OSHER LIFELONG LEARNING INSTITUTE

Demystifying Climate Change

Session 6

CO_2 and Other Greenhouse Gases:

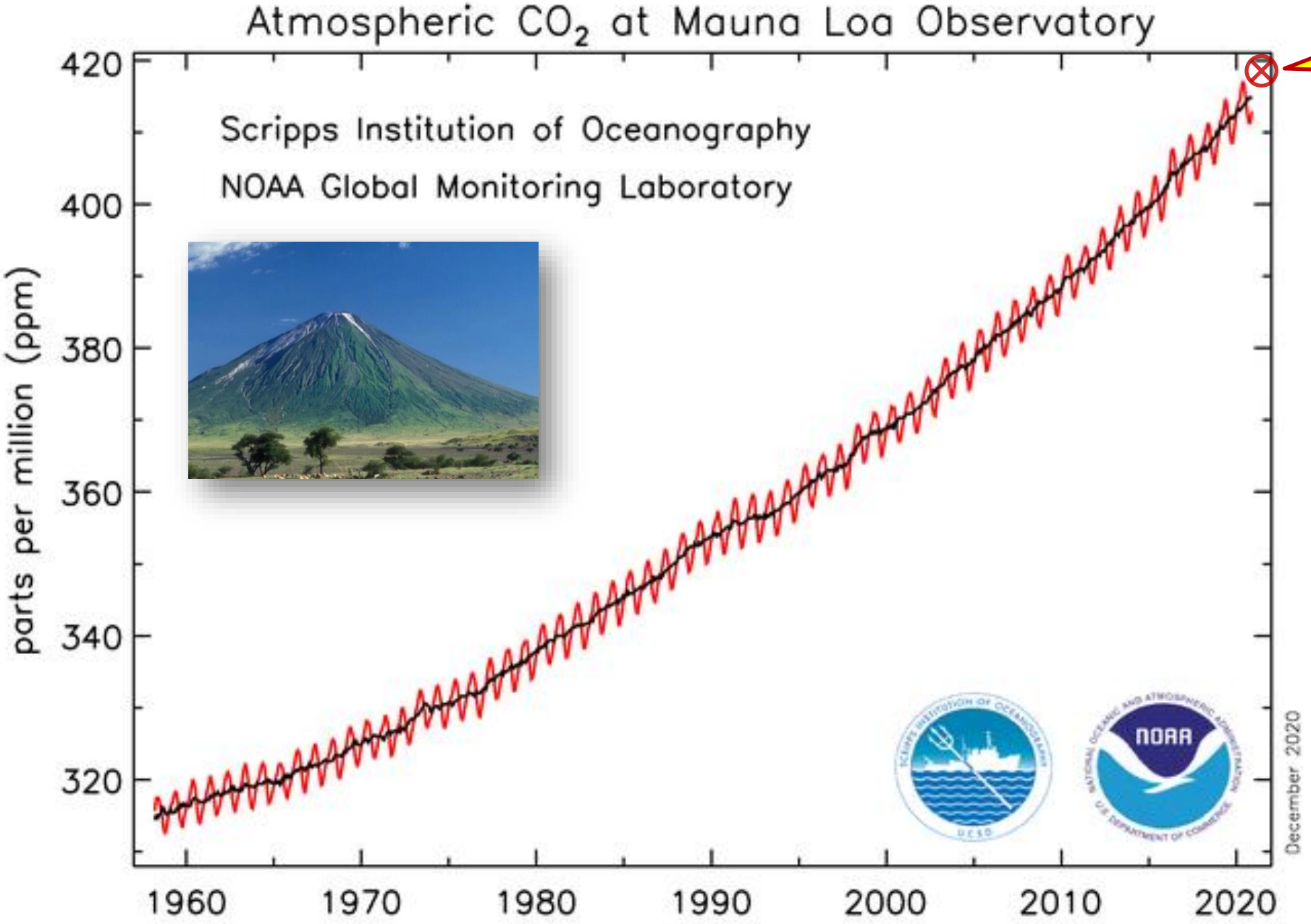
Where do they come from?

Where do they go?

How are they regulated?

OLLI at Illinois
Spring 2021

D. H. Tracy
DavidHTracy@gmail.com

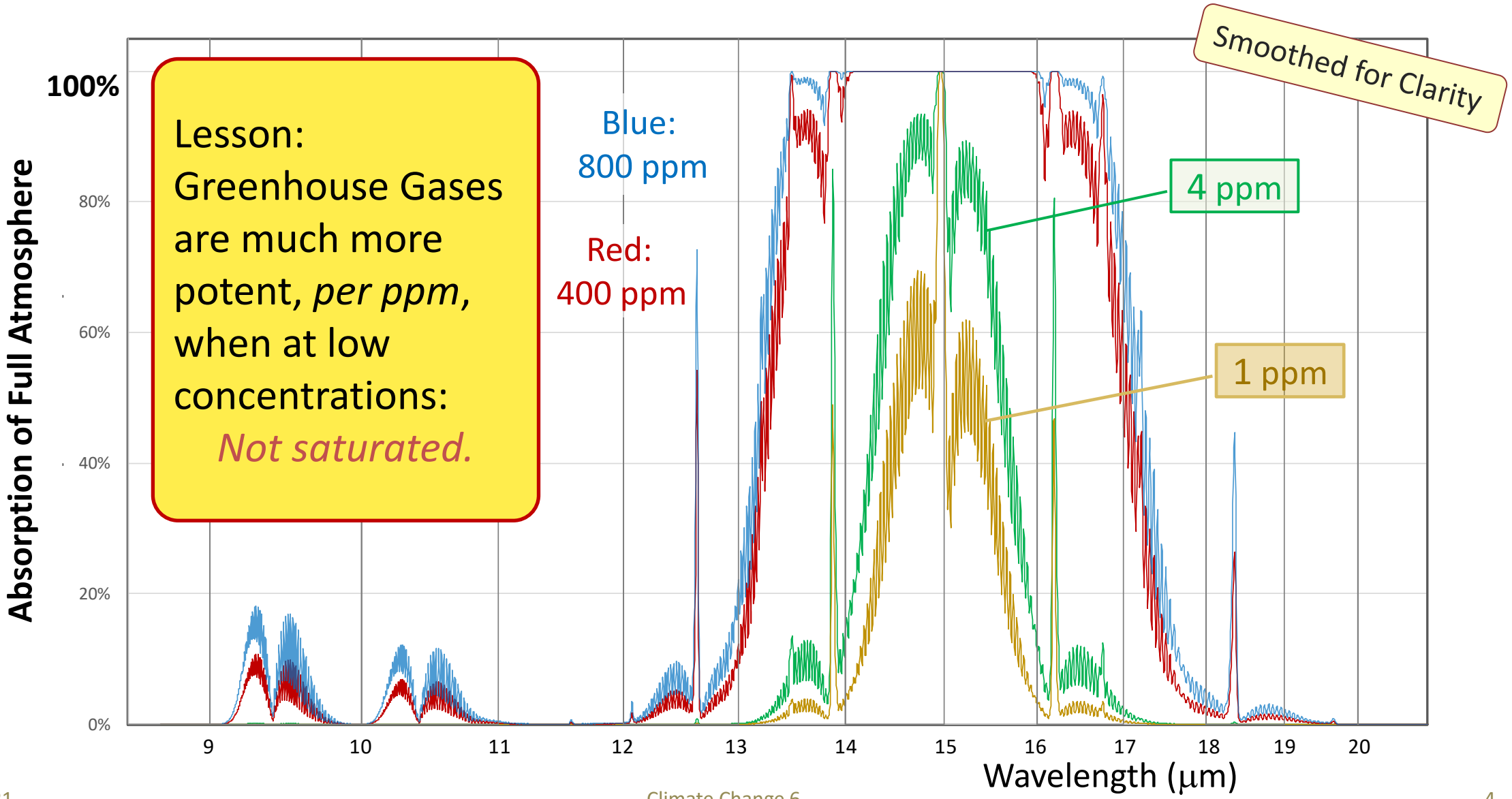


418.53 ppm
Mar 6, 2021

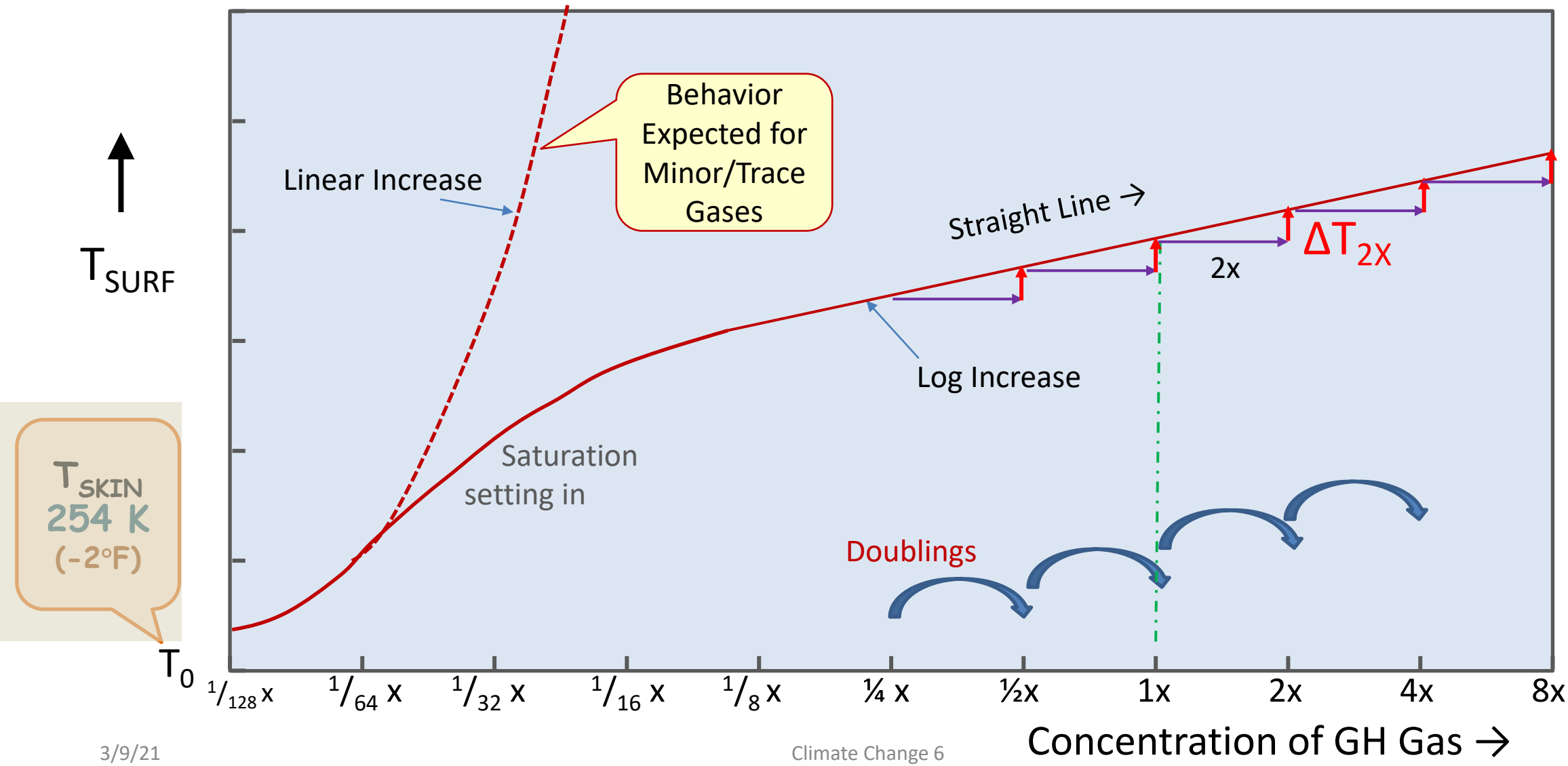
Course Outline

1. Building Blocks: Some important concepts
2. Our Goldilocks Earth: a Radiative Balancing Act
3. The Role of the Atmosphere: Greenhouse Gases & Clouds
4. Global Circulation and Dynamics of the Earth System:
   Oceans, Atmosphere, Biosphere, Cryosphere, People, Lithosphere
5. Natural Variability of the Climate, short and long term. Ice Ages
6. **Carbon Dioxide and other Greenhouse Gases:**
   Where do they come from, where do they go, how are they regulated?
7. Impacts and Future Projections for Global Warming -- Uncertainties
8. Amelioration Strategies. The Climate Debate. Policy Options.

Remember CO_2 Saturation?



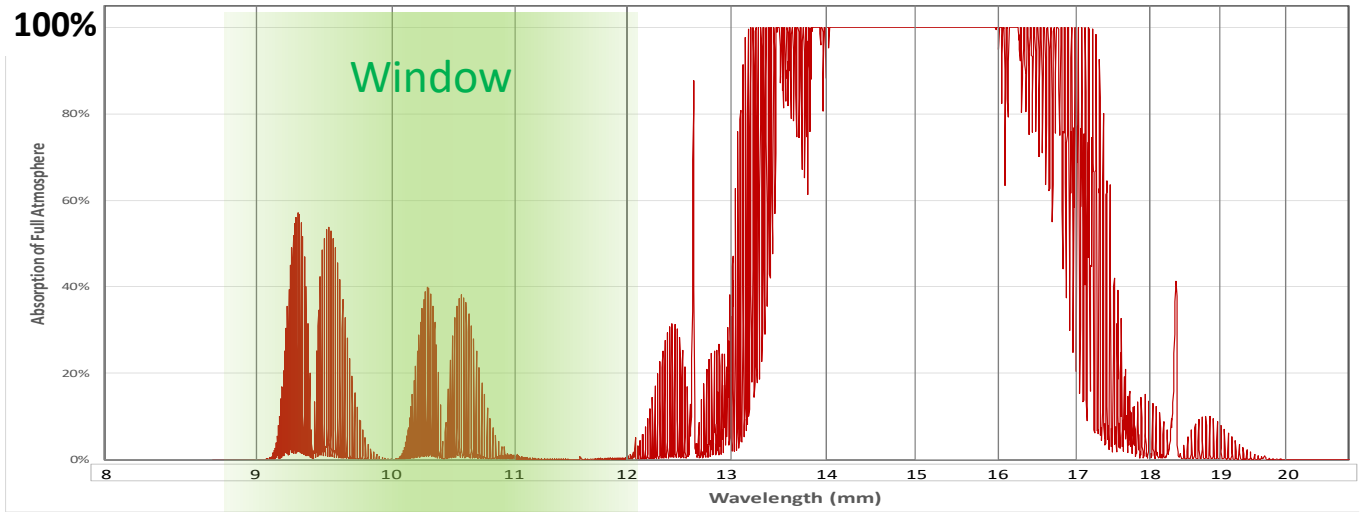
Actual Surface Temperature *vs.* GH Gas Concentration Doublings

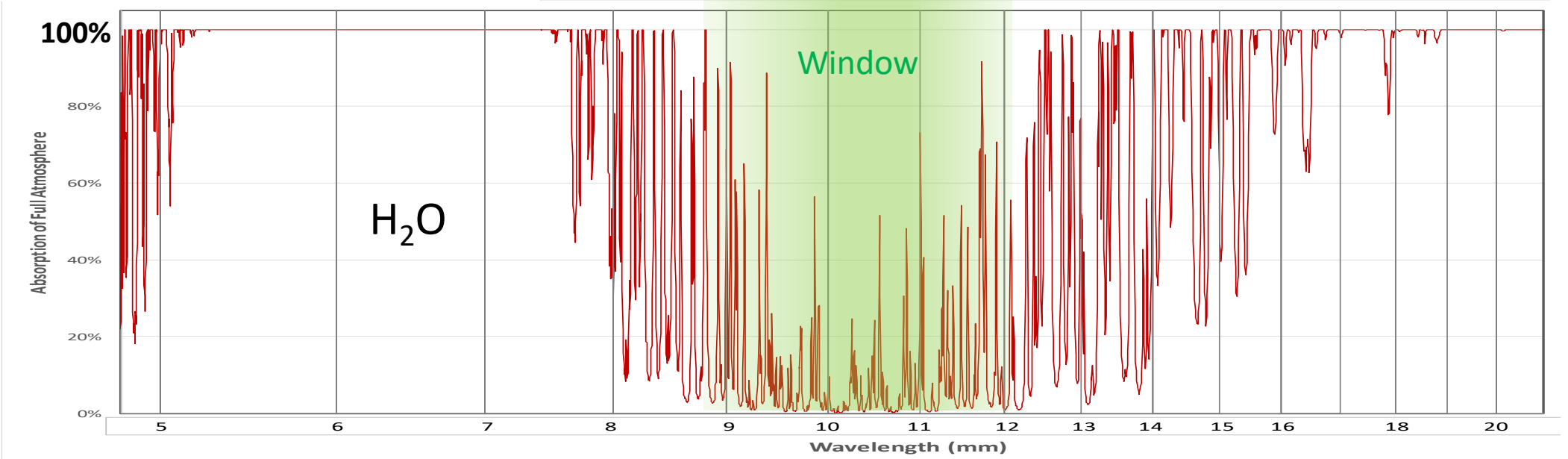


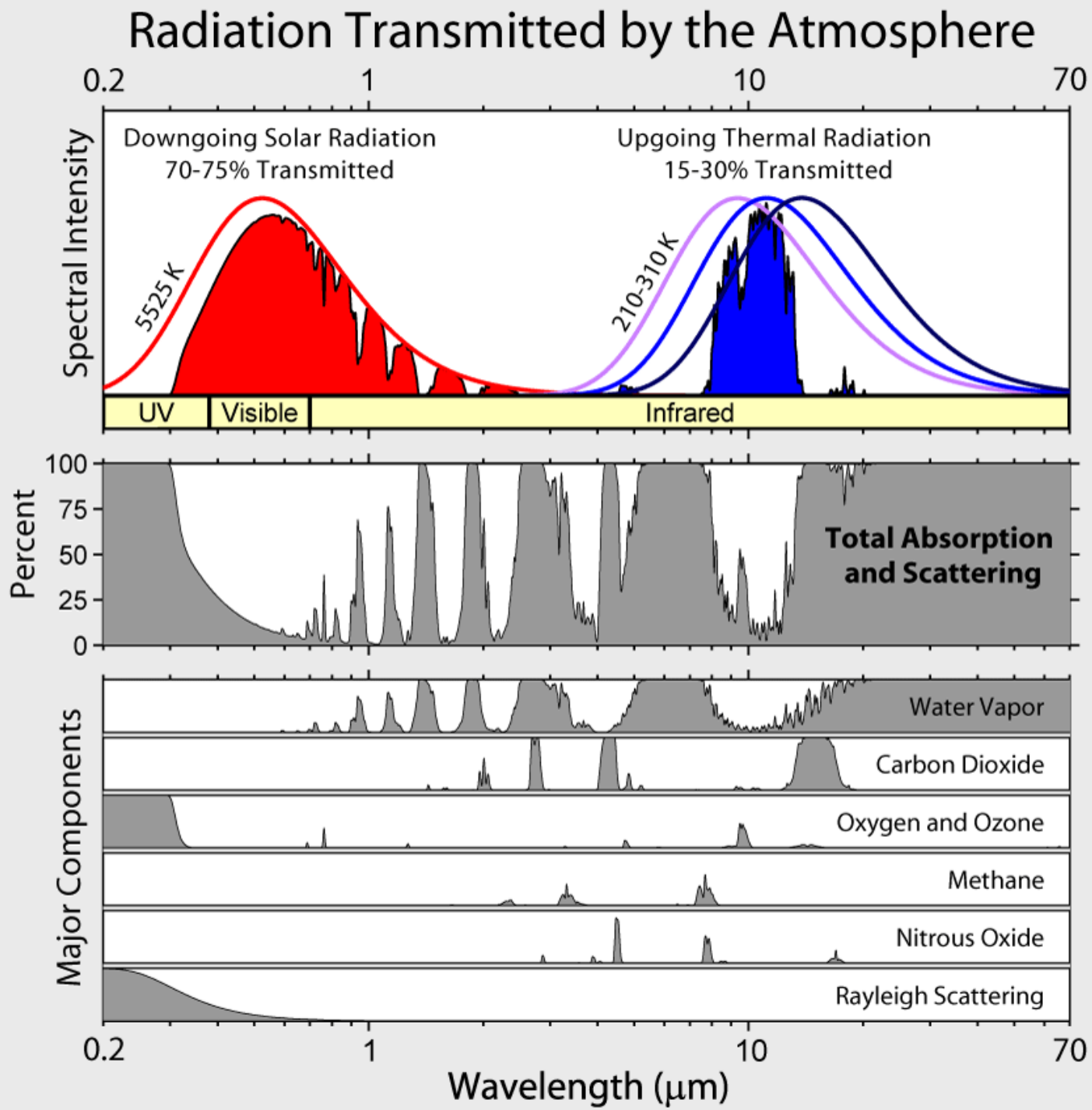
Full Atmosphere: Water Vapor + CO_2 Leave A Window at 10-11 μm

Origin of the LW IR Atmospheric Window

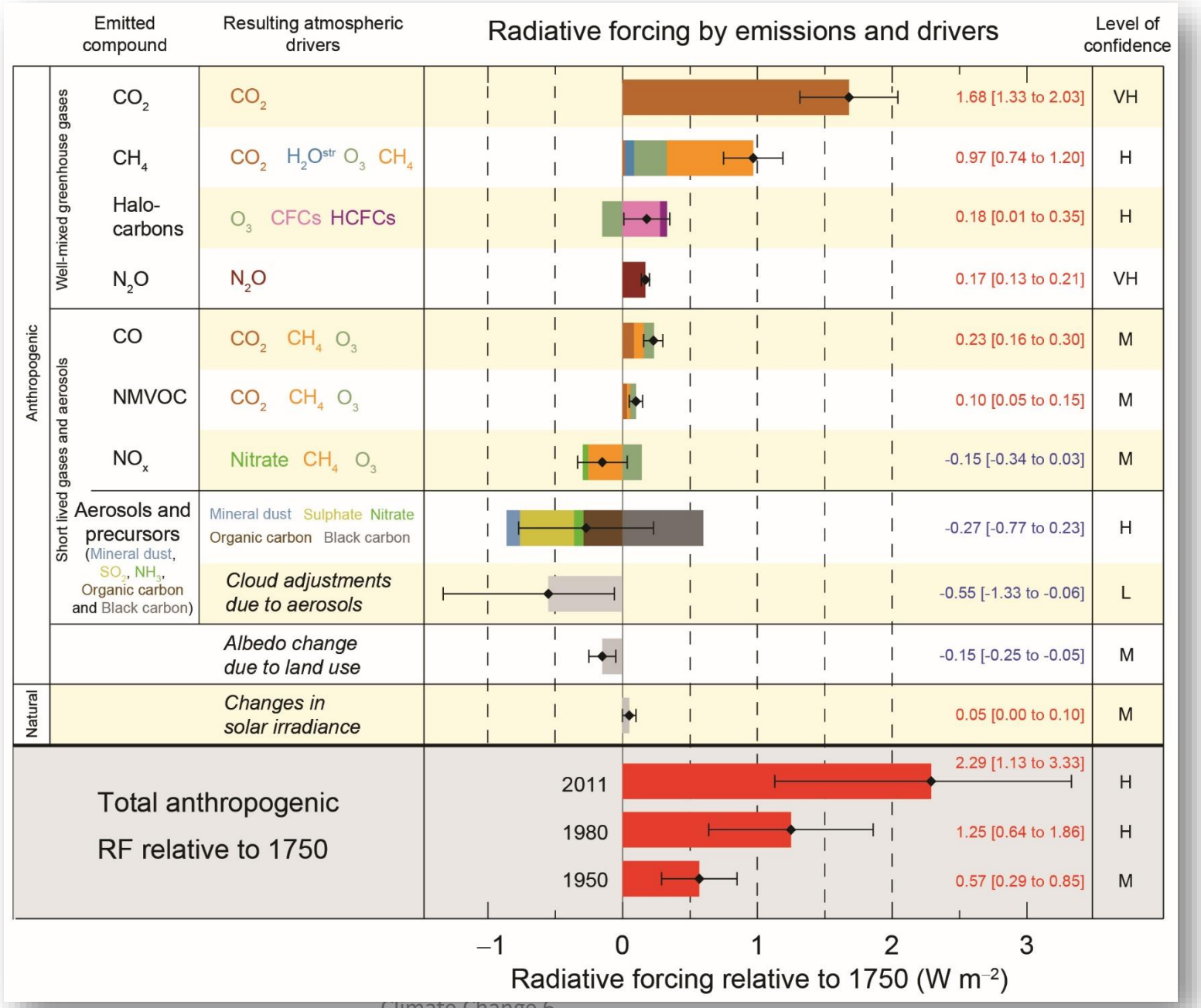
CO_2





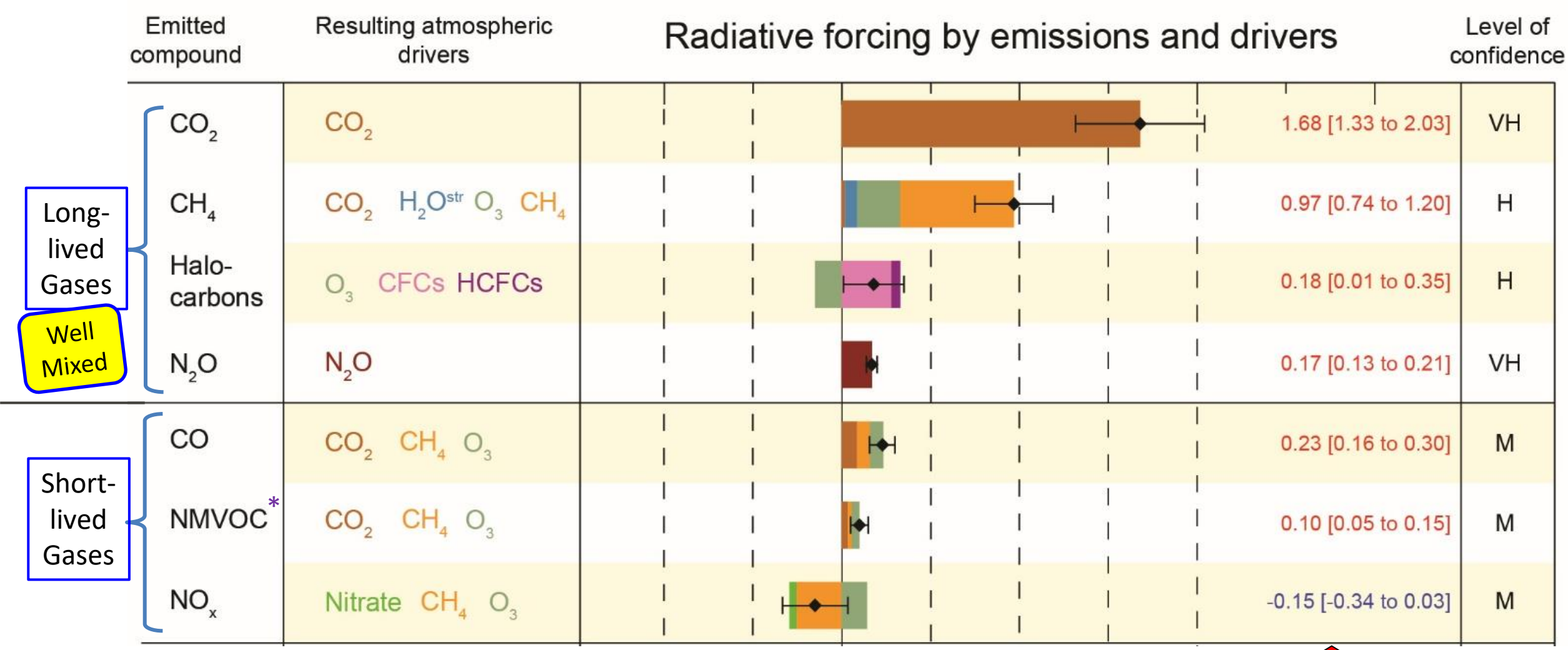

Radiation Transmitted by the Atmosphere
0.2
1
10
70
Spectral Intensity
Downgoing Solar Radiation
70-75% Transmitted
Upgoing Thermal Radiation
15-30% Transmitted
5525 K
210-310 K
UV
Visible
Infrared
Percent
100
75
50
25
0
Total Absorption and Scattering
Major Components
Water Vapor
Carbon Dioxide
Oxygen and Ozone
Methane
Nitrous Oxide
Rayleigh Scattering
0.2
1
10
70
Wavelength (μm)

Radiative Forcing as of 2011 (IPCC AR5)



IPCC AR5
SPM-5

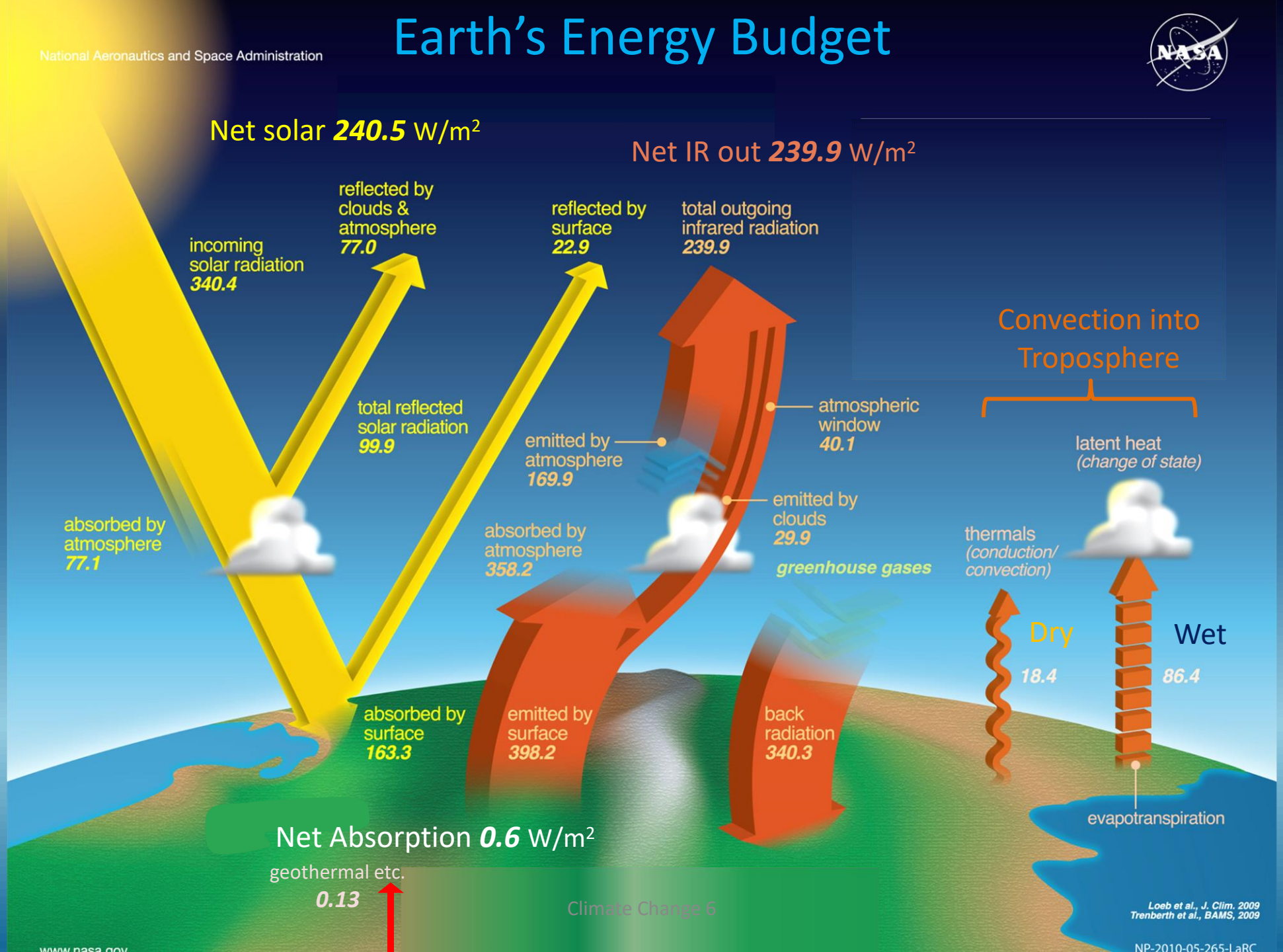
Greenhouse Gas Radiative Forcing as of 2011 (IPCC AR5)



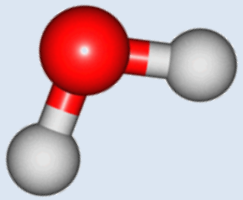
IPCC AR5 SPM-5

*Non-Methane VOC's
like Ethanol, Acetone, Formaldehyde

Earth's Energy Budget



Greenhouse Gases

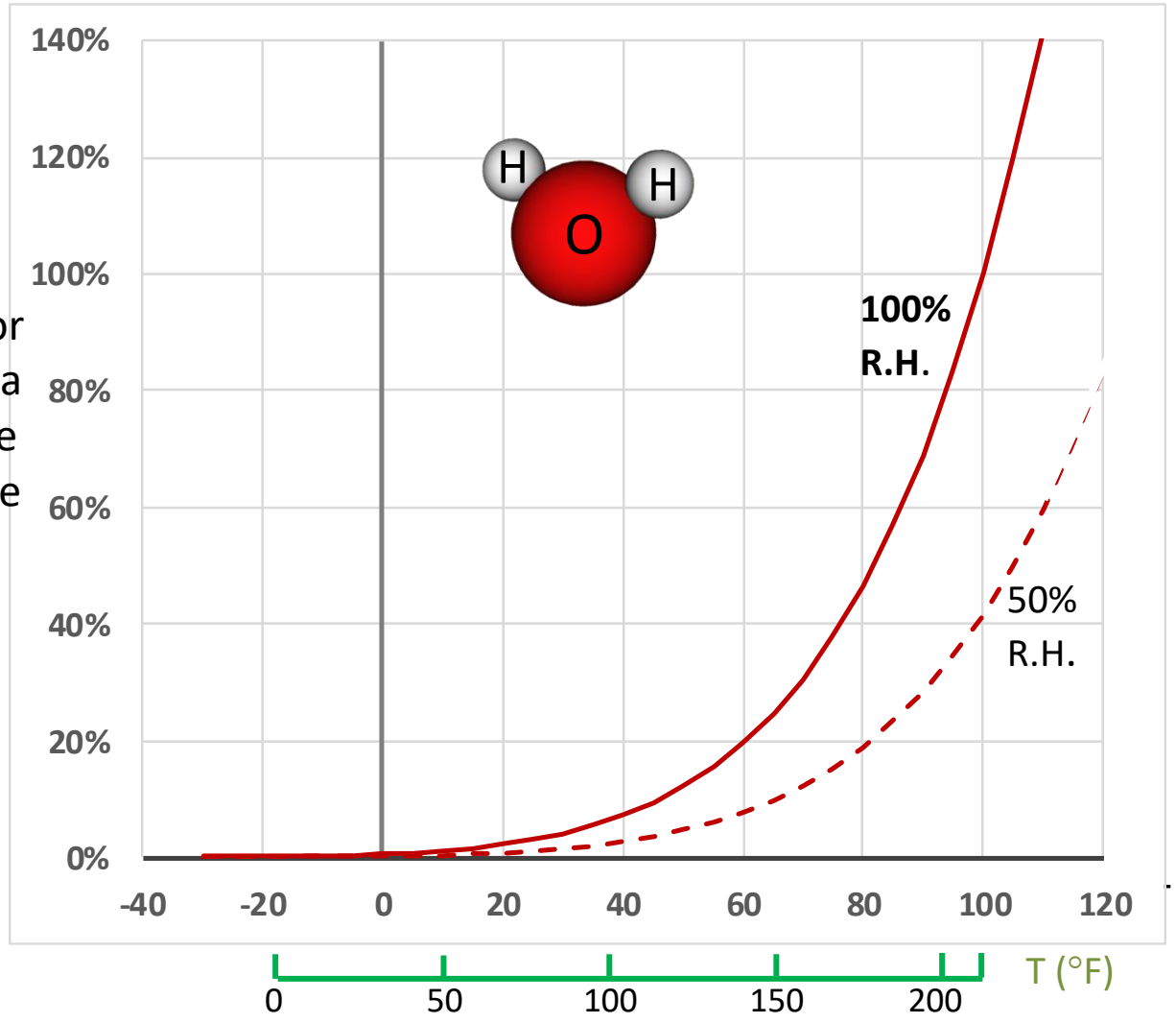


Water H_2O

a very important GH Gas

-- but not considered a Radiative Forcing agent

Water Content of Atmosphere Limited by Condensation



Changes in Surface Temperature will **automatically** cause the amount of water vapor in the atmosphere to change.

T ↑ H_2O ↑ Greenhouse ↑ T ↑↑

T ↓ H_2O ↓ Greenhouse ↓ T ↓↓

Positive Feedback

Water Feedback Approximately Doubles the Effect of Any Forcing

Water is on Autopilot

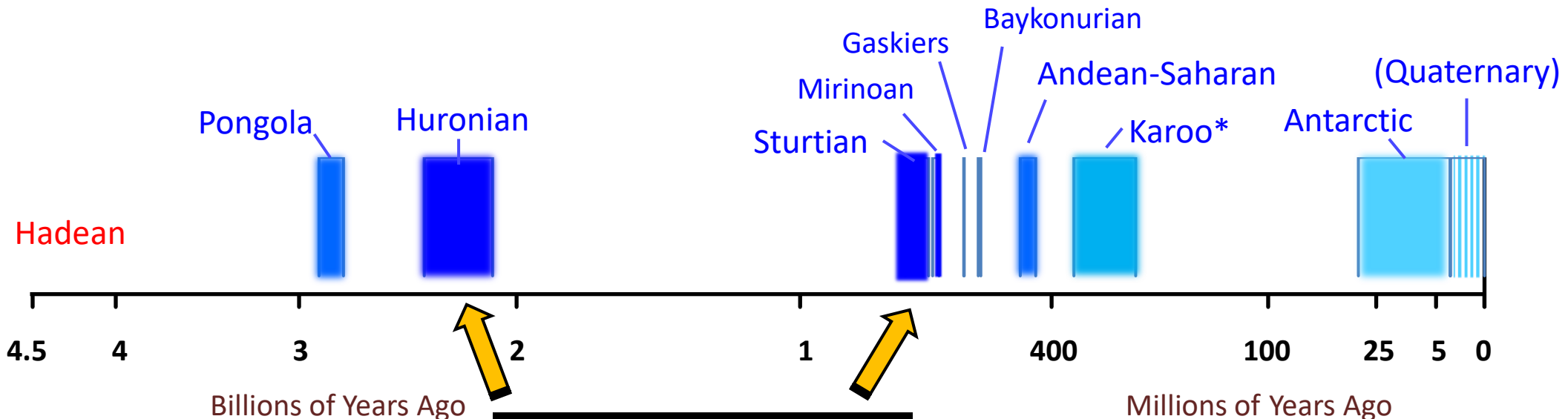
- No external intervention could feasibly *directly* affect H_2O vapor content of atmosphere
  - but *indirectly* any Forcing can and does affect water vapor

- Could the Positive Feedback run away?
  - Inducing Iceball Earth

    or
  - Venus-like Sauna Earth

* van der Ent & Tuinenburg (2017)

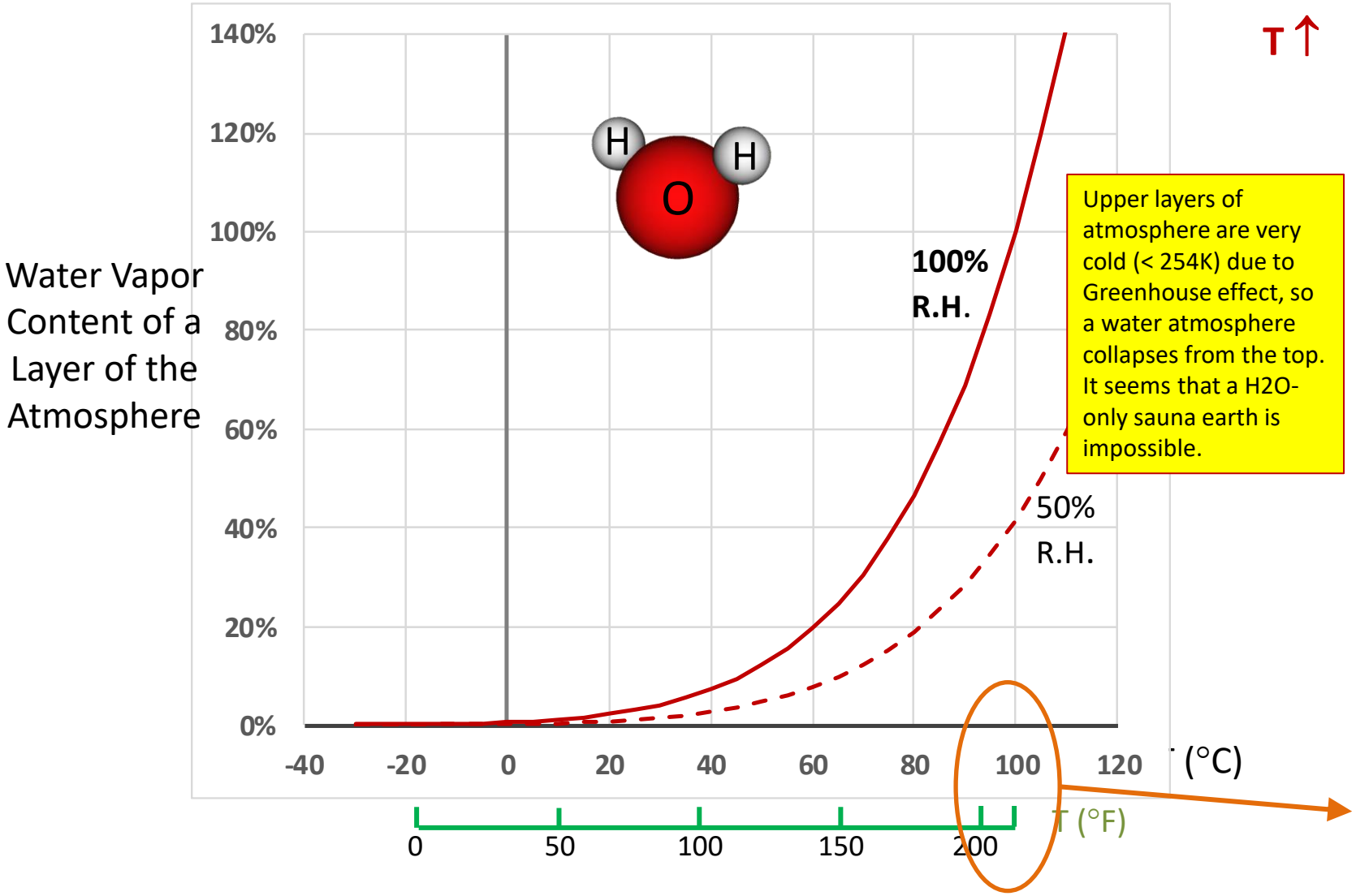
Rough Timeline of Past Glaciations



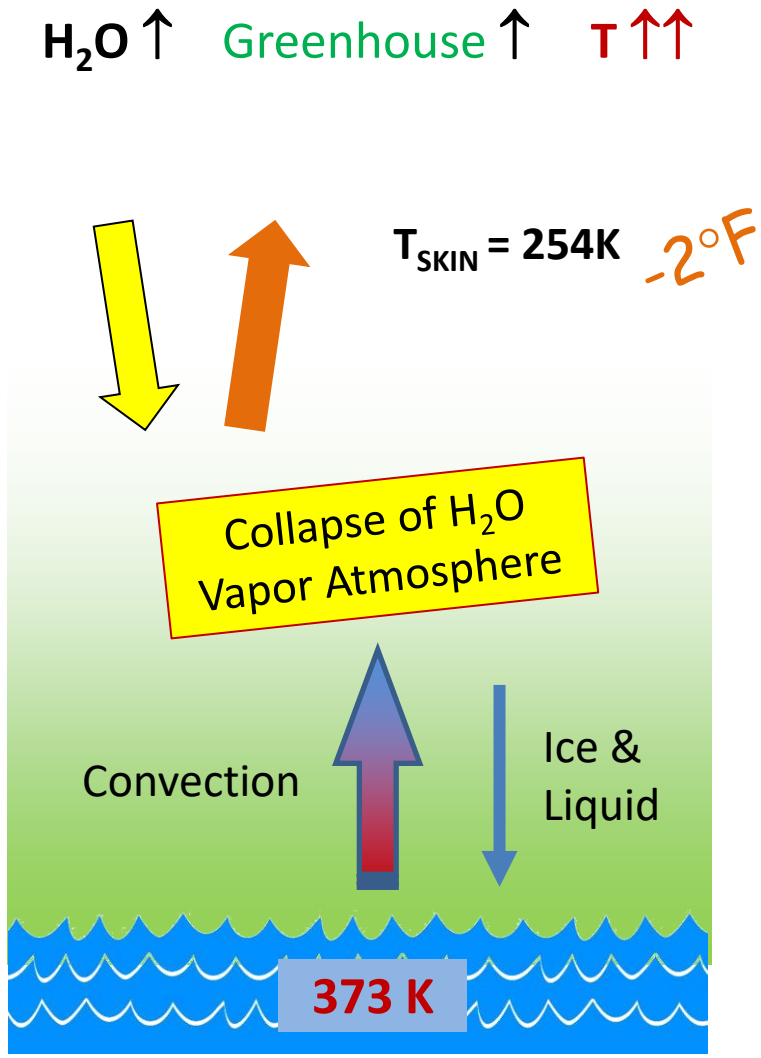
Data source: Wikipedia
"Late Paleozoic Icehouse" Table

* AKA Late Paleozoic Icehouse

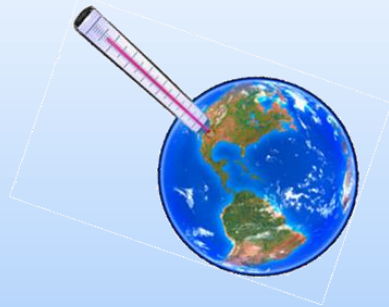
Sauna Earth?

