Exam 4: Average = 86.2

Scores:

100 96 96 96 94 94 93 93 93 92 92 91 91 89 88 87 87 87 86 83 83 83 83 80 78 77 73 72 70 58

IMPORTANT ANNOUNCEMENT

TOMORROW I am asking the Class to take a 50 min. Standardized ACS Physical Chemistry Exam. Please make a strong effort to do this:

Why?

1. The Department needs the results as part of mandated proof of "Learning Outcomes".

Your participation will be greatly appreciated by me and by Mary Cloninger (Chemistry and Biochem. Dept. Head)

Other information about this:

1. It is voluntary, but will be appreciated by the Department.
Participation was nearly 100% the last 3 years.

2. It will not affect your grade in any way. It is only for comparing long term trends.

3. You are not expected to study for this exam.

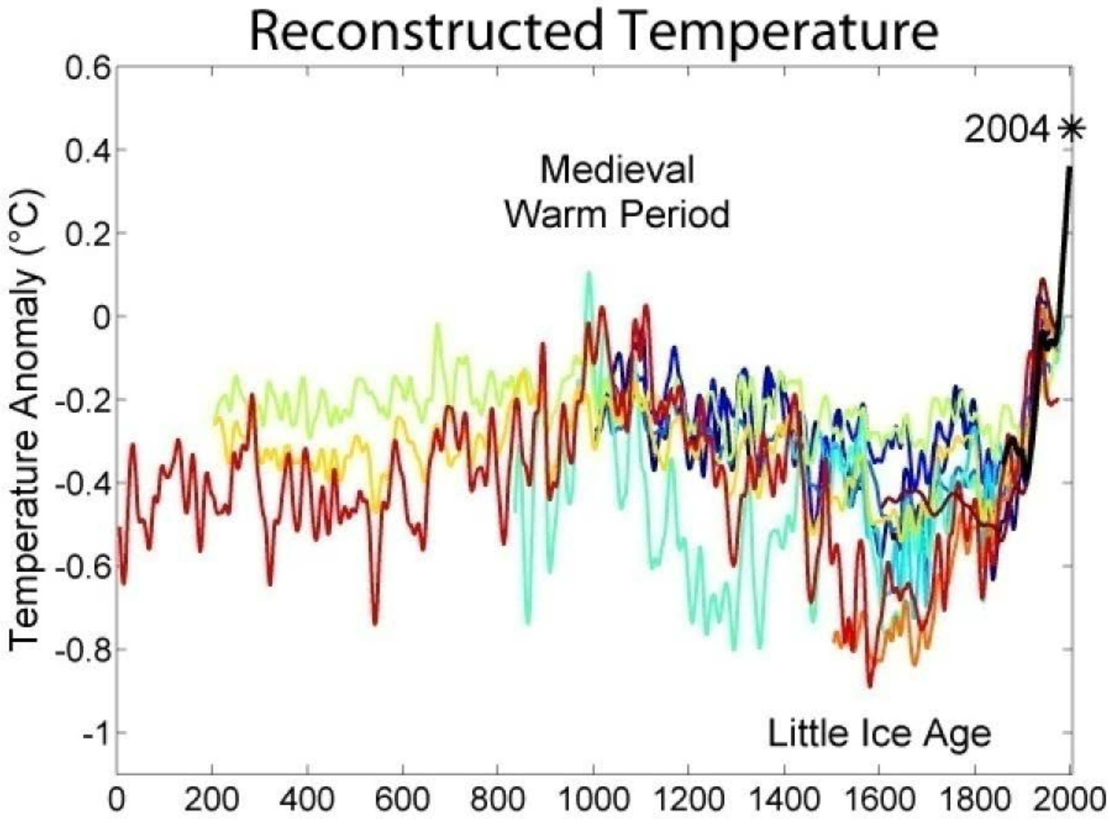
4. Expectations are not so high; this exam is assuming 6 semester credits, whereas you are taking only 4. Normally 110 minutes is allowed, but you get 50.

Last year's class scored 43% of 60 multiple 4-choice questions (the national average was 52%). (Four people scored well above the national average). This is good!

There are 3 sections: Thermodynamics, Kinetics, and Quantum/Spectroscopy; There is no penalty for guessing.

6. The Arctic ice has been melting for 15,000 years. This was not caused by humans, but we may—or may not—be hastening the process now.
--Callis

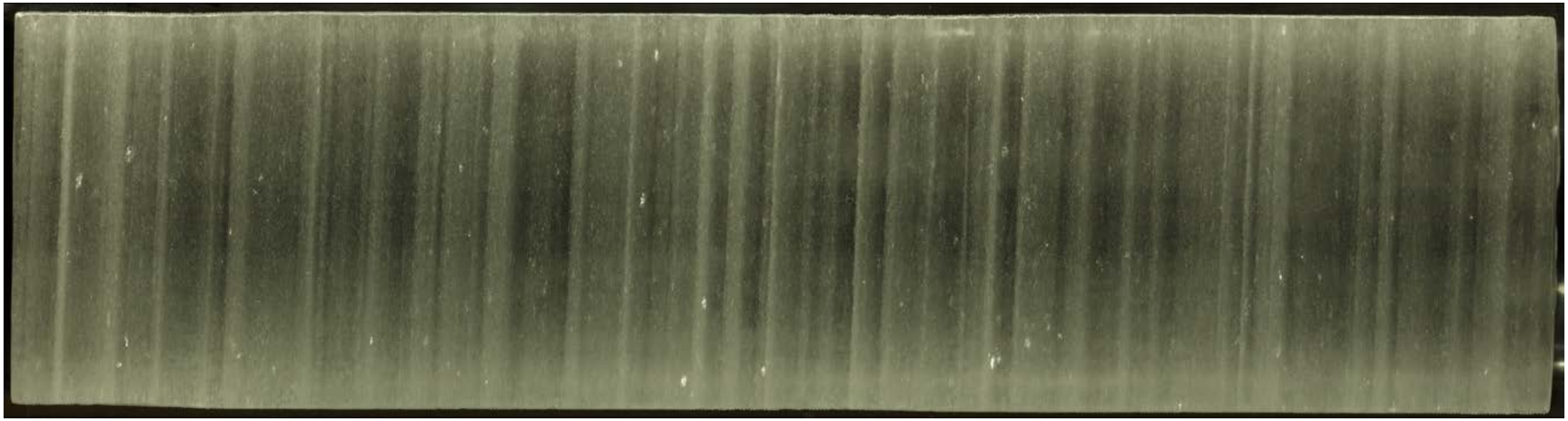
Last 2000 yrs



The Ice Core Record of Antarctica and Greenland

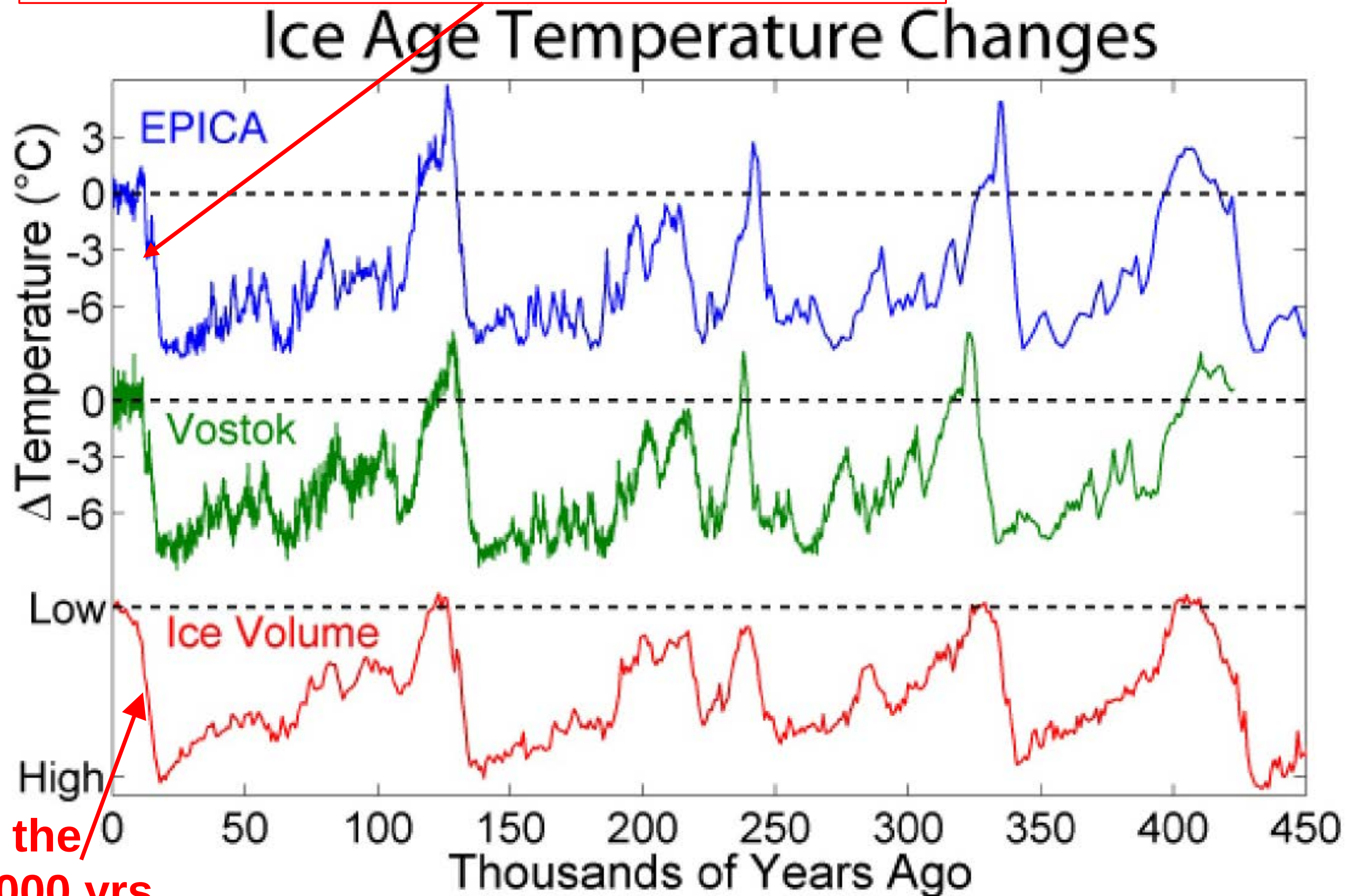
ice core samples provide a record of the previous 800,000 years

- Taken from both Greenland and Antarctica
- Gases trapped in bubbles include CO_2, CH_4, and N_2O
- Deuterium and ^{18}O content in water indicates Temperature
  (that is DHO content in H_2O)



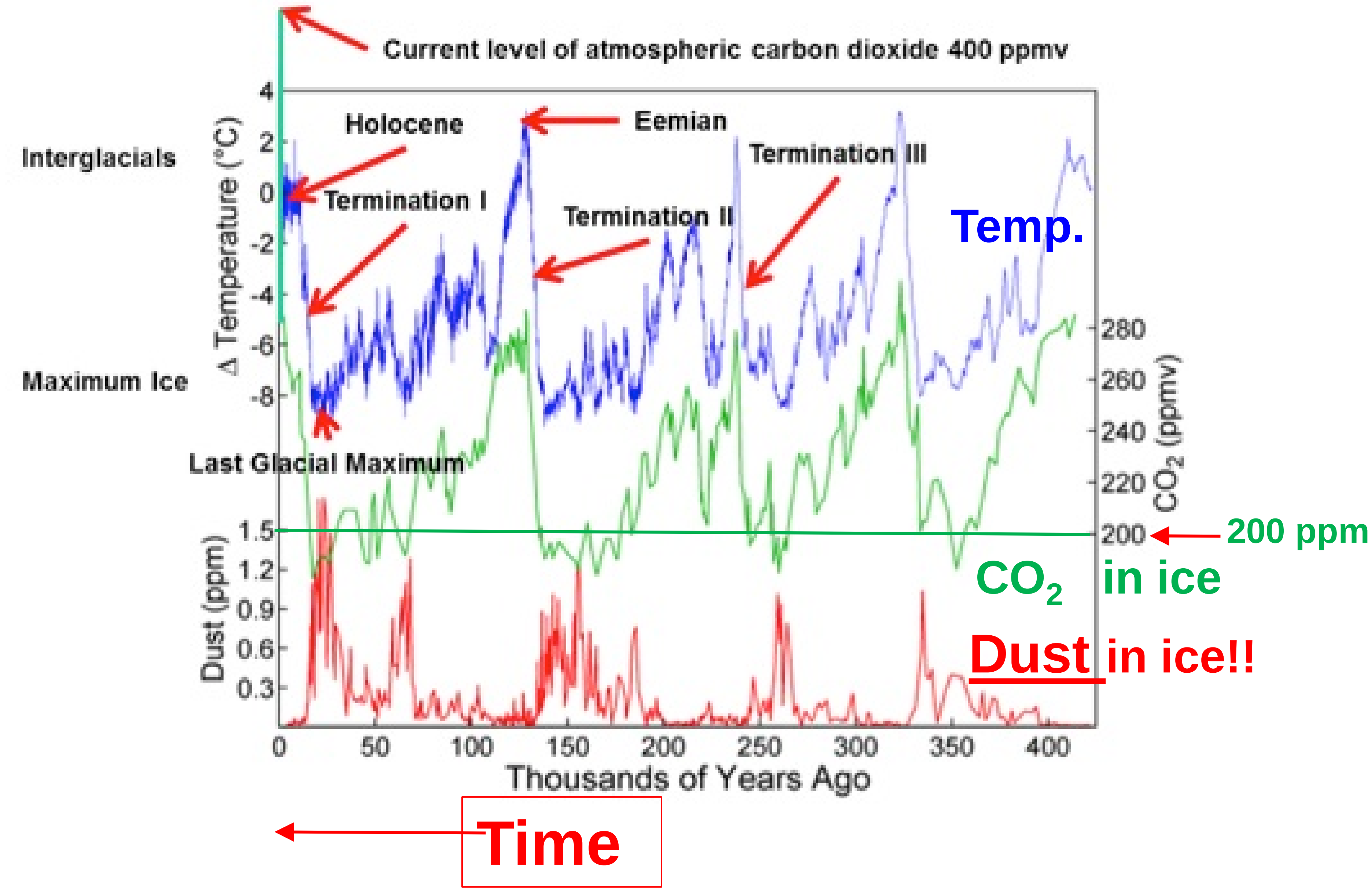
Cores are about 6 inches in diameter by several miles long.

