Sulfur Dioxide Initiates Global Climate Change in Four Ways Notes for Science Writers

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This document is a supplement to my paper *Sulfur Dioxide Initiates Global Climate Change in Four Ways* (doi: 10.1016/j.tsf.2009.01.005) intended to assist science writers in focusing on the key issues and understanding the science behind them.

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Key Issues

- 1) Eighteen months ago, I discovered an <u>enigma</u>, a mystery: Moderate increases in the rate of volcanism caused the beginning of ice ages and major increases in the rate of volcanism caused the end of ice ages. How?
- 2) The earth-science evidence for both conditions is surprisingly robust.
- 3) Understanding this enigma has led to a total <u>shift in paradigm</u> for both the science and the politics of global warming.
- 4) Before the 20th century, sulfur dioxide emitted from volcanoes initiated most changes in climate from rapid warming to slower cooling to decadal drought.
- 5) Before the 20th century, increases in carbon dioxide <u>followed</u> increases in global temperature by 500 to 1000 years. Carbon dioxide compounds global warming. It does not initiate it.
- 6) All known significant increases in global temperatures in the past 46,000 years match periods of very high rates of volcanism except during the 20th century.
- 7) During the 20th century, the amount of sulfur dioxide emitted by man burning fossil fuel was as high as the highest rates emitted by volcanoes in the past 46,000 years.
- 8) There is no doubt that **man is responsible** for rapid global warming since the 1920s.

- 9) By 1980, man began to cut sulfur dioxide emissions in order to reduce acid rain.
- 10) By 1990, the rate of increase of methane in the atmosphere began to decrease.
- 11) By 2000, both the atmospheric concentration of methane and global temperature leveled off.
- 12) Decreasing sulfur dioxide emissions led to an increase in the oxidizing capacity of the atmosphere, the ability of the atmosphere to cleanse itself.
- 13) These earth science observations come as a total shock to most climatologists.
- 14) Most climatologists know that large volcanic eruptions cause cooling of the earth typically for three years. Such eruptions have occurred every 100 years since the birth of Christ.
- 15) Climatologists do not realize there have been times when large eruptions occurred every few months.
- 16) Climatologists also know that sulfur dioxide normally remains in the atmosphere for only a few weeks. They thought this was too short a time to affect global warming.
- 17) I differ with the IPCC by emphasizing <u>sulfur dioxide</u> instead of <u>carbon dioxide</u> and by emphasizing atmospheric <u>consumption</u>, or more properly the atmosphere's ability to cleanse itself of pollutants, rather than the <u>emissions</u> of pollutants.
- 18) Volcanoes caused sudden climate change. Other sources for climate tipping points are less likely.
- 19) Sulfur dioxide emissions are now increasing again because of the large number of new fossilfuel burning electric power plants being built around the world.
- 20) Reducing sulfur emissions is much more important than reducing carbon dioxide emissions.
- 21) Good news. We know how to do it! It is much easier to do.
- 22) We know how to burn coal with minimal sulfur emissions. Coal reserves are greater than the reserves of all other fossil fuels combined. The largest deposits of coal are in the United States. Coal will ultimately become a major component of an energy independence program in the United States.
- 23) A major international effort to reduce sulfur dioxide emissions should have the highest priority as we try to reduce global warming.

What follows is an explanation of the science behind these issues.

The Atmosphere

The atmosphere is a very thin blanket of gases, aerosols, and minute particles that keeps the earth warm enough to be habitable. Without any atmosphere, the surface of the earth would approach - 19°C (-2°F). Approximately 99% of the air in the atmosphere is within 30 km (18.6 mi) of the earth's surface, 0.5% of the earth's radius. The atmosphere is a thin film on the earth's surface.

The atmosphere reflects, absorbs, and transmits broadband radiant energy coming in from the sun and infrared (longwave) energy radiated outwards by the earth. The atmosphere shields us from harmful ultraviolet light from the sun and from cosmic rays bombarding the earth from all directions.

Figure 1 from Kiehl and Trenberth (Bulletin of the American Meteorological Association, 1997, volume 78, page 206) shows how the incoming solar radiation and outgoing radiated energy are reflected, absorbed and transmitted in today's atmosphere. The net radiation (reflected solar



Figure 1: The flow of radiant energy in today's atmosphere.

radiation plus outgoing longwave radiation) emitted into space by the atmosphere equals the net energy received from the sun (incoming solar radiation).

