Introduction to the Greenhouse Effect

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Planetary Temperature

Over the past 10-15 years there has been growing concern over changes in the climate and the possibility that these changes are linked to human activity. Perhaps the peak in concern came during the summer of 1988 when the US experienced the worst summer in terms of heat and drought in its history. Globally, the 1980's were the warmest decade in recorded history. Atmospheric scientists are concerned that these climactic extremes are the result of a trend launched by CO_2 emissions accompanying the industrial revolution. The impact of CO_2 on the atmosphere has been to enhance the so-called "Greenhouse Effect." While the heavy debate that has accompanied discussions on global warming has led to as many questions as purported answers, one thing is not in question: The greenhouse effect is a real effect and is one of the firmer theories in atmospheric science.

To understand what is meant by the greenhouse effect, one can look to comparisons between three planets' atmospheres and climactic conditions - those of Venus, Earth and Mars. Consider Table 1:

Table 1. Some physical constants relevant to the radiation budgets of the planets.

Planet	Dist. to sun (km)	Solar constant	Albedo	Radiative temp. (˚C)	Surface temp. (˚C)
Venus	1.08×10^8	$2613 \frac{W}{m^2}$	75%	-39	427
Earth	1.50×10^8	$1367 \frac{W}{m^2}$	30%	-18	15
Mars	2.28×10^8	$589 \frac{W}{m^2}$	15%	-56	-53

To understand this table, consider what each piece of data means. The distance from the sun is a straightforward concept, and it affects the solar constant, which is the amount of solar energy that falls outside the planet's atmosphere on a plane perpendicular to the sun's rays. The closer the planet the higher the value of the solar constant (1 Watt (W) = 1 J/sec). Note that the solar constant represents a maximum value for incoming radiation. When averaged over the entire earth, the **Earth-averaged solar constant** is 340 $^{W}/_{m^2}$. This number is less than 1367 $^{W}/_{m^2}$, because only a small fraction of the earth's surface is perpendicular to the sun's radiation.

One variable between the planets that is less obvious is the **albedo**. This value defines the percentage of the sun's radiation that is reflected from the planet. The number depends on a number of factors, such as cloud cover, color of the planet surface, atmospheric dust and so on. For example, snow covered mountains and clouds reflect more light than forests and blacktop. Taking the solar constant and the albedo together, one can calculate an **effective radiative temperature** which corresponds to the heating of a planetary surface/atmosphere due to the portion of the solar radiation that is absorbed (when light is absorbed, the energy is typically converted to heat). Interestingly, one sees that earth should be the warmest planet at an uncomfortable -18˚C (-0.4˚F), while Venus and Mars are lower yet. Venus is perhaps a surprise given its proximity to the sun, but that is related to its high albedo – a reflection of the 100% cloud cover over Venus. Now, take a look at the actual surface temperatures of the three planets. Venus is cooking, while earth is actually quite livable. A major change away from the effective radiative temperatures has occurred, the result of the phenomenon described as the Greenhouse Effect.

The Solar Radiation Budget

Before we get into the specifics of why the actual surface temperature differs from the radiative temperature, it is worth expanding our understanding of the nature of the solar radiation budget. As with any budget, income must equal outgo, and in the solar radiation scheme for any planet, incoming solar radiation must equal outgoing radiation if the overall planetary temperature is to stay roughly constant. As a first point of examination, consider the implications of Earth's albedo. Thirty percent of incoming radiation is reflected. What happens to the remaining 70%? It is absorbed by the earth (and its atmosphere) to create a body that we know is about 15˚C overall. All objects above absolute zero radiate light (called black body radiation), and the earth is no exception. Black body radiation is light that is emitted from an object solely due to the object's temperature. Increasing the temperature of the object results in emission of shorter wavelength black body radiation. Earth is much cooler than the sun (15˚C vs. 5500˚C) so while the sun glows with light centered in the visible region, we expect the earth to "glow" with much longer wavelengths of light – in the infrared region. Figure 1 shows how the wavelength shift appears. The peak in the earth's blackbody radiation is located at about 20 μm (or 20000 nm), but the emission spectrum ranges from 5 μm to 100 μm. Clearly this is well outside the visible range and will not be observable by human eyes.