Note the “fast” (1000 year) temperature rise and melting near the peaks

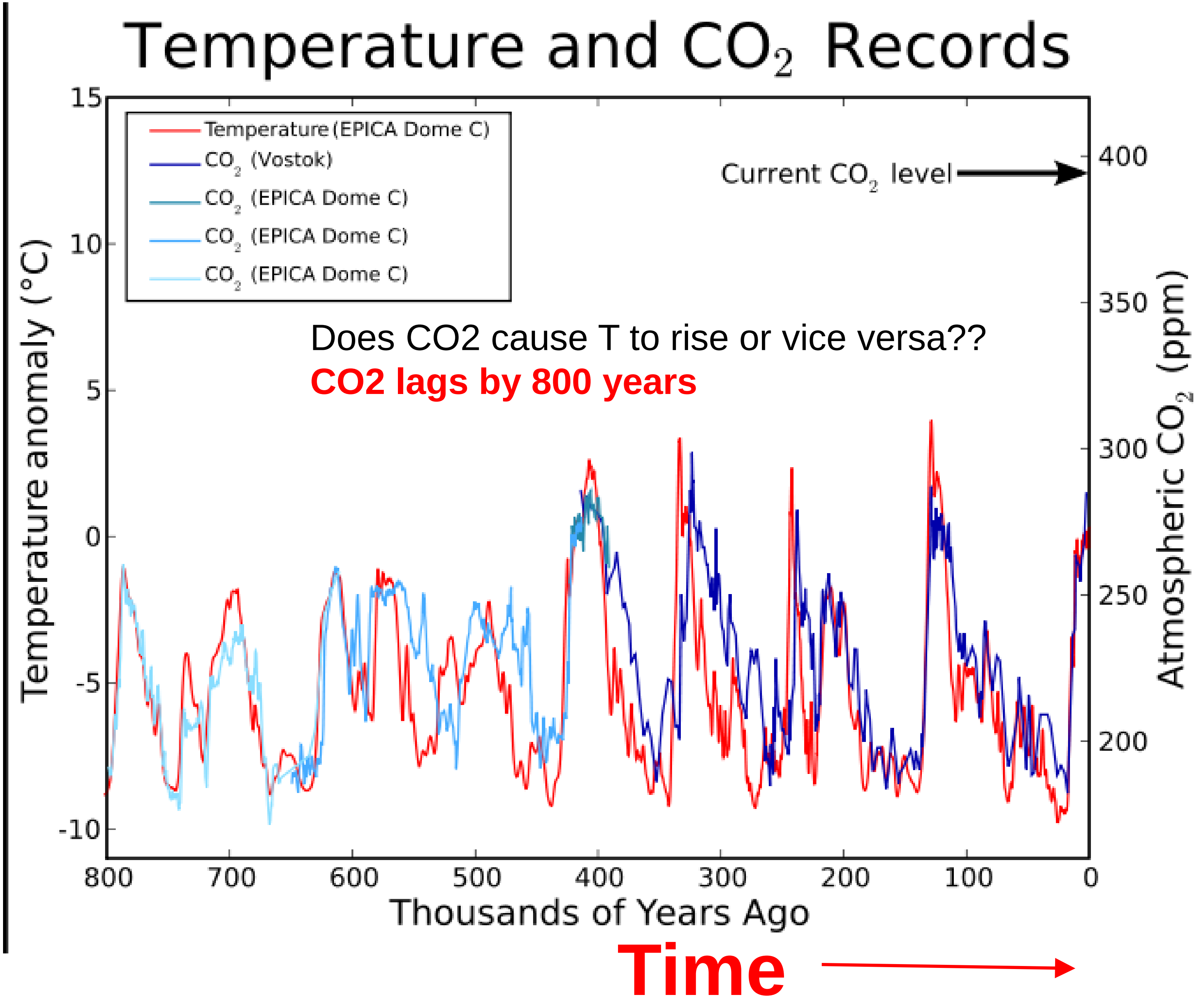


Melting the last 20,000 yrs

Time



Current level of atmospheric carbon dioxide 400 ppmv
Interglacials
Holocene
Eemian
Termination I
Termination II
Termination III
Maximum Ice
Last Glacial Maximum
Δ Temperature (°C)
4
2
0
-2
-4
-6
-8
Temp.
280
260
240
220
200
CO_2 (ppmv)
200 ppm
CO_2 in ice
Dust in ice!!
Dust (ppm)
1.5
1.2
0.9
0.6
0.3
0
50
100
150
200
250
300
350
400
Thousands of Years Ago
Time


Temperature and CO_2 Records
Temperature (EPICA Dome C)
CO_2 (Vostok)
CO_2 (EPICA Dome C)
CO_2 (EPICA Dome C)
CO_2 (EPICA Dome C)
Current CO_2 level
Does CO2 cause T to rise or vice versa??
CO2 lags by 800 years
Temperature anomaly (°C)
Atmospheric CO_2 (ppm)
15
10
5
0
-5
-10
400
350
300
250
200
800
700
600
500
400
300
200
100
0
Thousands of Years Ago
Time

Geoscience Frontiers 7 (2016) 891–909

HOSTED BY

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Contents lists available at ScienceDirect

China University of Geosciences (Beijing)

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journal homepage: www.elsevier.com/locate/gsf

Research paper

Modulation of ice ages via precession and dust-albedo feedbacks

Ralph Ellis [a,*], Michael Palmer [b]

[a] 105 – 6817 Route Pommier, St Martin Bellevue 74370, France
[b] University of Waterloo, Department of Chemistry, Waterloo, Ontario, Canada

ARTICLE INFO

Article history:
Received 23 March 2016
Received in revised form
17 April 2016
Accepted 30 April 2016
Available online 26 May 2016

Keywords:
Paleoclimatology
Ice-age
Precession
CO_2
Albedo
Dust

ABSTRACT

We present here a simple and novel proposal for the modulation and rhythm of ice-ages and interglacials during the late Pleistocene. While the standard Milankovitch-precession theory fails to explain the long intervals between interglacials, these can be accounted for by a novel forcing and feedback system involving CO_2, dust and albedo. During the glacial period, the high albedo of the northern ice sheets drives down global temperatures and CO_2 concentrations, despite subsequent precessional forcing maxima. Over the following millennia more CO_2 is sequestered in the oceans and atmospheric concentrations eventually reach a critical minima of about 200 ppm, which combined with arid conditions, causes a die-back of temperate and boreal forests and grasslands, especially at high altitude. The ensuing soil erosion generates dust storms, resulting in increased dust deposition and lower albedo on the northern ice sheets. As northern hemisphere insolation increases during the next Milankovitch cycle, the dust-laden ice-sheets absorb considerably more insolation and undergo rapid melting, which forces the climate into an interglacial period. The proposed mechanism is simple, robust, and comprehensive in its scope, and its key elements are well supported by empirical evidence.

This happens in **Phoenix Arizona** about 2 times a year!

Happened frequently in mid West USA during dust bowl years (1930s)

Figure 12. A large dust storm approaches Phoenix Arizona. High winds can move vast quantities of dust, and while the heavier dust particles seen here will soon settle out the finer particles can be transported for thousands of kilometers. Photo courtesy Daniel Bryant.

Figure 12. A large dust storm approaches Phoenix Arizona. High winds can move vast quantities of dust, and while the heavier dust particles seen here will soon settle out the **finer particles can be transported for thousands of kilometers.** Photo courtesy Daniel Bryant.

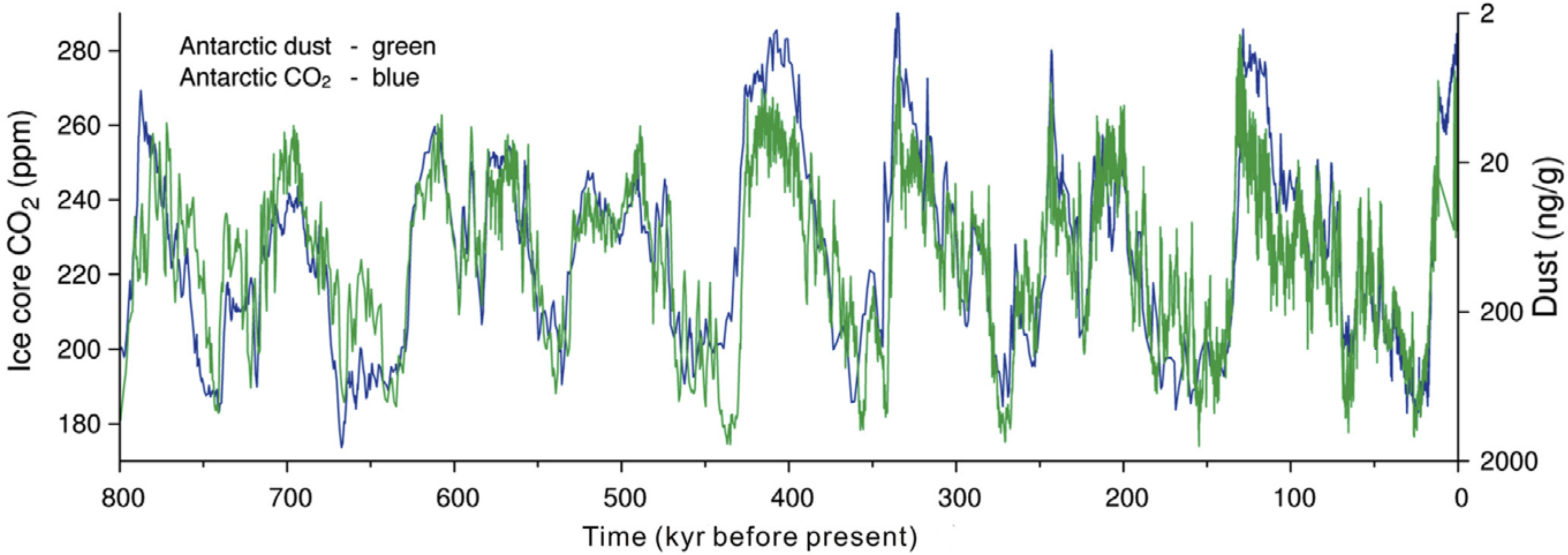


Figure 9. Dust deposition vs. CO_2 concentrations in ppm. The dust plot is inverted and to a logarithmic scale, to reduce amplitude peaks. So dust is closely but inversely correlated to CO_2 concentrations. Source: Epica, 2007.

