large mass, considering the small magnitude of the eruption.

The 1982 eruption of El Chichon volcano in Mexico led to the greatest enhancement of stratospheric aerosols since the 1963 Agung eruption in Indonesia and produced 3x10^{12} kg of magma. The El Chichon plume consisted of two major layers: at about 25 km height and a lower layer which extended from the tropopause to about 21 km height. The longitudinal spread of the cloud was quite fast and circled the globe in 21 days, with a mean speed of 22 m/s, or comparable with the longitudinal propagation of the 1883 Krakatau cloud at about 30 m/s. The latitudinal or poleward velocity of the El Chichon plume was between 0.13 and 0.19 m/s. Ballon-borne measurements showed that the El Chichon aerosol was dominated by sulfuric acid droplets, but the stratospheric plume also contained solid silicate particles between 2 and 40 microns in size. Over 80% of the solid particles were angular glass shards and the remainder were crystals of plagioclase, pyroxene, anhydrite, amphibole and magnetite. The silicate particles are generally coated by spherical droplets of sulfate gel that are less than 1 micron in diameter, and even smaller droplets of relatively unstable sulfuric acid. Fallout of silicate glass from the El Chichon eruption affected all of the northern hemisphere and glass shards from the eruption a few micron in diameter are even found in snow that accumulated in central Greenland in 1982 and early 1983. Tracking of the volcanic cloud by satellite shows that a total of 3.3x10^9 kg SO2 was injected to the atmosphere, corresponding to about 6.7x10^9 kg sulfuric acid aerosol. In contrast, airborne lidar surveys showed an aerosol mass of about 12x10^9 kg remaining in October 1982, and total aerosol mass from the event is estimated as 20x10^9 kg. The El Chichon stratospheric volcanic aerosol led to warming of the stratosphere by up
to 6°C in the months following the eruption, due to absorption of solar radiation by the aerosol. As this represented loss of heat, that would normally be transmitted to the Earth's surface, it was predicted on theoretical grounds that the eruption would lead to surface cooling. However, the effect was too small to cause significant climate perturbation.

Eruptions of sufficient magnitude to lead to climate modification occur at intervals of several decades or even hundreds of years. Because of their low frequency, their aerosols have not yet been observed or studied directly, and the study of the aerosol output of such large-magnitude eruptions must therefore rely on a study of their deposits. The yield of volcanic volatiles to the atmosphere from past volcanic eruptions can be evaluated from acidity layers in ice cores, and from petrologic studies of the tephra deposit. In the latter method, pre-eruption volatile concentration of the magma can be determined by electron microprobe analysis of glass inclusions in phenocrysts from the tephra, and the post-eruption concentration is determined from the degassed matrix glasses. These studies show, that typically 0.5 to 0.9 of the total sulfur mass fraction is degassed during eruption (Figure 4), whereas the fraction of chlorine and fluorine degassed from the magma is considerably smaller, or typically 0.2 to 0.5 of that dissolved in the melt prior to eruption (Figures 5 and 6). The yield of a given volcanic volatile species, i.e. the mass fraction released to the atmosphere, varies strongly with the composition of the magma, as shown in plot of sulfur yield versus SiO₂ content of the magma in figure 7. In the case of sulfur, where the data is most abundant, the results demonstrate clearly that the yield is highly dependent on the magma composition, and that eruptions of basaltic and trachy-andesite magmas can potentially have greatest impact on the atmosphere.

The petrologic estimates of volatile yield are clearly minimum estimates, as they only include the degassing of erupted magma. Studies of some small, recent eruptions show that in addition, a significant portion of volatile output to the atmosphere may occur from non-erupted magma at depth in the volcanic system. In the small eruptions of Fuego in 1974, El Chichon in 1982 and Nevado del Ruiz in 1985, degassing of the erupted magma accounts for only 10 per cent of the total sulfur emission. In case of El Chichon, the additional sulfur yield, over and above the amount from degassing of erupted magma, is probably related to sulfur released by break-down of erupted anhydrite phenocrysts. In case of the Ruiz eruption, the excess sulfur could be attributed to degassing of non-erupted magma at depth.

During the 1985 Ruiz eruption a total of 7x10¹⁰ kg magma was erupted. In addition to the observed atmospheric sulfur output of 6.6x10⁸ kg SO₂, about 3900 ppm or 1.4x10⁸ kg of sulfur had been adsorbed onto tephra particles and deposited with fallout from the plinian eruption. Thus the total yield from the eruption is estimated as 4.7x10⁸ kg sulfur, corresponding to 0.67 wt.% of the erupted magma.

The concentration of sulfur dissolved in Ruiz magma shows a range from
about 100 to 700 ppm (Figure 3). Even the highest pre-eruption dissolved sulfur concentration in the magma is an order of magnitude lower than the 0.67 wt.% sulfur concentration observed in the total erupted products, and the source of the excess sulfur emission from Ruiz thus presents an intriguing enigma. The mass of sulfur degassed from the erupted magma is about 650 ppm, which represents an atmospheric yield of about 4.6x10^7 kg sulfur, or an order of magnitude lower than the total erupted observed sulfur mass. Thus a major part of the sulfur emission during the Ruiz eruption is from a source other than degassing of the erupted magma, either the degassing of non-erupted magma in the Ruiz magma reservoir, from break-down of anhydrite crystals present in the magma, or the excess sulfur may have been present as a free volatile phase in the magma prior to eruption. The free sulfur volatile phase would have represented up to 4 to 7 vol.% of the magma volume in the reservoir system.