The atmosphere consists of gases, very small particles, and aerosols. Aerosols are gaseous suspensions of solid and liquid particles similar in form to what is sprayed from a spray can of insecticide or paint. Infinitesimal changes in the nature of these gases, particles and aerosols can change how incoming and outgoing radiation is reflected, absorbed or transmitted. A simple analogy is to think of slat or venetian window blinds. It takes a miniscule amount of energy to rotate the slats compared to the huge amounts of energy from the sun that is thereby reflected or transmitted. Solar energy dominates the earth. Just tinkering slightly with the chemical nature of the thin atmospheric blanket, changing the amounts of energy reflected or transmitted by less than one percent, can make substantial changes in temperature at the surface of the earth. **This is a very important point in trying to understand global warming**.

During and after large volcanic eruptions such as Mt. Pinatubo in the Philippines in June, 1991, sulfur dioxide and water erupted into the lower stratosphere, combined to form an aerosol that was 99% pure sulfuric acid and water (75% sulfuric acid, 25% water). This aerosol formed in the lower

stratosphere at altitudes of 20 to 23 km (12 to 14 mi). (This height would decrease for volcanoes located closer to the poles.) Within 21 days the aerosol layer circled the earth and began to spread slowly towards the poles.

This sulfuric acid aerosol reflected some of the incoming solar radiation, reducing it by approximately 2.5 Wm⁻² or 0.7% in the case of Pinatubo compared to Figure 1. The result was to lower the world's average temperature approximately 0.5° C (0.9° F) for three years.

All known major historic volcanic eruptions caused similar cooling. There is often reference in historic accounts to the year(s) without summer. Typically crops failed, causing widespread famine in earlier times when food supplies were limited in many parts of the globe.

Pinatubo added 15 to 19 megatons of sulfur dioxide to the atmosphere and 491 to 921 megatons of water. Together they increased the mass of the atmosphere by only 0.23 parts per million. Sulfur dioxide alone increased the mass of the atmosphere by only 3.3 parts per billion. A very small change for a very big effect. For comparison, the Medieval Warm Period (820 to 1120 AD) had an average temperature that was only 0.1°C warmer than the Little Ice Age (1300 to 1850 AD).

Southern Greenland was quite habitable by the Vikings during the Medieval Warm Period, but they all died off during the Little Ice Age because they refused to give up their traditional ways of farming and adapt to the colder climate the way the Inuit had done long before.

The Ocean

The ocean is the second most important part of the earth system when trying to understand global warming. The ocean, which covers more than 70% of the earth's surface, has a huge capacity for storing heat. Think of the ocean as a giant thermal battery: you can store heat in the ocean by raising the temperature of the air touching the ocean. When air temperature decreases, heat from the ocean dissipates back into the air, raising air temperature. Air temperatures can oscillate very quickly; ocean temperatures change very slowly. It takes a lot of calories to warm the ocean.

Since the ocean does not generate heat as a chemical battery generates electricity, a more technically correct but less widely understood analogy is a capacitor. A capacitor stores electricity when the voltage is high and returns electricity when the voltage is low. The effect is to smooth out the high frequency changes. Without the ocean, the extremes of temperature on earth could be a lot greater and ice ages would be shorter but more frequent.

The ocean during the last ice age was approximately $3^{\circ}C$ (5.4°F) cooler than it is today. The cooling of the atmosphere caused by the eruption of Pinatubo, reduced the ocean heat content by 3 x 10^{22} joules. The heat capacity of the ocean is approximately 1.5 x 10^{21} joules per degree Celsius per meter (3.3 feet) of depth. The heat capacity of the whole atmosphere is only equivalent to the heat capacity of the ocean. The heat necessary to raise the temperature of the atmosphere 1°C is the same necessary to raise the upper 360 meters of the ocean by only about 0.01°C (The Turbulent Ocean by S.A. Thorpe, 2005, page 17, available on line).

Essentially, after the eruption of Pinatubo, the temperature at the surface of the water was reduced by approximately 0.3° C (0.5° F) for three years. The cooling caused the ocean to shrink, lowering sea level by ~5 millimeters (0.2 inches). Computer modeling of this change showed the average surface temperature of the ocean had not returned to its pre-Pinatubo level by 2000, the end of the model run. Thus if Pinatubo-sized eruptions begin happening more frequently than every decade or two, there will be a net cooling of the ocean. This must continue on average for thousands to millions of years to move the world into an ice age. This demonstrates how a long sequence of large volcanic eruptions can ratchet the world down into an ice age.

