

Climate/Energy: Acidification

TEAC8, <http://tinyurl.com/zprh78l> (2015) <http://tinyurl.com/hhlrd4o>

What we must know to prevent oceanic extinctions, on track to occur by 2050.



**“Let’s work the problem.
Let’s not make things worse by guessing.”**

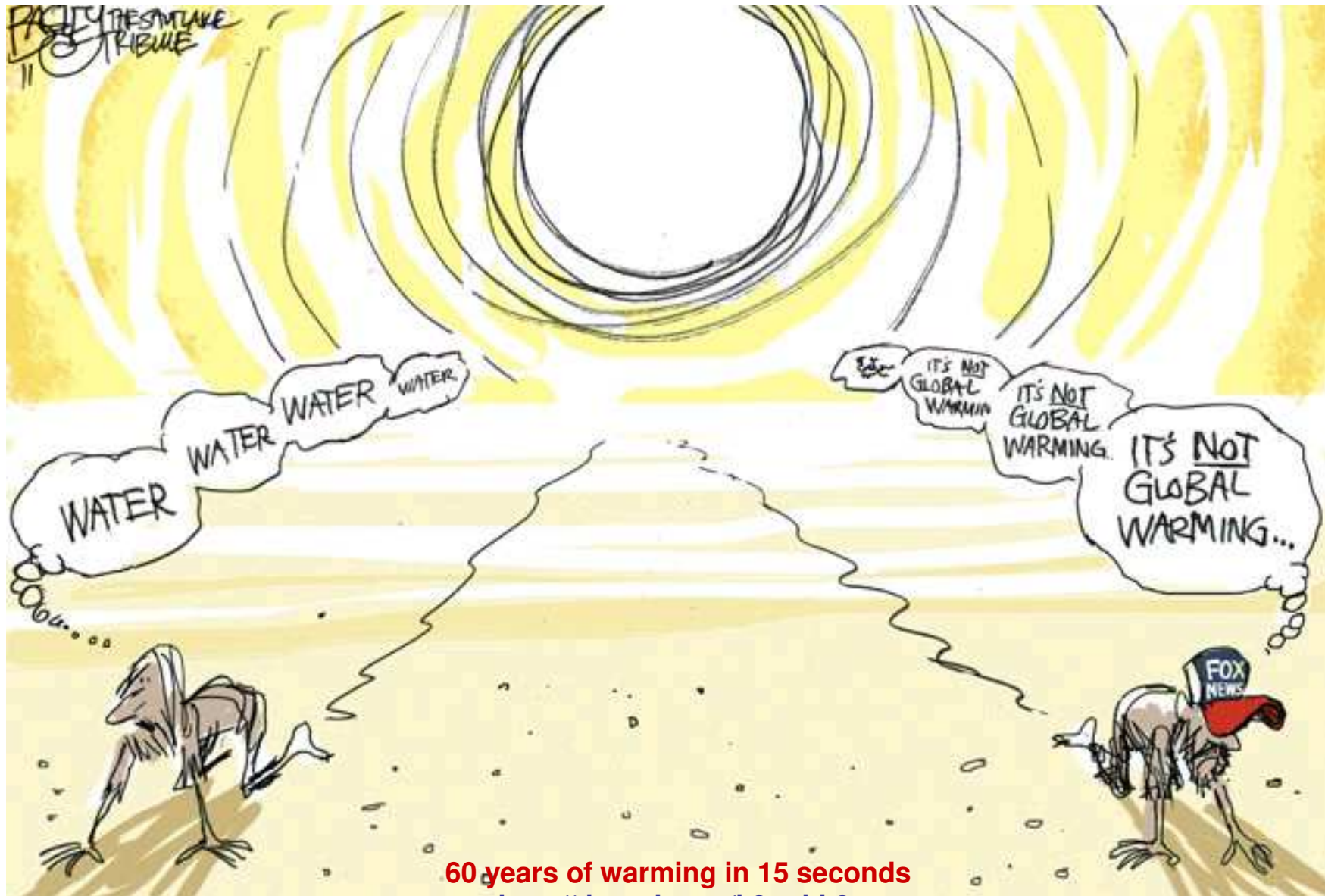


***Eugene Kranz,
Apollo 13
Flight Director,
April 1970.***



Dr. Alexander Cannara
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650-400-3071
17 Jan. 2018

Why Energy From Fire Must Go

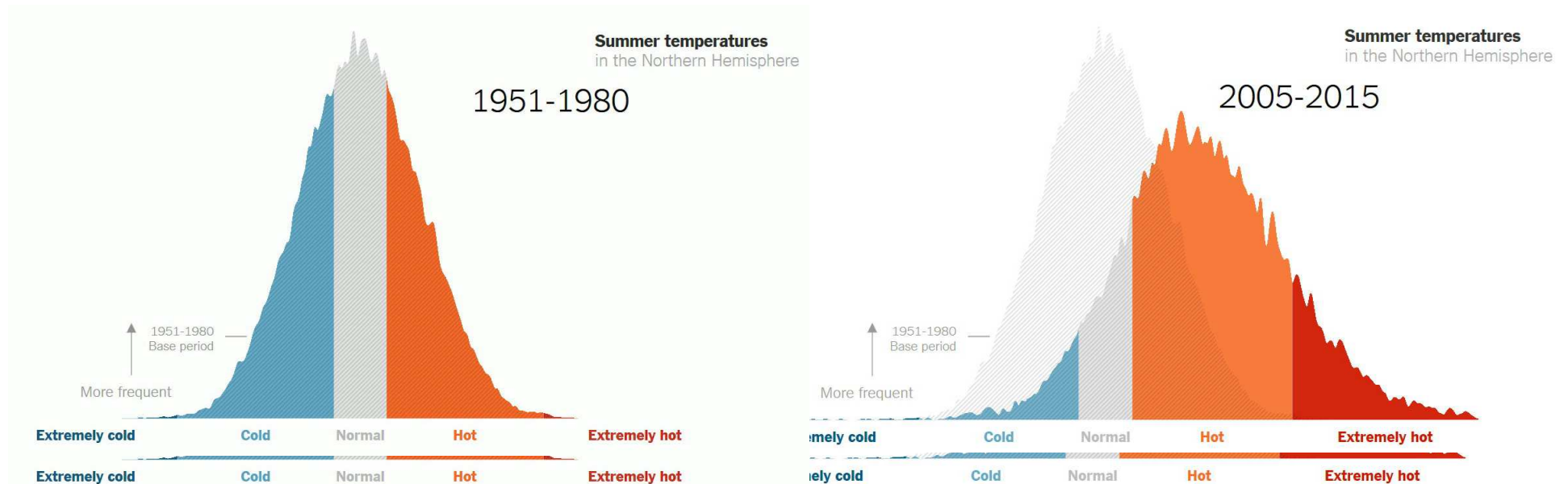


60 years of warming in 15 seconds

<http://tinyurl.com/k3guhk2>

Warming (1951-2015)

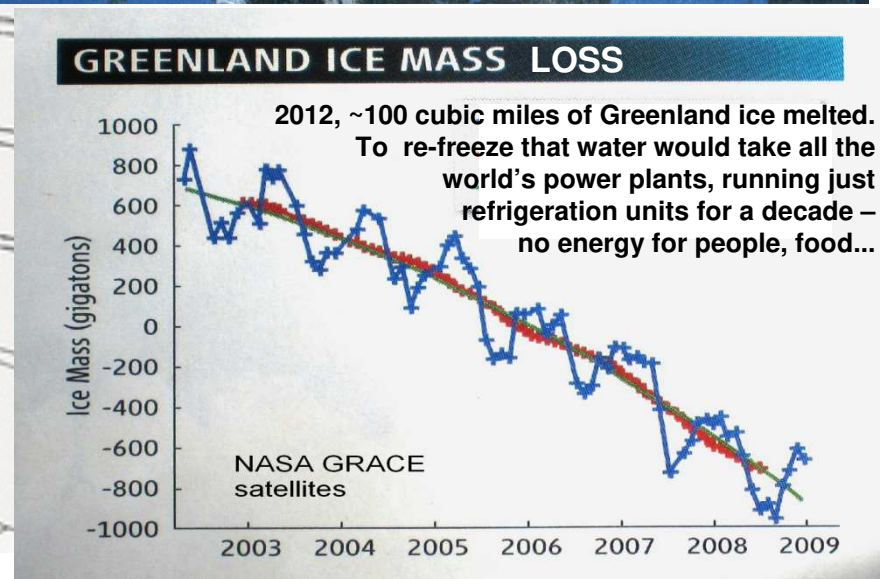
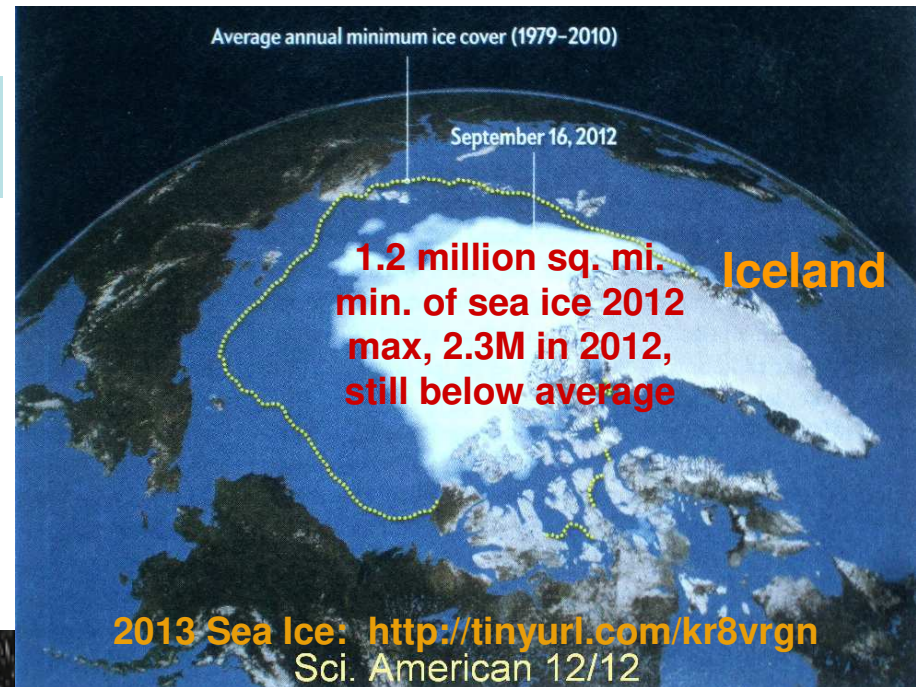
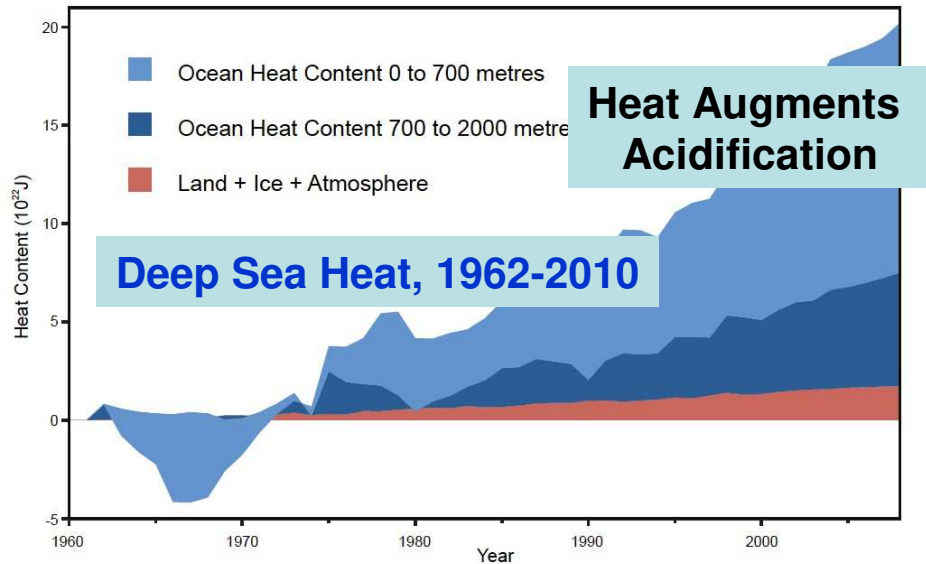
<http://tinyurl.com/yaaewjkm>
(note animation)



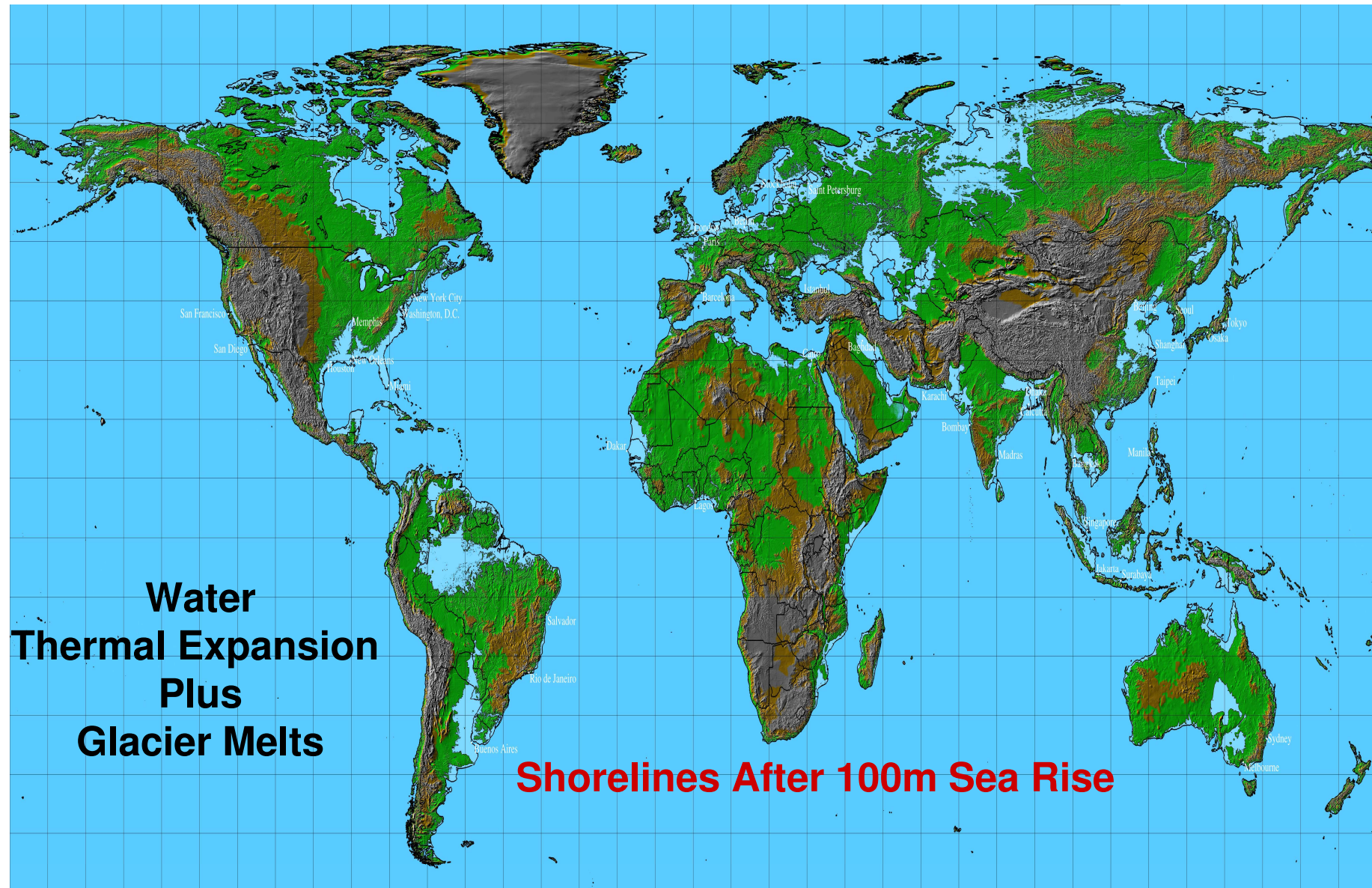
Extraordinarily hot summers (red), that were virtually unheard-of in the 1950s, have become commonplace.

Northern Hemisphere

Emissions Effects: Sea Warming

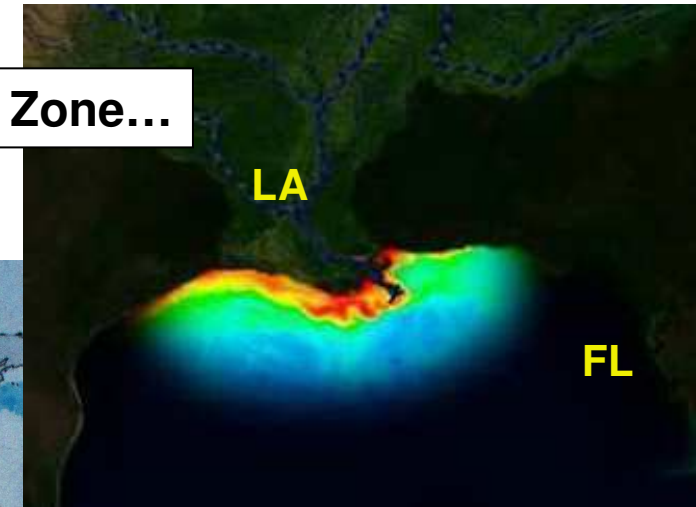
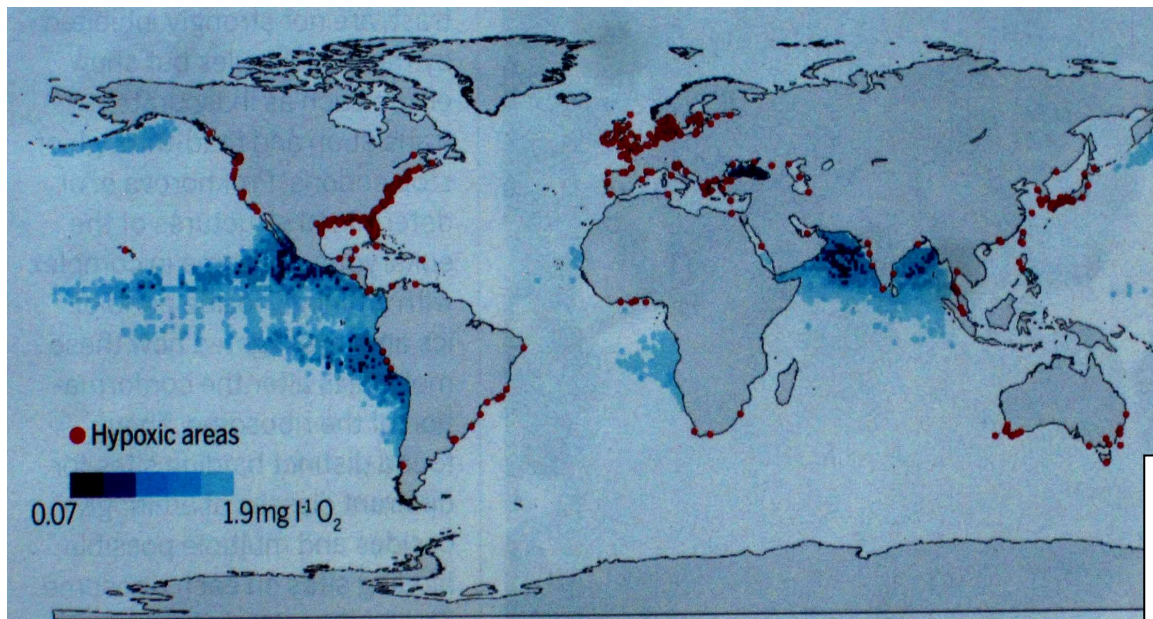


Warming => Sea Rise



Oceanic Oxygen Loss & Extinctions

Gulf of Mexico & Mississippi Dead Zone...



