Three Puzzling Observations Regarding Global Warming

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Atmospheric concentrations of CO_2 increased 6.8% since 1998 while mean global surface temperatures remained relatively constant. How can this divergence be explained if temperature is primarily a function of CO_2 concentration? Ice-layers beneath Summit Greenland containing the highest concentrations of volcanic sulfate also contain the $\delta^{18}O$ evidence for the greatest increases in temperature. How can volcanism be associated with warming when explosive volcanoes clearly cause cooling of up to 0.5°C over 3 years? CO_2 concentrations during two of the four major glacial epochs in the past 540 million years were five to ten times greater than preindustrial values. What is the relationship of CO_2 to ice ages?

The most efficient heating of the atmosphere is caused by photodissociation of molecular oxygen, ozone, and nitrogen dioxide at ultraviolet wavelengths. Global warming past and present appears to be caused primarily by thinning of the ozone layer allowing more photodissociation in the troposphere.

Puzzling Observation 1: Yearly and monthly global mean surface temperatures in the northern hemisphere (*1*) have changed very little since 1998 (Figure 1). Knight et al. (*2*) calculate that the temperature trend of these HadCRUT3 data from 1999 to 2008 was 0.07°±0.07°C per decade, more than two standard deviations less than the 0.18°C per decade recorded between 1979 and 2005 and the 0.2°C per decade anticipated during the next decade by global climate models (*3*). All major global temperature datasets show a similar trend although there are differences in detail especially when only continental sites are used.

Temperatures have remained high due to the substantial thermal capacity of the ocean; 13 of the last 15 years have annual temperature anomalies (relative to the mean temperature at each station from 1961 to 1990) between 0.41°C and 0.63°C while yearly mean temperature anomalies before 1982 were all <0.22°C (*1*). Earth's thermostat has been raised ~0.8°C since 1960 and the new heat stored in the oceans cannot be removed without some type of physical process that cools Earth, the best known being large explosive volcanic eruptions (*4, 5*).

Meanwhile annual mean concentrations of CO_2 at Mauna Loa increased 6.8% from 366 ppm in 1998 to 392 ppm in 2011 (*6*). Greenhouse gas theory posits that increased concentrations of CO_2 will absorb increased energy, raising atmospheric temperatures. The sensitivity of climate to a doubling in CO_2 concentration "is likely to be in the range 2.0°C to 4.5°C" (*3*). How can this observed divergence between temperature and CO_2 concentrations be explained?

Natural variability of temperature is often cited as the cause; global climate models show that periods of no temperature increase can last for 10 years but are highly unlikely to last for 15 years, which they now have (*2, 7-11*). Natural variability means energy is being shifted within the climate

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system. Where did the energy absorbed by an increase in CO_2 go? The primary heat sink is the ocean, but "ocean temperature measurements from 2004 to 2008 suggest a substantial slowing of the increase in global ocean heat content" (*12, 13*) although the possibility of the ocean warming below 700 meters cannot be ruled out (*14*). Warming due to CO_2 might have been offset by other sources (*15*), but Trenberth (*16*) examines a broad range of possible explanations and none of them can account for the missing energy. Is it possible that no net energy has been added to the atmosphere since 1999?

Puzzling Observation 2: Ice layers beneath Summit Greenland containing the highest concentrations of volcanic sulfate per century also contain the $\delta^{18}O$ evidence for the greatest warming during the Bolling (B) and the Preboreal (P) periods and low concentrations of sulfate during the intervening return to glaciation, the Younger Dryas (Y) (Figure 2) (*17, 18*). Sulfate concentrations remained high between 11,700 and 9800 years before present (BP) as the world was finally warmed out of the last ice age. In Iceland, eruption rates from basaltic fissures forming distinctive table mountains or tuyas under thick glaciers were up to 100 times larger during the Bolling and Preboreal warmings than during the glacial periods and during the last 5000 years (*19-26*). Volcanism was also high in Germany, France, Italy, Japan, Kamchatka, Korea, and New Zealand (*23, 27*). This volcanism may have been enhanced as it melted a thick ice sheet, reducing pressure on subterranean magma chambers (*19, 28*).

Sulfate concentrations deposited in Greenland ice were also very high during the 20th century (Figure 2) when trace elements show the sulfur dioxide (SO_2) precursors came from power plants and factories in northern Europe, Russia and central North America (*29, 30*).

There are many details to these sulfate data discussed elsewhere (*17, 31, 32*), but the basic signals associating high concentrations of oxidized volcanic and anthropogenic SO_2 with high rates of global warming are far above the noise (Figure 2). Yet SO_2 ejected into the stratosphere by explosive volcanoes is well known to cause global cooling of up to $0.5^{\circ}C$ over ~3 years. How can major volcanic activity be contemporaneous with both cooling and warming?