Ocean heat capacity has a big effect on 20th century global warming. If we reduce sulfur dioxide emissions to pre-industrial levels (before 1850), we can stop the increase of global temperature but we will not reduce global temperature. We have simply changed the setting on the thermostat because of the new heat stored in the ocean. It will take substantial cooling processes to cool the ocean and thereby reduce world temperatures to their pre-industrial level.

Oxidizing Capacity

The flow of energy shown in Figure 1 is also controlled by which gases and particles are in the atmosphere and how these combine into clouds and aerosols. New gases are added primarily by volcanoes, by fires, by biologic processes such as generation of methane, and now by man. New particles are added primarily by volcanoes, by fires, and by wind blowing dust or seawater into the air.

Atmospheric gases are modified by plants breathing carbon dioxide to produce oxygen, by animals breathing oxygen to produce carbon dioxide, by biologic processes, by chemical weathering of the earth's surface, by man, and by chemical processes in the atmosphere.

Of all these processes generating and modifying atmospheric gases and particles, by far the most important is oxidation, combining molecules of gases with oxygen to make bigger

molecules. These larger molecules can then either combine more easily with particles to create bigger molecules, fall out of the sky because of their increased size and weight, or be washed out of the sky by rain. This is how the atmosphere cleans itself.

A dirty atmosphere loaded with greenhouse gases absorbs more energy from the sun and energy radiated from the earth and radiates more energy back to the earth. Note in Figure 1 that 83% of the energy radiated by the earth is radiated back from the clouds to the earth. A dirty atmosphere is a warmer blanket, warming the earth.

A clean atmosphere has less gases and particles to absorb energy, transmits the energy to and from the earth's surface more effectively, leading to a cooler earth. But a clean atmosphere also allows more harmful ultraviolet light and cosmic rays to reach the surface of the earth. A clean atmosphere also does not nucleate clouds as effectively, reducing rain and causing drought on earth.

The chemical molecules that cause oxidation are primarily ozone (O_3) , the hydroxyl radical (OH) and hydrogen peroxide (H_2O_2) . Ozone is created by the effects of ultraviolet sunlight on oxygen (O_2) . The hydroxyl radical and hydrogen peroxide are similarly generated by the decomposition of ozone due to ultraviolet light.

Ozone, the hydroxyl radical, and hydrogen peroxide are highly reactive chemically; they do not last very long. Since oxidants are created in the atmosphere by sunlight, they are not created at night and they are created in greater abundance in the atmosphere above tropical regions. Oxidants, therefore, are in limited supply.

The amount of oxidants available is called the oxidizing capacity of the atmosphere. High oxidizing capacity "eats up" greenhouse gases, causing cooling. Low oxidizing capacity lets greenhouse gases accumulate, causing warming. Therefore, the concentration in the atmosphere of a greenhouse gas such as methane is an inverse indicator of oxidizing capacity. A high concentration of methane means low oxidizing capacity and global warming. A low concentration of methane means high oxidizing capacity and global cooling.

The IPCC emphasizes that methane is a greenhouse gas that absorbs much more energy than carbon dioxide. They explain the increasing amounts of methane as resulting from increases in methane sources on earth such as changes in the number of cows, peat bogs or rice paddies.

The increase in methane can be explained in another way. The hydroxyl radical reacts with sulfur dioxide in a fraction of a second. It reacts more slowly with methane, oxides of nitrogen and other greenhouse gases. Thus sulfur dioxide "steals" the oxidants that become available. Too much sulfur dioxide causes methane and other greenhouse gases to accumulate. Low concentrations of sulfur dioxide leave oxidants available to react with methane and other greenhouse gases, lowering world temperatures. **This is another very important concept in understanding global warming**: Large quantities of sulfur dioxide reduce the oxidizing capacity of the atmosphere, thereby changing the atmosphere's ability to cleanse itself and thereby increasing concentrations of methane. To belabor the point: The IPCC is primarily concerned with emissions. I am primarily concerned with the atmosphere's ability to remove these emissions through oxidation. Both affect atmospheric concentrations, but I argue that oxidation is far more important.

Sulfur dioxide opens and closes two types of venetian blinds. Sulfur dioxide and water emitted during a large volcanic eruption forms an aerosol in the lower stratosphere that closes those venetian blinds that govern <u>incoming</u> solar radiation, reflecting sunlight and thereby cooling the earth. Sulfur dioxide in the troposphere is largely oxidized. <u>Too much</u> sulfur dioxide, especially in the troposphere, reduces the oxidizing capacity of the atmosphere, closing a different set of venetian blinds that govern <u>outgoing</u> longwave radiation and thereby warming the earth. What closes these blinds is the rapid buildup of greenhouse gases, including sulfur dioxide, in the troposphere. How much sulfur dioxide is too much? These are details that will need to be worked out by atmospheric chemists, but my observations demonstrate that warming becomes a problem when there is at least one large, Pinatubo-sized volcanic eruption every two years.