AAAS Science 5 Jan 2018 p46
and

<http://tinyurl.com/yd6mkoec>

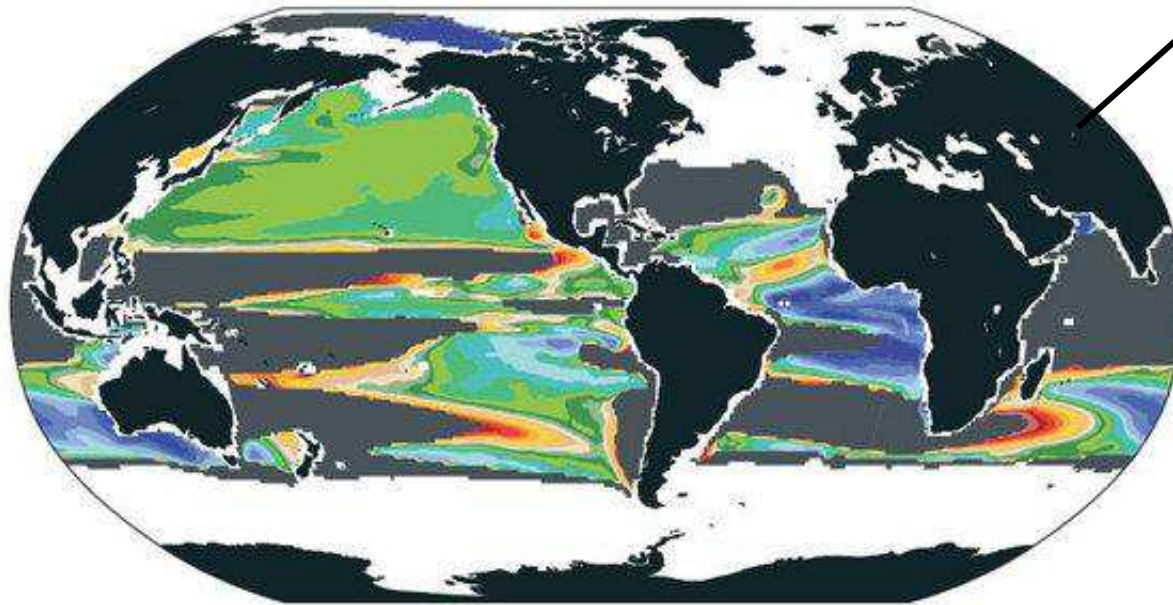
Low and declining oxygen levels in the open ocean and coastal waters affect processes ranging from biogeochemistry to food security. The global map indicates coastal sites where anthropogenic nutrients have exacerbated or caused O_2 declines to $<2 \text{ mg liter}^{-1}$ ($<63 \mu\text{mol liter}^{-1}$) (red dots), as well as ocean oxygen-minimum zones at 300 m of depth (blue shaded regions). [Map created from data provided by R. Diaz, updated by members of the GO₂NE network, and downloaded from the World Ocean Atlas 2009].

Oceanic Oxygen Loss & Extinctions

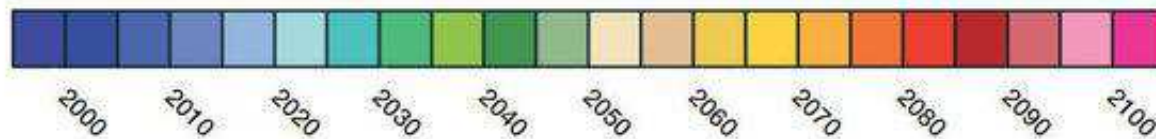
Oxygen loss in the oceans

Timeframe when ocean deoxygenation due to climate change is expected to become detectable

<http://tinyurl.com/z8dahhk>



Dark gray = unaffected until 2100+



Likely detection dates

Fluvial chemical threats: <http://tinyurl.com/yd6mkoec> and...
“A short history of ocean acidification science in the 20th century:
a chemist’s view”, P. Brewer, 2013, www.biogeosciences.net/10/7411/2013/

Warming/Acidification Warnings

- Tyndall & Chamberlin (1800s)...

- www.aip.org/history/climate/co2.htm

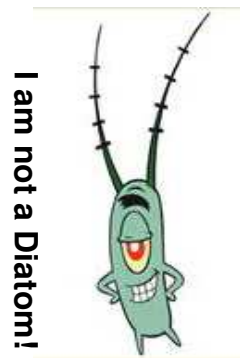
- <https://theconversation.com/life-on-earth-was-nothing-but-slime-for-a-boring-billion-years-23358>

- “How Oxygen Stifled Animal’s Emergence”, AAAS Science, 31 Oct. 2014, p537.

While Each CO₂ Molecule Stays in Air, It Heats Air ~100,000 Times More Than The Energy Released When Its C Was Burned

- Arrhenius (1896, 1905)...

CO₂ + H₂O => H₂CO₃ = Carbonic Acid



*On the Influence of Carbonic Acid
in the Air upon the Temperature of
the Ground*

Svante Arrhenius

Philosophical Magazine and Journal of Science
Series 5, Volume 41, April 1896, pages 237-276.

LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[FIFTH SERIES.]

APRIL 1896.

XXXI. *On the Influence of Carbonic Acid in the Air upon the Temperature of the Ground.* By Prof. SVANTE ARRHENIUS *.

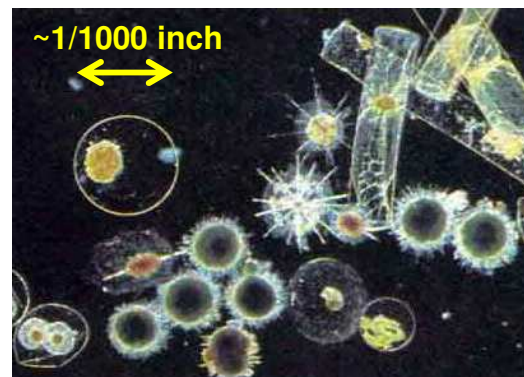
I. Introduction : Observations of Langley on Atmospheric Absorption.

A GREAT deal has been written on the influence of the absorption of the atmosphere upon the climate. Tyndall† in particular has pointed out the enormous importance of this question. To him it was chiefly the diurnal and annual variations of the temperature that were lessened by this circumstance. Another side of the question, that has long attracted the attention of physicists, is this: Is the mean temperature of the ground in any way influenced by the presence of heat-absorbing gases in the atmosphere? Fourier‡ maintained that the atmosphere acts like the glass of a hot-house, because it lets through the light rays of the sun but retains the dark rays from the ground. This idea was elaborated by Pouillet§; and Langley was by some of his researches led to the view, that “the temperature of the earth under direct sunshine, even though our atmosphere were present as now, would probably fall to –200° C., if that atmosphere did not possess the quality of selective

“Carbonic Acid” is what CO₂ makes when combined with water – soda pop.

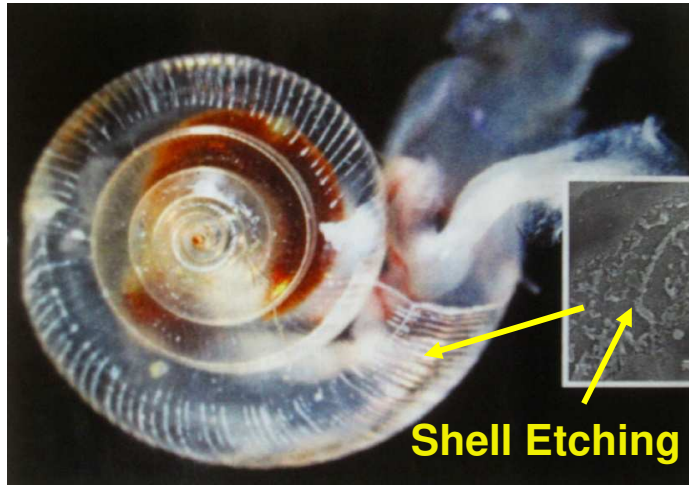
Since seas dissolve CO₂ well, they become more acidic every year we overload the natural Carbon Cycle (among plants, air, water & land) by burning fossil Carbon compounds made millions of years ago by plants, especially ocean Plankton...

Plankton are the initial prey for almost all fish larvae. Their Carbonate shells sink when they die, removing Carbon to sea floors & they make most of our Oxygen.