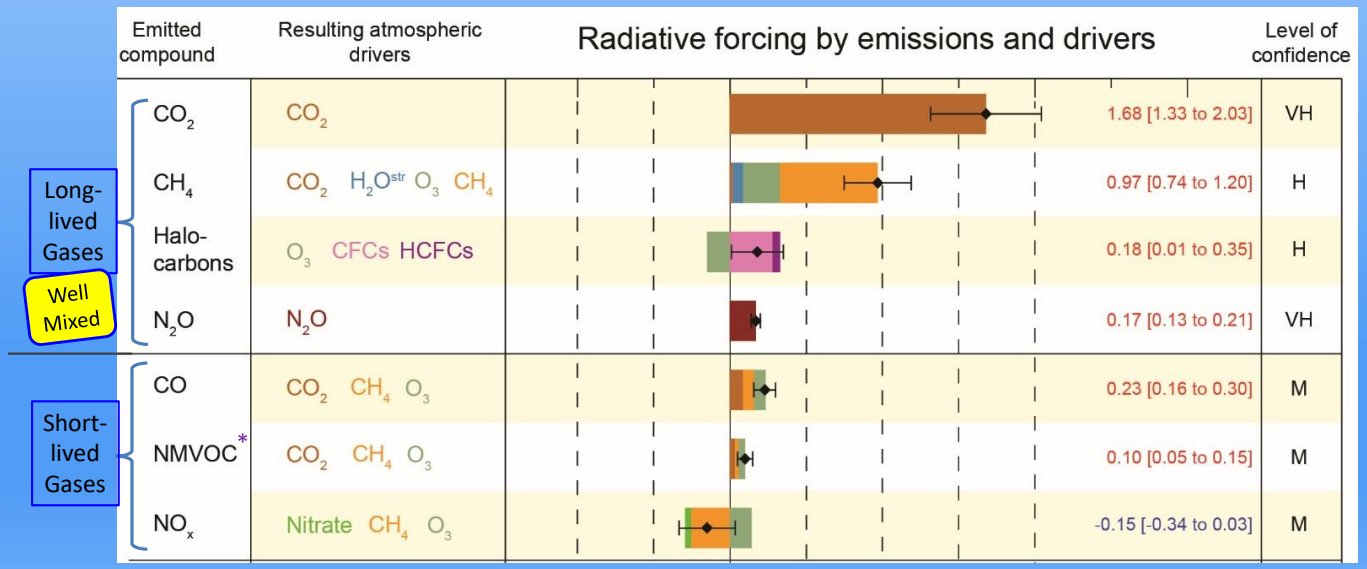


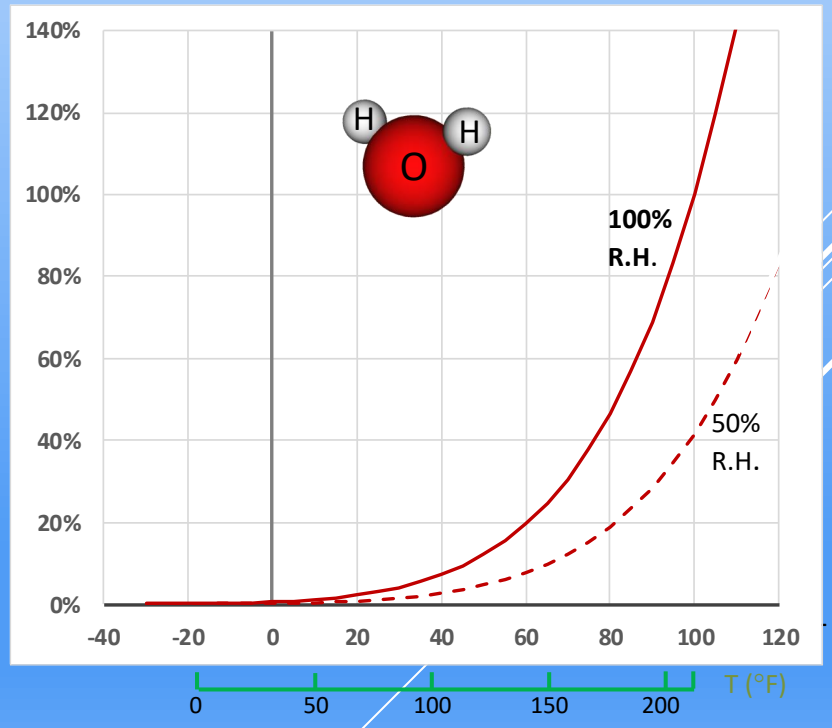
Upper layers of atmosphere are very cold (< 254K) due to Greenhouse effect, so a water atmosphere collapses from the top. It seems that a H2O-only sauna earth is impossible.



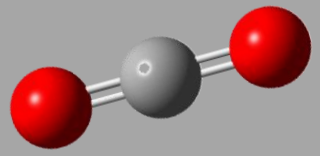
Questions about Greenhouse Gases in General or Water in Particular?







Greenhouse Gases



Carbon Dioxide CO_2

…the Gorilla in the room

Greenhouse Gases

Carbon Dioxide CO_2

Elemental Abundances

Solar System:

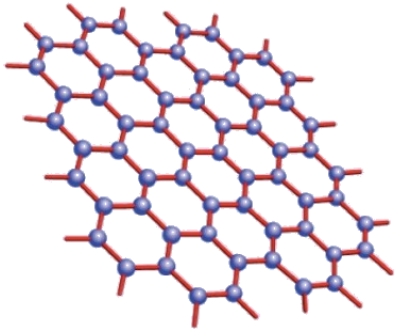
1. Hydrogen
2. Helium
3. **Oxygen**
4. **Carbon**
5. Nitrogen
6. Neon

Earth Crust:

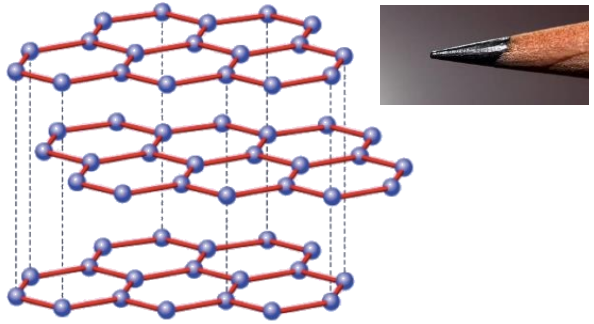
1. **Oxygen**
2. Silicon
3. Aluminum
4. Iron
5. Calcium
6. Sodium

10-15 **Carbon**

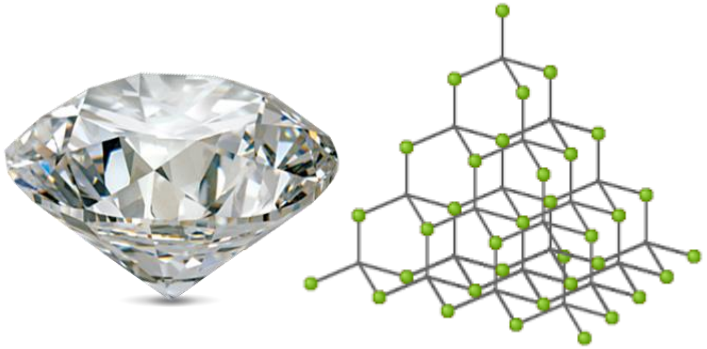
Elemental Carbon (^{12}C) Forms (Allotropes)



Graphene



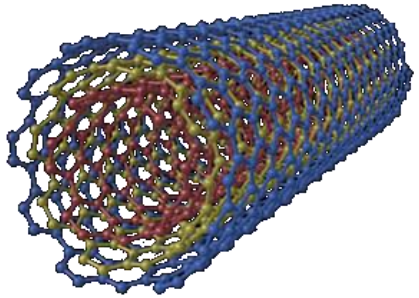
Graphite



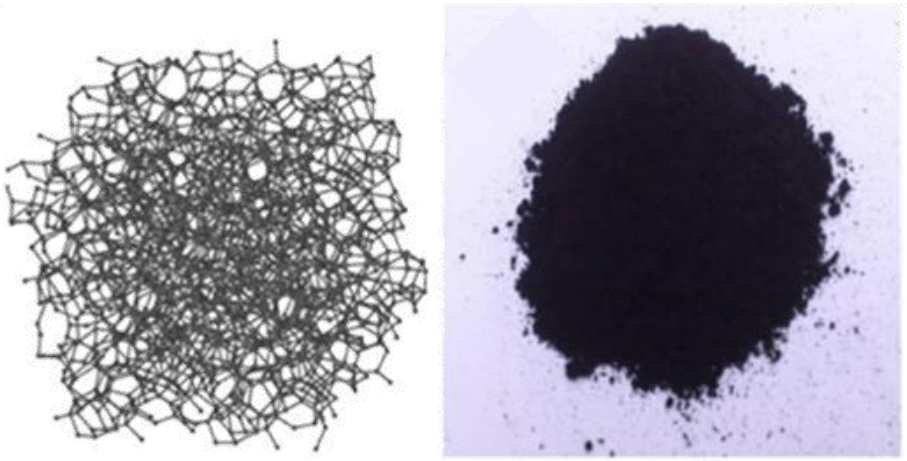
Diamond

C_{60}

Buckminsterfullerene



Carbon Nanotubes



Amorphous Carbon

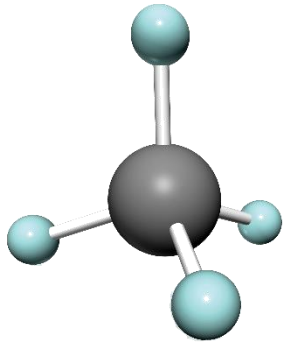
Carbon Compounds

Gases

CO_2

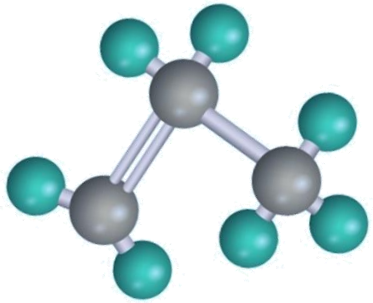
Methane

CH_4



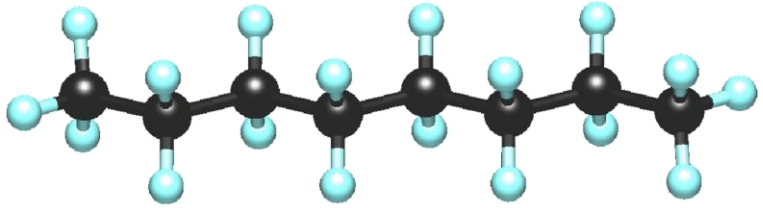
Propane

C_3H_6

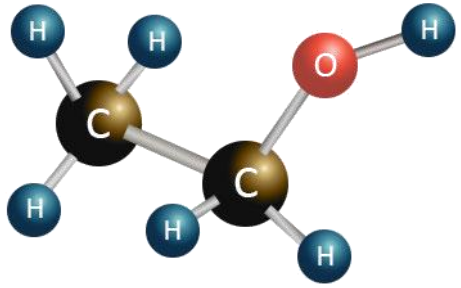


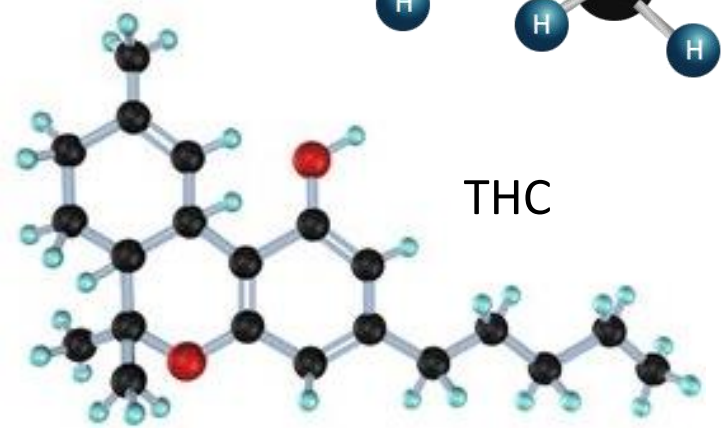
Organic Compounds

Octane



Ethanol

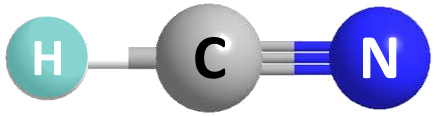




THC

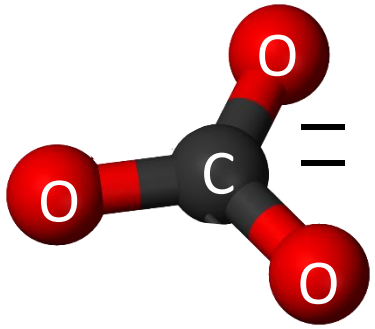
Inorganic Compounds

Hydrogen Cyanide



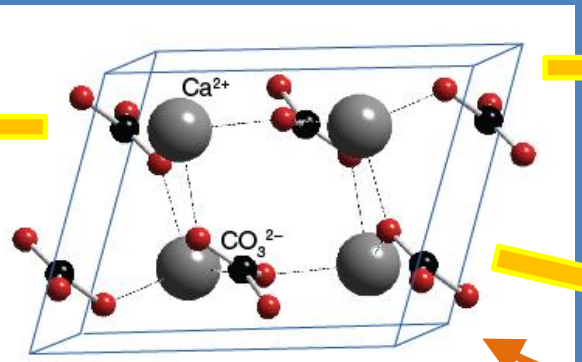
Calcium Carbonate

$Ca^{++}CO_3^{=}$



Carbon Compounds

Chalk



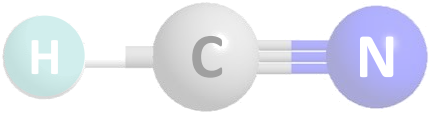
Calcite

Polarizers

Forams

Inorganic Compounds

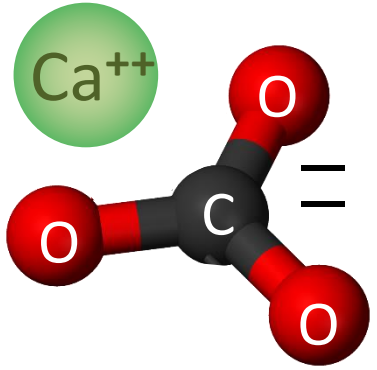
Hydrogen Cyanide



Mollusc Shells

Calcium Carbonate

$Ca^{++}CO_3^{=}$



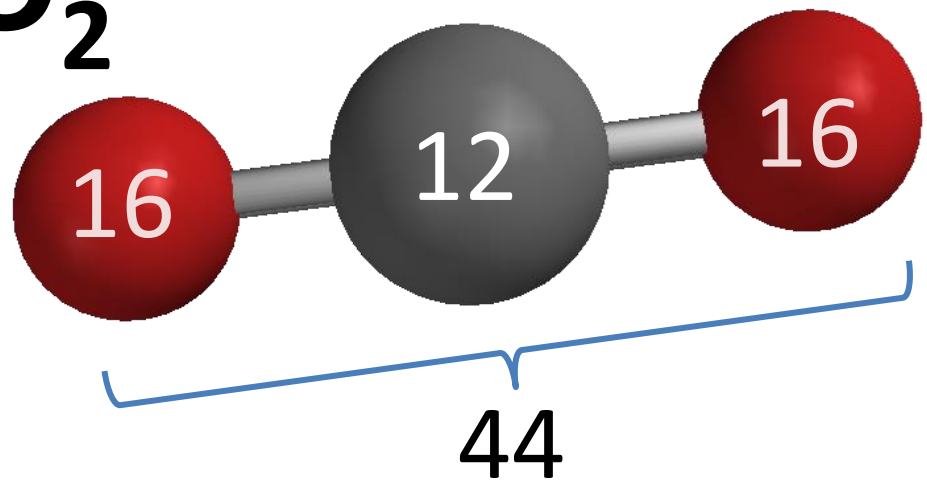
Aragonite

Corals

Tonnage of Carbon *vs.* CO_2

C

CO_2

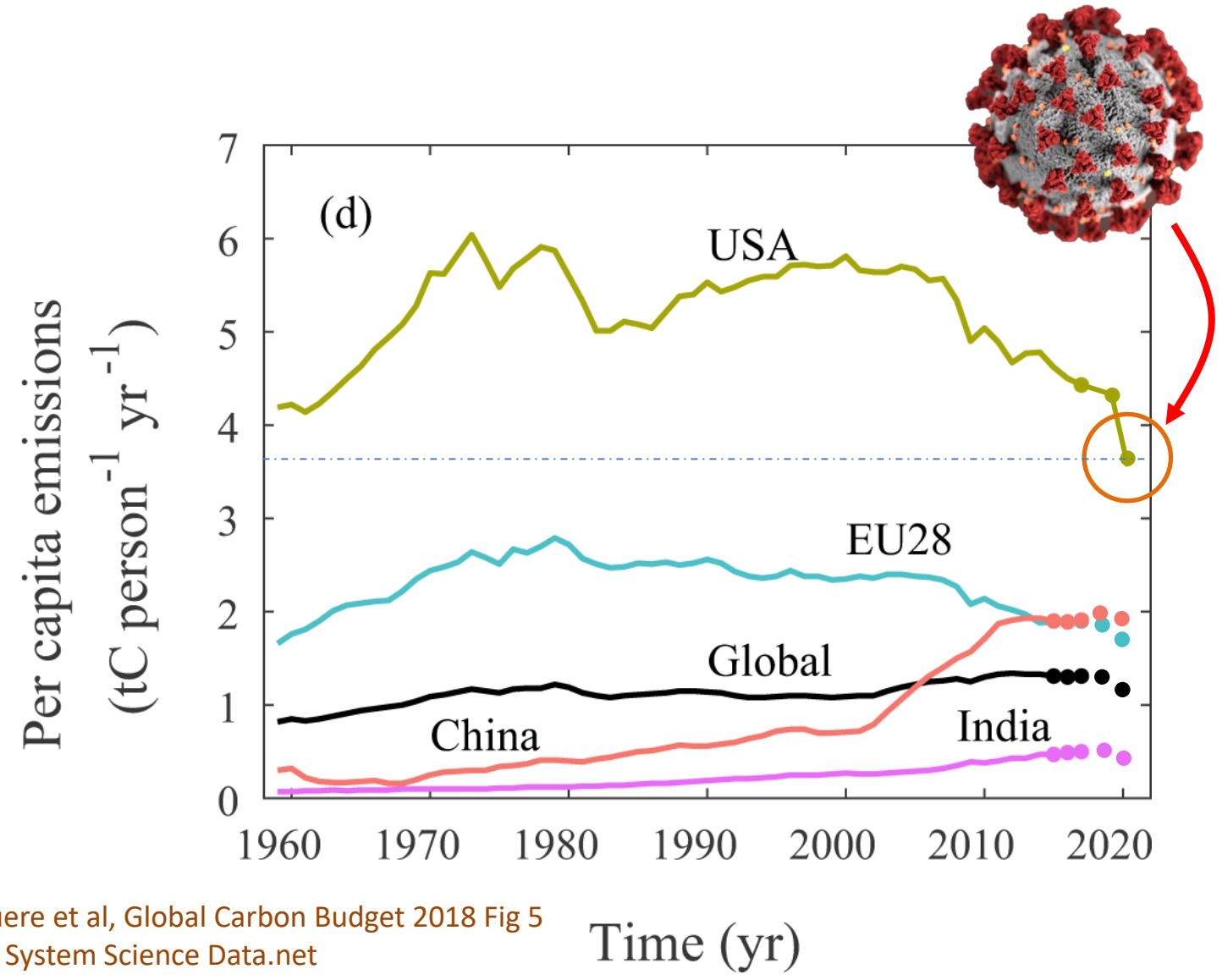


1 Ton of Carbon ….

makes

3.7 Tons of CO_2

Pay attention to units when you see Carbon emissions quoted…



Example:

2020 US Per Capita Carbon Emissions

3.7 tons of Carbon

or

13.7 tons of CO_2

per capita, per year

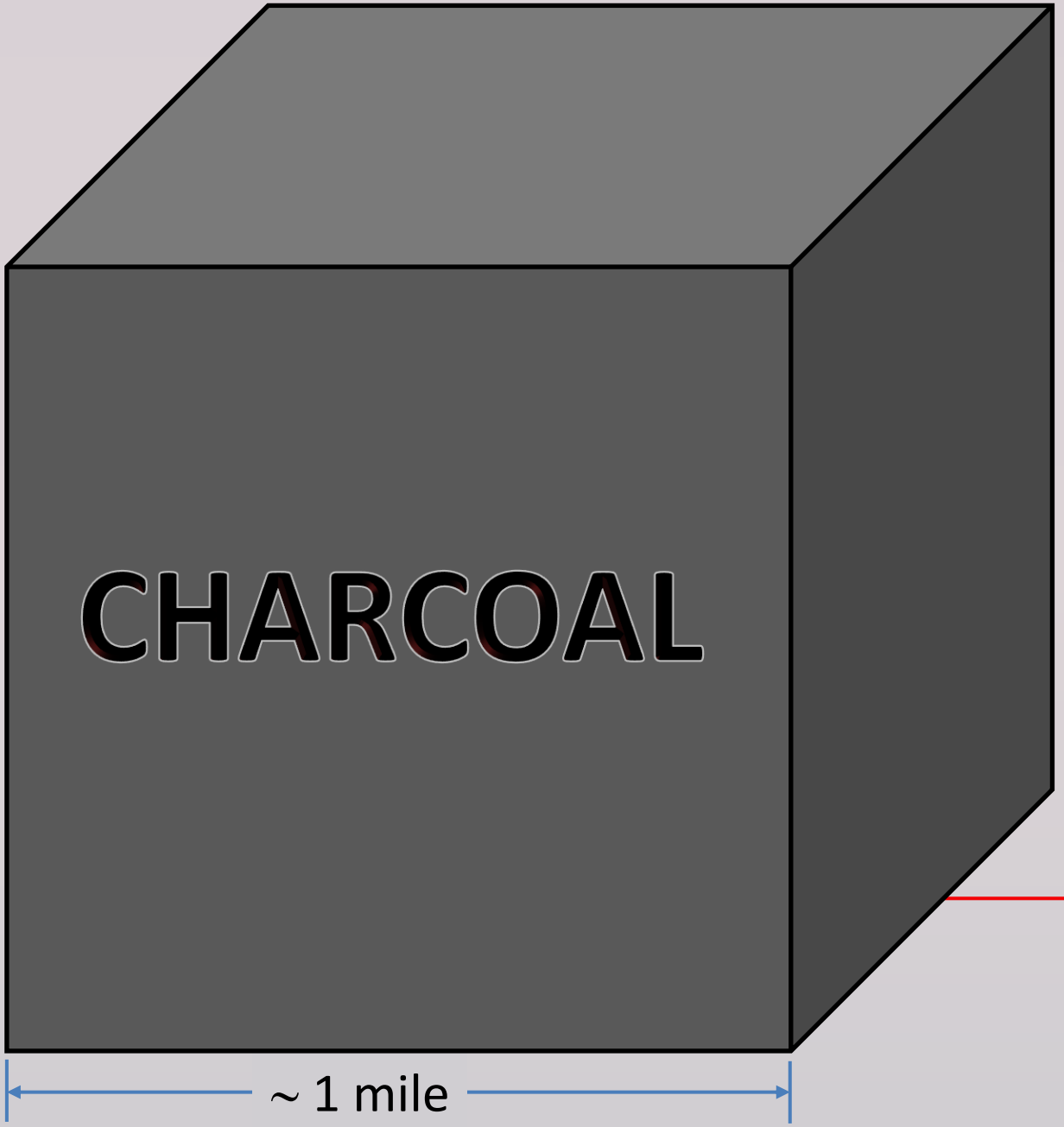
Le Quere et al, Global Carbon Budget 2018 Fig 5
Earth System Science Data.net
edgar.jrc.ec.Europa.eu for 2019
carbonbrief.org for 2020

1 Gigaton of Carbon (GtC)

Willis Tower Chicago

Brilliant—cut diamond

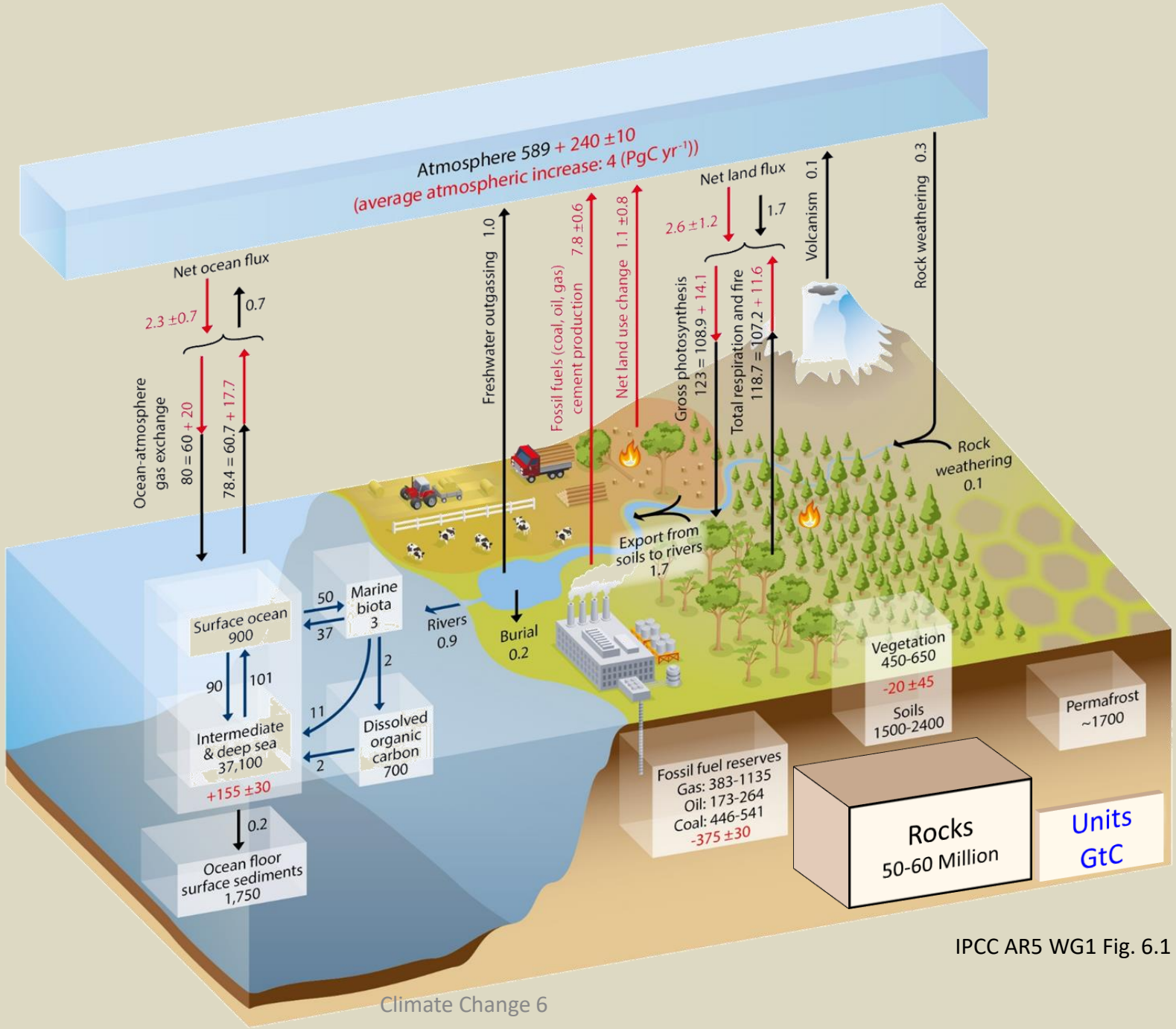
1 Gigaton of Carbon (GtC)



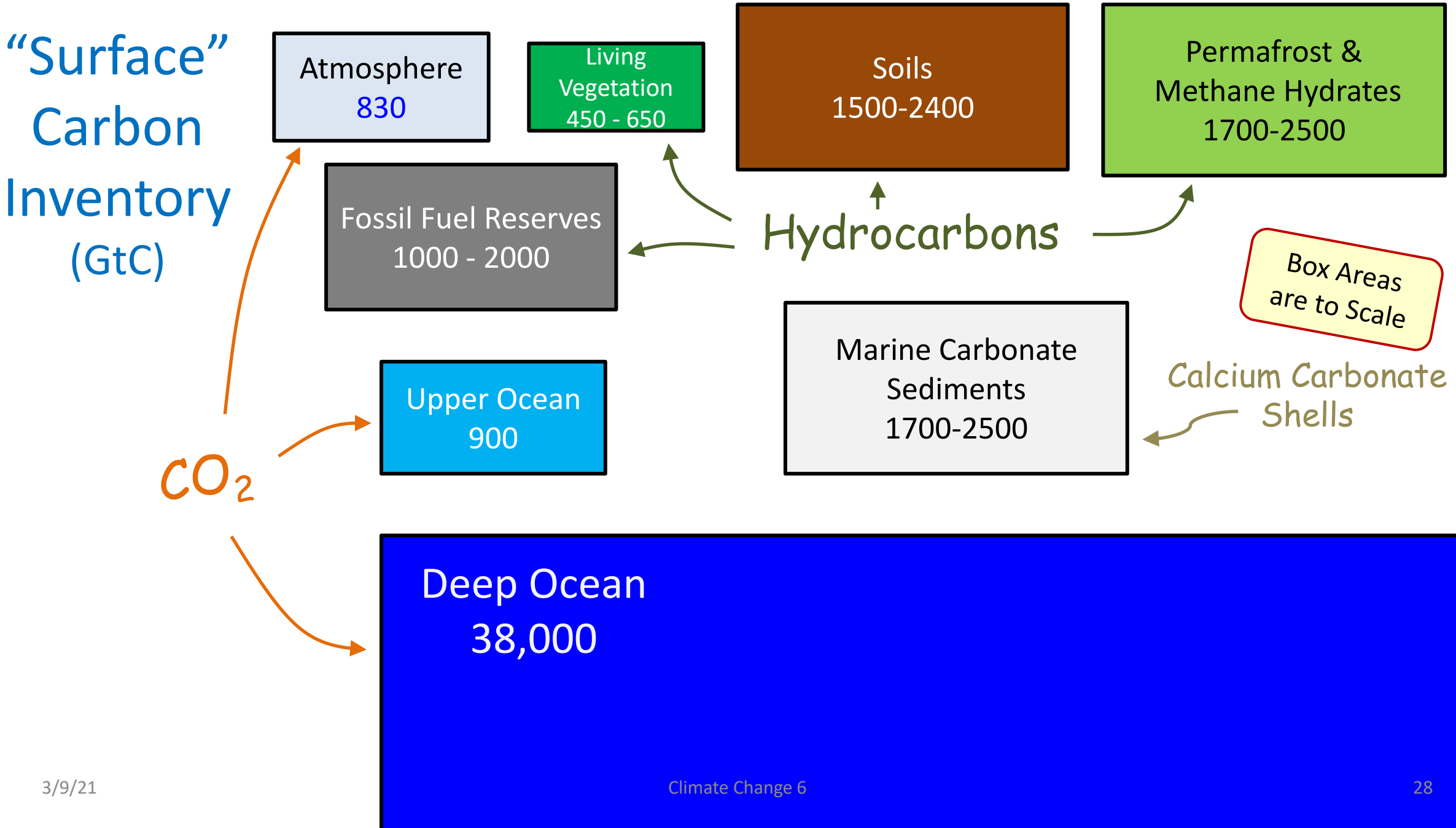
Willis Tower Chicago

Carbon Cycle

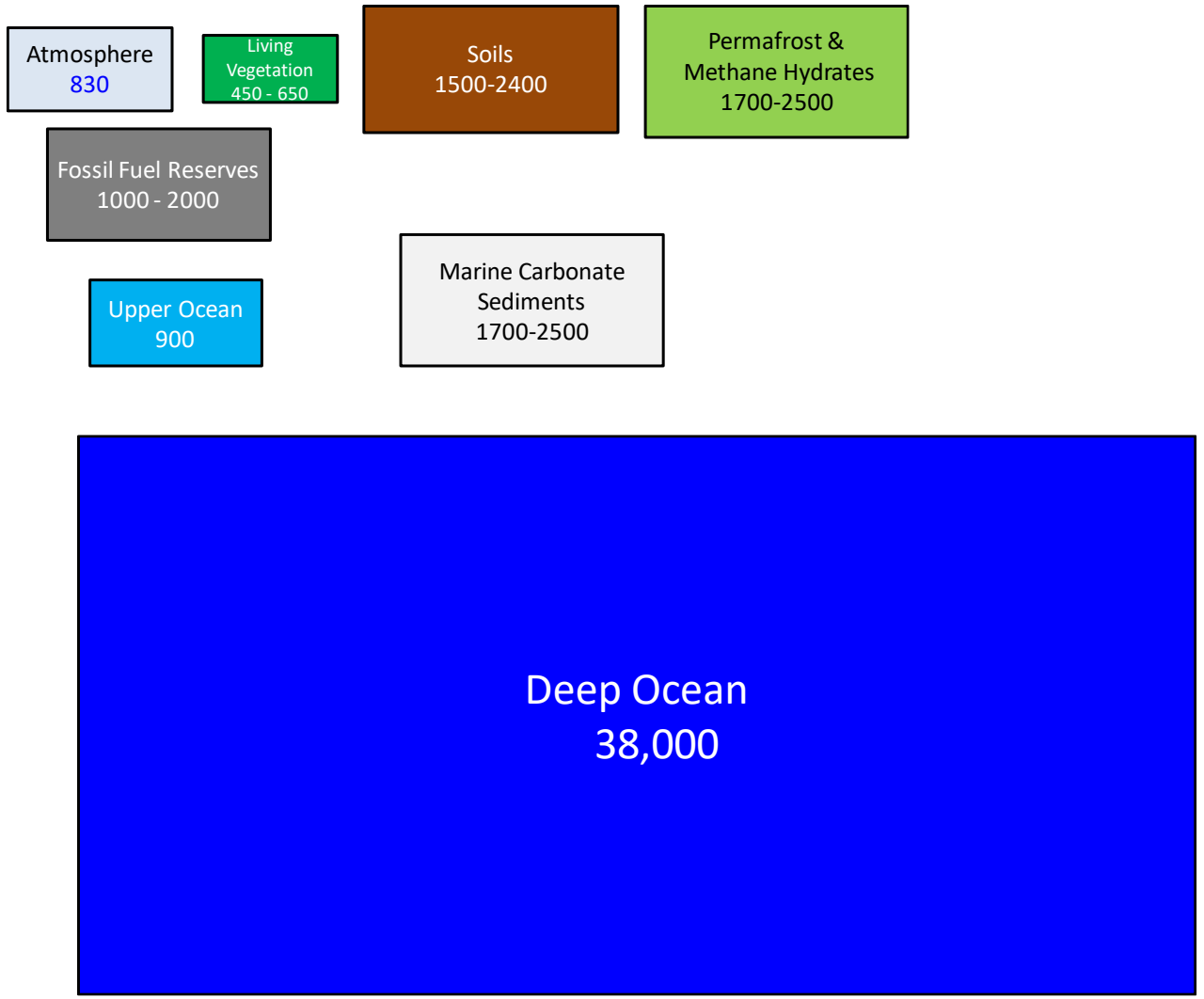
as of 2011



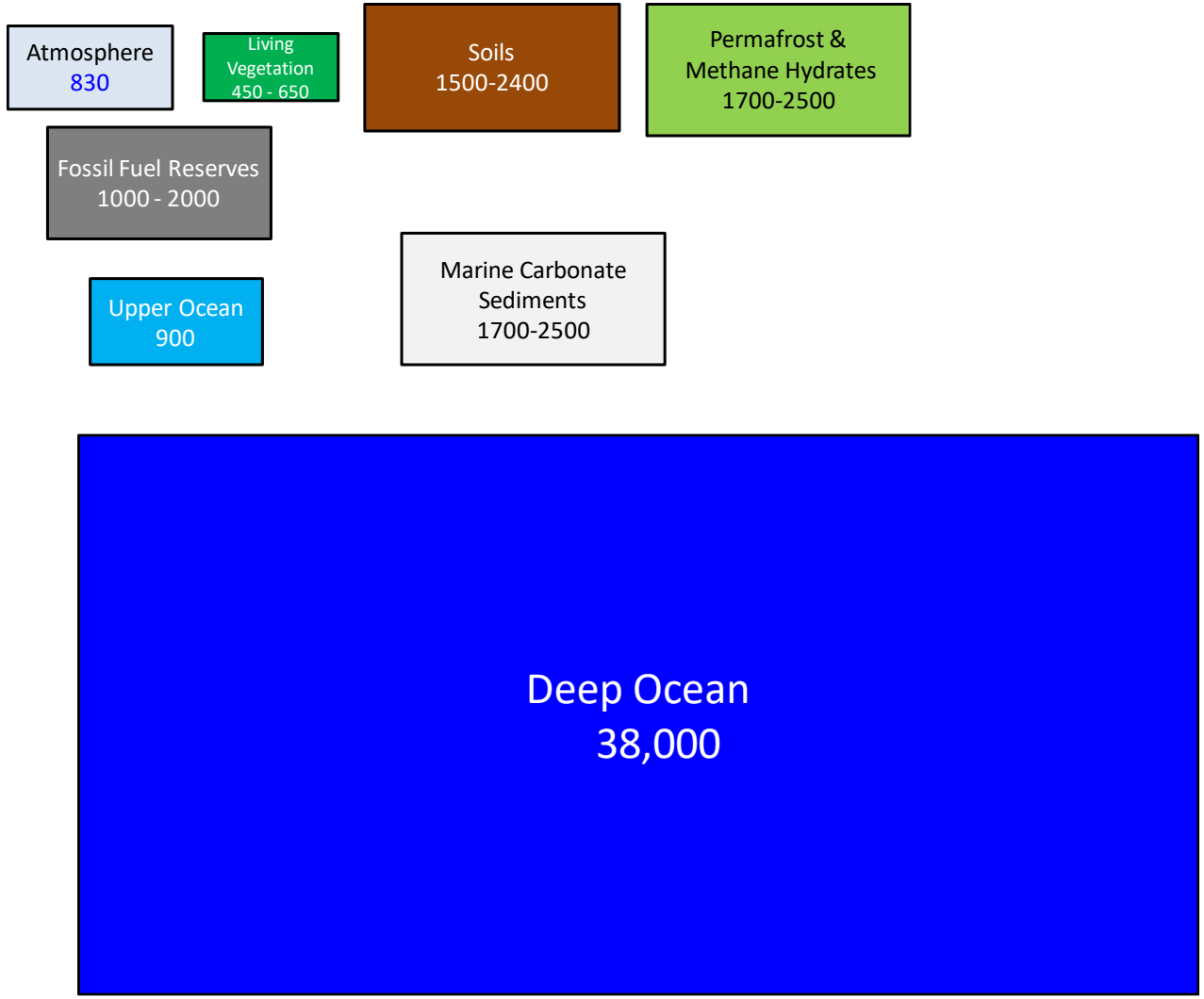
IPCC AR5 WG1 Fig. 6.1


"Surface" Carbon Inventory (GtC)
Atmosphere 830
Living Vegetation 450 - 650
Soils 1500-2400
Permafrost & Methane Hydrates 1700-2500
Fossil Fuel Reserves 1000 - 2000
Hydrocarbons
Box Areas are to Scale
Marine Carbonate Sediments 1700-2500
Calcium Carbonate Shells
Upper Ocean 900
CO_2
Deep Ocean 38,000

