Holocene Concentrations of Methane in the Atmosphere are in Part Proportional to Concentrations of Sulfur Dioxide and Inversely Proportional to the Oxidizing Capacity of the Atmosphere

U31A-0005

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December 17, 2008

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(1) Primary Conclusions

1. Global climate change, prior to the 20th century, was initiated primarily by changes in the rate of sulfur dioxide emitted from volcanoes. Changes in levels of carbon dioxide followed changes in temperature.

2. Man is currently emitting as much sulfur dioxide as what caused global warming in the past.

3. Global warming is caused by decreasing the oxidizing capacity of the atmosphere.

4. Concentrations of methane are inversely proportional to the oxidizing capacity of the atmosphere.

5. The increase in methane over the past 5000 years appears to have been influenced by volcanic activity.

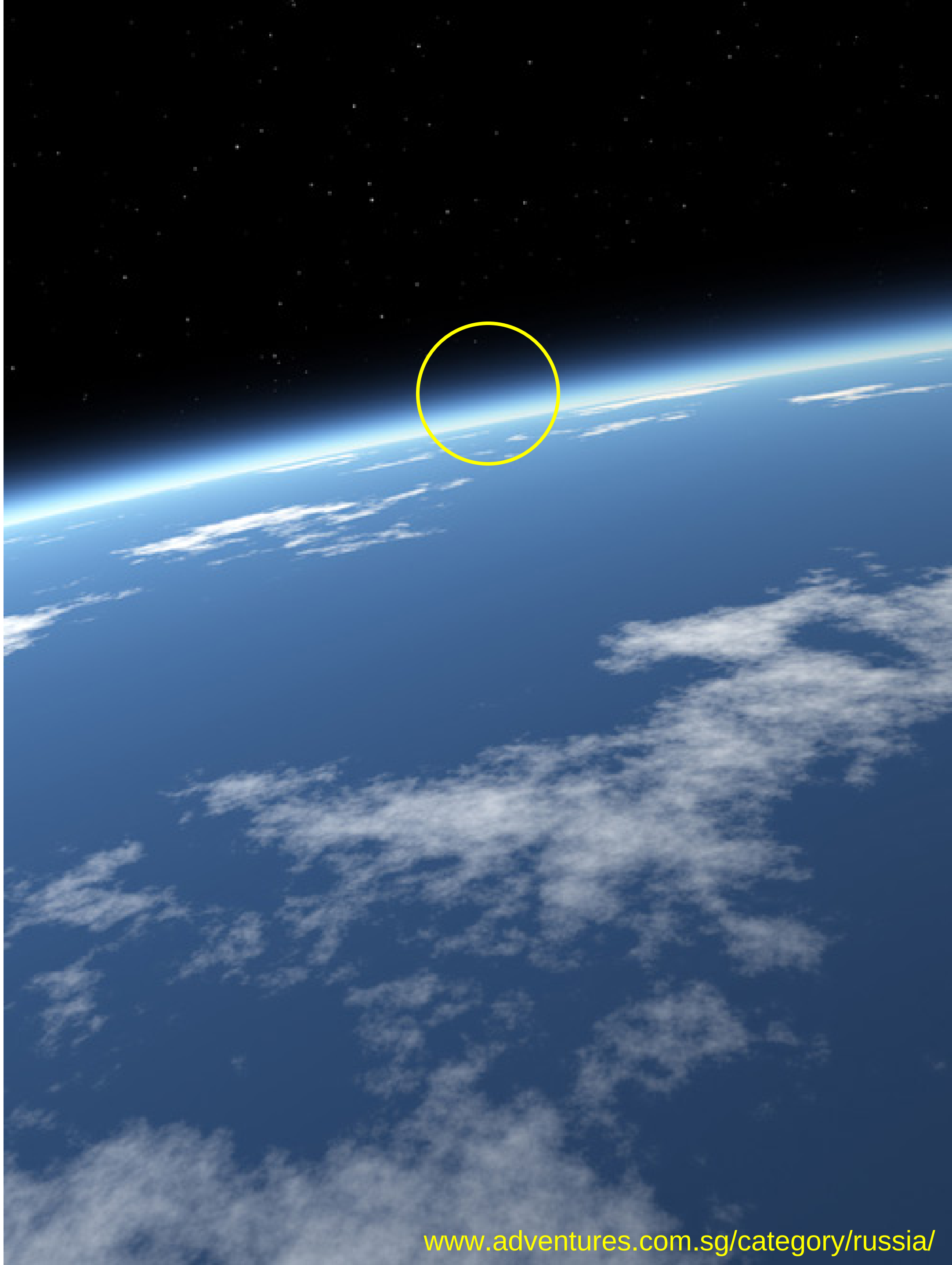
(2)

<u>Earth's atmosphere is a thin blanket that warms the Earth.</u>

99% of the air is within 30 km of the earth's surface

0.5% of the earth's radius

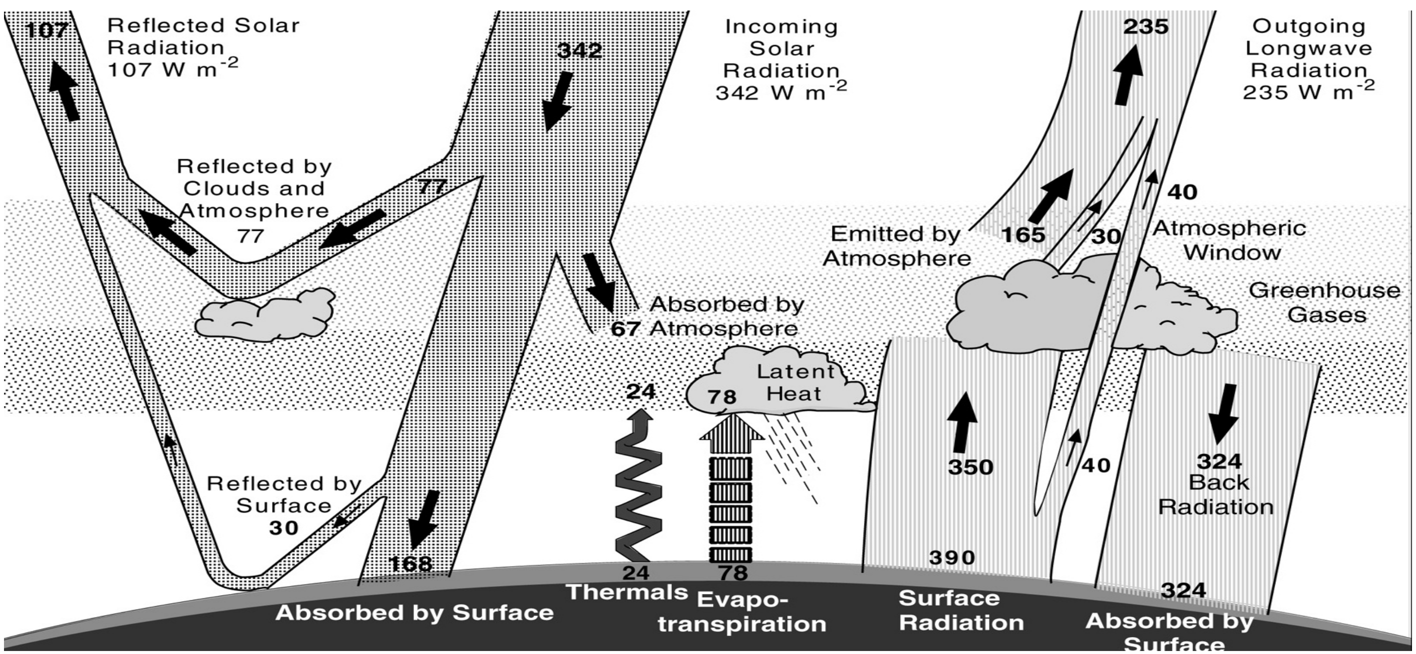
If no atmosphere, then the surface temperature would be -19^{o}C (-2^{o}F)



(3) The atmosphere selectively reflects, refracts, scatters, absorbs, or transmits broadband radiant energy from the sun, infrared energy radiated outwards by the earth, and cosmic rays bombarding the earth from all directions.

