Understanding Volcanoes May Be the Key to Controlling Global Warming

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Abstract

Volcanoes are the primary source of gases in the earth’s atmosphere and have been the primary cause of short-period climate change throughout geologic history. The large eruption of Pinatubo volcano in 1991 added ~17 Mt (megatons) sulfur dioxide (SO₂) primarily to the lower stratosphere where it spread rapidly around the world, forming an aerosol that scattered sunlight, cooling the earth ~0.5°C for ~3 years, decreasing precipitation, decreasing concentrations of the hydroxyl radical, ozone, and carbon dioxide while increasing concentrations of methane and carbon monoxide. Temperatures in the lower stratosphere increased ~3°C. All of these changes were initiated primarily by adding merely 3.4 ppb (parts per billion) SO₂ to the atmosphere.

In 1783, the larger but less explosive Laki fissure volcano added 122 Mt SO₂ primarily to the troposphere that led to a “dry fog” over Europe and western Asia for three months with average concentrations of ~60 ppb SO₂. This haze caused widespread respiratory problems and acid damage to vegetation, leading to famine and the death of more than 40,000 people. When this haze was present, temperatures near the earth’s surface increased up to 3.3°C above normal during the day but were unseasonably cold at night. The daytime warming is best explained by the fact that SO₂ is a strong absorber of ultraviolet solar energy in the UV-A and UV-B wavelengths.

By 1979, humans burning fossil fuels were emitting a similar 122 Mt SO₂ into the troposphere every ten months, 150 Mt each year. Constant emissions led to measured concentrations in 1980 of 4 to 20 ppb SO₂ in the United States and up to 93 ppb in some cities in China. The effects on climate of ultraviolet heating of such concentrations of SO₂ are not included in global climate models used widely to understand global warming. When anthropogenic emissions of sulfur were decreased 18% between 1979 and 2000 in an effort to reduce acid rain, the rapid rise in global temperatures and concentrations of methane that had prevailed for many decades approached zero by 1998. Temperatures for the past decade have remained relatively constant while the concentration of carbon dioxide continues to increase rapidly. Understanding how volcanoes have initiated abrupt climate change over the eons suggests ways for us to understand global warming during the last century and to mitigate global warming in the future.

Introduction

Large volcanic eruptions propel megatons of sulfur dioxide gas (SO₂) into the lower stratosphere where it is oxidized to sulfuric acid, forming a thin aerosol layer that circles the globe, scattering sunlight for a period of approximately three years. Global temperatures typically fall ~0.5°C for much of that period. This process in the lower stratosphere is widely observed and well understood.

But observations suggesting that SO₂ erupted or emitted into the troposphere might, under certain circumstances, cause global warming are not widely recognized or considered. Climate scientists observe that SO₂ emitted into the atmosphere lasts only a few days to weeks, under normal circumstances, while carbon dioxide (CO₂) may last 100 years. Thus they have every reason to believe that high concentrations of SO₂ are unlikely to build up.

They also observe that SO₂ absorbs infrared blackbody radiation from the earth, much like CO₂, but that the concentration of SO₂ in the atmosphere, under normal conditions, is four orders of magnitude less than the concentration of CO₂ and thus it would appear that SO₂ could not have significant radiative influence on global warming.

The very thorough 2007 technical report of the Intergovernmental Panel on Climate Change (IPCC) [1] discusses “sulphate aerosols,” but “sulphur dioxide” is not listed in the Index and is mentioned only 9 times in 996 pages, mostly as a precursor to aerosols. Most climate scientists are convinced beyond a reasonable doubt that SO₂ is unimportant to climate change except for causing cooling. Studies of the effects of volcanoes on climate suggest that this widespread assumption needs to be reevaluated.

The 14 multi-decadal periods of most rapid global warming during the past 46,000 years are each contemporaneous with the 14 short periods of highest concentrations of SO₂ in the atmosphere as measured by deposits of sulfate (SO₄²⁻) in the Greenland ice sheet [2]. Thirteen of these are associated with major increases in volcanism. The fourteenth is associated with major increases in emissions of SO₂ by humans burning fossil fuels, especially coal, during the 20th century.