“Surface” Carbon Inventory (GtC)

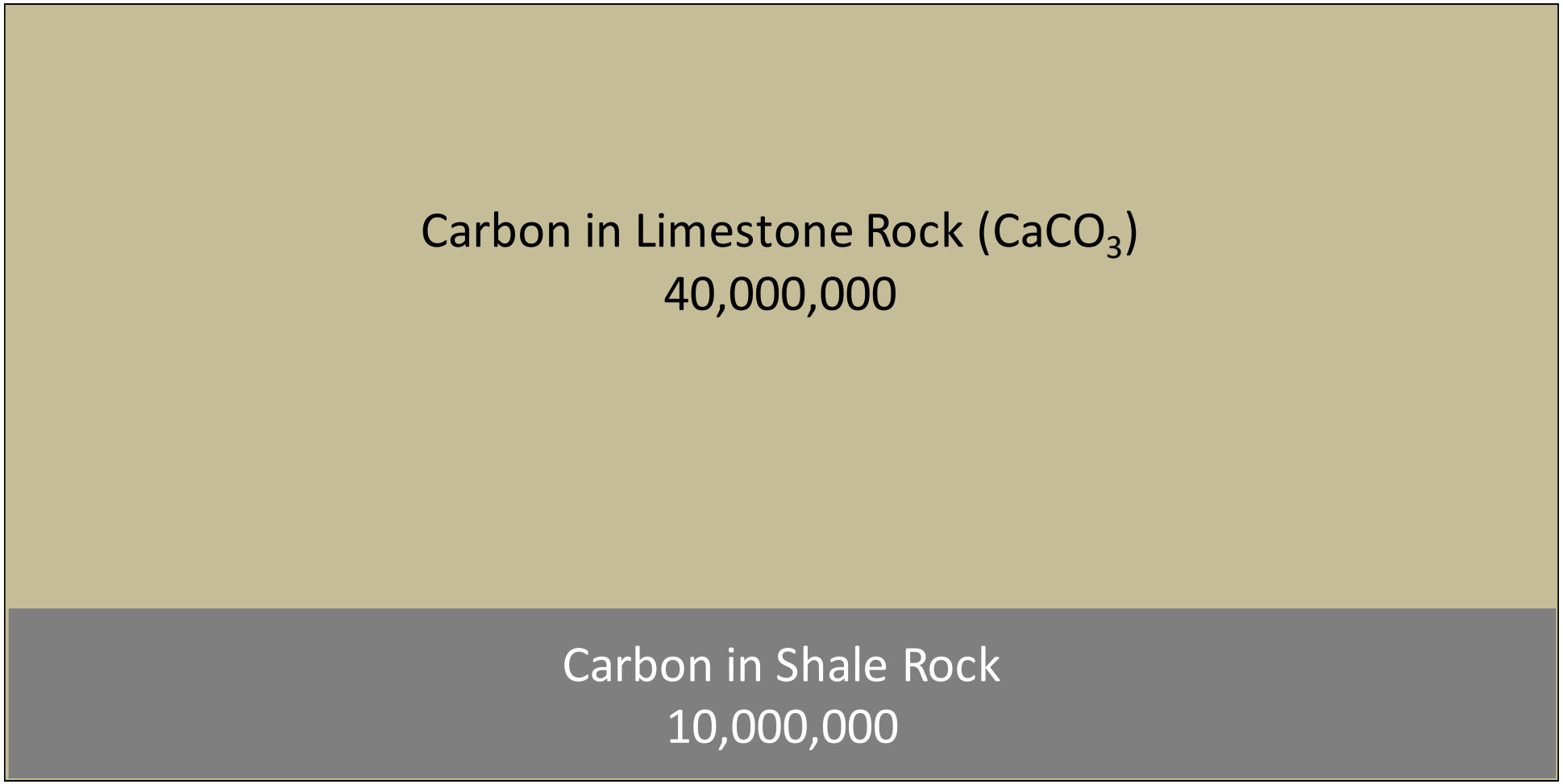


Total Carbon Inventory (GtC)

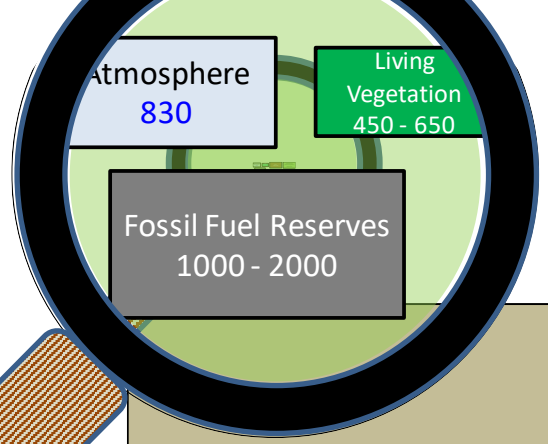


Carbon in Rocks
50,000,000

Total Carbon Inventory (GtC)



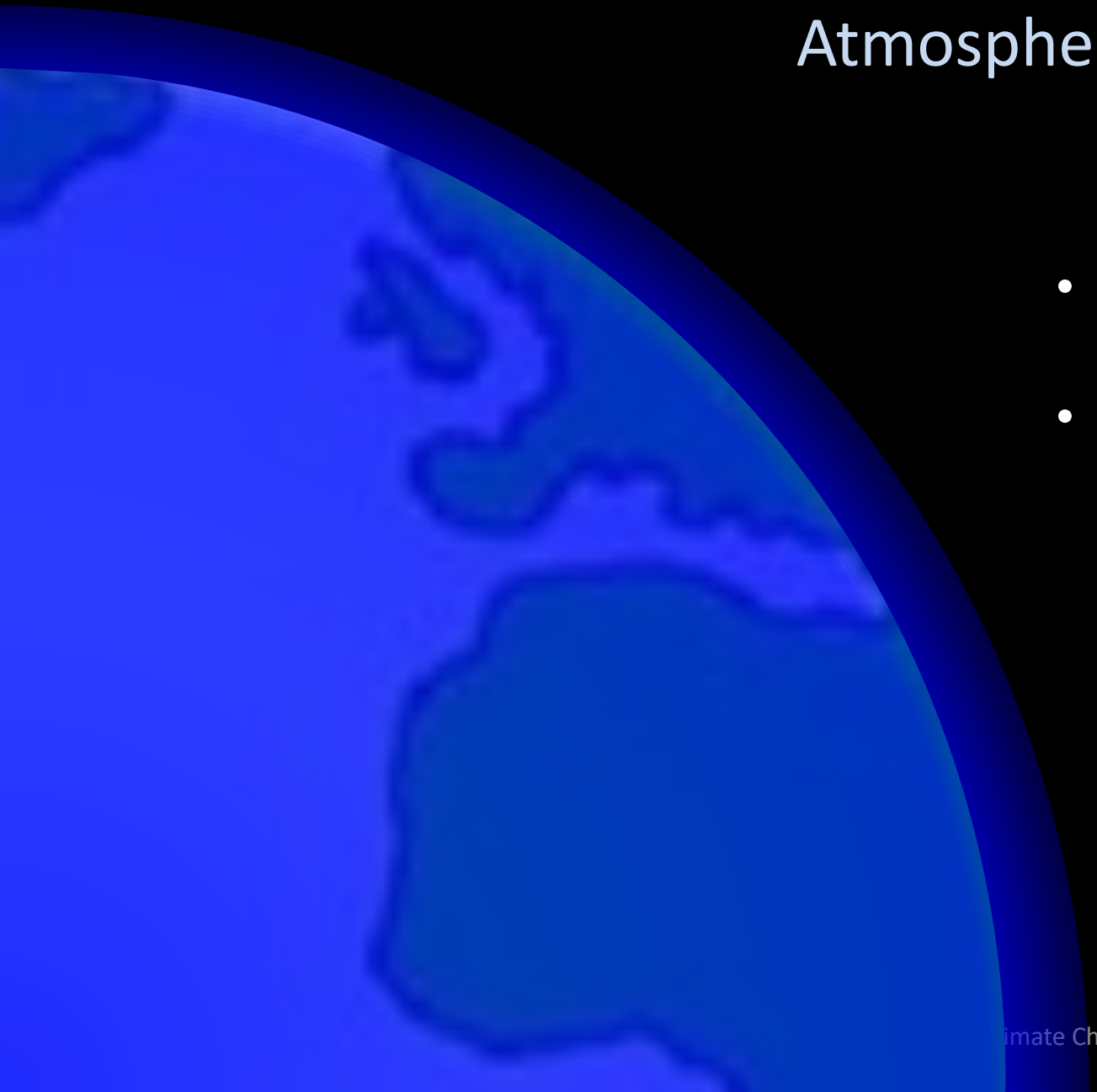
Total Carbon Inventor (Gt



Carbon in Limestone Rock ($CaCO_3$)
40,000,000

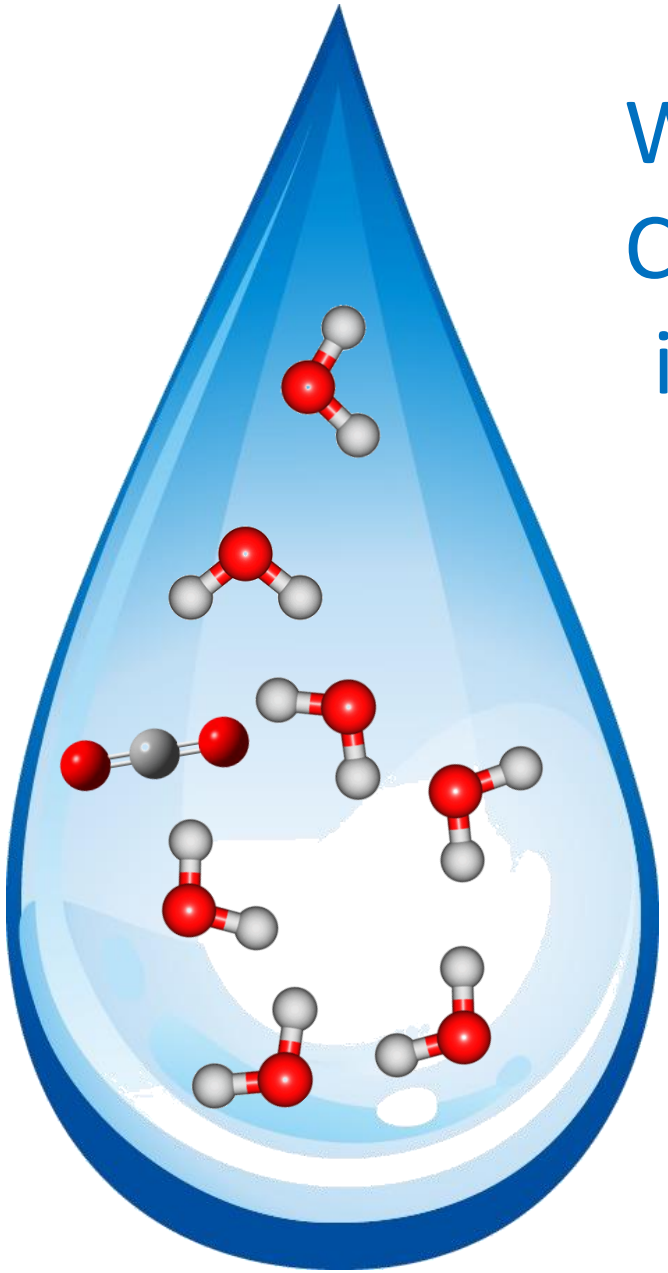
Carbon in Shale Rock
10,000,000

If All those 50 Million Gigatons of Carbon were put into the Atmosphere as CO_2



- CO_2 would increase 60,000 fold
- Air would contain ~37 atmospheres of CO_2
  - That's just 40% of Venus CO_2 , but enough to cook the surface to many hundreds of °F

What's keeping our CO_2 within bounds?

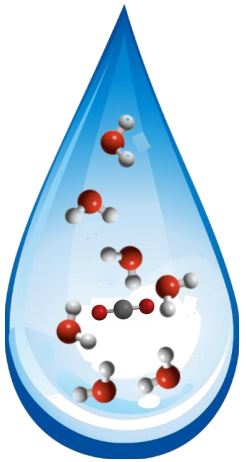


What Happens When a CO_2 Molecule Wanders into a Drop of Water?

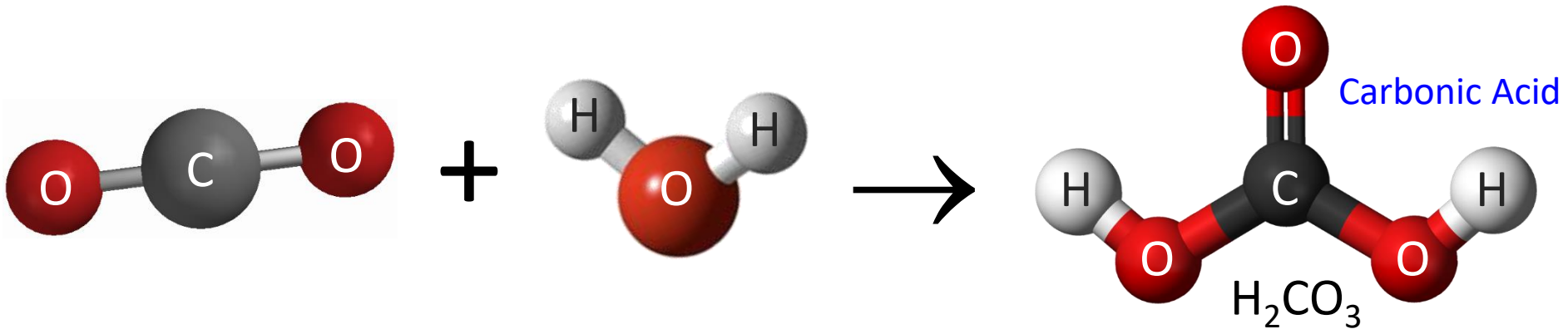
It may just dissolve in the water and float around

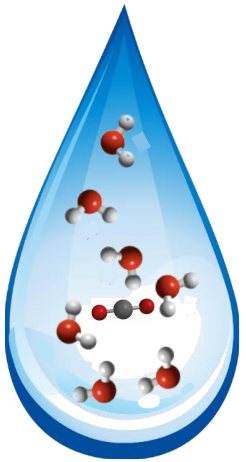
or

It may react with the water



A CO_2 Molecule and an H_2O can join up to form Carbonic Acid





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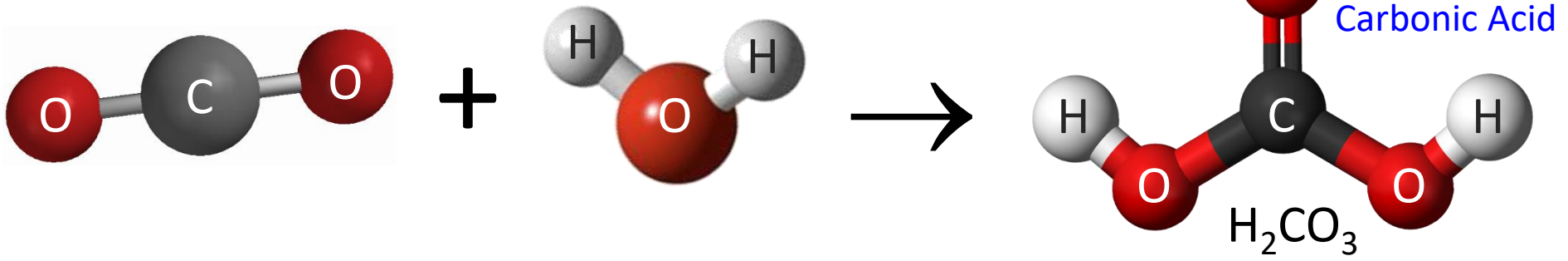
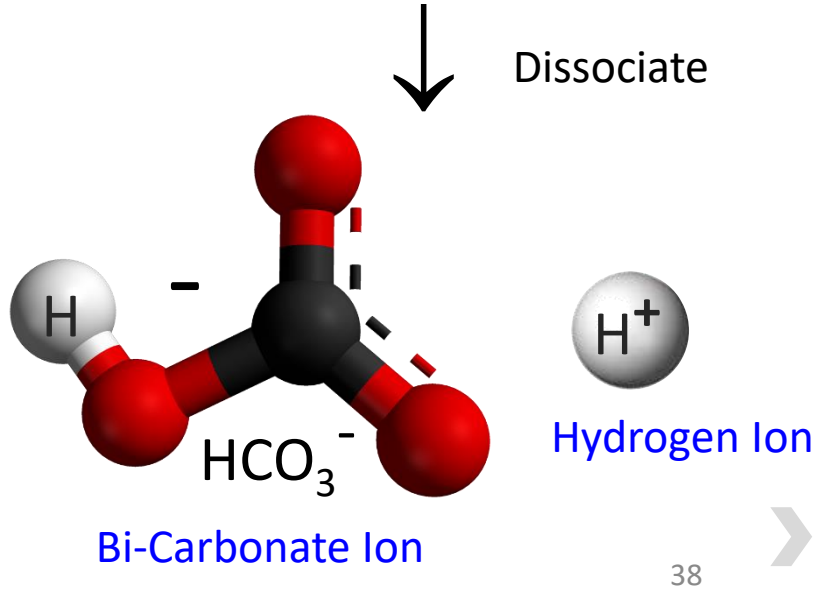
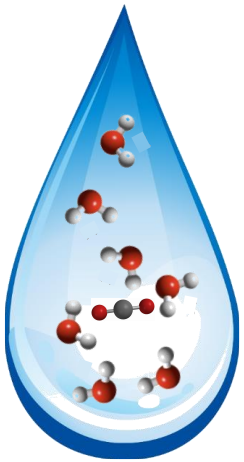
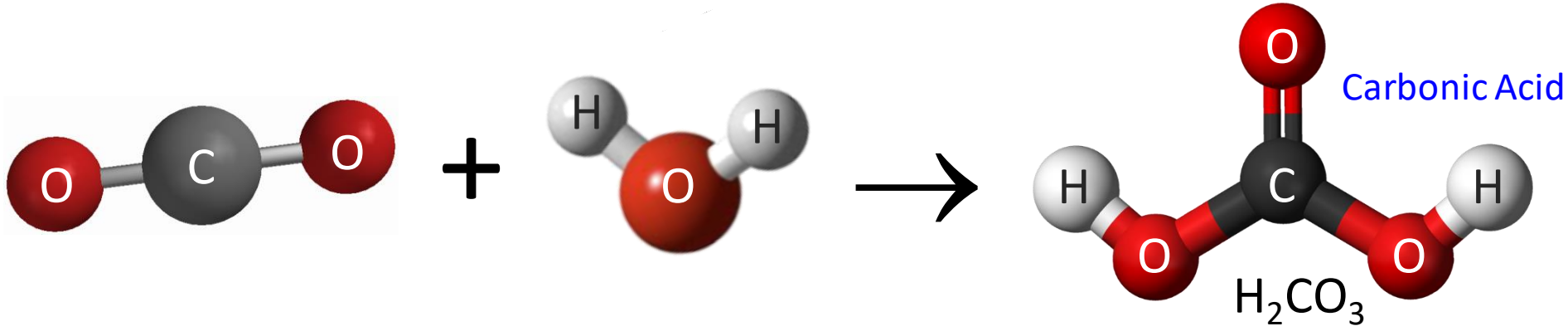


… which can dissociate under the right conditions to form a Bi-Carbonate ion + a Hydrogen ion…

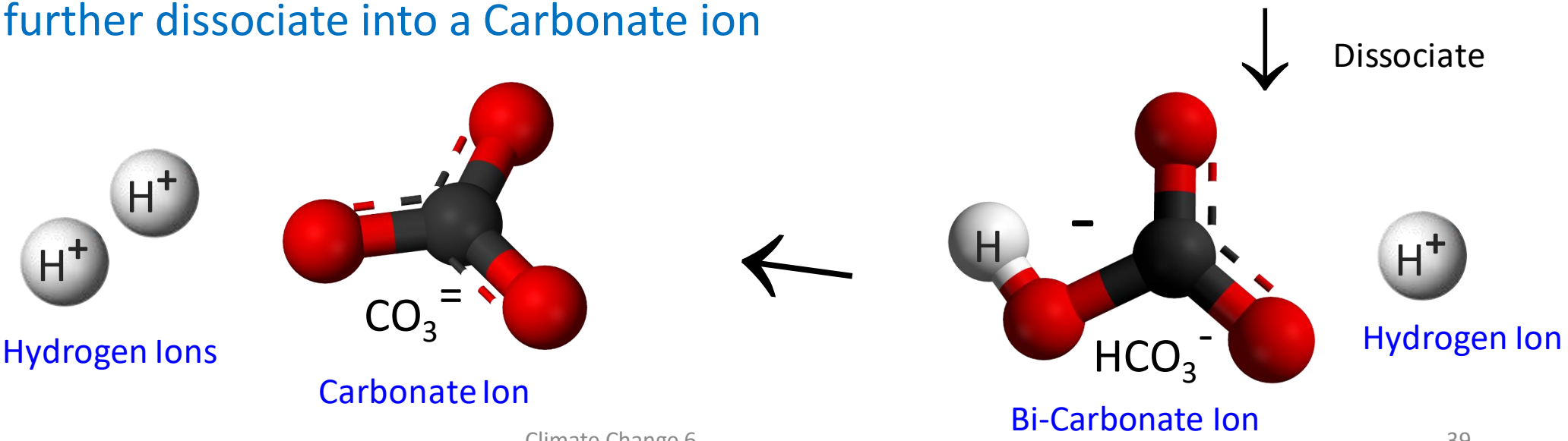


A CO_2 Molecule and an H_2O can join up to form Carbonic Acid





… and can further dissociate into a Carbonate ion



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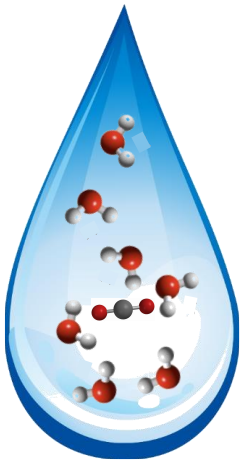
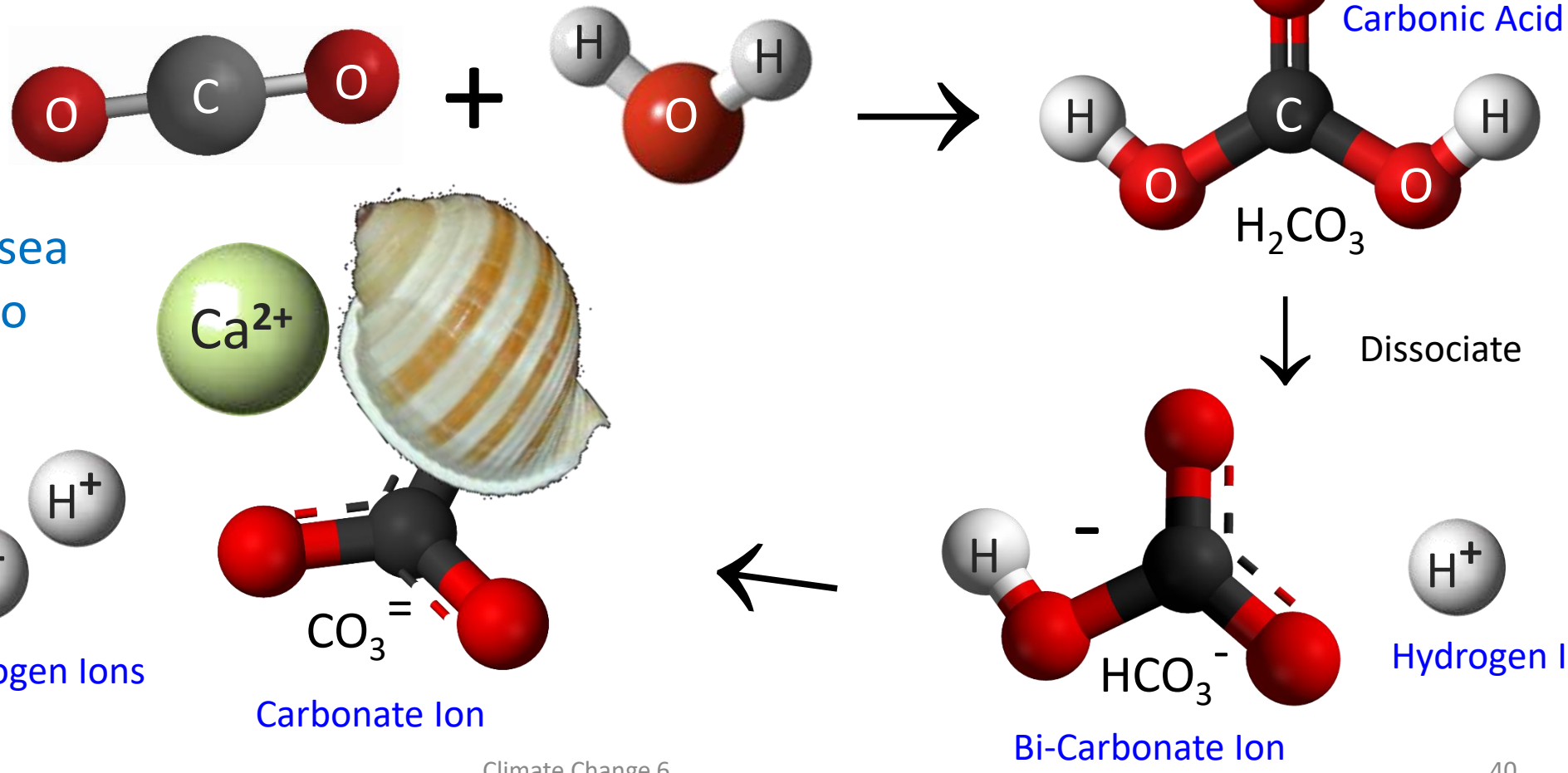
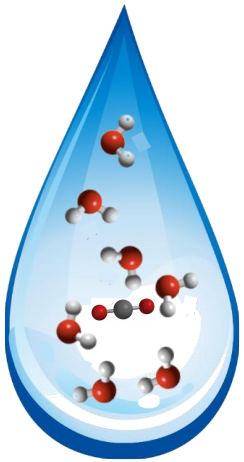




… which is what sea animals need to make shells…



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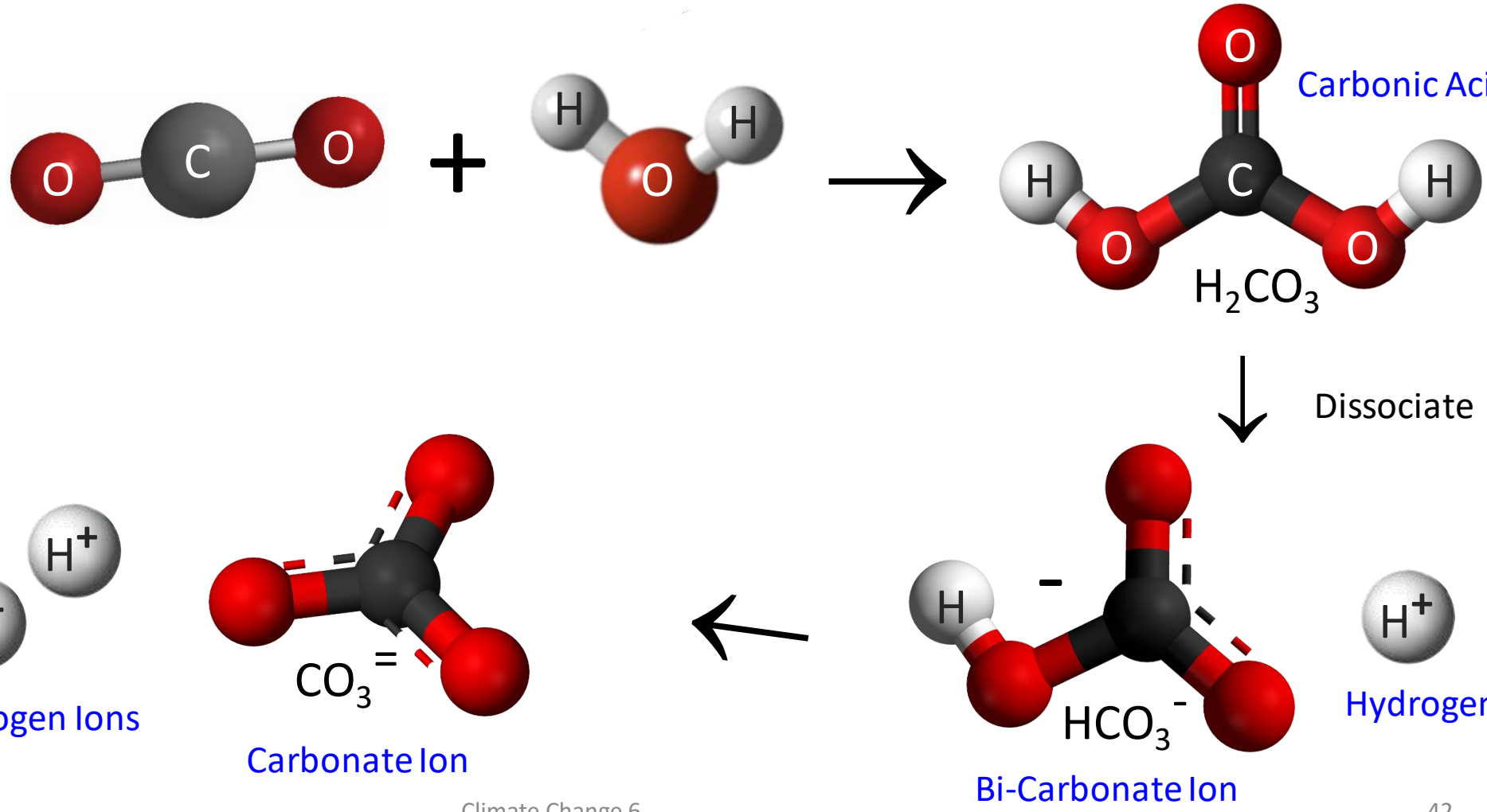
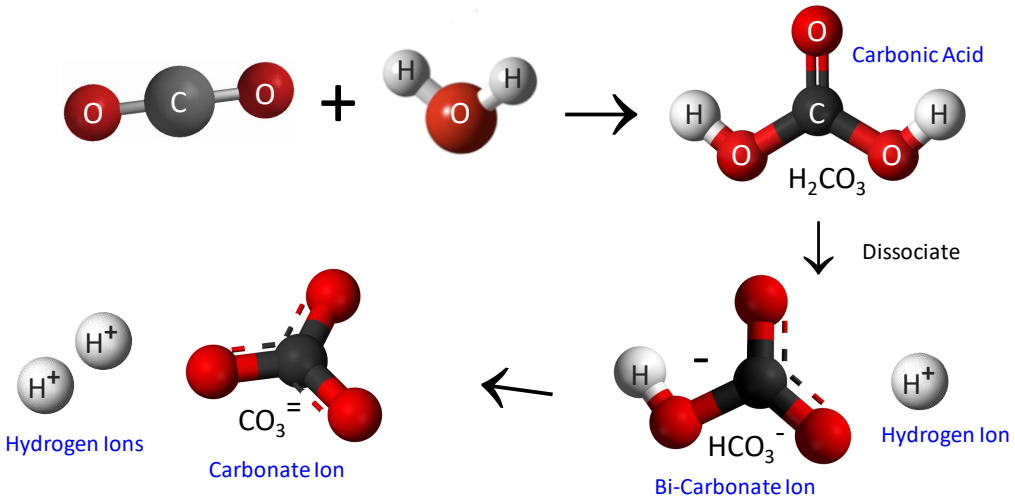


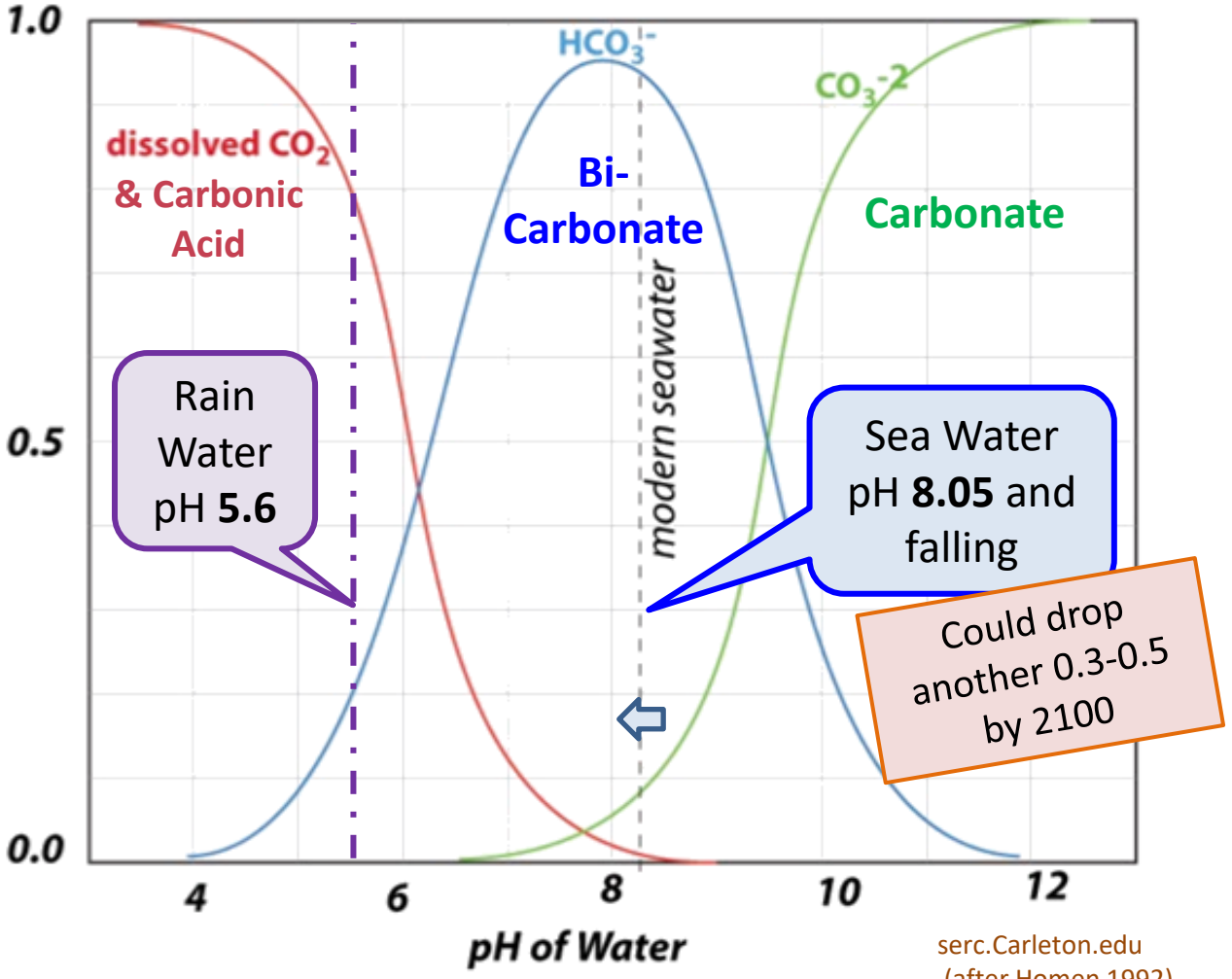
The Form CO_2 Takes in Water Depends on pH



… form depends on pH of water:

Low pH acidic

High pH basic



serc.Carleton.edu
(after Homen 1992)

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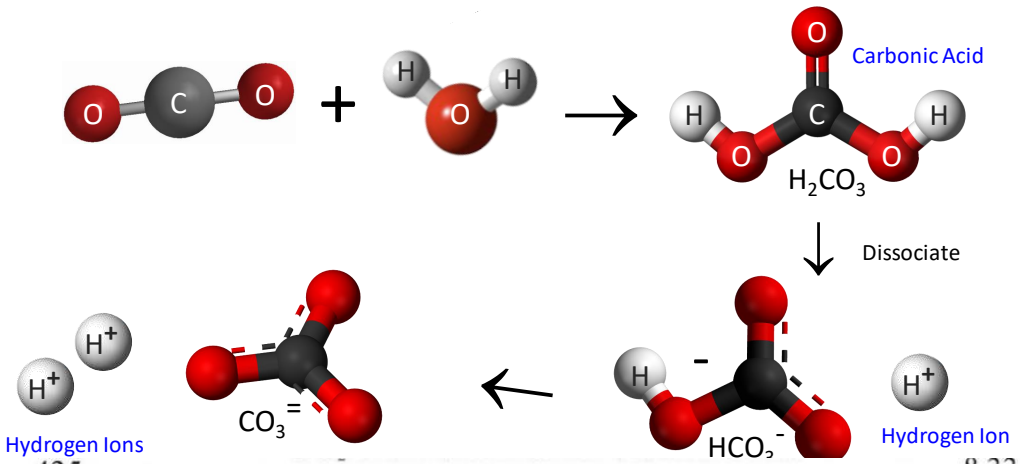

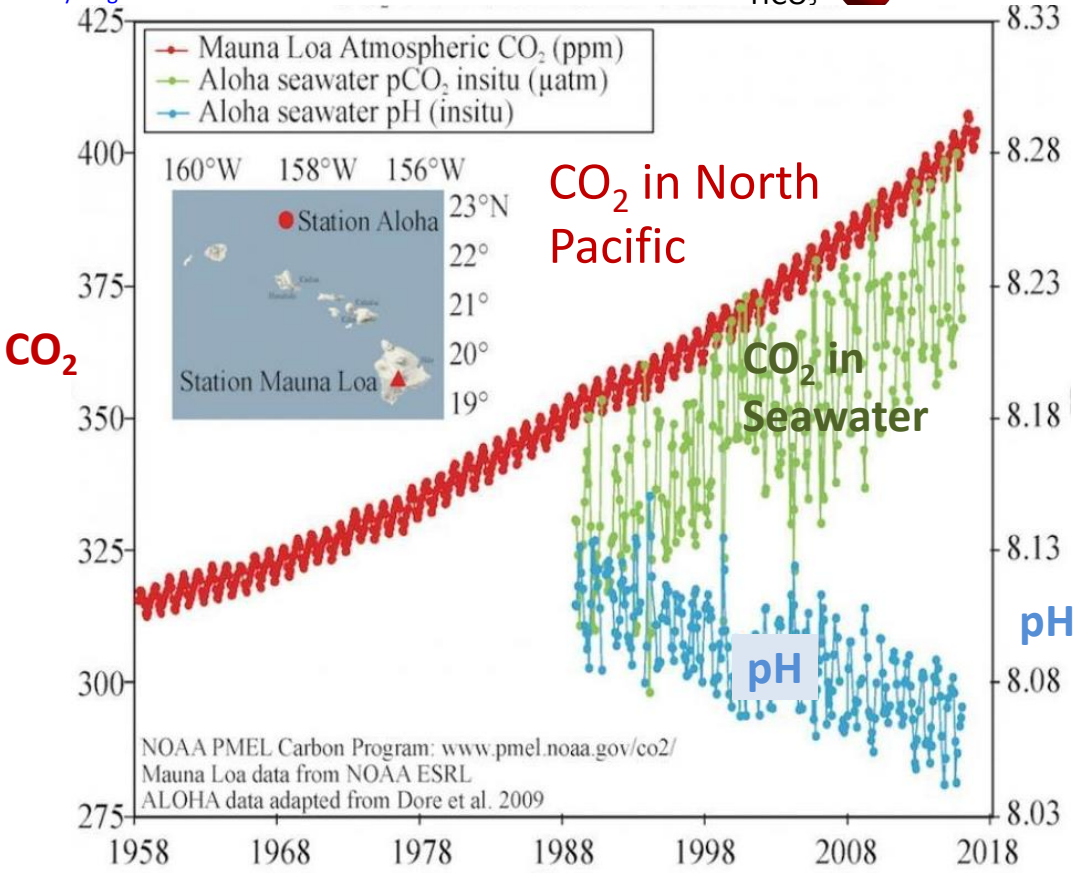

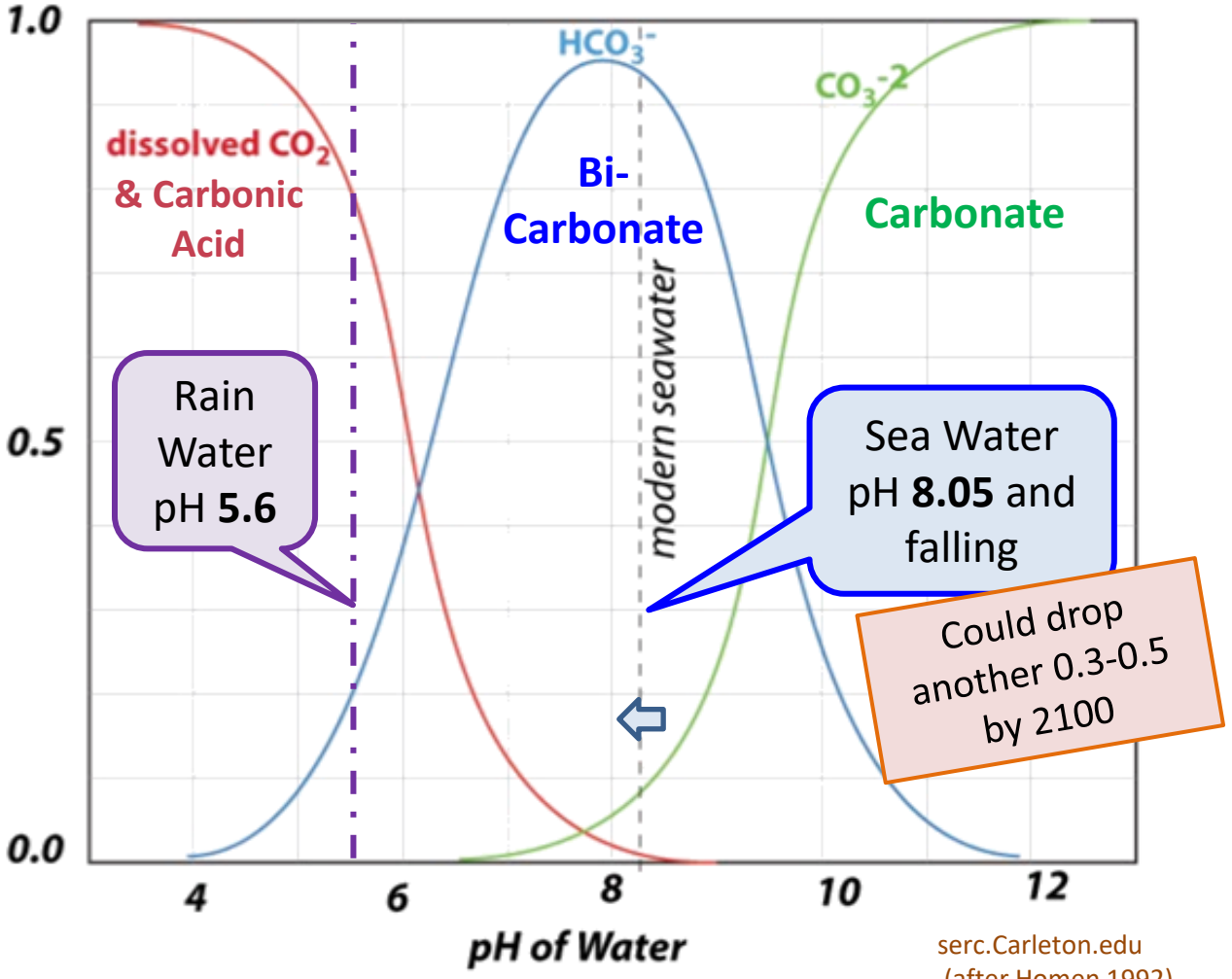

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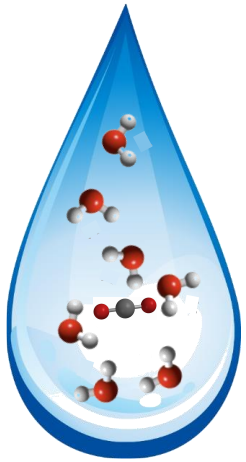
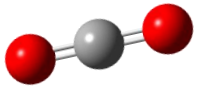
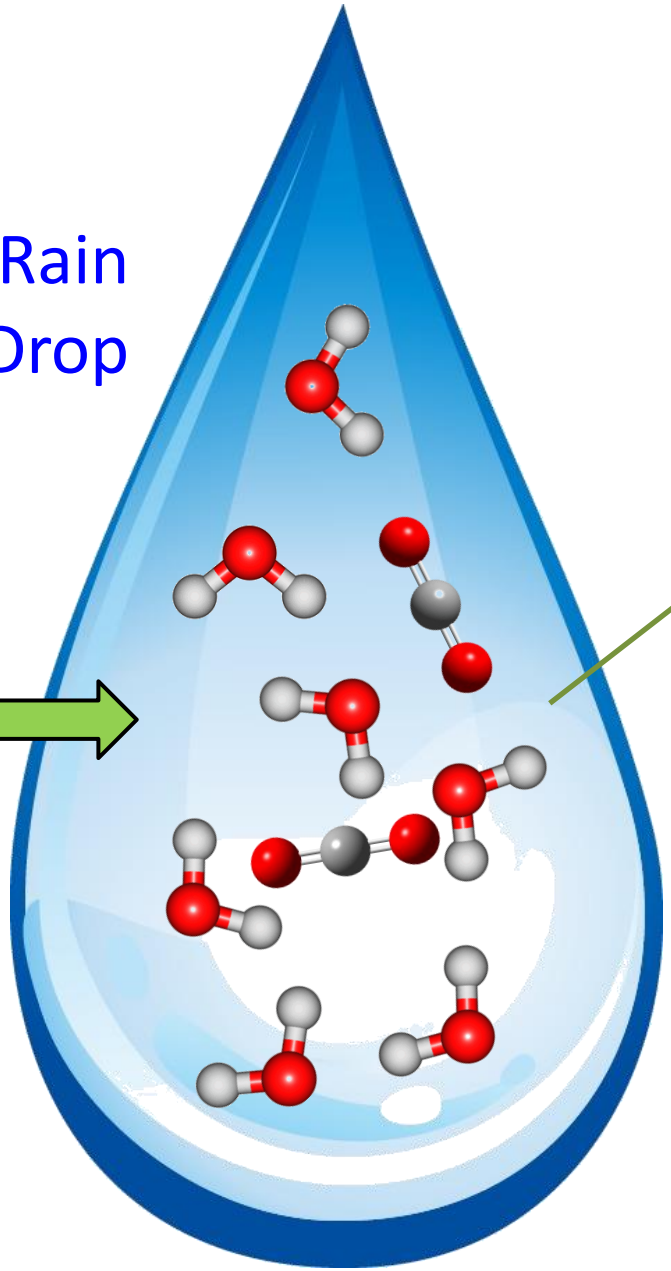
Weathering