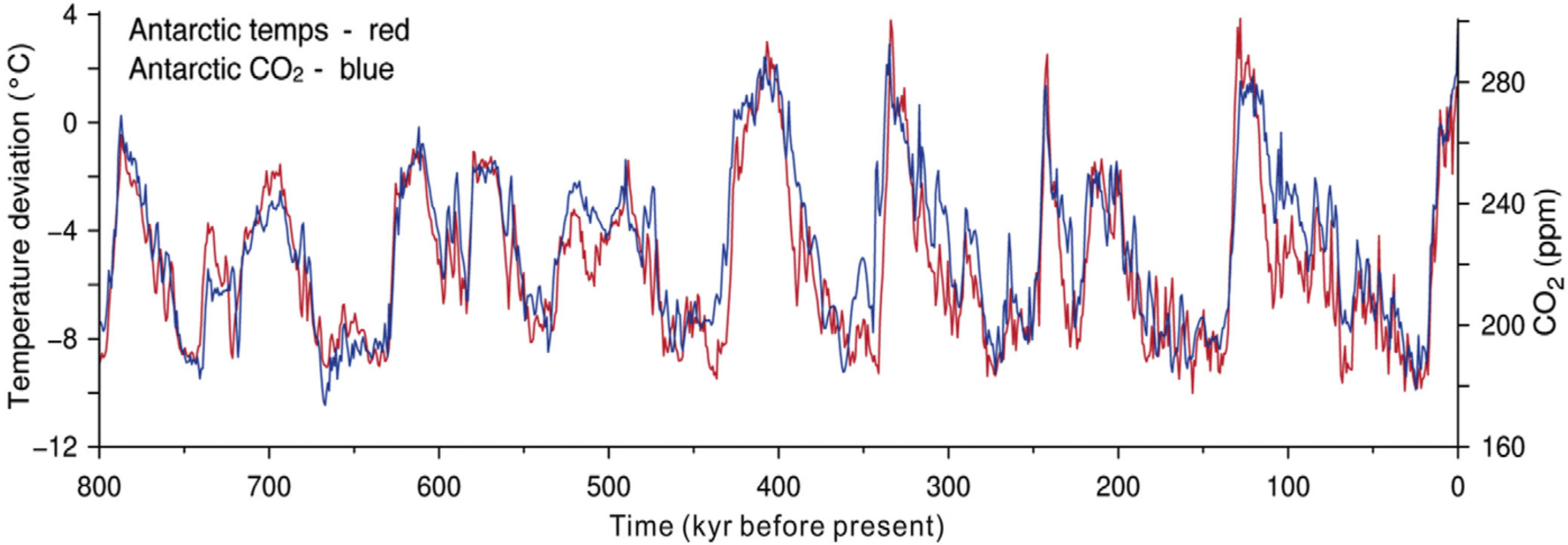
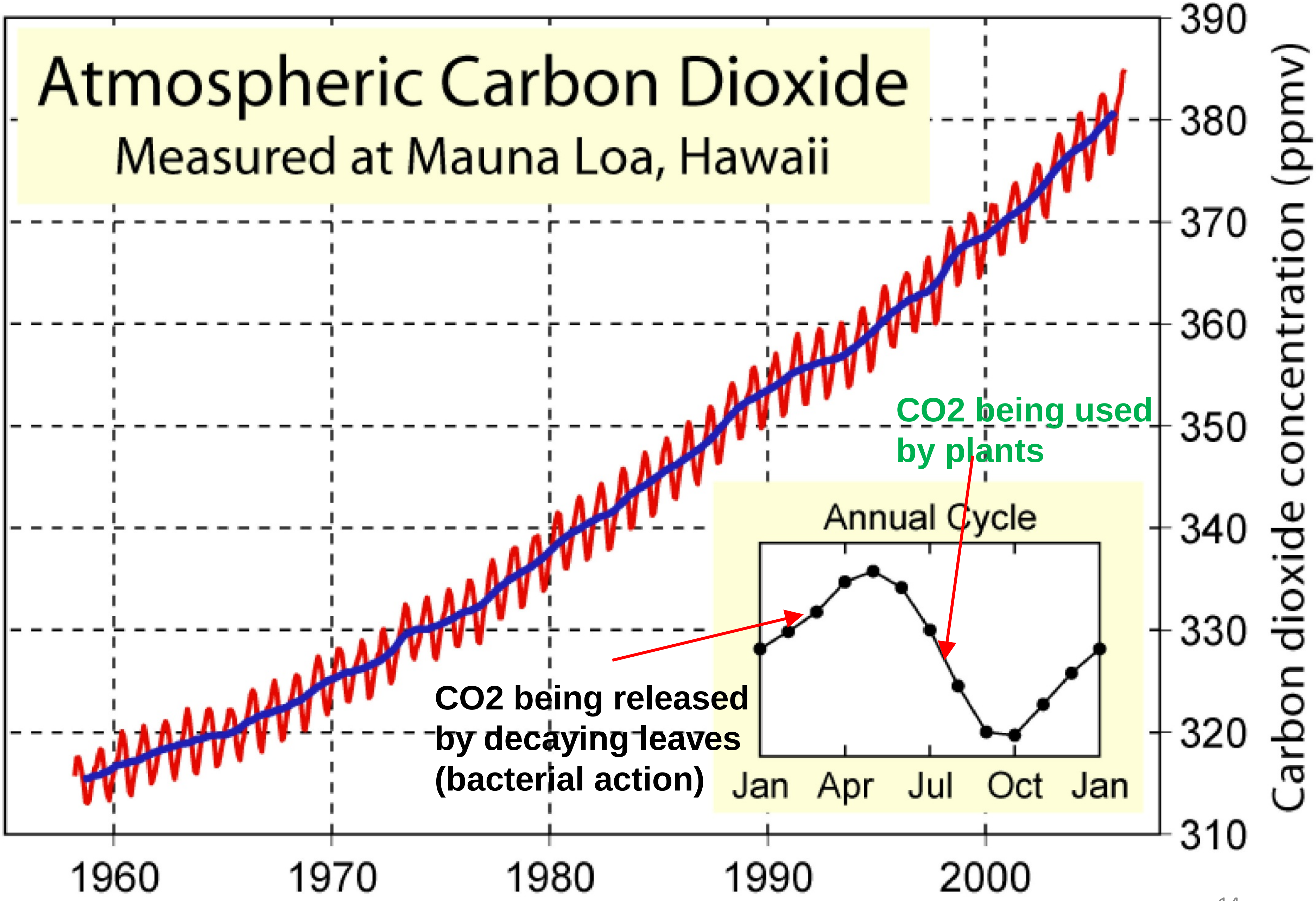
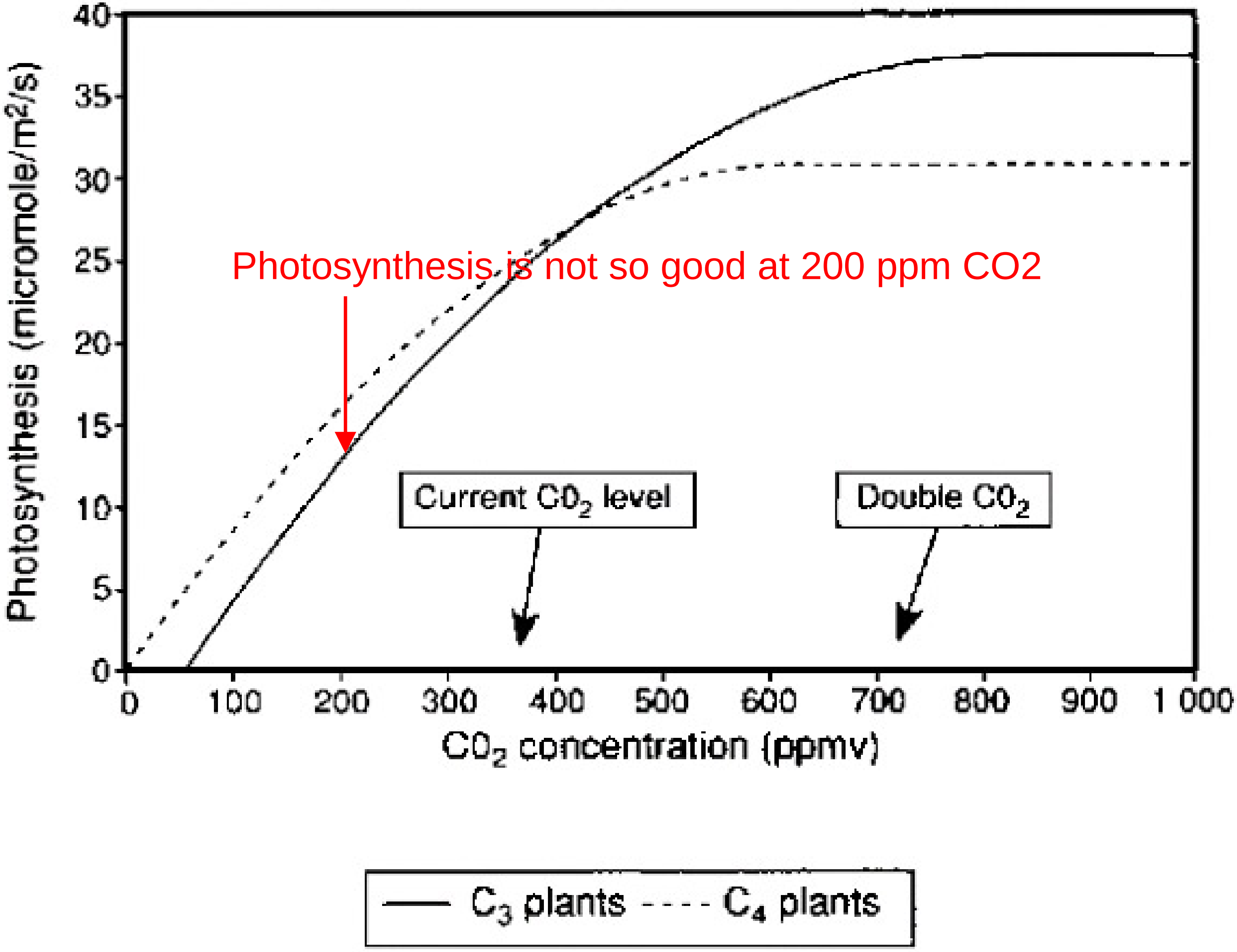


Figure 1. Antarctic temperature vs. CO2 over 800 kyr from the Epica3 ice core. Note that CO2 concentrations follow global temperatures very closely, giving the **illusion** of CO2 being the primary causal feedback factor. Source: Epica3, 2007.


Atmospheric Carbon Dioxide
Measured at Mauna Loa, Hawaii
CO2 being used by plants
Annual Cycle
CO2 being released by decaying leaves (bacterial action)
Jan
Apr
Jul
Oct
Jan
390
380
370
360
350
340
330
320
310
Carbon dioxide concentration (ppmv)
1960
1970
1980
1990
2000

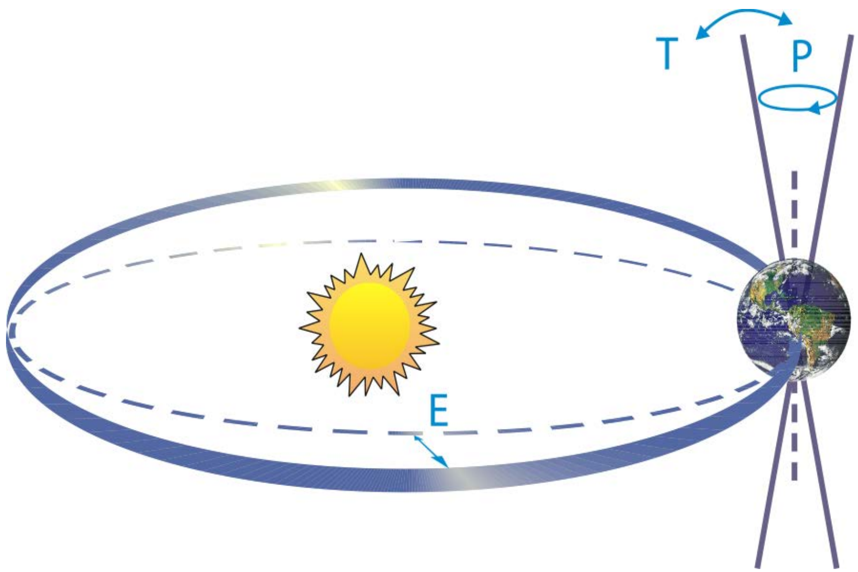


Photosynthesis is not so good at 200 ppm CO2
Photosynthesis (micromole/m²/s)
40
35
30
25
20
15
10
5
0
0
100
200
300
400
500
600
700
800
900
1 000
C0₂ concentration (ppmv)
Current C0₂ level
Double C0₂
C₃ plants
C₄ plants