When national regulations in a number of developed countries aimed at reducing acid rain led to an 18% decrease in sulfur emissions between 1979 and 2000, the rapid increases in global temperatures that had persisted especially since 1970 decreased to zero by 1998 [2] and global dimming, a decrease in solar radiation received at the earth’s surface that was widespread in the most polluted mid-northern latitudes, changed to global brightening [3-5]. Since 1998, average global temperatures have been among the warmest in recorded history [6], but they have not been increasing. Meanwhile atmospheric concentrations of CO₂ continue to rise at the same rate typical since 1970 [7].

This paper summarizes the evidence for very small amounts of SO₂ influencing climate in many more ways than just cooling. What has not been adequately examined is the fact that SO₂ absorbs solar energy strongly in the near ultraviolet range and may, in this way, have caused both global warming and global dimming during the 20th century. There is much more energy in solar radiation than in infrared radiation emitted by the earth and absorbed by greenhouse gases.

Volcanoes Created and Regularly Change the Atmosphere

Our life-sustaining atmosphere is a very thin blanket of gases, 99% of which lie within 30 km of the earth’s surface (0.4% of the earth’s radius). Most of these gases were erupted from volcanoes over the eons and then modified by biological, chemical, photochemical, and microphysical processes. Some gases leak off into space, dominantly hydrogen and helium [8], but volcanoes keep replenishing the supply.

Volcanoes appear to have played a significant role in the rise of atmospheric oxygen. When water is lofted into the mesosphere (50 to 80 km), high energy ultraviolet light from the sun decomposes it into hydrogen and oxygen ions [8]. The lighter hydrogen can leak into outer space and the heavier oxygen typically sinks back into the atmosphere. Large volcanic eruptions are the only natural processes that eject large amounts of water and SO₂ more than 30 km above the earth. Photolysis
by high-energy ultraviolet light causes mass-independent fractionation of sulfur, which leaves a distinctive δ³³S signature [9-10]. This signature was particularly strong on earth around 2.45 billion years ago [11], contemporaneous with the Great Oxidation Event when the atmosphere first showed signs of significant oxygen [12-13], and with the onset of the first major subaerial volcanism [12, 14-15] capable of lifting water high into the atmosphere. The rise in concentration of oxygen in the atmosphere appears to have involved volcanoes as well as cyanobacteria that carried out oxygenic photosynthesis. My detailed unpublished analysis shows that periods of higher concentrations of atmospheric oxygen throughout geologic history [16] tend to be contemporaneous with periods of particularly high rates of tectonic plate motions and accompanying subaerial volcanoes. An excellent example is the high oxygen concentration during the last 5 million years associated with rapid subduction of plates around the Pacific Ocean.

Volcanoes are not only the primary source of gases in the atmosphere but they are the primary source of rapid changes in atmospheric content. An eruption such as that of Mount Pinatubo in the Philippines on June 15, 1991, put as much as 921 Mt (megatons) of water, 234 Mt CO₂, 19 Mt SO₂, 16 Mt chlorine, and 7 Mt fluorine into the atmosphere primarily within 9 hours [17]. The chlorine and fluorine are mostly washed out in the eruption column [18], but the water and SO₂ have major effects on climate.

By 1979, humans were continuously emitting sulfur into the atmosphere at a rate of 75 Mt per year (roughly the equivalent of 150 Mt SO₂ per year), primarily into the mid-latitudes of the Northern Hemisphere [19-20]. In years without major volcanic eruptions, the typical amount of sulfur cycled per year between the earth and the atmosphere is between 30 and 60 Mt [21-22]. Thus humans doubled if not tripled the natural sulfur cycle while only increasing the much larger carbon cycle by 36% through prodigious emissions of CO₂. Even though SO₂ only lasts in the atmosphere for a matter of weeks under normal circumstances, humans have been adding SO₂ continuously, allowing concentrations to build up. In this way the rate of emissions becomes more important than the amount.