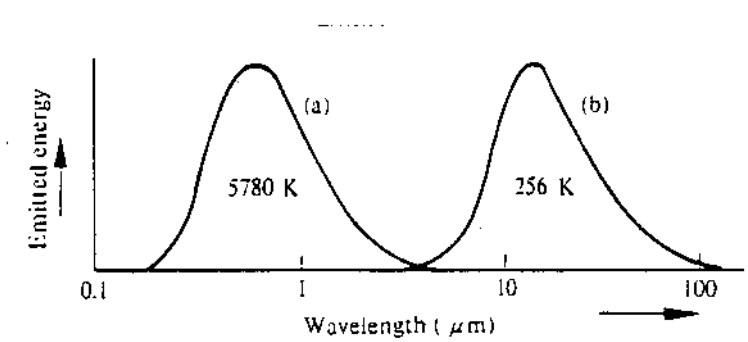


Figure 1. Blackbody radiation diagrams for (a) Sun and (b) Earth.

Under the simplest of circumstances (which actually is similar to the case on Mars as will be shown), the 70% of the radiation that was absorbed by the earth will be re-emitted at longer wavelengths and escape into the atmosphere. That does not happen, however, since the earth is far from the simplest set of circumstances. Consider Figure 2, which shows the full radiation budget diagrammatically.

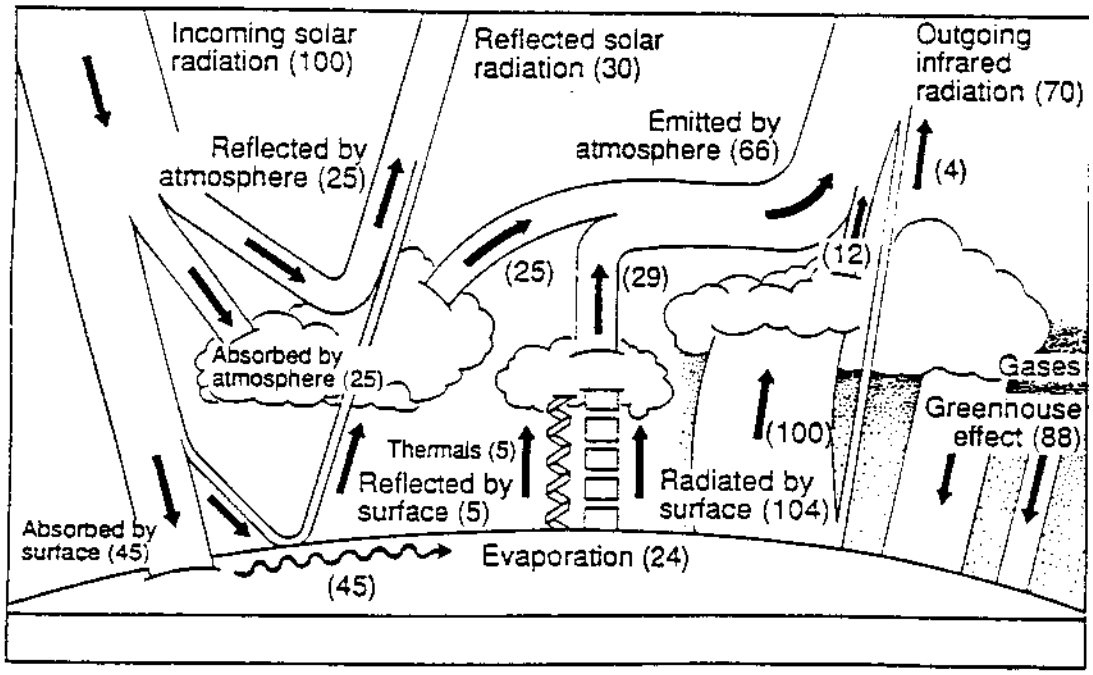


Figure 2. The radiation budget illustrated. The numbers in parentheses represent percentages.