It is unclear how such degassing of non-erupted magmas may affect sulfur yield during very large eruptions, such as those that have climatological impact. Judging from the good correspondence between petrologic estimates of volcanic aerosol yield and ice core aerosol mass estimates for the same eruptions, it seems unlikely that the volatile yield of very large eruptions contains a significant contribution from non-erupted magmas.

**Oxidation Reactions and Aerosol Formation**

The dominant sulfur gases emitted to the atmosphere during volcanic eruptions are H$_2$S and SO$_2$. The relative abundance of these sulfur species in magmas depends on oxygen fugacity and sulfur fugacity, but the H$_2$S/SO$_2$ ratio is typically quite low. A number of reactions in the atmosphere lead to oxidation of the sulfur dioxide, both in the gas phase, in the aqueous phase and by catalysis on aerosol surfaces. It is generally recognized that a reaction with the hydroxyl radical (OH') is most important in oxidation of sulfur dioxide in the gas phase:

\[
\text{OH} + \text{SO}_2 + \text{M} \rightarrow \text{HOSO}_2 + \text{M}
\]
\[
\text{HOSO}_2 + \text{O}_2 \rightarrow \text{HO}_2 \text{SO}_3
\]
\[
\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4
\]

In the aqueous phase, SO$_2$ oxidation to H$_2$SO$_4$ occurs by reactions with O$_3$:

\[
\text{HSO}_3^- + \text{OH} + \text{O}_3 \rightarrow \text{SO}_4^{2-} + \text{H}_2\text{O} + \text{O}_2
\]

and by reactions with H$_2$O$_2$:

\[
\text{H}_2\text{O}_2 + \text{HSO}_3 \rightarrow \text{A}^- + \text{H}_2\text{O} \rightarrow \text{A}^- + \text{H}^+ \rightarrow \text{H}_2\text{SO}_4
\]

These reactions in the aqueous phase occur at a much higher rate than the gas phase oxidation, but they may be limited by the relatively low atmospheric abundances of ozone and hydrogen peroxide. However, because of the low H$_2$O content of air, homogeneous gas phase reaction is likely to be the main process of SO$_2$ oxidation in the stratosphere, where most of the volcanic SO$_2$ of
climatological significance resides following major volcanic eruptions. Recent discovery of nearly complete peroxide depletion in association with volcanic sulfate aerosol deposition events in Greenland ice cores following the Laki (1783) and Tambora (1815) eruptions has dramatically shown the importance of the peroxide reaction in sulfate formation (Figures 8 and 9). Finally, SO₂ conversion to sulfuric acid is aided by adsorption of SO₂ on aerosol surfaces and catalysis by metallic species such as Mn and V which are present in the volcanic dust.

Climate Impact

The petrologic estimate of sulfur yield to the atmosphere during a volcanic eruption correlates well with the observed decrease in northern hemisphere surface temperature, as shown in Figure 10. The observed temperature decrease (ΔT) is related to the volcanic sulfur output by a power function, with the sulfur mass raised to a power close to a cube root law:

\[ \Delta T = 5.9 \times 10^{-5} S^{0.31} \]  

where S is the volcanic sulfur mass yield to the atmosphere, in grams. It has been argued that a linear change in the mean surface temperature of the Earth occurs in response to increase of the optical depth perturbation due to volcanic sulfuric acid aerosols. With constant relative humidity profile and stratospheric temperature, the expected surface temperature change (ΔT) versus optical depth perturbation (Δt) due to sulfuric acid aerosol loading is according to the equation:

\[ \Delta T °K = 0.35 - 6.8 (\Delta t) \]  

where Δt is the enhancement of the stratospheric aerosol optical depth at a reference wavelength of 0.55 μm. These results indicate a linear variation of optical thickness with the cube root of the change in mass of the sulfuric acid aerosol.

The relationship between volcanic sulfuric acid aerosol mass and surface temperature response (Figure 10) can be combined with the trends of typical sulfur yield from volcanic eruptions (Figure 7) in order to extrapolate to the sulfur loading of the atmosphere from truly climate-modifying events. The derived equation (2) implies that emission of $10^{12}$ kg sulfur would cause a major climatic event, with surface temperature decrease of the order ~4°C. On the basis of the sulfur yield as a function of magma composition (Figure 7), this would require an eruption of $10^{15}$ kg or approx. 400 km³ of basic magma (typical sulfur yield of 1000 ppm), or about 2×$10^{15}$ kg or 800 km³ of trachytic (Tambora-type) magma, and greater than $10^{16}$ kg or >4000 km³ of silicic magma. These results further amplify the importance of magma type when considering the potential impacts of volcanic eruptions.

As is evident from Figure 10, eruptions of sufficient magnitude to cause major climatological effects are rare. The most recent and largest such Quaternary explosive event was the silicic Toba eruption in Indonesia about 75,000 years ago, with ...

\[ \text{about } 2800 \]
km$^3$ dense-rock equivalent ($7 \times 10^{15}$ kg) and estimated sulfur dioxide emission of $6.5 \times 10^{12}$ kg. A surface temperature decrease of about $4^\circ$C would be predicted from such an event on the basis of equation (2), and the eruption has been correlated with abrupt lowering of sea water temperatures in the Indian Ocean at the stage 4-5 isotopic boundary.