Puzzling Observation 3: Atmospheric concentrations of CO_2 increased in the same manner as SO_2 coming out of ice ages (*33, 34*), but a cold soda drink is well known to lose CO_2 as it warms and much of the observed increase in CO_2 can be attributed to warming oceans (*35-38*). Pinatubo, on June 15, 1991, erupted up to 434 megatons of CO_2 (*39*), ~14 times more than SO_2, but the yearly increase in CO_2 concentrations at Mauna Loa was only 1.2 ppm in 1991, 0.8 ppm in 1992, and 0.7 ppm in 1993 compared to 1.3-1.9 ppm during the previous 14 years and 1.7-2.9 ppm in subsequent years (*6*). This decreased rate of increase stems, most likely, from cooling of the ocean surface during the three years of lower surface temperatures caused by sulfate aerosols in the lower stratosphere.

Most detailed studies find that increases in CO_2 concentrations at the end of ice ages follow increases in temperature by hundreds of years (*40-44*) suggestive of the thermal time lag necessary to warm the deep ocean (*45-47*). Arrhenius (*48*) concludes that "the temperature in arctic regions would rise about 8° to 9° C if the carbonic acid [CO_2] increased to 2.5 or 3 times its present value." But Figure 3 shows that during 2 of the 4 major epochs of glaciation in the past 540 million years, CO_2 concentrations were 5 to 10 times larger than pre-industrial values. Concentrations of CO_2 do not appear to play an obvious role in the timing of major glacial epochs.

What did cause ice ages? Milankovitch cycles most likely played a role (*32*) but they are too long-period to explain the return to glaciation during the Younger Dryas (Y, Figure 2). All three puzzles are robust observations that do not make sense under current climate theories. What are the relationships between volcanism, SO_2, CO_2, warming and cooling?

Depletion of the Ozone Layer by Man and by Volcanoes

Warming during the last few decades and during the end of the last ice age share a common feature: a decrease in the concentration of ozone, commonly referred to as the optical thickness of the ozone layer, which is most concentrated between altitudes of 12 and 22 km. The amount of ozone has a major effect on how much high-energy ultraviolet radiation reaches the troposphere.

The longest continuous measurements of total column ozone from the Earth's surface were made at Arosa, Switzerland (Figure 4) (*49, 50*). Total ozone averaged ~331 Dobson Units (DU) from 1927 until 1974, fell precipitously to 300 DU in 1993 (9%) and began rising again. This long-term decrease in ozone has been reliably associated with an increase in concentrations of anthropogenic chlorine (green line) through discovery of the influence of stratospheric nitrogen oxides (*51*), chlorine catalyzed destruction of ozone (*52*), and the Antarctic ozone hole (*53*). The resulting Montreal Protocol on Substances That Deplete the Ozone Layer was signed beginning in 1987, leading to phasing out the production of chlorofluorocarbons and hydrochlorofluorocarbons and a decrease in total tropospheric chlorine beginning in 1993. Long-term ozone concentrations are expected to return to late-1970's levels by 2040 (*54*).

Short-term peaks in ozone are observed in Figure 4 during years containing atmospheric nuclear tests with yield >10 Mt (*55*). The largest peak was in 1940-41 as Germany invaded most of Europe at the start of World War II. There is a peak in 1998 during one of the largest El Niños in history but no obvious peak in 1982-1983 during an equally large El Niño (*56*), although this observation may have been complicated by the eruption of El Chichón in 1982.

The most consistent short-term changes in ozone are associated with volcanic eruptions in the tropics and the northern hemisphere (Figure 4). The largest volcanic eruption since 1912 was in 1991 from Mt. Pinatubo in the Philippines with a logarithmic Volcano Explosivity Index (VEI) of 6. Pinatubo is 10,300 km east-southeast of Arosa. An even larger ozone anomaly in 2010 is associated with the relatively small basaltic fissure eruption of Eyjafjallajökull, Iceland (VEI=4), which is only 2600 km upwind from Arosa. Both anomalies may have been enhanced by the high level of tropospheric chlorine at the time. Anomalies appear associated with the 1970 eruption of Hekla in Iceland (VEI=3) and with the larger but more distant eruptions of El Chichón in Mexico (VEI=5, 4+) during 1982 and Agung in Bali (VEI=5, 4) during 1963. Mt. St. Helens in Washington state erupted in 1980 with VEI=5 but had little effect on global temperature or ozone most likely because it exploded much of its debris laterally rather than upward into the stratosphere (*57, 58*). The apparent increase in ozone during the year of each major eruption is discussed in the Supporting Online Material (SOM).

The depletion of ozone in the years following an eruption has been widely observed especially related to Pinatubo (*59, 60*) and is believed caused primarily by the new aerosols formed in the lower stratosphere providing substantial new surfaces for heterogeneous chemical reactions to form ozone-destroying chlorine at cold temperatures (*61-63*). Ozone depletion may also have been enhanced by the large volumes of erupted water leading to more OH (*64*), a small amount of erupted halogens (*64*) that were not immediately removed in condensed supercooled water from within the eruptive cloud (*65*), and increased regional anthropogenic pollution. Related major changes in atmospheric chemistry after the Pinatubo eruption are well documented by a 45% drop in total column NO_2 measured at Jungfraujoch, Switzerland, beginning five months after the Pinatubo eruption and returning to normal with an e-folding time of 24 months (*66*), a 40% decrease in NO_2 column observed above New Zealand (*67*), and substantial increases in HNO_3 concentrations due to heterogeneous conversion of N_2O_5 (*64, 68, 69*). The aerosol and related decreases in the concentrations of ozone and NO_2 lasted for several years.

