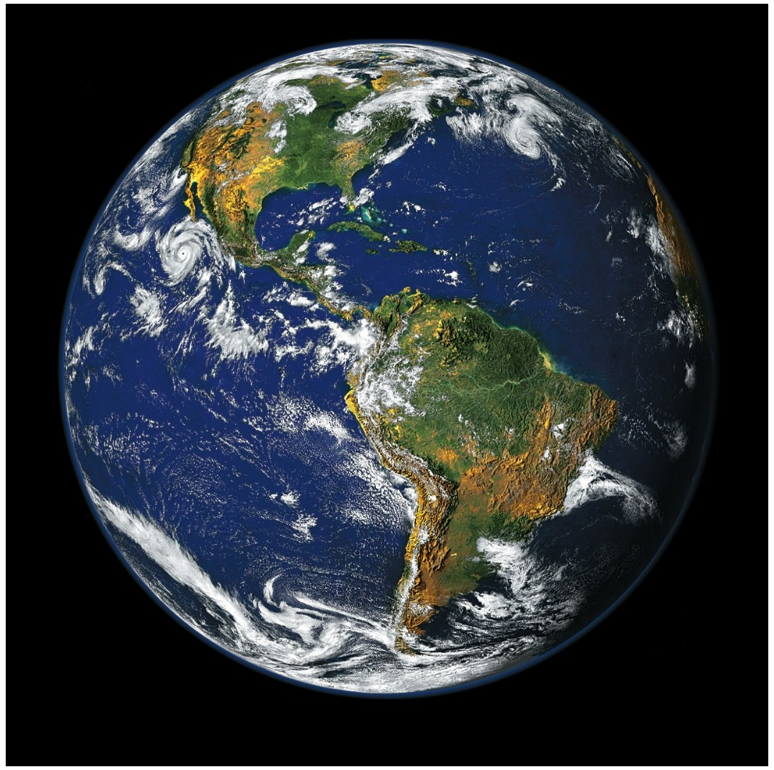

Wind Crest Learners

Lecture 3: Human causation?

Climate Redux:

February 19, 2021

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Switch order of lectures

- Today talk about CO_2 and human causation
- Next week paleoclimate

- Last week we saw that global temperature is like our “patient’s temperature”
- CO_2 is a measure of the viral load of “patient” Earth
- Where does all this CO_2 come from?

Today's lecture

- Refresher on isotopes
  - Which is heavier?
  - Heavier takes more energy
- Fractionation by plants
  - Lighter isotopes preferred
- How Nature makes ^{14}C
- The data and what it tells us

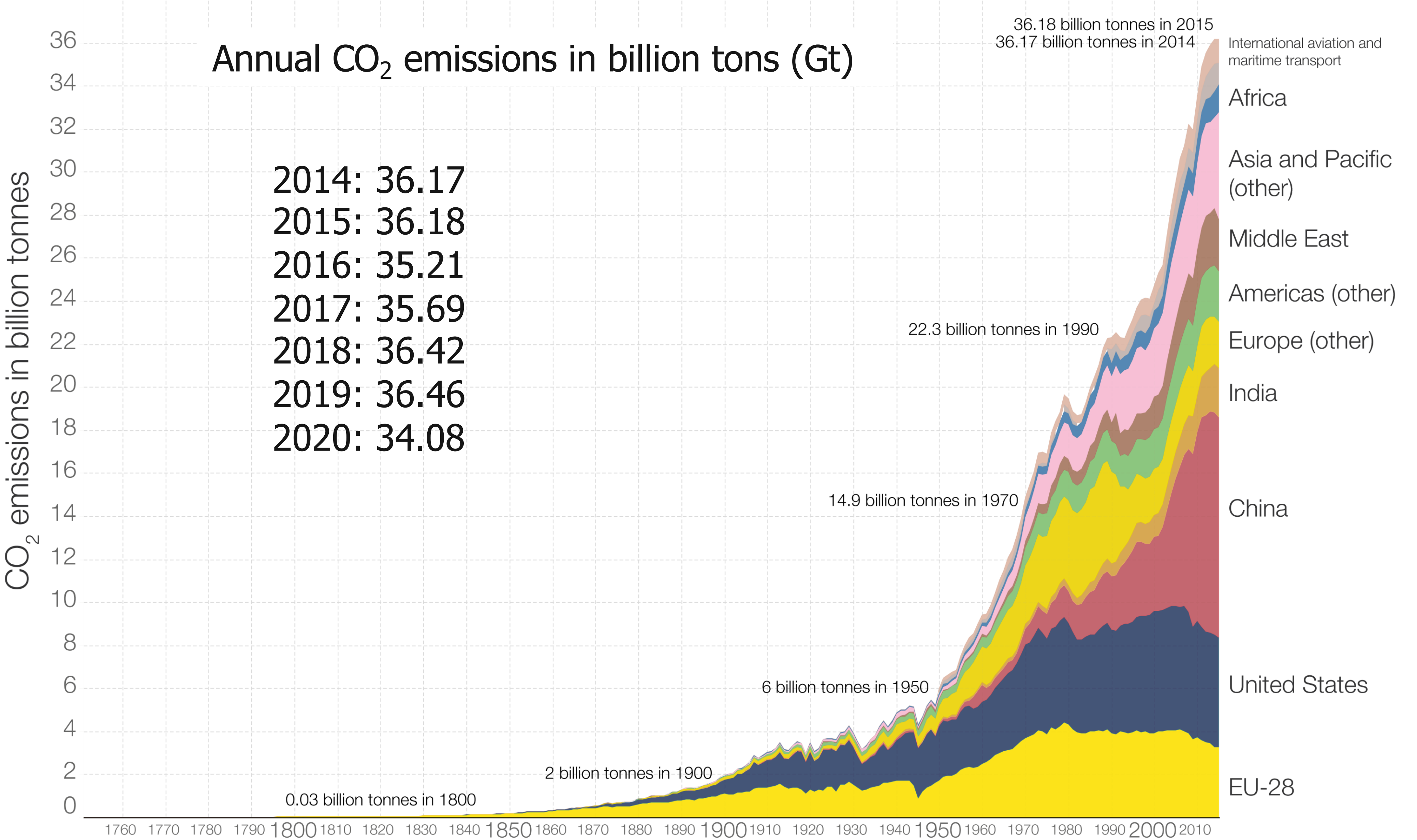
CO_2 is a greenhouse gas.
It is released by burning fossil fuels.

Fossil fuels have driven an extraordinary period of human expansion and prosperity. We have all benefitted greatly from inexpensive energy. Is the piper is asking to be paid?

Global CO_2 emissions by world region, 1751 to 2015

Annual carbon dioxide emissions in billion tonnes (Gt).

Our World in Data

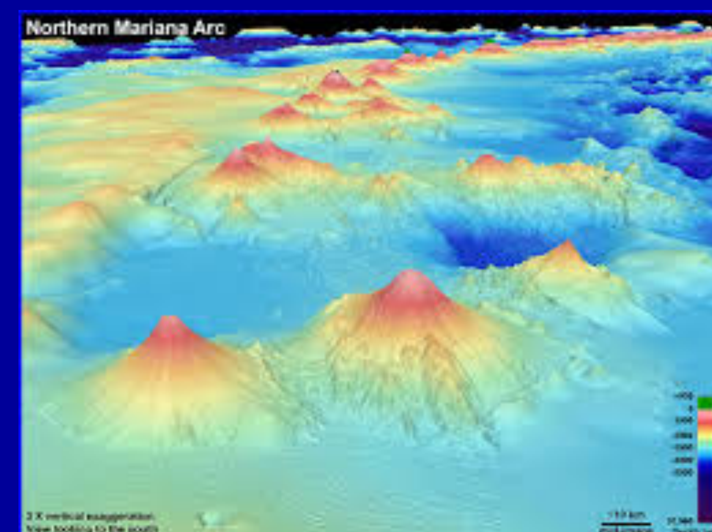


Data source: Carbon Dioxide Information Analysis Center (CDIAC); aggregation by world region by Our World In Data.
The interactive data visualization is available at OurWorldinData.org. There you find the raw data and more visualizations on this topic.

Volcanic contribution

Well known that volcanoes contribute gas and dust to the atmosphere that cools the planet on the short term – 2-5 years.

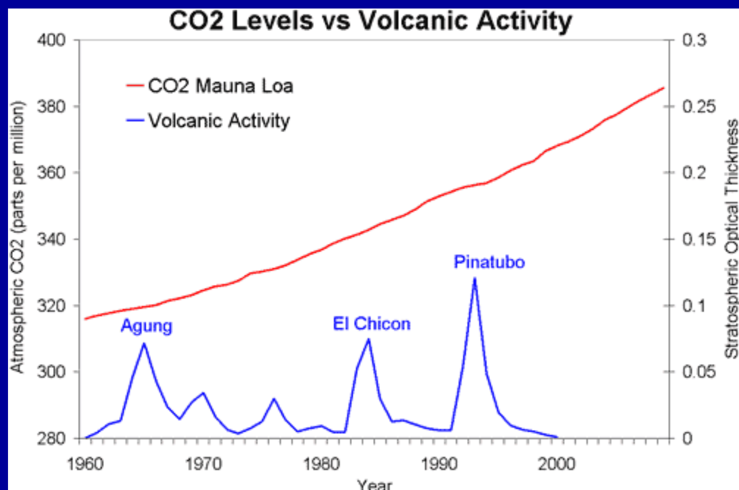
Uncertainty comes from undersea eruptions.



