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.

Light emitted by all objects not at 0 Kelviin.

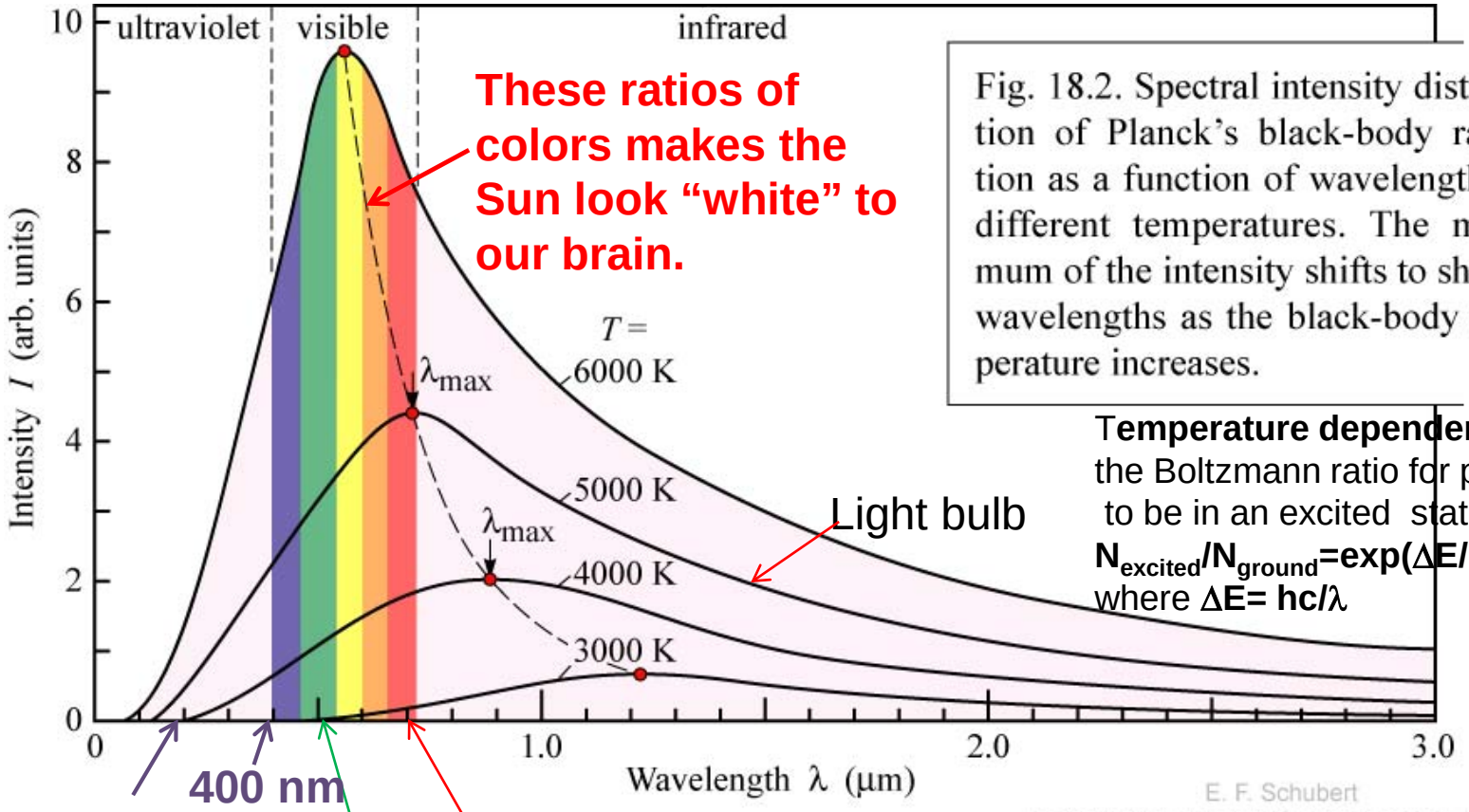


Fig. 18.2. Spectral intensity distribution of Planck's black-body radiation as a function of wavelength for different temperatures. The maximum of the intensity shifts to shorter wavelengths as the black-body temperature increases.

These ratios of colors makes the Sun look "white" to our brain.

Light bulb

T**emperature dependence** is from the Boltzmann ratio for probability to be in an excited state:
$N_{excited}/N_{ground}=\exp(\Delta E/k_B T)$,
where $\Delta E = hc/\lambda$

200 nm
Where N2 and O2 start to absorb

400 nm

500 nm

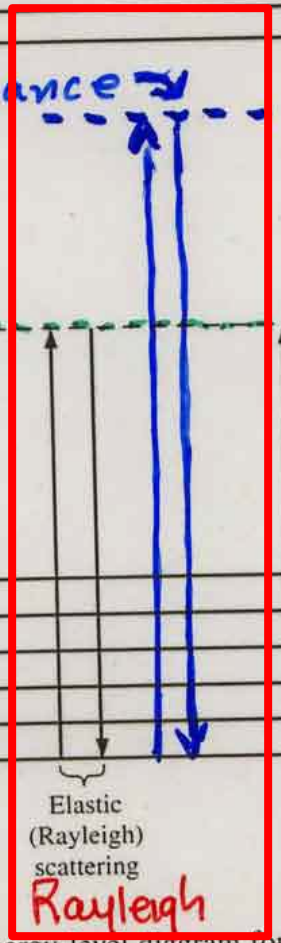
700 nm

E. F. Schubert
Light-Emitting Diodes (Cambridge Univ. Press)
www.LightEmittingDiodes.org

FIG 10.27

scattering.

Closer to resonance



Rayleigh

inelastic (Raman) scatte

ground electronic stat

tions are allowed. For elastic scatteri

equal to the frequency of the scattere

quency of the scattered light is differe

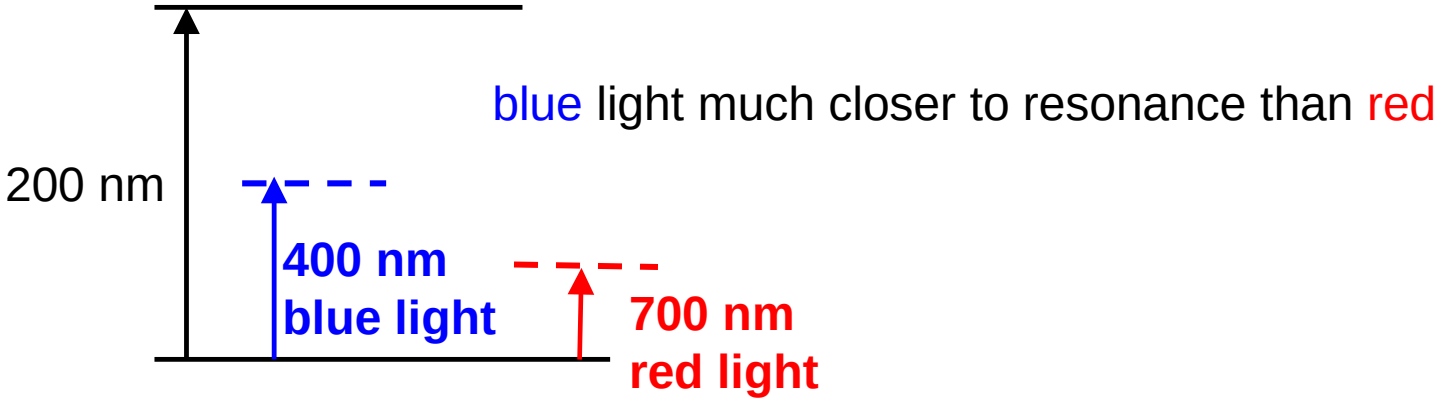
tual state shown can have any energy;

of the spectrum.

Why is the sky BLUE, but sunsets are RED?

This question may be on the Final Exam (demo with pendulums)

N_2 and O_2 are small. Therefore quantum <u>electron energy levels</u> are <u>spaced far apart</u>: They absorb at 200 nm, far in UV



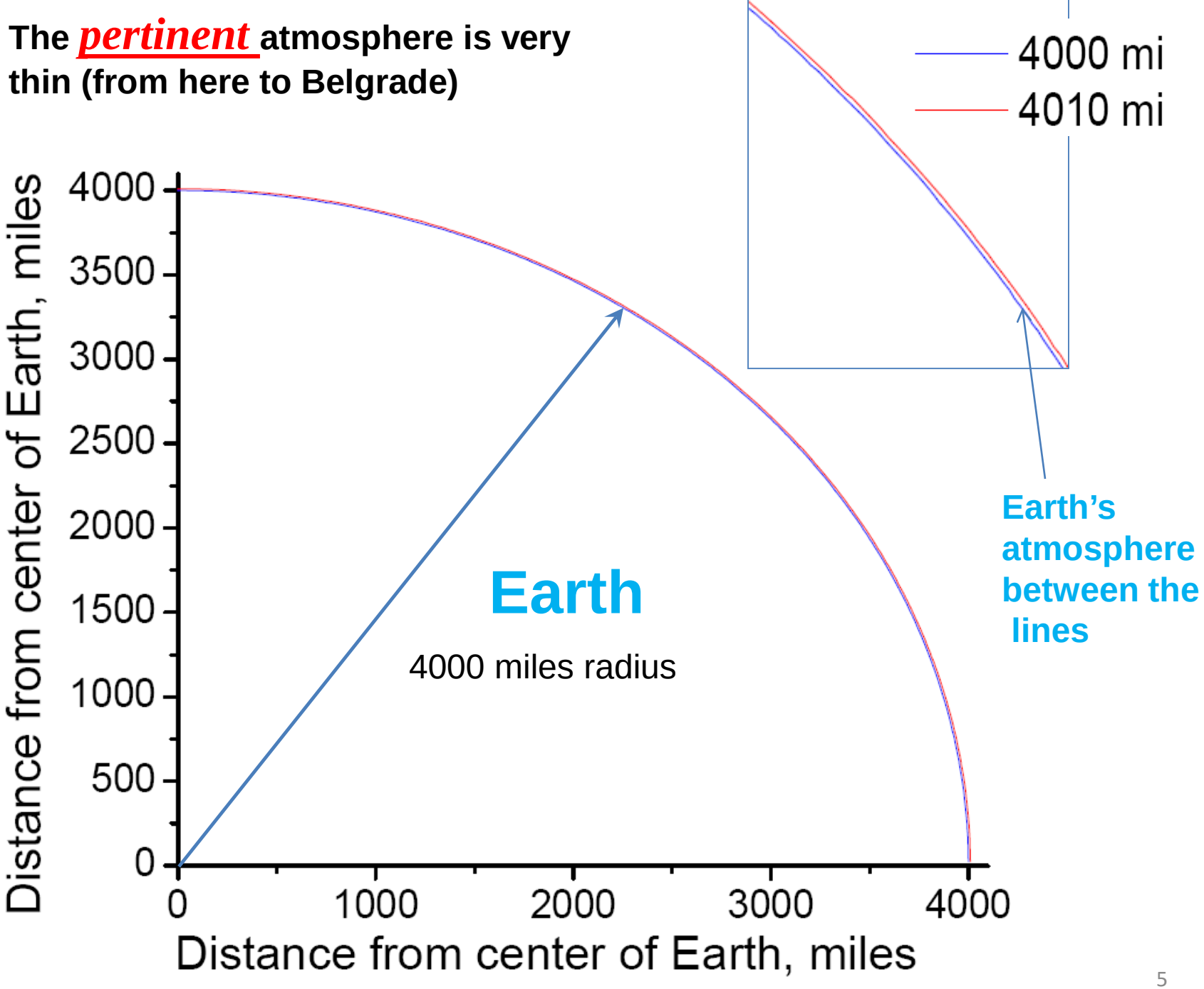
Rayleigh scattering efficiency increases as λ^{-4}

$(700/400)^4 = 9.4$

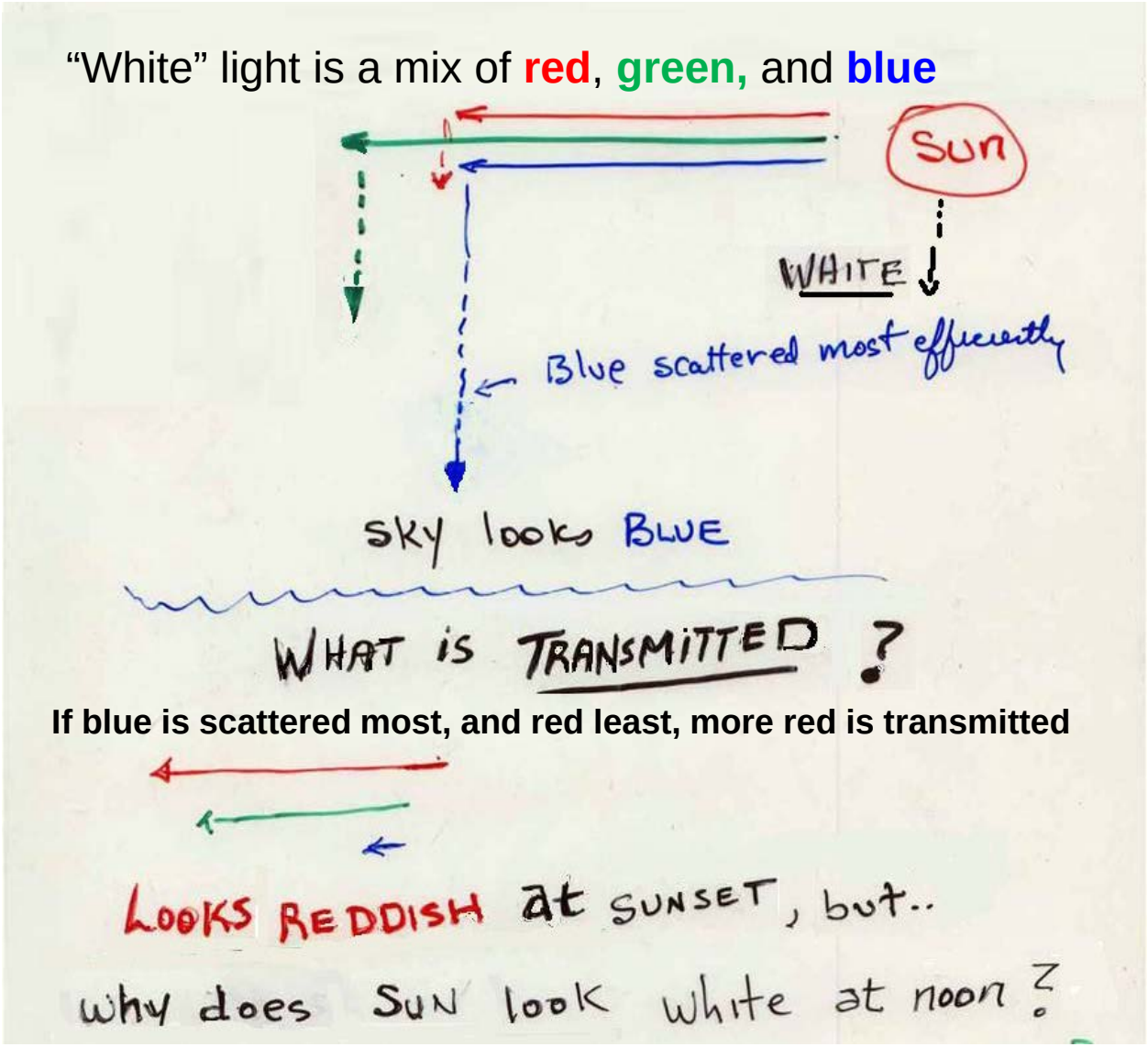
so blue light scatters far more than red;

The scattered sunlight is greatly enriched in blue

1. **The *pertinent* atmosphere is very thin (from here to Belgrade)**



Space Shuttle *Endeavour* appearing to straddle the stratosphere and mesosphere. The orange layer is the troposphere, which gives way to the whitish stratosphere and then the blue mesosphere.[14] (Why is the troposphere reddish?)



Why is steam white, but smoke and viruses are often bluish?

Selected Essentials of Climate Physical Chemistry

1. The *pertinent* atmosphere is very thin (from here to Belgrade)

2. The *pertinent* ocean is very thin (only the top layer appears to be important for the next 1000 years)

3. The CO_2 level is going to rise to much higher levels, *unless something very unexpected* is discovered. This *suggests* that temperatures will continue to rise, because CO_2 is a "greenhouse gas".

4. The Earth cools itself by fluorescing infra-red radiation in the region of 10 μm (1000 cm^{-1})—just where water molecules do not absorb.

5. "Greenhouse" in this context means that CO_2 (also CH_4) absorbs IR in this same " frequency window of cooling", thereby intercepting radiation that would have left the planet, and sending some of it back to earth.