The March 1963 Agung explosive eruption on the island of Bali in Indonesia represents a very instructive recent case, when a major decrease in mean solar transmittance to the Earth of approximately 1.5 % occurred as a result of the eruption, representing a change which is order of magnitude larger than observed short-term variations in the so-called solar constant. Greatly elevated sulfate concentration levels were measured in the stratosphere following the eruption, reaching a peak value of $40 \mu g/SCM$ about one year after the event, but the significant time delay is in part due to the slow rate of conversion of sulfur gases to sulfurous acid aerosols.

Agung produced about $2.5 \times 10^{12}$ kg of magma during the 1963 eruption. Degassing of volatiles from this magma, on basis of petrologic evidence, yielded a minimum of $5 \times 10^9$ kg total acids to the atmosphere: $2.8 \times 10^9$ kg H$_2$SO$_4$, $1.5 \times 10^9$ kg HCl, and $0.8 \times 10^9$ kg HF. An estimate of total volcanic acids deposition on basis of Greenland ice core evidence is $2 \times 10^{10}$ kg, or factor of four higher than the petrologic estimate. An optical depth perturbation of the atmosphere of 0.3 occurred after the Agung eruption.

A stratospheric warming of the order $6^\circ$C was observed for three years following the eruption, mainly due to the absorption of infrared thermal radiation by the volcanic stratospheric aerosol and in part due to direct absorption of solar radiation. A global surface cooling was also observed following the Agung eruption, which may in part be attributed to scattering of sunlight back to space by the volcanic aerosol. Thus a mean annual northern hemisphere surface temperature decrease of $0.3^\circ$C is reported after the eruption.

The 29 March and 4 April 1982 explosive eruptions of El Chichon volcano in southern Mexico was followed by stratospheric warming of the equatorial lower stratosphere, of about $6^\circ$C at 30 mbar (24 km) and about $4^\circ$C at 50 mbar (20 km). The global stratospheric mass of volcanic aerosol from the eruptions was concentrated between 21 and 25 km altitude, and has been estimated in the range 1.2 to $2 \times 10^{10}$ kg, consisting 99% of sulfuric acid. The eruptions were relatively minor, producing a total of only 1.09 km$^3$ magma ($2.7 \times 10^{12}$ kg), from eruption columns with column heights ranging from 20 to 24 km. Thus the volcanic aerosol mass represents approximately one per cent of the total erupted magma, which is far in excess of volatile yield that can be accounted for by the degassing of the erupted magma. The source of the excess sulfur from the eruption remains a mystery, but a likely culprit may be breakdown of the anhydrite phenocrysts present in the erupted magma.
Because of the large aerosol mass and observed stratospheric warming after the El Chichon eruption, climate models predicted temperature reduction of 0.5°C at the surface. Any temperature signal associated with the eruption was, however, swamped by the effects of an unusually strong El Nino, resulting both in extreme sea surface warming and tropospheric warming.

The great 1912 Katmai eruption in Alaska was the most voluminous eruption of this century, producing about 15 km\(^3\) magma, with eruption column heights of 20 to 30 km. Petrologic estimates of volcanic volatile yield to the atmosphere are 7.9x10\(^9\) kg H\(_2\)SO\(_4\), 3.2x10\(^9\) kg HCl, and 6.6x10\(^7\) kg HF. The petrologic estimate of total volcanic acids is thus 1.1x10\(^10\) kg, whereas other volcanic aerosol estimates range from 1.34x10\(^10\) to 3x10\(^10\) kg, on basis of atmospheric studies and ice cores, respectively. From June to August 1912, up to 20% change in direct radiation has been reported over a large area in both Europe and America, after the Katmai eruption, fading to background level in mid-1913. The northern hemisphere surface temperature decrease associated with the eruption is estimated as 0.2°C.

The largest explosive volcanic eruption in historical time is the April 1815 explosive eruption of Tambora volcano in Indonesia, which also led to the largest documented volcano-related atmospheric disturbance. The event caused the eruption of over 50 km\(^3\) dense-rock equivalent of magma, in two plinian explosions with eruption column height of 33 and 43 km, followed by a major ignimbrite eruption. It is generally accepted that the remarkable global meteorological and optical phenomena, observed months and years after the Tambora eruption, had a strong connection with activity of the volcano. Most of these phenomena can be attributed to the effect of the stratospheric volcanic aerosol. The optical depth of the Earth’s atmosphere increased rapidly after the eruption and reached a maximum of 1.4 in about five months, but did not decay to background levels until three years after the event.

Various features of the Earth’s climate exhibited highly abnormal behaviour following the Tambora eruption. The annual deviation of the northern hemisphere mean temperature due to the eruption was -0.7°C in 1816. In the eastern United States, the great climate anomaly of the year 1816 is a unique event which also persists in 1817 (figure 11). Summer temperature was about 1.5°C below the two-hundred year average, and the June 1816 temperature about 3°C below average. The climate effect of the Tambora event cannot be considered in isolation, however, as it was coincident with a depression in solar activity between about 1790 to 1830, i.e. the Dalton Minimum in sunspot numbers and aurorae. During these decades the characteristic eleven-year cycle in solar activity persists, but the amplitude is reduced by an order of magnitude or more. Variations in sunspot frequency have been linked to changes in the solar “constant” and in turn related to climate changes. It therefore appears likely that climate was already
deteriorating by the beginning of the nineteenth century, due to reduction in solar activity. This climate trend was then greatly amplified by the impact of the Tambora volcanic aerosol, culminating in the "year without summer" in 1816. Both ΔO18 data on ice cores and northern hemisphere decadal temperature trends support the contention that a climate change had set in by the first decade of the nineteenth century. Thus for example evidence from Peru ice cores show that the decade 1810 to 1820 is characterized by the most negative ΔO18 values (coldest temperatures) of the entire record, culminating in the southern hemisphere wet season of 1819-20. The relative contribution of solar variability to the deterioration occurring after 1815 is estimated 10 to 20%.