Volcanoes: 0.13 to 0.44 billion tons per year

Human activities: 35 billion tons/yr (2020)

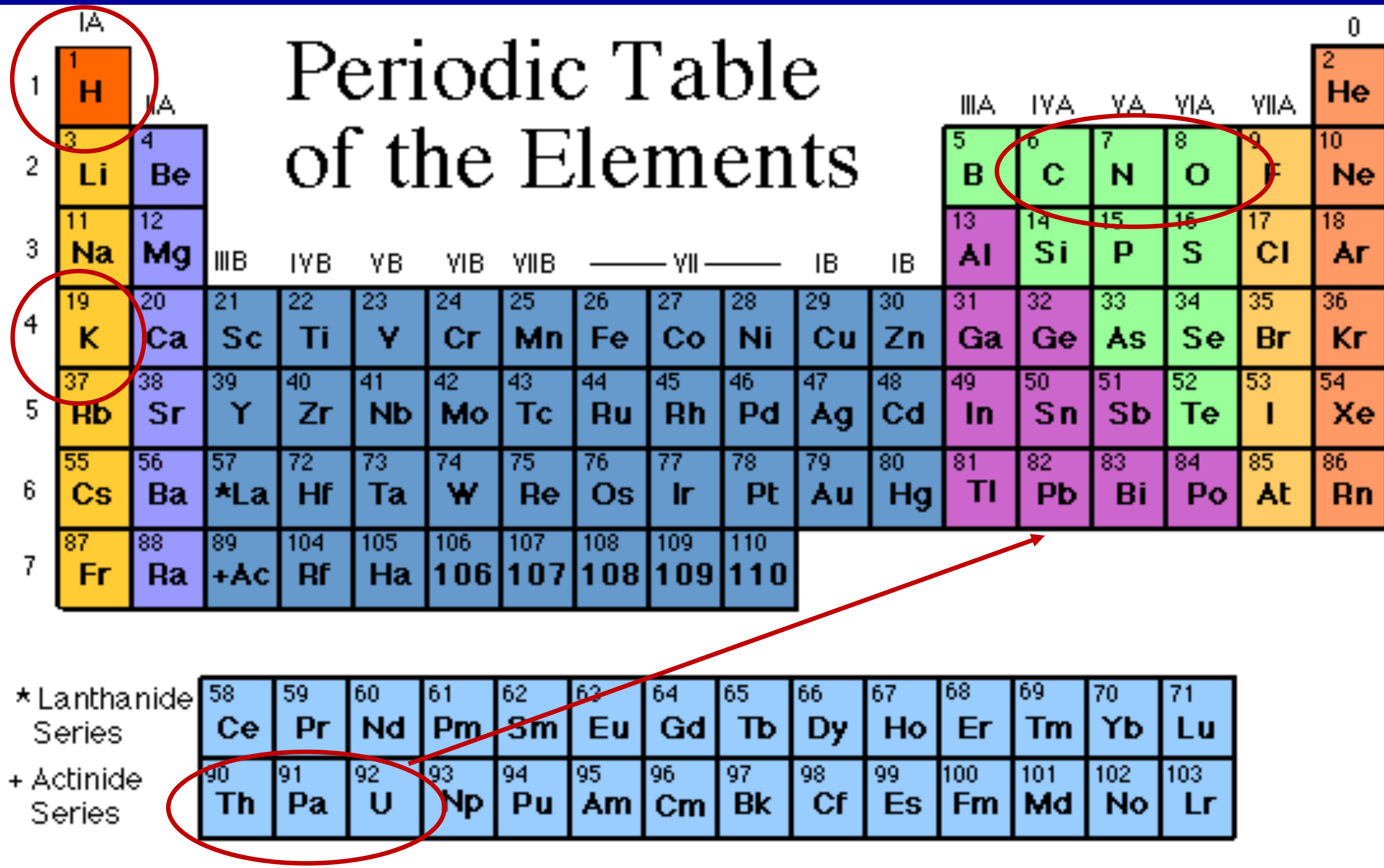
Volcanoes emit CO_2



CO_2 from volcanic eruptions cannot be seen in Keeling plots, plots of CO_2 in atmosphere vs. time.

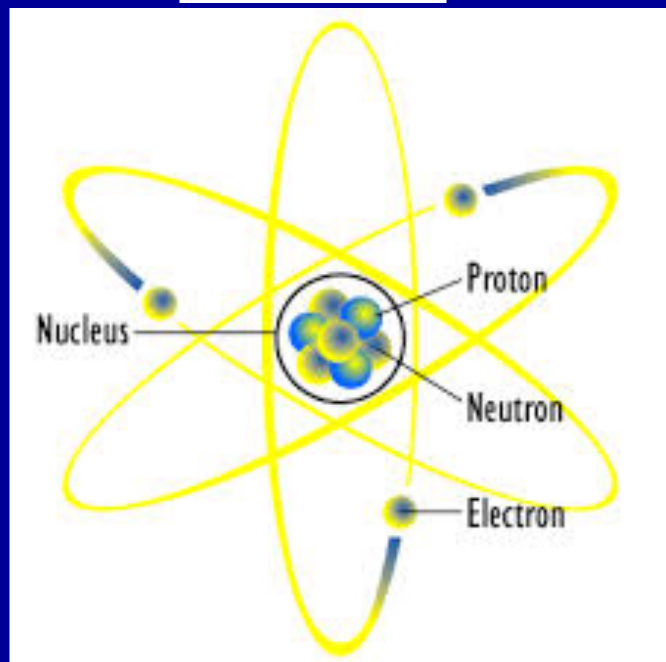
British Geological Survey
Average 300 M tons CO_2/yr

Chemistry


Periodic Table
of the Elements
IA
IIA
IIIA IVA VA VIA VIIA
0
IIIB IVB VB VIB VIIB — VII — IB IB
1 2 3 4 5 6 7
1 H
2 He
3 Li 4 Be 5 B 6 C 7 N 8 O 9 F 10 Ne
11 Na 12 Mg 13 Al 14 Si 15 P 16 S 17 Cl 18 Ar
19 K 20 Ca 21 Sc 22 Ti 23 V 24 Cr 25 Mn 26 Fe 27 Co 28 Ni 29 Cu 30 Zn 31 Ga 32 Ge 33 As 34 Se 35 Br 36 Kr
37 Rb 38 Sr 39 Y 40 Zr 41 Nb 42 Mo 43 Tc 44 Ru 45 Rh 46 Pd 47 Ag 48 Cd 49 In 50 Sn 51 Sb 52 Te 53 I 54 Xe
55 Cs 56 Ba 57 *La 72 Hf 73 Ta 74 W 75 Re 76 Os 77 Ir 78 Pt 79 Au 80 Hg 81 Tl 82 Pb 83 Bi 84 Po 85 At 86 Rn
87 Fr 88 Ra 89 +Ac 104 Rf 105 Ha 106 106 107 107 108 108 109 109 110 110
* Lanthanide Series
58 Ce 59 Pr 60 Nd 61 Pm 62 Sm 63 Eu 64 Gd 65 Tb 66 Dy 67 Ho 68 Er 69 Tm 70 Yb 71 Lu
+ Actinide Series
90 Th 91 Pa 92 U 93 Np 94 Pu 95 Am 96 Cm 97 Bk 98 Cf 99 Es 100 Fm 101 Md 102 No 103 Lr

Atoms and their nuclei

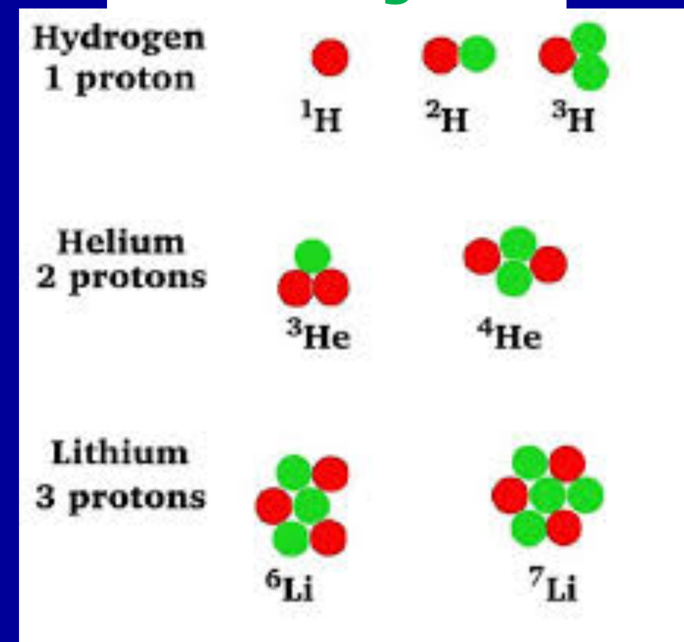
An atom



Number of electrons (-)
= number of protons (+)