**Volcanoes Cool the Globe**

Pinatubo erupted ash and gases to elevations as high as 40 km before the eruption cloud spread horizontally between 17 and 25 km in the lower stratosphere [23]. Temperatures in the stratosphere increase with height because ozone, the dominant molecules present, generates heat by absorbing ultraviolet light from the sun and re-emitting longwave infrared radiation. This warming forms the stratosphere and the resulting temperature inversion causes a strong stratification of the stratosphere so that air parcels move far more efficiently in the horizontal direction than in the vertical direction. The SO₂ erupted from Pinatubo circled the earth within 22 days and covered 42% of the earth’s surface within 2 months [24]. The SO₂ was oxidized primarily by the hydroxyl radical (OH) to form an aerosol layer that was a 99% pure mixture of sulfuric acid (H₂SO₄) (75%) and water (25%). Within 28 days, approximately half of the SO₂ had been converted to aerosols [25] but SO₂ could still be detected above background level by satellites 170 days after the eruption [23]. The aerosol particles, typically in the 0.3 to 0.5 µm range, scattered sunlight, increasing atmospheric optical depths to as high as 0.4, reducing solar radiation into the troposphere by up to 3 Watts/m² and thereby cooling the earth 0.5 to 0.7°C before recovering to normal in ~3 years [23, 26-27].

The cooler temperatures reduced evaporation of water. Global water vapor decreased as much as ~0.75 mm (~3%) [28], decreasing continued on page 24
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global precipitation 3 standard deviations below normal, decreasing river discharge 3.7 standard deviations below normal [29], and further decreasing temperatures since water vapor is the most potent and voluminous greenhouse gas. Computer models suggest that the global sea surface cooled by ~0.15°C [30], that the colder atmosphere decreased ocean heat content by ~3 x 10^22 J [31], and that sea level rose 9±3 mm in the first year after the eruption as rivers continued to feed old rainfall into the ocean, but fell this amount plus an additional 7±3 mm in the period 2 to 3 years after the eruption [32]. Global climate models also show that water cooled at the ocean surface following major volcanic eruptions tends to sink several hundred meters where it remains cooler than normal for many decades [33] and that a sequence of volcanic eruptions less than decades apart, cool the ocean incrementally [34]. Ward [2] argues that a sufficiently long and moderately rapid sequence of large volcanic eruptions in this way complements Milanković cycles to increment the world into an ice age.

The diffused sunlight enhanced noontime photosynthesis of a deciduous forest by 23% [35]. Between cooler temperatures and enhanced photosynthesis, the rise in concentration of CO_2 in the atmosphere slowed for a couple of years [36-37] despite the fact that Pinatubo added as much as 234 Mt CO_2 to the atmosphere.

Formation of the aerosol caused a reduction of OH on the order of 10% during the first year [38]. OH is known as “the tropospheric vacuum cleaner” because it oxidizes most impurities in the atmosphere, allowing them to be washed out or to settle out. Thus concentrations of carbon monoxide, methane, ethane, etc. increased [38]. OH is formed photochemically from ozone, and ozone can under some circumstances oxidize SO_2. Ozone concentrations decreased as much as 20% in the lower tropical stratosphere (16 to 25 km) 3 to 6 months after the eruption [39]. The ozone hole in the Southern Hemisphere grew to an unprecedented 27 x 10^22 m^2 in area in early 1992 [40-42]. Erupted chlorine and fluorine and heterogeneous chemical processes on the surface of the aerosol may have contributed to ozone loss [43-44].

While temperatures at the earth’s surface cooled ~0.5°C, temperatures in the tropical lower stratosphere warmed 3°C by late 1991 [45]. A warmer stratosphere would affect the radiation of heat from earth into space. Heating of the aerosol and gases would also cause both the aerosols and the gases to rise, leading to evaporation and re-condensation of the aerosols, prolonging their lifetimes and possibly increasing aerosol particle size. Numerous authors modeled this warming assuming the aerosol absorbs radiant energy from the earth [44, 46-50], but the greatest stratospheric warming occurred before the aerosol had fully formed. Solar heating of SO_2 is known to play an important role in eruption dynamics [51] and thus it would not be surprising if it played a major role in heating of the atmosphere for the first few months after the eruption, before the majority of the SO_2 has been oxidized to form the aerosol.

