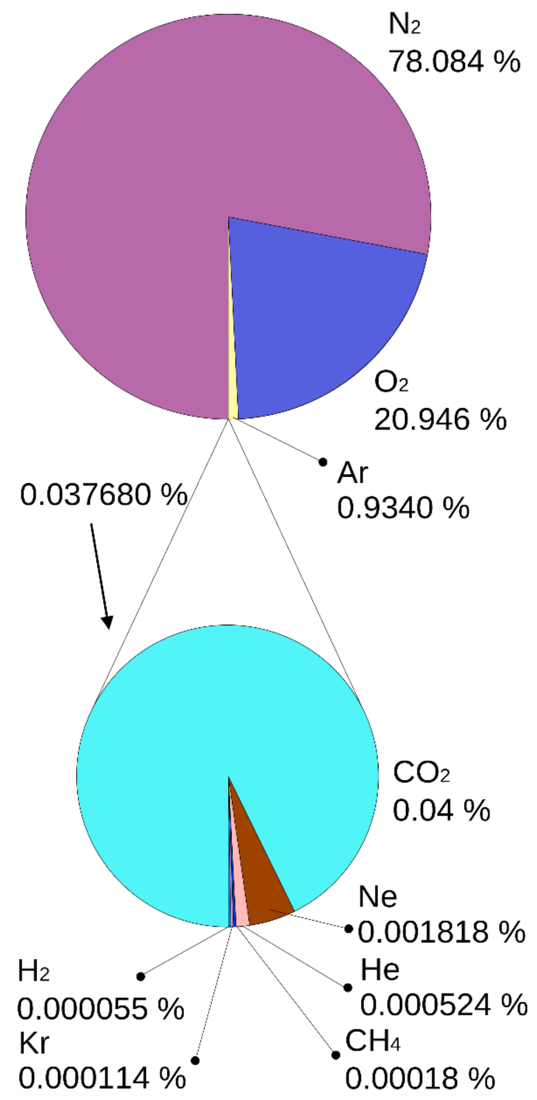
Chemistry of the Global Climate

1. Composition of Earth's Atmosphere
2. Radiative Energy Balance
3. Greenhouse Gases and Aerosols
4. Radiative forcing and global warming potentials (GWP)
5. Energy Resources Fossil and Renewable

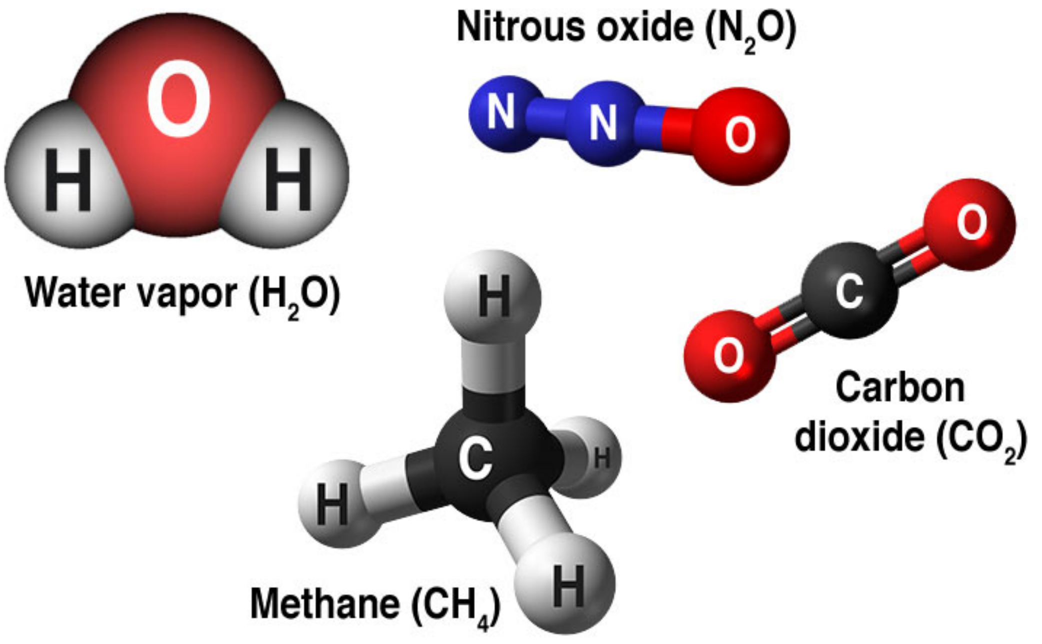
1. Atmospheric composition

Mixing ratios of present day dry Earth atmosphere

Nitrogen	78.08 %
Oxygen	20.95 %
Argon	0.934 %
Carbon dioxide	~400 ppm_v (increasing)
Neon	18.2 ppm_v
Helium	5.24 ppm_v
Methane	~1.8 ppm_v (increasing)
Krypton	1.14 ppm_v
Hydrogen	0.5 ppm_v
Nitrous oxide	~0.3 ppm_v (increasing)
Xenon	0.09 ppm_v



Major ‘Greenhouse’ Gases



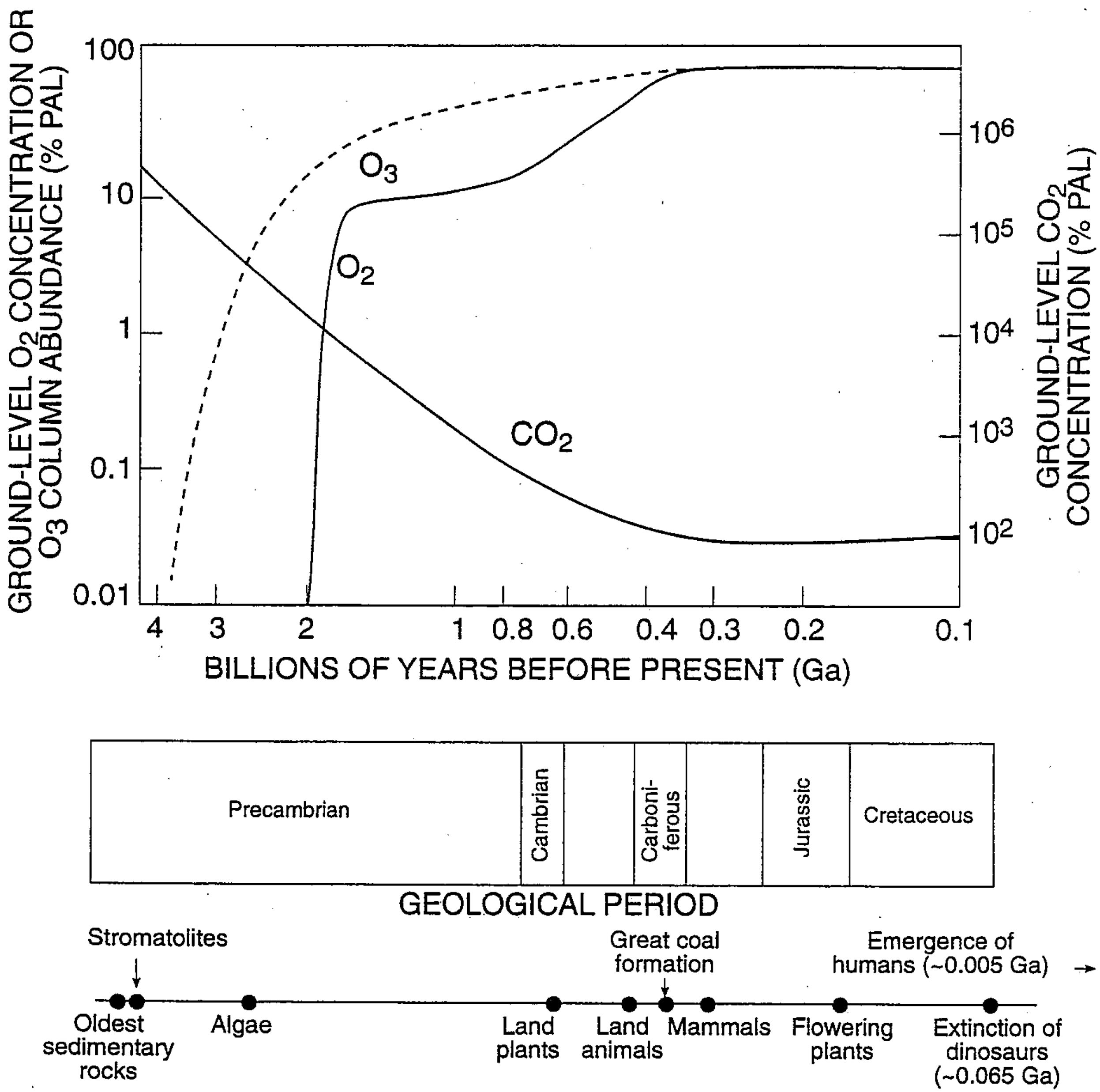
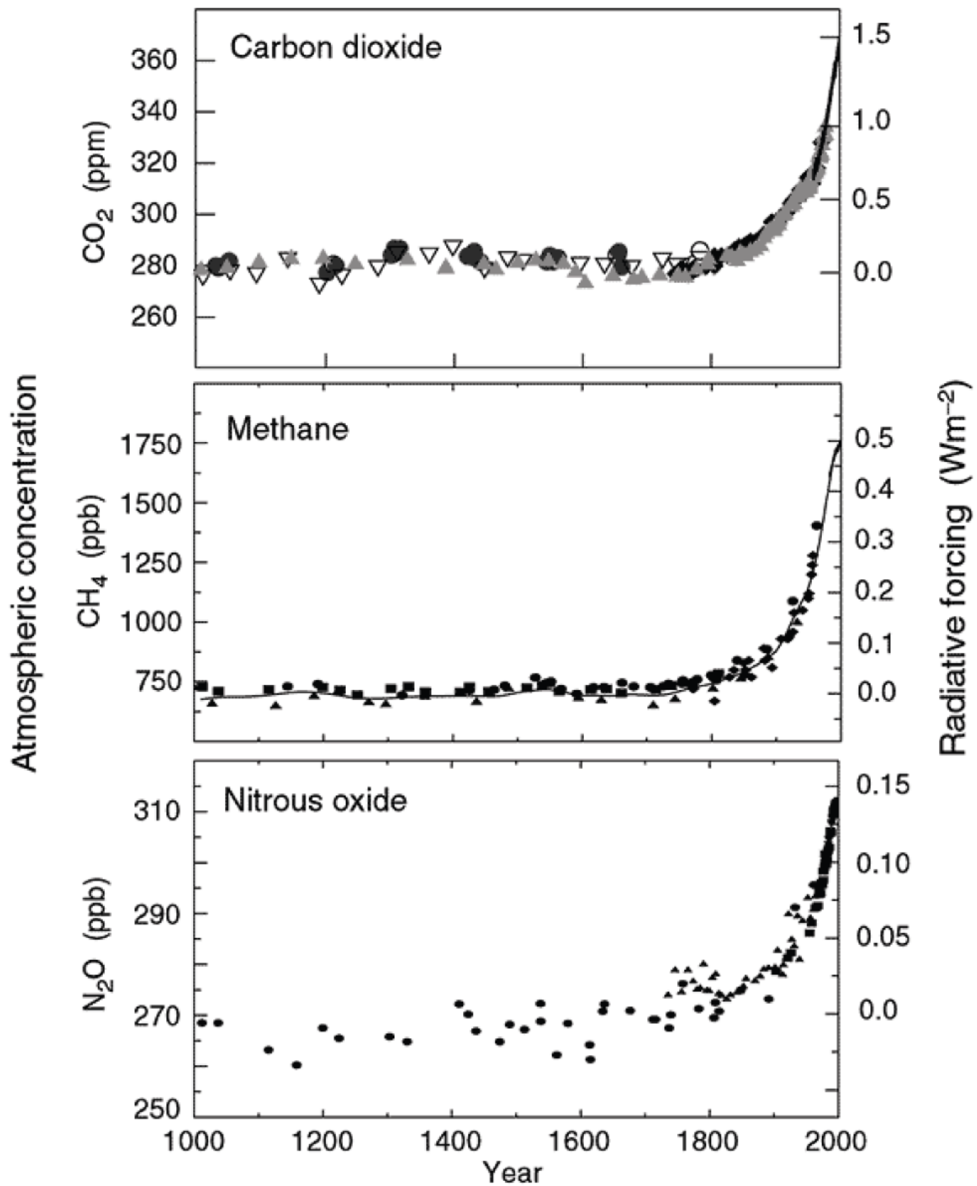


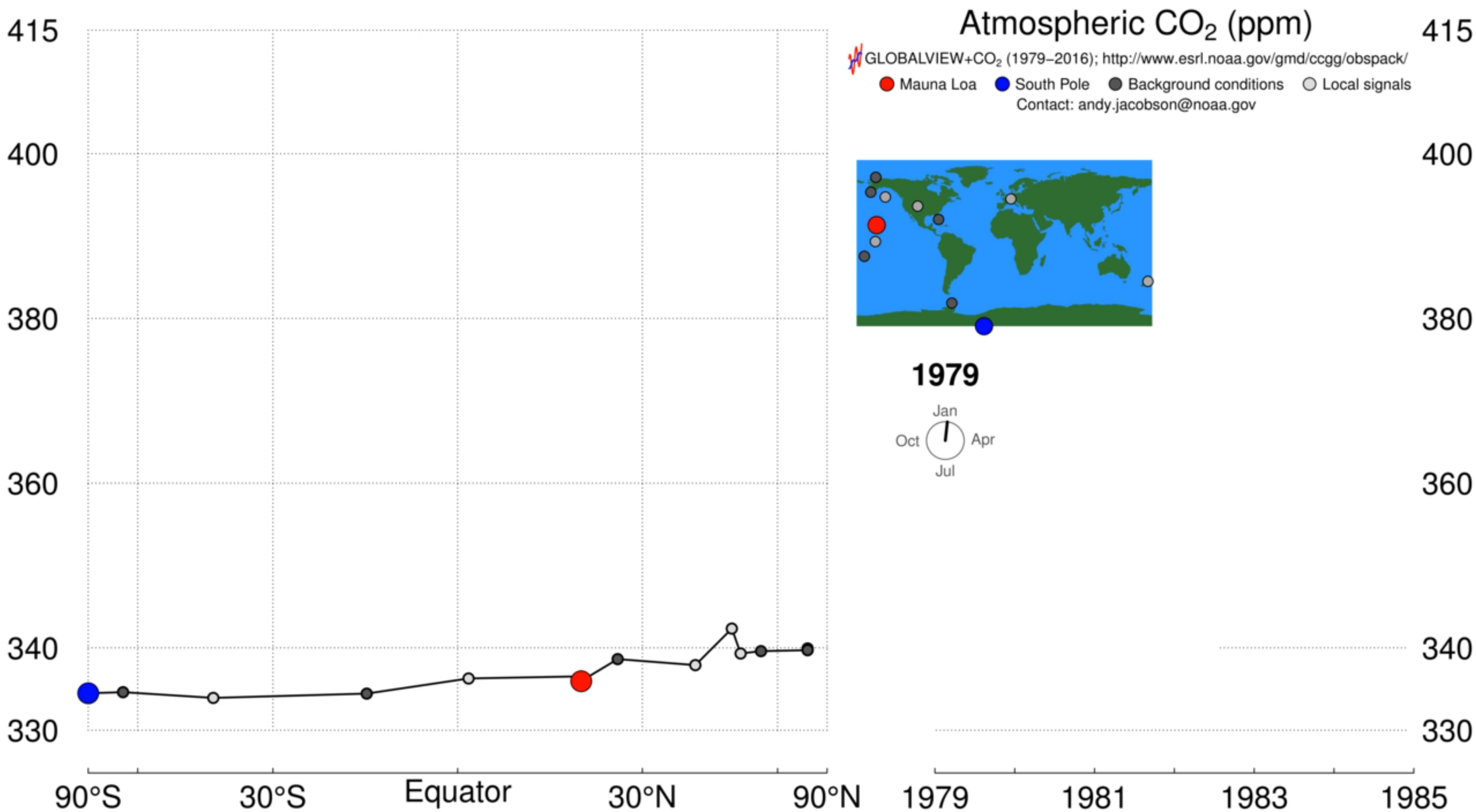
Figure 1.2. Schematic diagram showing predictions of the evolution of oxygen, ozone and carbon dioxide to present atmospheric levels (PAL). [After R. P.

Changes in GHGs in the Modern Era

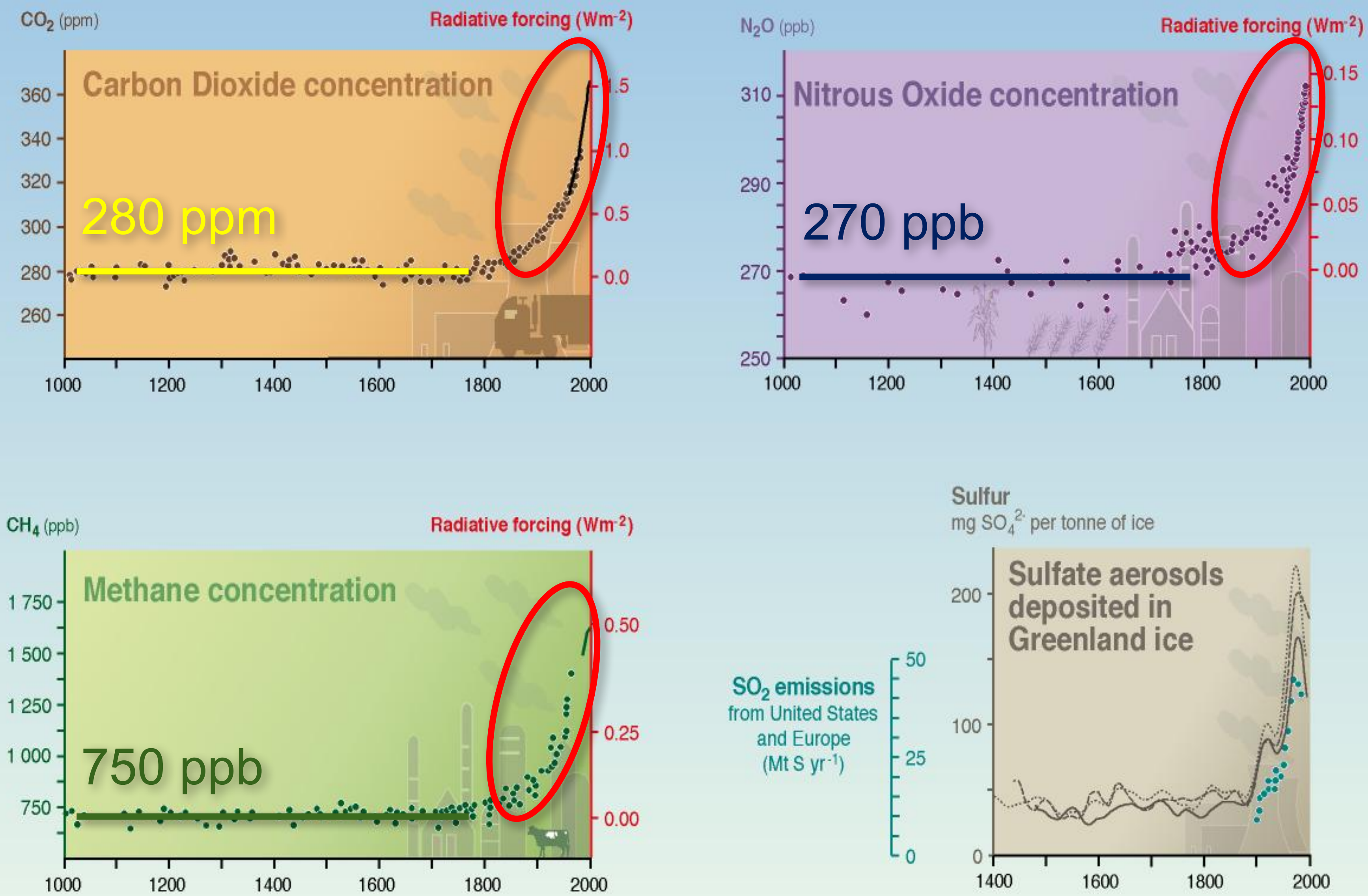


Observations

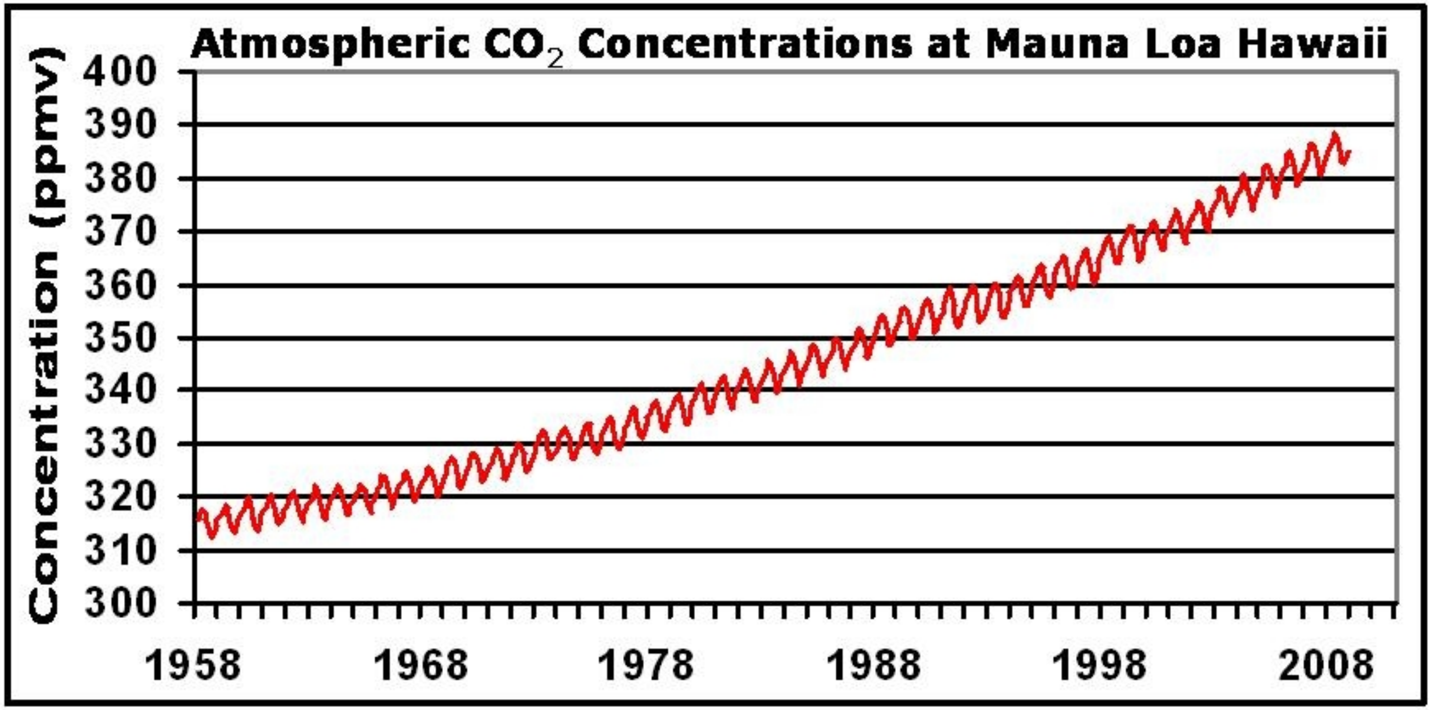
reproducibility



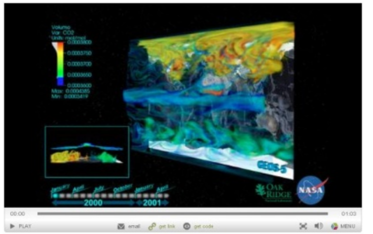
Changes in Atmospheric Composition



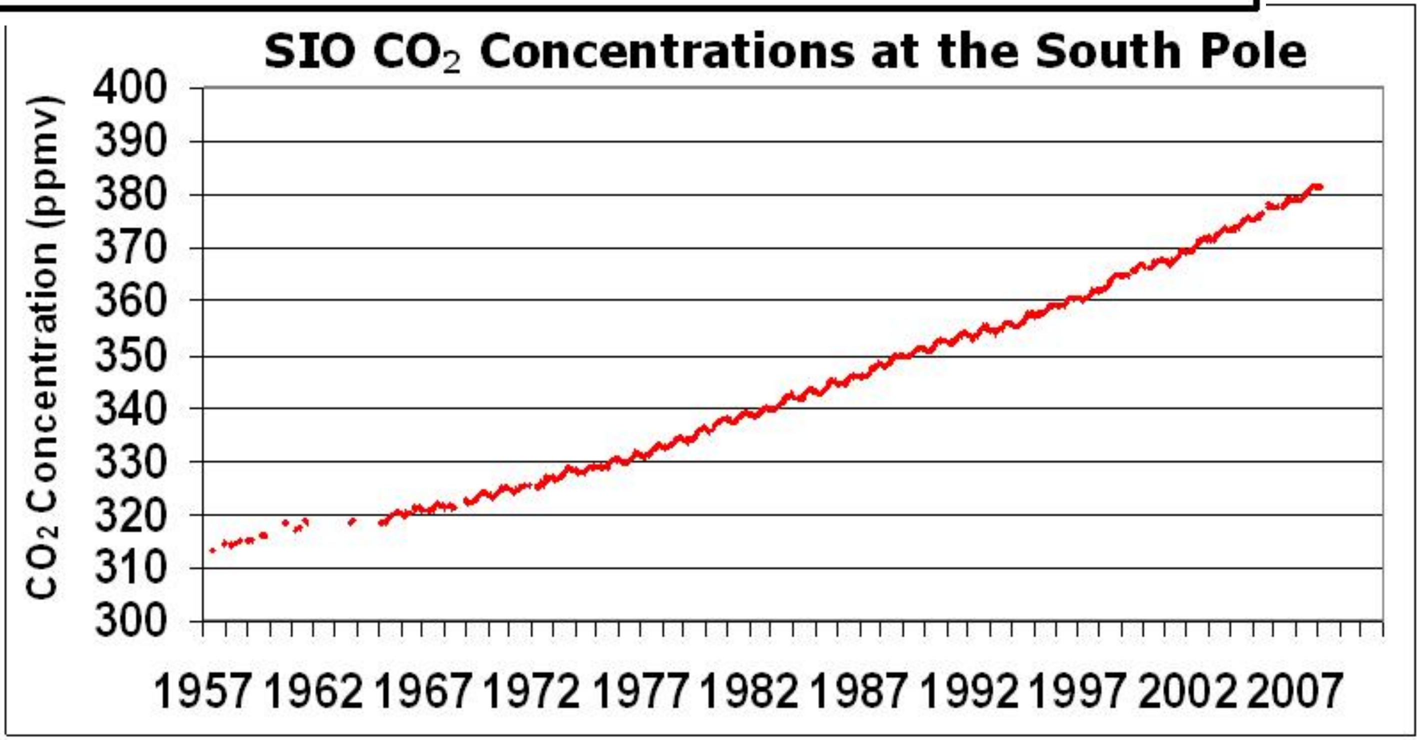
Adapted from IPCC third assessment report, 2007



CDIAC, 2010



Go to NASA/Oak Ridge Video



How Much CO_2 in ppm Does a Barrel of Oil Produce?