Acidification

"Lethal Seas" -- PBS Nova 2015



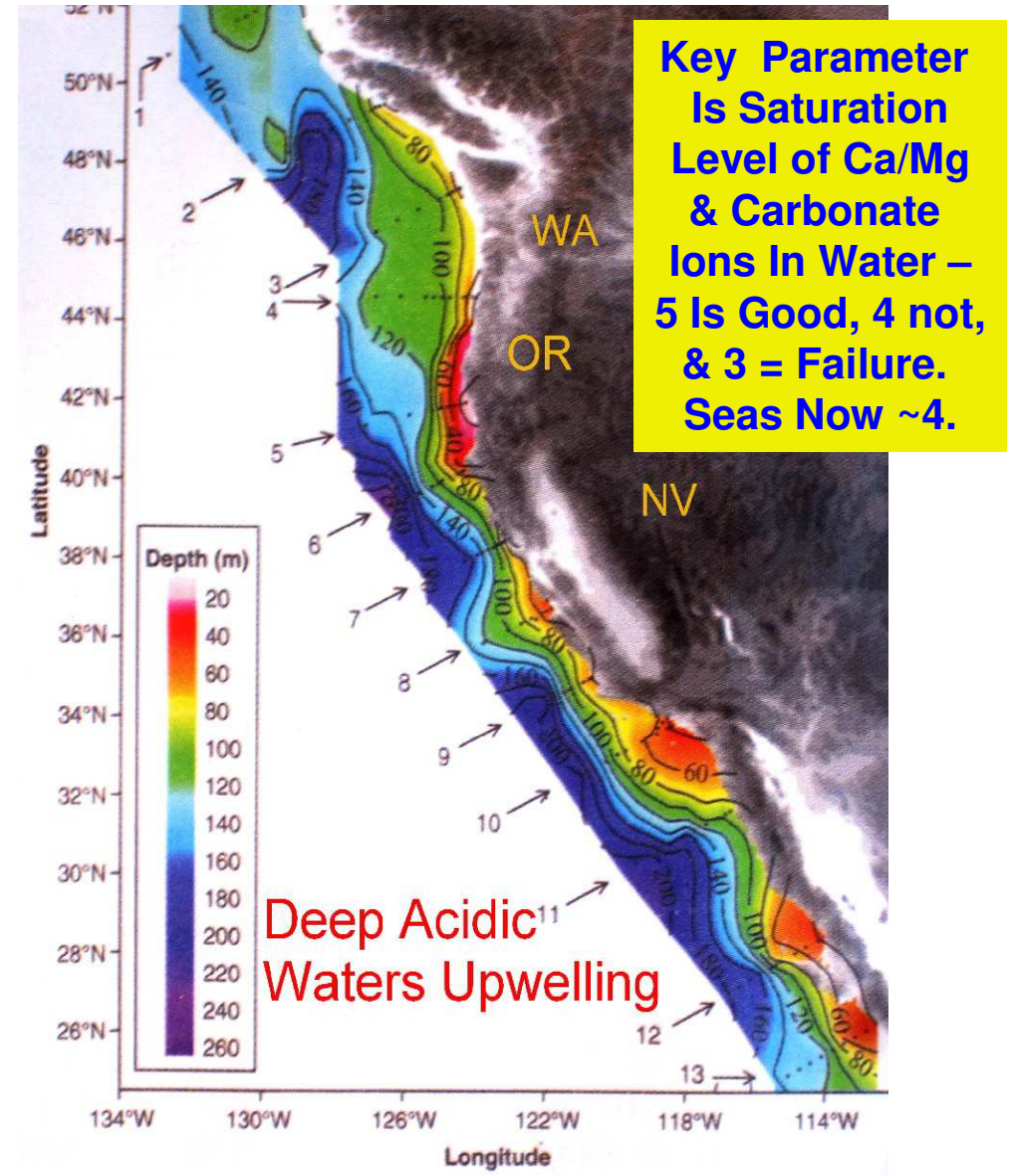
AAAS Science, Vol 344, 9 May 2014, p569

Oyster Stress, <http://tinyurl.com/lqrj5v7>
<http://tinyurl.com/pfjc4ud>



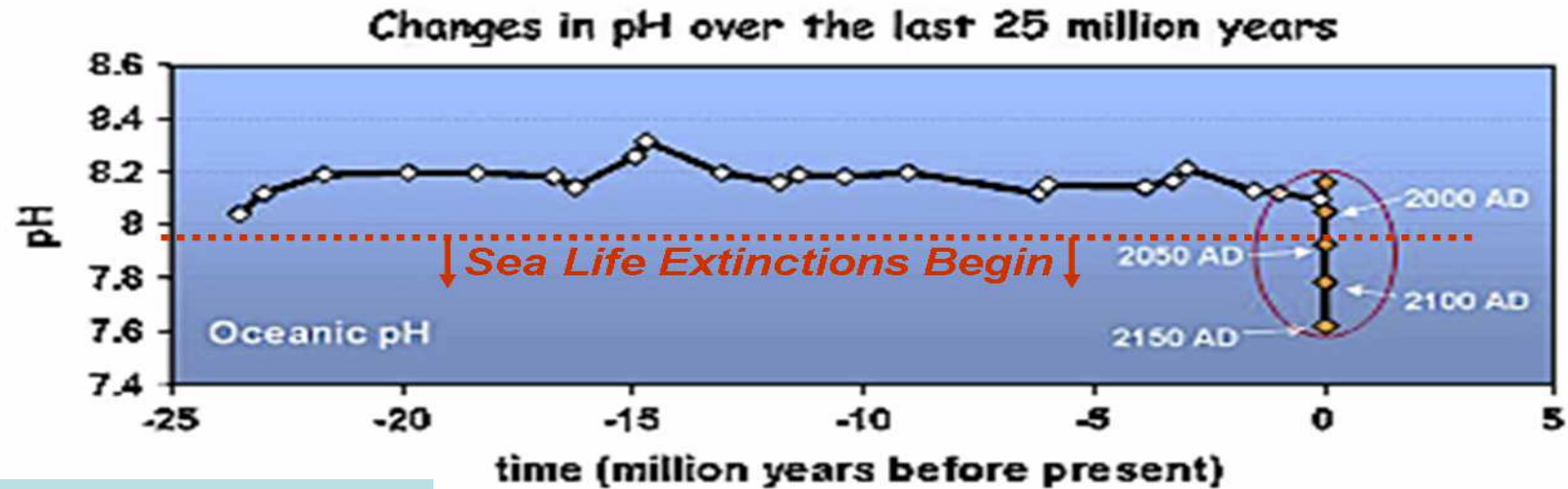
Also see April 2013 Scientific American

www.tos.org/oceanography/archive/22-4_kump.html



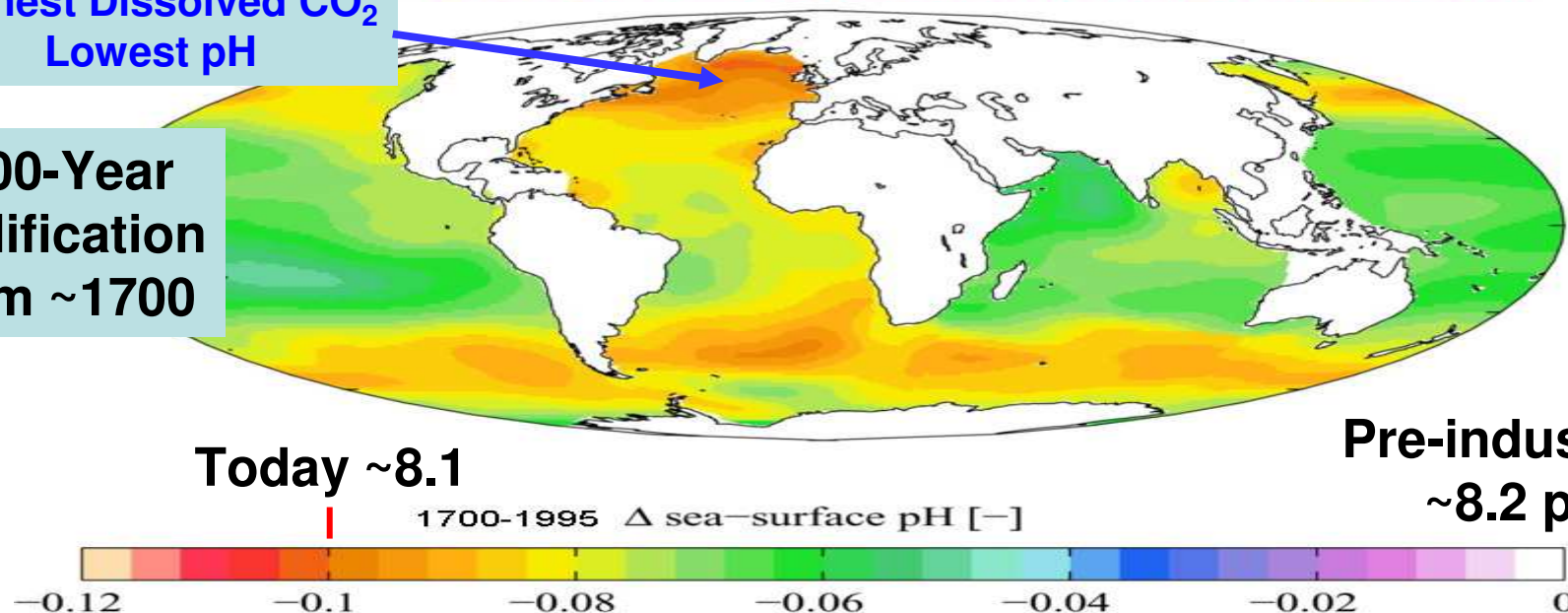
Emissions Effects: Sea Chemistry

Oceans are Acidifying Fast -- Ceasing All CO₂ Emissions Has Little Effect



Highest Dissolved CO₂
Lowest pH

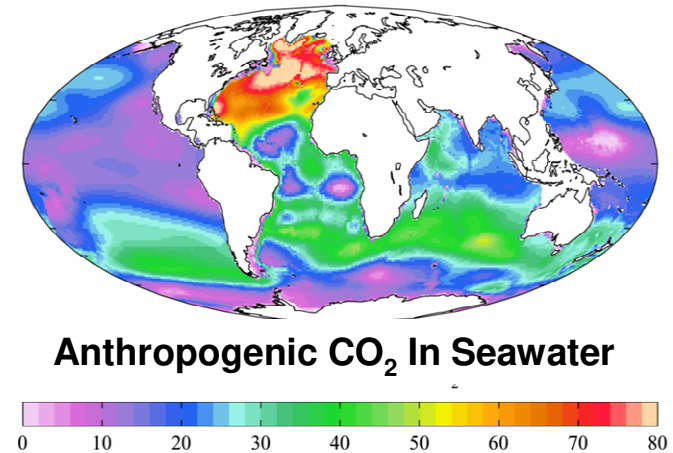
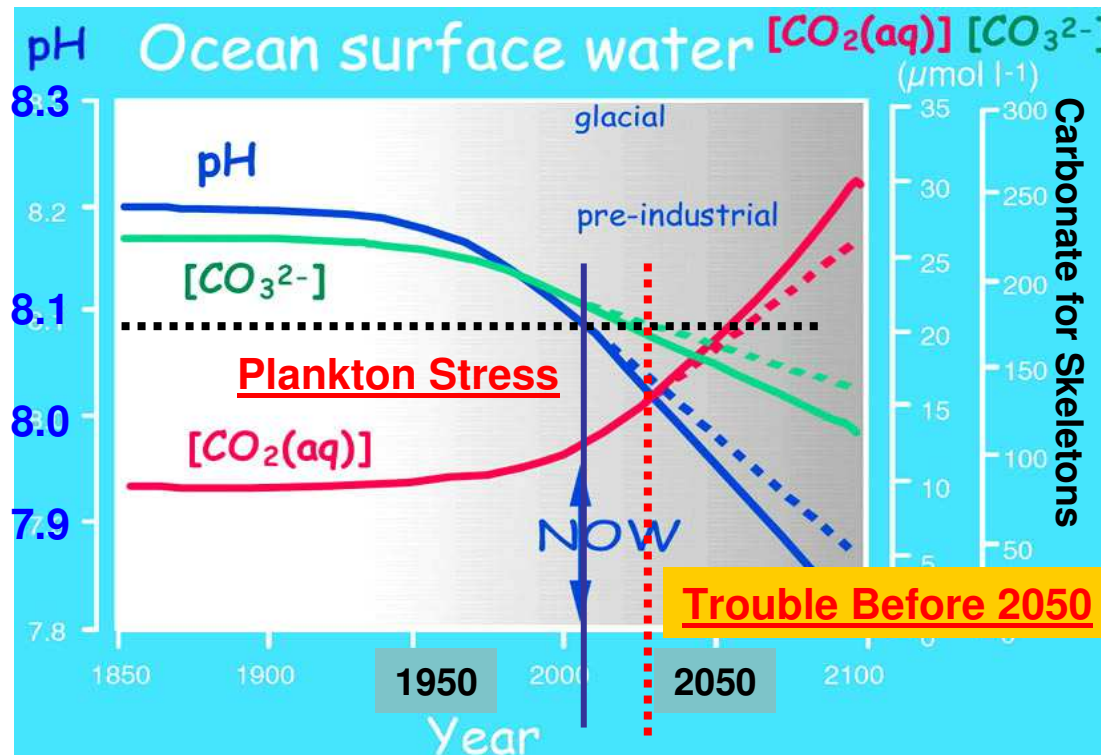
~300-Year
Acidification
From ~1700



Acidification & Extinctions

~30% of all ~1.5 trillion tons of CO₂ emissions are now in oceans creating less alkaline seawater, affecting entire sea food chains -- sea life provides ~20% of all human food protein – “The Sixth Extinction” by Kolbert 2014

www.kqed.org/a/forum/R201405260900



Anthropogenic CO₂ In Seawater



Deformed Larvae

Normal Larvae:

Warmer, acidifying North Atlantic

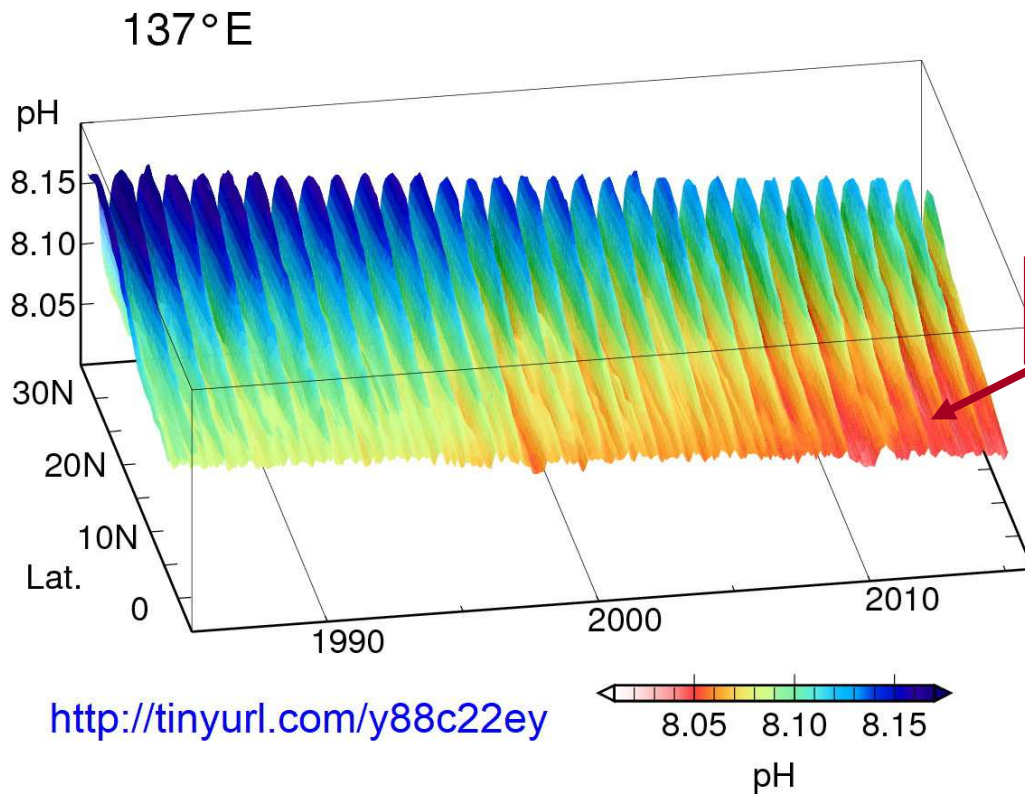
www.ocean-acidification.net/

<http://tinyurl.com/6mtd8db>

www.noaa.gov/video/administrator/acidification/index.html

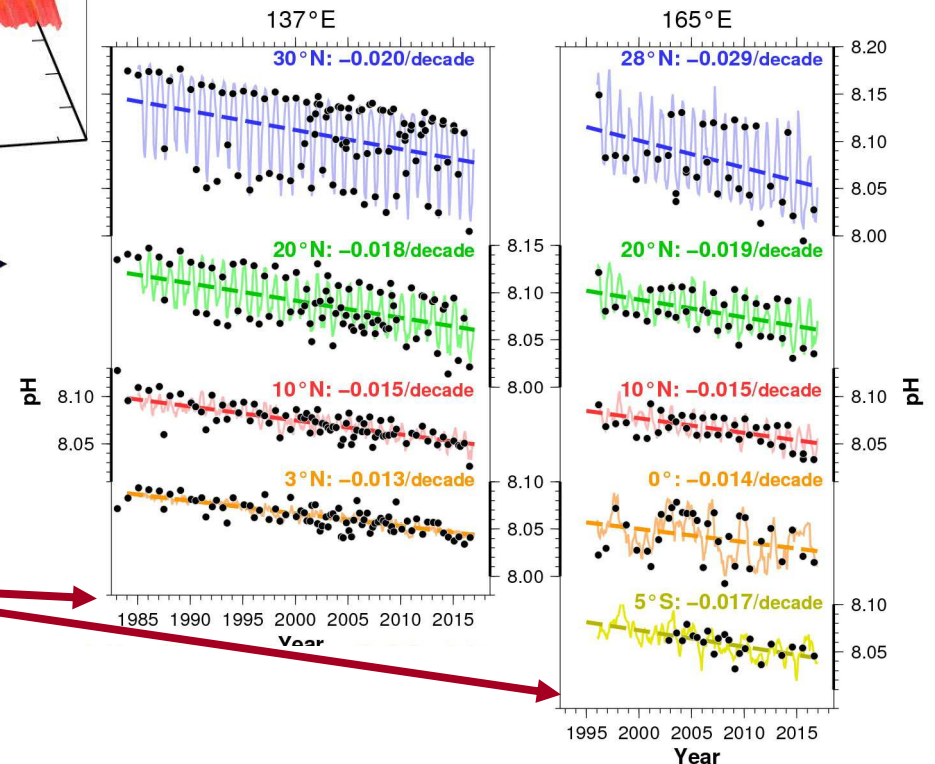
www.bbc.co.uk/news/science-environment-18938002

Western Pacific pH 1986-2016



Extinctions Below 8.0pH

Extinctions Below 8.0pH



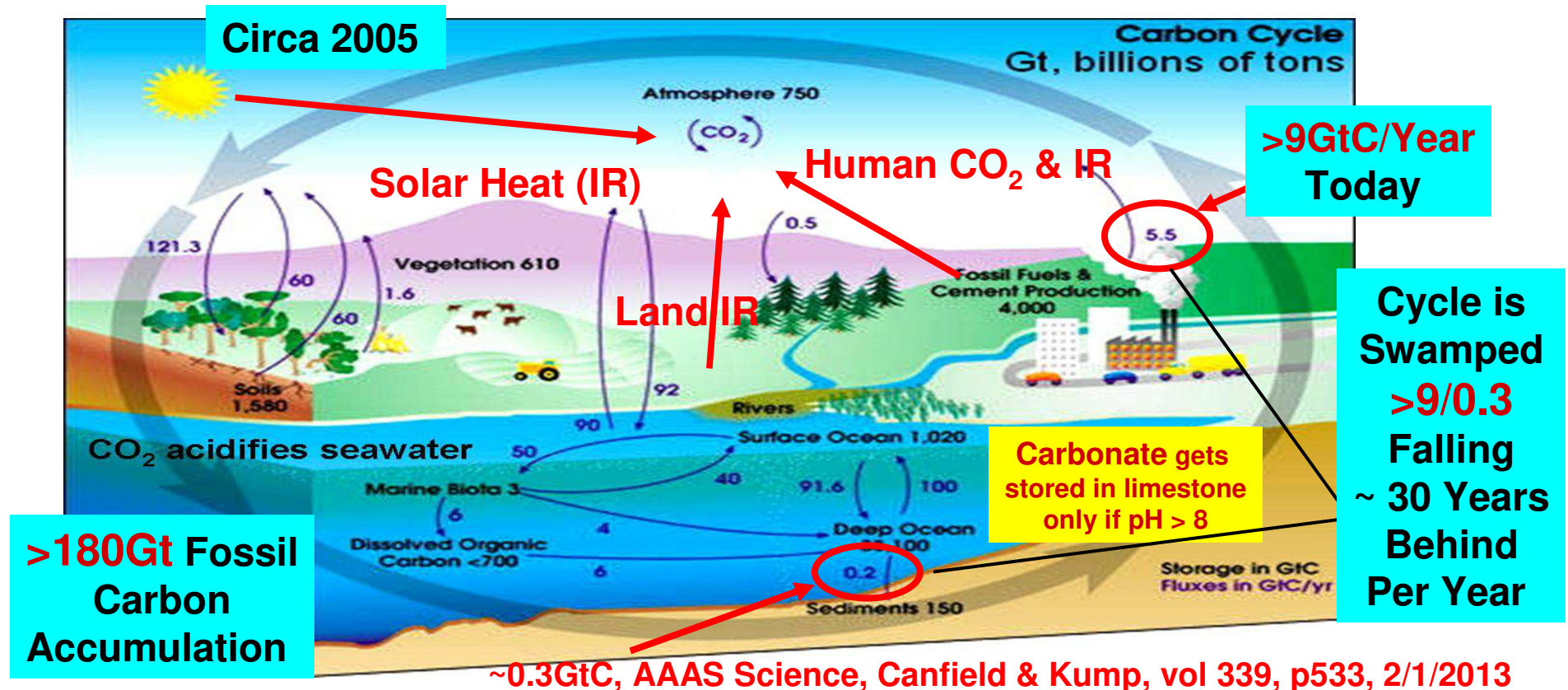
Acidification & Remediation (**3 Numbers**)

Cyanobacteria, plankton & algae produced most of the Oxygen we have to breathe & use, starting >2 billion years ago, with earliest photosynthesizing ocean life. Land plants later evolved & helped. All fossil fuels we dig up were made from plant decay. Carbon emissions today are **>9GtC** (>30Gt CO₂)

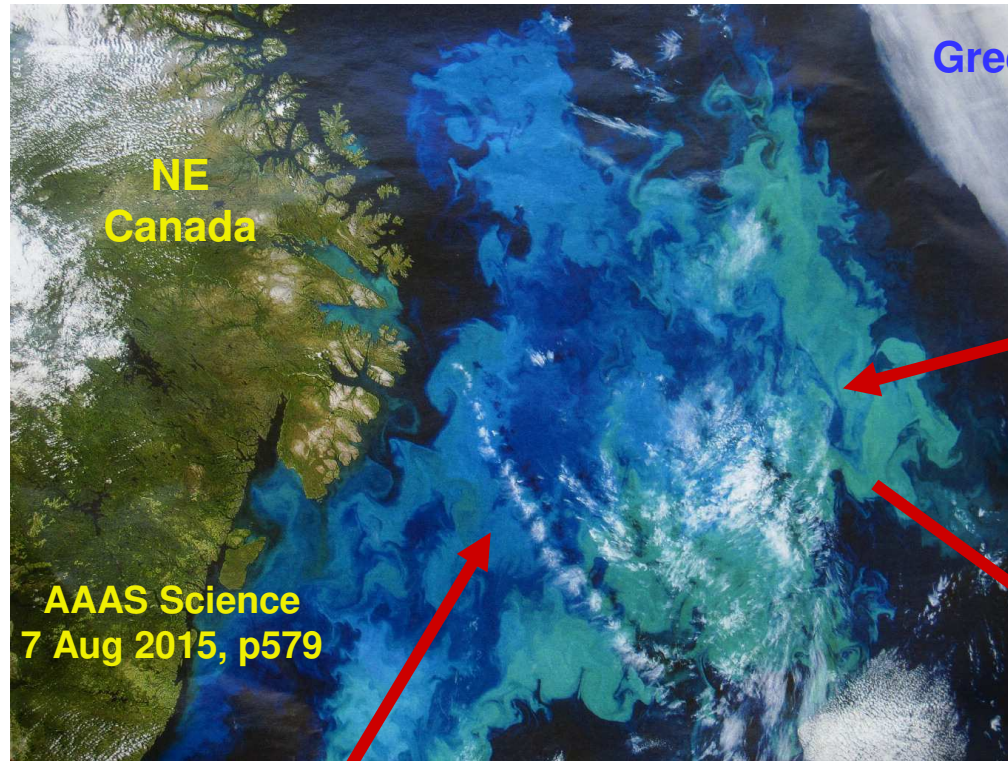
www.ocean-acidification.net

www.atmo.arizona.edu/courses/fall07/atmo551a/pdf/CarbonCycle.pdf

www.annualreviews.org/doi/abs/10.1146/annurev.earth.031208.100206?journalCode=earth

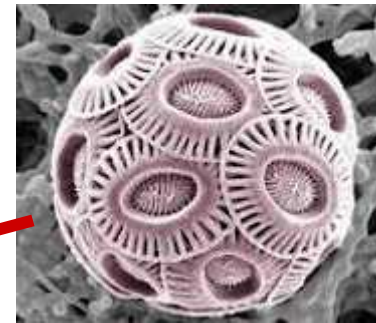


Emissions Effects: Algal Blooms



Greenland

~0.000001 Meter



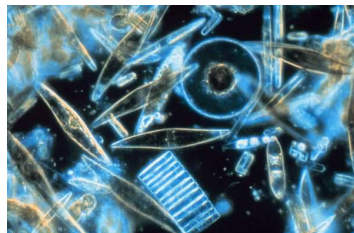
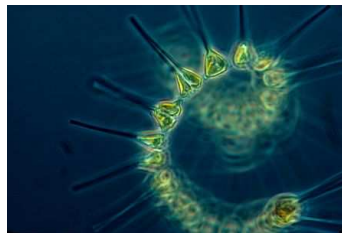
Coccolith:
Calcite Shields
Around Single
Algal Cell of
*Emiliania
Huxleyi*