Volcanically erupted SO_2 cools the earth efficiently when it is placed primarily in the lower stratosphere where predominantly horizontal winds spread it rapidly around the world, because it forms near the base of the ozone layer where sufficient OH is available, because sulfuric acid has a very low vapor pressure that allows it to nucleate and grow aerosol particles large enough to scatter sunlight effectively, and because a variety of microphysical processes allows the aerosol to persist for a few years. All of the global changes following the eruption of Pinatubo were initiated primarily by adding only 3.4 parts per billion SO_2 (17 Mt) to the mass of the atmosphere (5 x 10^12 Mt) together with sufficient water (3 times as much as SO_2) to form the aerosol layer [52], although these additions were concentrated into a stratospheric layer between 20 and 25 km in height that makes up only 17% of the volume of the atmosphere below 30 km.

Humans cause emission of that much SO_2 into the atmosphere every 41 days, but mostly into the lower troposphere where convective turbulence is dominant and a distinctly different set of chemical and microphysical processes take place.

Volcanoes Warm the Globe

Between June 8, 1783, and February 7, 1784, the Laki fissure volcano in southern Iceland erupted in 10 phases, spewing ~122 Mt of SO_2 into the

Figure 1. The density of haze observed following the ten eruptive phases of the Laki fissure volcano in southern Iceland shows a close relationship to the amounts of SO_2 emitted (red numbered circles). The arbitrary haze density index was assigned by Thordarson based on an extensive compilation of historical observations [53, 93]. SO_2 was emitted explosively from the eruptive vents and effusively from the resulting lava flows. Haze density is also a function of weather conditions. The gray shaded area shows observations above Grund, Iceland (130 km to the N17°W). The line shows observations above Mannheim, Germany (2250 km to the S55°E). The numbered circles show the time of onset of each eruptive phase and the total amount of SO_2 erupted during that phase. Note how the haze dissipates after each eruptive phase and is replenished by the next eruptive phase.
atmosphere, five times the emission of Pinatubo [53]. But this basaltic eruption, similar to eruptions in Hawaii, was not particularly explosive. Most of the $\text{SO}_2$ was left in the troposphere (the lower 10 km of the atmosphere at this latitude) with perhaps only 20% reaching the lower stratosphere and causing cooling for several years as discussed above [53]. Most of the $\text{SO}_2$ traveled into the southeast quadrant via the jet stream to Europe similar to the ash erupted by Eyjafjallajökull during March to May, 2010. By June 21, 1783, a “dry fog” or haze settled over England, reaching Eastern Europe by June 23 and Moscow by June 30. Ultimately noticeable haze covered the area from North Africa to the North Pole, to the Altai Mountains in central Asia, ~7000 km from the source [53]. The estimated density of the haze recorded in Grund, northern Iceland, and Mannheim, Germany, is shown in Figure 1 together with the amounts of $\text{SO}_2$ emitted during each of the ten eruptive phases [53]. Note that the high densities of the haze would not have lasted for three months had there not been a new eruption, on average, every two weeks.

The haze looked like fog but it was very dry. It often had a noticeable odor of sulfur dioxide (the smell of a strike-anywhere burnt match), it caused irritation to respiratory passages [54], and it significantly damaged vegetation throughout Europe from the British Isles to Finland and Italy [55]. Between August, 1783, and February, 1784, more than 20,000 people died in England [56] and similar numbers in France [57] from health issues related to the haze and to famine. There is little question from extensive contemporary accounts that most of the dry fog was $\text{SO}_2$, which damaged the vegetation by dry deposition (typically blown onto vegetation by near ground turbulence and then oxidized) and that was, in some cases, oxidized directly in the troposphere to sulfuric acid rain. The mean concentration, based on the amount of $\text{SO}_2$ erupted, was ~60 ppb across western Eurasia north of 35°N and may have been concentrated in excess of 1,000 ppb on the ground in Europe based on the damage done to vegetation [53].

The haze appeared to extend throughout the troposphere but was thinner higher up [53]. Near the ground, the intensity grew during the night but then $\text{SO}_2$ floated upward with heating during the day. The haze caused considerable dimming of sunlight [53].