Here's a list that will explain exactly what is going on here, by breaking down the categories (the following percent signs are relative to the original radiation):

100% Incoming solar radiation

25% reflected by atmosphere

5% reflected by earth's surface

70% absorbed by planet (atmosphere and lithosphere combined)

70% Absorbed by planet (expanding the last category)

25% absorbed by atmosphere - and is then re-emitted by atmosphere eventually

45% absorbed on the surface of the earth

45% Absorbed by surface

24% lost through evaporation

5% lost through direct heating of air

Which leaves at this point leaves us with 16% of initial radiation to be re-emitted as blackbody radiation. But wait! Here's where the Greenhouse effect comes in. In fact, the atmosphere is also emitting blackbody radiation, and a significant quantity of that is being directed at the earth's surface. In fact this radiation (also in the infrared) is equal in energy to 88% of the original solar radiation and it, too, is absorbed by the earth.

16% + 88% = 104% of absorbed energy at earth's surface (which is why we're warm).

104% Earth's absorbed energy

4% radiated straight into space

100% radiated by the earth and absorbed by atmosphere

100% Atmosphere's absorbed energy

12% released to space as IR radiation

88% returned to earth as IR radiation (the Greenhouse Effect)

All of this is fairly complicated, but the end result is balance. What comes in, leaves eventually. Once it is accepted that the earth is already warm, then the steady state temperature is maintained by matching income to outgo. The big question now must be, why does the atmosphere trap energy? The answer comes from its chemical composition. Compare Venus, Earth and Mars again:

Table 2. Atmospheric composition of planetary atmospheres.

Planet	***Atmospheric Pressure***	***Chemical Composition of Atmosphere (%)***			
		N_2	**O_2**	**H_2O**	**CO_2**
Venus	92 atm	<2	<0.001	0.0001-0.3	>98
Earth	1 atm	78	21	0.0001-4	0.035
Mars	0.006 atm	2.5	<0.25	<0.001	>96

One trend that is evident is that the planets with the greater quantities of atmosphere have warmer temperatures. Because Mars has such a sparse atmosphere, it is incapable of sustaining habitable temperatures, because there is no Greenhouse Effect available. However, on Venus there is an incredibly dense atmosphere that is capable of absorbing quite a bit of energy, despite the fact that most of the sun's rays are reflected. This is due, in large part, to the high concentrations of CO_2 in Venus' atmosphere. As it turns out, two chemical species are the most significant natural contributors to the Greenhouse effect, CO_2 and water. The reason is because of their ability to absorb and re-radiate infrared radiation.

Molecular Vibration and the Infrared Spectrum

In examining the interaction between light and molecules, UV and visible photons have sufficient energy to excite electrons in low energy molecular energy levels to higher levels, sometimes with bond breaking as a result. Infrared radiation, which occurs at wavelengths between 700 nm and 30000 nm (0.7 μm and 30 μm) is much lower in energy and generally lacks the oomph necessary to advance electrons to higher energy levels.

Nevertheless, molecules in fact, absorb infrared radiation. Instead of exciting electrons between quantized energy levels, molecules absorbing IR radiation become excited to higher quantum "vibrational energy levels." All molecules are vibrating constantly, and the more rapid the vibration, the higher the energy of the molecule. However, just as electron energy is quantized, vibrational energy is also quantized and the frequency of a vibration is identical to the frequency of the (IR) photon necessary to excite the molecule to that vibrational energy level from the next lower vibrational level. For example, the HCl molecule can vibrate at a series of frequencies, all of them integer multiples of 8.66×10^{13} Hz. So HCl vibrates at $1 \times (8.66 \times 10^{13}$ Hz) and $2 \times (8.66 \times 10^{13}$ Hz) and $3 \times (8.66 \times 10^{13}$ Hz) and so on, but it turns out that molecules can only be excited between adjacent vibrational energy levels. Note, then, that the difference in frequency is always 8.66×10^{13} Hz. Wavelength can be calculated as follows:

$$\lambda = {}^{c}/_{\nu} = (2.998 \times 10^{8}\ {}^{m}/_{s})/(8.66 \times 10^{13}\ s^{-1}) = 3.46 \times 10^{-6}\ \text{m or } 3.46\ \mu\text{m}$$

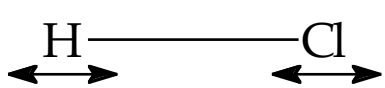
3.46 μm is solidly in the IR region of the spectrum.