protons red
neutrons green

Charge increasing



Mass increasing

Charge affects the chemistry
Mass affects the physics

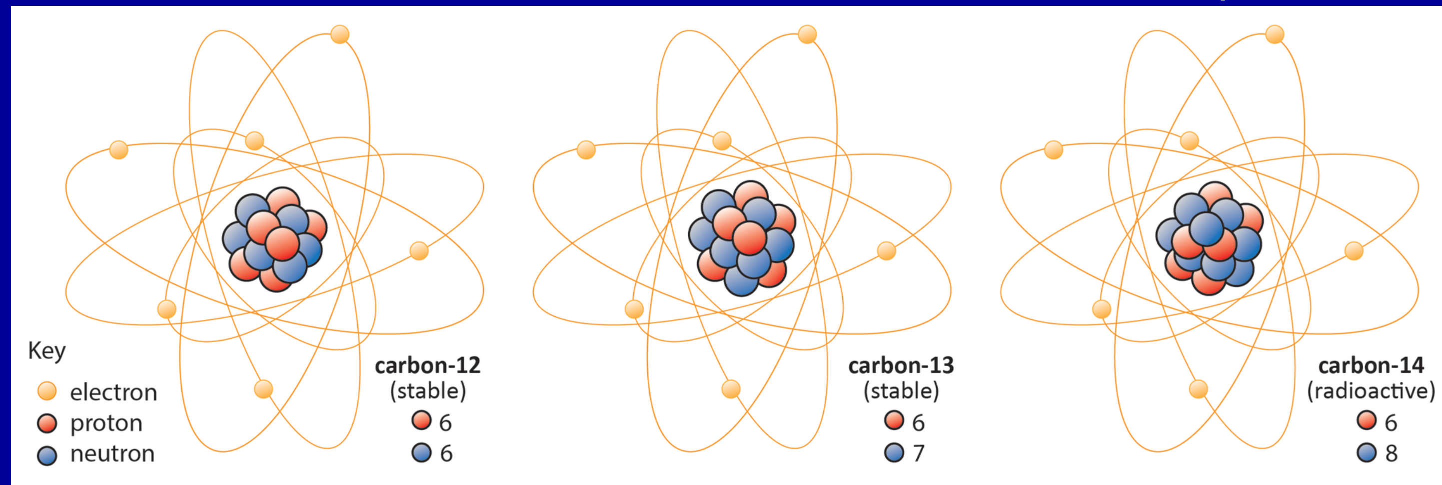
Carbon Isotopes

Stable isotopes

^{12}C Atom 99%

^{13}C Atom 1%

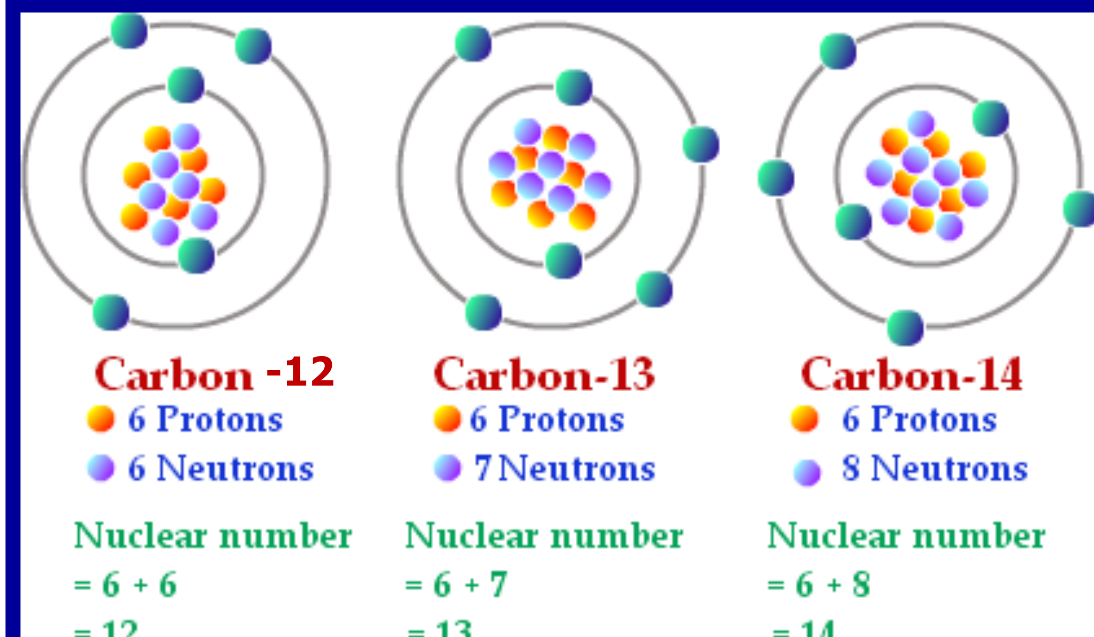
^{14}C Atom
half-life of
5,700 years