By January-April, 1993, the total ozone column was 11 to 17% below normal throughout Canada with a peak loss of 30% at ~16 km (*70*). On average, total ozone decreased 8% in Europe, 5-6% in North America, Russia, and Asia and <2% in the tropics (*60*). Following Agung and El Chichón, the deceases were 5%, 2-3%, and <2% in these same regions. Volcanism clearly lowers total column ozone especially from the mid-latitudes to the poles. The green line for chlorine in Figure 4 is inverted and has been scaled so that the increase in chlorine from 1965 to 1993 has approximately the same slope as the corresponding long-term decrease in ozone. This scaling will need to be quantified through modeling, but the visual fit as shown confirms the observation above that the decrease in ozone resulting from the Pinatubo eruption lasted for several years. At the end of the last ice age when rates of volcanism were ~100 times higher than now, i.e. one Pinatubo-sized eruption every year, such ozone depletion would have accumulated and would have lasted as long as the volcanoes continued to erupt frequently (11,700-9800 BP).

Reduced ozone increases the amount of ultraviolet energy reaching the Earth's surface. Surface erythemal (sun-burning) radiation (wavelengths predominantly between 300 and 320 nm) at mid-latitudes in the Northern Hemisphere was estimated in 1998 to have increased 7% in winter/spring and 4% in summer/fall compared to 1970 (*71*). Increases were 22% in Arctic spring and 130% in Antarctic spring during formation of the ozone hole (*72, 73*). At Toronto, Canada, between 1989 and 1993, ozone levels decreased 4.1% per year in the winter and 1.8% in the summer while ultraviolet radiation at 300 nm increased 35% per year for winter and 6.7% per year for summer (*74*). Yet no significant change in radiation was noted at 324 nm. Why?

The fuchsia line in Figure 5 shows the absorption cross section for O_3 as a function of wavelength (*75*). The absorption at 300 nm is 43 times stronger than the absorption at 324 nm. As the optical thickness of the ozone layer decreases, especially in the winter, the biggest increases in radiation reaching the troposphere will have wavelengths around 300 nm. These are precisely the wavelengths absorbed most strongly in a troposphere polluted with anthropogenic or volcanic SO_2 (black line) (*76, 77*) and anthropogenic ozone. These ultraviolet wavelengths do not seem to be absorbed or dispersed by the sulfuric acid aerosols in the lower stratosphere (*78-80*), although the aerosols increase dispersion towards sunrise and sunset.

Thinning the ozone layer cools the stratosphere (*81*), moving heating from the lower stratosphere down to the level of pollution in the troposphere. A good example of such heating was observed during the first two northern winters following the eruption of Pinatubo when tropospheric anthropogenic pollution and ozone depletion were both high in northern China, Russia, Europe, and mid-western North America. Lower tropospheric warming of up to 3°C was observed on the more northerly parts of these polluted areas (*82*), the parts with greater depletion of ozone. The northern winters (January to April) of 2011 and 2012 are similarly unusually warm associated with the ozone depletion following the eruption of Eyjafjallajökull in Iceland during April and May, 2010 (Figure 4). Pinatubo and Eyjafjallajökull are two well-documented examples of regional winter warming caused by volcanism that also caused global cooling.

Warming is typically many times greater in the Arctic than in equatorial regions (*83, 84*) because during the winter ozone depletion is high and oxidation rates of pollution are low (*85, 86*).

Temperature in the Atmosphere

The widely accepted kinetic theory of gases, developed primarily by Maxwell in 1859 and Boltzmann in 1871, postulates that the temperature of a gas is directly proportional to the average translational kinetic energy of its components, $E_M=½mv^2$ where m is mass, v is the translational velocity, and E_M means the energy is related to the translational motion of mass. Planck (*87*) showed that for electromagnetic radiation $E_R=h\nu$ where h is Planck's constant, ν (the Greek letter nu) is frequency and E_R means the energy is the oscillatory energy contained in radiation, i.e. simply the frequency times a constant. E_R increases rapidly at ultraviolet wavelengths as shown by the dashed green line plotted on the traditional logarithmic scale for wavelength in Figure 5.