Clean Air with 410 ppm CO_2



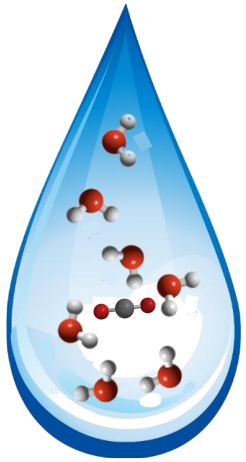
Rain Drop



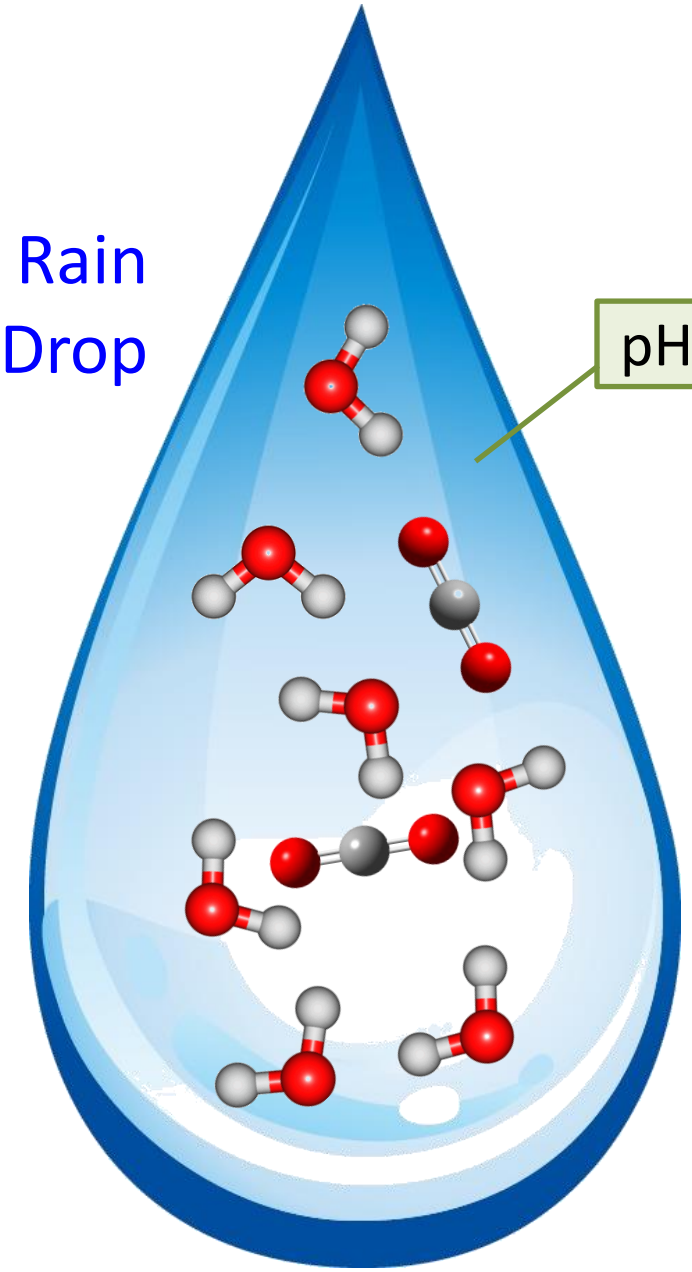
pH **5.6**

- pH 7 is neutral
- pH 5.6 weakly acidic
- Can dissolve limestone, e.g.

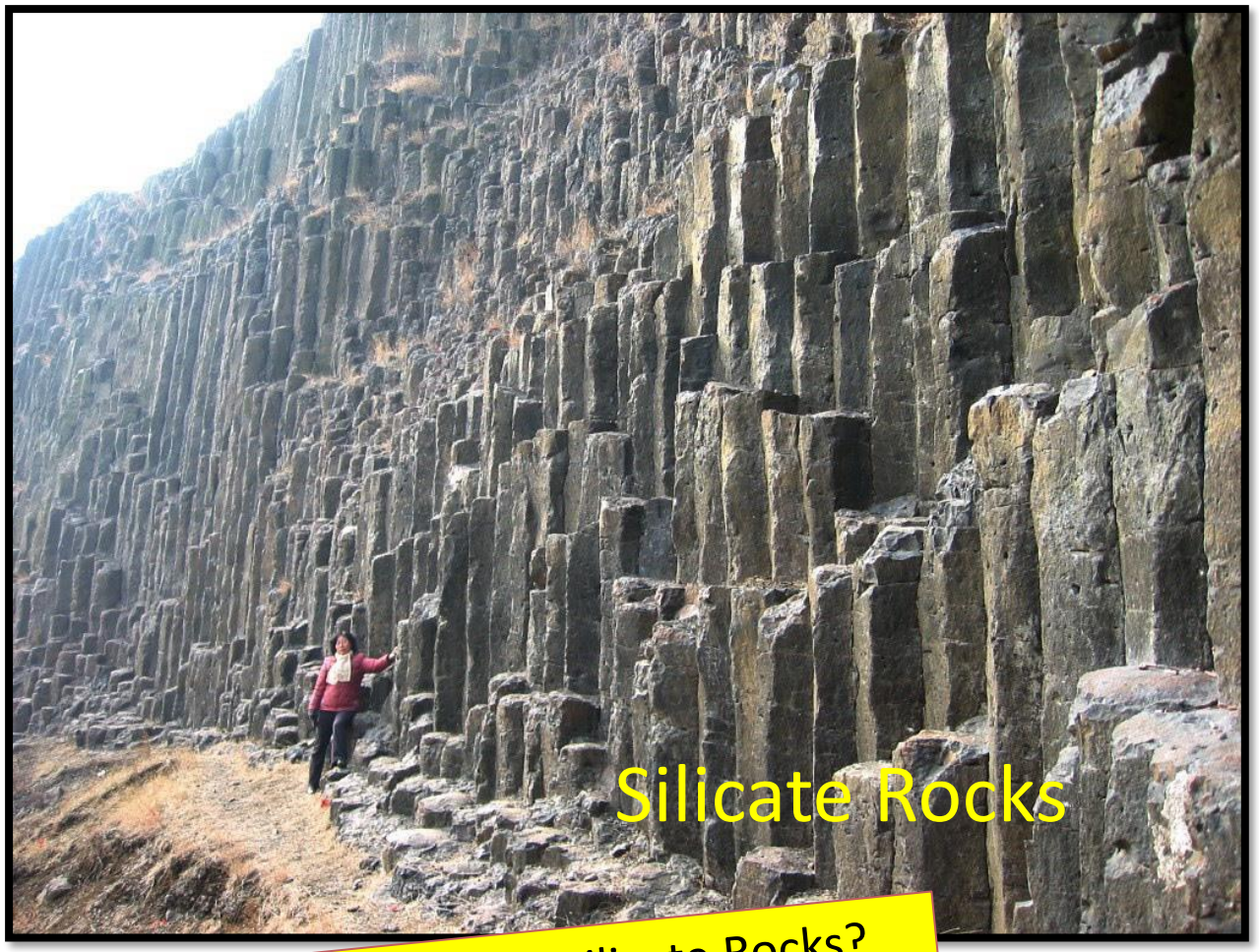
Weathering



Rain Drop

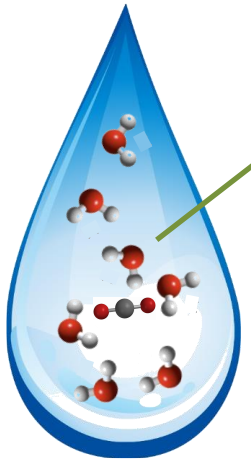


?



What will rain do to Silicate Rocks?

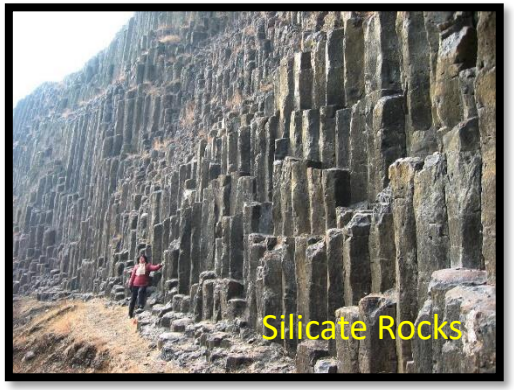
Weathering



~90% of Earth's Crust is Silicates

Simple Example:

Wollastonite
Calcium Silicate
$CaSiO_3$



$$2\,CO_2 + 3\,H_2O + CaSiO_3 \xrightarrow{\textit{Rivers to Ocean}} Ca^{++} + 2\,HCO_3^{=} + H_4SiO_4$$

Rain Water

Rock

Bicarbonate

Silicic Acid

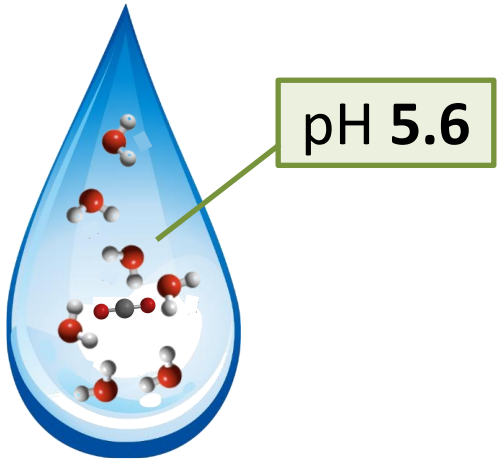
Makings of **$CaCO_3$ Shells** for Molluscs, Forams, Corals etc.

Diatoms

$2\,H_2O + \mathbf{SiO_2}$

Silica or Quartz

Weathering



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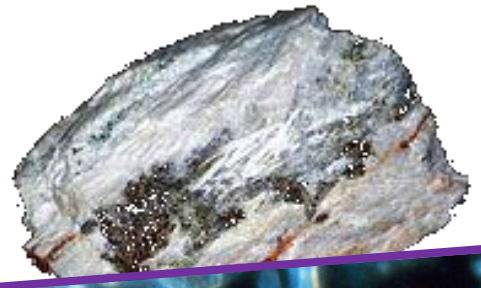
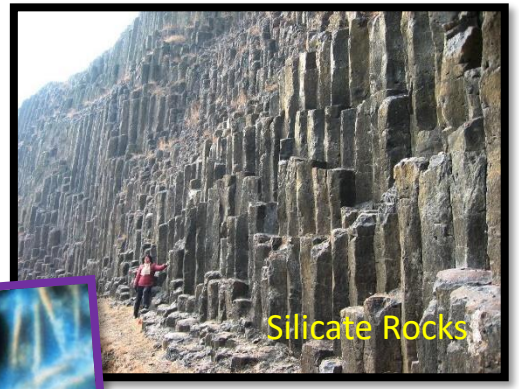




$2\ CO_2 + 3\ H_2O$ + ...nate → H_4SiO_4 + $CaCO_3$

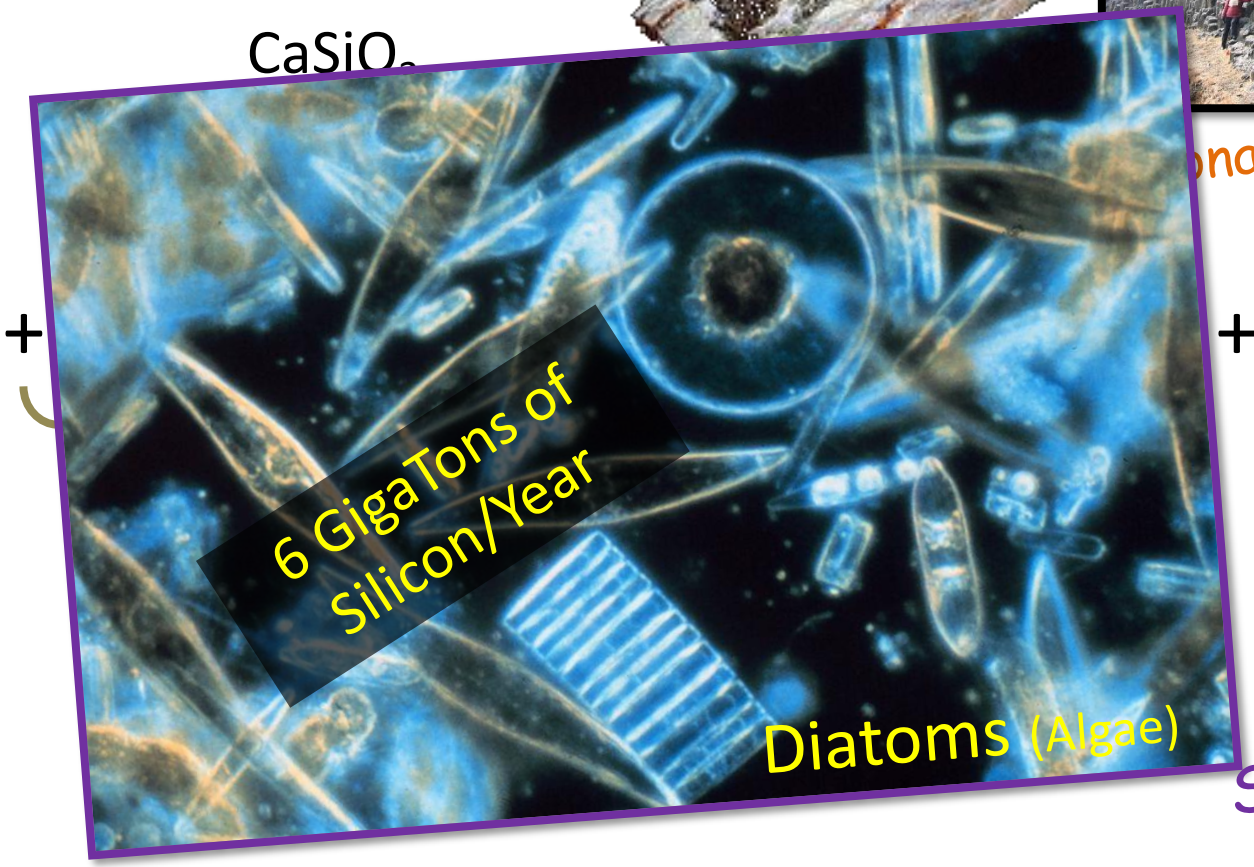
Rain Water

Silicic Acid

Diatoms

$2\ H_2O + \mathbf{SiO_2}$

Silica or Quartz



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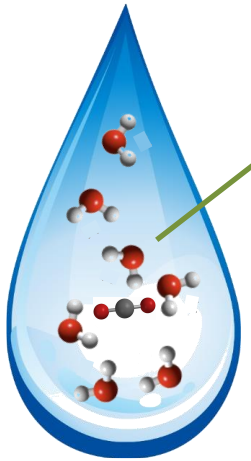
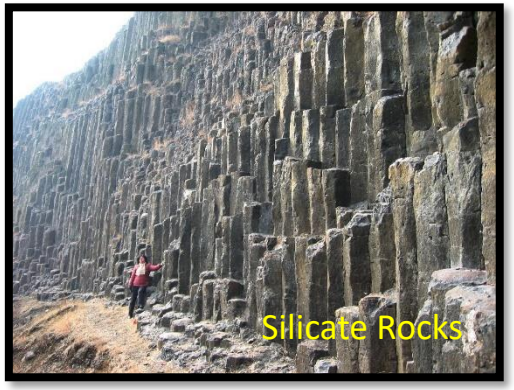


Removing CO_2 from the Air (and hence from all Surface Reservoirs)

Simple Example:
Wollastonite
Calcium Silicate
$CaSiO_3$



Rivers to Ocean

Bicarbonate

Silicic Acid

$$2\,CO_2 + 3\,H_2O + CaSiO_3 \rightarrow Ca^{++} + 2\,HCO_3^{=} + H_4SiO_4$$

Rain Water

Rock

Makings of $CaCO_3$

Diatoms

$$2\,H_2O + \mathbf{SiO_2}$$

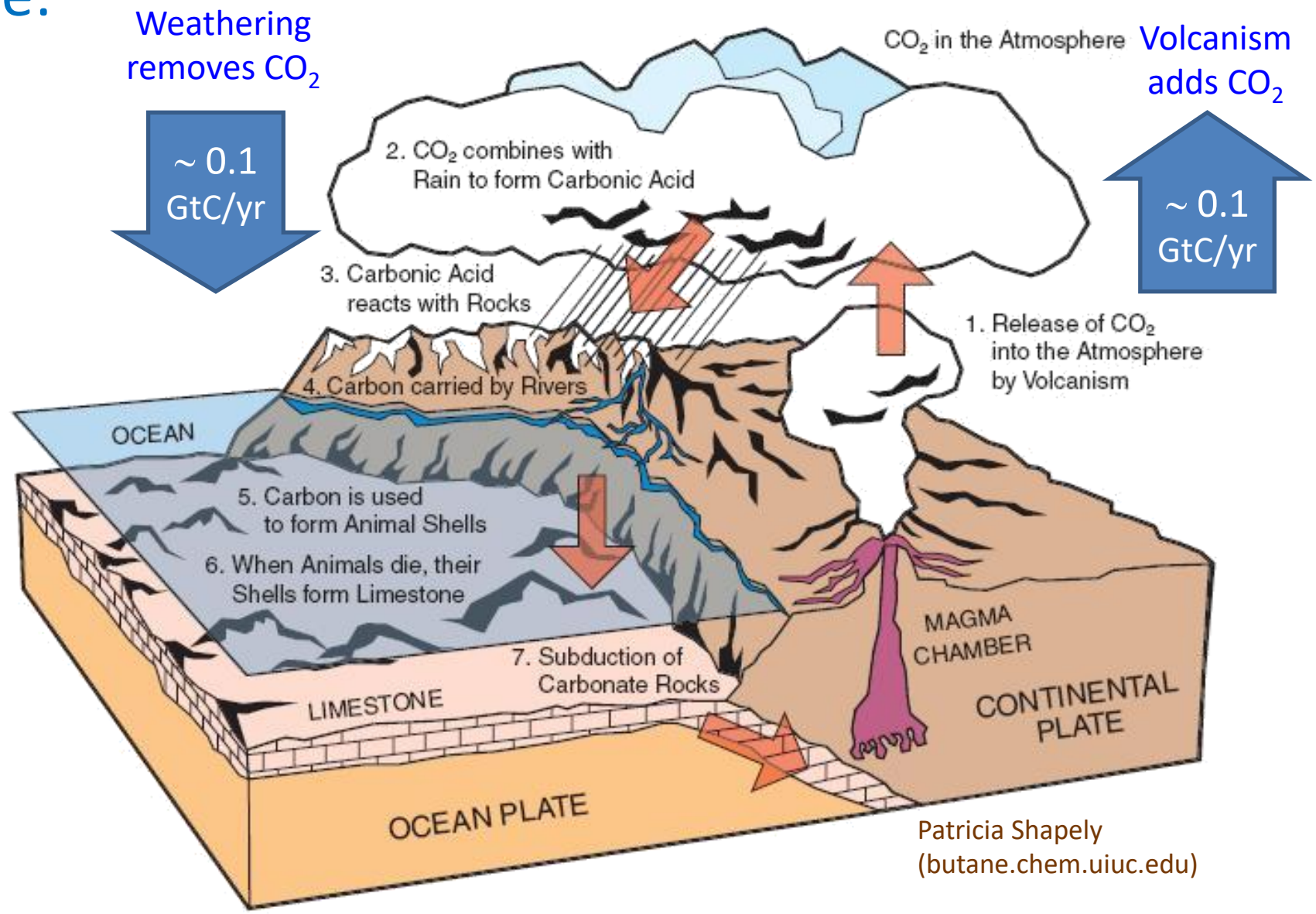
Silica or Quartz

Very slow reaction!
Global Total is only ~0.1 GtC/year

Long Term Carbon Cycle:

Our Carbon "Thermostat"

- Weathering reaction **removes** CO_2, sends $CaCO_3$ to oceans
- Ocean animals make **shells** of $CaCO_3$ which fall to bottom
- **Limestone subducts** under continents via plate tectonics, into the molten mantle
- Carbonates break down in mantle and **release CO_2**
- **CO_2 escapes** via volcanism to atmosphere and ocean



Patricia Shapely
(butane.chem.uiuc.edu)

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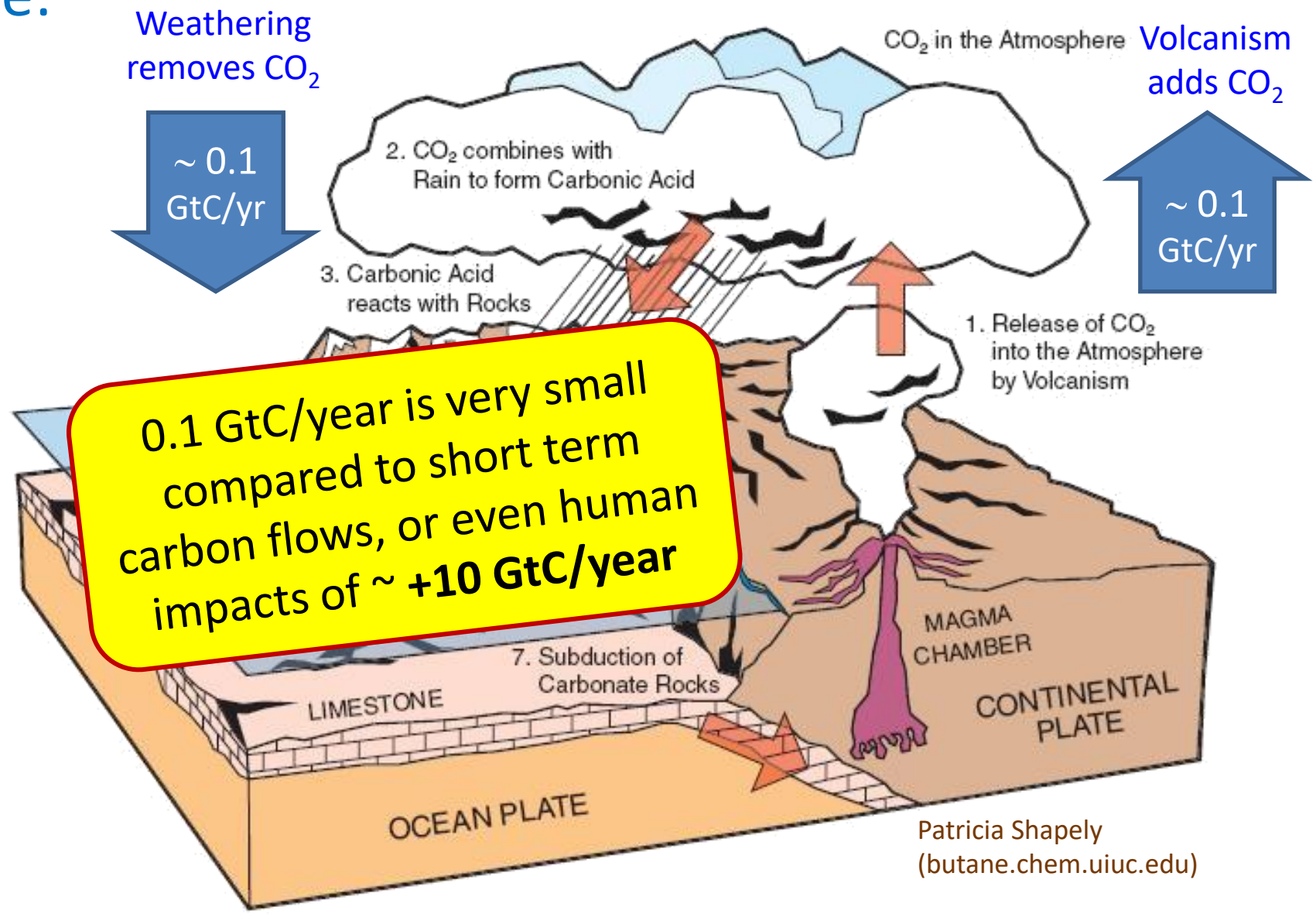

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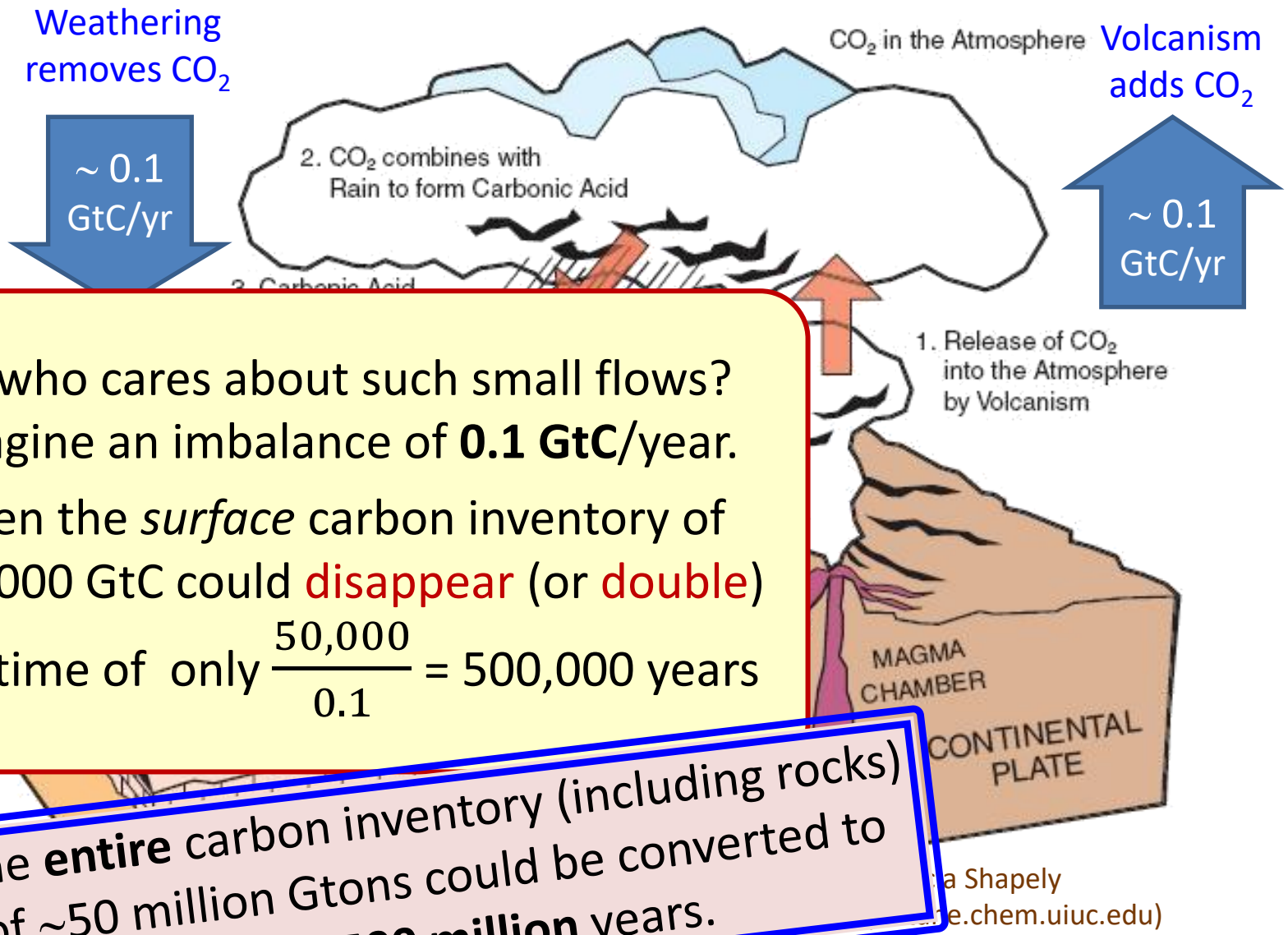

So who cares about such small flows? Imagine an imbalance of **0.1 GtC**/year.

Then the *surface* carbon inventory of ~50,000 GtC could disappear (or double)

in a time of only $\frac{50{,}000}{0.1}$ = 500,000 years

The **entire** carbon inventory (including rocks) of ~50 million Gtons could be converted to CO_2 in ~**500 million** years.

a Shapely
e.chem.uiuc.edu)

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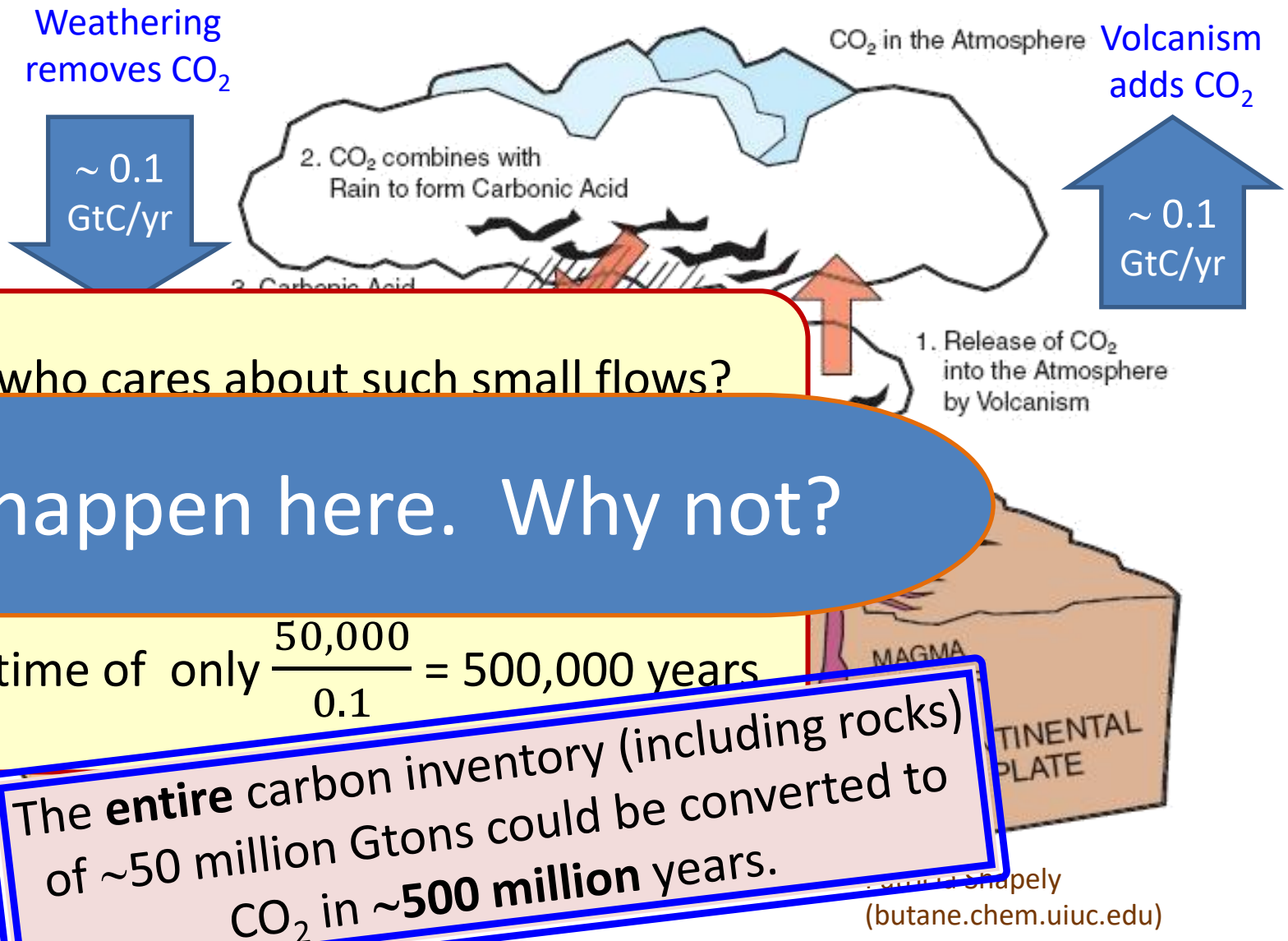

So who cares about such small flows?

It didn't happen here. Why not?

in a time of only $\frac{50{,}000}{0.1}$ = 500,000 years

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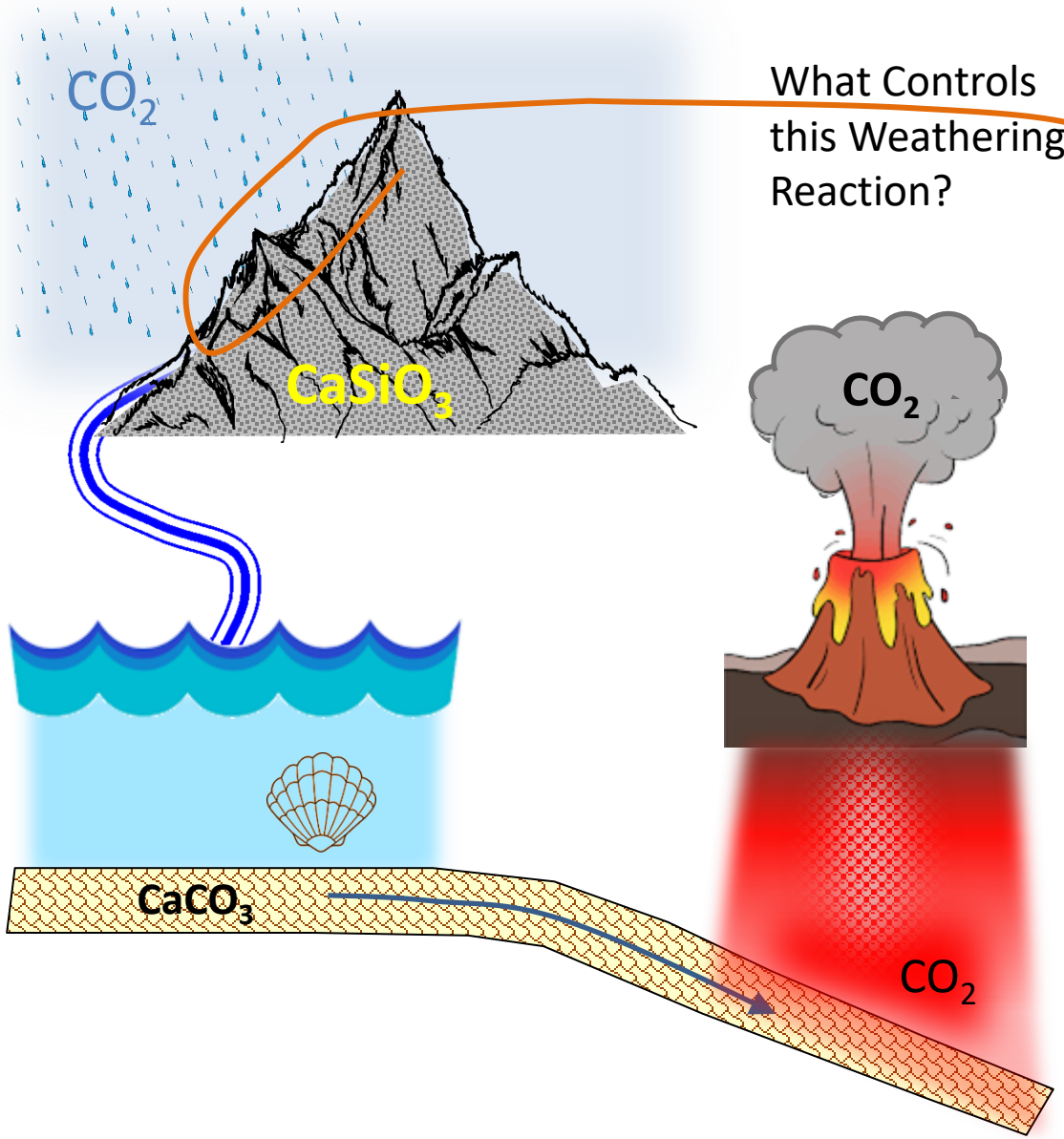
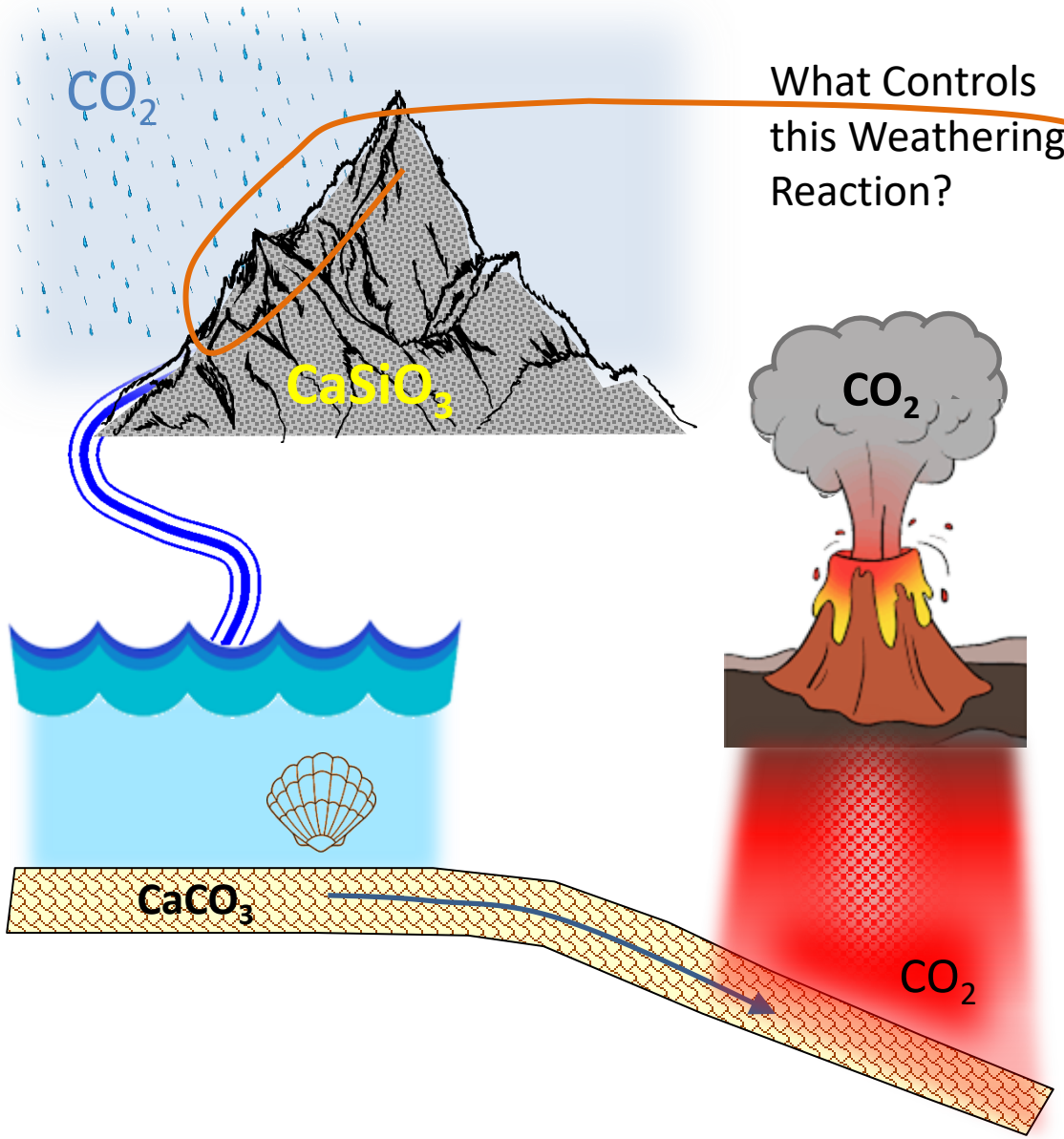
Regulation of Long Term Carbon Cycle



- Amount of CO_2
- Temperature
- Amount of H_2O
- Fresh Exposed Rock

Regulation of Long Term Carbon Cycle



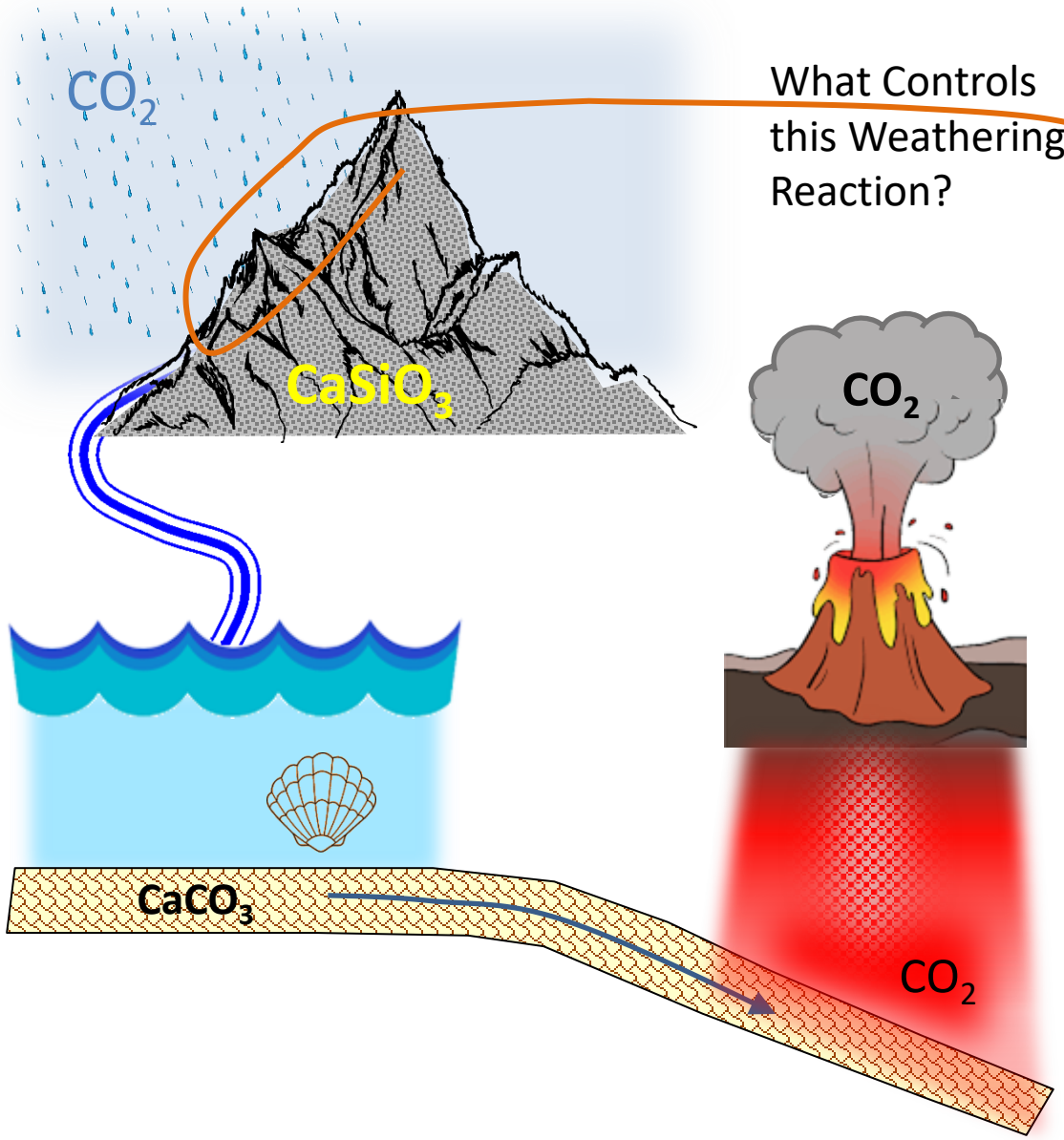
What Controls this Weathering Reaction?