6. The Arctic ice has been melting for 10,000 years. This was not caused by humans, but we may be hastening the process now. --Callis

Selected slides on climate change, greenhouse effect, and global warming

Links:

http://www.aip.org/history/climate/index.htm#contents

http://www.aip.org/history/climate/summary.htm

http://www.aip.org/history/climate/co2.htm

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

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

ericgrimsrud

On the science and implications of climate change

http://ericgrimsrud.org/

http://ericgrimsrud.org/scientific-basics/

Our Atmosphere and its Essential Functions

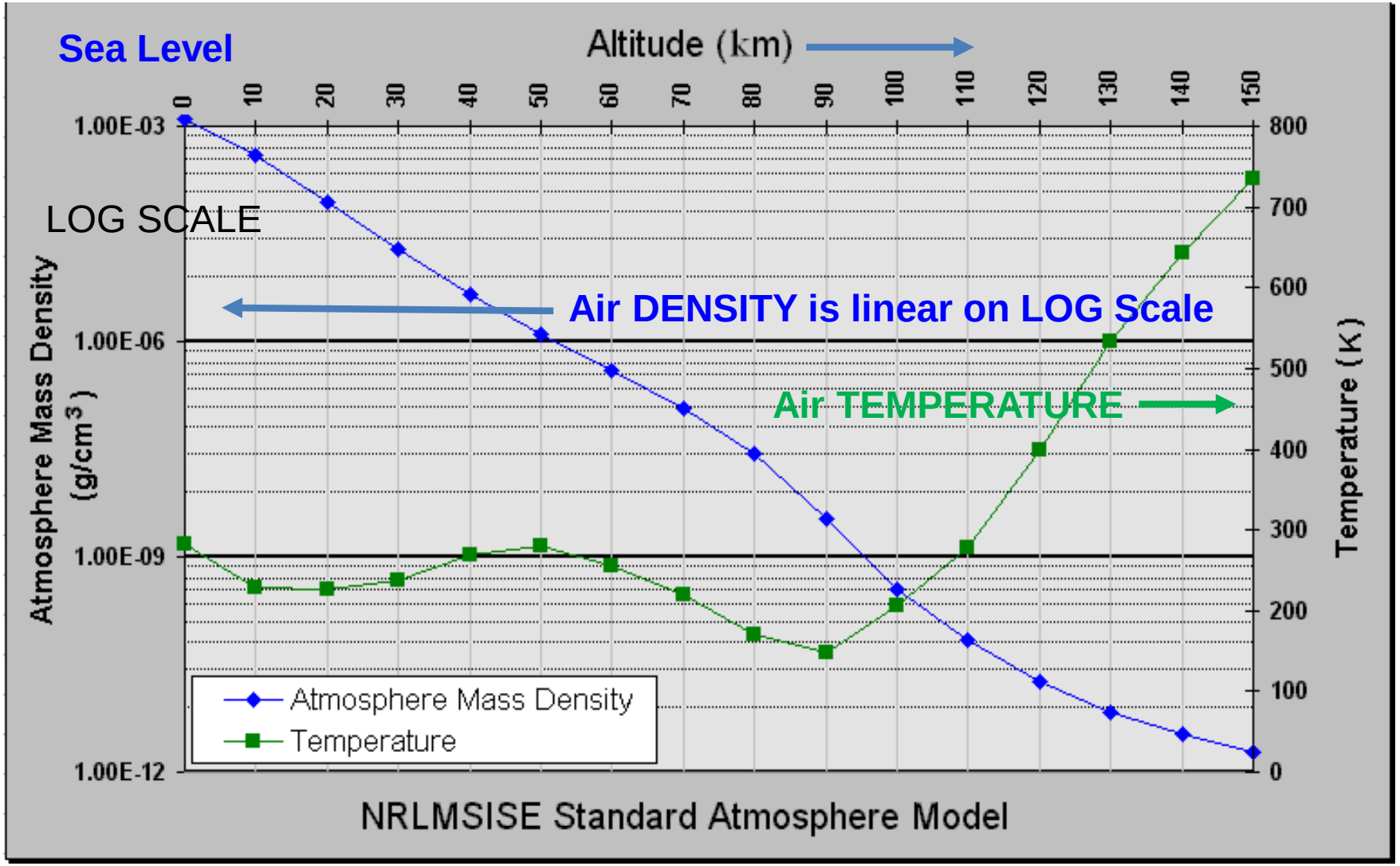
(1) filters out UV light
(2) regulates surface temperatures
(3) cleans itself
(4) others?

Note: **The atmosphere is not very deep!**

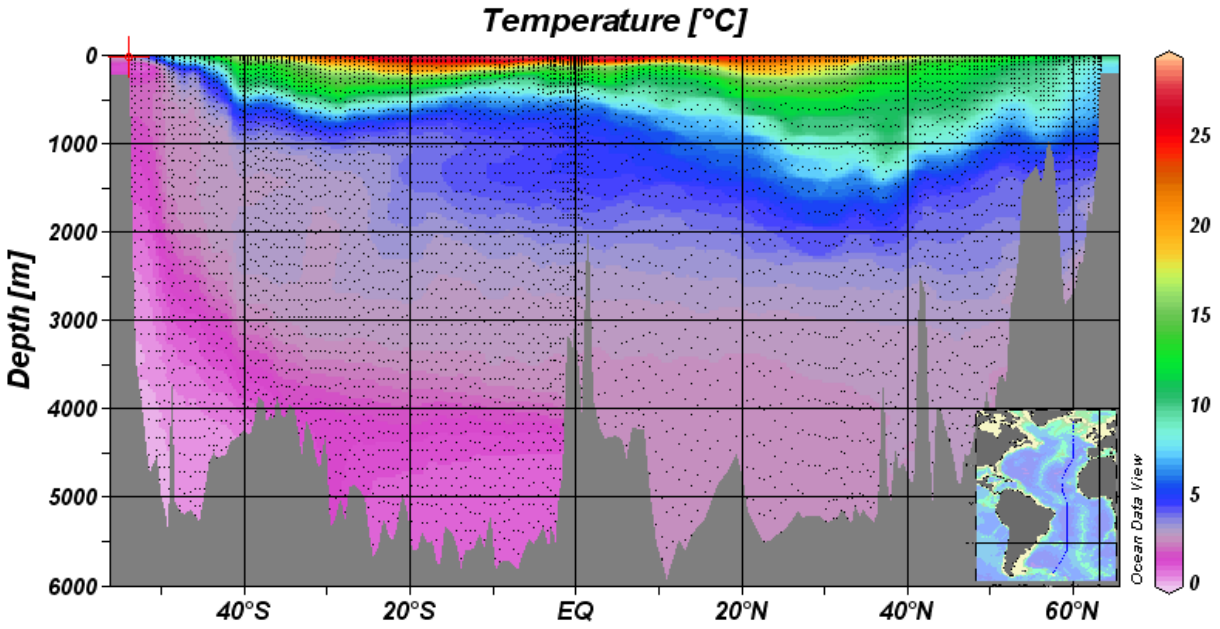
Air pressure **halves every 3.4 mi**

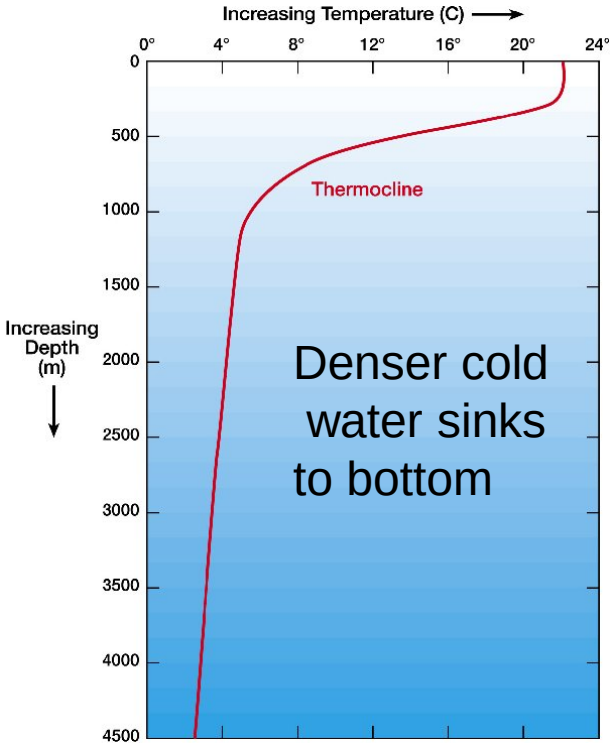
1 bar at sea level
0.5 bar at 3.4 miles
0.25 bar at 6.8 miles
0.125 bar at 10.2 miles
(About the distance to Belgrade)

The Atmosphere is layered



The Ocean is layered

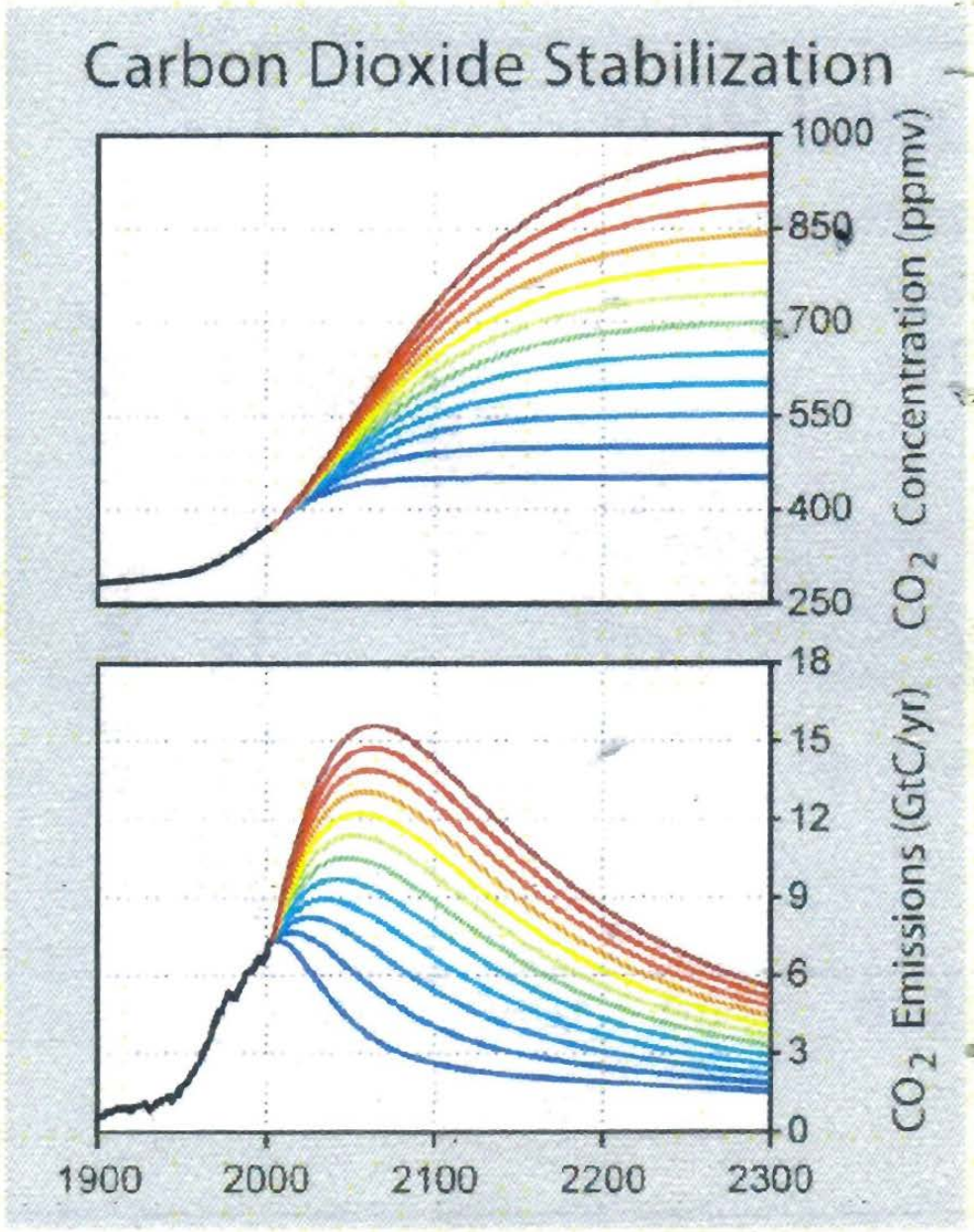




This is a simple temperature-depth ocean water profile. You can see temperature **decreases with increasing depth**.

Mixing of the thin top layer with the vast deeper bulk takes **~1000 years!**

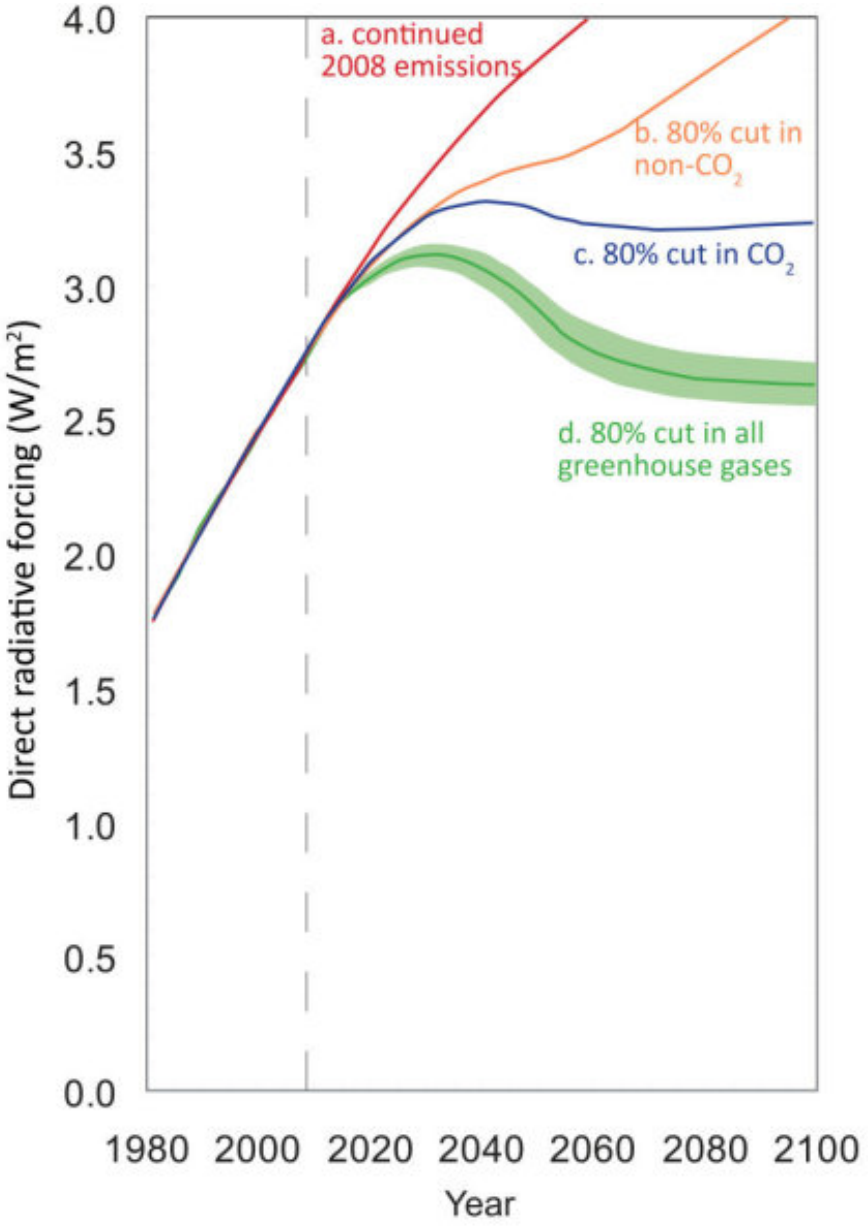
Windows to the Universe original image



NOTE:

The CO2 "overload" due to the extra CO2 put into the biological cycle by the combustion of fossil fuels has a very long lifetime, on the order of a millennium.

What we decide to do in the coming decades is likely to last for a millennium. That is essentially "forever" on the time scale of western civilization.



Science News
from research organizations

Long-term Stabilization Of Carbon Dioxide In Atmosphere Will Require Major Cuts In Emissions

Date:

November 3, 2008

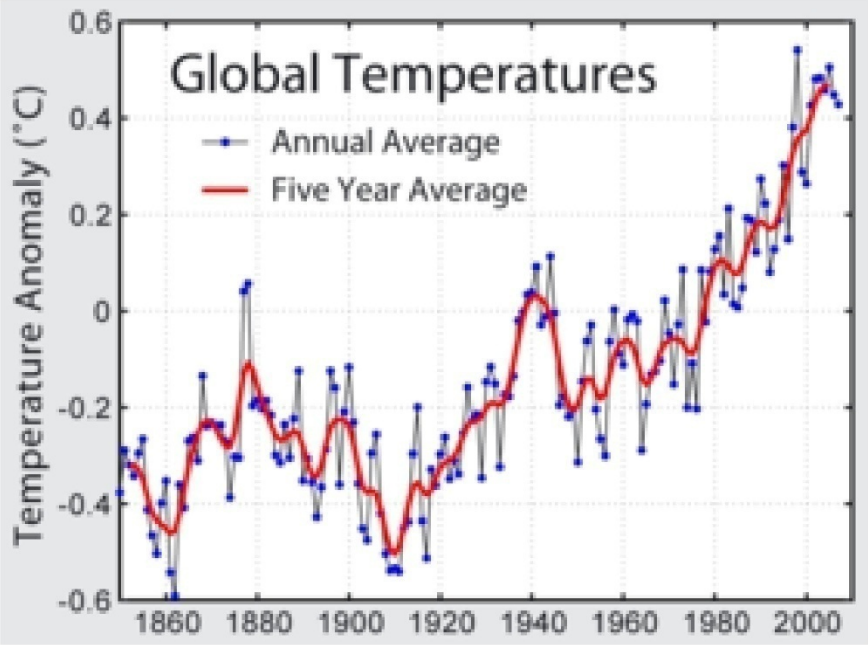
Source:

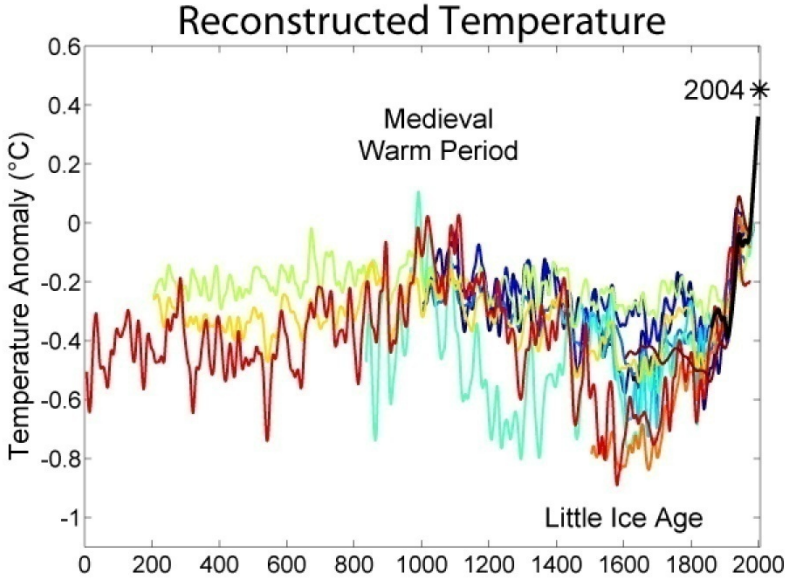
Natural Environment Research Council (NERC)

Summary:

Carbon dioxide, the greenhouse gas that has had the largest impact on our climate, will continue to rise even if current national and international targets for reducing emissions are met, scientists warn.