The glacial / interglacial cycles

(a theory proposed in the 1920's)

the Milankovitch cycles



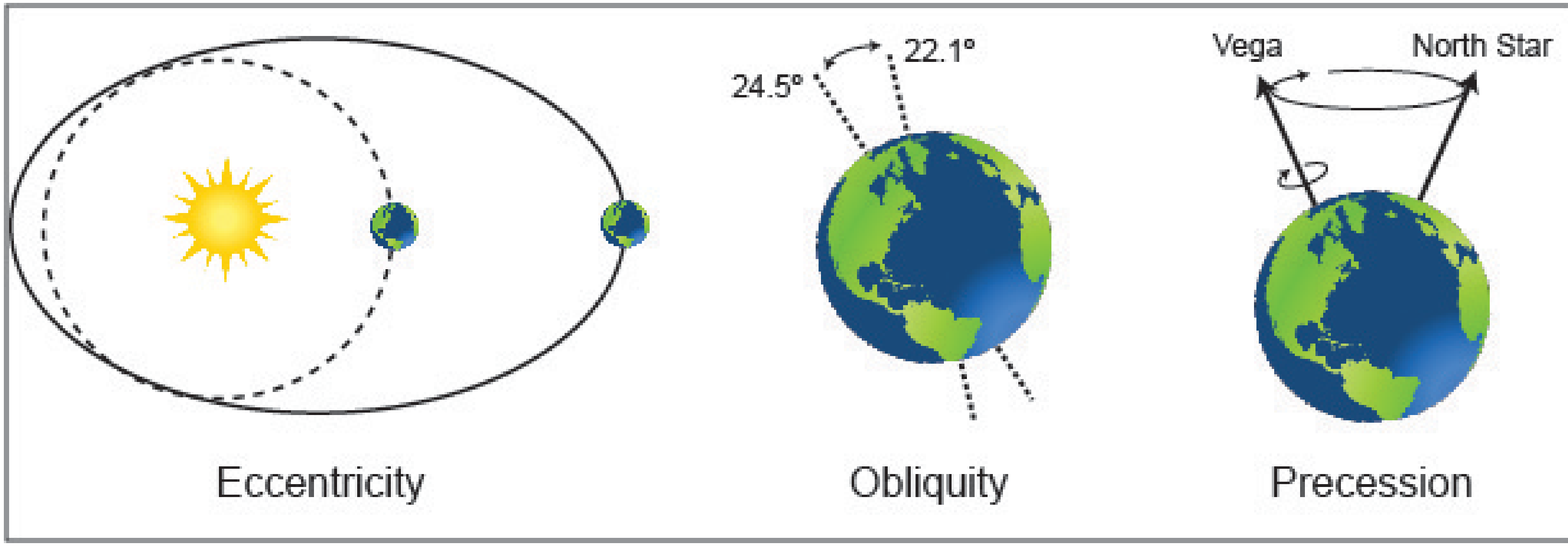
E - distance from sun

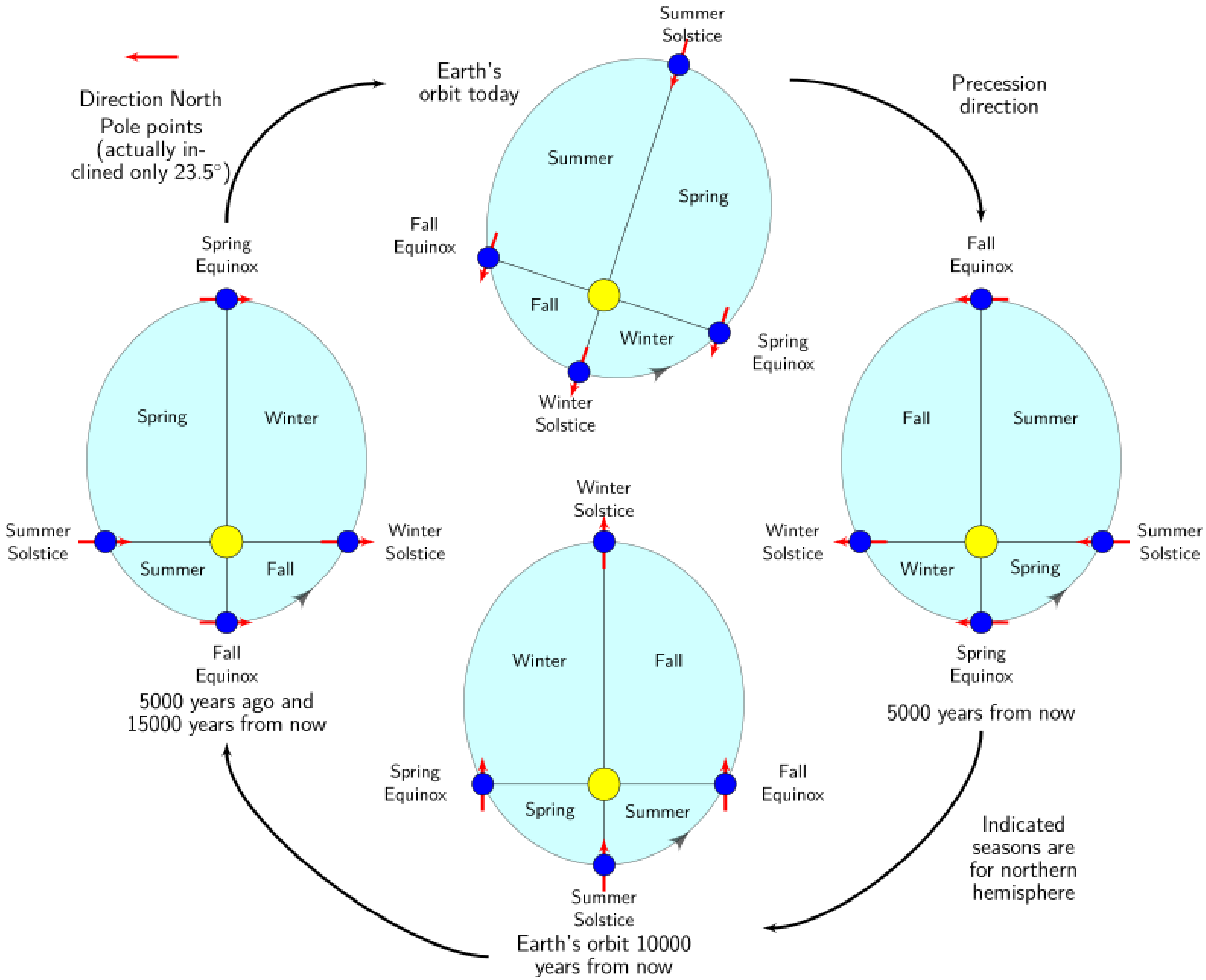
T - magnitude of tilt

P - direction of tilt

the determining factor here is how warm a summer the Northern Hemisphere has.

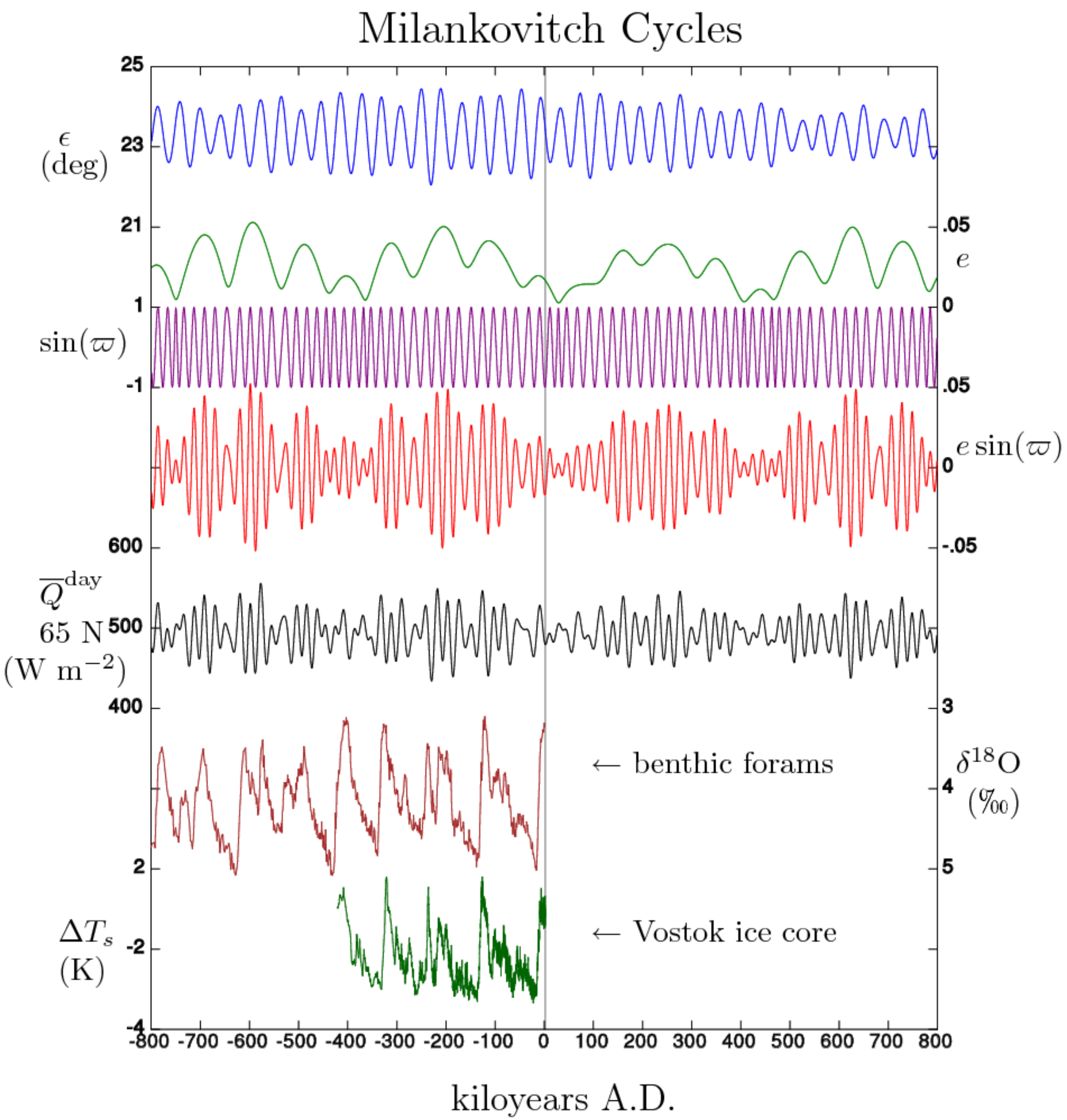
These small changes were greatly amplified by the **albedo and then greenhouse feedbacks.**


24.5°
22.1°
Vega
North Star
Eccentricity
Obliquity
Precession



Direction North
Pole points
(actually in-
clined only 23.5°)
Earth's
orbit today
Summer
Solstice
Summer
Spring
Fall
Equinox
Fall
Winter
Spring
Equinox
Winter
Solstice
Precession
direction
Spring
Equinox
Spring
Winter
Summer
Solstice
Summer
Fall
Winter
Solstice
Fall
Equinox
5000 years ago and
15000 years from now
Fall
Equinox
Fall
Summer
Winter
Solstice
Winter
Spring
Summer
Solstice
Spring
Equinox
5000 years from now
Winter
Solstice
Winter
Fall
Spring
Equinox
Spring
Summer
Fall
Equinox
Summer
Solstice
Earth's orbit 10000
years from now
Indicated
seasons are
for northern
hemisphere

http://en.wikipedia.org/wiki/Milankovitch_cycle



Past and future Milankovitch cycles. VSOP allows prediction of past and future orbital parameters with great accuracy.

— ε is obliquity (axial tilt).

— *e* is eccentricity.

— ϖ is longitude of perihelion.

— *e* sin(ϖ) is the **precession index**, which together with obliquity, controls the seasonal cycle of insolation.

— is the calculated daily-averaged insolation at the top of the atmosphere, on the day of the summer solstice at 65 N latitude.

— *Benthic forams* and — *Vostok ice core* show two distinct proxies for past global sealevel and temperature, from ocean sediment and Antarctic ice respectively. The vertical gray line shows current conditions, at 2 ky A.D.