When a molecule of gas absorbs most infrared frequencies via rotational and vibrational transitions, E_R is absorbed as oscillatory kinetic energy within the molecule, which must then be shared with all other molecules through collisions that convert oscillatory kinetic energy into translational kinetic energy. When a molecule of gas absorbs ultraviolet radiation, electronic transitions become involved. The oscillatory kinetic energy associated with rotational and vibrational transitions is shared via collisions, but the energy in the electronic transitions is typically reemitted by fluorescence at a slightly lower frequency (longer wavelength). When a molecule of gas absorbs ultraviolet radiation whose energy is greater than the energy of a molecular bond, the molecule dissociates and all of the oscillatory kinetic energy (E_R) in that bond is converted immediately into the translational kinetic energy (E_M) of the resulting molecular pieces. Photodissociation not only absorbs high-energy radiation but facilitates the gas reaching thermal equilibrium most efficiently and most rapidly. The energy absorbed by a molecule of ozone at 300 nm (4.13 eV) is 14.2 times greater than the energy absorbed by a molecule of CO_2 at 4250 nm (0.292 eV).

Ultraviolet energy drives essentially all photochemistry in the atmosphere. For example, the equation

$$O_2 + h\nu\ (\lambda<242.4\text{ nm}) \rightarrow O(^3P) + O(^3P)$$

means that energy (hν) in radiation with wavelengths (λ) less than 242.4 nm ($E_R=h\nu>5.11$ eV) is sufficient to dissociate molecular oxygen into two ground state oxygen atoms.

The thermal structure of the atmosphere is a balance between the highest energy solar radiation to penetrate to a given level, the concentration of molecules that can absorb it, and the number of molecules whose translational kinetic energy must be increased. The small amount of solar radiation in the extreme ultraviolet ($\lambda<124$ nm, $E_R>10$ eV) is typically absorbed above ~85 km altitude primarily through photoionization of N_2, O_2, and NO. In the mesosphere, wavelengths <242.4 nm photodissociate O_2. The stratopause is the altitude (~55 km) where there are sufficient O_2 molecules being dissociated by sufficiently energetic ultraviolet radiation to cause the maximum increase in temperature, up to 60°C warmer than the temperature at the tropopause (~11 km at the poles to ~17 km in the tropics). Oxygen atoms formed by photodissociation of O_2 combine with O_2 to form ozone (O_3) which is photodissociated by ultraviolet radiation with $\lambda<300$ nm ($E_R>4.00$ eV). At decreasing altitudes in the stratosphere, lower and lower energy radiation is still available, so that even though the concentrations of O_2 and O_3 increase, the translational velocities of particles of dissociated atomic oxygen decrease, lowering temperature.

Theoretically ozone is dissociated into O_2 and the excited oxygen atom $O(^1D)$ for $\lambda<310$ nm. The $O(^1D)$ then reacts with H_2O to form OH. Yet dissociation is observed in the laboratory for $\lambda<336$ nm probably because of the complicating effects of the simultaneous vibrational and rotational transitions (*88*). Longer wavelengths (440-850 nm) can split ozone into O_2 plus the ground state oxygen atom $O(^3P)$, which reacts with O_2 to form ozone again. The amount of ozone does not change, but continued photodissociation converts radiant energy into higher velocities of the molecules and thus higher temperature. Photodissociation of NO_2 can similarly produce $O(^3P)$ in this wavelength range. Photodissociation due to ultraviolet radiation can thus remain the primary source of heating a polluted atmosphere all the way to the ground.

The spectrum of radiation reaching an altitude of 15 km, the lower part of the ozone layer, is shown by the dashed red line in Figure 5. The solid red line shows the spectrum reaching the Earth's surface. This actinic flux is the total intensity of electromagnetic radiation available from all directions to a molecule of air for absorption estimated by Madronich, who made certain assumptions about the total atmospheric ozone column and surface albedo, and calibrated his calculations against observed spectral intensities and the rate of decay for species such as NO_2 (*89*). The difference between these lines essentially represents the solar energy absorbed in the troposphere. When the ozone layer is thinned, the dashed line will move to the left (shorter wavelengths). Heating of the whole atmosphere above the troposphere as much as 60°C is done primarily by photodissociation caused by wavelengths less than 320 nm that constitute only 3.7% of total solar irradiance (*90*). Thinning the ozone layer allows more energy into the troposphere in the 300 to 320 nm band that contains nearly half of this total solar irradiance. This energy should be more than adequate to warm the lower troposphere one degree, even though the density of the atmosphere increases rapidly toward the surface.

Without sufficient tropospheric pollution, this increase in ultraviolet energy would cause more sunburn and other damage to DNA and would be absorbed at the Earth's surface causing slow warming of this large mass. On land, much of the energy absorbed during the day would be radiated back into the atmosphere at night. At sea, ultraviolet radiation is absorbed at depths >10 meters (*91*) and is thus more effective at heating the ocean that infrared radiation absorbed near the surface where there is cooling at night.

Relative Timing of Atmospheric Changes

The phasing of a number of changes in the atmosphere since 1930 (Figure 6) is particularly instructive:

1. **Red line**: Annual mean surface temperatures remained essentially constant from 1930 to 1975, rose rapidly until 1998, and have remained relatively constant since. The temperature increase

was 30% greater in the northern hemisphere containing 90% of human population and most of the anthropogenic pollution.