But, they say, strong action taken now – such as the 80% target recently announced by the UK government – will continue to have be


Global Temperatures
Annual Average
Five Year Average
Temperature Anomaly (°C)
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
1860
1880
1900
1920
1940
1960
1980
2000

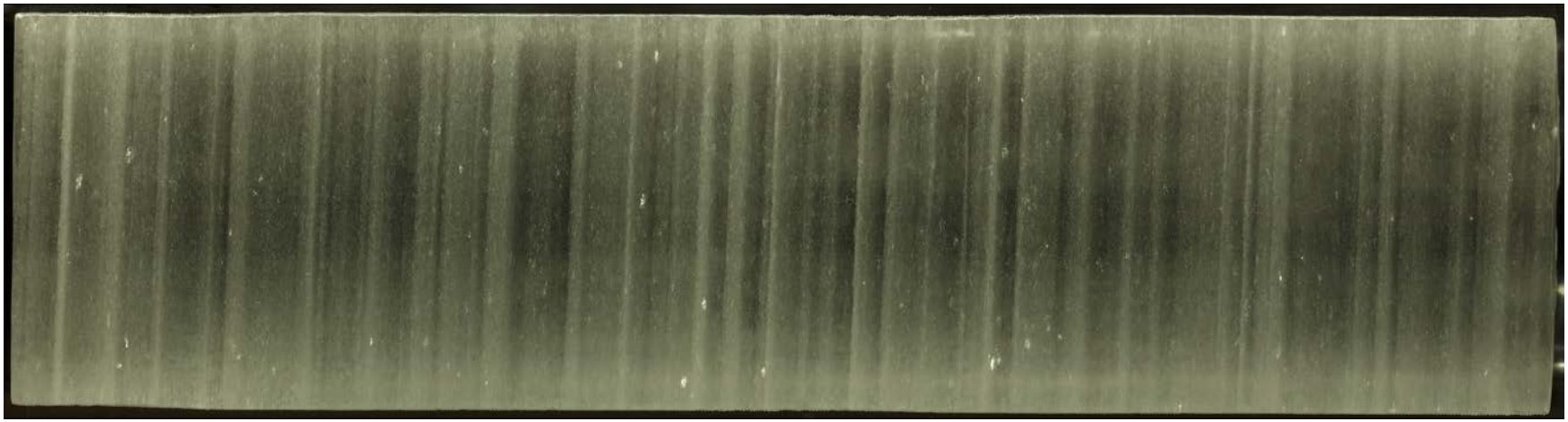

Reconstructed Temperature
2004
Medieval
Warm Period
Little Ice Age
Temperature Anomaly (°C)
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1
0
200
400
600
800
1000
1200
1400
1600
1800
2000

The Ice Core Record of Antarctica and Greenland

4C

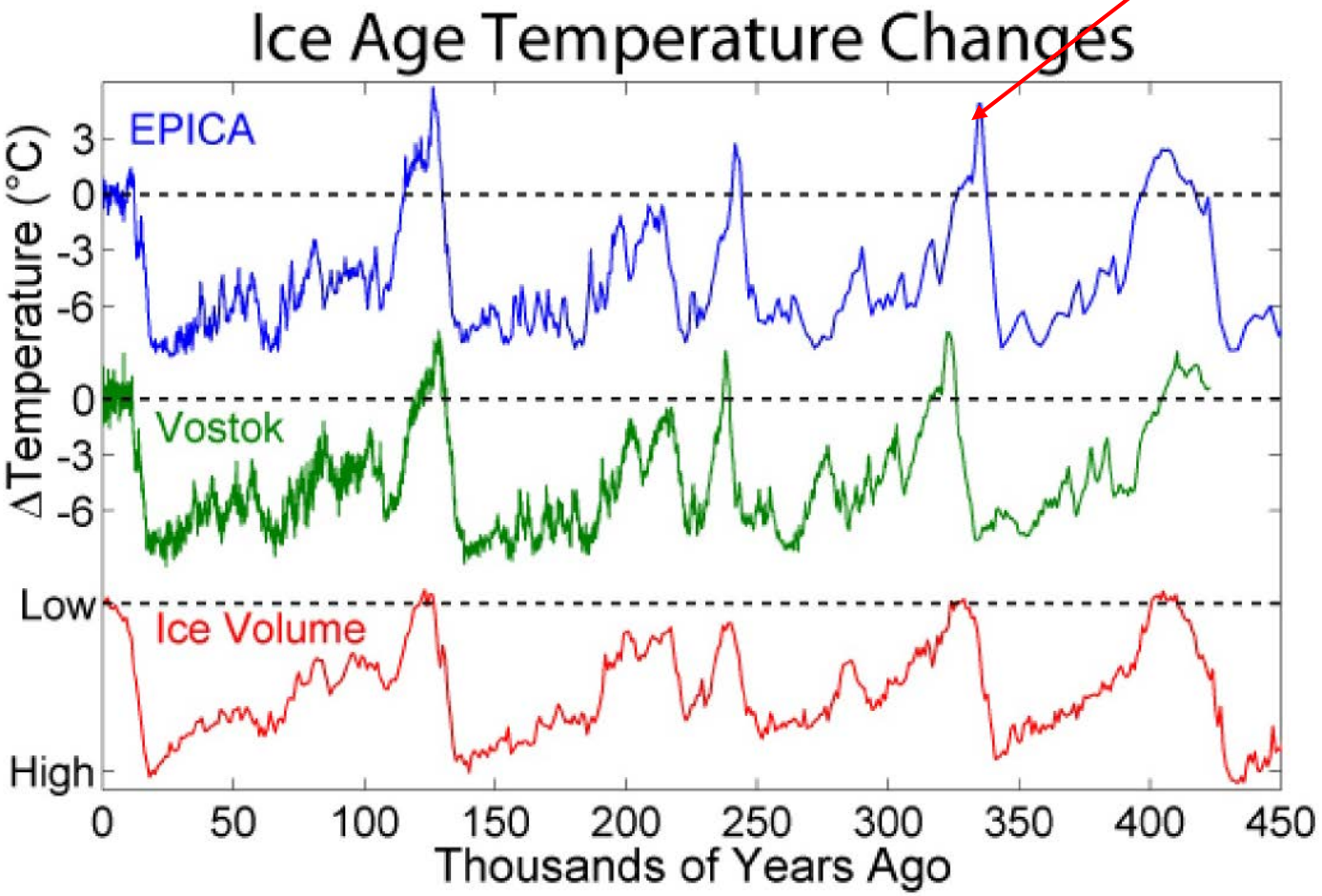
ice core samples provide a record of the previous 800,000 years

- Taken from both Greenland and Antarctica
- Gases trapped in bubbles include CO2, CH4, and N2O
- Deuterium content in water indicates Temperature
  (that is DHO content in H2O)



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

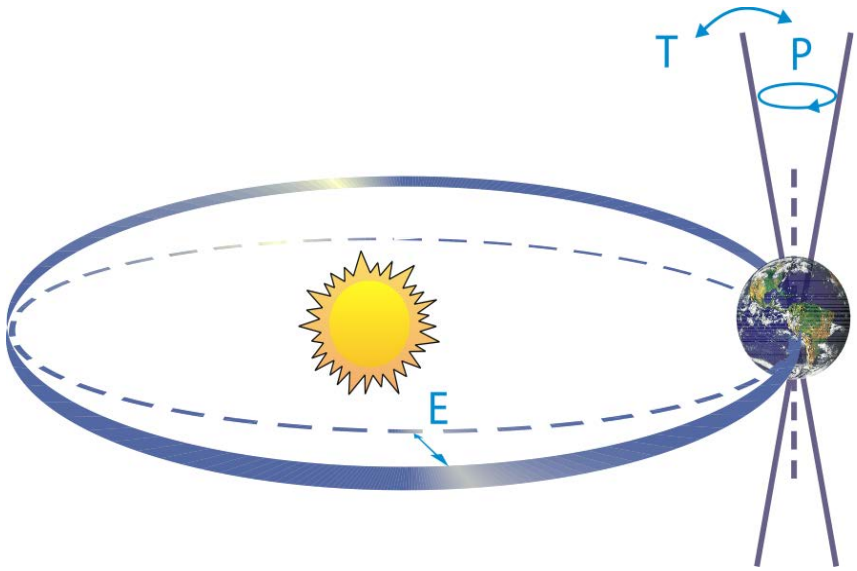
Note the “fast” (1000 year) temperature rise and melting near the peaks



The glacial / interglacial cycles

(a theory proposed in the 1920's)

the Milankovitch cycles



E - distance from sun

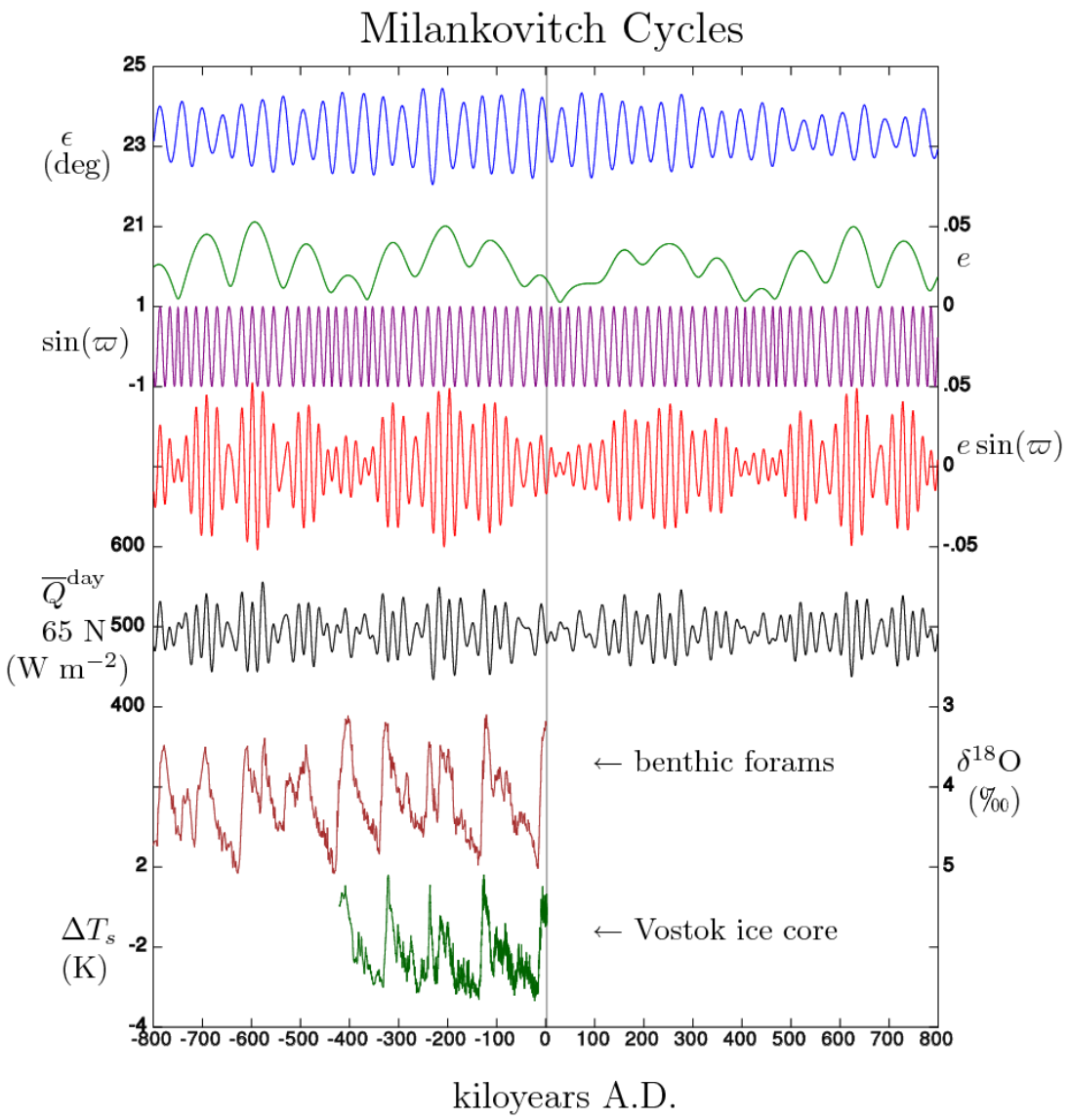
T - magnitude of tilt

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.**

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.

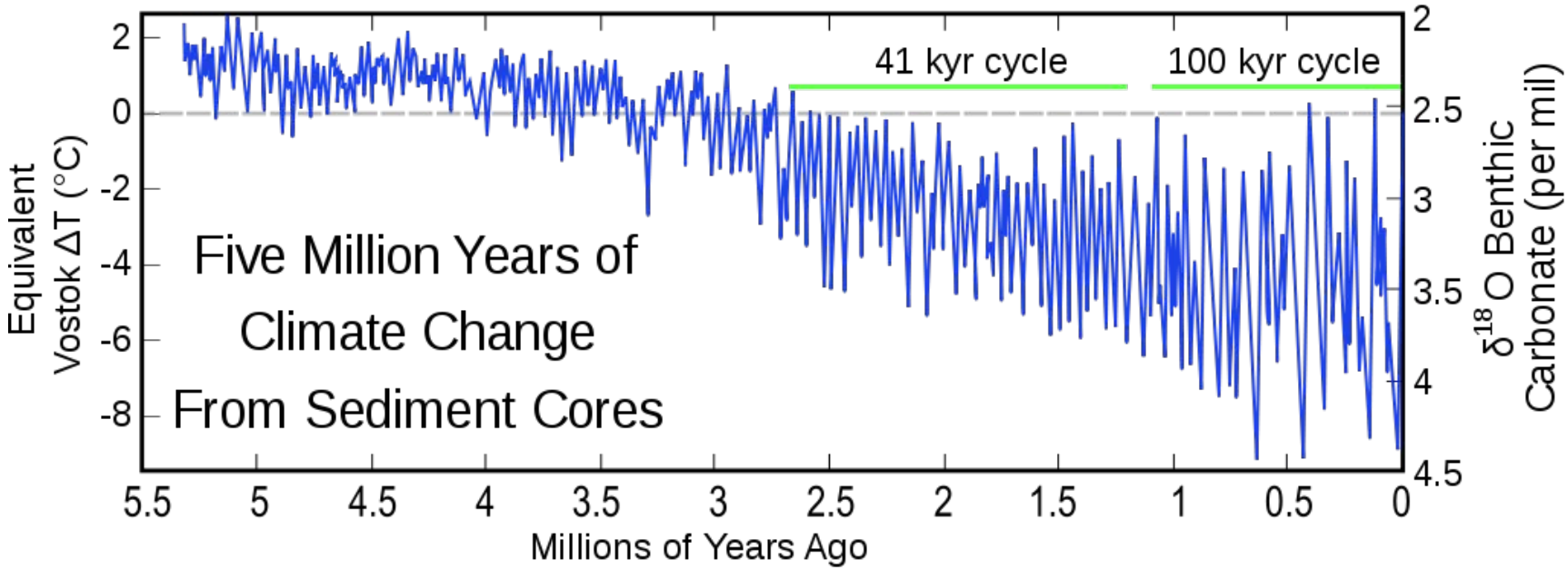
— ϖ is longitude of perihelion.

— *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.



Because of their diversity, abundance, and complex morphology, fossil foraminiferal assemblages are useful for biostratigraphy, and can accurately give relative dates to sedimentary rocks. The oil industry relies heavily on microfossils such as forams to find potential hydrocarbon deposits.[26]

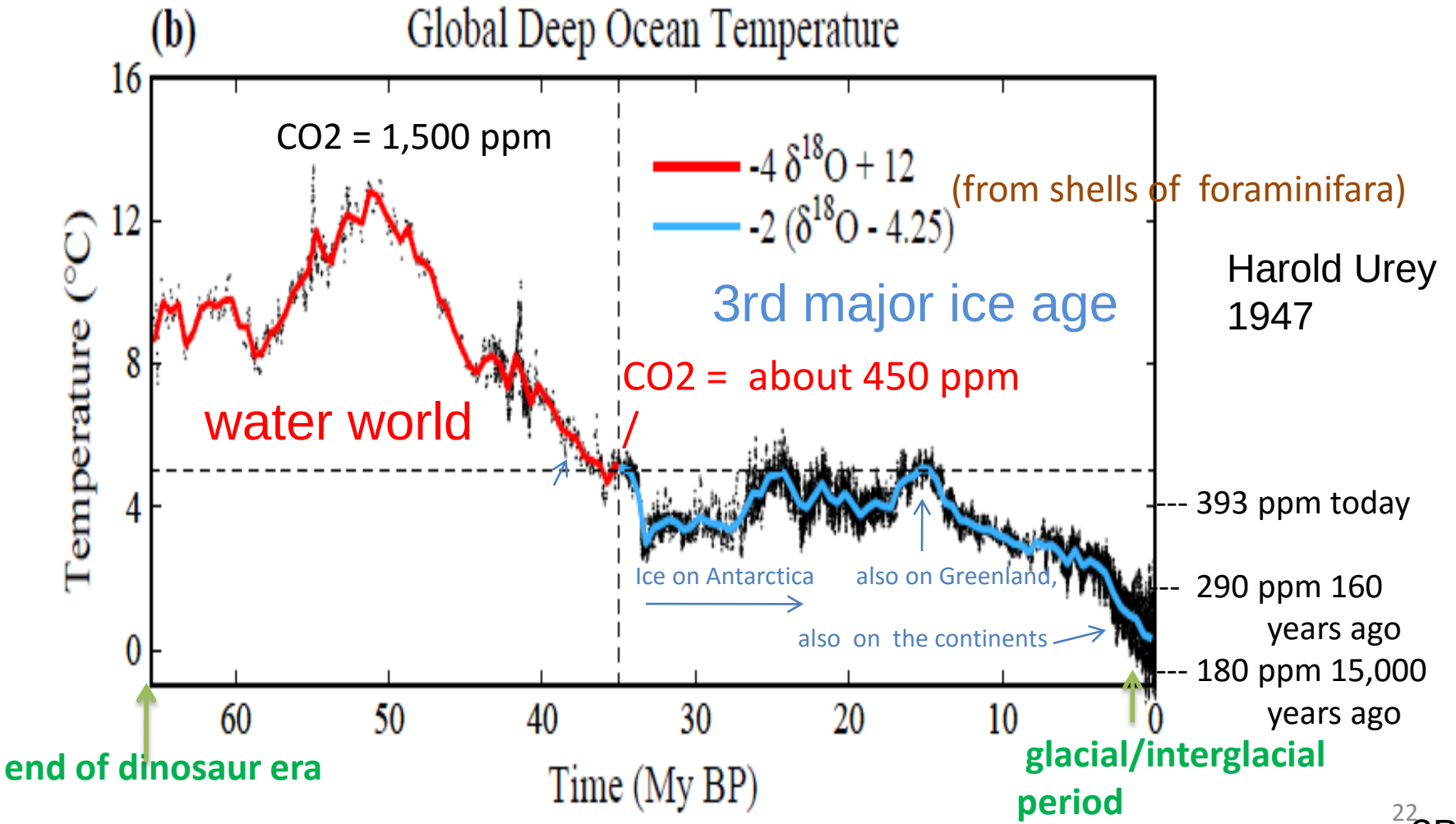
Calcareous fossil Foraminifera are formed from elements found in the ancient seas they lived in. Thus they are very useful in paleoclimatology and paleoceanography. They can be used to reconstruct past climate by examining the stable isotope ratios and trace element content of the shells (tests). Global temperature and ice volume can be revealed by the isotopes of oxygen, and the history of the carbon cycle and oceanic productivity by examining the stable isotope ratios of carbon;[27] see δ18O and δ13C. The concentration of trace elements, like magnesium (Mg),[28] lithium (Li)[29] and boron (B),[30] also hold a wealth of information about global temperature cycles, continental weathering and the role of the ocean in the global carbon cycle. Geographic patterns seen in the fossil records of planktonic forams are also used to reconstruct ancient ocean currents. Because certain types of Foraminifera are found only in certain environments, they can be used to figure out the kind of environment under