The Tambora magma was enriched in volatile components, with 2.4 wt % H2O, 570 ppm sulfur, 2220 ppm chlorine and 570 ppm fluorine. The sulfuric acid aerosol mass injected to the stratosphere from Tambora ranges from 1 to 2×10^{11} kg on basis of petrologic data, ice cores and atmospheric phenomena. In addition to the large sulfur yield, petrologic data indicate major emission of halogens to the atmosphere from the eruption, or 10^{11} kg of chlorine, and 7×10^{10} kg fluorine. The fate of these volcanic halogens in the atmosphere is unclear. Fluorine and chlorine most likely form HCl and HF gas molecules upon degassing from the magma. The latter is relatively inert in the stratosphere, as HF photolysis is shielded by oxygen and HF is also relatively indifferent to OH abundance.

Chlorine was probably removed in significant amounts from the high-temperature region of the Tambora eruption column by adsorption onto tephra. Although HCl is not known to form stratospheric aerosols, chlorine may conceivably enter other aerosol droplets. Studies of ice cores cited above indicate that acidity layers from some eruptions contain significant chlorine, requiring incorporation of this species into the aerosol by some process. While HCl is relatively inert in the stratosphere, reaction with OH or by photolytic reactions leads to formation of atomic chlorine. As the Tambora eruption cloud was dominantly in the region below 30 km which is photolytically inactive, formation of Cl and ClO by the latter process would have been minor. On the other hand, water vapor was injected in large quantities, involving both magmatic and atmospheric water. Thus OH radicals were abundant in the eruption column and available for reaction with HCl to produce atomic chlorine. Reactions of atomic chlorine with ozone are catalytic, and a single chlorine atom may destroy thousands of ozone molecules before it becomes inert and enters the HCl reservoir. Independent of their role in generation of single chlorine atoms, OH radicals from the eruption cloud would also lead directly to destruction of ozone.

Flood Basalt Eruptions

The potential environmental impact of large-scale basaltic volcanism has received increased attention in connection with the debate of causes of the terminal Cretaceous extinctions. Basaltic volcanism is an attractive mechanism for inducing climate change for two reasons: basalts display the highest solubility of
sulfur of all magmas and therefore have the highest potential sulfur yield to the atmosphere per unit mass of erupted magma. Secondly, basaltic magma is the dominant magma type extruded on Earth, with a combined annual mass eruption rate of \(20 \times 10^{12}\) kg yr\(^{-1}\) for hotspots and ocean ridge basaltic volcanism, compared to \(5 \times 10^{12}\) kg yr\(^{-1}\) for the dominantly andesitic volcanism of volcanic arcs. As mid-ocean ridges are almost entirely submerged, however, the sulfur associated with submarine eruptions is largely trapped in quenched glassy pillow lavas or dissolved in the oceans. On the other hand, the dominantly subaerial hotspots exhibit a total magma discharge rate comparable to that of volcanic arcs, and their sulfur yield is directly to the atmosphere.

Although basaltic volcanism is clearly a major potential source of sulfur injection to the atmosphere, there are other factors, however, which cast some doubt on the ability of this type of volcanism to form stratospheric sulfate aerosol layers that lead to climate change. Basaltic explosive eruptions are extremely rare in the geologic record, but very large basaltic fissure eruptions have been considered as a potential climate modifiers. Numerical simulation of a very large basaltic fissure eruption has indicated that little or no stratospheric injection would result from such an event. On basis of these results, it is unlikely that flood-basalt volcanism can have major climate effects, except perhaps in the case of high-latitude basaltic eruptions, where the tropopause is at lower altitude, such as in the case of the 1783 Laki eruption in Iceland.

This basaltic fissure eruption is the only one that has received detailed petrologic study for the determination of volatile loss to the atmosphere. The pre-eruption CO\(_2\) and H\(_2\)O content dissolved in the Lakagigar magma has been determined by infra-red spectrophotometry analysis of glass inclusions trapped in phenocrysts. The CO\(_2\) content of 430 to 510 ppm is consistent with a reservoir at a depth of about 4 km. On basis of Quadropol mass spectrometry, the bulk CO\(_2\) content of glass inclusion-bearing crystals from the Lakagigar eruption may be as high as 0.85 wt.%, indicating a free CO\(_2\)-dominated volatile phase in the magma. The H\(_2\)O content of glass inclusions is about 0.47 wt.% indicating that water exsolution would not have occurred in the magma reservoir at the depth indicated by the CO\(_2\) solubility estimates. The volatile gradient in the reservoir and the observed correlation between vesicularity and chemical composition of the magma (Figure 12A) is therefore attributed to a gradient in the abundance of a CO\(_2\)-dominated volatile phase, ranging from vesiculated quartz tholeiite magma (Mg\# 38 to 40) in the uppermost part of the reservoir, to volatile-poor tholeiite (Mg\# 44 to 47) at deeper levels. We envisage CO\(_2\) nucleation at depths corresponding to lower parts of the reservoir, and bubble rise by buoyancy through the reservoir, leading to a vesiculation gradient and volatile accumulation in the roof zone.