2. **Black line**: SO_2 emissions, 88% from burning fossil fuels (*92*), rose rapidly from 1950 until 1973, when concern over acid rain led to the addition of smokestack-scrubbers and other technologies, primarily to electric generating and certain mineral processing facilities, as well as substitution of North Sea oil for coal in Europe. The result was a 20% decrease in SO_2 emissions by 2002. But rapid growth in industry and particularly electric power generation in Asia caused global SO_2 emissions to begin increasing again in 2002. Surface solar radiation decreased while concentrations of SO_2, NO_X, methane, and black carbon increased as discussed in the SOM.
3. **Fuchsia line**: Total tropospheric chlorine, caused primarily by anthropogenic chlorofluorocarbons, increased rapidly after 1970 but reached a peak in 1993 due to implementation of the Montreal Protocol (*54*).
4. **Green line**, y-axis reversed: The annual total ozone column at Arosa, Switzerland, fell rapidly from 1975 to 1994 as a result of the rise in tropospheric chlorine and volcanic eruptions, and has been increasing ever since (*49*).
5. **Blue line**: The annual rate of increase in CO_2 concentrations had been <0.1 ppm/yr from 1938 to 1947 but began increasing to 0.7 ppm/yr by 1960 as other anthropogenic pollutants were rapidly increasing. From 1976, the annual rate of increase has been between 1.3 and 2.7 ppm/yr. Annual CO_2 concentrations increased with industrialization and, most likely, with ocean temperature.

The primary time delay in the atmospheric system involves the heat capacity of the ocean covering 71% of the Earth. A mere 3.2 meters of the ocean holds as much heat as the whole atmosphere yet the average depth of the ocean is 3800 meters (*47*).

The ozone column began decreasing a few years after chlorine increased, a reasonable timeframe given that most ozone is formed above the tropics and circulates slowly to high latitudes where most ozone destruction occurs in mid to late winter, when temperatures are very low.

The observation that ocean surface temperature rose ~5 years after the decrease in ozone is in the range of the calculations by Hansen et al. (*45*) for a 3.5-year e-folding time for warming the ocean if the equilibrium temperature of Earth suddenly increased a small amount and a 10-year e-folding time taking in to account an ocean with a 100-meter-thick, mixed-layer.

Note that the increase in SO_2 and related pollution, on the other hand, began ~30 years before the onset of the major increase in temperature and ~25 years before the major increase in chlorine. Major increases in anthropogenic ozone, NO_x, SO_2, methane and black carbon, discussed in the SOM, did not seem to increase global warming until the ozone layer was thinned.

The phasing of these different changes in gases and radiation should be modeled in detail once new models are developed that deal with the issues raised in this paper.

Absorption versus Temperature

Laboratory studies of absorption by gases in the atmosphere are extensive; absorption is well observed and precisely quantified (*75, 93*). But the oscillatory kinetic energy of radiation is absorbed to become oscillatory kinetic energy in the gas molecule while temperature of a gas is related to translational kinetic energy. It has been assumed that all oscillatory energy is converted to translational kinetic energy during the very frequent collisions of gas molecules and that the more molecules absorbing radiant energy, the greater the increase in temperature. Neither of these assumptions has been proven. The Achilles heel of current greenhouse gas theories is that the sensitivity of climate, the change in temperature caused by a doubling of CO_2, is not observed data, but is modeled based on these two unproven assumptions. Only some of the oscillatory energy absorbed may be converted to translational energy unless dissociation occurs, and even then the conversion is complete only for the energy stored in the chemical bond that dissociates. Energy is conserved whether conversion occurs or not.

Many observations imply that absorption may not be as important as photodissociation for determining temperature. For example:

1. Temperature in the stratosphere is highest at the stratopause where dissociation clearly prevails and lowest in the lower stratosphere where the concentration of O_3 is highest and thus absorption could prevail.
2. Water vapor absorbs a much broader range of wavelengths at higher energies than CO_2 (*94*) and the percentage of water vapor in the atmosphere can be as large as 4% compared to 0.04% for CO_2.

Conclusions

Photodissociation of O_2 leading to formation of ozone raises the temperature of the upper stratosphere by tens of degrees. In the lower stratosphere, photodissociation of ozone becomes the most important exothermal photochemical process. When the ozone layer is thinned following volcanic eruptions or during substantial anthropogenic releases of chlorine forming gases that destroy ozone at cold temperatures, more ultraviolet radiation with wavelengths around 300 nm reaches the troposphere, increasing photodissociation of anthropogenic ozone. Thinning the ozone layer moves some warming from the lower stratosphere to the lower troposphere.

Sulfate recorded in Greenland ice shows when volcanic eruptions were frequent and when anthropogenic pollution was high, but absorption by its precursor, SO_2, was not adequate to cause global warming (Figure 6). Warming occurred only when pollution or volcanism thinned the ozone layer, promoting increased photodissociation of O_3 and NO_2 in the troposphere. SO_2 and CO_2 can only be dissociated high in the atmosphere by radiation with wavelengths <200 nm and <167 nm respectively. SO_2 ejected into the stratosphere by explosive volcanoes does cause short-term cooling as discussed in the SOM and can increment the world into an ice age when large, Pinatubo-sized eruptions occur on the order of once every decade (*32*).