In a single molecule, there may be a variety of different types of vibrations that are occurring simultaneously. These types are called "fundamental" vibrations and the number of possible fundamental vibrations are restricted by the number of atoms (N) in a molecule:

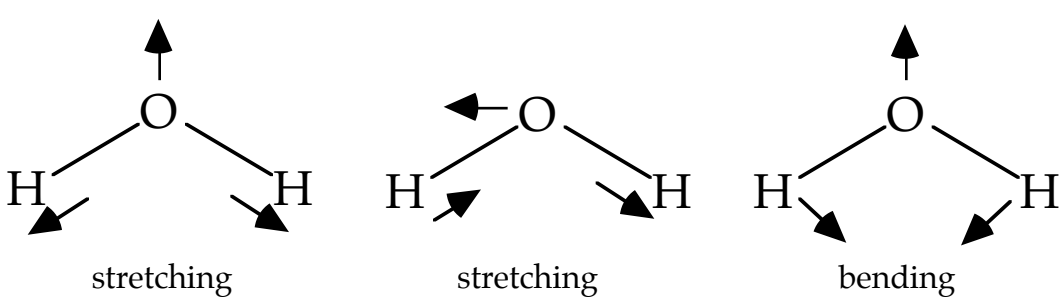
3N–5 For a linear molecule (all the atoms arranged in a line)

3N–6 For a non-linear molecule

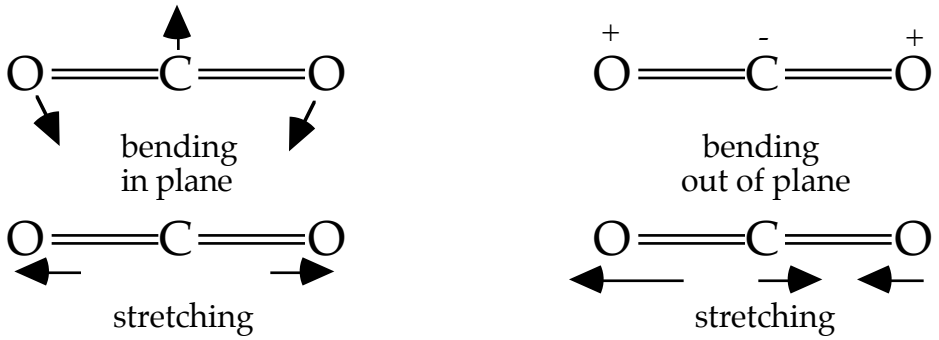
For example, HCl has only 3(2) – 5 = 1 fundamental vibration, namely the H and Cl bond stretching and contracting:



For more complicated molecules there are greater numbers of fundamental vibrations as N increases. For example, consider water, which has three atoms in a "bent" configuration. The number of fundamental vibrations is 3(3) – 6 = 3:



For CO_2, which is a linear molecule, there are 3(3) – 5 = 4 fundamental vibrations:



There is one more rule to be aware of in understanding how light excites a molecule vibrationally: **Vibrations that do not change the overall dipole of the molecule do not lead to IR absorption.** Consider the symmetric stretching vibration of CO_2 (on the left). In that case, both oxygen atoms have more electron density than carbon, but the center of electron density is at the carbon, half way between the two oxygen atoms. As the oxygen atoms both stretch away from the carbon, they do so symmetrically, so that the carbon always remains at the center. The H-Cl stretching vibration is not symmetric because the dipole "stretches" with the increase in bond distance.