The yield of sulfur to the atmosphere from the Lakagigar eruption is one of the largest volcanic pollution events in historical time, and comparable to the
great eruption of Tambora. Studies of Greenland ice core acidity layers from the eruption indicate a total $\text{H}_2\text{SO}_4$ volcanic aerosol mass of $2.8 \times 10^{11}$ kg, whereas estimate of sulfur degassing, based on the difference of sulfur concentration between glass inclusions and matrix glasses, is equivalent to $1.35 \times 10^{11}$ kg $\text{H}_2\text{SO}_4$ aerosol. The close correspondence of these independent estimates indicates that degassing of sulfur dissolved in the magma was the dominant mechanism, and that other sources of the sulfur aerosol need not be invoked, such as an immiscible sulfide phase.

As shown in Figures 13 and 14, sulfur degassing during the eruption was strongly dependent upon both the vesicularity of the magma and its chemical composition. Thus degassing was most efficient from the evolved quartz tholeiite, which was also most vesicular and presumably highest in volatile content. On the other hand, sulfur loss was relatively minor from the less evolved and poorly vesiculated matrix glasses. These results demonstrate the critical role of the abundance of a major exsolving volatile phase in the degassing of sulfur during eruption.

The Halogens

Diffusion of anthropogenic chlorofluoromethanes (CFC) from the troposphere is currently the principal source of stratospheric chlorine, but volcanic emissions are also a potential source of stratospheric chlorine during major eruptions. The large-scale introduction of odd-chlorine species into the stratosphere during eruptions is important because of the potential of chlorine in catalyzing the removal of $\text{O}_3$ and thus damaging the Earth's ozone layer, which shields the biosphere from the effects of damaging solar ultraviolet radiation, such as effects on DNA and the immune system response, skin cancer and sunburn.

The stratospheric injection rate for volcanic chlorine is normally quite low, or about $2 \times 10^7$ kg yr$^{-1}$. During major eruptions, however, such as the 1815 Tambora event, the HCl emission is of the order $10^{11}$ kg. By comparison, the annual release of chlorofluorocarbons is about $7 \times 10^8$ kg yr$^{-1}$ and the budget of stratospheric chlorine is about $10^9$ kg yr$^{-1}$. HCl is generally the principal chlorine molecule in volcanic gases, but studies of the Mount St. Helens 1980 stratospheric cloud show that concentrations of methyl chloride ($\text{CH}_3\text{Cl}$) were as high or higher than concentrations of HCl. As HCl is highly soluble in water, it is possible that large quantities of the emitted HCl are dissolved in eruption cloud water and returned to the surface of the Earth as precipitation during or shortly after eruption.

A very large volcanic chlorine emission to the atmosphere, such as during the Tambora eruption, is of potential concern for the stability of the Earth's stratospheric ozone layer. Stratospheric HCl injection was documented during the small 1982 El Chichon eruption and some workers have previously alerted to the possible consequences of large volcanic chlorine emissions. HCl in the
stratosphere may react with OH radicals from magmatic water, thus forming odd-chlorine atoms which can lead to catalytic decomposition of ozone. Similarly, dissociation of magmatic water in the eruption column can form OH radicals, which alone can destroy ozone.

Although large quantities of chlorine and fluorine are shown to be emitted by Tambora, it should not be assumed that these gases form aerosols in the stratosphere, as physical and chemical data indicate that HCl and HF gases are unlikely to form liquid aerosols under normal stratospheric conditions. The halogen aerosols may conceivably form at higher temperatures in the eruption column, and the presence of elevated concentrations of HCl and HF in volcanic acidity layers in Greenland ice cores suggests that halogens have indeed become incorporated into some volcanic aerosols. Thus the acidity layer from the 934 AD Eldgja eruption in a Greenland ice core contains 65% HCl and high levels of F. Similarly elevated Cl levels have been noted in the Greenland ice core acidity layer from the Laki 1783 eruption. In general, the ice core data thus suggest that Cl and possibly F may enter the volcanic aerosol. This may not imply the formation of a discrete halogen aerosol, but rather that HCl and HF may be absorbed and dissolved in the sulfuric acid aerosol.

HCl is inert toward ozone, but reaction of HCl with OH leads to formation of atomic chlorine, followed by the catalytic decomposition of the ozone by the Cl. Thus in the stratosphere Cl can be released from HCl by reactions of the type:

\[ \text{HCl} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{Cl} \]

Similarly, methyl chloride can produce atomic chlorine by photolytic decomposition and attack by OH. Several reactions involving gaseous chlorine have the effect of converting odd-oxygen molecules (including ozone) to diatomic oxygen by ClO catalysis. They are reactions of the type:

\[ \text{O}_3 + \text{Cl} \rightarrow \text{O}_2 + \text{ClO} \]
\[ \text{O} + \text{ClO} \rightarrow \text{O}_2 + \text{Cl} \]

A Krakatau-size emission, involving \(3 \times 10^8\) kg Cl, would result in about 7% depletion of the ozone layer. Chlorine output was two orders of magnitude higher than this value during the 1815 Tambora eruption, and major ozone depletion by that event cannot be ruled out. Given the great importance of the ozone layer to the biosphere and climate, the modeling of the potential impact on atmospheric chemistry by a Tambora-size eruption is timely.