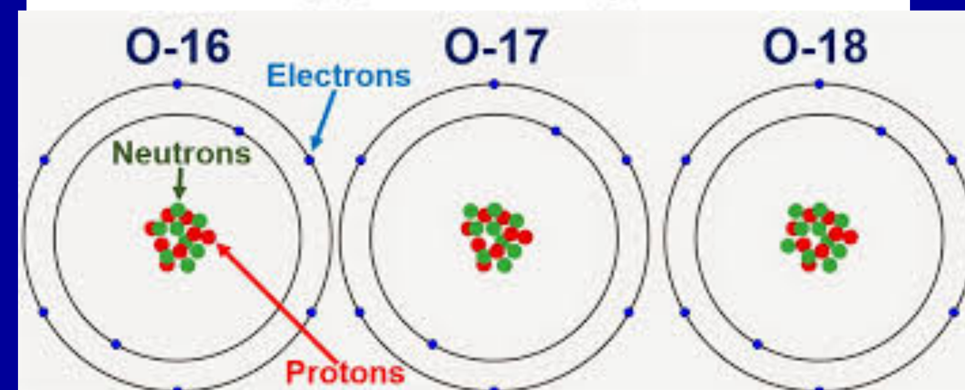
Z=6, A = 12

Z=6, A = 13

Z=6, A = 14



Oxygen Isotopes



99.76%	0.04%	0.20%

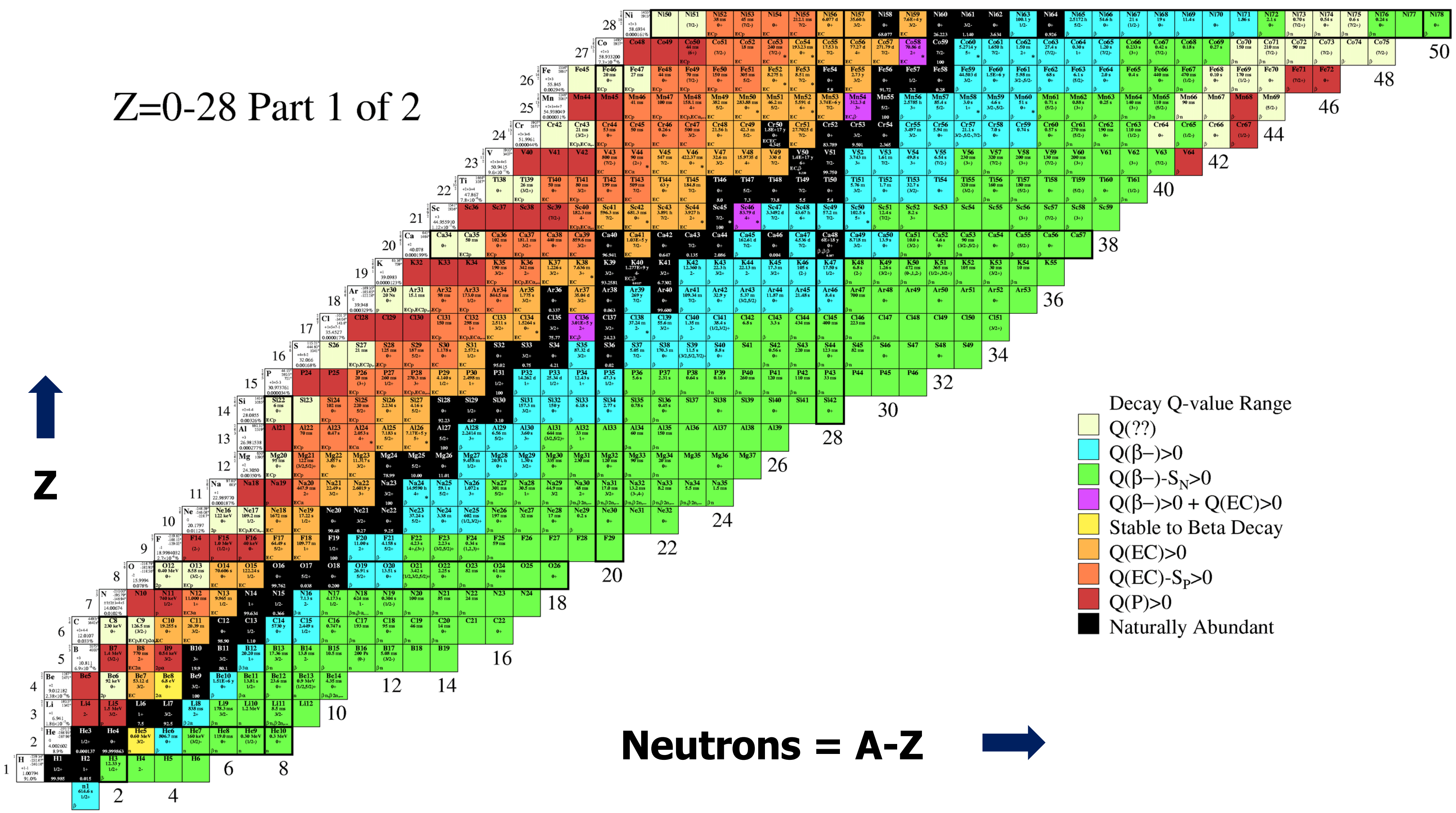
neutrons

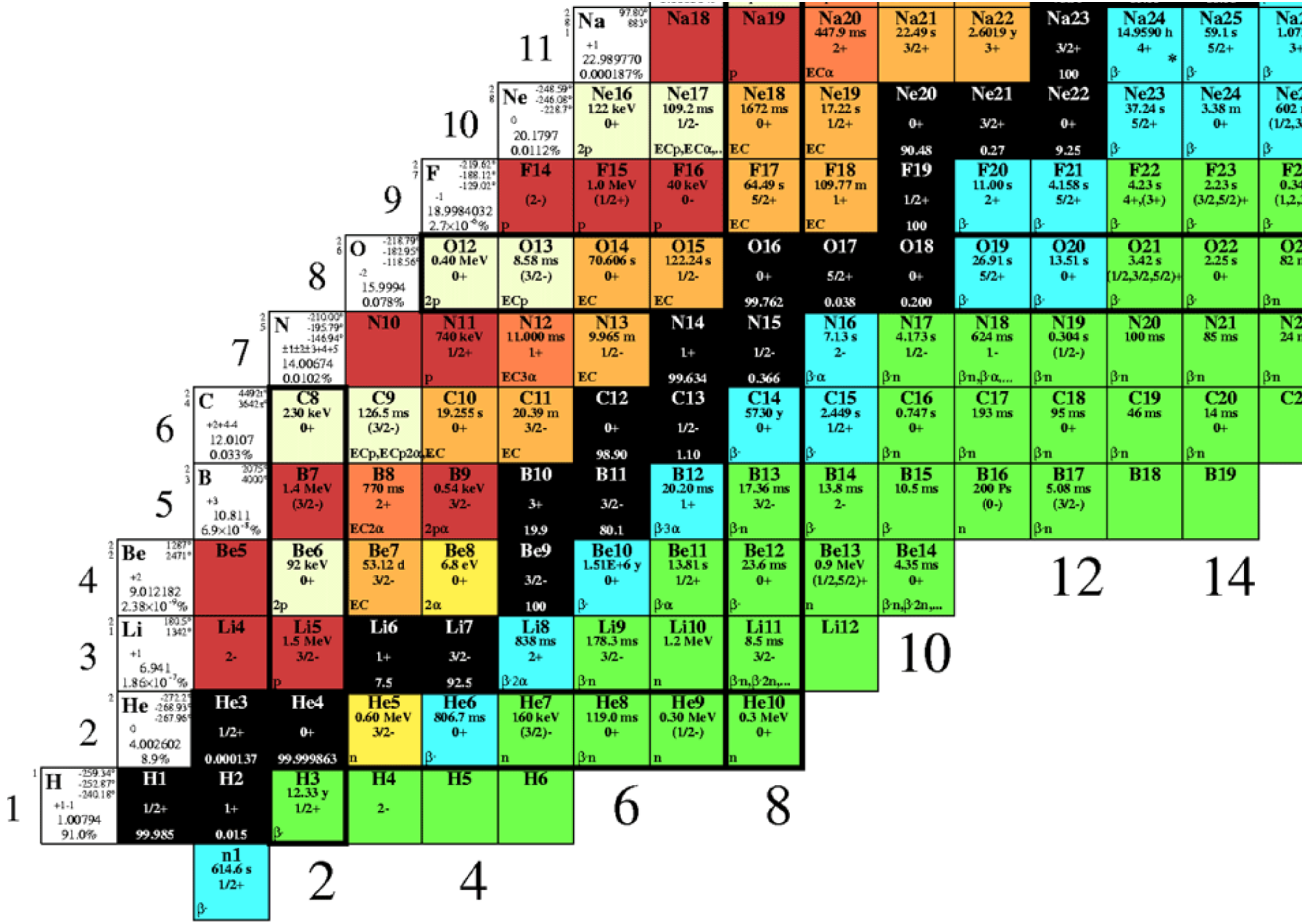
8	9	10

protons 8

Chart of nuclei

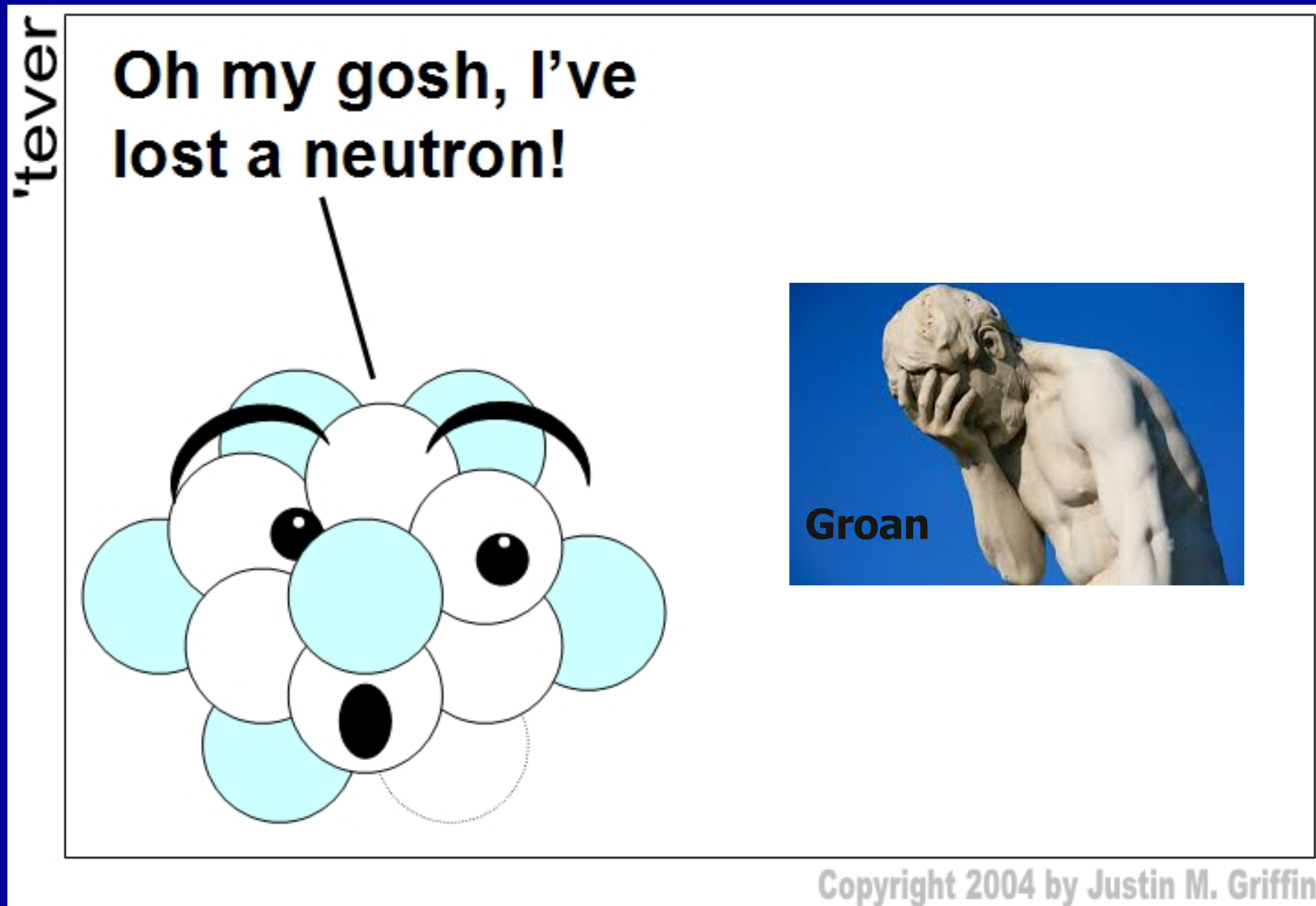
Table of Isotopes (1999)