The most remarkable feature of the haze was that in July, 1783, during times and in locations of greatest density, daily temperatures in Europe were as much as 3.3°C warmer than the 1768-1784 mean[53]. The warmest recorded temperatures extended from the English Channel to southern Sweden, a region often occupied by high pressure cells during that month [58]. In England, 1783 was the warmest summer on record until 1995. Gases in the troposphere moved rapidly southeast propelled by the jet stream. But gases in the lower stratosphere would have moved primarily toward the east and poleward as the aerosol formed, explaining why summer temperatures were cooler than normal in Iceland, the Faeroe Islands, and northernmost Europe. The cooling effects of the aerosol were dominant north of 60°N while the warming effects of $\text{SO}_2$ were more dominant in the troposphere south of 60°N. Nights in Europe were colder than normal with many reports of unseasonable frost, although acid damage to plants might have been confused with frost damage [53].

The cooling was caused by the stratospheric aerosol scattering sunlight, but the heating had to come from absorption of radiant energy by the haze. Since the heating was greatest during the daytime, it had to be caused by radiant energy from the sun. $\text{SO}_2$ is strongly absorbent in the ultraviolet range beginning with UV-A (315-400 nm (nanometers)) and UV-B (280-315 nm) [59] (Figure 2). Ozone is the other major absorber of UV, but nearly two orders of magnitude less absorbent than $\text{SO}_2$ in the 350 to 400 nm range (Figure 2) [60]. We know that this energy is plentiful at the earth’s surface because these are the wavelengths that cause sunburn and skin cancer (310-320 nm) [61] and cause the skin to form vitamin D$_3$ (270-300 nm) [62]. Plus, following volcanic eruptions, decreases in concentrations in ozone discussed above leave more solar energy to be absorbed by increased concentrations of $\text{SO}_2$. 

Figure 2. Sulfur dioxide ($\text{SO}_2$) [59] and ozone ($\text{O}_3$) [60] absorb sunlight strongly at near ultraviolet wavelengths. The absorption by $\text{SO}_2$ is nearly two orders of magnitude greater than the absorption by $\text{O}_3$ between 400 and 350 nm.

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Humans Warmed the Globe

The Industrial Revolution led to a significant increase in sulfur emitted by humans burning coal and other fossil fuels from 1.5 Mt per year in 1850 to a peak of 74.9 Mt per year in 1979 when nations started reducing sulfur emissions in an attempt to reduce acid rain (black line in Figure 3) [19-20]. Sulfate measured in layers of ice below the summit area of Greenland showed the same increase (red bars in Figure 3) [63]. During the 2000 years prior to 1850, 76% of the two-year layers of ice contained no sulfate. Yet all layers since 1927 contain sulfate in increasing amounts proportional to known anthropogenic emissions as shown. While the tallest bars are contemporaneous with moderate volcanic eruptions, trace element analysis leaves little doubt that the bulk of the sulfate measured in the summit area of Greenland comes from smokestacks in northern Europe and Asia with sporadic contributions from the industrial areas within the United States and Canada [64-67]. Note that sulfate deposits began to decrease when anthropogenic emissions began to decrease.

Christian Junge, the father of atmospheric chemistry, emphasized in 1960 [68] that “sulfur is one of the trace substances which is always found in the atmosphere ... usually present in the gaseous state as SO$_2$ or H$_2$S.” He predicted that the rise in anthropogenic sulfate emissions should be observable in snow layers in Greenland as shown in Figure 3. His attempts to measure this increase were inconclusive, but more recent observations by many different groups show that his prediction was accurate.

Anthropogenic emissions are shown again in Figure 4 (purple line) compared to global mean temperature smoothed to fit 5 cycles (black line) [69]. The cooling between 1883 and 1920 is most likely related to a sequence of large volcanic eruptions (Kra Katatua, 1883, Okataina, 1886, Santa Maria, 1902, Ksudach, 1907, and Katmai/Novarupta, 1912) and the drop in temperature in 1945 has been shown to be the result of an abrupt change during World War II in the methods used to measure the majority of sea surface temperatures [70]. Removing these effects qualitatively, you can see that the temperature curve has an exponentially increasing trend remarkably similar to the sulfur emissions curve. There is a time lag related to the time it takes to heat the ocean.