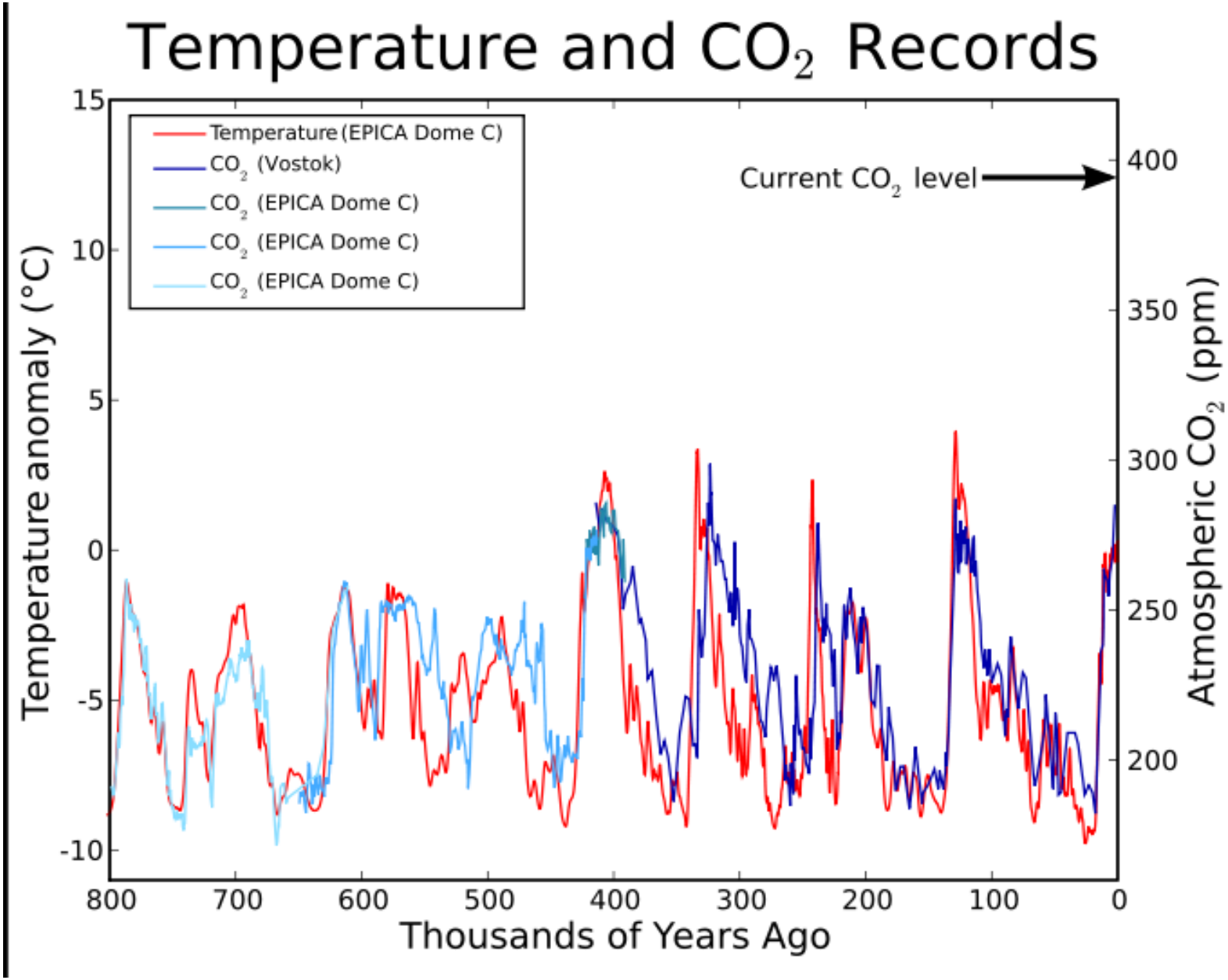


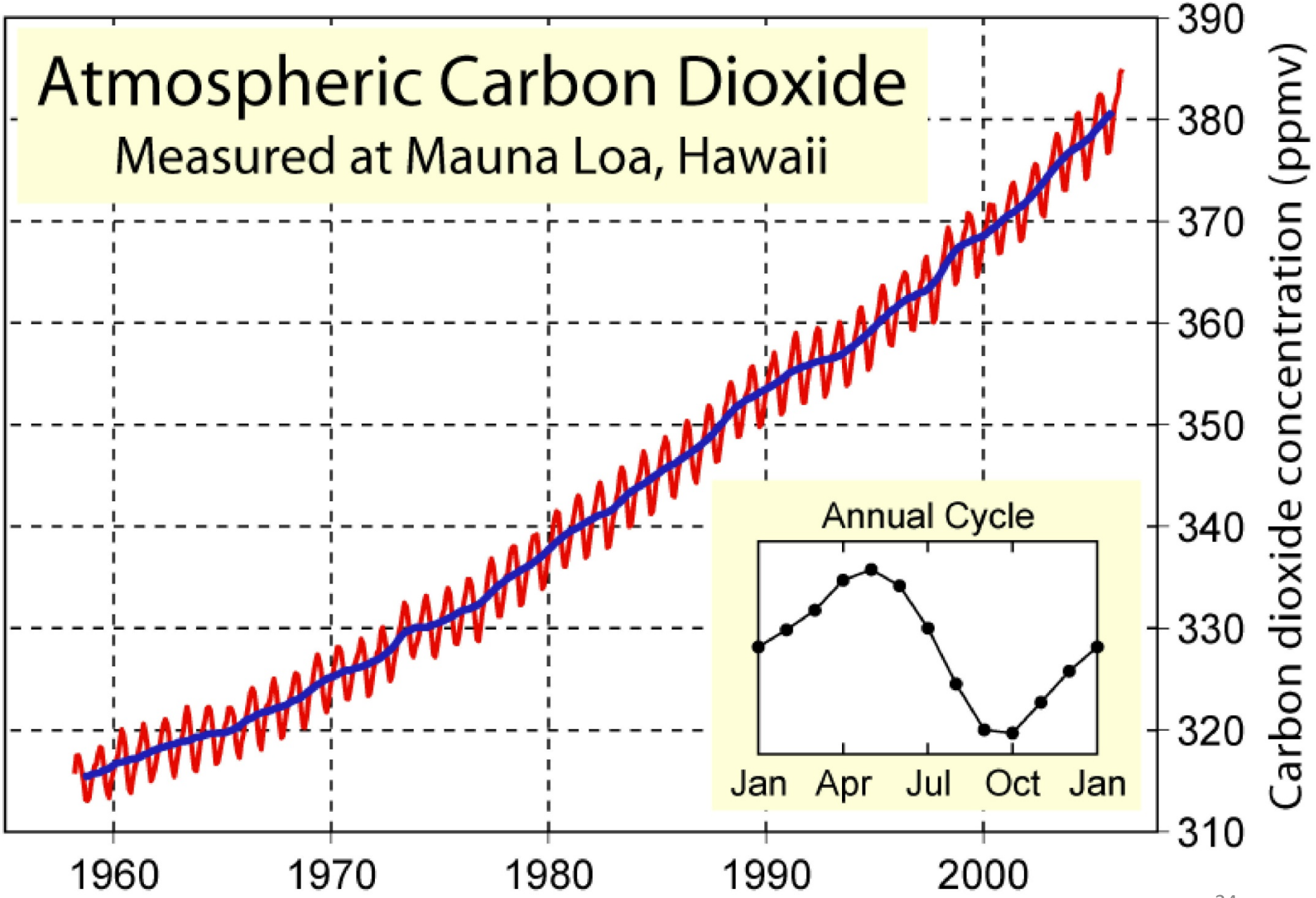
The Earth's temperature record of last 65 Myears

(the Cenozoic Period - from ocean bottom core samples)

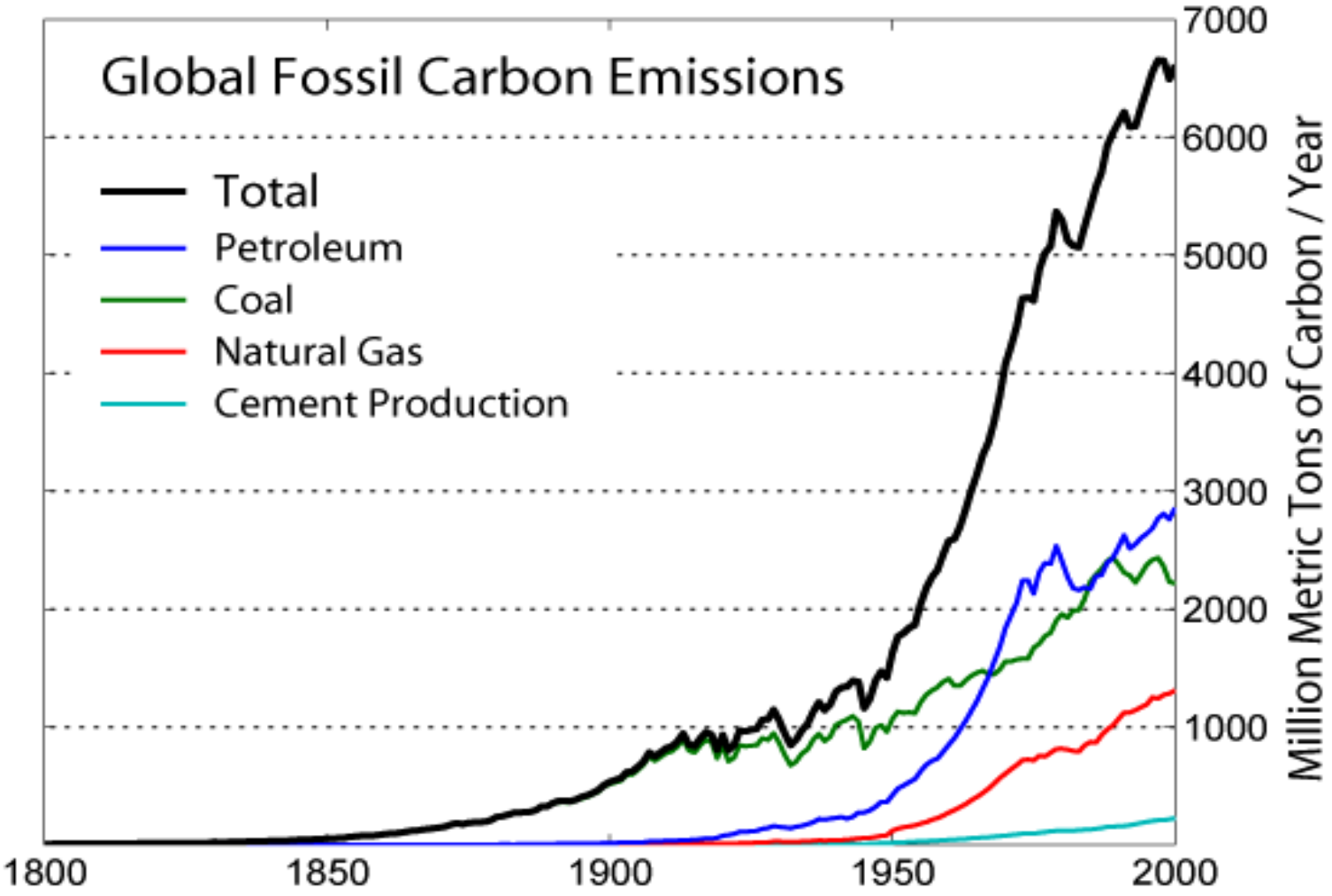


3B

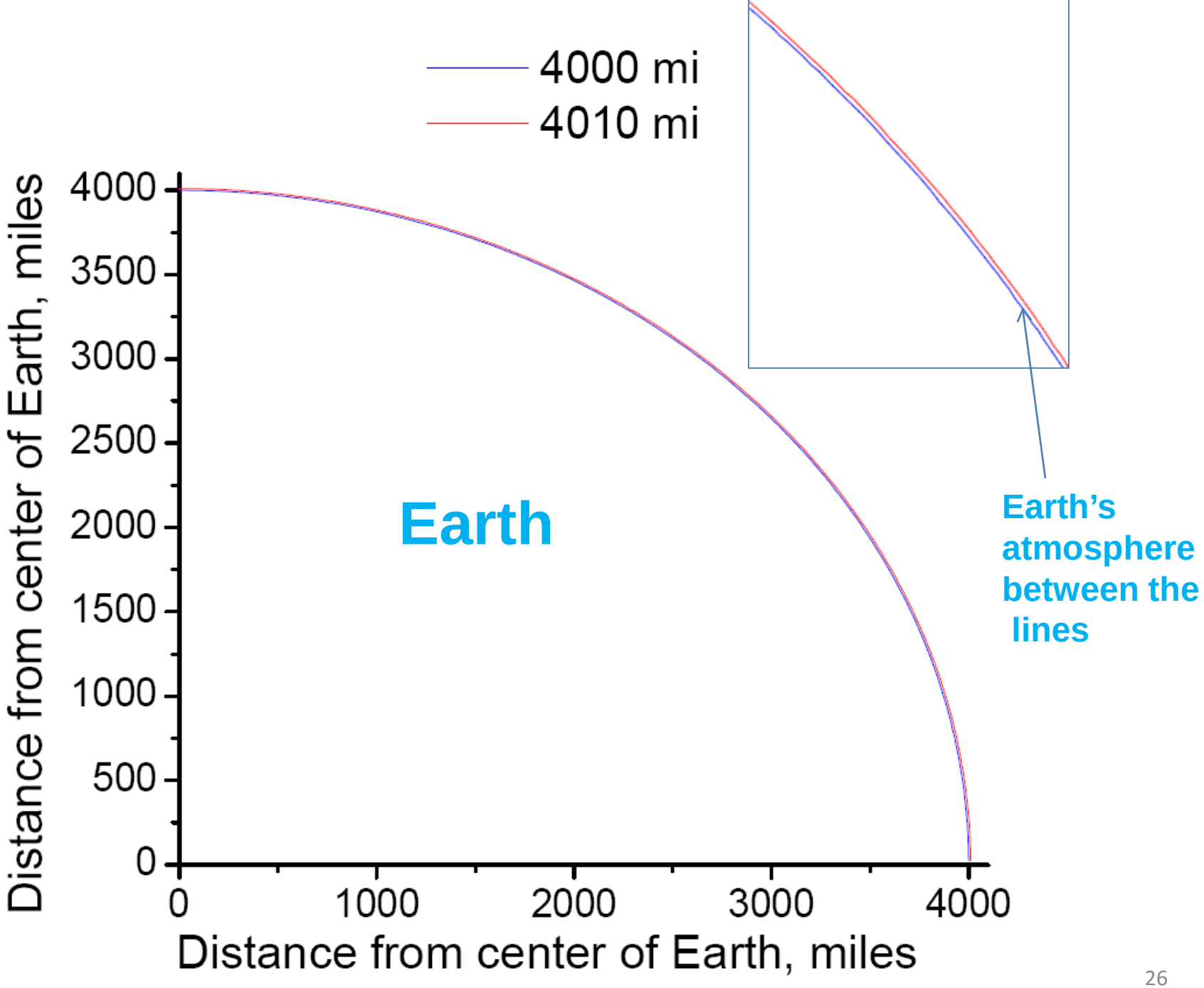

Temperature and CO_2 Records
Temperature (EPICA Dome C)
CO_2 (Vostok)
CO_2 (EPICA Dome C)
CO_2 (EPICA Dome C)
CO_2 (EPICA Dome C)
Current CO_2 level
Temperature anomaly (°C)
Atmospheric CO_2 (ppm)
Thousands of Years Ago
15
10
5
0
-5
-10
400
350
300
250
200
800
700
600
500
400
300
200
100
0

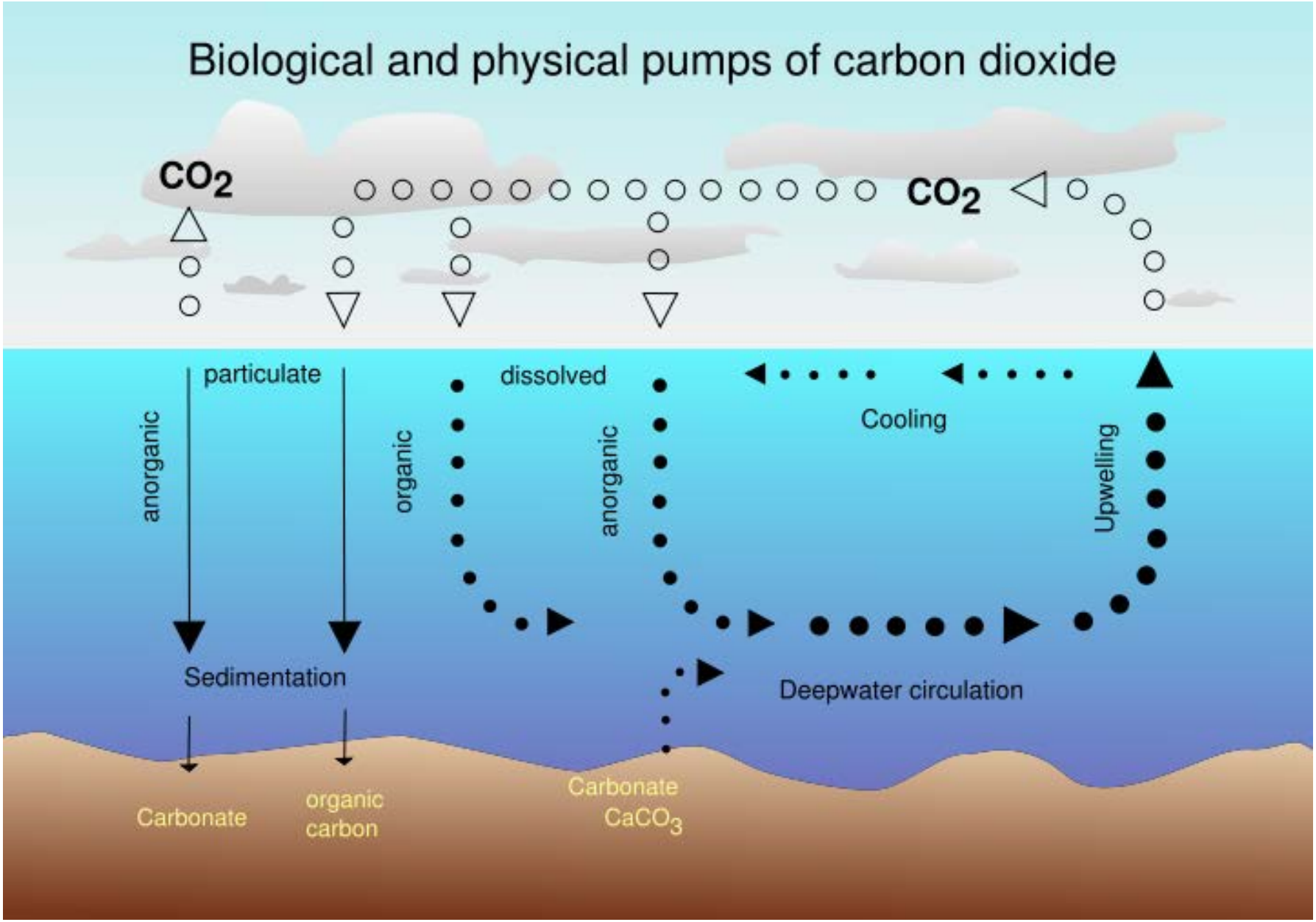

Atmospheric Carbon Dioxide
Measured at Mauna Loa, Hawaii
Annual Cycle
Jan
Apr
Jul
Oct
Jan
1960
1970
1980
1990
2000
310
320
330
340
350
360
370
380
390
Carbon dioxide concentration (ppmv)