The two most important ways to reduce global warming are to reduce emissions that lead to ozone-destroying chlorine and that lead to tropospheric ozone, predominantly nitrogen oxides, carbon monoxide, and volatile organic compounds (*95*). Ground-level ozone in the United States has been reduced through extensive efforts to reduce pollution from a mean of 100 ppb in 1980 to 73 ppb in 2010 where 90% of the data is less than 129 ppb in 1980 and 83 ppb in 2010 (Figure S3 in SOM). But mean springtime concentrations of ozone primarily at 3 to 8 km above the Pacific Ocean just west of North America increased from 47 ppbv in 1984 to 64 ppbv in 2008 with some values exceeding 90 ppbv. Model studies suggest that 50% of the ozone was formed in Asia and 50% was formed during Pacific transport from Asian precursors and emissions from ships (*96, 97*). Reducing both tropospheric ozone, which is very toxic to all life forms, as well as black carbon will improve world health substantially (*95, 98*).

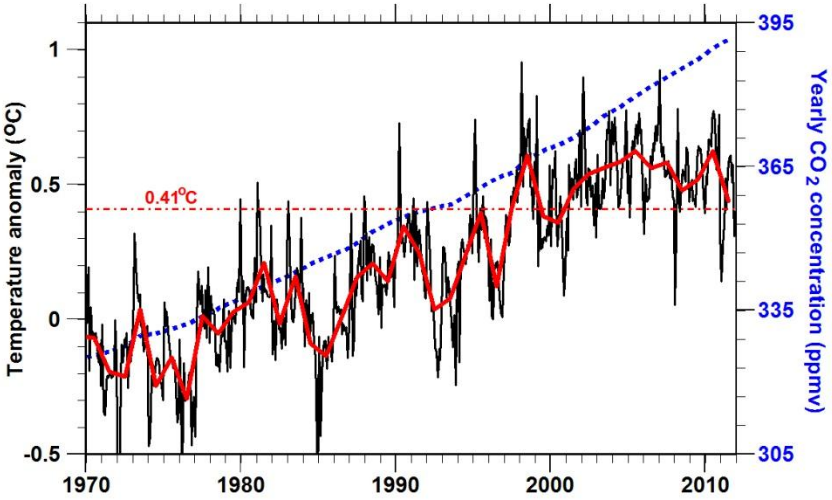


Fig. 1. Trends in surface temperature anomaly and yearly CO_2 concentration have diverged since 1998. Monthly (black line) and yearly (red line) temperature anomalies from the 1961-1990 mean at each station spatially averaged for land and marine sites in the northern hemisphere (HadCRUT3_NH) are shown compared to yearly CO_2 concentrations measured at Mauna Loa, Hawaii (blue dashed line).

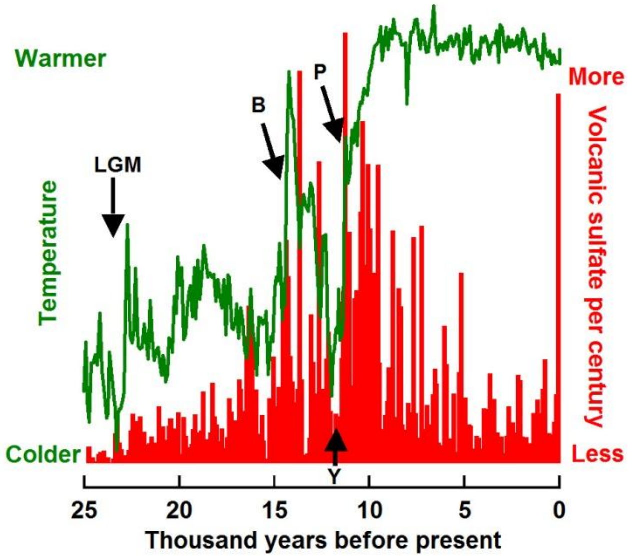
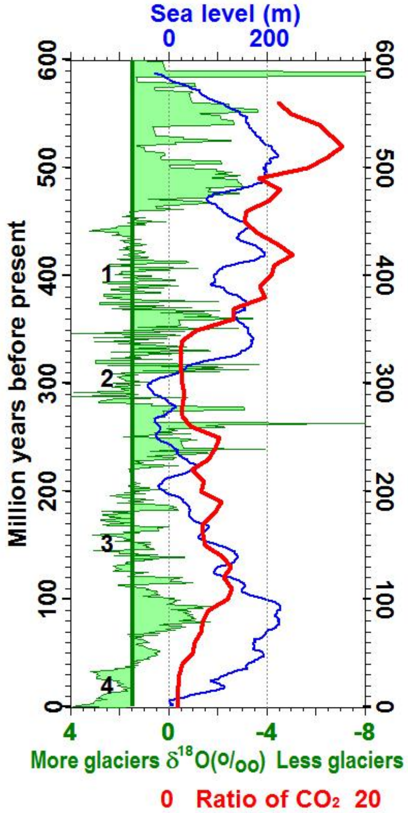