Small changes in gas chemistry and cloud content can modulate large changes in solar and radiated energy flow.

An analogy would be a venetian blind where the very small amount of energy needed to rotate the blind could have a major effect on the solar energy reflected and transmitted.



(Kiehl and Trenberth, 1997)

(4) Volcanoes erupt large amounts of sulfur

Summit of Mt. Trident, Alaskan Peninsula, August 7, 1963
Trident erupted in April and October, 1963, Fumarole temperature > 500^{o}F

(5) The Four Cardinal Rates of SO_2 Emission

	Rate of SO_2 Emission	Eruption Rate	Effect	Cause
I	Low	No large volcanic eruptions for decades	Cooling and decadal droughts	Lack of significant SO_2 allows the oxidizing capacity of atmosphere to be restored, purging all greenhouse gases and pollutants, reducing the insulating capacity of the atmosphere and inhibiting rain.
II	Moderate	One large volcanic eruption (VEI>=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.

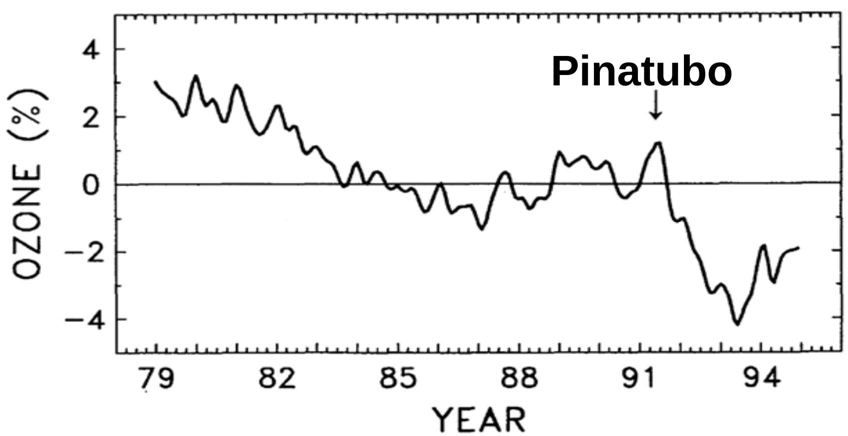
(6) An occasional large volcanic eruption cools the Earth for several years but uses up ozone

Pinatubo (1991) was the largest volcanic eruption in 87 yrs

Erupted 17 Mt SO_2 and 491+ Mt H_2O forming an aerosol layer between 20 and 23 km high that was 99% pure H_2SO_4 and H_2O

The aerosol reflected sunlight, lowering world temperatures 0.4°C over 3 years with some winter warming over continents.

Reduced Ozone levels to lowest known level since satellite measurements began.



TOMS Satellite global mean anomaly less Quasi-Biennial-Oscillation (Randel et al., 1995)

Reduced ocean heat content by 3 * 10^{22} J, lowering sea level by 5 mm.

Very small change in atmospheric mass: $\frac{\text{Mass } SO_2}{\text{Mass Atmosphere}} = \frac{17 \text{ Mt}}{5.15 * 10^9} =$ 3.3 ppb

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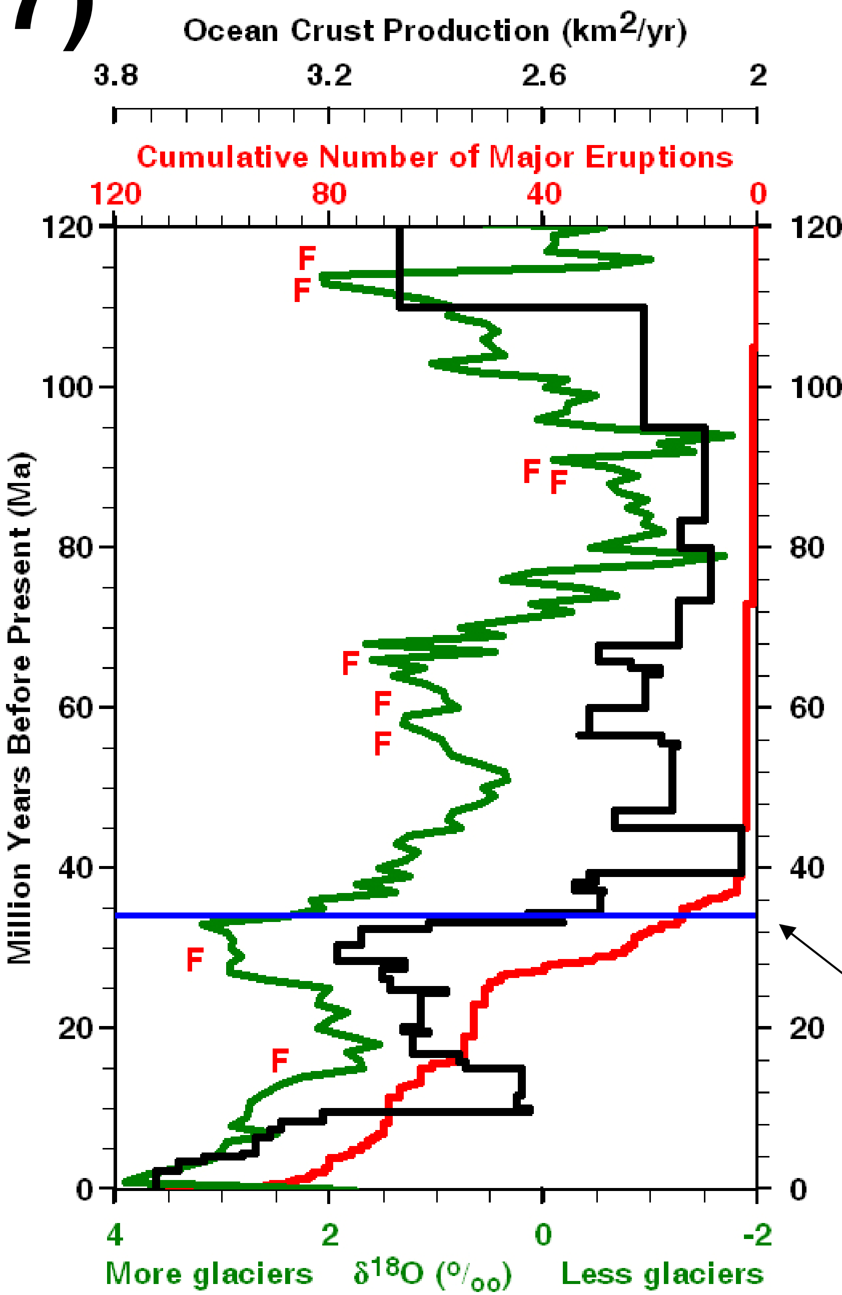


The most recent glacial epoch began with a major increase in volcanic activity.

