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Special Feature

Sulfur dioxide initiates global climate change in four ways

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ABSTRACT

Global climate change, prior to the 20th century, appears to have been initiated primarily by major changes in volcanic activity. Sulfur dioxide (SO^2) is the most voluminous chemically active gas emitted by volcanoes and is readily oxidized to sulfuric acid normally within weeks. But trace amounts of SO_2 exert significant influence on climate. All major historic volcanic eruptions have formed sulfuric acid aerosols in the lower stratosphere that cooled the earth's surface ~0.5 °C for typically three years. While such events are currently happening once every 80 years, there are times in geologic history when they occurred every few to a dozen years. These were times when the earth was cooled incrementally into major ice ages. There have also been two dozen times during the past 46,000 years when major volcanic eruptions occurred every year or two or even several times per year for decades. Each of these times was contemporaneous with very rapid global warming. Large volumes of SO_2 erupted frequently appear to overdrive the oxidizing capacity of the atmosphere resulting in very rapid warming. Such warming and associated acid rain becomes extreme when millions of cubic kilometers of basalt are erupted in much less than one million years. These are the times of the greatest mass extinctions. When major volcanic eruptions do not occur for decades to hundreds of years, the atmosphere can oxidize all pollutants, leading to a very thin atmosphere, global cooling and decadal drought. Prior to the 20th century, increases in atmospheric carbon dioxide (CO_2) followed increases in temperature initiated by changes in SO_2.

By 1962, man burning fossil fuels was adding SO_2 to the atmosphere at a rate equivalent to one “large” volcanic eruption each 1.7 years. Global temperatures increased slowly from 1890 to 1950 as anthropogenic sulfur increased slowly. Global temperatures increased more rapidly after 1950 as the rate of anthropogenic sulfur emissions increased. By 1980 anthropogenic sulfur emissions peaked and began to decrease because of major efforts especially in Japan, Europe, and the United States to reduce acid rain. Atmospheric concentrations of methane began decreasing in 1990 and have remained nearly constant since 2000, demonstrating an increase in oxidizing capacity. Global temperatures became roughly constant around 2000 and even decreased beginning in late 2007. Meanwhile atmospheric concentrations of carbon dioxide have continued to increase at the same rate that they have increased since 1970. Thus SO_2 is playing a far more active role in initiating and controlling global warming than recognized by the Intergovernmental Panel on Climate Change. Massive reduction of SO_2 should be a top priority in order to reduce both global warming and acid rain. But man is also adding two to three orders of magnitude more CO_2 per year to the climate than one “large” volcanic eruption added in the past. Thus CO_2, a greenhouse gas, is contributing to global warming and should be reduced. We have already significantly reduced SO_2 emissions in order to reduce acid rain. We know how to do it both technically and politically.

In the past, sudden climate change was typically triggered by sudden increases in volcanic activity. Slow increases in greenhouse gases, therefore, do not appear as likely as currently thought to trigger tipping points where the climate suddenly changes. However we do need to start planning an appropriate human response to future major increases in volcanic activity.

1. Introduction

The atmosphere is a very thin blanket of gases, aerosols, and minute particles that makes the earth habitable. Over 90% of the atmosphere by mass is within 16 km of the earth's surface [1]. Without an atmosphere, world temperatures would approach −19 °C (−2 °F) [2] but with the atmosphere the average world temperature has been within 0.7 °C of 14 °C (57.2 °F) since 1880 [3]. A small difference of 0.1 °C between the mean temperatures of the Medieval Warming Period and the Little Ice Age [4] had a major effect on climate change, glacial length, food supplies, and population growth [5,6].

The atmosphere selectively reflects, refracts, scatters, absorbs, or transmits broadband radiant energy from the sun, infrared energy

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Fig. 1. Fresh sulfur deposits on the summit of Trident Volcano, Katmai National Park, southwestern Alaska. This picture was taken on August 7, 1963, looking northwest. The thermometer went off scale above 400 °F. Access was possible because very strong winds kept the hot toxic gases close to the ground. Trident erupted in April and October, 1963. (Photo by Peter L. Ward).

radiated outwards by the earth, and cosmic rays bombarding the earth from all directions. Gases, aerosols, and particles in the atmosphere maintain a delicate and very dynamic balance such that the energy at the top of the atmosphere received from the sun equals the energy reflected or radiated by the earth and its atmosphere [7]. We will see below that very small changes in atmospheric chemistry can lead to major changes in reflection, refraction, scattering, absorption, and transmission that change global climate. An analogy would be a horizontal slat window shade (venetian blind) where the very small amount of energy needed to rotate the slats could have a major effect on the solar energy reflected and transmitted.

The atmosphere originally formed from outgassing of the earth, primarily through volcanoes. The atmosphere changed from reducing to oxidizing around 2.5 Ga (billion years ago) when volcanism shifted from being primarily submarine to having a major subaerial component [8]. The major source of new gases in the atmosphere has been from volcanoes. Volcanic gases are modified, for example, by chemical processes in the atmosphere, by plants converting carbon dioxide (CO_2) to oxygen (O_2), by animals doing the reverse, by decay of animal and vegetable matter, by forest fires, and by chemical weathering of geologic materials. The single most important chemical process in the atmosphere today is oxidation. The atmosphere cleans itself of impurities by oxidizing them to form larger molecules that settle out or are rained out.

Similarly, the only well-known sources of regular major changes in atmospheric chemistry throughout geologic time are volcanoes, major fires and now human burning of fossil fuels. Large volcanic eruptions that spew hundreds of megatons of water and gases occur today approximately once every 80 years, but have been known in the past to occur as often as several times each year. Large meteoroids, the methane "clathrate gun hypothesis" [9], sudden draining of glacial lakes [10], massive iceberg discharges [11], and other possible climate changing events are orders of magnitude less common.

The Intergovernmental Panel on Climate Change (IPCC) Working Group I published an extensive report in 2007 [12] that concludes that carbon dioxide (CO_2) is the most important cause of climate change and that the only important effect of volcanoes on climate change is to cause global cooling for a few years following large volcanic eruptions. While the concentration of CO_2 clearly has changed in phase with changes in global temperature in the past, recent data suggest that these changes actually followed changes in temperature. For example, Stott et al. [13] observed that at the end of the last ice age, deep-sea temperatures warmed by ~2 °C between 19 ka (thousand years ago) and 17 ka, preceding the rise in atmospheric CO_2 and tropical sea-surface warming by ~1000 years. Similar delays were observed at the end of the last three glacial periods at 19 ka, 125 ka and 240 ka [14–17]. CO_2 is soluble in water and more soluble in cold water. Ocean temperature is therefore the primary natural control for atmospheric CO_2 concentration [18]. Similarly, before the widespread growth of plants (~350 Ma, million years ago), the mass of atmospheric CO_2 may have been as large as 17 times the mass of pre-human atmospheric CO_2 but global temperatures were not significantly higher [19]. In fact, glaciers were common. These extremely important observations must be explored in detail before we can assess how much the 7.8 Gt of carbon added to the atmosphere yearly by humans burning fossil fuel and manufacturing cement [20] is influencing global warming.

Volcanoes erupt large amounts of sulfur (Fig. 1) and the most chemically active gas erupted by volcanoes in significant volumes is sulfur dioxide (SO_2) [21], which is readily oxidized to sulfuric acid. Sulfuric acid, "because of its low vapor pressure, quickly attaches to aerosol particles" [22]. The primary oxidant is the hydroxyl radical (OH) which is formed high in the atmosphere from ozone (O_3) primarily through photodissociation in the near ultraviolet [23]. Ozone and OH are in limited supply. If large amounts of SO_2 are erupted frequently enough, as will be explained in detail below, the atmosphere loses its oxidizing capacity, its ability to cleanse itself. Greenhouse gases such as water vapor, methane and carbon monoxide, and other pollutants increase, causing global warming.

This paper explains the evidence for each of the four cardinal rates of SO_2 erupted by volcanoes and their effects on global climate change (summarized in Table 1). The IPCC only discussed the moderate rate (II). The other three rates are quite unexpected in the prevalent

Table 1
The four cardinal rates of SO_2

Rate of SO_2 emission	Eruption rate	Effect	Cause
I Low	No large volcanic eruptions for decades	Cooling and decadal droughts	Lack of significant SO_2 allows the oxidizing capacity of atmosphere to be restored, purging all greenhouse gases and pollutants, reducing the insulating capacity of the atmosphere and inhibiting rain.
II Moderate	One large volcanic eruption (Volcano Explosivity Index ≥6) every few decades or longer	Cooling for a few years	Erupted SO_2 forms sulfuric acid layer in the lower stratosphere, reflecting heat from the sun typically for three years. Eruptions spaced a few years to decades apart cool the earth incrementally into ice ages.
III High	More than one large volcanic eruption each year for decades	Global warming	Erupted SO_2 uses up the oxidizing capacity of the atmosphere causing greenhouse gases and other pollutants to accumulate.
IV Extreme	More than 100,000 large flood basaltic eruptions in less than one million years	Extreme global warming and mass extinctions	Erupted SO_2 causes extreme global warming and acid rain over tens of thousands of years.

climatological thinking of today. For those who understand the widespread distribution of volcanoes, their sometimes extremely high rates of eruption, and the large volume of water and gases erupted, what is unexpected is why it has taken so long to recognize their important role in climate change. SO_2 is also emitted when fossil fuels are burned. This paper provides the clearest link yet published between human activities and global climate change.

There are numerous ideas about what initiates climate change. Many of these processes may be at work, but in this paper, I propose that the concentration of SO_2 has been the primary initiator of climate change prior to the industrial revolution beginning in 1850. The climate appears to have maintained a delicate balance among the four cardinal rates of SO_2. This is good news, because we have already developed effective technological and political ways to reduce SO_2 emissions in order to reduce acid rain. Throughout geologic history, changes in CO_2 have been the result of climate change. The prodigious emission of greenhouse gases by man may now have become a secondary initiator of climate change.

2. Moderate rate: Occasional large volcanic eruptions, short-term global cooling

The largest volcanic eruption in the past 95 years was from Mt. Pinatubo in the Philippines in 1991 [24]. Pinatubo erupted into the atmosphere 491 to 921 Mt (megatons) of water (H_2O), 42 to 234 Mt CO_2, 15 to 19 Mt SO_2, and 3 to 16 Mt chlorine (Cl) [25]. This eruption increased the total mass of the atmosphere [26], primarily with water, by only 0.23 ppm (parts per million). The amount of SO_2 added to the atmosphere was only 3.3 ppb (parts per billion), although the changes were much greater near the volcano. Within 21 days, an aerosol layer circled the earth at altitudes of 20 to 23 km that was 99% pure sulfuric acid/water solution droplets (~75% H_2SO_4 and 25% H_20) [27,28]. These aerosols increased the optical depth of the atmosphere to 0.4, reflecting and absorbing incoming solar energy, reducing globally averaged net radiation at the top of the atmosphere by about 2.5 W m^{-2}, causing an average global cooling of surface temperatures by 0.5 °C over three years [28,29] and warming the tropical lower stratosphere 3 °C [30]. While there was global average cooling, winter surface temperatures over Eurasia and North America were slightly higher [31].