- Amount of CO_2 ↑
- Temperature ↑
- Amount of H_2O ↑
- Fresh Exposed Rock

If CO_2 in atmosphere goes up for *any reason*…..

- Temperature Increases
- Precipitation Increases

Regulation of Long Term Carbon Cycle



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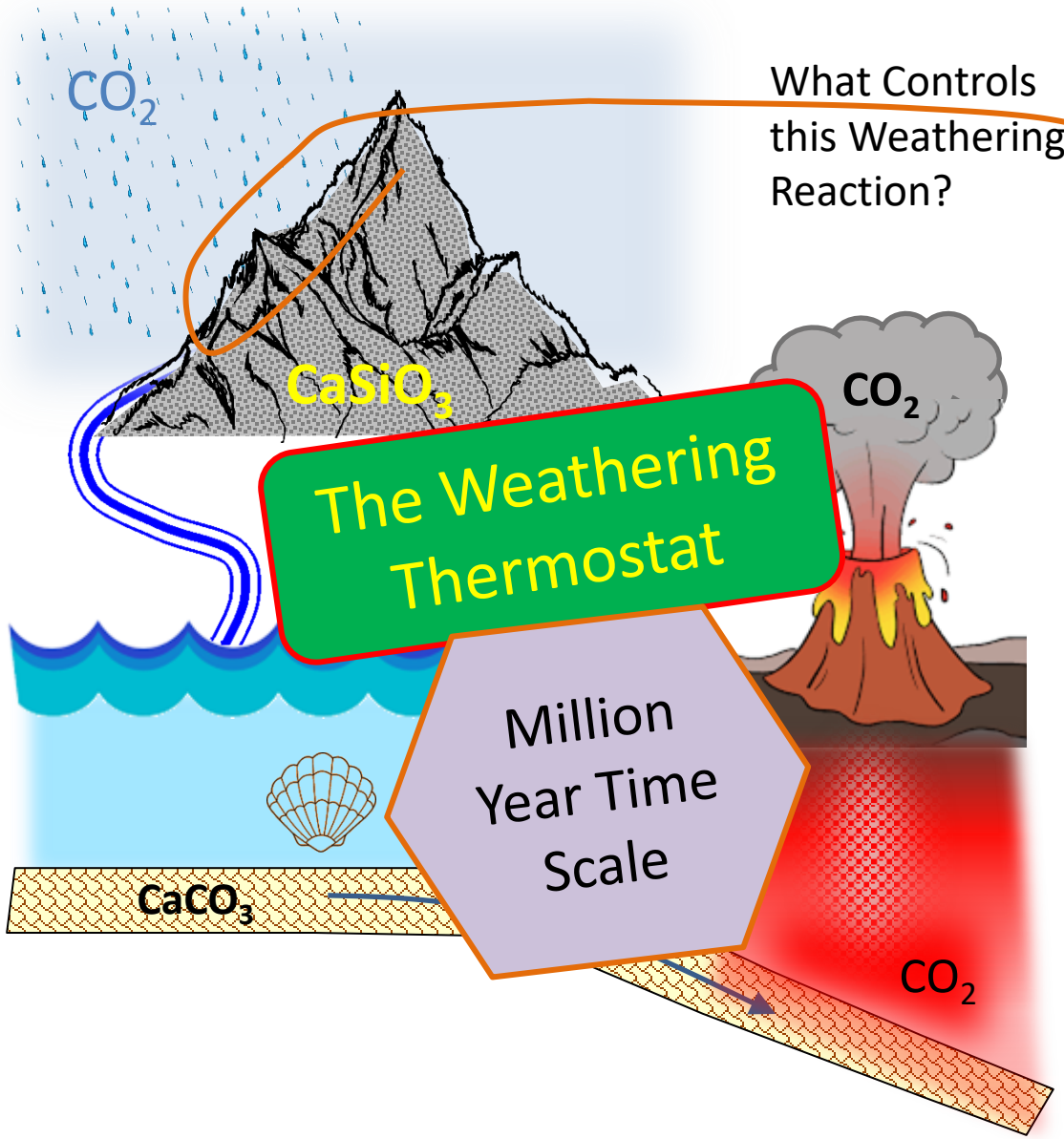
So

if CO_2 in atmosphere goes **up** ↑,

- the Weathering removal reaction *speeds up*
- … and CO_2 goes **down** ↓

Classic Negative Feedback

Regulation of Long Term Carbon Cycle



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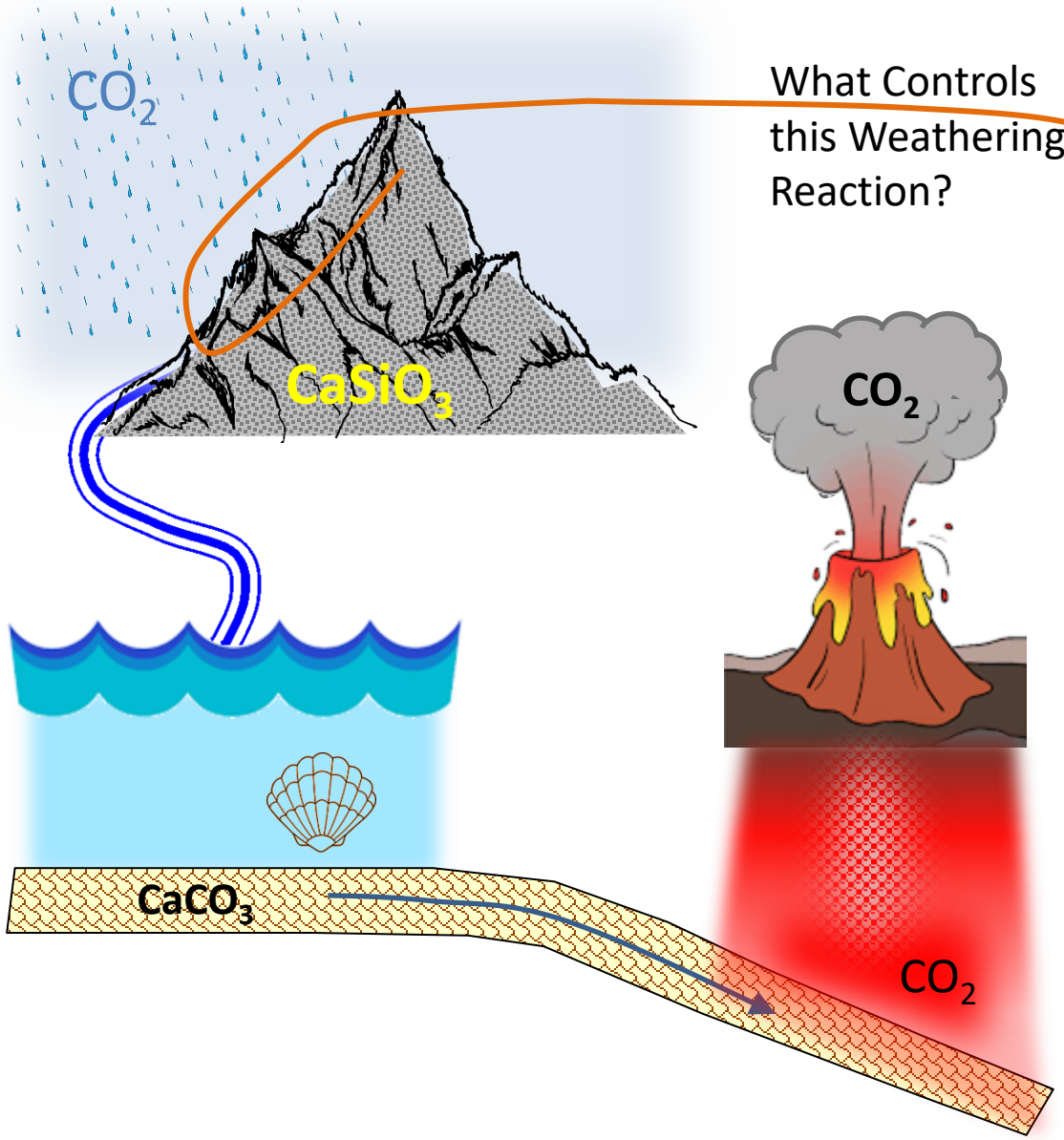


What Controls this Weathering Reaction?

- Amount of CO_2
- Temperature
- Amount of H_2O
- Fresh Exposed Rock

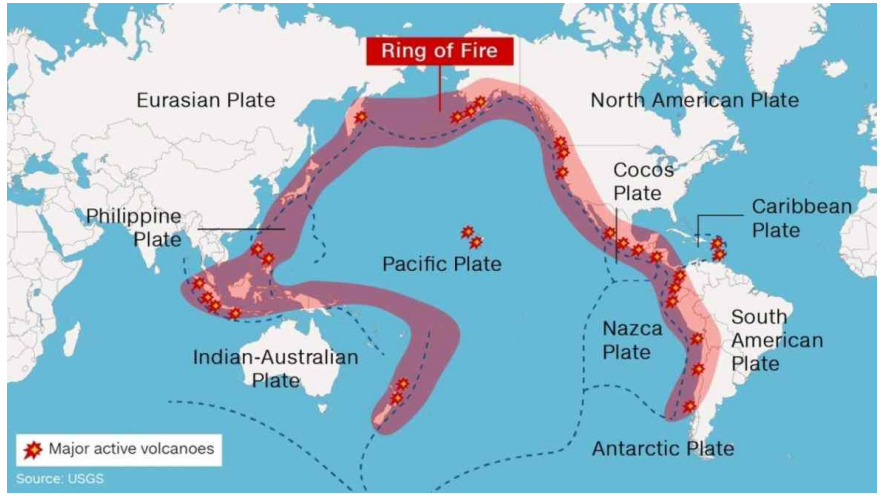
Negative Feedback

- Relatively *new* tropical mountain ranges play key role
- These occur along volcanic arcs
- Volcanic arcs occur intermittently as continents drift

Tropical Mountain Building Eras may Trigger Glaciation Periods

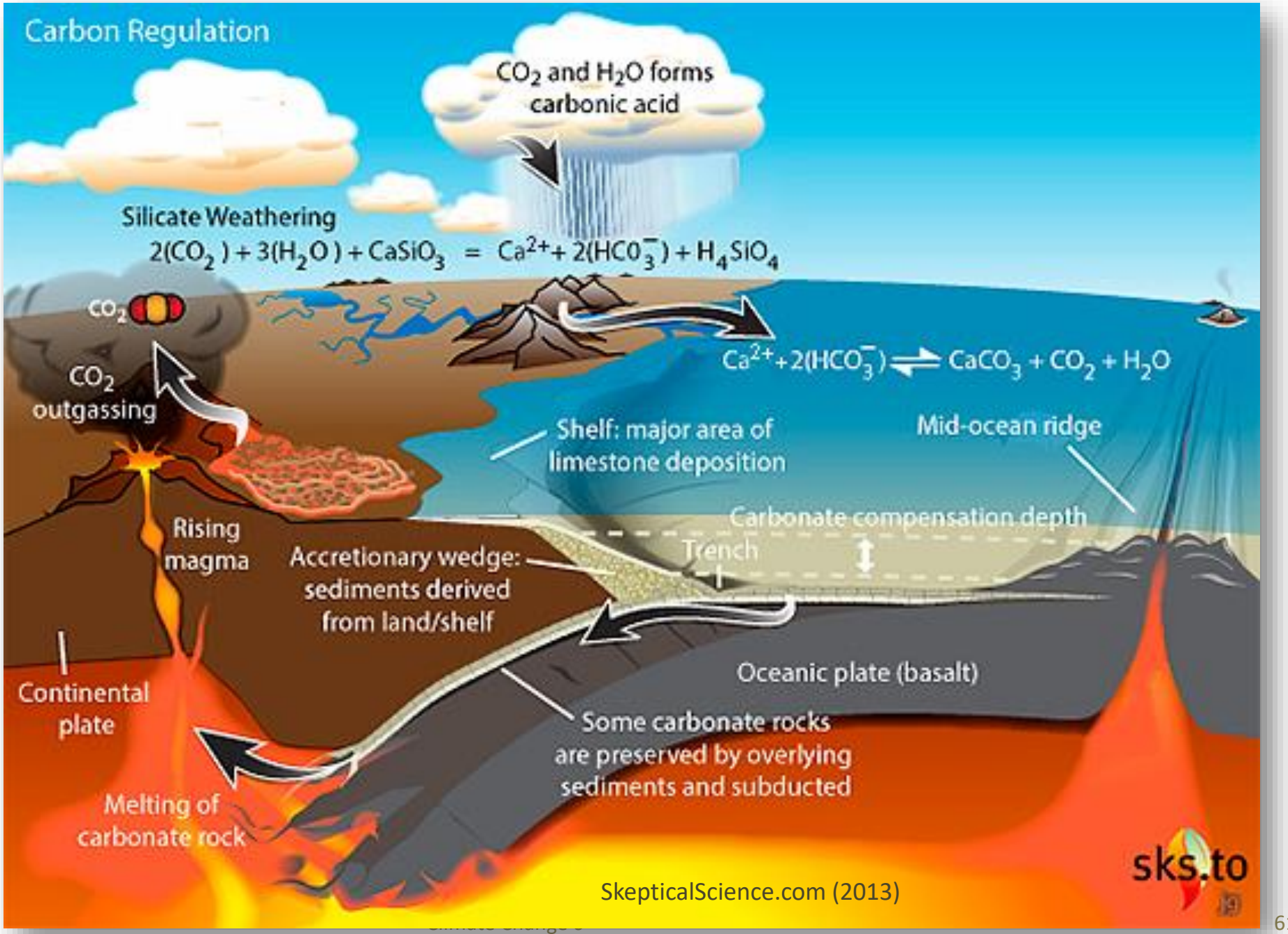
(like the one we are in)

Francis Macdonald
(UC Santa Barbara 2018)



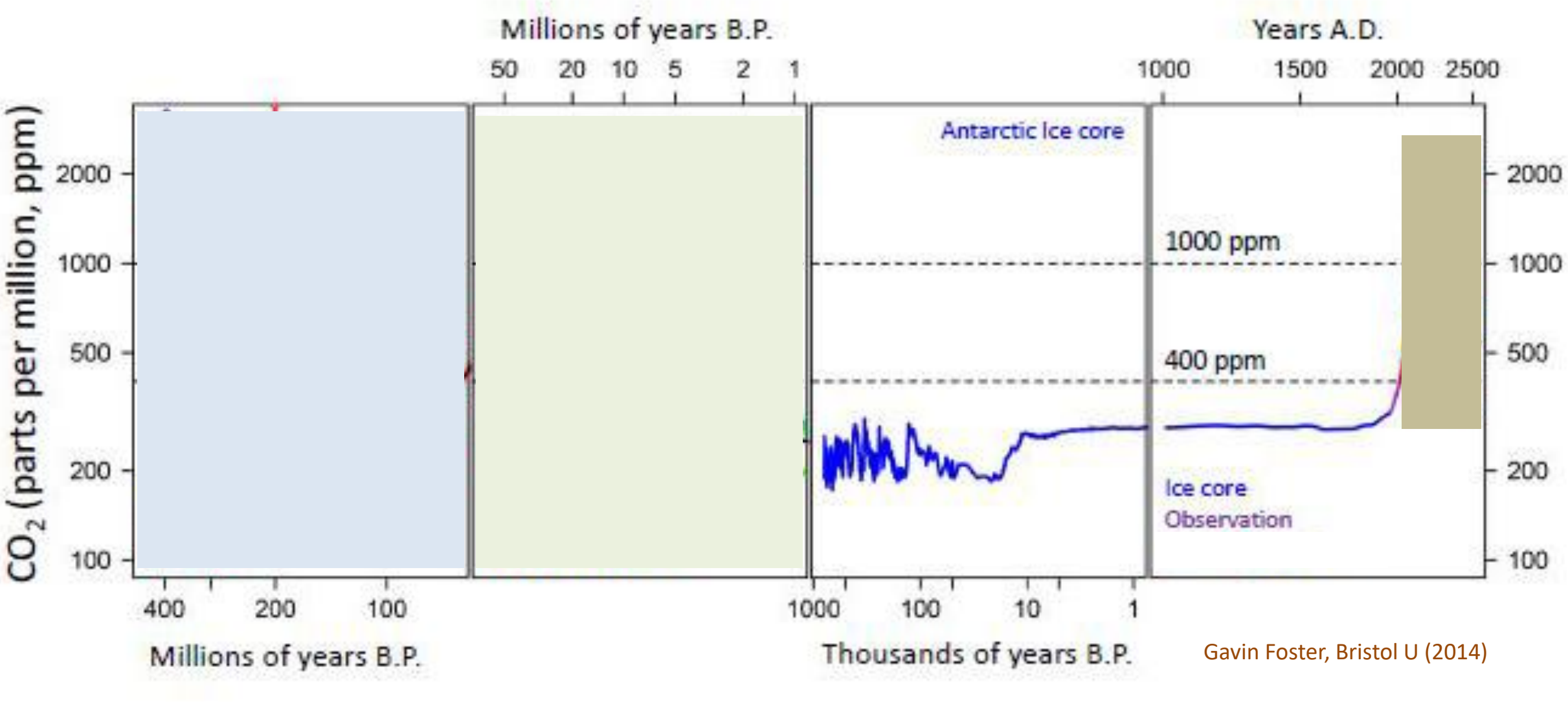
Group claims high correlation between *tropical* volcanic mountain building periods and glacial ages over last 500 Million years.

Yet Another Graphic Showing Long-term Carbon Cycle



SkepticalScience.com (2013)

Mashup of Paleo-CO_2 Estimates



Gavin Foster, Bristol U (2014)

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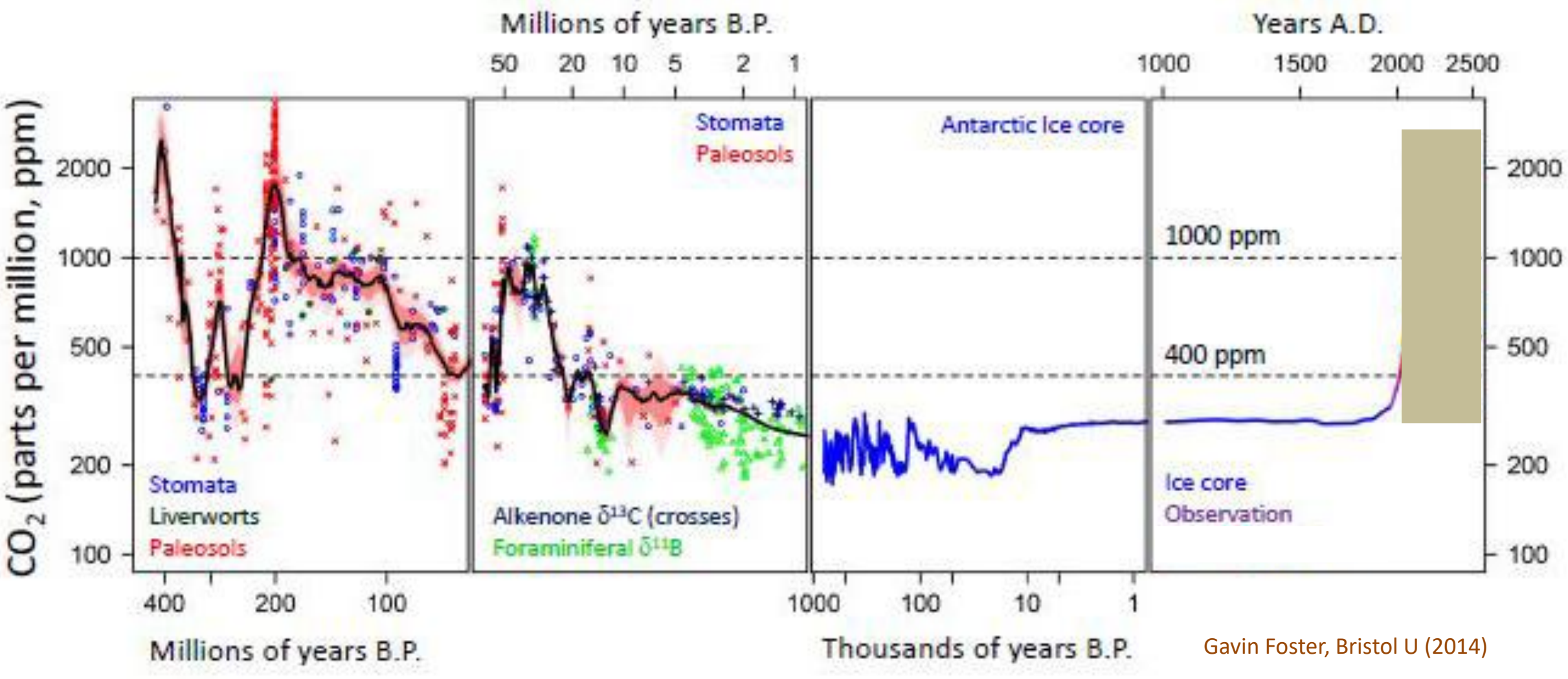

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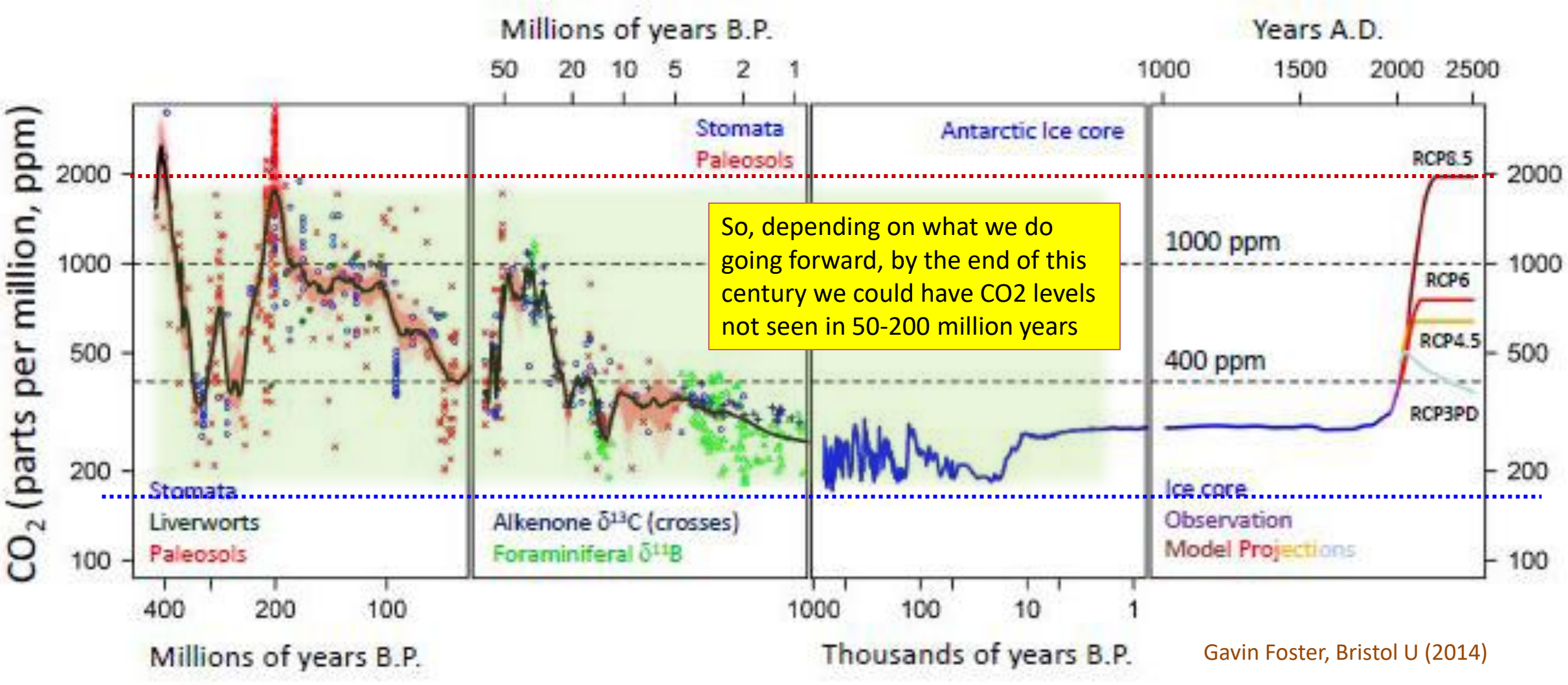
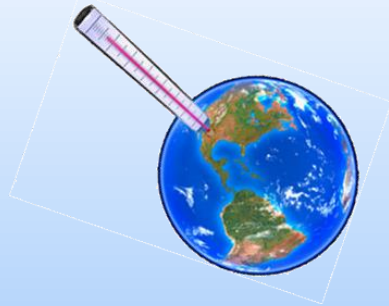
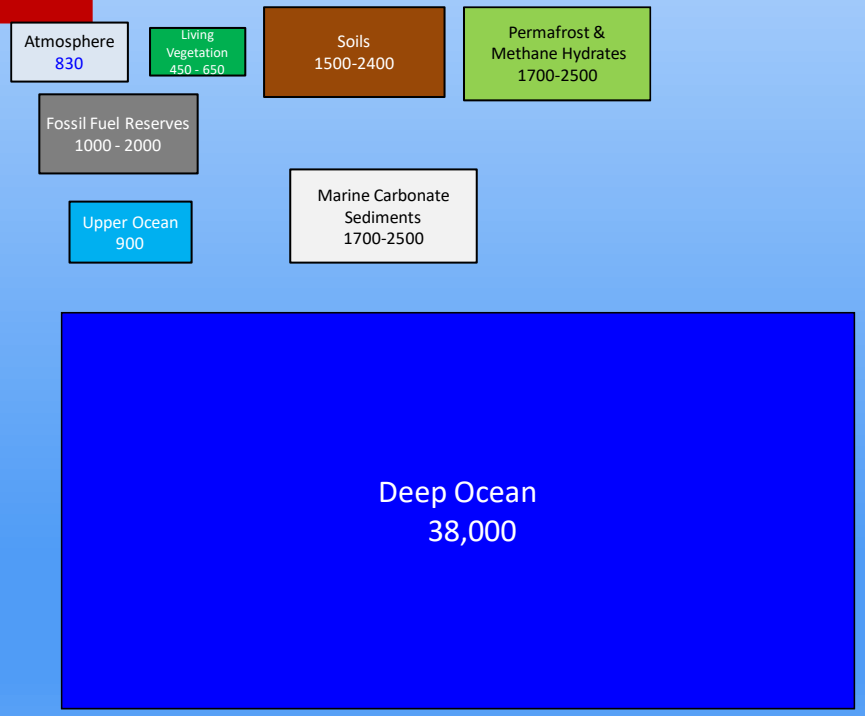
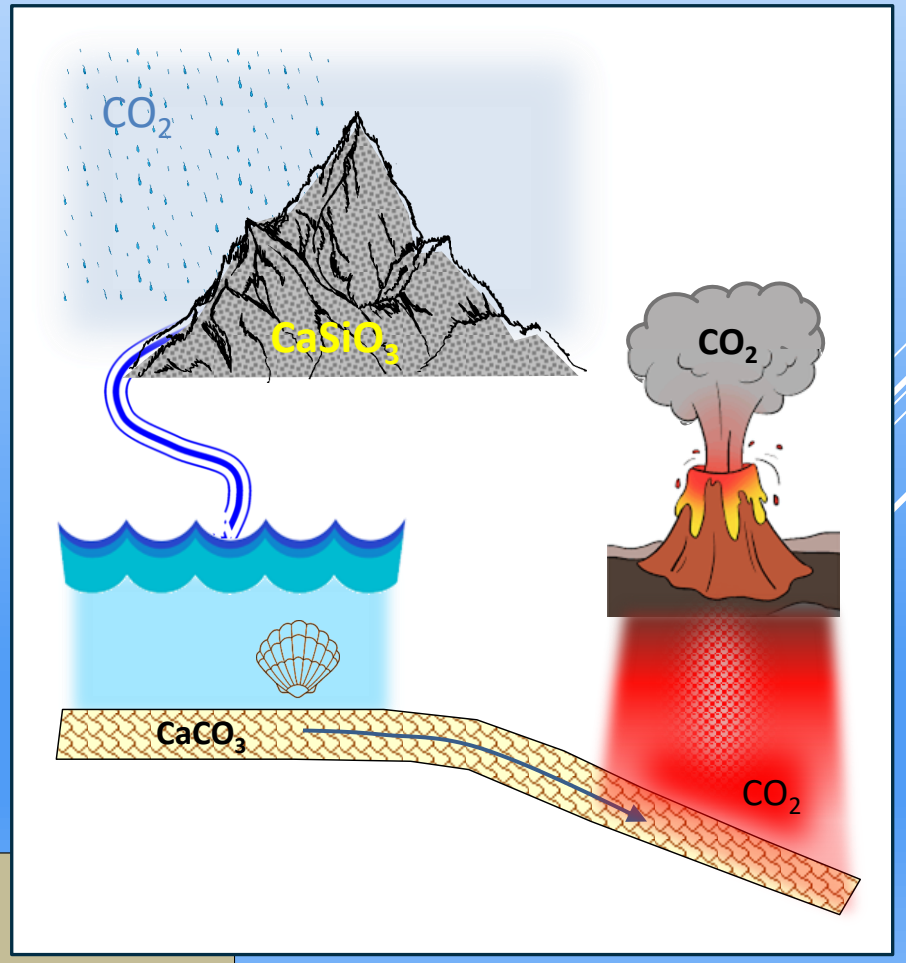


Gavin Foster, Bristol U (2014)

Questions about CO_2 and the Long Term Carbon Cycle?

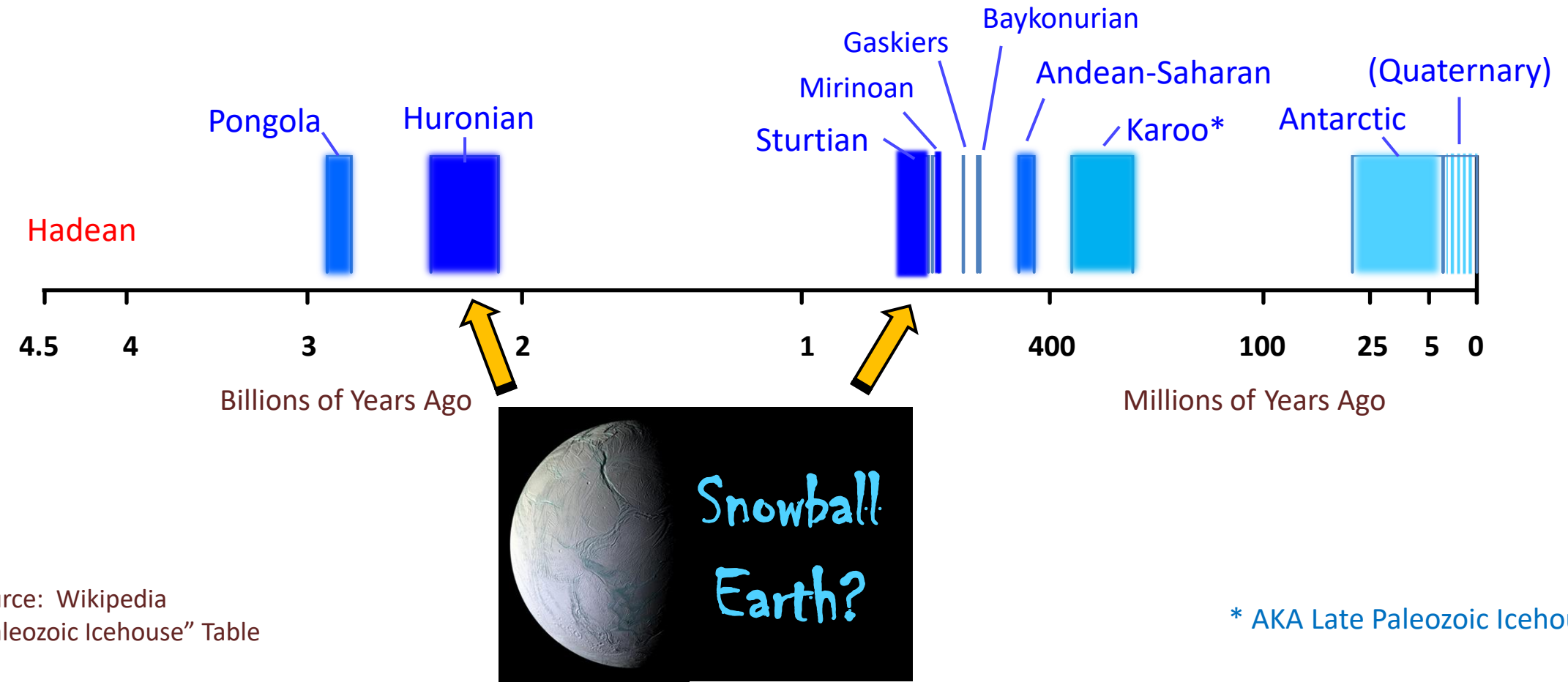






Carbon in Rocks
50,000,000

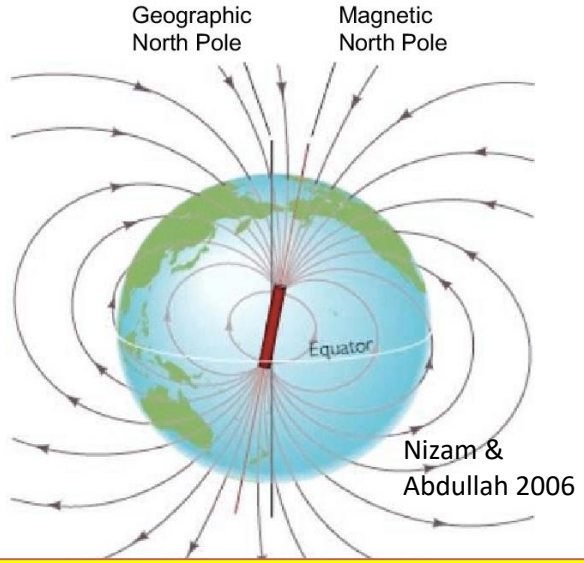
Rough Timeline of Past Glaciations



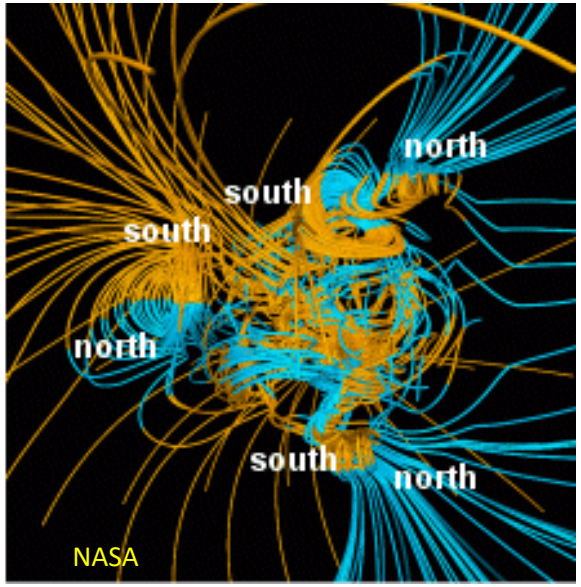
Data source: Wikipedia
"Late Paleozoic Icehouse" Table

* AKA Late Paleozoic Icehouse

Figuring Out Where a Glaciated Rock *Was*… Way Back Then

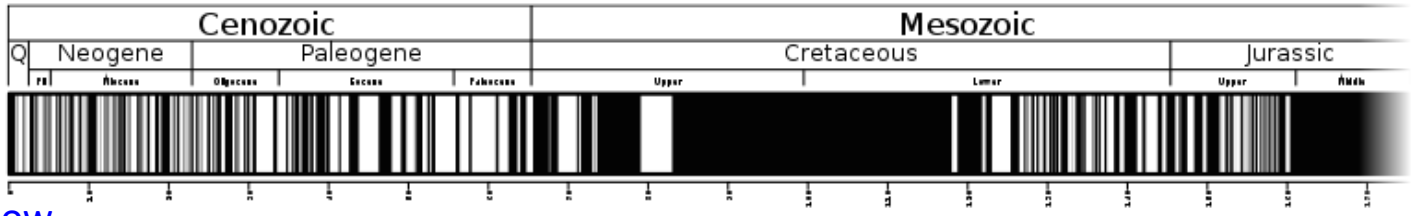


Nizam & Abdullah 2006



Modeled Magnetic Field During a Reversal

When geologists find a glaciated rock formation, they have to figure out where it was at the time…