https://en.wikipedia.org/wiki/Foraminifera

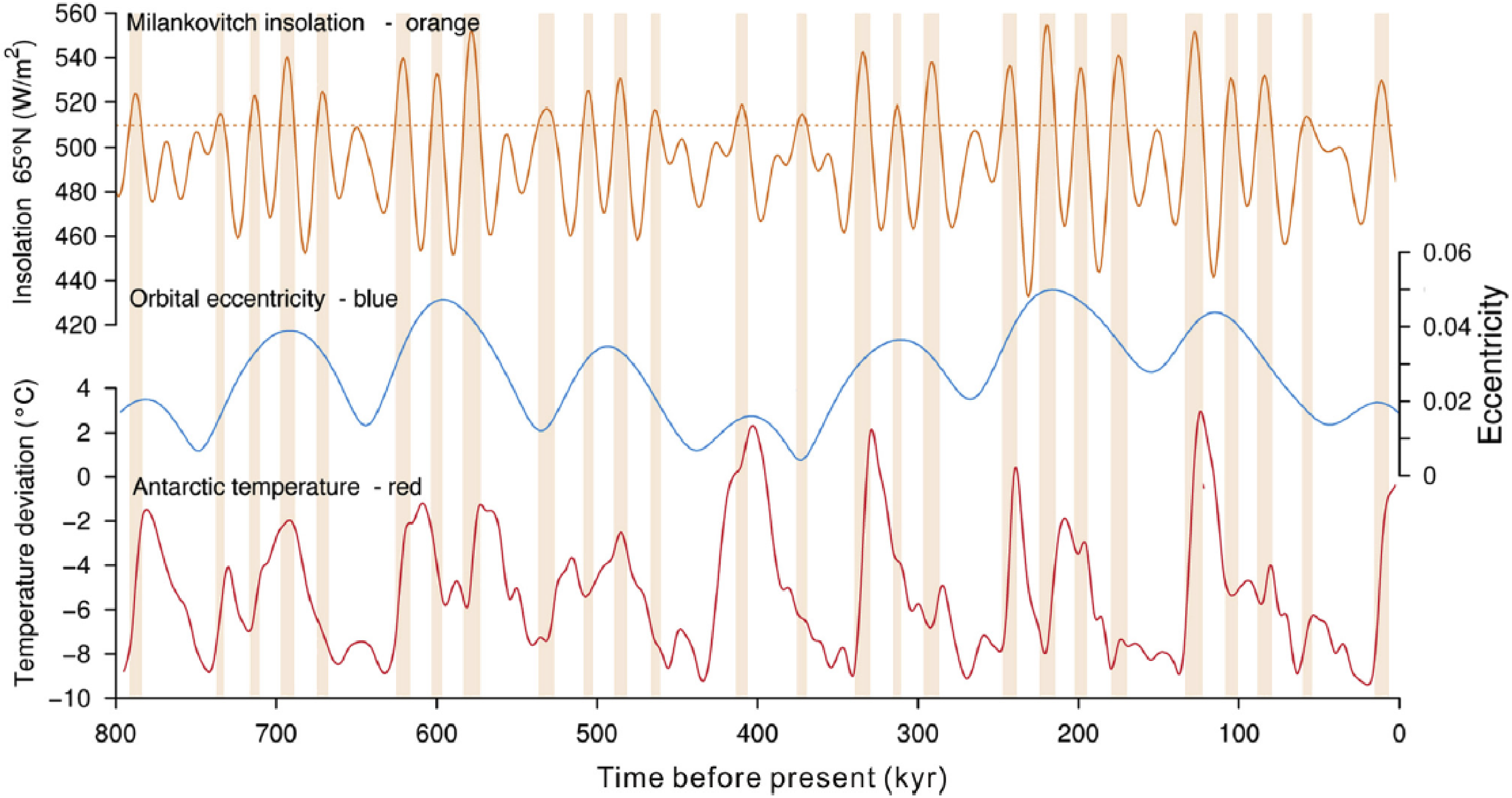


Figure 2. An illustration of why ice-ages follow the Earth's orbital eccentricity. Eccentricity-enhanced precessional Great Summers over 510 W/m^2 are marked with orange shading, and these clusters of shaded Great Summers are closely correlated with the ice-age cycle. Source: Laskar et al., 2004 orbital data. Epica3 Antarctic temperature data.

northern hemisphere **Great Summer seasons**

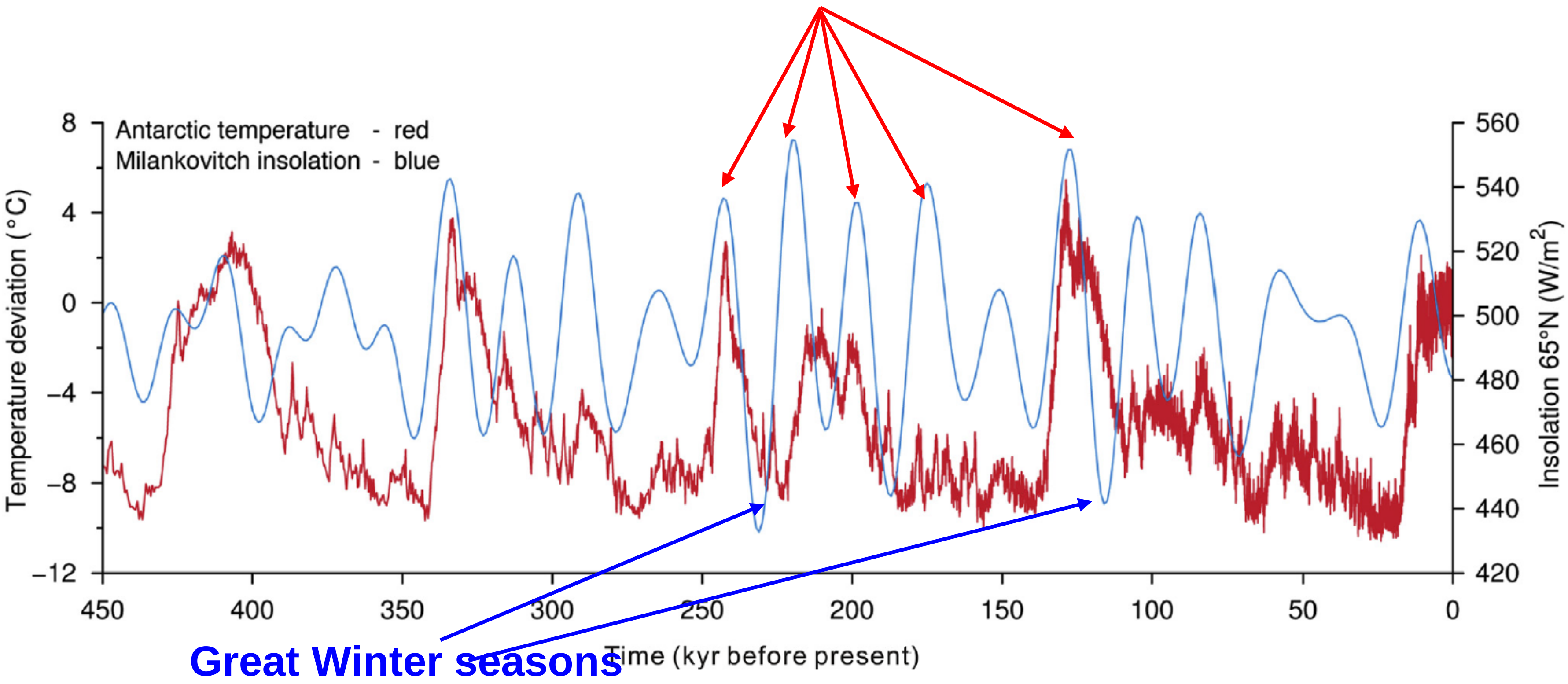


Figure 3. Graph of Milankovitch insolation at 65N (blue) vs. Antarctic temperature (red). The graph plots the last 21 **precessional Seasonal Great Years** in W/m2. The insolation peaks represent northern hemisphere Great Summer seasons, and the insolation troughs represent northern hemisphere Great Winter seasons. Sources: Laskar et al., 2004; Epica3, 2007.

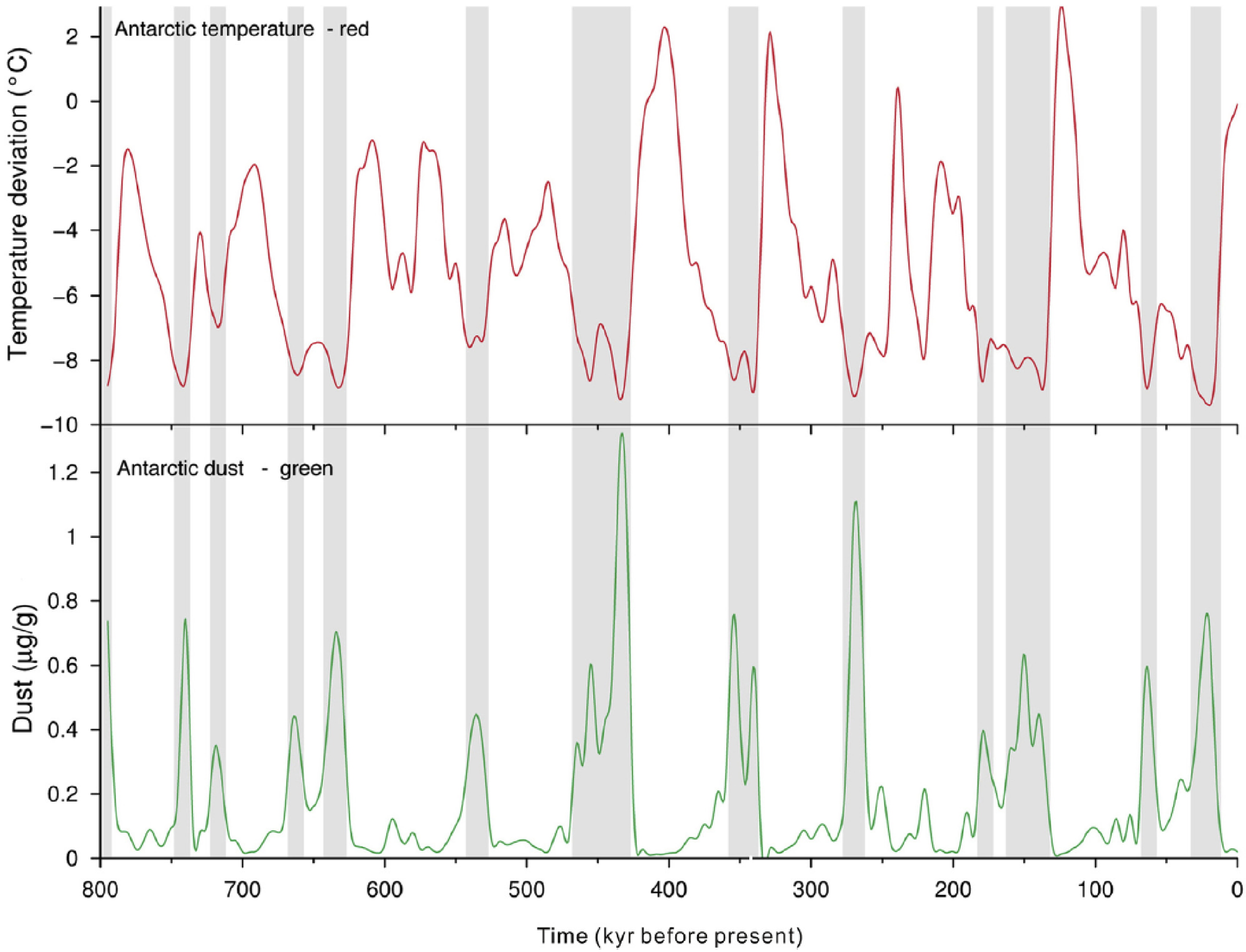


Figure 4. Dust concentrations in ug/g vs. temperature for the last 800 kyr, from the Epica3 ice core. Shaded bands highlight dust >0.35 ppm. Note that **increased dust deposition occurs just before each interglacial warming**. Source: Epica3, 2007.

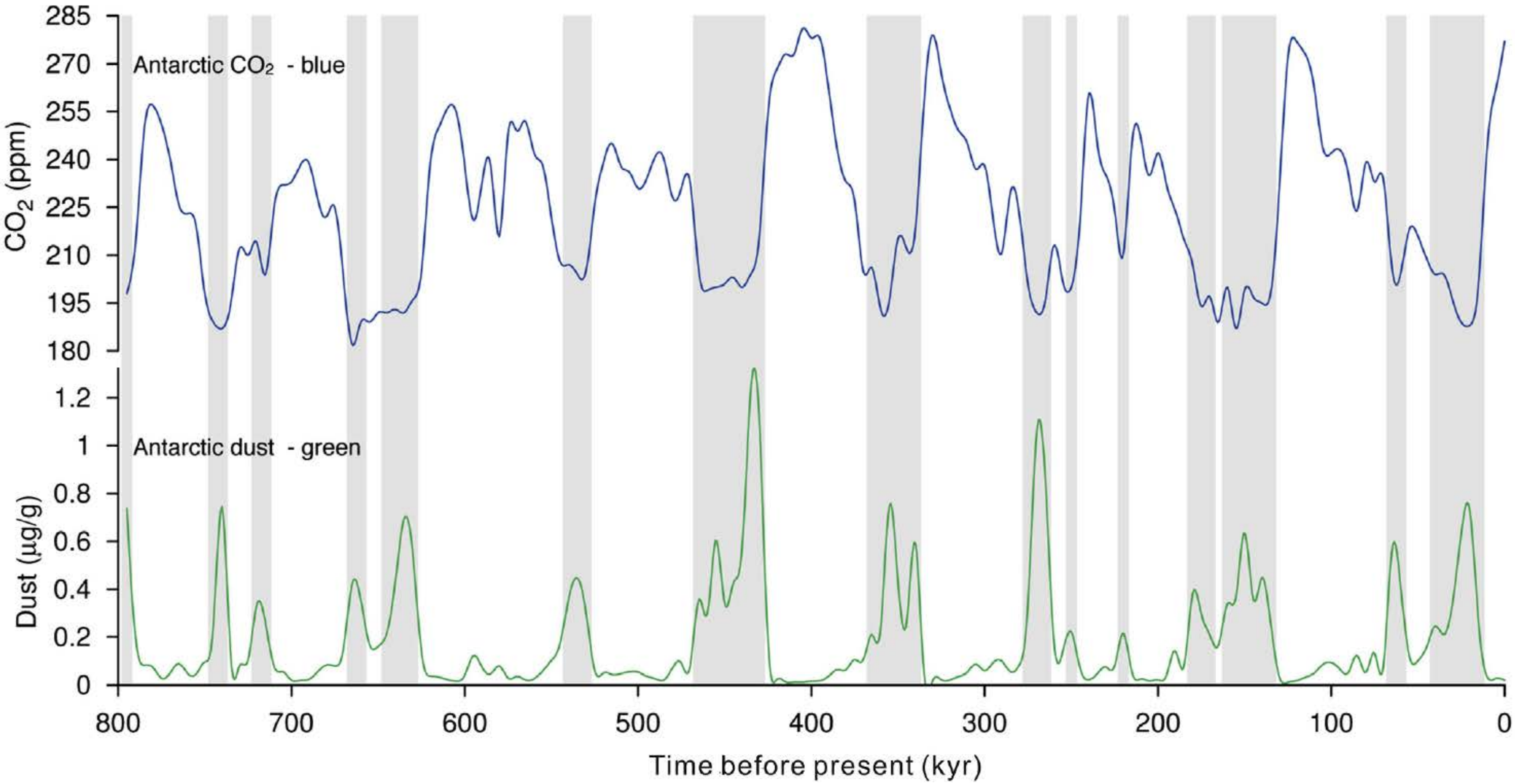


Figure 8. Dust deposition vs. CO2 concentrations in ppm. **Note that low CO2 concentrations always result in high dust concentrations**. It is likely that [LOW] CO2 concentrations are the causal factor [of dust] here. Source: Epica3, 2007.