Fuels + O2 ---> CO2 + H2O



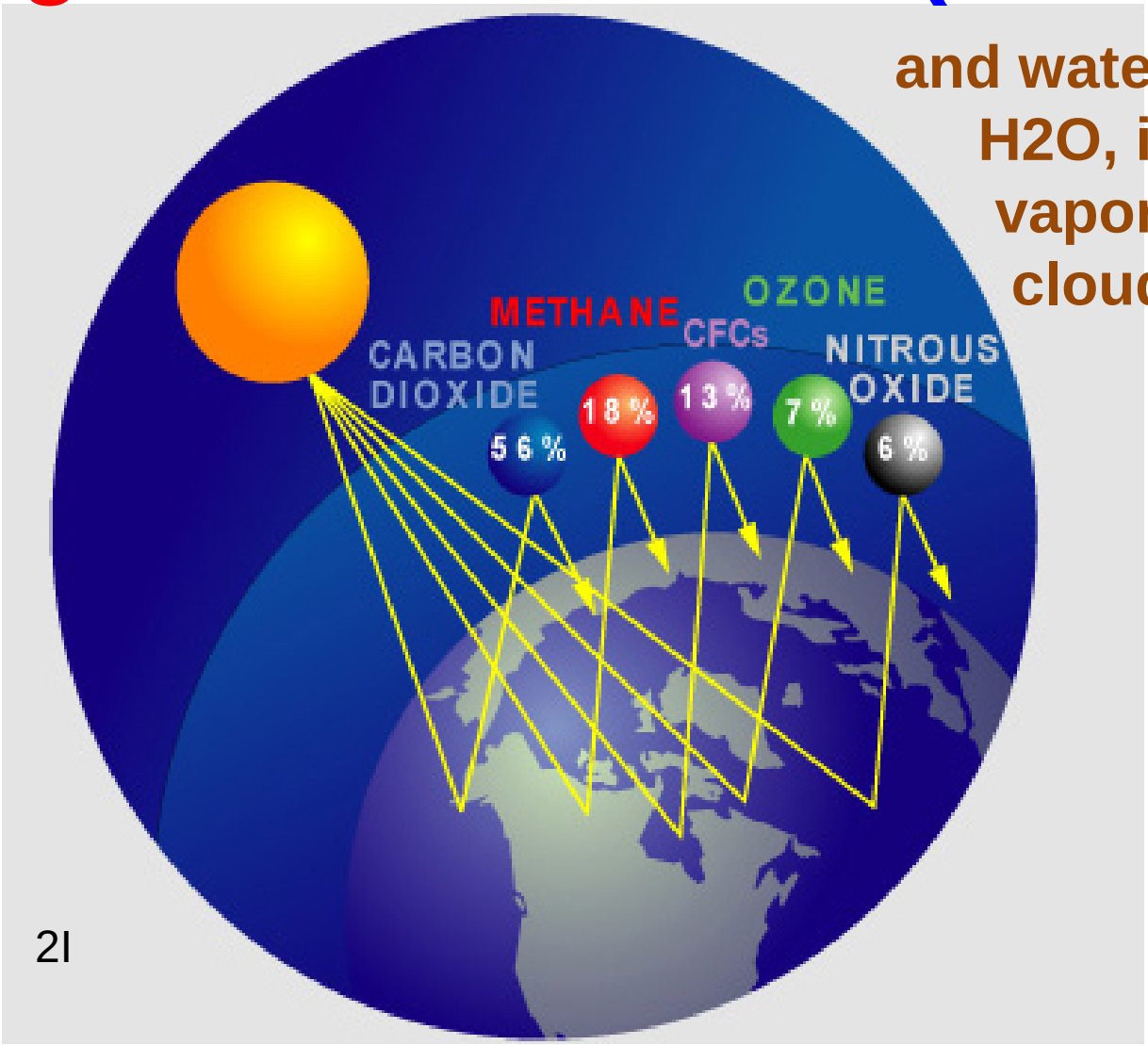
5E


4000 mi
4010 mi
Distance from center of Earth, miles
4000
3500
3000
2500
2000
1500
1000
500
0
0
1000
2000
3000
4000
Distance from center of Earth, miles
Earth
Earth's atmosphere between the lines


Biological and physical pumps of carbon dioxide
CO_2
CO_2
particulate
dissolved
anorganic
organic
anorganic
Cooling
Upwelling
Sedimentation
Deepwater circulation
Carbonate
organic carbon
Carbonate $CaCO_3$

Fortunately, the Earth's surface enjoys a strong

greenhouse effect (otherwise very c

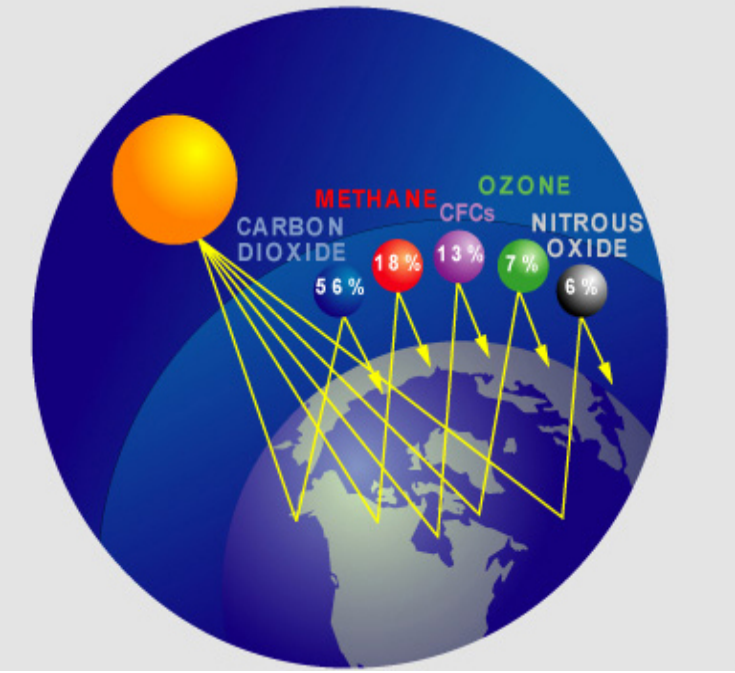


and water, H2O, in vapor and cloud forms.

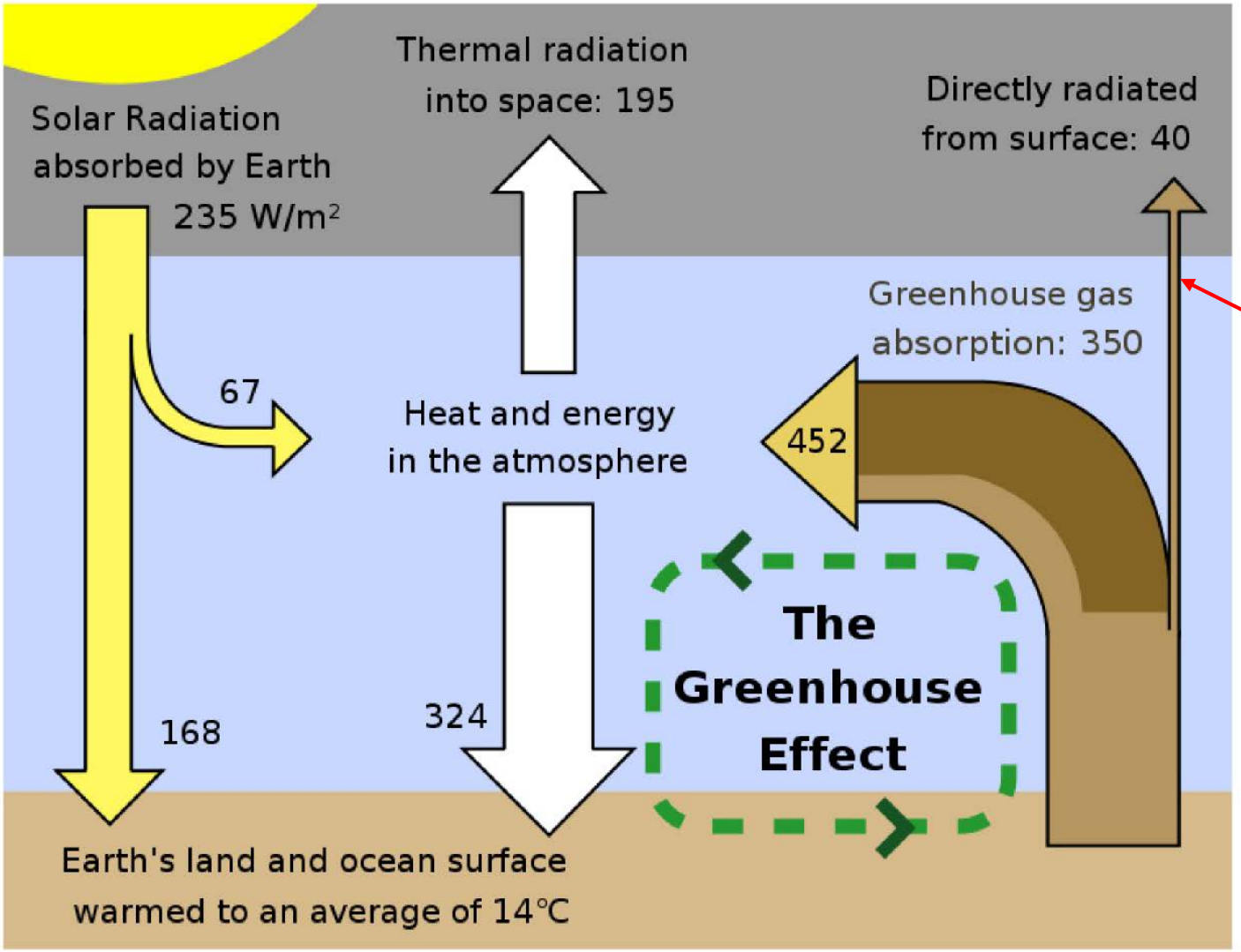
2l

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)

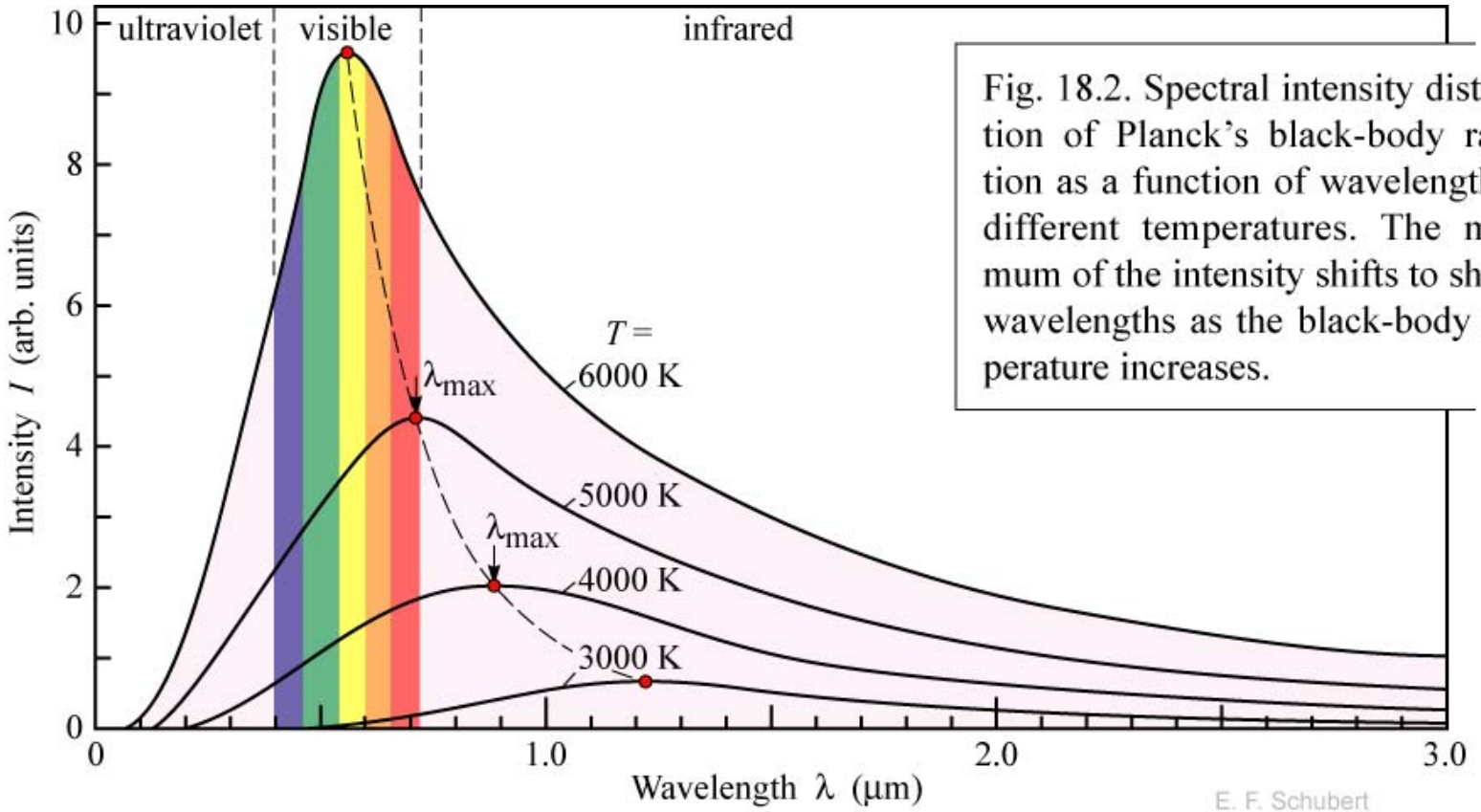
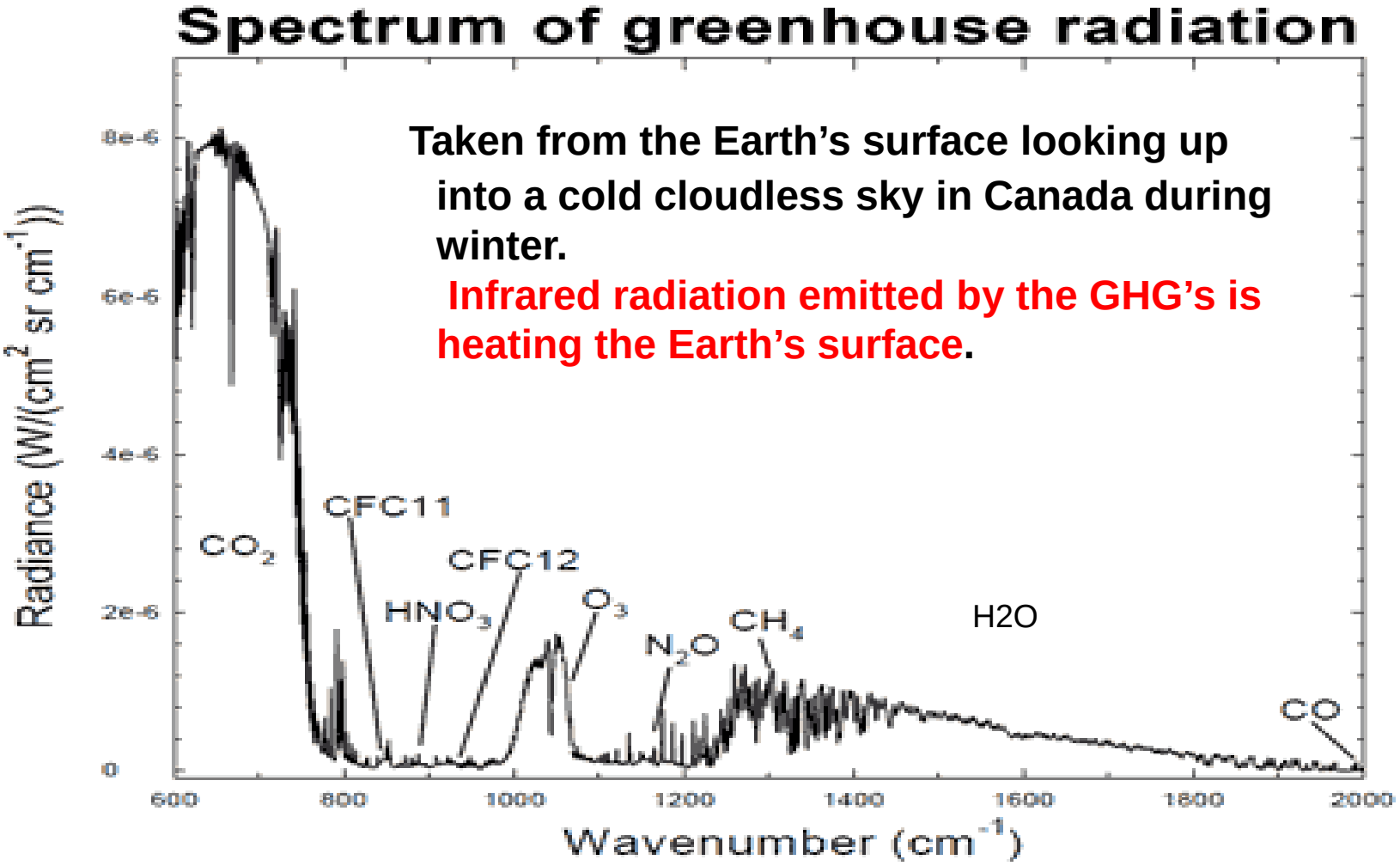


Fig. 18.2. Spectral intensity distribution of Planck's black-body radiation as a function of wavelength for different temperatures. The maximum of the intensity shifts to shorter wavelengths as the black-body temperature increases.