The above rule becomes important when you consider the composition of earth's atmosphere. N_2 and O_2 constitute 78% and 21% of the atmosphere. However each of them has only 3(2) – 5 = 1 fundamental vibration and it is symmetric:

Therefore, neither O_2 nor N_2 absorbs IR light. On the other hand the next most abundant species is Ar, an atom that does not vibrate at all (no bonds!) So finally we come to CO_2 and water, which both have non-symmetric vibrations. These are the principle chemical species that can both absorb and emit infrared radiation in the atmosphere. Without them, earth would be quite cold (like Mars). Other trace gasses in the atmosphere are also important with regards to the greenhouse effect. Figure 3 shows the IR absorption spectra of a number of greenhouse gases, including CH_4, N_2O and O_3 and how these contribute to the total IR absorption of the atmosphere. Note also in Figure 3 that CO_2 absorbs in a region where H_2O does not, providing a complementary effect in trapping IR radiation more efficiently.

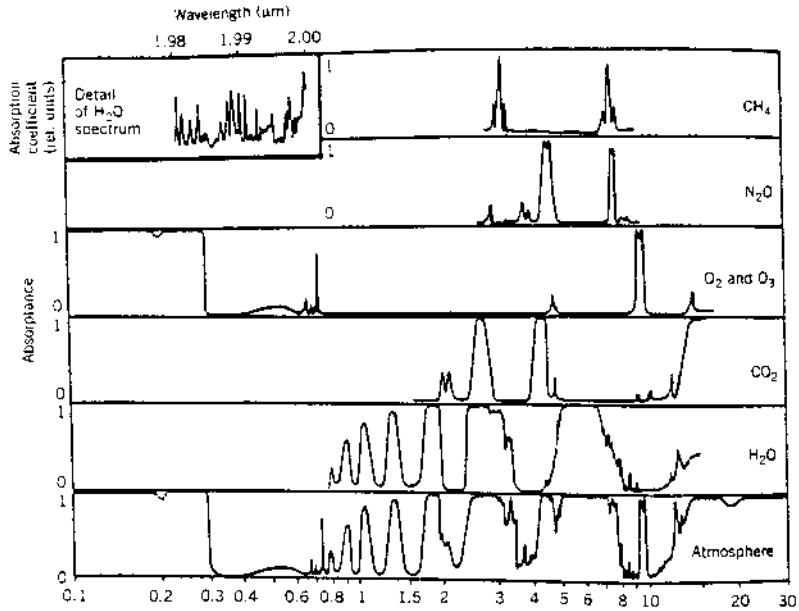


Figure 3. Infrared absorption spectra of the earth's atmosphere and several greenhouse gases. The unlabeled x-axis represents wavelength in μm.

As with the solar radiation budget, there is an infrared radiation budget. Income must equal outgo. The infrared energy that is given off by the earth's surface and absorbed by the atmosphere must be emitted again. Vibrationally excited molecules can release photons in the infrared by dropping to lower vibrational states. When the IR radiation is emitted it is felt as heat when absorbed again at the earth's surface, and so a cycle of IR emission and absorption is set up.

Perturbing the Greenhouse

As noted previously, Earth has developed a relatively stable solar radiation budget that provides the inhabitants of this planet with a comfortable environment (of course they have evolved to find this environment comfortable). As it currently stands, the majority of the radiation hitting the surface of the earth is furnished by infrared radiation emitted by greenhouse gasses as they drop to lower vibrational energy states. Based on some relatively commonplace observations, one is led to believe that the higher the content of greenhouse gasses, the warmer the climate. Aside from comparisons to Venus, we only need look at the impact of atmospheric water vapor. In areas of high humidity, such as the Midwest in the summer, surface temperatures remain roughly constant from day to night, uncomfortably so. However, in areas of low humidity the difference between daytime and nighttime temperatures is remarkable in places like Death Valley, where no water vapor is present to continue to heat the surface after the sun has set. This variation in humidity is something we are familiar with and tends to average out over the globe to provide a balanced warming that has a median temperature of 15°C.