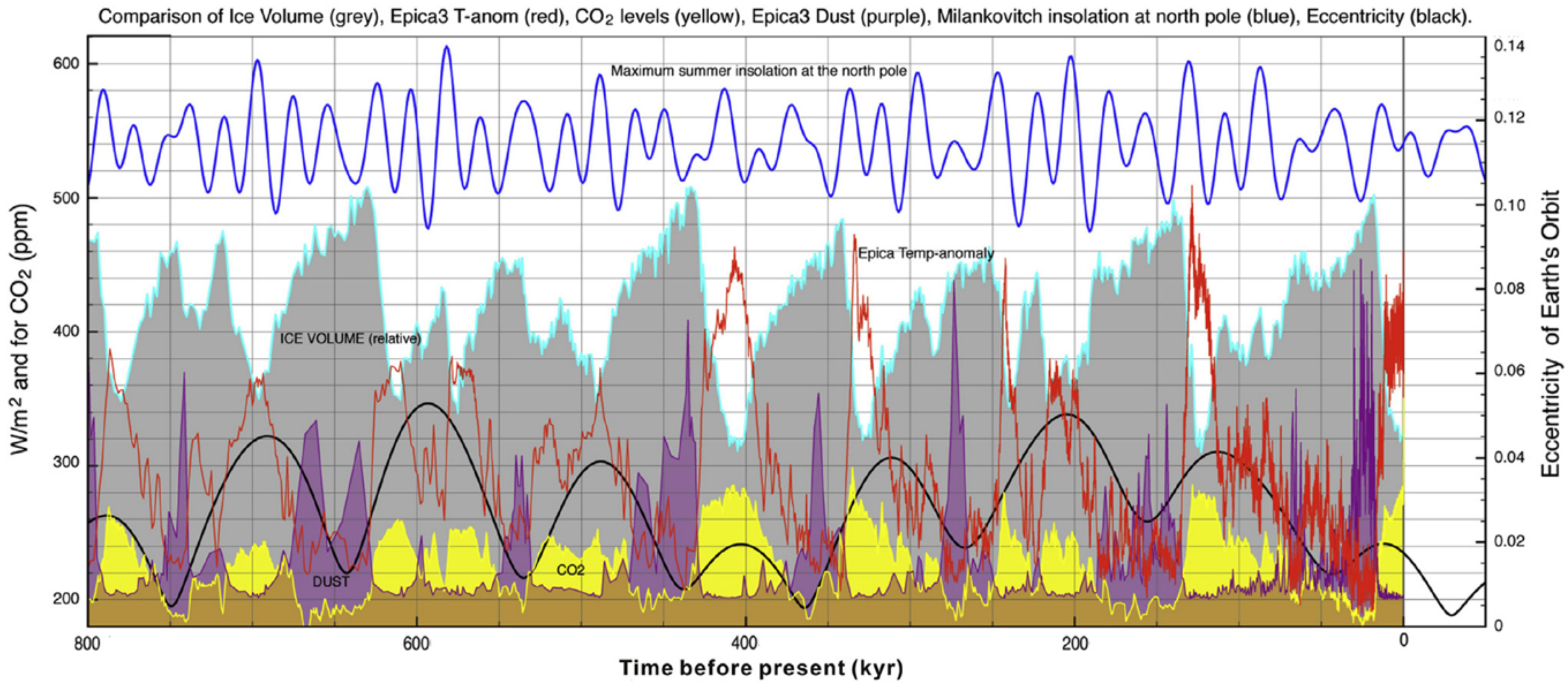
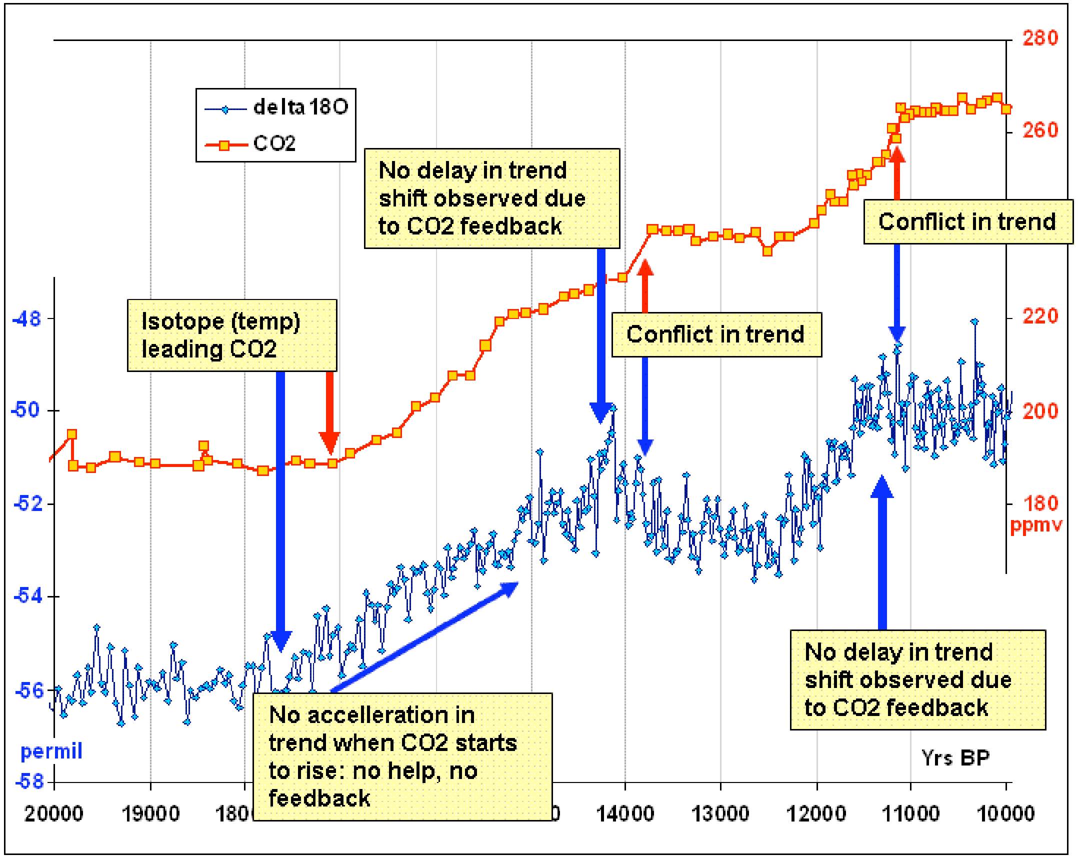


Figure 14. A summary graph of all the factors that play a role in glacial modulation. Key: Ice Volume (grey), Epica3 temperature (red), CO_2 levels (yellow), Epica3 Dust (purple), Laskar Precessional Forcing (blue), Laskar Eccentricity (black). Diagrammatic only - scales adjusted to suit the diagram. Note that there are no strong Great Summers or Great winters for at least 50 kyr into the future, and so the world is unlikely to experience another ice-age for many millennia. Image courtesy of Prof Clive Best.



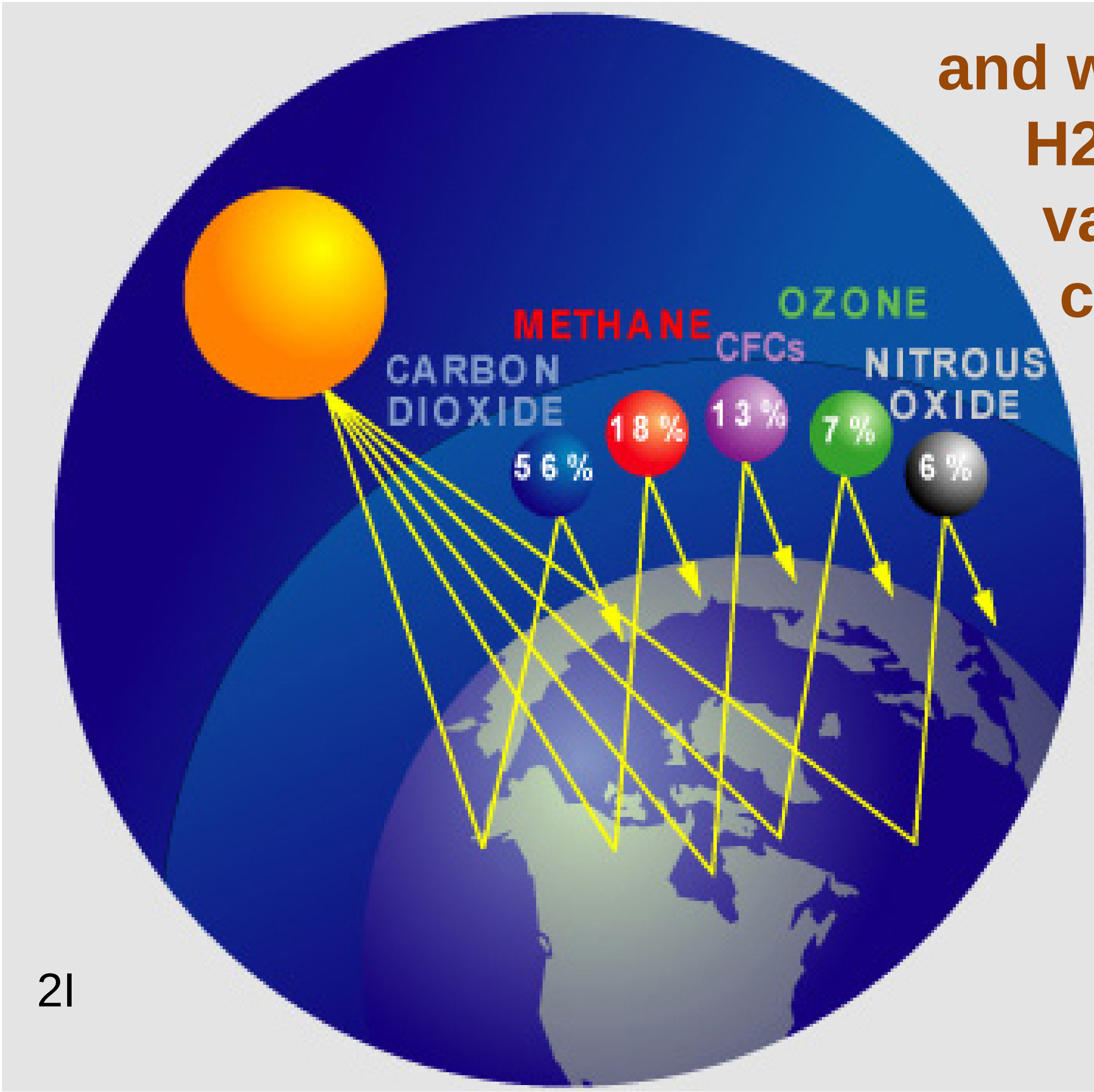
High resolution ice core analysis of the end of the last ice age: No influence from CO2 on temperature. Influence is from temperature to CO2 with 800 years delay. Ocean outgassing follows roughly CO2 solution thermodynamics. No CO2 feedback observed.

Noor van Andel

A similar opinion has been expressed by Noor van Andel

Fortunately, the Earth's surface enjoys a strong

greenhouse effect (otherwise very cold)

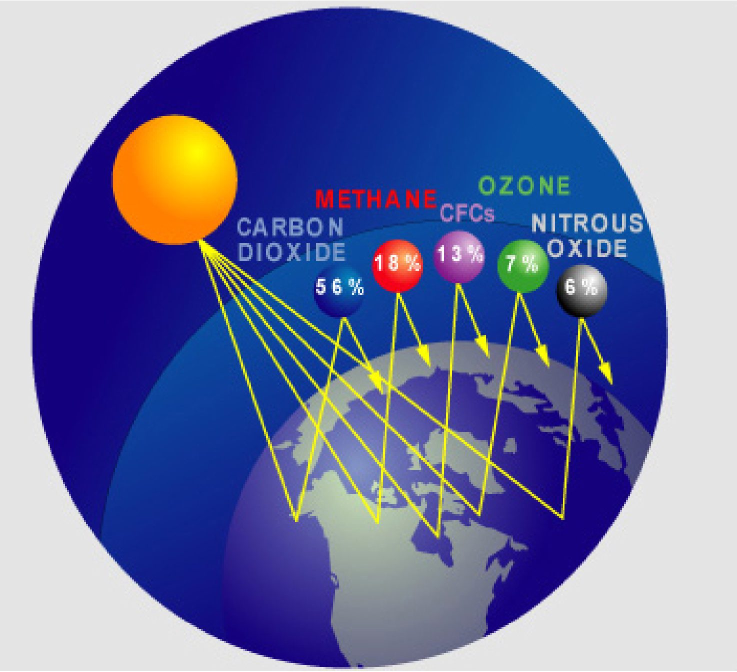


and water, $H2O$, in vapor and cloud forms.