Pinatubo erupted 2.5 to 14 times more CO_2 than SO_2 and 29 to 54 times more water than SO_2. Yet the constant rate of growth of CO_2 in the atmosphere decreased after the eruption from 1 to 2 ppmv per year between 1982 and 1990 to less than 1 ppmv per year in 1992–1993 [32,33]. This decrease was most likely caused by the decrease in global temperature, cooling the water that then absorbed more CO_2. The aerosols following the eruption also increased diffuse radiation, enhancing noontime photosynthesis of a deciduous forest by 23% in 1992 and 8% in 1993 under cloudless conditions and therefore absorbing more CO_2 [34]. Similarly the cooling decreased total water vapor in the atmosphere [35]. In this way the sulfate (SO_4^{2-}) aerosols negated the potential global warming effects of both erupted water, the dominant greenhouse gas [7], and erupted CO_2.

But the erupted water did play a key role. Sulfate aerosols are hygroscopic; their formation depends on availability of one molecule of OH and ~3 molecules of water for each molecule of SO_2 oxidized in the stratosphere [36]. Since the stratosphere is normally almost completely dry [37,38], the presence of erupted water is extremely important in formation of these aerosols [39].

Cooling of the earth for several years has been observed after all large volcanic eruptions throughout history [40–49], has been successfully modeled [50–55], is discussed clearly by the IPCC [12] and will therefore not be discussed further here (Cardinal Rate II, Table 1).

Church et al. [56] estimate that the eruption of Pinatubo caused a rapid "reduction in ocean heat content of about 3×10^{22} J and a global sea-level fall of about 5 mm" and that "recovery was not complete at the end of the simulations in 2000," 8.5 years later. The only way to move the earth into an ice age is to reduce the massive heat capacity of the ocean. These calculations suggest that a sequence of large volcanic eruptions only a few years to a few decades apart could cool the ocean incrementally into an ice age.

3. Volcanism and glacial epochs

Table S1 (see Supplementary data) provides the most complete list available of all known large volcanic eruptions through the last 542 million years. These events typically have a Volcano Explosivity Index (VEI) [24,57] of 6 or greater. The red line in Fig. 2 shows the cumulative number of the largest known volcanic eruptions in the past 120 m.y. (million years) based on the red highlighted entries in Table S1. The general shape of this curve is what is most important and is probably a reasonable estimate. The actual number of largest eruptions is a major underestimate. For example, more than 50% of the eruptions shown are within the United States portion of the largest known Silicic Volcanic Province extending from central Colorado to central Mexico and active primarily between 32 and 27 Ma as described in detail by Ward [58,59]. Yet more than 75% of this province is in Mexico where insufficient fieldwork has been done to delineate the date and volume of most specific eruptions [60]. Thus the major increase in number of large

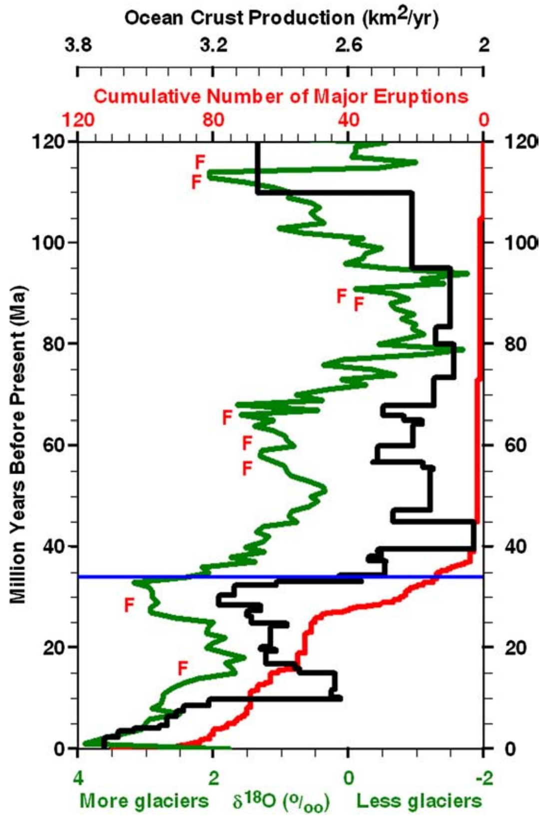

Fig. 2. A major increase in volcanism led to the modern glacial epoch. The red line is the cumulative number of known major volcanic eruptions (Table S1). The green line is $\delta^{18}O$ measured in shells of foraminifera, a proxy for mean paleotropical sea-surface temperature and global ice volume with lowest temperatures and more glaciers to the left [70]. The range in temperatures is approximately 7 °C [71]. The blue line at 33.9 Ma shows the time of major cooling of the earth leading to sudden major glaciation in Antarctica and major changes in flora and fauna in North America and Eurasia [62–65]. The black line shows the area of ocean crust formed per year [72]. Note the major increase in seafloor production and volcanism around 34, 12 and 3 Ma. Red "F" symbols show times of major flood basalts (Table S1).

eruptions between 32 and 27 Ma could be 4 times greater than shown.

Despite these limitations, there is clearly a significant increase in the rate of large volcanic eruptions between 37 and 27 Ma, between 17 and 10 Ma, and since 5 Ma. Around 33.9 Ma (blue line), major cooling of the earth occurred in two 40 k.y. (thousand years) phases separated by 200 k.y. leading to sudden major glaciation in Antarctica [61]. At the same time the temperature in central North America decreased by 8.2 °C [62] and abrupt cooling was observed in China [63]. There were dramatic changes toward colder climate in flora and fauna in North America and Eurasia [64,65]. Major increases in ice volume in Antarctica also began at 23.7, 16–12, and 2.7 Ma [66,67]. Extensive ice-rafted debris appeared in the Norwegian–Greenland Sea between 38 and 30 Ma [68]. Other major increases in glaciation in the Arctic began around 14 and 3.2 Ma [69].

The green line in Fig. 2 is an estimate of the mean paleotropical sea-surface temperature based on δ^{18}O, which is the ratio of the isotopes ^{18}O to ^{16}O measured in the shells of foraminifera and compared to some standard [70]. Increasing δ^{18}O is sensitive to decreasing temperature and to increasing world ice volume and is therefore a good proxy for the amount of glaciation. Individual measurements were averaged for each million years. Independent calibration of δ^{18}O for temperature using Mg/Ca suggests a difference of 2.8 ± 0.7 °C between the Last Glacial Maximum and the present [71]. Therefore the range shown may be as much as 7 °C with the coldest temperatures to the left. Clearly cooling has increased most around 33.9 Ma and since 15 Ma when the rate of major volcanic eruptions was high.

The black line shows the ocean crust production per year [72]. The rate of ocean crust formation similarly is higher for periods of rapid cooling. One might assume that submarine volcanoes would heat the ocean, but for new ocean floor to form, similar amounts of ocean floor must be subducted elsewhere around the globe. Increased subduction leads to increased volcanic activity above subduction zones. Such eruptions are largely unreported in Table 1 before 5 Ma because of the difficulty of mapping their deposits under piles of more recent volcanic debris. The rapid increase of ocean crust production around 40 Ma, 33 Ma and 10 Ma are contemporaneous with global cooling. The net cooling after major volcanic eruptions demonstrates that the reduction of incoming solar heat caused by volcanic atmospheric aerosols is considerably greater than the heat released directly by subaerial or submarine volcanoes.

Starting after 4 Ma, the world is slipping into the coldest part of the ice age. Ice Rafted Debris (IRD) are first observed in the North Atlantic around 3 Ma [73] as forests in Africa turn into open savannah [74,75]. At 2.65 Ma there are major increases of IRDs and deep-sea volcanic sediments in the North Pacific [76,77] marking the beginning of the Pleistocene Ice Age preferred by climatologists (2.58 Ma). Geologists think of the Pleistocene as starting at 1.81 Ma [78]. This increase in volcanism correlates with the major increase in the rate of subduction under Alaska and Asia.

The red Fs in Fig. 2 show times of major flood basalts listed in Table S1. The dates of individual flood basalt eruptions are unknown and are not included in the red curve. As will be discussed below, major flood basalts normally cause major short-term global warming for periods of less than 1 million years. Such warmings have largely been averaged out of the green curve, which shows one mean value per million years.

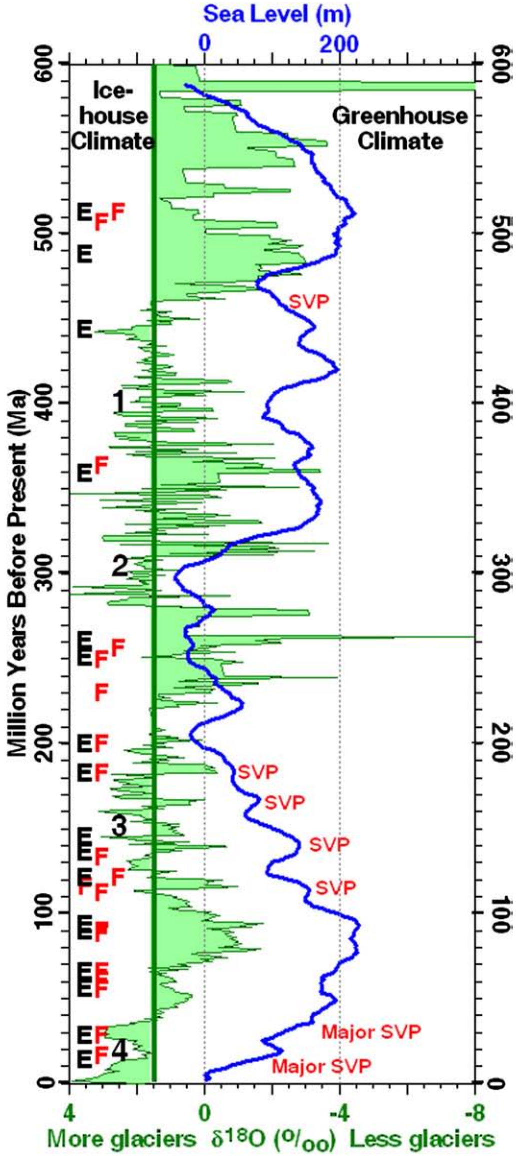

Fig. 3. Major volcanic activity in Silicic Volcanic Provinces (SVP) typically precedes an increase in glaciation and a decrease in sea-level throughout the last 600 million years. Times of SVP are shown in red from Table S1.The shaded green areas show the δ^{18}O proxy for tropical sea surface temperature [70]. Values to the left of the vertical green line show times of glaciation (icehouse). Values to the right of the line show times of little of no glaciation (greenhouse). The blue curve shows sea level [81–84]. The black "E" symbols are times of major mass extinctions [180] and the red "F" symbols are times of major flood basalts (Table S1).

The same paleotropical sea-surface temperature data are shown by the shaded green curve about a vertical axis in Fig. 3 for the past 600 m.y. (million years). Essentially, data to the left of the green vertical axis (average δ^{18}O per m.y. = 1.45‰ (per mil)) represent times of extensive glaciation or Icehouse Climate and data to the right of this axis represent warmer times of limited glaciation or Greenhouse Climate. Note the four numbered basic epochs of glaciation. Times of these epochs and the specific times of major glaciation shown agree well with detailed geologic evidence for glaciation throughout the world within the temporal resolution of both data sets [79,80]. Note that most major Silicic Volcanic Provinces (SVP) listed in Table S1 and shown in this figure occur near the onset of major glaciation and that the largest known SVP at 32 Ma begins the largest known glacial epoch in the past 600 m.y.