Red = Cumulative number of major volcanic eruptions

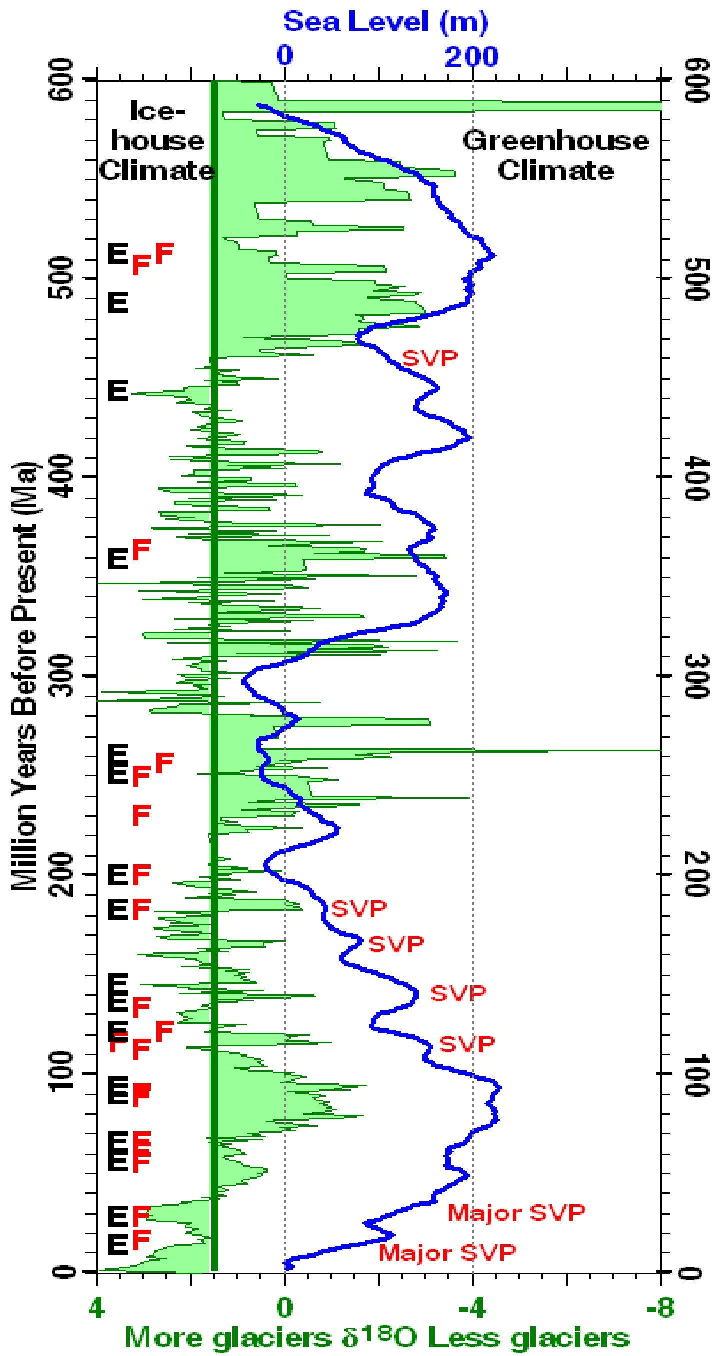
Green = Proxy for temperature

Black = Ocean crust production

F = Times of major flood basalts

Blue = 33.9 Ma, onset of major glaciation, boundary between the Eocene and the Oligocene

(8)



__Ice ages are typically preceded by large numbers of volcanic eruptions in Silicic Volcanic Provinces (SVP) and coincide with decreases in sea level.__

Green = Proxy for temperature

Blue = Sea-level

E = Times of mass extinctions

F = Times of major flood basalts

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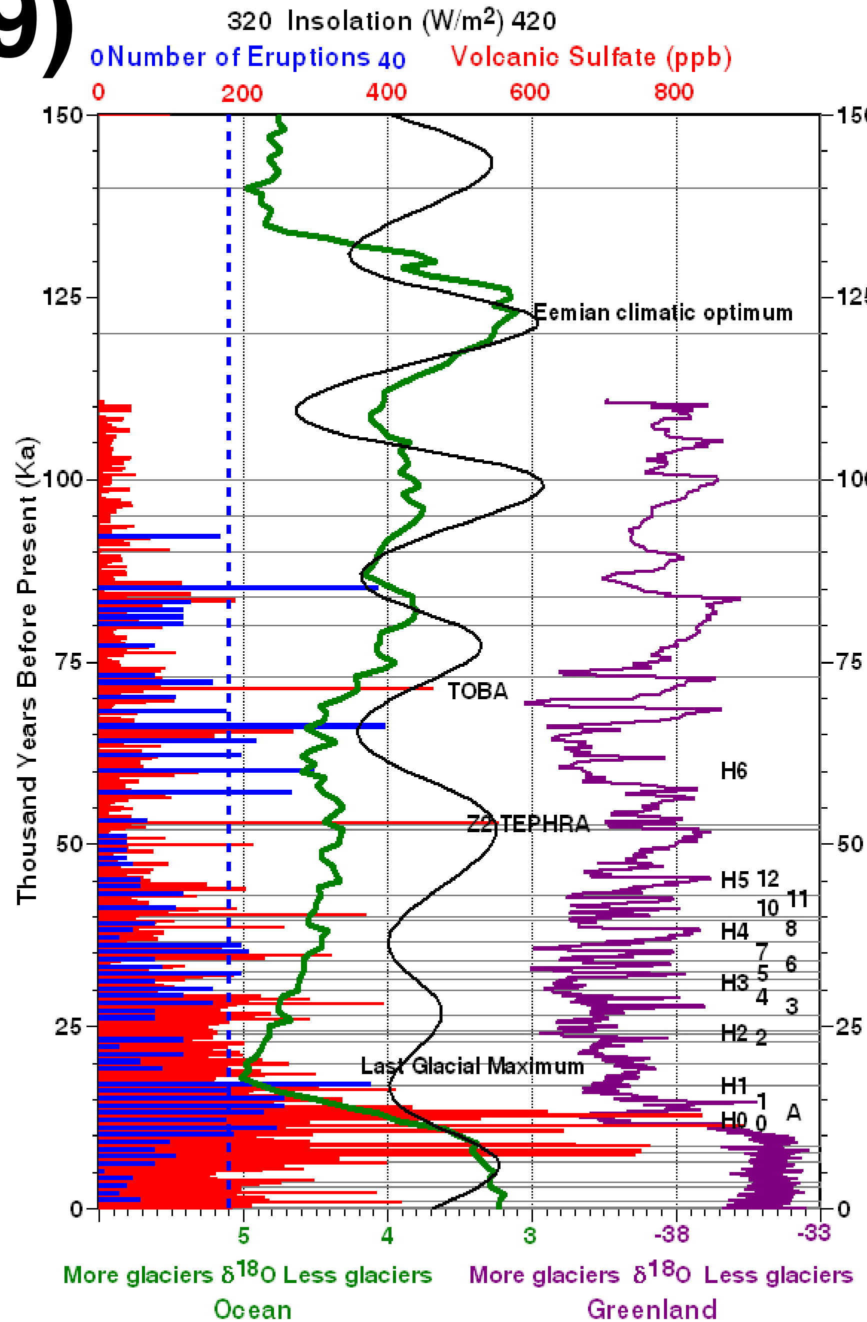

Earth cools incrementally into an ice age and warms very rapidly.