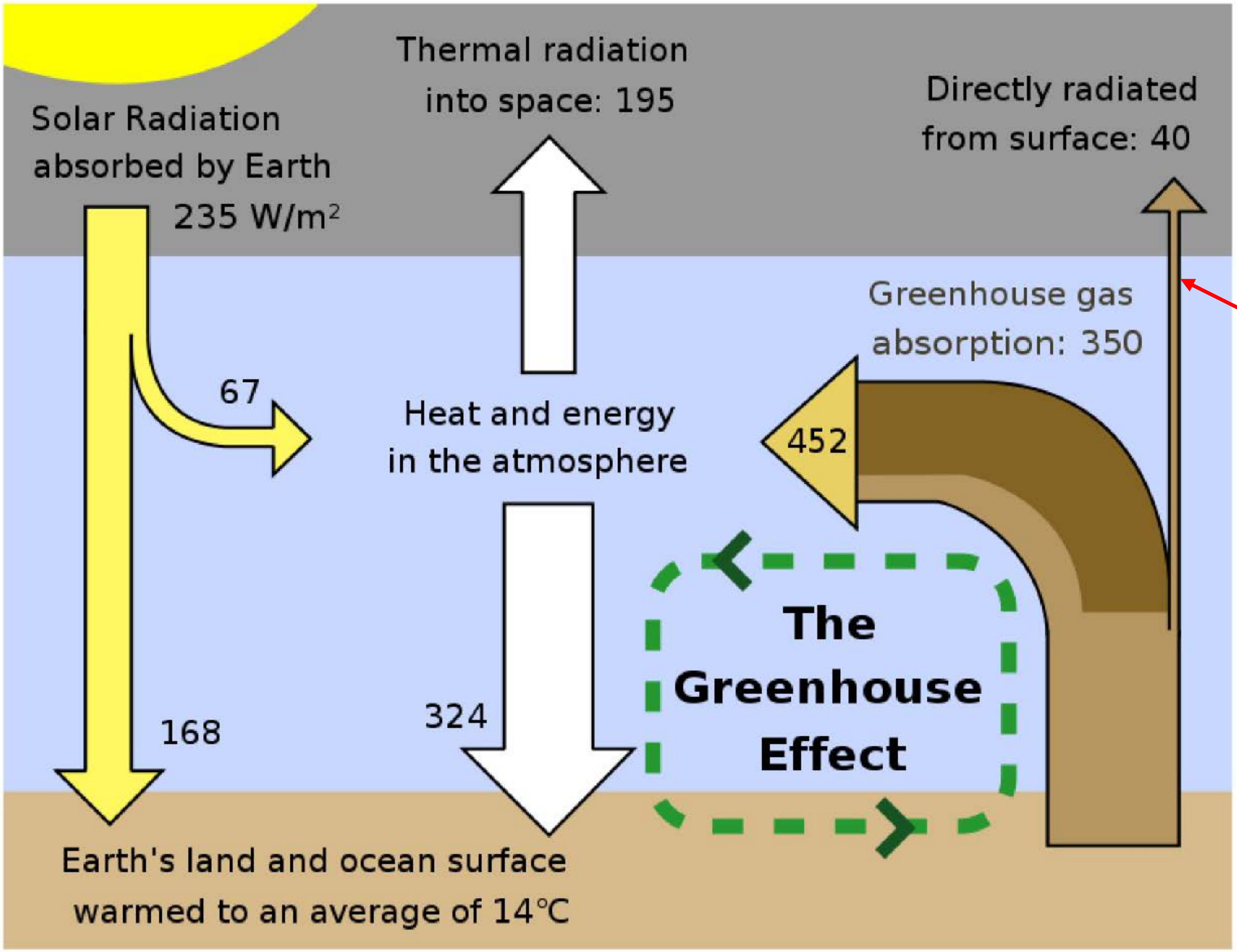
2l

greenhouse effect

1. Fluorescence of sun (6000 K UV, Vis IR)
2. Absorption by earth
3. Fluorescence of earth (260 K, IR only)
4. Absorption by atmosphere (IR only)
5. Fluorescence by atomosphere (back to earth, or space)



Greenhouse Effect



Only 10% of heat on surface is directly radiated to space, but is very important in keeping temperature low

Fluorescence of sun (6000 K : UV, Vis IR)

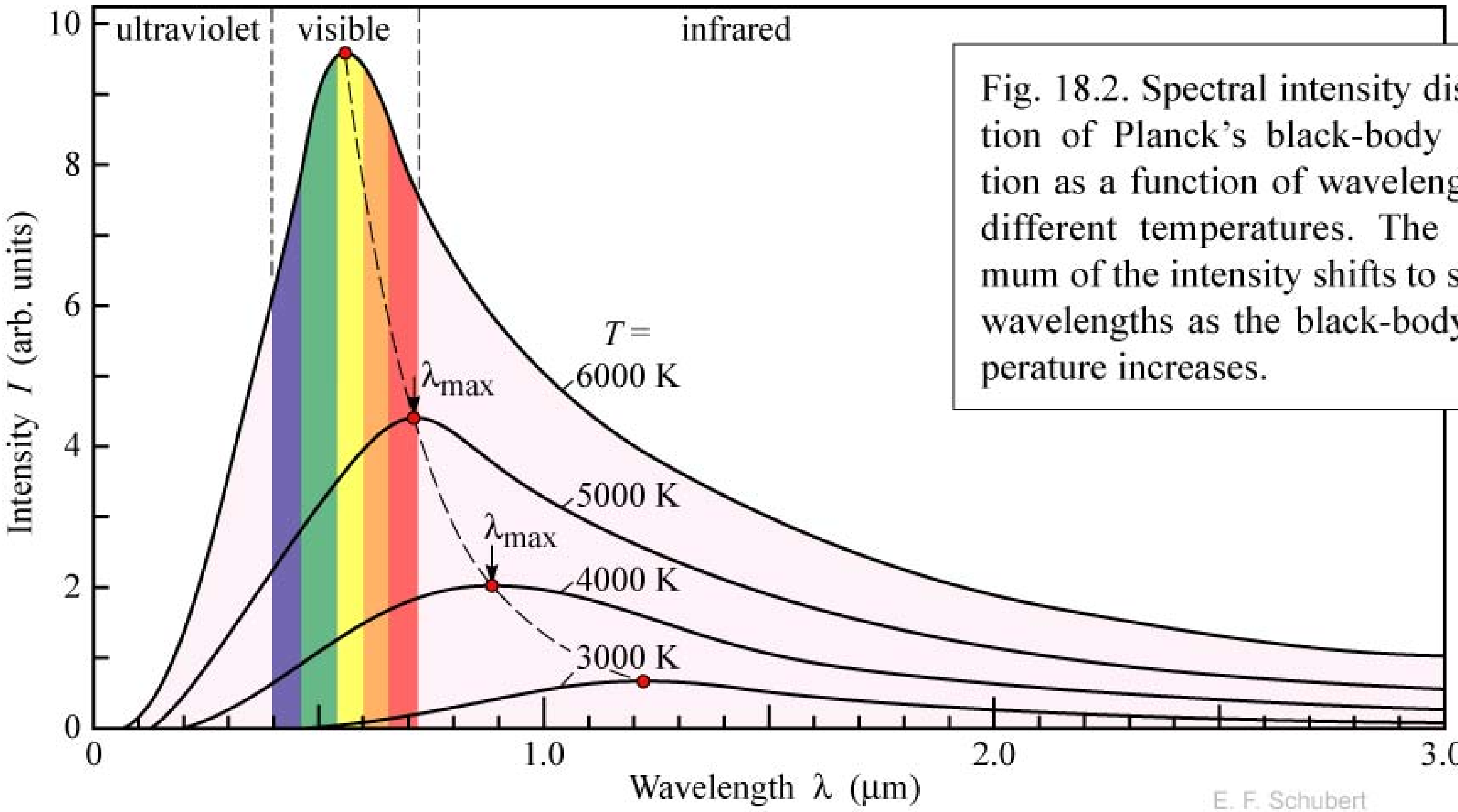
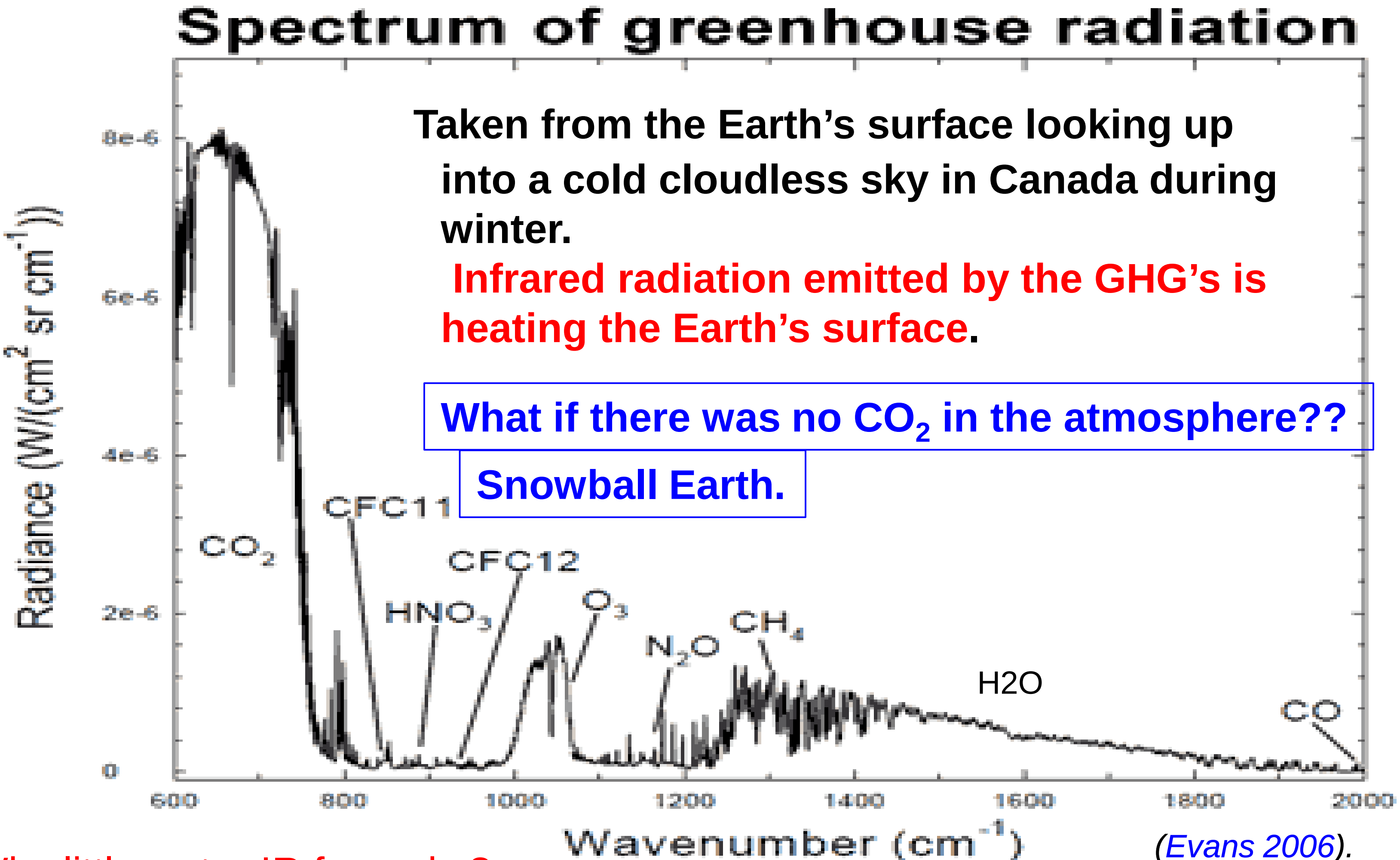


Fig. 18.2. Spectral intensity distribution of Planck's black-body radiation as a function of wavelength for different temperatures. The maximum of the intensity shifts to shorter wavelengths as the black-body temperature increases.

IR fluorescence from the atmosphere.

Evidence: looking skyward with an IR spectrometer:



Taken from the Earth's surface looking up into a cold cloudless sky in Canada during winter.

Infrared radiation emitted by the GHG's is heating the Earth's surface.

What if there was no CO_2 in the atmosphere??

Snowball Earth.

(Evans 2006).

Why little water IR from sky?