The blue curve in Fig. 3 shows sea-level [81–86]. Note that SVPs, as far back as they have been mapped, typically occur at the onset of decreases in sea-level most likely associated with increased glaciation.

Fig. 4 shows the relationship of volcanism to global temperature during the last glacial cycle since 125 ka. The green line shows stacked δ^{18}O data measured in the shells of foraminifera from 57 globally distributed benthic sites [87]. Note that it took 100,000 years to cool

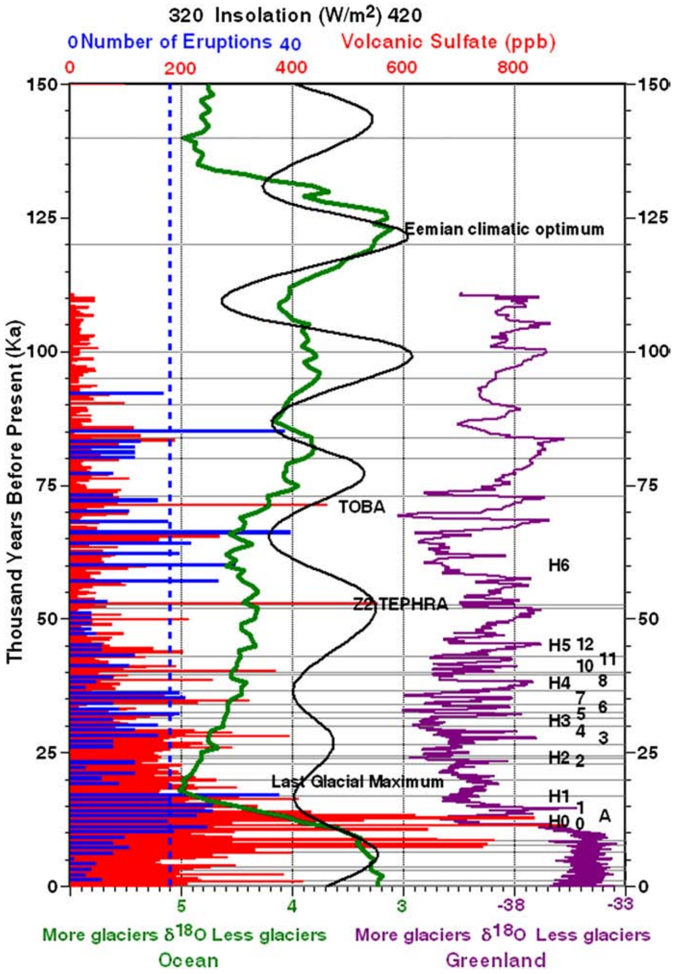

Fig. 4. The most recent glacial cycle involves incremental decreases in temperature over 100,000 years followed by rapid warming of the same amount in less than 8000 years. The green line is the stacked $\delta^{18}O$ proxy for tropical benthic temperature and ice volume [87] with lowest temperatures to the left and a temperature range of approximately 2.8 °C between the Last Glacial Maximum and the present [71]. The black curve shows the changes in temperature resulting from earth orbital changes as predicted by Milanković [89]. The purple line is the $\delta^{18}O$ proxy for temperature and glaciation on the glacial surface in Greenland [91]. Horizontal black lines are major volcanic eruptions (Table S1). Red bars show individual sulfate anomalies measured in the GISP2 ice core [96]. Blue bars show the number of eruptions per century inferred by Zielinski et al. [96] to correct for ice compaction. The dashed blue line at 18 eruptions per century is the approximate boundary between the cooling effects of a small number of eruptions and the warming effects of a large number of eruptions. Toba is the largest known volcanic eruption since 28 Ma and the Z2 tephra is a volcanic ash widely recognized in deep-sea sediment cores. H0 thru H6 are Heinrich events. Numbers 0 thru 12 and the letter A are Dansgaard–Oeschger sudden warming events. The largest sulfate anomalies clearly coincide with the rapid warming since the Last Glacial Maximum.

the earth incrementally but less than 9000 years to warm it up again. Why?

In 1920, Milanković first published an explanation for ice ages that has been the only widely accepted mechanism [88]. He noted that the amount of solar energy reaching the earth is controlled primarily by periodic changes in the earth's precession, obliquity, and eccentricity and proposed that the net effect could explain the origin and termination of ice ages. The insolation in August at 65°N predicted by Milanković is shown in black in Fig. 4 [89,90]. The long period components of the green curve are similar to the black curve but the temperature varies much more frequently.

The purple line in Fig. 4 shows $\delta^{18}O$ measured in the GISP2 ice cores in Greenland [91]. Various data show that the surface temperature in Greenland cycles through a range of as much as 16 °C [92,93] with modest change of mean until the end of the ice ages while the green line suggests that ocean temperatures changed less than 3 °C [71], ratcheting incrementally down into the depths of the ice age and then warming rapidly.

Major volcanic eruptions listed in supplementary Table S1 (horizontal black lines in Fig. 4) typically occur at the beginning of sudden decreases in $\delta^{18}O$. The precision of the age dates for most of these eruptions is limited, but this temporal relationship is particularly clear for the few precisely dated eruptions [94,95]. The record of specific eruptions during this time period is fairly limited, but evidence in the latter part of Table S1 suggests there were enough major eruptions to have at least one occur for each and every inflection point along the $\delta^{18}O$ curve.

The red bars in Fig. 4 show the concentrations of volcanic sulfate (SO_4^{2-}) measured by ion chromatograph in specific layers in the GISP2 ice core [96]. The amount of sulfate designated as volcanic is determined by an empirical orthogonal function (EOF) analysis on the entire glaciochemical time series [97,98]. The primary sources of sulfate are continental dust rich in calcium, sea salt rich in sodium, and volcanoes rich in a host of other elements. The EOF analysis essentially uses the proportions of all elements to separate sources.

Ice layers become more compacted and more difficult to decipher with increasing depth. The blue bars in Fig. 4 show the number of eruptions per century inferred by Zielinski et al. to correct for such compaction [96]. Note that while most red bars before the Last Glacial Maximum correspond to cooling, some red bars and all blue bars longer than 18 eruptions per century (blue dashed line) occur during brief warming phases. Also note that the greatest levels of volcanic sulfate by a factor of 3–4 correspond to the period of most rapid warming after the Last Glacial Maximum (LGM). Moderate rates of volcanism appear to cause cooling (Cardinal Rate II, Table 1) while high rates of volcanism appear to cause warming (Cardinal Rate III, Table 1).

4. The oxidizing capacity of the atmosphere is limited

The primary oxidants in the atmosphere are ozone, the hydroxyl radical (OH) and hydrogen peroxide (H_2O_2) [23]. OH has been called the “tropospheric vacuum cleaner” [99] because it reacts with dozens of gases. In fact OH is responsible for removing ~2380 Mt of carbon monoxide (CO), ~90 Mt of SO_2, and ~1180 Mt of other trace gases from the atmosphere each year [22]. Ozone in the stratosphere forms from the effects of ultraviolet sunlight on oxygen. OH and H_2O_2 form from ozone by photodissociation in the near-ultraviolet [23]. All three oxidants are highly reactive, short lived, and in limited supply, especially at night, at high latitudes, and during the winter. The availability of these three oxidants is called the “oxidizing capacity” of the atmosphere.

Immediately following the eruption of Pinatubo in 1991, ozone levels in the lower stratosphere dropped by as much as 25%, the lowest level since satellite measurements began in 1979 [100,101]. There was a strong downward trend in OH concentration [102–105] and sharp increases in the growth rates of CH_4 and CO concentrations in the tropics and at high southern latitudes [105,106]. Manning et al. [107] calculated that an OH reduction of the order of 10%, decaying over about a year, is consistent with anomalously high CH_4 growth rates during this period.

Small changes in SO_2 can cause large changes in atmospheric chemistry for several reasons:

A. SO_2 when oxidized, forms sulfuric acid, which has a particularly low vapor pressure allowing it to adsorb on tiny dry particles and then to increase the size of these particles by molecular condensation of more acid [22]. The resulting molecules “nucleate new particles under favorable conditions, increasing aerosol number density and the population of cloud condensation nuclei" [108]. Sulfuric acid is formed in the lower stratosphere via the following three cascading chemical reactions [22]:

$$SO_2 + OH + M \rightarrow HSO_3 + M$$

$$HSO_3 + O_2 \rightarrow HO_2 + SO_3$$

$$SO_3 + H_2O + M \rightarrow H_2SO_4$$

where M is either N_2 or O_2, the most common molecules in the atmosphere.

B. Other oxidation pathways can become important including the $SO_2 + O(^3P)$ reaction which tends to deplete ozone [109]. Modeling of these changes suggests that H_2SO_4 is converted to ultrafine sulfate particles (radius ~0.01 µm or even less) and therefore their residence time in the stratosphere is increased by at least a factor of 2 [110,111].

C. SO_2 reacts immediately with any available OH leaving little OH to oxidize slower reacting gases such as CH_4 and CO. Therefore increasing concentrations of CH_4 and CO indicate decreasing oxidizing capacity.

D. SO_2 gas absorbs ultraviolet light at wavelengths of 290–330 nm. As a result, SO_2 reduced production of OH by reducing the actinic flux by ~12% immediately after the eruption of Pinatubo [106].

E. Scattering by the sulfate aerosols perturbed the actinic flux for up to one year after the eruption [106].

F. Oxidation of SO_2 after the eruption of Pinatubo had an e-folding time of 35 days, which means it took 35 days to oxidize 1/e or 37% of the gas [112]. The rate controlling molecule in the oxidation of SO_2 is OH [22]. Therefore it took 35 days for enough OH to be available to oxidize 37% of the SO_2. Most SO_2 was in the atmosphere for less than a few months. Its effect on the availability of OH was greatest in the months following the eruption, but continued for several years while the sulfate aerosols remained in the lower stratosphere.

G. SO_2, in sufficient concentration, condenses to a liquid below −10 °C. The temperature of the troposphere decreases with increasing altitude at −6.4 °C/km to −55 °C at the tropopause and then increases with altitude in the overlying stratosphere. Thus in most of the troposphere and lower stratosphere, SO_2 is potentially a liquid. This liquid has good solubility and can be oxidized readily by H_2O_2 in cloud droplets and in precipitation [22]. Ehhalt [22] argues that 70% of the available SO_2 is oxidized in this way. Such oxidation does not lead to nucleation of new particles [108]. Yet Carslaw et al. [113] write "An important source of new aerosol particles in the atmosphere is the nucleation of ultrafine condensation nuclei from trace condensable vapors such as sulfuric acid. Despite intensive research over several decades, the sources of the ubiquitous background of ultrafine aerosols in the troposphere have not been conclusively identified." I propose that the SO_2 gas/liquid, which exists in the troposphere for at least months after volcanic eruptions, is the likely source of such vapors. I will discuss below the fact that man is adding SO_2 to the atmosphere constantly by burning fossil fuels.

Laj et al. [114] argue that the depletion of H_2O_2 in the ice in Greenland suggests that SO_2 reached Greenland as a gas and was then oxidized in precipitation. Barrie and Hoff [115] studied SO_2 in the arctic originating from fossil fuel burning in Eurasia. They conclude that the residence time is 14–20 days in late fall, 16–32 days in mid-winter and 10–19 days in April.