Sudden global warming is contemporaneous with major volcanic activity.

Temperature in Greenland (purple) oscillates rapidly by 10ºC while ocean temperature (green) decreases slowly (2.8ºC) but with brief warming spells that are contemporaneous with increased volcanism. Milanković predicted changes in insolation (black) are more sinusoidal.

The period of most rapid warming between 15 and 8 Ka is clearly contemporaneous with highest rates of volcanism (red sulfate per layer, blue eruptions per century after Zielinski et al, 1996).

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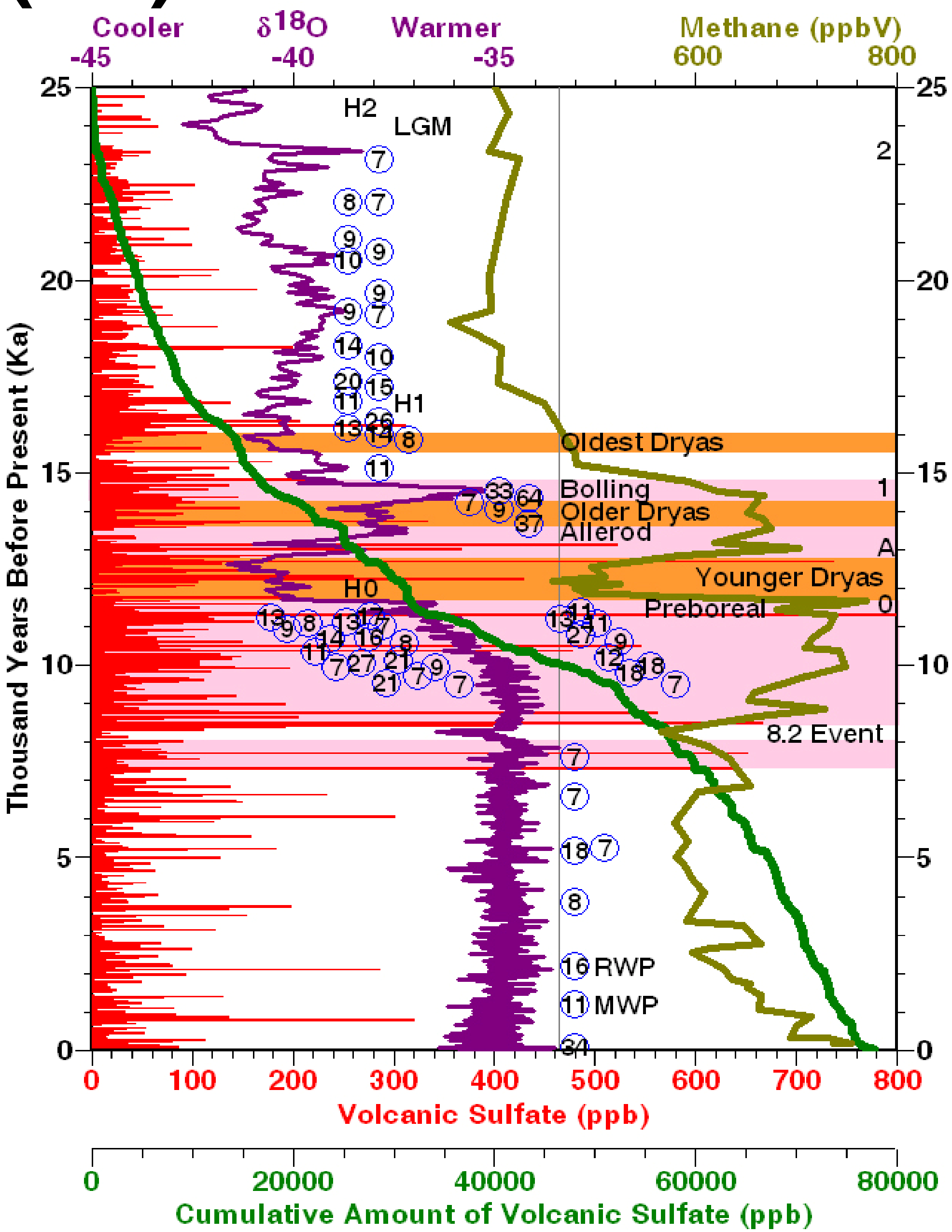

Periods of greatest global warming are contemporaneous with times when seven or more contiguous layers of snow in Greenland contain volcanic sulfate.

Circles show the number of contiguous layers containing sulfate.

Periods of re-glaciation (orange) are contemporaneous with low levels of volcanic activity.

Methane levels are high when volcanic sulfate levels are high.

(11) The oxidizing capacity of the atmosphere is limited.

1. Pollutants of the atmosphere are removed primarily by oxidation and then rain

2. Oxidation is caused primarily by OH, H_2O_2 and O_3, which are in limited supply

3. OH forms primarily from ozone by photodissociation in the near-ultra-violet

$$O_3 + h\nu \rightarrow O(^1D) + O_2$$
$$O(^1D) + H_2O \rightarrow OH + O$$
(Thompson, 1992)

4. Oxidation of SO_2 is limited primarily by availability of OH and H_2O

$$SO_2 + OH + M \rightarrow HOSO_2 + M$$
$$HOSO_2 + O_2 \rightarrow SO_3 + HO_2$$
$$SO_3 + H_2O \rightarrow H_2SO_4$$
(Coffey, 1996)

5. Pinatubo e-folding time for this reaction = 35 days (Bluth et al., 1992)

6. Atmospheric methane is inversely proportional to oxidizing capacity

$$CH_4 + OH \rightarrow CH_3 + H_2O$$ (Lifetime 9.6 years) (Wikipedia/Methane)