During the 1815 Tambora eruption, about \(7.4 \times 10^{10}\) kg HF gas emission occurred to the atmosphere. In general, HF is assumed to be inert in the stratosphere. The photolysis of HF is shielded by oxygen, and the reaction of HF with OH is endothermic, so that it is believed that F atoms do not play the same role in stratospheric chemistry as chlorine atoms. Furthermore, fluorine and to some extent chlorine, are known to adsorb onto tephra particles and thus may be relatively rapidly removed from the atmosphere in the tephra fallout.

Large fraction of the fluorine is stripped from the high-temperature region
of the eruption column (338 to 700°C) by adsorption onto tephra and thus incorporated in the fallout deposit near source. Majority of the Tambora fluorine emission may have been removed by this process, and led to fluorosis and thus accounting for the observed death of livestock. During the 1970 Hekla eruption in Iceland, fluorine-rich fallout led to poisoning of large numbers of livestock up to 200 km from the volcano. The tephra fall from the eruption was unusually rich in adsorbed fluorine (2000 ppm). The concentration of the adsorbed fluorine in the fallout deposit was directly dependent on surface area of the tephra grains, and thus the concentration increased with decreasing grain size. The total mass of fluorine deposited is estimated as $3 \times 10^7$ kg or corresponding to 700 ppm of the total erupted mass from Hekla.

**CO$_2$ Output from Volcanoes**

In view of the major role that CO$_2$ plays in the Earth - atmosphere system, it is appropriate to evaluate the contribution of volcanism in general, and that of very large Tambora-size eruptions of CO$_2$ to the atmosphere. As shown below, however, the output of this gas from even the largest eruptions is trivial in the context of the huge atmospheric CO$_2$ reservoir. The degassing of CO$_2$ from the Earth's mantle occurs dominantly during submarine volcanism at the mid-ocean ridges, and consequently most of the gas is dissolved in the oceans and does not enter directly the Earth's atmosphere. Estimates of total mantle CO$_2$ degassing via mid-ocean ridge volcanism range from 0.3 to $2.4 \times 10^{11}$ kg yr$^{-1}$. The output of carbon dioxide from subaerial events such as the Tambora eruption could be determined by infra-red spectroscopy measurement of carbon in glass inclusions trapped in crystals in the tephra, but such analyses have yet to be made. Estimates of CO$_2$ output can be made, however, on the basis of known solubility of carbon dioxide in magmas. CO$_2$ solubility of Tambora magma is likely to be of the order of 500 ppm judging from experimental evidence and almost all of the carbon dioxide is likely to have exsolved or degassed, by analogy with the gas budget of the Hawaiian volcano Kilauea. With total magma output of $2.4 \times 10^{14}$ kg, the CO$_2$ yield from the Tambora eruption would be $1.2 \times 10^{11}$ kg, or approximately equal to the annual mantle output. Much more meaningful estimates of CO$_2$ degassing can be made for the Laki basaltic fissure eruption in Iceland in 1783, based on infra-red spectroscopy measurements of CO$_2$ content of glass inclusions in crystals and bulk CO$_2$ content of crystals and trapped glass. These studies show, that while the magma contained 400 to 500 ppm dissolved CO$_2$ prior to eruption, the magma also contained a free CO$_2$-dominated vapor phase, with a bulk CO$_2$ concentration of 0.85 wt.%, representing a total release of about $3 \times 10^{10}$ kg of the gas during this large
eruption. The high yield from the Laki eruption is surprising, and if the results may be applied to eruptions of other hotspots, they indicate that weight fraction estimates of 0.005 CO$_2$ for the Deccan basalts may be quite reasonable. It has been proposed, that massive CO$_2$ degassing during extrusion of the Deccan Traps at time of the Cretaceous-Tertiary transition destabilized atmospheric and marine mixed-layer pCO$_2$, leading to terminal extinctions. Results of numerical models of Deccan Traps degassing indicate that while a significant "greenhouse" effect is likely, with a global warming less than 2 °C the process was on too small a scale to have produced massive extinctions.

The anthropogenic production rate of CO$_2$ from the burning of fossil fuels is estimated as $4 \times 10^{14}$ mole yr$^{-1}$, or $1.8 \times 10^{13}$ kg yr$^{-1}$. Thus the Laki and Tambora volcanic output was only approximately one percent of the current anthropogenic CO$_2$ output. Consequently these eruptions would have represented a very minor addition to the total CO$_2$ atmospheric reservoir, which is estimated as $5.5 \times 10^{20}$ moles in 1985, or $2.4 \times 10^{19}$ kg. Thus the CO$_2$ output from a Tambora-size eruption would represent only an addition at the 5 ppb level to the huge atmospheric reservoir of this gas.