All of these observations show that the oxidizing capacity of the atmosphere is limited over periods of months to a few years following major volcanic eruptions. It typically takes from one to ten years for the atmosphere to recover totally. Therefore the oxidizing capacity of the atmosphere can be overwhelmed if large volcanic eruptions begin occurring every year or several times a year. The result is global warming.

5. High rate: Frequent large volcanic eruptions, global warming

Volcanic sulfate anomalies in the Greenland ice layers are significantly larger and more frequent between 15 and 7 ka as shown by the red bars in Fig. 4. This is exactly the time of greatest global warming coming out of the last ice age (green line). Fig. 5 shows this relationship in more detail. The purple line shows the GISP2 $\delta^{18}O$ proxy for temperature and ice volume for the past 25,000 years [91]. The world was coldest during the Last Glacial Maximum (LGM) between 22 and 24 ka, depending on the data set. Warming was slow until between 15 and 9 ka when temperature increased abruptly. The green line shows the cumulative amount of volcanic sulfate. The slope of the green line is the inverse of the rate of sulfate per thousand years. The more horizontal the green line, the greater the rate of sulfate deposition. The slope is most horizontal, which means the volcanic activity is highest between 11.3 and 9.5 ka, the time of greatest global warming, the Preboreal warming.

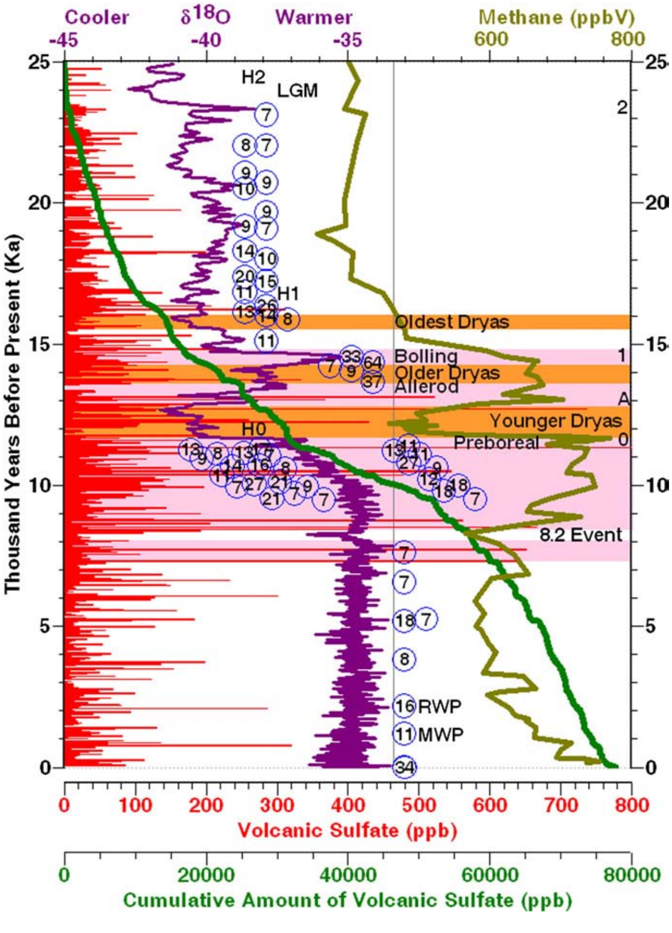

Fig. 5. Warming correlates with high rates of volcanism, times of continuous volcanism within contiguous layers and increases in methane. Red bars show volcanic sulfate [96], the purple line shows the $\delta^{18}O$ proxy for surface temperature in Greenland [91], and the olive line shows methane since 25 ka from the GISP2 drill hole [116]. The green line is cumulative volcanic sulfate; the more horizontal the slope, the higher the rate of volcanism. The blue circles with numbers show the time and number of contiguous layers in the GISP2 cores containing volcanic sulfate. These are the periods of greatest warming. The brown shaded areas show times of increased glaciation. The pink shaded areas show times of lush vegetation in Egypt, Sudan, Libya and Chad [117]. The largest sulfate anomalies are contemporaneous with times of rapid warming, increases in methane, and northward movement of the ITCZ in Africa. RWP is the Roman Warming Period. MWP is the Medieval Warm Period. H0–H2 are Heinrich glacial surges. Black 0, A, 1–2 are Dansgaard–Oeschger sudden warming events.

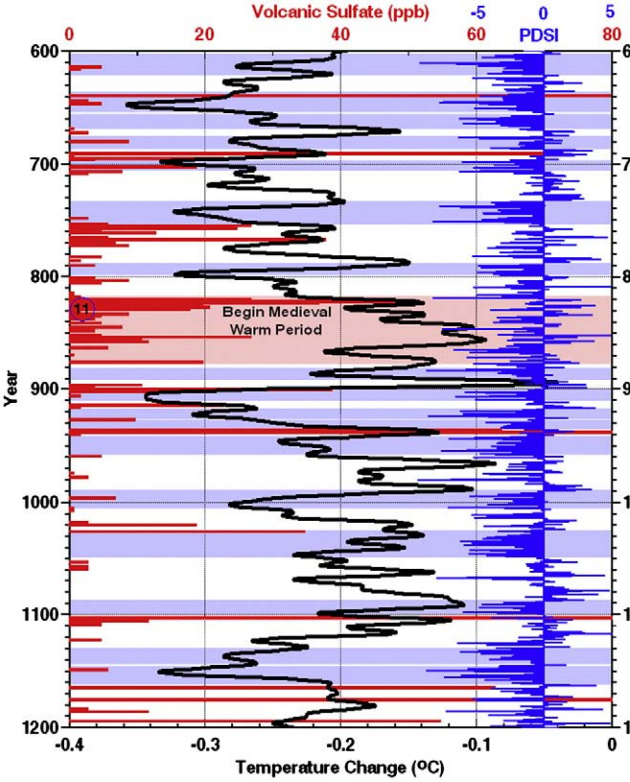

Fig. 6. The Medieval Warming Period began with a burst of volcanism. The black line is temperature change based on multiple proxies [4] which shows that the Medieval Warming Period began around 820 AD and ended sometime after 1120 AD. The red bars show volcanic sulfate anomalies in individual layers of the GISP2 borehole [96]. The blue circle shows the time when 11 contiguous layers in the borehole had sulfate anomalies, which coincides exactly with the increase in temperature. Volcanism was high throughout the time shown shaded in pink. Individual large sulfate anomalies tend to be followed by short-term cooling. The Palmer Drought Severity Index (PDSI) is shown in blue for southeastern Utah [241]. Negative numbers are drought; positive numbers imply rain. Times of extended drought (shaded blue) tend to be times with little or no evidence of volcanism.

In the process of warming, there were several times when ice-age conditions returned for hundreds to thousands of years. These times of reduced temperatures and glacial advance are known as the Oldest, Older, and Younger Dryas (light brown bands in Fig. 5) separated by the Bolling, Allerod, and Preboreal warmings. Note that the rates of volcanism are lowest during the Dryas phases and highest during the warming phases. The olive curve shows methane measured in the GISP2 ice cores [116]. Note the high methane concentrations during the periods of most rapid warming. Methane concentration increases as oxidation capacity decreases (Paragraph C in Section 4 above).

The light-red shaded areas show times of global warming when Egypt, Sudan, Libya and Chad were verdant and lush [117]. The African humid period began at ~14.8 ka, ceased during the Younger Dryas (12.7–11.5 ka), moved suddenly south at 7.3 ka leaving Egypt dry, and continued until 5.1 ka. Warming during the highest sulfate levels appears to have moved the Intertropical Convergence Zone (ITCZ) northward [118]. Since ~70% of land is in the northern hemisphere, this motion could be driven simply by greater than usual heating of the land surfaces.

Each red bar in Fig. 5 shows the amount of volcanic sulfate deposited in one layer of ice in Greenland. The eruption of Tambora (Volcano Explosivity Index (VEI) = 7, Table S1) caused a sulfate anomaly in Greenland of 83 ppb while the eruptions of Kuwae, Huayaputina, Krakatoa, Santa Maria and Katmai (all VEI = 6) caused an average sulfate anomaly of 47 ppb. Let's define “large” volcanic eruptions as those erupting >10 km^3 of tephra (air-fall material) >25 km into the stratosphere (VEI ≥ 6) [24]. The size of the sulfate anomaly depends not only on VEI, but also on the gas content of the eruption and latitude of the volcano. Let's assume for simplicity, however, that a “large” volcanic eruption typically produces a sulfate anomaly of 50 ppb. The sulfate anomaly of 801 ppb at 11.292 ka, then, represents 16 “large” eruptions in 2.08 years, or one “large” eruption every 47 days. This is the highest rate of sulfate deposition in the GISP2 ice cores, but there are 183 layers with sulfate > 100 ppb and many are sequential. For example, between 11.292 and 11.229 ka, a total of 1858 ppb sulfate implies one large eruption every 7 months over a period of 63 years. This was the time of the very rapid Preboreal warming (Fig. 5) [119].

The circles with numbers show the number of contiguous layers (7 or greater) that contain a sulfate anomaly plotted at their average age. Warming should be greatest when “large” volcanic eruptions occur in the most rapid sequences. Note the high concentration of numbered circles during the Bolling, Allerod, and Preboreal warmings. The youngest circle is related to anthropogenic warming and will be discussed below.

The second youngest circle marks the beginning of the Medieval Warm Period (MWP) shown in more detail in Fig. 6. The red bars show individual sulfate anomalies from 600 to 1200 AD [96]. The black line shows the temperature in the Northern Hemisphere based on multiple proxies [4]. The blue circle with the number 11 is centered

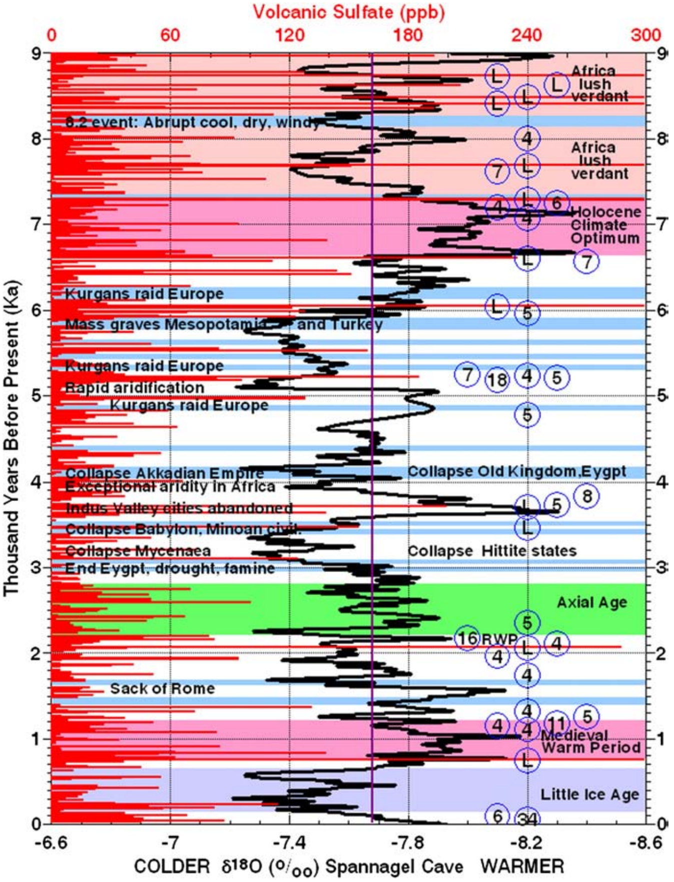

Fig. 7. In the last 9000 years, most of the warmest times are contemporaneous with times when sulfate anomalies occurred in numerous contiguous layers (numbers in blue circles). Red bars show individual sulfate anomalies measured in the GISP2 ice core [96]. The black line shows relative temperature based on $\delta^{18}O$ data from three stalagmites located in the Spannagel Cave, Austria [120]. Times of sudden cooling (narrow blue bars) tend to be during times of little or no volcanic activity when numerous empires fell and there are other signs of fighting over food. The Axial Age (green) was the time when temperatures were most constant.