11
Na 97.80° 883° +1 22.989770 0.000187%
Na18 p
Na19 p
Na20 447.9 ms 2+ ECα
Na21 22.49 s 3/2+
Na22 2.6019 y 3+
Na23 3/2+ 100
Na24 14.9590 h 4+ * β-
Na25 59.1 s 5/2+ β-
10
Ne -248.59° -246.08° -228.7° 0 20.1797 0.0112%
Ne16 122 keV 0+ 2p
Ne17 109.2 ms 1/2- ECp,ECα,...
Ne18 1672 ms 0+ EC
Ne19 17.22 s 1/2+ EC
Ne20 0+ 90.48
Ne21 3/2+ 0.27
Ne22 0+ 9.25
Ne23 37.24 s 5/2+ β-
Ne24 3.38 m 0+ β-
9
F -219.62° -188.12° -129.02° -1 18.9984032 2.7×10^-6%
F14 (2-) p
F15 1.0 MeV (1/2+) p
F16 40 keV 0- p
F17 64.49 s 5/2+ EC
F18 109.77 m 1+ EC
F19 1/2+ 100
F20 11.00 s 2+ β-
F21 4.158 s 5/2+ β-
F22 4.23 s 4+,(3+) β-
F23 2.23 s (3/2,5/2)+ β-
8
O -218.79° -182.95° -118.56° -2 15.9994 0.078%
O12 0.40 MeV 0+ 2p
O13 8.58 ms (3/2-) ECp
O14 70.606 s 0+ EC
O15 122.24 s 1/2- EC
O16 0+ 99.762
O17 5/2+ 0.038
O18 0+ 0.200
O19 26.91 s 5/2+ β-
O20 13.51 s 0+ β-
O21 3.42 s (1/2,3/2,5/2)+ β-
O22 2.25 s 0+ β-
7
N -210.00° -195.79° -146.94° ±1±2±3+4+5 14.00674 0.0102%
N10
N11 740 keV 1/2+ p
N12 11.000 ms 1+ EC3α
N13 9.965 m 1/2- EC
N14 1+ 99.634
N15 1/2- 0.366
N16 7.13 s 2- β-α
N17 4.173 s 1/2- β-n
N18 624 ms 1- β-n,β-α,...
N19 0.304 s (1/2-) β-n
N20 100 ms β-n
N21 85 ms β-n
6
C 4492t° 3642s° +2+4-4 12.0107 0.033%
C8 230 keV 0+
C9 126.5 ms (3/2-) ECp,ECp2α,...
C10 19.255 s 0+ EC
C11 20.39 m 3/2- EC
C12 0+ 98.90
C13 1/2- 1.10
C14 5730 y 0+ β-
C15 2.449 s 1/2+ β-
C16 0.747 s 0+ β-n
C17 193 ms β-n
C18 95 ms 0+ β-n
C19 46 ms β-n
C20 14 ms 0+ β-n
5
B 2075° 4000° +3 10.811 6.9×10^-8%
B7 1.4 MeV (3/2-)
B8 770 ms 2+ EC2α
B9 0.54 keV 3/2- 2pα
B10 3+ 19.9
B11 3/2- 80.1
B12 20.20 ms 1+ β-3α
B13 17.36 ms 3/2- β-n
B14 13.8 ms 2- β-
B15 10.5 ms β-
B16 200 Ps (0-) n
B17 5.08 ms (3/2-) β-n
B18
B19
4
Be 1287° 2471° +2 9.012182 2.38×10^-9%
Be5
Be6 92 keV 0+ 2p
Be7 53.12 d 3/2- EC
Be8 6.8 eV 0+ 2α
Be9 3/2- 100
Be10 1.51E+6 y 0+ β-
Be11 13.81 s 1/2+ β-α
Be12 23.6 ms 0+ β-
Be13 0.9 MeV (1/2,5/2)+ n
Be14 4.35 ms 0+ β-n,β-2n,...
12
14
3
Li 180.5° 1342° +1 6.941 1.86×10^-7%
Li4 2-
Li5 1.5 MeV 3/2- p
Li6 1+ 7.5
Li7 3/2- 92.5
Li8 838 ms 2+ β-2α
Li9 178.3 ms 3/2- β-n
Li10 1.2 MeV n
Li11 8.5 ms 3/2- β-n,β-2n,...
Li12
10
2
He -272.2° -268.93° -267.96° 0 4.002602 8.9%
He3 1/2+ 0.000137
He4 0+ 99.999863
He5 0.60 MeV 3/2- n
He6 806.7 ms 0+ β-
He7 160 keV (3/2)- n
He8 119.0 ms 0+ β-n
He9 0.30 MeV (1/2-) n
He10 0.3 MeV 0+ n
1
H -259.34° -252.87° -240.18° +1-1 1.00794 91.0%
H1 1/2+ 99.985
H2 1+ 0.015
H3 12.33 y 1/2+ β-
H4 2-
H5
H6
6
8
n1 614.6 s 1/2+ β-
2
4

Alchemy by neutron bombardment



How to indicate which isotope

- Normally we write CO_2 (ignoring the isotopes)
- We can add the mass number, e.g. $^{12}CO_2$, $^{13}CO_2$ or $^{14}CO_2$
- We could also indicate which oxygen isotope: $^{12}C^{18}O^{16}O$ (CO_2 with one ^{18}O atom)
- This will indicate which isotope of the carbon we are talking about.
- You have all heard about carbon dating. It uses the isotope ^{14}C.

Human Causation

How do we know the increasing CO_2 doesn't come from volcanos?

Was it because we burned a lot of wood in our wood stoves or burned trash to make electricity? Is it from decaying plants?

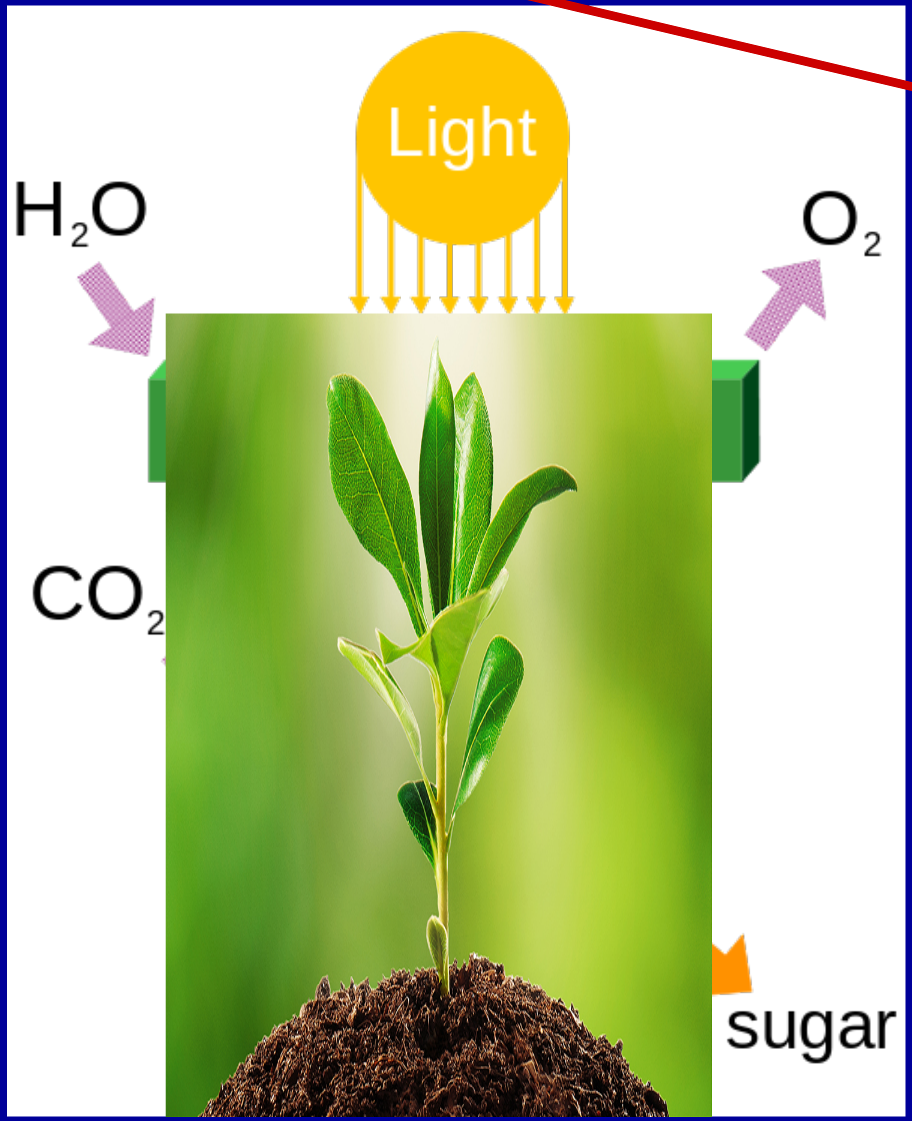
Can we find a "smoking gun" that shows CO_2 is coming from burning ancient hydrocarbons?

Photosynthesis

$6CO_2 + 12H_2O + \text{light} \rightarrow C_6H_{12}O_6 + 6O_2 + 6H_2O$

Isotopes!

The C can be ^{12}C, ^{13}C or even ^{14}C



Aside: This explains why you have to water plants (12 in 6 out).

The plant can use $^{12}CO_2$ or $^{13}CO_2$ or even $^{14}CO_2$ to make the sugar.

Light provides the energy to drive the process. It takes less energy to use the lightest carbon isotope, ^{12}C, so the plant does this preferentially.

Different plants use different photosynthetic processes (C3 & C4), but both processes deplete ^{13}C & ^{14}C relative to ^{12}C.