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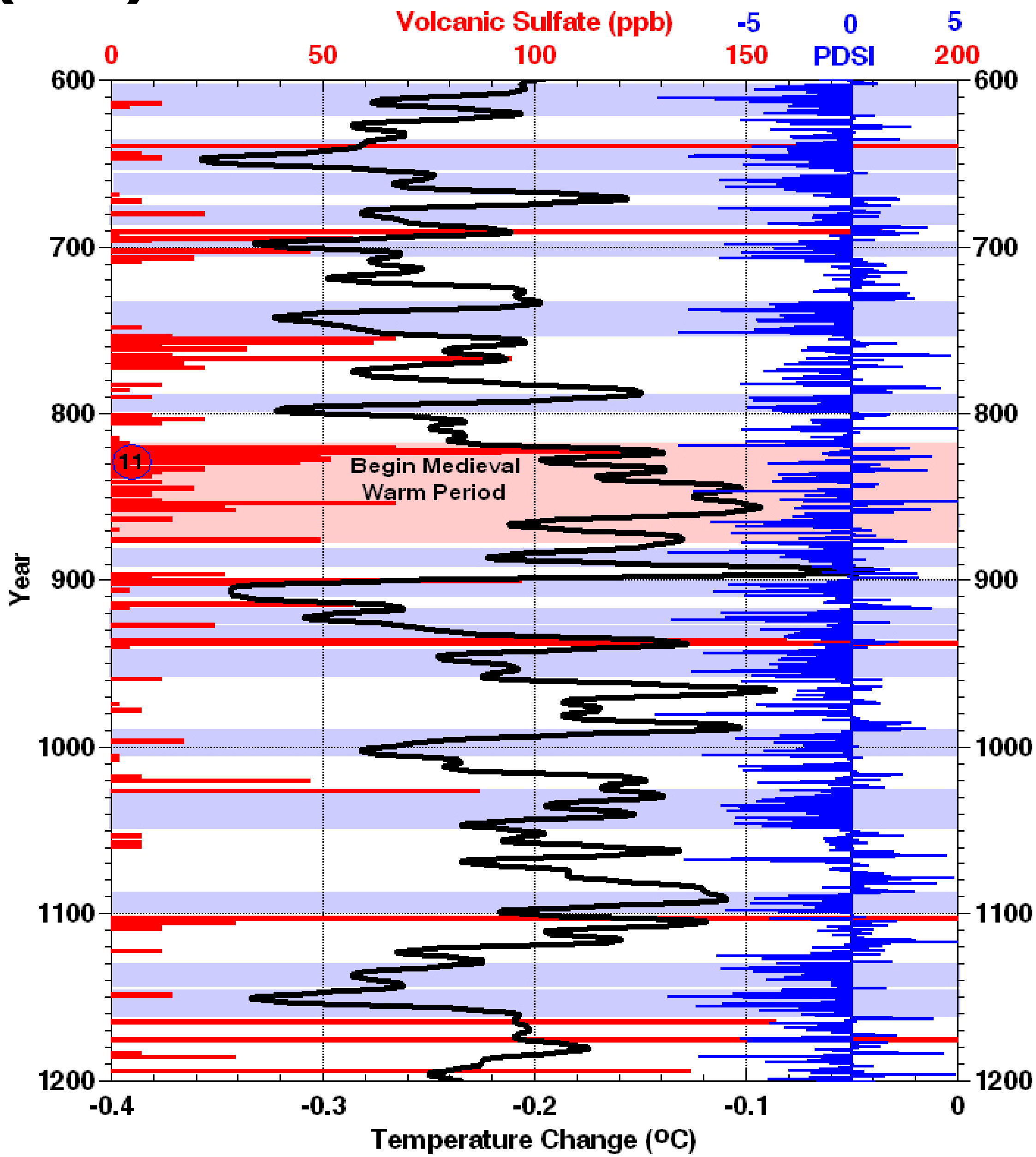

Onset of the Medieval Warm Period coincides with 11 contiguous layers of volcanic sulfate from 818.2 to 837.8 = 19.6 years.

Most large volcanic eruptions are followed by cooling for a few years.

Most periods of no volcanic activity (blue) coincide with periods of prolonged drought.

(PDSI for SE Utah, North American Drought Atlas, Cook & Krusic, 2004)

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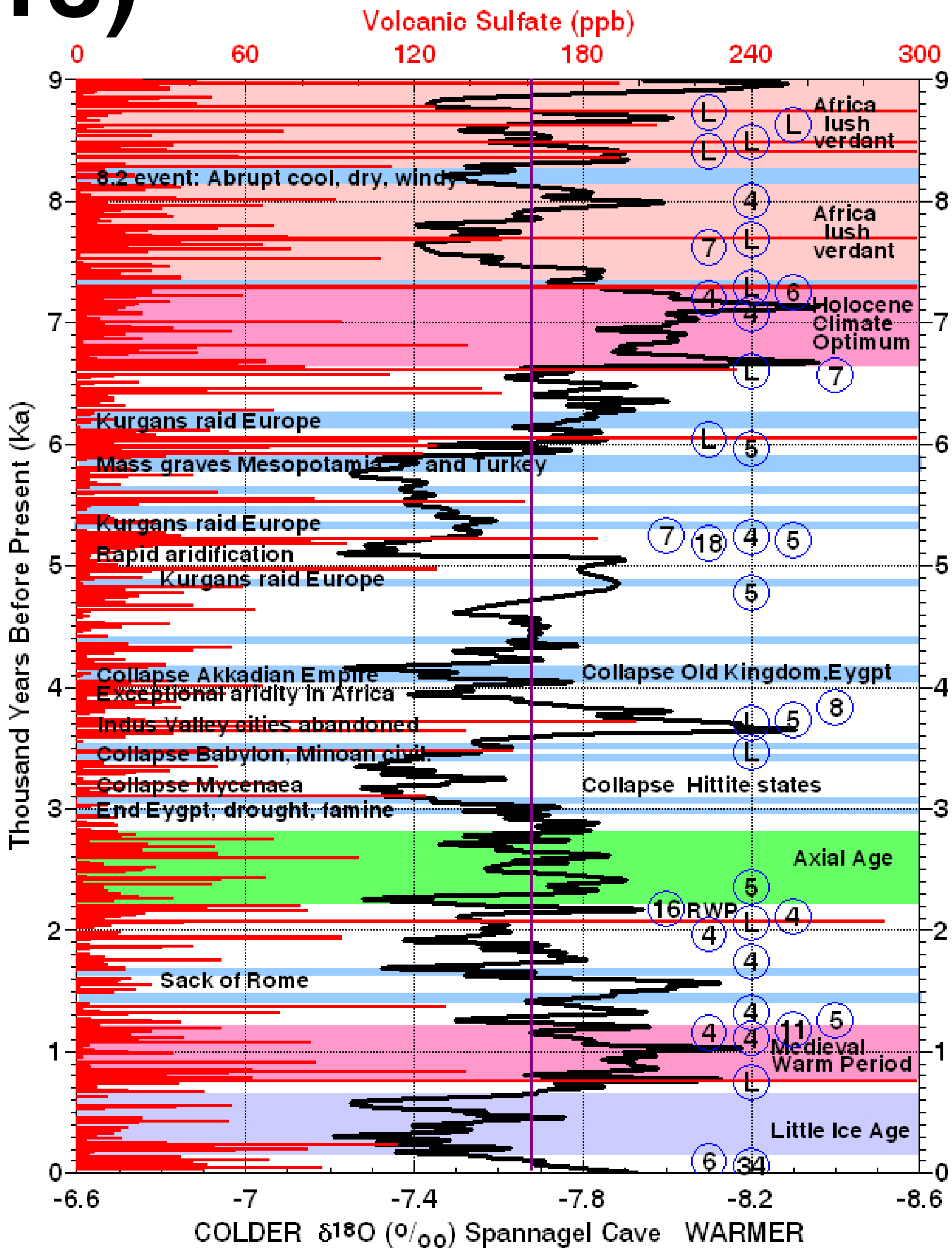