Table 2
Times of a high rate of volcanic activity shown by sulfate anomalies within 4 or more contiguous layers or by sulfate anomalies of at least 200 ppb within one or two contiguous layers (L in column 1)

Number of contiguous layers	Begin years before 2007	End years before 2007	Total number of years	Total sulfate (ppb)	Sulfate per year (ppb)
34	23	81	58	1049	18
6	86	97	11	172	16
L	745	749	4	329	82
4	1103	1111	8	75	9
4	1148	1155	7	55	8
11	1168	1189	21	197	9
5	1244	1254	10	76	8
4	1309	1316	7	101	14
4	1736	1746	10	108	11
4	1953	1968	15	33	2
L	2056	2063	7	309	44
4	2101	2111	10	57	6
16	2149	2188	39	380	10
5	2340	2351	11	27	2
L	3459	3466	7	288	41
L	3700	3702	2	200	100
5	3718	3729	11	96	9
8	3813	3836	23	187	8
5	4766	4777	11	77	7
18	5163	5204	41	808	20
5	5206	5218	12	237	20
4	5229	5238	9	79	9
7	5240	5256	16	68	4
5	5953	5964	11	97	9
L	6040	6042	2	303	152
7	6557	6571	14	233	17
L	6601	6603	2	236	118
4	7060	7069	9	79	9
4	7195	7205	10	54	5
6	7238	7252	14	107	8
L	7282	7286	4	1052	263
7	7606	7621	15	82	5
L	7679	7683	4	806	202
4	7995	8005	10	113	11
L	8402	8405	3	500	167
L	8479	8484	5	785	157
L	8619	8621	2	207	104
L	8723	8729	6	952	159

The last column, sulfate per year, provides a way to compare intensity of volcanism.

on the period with volcanic sulfate in 11 contiguous layers (819 to 840 AD). This high rate of volcanism continues until 878 AD shown by the red shaded area. Note how the beginning of the Medieval Warm Period coincides exactly with the high contiguous rate of volcanism (Cardinal Rate III, Table 1). Most individual major volcanic sulfate anomalies in Fig. 6 are followed by short-term cooling (Cardinal Rate II, Table 1), although this is pushing the accuracy of the temperature data.

The red bars in Fig. 7 show volcanic sulfate anomalies for the past 9000 years [96]. The black line is temperature based on δ^{18}O data from three stalagmites located in the Spannagel Cave, Austria [120]. The numbers in the blue circles again show the number of contiguous layers containing volcanic sulfate anomalies (4 or greater). Very high volcanic activity is sometimes confined to one or two layers. An L in a blue circle denotes a time when total sulfate in one or two layers is at least 200 ppb. The data in the blue circles are summarized in Table 2. Note that the warmer temperatures ($\delta^{18}O < -7.8$) are contemporaneous with high volcanic activity shown by the blue circles. This is true for the Medieval Warm Period, the Roman Warm Period (RWP), the warm peaks around 3.7 ka and 5.2 ka [121], the Holocene Climate Optimum, and the period from 8.4 to 9 ka. The Little Ice Age, on the other hand is a time of relatively low volcanism.

The correlation between warming and high volcanic activity in Fig. 7 appears particularly robust when you realize that the width of the red lines tends to obscure the fact that 74% of the ice layers formed since 9 ka contain zero volcanic sulfate. Note that climate change appears to be initiated by levels of sulfate far less than one "large" volcanic eruption per year (50 ppb). The more I work with the raw data in Fig. 7 and Table 2, the more convinced I become that when we have developed the best model integrating the four cardinal rates of SO_2 (Table 1), we should be able to input observed volcanic sulfate levels and predict a temperature profile within the error bars of observed temperature profiles.

The red bars in Fig. 8 show volcanic sulfate anomalies between 9 and 16 ka [96]. The numbers in the blue circles show the number of contiguous layers containing volcanic sulfate anomalies (7 or more). The purple line is temperature based on δ^{18}O data from layers of snow in the GISP2 borehole [91]. As snow accumulates, it forms firn, a layer of ice with interconnected air passages. The gases are not trapped within the ice until buried by 40 to 120 m of snow [122,123]. Therefore the gas age is less than the layer age. The Meese/Sowers timescale relates depth in the GISP2 holes to layer age and to gas age [124]. Gas ages are typically 220 years younger from 0 to 10,000 years and 550 years younger around 15,000 years ago. The purple line is plotted as a function of gas age. The largest sulfate anomaly of 801 ppb at 11.292 ka followed by numerous contiguous layers of volcanic activity is contemporaneous with the rapid Preboreal warming. The Bolling Warming begins with 33 contiguous layers (14.484 to 14.586 ka) and then with 64 contiguous layers (14.235 to 14.457 ka). The Allerod Warming coincides with 37 contiguous layers (13.577 to 13.732 ka) of

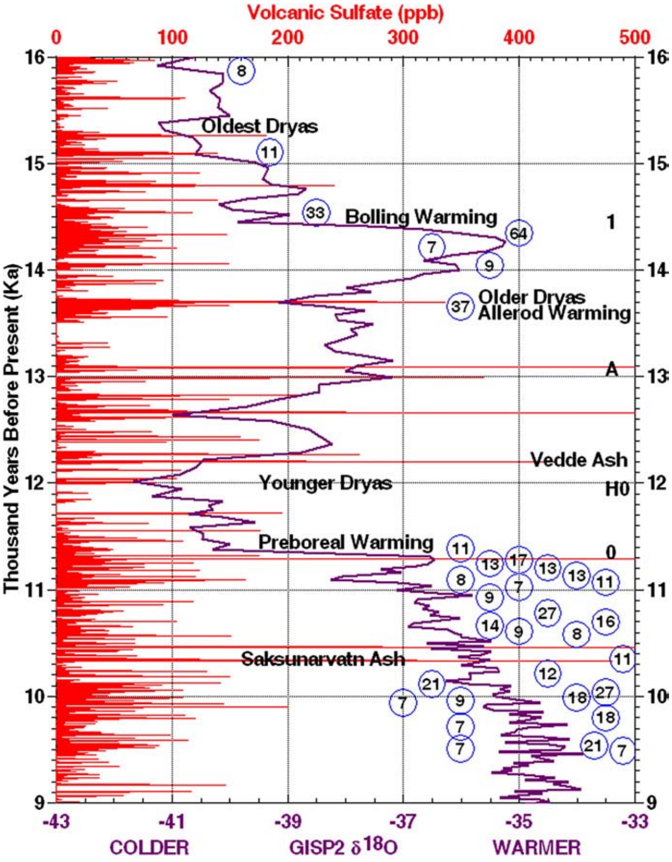

Fig. 8. Periods of greatest warming coming out of the last ice age are contemporaneous with times of sulfate anomalies in numerous contiguous layers (blue circle and number of layers). Red bars show sulfate anomalies in individual layers of ice in the GISP2 borehole [96]. The purple line shows the δ^{18}O proxy for temperature adjusted for gas age [91]. The Preboreal warming coincides with the largest sulfate anomaly observed. The Bolling Warming coincides with the largest number of contiguous layers containing volcanic sulfate. Dryas periods of increased glaciation coincide with little or no volcanism.

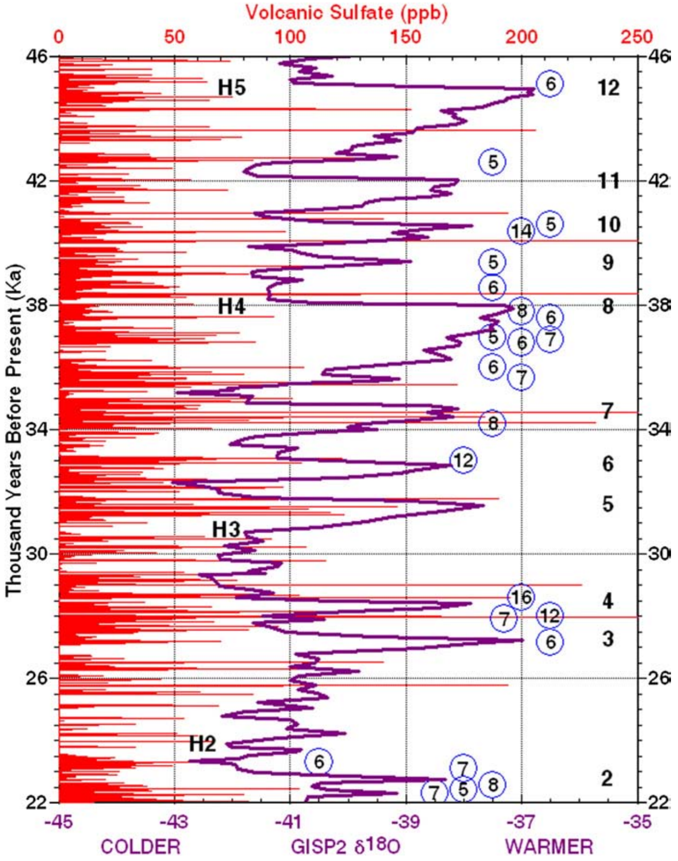

Fig. 9. Dansgaard–Oeschger sudden warming events (numbers on the right side) all correspond to times of high volcanism. Red bars show sulfate anomalies in individual layers of ice in the GISP2 borehole [96]. The purple line shows the $\delta^{18}O$ proxy for temperature adjusted for gas age [91]. Numbers in blue circles show the number of contiguous layers containing sulfate anomalies at the time plotted. H2 to H5 are Heinrich events when large numbers of icebergs suddenly appeared in the northern Atlantic Ocean.

volcanic sulfate anomalies. Single, even large, sulfate anomalies tend to be contemporaneous with cooling (Cardinal Rate II, Table 1) while sulfate in multiple contiguous layers tends to be contemporaneous with warming (Cardinal Rate III, Table 1). Steffensen et al. [125] document from detailed sampling of ice layers in Greenland that warming of as much as 10 °C occurred within 3 years during the Bolling Warming and 60 years during the Preboreal Warming with corresponding increases in layer thickness (precipitation) of 40%.