<https://en.wikipedia.org/wiki/Coccolith>

AAAS Science
7 Aug 2015, p579

Ocean Food Chain:
Sun & Plankton
to Krill, Fish,
Whales, Birds;
pH >8.0

Arctic Algae Blooms 2015

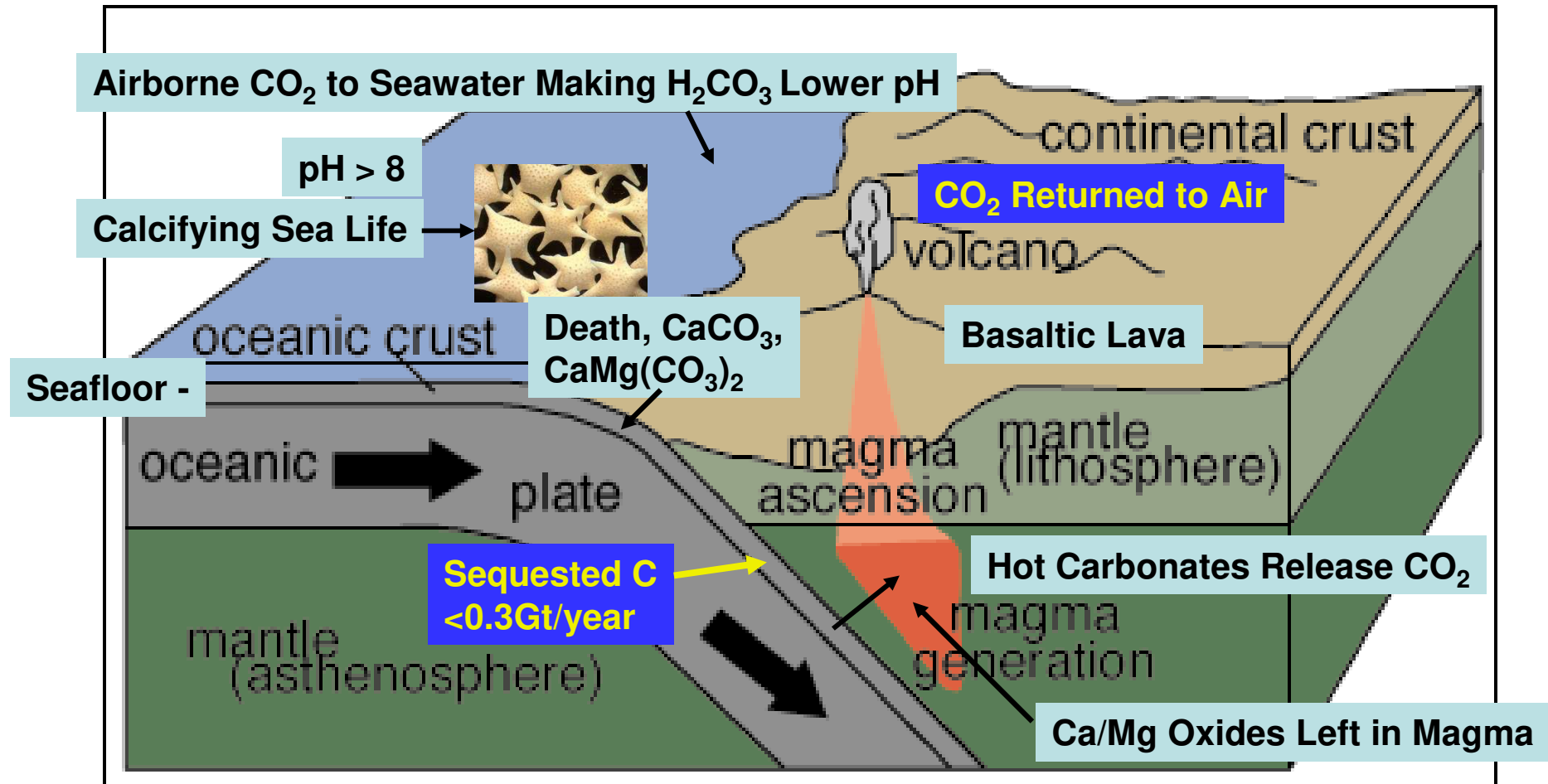


<https://en.wikipedia.org/wiki/Phytoplankton>

The hexacoel
observed humpback
whales engaging in
"bubble-net feeding."



Seafloor C Sequestration/Subduction



Subduction Animation...

http://earthguide.ucsd.edu/eoc/teachers/t_tectonics/p_subduction.html

Lime Cycle & Cement Making

Possible CO₂ Sequestration to Basalt

Sodium aluminate: NaAlO_2 , Na_5AlO_4 , $\text{Na}_7\text{Al}_3\text{O}_8$...
Tricalcium aluminate: $\text{Ca}_3\text{Al}_2\text{O}_6$ plus many possible mixed oxides with B, Be, Mg...

750g

Limestone (750gr)

Silica (150gr)

Aluminate (50gr)

Iron (50gr)

1
Grind and carefully mix the ingredients.

1kg

48%)

CO₂ 360g

2
~300kWhr/ton
~1500C

4 Add 50 g of gypsum

Gypsum
 $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

3
Cool rapidly

640g

5
Grind the mixture into a fine powder.

690g

6
Cement

This will give you 690 g Portland cement. Store in dry conditions until ready for use.

CO₂

Carbonated

Limestone
 CaCO_3

Heated

Slaked lime
 $\text{Ca}(\text{OH})_2$

Quicklime
 CaO

Water added

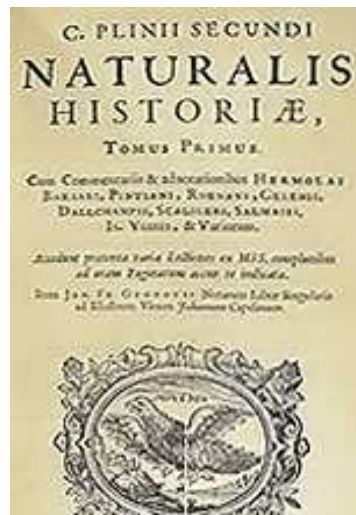
Wikipedia

**CaO Yield = 390/750
= 52% (no additives)
~5000 tons/day/plant**

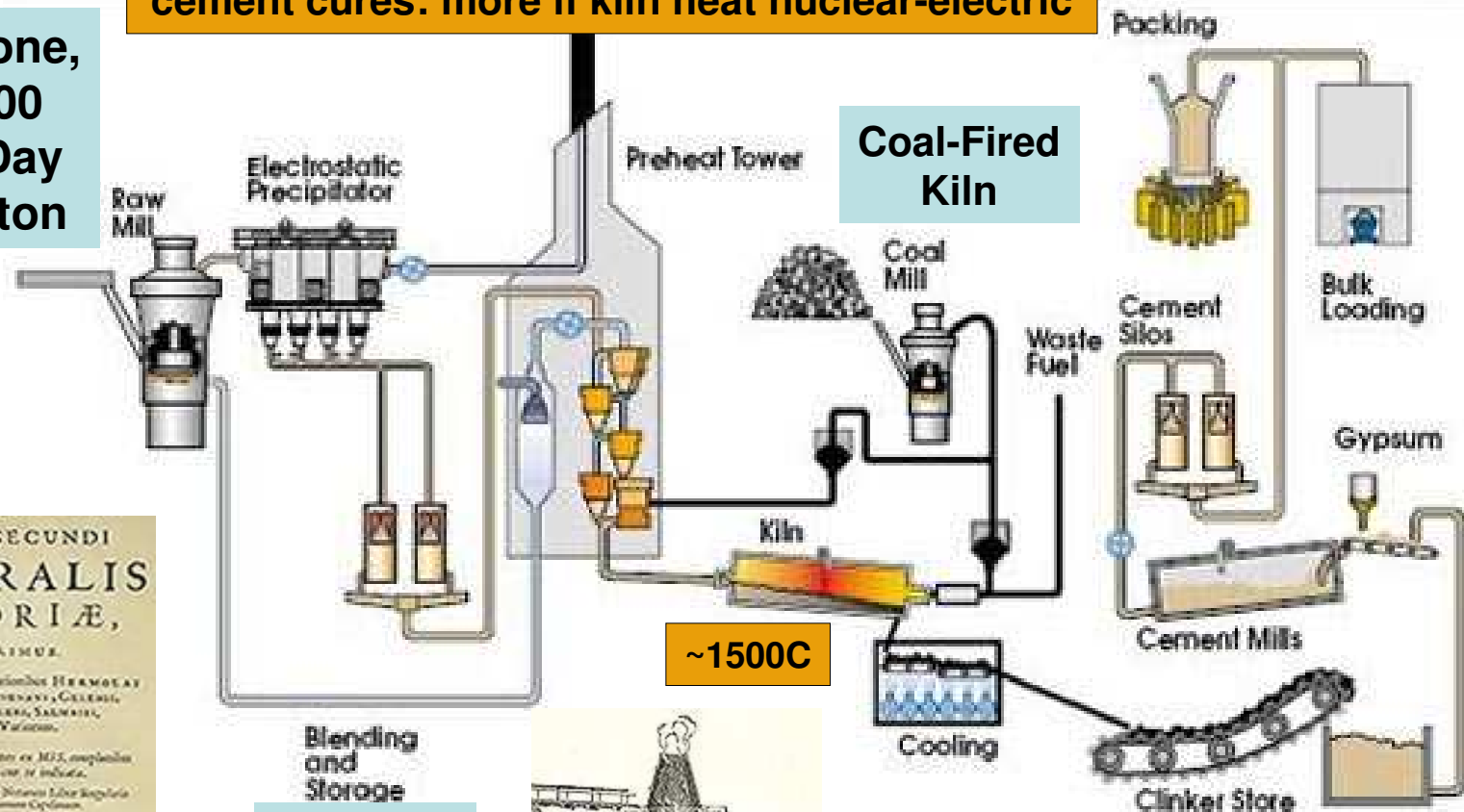
Cement Making

CO₂ exhaust, ~40% removed from air as cement cures: more if kiln heat nuclear-electric

Limestone,
~10,000
Tons/Day
@1GJ/ton



Pliny The Eklder ~50ce



Blending
and
Storage
Additives

Chatellier Kiln 1896

Wikipedia

Lime

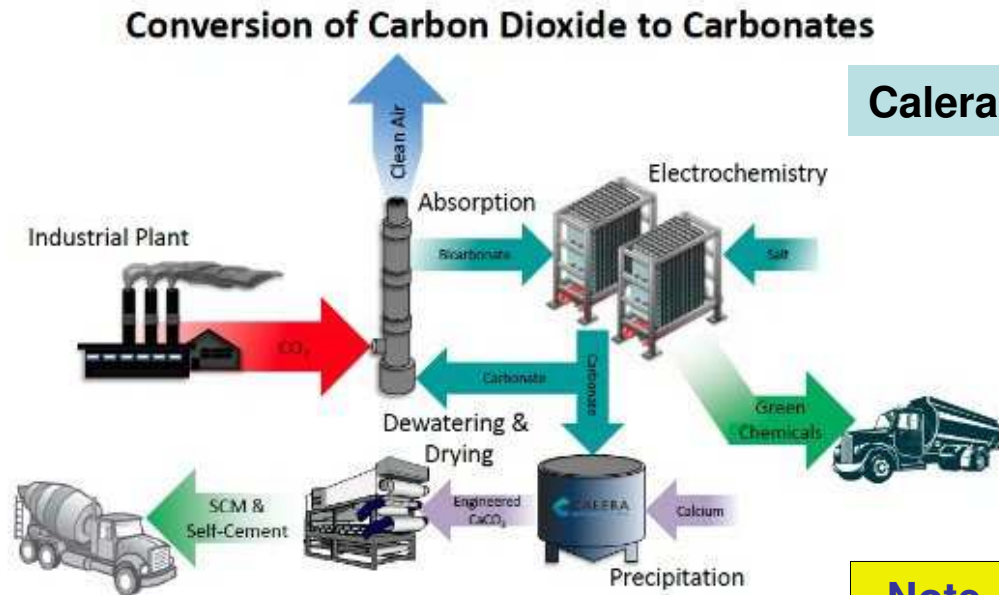


Fire

**Lime + Additives,
~5000 Tons/Day**

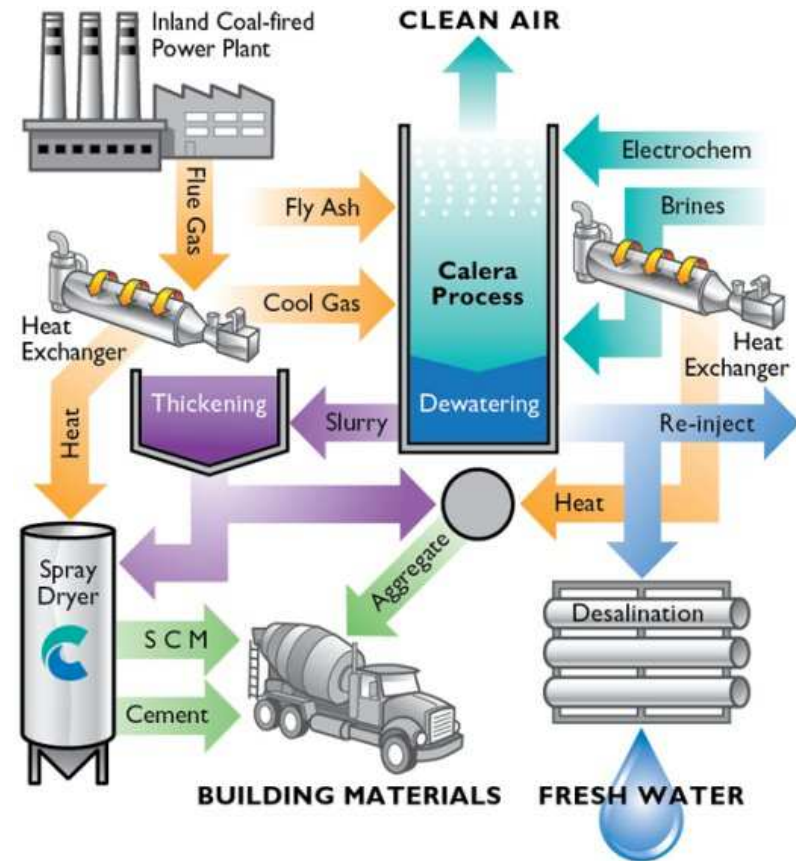
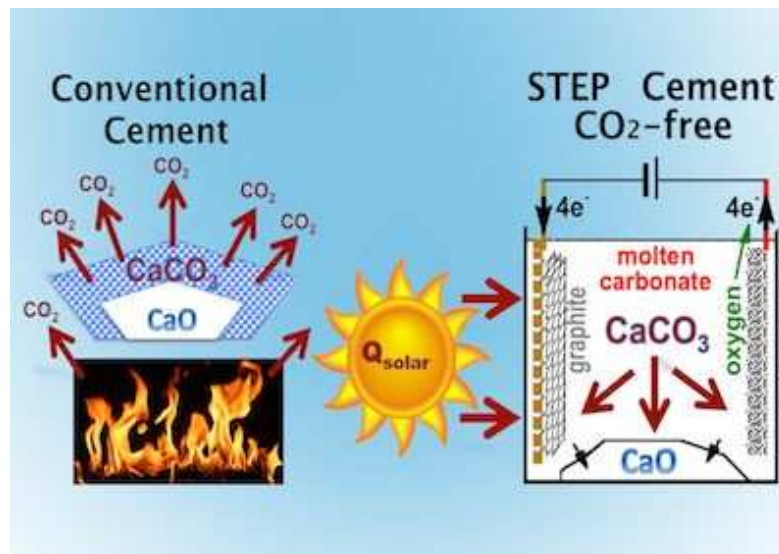
Reactions between Ca and Silicate compounds form the primary constituents of cement (calcium silicate). Material reaching the lower part of the kiln takes the shape of a clinker.

Alternative Cement Making



Calera

**Note
All
Power
Inputs**



**Electrolytic
Carbon & Lime
Precipitation
 $T > 600^\circ\text{C}$**

**Calera Process Needs
Additives for Strength
But Yields Clean Water**

Cement Making

Typical Cement Plant



Flooded German Plant

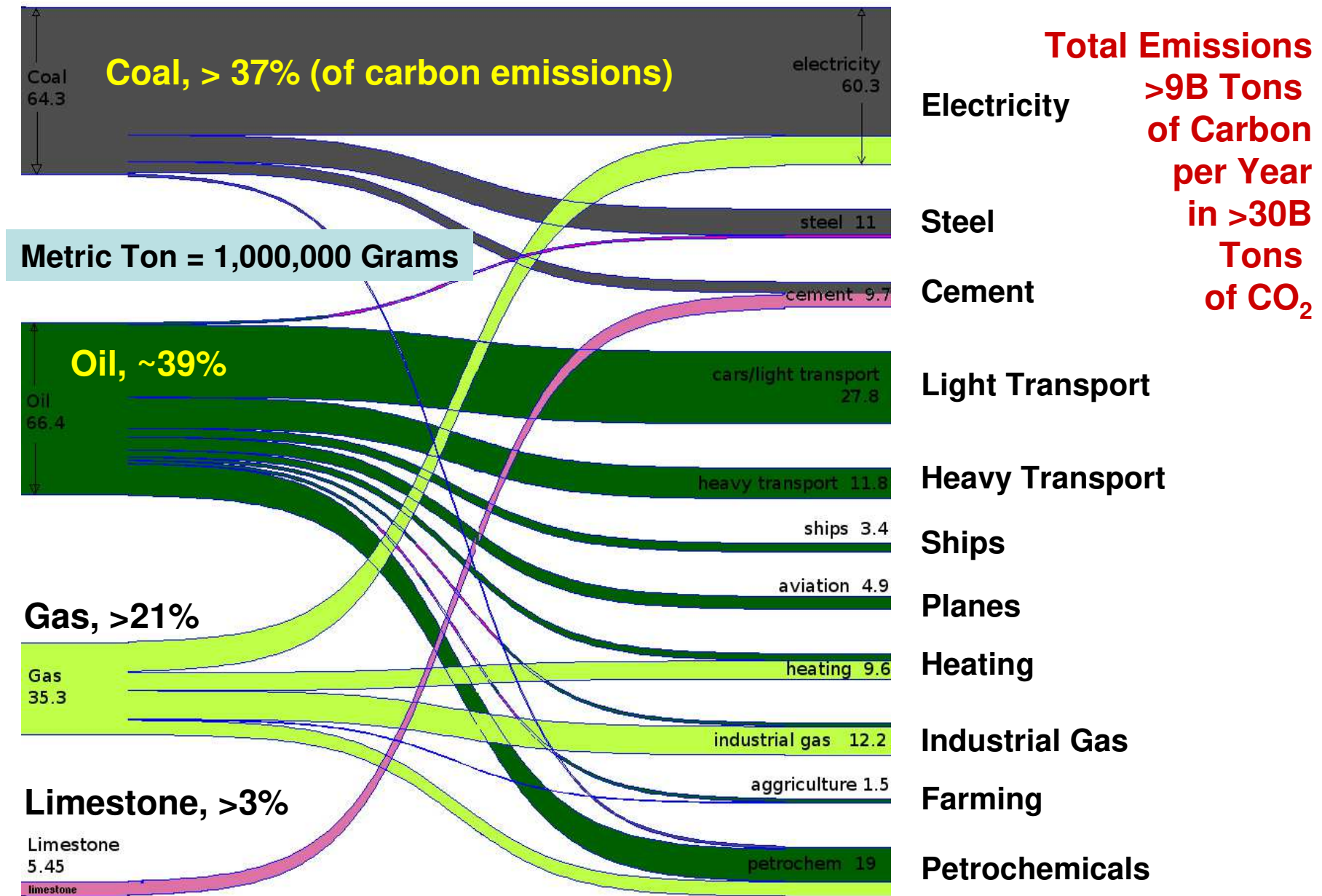


Typical Kiln Is ~150ft Long & Several Feet in Diameter, Lined Inside With Refractory Brick. Final Lime Conversion Occurs in the Last (Lowest & Hottest) Several Feet.