Reduced [$^{13}C/^{12}C$] in plants and fossil fuels.

- Plants find it easier (takes less energy) to use the lightest isotopes when they convert sunlight and CO_2 into food. This is true for all forms of plant life.

Young plants

Living forest

Ancient plants

$[^{13}CO_2/^{12}CO_2]$ inside plants is less than $[^{13}CO_2/^{12}CO_2]$ in air

[ ] indicate the abundance ratio of

550Myr old plants

Plants fractionate carbon

- Plants live off of CO_2; let's focus on the C
- Most carbon is ^{12}C.
- There is less ^{13}C (and ^{14}C) in wood,
  - in fossil fuels, coal, oil or natural gas,
  - in plastics
  - than in the air they used when they grew.

  ∴ the [$^{13}C/^{12}C$] and [$^{14}C/^{12}C$] ratios are lower

The [$^{13}CO_2/^{12}CO_2$] story

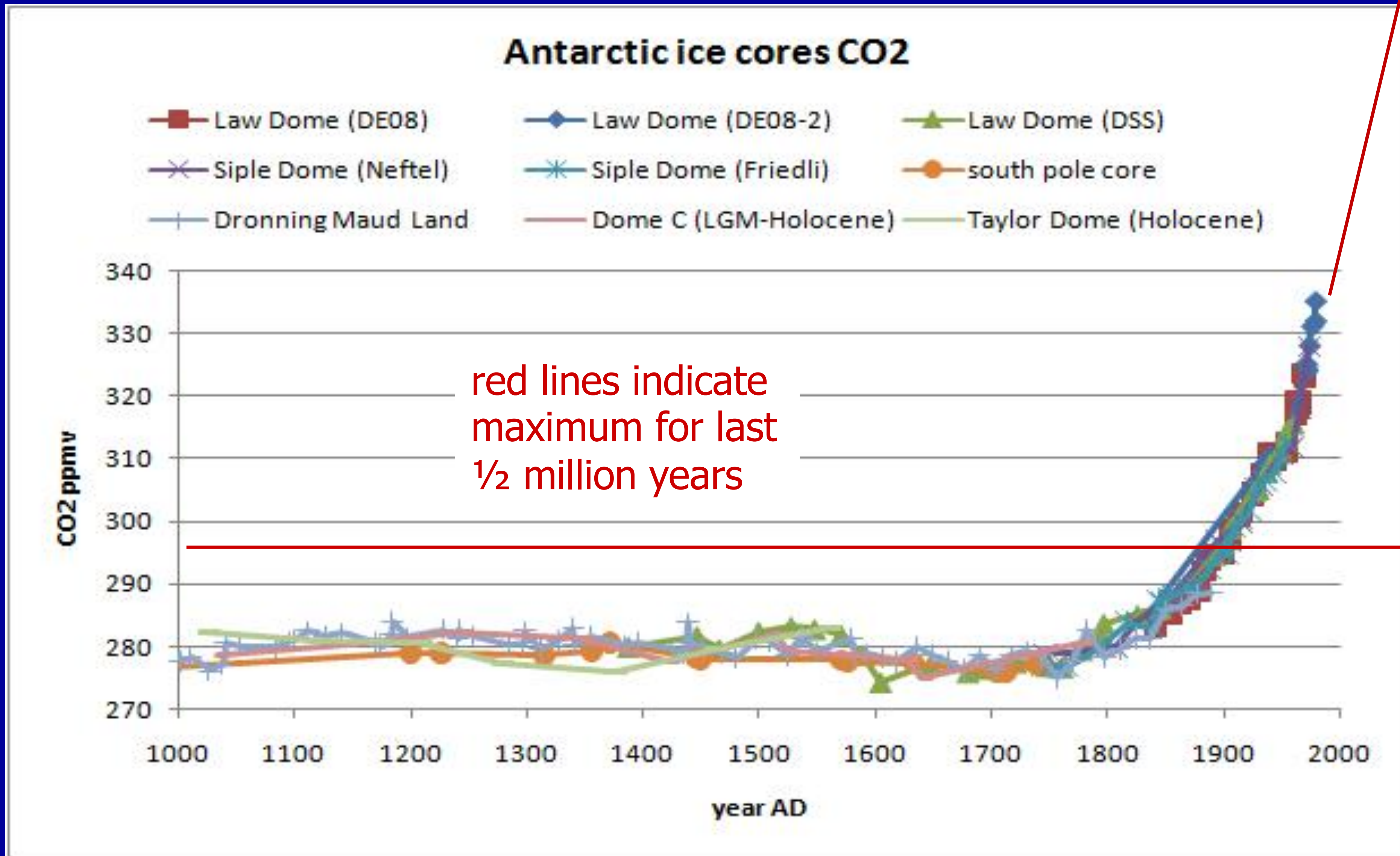
"In the beginning" [$^{13}C/^{12}C$] ratio has the "natural" or universal abundance.

- Ratio of [$^{13}CO_2/^{12}CO_2$] in the air was the "natural" abundance when the plants grew.
- Growing plants decrease the [$^{13}CO_2/^{12}CO_2$] ratio.
- The reduced [$^{13}CO_2/^{12}CO_2$] ratio was frozen in when the plant died.

That reduced ratio appears in the CO_2 released when the plant (now a fuel) is burned.

Current 415 ppm
32% of CO_2 in air added since 1800

Now CO_2 is a mix of old and new CO_2.



An example

white water

old CO_2 with
$^{13}C/^{12}C = {}^{13}C/^{12}C_{ref}$

blue water

add CO_2 with
less ^{13}C from
burning
fossil fuels

Not so blue water

$^{13}C/^{12}C$ will decrease as
the "blueness" decreased

The [$^{13}CO_2$/$^{12}CO_2$] story

- There is now 415 ppm of CO_2 {$^{12+13+14}CO_2$} in the atmosphere (after contamination by the burning of carbon-based fuels became significant – our hypothesis, 285 ppm).

- So (415ppm-285ppm)/410ppm = 32% of the CO_2 (in air) comes from burning carbon-based materials.

The [$^{13}CO_2/^{12}CO_2$] story

- Outgassing of C from volcanoes has the "natural" or universal abundance.
  - Ratio of $^{13}CO_2/^{12}CO_2$ in the air was the "natural" abundance when coal & oil were formed.

- There is now 415 ppm of CO_2 [$^{12+13+14}CO_2$] in the atmosphere (after contamination by the burning of fossil fuels became significant – our hypothesis, 280 ppm).
- So (415-280)/415 = **32%** of the CO_2 (in air) comes from burning something.

How do we measure this deficit of ^{13}C? It's a small number!

$$\delta^{13}C = \frac{\left[\left(\frac{^{13}C}{^{12}C}\right)_{sample} - \left(\frac{^{13}C}{^{12}C}\right)_{standard}\right]}{\left(\frac{^{13}C}{^{12}C}\right)_{standard}} * 1000\%$$

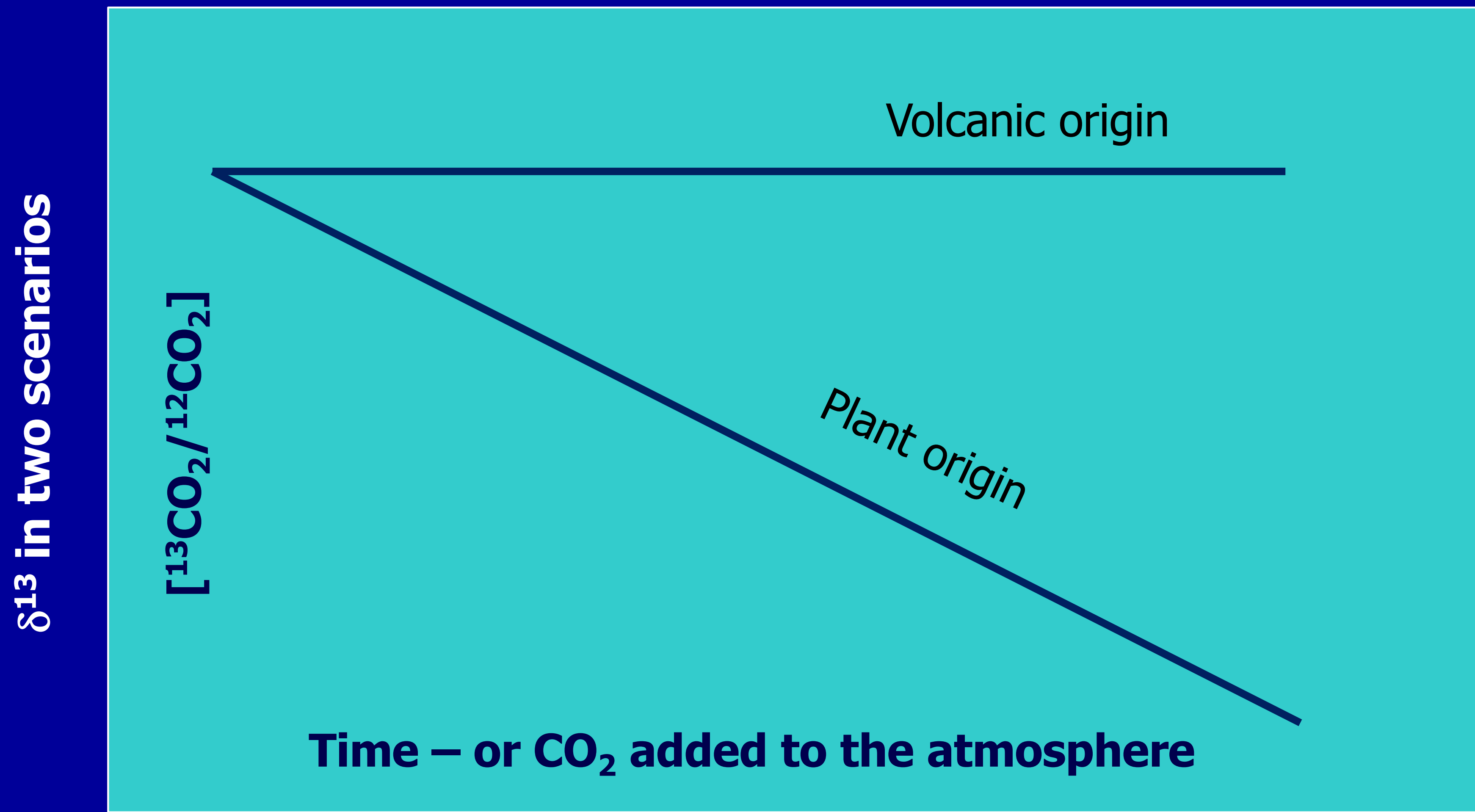
Multiply by 1000% to make the number reasonable.