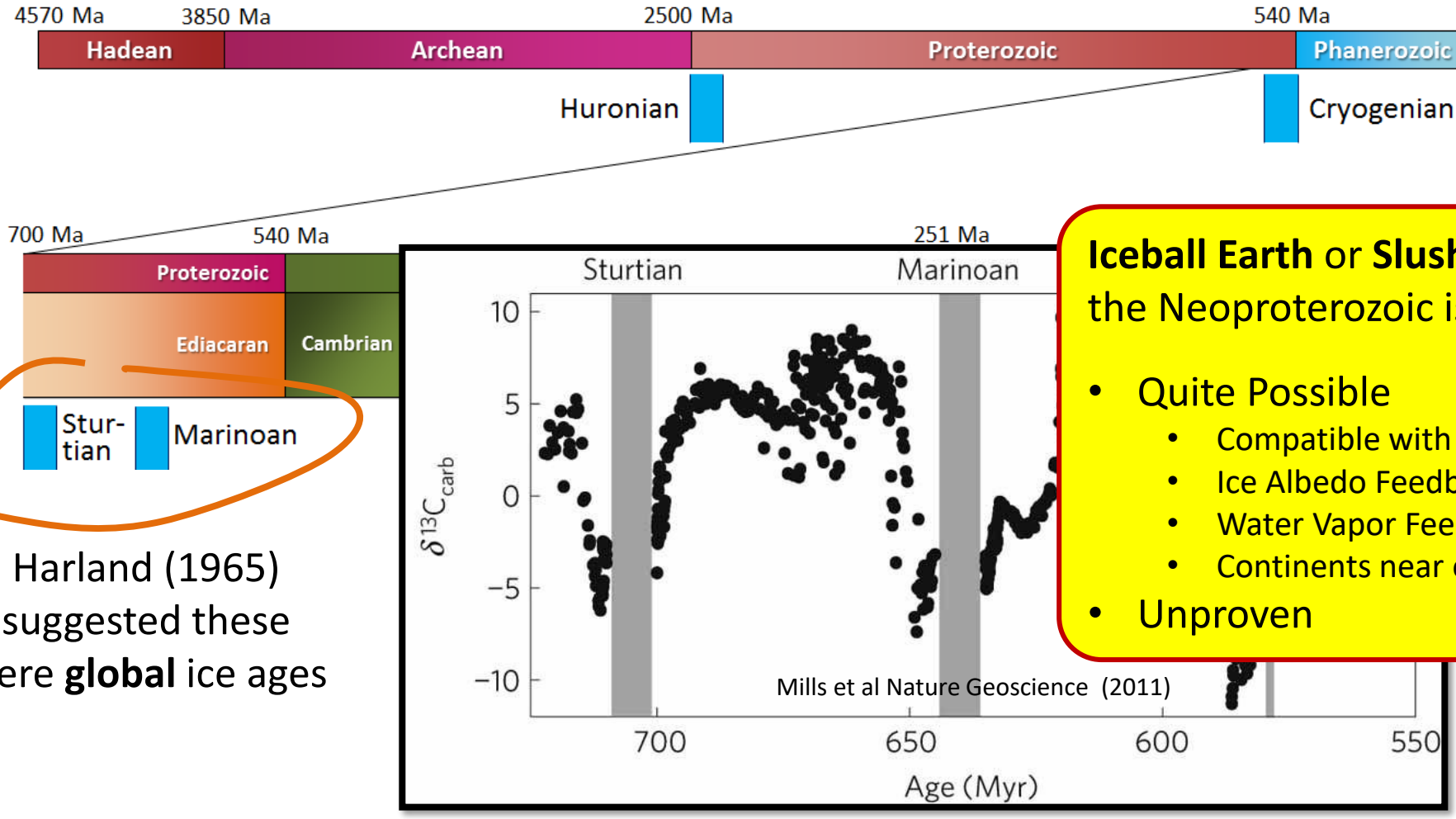


Hundreds of Random Flips

Wikimedia (from USGS)

The embedded magnetic field is one way – but it is tricky due to the many field reversals over time…

There Have Been Several Glaciated Periods



Harland (1965) suggested these were **global** ice ages

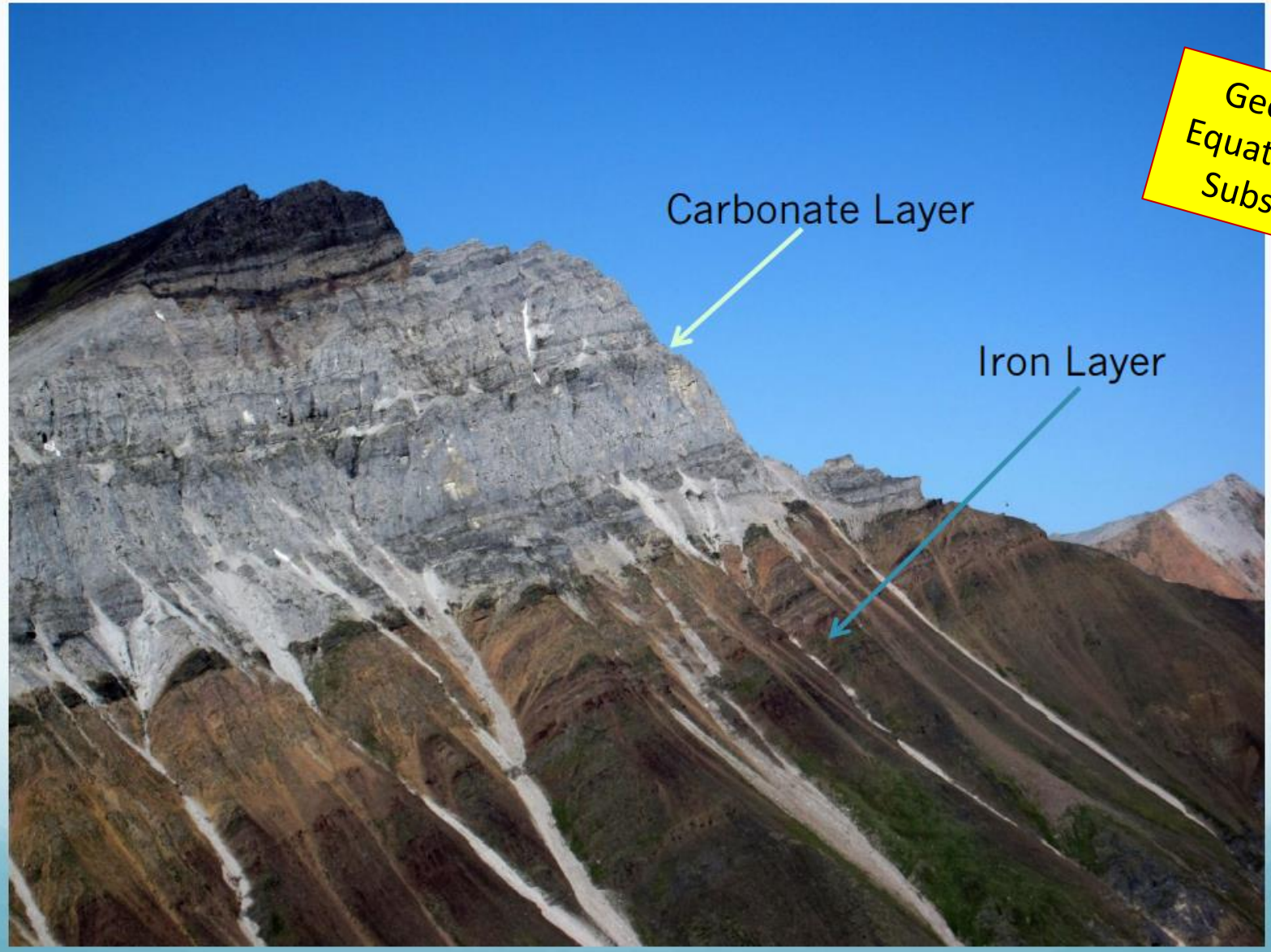
Iceball Earth or **Slushball Earth** in the Neoproterozoic is

- Quite Possible
  - Compatible with Models
  - Ice Albedo Feedback
  - Water Vapor Feedback
  - Continents near equator
- Unproven

Snowball Earth Scenario according to Dennis Hartmann (U Washington)

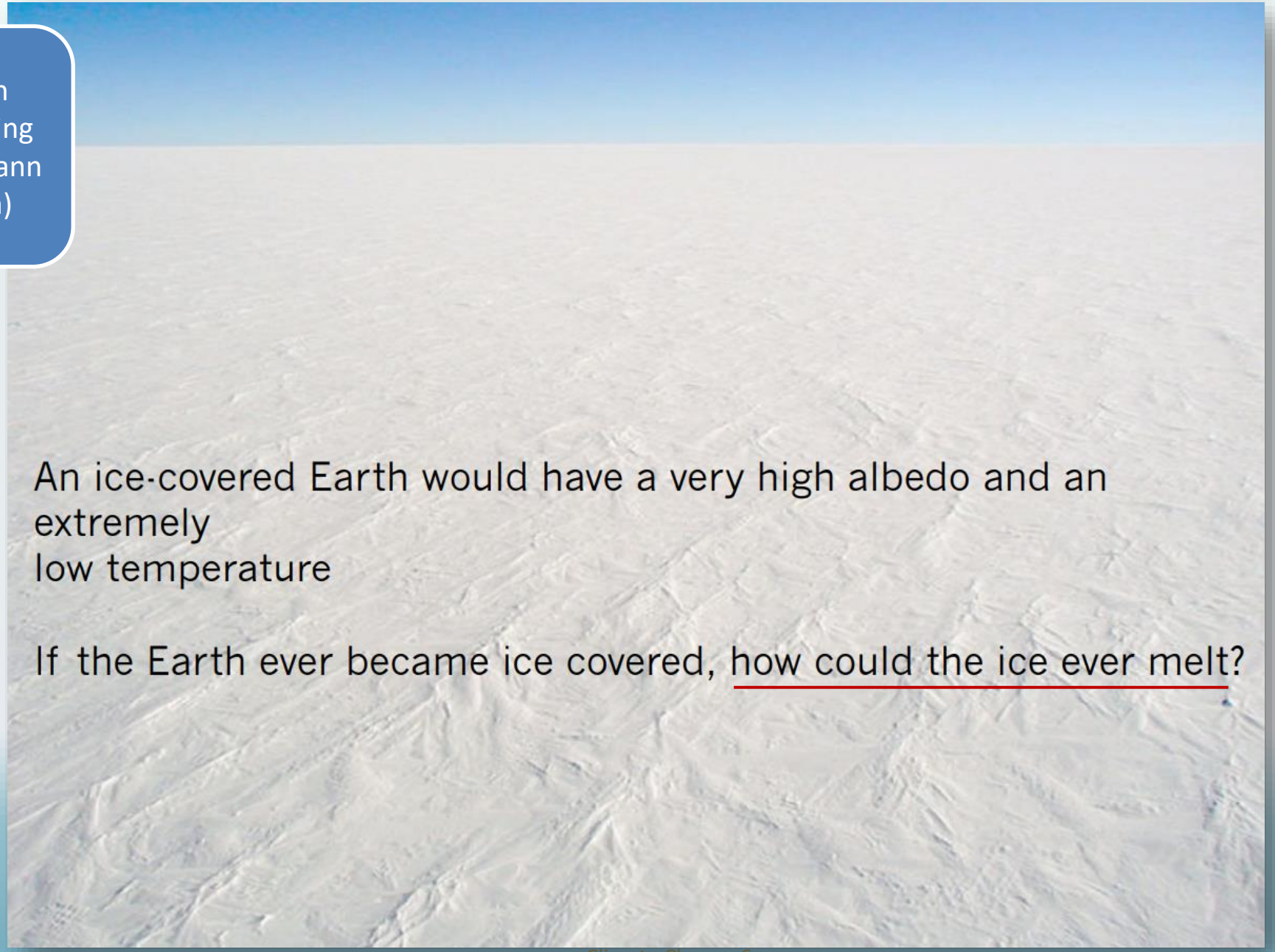
Rocks in Yukon that were once at the equator at sea level and covered by ice.

Snowball Earth Scenario according to Dennis Hartmann (U Washington)

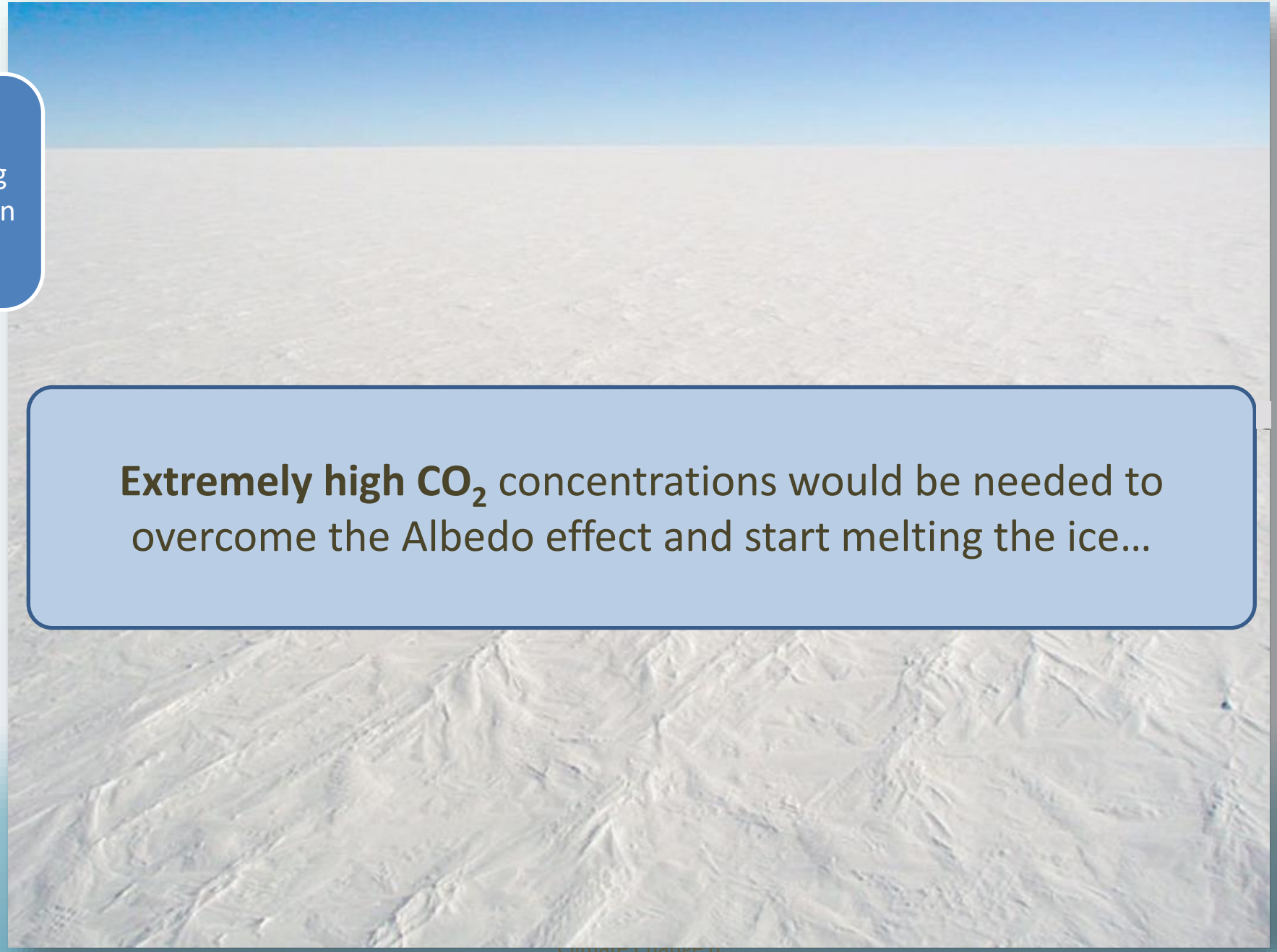


Geologic evidence for Equatorial Glaciation and Subsequent High CO_2

Snowball Earth Scenario according to Dennis Hartmann (U Washington)



Snowball Earth Scenario according to Dennis Hartmann (U Washington)



Extremely high CO_2 concentrations would be needed to overcome the Albedo effect and start melting the ice…

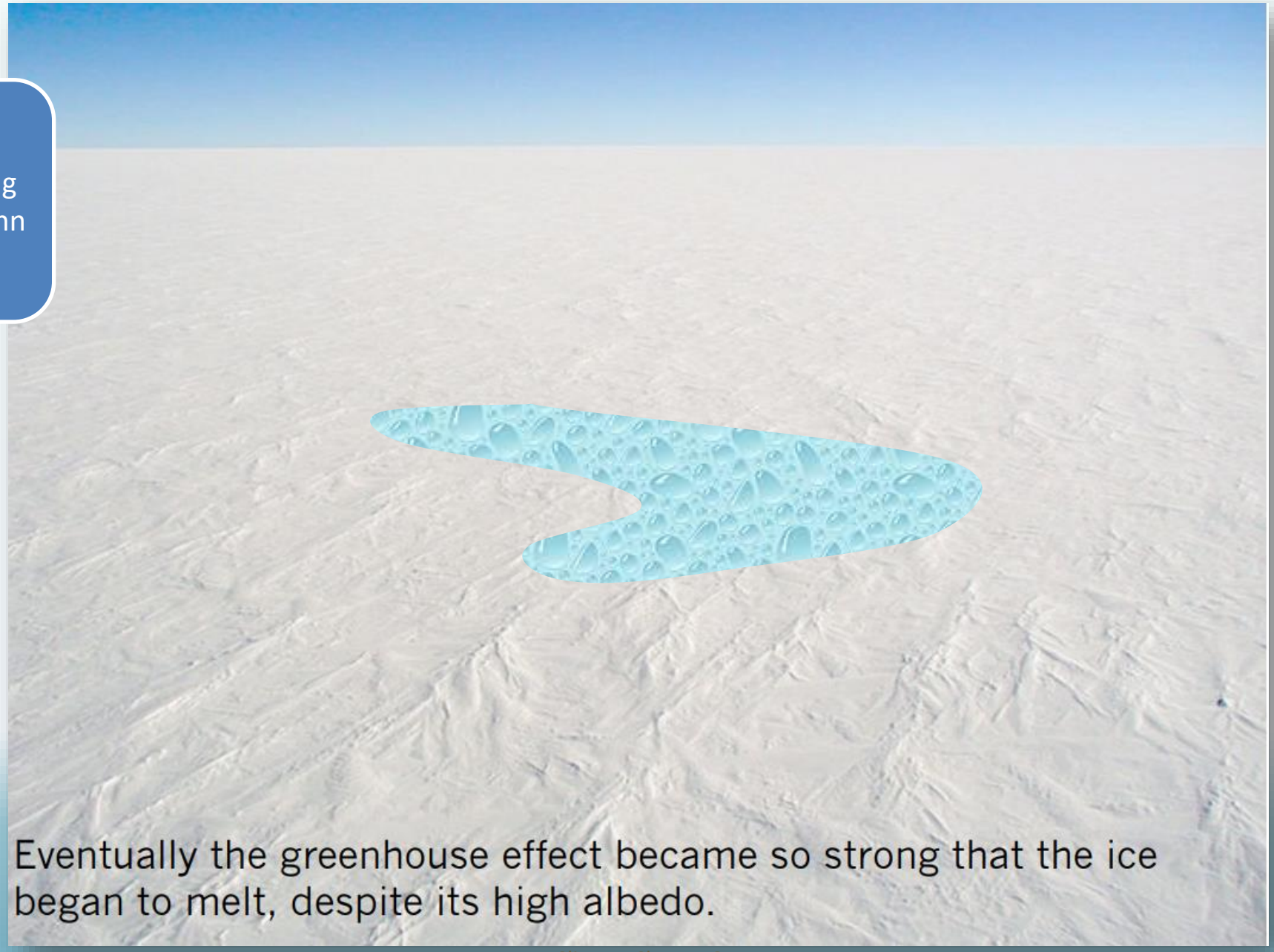
Snowball Earth Scenario according to Dennis Hartmann (U Washington)

During Snowball Earth, volcanic activity injected CO2 into the atmosphere

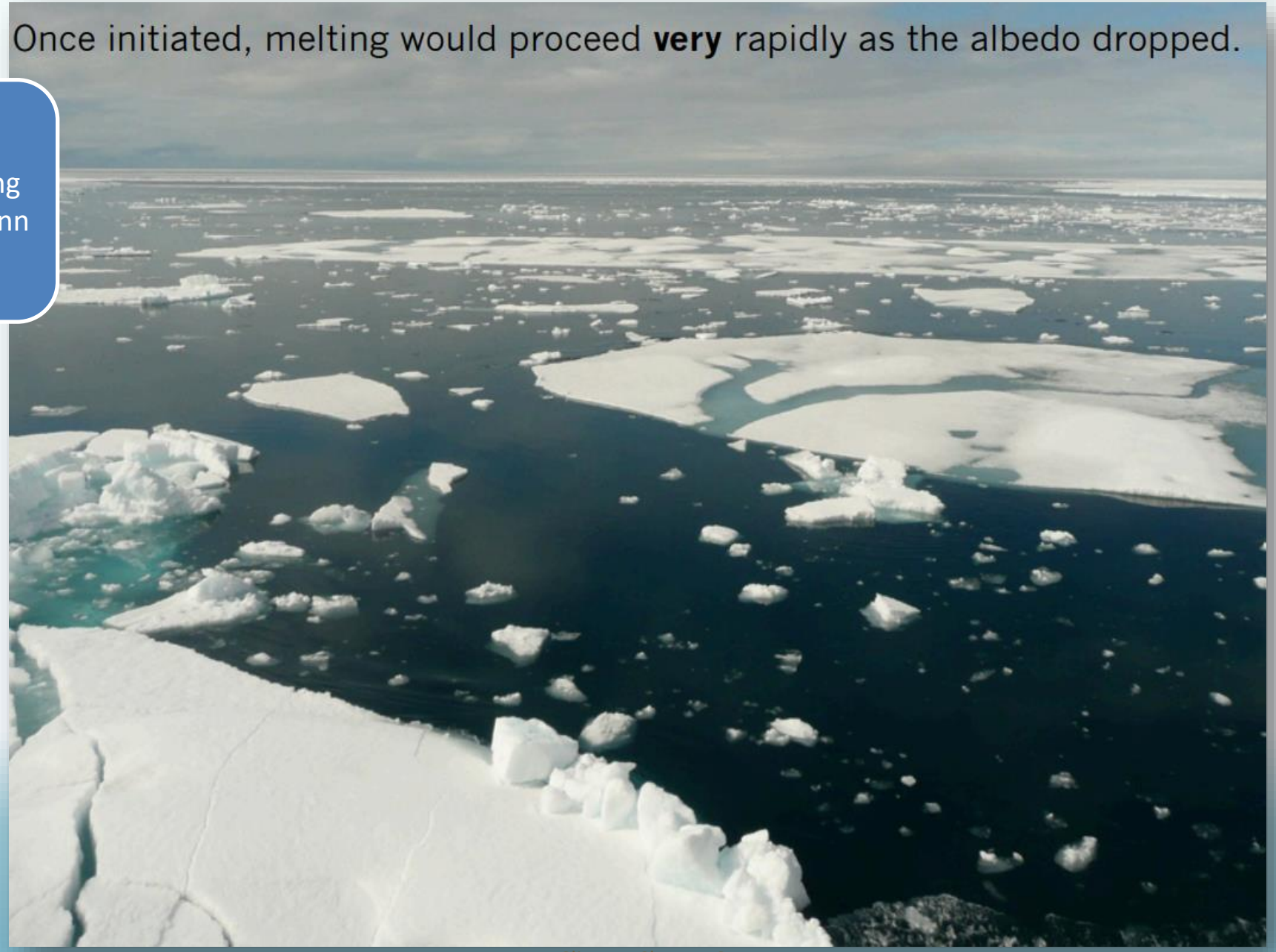
… a continuation of the normal process

But with land and oceans mostly covered with ice, there was *no chemical weathering* to remove CO_2 from the atmosphere … so it continued to accumulate for millions of years

Snowball Earth Scenario according to Dennis Hartmann (U Washington)



Snowball Earth Scenario according to Dennis Hartmann (U Washington)



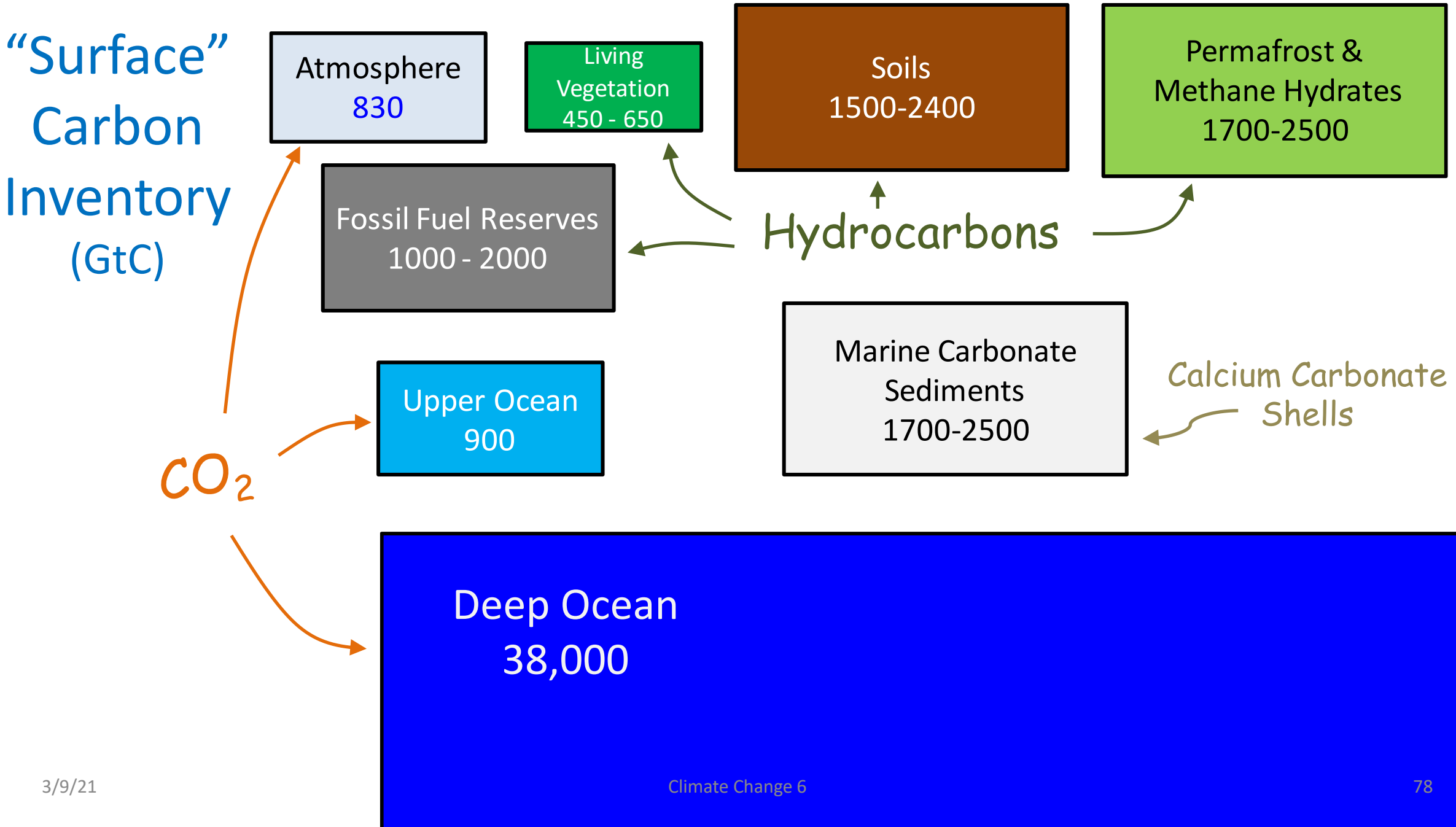
Snowball Earth Scenario according to Dennis Hartmann (U Washington)

Post-Snowball "Hothouse" Climate

- Immediately after Snowball Earth thaws, CO_2 concentrations would have been tremendously high
- Was likely the **hottest period** in Earth's history right after the **coldest**!
  - Temperatures jumped from -50° C to 50° C in only 1000 years!

Disclaimer: This story is a reasonable one, even likely, but cannot be considered proven. The evidence is somewhat circumstantial…

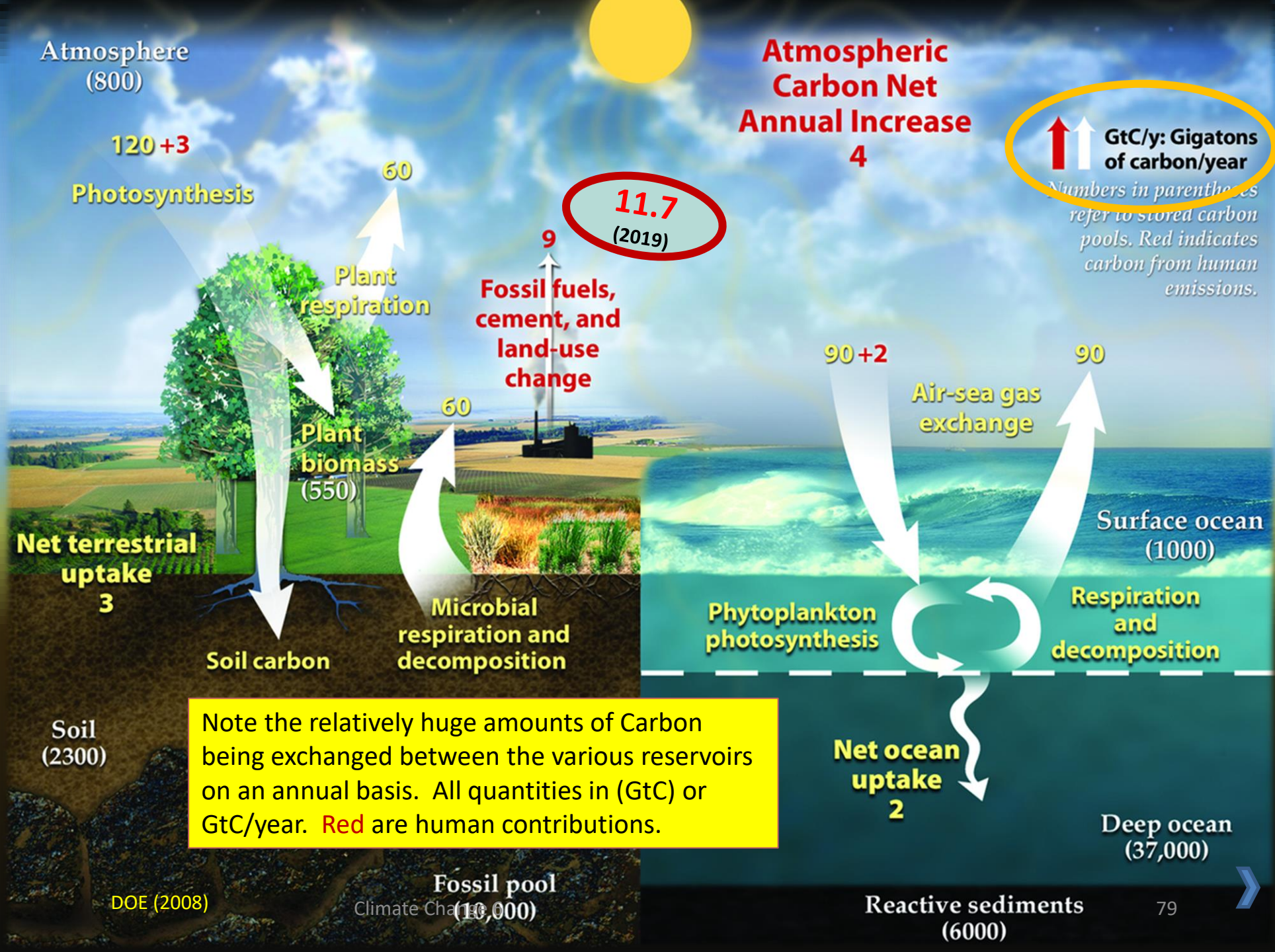
Short Term Carbon Cycles


"Surface" Carbon Inventory (GtC)
Atmosphere 830
Living Vegetation 450 - 650
Soils 1500-2400
Permafrost & Methane Hydrates 1700-2500
Fossil Fuel Reserves 1000 - 2000
Hydrocarbons
Marine Carbonate Sediments 1700-2500
Calcium Carbonate Shells
Upper Ocean 900
CO_2
Deep Ocean 38,000

Highly Simplified Depiction of Major Short-term Carbon Flows

(as of ~12 years ago)

- Atmosphere
- Plants
- Soil
- Fossil Fuel
- Ocean Surface
- Deep Ocean

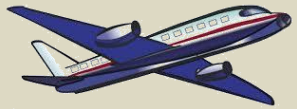


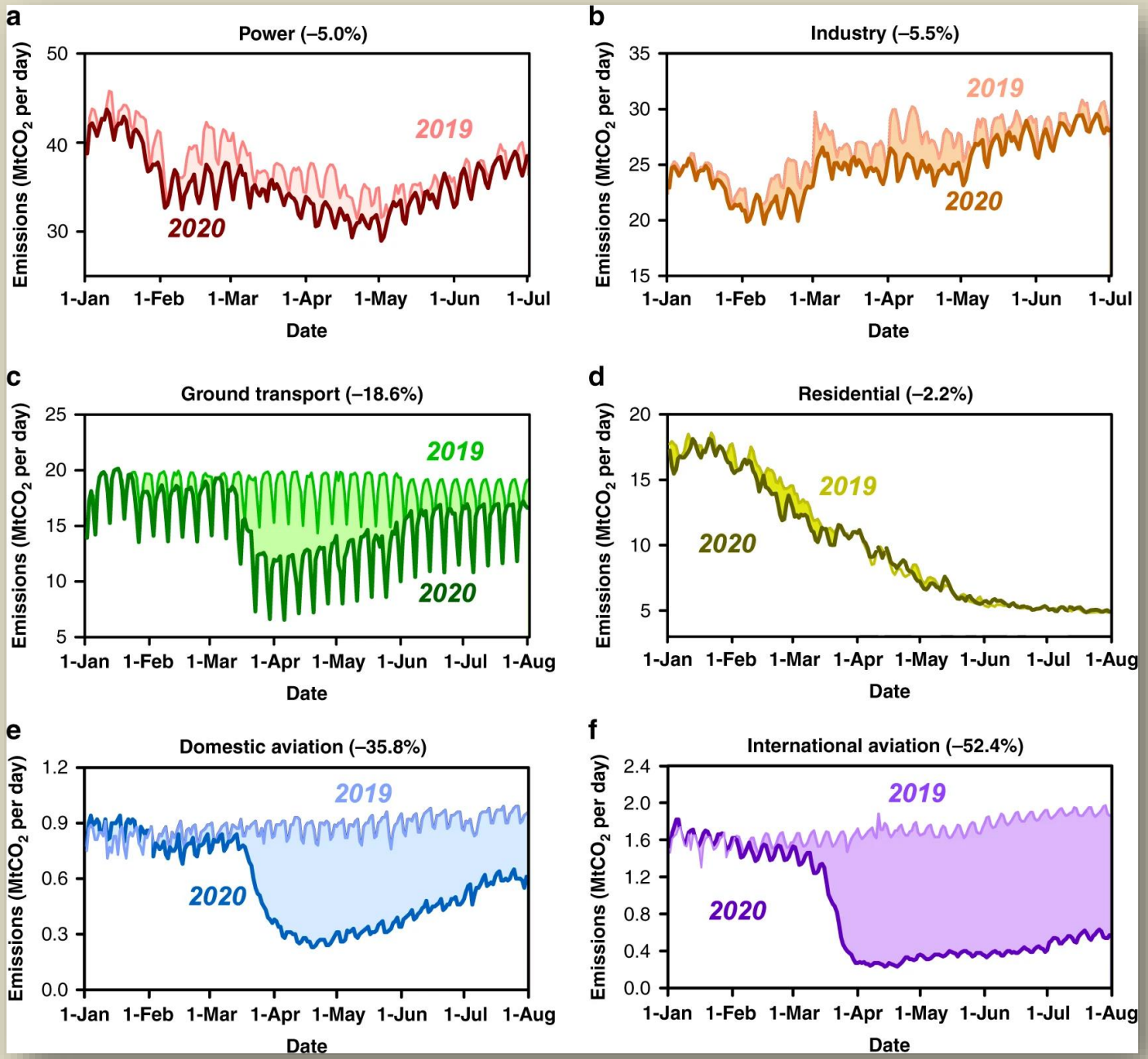
Note the relatively huge amounts of Carbon being exchanged between the various reservoirs on an annual basis. All quantities in (GtC) or GtC/year. Red are human contributions.

DOE (2008)

The COVID Effect:

CO_2 emissions dipped in 2020





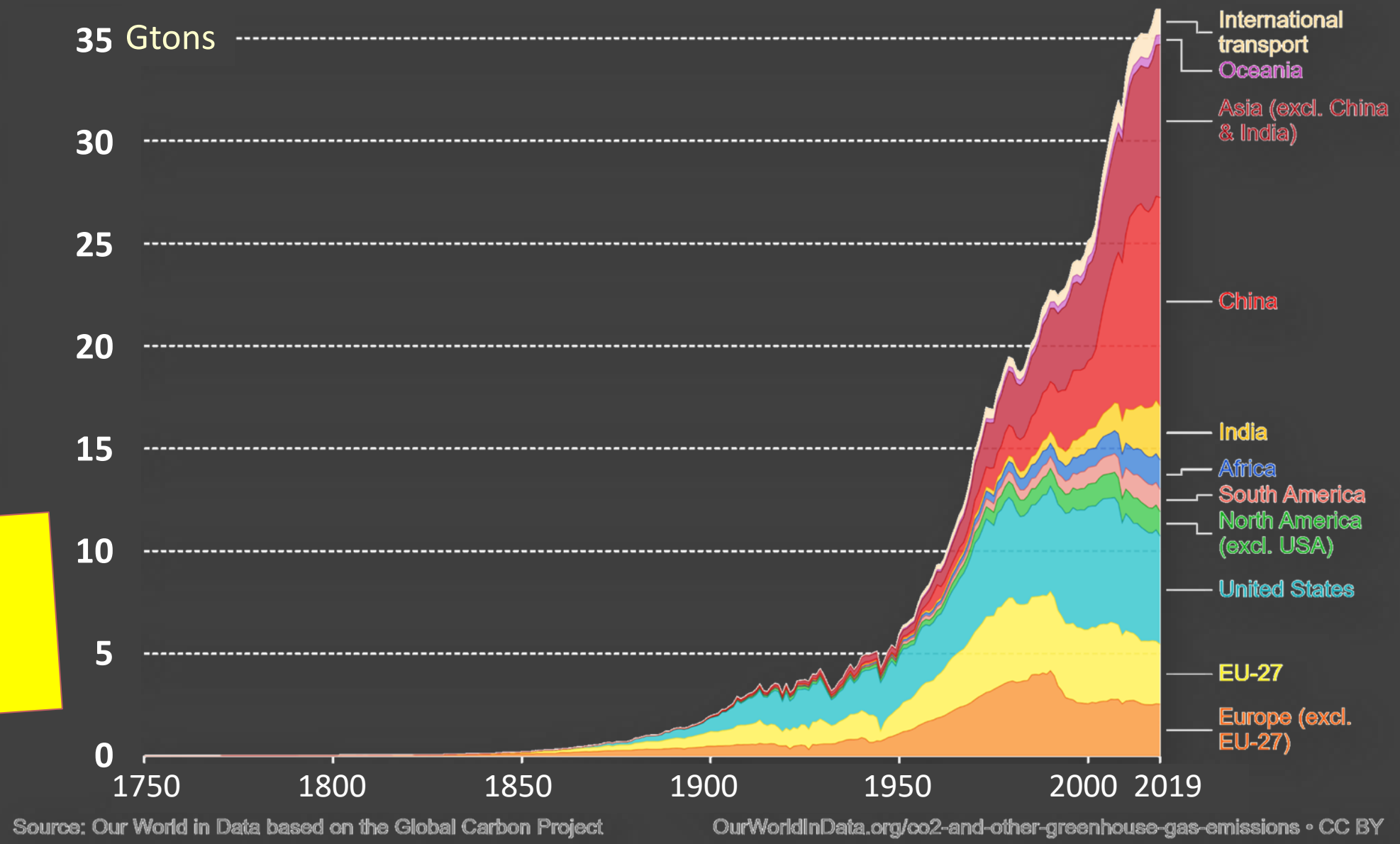
Zhu Liu et al, Nature Communications (2020)

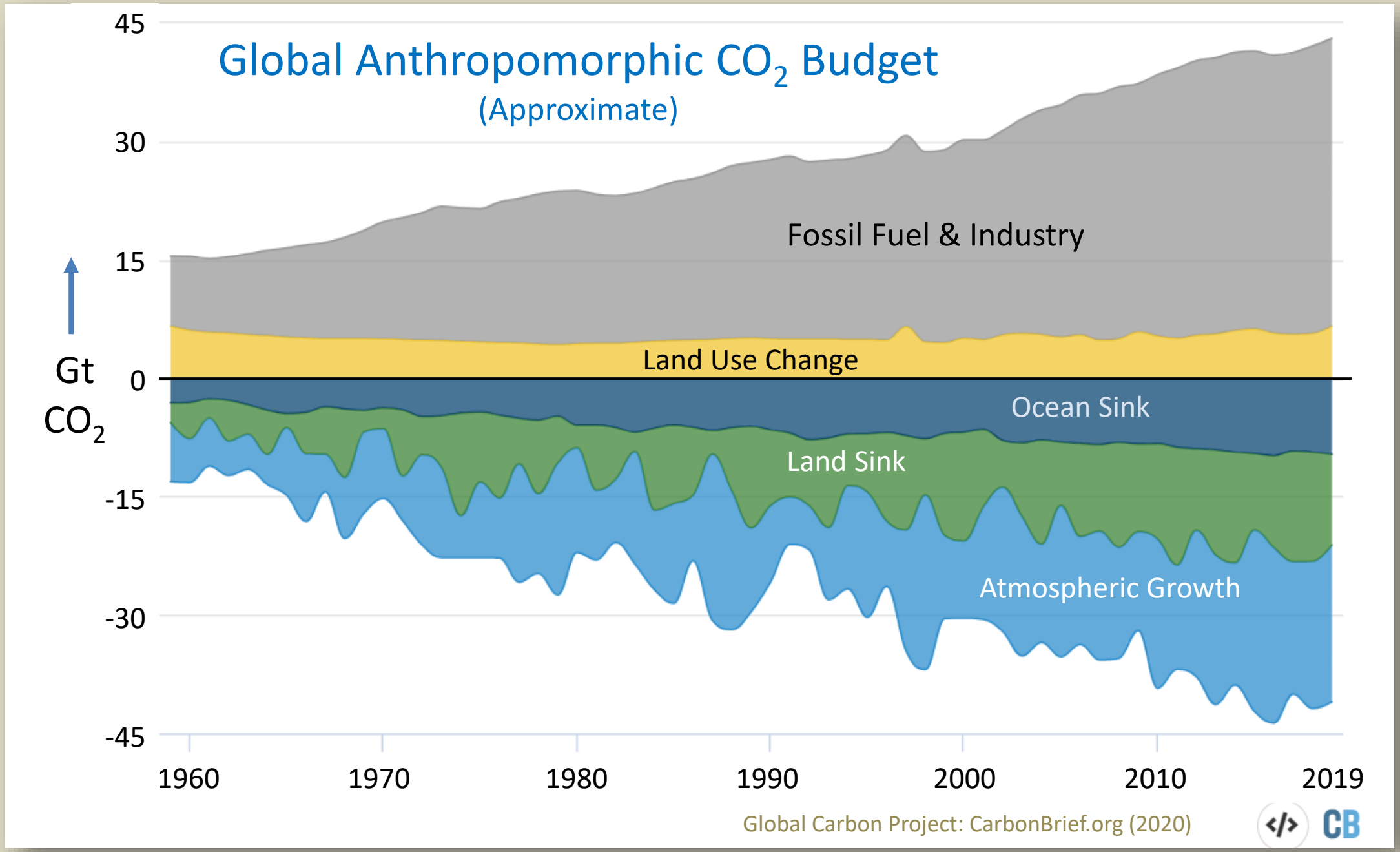
World CO_2 Emissions

1750-2019

[Fossil Fuel and Cement only]

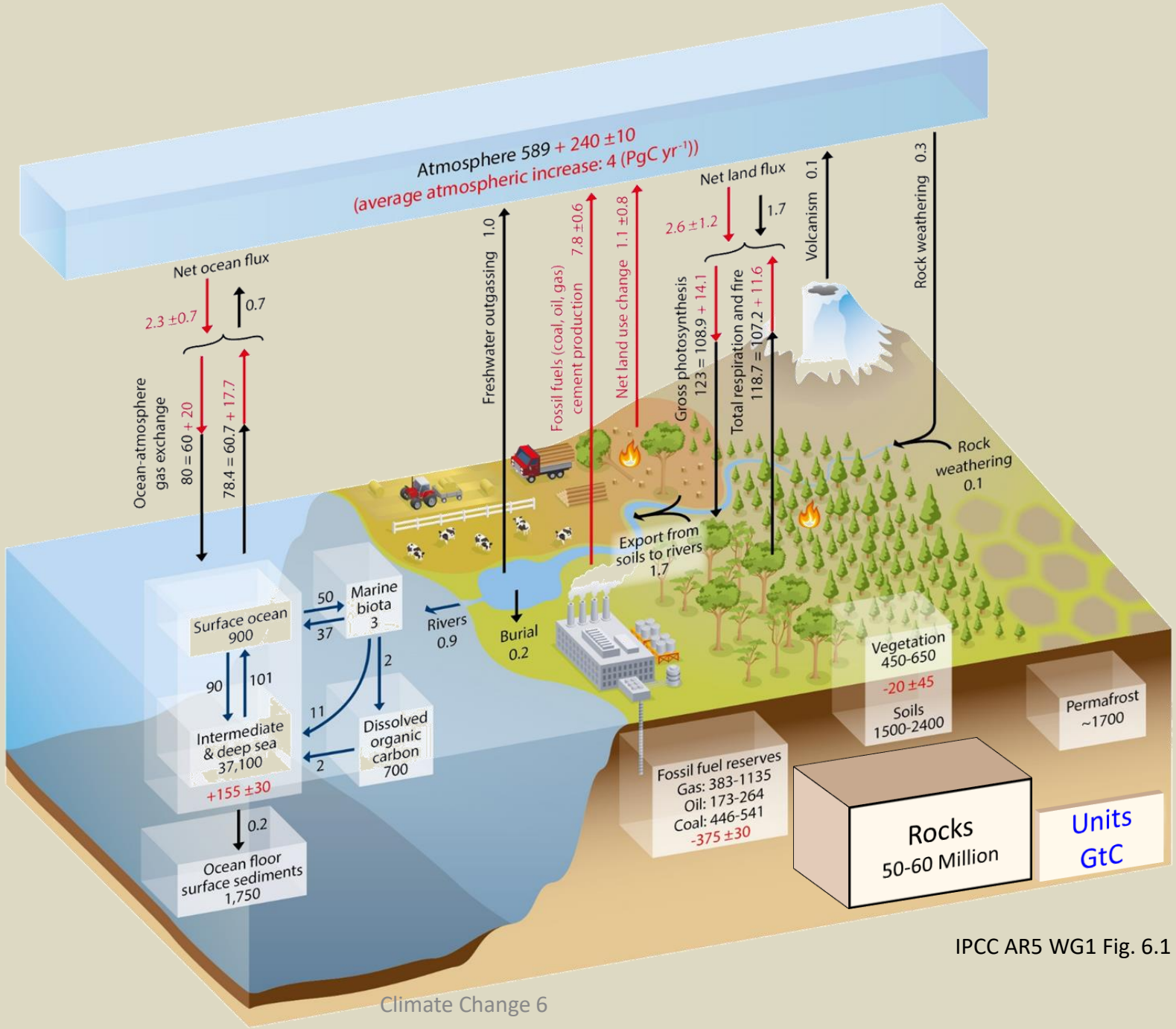
These are the anthropomorphic contributions only, not including the natural ones.