Unfortunately, well enough has not been left alone. The industrial revolution, powered largely by combustion of fossil fuels, began roughly 150 years ago and has had an enormous impact on the composition of the atmosphere. Its most impressive impact, however, has been in

the significant alteration of the fourth most abundant component of dry air, carbon dioxide. Remember that the two chief combustion products from hydrocarbon burning are water and carbon dioxide. In the nineteenth century, CO_2 concentrations averaged around 280 ppm, while current concentrations are now closer to 350 ppm and rising. Fossil fuels contain carbon that has been sequestered from the atmosphere/biosphere for tens of millions of years. By releasing a substantial fraction of this carbon in a short time span, we are dramatically altering the quantity of available carbon in the atmosphere. A second trend that is no less to blame is the deforestation of large areas in both the Northern and Southern Hemispheres. Carbon dioxide is, in part, removed from the atmosphere by carbon fixation in plants. The huge loss in forest biomass in the Amazon rain forest and even in the Northwest reduces the ability of the biosphere to absorb the carbon dioxide we are emitting.

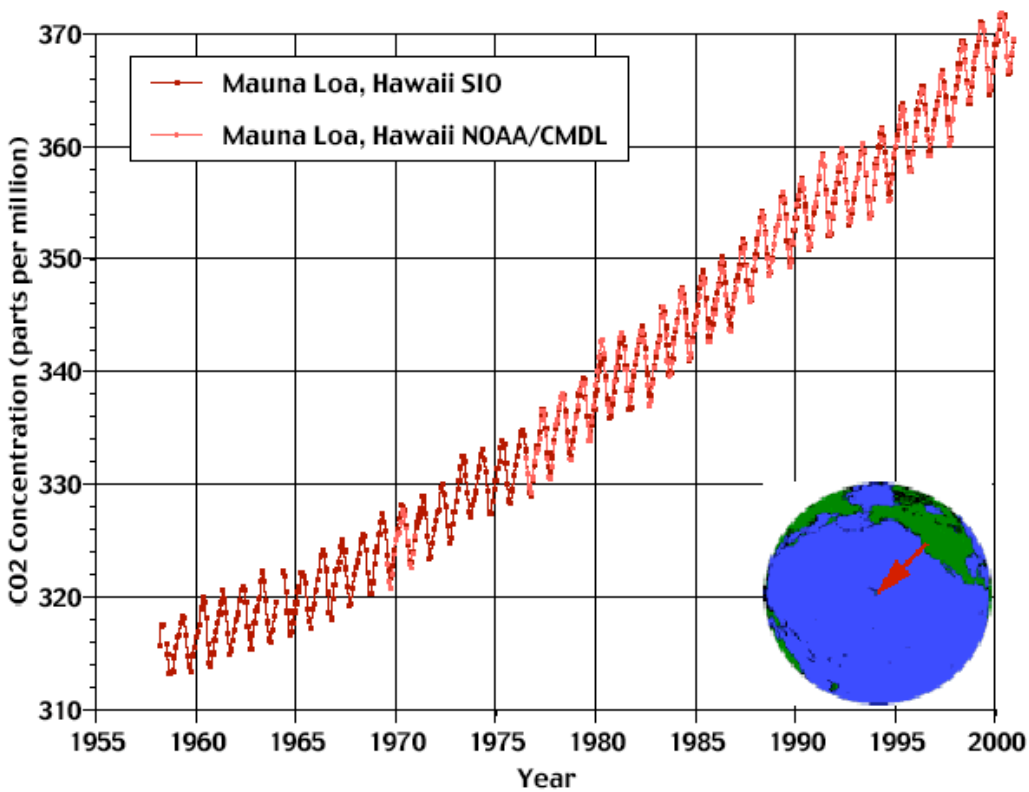


Figure 4. Atmospheric concentrations of CO_2 measured at Mauna Loa in Hawaii. Graphic copied from http://chemistry.beloit.edu/Warming/pdf/CO2.pdf.

An atmospheric station on Mauna Loa in Hawaii (see Figure 4) has been recording CO_2 concentrations since 1958, and the steady trend upwards is both obvious and alarming. (Note that the annual cycle of CO_2 variation is due to increased photosynthesis in summer months in the Northern Hemisphere.) One bright point that has people perplexed however, is the slight leveling at the top end of the curve. No explanation has been given for that yet. The rapid rise in CO_2 concentrations in the last part of this century is expected to continue, since little action has been taken at an official level to curb CO_2 emissions. Some predictions of future CO_2 concentrations go as high as 750 ppm, which has never before been encountered on earth.