The downturn in sulfur emissions in Figure 4 is in 1979 while the downturn in temperatures is in 1998, after a very large El Niño. Raising atmospheric temperatures warms the ocean, which then maintains the warmer air temperatures. It takes time for the atmosphere and ocean to reach thermal equilibrium and El Niños may be an important part of this process. Since 1850, we appear to have warmed the ocean ~0.8°C, resetting the thermostat of the earth’s atmosphere. The only natural short-term way to cool the earth is by a sequence of large volcanic eruptions, which, as shown above, may cause warming if they occur too frequently.

The green line in Figure 4 shows the rapid increase in atmospheric concentration of methane [71-72], which is oxidized and thus removed from the atmosphere by OH. Reducing SO$_2$ emitted after 1979 would leave more OH available to oxidize methane, the most likely reason why the growth in concentration of methane approached zero by 1998. This suggests an hypothesis to be tested: the rapid increase in methane concentrations during the 20th century was not caused primarily by increased methane emissions, but rather by a decrease in the atmosphere's ability to oxidize and thus remove the methane being added. Methane is a potent greenhouse gas and its rise must have contributed to global warming.

The red line in Figure 4 shows the rapid rise in atmospheric concentration of CO$_2$ [73-74]. If CO$_2$ is the principal cause of global warming, why does its concentration continue to rise at a rapid rate while the temperature and the concentrations of SO$_2$ and methane have all leveled off or even decreased?

Thus it appears that humans, by constantly emitting more and more SO$_2$, built up an atmospheric concentration sufficient to cause tropospheric warming primarily by absorption of solar ultraviolet energy similar to the even greater warming caused by higher concentrations of SO$_2$ during the eruptions of Laki volcano in 1783. Global climate models need to be updated to represent accurately the absorptive, chemical and photochemical properties of SO$_2$ with atmospheric concentrations of...
less than 100 ppb. Then it should be possible to estimate accurately the relative importance of CO$_2$ with current atmospheric concentrations of 387,000 ppb.

**Humans Dimmed Global Sunlight**  
The blue line in Figure 4 shows the average daily temperature range (DTR), maximum minus minimum, compared to the 20th century average [75] and smoothed with a running average over 8 years. DTR is a proxy for global dimming, the reduction of solar radiation received at the earth’s surface. Other factors may influence DTR, but it is widely regarded as the most reliable long-term measure of global dimming over the past century [75]. Note that as anthropogenic sulfur emissions increased, dimming increased, and as sulfur emissions decreased, dimming rapidly decreased (or, we can say, solar brightening rapidly increased).

Dimming of the sunlight by the SO$_2$ haze following the Laki eruption in 1783 was widely observed throughout Europe. This dimming was significant during the three months that the eruptions continued (Figure 1) but then gave way to the lesser dimming caused by the stratospheric aerosol scattering sunlight, which lasted for ~3 years. Concentrations of SO$_2$ during the period of widespread haze were, most likely, rarely more than tens of parts per billion [53].

The mean concentration of SO$_2$ measured in the lowermost troposphere during 1980 at 141 sites throughout the United States by the Environmental Protection Agency was 12 ppb, with 90% of the data falling between 22 and 4 ppb [76]. By 2008, the mean had fallen to 3.4 ppb, with 90% of the data between 6.3 and 0.1 ppb. The highest concentrations were in the eastern United States, downwind from the industrial areas and electric generating plants of the Midwest. Daily heating of SO$_2$ by UV-A would cause lofting, dispersing the gas throughout the troposphere and thus increasing the thickness of the layer of gas that can absorb sunlight.

Global dimming and brightening on a decadal time scale cannot be explained by changes in the intensity of light received at the top of the atmosphere from the sun [75]. Many groups have modeled changes in solar intensity due to changes in clouds and aerosols with modest success [77], but these models do not include the radiative effects of gases except for Kvalevåg et al. [4], who do not include the effects of SO$_2$. New modeling is needed.

**But How Can SO$_2$ Be So Important?**  
How can SO$_2$, measured in concentrations of tens of parts per billion, be more important radiatively than CO$_2$, measured in concentrations of hundreds of parts per million, four orders of magnitude more?