Basic Facts:

- Carbon-based fuel releases 3.15 times its mass in CO_2
- Mass of a barrel of oil is about 135 kg
- 1 barrel releases 425 kg CO_2
- CO_2 has a molar mass of 44g/mol

1 barrel releases 425 kg of $CO_{2;}$ in moles this is

$$\frac{425\,kg}{0.044\,kg\,/\,mol} = 10^4\,mol$$

Since the atmosphere contains 1.7 X 10^{20} mol of air, one barrel will release

$$\frac{10^4}{1.7 \times 10^{20}} = 6 \times 10^{-17}$$

This is the fraction of CO_2 relative to the entire atmosphere – multiply by 1 million to get the parts-per-million or ppm. So, 1 barrel releases an additional

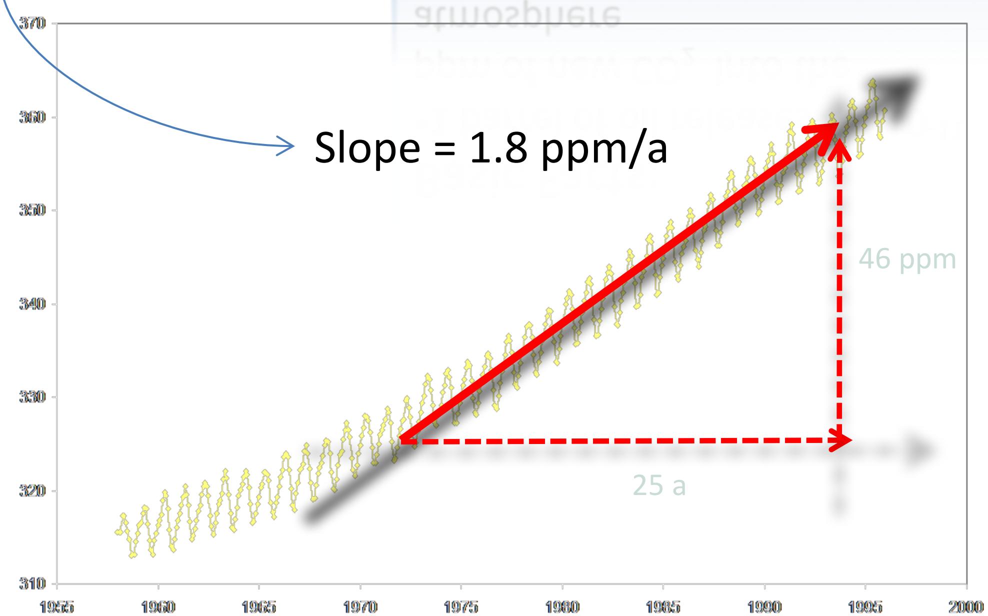
$$6 \times 10^{-11}\,ppm$$

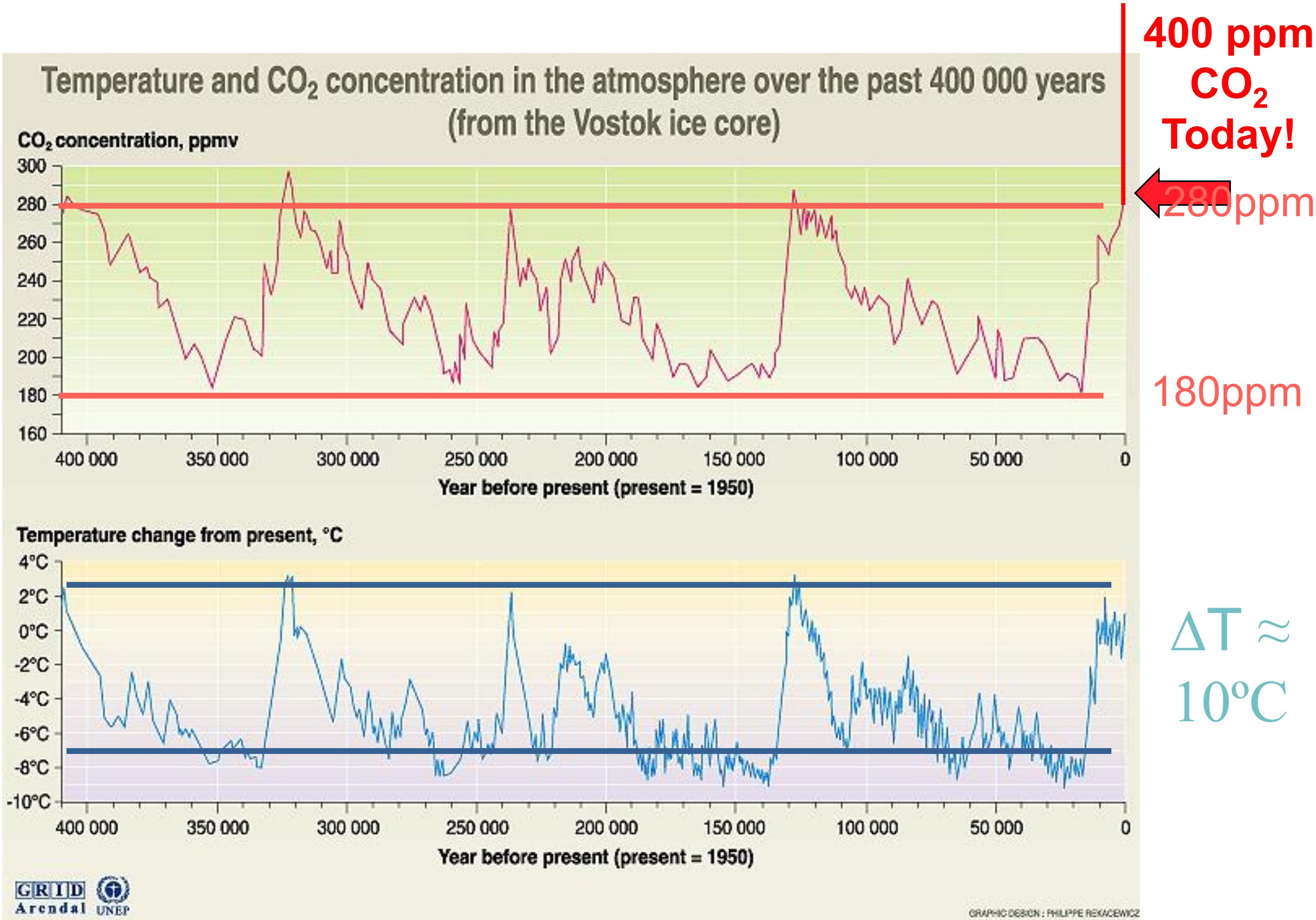
Is the observed increase in CO_2 "natural" or …

$$(30 \times 10^{9}\ bbl/a)(6 \times 10^{-11}\ ppm/bbl) = 1.8\ ppm/a$$

Basic Facts:

- 1 barrel of oil releases 6×10^{-11} ppm of new CO_2 into the atmosphere
- 30 billion barrels of oil are consumed annually





Source: J.R. Petit, J. Jouzel, et al. Climate and atmospheric history of the past 420 000 years from the Vostok ice core in Antarctica, Nature 399 (3JUne), pp 429-436, 1999.

Hypothesis

Svante Arrhenius
1896 Artic Balloon Expedition
Nobel Prize in Chemistry 1903

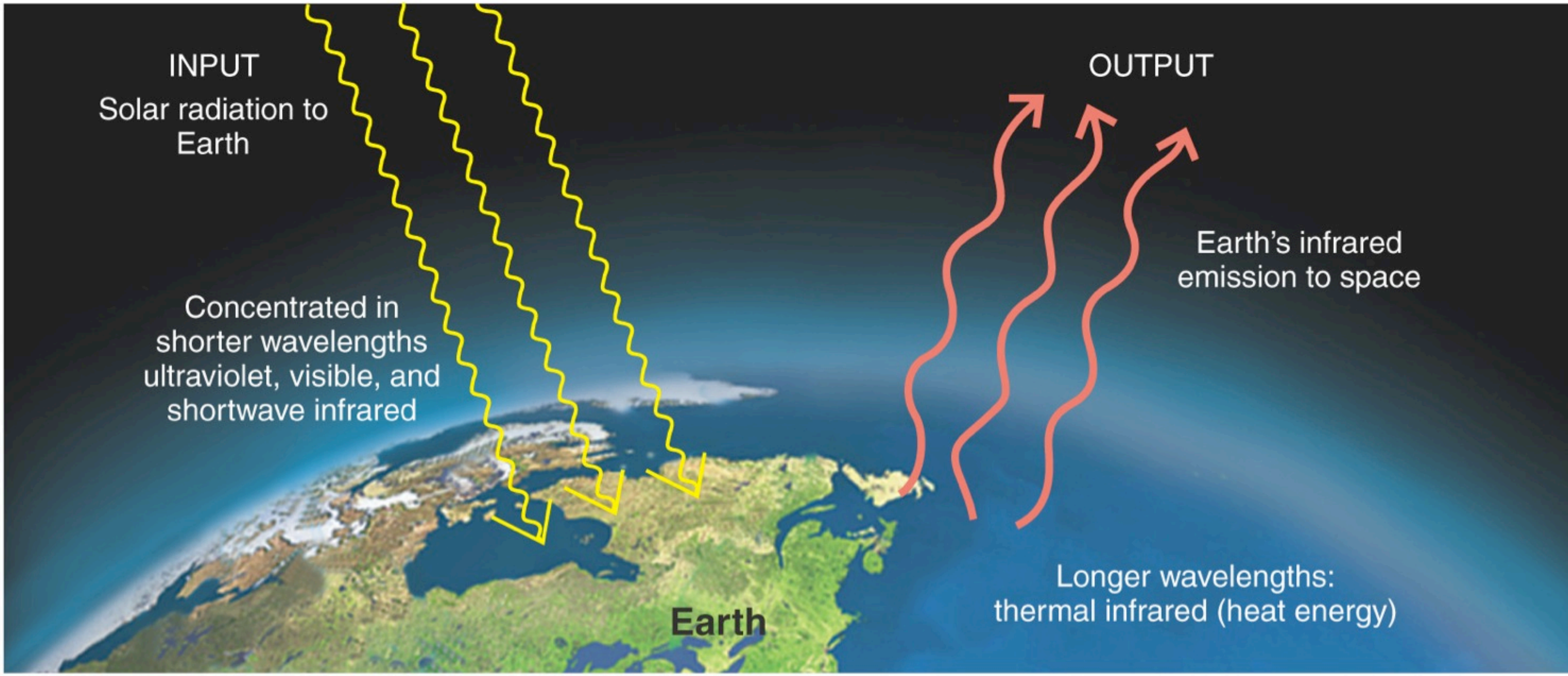
The Rodney & Otamatea Times
WAITEMATA & KAIPARA GAZETTE.
PRICE—10s per annum in advance
WARKWORTH, WEDNESDAY, AUGUST 14, 1912.
3d. per Copy.

Science Notes and News.

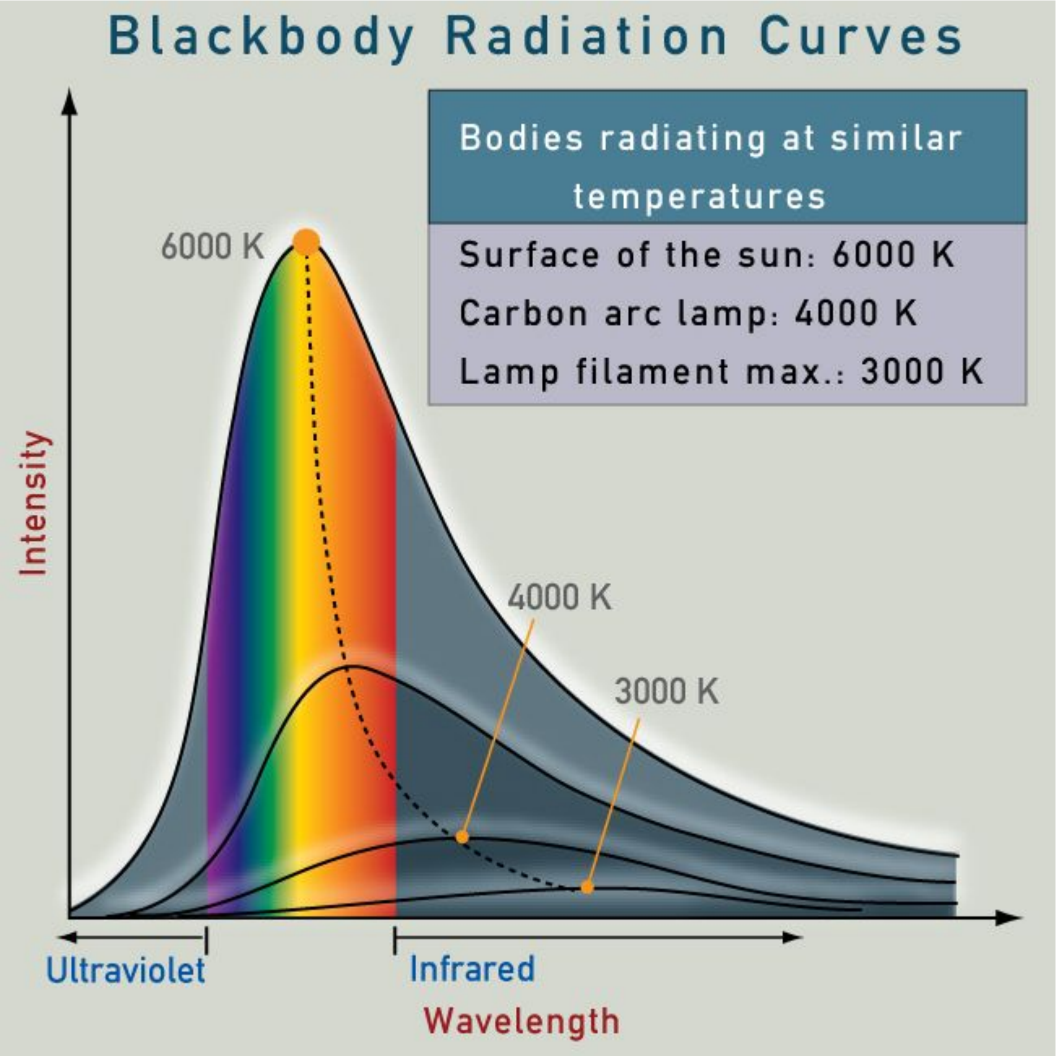
COAL CONSUMPTION AFFECTING CLIMATE.

The furnaces of the world are now burning about 2,000,000,000 tons of coal a year. When this is burned, uniting with oxygen, it adds about 7,000,000,000 tons of carbon dioxide to the atmosphere yearly. This tends to make the air a more effective blanket for the earth and to raise its temperature. The effect may be considerable in a few centuries.

2. Radiative Energy Balance



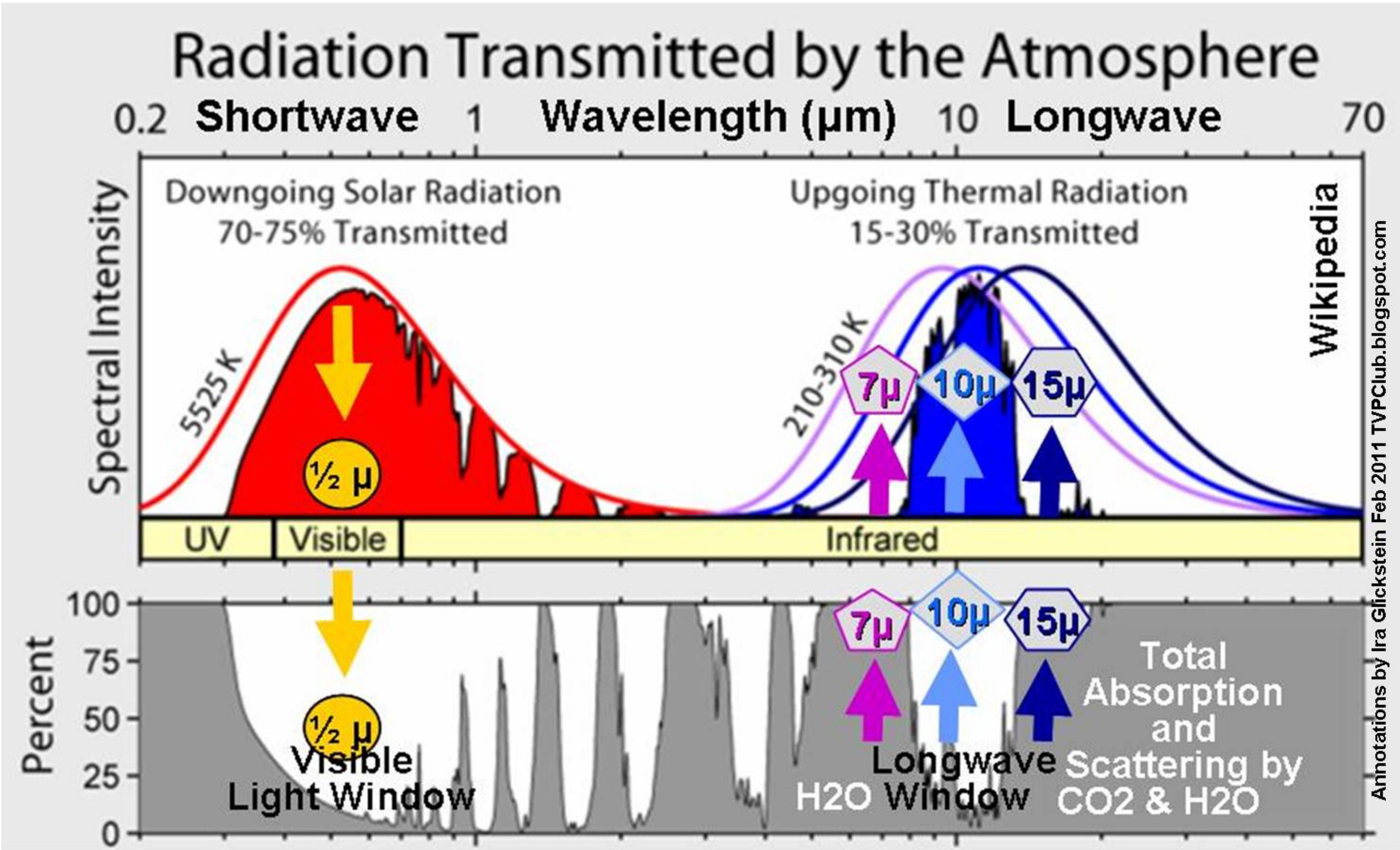
Black Body Radiation



The sun is very hot and so it's radiation is mostly in the visible spectrum.

The Earth is much cooler then the sun so it emits in the infrared.

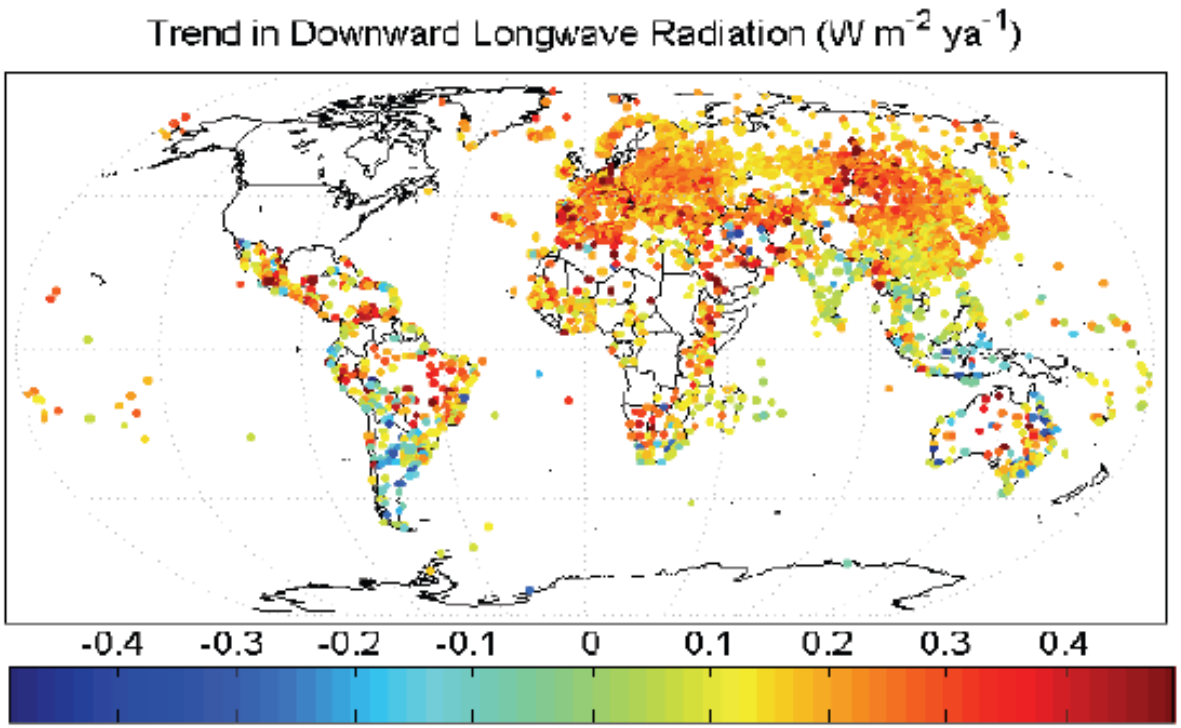
Humans, like the Earth emit in the infrared.



Radiation Transmitted by the Atmosphere
0.2 Shortwave 1 Wavelength (μm) 10 Longwave 70
Downgoing Solar Radiation
70-75% Transmitted
Upgoing Thermal Radiation
15-30% Transmitted
Spectral Intensity
5525 K
210-310 K
½ μ
7μ
10μ
15μ
Wikipedia
UV
Visible
Infrared
Percent
100
75
50
25
0
½ μ
Visible
Light Window
7μ
10μ
15μ
Longwave
H2O Window
Total
Absorption
and
Scattering by
CO2 & H2O
Annotations by Ira Glickstein Feb 2011 TVPClub.blogspot.com

Observational Evidence for an Enhanced Greenhouse effect

More incoming long wavelength infrared energy

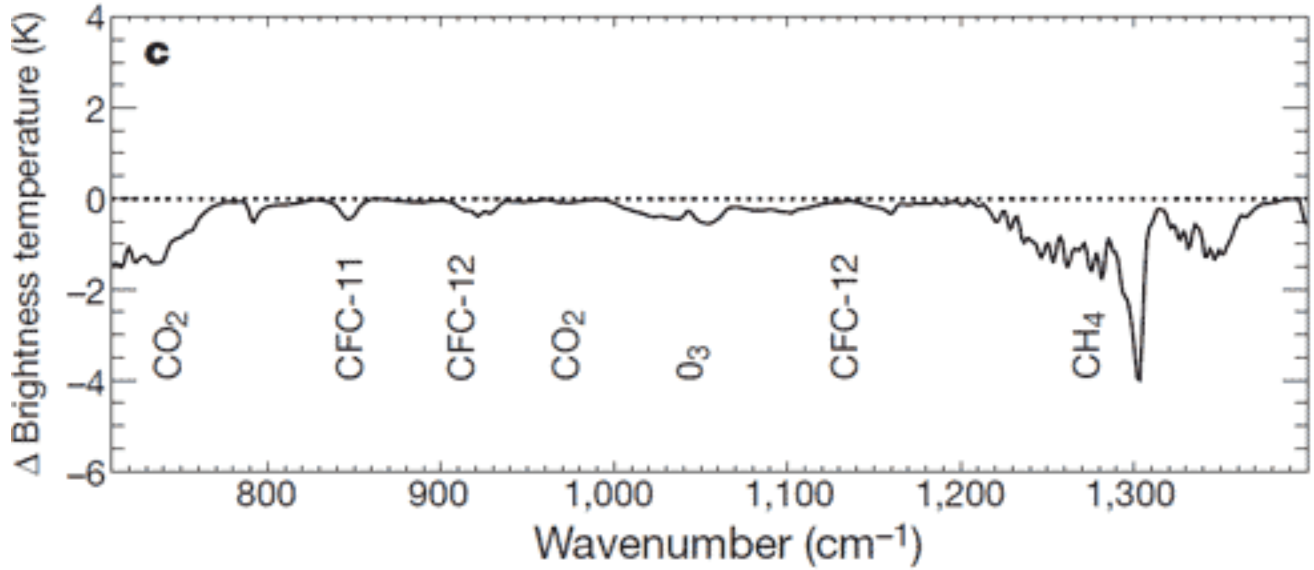


Linear trend of daily (L_d) over 3200 global weather stations where data are available for at least 300 months (25 years) during the period of 1973-2008.