Warm periods are contemporaneous with times of high volcanic activity

Cold periods are contemporaneous with lack of volcanism

Black = proxy for temperature

Red bars = volcanic sulfate

Blue shading = times of low volcanic activity

Circles show number of contiguous layers containing sulfate

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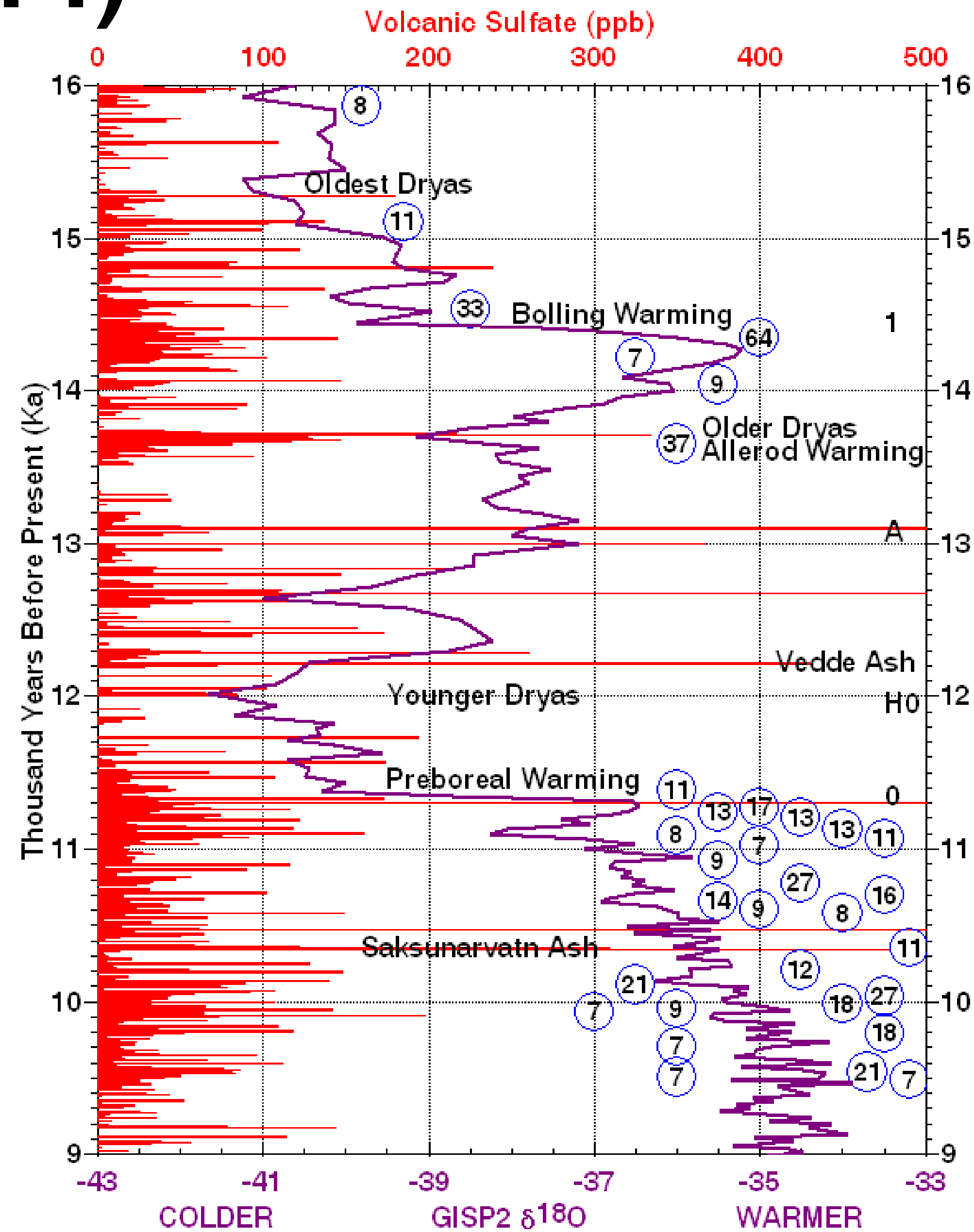

Times of most rapid warming are contemporaneous with times of highest volcanic activity

Preboreal warming

801 ppb sulfate in 2.08 years = one large eruptions every 1.5 months

1858 ppb in 63 years is one large eruption every 7 months

Purple = temperature proxy

Red = volcanic sulfate

Circles show number of contiguous layers with volcanic sulfate

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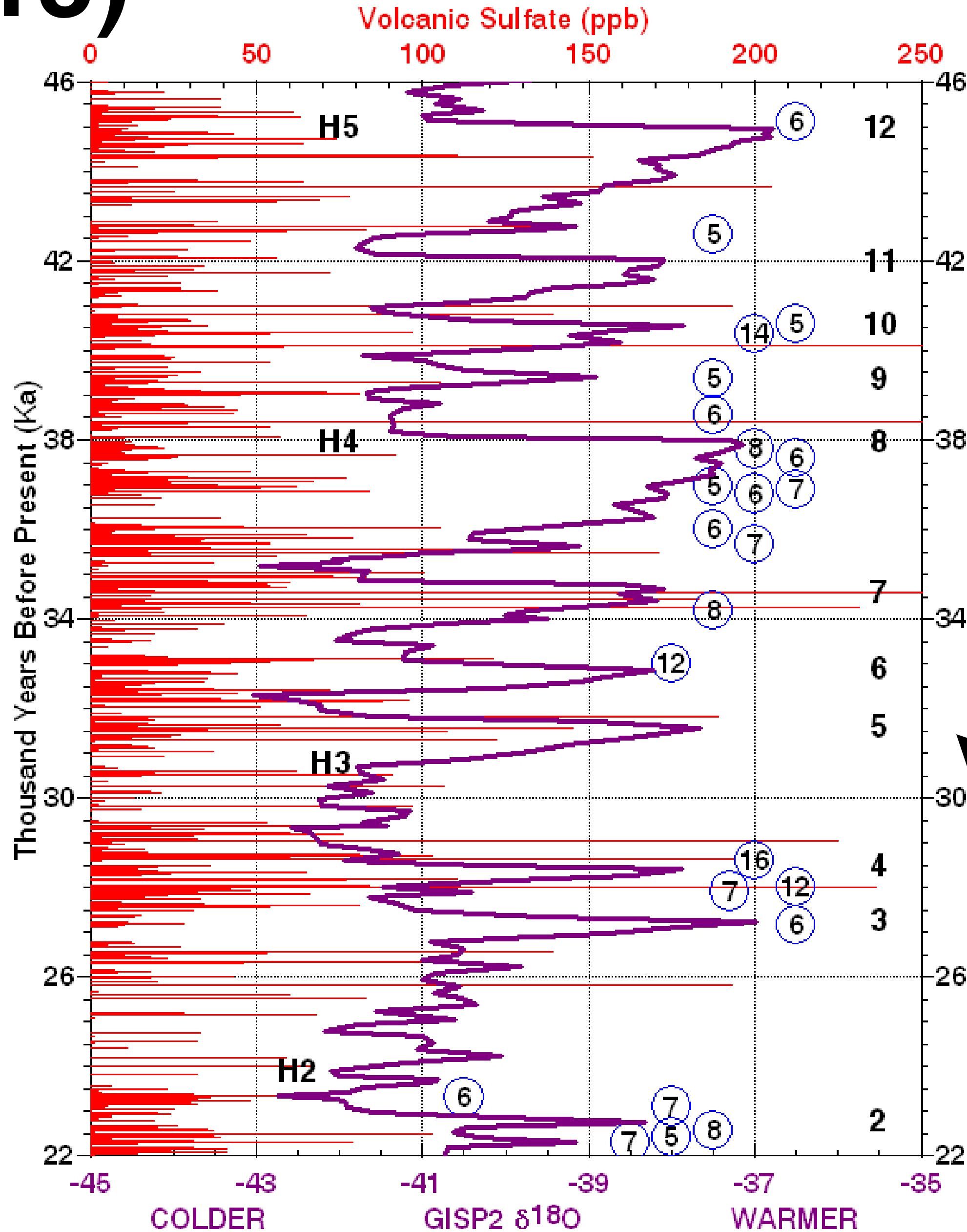