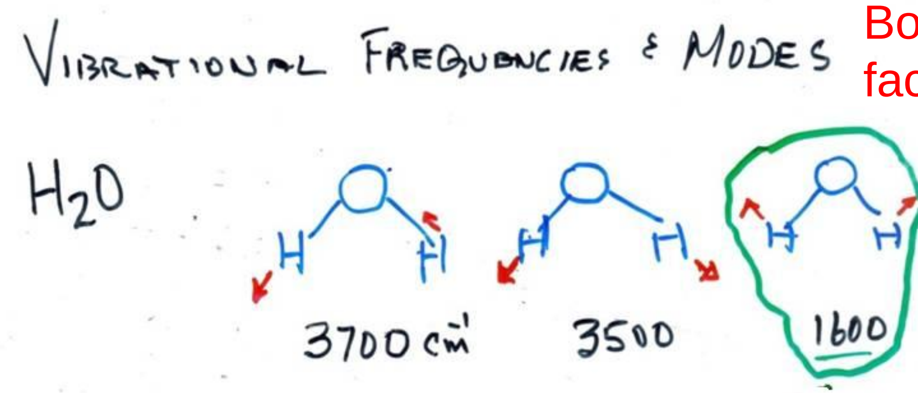
Boltzmann factors

$$CO_2 = e^{-\frac{700}{200}} = e^{-3.5} = (2.718)^{-3.5} = \frac{1}{2.718^{3.5}} = 10^{\frac{-3.5}{2.3}} = 10^{-1.5} = \mathbf{0.030}$$

$$H_2O = e^{-\frac{1600}{200}} = 10^{\frac{-8}{2.3}} = 10^{-3.5} = \mathbf{0.00034}$$

Water absorbs much infrared but **reguates itself by condensation**

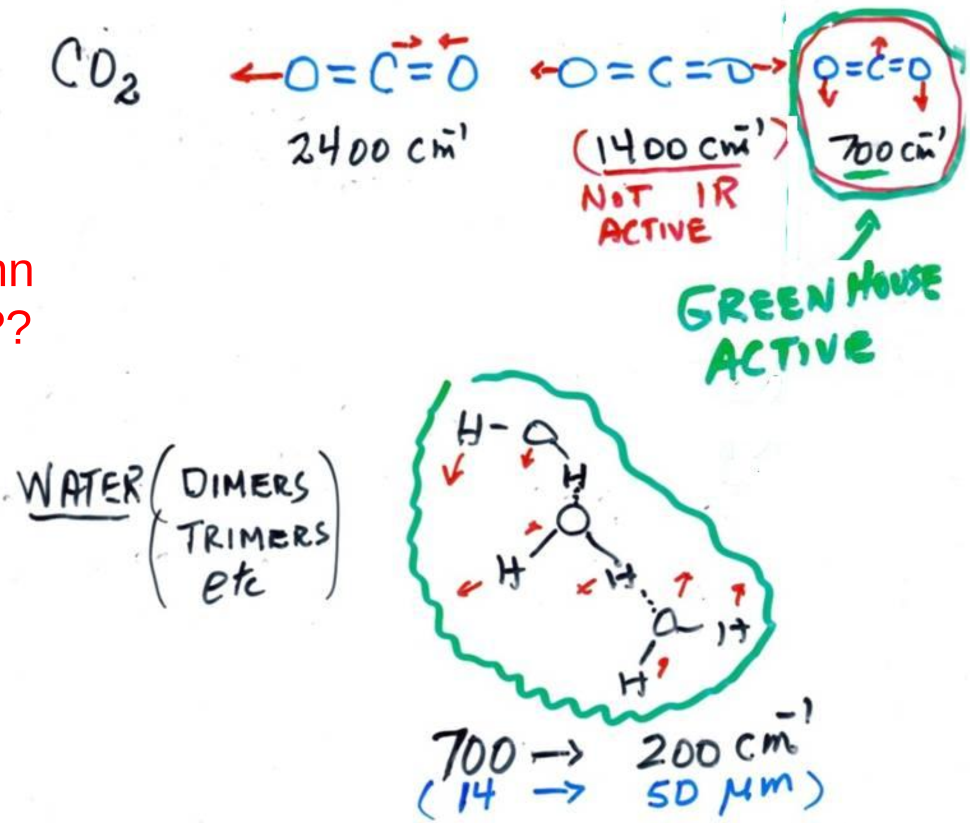
Boltzmann factors???



1/1600 c
= 6.25 r

“Greenhouse” Gases: CO2 and Methane

Boltzmann factors???



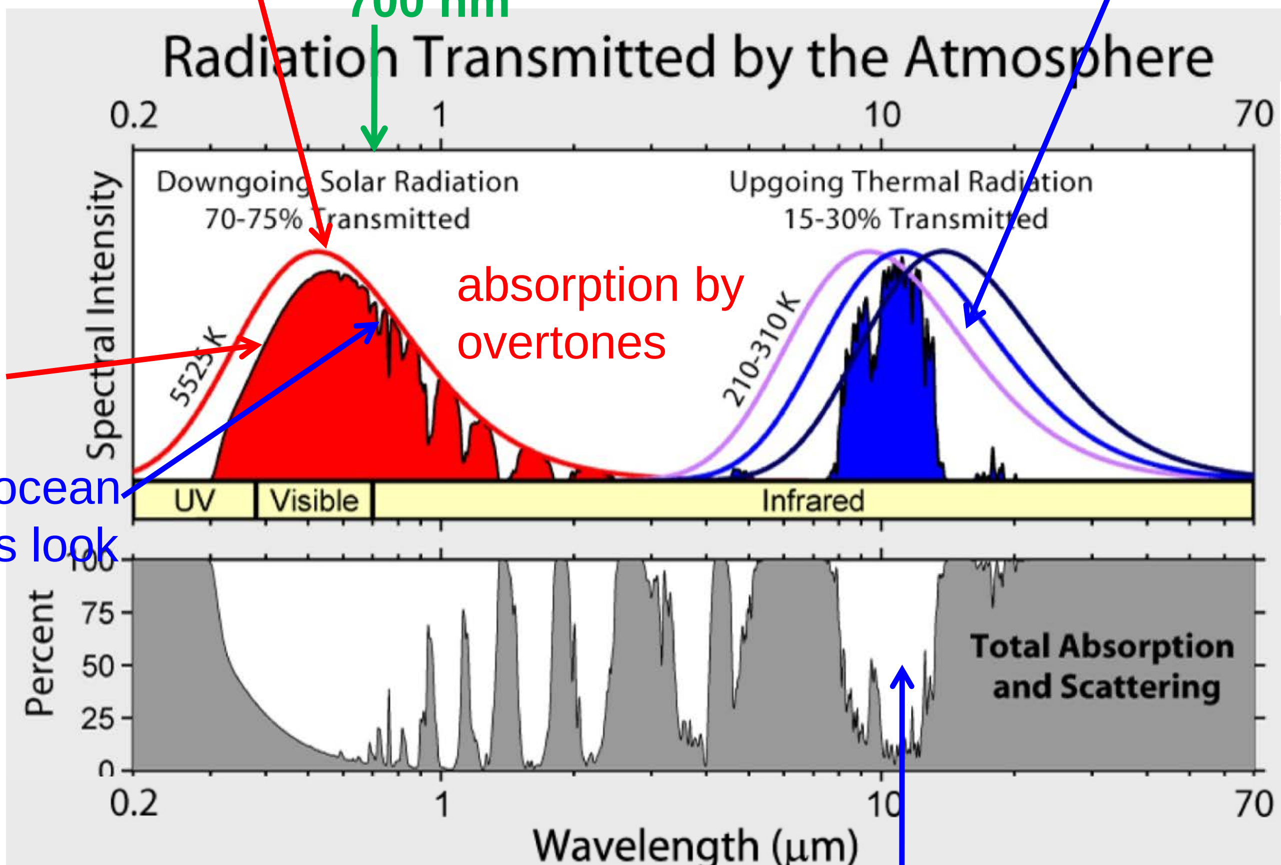
Green House Effect

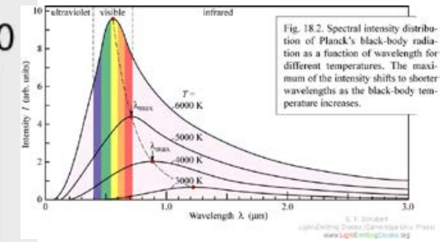
Emission Spectrum of the Sun

Emission spectra of the Earth at different places (proportional to T^4)

700 nm

Fluorescence of sun (6000 K : UV, Vis IR)





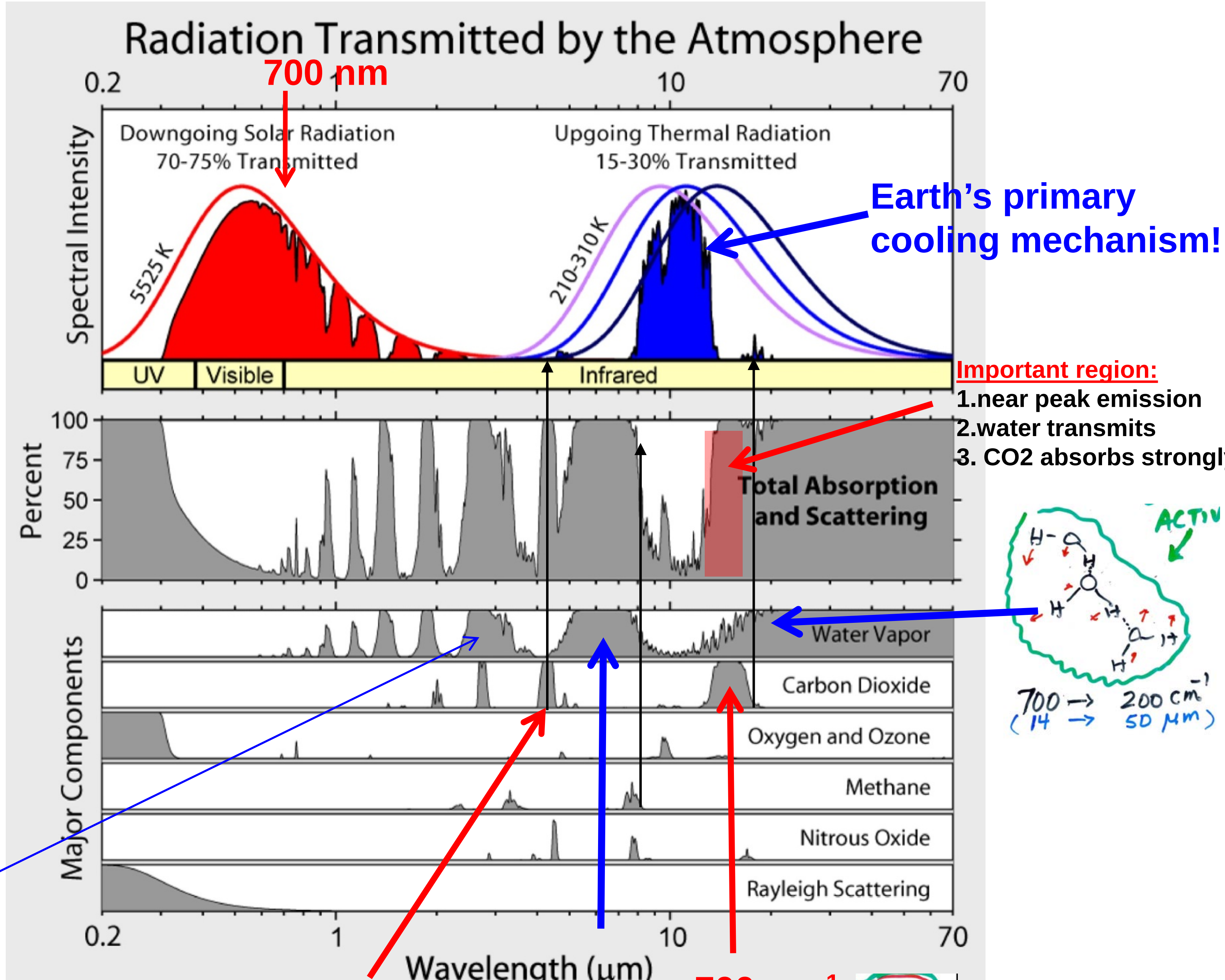
absorption by overtones

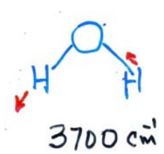
At earth surface

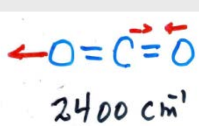
why the ocean and lakes look blue

Infrared at 10 micrometers is the only place where Earth emits <u>AND</u> no molecules absorb; ALL cooling is at this narrow band of wavelengths!

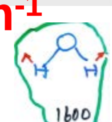
1-T%





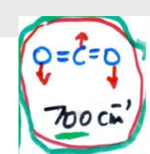


2400 cm^{-1}
CO_2



1600 cm^{-1}
H_2O 6.25 µm

700 cm^{-1}
CO_2



So, back to the bottom line:

Have temperatures increased during the last 150 years ?

These is a lot of indirect evidence concerning this question:

Courtesy: https://ericgrimsrud.org/2012/06/09/home/