Wang, K., and S. Liang, (2009), Global atmospheric downward longwave radiation under all-sky conditions from 1973 to 2008, *Journal of Geophysical Research*, 114, D19101, doi:10.1029/2009JD011800

Observational Evidence for an Enhanced Greenhouse effect

Less long wavelength infrared radiation escaping to outer space at the wavelengths associated with greenhouse gases absorb.

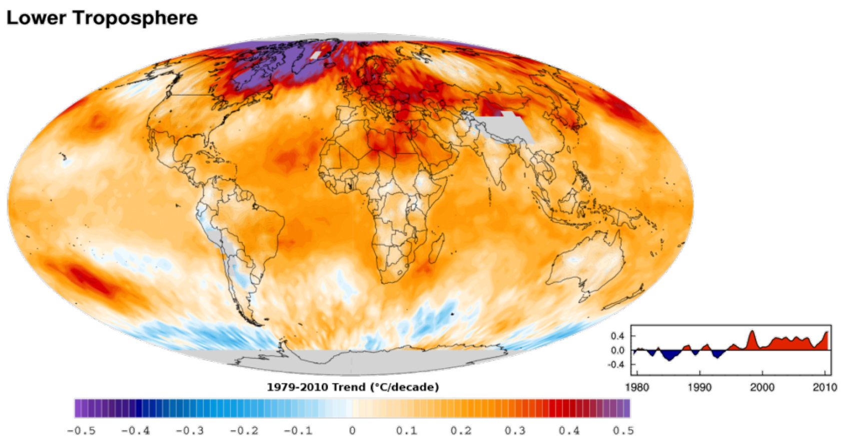


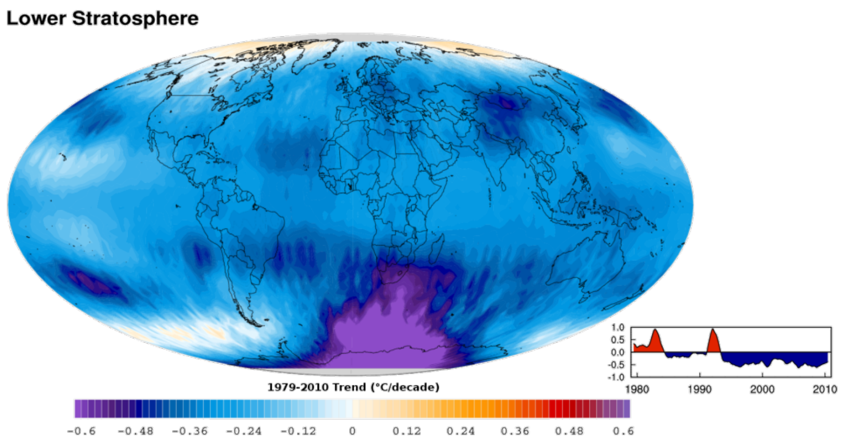
Change in outgoing IR from 1970 to 1997. Reductions attributed to known spectroscopic properties of GHGs.

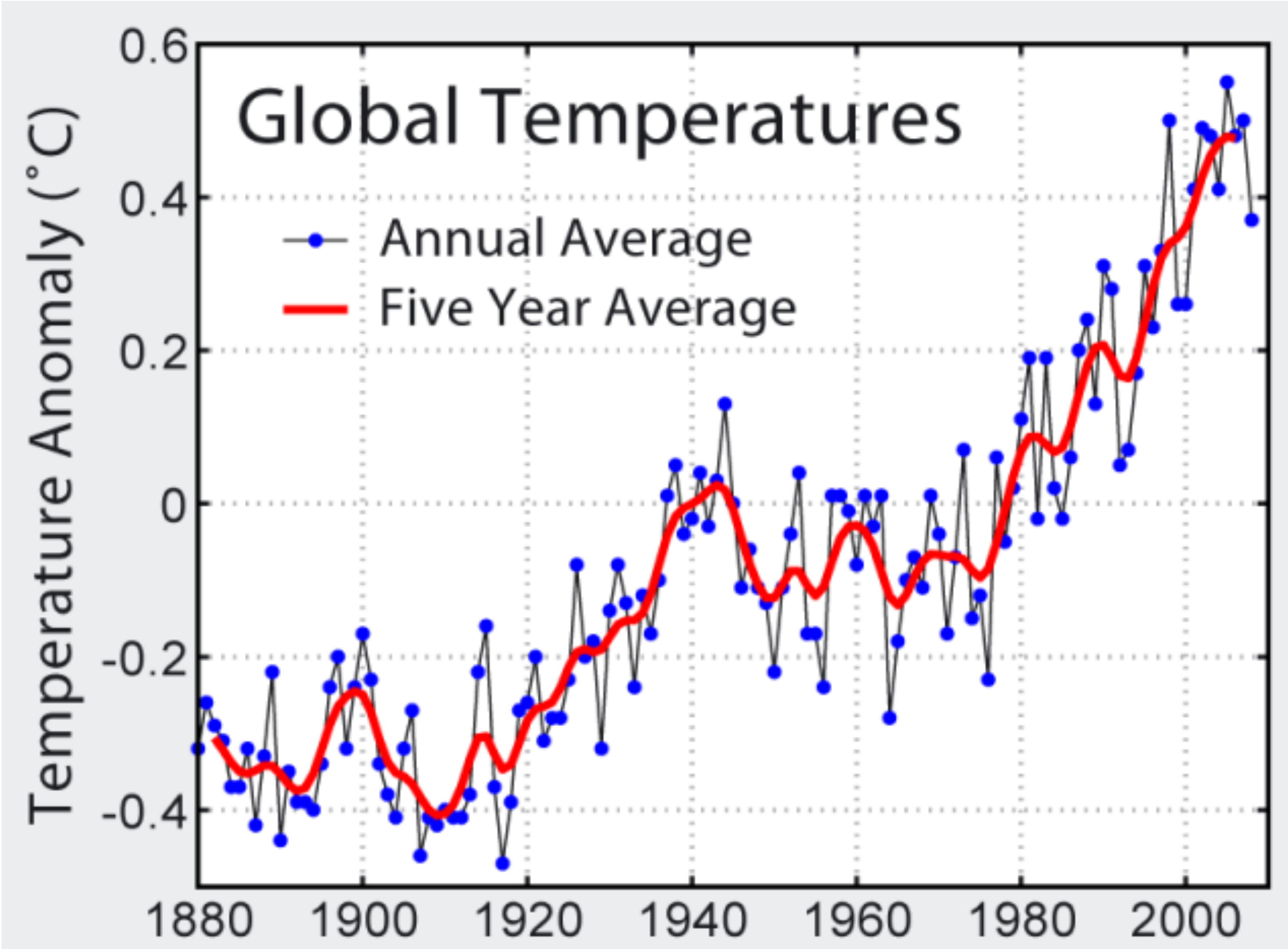
John E. Harries et al. *Nature* **410**, 355-357 (15 March 2001) | doi:10.1038/35066553

Observational Evidence for an Enhanced Greenhouse effect

Tropospheric warming and stratospheric cooling

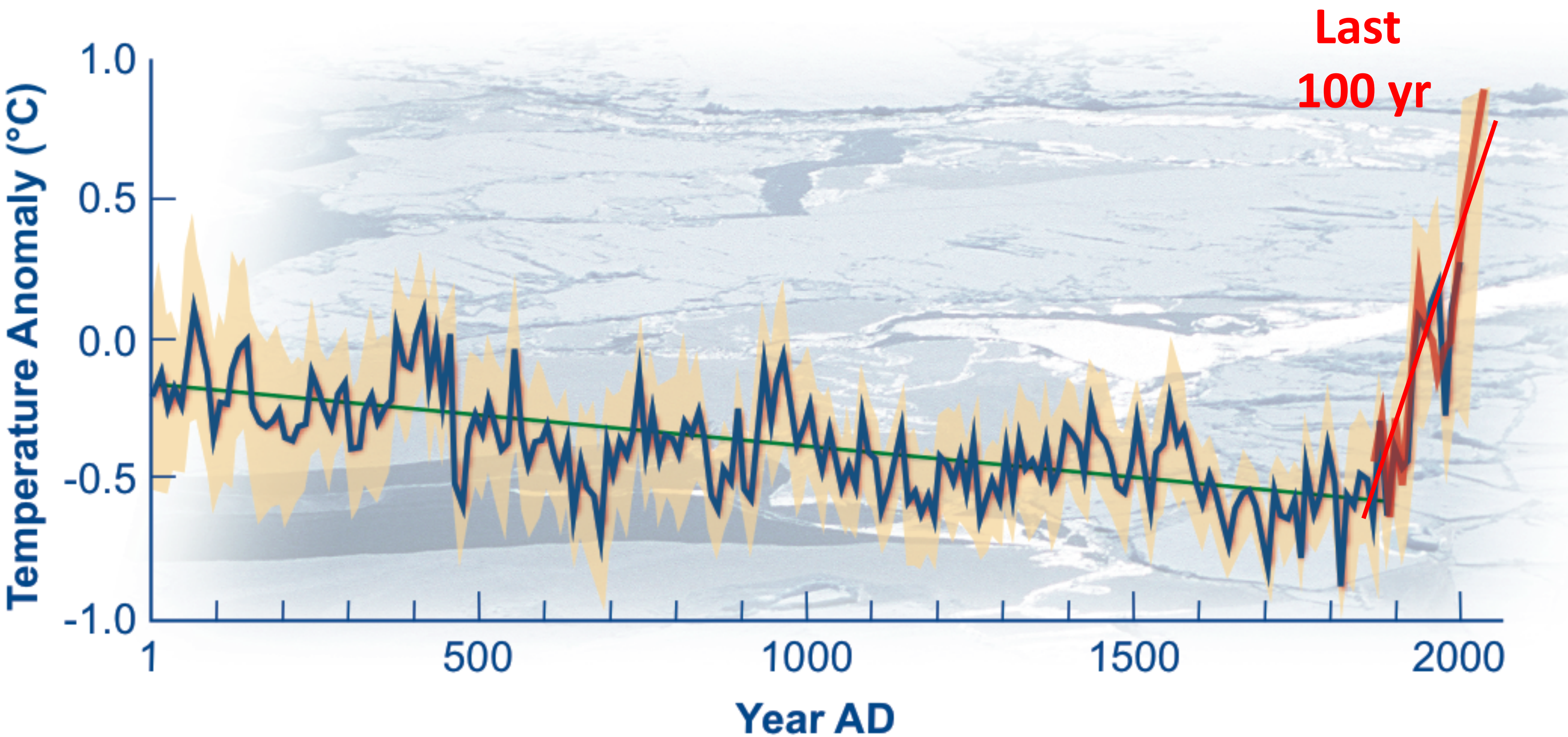






Global Temperatures
Annual Average
Five Year Average
Temperature Anomaly (°C)
0.6
0.4
0.2
0
-0.2
-0.4
1880
1900
1920
1940
1960
1980
2000

Observation
temperature record

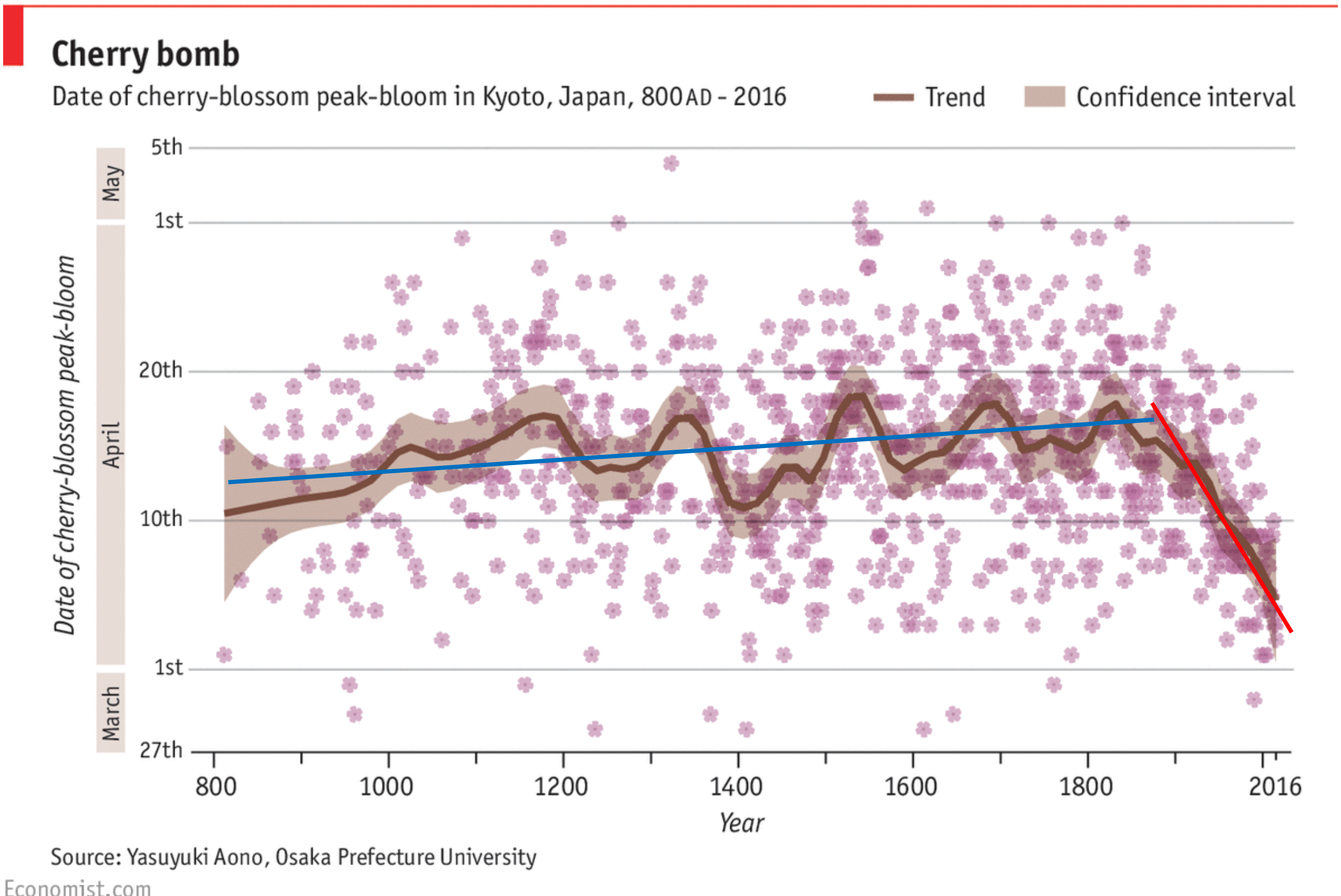


Arctic air temperature change reconstructed (blue), observed (red)

http://www.copenhagendiagnosis.com/

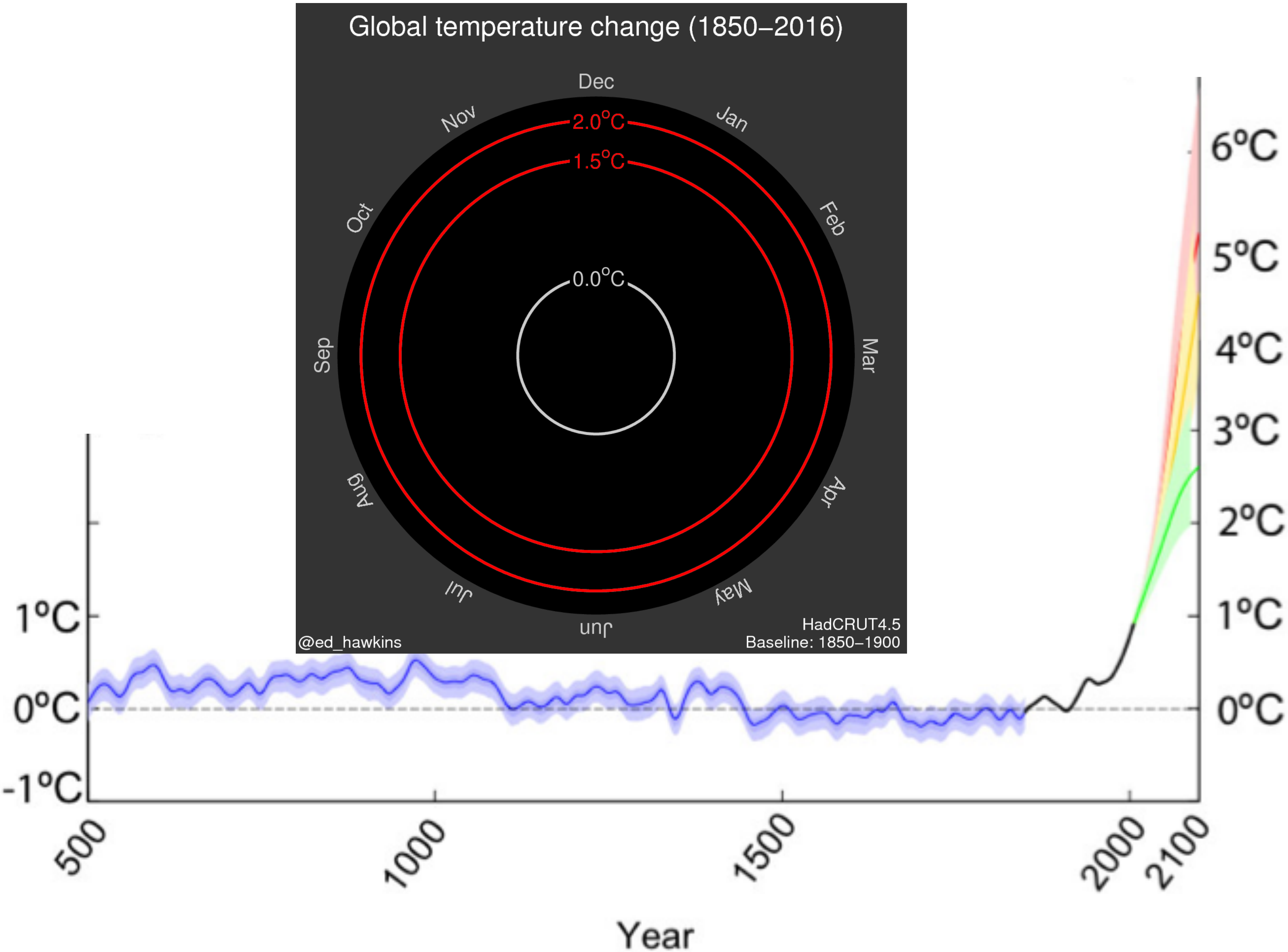
Observation

cherry blossom bloom date



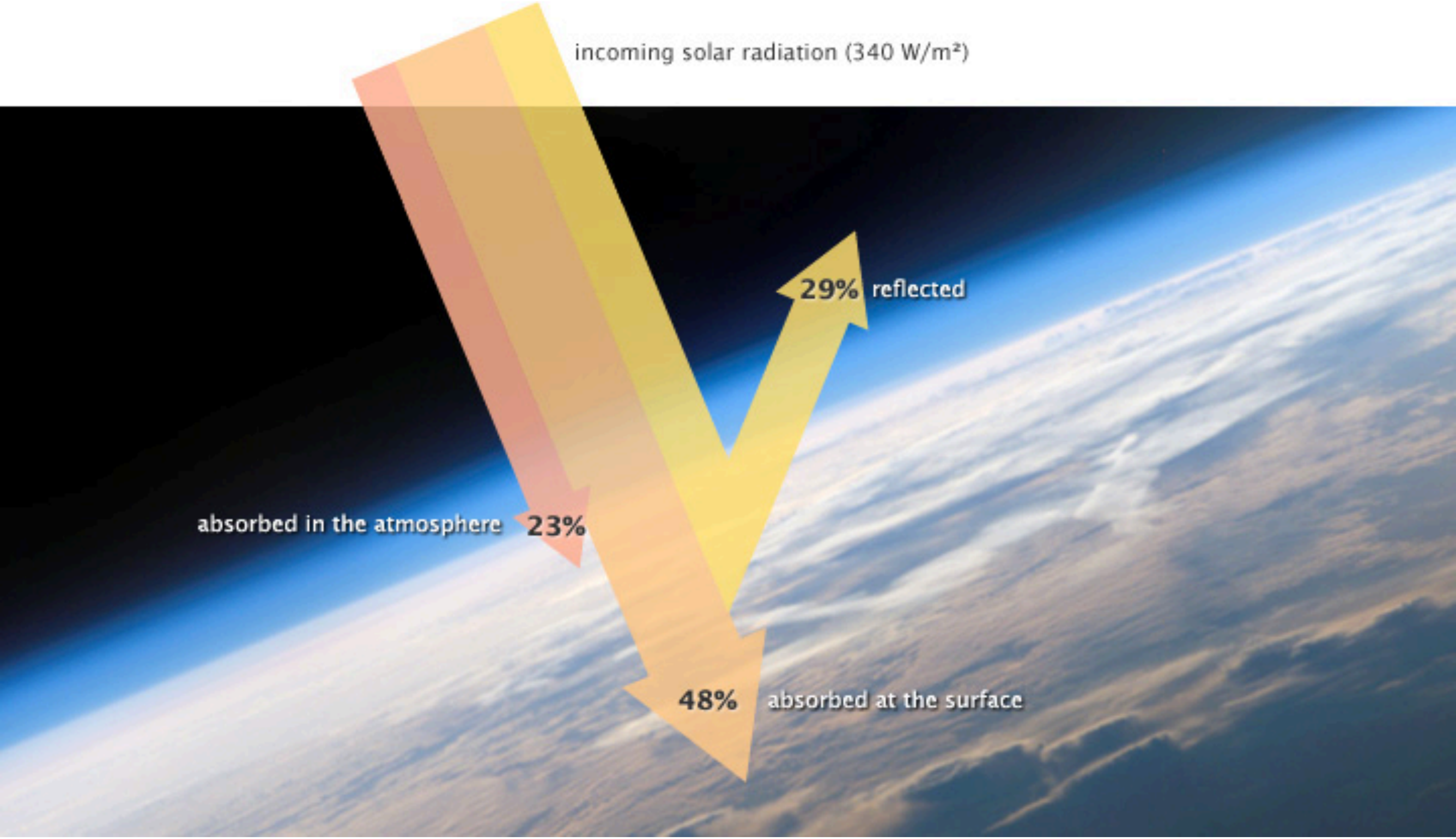
https://www.economist.com/blogs/graphicdetail/2017/04/daily-chart-4

Global Temperature Relative to 1800-1900 (°C)



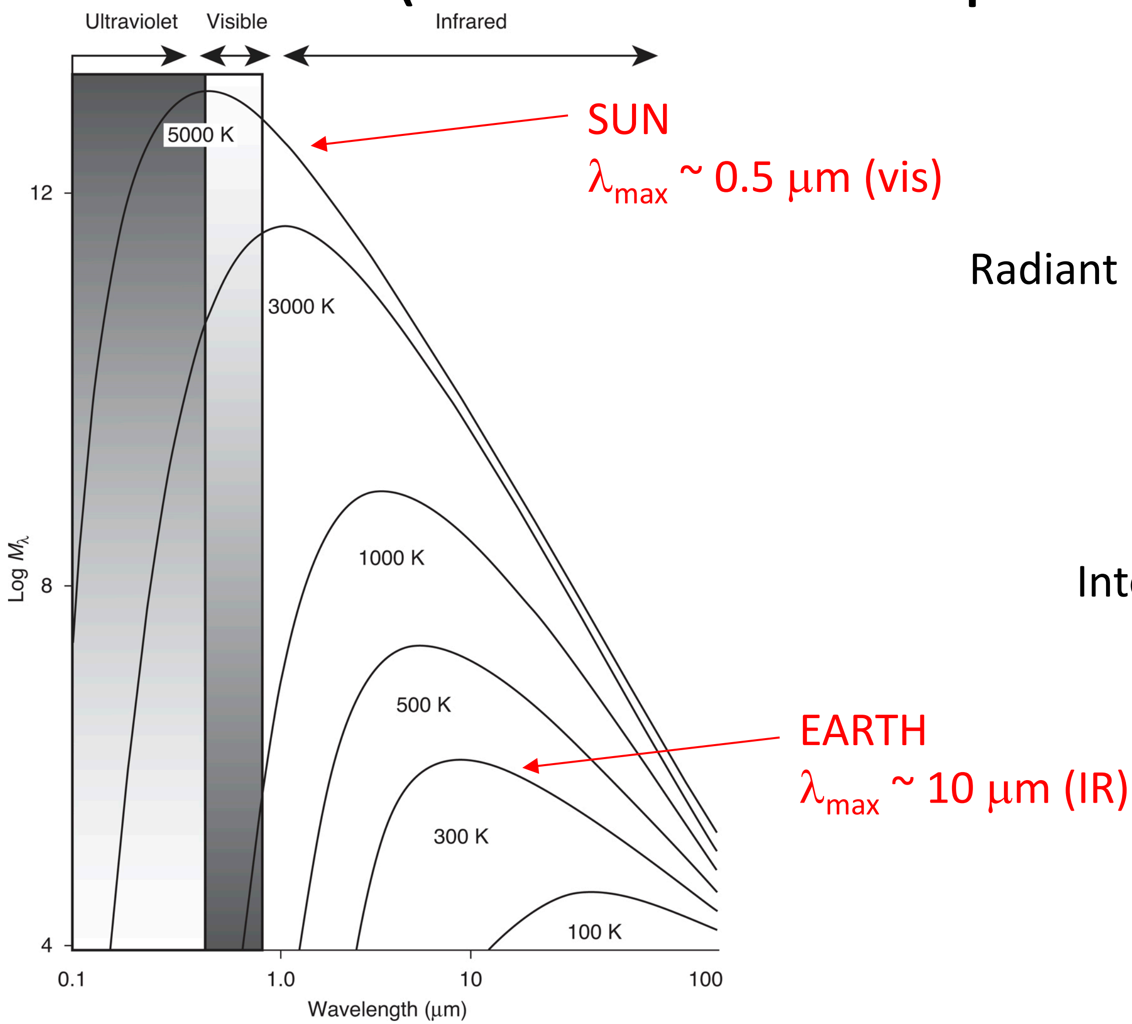
Incoming Solar Radiation

(short wavelength)