Time of most rapid warming are contemporaneous with times of highest volcanic activity

Paleolithic Revolution: humans spread rapidly. Major increase in sophistication of stone-working, art, music, elaborate burials, etc.

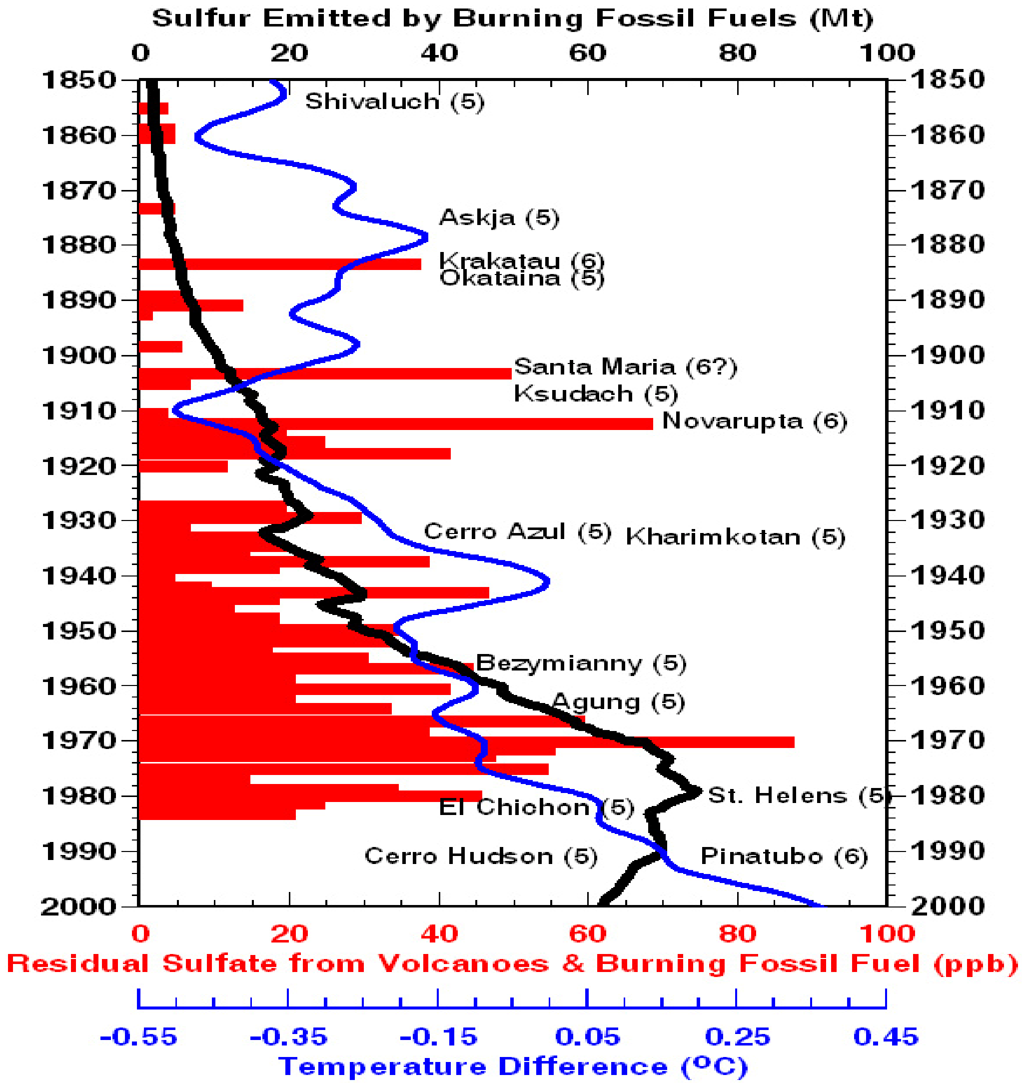
Unusually high sulfate of 795 ppb from 31.632 to 31.203 Ka

Purple = temperature proxy

Red = volcanic sulfate

Circles show number of contiguous layers with volcanic sulfate

(16) Sulfur emitted by humans burning fossil fuels is depositing sulfate in Greenland equivalent to one major volcanic eruption per year.