Carbon dioxide, on the other hand, is not strongly affected by oxidizing capacity. Carbon dioxide is soluble in water, forming carbonic acid. Cold water absorbs more carbon dioxide. Warm water releases carbon dioxide. The atmospheric content of carbon dioxide prior to the industrial era is thus a proxy for temperature. There is a time lag introduced by ocean circulation. The coldest waters are the deep bottom waters that settle into the deepest ocean basins. Ocean circulation is driven in part by density differences of water of different temperatures and of slightly different salinities. These reservoirs of deep water have already sunk as deep as they can go and thus they do not participate directly in the mixing of the upper layers of the ocean. It takes time to warm these layers.

Since the beginning of the industrial revolution, man has been adding prodigious amounts of carbon dioxide to the atmosphere. Carbon dioxide is a greenhouse gas that absorbs radiant energy, contributing to global warming. But the effects of the radiative properties of carbon dioxide gas on the atmosphere appear to be small compared to the effects of oxidizing capacity. Prior to the widespread growth of plants (~ 350 Ma, million years ago), the mass of atmospheric CO₂ may have been as large as 17 times the mass of pre-human atmospheric CO₂ but global temperatures were not significantly higher. This suggests that CO₂ alone does not cause global warming.

A second argument against CO_2 alone causing global warming is found on Mars where the atmosphere consists of 95% carbon dioxide. During Martian winter, the surface near the poles becomes so cold that as much as 25% of the atmospheric carbon dioxide condenses into dry ice. Mars is 52% farther from the sun than earth, but if the radiative properties of carbon dioxide are as important as the IPCC emphasizes, Mars should probably have a very warm climate.

Global Warming

Figure 2 shows that the concentration of volcanic sulfate in individual layers of ice in the Greenland ice sheet is highest during the times when global warming was greatest (W) and was lowest when re-glaciation was greatest (C). Sulfate comes primarily from volcanoes, sea salt, and blown dust. Sea salt also contains sodium and blown dust contains calcium. Thus the amounts of sulfate from sea salt and dust can be estimated by the amounts of sodium and calcium and then subtracted from the total sulfate to determine the amount of "volcanic" sulfate. In analyzing the data from Greenland shown in Figure 2, Paul Mayewski (Journal of Geophysical Research, 1997, volume 102, page 26345) used a mathematic method called empirical orthogonal function that looks at the concentrations of all of the chemicals measured and groups them in the most chemically sensible ways. Thus the amounts of "volcanic" sulfate shown in Figure 2 are a reasonable proxy for the amount of volcanic activity (except in the 20th century when sulfur emissions by man became important). It turns out that one large volcanic eruption typically causes a deposit of approximately 50 parts per billion sulfate in Greenland. This value changes with the size of the eruption, the latitude of the volcano, the distance from Greenland, and the chemistry of its magma, but 50 ppb is a reasonable approximation.

Sulfate comes from oxidizing sulfur dioxide. The association of sulfate (sulfur dioxide) in Figure 2 with global warming is very clear and unambiguous. A more detailed look at all the data shows that the amount of warming is typically proportional to the amount of sulfate, especially when the warming lasts for several hundred years. The tall peak in sulfate at 13,600 years is accompanied by warming, but not as great warming as the peaks surrounded by other peaks. The duration of high sulfate is more important than the amount.

One could develop statistics to quantify the relationship, but statistics of small numbers are unreliable and the correlation is extremely clear to the eye. I show in Figures 7, 8, and 9 in the main paper that each known time of significant warming going back 46,000 years is contemporaneous, within the errors of the data, with each peak in major volcanic activity and visa versa. The sulfate record in the GISP2 hole goes back to 100,000 years before present. I stopped at 46,000 because the



Figure 2: Volcanic sulfate measured in ice layers in Greenland has its highest concentrations during times when global warming was greatest (W) at the end of the last ice age and its lowest when reglaciation occurred (C).

signal levels were getting too small to be reliable. There is very low noise in this relationship because more than 70% of the ice layers contain no volcanic sulfate.

One can argue about the fine details of the correlation, **but the main correlation between volcanism and global warming cannot be denied** other than to argue that it might just be fortuitous. The clear correlation of low volcanism and re-glaciation argues against chance.