**Volcanic Water**

Observations and theory shows that the solid particle weight fraction in high eruption columns (1-$n_c$) is only of the order 0.018; the remainder being almost entirely entrained atmospheric air and expanding volcanic gases. Assuming that most of the tephra which generated the fallout deposit ($5.8 \times 10^{13}$ kg) had entered the lower stratosphere, the mass of associated air lofted to the stratosphere would then be about equal, and equivalent to approximately $7 \times 10^{13}$ m$^3$ at the surface. The water content of saturated air at 1 atm and 14°C is about 0.01 kg H$_2$O/kg air. Thus total mass of atmospherically derived water entrained into the stratospheric eruption column could have been as high as $5 \times 10^{11}$ kg. A portion would condense with rise in the eruption column and cause precipitation, but some portion would enter the stratosphere. Although large, this figure is only one third of the mass of magmatic water introduced into the atmosphere ($1.7 \times 10^{12}$ kg), as discussed in a previous section. Normally the content of water vapor decreases with height due to lowering of both temperature and saturation vapor pressure and condensation. However, water vapor is likely to be introduced to high levels under the conditions of elevated temperatures and turbulence within a buoyantly rising eruption column.

Water vapor introduced to the stratosphere by an eruption column could be a major source of OH radicals by reaction of water vapor with photodissociated oxygen atoms. Evidence from ground-based spectroscopic measurements of OH
during the 1982 El Chichon eruption indicates that water vapor was injected at the level of 20 ppm, or two to four times normal and may have been responsible for the large ozone depletion observed in 1982-1983. Elevated levels of volcanically derived OH from Tambora may have played a major role in generation of H$_2$SO$_4$ by reaction with SO$_2$, in the regeneration of free Cl atoms from HCl and in direct reactions with stratospheric ozone.

Conclusions

The principal effects of volcanism on the Earth's climate are related to the effects of volcanic aerosols on the radiation budget of the Earth, both in terms of incoming sunlight and outgoing terrestrial radiation. Although silicate particles (volcanic ash) form a major part of the erupted component from volcanoes, they are probably not important component of the volcanic aerosol due to the process of particle aggregation and thus a short residence time of volcanic ash in the atmosphere. On the other hand, sulfuric acid aerosols formed by gas-to-particle conversion from SO$_2$ and H$_2$S volcanic gases are potentially most important in climate modification due to a long stratospheric residence time of this aerosol. Examples of petrologic estimates of sulfuric acid aerosol mass for several eruptions are shown in Figure 15.

The potential climate impact of volcanism is thus largely dependent on the mass yield of sulfur gases from an eruption which is capable of penetrating the tropopause and forming a stratospheric aerosol. Petrologic studies indicate that eruptions of low-silica magmas, such as basalts and trachy-andesites, have the highest sulfur yield, whereas high-silica magmas, such as rhyolites and dacites, transport relatively minor quantities of sulfur to the atmosphere. Similar dependence of volcanic mass yield and magma composition is exhibited also for chlorine and fluorine gases. Empirical data on climate effects of several historic eruptions correlate very well with the mass yield of sulfur to the atmosphere during these volcanic events. When this relationship is applied as a basis for climate prediction following volcanic events, it is evident that the eruption of very large volumes (>1000 km$^3$) of silicic magmas would be required to have major climate effects (>2°C). Only one eruption of this magnitude is known in the last one hundred thousand years: the Toba eruption in Indonesia 75,000 years ago.

The largest known sulfuric acid aerosols have been formed by trachyte or trachy-andesite explosive eruptions, such as the Tambora event in 1815, with column height up to 43 km. Both ice core evidence, atmospheric phenomena and petrologic studies indicate that the sulfur output during this event was exceptionally large, and a climatic deterioration followed the eruption, as discussed above. However, some uncertainty exists regarding the magnitude of the climate event that is purely due to the Tambora volcanic aerosol, as there is some indication that the eruption occurred during a decade of cool climate. Tambora and several other volcanoes also emit very large masses of halogen gases during eruption, but the atmospheric impact of volcanic chlorine and fluorine during
such events has not been explored. While fluorine may be largely stripped out of
the eruption column by adsorption onto tephra particles, it is possible that
chlorine may be injected into the stratosphere during such events, where odd-
chlorine may severely deplete the Earth's ozone layer. Similarly, stratospheric
deposition of ozone by volcanic hydroxyl radicals derived from magmatic water
vapor must be considered during very large explosive eruptions.

Recent moderate-size volcanic eruptions such as Agung 1963 and El Chichon
1982, which produced comparable stratospheric aerosols and both led to
stratospheric warming, yet their effects on the Earth's northern hemisphere
surface temperature were quite different, with 6 °C decrease in the case of Agung,
and no observable effect in the case of El Chichon. These differences serve as a
reminder of the great buffer of short-term climate change: the heat capacity
reservoir of the ocean. The thermal inertia of the ocean-atmosphere system is
dramatically underscored when one considers that the heat capacity of the
atmosphere corresponds to only 3 m thick layer of sea water. Therefore, while
El Chichon-size volcanic events have significant effects on the thermal radiation
budget and generally heat the stratosphere, their ability to cool the troposphere and
the Earth's surface is tempered by the ocean heat reservoir. Storage and re-
distribution of heat from the ocean can thus dominate short-term climate.
Figure Captions

Figure 1: Typical ranges of eruption column height (A), intensity or magma discharge rate (B), and magnitude (total erupted mass) for fifty recent explosive eruptions. The equations describe the curve fit to the relations between column height, discharge rate and magnitude, with correlation of 0.88 and 0.82, respectively.

Figure 2: Relationship between sulfur solubility and oxidation state of magmas.

Figure 3: Sulfur solubility vs. FeO content of magma, from melting experiments on Mt St Helens 1980 magmas (crosses) and for glass inclusions in phenocrysts in Nevado del Ruiz 1985 magmas.