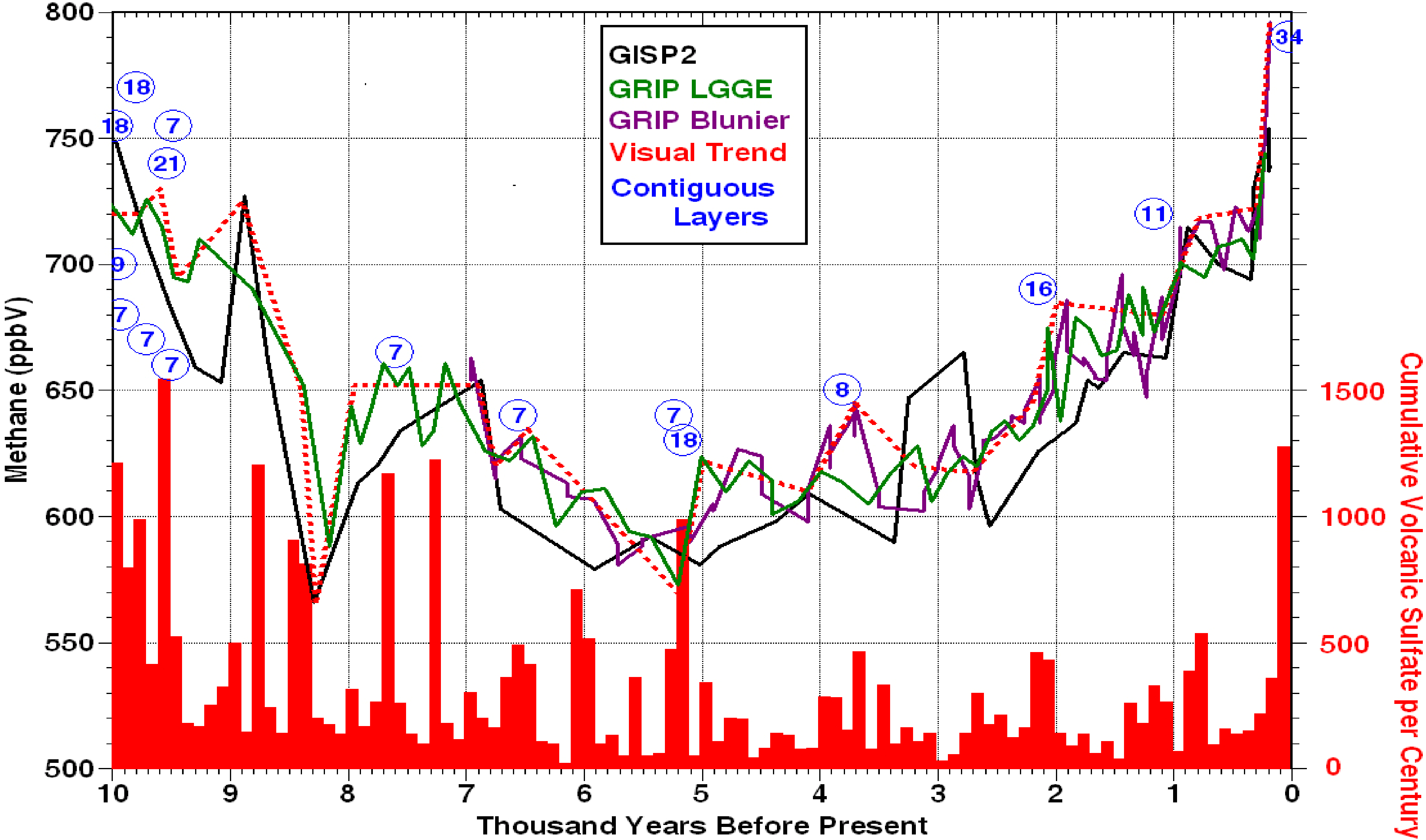
Sulfur Emitted by Burning Fossil Fuels (Smith et al., 2004)

Global Temperature Changes (Brohan et al., 2006)

Volcanic Sulfate GISP2 (Mayewski et al., 1997)

Volcanic Eruptions (VEI) (Simkin & Siebert, 1994)

(17) Methane increases during times of high rates of volcanism shown by both sulfate per century and the number of contiguous layers containing sulfate.



(18)

But What About CO_2?

Man is causing 7.8 Gt Carbon to be emitted each year by burning fossil fuels and manufacturing cement

If all carbon is released as CO_2, then this is 28.6 Gt of CO_2

Pinatubo emitted 42 to 234 Mt of CO_2

Man is emitting two to three orders of magnitude more CO_2 than a large volcanic eruption like Pinatubo

Only in the past 100 years has CO_2 become an environmental problem

<u>We must reduce significantly both SO_2 and CO_2</u>

Need detailed modeling to determine relative effects of SO_2 and CO_2

(19) Largest historic basaltic eruption Lakigigar, Iceland 1783, VEI = 4

14.7 km^3 basalt
27 km-long fissure
122 Mt SO_2
(5 times Pinatubo)

<u>Deaths</u>
10,521 Iceland
20,000 England
16,000 France
Japan, Alaska

Trees and crops damaged from acid rain from Iceland to Scandinavia to Italy

Very cold, harsh summer from Iceland to Siberia
Very dry and hot in western Europe
Winter 1783-4 one of most severe on record
Crops failed 1783 thru 1788
Helped spawn French Revolution

<u>Basaltic eruptions typically erupt 10 to 100 times more volatiles per km^3 than silicic volcanoes</u>

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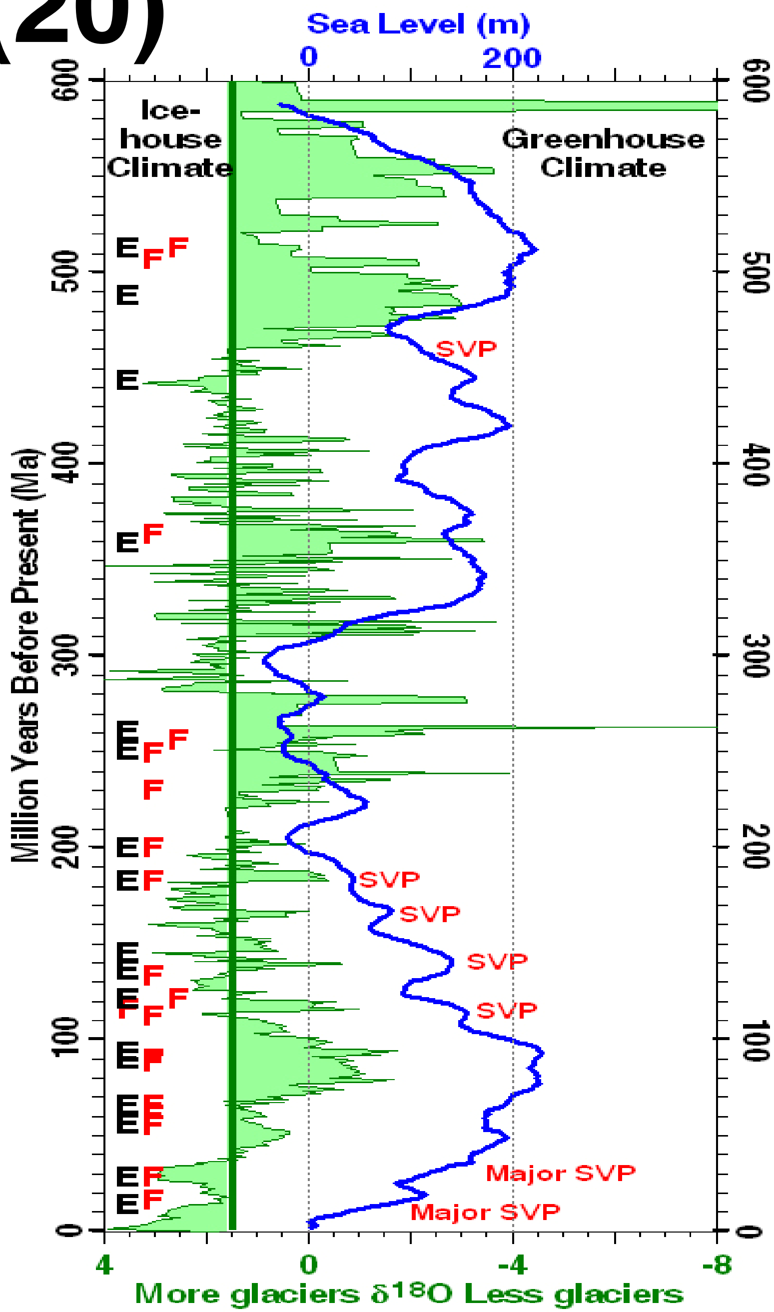

Most mass extinctions are contemporaneous with most major flood basalts within the accuracy of the best dating.

(Courtillot and Renne, 2003)

E = Age of mass extinction
F = Age of flood basalt
SVP = Silicic Volcanic Provence

"Humans are responsible for the sixth largest major extinction event"

United Nations Millennium Ecosystem Assessment and the Global Biodiversity Outlook 2 (2005)