<u>This observation correlating volcanism and global warming in time is totally unexpected.</u> For climatologists, it comes totally out of left field. They know that volcanoes cause cooling of the earth for a few years after large eruptions. How could volcanoes cause warming too?

The key to understanding this enigma is to understand the <u>rate</u> of emission. Sulfur dioxide in today's atmosphere lasts only for weeks. Following the eruption of Pinatubo, the observed "e-folding" time was 35 days. E-folding time means the amount of time it takes for 1/e or 35% of the gas to be oxidized. Sulfur dioxide from Eurasia seemed to reside 14 to 32 days in the atmosphere while propagating into the Arctic.

The concepts of e-folding time and residence time are misleading. Sulfur dioxide remains in the atmosphere until it is oxidized. In an atmosphere with high oxidizing capacity, residence time will be very short. In an atmosphere with low oxidizing capacity, residence time can be much longer. The rate-controlling molecule in the oxidizing reactions is the oxidant: OH or H_2O_2 . These are being generated in sunlit parts of the atmosphere at highest rates near the equator and lowest rates near the poles. Oxidants are also being generated near the top of a dirty atmosphere and at lower altitudes in a clean atmosphere where ultraviolet light can reach farther down into the atmosphere.

When a molecule of oxidant is generated, it will react immediately with whatever is available. In the case of sulfur dioxide, the reaction time is a miniscule part of a second. The reaction time is much longer for methane. Thus "residence time" for each type of oxidizable molecule in the atmosphere depends on oxidizing capacity, amount of day light, latitude, altitude, concentration, and chemical reaction time. The depletion of hydrogen peroxide in the snow in Greenland, suggests the sulfur dioxide was oxidized as it was deposited, meaning during the snow forming processes. Thus the presence of rainmaking and snowmaking processes influence "residence time."

Atmospheric chemistry is very complex in detail. Radiant energy from the sun, especially ultraviolet energy, is changing upper atmospheric chemistry all the time in sun lit areas. The chemical properties of each gas and their rates and types of changes are critically dependent on the frequency of the incoming radiation. Concentrations are very low so that the chemistry of solutions typically does not apply. Temperatures are low and vary significantly with altitude changing the



Figure 3: Human emissions of sulfur began to decrease around 1980 through efforts to reduce acid rain. The rate of increase of the concentration of methane began to decrease by 1990. Methane and temperature became relatively constant soon after 2000. It took 20 years to increase the oxidizing capacity of the atmosphere enough to reverse the increase in temperature.

types and rates of chemical reactions. Most chemical and physical processes are constantly changing. It is difficult to recreate upper atmospheric conditions in the laboratory and it is difficult to observed them in detail in situ. But the earth's atmosphere is an oxidizing atmosphere, meaning that chemical processes are dominated by oxidation. We can observe oxidizing capacity in a number of ways.

Figure 3 shows that in the last 60 years as human-generated sulfur emissions increased, the concentration of methane increased and therefore the oxidizing capacity of the atmosphere decreased. The result was an increase in average global temperature.

Around 1980, the sulfur emissions decreased because of major efforts to reduce acid rain, especially in Japan, Europe, and North America. The acidity in acid rain is primarily sulfuric acid formed by the reaction of sulfur dioxide with water. Note that the rate of increase in methane concentration began to decline by 1990 and reached zero by 2000. Since 2000, the concentration of methane in the atmosphere remained nearly constant. Since 2000, the temperature has similarly been constant or even decreased some. The time delays for the temperature and the concentration of methane to level off after the peak in sulfur emissions make perfect sense. It took time for the oxidizing capacity of the atmosphere to increase. As the amounts of sulfur dioxide slowly decreased, the amounts of oxidants could increase.

Meanwhile notice in Figure 3 that carbon dioxide (CO_2) has simply continued to increase. This increase is due in part to the warming of the ocean and in part to emissions from burning fossil fuels. Figure 3 is, in my mind, the smoking gun for the IPCC explanation for global warming.

The temperature shown in Figure 3 is based on the HadCRUT3 yearly averages (<u>www.cru.uea.ac.uk/cru/temperature/</u>) smoothed with a running centered average of 5 data points. The smoothing shows the trend more clearly but also rounds the peak around 2004. Temperature since 2000 was fairly constant until 2007 when it began to decrease. See globalwarmingart.com/wiki/Temperature Gallery.