E. F. Schubert
Light-Emitting Diodes (Cambridge Univ. Press)
www.LightEmittingDiodes.org

IR fluorescence from the atmosphere.

Evidence: looking skyward with an IR spectrometer:



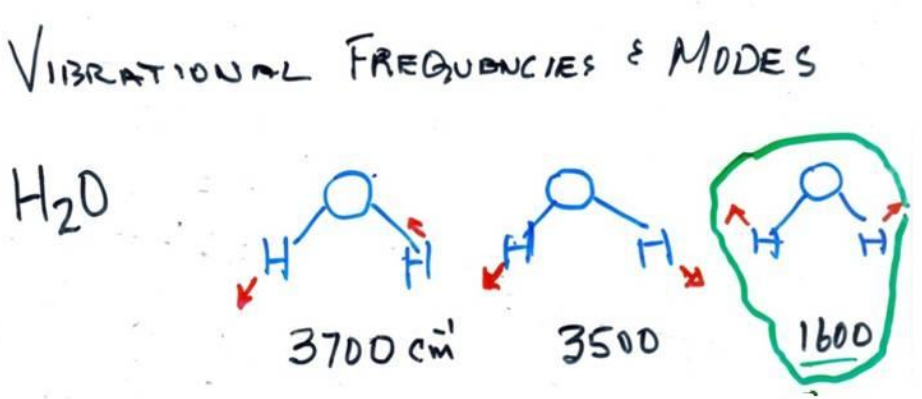
Taken from the Earth's surface looking up into a cold cloudless sky in Canada during winter.

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

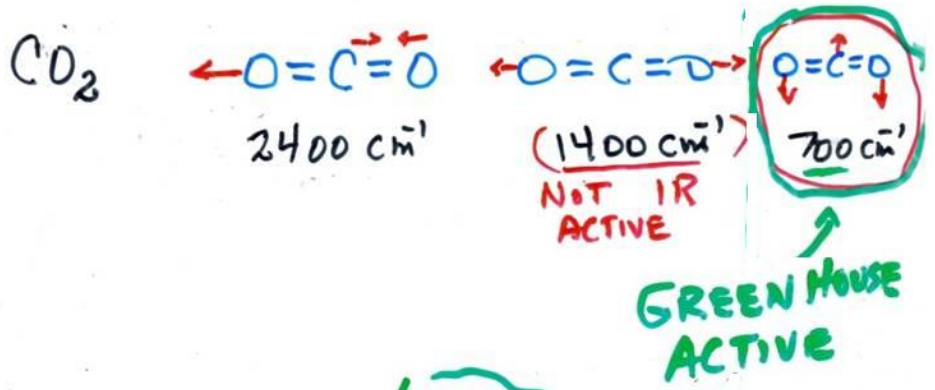
2 J

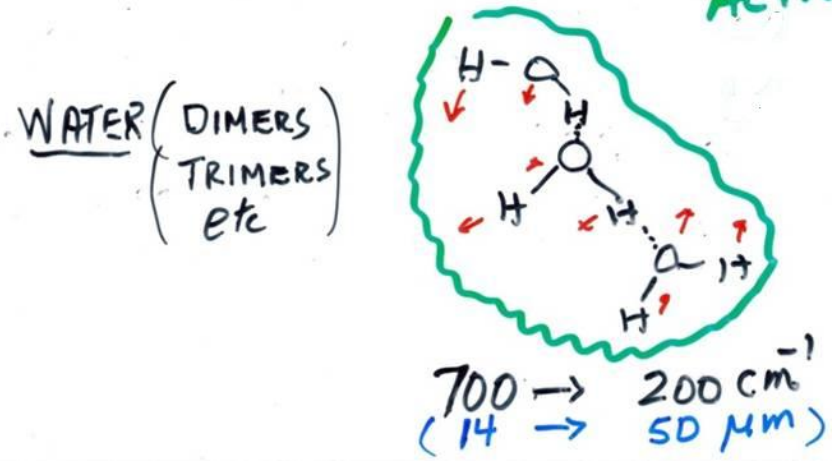
(*Evans 2006*).

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



"Greenhouse" Gases: CO2 and Methane



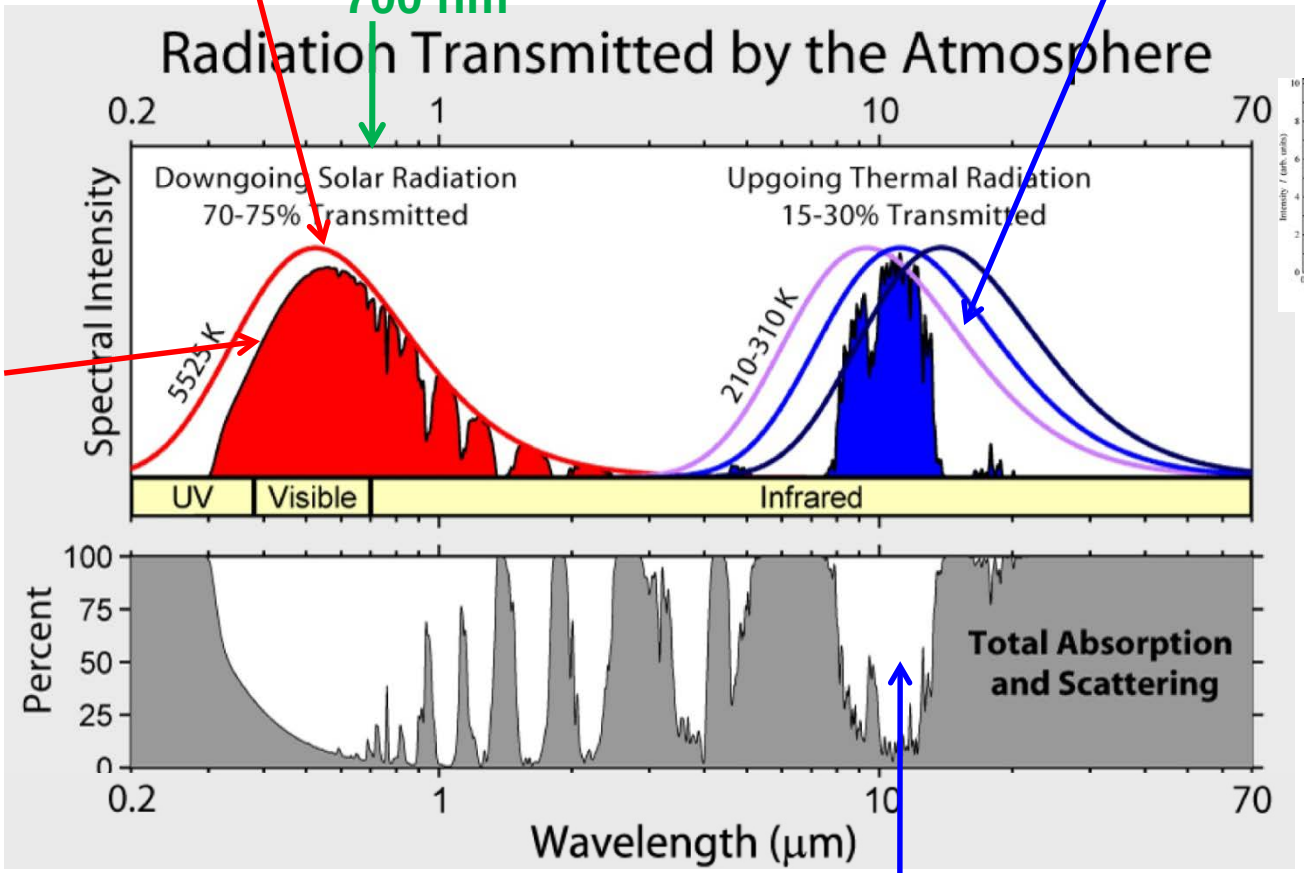


Green House Effect

Emission Spectrum of the Sun

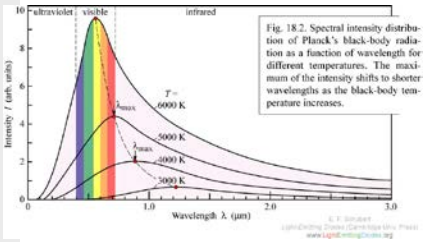
Emission spectra of the Earth at different places (proportional to T^4)

700 nm



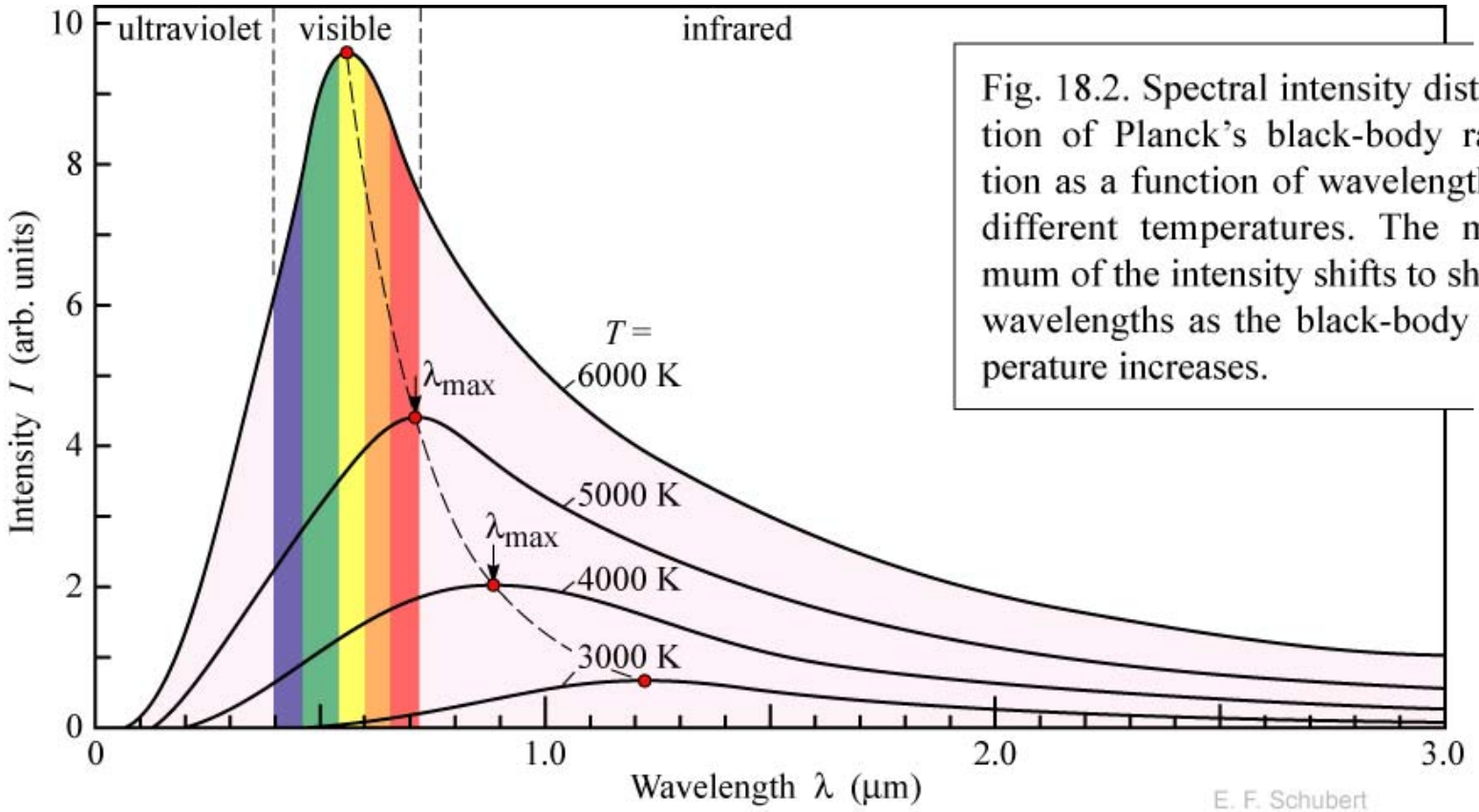
At earth surface

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



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

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



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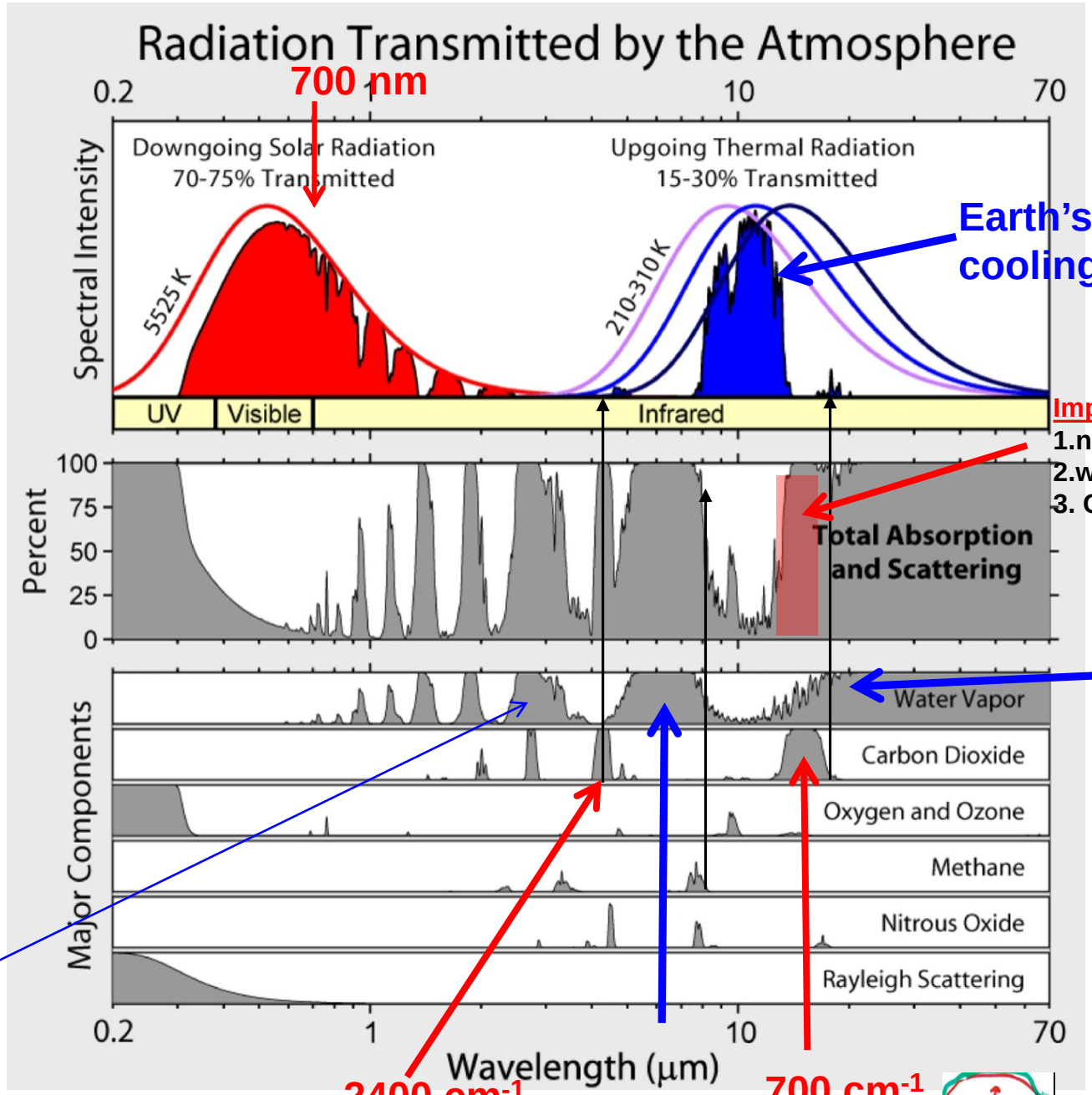
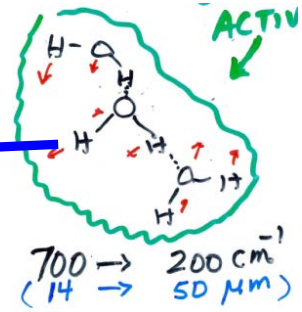


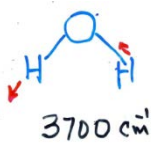
Earth's primary cooling mechanism!