Global Anthropomorphic CO_2 Budget
(Approximate)
45
30
15
0
-15
-30
-45
Gt CO_2
Fossil Fuel & Industry
Land Use Change
Ocean Sink
Land Sink
Atmospheric Growth
1960
1970
1980
1990
2000
2010
2019
Global Carbon Project: CarbonBrief.org (2020)
CB

Short Term Carbon Cycle

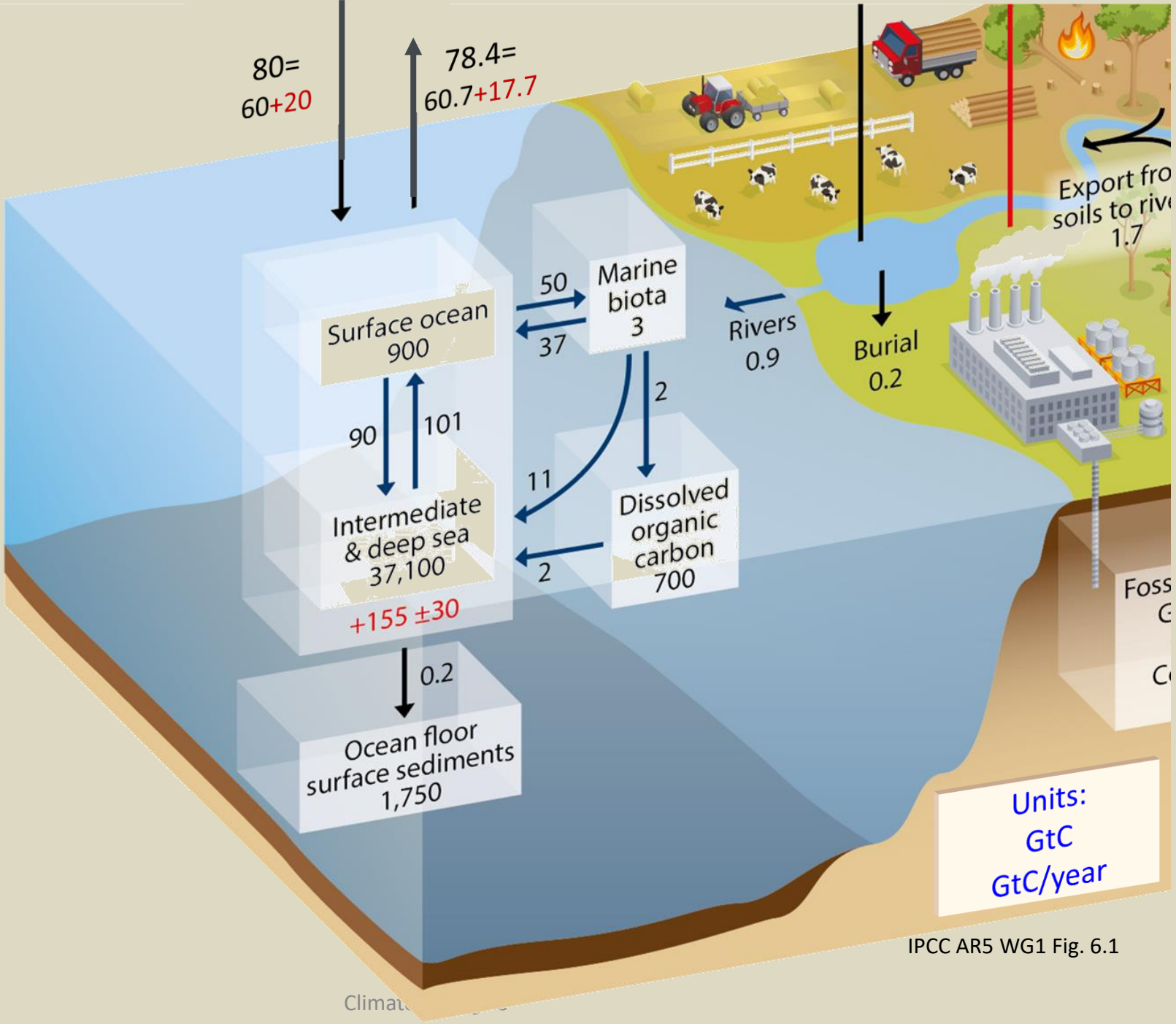
as of 2011



IPCC AR5 WG1 Fig. 6.1

Short Term Carbon Cycle in Ocean

as of 2011

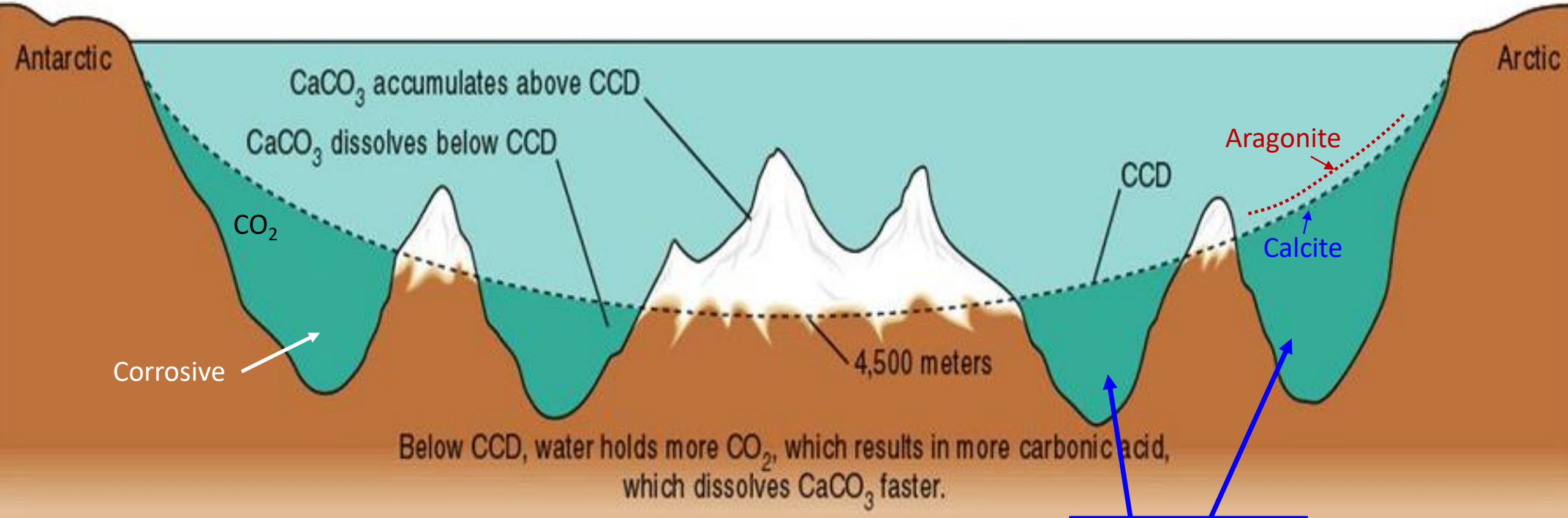


IPCC AR5 WG1 Fig. 6.1

$CaCO_3$ Dissolves below the CCD
(Carbonate Compensation Depth)

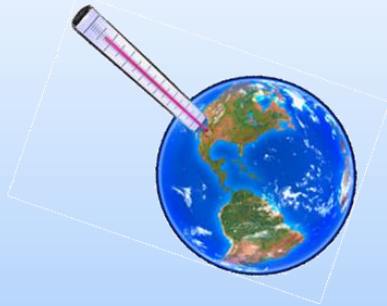
Calcium Carbonate more soluble at:

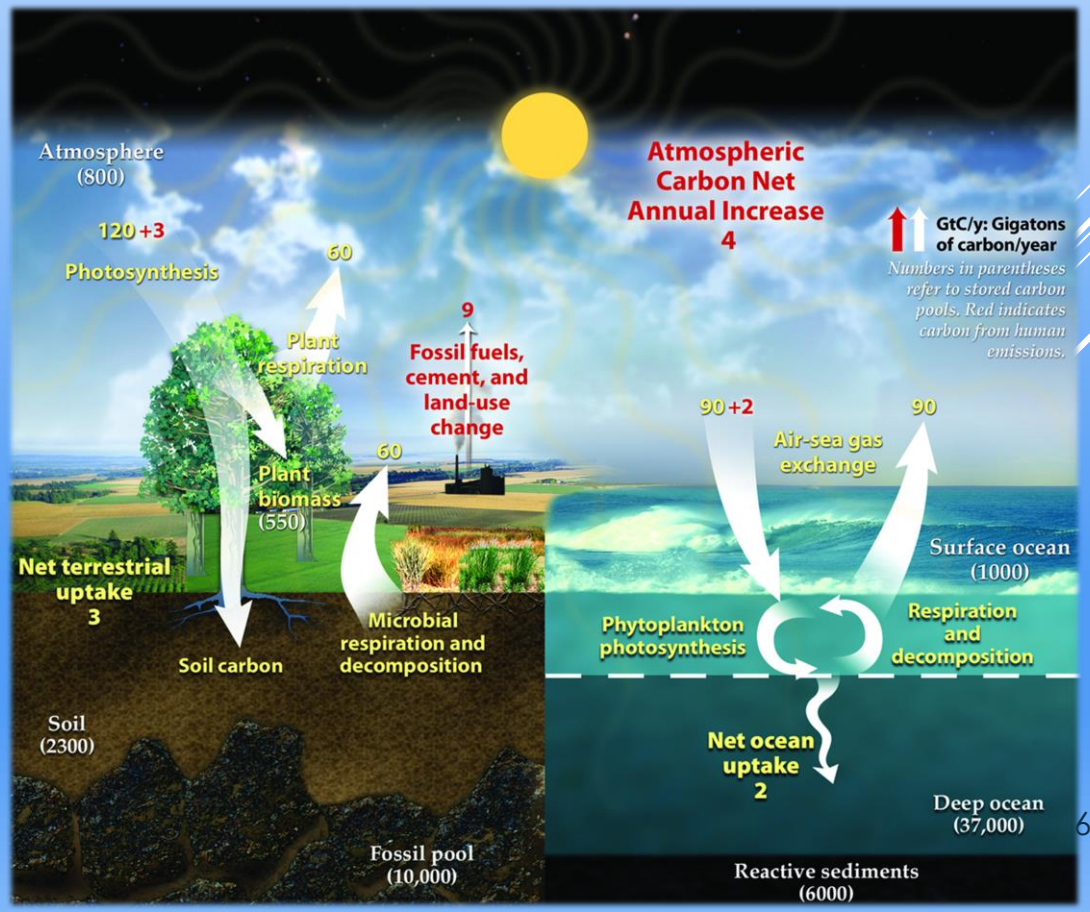
- Lower temperatures
- Higher pressures
- lower pH (more CO_2)



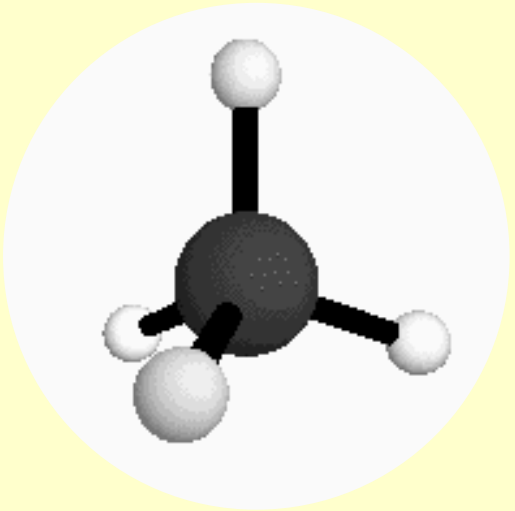
Hope Owen (Oregon State U)

Questions about Snowball Earth or the Short Term Carbon Cycle?



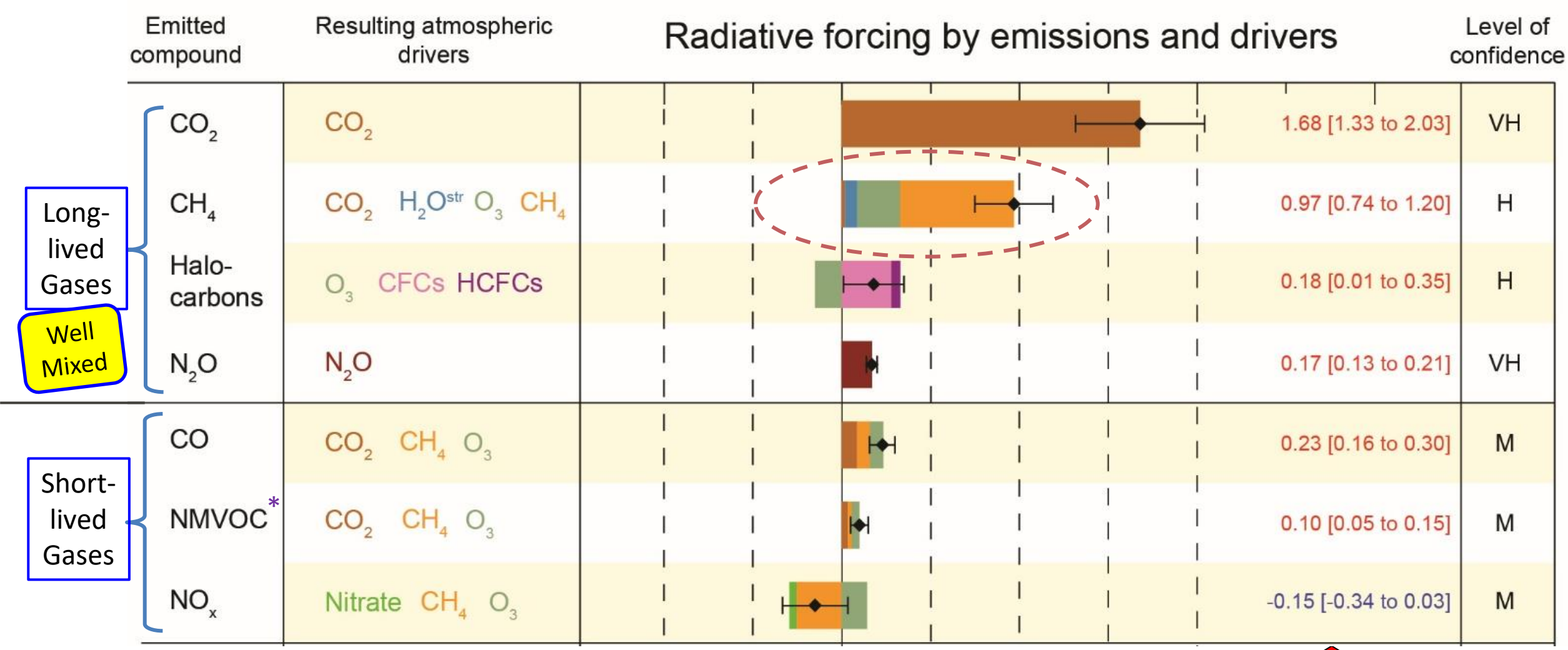


Greenhouse Gases



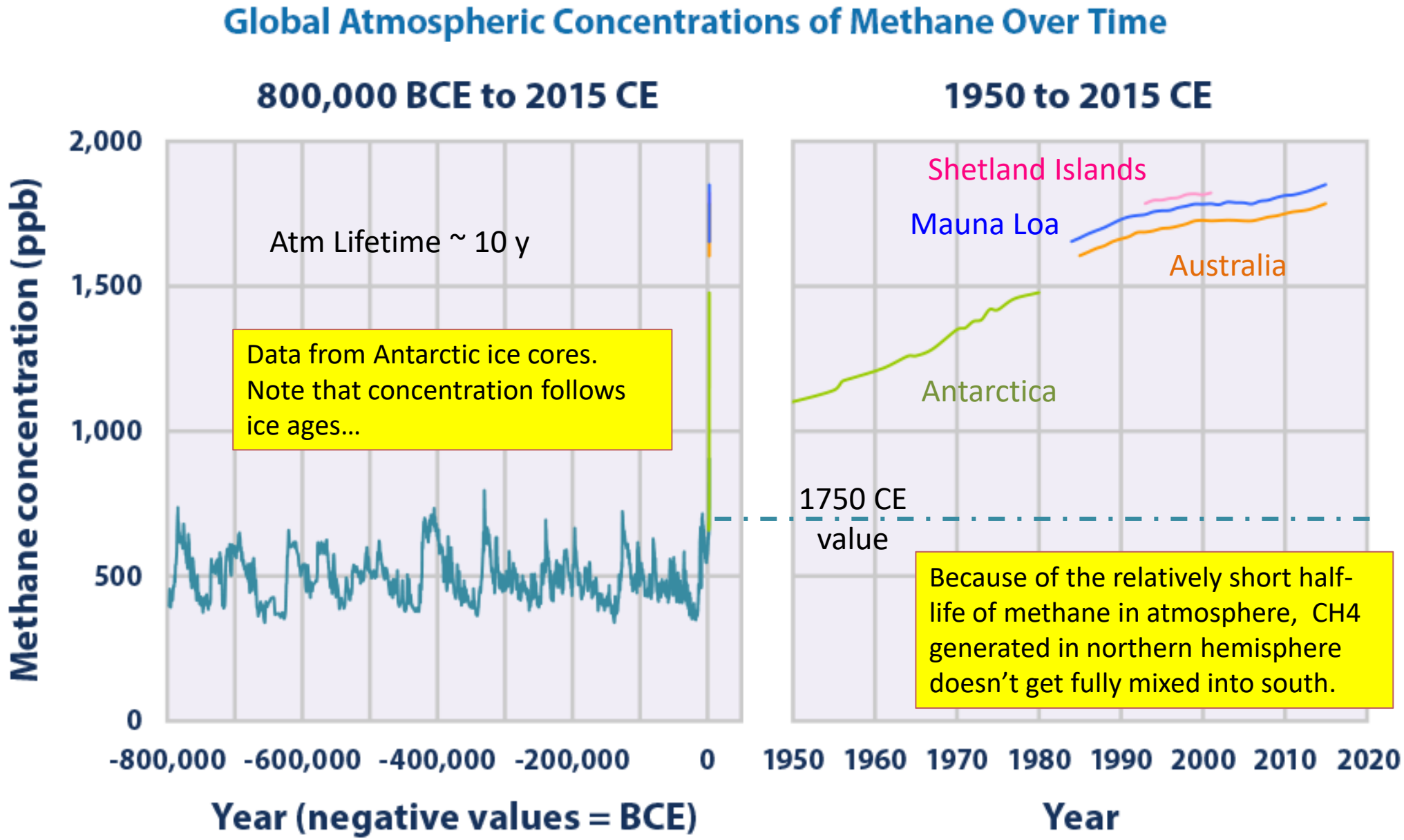
Methane CH_4

Greenhouse Gas Radiative Forcing as of 2011 (IPCC AR5)



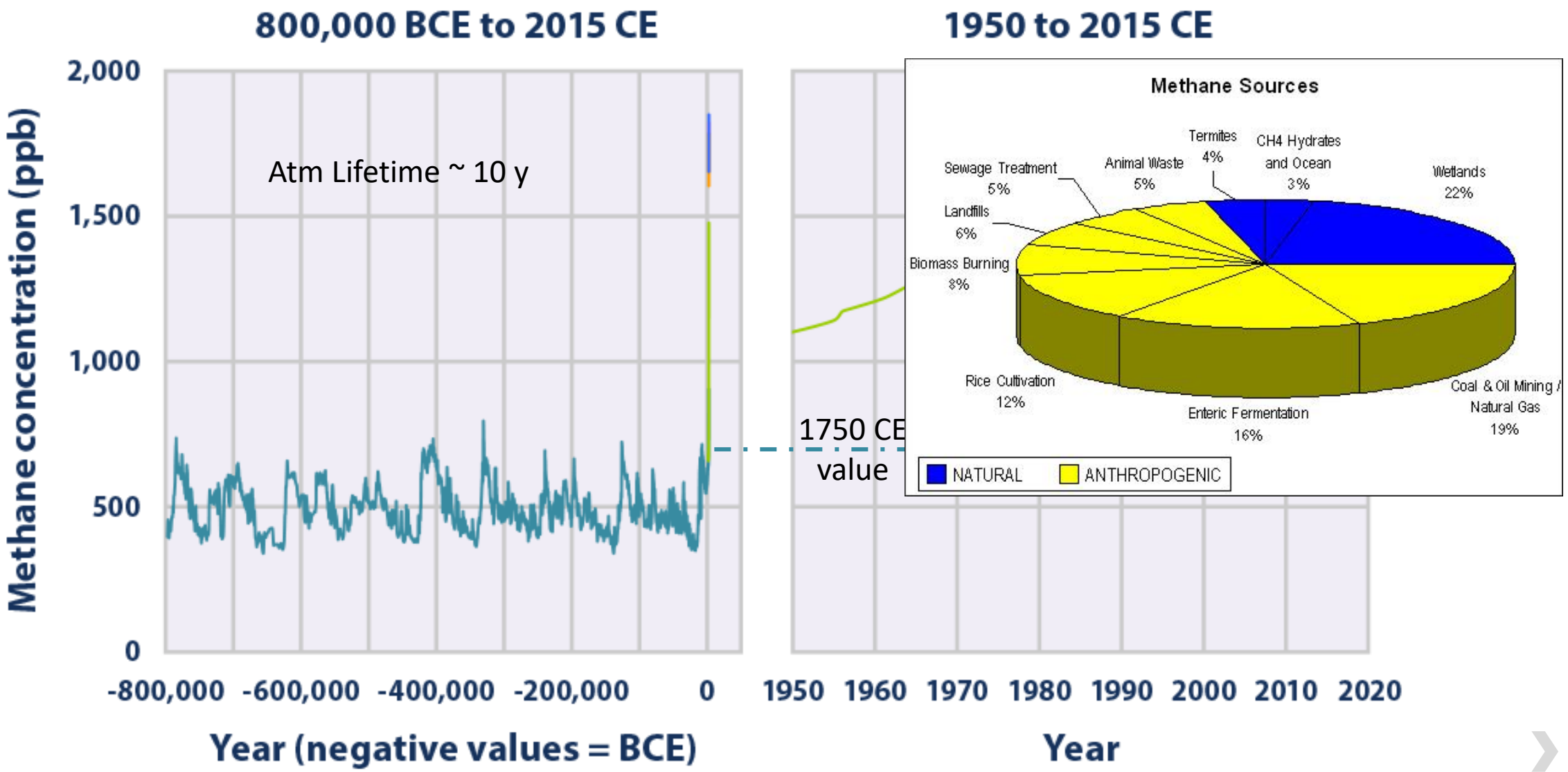
IPCC AR5 SPM-5

*Non-Methane VOC's
like Ethanol, Acetone, Formaldehyde


Global Atmospheric Concentrations of Methane Over Time
800,000 BCE to 2015 CE
1950 to 2015 CE
Methane concentration (ppb)
2,000
1,500
1,000
500
0
Atm Lifetime ~ 10 y
Data from Antarctic ice cores. Note that concentration follows ice ages…
-800,000
-600,000
-400,000
-200,000
0
Year (negative values = BCE)
Shetland Islands
Mauna Loa
Australia
Antarctica
1750 CE value
Because of the relatively short half-life of methane in atmosphere, CH4 generated in northern hemisphere doesn't get fully mixed into south.
1950
1960
1970
1980
1990
2000
2010
2020
Year

EPA 2016

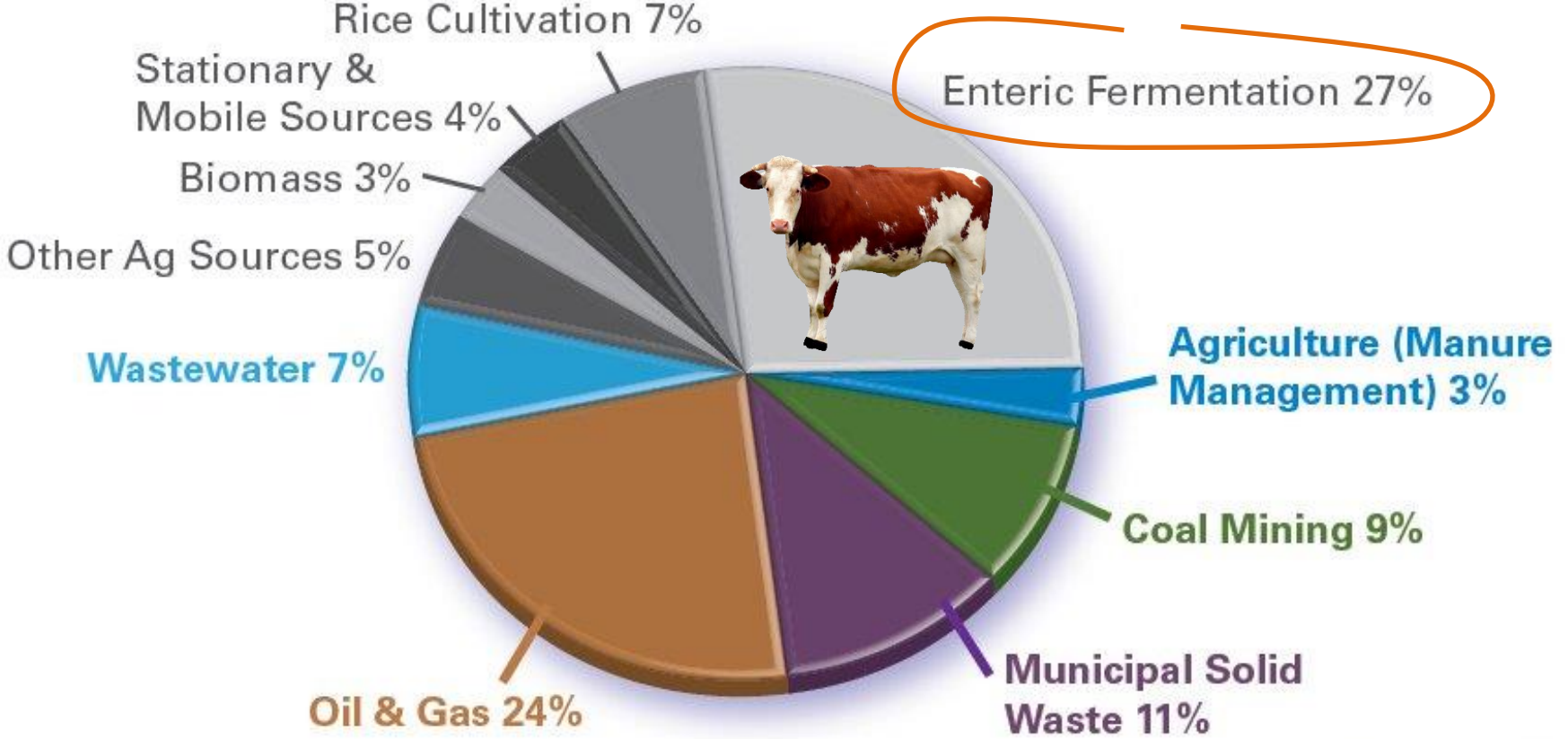
Global Atmospheric Concentrations of Methane Over Time



EPA 2016

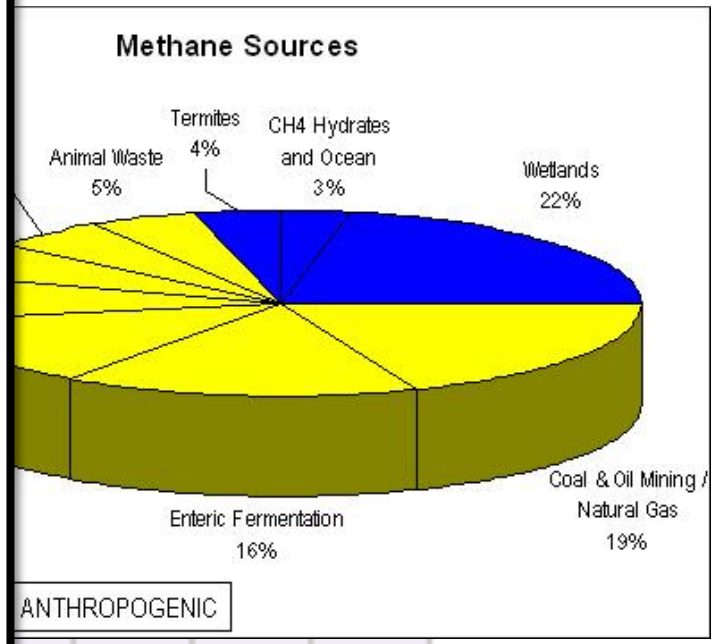
Global Atmospheric Concentrations of Methane Over Time

Estimated Global Anthropogenic Methane Emissions by Source, 2020



Source: Global Methane Initiative

2015 CE



1990 2000 2010 2020

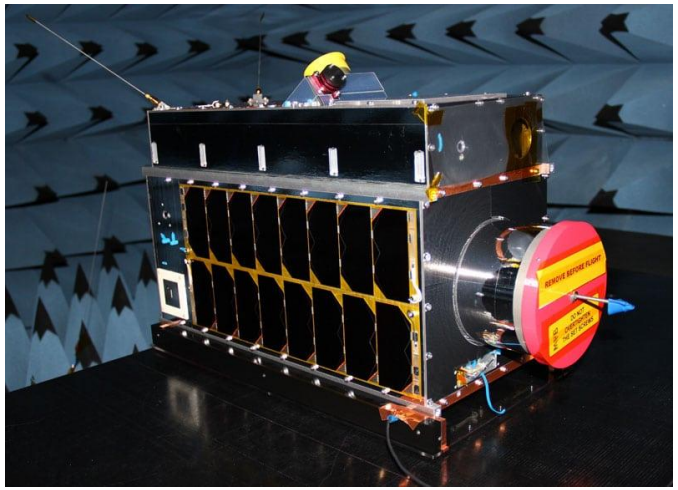
ar

EPA 2016

GHGSAT

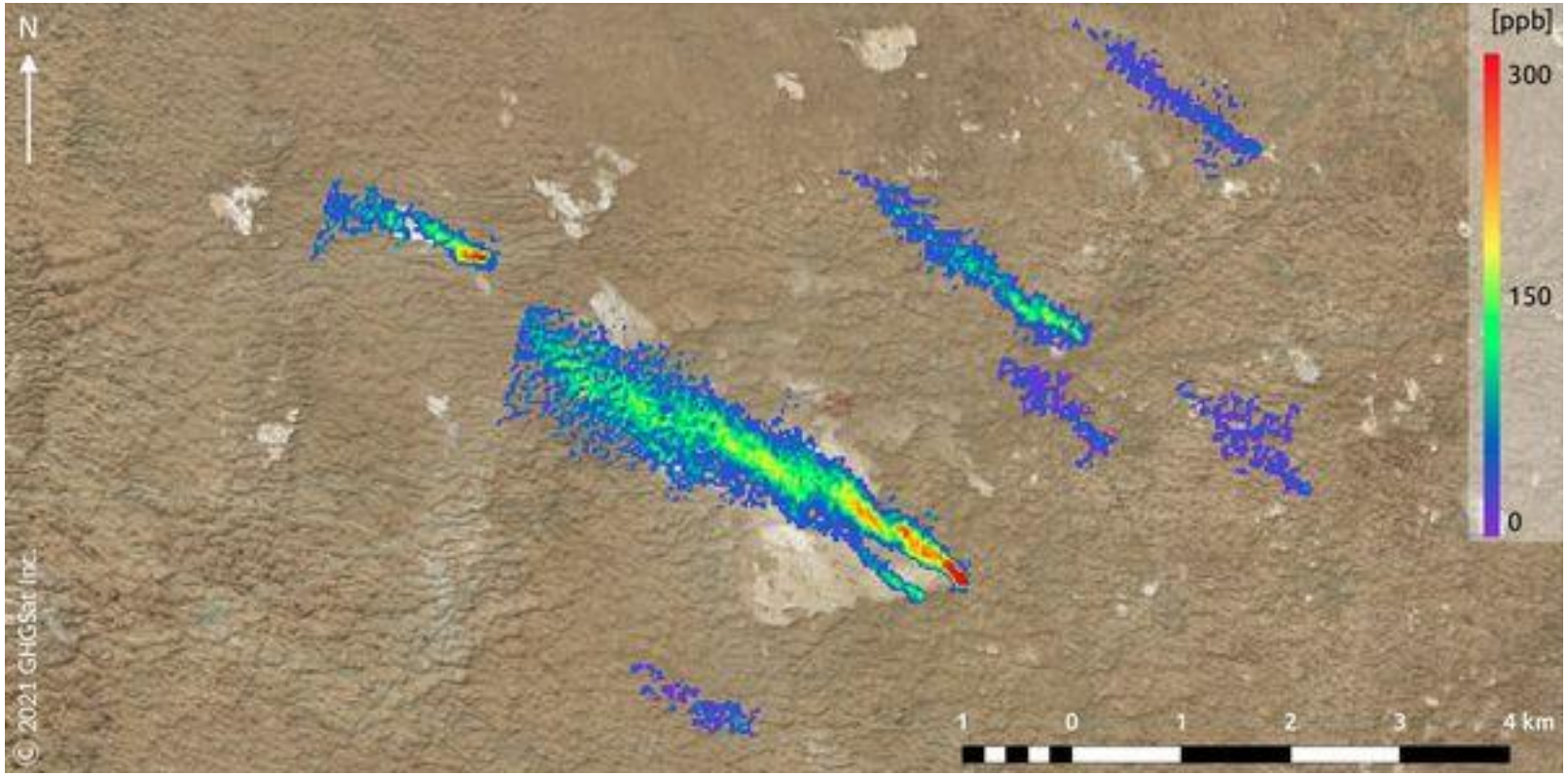
[GreenHouse Gas Satellite]
Detects Methane
Emissions from Space

GHGSAT Iris & Hugo
Satellites

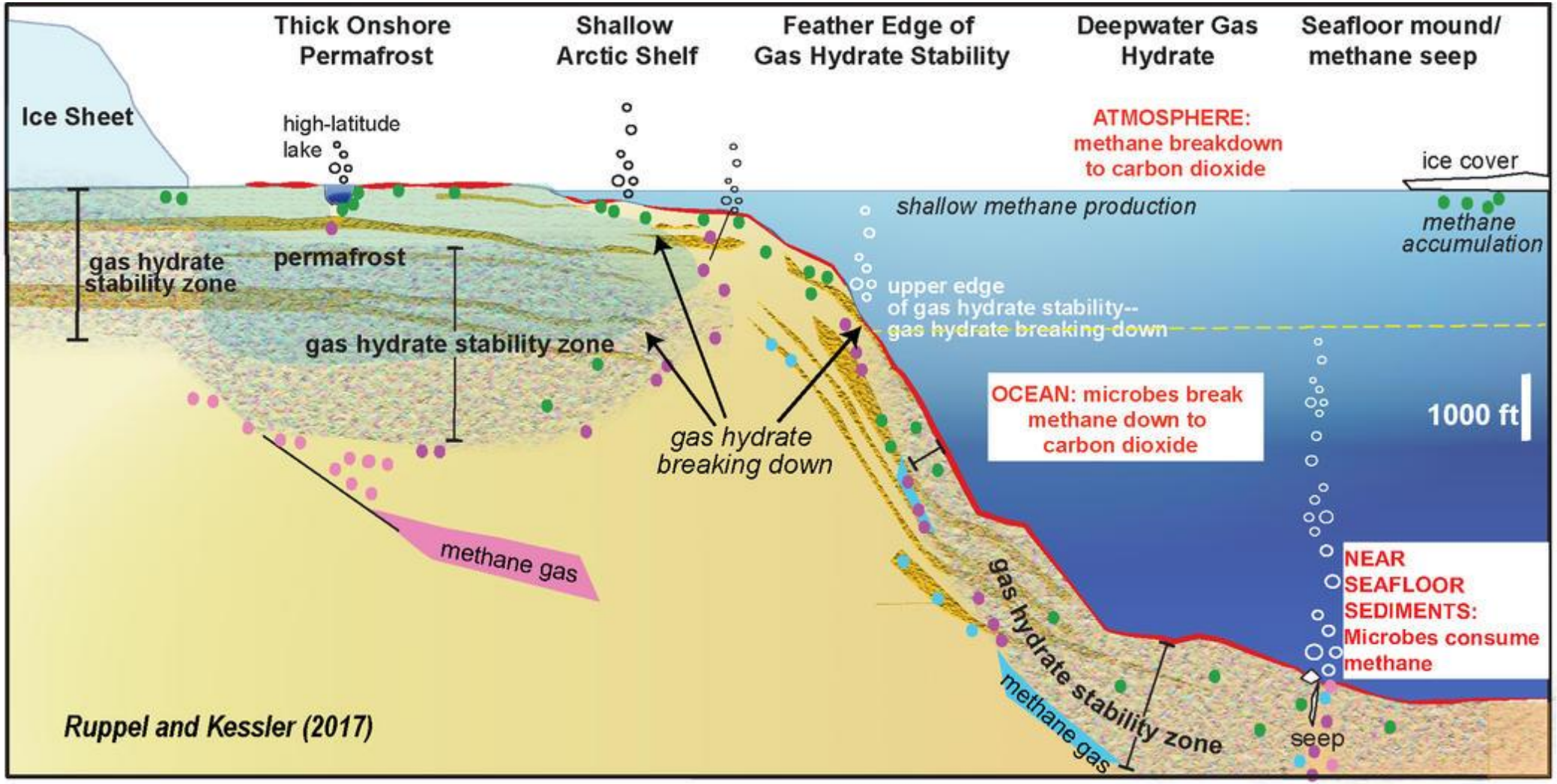


Eight Methane Leaks Observed in Oil Field in Central Turkmenistan

Feb. 1, 2021



Methane from Permafrost and Hydrates

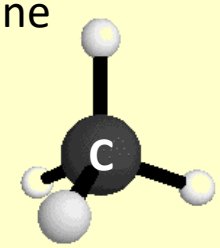


USGS

Greenhouse Gases

Halogenated Gases

Methane
CH_4

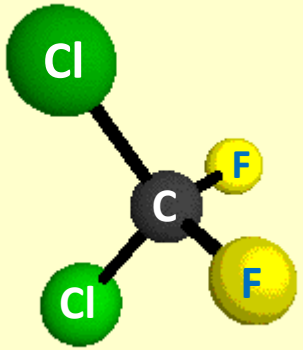


CFC's ChloroFluoroCarbons

Simple hydrocarbons with Hydrogens replaced by halogens like Chlorine and Fluorine