Cooling and Drought

As discussed in detail in the main paper, extended periods with very low volcanic activity are contemporaneous with times of cooling and drought. The effect seems greatest following periods of very high volcanic activity such as 8,175 years ago. I have listed times in history when very low volcanic activity appears to be associated with decades of drought and crop failure typically causing the demise of major civilizations. This provides an explanation for why large cities appear to have been abandoned relatively rapidly as people had to fend for themselves to find food. It also explains why waterworks appear to be so important in these cities. There is considerable work to be done by historians and volcanologists to refine the association I sketched.

Theoretically, cooling and drought makes perfect sense. As the emissions of sulfur dioxide decrease, the oxidizing capacity of the atmosphere increases, cleaning the atmosphere. As the atmosphere becomes cleaner, ultraviolet sunlight penetrates closer to earth, increasing oxidation. Effectively the atmosphere gets scrubbed from the top down. Perhaps the most important greenhouse gas is water. As the atmosphere becomes better oxidized, water content decreases, in part because sulfurous vapors are very important for nucleating clouds.

Changes in atmospheric content of trace greenhouse gases vary by latitude and over land and sea, causing changes in atmospheric and thus oceanic currents. I show in Figure 6 how the drought index determined from tree rings decreases in southeastern Utah indicating increased drought during periods of very low volcanic activity. Droughts in Utah are typically associated with La Niña ocean currents in the Pacific. I show in Figure 5 that the periods of very large volcanic activity are associated with movement of the Intertropical Convergence Zone (monsoon alley). I show in Figure 11 that sudden major peaks in global temperatures are associated with the largest known El Niño

currents. Changes in atmospheric chemical content will change which regions of the world will be good for growing crops and which regions will be bad. Such changes in climate will also affect natural vegetation, probably explaining why early man had to migrate at specific times.

Mass Extinctions

Eruptions of basalt typically emit 10 to 100 times more sulfur dioxide per cubic kilometer of magma than the "large" silicic eruptions discussed throughout most of the paper. Basalt is a primitive magma that forms from the partial melt of peridotite that makes up the parts of the earth below the crust and uppermost mantle layers called the lithosphere. When the lithosphere cracks or is broken, basalt rises. If the lithosphere is thin, such as is typical under ocean basins, the basalt rises to the surface and is erupted forming a mid-ocean ridge or a line of volcanic islands. If the lithosphere is thick, such as is typical under continents, the basalt is not buoyant enough to erupt. It forms magma chambers at depths such as 5 to 15 kilometers (3 to 9 miles) where it cooks with the surrounding rocks forming silicic volcanics that are lighter and can ultimately erupt with the help of the gases that separate from the magma.

While I have not developed the concept in the scientific literature, I believe that flood basalts tend to be erupted where mid-ocean ridge triple points approach a trench and clog the trench, ending subduction. See en.wikipedia.org/wiki/Plate tectonics to understand this terminology. The eruption of flood basalts causes the thermal anomaly under the ridge to grow downward into the mantle thereby forming a volcanic hotspot that can continue to erupt more magma than surrounding lithosphere for millions to tens of millions of years. This may be the physical reason why massive flood basalts and mass extinctions only occur on average every 20 million years. Many flood basalts are massive with volumes as large as 3 million cubic kilometers (720,000 cubic miles). The largest historic basaltic eruption was from the Laki fissure in southern Iceland, on the Mid-Atlantic Ridge. The damage from this eruption of less than 15 cubic kilometers (3.6 cubic miles) of basalt was prodigious. I describe these effects in some detail in the paper to help readers imagine what the effect of erupting 200,000 times as much basalt would be. This provides a way to understand what the climate might have been like during a major mass extinction. The surprise for me was the conclusion cited in the paper from 1360 scientists that "Humans are currently responsible for the sixth major extinction event in the history of the earth." Twentieth century concentrations of sulfur dioxide compare not only with the concentrations during the major warming phases coming out of the last ice age (Figure 2) but also with the concentrations during many mass extinctions throughout geologic time.

Complications

Sulfur dioxide emitted in large volcanic eruptions has the primary effect on climate. There are other sources of sulfur dioxide and other chemically active gases that must ultimately be taken into account in modeling global climate change. Their effects will be much less, but they will have some effect.

Sulfur dioxide is also emitted from volcanoes continuously, such as from Mt. Trident shown in Figure 1 of the paper. It is also emitted in volcanic eruptions of all sizes. It is also produced in the atmosphere from dimethyl sulfide produced by phytoplankton in the ocean. All of these sources must be included in detailed models of the atmosphere.