The most logical answer is that the photochemical and microphysical processes for how photons are absorbed and scattered and how the energy involved is converted to increased temperature must be fundamentally different for solar-energy-absorbing SO$_2$ and for terrestrial-energy-absorbing CO$_2$. We have already seen above that a mere 3.4 ppb SO$_2$ concentrated in the stratosphere can cause global cooling of ~0.5°C for ~3 years, a much larger radiative effect than anything attributed to orders of magnitude greater changes in CO$_2$. This difference stems from a clear difference in photochemistry and microphysics. Similarly the temperature inversion in the stratosphere, the reason the stratosphere exists, is caused primarily by the radiative effects of only tens of parts per billion of ozone, again because of very different photochemical and microphysical processes.

There are a number of reasons to suspect a similar major difference between absorption and scattering of solar energy versus greenhouse absorption of terrestrial energy:

1. SO$_2$, just like ozone and water, the strongest and most important absorbers in the atmosphere, is a non-linear, triatomic, aspherical top

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molecule with a significant electric dipole causing a strong continuum absorption and providing a highly efficient way to convert solar ultraviolet energy to increased kinetic energy, which is proportional to temperature [61]. CO₂ is triatomic, but linear without an electric dipole that can acquire oscillating momentum during vibration.

2. SO₂ absorbs solar energy strongly in the UV-A range where each photon has 43 times more energy than infrared photons emitted from the earth and absorbed by CO₂. Photons of UV light, unlike infrared, have sufficient energy to cause electronic transitions, increasing the orbits of the electrons orbiting the atoms in the SO₂ molecule and ultimately providing more efficient heating. The strong absorption by O₃ between 200 and 310 nm is based on electronic transitions [61]. The photons absorbed strongly by SO₂ (350–400 nm) are the most energetic photons from the sun that reach the lower atmosphere and the atmosphere is very transparent in the UV-A spectral range.

3. The sun is the primary source of heat on earth. The total solar irradiance is 1361 W m⁻² during the day while earth’s irradiance averages only 396 W m⁻² over 24 hours [78]. Photons in the UV-A and upper UV-B range (300–400 nm) provide 10.3% of all of the sun’s irradiance at the top of the atmosphere [79].

4. Rayleigh scattering is proportional to the inverse of wavelength to the fourth power and thus increases rapidly in the UV-A spectrum. The Rayleigh scattering optical depth increases from 0.027 at 750 nm (top of visible spectrum) by a factor of 15 to 0.40 at 390 nm (bottom of the visible spectrum) and by a factor of 34 to 0.93 at 320 nm (bottom of the UV-A spectrum)[80]. Raman scattering is also important for SO₂. Scattering tends to increase the kinetic energy and thus temperature in any given layer and is largely unimportant for CO₂.

5. It takes 25% less heat to raise the temperature of a molecule of SO₂ than a molecule of CO₂ based on a comparison of their specific heat capacities [81].

6. A molecule of SO₂ in the atmosphere can absorb a photon from the sun just as efficiently from any azimuth. Thus heating will be most efficient just after sunrise and just before sunset when photons travel the longest ray paths through the atmosphere and thus have the greatest likelihood of striking an SO₂ molecule [82]. This effect helps explain why temperatures in the Arctic tend to rise more than in lower latitudes during episodes of global warming and are compounded during the 20th century by Arctic Haze containing significant amounts of SO₂ from industrial sources [83].

7. Concentrations of SO₂ are greater close to the ground where increased pressures broaden spectral absorption lines and increase the likelihood of collisions that redistribute rotational, vibrational, and electronic energy transitions into kinetic energy and thus increase temperature.

8. Heating of individual molecules of SO₂ causes them to rise upward in the troposphere and therefore last longer. This settling at night and rising during the day was well observed qualitatively after the Laki eruption.

For all of these reasons, SO₂ and the resulting haze and dry fog are very effective warming the atmosphere, diffusing sunlight, and causing global dimming that allows less sunlight to be absorbed at the earth’s surface. These and related details will need to be worked out and modeled, to show whether they can quantitatively explain the observations of SO₂ reported in this paper.

What Next?