Freon-12

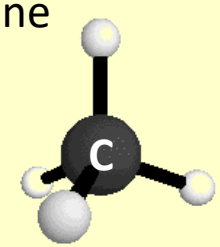
CCl_2F_2



Greenhouse Gases

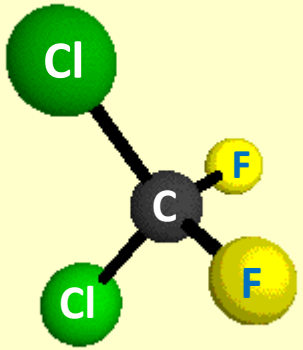
Halogenated Gases

Methane
CH_4



Freon-12

CCl_2F_2



CFC's **C**hloro**F**luoro**C**arbons

Stratospheric Ozone Killers

largely phased out in favor of…

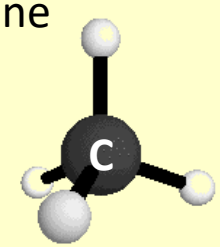
HFC's **H**ydro**F**luoro**C**arbons

Safe for Ozone– no Cl

Greenhouse Gases

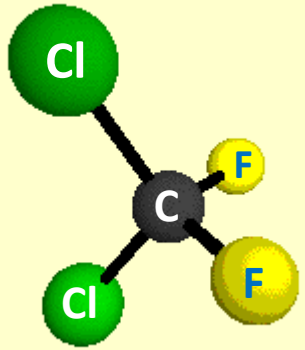
Halogenated Gases

Methane
CH_4



Freon-12

CCl_2F_2



CFC's **C**hloro**F**luoro**C**arbons

Stratospheric Ozone Killers

largely phased out in favor of…

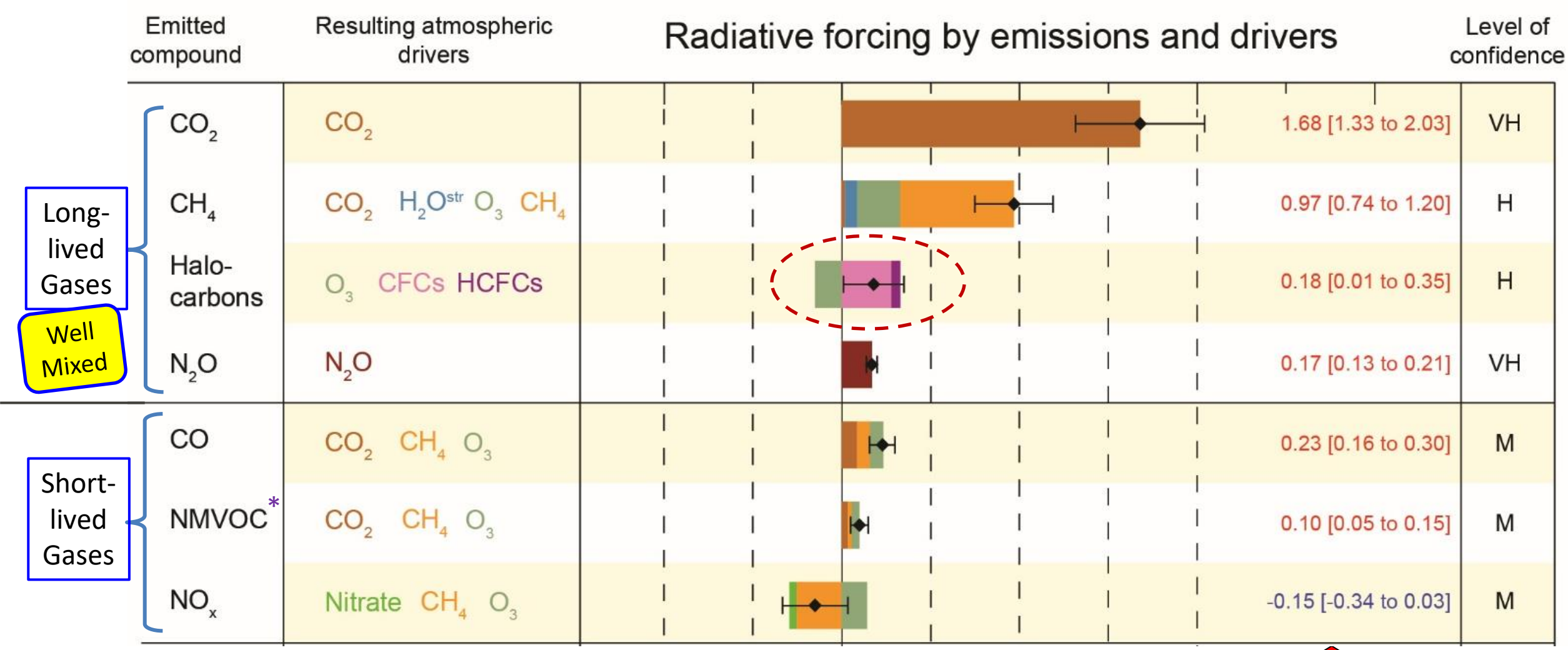
HFC's **H**ydro**F**luoro**C**arbons

Safe for Ozone

Unfortunately, all are Greenhouse Gases

- some very potent
- some very long lasting

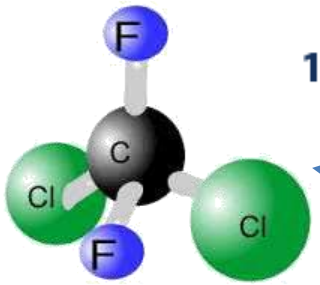
Greenhouse Gas Radiative Forcing as of 2011 (IPCC AR5)

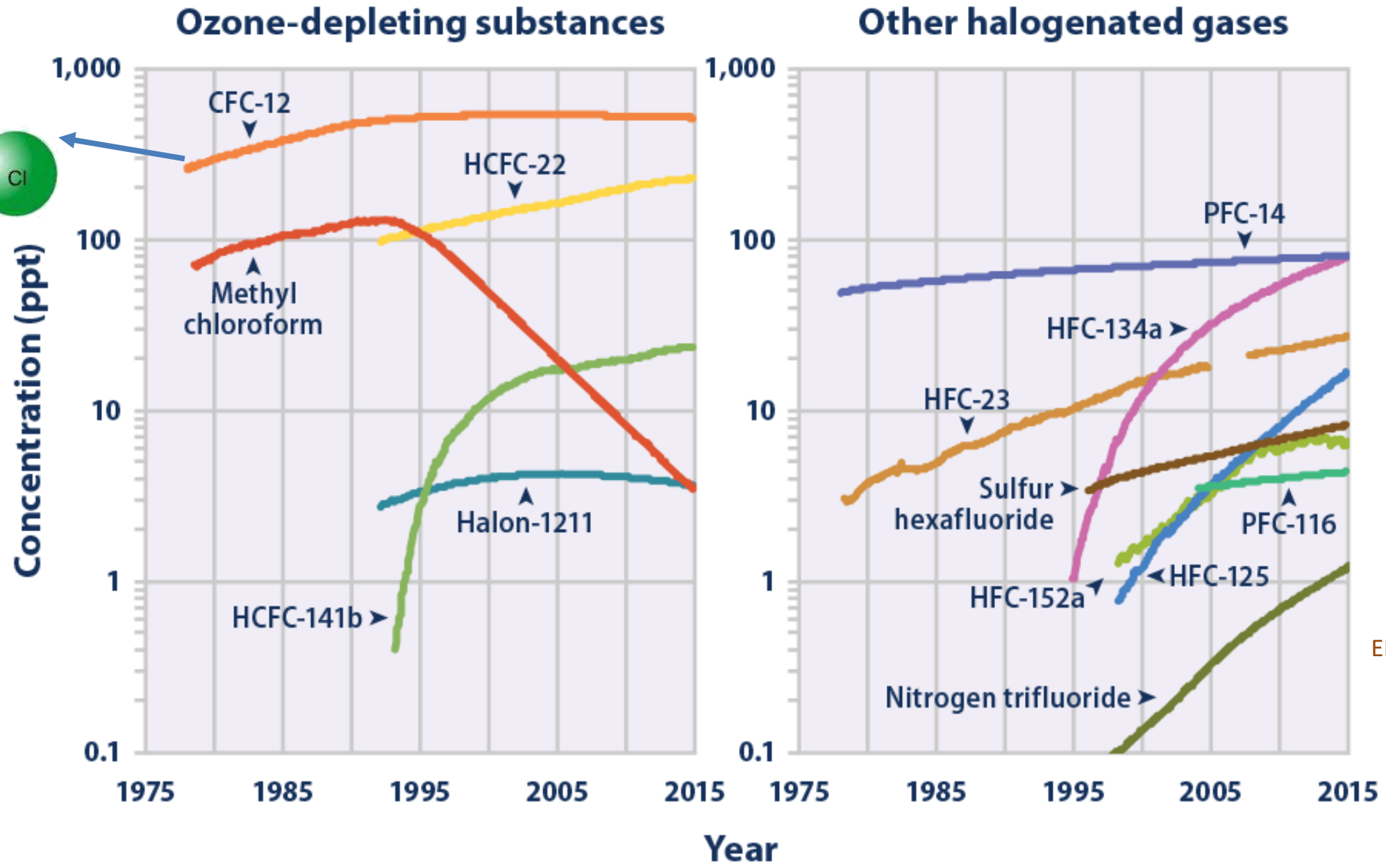


IPCC AR5 SPM-5

*Non-Methane VOC's
like Ethanol, Acetone, Formaldehyde

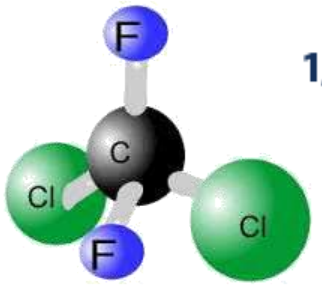
Du Pont
Freon-12

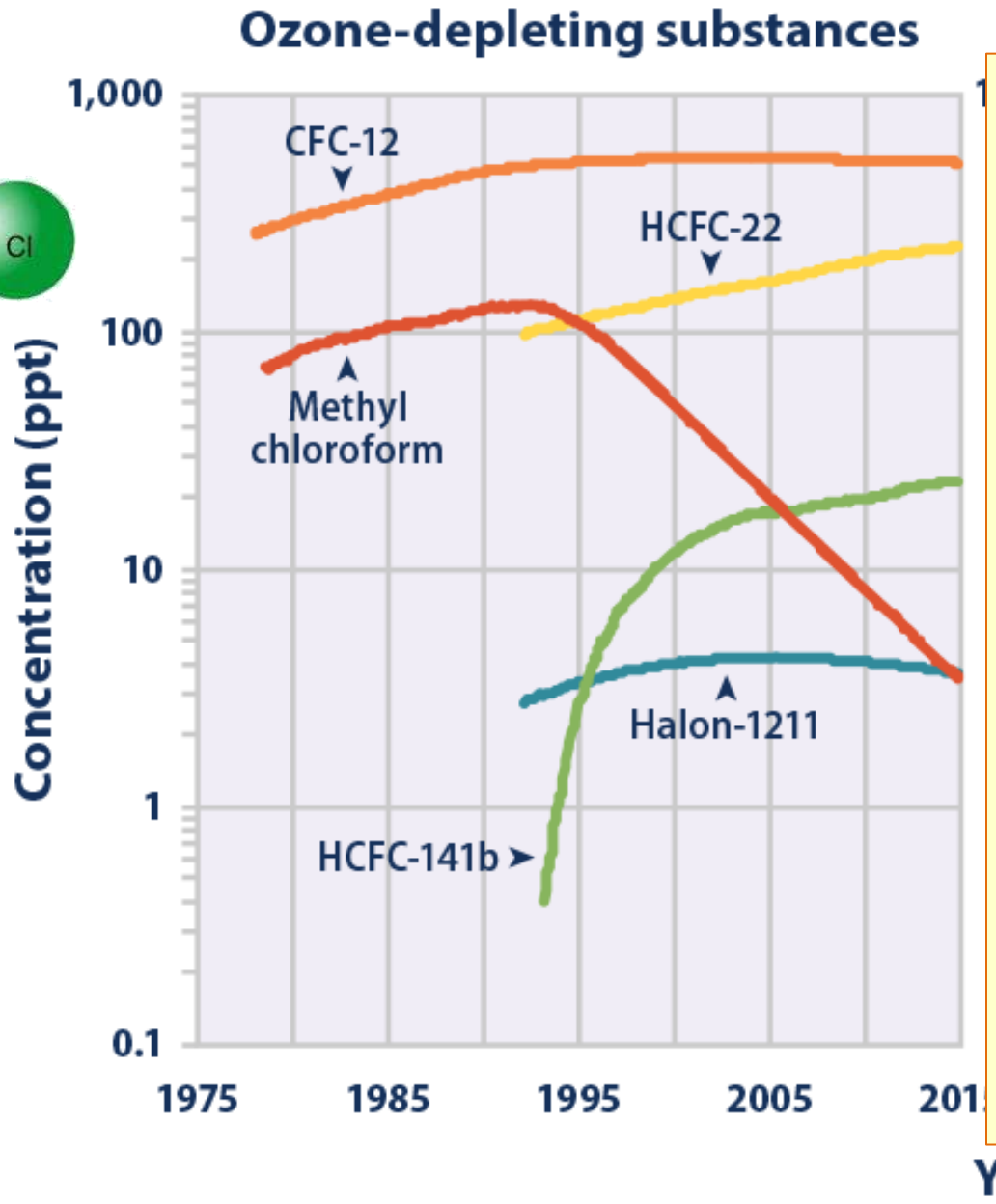




EPA 2016

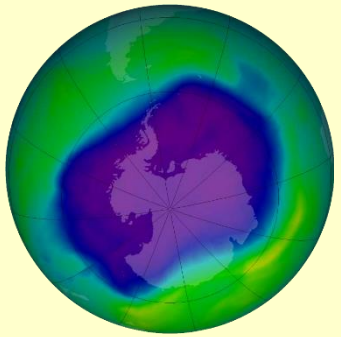
Global Atmospheric Concentrations of Selected Halogenated Gases, 1978–2015





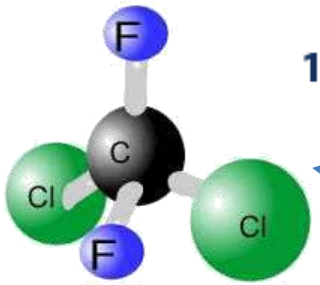
Montreal Protocol (1987)

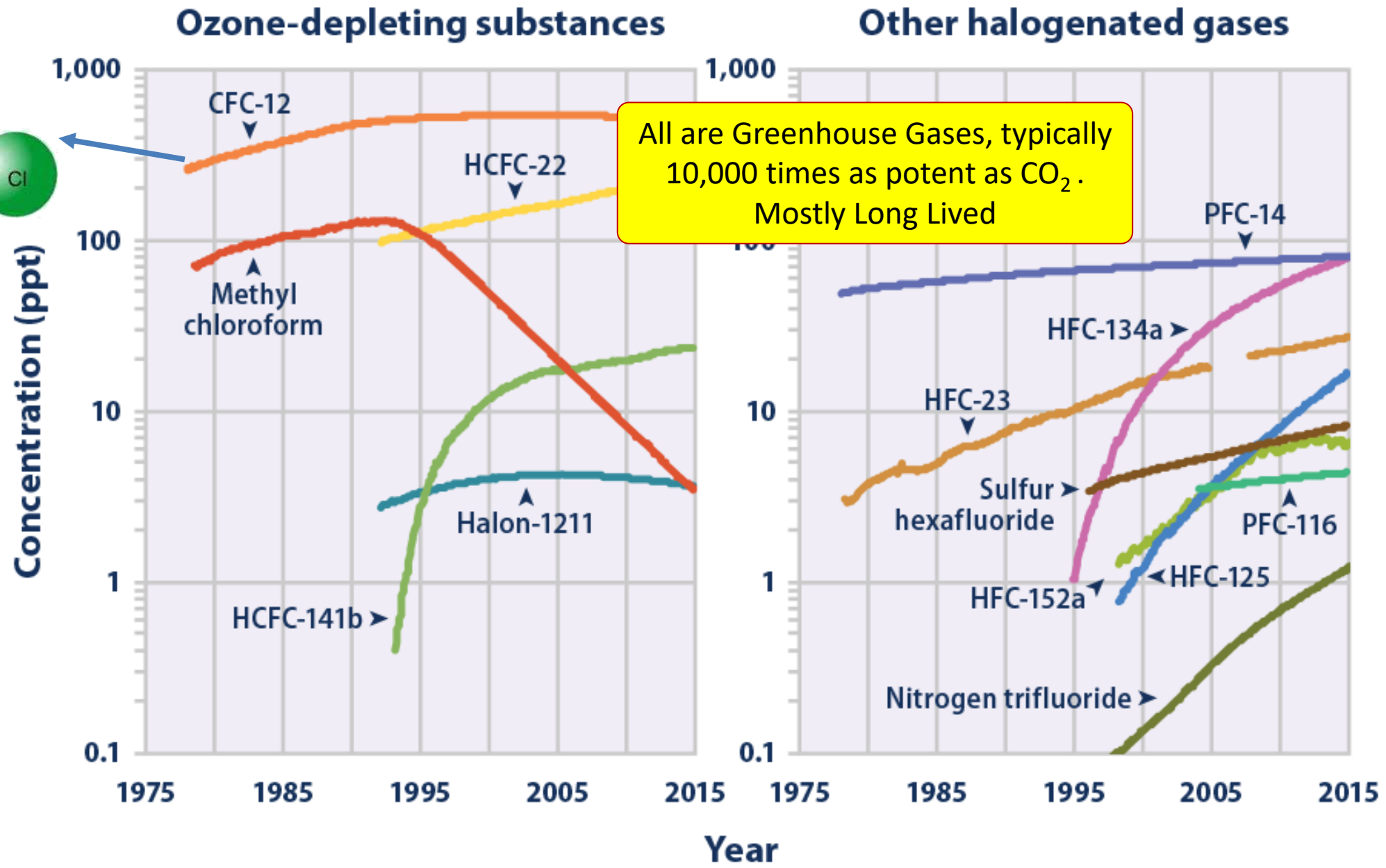
- International Agreement to phase out Chlorine- and Bromine-containing hydrocarbons which attack Stratospheric Ozone.
  - Used as refrigerants, fire suppressants, aerosol propellants.
- Universally adopted, big success.
  - Substituted by Fluorine-containing compounds.
- Note:
  All are GHG's.



Antarctic Ozone Hole
September 2006

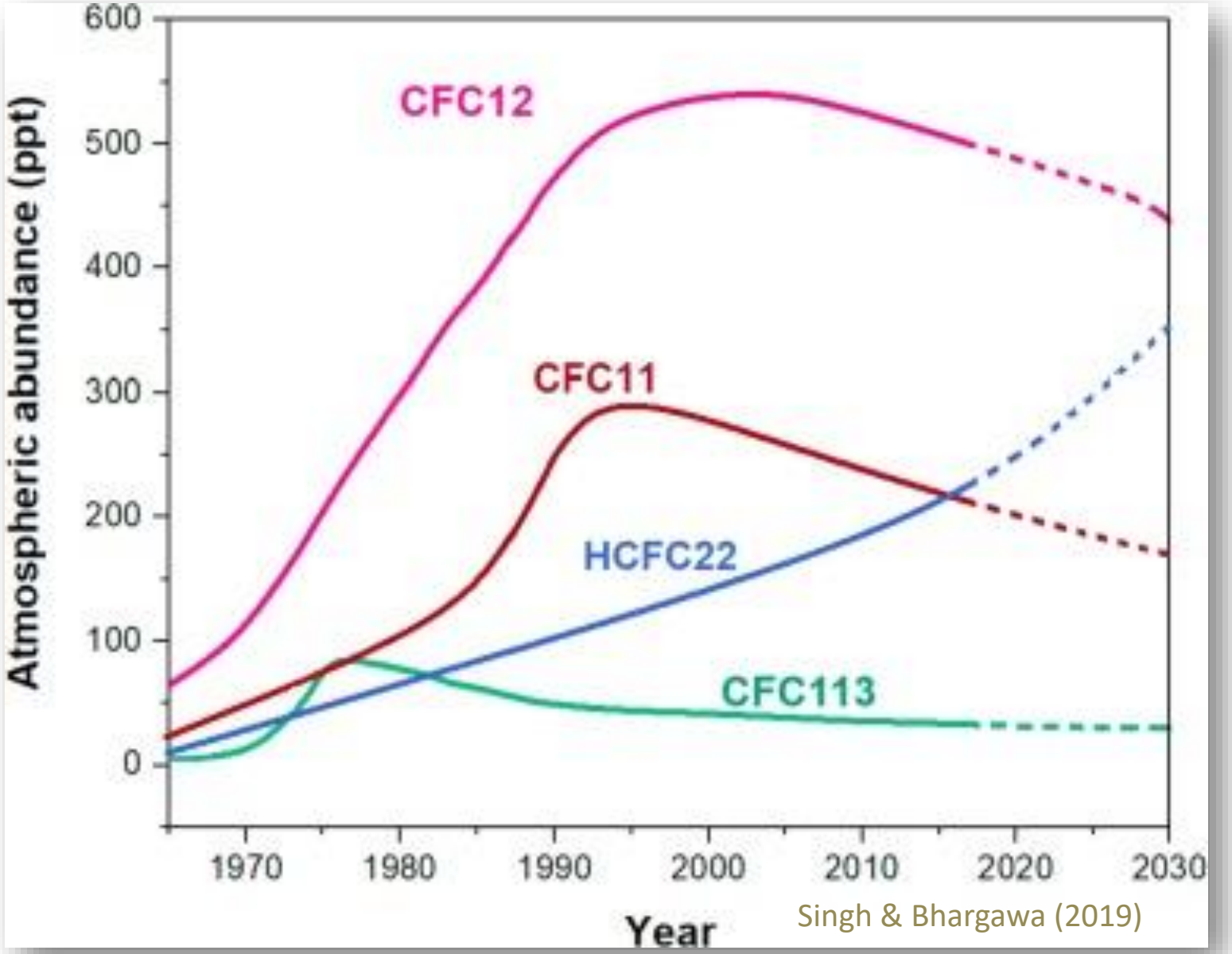
Du Pont
Freon-12





EPA 2016

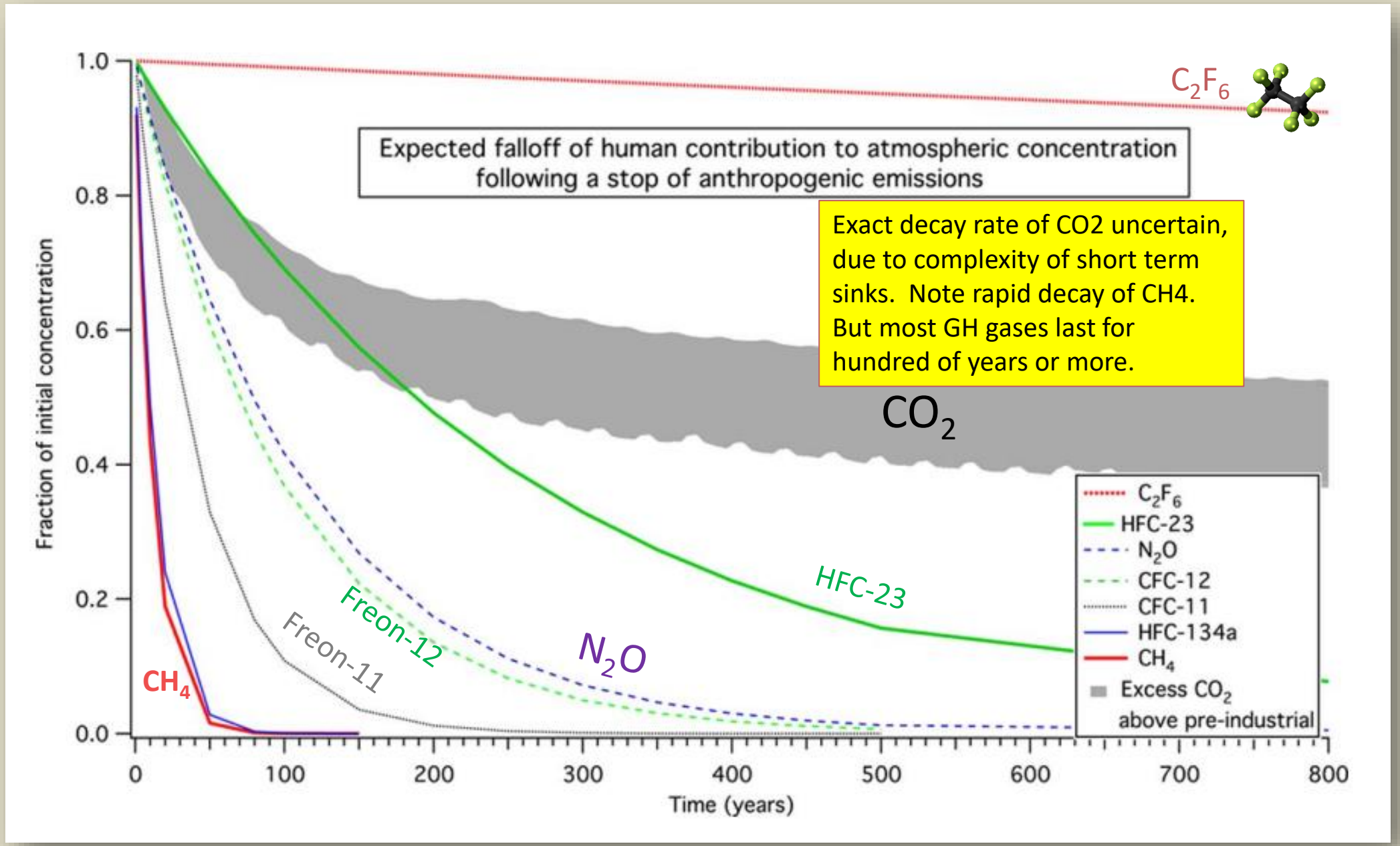
As CFC's are phased out, HFC's are growing



Singh & Bhargawa (2019)

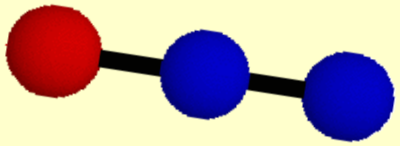
Lifetimes of GH Gases:

Cold Turkey Cutoff

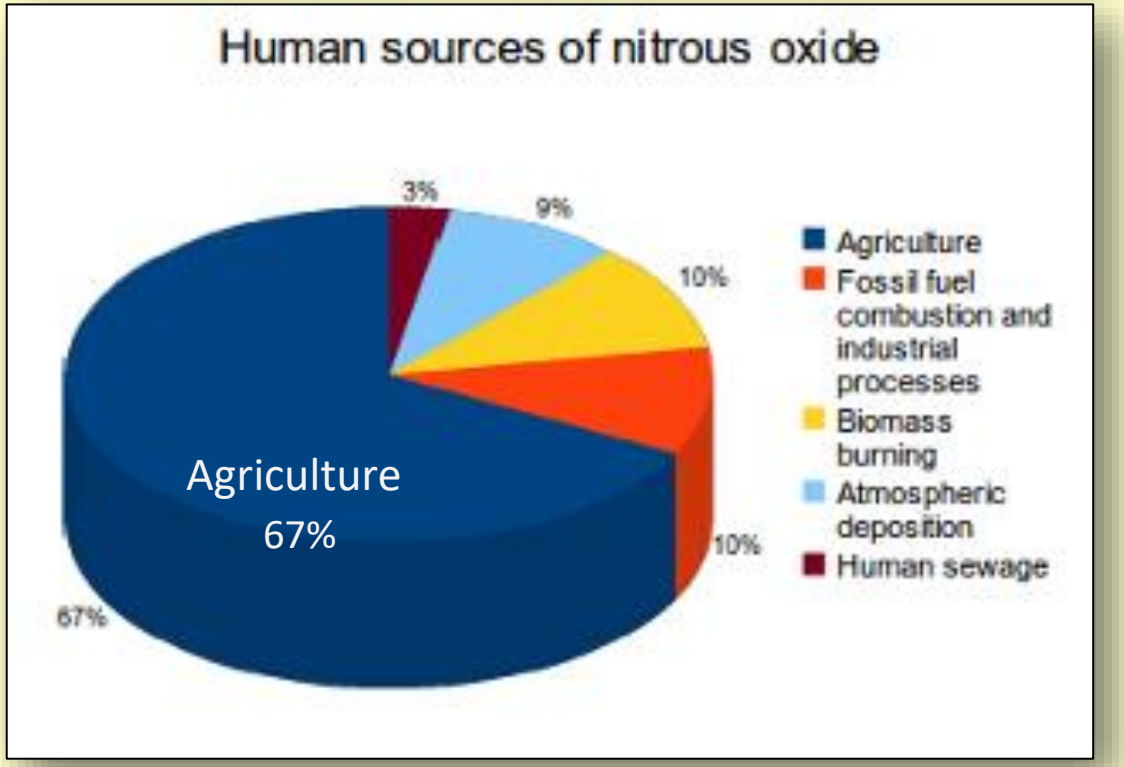


Greenhouse Gases

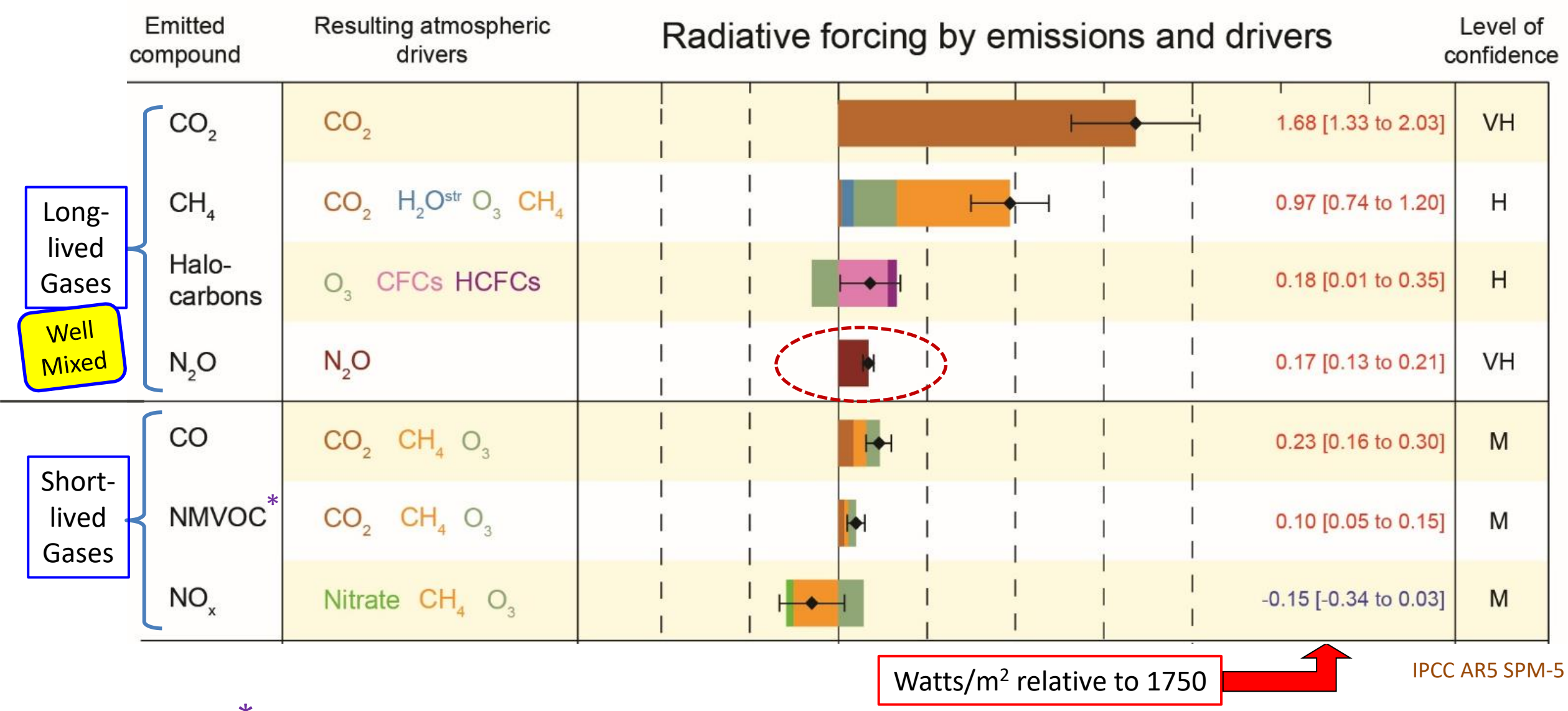
Nitrous Oxide N_2O



7.7 μm

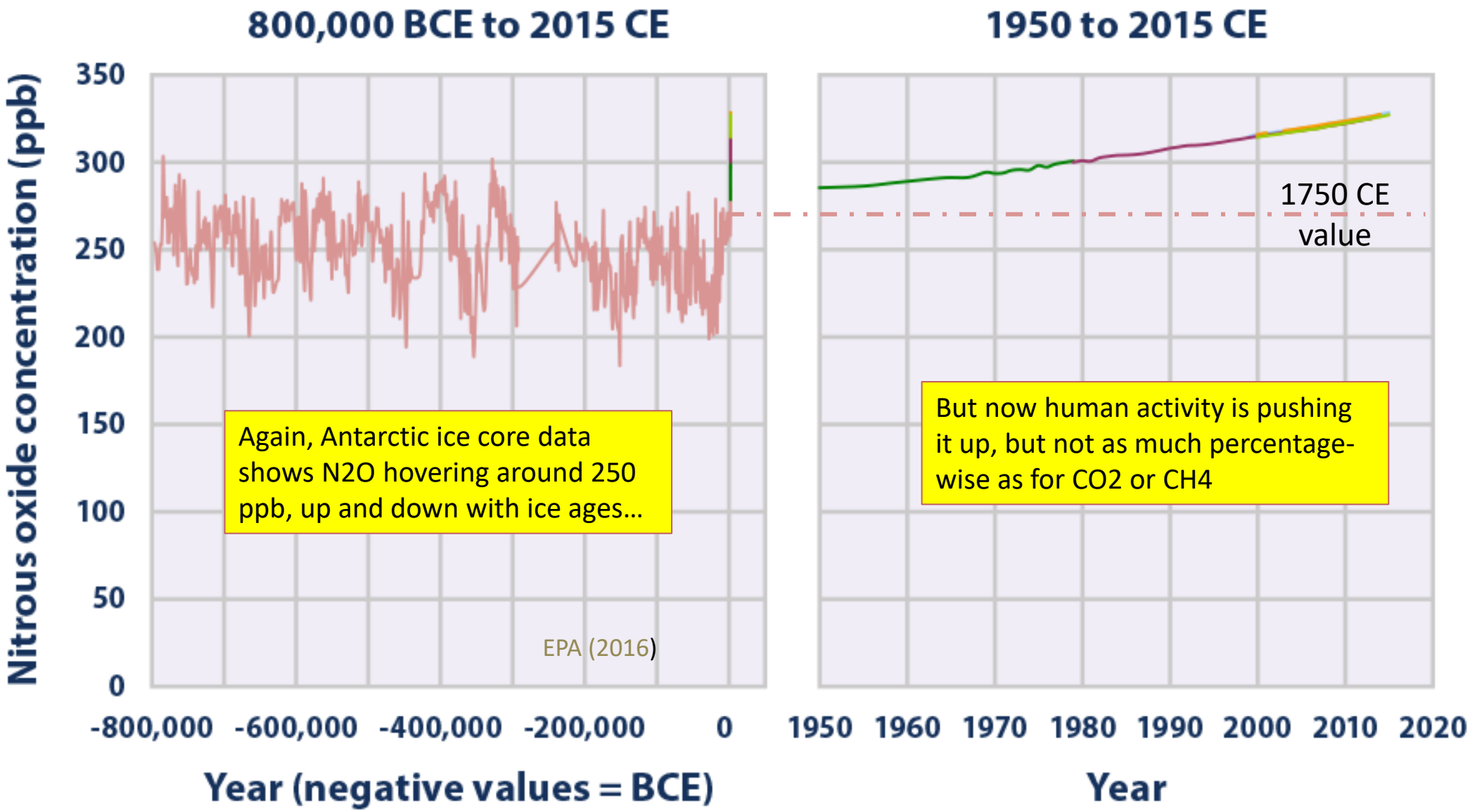


Greenhouse Gas Radiative Forcing as of 2011 (IPCC AR5)

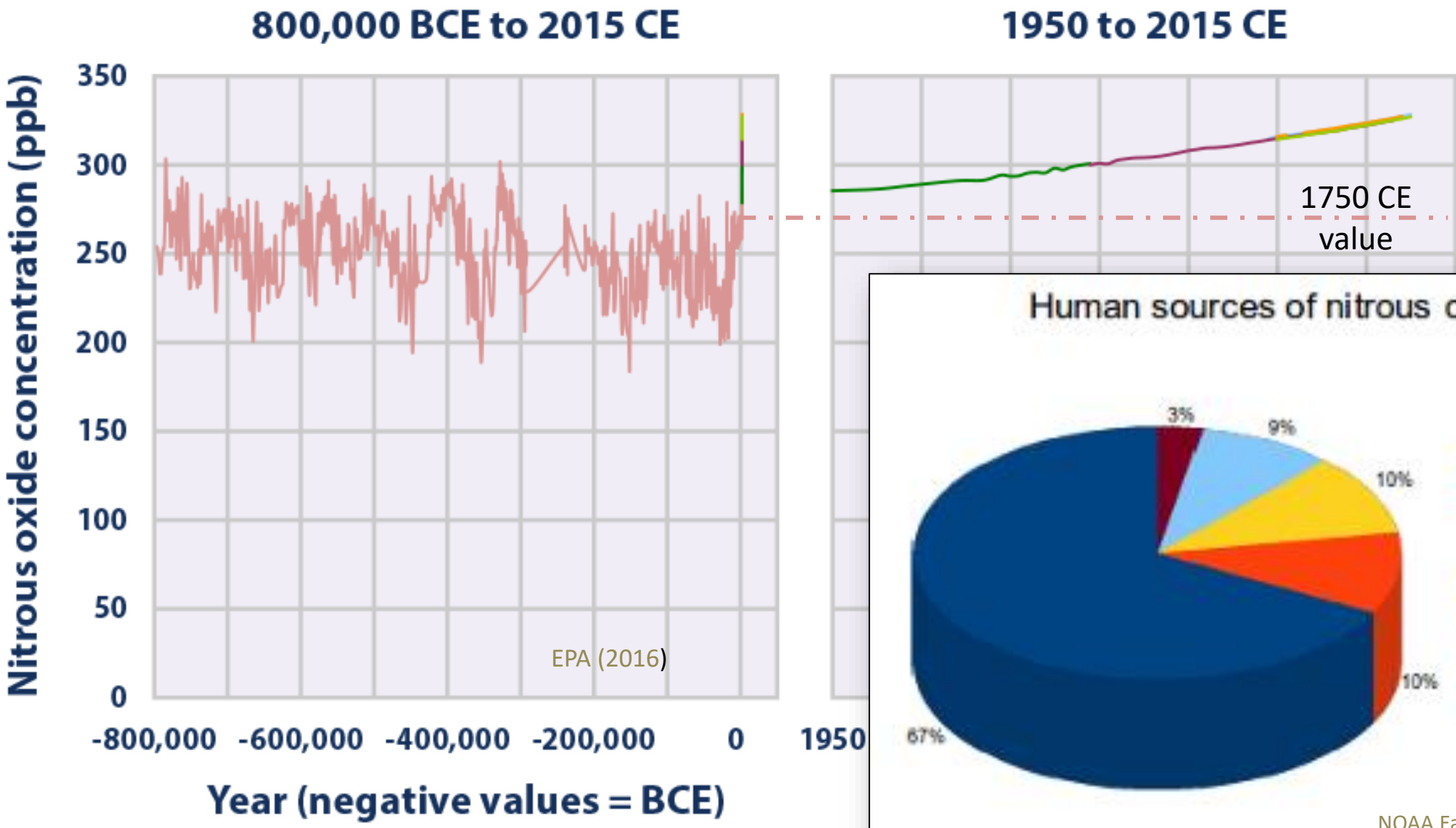


*Non-Methane VOC's
like Ethanol, Acetone, Formaldehyde

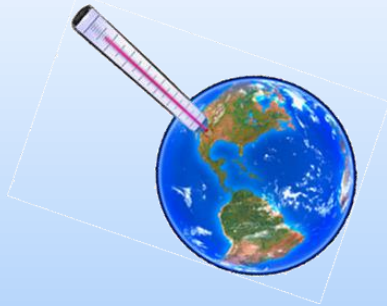
Global Atmospheric Concentrations of Nitrous Oxide Over Time



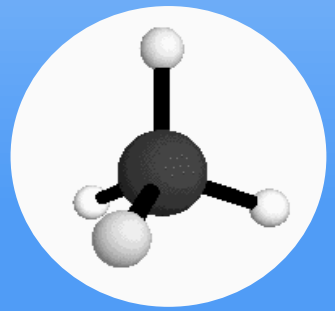
Global Atmospheric Concentrations of Nitrous Oxide Over Time



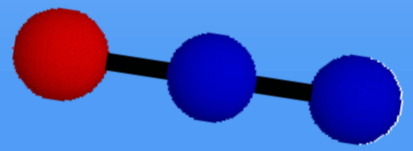
Questions about Other Greenhouse Gases?



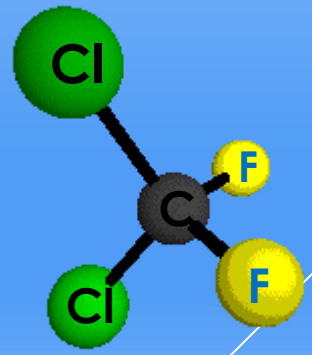
CH_4



N_2O



CFC's *etc.*



Course Outline

1. Building Blocks: Some important concepts
2. Our Goldilocks Earth: a Radiative Balancing Act
3. The Role of the Atmosphere: Greenhouse Gases & Clouds
4. Global Circulation and Dynamics of the Earth System:
   Oceans, Atmosphere, Biosphere, Cryosphere, People, Lithosphere
5. Natural Variability of the Climate, short and long term. Ice Ages
6. **Carbon Dioxide and other Greenhouse Gases:**
   Where do they come from, where do they go, how are they regulated?
7. Impacts and Future Projections for Global Warming -- Uncertainties
8. Amelioration Strategies. The Climate Debate. Policy Options.