Fig. 2. Layers of ice beneath Summit Greenland (GISP2) containing the largest concentrations of volcanic sulfate per century (red) also contain $\delta^{18}O$ evidence for rapid global warming (green). Volcanic sulfate is total measured sulfate minus the small contributions from sea salt and dust based on sodium and calcium content (*99*) and ranges from 0 to 2028 ppb. Sulfate in the 20th century is anthropogenic and the value shown is twice the sum for 1935 through 1984 (1910 ppb). The range of equatorial Pacific sea surface temperature from the last glacial maximum (LGM) is on the order of 2.8°C (*100*).

Fig 3. Atmospheric concentrations of CO_2 (red line) were 5 to 10 times greater than recently during major epochs of glaciation 150 and 400 million years before present. The red line shows the ratio of the mass of atmospheric CO_2 then to the mass of pre-industrial CO_2 based on a model for the long-term cycles of carbon and sulfur resulting from the weathering of silicate and carbonate rocks, the burial of organic matter, and degassing of volcanoes (*101, 102*) with independent verification from fossil leaf stomatal densities (*103*). The green shaded area shows the $\delta^{18}O$ proxy for tropical sea surface temperature (*104*). Values to the left of the vertical green line show times of glaciation; values to the right of the line show times of little of no glaciation. Geologic evidence of widespread glaciation is found primarily within the four numbered epochs (*105, 106*). Decreases in sea level (blue curve) (*107-109*) provide an estimate of how much water was tied up in ice sheets during the four major glacial epochs.



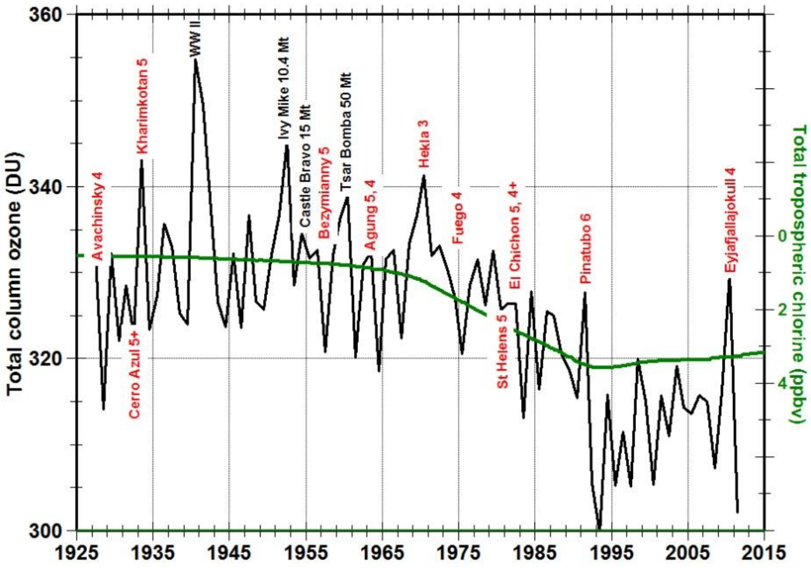


Fig. 4. Total column ozone peaks during years with major volcanic eruptions and then drops precipitously by more than twice as much during the following year. These data were measured at Arosa, eastern Switzerland, at an elevation of 1820 meters since 1927 (*49, 50*). Yearly values are plotted in the middle of each year. The names of the erupting volcanoes and the Volcano Explosivity Index for each large eruption are labeled in red. The green line shows the annual mean tropospheric ozone with the scale reversed to show that long-term decreases in ozone correlate with increases in tropospheric chlorine.