Typical Kiln



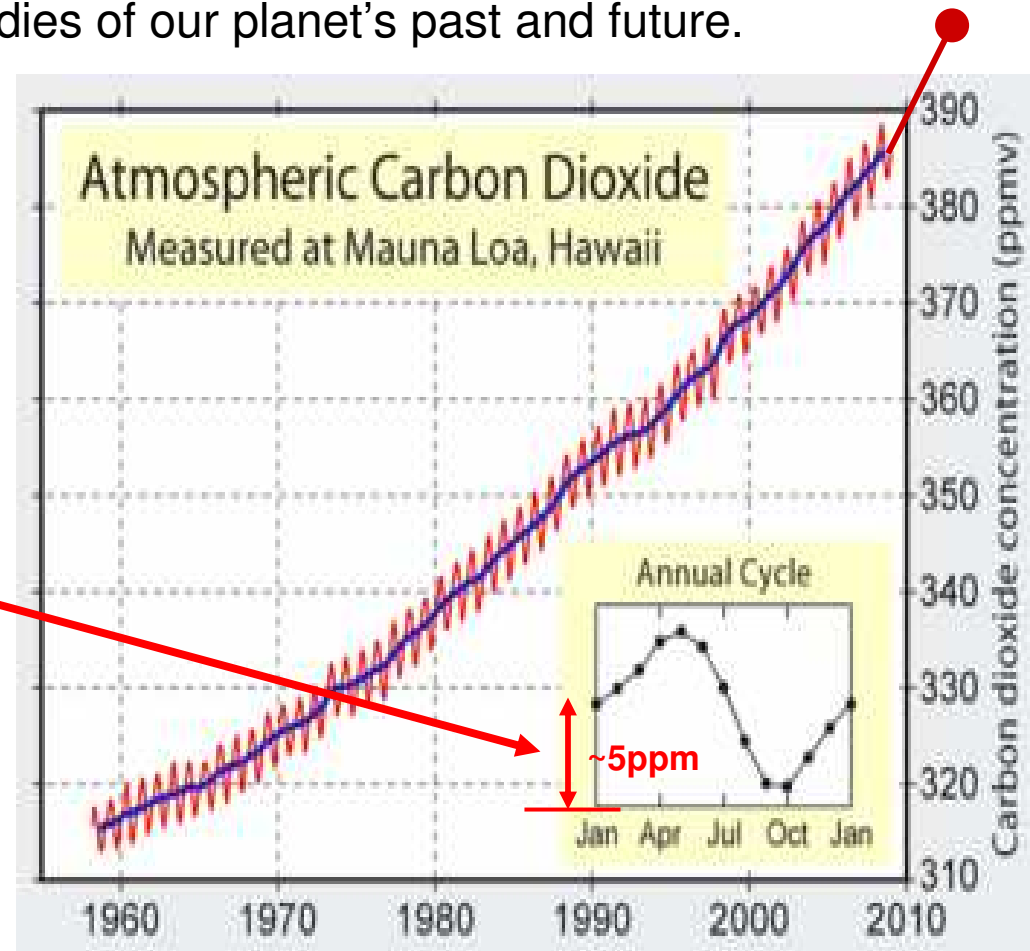
Where Emitted C Comes From (2010)



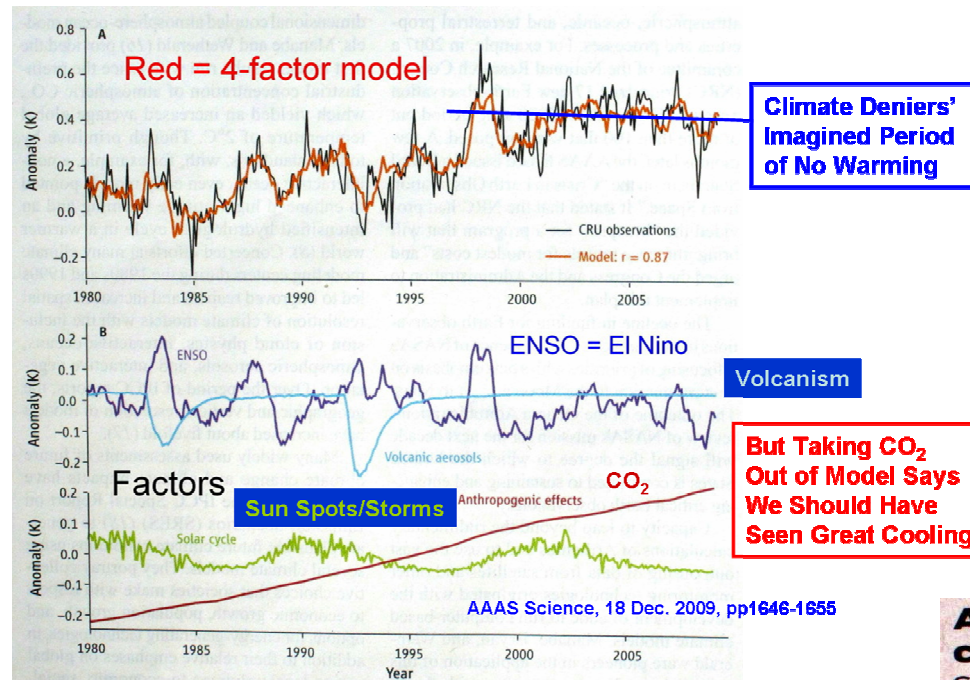
Recent CO₂ History

Our recent GHG awareness stems from the U. of Hawaii measurements of CO₂, beginning in 1957 – the first IGY (International Geophysical Year), when scientists worldwide began the intensive studies of our planet's past and future.

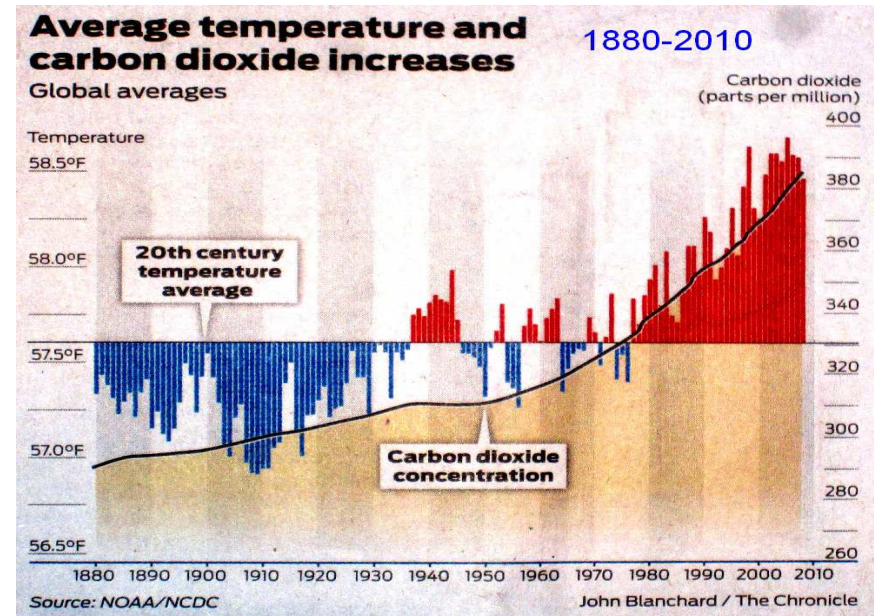
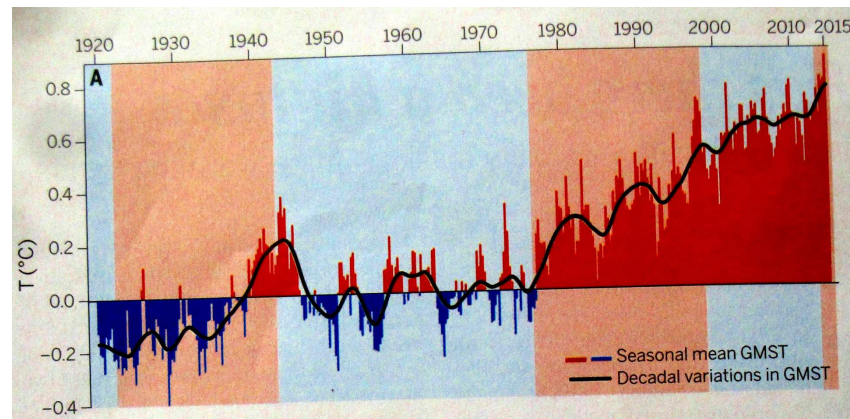
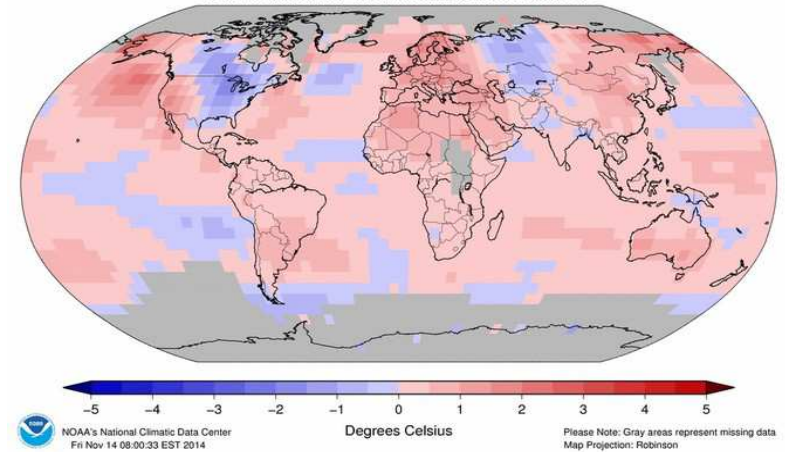
Note the important fact the **Annual Cycle** exposes -- it shows **what natural, sea & land photo-synthesizing organisms might do for us each year to reduce CO₂ levels -- about 4ppm/year, if no natural sources of CO₂ existed & we stopped all Hydrocarbon combustion -- $(400-280)/4 = 30$ years.**



Temperature History



Land & Ocean Temperature Departure from Average Jan–Oct 2014
(with respect to a 1981–2010 base period)
Data Source: GHCN–M version 3.2.2 & ERSST version 3b



C & CO₂ Emissions (2013)

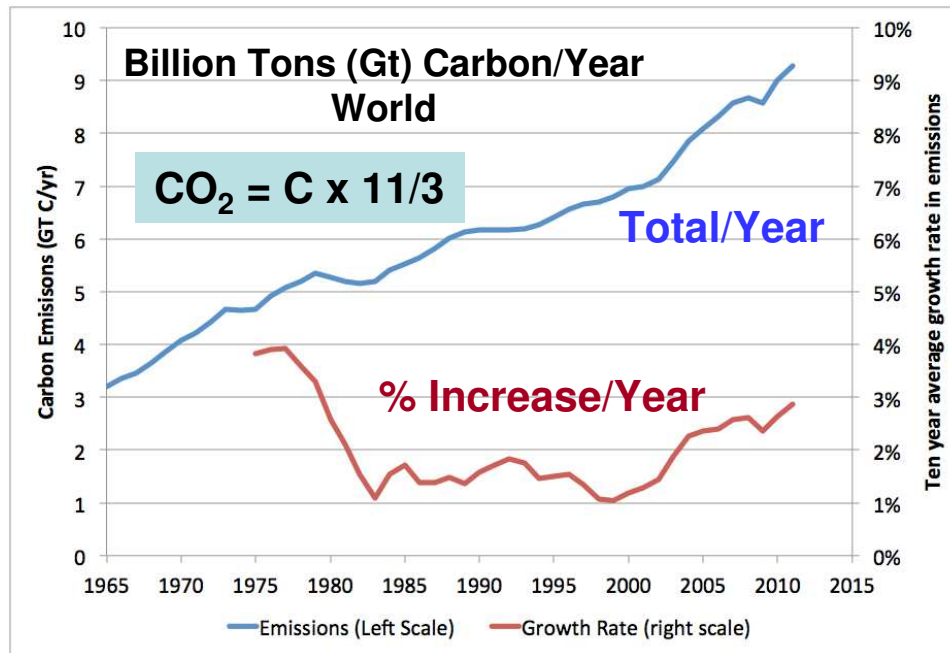
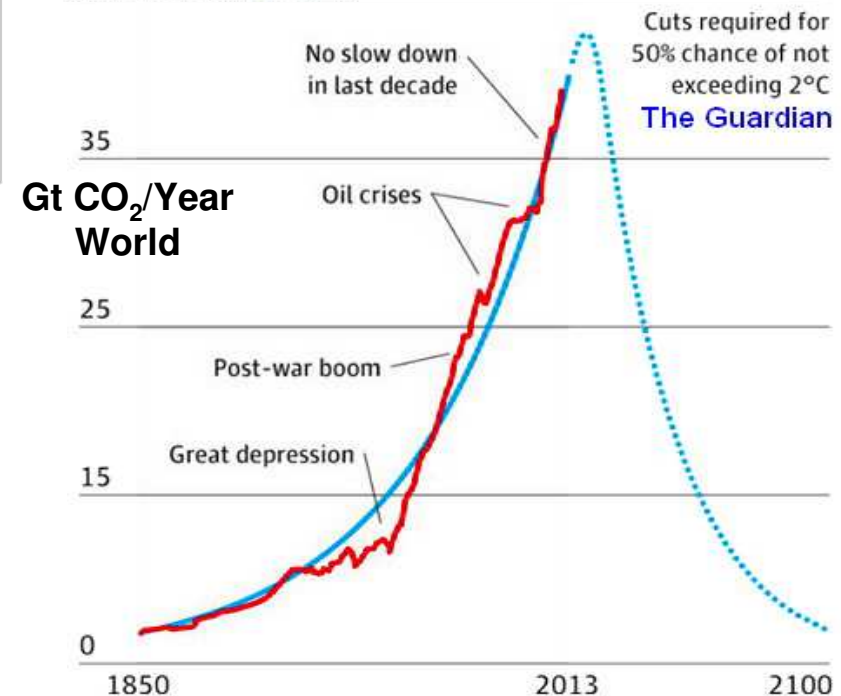
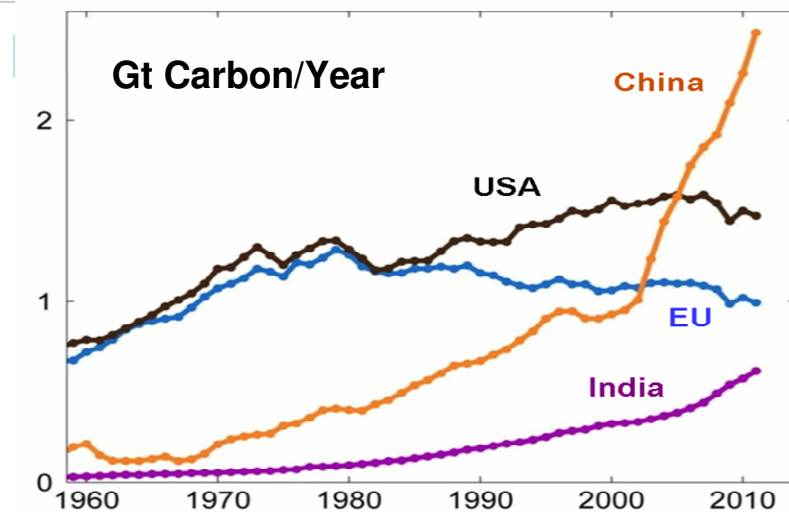
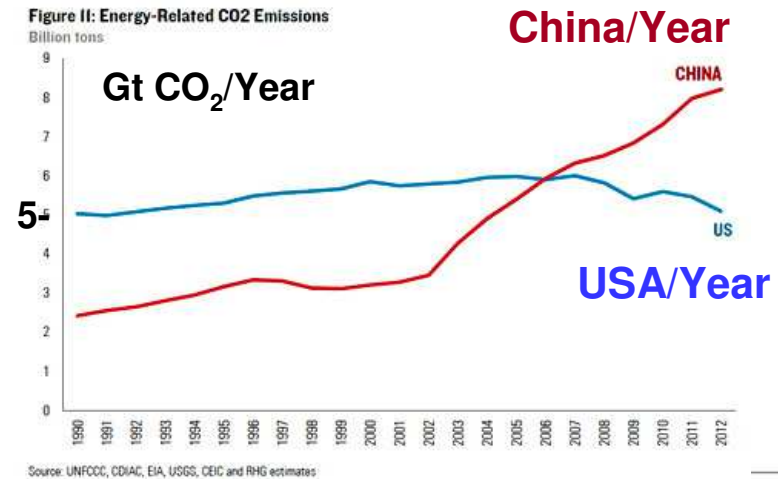