We have seen that SO₂ is oxidized in the lower stratosphere to form aerosols that diffuse sunlight and cool the earth. It is widely assumed that SO₂ is oxidized similarly in the troposphere, and there is much published about the cooling effects of tropospheric aerosols. But SO₂ is oxidized by OH, which is produced from ozone by high energy ultraviolet light. Since most high-energy UV has been absorbed by the ozone layer and the stratospheric aerosols that form near the base of the ozone layer, little high-energy UV penetrates into the troposphere. In the aqueous phase, SO₂ is oxidized by hydrogen peroxide (H₂O₂), which is also produced by high energy UV. Thus some SO₂ can be oxidized in cloud processes, producing acid rain. But much of the damage to vegetation attributed to acid rain is actually caused by dry deposition of SO₃ as near-ground turbulence “paints” the gas onto leaves where it then is oxidized [84-87]. Even sulfate deposited in snow in Greenland is associated with a depletion of H₂O₂ implying oxidation after deposition [88-89].

SO₂ is not removed from the troposphere as easily as widely assumed and is observed to accumulate strongly during volcanic eruptions such as Laki. During the 20th century, continued emissions of SO₂ by humans burning fossil fuels accumulated in phase with global warming and global dimming. As the concentration of SO₂ decreased, temperature increases slowed and global dimming changed to global brightening. The ability of this accumulated SO₂ to absorb solar energy strongly in the UV-A and UV-B spectral bands has not been widely recognized and has not been included in global climate models, which are so important for our understanding of global climate change.

The apparent primary role of SO₂ is good news however. We know how to reduce SO₂ emissions. We have done it very successfully through government regulation since the Clean Air Act of 1970 with amendments in 1977 and 1990. The cost has been covered through the normal cost of doing business such as the operation of coal-burning electric power plants. These reductions, primarily in North America, Europe, and Japan, accidentally slowed global warming. Whether reduction of CO₂ emissions is still required, can only be shown when current global climate models properly account for the hitherto underappreciated effects of SO₂.

The global decline in SO₂ emissions is being rapidly offset by emissions in China that rose from 0.6 Mt in 1950 to 25.8 Mt in 2004 [90]. By 2003, damage from acid rain to forests, crops, fisheries, and buildings exceeded 0.8% of China’s gross domestic product [90] and premature deaths from SO₂-rich pollution are at least 400,000 per year [91]. 72% of China’s primary energy use and 79% of their electricity comes from coal. China has major programs to reduce SO₂ emissions primarily by shutting down the smallest and most inefficient coal-burning plants and by installing flue gas desulfurization equipment. Concentrations of SO₂ in Chinese cities fell from 93 ppb in 1980 to 46 ppb in 2006 partly by building taller smokestacks that simply spread the problem over larger areas, but pressure to maintain high rates of economic growth are taking precedence over environmental protection [90]. Atmospheric haze from SO₂ and other pollutants are readily observed from China crossing over Japan to the western parts of North America [92]. There are similar problems with SO₂ pollution in India and other developing countries with major populations. These countries, and especially China, provide excellent laboratories for studying and verifying the effects of SO₂ discussed in this paper.

I have emphasized the role of SO₂ because it is the dominant chemically and radiatively active gas erupted by volcanoes. Anthropogenic pollution, on the other hand, also includes N₂O and O₃ formed in the lowermost troposphere that absorb strongly in the ultraviolet range. While their concentrations are typically much less than SO₂, their effects will need to be evaluated as we seek a long-term solution to anthropogenic global warming [88].
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82. Peter L. Ward

Peter L. Ward has studied active volcanoes since 1963, received a B.A. from Dartmouth, a Ph.D. from Columbia, and worked 27 years with the U.S. Geological Survey in Menlo Park, California. He was a primary leader in developing and managing the National Earthquake Hazards Reduction Program. He received two national awards for a magazine about living safely with earthquakes that he wrote, produced, and distributed to 3.3 million families in northern California. In 1997 and 1998, he chaired the Working Group on Natural Disaster Information Systems at the White House. He has been published widely on volcanoes, earthquakes, earthquake prediction, public warning, plate tectonics, the geology of western North America and now climate.

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