Outgoing Blackbody Radiation

(function of Temperature)



Radiant Energy at specific wavelength

$$E_\lambda = \frac{2\,\pi\,h\,c^2\,\lambda^{-5}}{\left(e^{\frac{hc}{\lambda kT}} - 1\right)}$$

Integrating over all wavelengths yields total radiant energy

$$E_{total} = \frac{2\,\pi^5\,k^4\,T^4}{15\,c^2\,h^3}$$

$$= \sigma\,T^4$$

Radiative Balance

Radiant Energy In = Radiant Energy Out

$\Omega \pi r^2 (1 - A)$

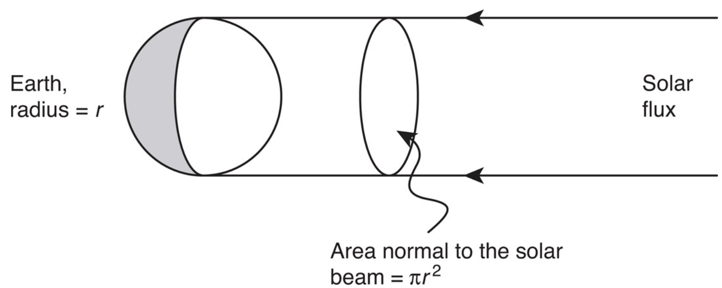
$4 \pi r^2 \sigma T^4$

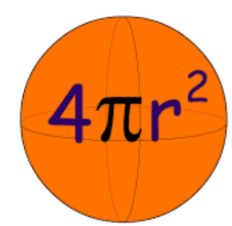
Solar flux

$\Omega = 1368 \text{ W m}^{-2}$

Stefan-Boltzmann

$\sigma = 5.67\text{x}10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$





Surface area of sphere x E_{total}

Radiative Balance

$$\Omega \; \pi \, r^2 \, (1 - A) = 4 \, \pi \, r^2 \, \sigma \, T^4$$

$$\Omega \, (1 - A) = 4 \, \sigma \, T^4$$

$$\therefore T = \left[\frac{(1 - A)\Omega}{4 \, \sigma} \right]^{1/4}$$

$$= 255 \, K \, (-18 \, {}^{o}C)$$

Predicted global average temperature

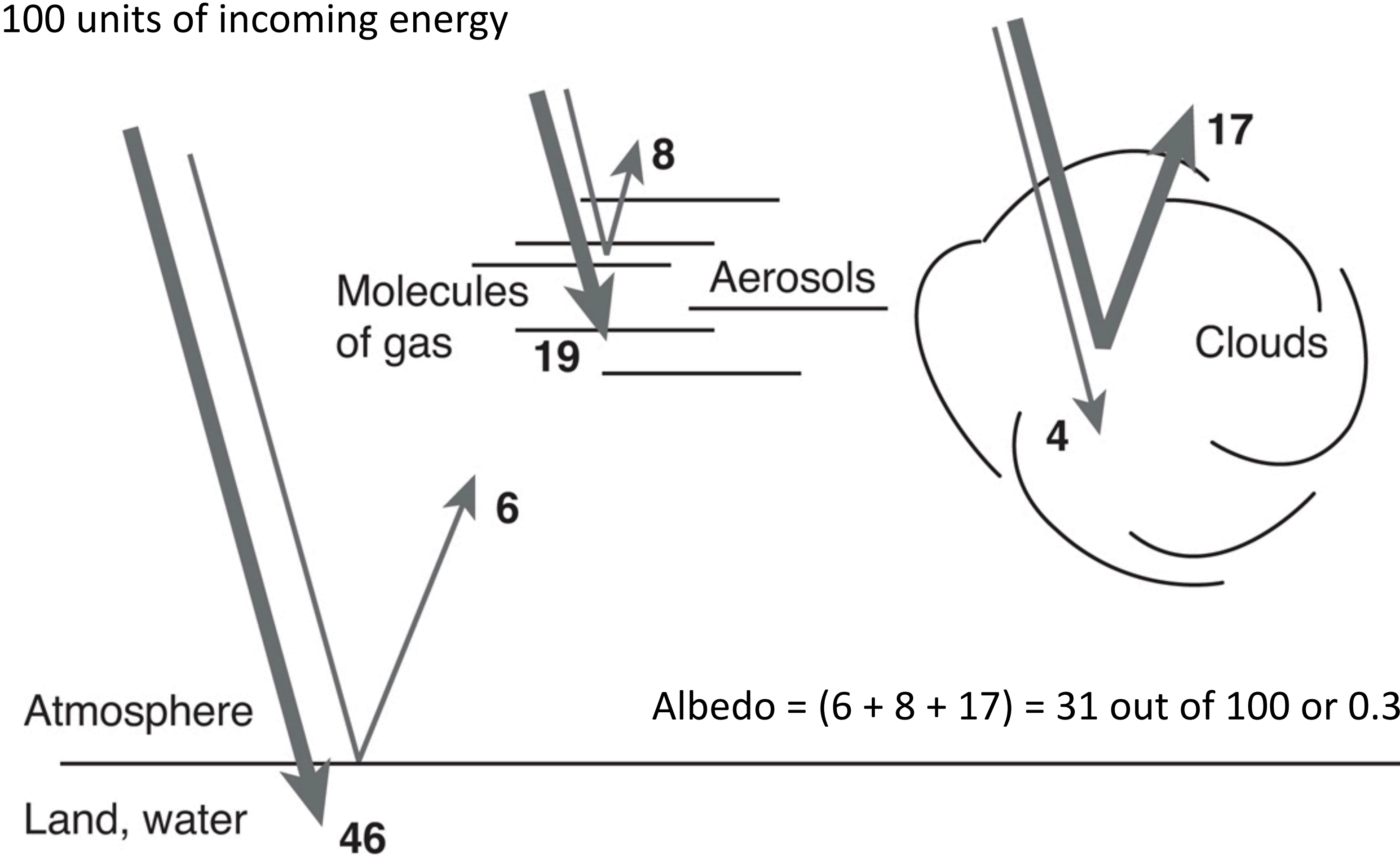
$$\sigma \, T^4 = \frac{(1 - A)\Omega}{4} + {}'\Delta E'$$

Radiant energy absorbed by Earth's atmosphere 'greenhouse' effect

Radiative Forcing (W m^{-2})

Incoming Solar Radiation
(short wavelength)

100 units of incoming energy



Albedo = (6 + 8 + 17) = 31 out of 100 or 0.31

Fig 8.4 (van Loon)

Outgoing Infrared Radiation

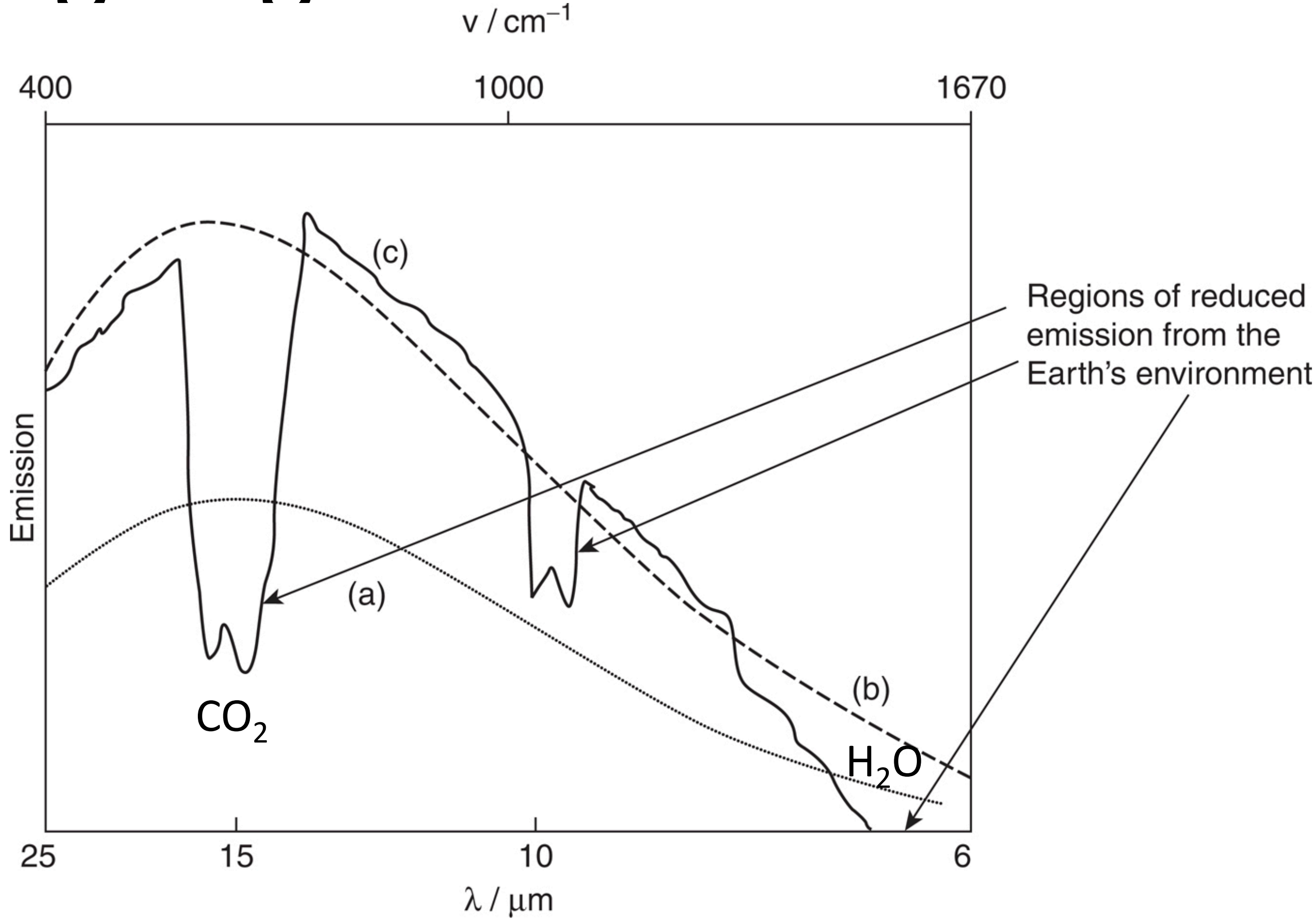


Fig 8.6 (van Loon)

'IR Windows' in Earth's Atmosphere

8 – 10 μm (1200 – 1400 cm^{-1})
11-14 μm (800 – 1000 cm^{-1})
16-25 μm (400 – 600 cm^{-1})

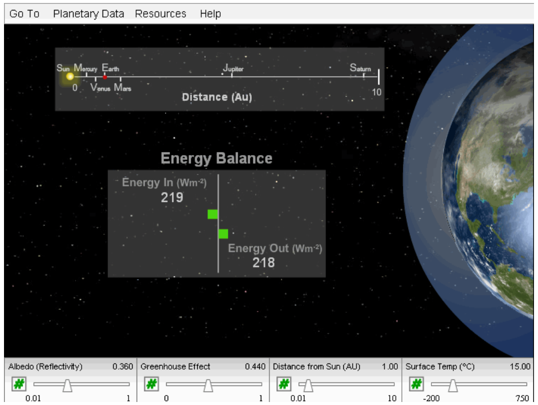
[King's Centre for Visualization in Science](http://kcvs.ca/concrete/visualizations/global-climate-change)

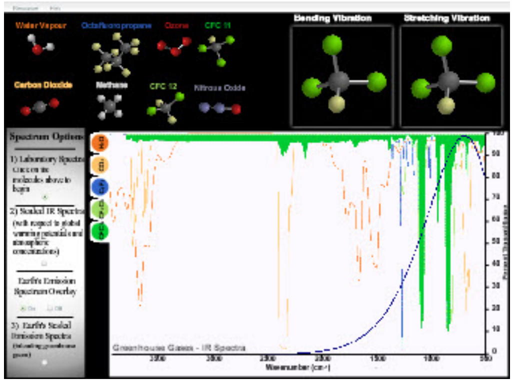
http://kcvs.ca/concrete/visualizations/global-climate-change

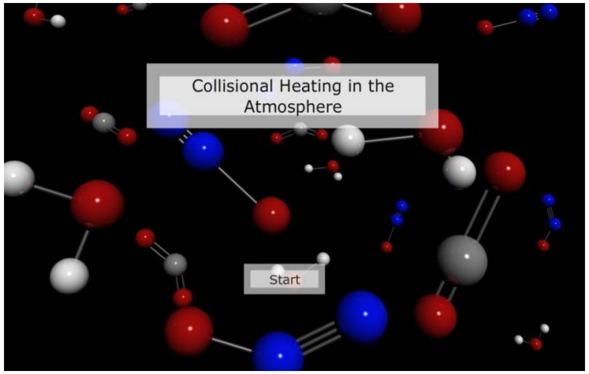
Planetary Climates: Radiative Energy Balance

Infrared Spectral Windows

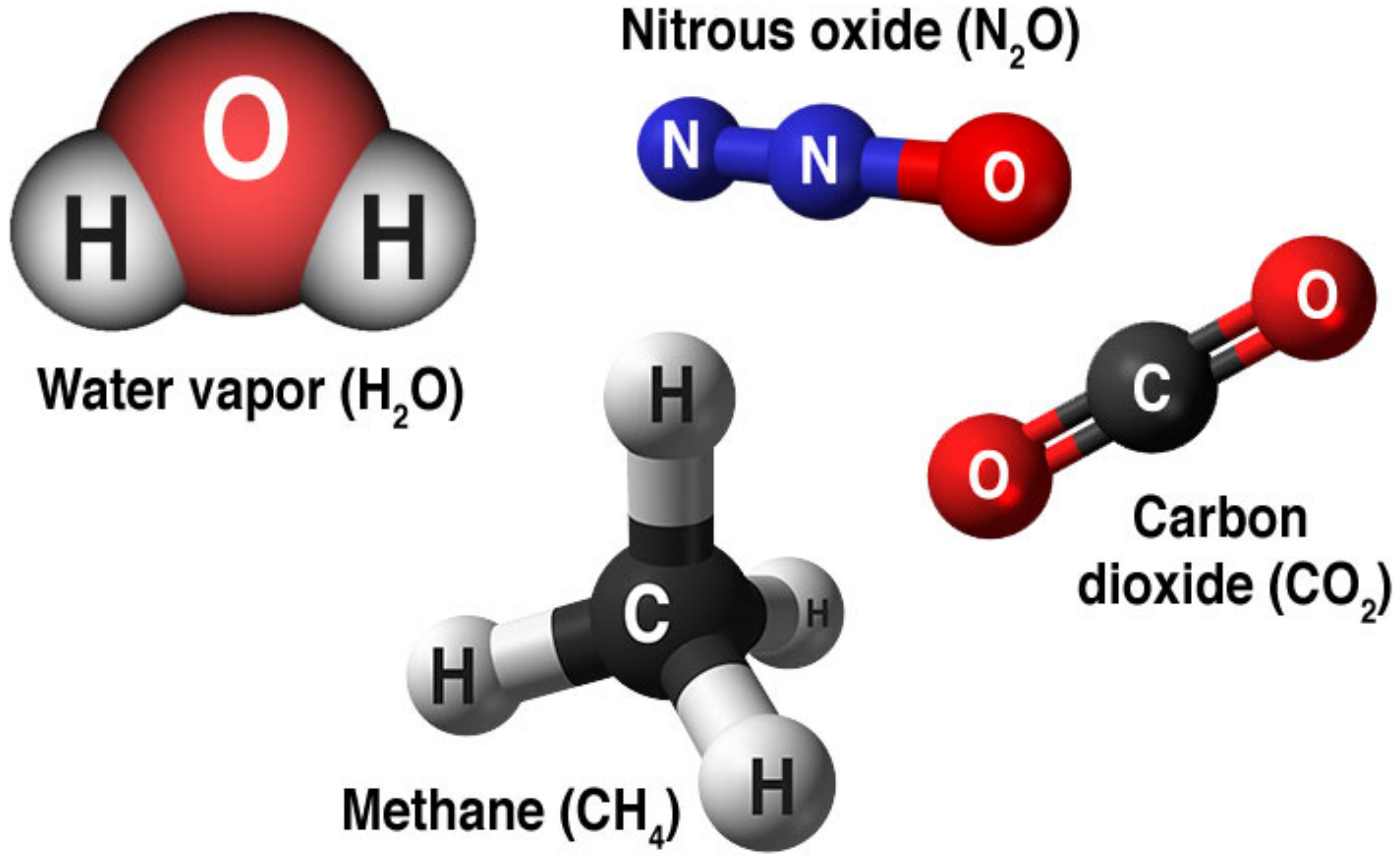
Collisional Heating in the Atmosphere





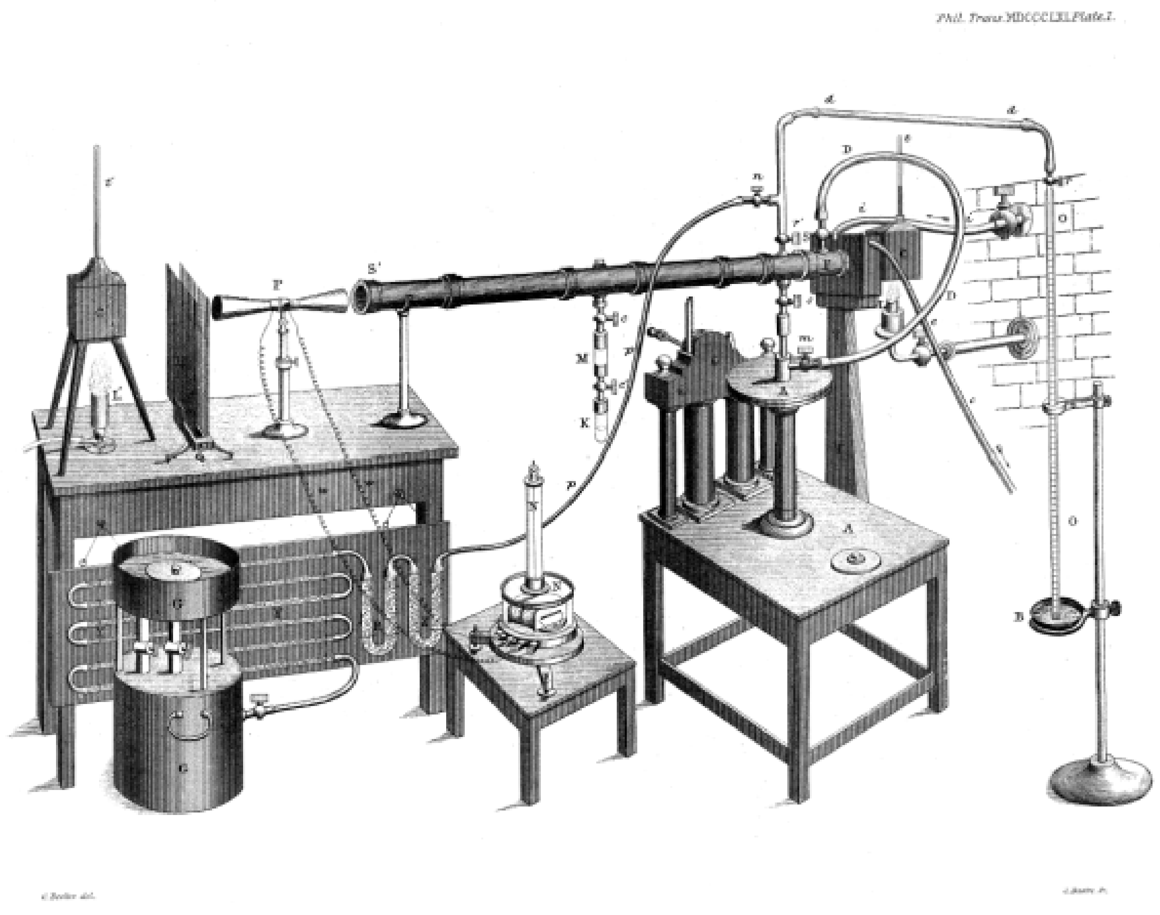


3. Greenhouse Gases and Aerosols



Demonstration of variable heat absorbing properties of atmospheric gases

John Tyndall, Royal Albert Hall, London, 1864



http://www.climate4you.com/images/JohnTyndall%202.jpg

IR Absorption
(spectroscopic property)

Transitions between quantized vibrational energy levels within molecules.

(does not apply to monoatomic gases, e.g. Ar and He)

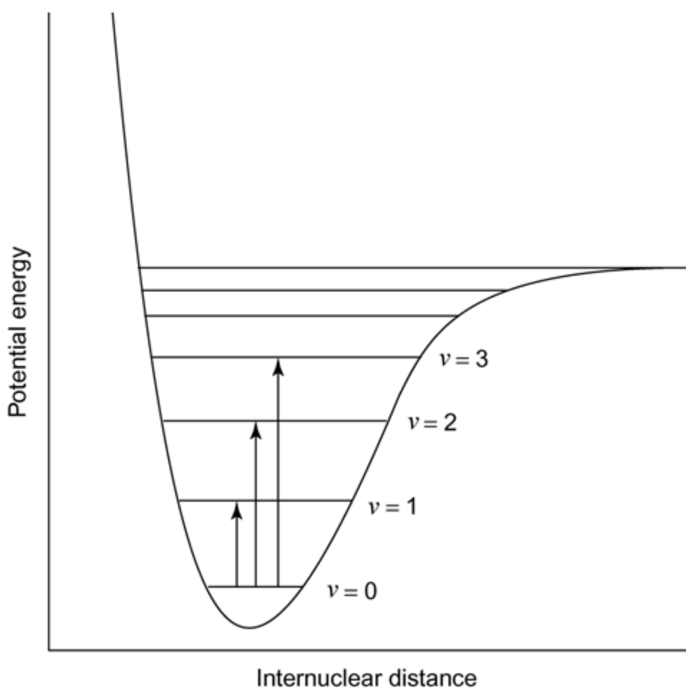
Governed by QM selection rules.