Other gases are involved. The eruption of Pinatubo in 1991 emitted 491 to 921 Mt (megatons) of water (H_2O), 42 to 234 Mt CO₂, 15 to 19 Mt SO₂, and 3 to 16 Mt chlorine (Cl). Basaltic fissure volcanoes, such as Laki, also erupt fluorine, hydrogen sulfide, ammonia and many other chemical elements. The atmospheric concentration of CO₂ actually decreases as discussed in the paper due to

Table 1: The Four Cardinal Rates of SO₂.

	Rate of SO ₂	Eruption		
	Emission	Rate	Effect	Cause
Ι	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.
п	Moderate	One large volcanic eruption (Volcano Explosivity Index \geq 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.

the cooling effect of the sulfur dioxide generated aerosols. Much of the chlorine is concentrated in the eruption cloud and falls out of the eruption cloud due to dynamics described in the paper cited in footnote 21 in the paper. Thus sulfur dioxide is the most voluminous chemically active gas erupted by volcanoes but it is not the only one. Other volcanic gases have some effect on climate.

The Beneficial Effects of Sulfur Dioxide

I argue in the paper that sulfur dioxide concentrations in the atmosphere vary between the first three options in Table 1 and every 20 million years or so the eruption of massive flood basalts causes extreme concentrations of SO_2 and mass extinctions. In this way, sulfur dioxide appears to initiate global climate change. Changes in insolation or energy arriving from the sun due to small changes in the earth's orbit and inclination have an effect as proposed by Milanković and shown in Figure 4 of the paper, but less cyclic changes appear to be initiated by random changes in the concentration of sulfur dioxide. Therefore, if there were no large eruptions of sulfur dioxide from volcanoes, the world might be considerably cooler, drier, and less habitable. Life on earth as we know it might only be possible because of the volcanic eruption of sulfur dioxide.

Implications for the Politics of Global Warming

The recognition that sulfur dioxide appears to play the primary role in initiating climate change is good news. We know how to reduce sulfur dioxide emissions. We did an excellent job by 1980. We have the technology and we have examples of legislation and other political agreements that led to SO_2 -emission reductions. We also have experience at developing new technologies.

The conclusion that CO_2 is much less important than SO_2 in causing climate change is a political shock. Countries around the world are looking for ways to reduce CO_2 emissions. It is not yet clear that reducing CO_2 is not important, but it is less important than reducing SO_2 .

The burning of all fossil fuels emits sulfur dioxide. A particularly strong source is the burning of high-sulfur content types of coal often used in large amounts in plants that generate electricity. The major reduction of SO_2 output around 1980 came from new methods of burning such coal, scrubbing SO_2 from smokestacks, and, especially in Europe, converting power plants to gas, oil, or nuclear. Known coal resources in the world are significantly greater than the known resources of all other types of fossil fuels combined. The greatest supplies of coal in the world are in the United States. Thus developing clean-coal technologies should be a high priority. Regulating the burning of high-sulfur oil used especially by ships traversing our oceans should also be a high priority

Because of the immediate political implications of this paper, it will be scrutinized more carefully by more people than most scientific papers. Scientists will take issue with some details and we will all learn. Some may continue to deny that man really is responsible for global warming. I look forward to the scrutiny. No scientist is ever totally right. But to those who want to deny the role of sulfur dioxide, I encourage them to look carefully at Figure 2 of this document. This figure shows a basic observation of the earth that must be explained. As Francis Bacon said, "To learn secrets of nature, we must first observe." Pope Benedict summed it up: "Our Earth is talking to us and we must listen to it and decipher its message if we want to survive."

What is Sulfur Dioxide?

Sulfur dioxide is a colorless, heavy, poisonous gas that has an irritating, pungent odor. It is readily soluble in cold water. It has antibiotic and antioxidant properties that are useful as a preservative for dried fruits such as apricots. It is a very important compound used in winemaking and winery sanitation. SO_2 is used as reducing bleach, as a refrigerant, a reagent, a solvent and to treat chlorinated wastewater. SO_2 is the precursor for sulfuric acid used widely in industrial processes.

History of the Published Paper

During the summer of 2007, while doing research totally unrelated to climate change, I noticed that the most recent Ice Age Epoch began around 34 million years ago, when volcanism began in the world's largest known silicic volcanic province extending from central Colorado nearly to Guadalajara, Mexico. I had written two papers about this province published in 1991 and 1995 and understood well its size and significance. Oh, I thought, a major increase in volcanism might cause glacial epochs. I started to dig for more information.