The red bars in Fig. 9 show volcanic sulfate anomalies from 22 to 46 ka [96]. The numbers in the blue circles again show the number of contiguous layers containing volcanic sulfate anomalies (5 or more). The purple line is temperature based on $\delta^{18}O$ data from layers of snow in the GISP2 borehole based on gas age [91]. Numbers 2 thru 12 are Dansgaard–Oeschger events when rapid warming of 10 to 16 °C in Greenland occurred in less than 40 years [92,93,126–129]. All warming phases except event 5 at 31.5 ka are contemporaneous with volcanic sulfate in 5 or more contiguous layers. Event 5 is contemporaneous with much higher volcanic sulfate (795 ppb) than usual between 31.632 and 31.203 ka, but not in more than 4 contiguous layers.

Heinrich events [130] (H0–H6 in Figs. 4, 5, 8 and 9) when large numbers of icebergs suddenly appeared in the northern Atlantic Ocean tend to occur when there is little volcanism. H2 and H3 in Fig. 9 appear to be contemporaneous with major cooling while H4 and H5 appear to be contemporaneous with rapid warming. The temporal resolution is not yet accurate enough for an unambiguous interpretation.

Figs. 4–9 and Table 2 show that all major warming events in the past 46 k.y. are contemporaneous with high rates of volcanism when “large” volcanic eruptions are occurring every few months to every year or two for years to decades (Cardinal Rate III in Table 1). No other processes are known that can cause such rapid warming so often. The reason for the warming appears to be reduction of oxidation potential causing an increase in gases such as carbon monoxide and methane. Once warming begins, the erupted water and CO_2 would compound the warming. Increasing temperatures would further increase atmospheric concentrations of water and CO_2. Such positive feedbacks help us understand how the global temperatures could change so rapidly.

In conclusion, prior to man, global climate change appears to be initiated primarily by changes in SO_2. Changes in CO_2 are a result, not a cause.

6. Anthropogenic warming

The red bars in Fig. 10 show sulfate anomalies in the GISP2 ice core in Greenland from 1850 to 1985 [96] along with the names of known volcanic eruptions with their VEI [24]. The blue line shows mean yearly global surface temperature [131,132]. The black line shows the amount of sulfur emitted by humans burning fossil fuel [133,134]. During the 19th century, 72% of the ice layers had no volcanic sulfate. Since 1927, all layers had sulfate and the amount of sulfate increases proportionally to the sulfur emitted by burning fossil fuels (black line).

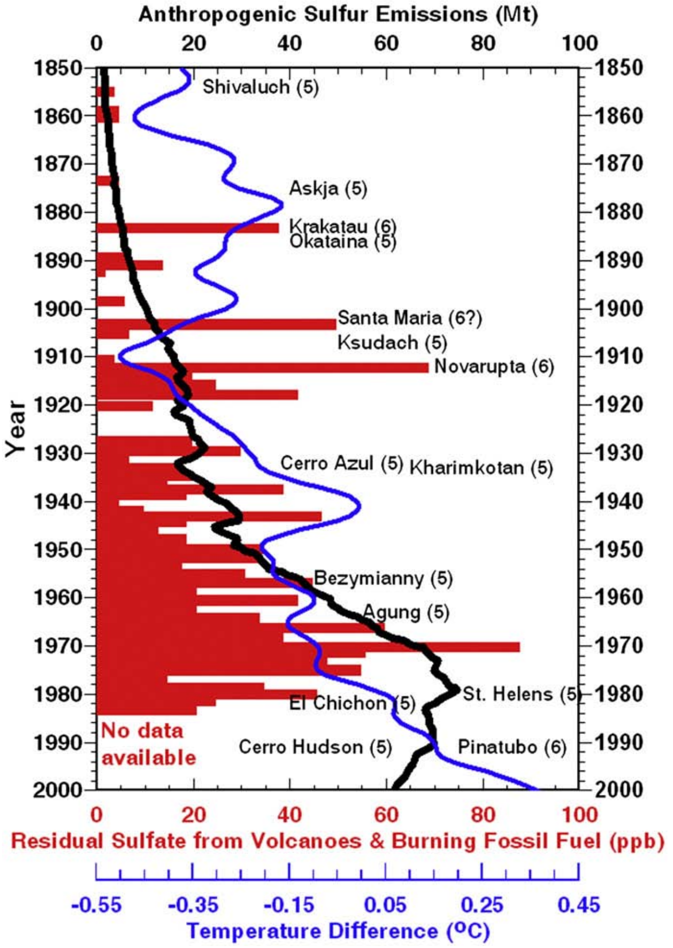

Fig. 10. Recent warming correlates with increases in sulfur from fossil fuels. Red bars show sulfate in each layer of ice in Greenland [96], the blue line shows average global temperature [132] and the black line shows sulfur emitted by burning fossil fuels [133,134]. Names of volcanoes (VEI) are shown with associated sulfate anomalies [24]. All layers since 1925 contain residual sulfate that increases yearly in proportion to the increase in anthropogenic sulfur emissions.

Such a linear increase in background sulfate has never been observed in any ice cores going back many hundreds of thousands of years. The sulfate in Greenland increases proportional to known human emissions and decreases after 1980 when the amount of anthropogenic sulfur was decreased through international efforts to reduce acid rain.

This same increase before 1980 and then decrease is seen in ice and shallow firn cores throughout Greenland in holes drilled as recently as 1999 [135–137]. Similar sulfate trends observed in the Alps correspond closely with known sulfate emissions in surrounding countries [138]. The rise and fall has been successfully modeled using known anthropogenic emissions [139,140] and known efforts to reduce sulfur dioxide emission throughout Europe [141]. Similar rise and fall is observed in ice cores from the Dasuopu glacier [142] and the East Rongbuk glacier [143] in the Himalayas, the Belukha ice core in the Siberean Altai [144], the Lomonosovfonna ice field on Svalbard [145] and from ice cores in Severnaya Zemlya, Eurasian Arctic [146]. The amount of sulfate varies with distance to industrial centers with very low anthropogenic signals observed in ice cores from the St. Elias Mountains in Yukon, Canada [147].

These sulfate signals corresponding closely to known anthropogenic emissions prove that SO_2 emitted from smokestacks around the world rises high enough and remains in the troposphere long enough to reach regional ice fields but not long enough to be thoroughly homogenized worldwide. Barrie and Hoff [115] conclude that the residence time for industrial SO_2 from Eurasia in the Arctic is 14–20 days in late fall, 16–32 days at mid-winter and 10–19 days in April. Laj et al. [114] found that high concentrations of sulfate in Greenland were associated with local depletions in H_2O_2, suggesting that the SO_2 remained a gas until oxidized as it was deposited in Greenland. All authors agree that the majority of anthropogenic sulfate in Greenland originated from northern Eurasia.

The amount of sulfate deposited in each layer (1.7 years) in Greenland had risen by 1962 to 50 ppb, the equivalent to one "large" volcanic eruption. Humans burning fossil fuels have raised the background SO_2 levels in the atmosphere to levels that throughout the past 46 k.y. have caused global warming.

Since 2000, the world reached a peak in global warming as shown in Fig. 11. The thin black line shows the monthly temperature data [131,132] with a running, centered, 12-point average. The thick black line shows a five-cycle trend fit to the data. Note that since 2000, global temperature has remained relatively constant and even decreased since autumn 2007. The peak in temperature during World War 2 (1939–1945) was discovered recently to be an artifact caused by a change in countries reporting ocean temperatures that used different methods for measuring [148]. The low in temperature around 1910 is most likely related to the large volcanic eruptions of Krakatau (1883), Santa Maria (1902), and Katmai (1912), all VEI 6. If these effects were corrected, the temperature data would approach a monotonically increasing line similar to the other lines in this Figure. Sudden peaks in temperature appear to correspond to the very largest known El Niño currents (Symbol "E" in Fig. 11) [149,150].

The purple line in Fig. 11 shows the sulfur emission resulting from man burning fossil fuels [133,134]. Note the moderate increase in temperature before 1950 when anthropogenic sulfur increased slowly and the rapid increase in temperature since 1950 when anthropogenic sulfur increased rapidly. Anthropogenic sulfur peaked around 1980.

The green line shows the atmospheric concentration of methane based on Etheridge et al. [151] prior to 1993 and Dlugokencky et al. [152] [153] since 1993. The levels of methane shown are higher than any values observed in the past 650,000 years [154] with current values being 2.3 times larger than any value known prior to the industrial era. Note that the methane peaks around the year 2000, which implies that the oxidizing capacity of the atmosphere had begun to recover by 2000. This is when the temperature peaked. The atmospheric lifetime of methane has increased 25–30% during the past 150 years to a current value of 7.9 years [155] implying gradually decreasing oxidizing capacity. Lifetime is based on the availability of OH and lifetime calculations do not consider continuing methane

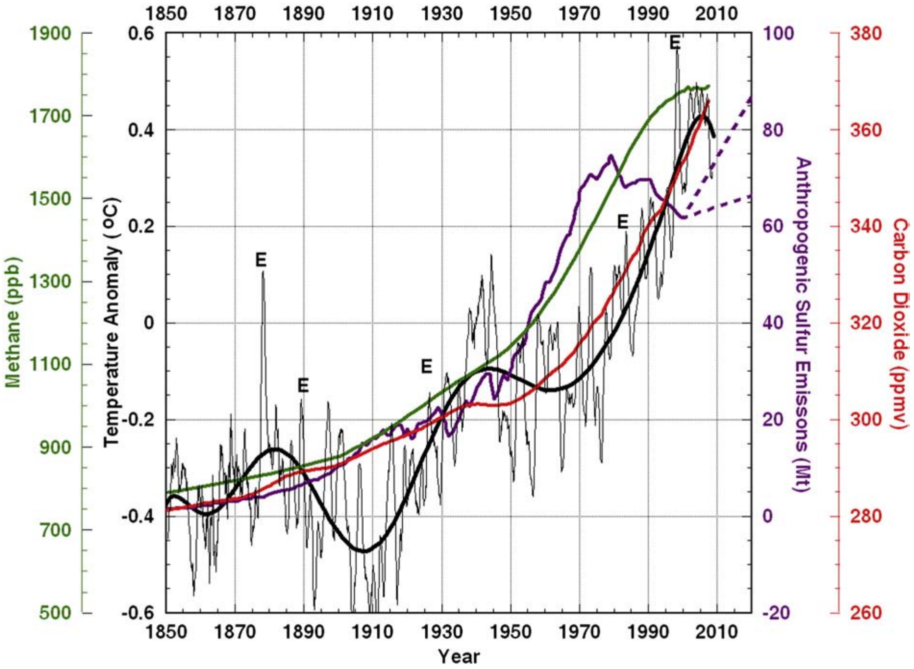

Fig. 11. Anthropogenic sulfur emissions peaked around 1980, followed by both methane concentrations and global temperatures around 2000. The atmospheric concentration for carbon dioxide meanwhile increases at the same rate. The thin black line is monthly average temperature smoothed with a 12-point, centered running average. The thick black line shows the temperature trend fit to five cycles. The solid purple line shows known anthropogenic sulfur releases [133,134]. The dashed purple line shows the likely range of anthropogenic sulfur releases until 2020 [158]. The green line shows annual average methane measured [151,152]. The red line shows annual average carbon dioxide measured [156,157]. Symbols "E" show times of the largest known El Niño events [149,150].

emissions. Thus the peaking of methane and temperature 20 years after the peaking of anthropogenic sulfur is a reasonable delay.