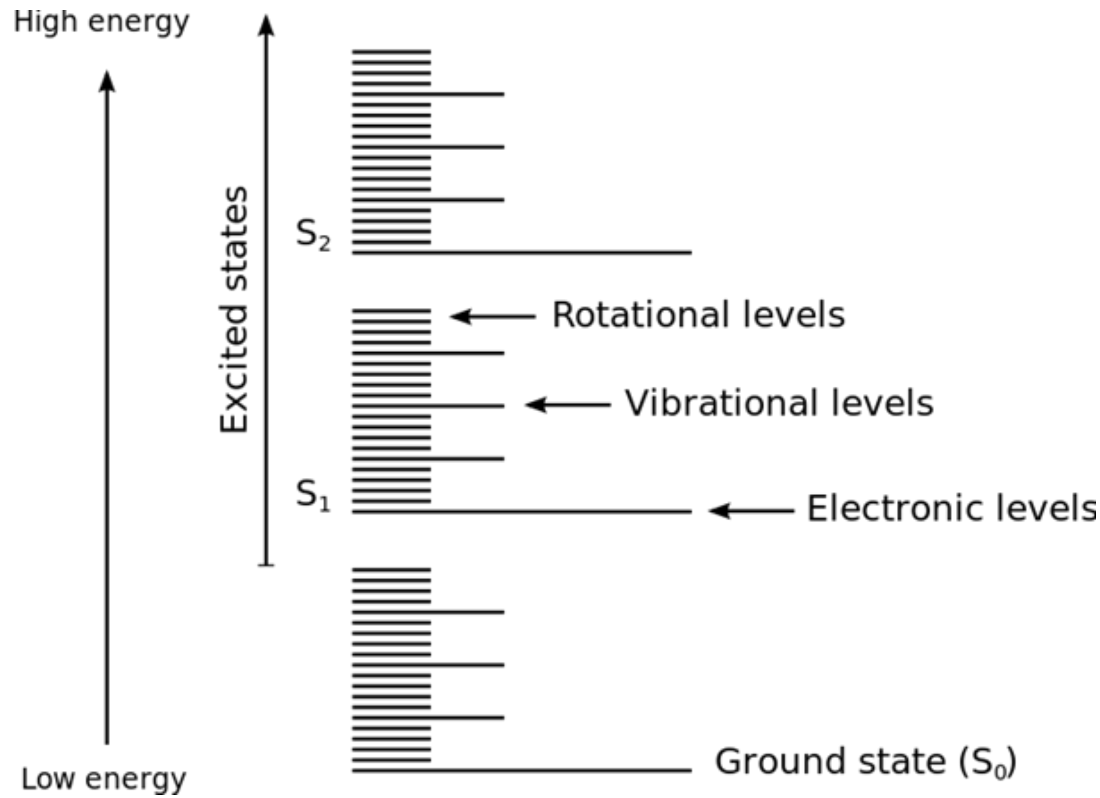
--> change in dipole moment between upper and lower vibrational state

(not met by homonuclear diatomics, e.g. N_2 and O_2)

3N – 5 vibrational modes (where N = #atoms in molecule)

Energy Level Diagrams





Carbon Dioxide

Symmetric stretching modes involve no change in dipole moment → IR inactive
Asymmetric stretching modes involve large change in dipole moment → IR active

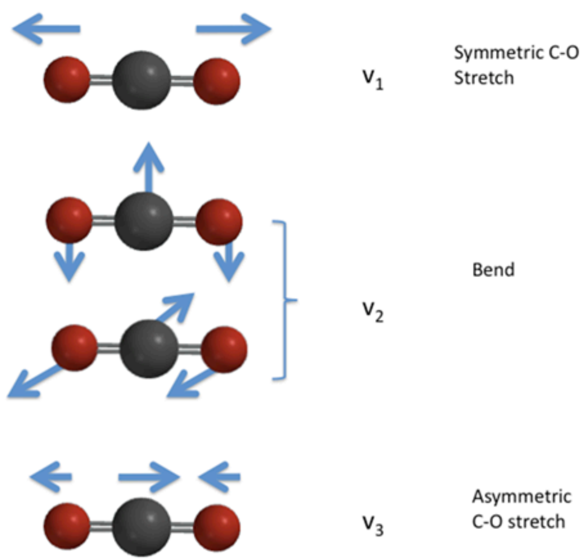
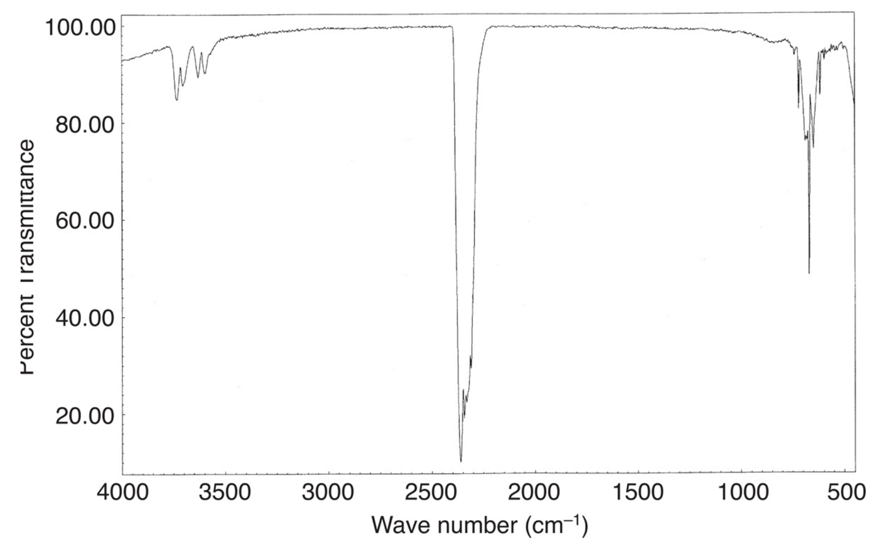
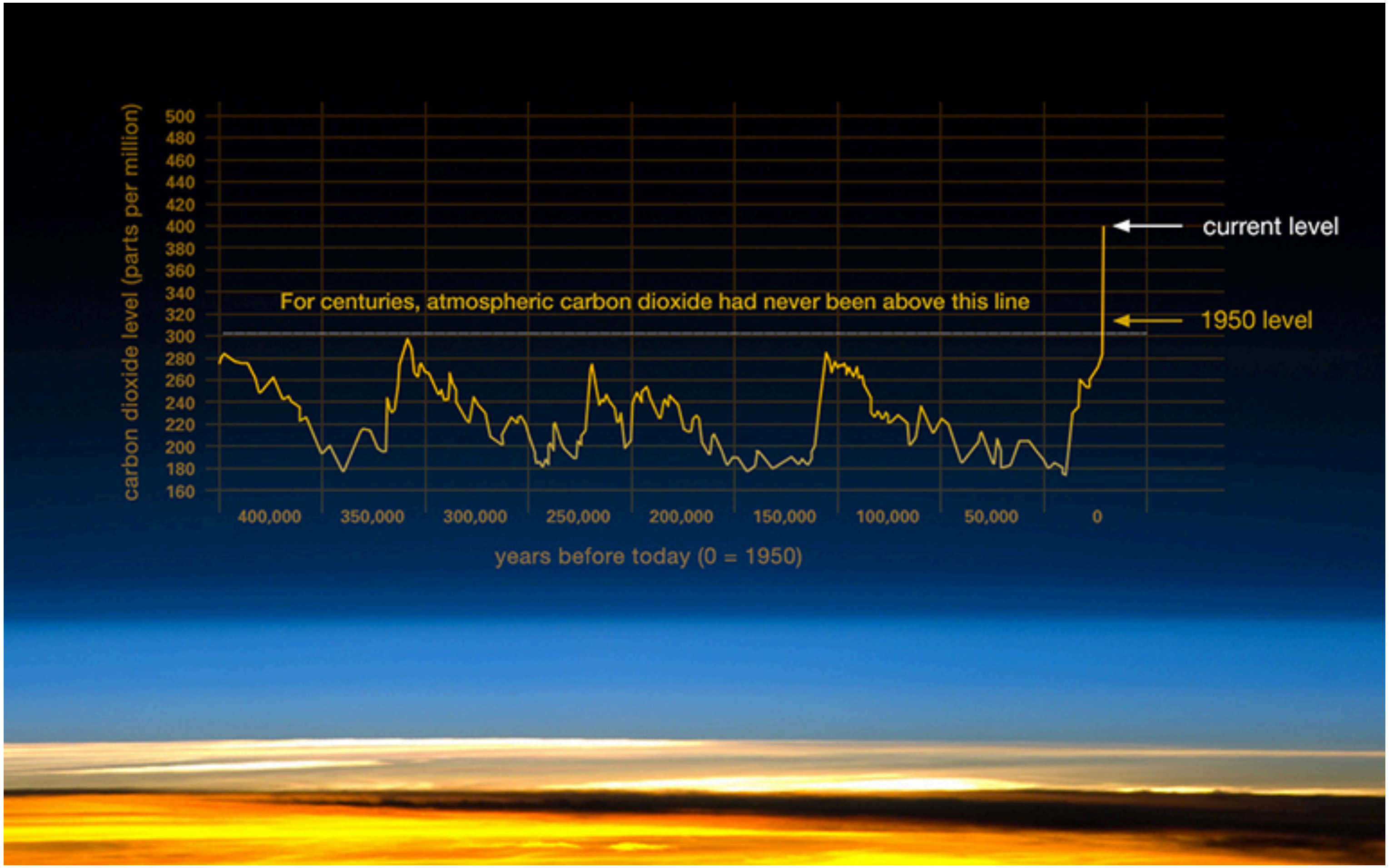


Fig. 1 Vibrational modes of CO_2



Carbon Dioxide



Carbon Dioxide

Sources

Sinks

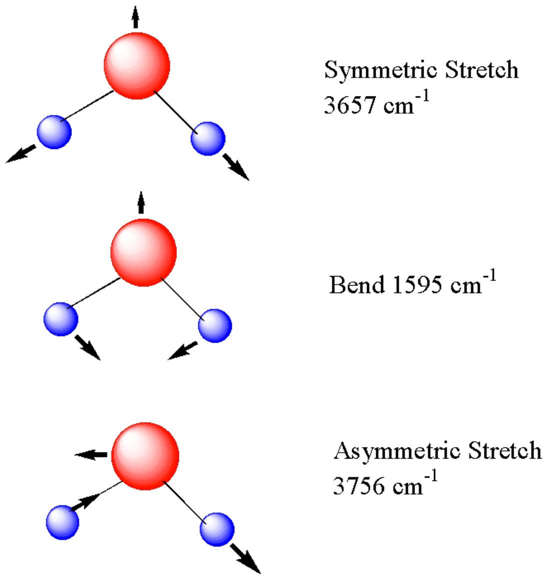
CO_2 –Temperature Feedback Loops

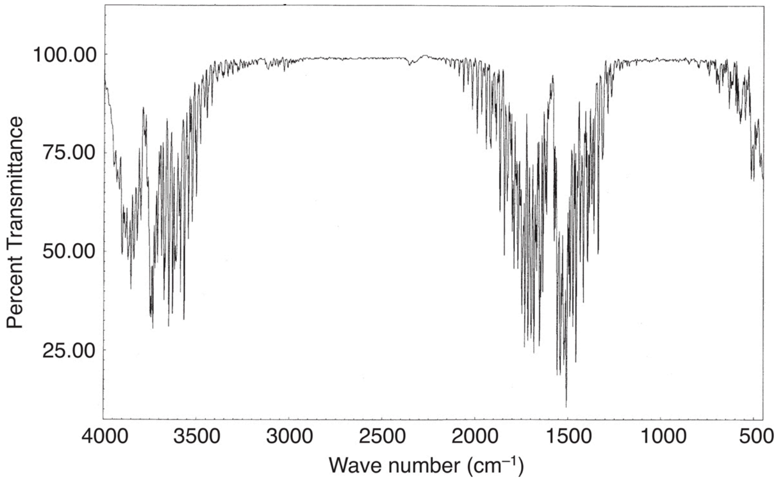
Decreasing solubility in water

Increasing biomass production

Water Vapour

Asymmetric stretching and bending modes involve large change in dipole moment
→ IR active



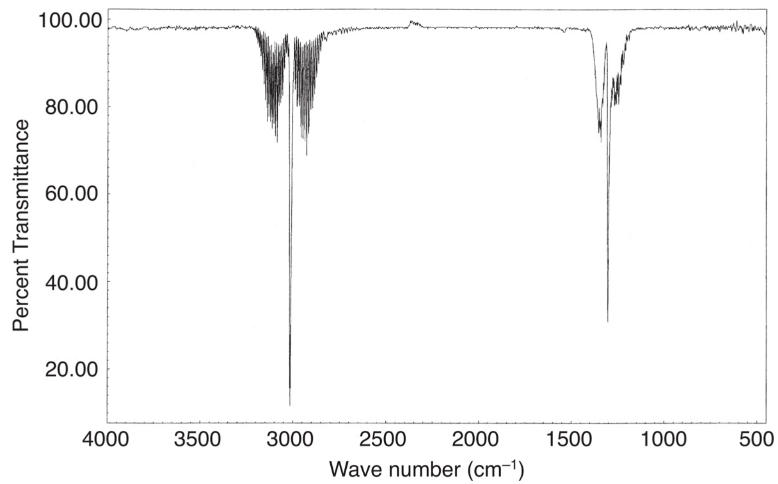


H_2O –Temperature Feedback Loops

Increased evaporation of water

Increasing Albedo

Methane

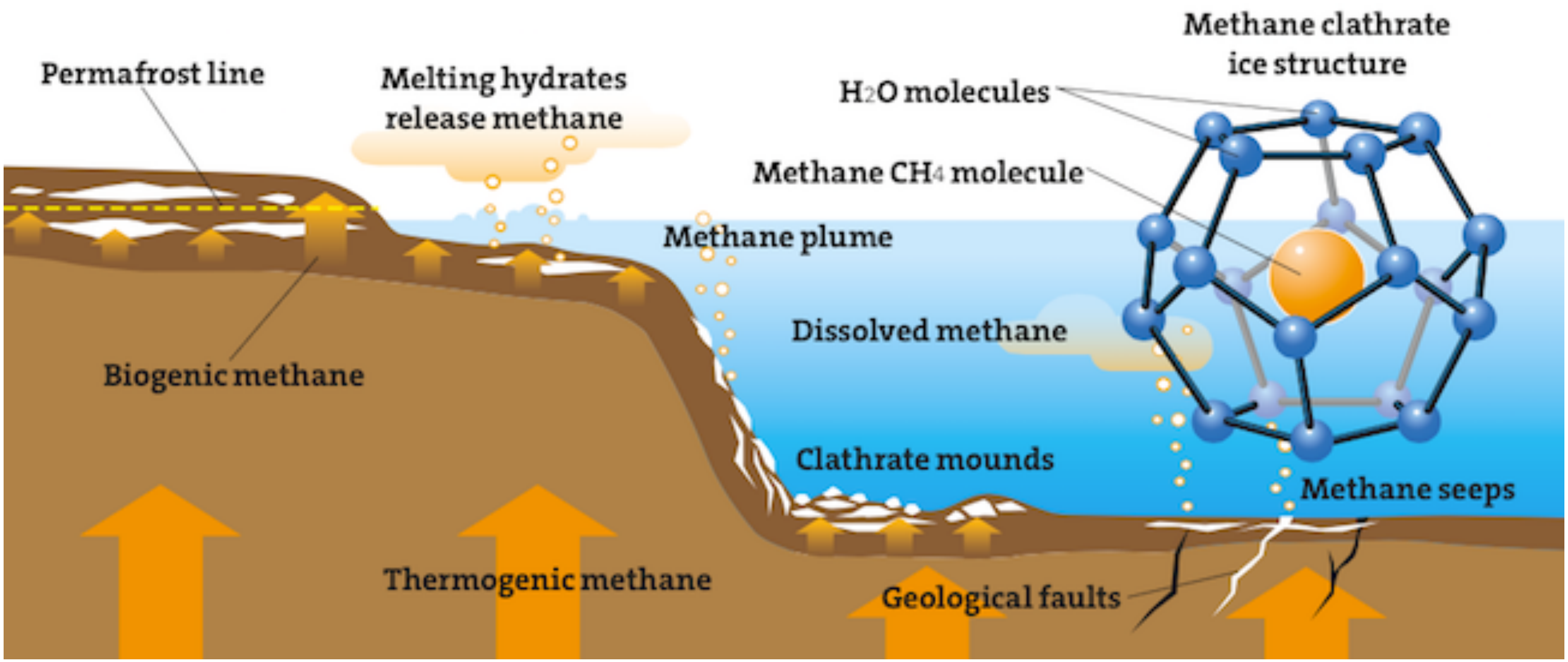


Sources

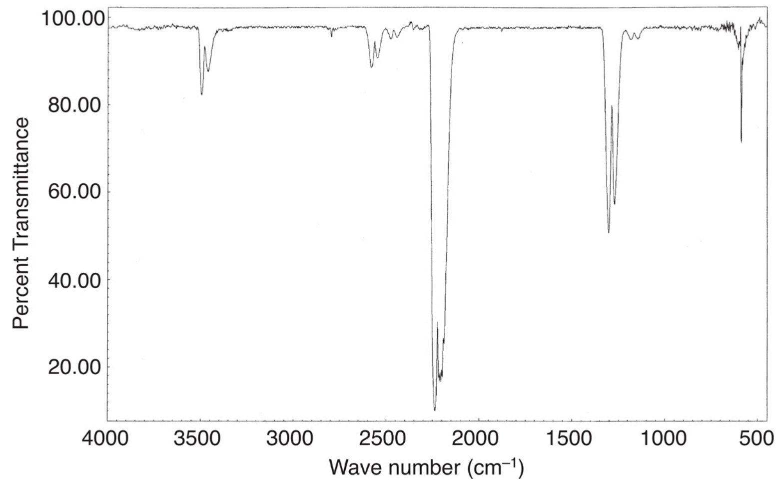
Sinks

CH_4 –Temperature Feedback Loops

Permafrost and clathrate destabilization



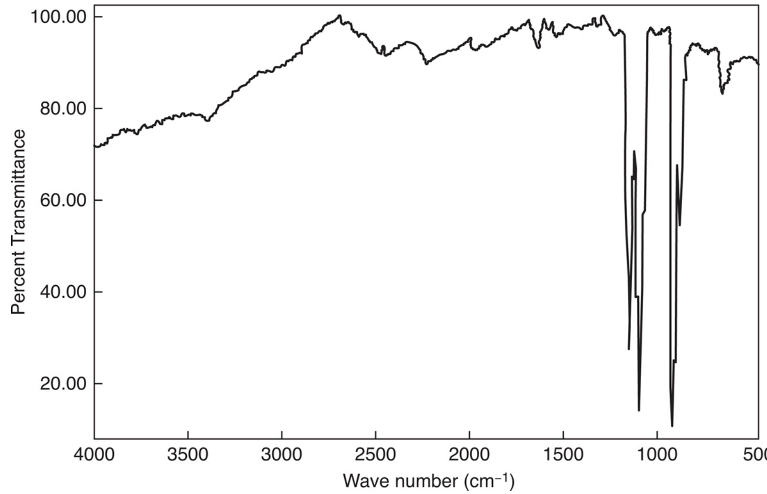
Nitrous Oxide



Sources

Sinks

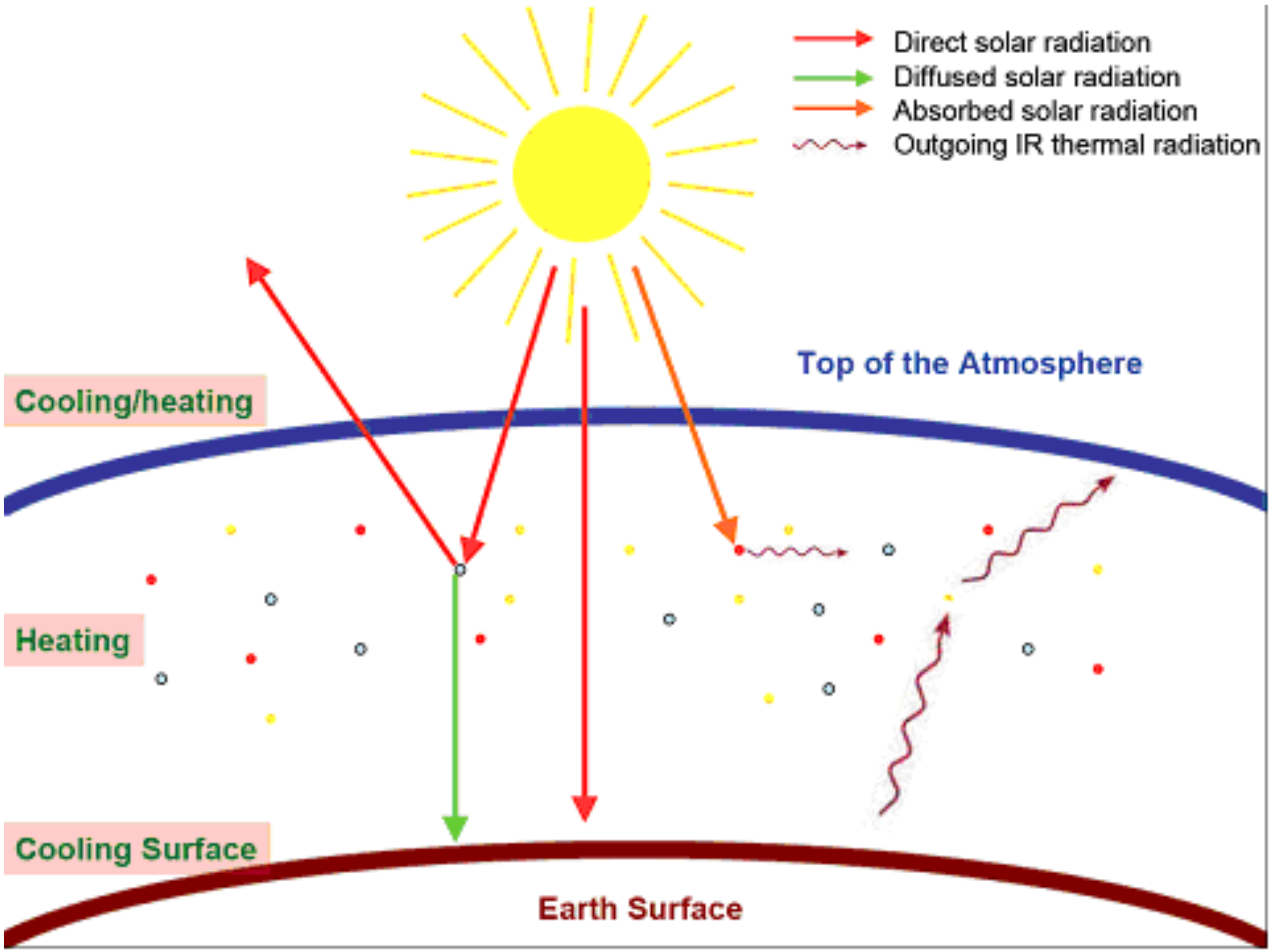
Ozone, CFCs, HCFCs and halocarbons



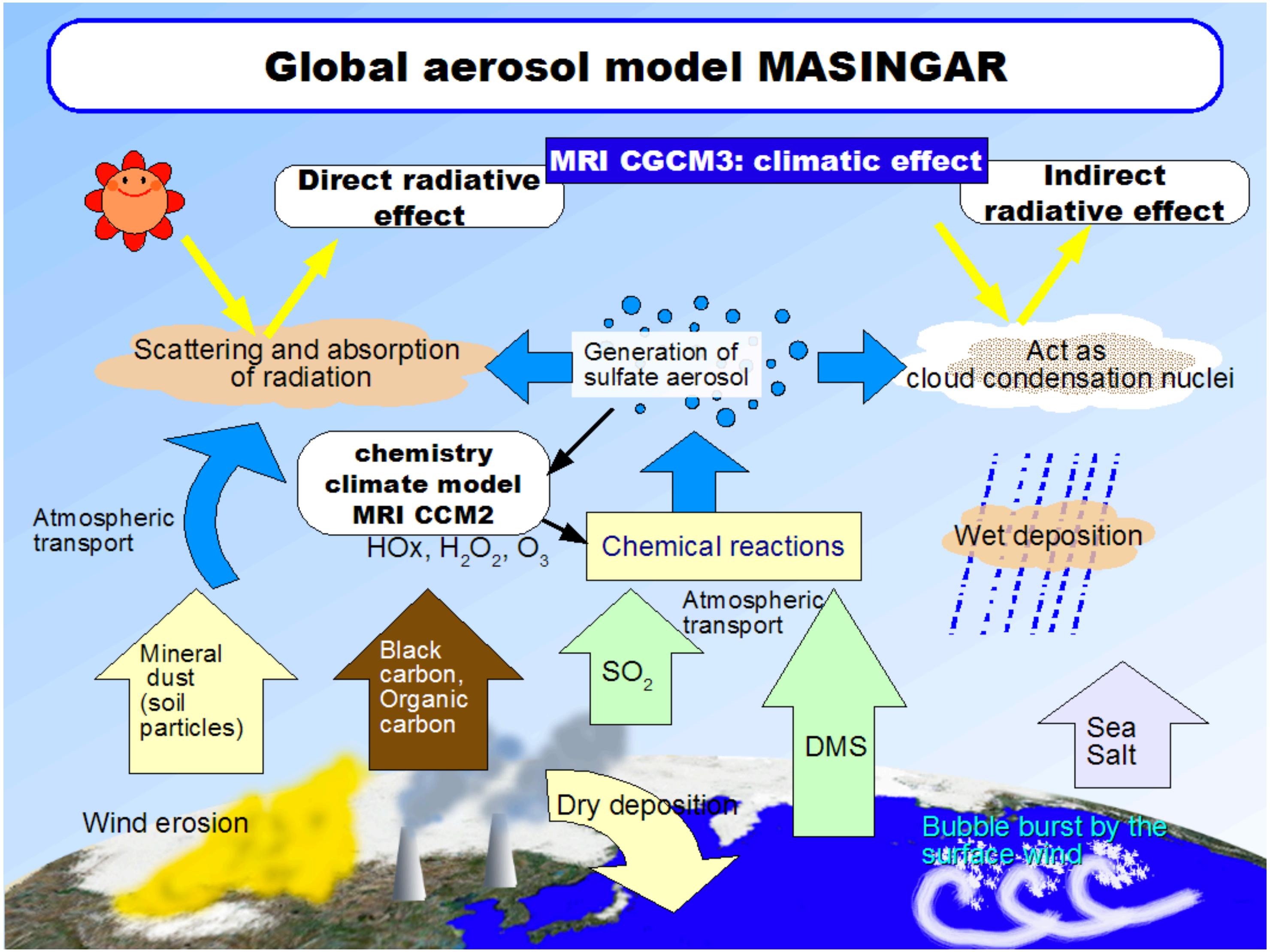
Sources

Sinks

Aerosols (absorb and reflect)