Figure II: Energy-Related CO₂ Emissions



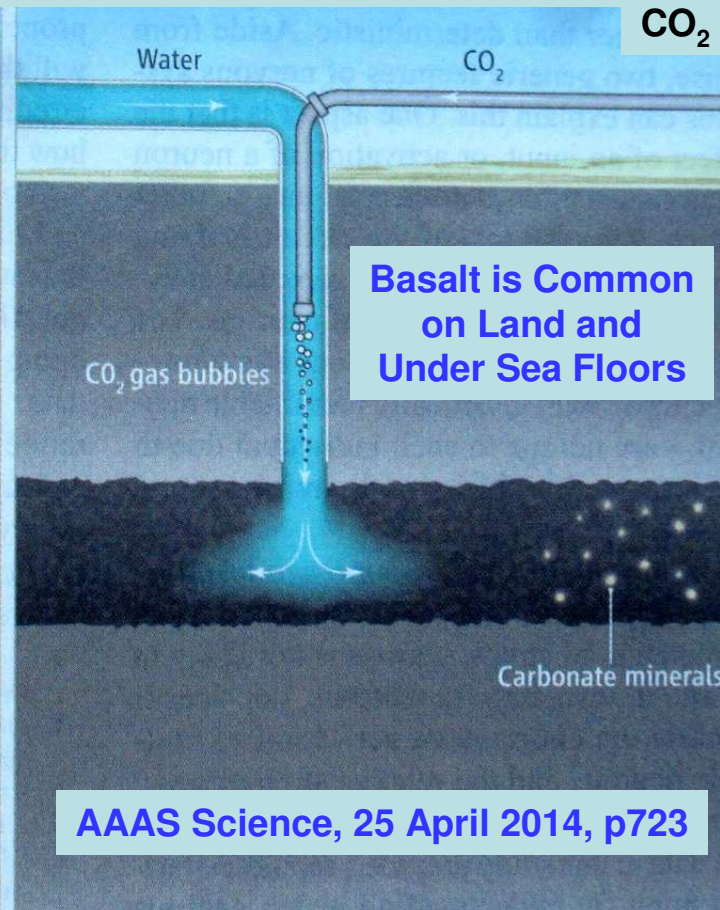
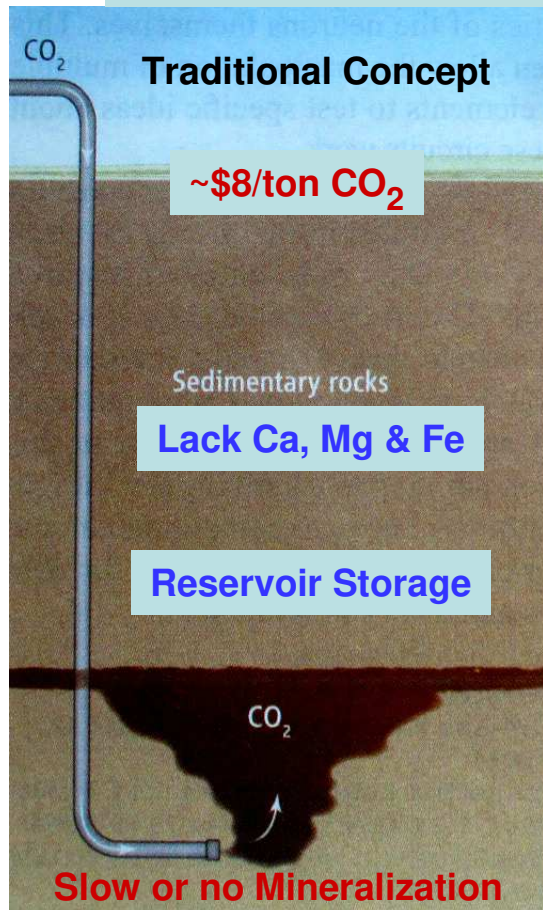
Acidification Remediation

Duplicate natural processes...

- a) Reverse ancient seafloor carbonate formation via heating dolomite/limestone from land deposits, just as subduction & heating in magma accomplishes.
- b) Capture freed CO₂.
- c) Return residue of Ca/Mg oxides (lime) to oceans.
- d) Sequester unusable CO₂ to geologic storage. Disso-
ciate CO₂ and H₂O, releasing Oxygen to air and capturing C & H₂ for feedstocks.
- e) Process C & H₂ into desired hydrocarbons for...
 - 1) Carbon-neutral fuels;
 - 2) Industrial feedstocks;
 - 3) Benign C-H compounds for geologic storage – in old wells/mines, etc.
- f) Store CO₂ permanently as carbonates in basalt.

CO₂ Sequestered to Basalt

CO₂ Capture from Emissions Sources ~\$60-120/ton



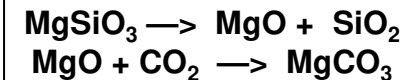
CO₂ Input = 5% of H₂O

~\$17/ton CO₂

Present EU Carbon Trades at ~\$7/ton

Porous Basalt Can Hold >50kg/m³ CO₂ as Permanent Carbonates

Example Reactions



Can also crush basalt with high alkali content and distribute in seas, If biologically safe.



Basalt is ~25% Ca, Mg & Fe Oxides.

Projects: Carbfix, 2012 in Iceland & BSCP, 2013 in Wallula, Washington

<http://tinyurl.com/hk6yxgv>

Env. Sci. & Tech. Ltrs. 2016; 10.1021/acs.estlett.6b00387

CO₂ & 1,000,000 Sq. Miles of Basalt

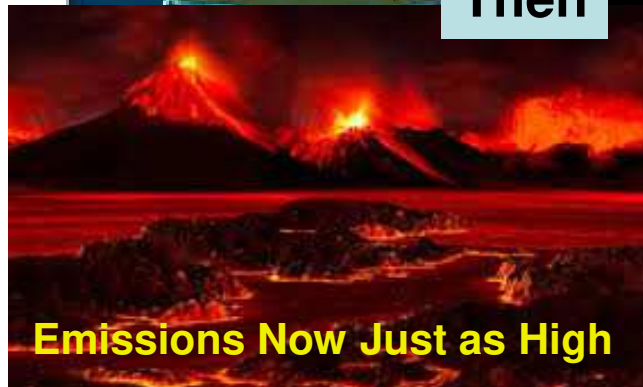


Coal, laid down in Carboniferous was ignited & burned underground for thousands of years.



Then

~90% of Species Gone



Emissions Now Just as High



Now



Siberian Traps

Coal & Carbonate (Limestone)

Alternating Swamps & Seas

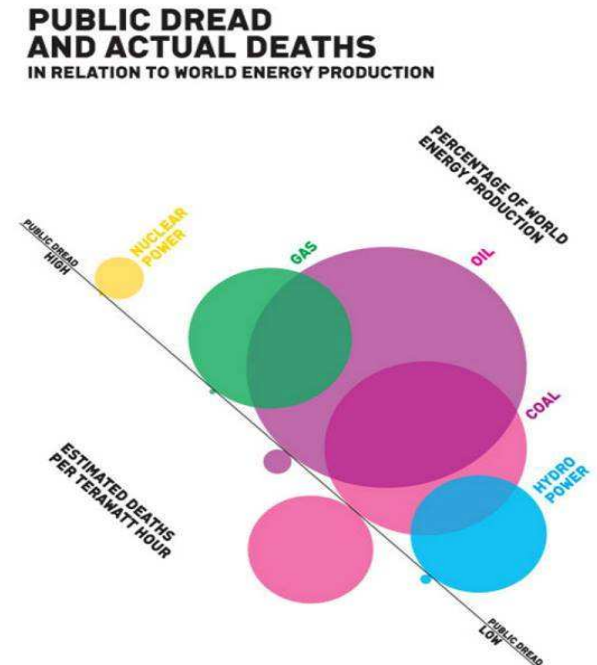
Cretaceous Chalk/Limestone



Carboniferous Coal

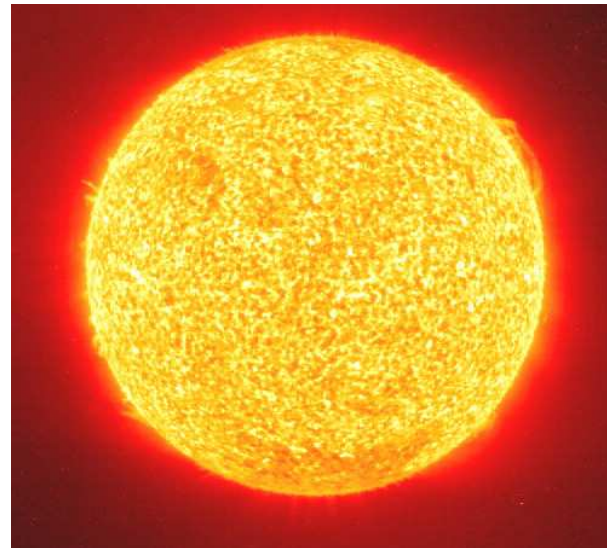
Remediation Power Choices

- **Features** – will not increase GHG emissions
- **Power Density** – resources needed to build & operate:
 - Processing limestone/dolomite to lime (~400kWHr/ton -- mining, transport, process temperature >1400C)
 - Lime transport to ocean (kW)
 - CO₂ storage & cracking (kW + temp)
 - CO₂ sequestration (kW)
 - H₂O acquisition & cracking (temp + kW)
 - C-H compound reforming (temp):
 - Fuels (for critical uses – aircraft, etc.)
 - Feedstocks (petroleum/gas/coal substitutes)
 - For sequestration
- **Reliability** – on human time scale:
 - Longevity
 - Safety



Energy Rate & Density

- **Rates** are everything in nature (and banking).
- **Power** is the rate of doing work – moving mass-energy.
- **Energy Density** is the power available each second in a standard volume of some material.
 - Arrange these from highest to lowest energy density...



Areas Needed to Replace US Fossil Fuels

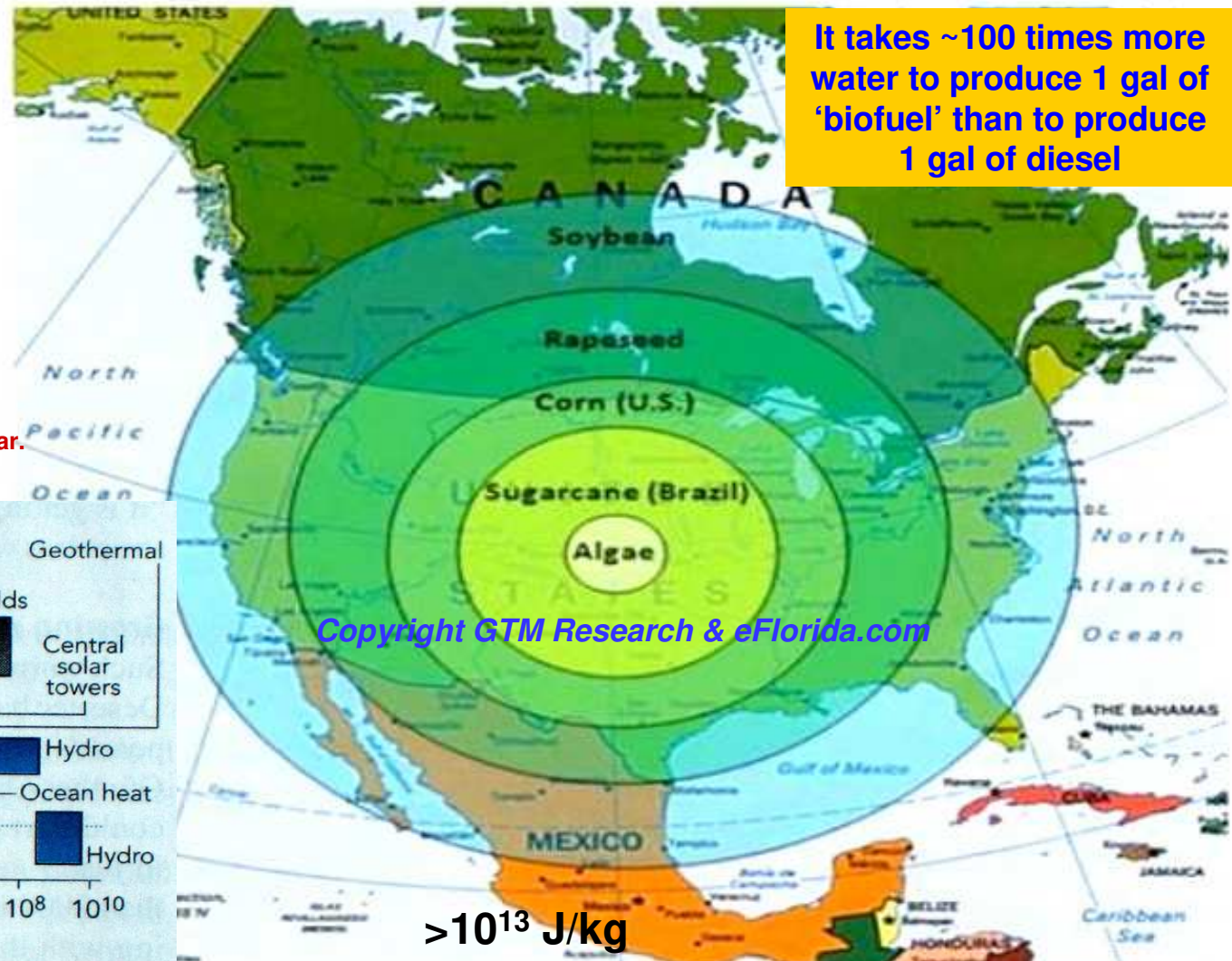
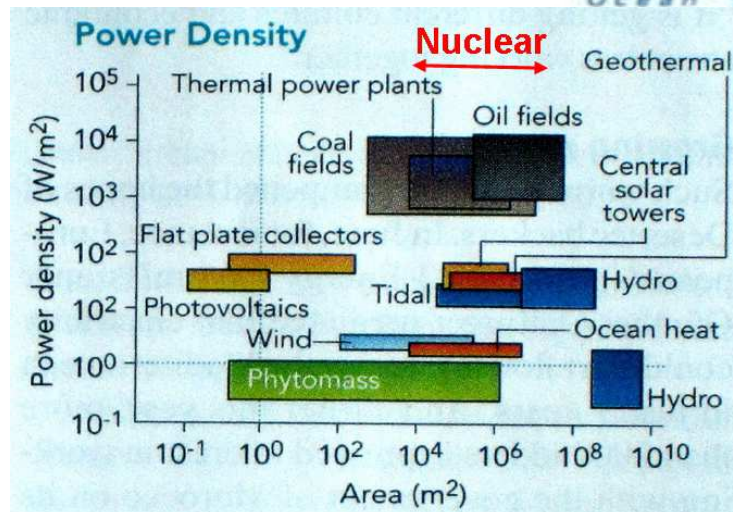
Area Needed
for Nuclear*



Area Needed for Solar PV*
(Wind is much larger)

* All mining, construction, power & vehicular uses included in nuclear & solar.

It takes ~100 times more water to produce 1 gal of 'biofuel' than to produce 1 gal of diesel