Important region:

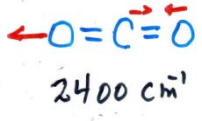
1. near peak emission
2. water transmits
3. CO_2 absorbs strongly

1-T%



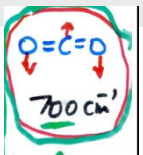


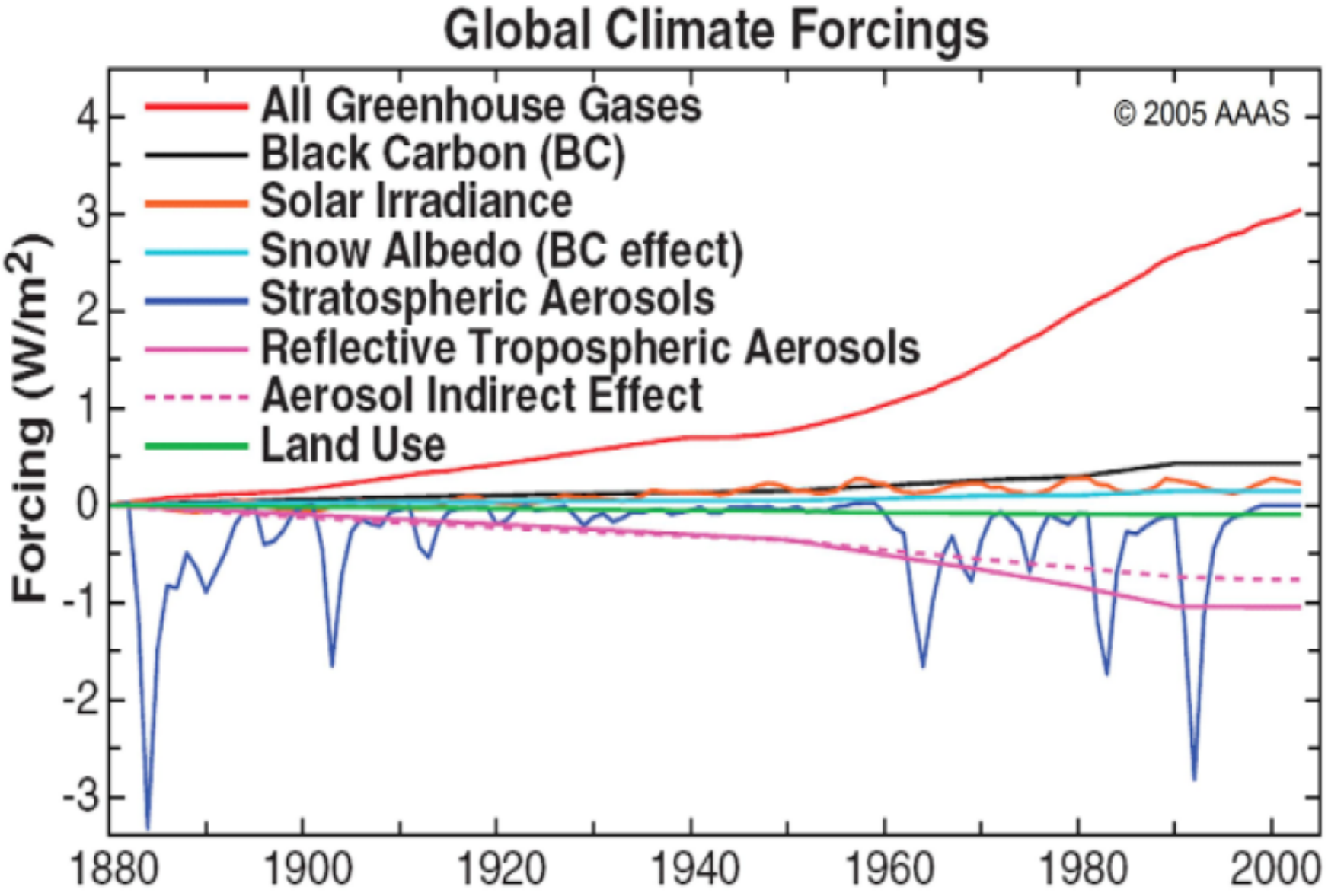
2400 cm^{-1} CO_2



1600 cm^{-1} H_2O

700 cm^{-1} CO_2

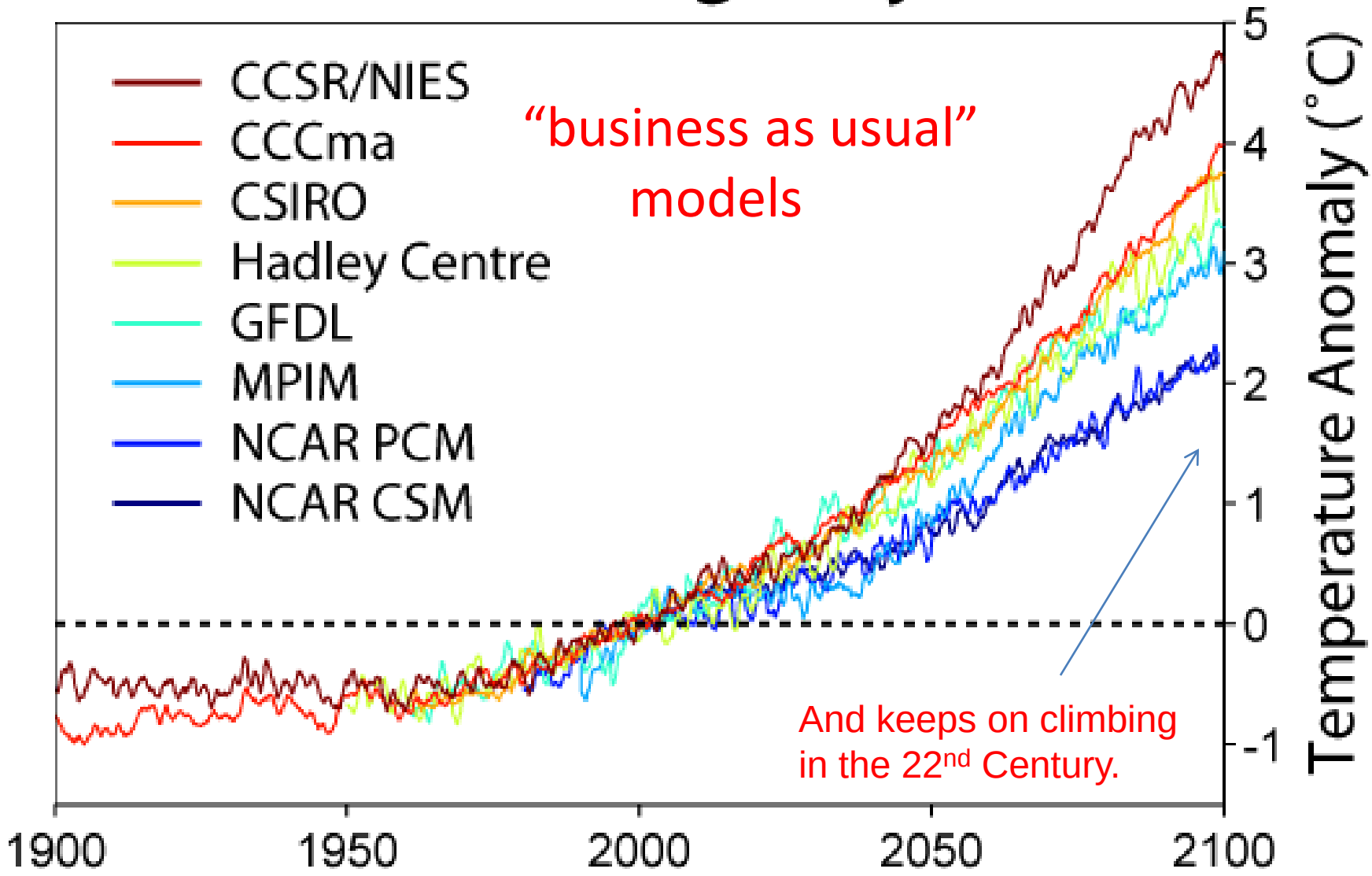




5R

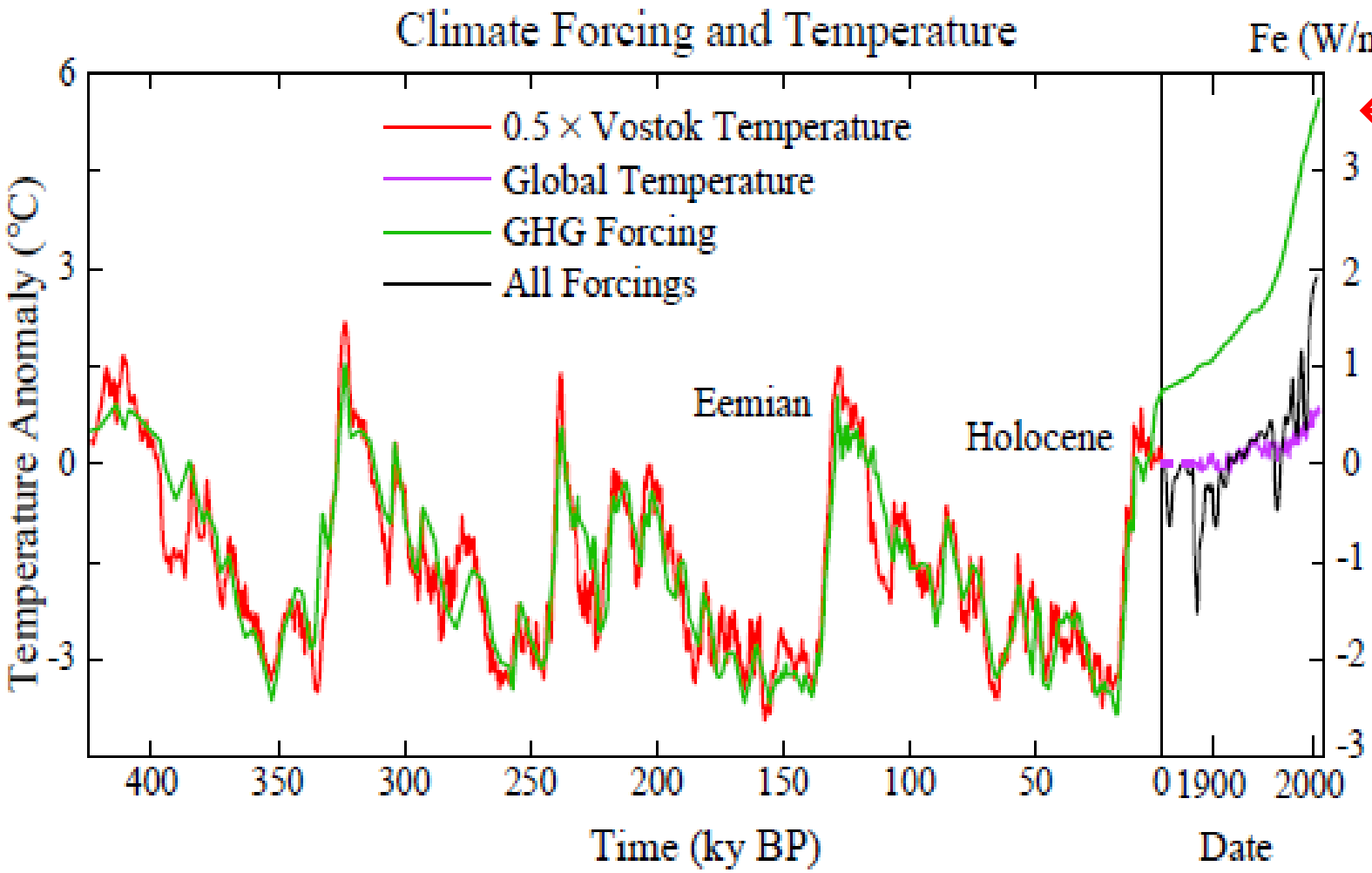
Figure 3. Forcings used to drive global climate simulations (From Hansen, Sato et al. 2005; Reprinted with permission from AAAS). Records of forcing history

Global Warming Projections



6C

"Image created by Robert A. Rohde / Global Warming Art"



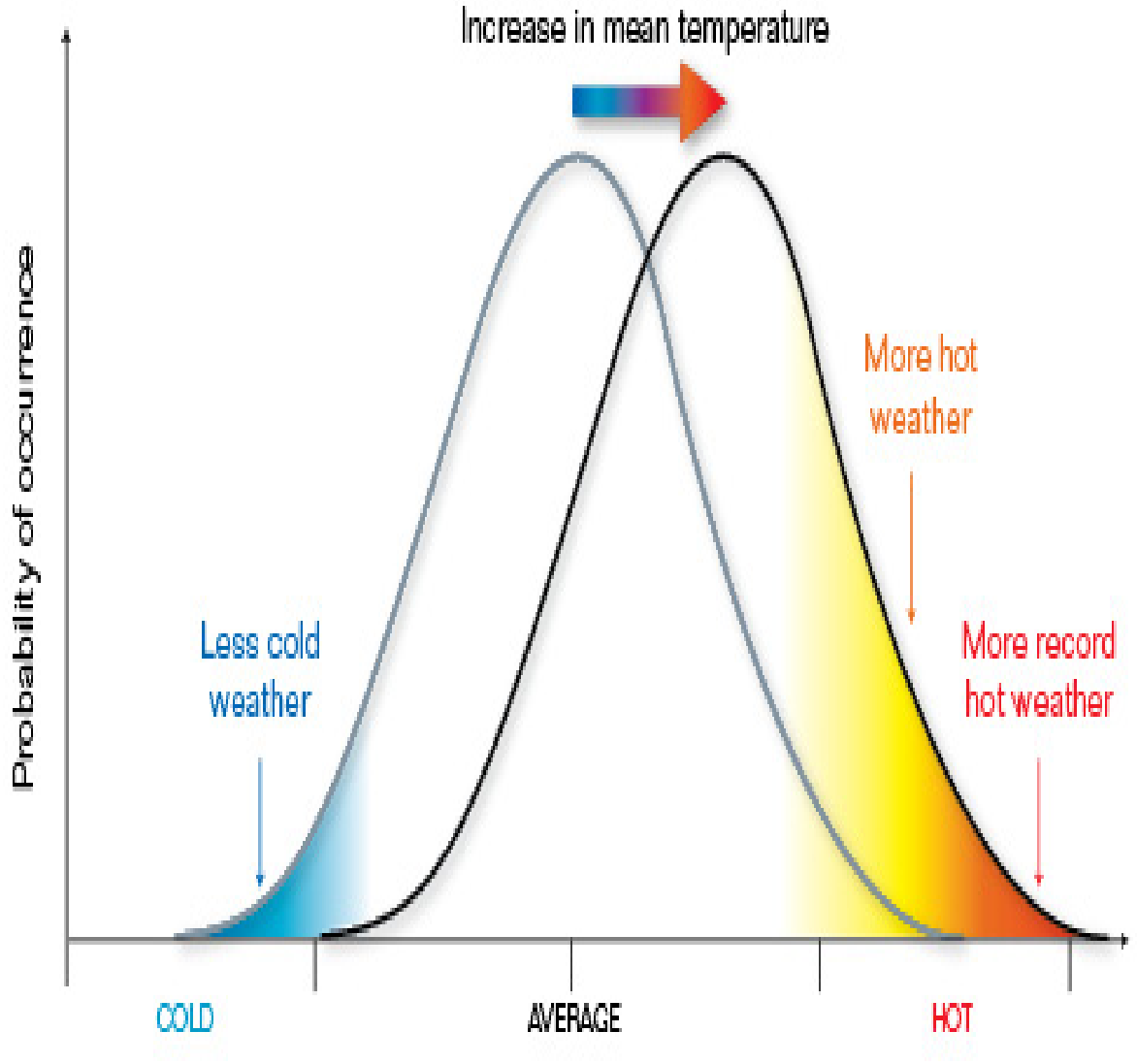
←Yikes!!!
way too much positive GHG forcing!

Note: the present level of Forcing by CO2 will last for a millennia unless brought down and temperature always catches up within a century. And note how quickly land ice melted in past glacial to interglacial transitions

8D

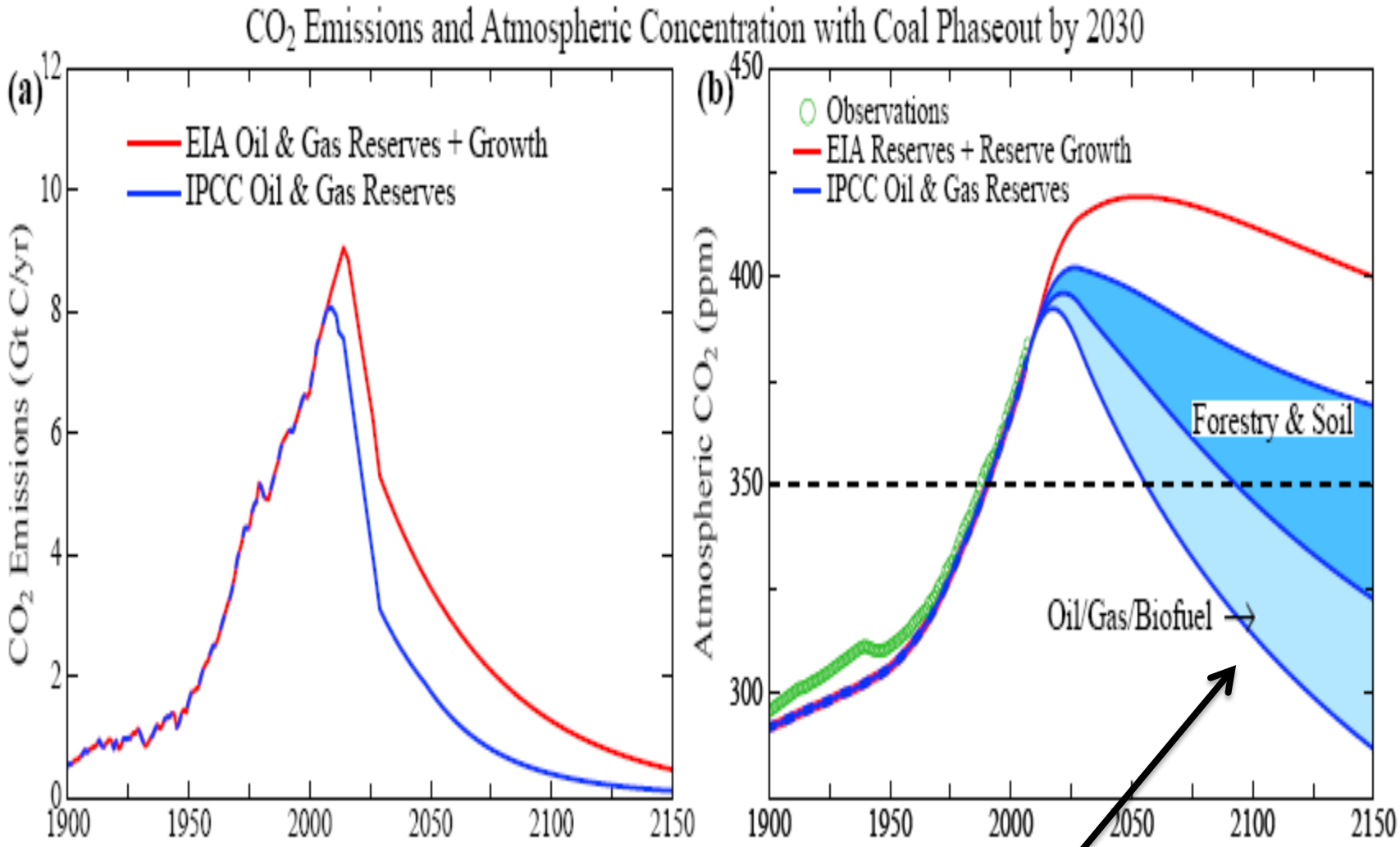
From "Target Atmospheric CO2: Where should humanity aim?" by Hansen et al., 2008,.