Aerosol Models



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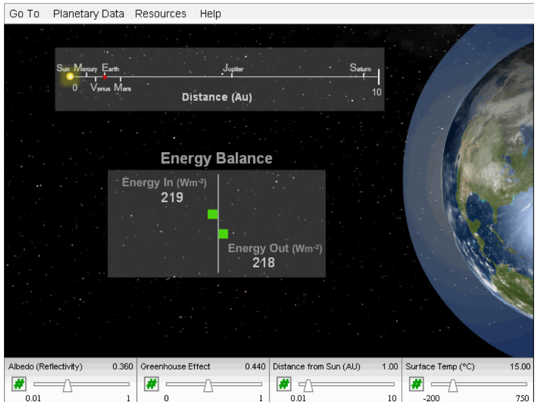
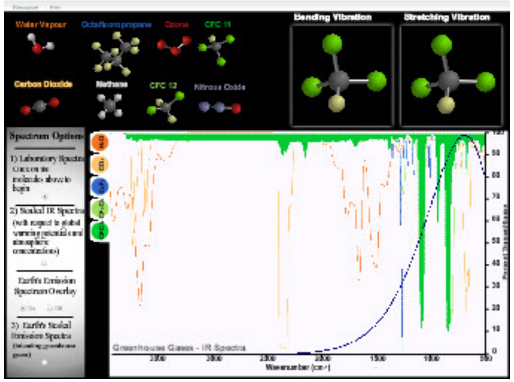
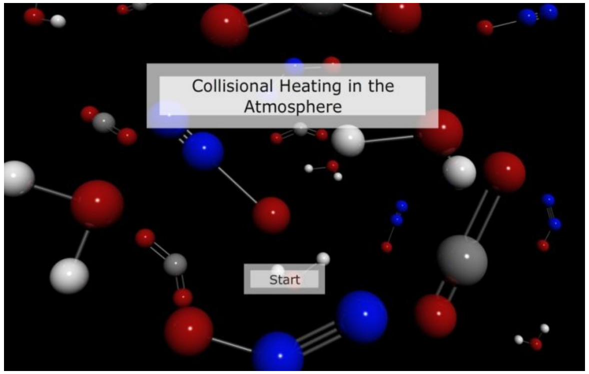






4. Radiative Forcing and GWP

Three factors to rank immediate relative importance of GHGs

1) Current atmospheric concentrations

2) Wavelength of IR absorption bands

3) Strength of IR absorption per molecule

Long term impact also requires atmospheric residence time (τ)

Definitions

Radiative forcing

$(W\ m^{-2})$

Relative instantaneous radiative forcing

(relative to equivalent mass of CO_2)

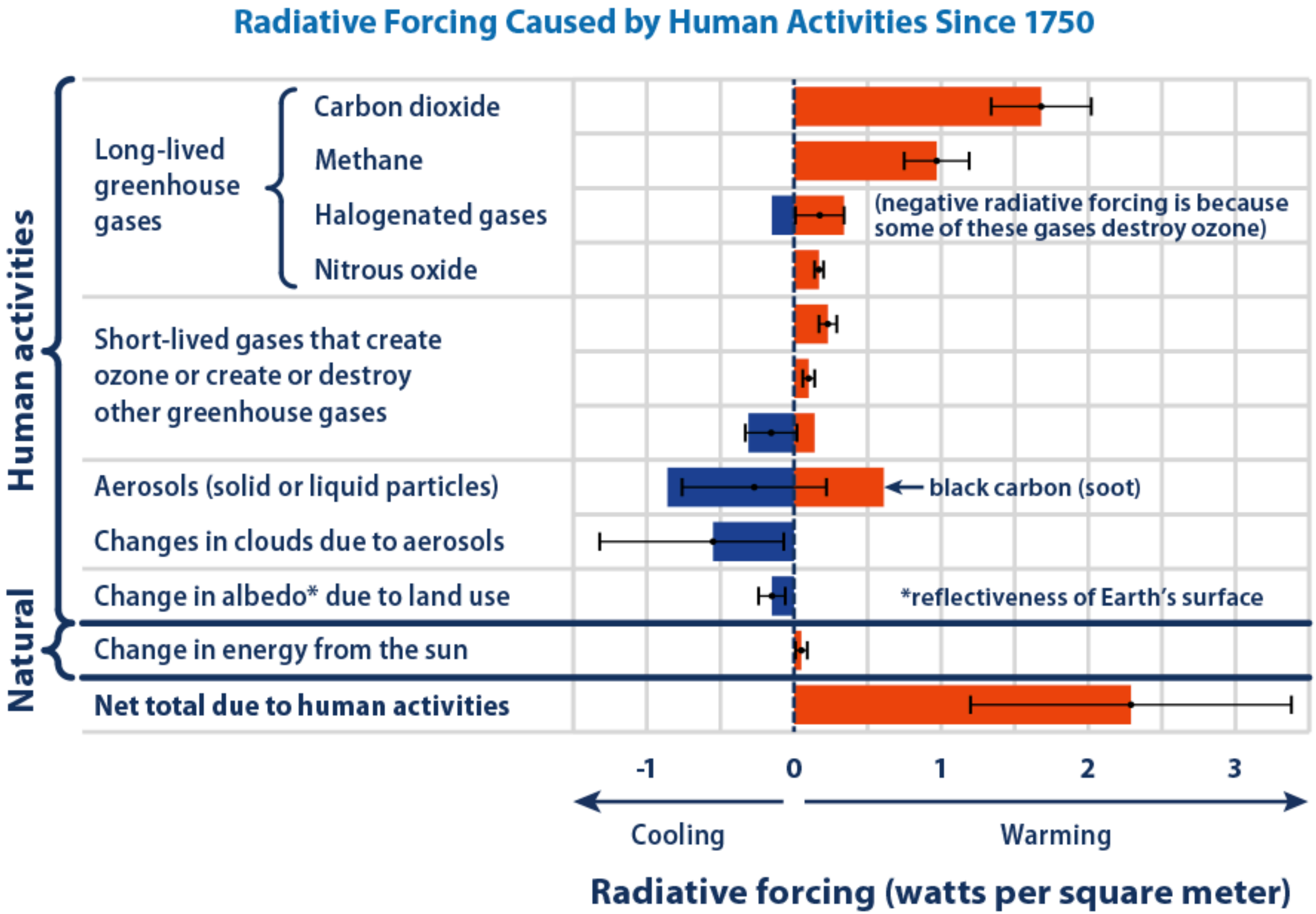
Global warming potential

(relative to equivalent mass of CO_2 over specified time)

Radiative Forcings and GWPs

	RF (W/m^2)	RRIF	τ (yr)	GWP - 100 yr
CO_2	1.7	1	50-100	1
CH_4	0.48	25	12	28-36*
N_2O	0.16	220	114	265-298
O_3	0.30			
CFC-12		23,000	100	10,900
HCFC-22		14,000	12	1,810
CCl_4		9,300	26	1,400
aerosols	-1.2 +/- ?			

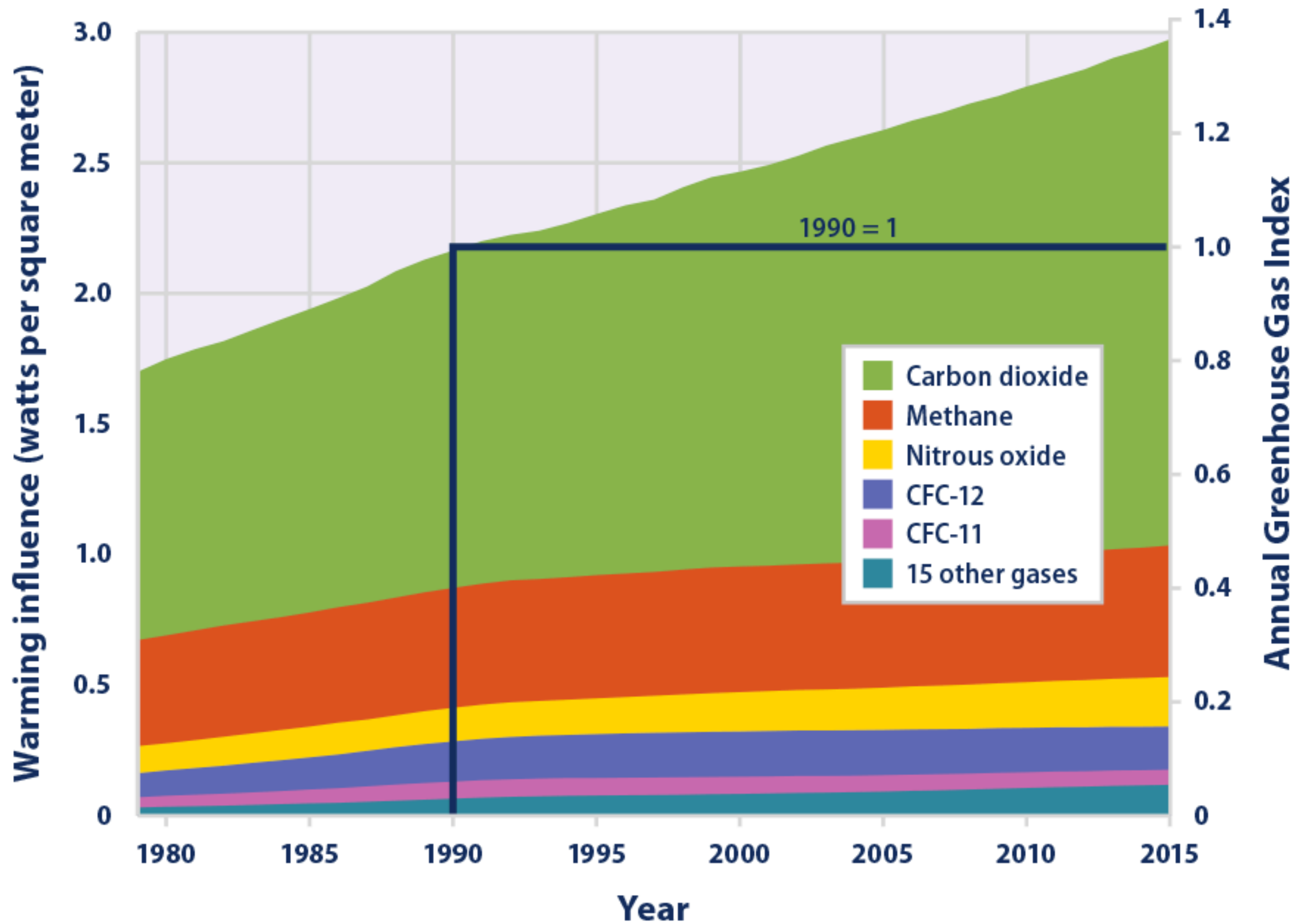
* Shine, K.P. et al., Radiative forcing of carbon dioxide, methane, and nitrous oxide: A significant revision of the methane radiative forcing, *Geophysical Res. Lett.*, 43(24), 12,614-12,623 (**2016**).



Data source: IPCC (Intergovernmental Panel onClimate Change). 2013. Climate change 2013: The physical science basis. Working Group I contribution to the IPCC Fifth Assessment Report. Cambridge, United Kingdom: Cambridge University Press. www.ipcc.ch/report/ar5/wg1.

For more information, visit U.S. EPA's "Climate Change Indicators in the United States" at www.epa.gov/climate-indicators.

Radiative Forcing Caused by Major Long-Lived Greenhouse Gases, 1979–2015



Data source: NOAA (National Oceanic and Atmospheric Administration). 2016. The NOAA Annual Greenhouse Gas Index. Accessed June 2016. www.esrl.noaa.gov/gmd/aggi.

For more information, visit U.S. EPA's "Climate Change Indicators in the United States" at www.epa.gov/climate-indicators.

Anthropogenic GHG
emissions and relative instantaneous forcing

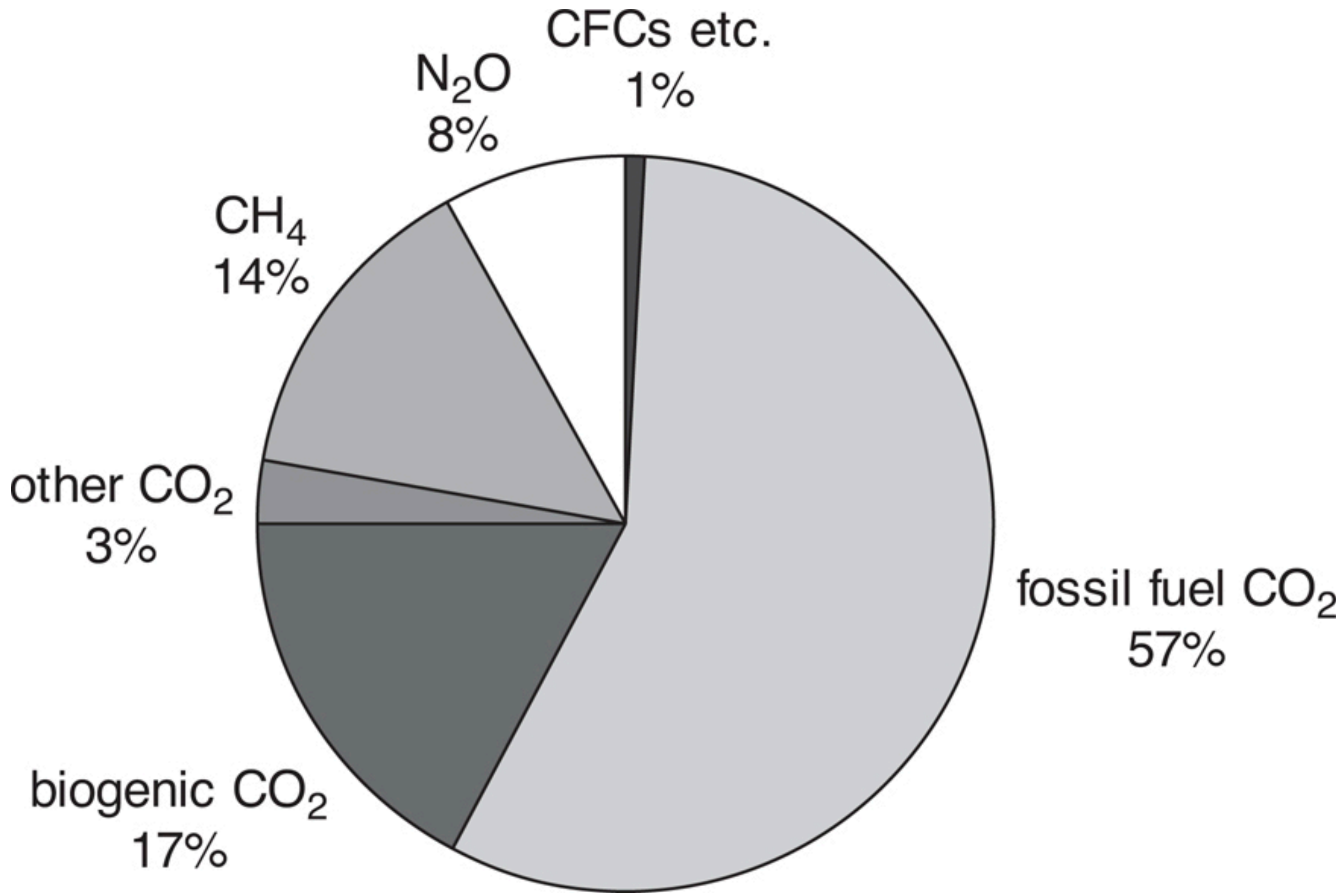


Fig 8.13 (van Loon)

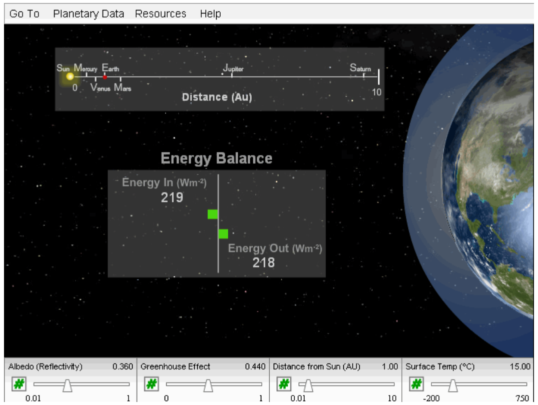
King's Centre for Visualization in Science

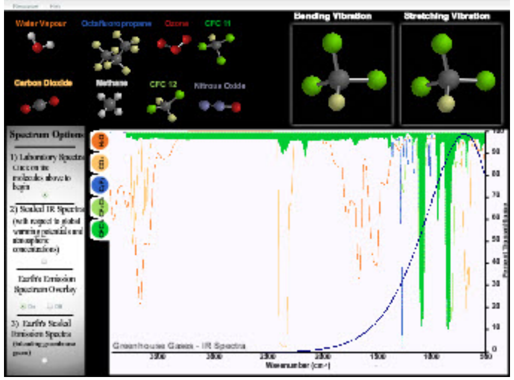
http://kcvs.ca/concrete/visualizations/global-climate-change

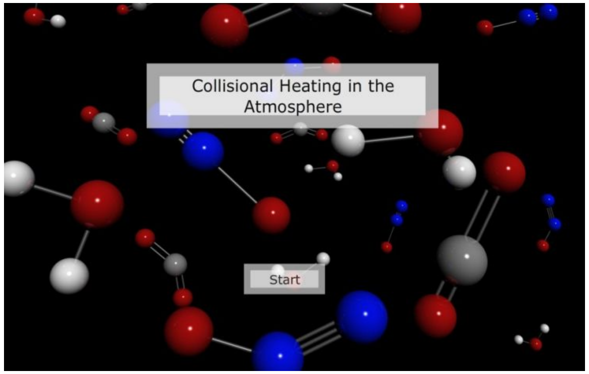
Planetary Climates: Radiative Energy Balance

Infrared Spectral Windows

Collisional Heating in the Atmosphere

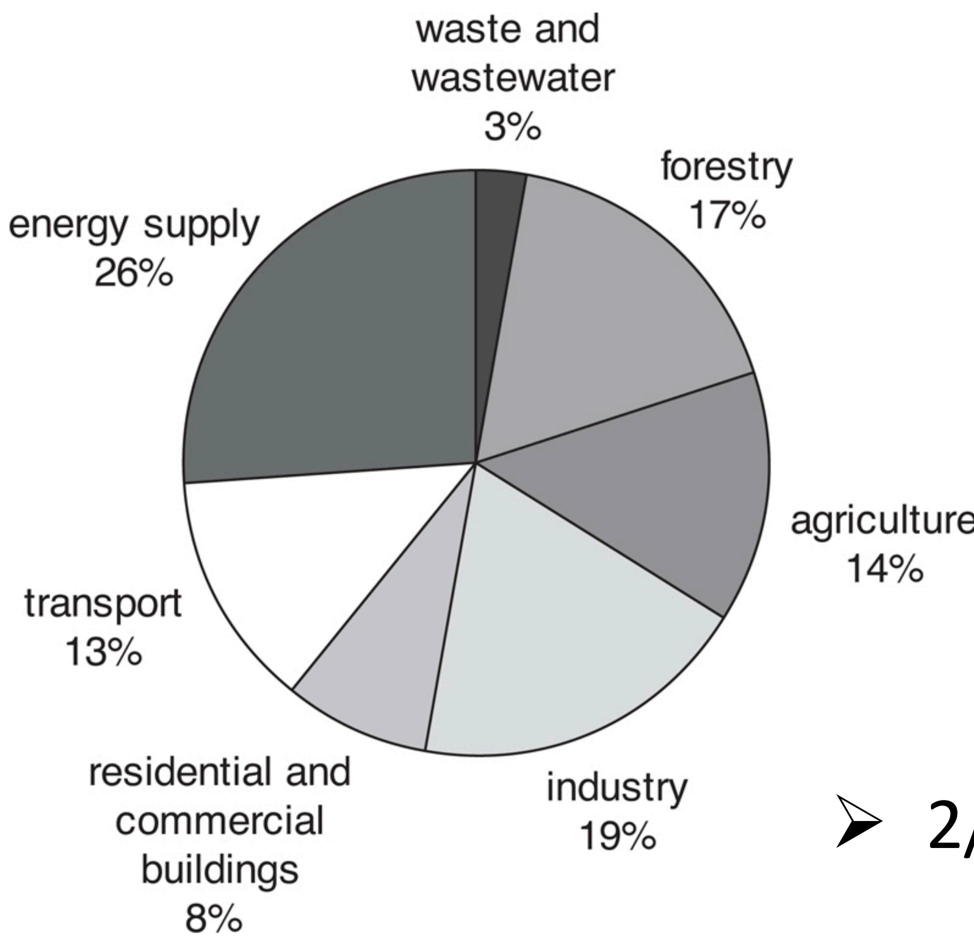






5. Energy Resources

Anthropogenic GHG Emissions (CO2 – equivalents)



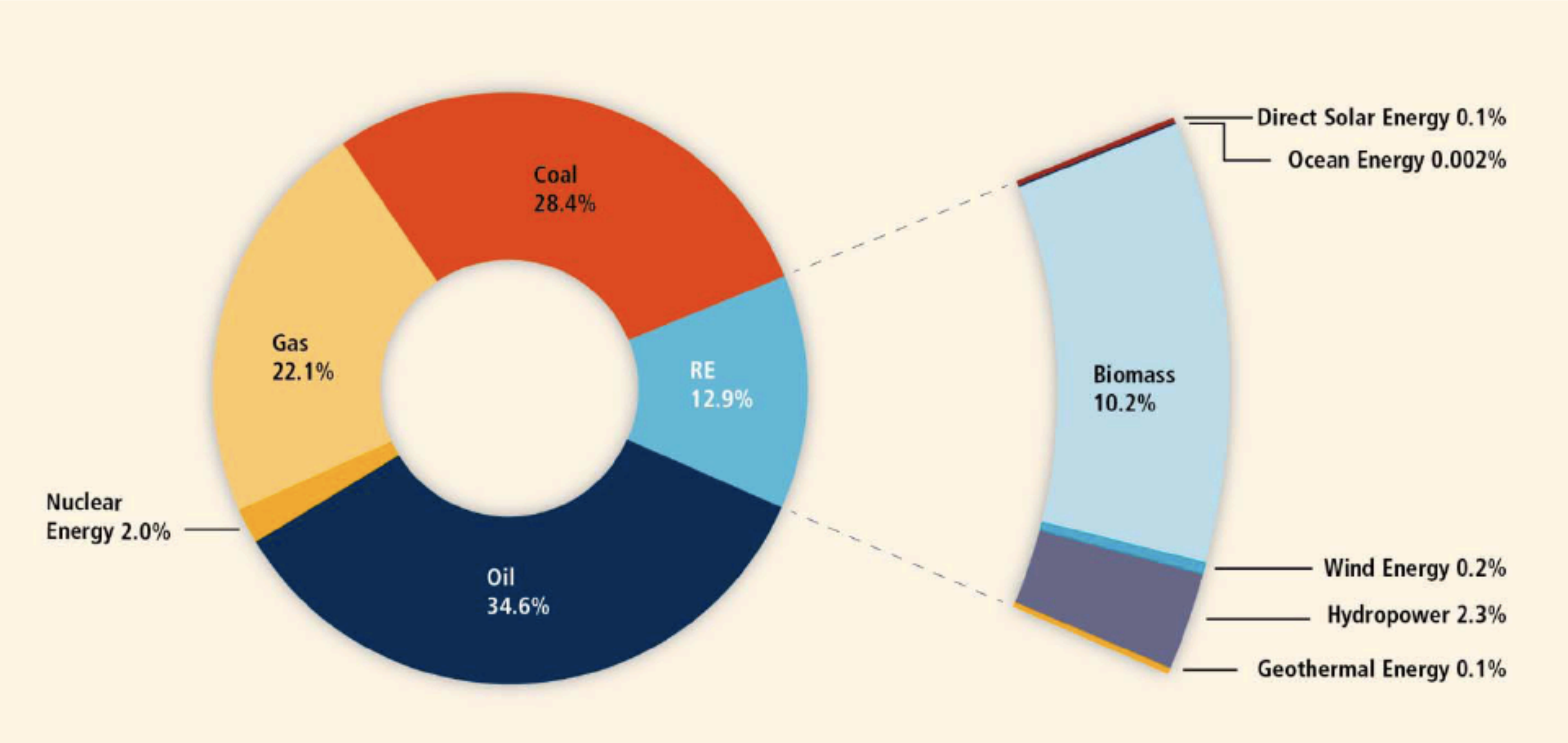
- 2/3 energy related

Fig 8.12 (van Loon)

Source	Reaction	ΔH_{comb} (kJ/mol)
Natural Gas	$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O$	-890
Petroleum	$C_{20}H_{42} + 30.5\ O_2 \rightarrow 20\ CO_2 + 21\ H_2O$	-13,300
Coal	$C + O_2 \rightarrow CO_2$	-393

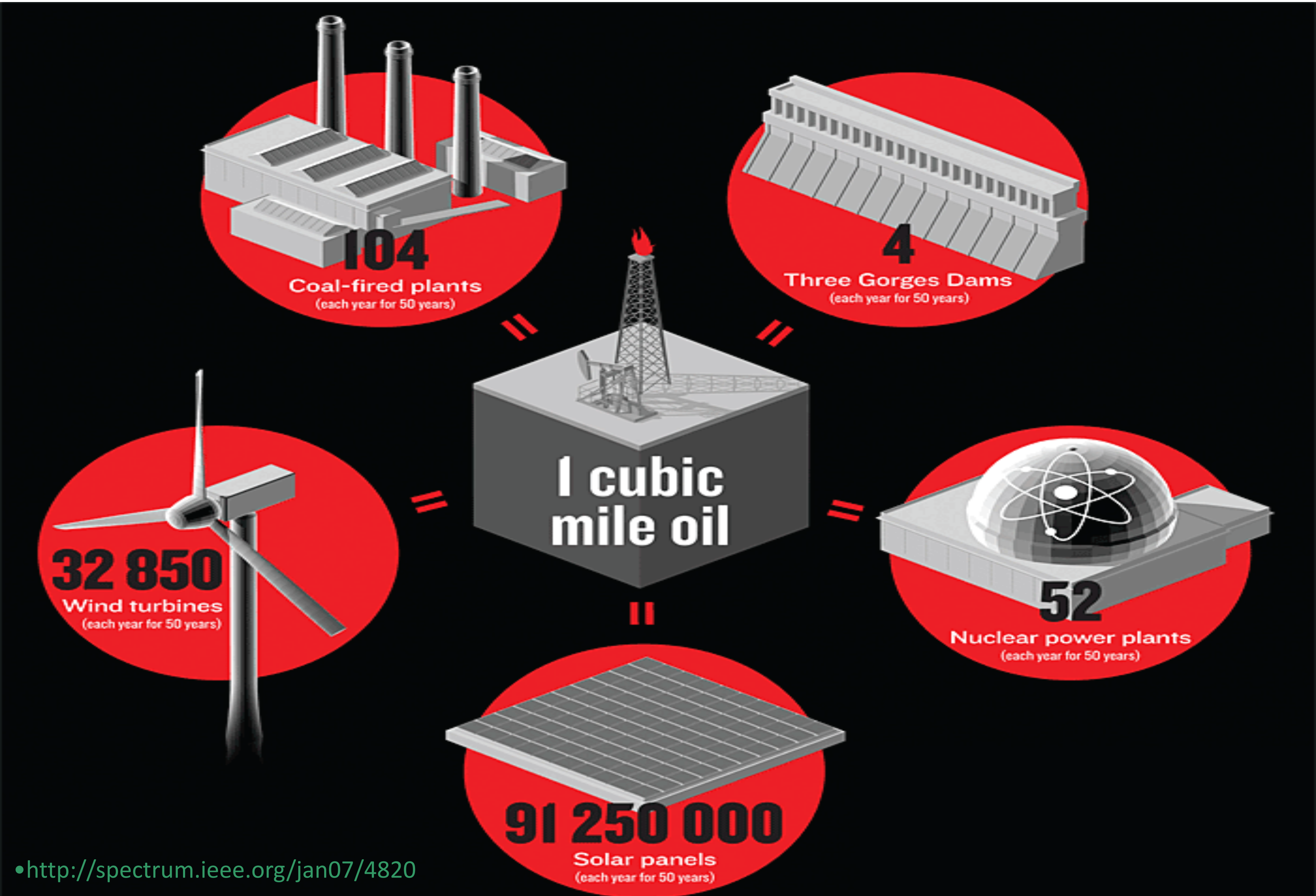
Source	Energy Content (J/amt)	GHG (kg CO_2/GJ)
Natural Gas	3.7×10^7 J/m^3	49
Petroleum	3.9×10^{10} J/tonne	66
Coal	$2\text{-}3 \times 10^{10}$ J/tonne	112
Biomass	$1\text{-}2 \times 10^{10}$ J/tonne	-

World Energy Consumption



Special Report on Renewable Energy Sources and Climate Change Mitigation (SRREN), IPCC, May, 2011.