This formula for δ is used for other isotopes, e.g. ^{14}C

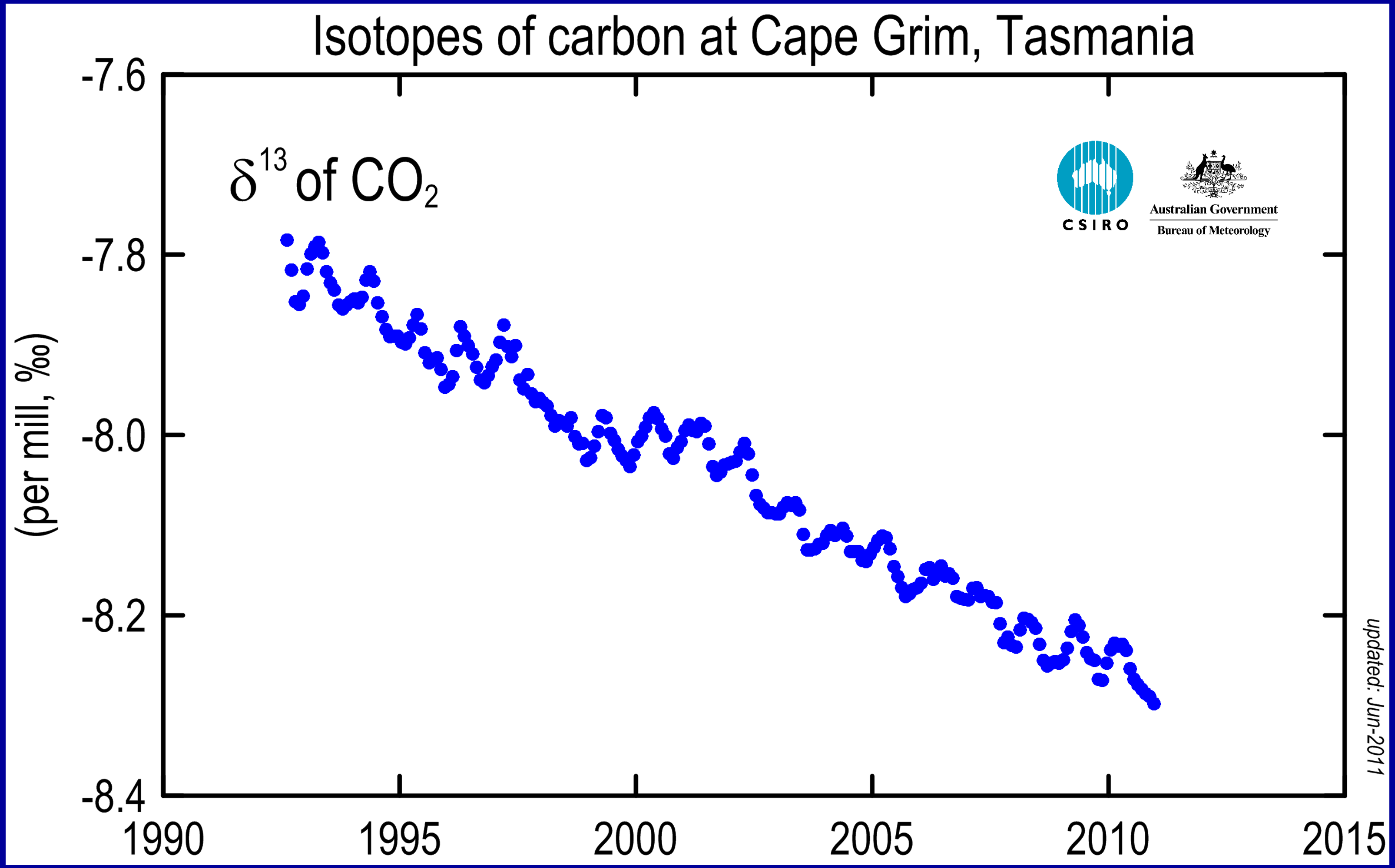
What happens when we burn carbon fuels?

- Plants take in ^{12}C more easily than they do ^{13}C (or ^{14}C).
- The standard ratio of [$^{13}C/^{12}C$] is 0.01123720 has been established as $\delta^{13}C$ value of zero.
  - This number doesn't matter. You just need to know there is a standard.
- We burn wood, plants, coal and oil now releasing the carbon to the atmosphere. Plants decay. There will be a lower [$^{13}C/^{12}C$] ratio because these plant that captured it took in less ^{13}C as they grew.

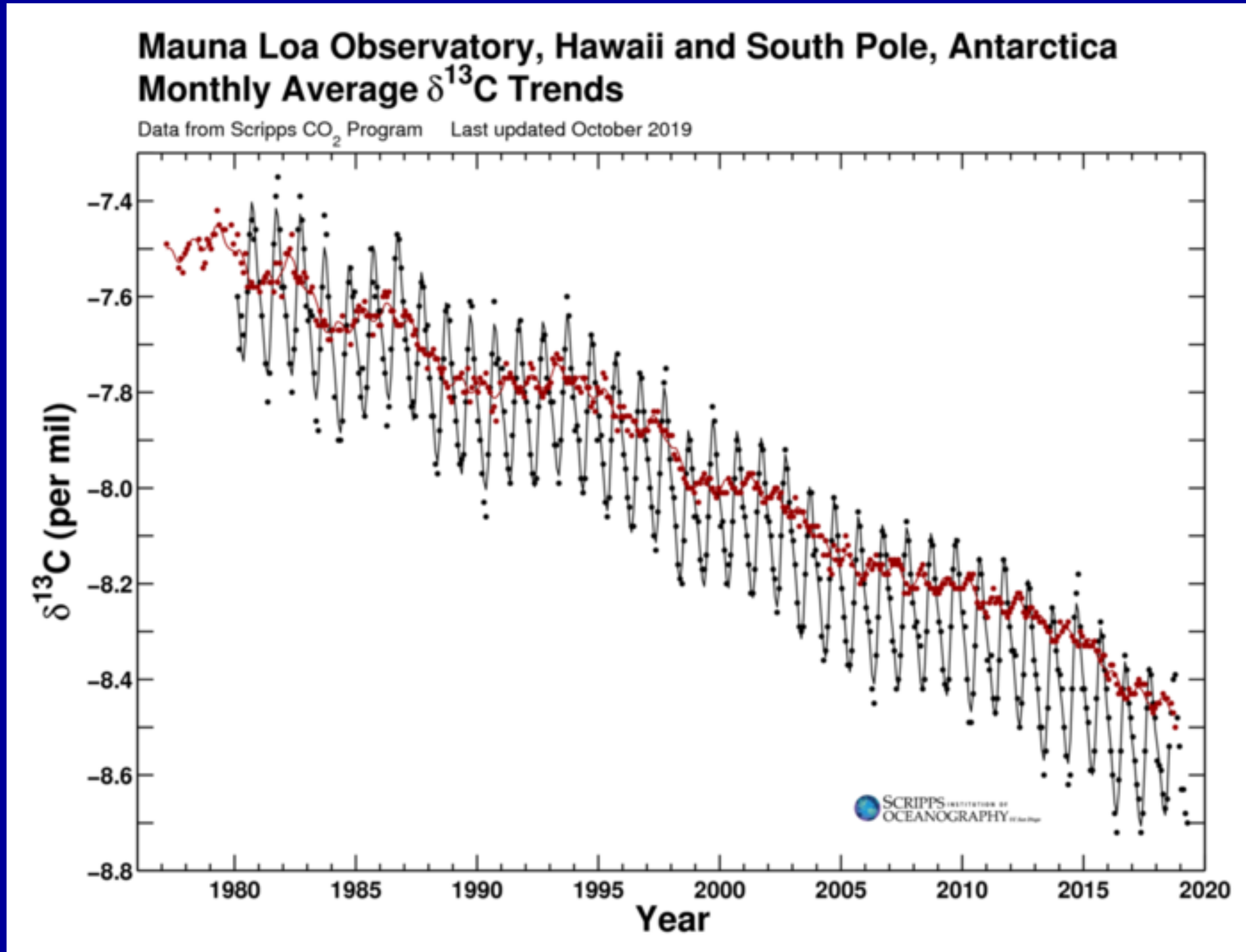
$\delta^{13}C$ vs. time, a measure of the fractional amount of $^{13}CO_2$ relative to $^{12}CO_2$