Note that the frequency of extreme hot-weather events will increase much more than the increase in average temperature.



6F

The problem can be solved !!!

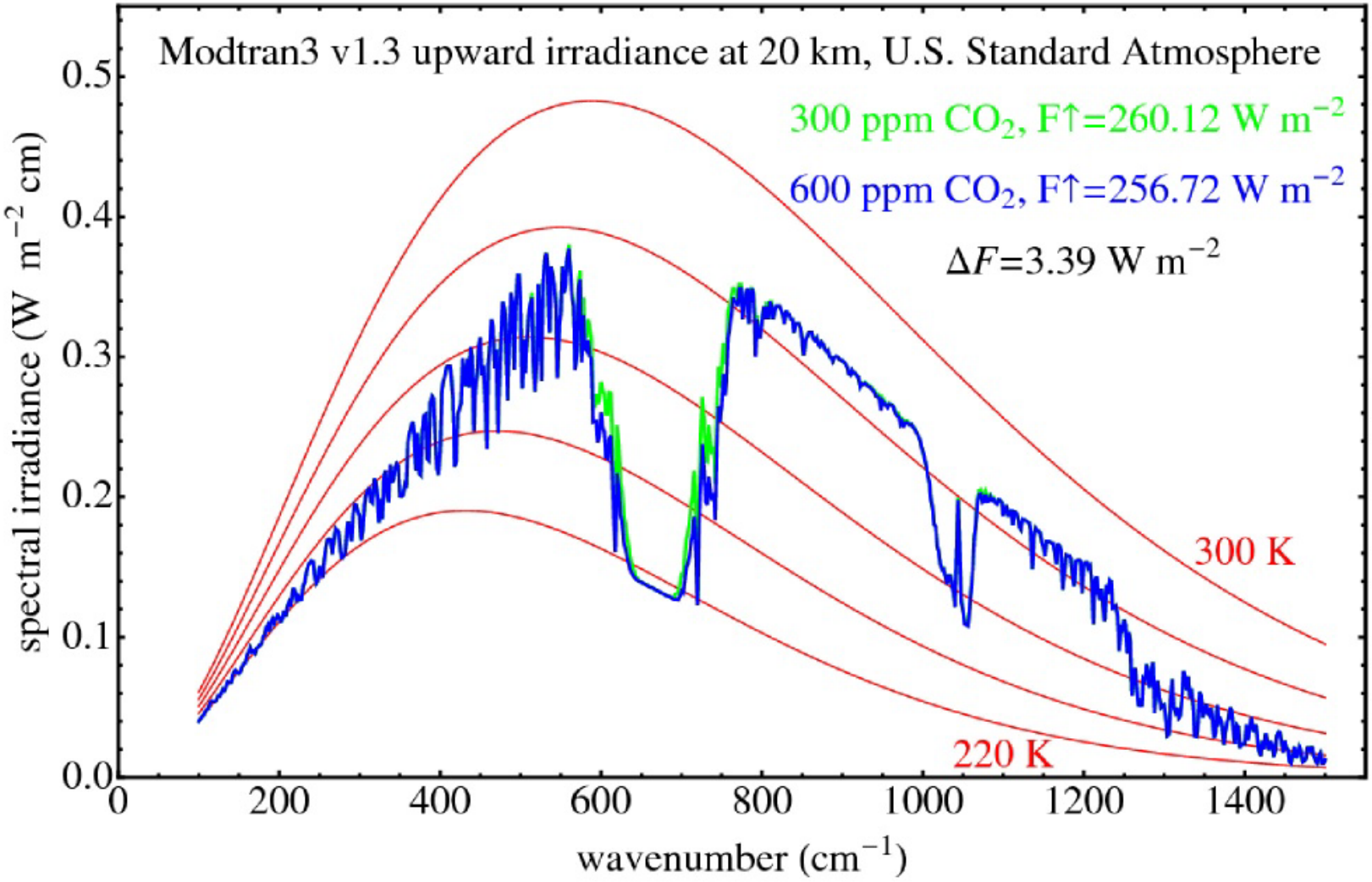


Using only known reserves of gas and oil, and BIOFUELS along with some CCS and reforestation !!

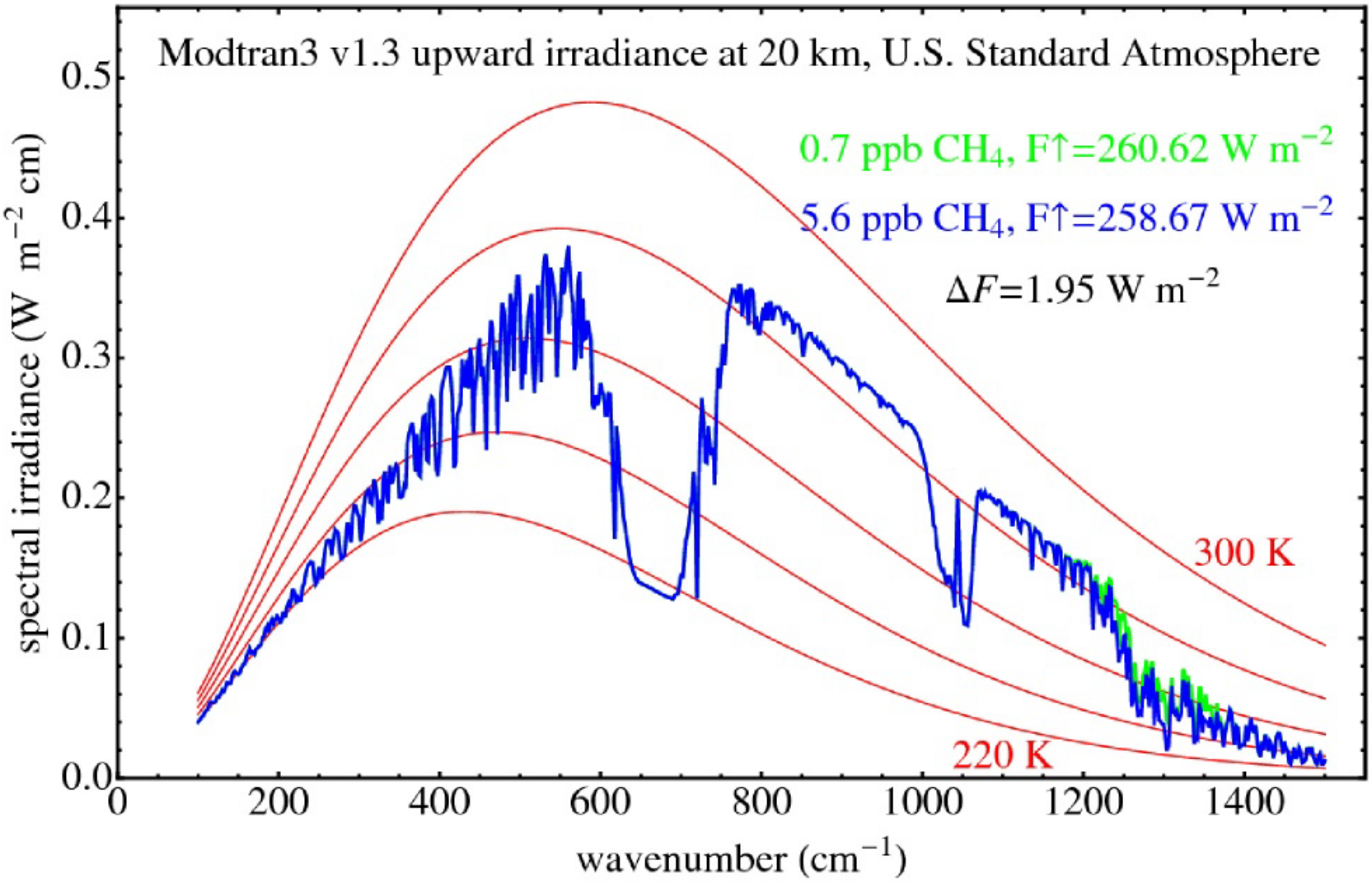
8H

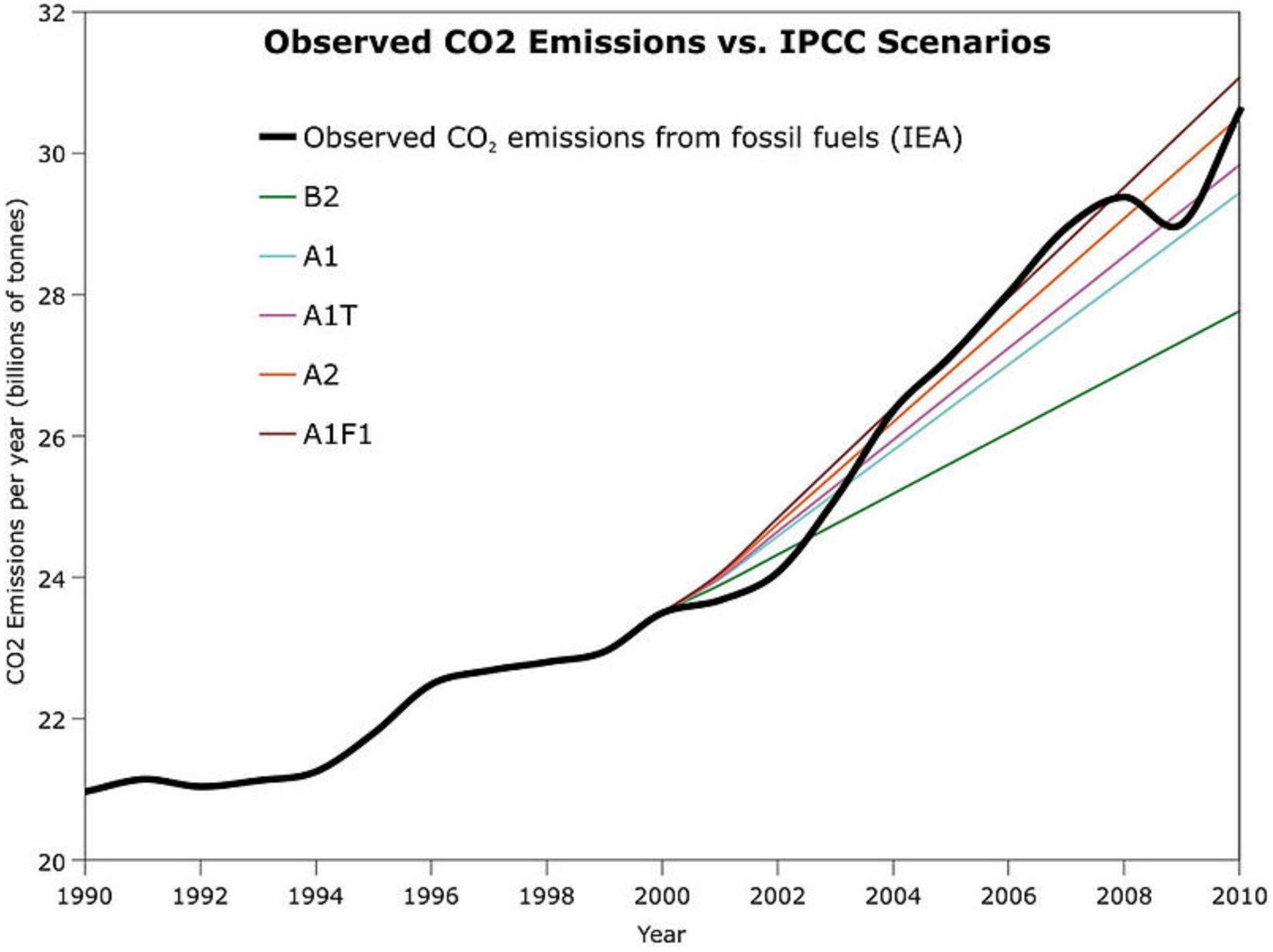

Sea-to-Air
Heat Transfer
Solar Warming
of Ocean Waters
Warm Shallow Current
Cold and Salty Deep Current

CO_2

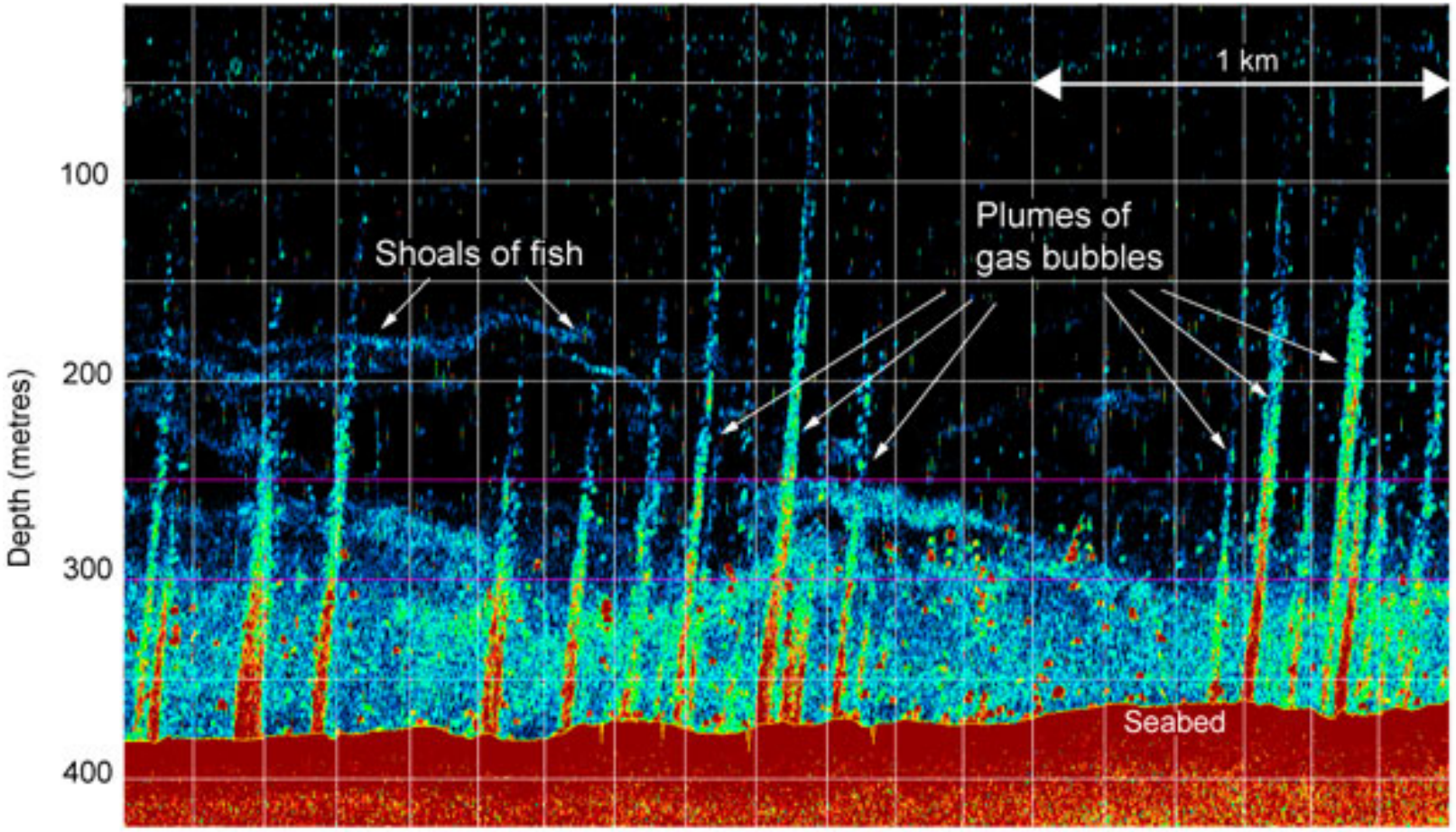

Modtran3 v1.3 upward irradiance at 20 km, U.S. Standard Atmosphere
300 ppm CO2, F↑=260.12 W m−2
600 ppm CO2, F↑=256.72 W m−2
ΔF=3.39 W m−2
300 K
220 K
spectral irradiance (W m−2 cm)
wavenumber (cm−1)
0.0
0.1
0.2
0.3
0.4
0.5
0
200
400
600
800
1000
1200
1400

Methane, CH_4


Modtran3 v1.3 upward irradiance at 20 km, U.S. Standard Atmosphere
0.7 ppb CH4, F↑=260.62 W m−2
5.6 ppb CH4, F↑=258.67 W m−2
ΔF=1.95 W m−2
300 K
220 K
spectral irradiance (W m−2 cm)
wavenumber (cm−1)
0.0
0.1
0.2
0.3
0.4
0.5
0
200
400
600
800
1000
1200
1400


Observed CO2 Emissions vs. IPCC Scenarios
Observed CO_2 emissions from fossil fuels (IEA)
B2
A1
A1T
A2
A1F1
CO2 Emissions per year (billions of tonnes)
32
30
28
26
24
22
20
1990
1992
1994
1996
1998
2000
2002
2004
2006
2008
2010
Year

Pictures of METHANE Plumes!

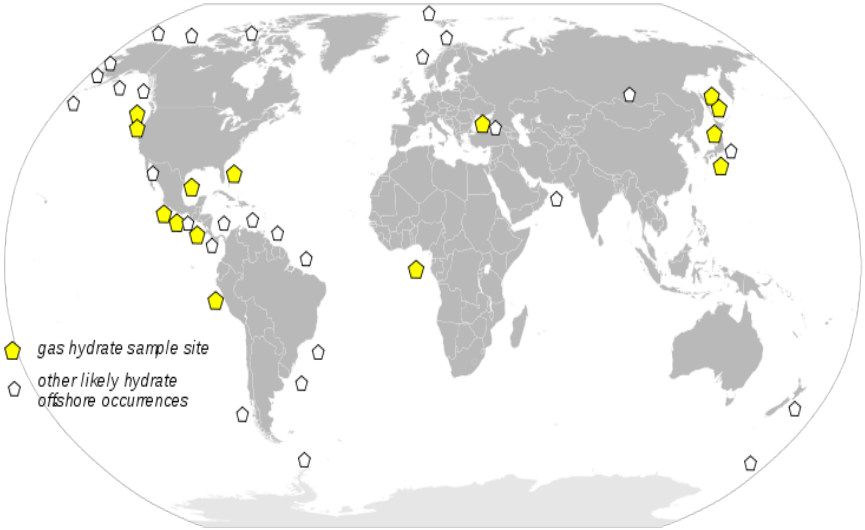


Sonar image near Svalbard

7 I

Methane Clathrates or Methane Hydrates

are found in deep and/or cold coastal ocean sea beds (in the top few hundred meters).



7H

"burning ice"