Figure 5 shows historical data taken from gas bubbles trapped in the Antarctic ice shield that show that over the past 20,000 years or so, CO_2 concentrations have correlated well with global temperature levels.* While there is no direct evidence that CO_2 levels are responsible for the climate changes of the past, there is some real concern that we are due to experience unusual levels of global warming due to increased concentrations of atmospheric CO_2.

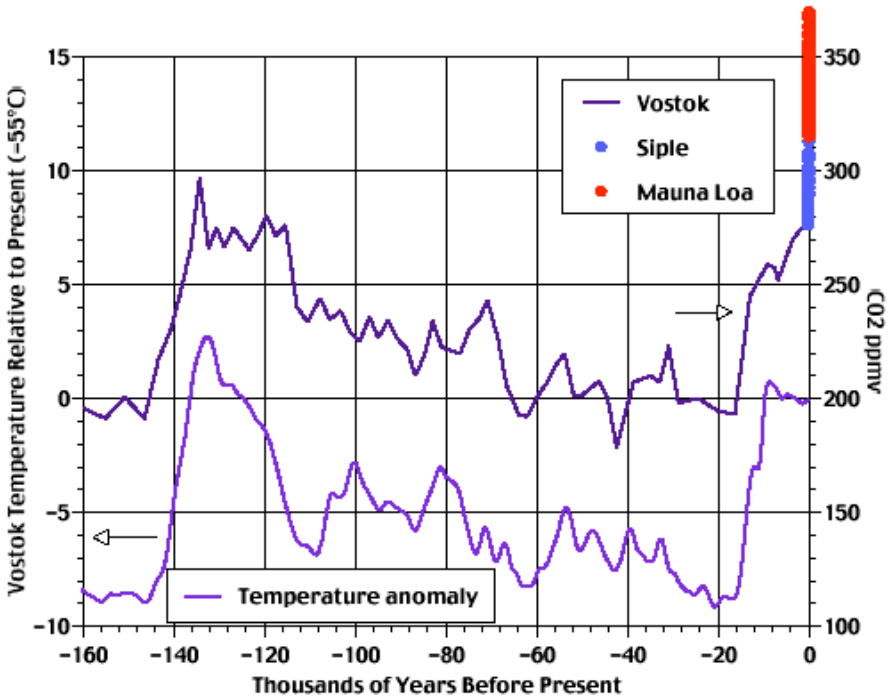


Figure 5. Long term temperature record* and CO_2 concentrations analyzed from trapped gas bubbles in ice core samples from Antarctica. Graphic copied from http://chemistry.beloit.edu/Warming/pages/temperature.html.

Furthermore, CO_2 is not the only greenhouse gas to be increasing in concentration in the atmosphere. The concentration of methane (CH_4) has doubled since 1850, both from industrial and agricultural sources (the latter related to an increased world ruminant population - cows, goats and sheep). Also, other anthropogenic pollutants play a significant role. CFC's, though relatively low in concentration, actually absorb infrared radiation that otherwise passes through the atmosphere, so they act as particularly effective insulators.

The Greenhouse Effect is real. There is no question that the presence of CO_2 and other greenhouse gases keeps this planet comfortably warm. The alarming crisis of Global Warming arises from the ever-increasing concentrations of greenhouse gases in our atmosphere as a direct result of human activity. All of the science suggests that increasing greenhouse gas concentrations will inevitably lead to a rise in global temperature. How much and how quickly temperature will rise is disputed. Nonetheless, as scientists and citizens, we have a responsibility to act now, to educate and work towards changing our habits and our impact on the planet.

* Temperature levels are discerned by the concentration of ^2H (deuterium) in the ice. Deuterium is a heavy isotope of hydrogen. Water containing deuterium has a lower vapor pressure at any given temperature, but volatilizes to a greater degree relative to water as temperature increases. The more ^2H in the ice, the warmer the global temperatures at the time.