Equivalent Energy Used in 1 Year



- http://spectrum.ieee.org/jan07/4820

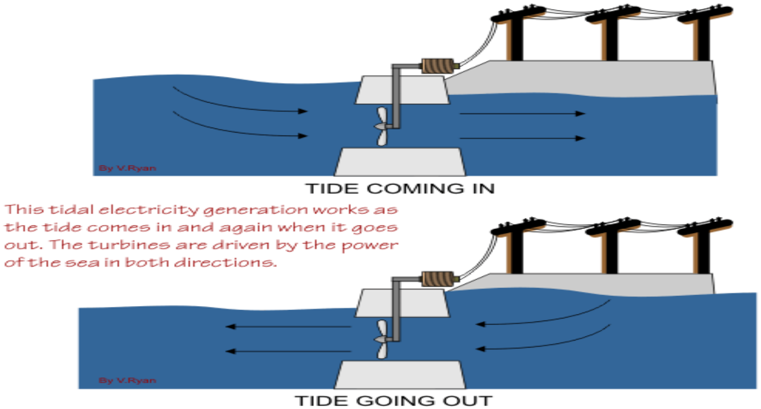
Renewable Energy Sources

Wind Power

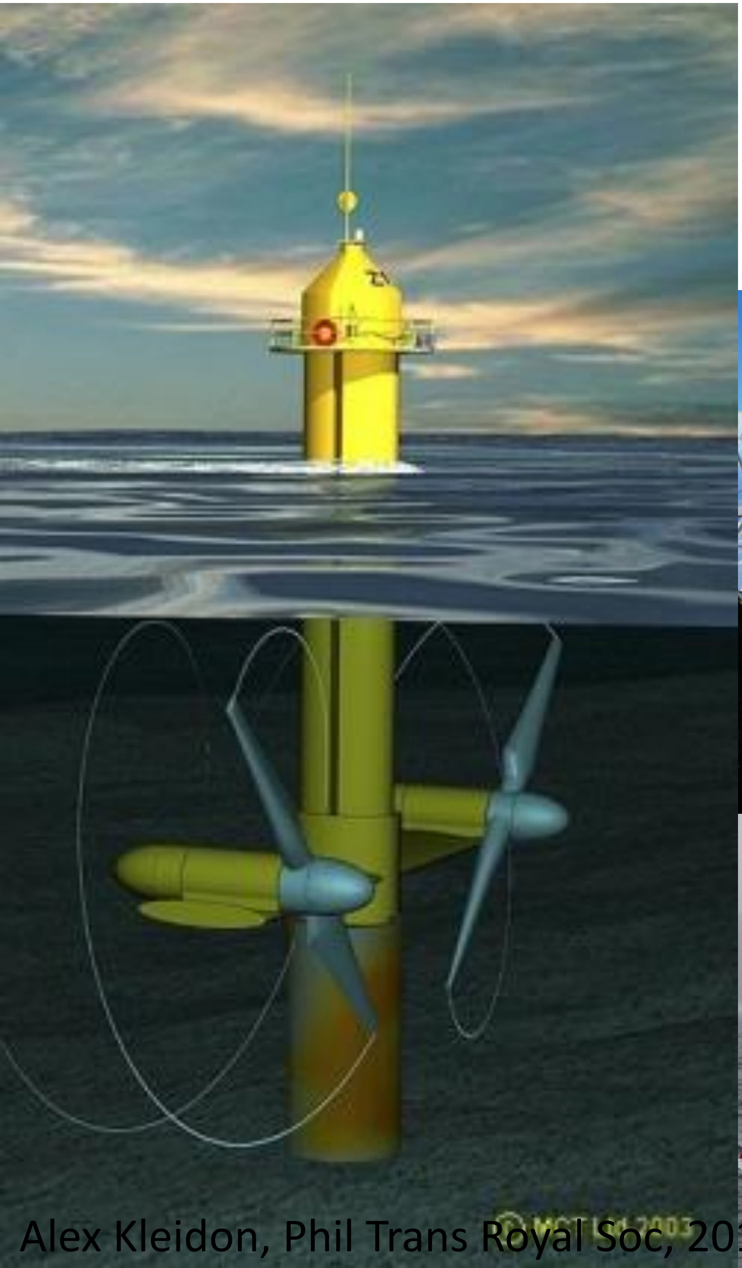
Solar Thermal

Photo Voltaics

Tidal Power

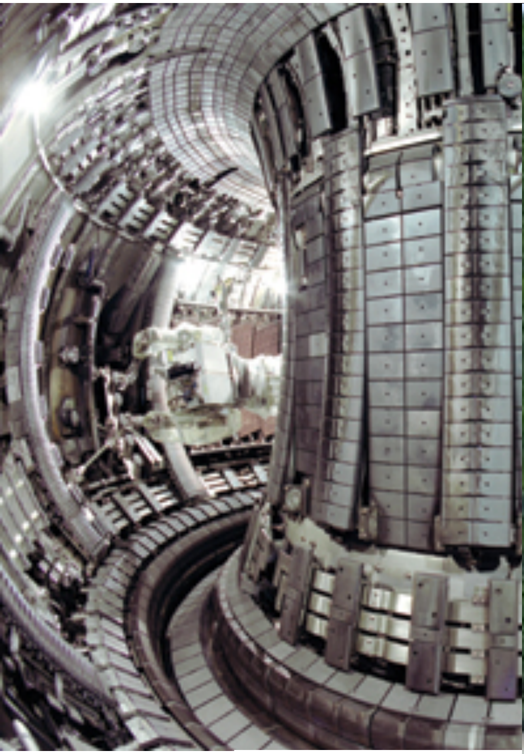


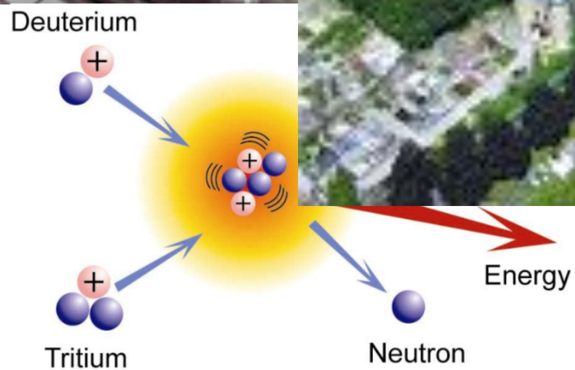
Renewables ?

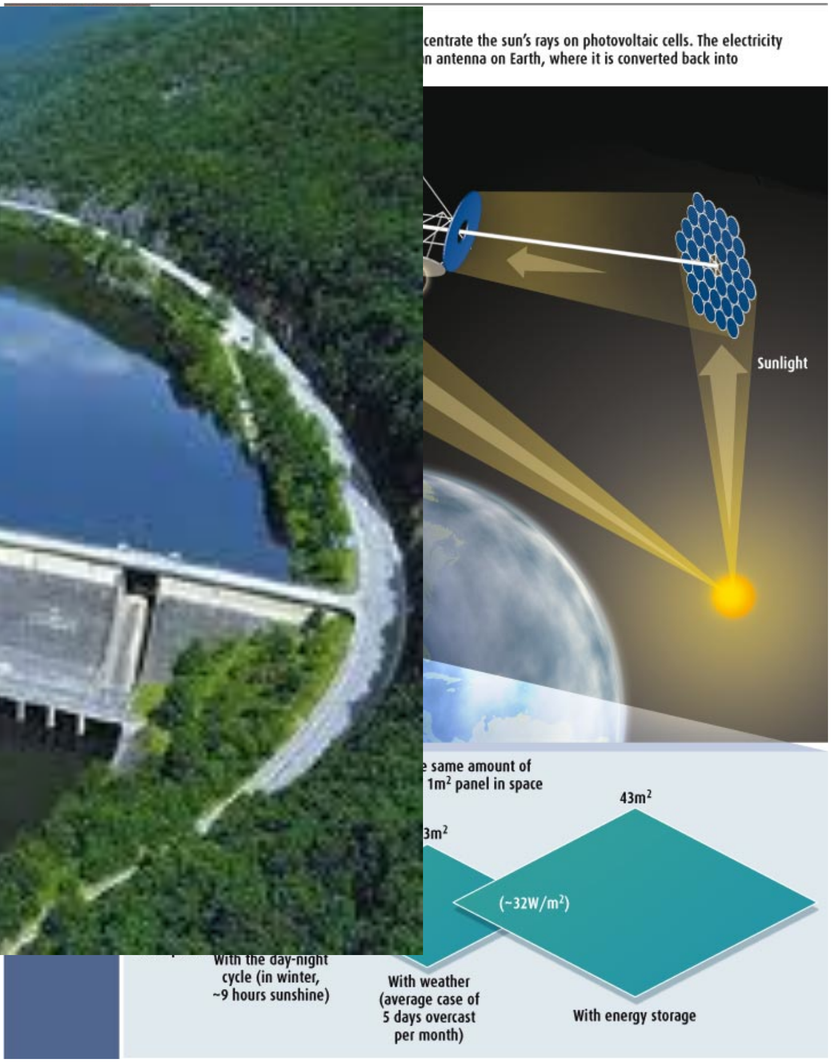


Alex Kleidon, Phil Trans Royal Soc, 2011

Other ‘Top Down’ Solutions?







Global Energy Demands

Current use	~ 14 TW
Future use (2050)	~ 30 TW

Global Resource Estimates (best case scenarios)

Tidal/Oceans	~ 2 TW
Hydro	~ 2 TW
Wind (10 m)	~ 4 TW
Biomass (all crops)	~ 7 TW
Nuclear (Fission)	~ 8 TW (200/yr forever)
Geothermal	~ 12 TW

Solar 120,000 TW (incident) ~ 800 TW(practical)

Lewis, N.S. & Nocera, D., *PNAS*, 2006, 103:15729

Energy Density for Storage

Compressed Air	~0.5 MJ/kg
Pump Water	~0.001 MJ/kg
Batteries	~0.1 – 0.2 MJ/kg (conventional)
	~0.5 - 0.7 MJ/kg (Li ion)

Chemical Bonds

Wood	~ 16 MJ/kg
Carbohydrates	~ 17 MJ/kg
Coal	~ 20 MJ/kg
Liq. Petrol	~ 40 MJ/kg
Natural gas	~ 50 MJ/kg
Hydrogen	~ 120 MJ/kg

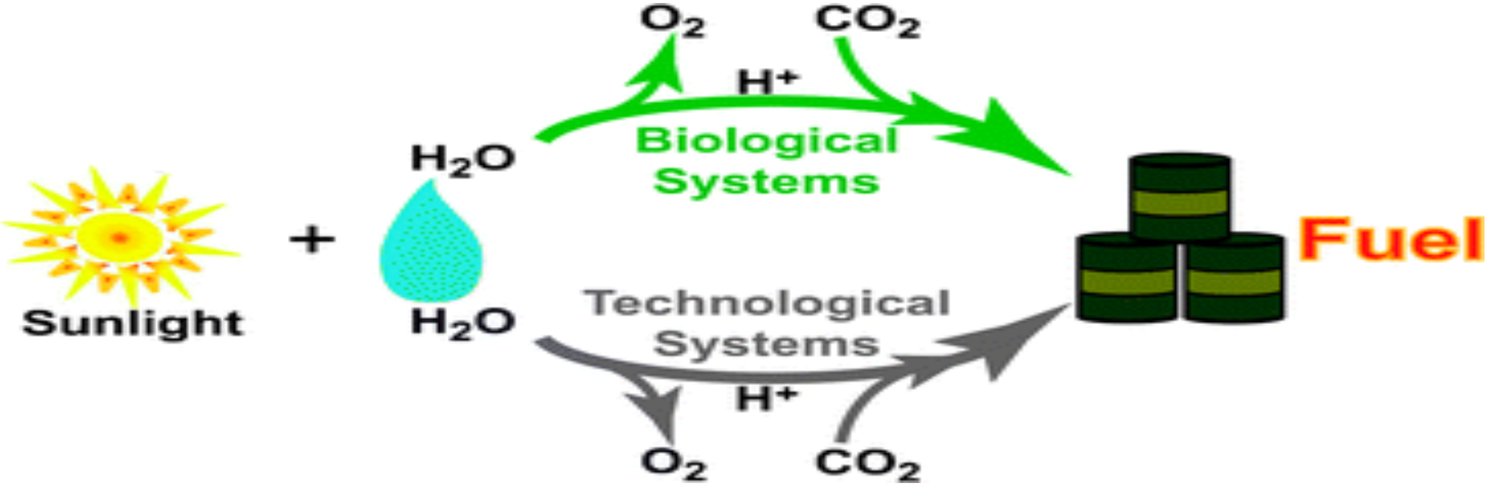
Qualities of Photosynthesis

Carbon sequestration

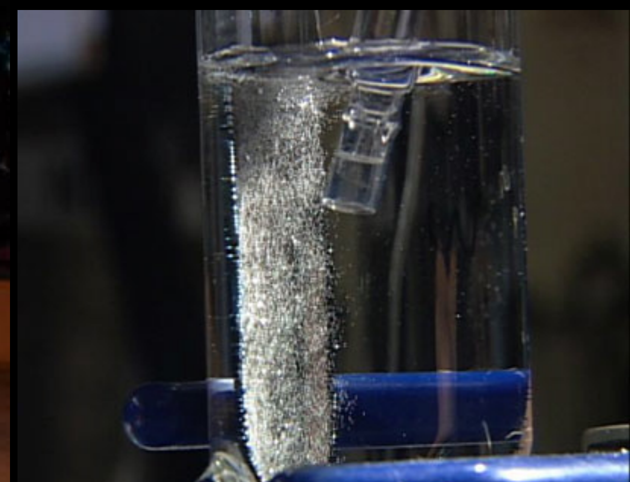
Energy storage 'Fuel'

Oxygen production

One hr of sunlight on Earth = global energy needs for 1 yr



Water splitting catalyst driven by sunlight



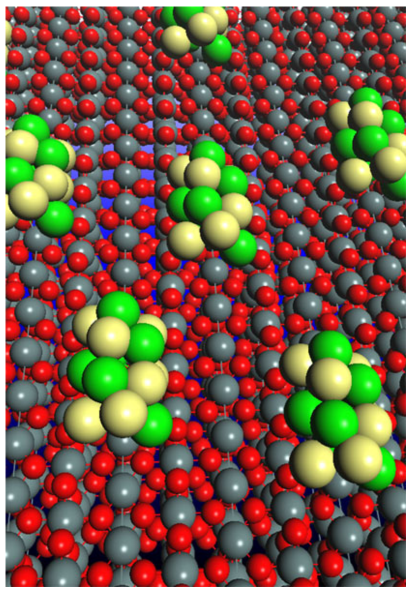
Daniel Nocera (2 mins)

Energy + Water → Hydrogen + Oxygen

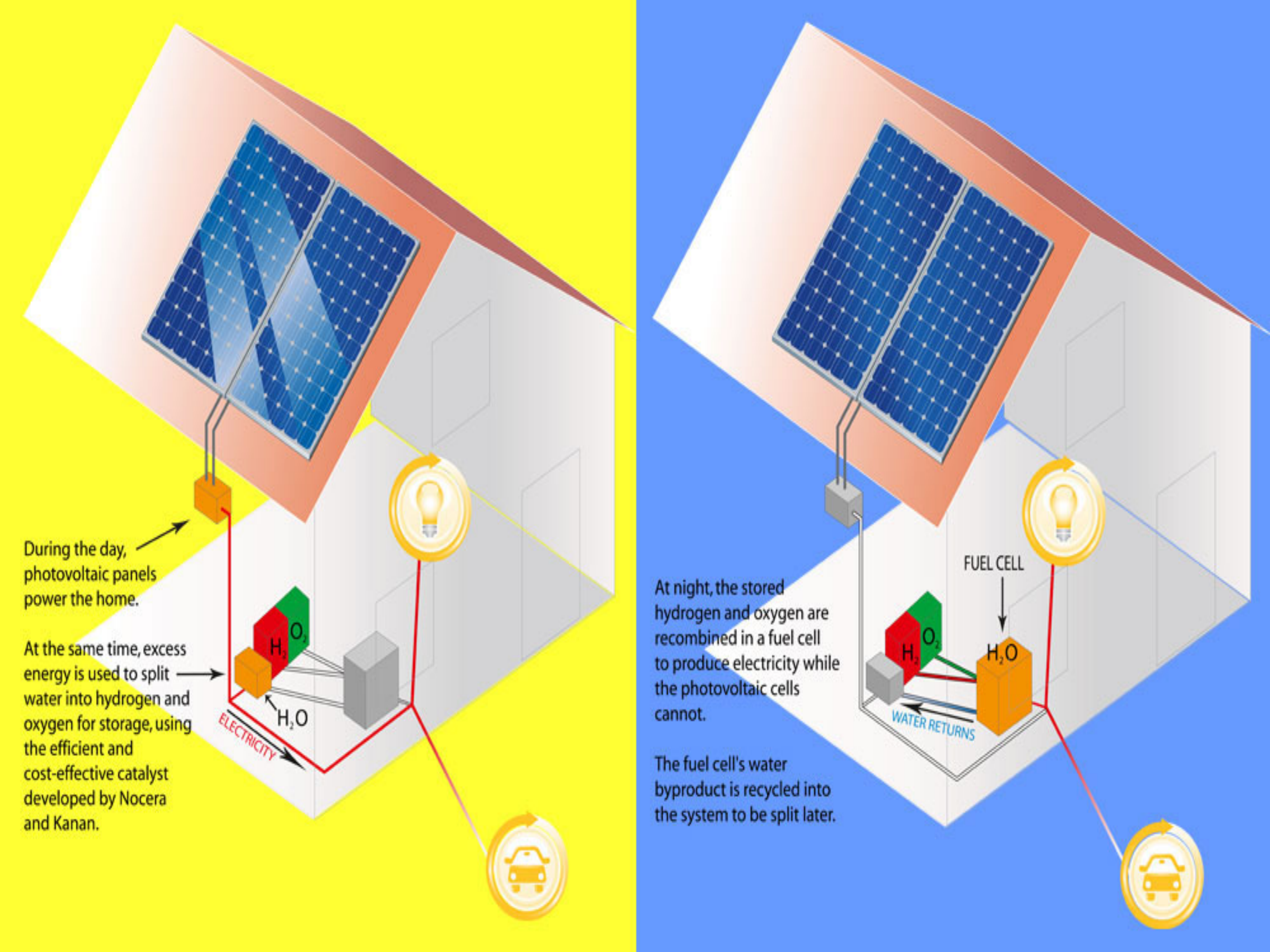
Hydrogen + Oxygen → Water + Energy

Methanol Fuel Economy

$$CO_2 + H_2 \rightarrow CH_3OH + H_2O$$

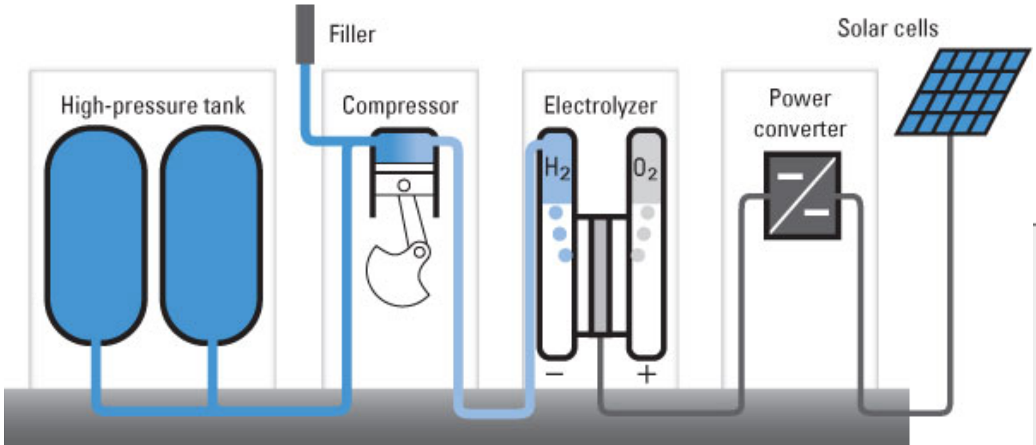


$$CH_3OH + O_2 \rightarrow CO_2 + H_2O + \text{ENERGY}$$

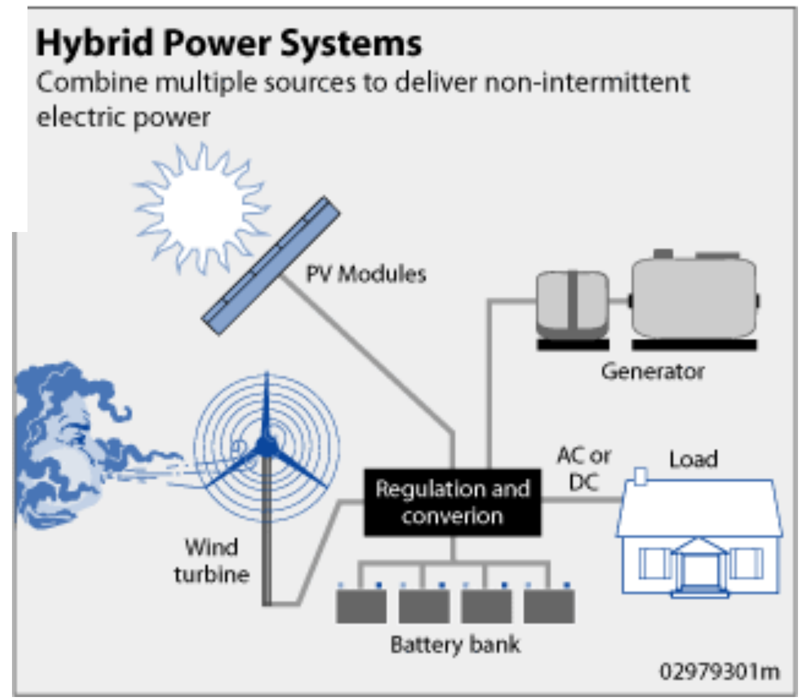

During the day, photovoltaic panels power the home.
At the same time, excess energy is used to split water into hydrogen and oxygen for storage, using the efficient and cost-effective catalyst developed by Nocera and Kanan.
H_2
O_2
H_2O
ELECTRICITY
At night, the stored hydrogen and oxygen are recombined in a fuel cell to produce electricity while the photovoltaic cells cannot.
The fuel cell's water byproduct is recycled into the system to be split later.
FUEL CELL
H_2
O_2
H_2O
WATER RETURNS