Not much later, I discovered the excellent work of Greg Zelinski analyzing sulfate from the GISP2 drill hole. I plotted his data and immediately noted that the highest rates of sulfate deposition are exactly contemporaneous with the highest rates of warming after the last ice age as shown in Figure 2. Oh, I thought, very high rates of volcanism cause the end of ice age epochs. Now there is an enigma. I knew that some of the most exciting discoveries in science came from trying to resolve an enigma. I realized immediately the potential significance of this enigma to both the science and the politics of global warming. In fact it took considerable effort to calm down in order to get the hard work done.

In October, two members of the IPCC Technical Committee I and a very senior earth scientist advising the British Parliament on climate came to Jackson, Wyoming, as part of an "Energy and Climate Summit." I explained the enigma to all three. Both members of the IPCC said in effect, "No way. Something must be wrong. That is not possible."

The first version of this paper was a massive memory dump covering a wide range of related issues. Numerous reviewers argued with details and expressed the need to be more focused. I wrote the second version starting from scratch for *Science* magazine. I submitted it on March 17, 2008. It was rejected without review on March 21st. I rewrote the paper for *Earth and Planetary Science*

Letters submitting it on March 23. It was rejected without review on April 10. I rewrote the paper from scratch for *Nature*, submitting it on May 4. It was rejected without review on May 14 and automatically sent to *Nature Geoscience* where it was rejected without review on May 22. The most favorable interpretation of the rejection letters is that I should publish this paper in a specialty journal where the average reader would be better able to determine the quality of my work.

I then submitted the paper to *GSA Today* on May 29. Meanwhile I had been receiving comments from many reviewers and integrating them into the text. I began to write version 7 of the paper from scratch, determined to say all that needed to be said in as short a version as possible. After integrating comments from numerous reviewers, I submitted this version to *Thin Solid Films* on November 4. The editor asked many prominent climatologists to review the paper. Most refused saying that sulfur dioxide could not have such effects. He did find some highly respected chemists and physicists to look over the paper. They all agreed that the paper "is lucid, reasonable, may well be correct (while admitting they are not experts), and, in any case, deserves publication and scientific distillation." The paper was accepted on January 3, 2009.

Meanwhile in October, I spoke to the editor of *GSA Today* at a national meeting. He had had extreme difficulty finding any climatologist who would agree to review the paper. He was still looking for one more reviewer. On November 11, he rejected the paper based on two very short reviews. One simply said "SO₂, because of its very short atmospheric lifetime due to oxidation by much more abundant O₂ [totally incorrect], is not an important greenhouse gas. Therefore, it exists

only at very low concentrations insufficient to affect global warming." The other reviewer said "This paper is almost irresponsible in its disregard for known science." Neither reviewer mentioned my data, my data analysis, or my methods of interpretation. They simply said my conclusions did not agree with known science. I knew that before I submitted any version.

Now that the paper is in press, climatologists are beginning to express interest.

Biographical Information for Peter L. Ward

Peter L. Ward was educated at Noble & Greenough School (1961), Dartmouth College (BA in Geophysics, 1965) and Columbia University (Ph.D. in Seismology, 1970). He began working on active volcanoes in 1963 in Alaska. His Ph. D. thesis was on a new interpretation of the geology of Iceland based on studies of small earthquakes and on the relationship of these earthquakes to volcanoes and geothermal power sources. He worked 27 years with the United States Geological Survey on volcanoes, earthquakes, and plate tectonics. In the early 1970s he developed a prototype global volcano surveillance system



Photo by Irene Mellion

using the ERTS satellite to collect data from ground instruments on volcanoes through-out the western U.S., Central America, and Iceland. In 1975, he became chief of the Branch of Seismology, a group of 140 scientists and staff. He helped sell to Congress, develop and guide the new U.S. National Earthquake Hazards Reduction Program in 1977–1978. In 1990, he wrote and produced a 24-page magazine about living safely with earthquakes. Editions in English, Spanish, Chinese and Braille were distributed primarily in 41 Sunday-morning newspapers throughout Northern California to 3.3 million people, winning him two national awards. His major publications in the 1990s explored the relationship between volcanoes and other geologic features of western North America with the motion of plates in the northeastern Pacific Ocean. This led to significant new ideas about the origins and nature of volcanoes, granites, silicic volcanic provinces, flood basalts, and volcanic hot spots. He currently lives in Jackson, Wyoming, continuing his research on the effects of volcanoes on man. See <u>www.tetontectonics.org</u> for more detail.