$>10^{13}$ J/kg

Combustion

Fission

Fusion

~10kWhr/lb

$\times 1,000,000$



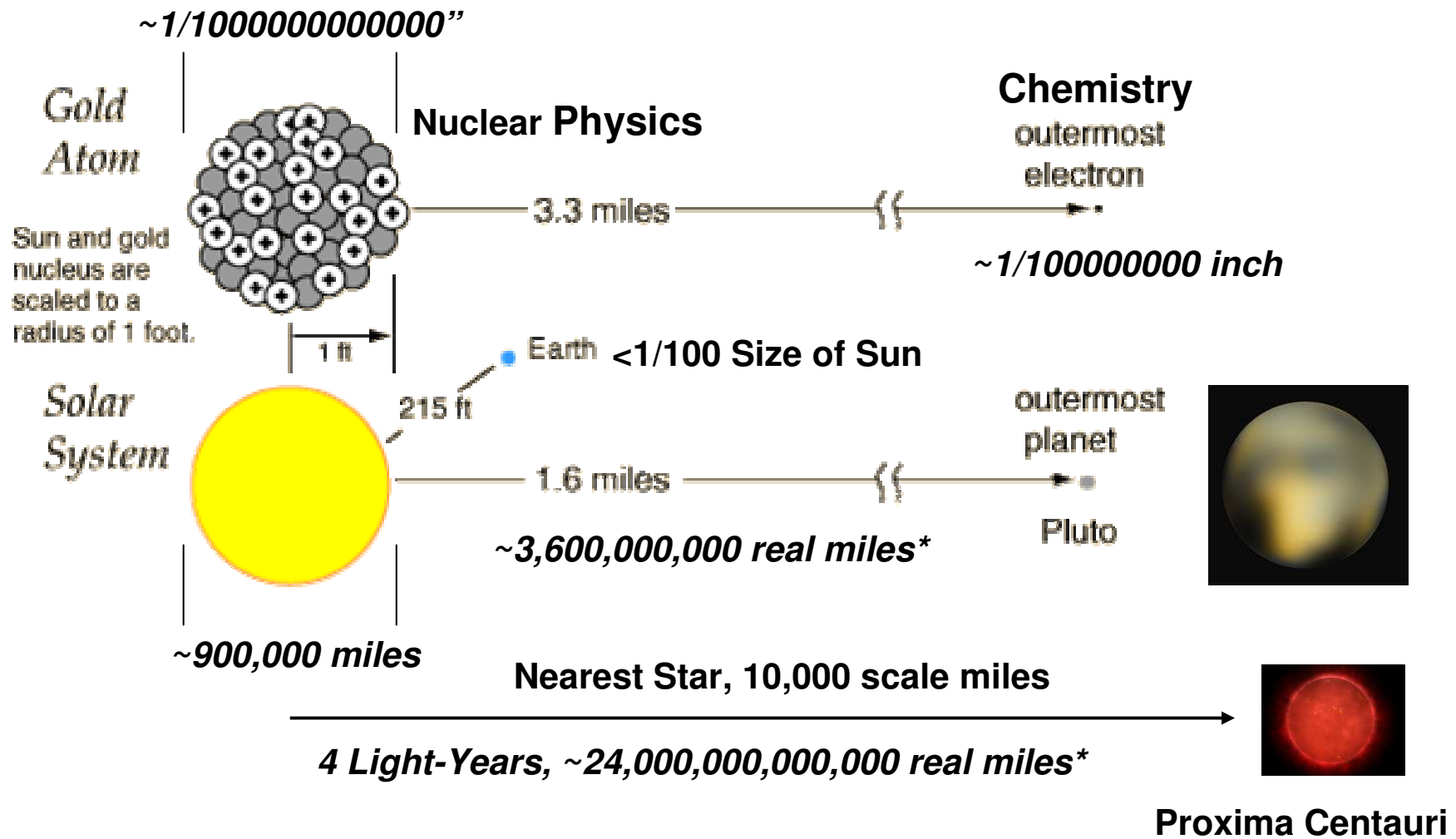
~3GWhr/lb

$\times 100$



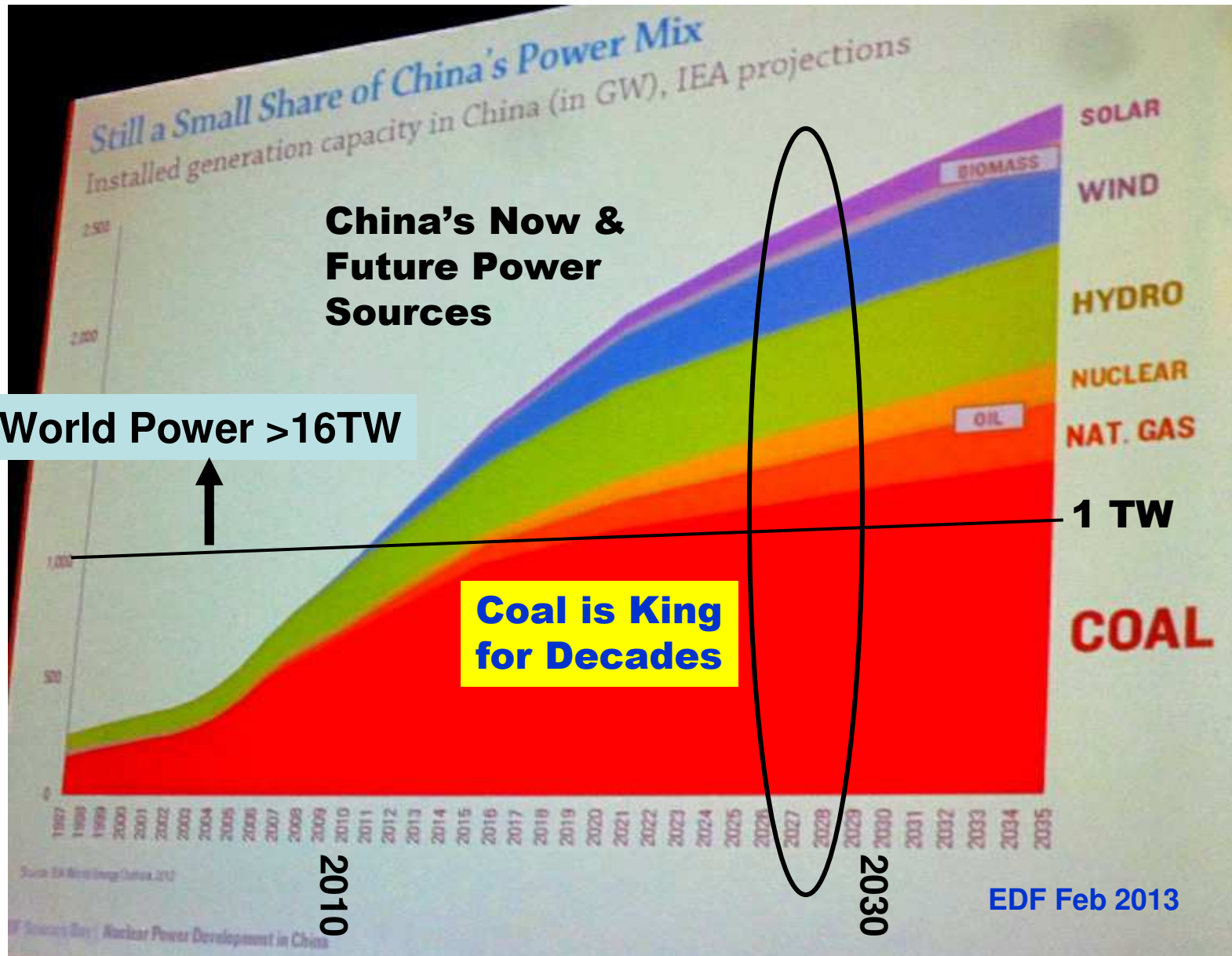
~ 10^{11} Whr/lb

A Worldly Scale

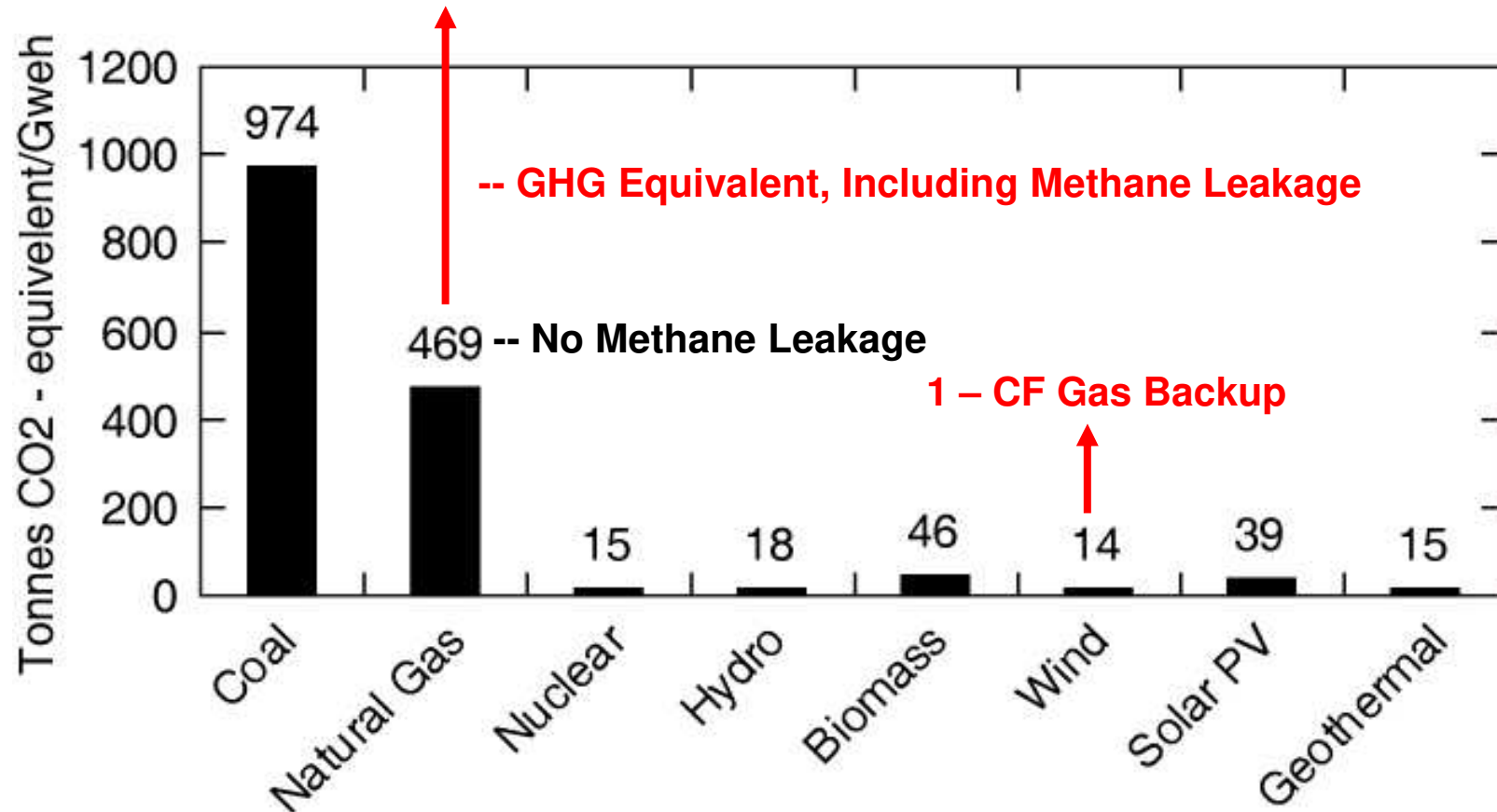


* Actual distances are in italics

Chinese Power 2010-2035

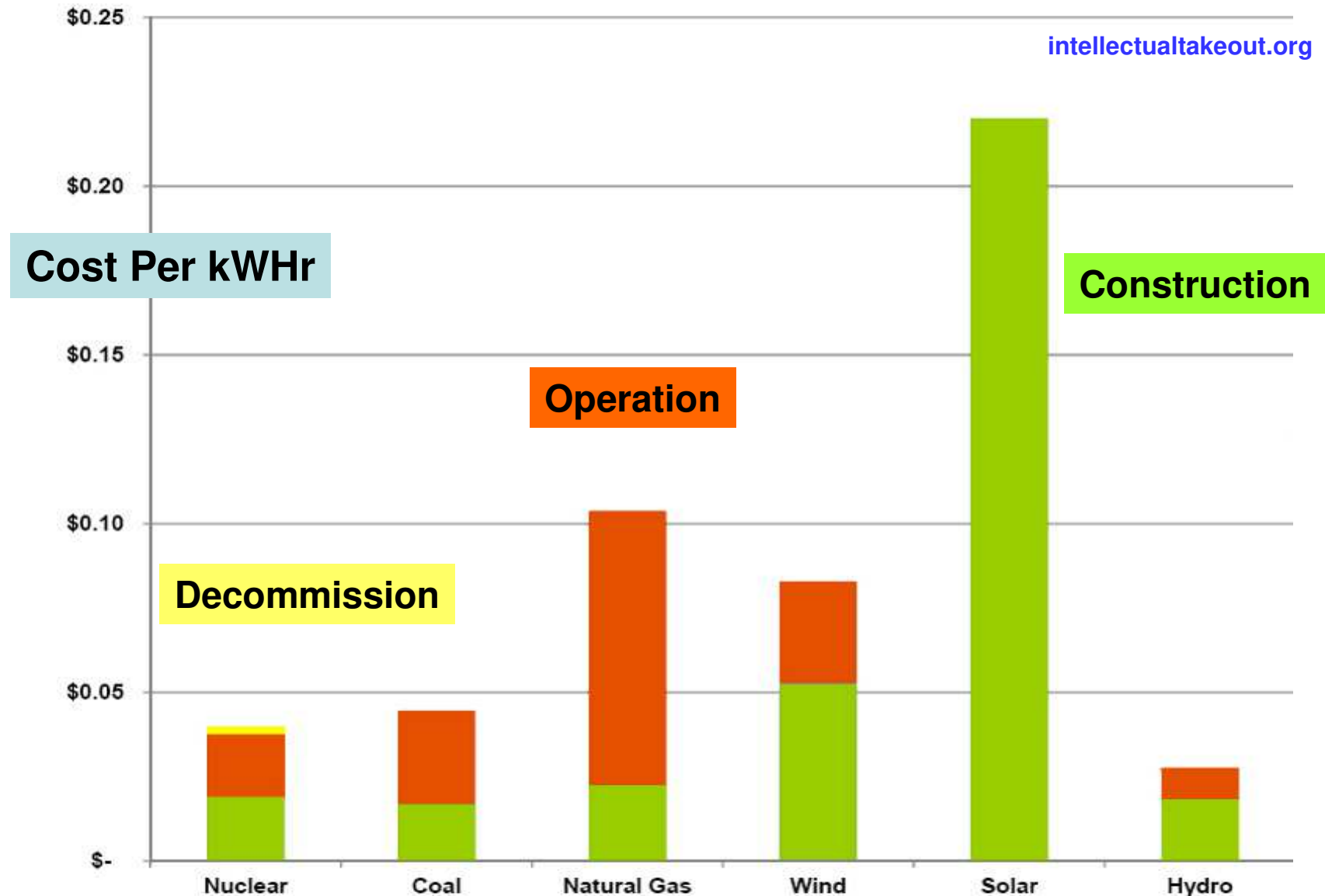


Lifecycle CO₂ Emissions

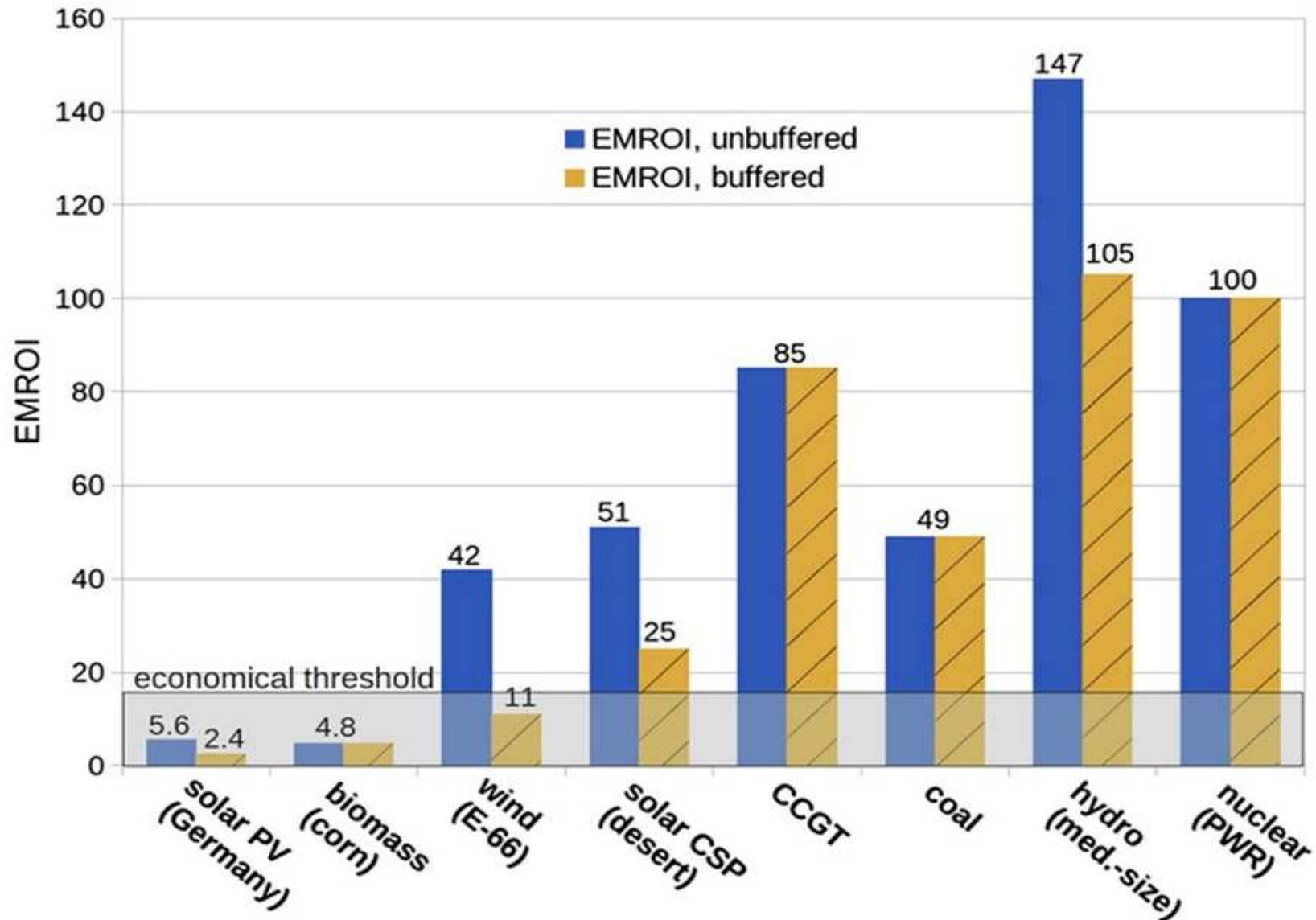


Courtesy Burton Richter -- Comparison of Life Cycle Emissions in Metric Tonnes of CO₂e per GW-hour for various modes of Electricity Production; P.J. Meier, *Life-Cycle Assessment of electricity Generation Systems with Applications for Climate Change Policy Analysis*,

Lifecycle Costs Per kWhr

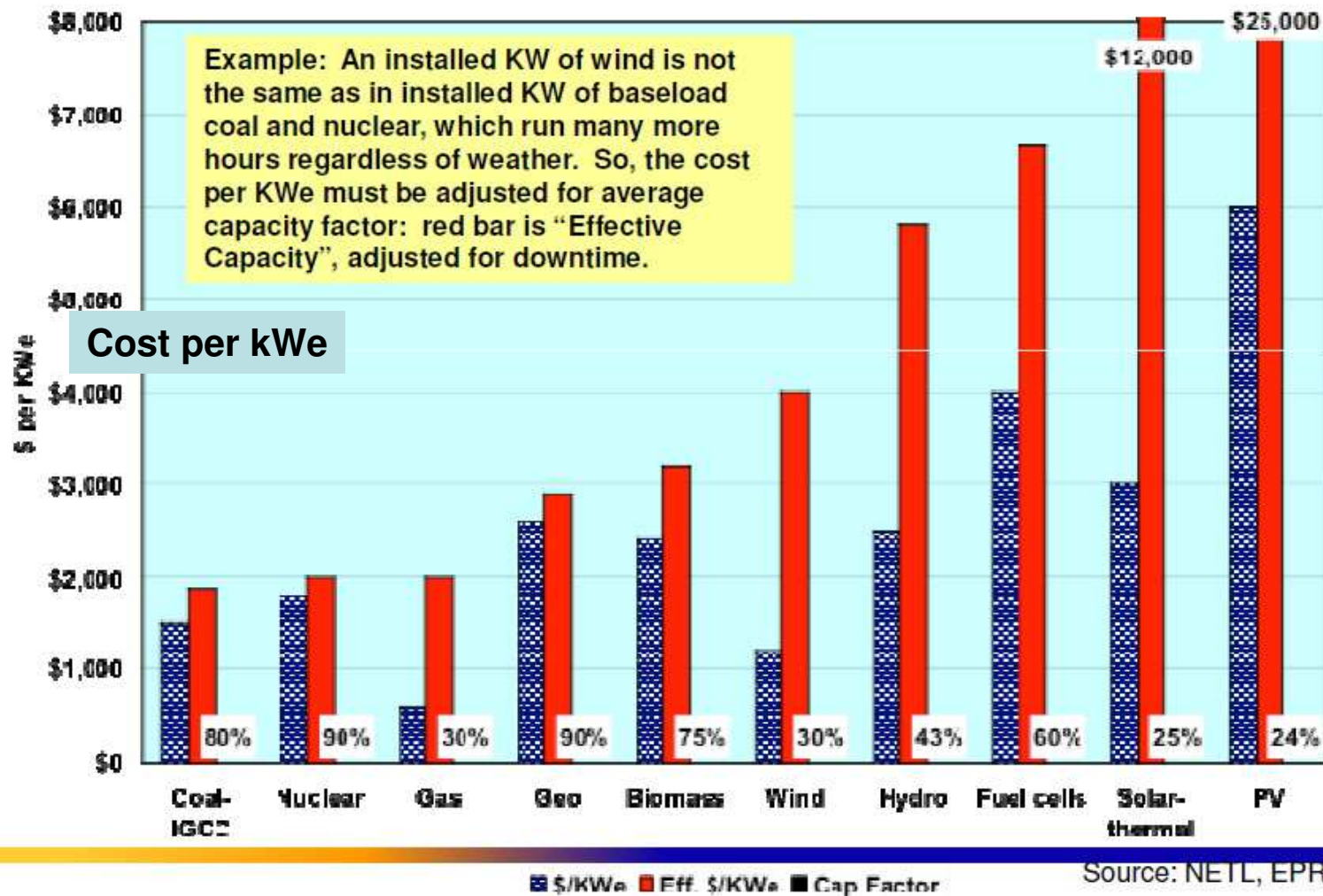


Lifecycle Return Per kWh



Real Cost of Power Sources Affected by Capacity Factor (2006)

Fuel costs, weather affect downtime of some sources, which impacts investment.