The red line shows the atmospheric concentration of CO_2 based on the annual fitted average of Keeling et al. since 1959 [156] and 20 year smoothed data measured in ice layers of the Law Dome in Antarctica with gas ages prior to 1959 [157]. Note that there is no change in the rate of increase of CO_2 since 1970 except for a small decrease and then increase after the Pinatubo eruption in 1991 caused by eruption induced global cooling [33]. There is no change in the rate of change of CO_2 concentration in the atmosphere that precedes or is contemporaneous with the flattening of the temperature profile since 2000. Thus it seems reasonable to accept the hypothesis that global warming during the 20th century was primarily initiated by a rapid increase in the rate of anthropogenic emission of sulfur by man, that the SO_2 reduced the oxidizing capacity of the atmosphere, leading to an increase in methane, water, and other greenhouse gases.

This does not mean that CO_2 did not have any role, but it does not appear to have had a lead role. Humans burning fossil fuels and manufacturing cement are releasing 7.8 Gt of carbon into the atmosphere yearly [20]. If all this carbon were in the form of CO_2, it would be 28.6 Gt, or 122 to 681 times greater than the amount of CO_2 emitted in the 1991 eruption of Pinatubo. Humans are putting two to three orders of magnitude more CO_2 into the atmosphere every year than one “large” volcanic eruption. There are many feedback loops in the carbon cycle, but there is little doubt that since the beginning of the industrial era, humans burning fossil fuels and making cement have been the primary cause for increasing the atmospheric mixing ratio of CO_2 globally from 285 ppm to 379 ppm [20]. CO_2 is a greenhouse gas that is also causing global warming as emphasized by the IPCC [12]. We need to incorporate the four cardinal rates of sulfur dioxide (Table 1) into atmospheric models before we can evaluate the net effect of CO_2.

The dashed purple lines in Fig. 11 show the upper and lower limits of likely future sulfur dioxide emissions [158]. Increase in methane beginning in early 2007 [159], suggests that sulfur values are already increasing. While the most developed countries have reduced and continue to reduce sulfur emissions, the problem is that the rest of the world wants to improve their standards of living. China [160] and India, for example, are adding two new coal-fired power plants typically each week [161]. Burning coal is a primary source of sulfur gas. Yet the use of coal is rapidly growing because more than 70 countries have coal reserves and coal reserves are significantly larger than all the other fossil fuel reserves worldwide [162]. The U.S. has the greatest coal reserves of any country and thus judicious use of coal is a key to American energy independence.

The good news is that during the past three decades we have made considerable progress reducing SO_2 emissions both technically and politically in order to reduce acid rain. Flue-gas desulfurization technologies can remove up to 98% of the sulfur gases from smokestacks and in some cases produce commercial products with the residue [163,164]. Improved combustion techniques such as pressurized fluidized bubbling-bed combustion can extract the energy from coal without releasing much sulfur [165]. The Clean Air Act Amendments of 1990 set legal limits for power plants that caused a reduction of SO_2 emissions in the U.S. by more than 50% as of January 1, 2000. Agreements in Europe led to a nearly 70% decrease in land-based sulfur emissions between 1980 and 2000 [166]. Clearly we need a major program to improve and implement these technologies worldwide as soon as possible [158]. We also need to improve technologies for reducing sulfur dioxide emissions from burning oil and natural gas. A significant source of sulfur emissions are ships that burn oil with as much as 5% sulfur by weight [167] and are largely unregulated. Reducing SO_2 emissions will not only reduce global warming, but will also reduce acid rain, and make the world healthier. The sulfur pollution produced by burning coal in China contributes to 400,000 premature deaths per year [168]. Significantly reducing global emissions of sulfur dioxide is well within out technical and political capabilities if we chose to give it top priority.

Thousands of papers have been written about very rapid changes of climate in the past, searching for their cause and expressing the fear that such changes could happen at any time in the near future when the climate reaches some unknown tipping point. Recognizing that the past 24 times of very rapid global warming were all caused by sudden increases in volcanic activity, allows us to stop worrying about tipping points and to begin worrying about what society should do when volcanoes become that active again in the future.

The emphasis in this paper has been on non-sea-salt sulfate measured in ice cores because this results from the largest volume of chemically active gas emitted from volcanoes. Other anthropogenic gases that have similar important effects with respect to aerosols include ammonium, nitrate, black carbon, and primary and secondary organics [169]. All will need to be addressed.

7. Extreme rate: Very frequent basaltic eruptions, mass extinctions

The largest known basaltic fissure eruption in the past 1000 years is Laki in southern Iceland, which produced 14.7 km^3 of basalt in 8 months beginning in June, 1783 [48]. The 10 eruption episodes were not all that spectacular (VEI = 4), with ash reaching altitudes of only 13 km, but this 27-km-long fissure complex emitted 122 Mt of SO_2, more than 5 times that of Pinatubo, as well as 235 Mt of H_2O, 15 Mt of chlorine, 7 Mt of fluorine, some hydrogen sulfide and some ammonia. Most of these gases were emitted into the troposphere but high enough to be caught in the jet stream headed for Europe. A dry fog covered the North Atlantic, Europe, North Africa and Asia with the greatest opacity between mid-June and mid-July.

It was a very cold and harsh summer in Iceland and Siberia, but very dry and hot in western Europe, most likely from solar heating of the dry fog. Intense thunderstorms and hail were unusually frequent. The winter of 1783–1784 was one of the most severe on record for Europe and North America with large floods in Europe in the spring. Cold winters and crop failures in Europe lasted into 1788 helping to spawn the French Revolution in 1789 [170]. Most birch trees, shrubs, and moss were killed in Iceland. Grass withered to the roots. Throughout Europe, from England to Sweden to Italy, trees and plants were damaged by acid rain and crops failed.

In Iceland, 50% of the cattle, 79% of the sheep, 76% of the horses and 24% of the people (10,521) perished from pollution of the air, water, and forage by the volcanic gases or from the resulting famine [171]. In England there were approximately 20,000 deaths related to the eruption [172], and more than 16,000 in France [173]. Famine and death even resulted among the Alaskan Inuit [174]. When similar mortality studies are completed throughout Europe, life loss from the eruption of Laki is likely to rival the largest known historic volcanic loss of 60,000 people during the eruption of Tambora in Indonesia in 1815 (VEI = 7) [175]. In fact one million people died during the Great Tenmei Famine in Japan exacerbated by the eruption of Laki and the local small eruption of Asama [176].

Basaltic eruptions typically emit 10 to 100 times more volatiles per cubic kilometer of magma than the “large” silicic eruptions discussed in earlier sections of this paper [177–179]. Given such major environmental effects from erupting less than 15 km^3 of basalt, what would be the effects of erupting more than 3,000,000 km^3 of basalt in the Siberian Traps around 249.4 Ma, the equivalent of 200,000 Laki eruptions? The Siberian Traps cover an area of 2,500,000 km^2, almost as large as Washington, Oregon, California and Nevada combined.

Courtillot and Renne [180] summarize studies of the twelve largest fissure basalt eruptions known in the past 360 m.y. and known mass extinctions and ocean anoxia events. They find a one-to-one correspondence between basaltic eruptions and extinctions within the precision of the dating for all the events (Fig. 3). The only exception is the Ordovician–Silurian mass extinction (443.7 Ma), probably the second largest, occurring in two separate prolonged events. Flood basalts of this age have not yet been recognized. Therefore there may be another explanation for at least one major mass extinction.

Only one mass extinction, on the other hand, clearly coincides with a meteorite impact, the Cretaceous/Tertiary boundary (65.5 Ma). Most paleontologists conclude that mass extinctions are not instantaneous; they tend to occur over at least thousands of years. While a meteorite may have complicated the extinction around 65.5 Ma, it is now clear that radiation did not kill the dinosaurs [181] and that large percentages of animals could have survived a large impact by sheltering [182]. Mass extinctions typically involve runaway greenhouse warming, major changes of acidity of air and water, dramatic increases in light carbon isotopes, and anoxia over hundreds to tens of thousands of years [183–188].

Given that massive increases in SO_2 appear to have caused mass extinctions in the past (Cardinal Rate IV, Table 1) and that there has been a significant increase in SO_2 gases since 1925 (Fig. 10), we should not be too surprised to discover that we are currently in the midst of a major mass extinction. In 2005, more than 1360 scientists under the auspices of the United Nations, completed the Millennium Ecosystem Assessment [189,190]. This was followed by the Global Biodiversity Outlook 2 under the Convention on Biological Diversity, a legally binding global treaty created in 1992 with nearly universal participation of countries. Among their conclusions are [191]:

1. “15 out of 24 ecosystem services are in decline including the ability to provide fresh water and the ability of the atmosphere to cleanse itself of pollutants.”
2. “Trends among 3000 wild populations of species show a consistent decline in average species abundance of about 40% between 1970 and 2000.”
3. “Between 12% and 52% of species within well-studied higher taxa are threatened with extinction.”
4. “The global demand for resources exceeds the biological capacity of the Earth to renew these resources by some 20%.”
5. “Humans are currently responsible for the sixth major extinction event in the history of the earth, and the greatest since the dinosaurs disappeared, 65 million years ago.”

8. Low rate: No volcanic eruptions, clean atmosphere, cooling and drought

The fourth type of abrupt climate change is very rapid cooling with widespread drought that appears to happen when the rate of volcanic activity decreases from a very high level to a very low level. The clearest example is known as the 8.2 ka event (Figs. 5, 7) (Cardinal Rate I, Table 1). At approximately 8175 years BP (Before Present) the temperature in Greenland dropped at least 3.3 °C in less than 20 years [192]. After 60 cold years, the temperature recovered in approximately 70 years. At the start of this event, methane in the ice core decreased 15% in 40 years perhaps lagging temperature by approximately 7 years [192]. Snow accumulation rate dropped and debris from wind-blown dust and forest-fire smoke increased [193]. Cooling (typically 1 °C), drought, and increased wind were observed throughout North America, Europe, Asia, and Africa [194,195]. This drought caused an end to the earliest known large farming settlement in the world (5000 people) founded around 9.3 ka at Çatalhöyük, Turkey [196]. The huge Lake Agassiz in Canada along the western edge of the ice sheet drained catastrophically into Hudson Bay at 8490 and 8290 years BP and models of this process can explain many of the observations of climate change [197–199]. But a surprising observation shown clearly in Figs. 5 and 7 is that the sulfate in the GRISP2 ice core had been very high but dropped to nearly zero around 8.2 ka. Similar sudden drops in sulfate are found throughout human history with the following disastrous consequences.

The largest drought in the past 5000 years occurred around 4.1 ka throughout all the continents of the northern hemisphere (Fig. 7). Widespread effects over 200 to 300 years included forest fires, dune reactivation, abrupt changes in forest composition, decreases in flood magnitudes, significantly increased dust, desiccation of lakes in mid-latitudes and positive moisture anomalies at high latitudes in Eurasia and North America [200–202]. This drought led to the collapse of the Akkadian Empire [203–206] and many early civilizations from Egypt to Greece. Empires collapse when they cannot feed their populous. Sulfate was particularly low at this time (Fig. 7).

Sulfate was similarly low around 5.8 ka. Mass graves with evidence of subsequent feasting implying fighting over dwindling food resources have been found in Turkey and Mesopotamia dating from this time [207]. Similarly the Kurgan pastoralists (Yamna Culture) from the steppes of Russia raided Europe most likely in search of food during sulfate lows at 6.2, 5.4, and 5 ka [208].