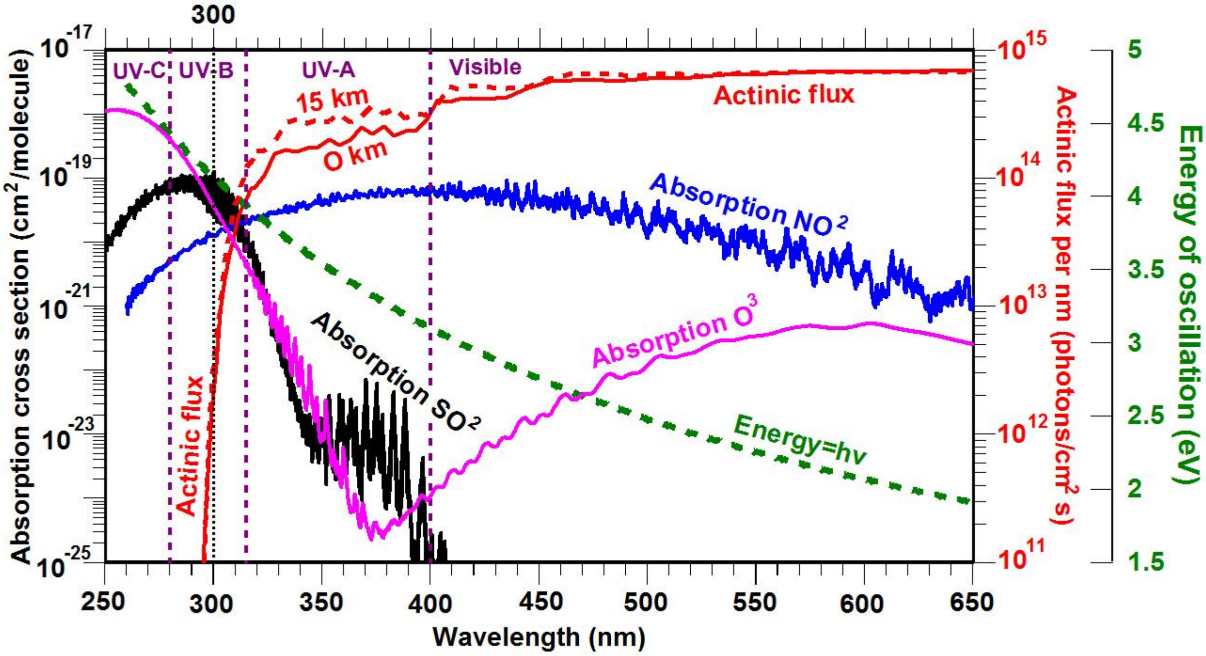


Fig. 5. O_3, SO_2, and NO_2 absorb solar energy strongly at wavelengths <400 nm. O_3 and NO_2 also absorb visible light. Absorption by O_3 and NO_2 typically leads to photodissociation throughout the range shown. Actinic flux shows the spectrum of solar radiation penetrating the atmosphere to altitudes of 15 and 0 km.

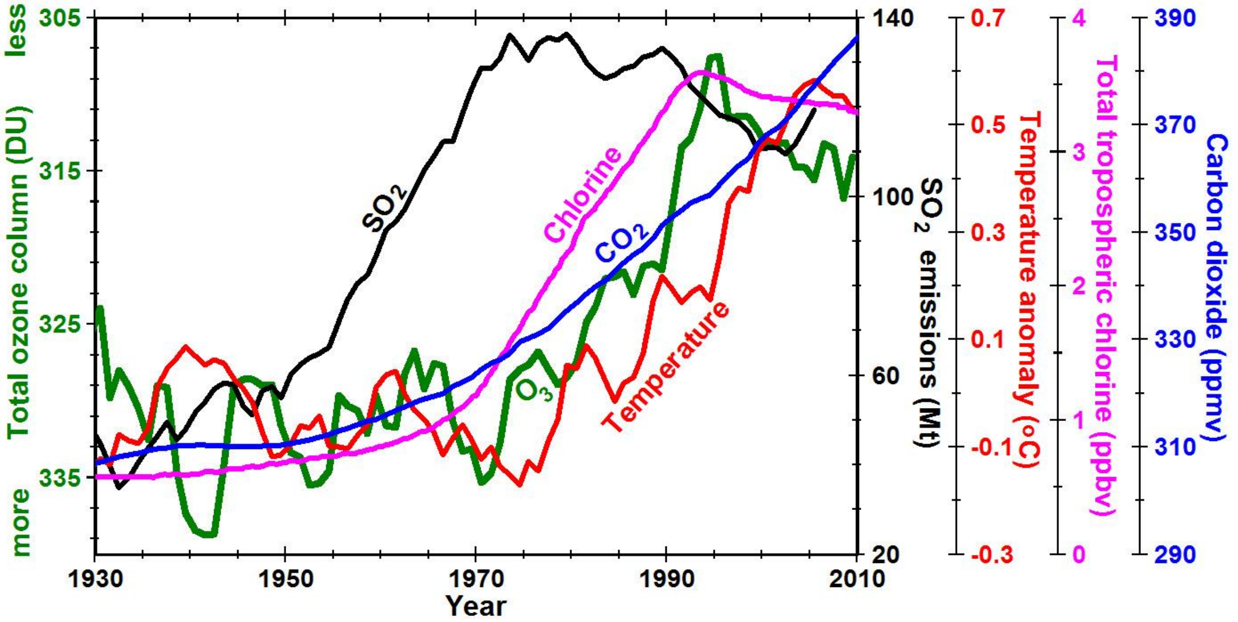


Fig. 6. Increased pollution did not contribute to global warming until the total ozone column decreased primarily due to increasing tropospheric chlorine. Annual total ozone column at Arosa, Switzerland (*49*), and mean annual temperature anomaly in the Northern Hemisphere (*1*) are smoothed with a centered 5 point running mean. Total tropospheric chlorine (green line) is from Solomon (*54*) and SO_2 from Smith et al. (*110*).

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