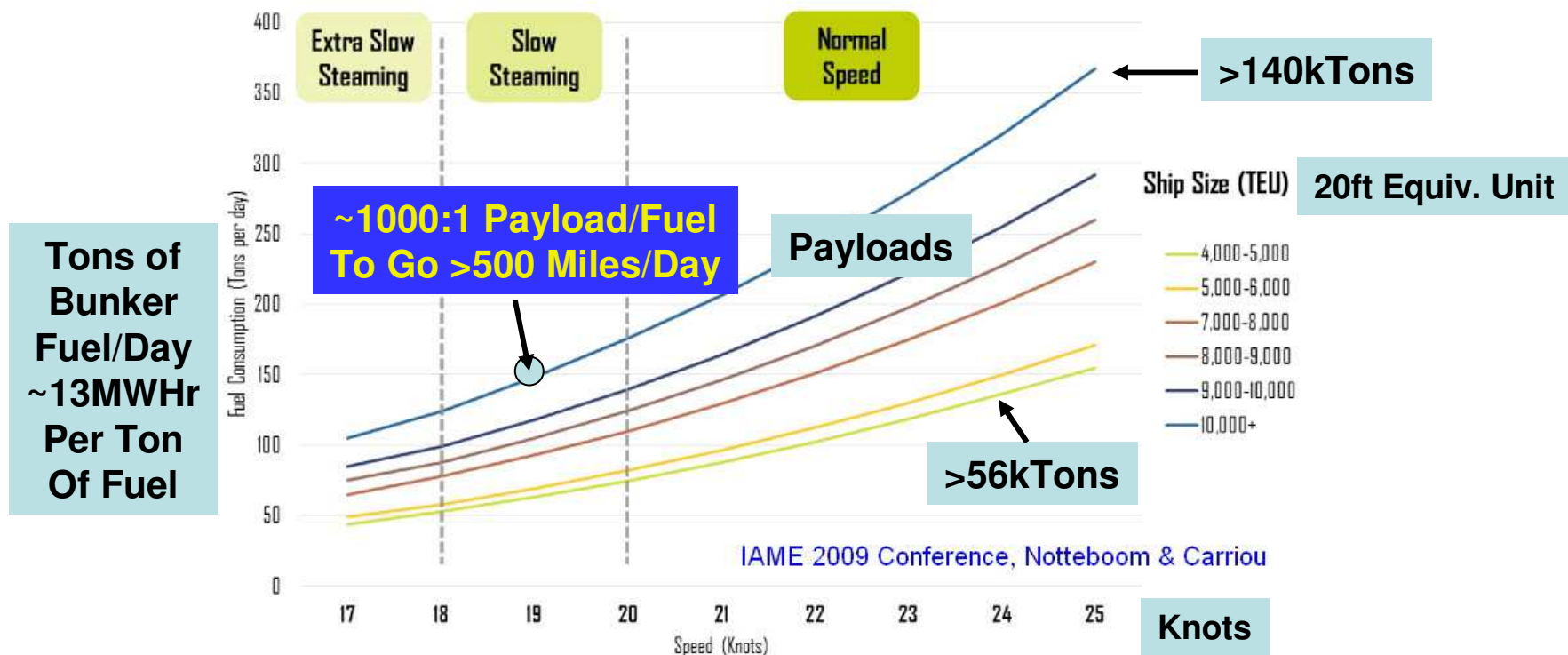


Remediation – The Numbers

- Processing limestone/dolomite to lime ~400kWHr/ton
- Lime transport to ocean (rail 0.085kWHr/ton-mile + ship 4kWHr/ton-mile)
- CO₂ cracking (assume electrochemical reduction of at least 505 kJ/mole ~1.5GJ/ton ~420kWHr/ton)
- H₂O cracking -- @2000C, or electrolysis @850C 225 GJ/ton H₂ (64% efficient incl electricity gen)
- C-H compound reforming (use H₂O cracking heat)
 - Fuels (for critical uses – aircraft, etc.)
 - Feedstocks (petroleum/gas/coal substitutes)
 - For geologic sequestration (waxes – C₂₅+)
- **Remediate 1/4 of yearly CO₂ emissions = 9Gt (dissolves)**
 - $(9 \times 10^9 (1 + 1.5) \times 10^9) \times 2.8 \times 10^{-7} = 2100 \text{ TWHrs} + \text{H}_2\text{O cracking}$
 - **~400, 1GWe 0-emission powerplants + H₂O cracking**

Remediation – Shipping

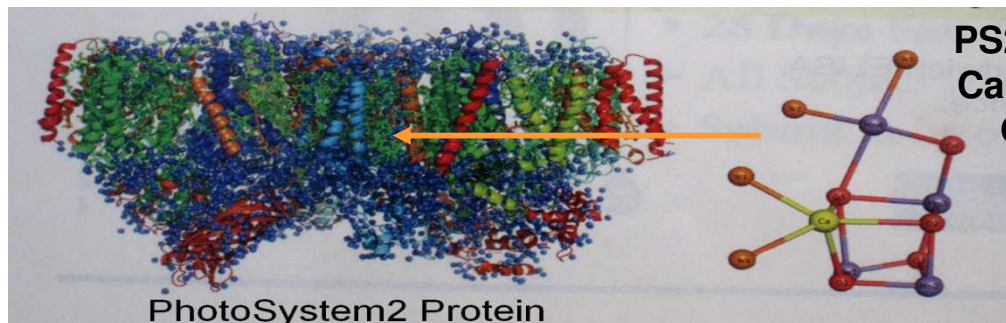
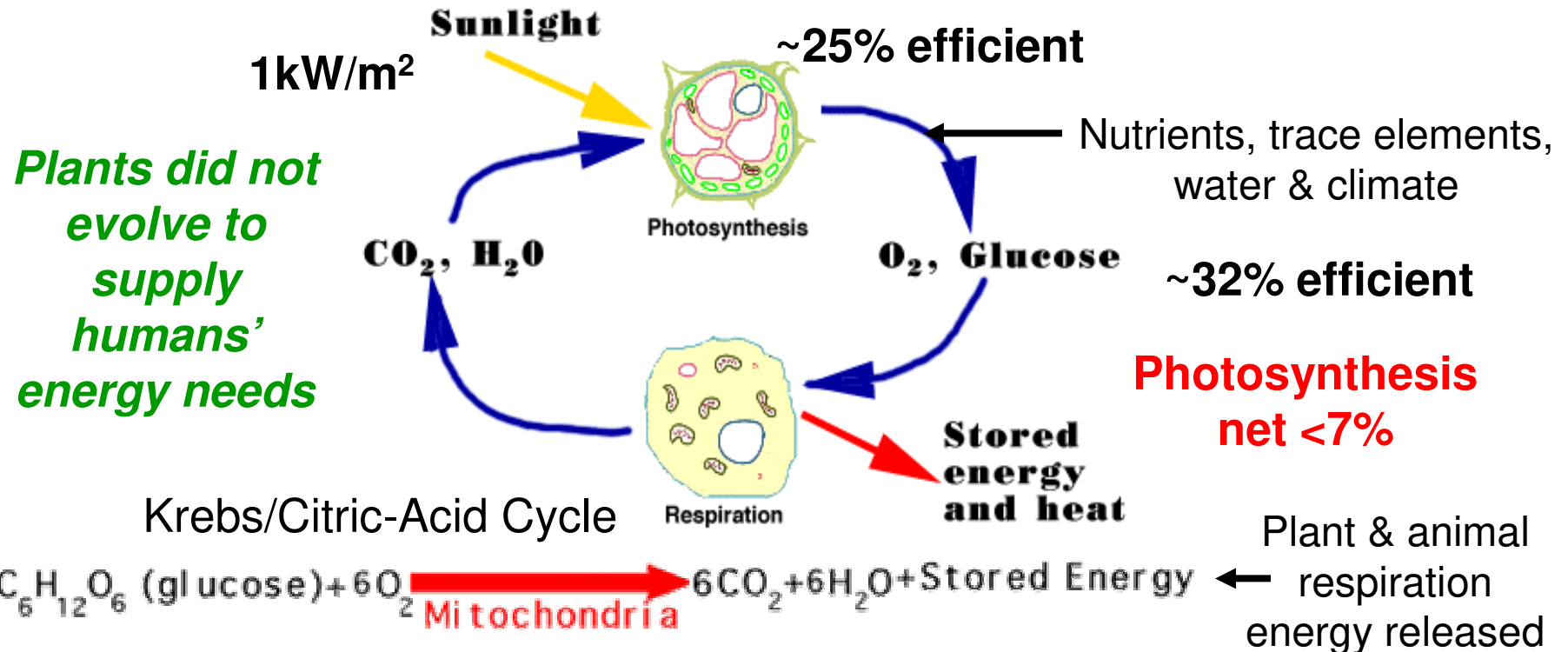
- Compounds for geologic sequestration
 - Rail: 400 ton-miles/gallon = 0.085kWhr/ton-mile
- Lime transport to ocean (~1 million yearly transits)
 - Rail: 0.085kWhr/ton-mile @1000mi/day
 - Ship: 14 tons/TEU, 10k TEUs, ~4kWhr/ton-mile @500mi/day



Photosynthesis – CO₂ Handling

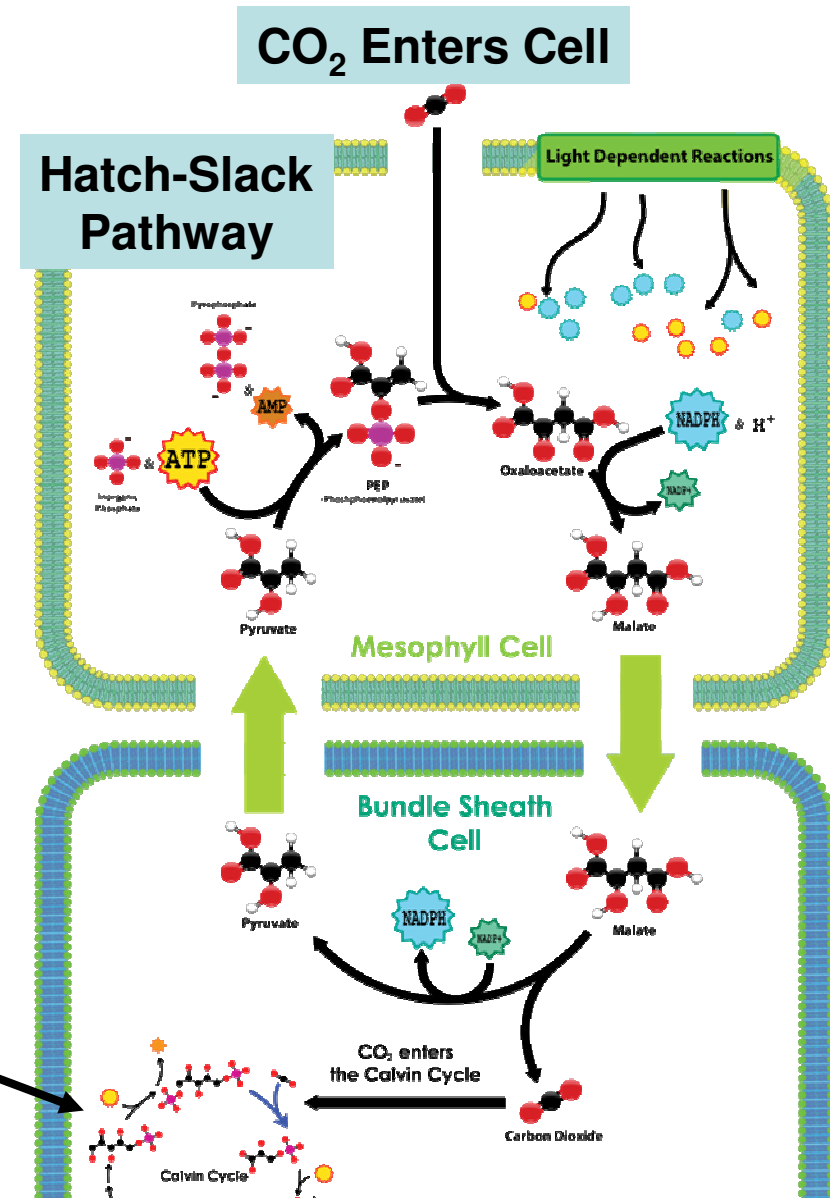
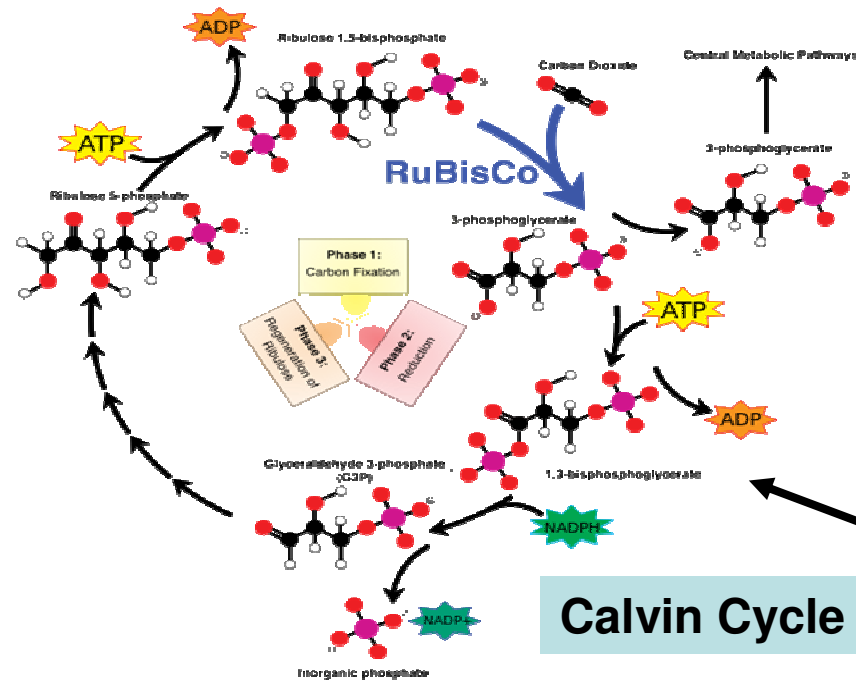
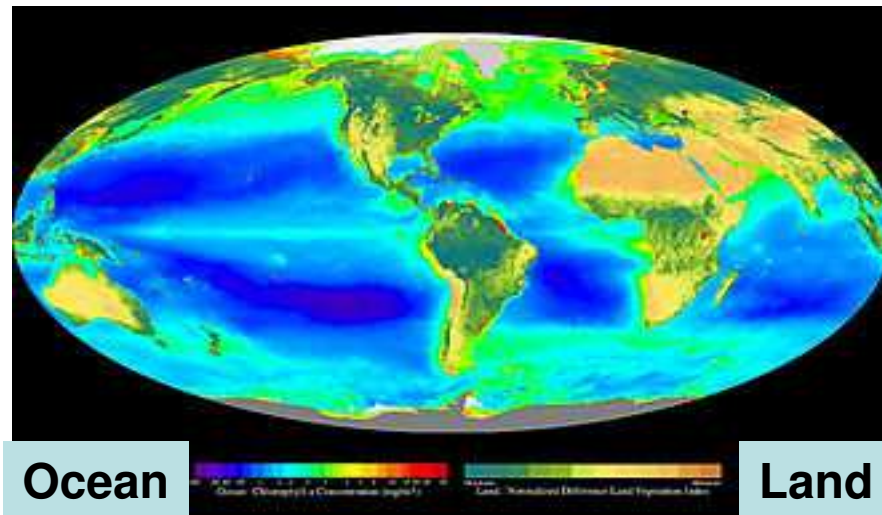


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PS2 Protein Houses a Calcium, Manganese, Oxygen Catalyst To Split H₂O

Photosynthesis – CO₂ Handling



17 April 1970



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