Personalized Energy

Solar H_2 production



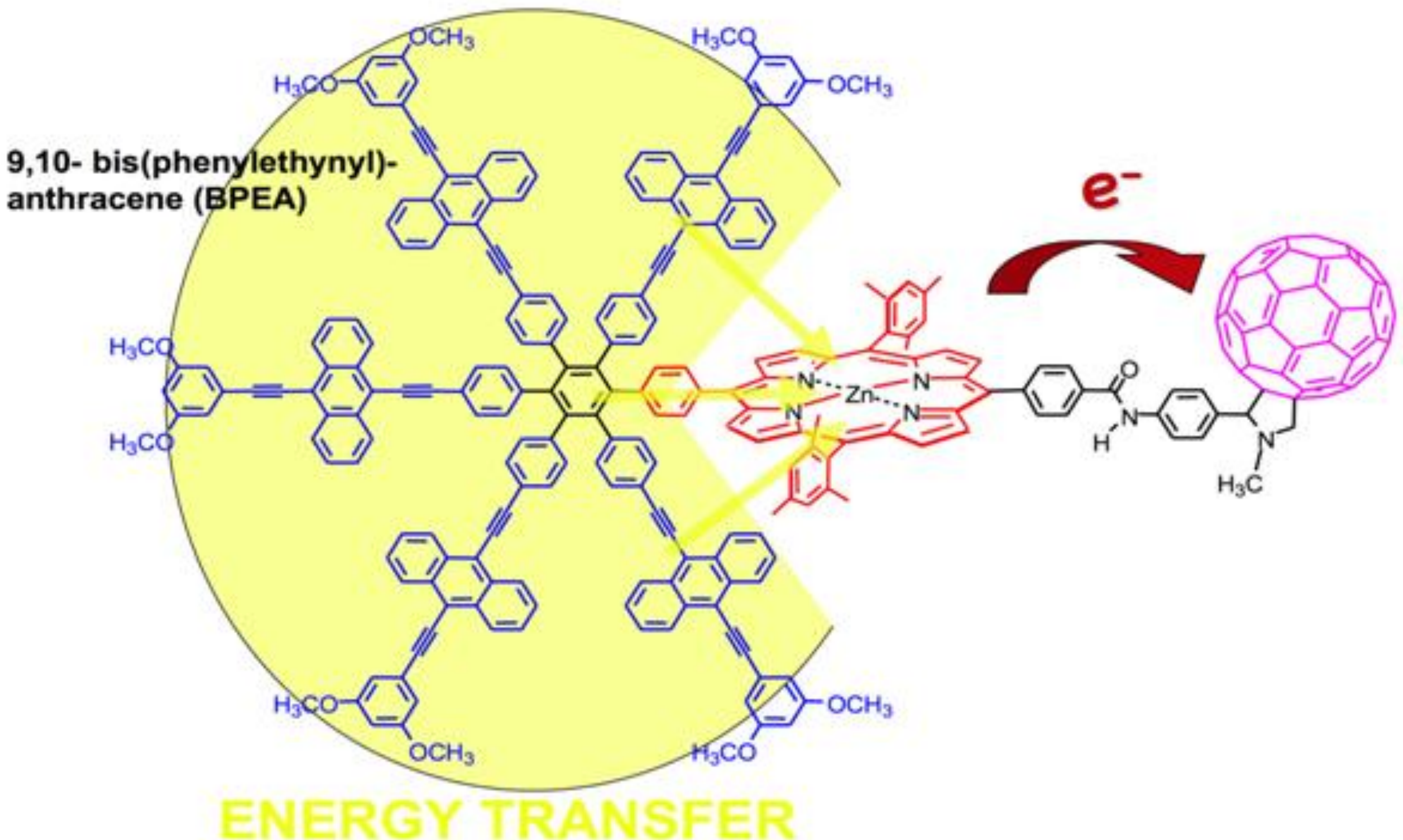
Photovoltaic roof tiles



Hydrogen Fuel Cells

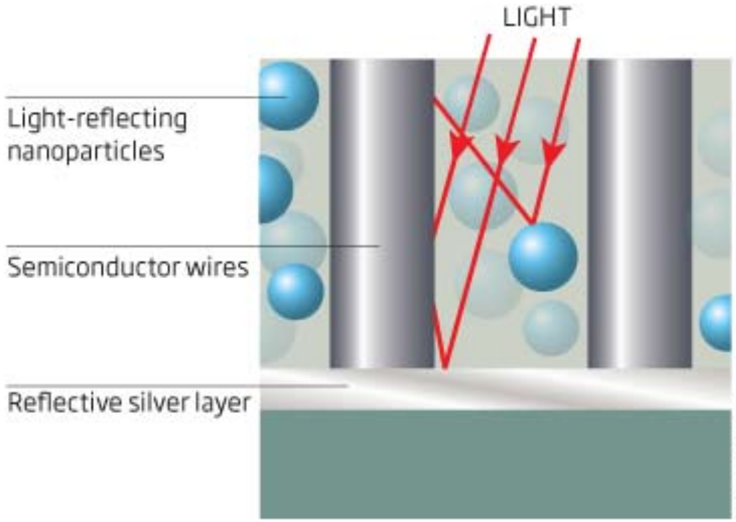
Climate Future Economics (1.5 min)

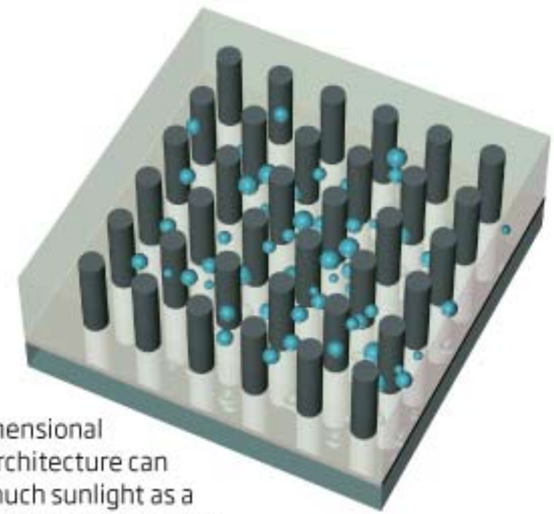
Bio-inspired Artificial Photosynthesis



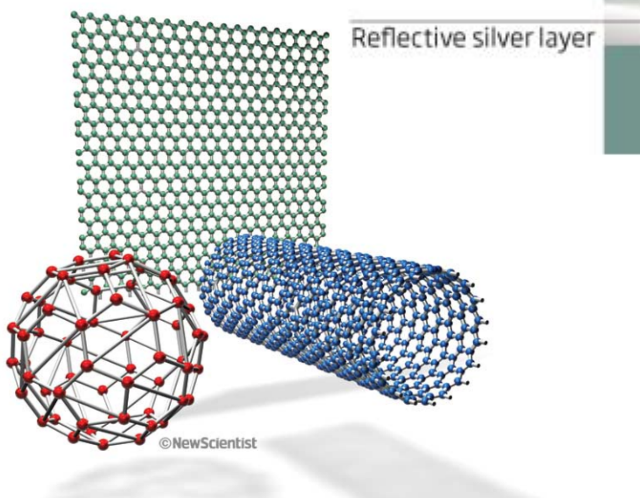
L'ActualitéChimique, 308, 50-56, 2007

Carbon Based Photovoltaics





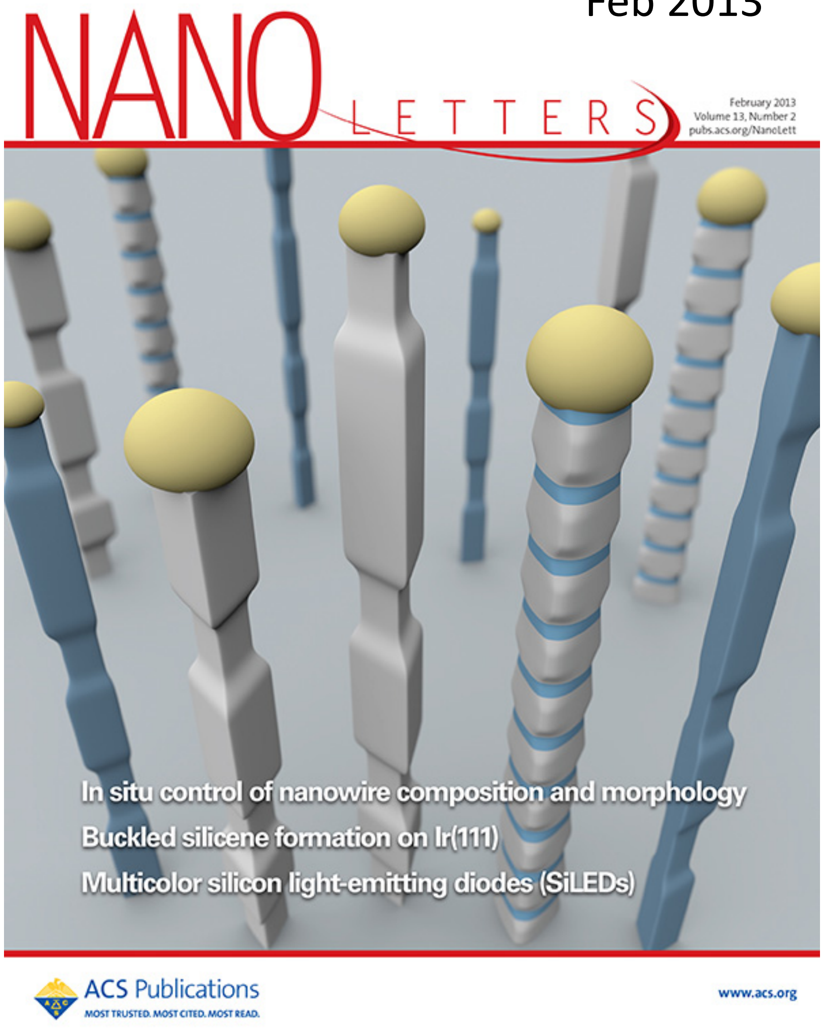
A three-dimensional nanowire architecture can absorb as much sunlight as a silicon crystal 100 times thicker

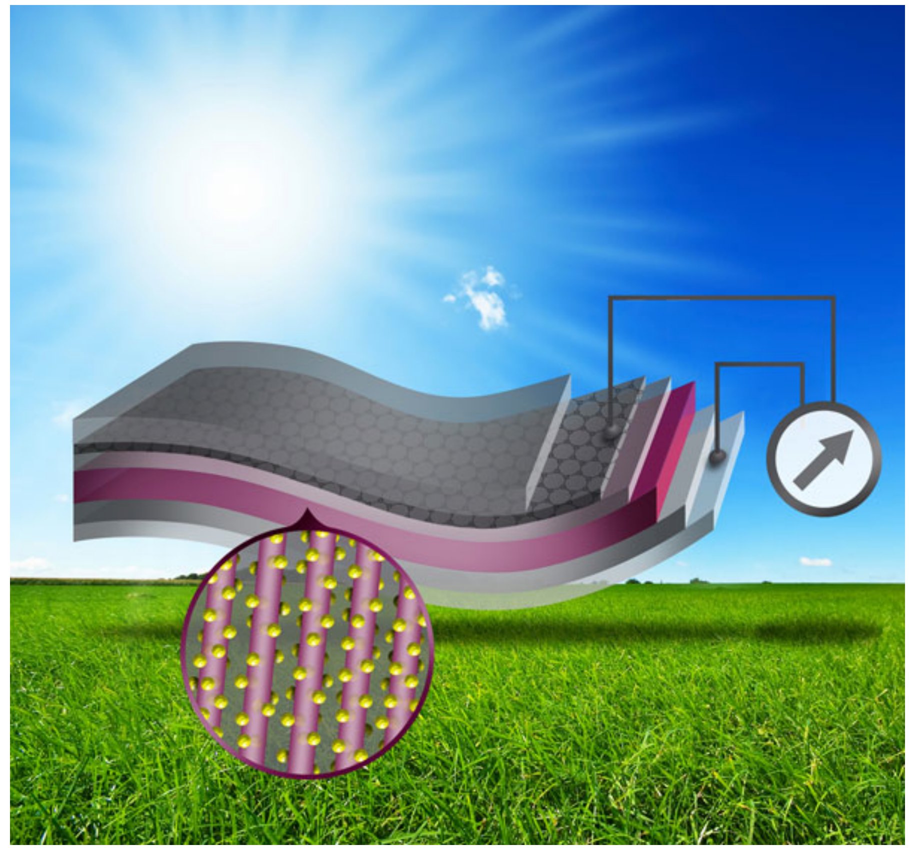


New Scientist, April 13, 2010

Nanowire coated graphene sheets for flexible solar cells

Feb 2013





ZnO nanowires and PbS quantum dots

S. Gradecak et al., *Nano Letters*, 2013

World's most energy efficient LED

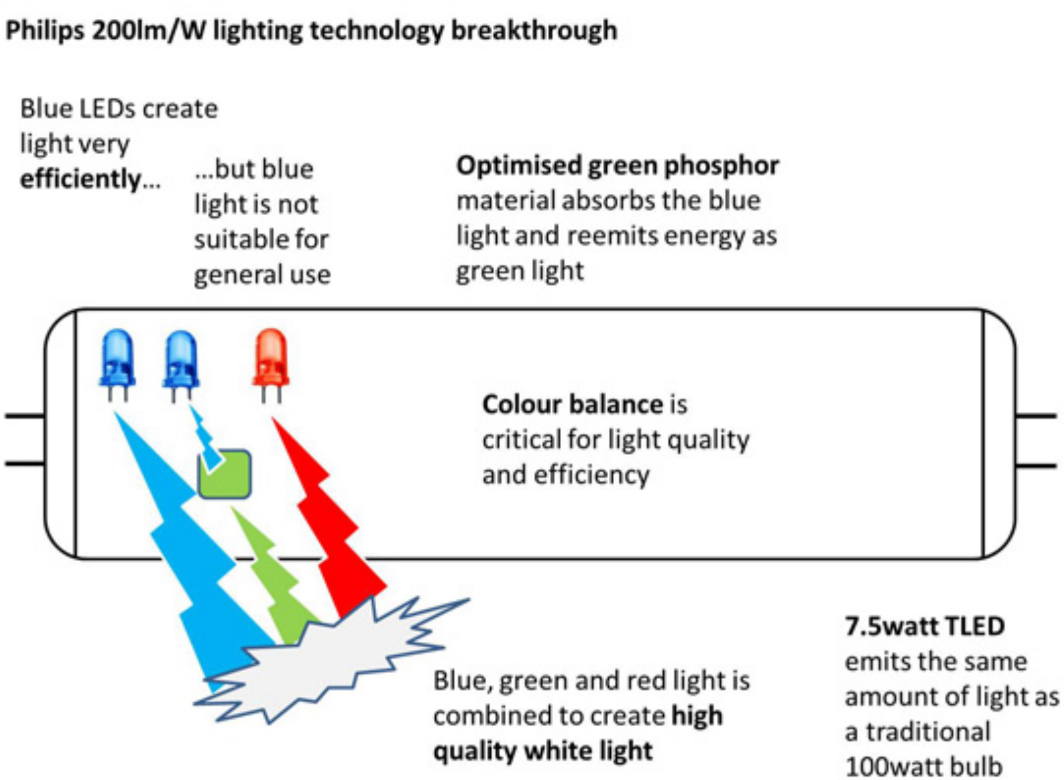
April 11, 2013

Replacing all US fluorescent bulbs

→ $12 billion

→ 60 million tons of CO_2

→ 50 mid-sized power plants

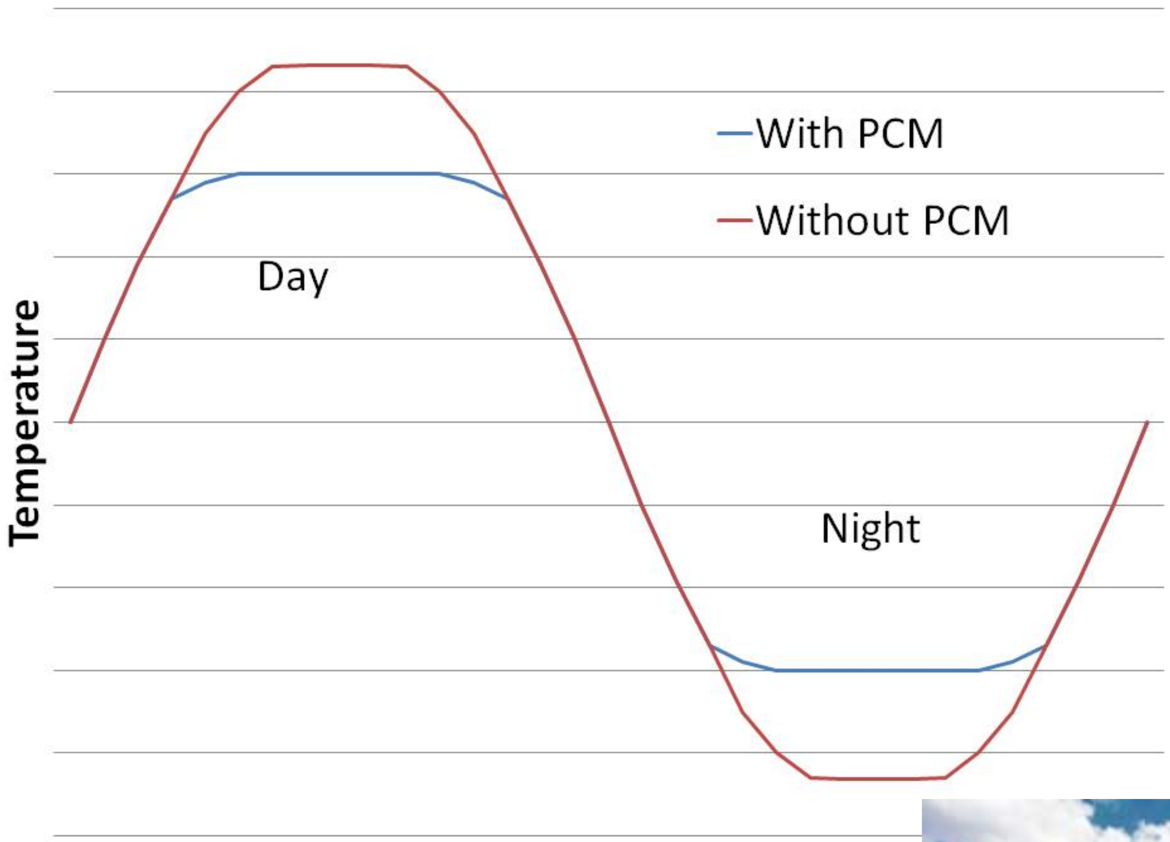


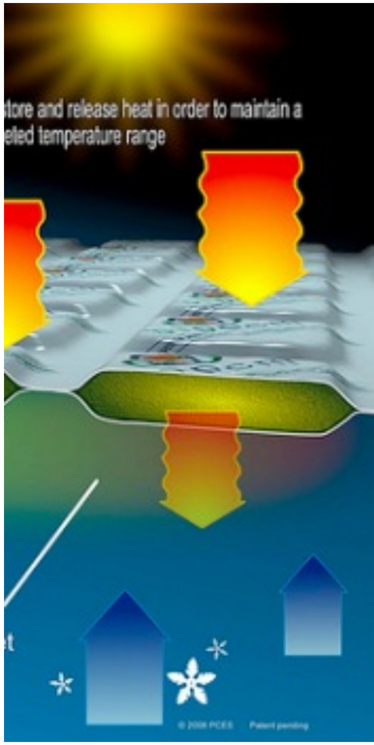
Replacing worldwide

→ Equivalent to 70% of all car emissions!

http://www.newscenter.philips.com/main/standard/news/articles/20130411

Phase Change Materials





BioPCM 23 – 29 ^{o}C

98% reduction in cooling costs

Molecular Engineering and Sciences Building,
Univ. Washington

“Most of this energy comes from fossil fuels such as coal, oil and natural gas that account for a majority of global carbon dioxide (CO_2) emissions. We know that CO_2 emissions are a leading contributor to climate change, and the world will need a portfolio of solutions to address this Grand Challenge”.

Incentivize and Accelerate new CO_2 conversion into ‘value added’ products

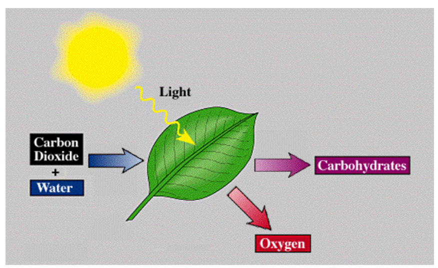
Real-world applications in flue stack of coal and CH_4 power stations

$20 million dollars

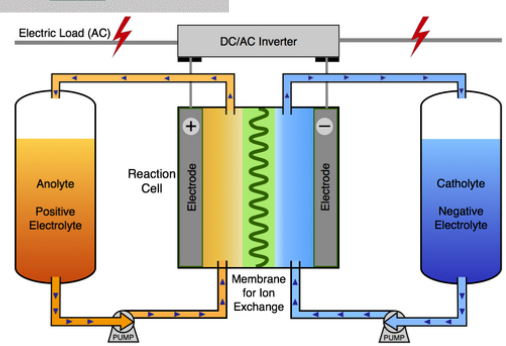
Clean Energy Investment Pact
Breakthrough Energy Coalition

Zero-carbon energy technologies
Long term investments > 10 years
Billions $ for 'lab' to 'marketplace' R&D

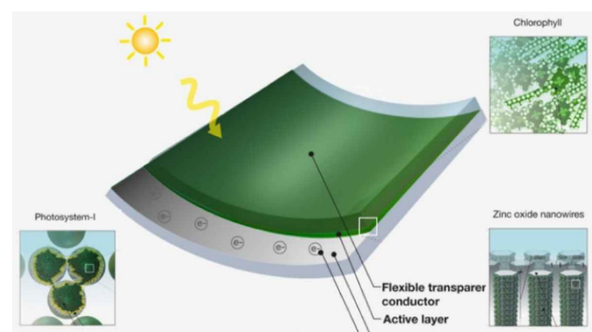
Solar Chemical

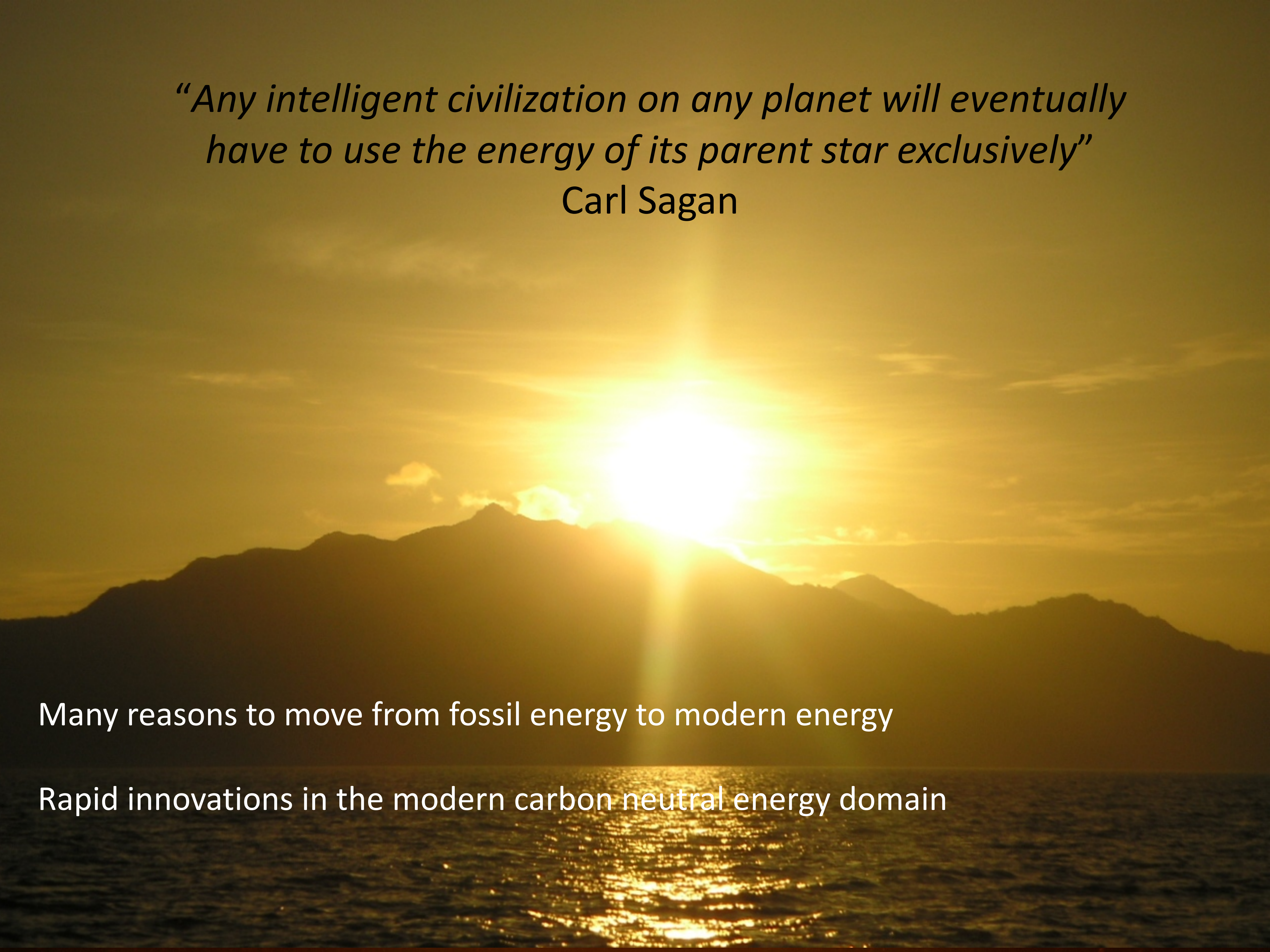


Flow Batteries



Solar Paint




“Any intelligent civilization on any planet will eventually
have to use the energy of its parent star exclusively”
Carl Sagan
Many reasons to move from fossil energy to modern energy
Rapid innovations in the modern carbon neutral energy domain

Social Sciences and Humanities Research Council of Canada

Conseil de recherches en sciences humaines du Canada

Canada

Awareness of Climate Change through Education and Research

ACER

Vancouver Island University Chemistry Student Initiatives

Awareness of
Climate Change through
Education and
Research

NSERC CRSNG

TD Friends of the Environment Foundation

VANCOUVER ISLAND UNIVERSITY