Figure 4: The relation between pre-eruption sulfur concentration in magmas (sulfur content in glass inclusions in phenocrysts) and sulfur content in degassed matrix glasses, in parts per million. The diagonal line shows no sulfur loss. For most eruptions, the fraction of sulfur which is degassed from the magma ranges from 0.5 to 0.9 of the initial concentration.

Figure 5: The relationship between pre-eruption chlorine concentration in magmas (chlorine in glass inclusions in tephra phenocrysts), and the chlorine concentration in degassed matrix glasses. The diagonal line shows no chlorine loss. Note that the chlorine fraction degassed from the magma is typically less than 0.5 of the initial amount present in the magma.

Figure 6: Relationship between pre-eruption fluorine concentration and matrix glass fluorine content for seven eruptions. Fraction of fluorine degassed during eruption is generally less than 0.5. The diagonal line shows no fluorine loss.

Figure 7: Yield of sulfur to the atmosphere as a function of magma composition (SiO₂). Note the high sulfur yield in the case of eruptions of basaltic (low-silica) magmas, in contrast to the low yield for eruptions of rhyolitic and other high-silica magmas.

Figure 8: The relationship between hydrogen peroxide and volcanic (non-sea salt) sulfate in the Laki 1783 volcanic acidity layer in a Greenland ice core.

Figure 9: The relationship between hydrogen peroxide and volcanic (non-sea salt) sulfate in the Tambora 1815 volcanic acidity layer in a Greenland ice core.

Figure 10: Correlation between sulfur yield to atmosphere from volcanic eruptions and the observed northern hemisphere surface temperature decrease for several volcanic events. Sulfur yield based on the petrologic estimates.
Figure 11: Observed climate response following the Tambora 1815 eruption. Upper curve is annual summer temperature data for the eastern United States, at the latitude of Philadelphia (Pa), based on several long temperature series. The solid horizontal line shows the 224-year average summer temperature. Lower curve is annual June temperature data for New Haven (Conn). The horizontal line shows the 145-year New Haven June mean temperature.

Figure 12: Vesicularity and crystal content of Laki 1783 basaltic glasses as a function of magma composition.

Figure 13: Vesicularity and sulfur content of Laki 1783 matrix glasses, demonstrating the importance of a major carrier gas (CO$_2$) in sulfur degassing.

Figure 14: Relationship between sulfur and iron content in Laki 1783 glass inclusions and matrix glasses. The dotted line is Mathes’ solubility curve for basaltic magmas. Note the extreme depletion of sulfur in matrix glasses as a function of degassing, whereas glass inclusions in phenocrysts contain pre-eruption sulfur concentrations.

Figure 15: Petrologic estimates of sulfuric acid aerosol mass for several historic and recent volcanic eruptions. The Minoan age eruption of Thera (Santorini) volcano has a relatively low sulfate yield, according to petrologic data, whereas the ice core acidity layer which has been tentatively correlated with the eruption is order of magnitude higher. The 1259 eruption is observed in ice cores; the source volcano of the huge sulfate input into the atmosphere is unknown, but is probably in the equatorial region.
Graph A:

Column Height vs. Log Total Mass, kg

\[ y = -60.4 + 7.2x \quad R = 0.88 \]

Graph B:

Log Magma Discharge Rate, kg/s vs. Log Total Mass, kg

\[ y = 2.59 + 0.43x \quad R = 0.82 \]
Fig. 4. Sulfur solubility as a function of oxidation state. All experiments done at 1025°C and approximately 200 MPa. Numbers in boxes are silicate melt FeO contents. The curved line represents a saturation surface for hydrous silicate melts with approximately 3 wt % FeO. The dotted vertical line schematically indicates an oxidation reaction whereby FeS breaks down to form CaSO₄. This reaction has not been closely bracketed, but at 1025°C it must lie between the QFM and MNO buffer curves. GCH and QFM experiments are sulfide (FeS-rich liquid) saturated, HM and MNO experiments are sulfate (CaSO₄) saturated. Diagram is polybaric in AS₂O₃, with log AS₂O₃ ranging (approximately) from -3.0 at GCH to -1.0 at HM (error ±1.0 log units).
Sulfur (ppm) vs. FeO* wt.%

\[ y = 9.18 + 76.48x \]
\[ R = 0.95 \]
CHLORINE IN GLASS INCLUSIONS PPM

CHLORINE IN MATRIX GLASS PPM

C-27
FLUORINE IN GLASS INCLUSIONS PPM

FLUORINE IN MATRIX GLASS PPM
$y = 2989 - 57x + 0.23x^2 \quad R = 0.77$
ACIDITY LAYER IN GREENLAND ICE CORE: AEROSOL FROM THE 1783 ERUPTIONS OF LAKI IN ICELAND AND ASAMA IN JAPAN

![Graph showing changes in H2O2 and nss.S04 concentrations over depth in ice core (m).](image-url)
ACIDITY LAYER IN GREENLAND ICE CORE:
AEROSOL DEPOSITION FROM THE 1815
ERUPTION OF TAMBORA IN INDONESIA
$y = 5.896 - 5 * \frac{SULFUR}{0.308}, R = 0.92$

SULFUR YIELD (GRAMS)

TEMP DECREASE °C

TAMBOA

KAMIA

KRAKATIAU

ST MARIA

AGUNG

FUETO

ST HELENS
C-36