Every time the level of sulfate per century measured in this Greenland ice core dipped close to zero (blue shaded areas in Fig. 7), severe drought and famine brought the demise of major civilizations. The Old Kingdom of Egypt ended with decades of drought and famine between 2200 and 2150 BC [209]. Egyptian power ultimately ended with the eruption of Hekla in Iceland from 1159 to 1140 BC followed by decades of drought and famine. The Minoan civilization, weakened by the eruptions of Santorini from 1627 to 1600 BC, ultimately collapsed during the sulfate low around 1450 BC [210]. The Kassites, a mountain tribe, were able to conquer Babylonia around 1595 BC because of widespread famine [211]. The Greek Dark Ages between 1100 and 750 BC is also known as the Bronze Age of Collapse when Mycenaean and Hittite civilizations collapsed. There were “fewer and smaller settlements suggesting famine and depopulation” [212]. The Roman Empire fell around 476 AD [213] during a sulfate low. The Fremont and Anasazi cultures of southwestern North America and the Mississippian Cahokian culture were severely stressed by droughts between 990 and 1060 AD, 1135 and 1170 AD and 1276 and 1297 AD (Fig. 6) [214]. Plagues were also common during these major times of colder climate and they show some relation to the cold years following volcanic eruptions [215–217].

The largest droughts are not worldwide. They show some relationship to movement of the Intertropical Convergence Zone (ITCZ) affecting different cultures. The African Humid Period shown in Figs. 5 and 7 is a clear example. Therefore we should not be too surprised to find that the Mayan civilization [218] and the Tang Dynasty [219] collapsed from droughts centered at approximately 810, 860, and 910 AD. Similarly the Indus Valley civilization collapsed from droughts around 1700 BC [220] when there were high levels of volcanic sulfate and most likely northward shifts in the ITCZ.

Droughts are particularly common in the American southwest. The Palmer Drought Severity Index as listed in the North American Drought Atlas [221] is shown in Fig. 6 for southeastern Utah. Data from western Colorado through eastern Nevada show similar results. Negative numbers imply drought. Note that periods of extended drought tend to be times with little or no volcanism (Cardinal Rate I, Table 1).

One gets the impression from Fig. 7 that humanity in populous cities tended to flourish when the temperature averaged the amount equivalent to a $\delta^{18}O$ value of -7.68 ± 2 (vertical purple line). This is true from the success of the Akkadian Empire and the Old Kingdom of Egypt prior to 4.1 ka, to the Axial Age from 800 to 200 BC when nearly all the religions of the world were created and when Greek democracy, literacy, philosophy, and science flourished, to the Tang dynasty, the golden age of poetry and sculpture (618–907 AD), to the Protestant Reformation (16th century), the Age of Reason, the Age of Enlightenment, the roots of the Industrial Revolution, and the roots of democracy through the American and French Revolutions. A similar relationship is seen during the period from 38 to 36 ka in Fig. 9. The unusually high volcanic activity and the associated warm period, coincides with the start of the Upper Paleolithic Revolution when modern humans spread rapidly into Eurasia and there was a sudden increase in sophistication of stone-working technologies, art, music, elaborate burials, and such [222].

When volcanoes are no longer erupting large amounts of SO_2, the oxidizing capacity of the atmosphere can increase, leading to more effective oxidation of methane, CO, and other pollutants. As the atmosphere becomes cleaner, ultraviolet rays penetrate closer to the earth, increasing production of OH and H_2O_2 in the troposphere and increasing oxidation. In this way, the atmosphere "scrubs" itself from the top down, cooling the earth. Rainfall depends on coagulation of pollutants around very small particles. With the decrease in volcanic activity, there are less particles and less sulfuric acid, inhibiting rain. Small particles can become condensation nuclei in the presence of ions, which are atoms or groups of atoms bearing an electric charge [223,224]. Ions are produced by cosmic rays that are also able to penetrate a thinner atmosphere. The net result of cosmic rays on these ultrafine particles is to increase cloud cover, cloud reflectivity, and cloud lifetime and to suppress rainfall [113]. The effects are greatest when there are the largest concentrations of ultrafine particles following either the largest volcanic eruptions or series of volcanic eruptions or following significant, continuous pollution by man. The effects are also greatest at the more polar latitudes because cosmic ray intensity at the top of the atmosphere is only about 5% near the geomagnetic equator, but 50% at the poles [113]. The effects are also greatest for low-altitude clouds and therefore for times when cosmic rays can penetrate most of the atmosphere.

There is an extensive literature reporting apparent correlations between solar cycles or proxies for solar cycles with climate change, but satellites now show that the variation in solar output is only 0.1% on decadal time scales, which can only explain temperature changes of about 0.1 °C [225]. Two proxies commonly used to infer solar cycles are ^{14}C in tree rings and ^{10}Be in ice cores [226,227]. Both of these light isotopes are generated by cosmic rays and their production probably increases during atmospheric purging events when there are no stratospheric or tropospheric aerosols and cosmic rays can therefore penetrate deep into the troposphere. ^{14}C levels also increase when methane is oxidized [228], which should happen as SO_2 levels decrease. These associations may give insight into why there are sudden changes in the slope of the curve relating ^{14}C dates to calendar dates.

Cooling the atmosphere encourages glaciers to grow, but drought inhibits glacial growth.

9. Discussion

The international debate over climate change has been between those who argue that periods of sudden warming have happened without man many times in the geologic past and those who argue that the prodigious amounts of gases emitted by man are causing the current warming. I have shown in this paper that both groups have merit and the mechanisms are similar. Sudden global warming has occurred dozens of times in the past 46,000 years and each of those times is contemporaneous with a significantly higher rate of "large" volcanic eruptions essentially every year for dozens of years. The most chemically active gas emitted by volcanoes in significant amounts is SO_2. Changing concentrations of SO_2 are observed to cause cooling, warming, acid rain, and drought. Measurements in Greenland show that man is currently putting as much SO_2 into the atmosphere every 1.7 years as one "large" volcanic eruption, enough to cause global warming. The only "large" volcanic eruption in the past 96 years was Pinatubo. Therefore, man is clearly responsible for current global warming even though man had nothing to do with earlier periods of global warming.

If too much SO_2 causes global warming and mass extinctions and too little causes cooling and drought, there must be an ideal level in between. Our first challenge is to reduce SO_2 emissions significantly to reduce warming. The second challenge will be to allow just enough SO_2 emissions to prevent drought. The third challenge will be to stop all human SO_2 emissions during volcanic eruptions and to discover other ways to mitigate the effects of volcanoes putting too much SO_2 into the atmosphere. Therefore geoengineering of a stable "ideal" climate might be scientifically feasible, although politically a nightmare. Current suggestions for geoengineering by injecting SO_2 [229,230] into the lower stratosphere are likely to cause more harm than good unless massive amounts of water are also injected.

SO_2 has its largest effect by changing how the atmosphere reflects, refracts, scatters, absorbs, or transmits broadband radiant energy from the sun, infrared energy radiated outwards by the earth, and cosmic rays bombarding the earth from all directions. The result is differential heating of the atmosphere and the earth's surface that then affect atmospheric and oceanic currents. Many different feedback loops are set into motion. In order to understand in detail the effects of the four cardinal rates of SO_2 on climate, we must adapt current climate models to be driven by changes in SO_2. This should involve more detailed studies of the effects of past volcanic eruptions. The results may not always be intuitive.

For example, beginning 6 years after the Laki eruption in 1783, when the cooling of the stratospheric aerosol is likely to have declined, the South Asia Monsoon failed leading to major prolonged droughts from 1790 through 1792 in southern India, southern Africa, Australia, Mexico and many Atlantic islands. In India more than 600,000 people died from the resulting famine [231]. A moderate El Niño current occurred in 1786, but an extraordinary El Niño formed in 1791. Many authors have suggested that volcanoes can affect El Niños [232–235]. The suggestion of an 8-year delay seems preposterous. Yet there was an apparent 8-year delay for a very severe El Niño following the large 1883 eruption of Krakatau, and a 9-year delay following the 1902 large eruption of Santa Maria as well as smaller but significant eruptions of Pelée and Soufriere. Such delays suggest that the very large El Niño of 1997–1998 might be the result of the large 1991 eruptions of Pinatubo and Cerro Hudson. Such correlations are complicated by the large number of El Niños in history that vary significantly in size [149,150], but the largest volcanic eruptions do seem to precede the largest El Niños by ~9 years. Delays of several years need to be considered and may well be related to delays in changing the huge heat capacity of the oceans with low heat capacity atmospheric currents. There are other sources of multi-year delays. For example, modeling the effects of the 1991 eruption of Pinatubo suggests that significant effects on atmospheric water in the stratosphere peaked 3.5 years after the eruption and decayed slowly after that [236].

El Niño currents are caused by heating of the atmosphere and therefore the ocean in the western Pacific. La Niña currents, on the other hand, are caused by cooling of the same region. La Niñas are closely associated with drought in southwestern North America [201,237–240]. Significantly reducing sulfur emissions leads to drought and cooling as discussed above. Therefore some care must be taken in the rate of SO_2 reduction. Note in Fig. 10 that there was low volcanic activity in the 1920s and a decrease in anthropogenic sulfur release in the early 1930s related to the Great Depression in the United States. It is conceivable that this decrease in SO_2 emissions is related to the extreme drought of the 1932–1939 in southwestern America. Similarly man's success in reducing sulfur emissions beginning around 1980 may have had an effect on the droughts of 1998–2002.

We have much to learn about climate. There have been many suggestions about what initiates climate change. The concept presented in this paper that changing concentrations of SO_2 is the primary initiator of climate change is new and should be evaluated in detail.

10. Conclusions

The concentration of SO_2 in the atmosphere appears to initiate global climate change in four ways:

I. Very low concentrations allow the atmosphere to cleanse itself by oxidizing most pollutants. This thins the atmospheric blanket, cooling the earth and causing drought.
II. Sporadic “large” volcanic eruptions cause cooling of the earth for approximately three years by forming a sulfuric acid aerosol in the lower stratosphere. A sequence of such eruptions can increment the world into an ice age.
III. When “large” volcanic eruptions occur in quick succession at the rate of at least one each year for ten or more years, the oxidizing capacity of the atmosphere is severely impaired, greenhouse gases accumulate, causing global warming.
IV. Every 20 million years or so, the eruption of millions of cubic kilometers of flood basalts overwhelms the oxidizing capacity of the atmosphere for tens of thousands of years or more, causing mass extinctions.

Humans burning fossil fuels are currently emitting as much SO_2 every 1.7 years measured in Greenland as one “large” volcanic eruption. Such a high level of SO_2 is causing not only global warming but widespread extinction of many species. Humans are also emitting 2 to 3 orders of magnitude more CO_2 than large volcanic eruptions, compounding global warming. Both CO_2 and SO_2 emissions must be reduced significantly to reverse global warming, but reducing SO_2 should be the highest priority.

Humans have developed many ways to reduce significantly the amount of SO_2 emitted; we need to implement them widely and aggressively. It might even be possible in the future to carefully maintain a constant ideal level of SO_2 by supplementing natural releases with controlled human releases.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tsf.2009.01.005.

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