Hypothesis is tested in air

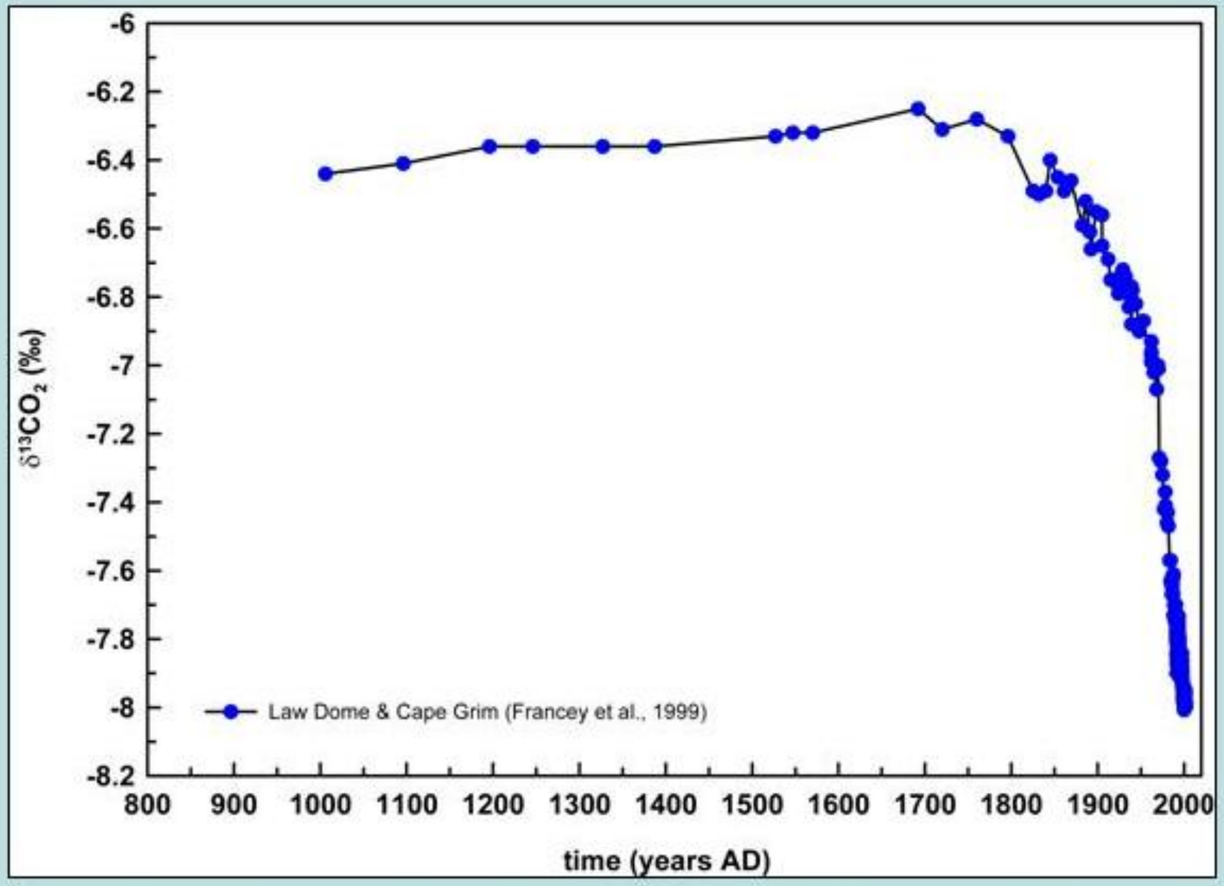


http://www.cmar.csiro.au/research/capegrim_graphs.html



Mauna Loa Observatory, Hawaii and South Pole, Antarctica
Monthly Average δ13C Trends
Data from Scripps CO2 Program
Last updated October 2019
δ13C (per mil)
−7.4
−7.6
−7.8
−8.0
−8.2
−8.4
−8.6
−8.8
1980
1985
1990
1995
2000
2005
2010
2015
2020
Year
SCRIPPS
OCEANOGRAPHY

Hypothesis is tested in ice cores

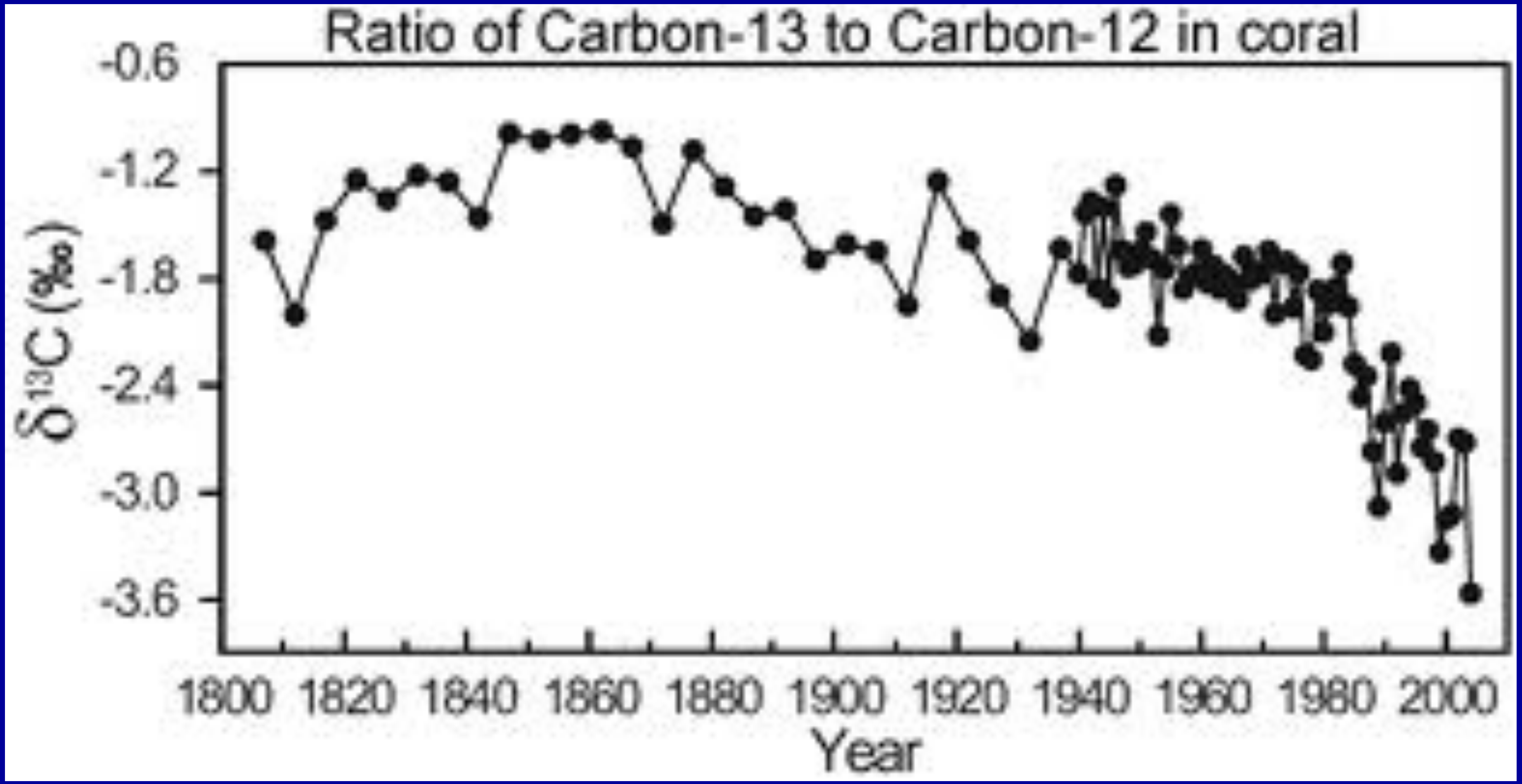


Reconstruction of the carbon isotope (C-13) of atmospheric CO2 from the Law Dome ice core (Francey et al., 1999) and the Cape Grim ambient air measurements (Allison et al., 2003).

pre-industrial value -6.4

http://www.bridge.bris.ac.uk/projects/pcmip/experiments.html

Hypothesis is tested in corals



"Evidence for ocean acidification in the Great Barrier Reef of Australia",
G. Wei et al., 2009, Geochimica et Cosmochimica Acta, **73**, 2332–2346

We proved the CO_2 comes from plants, but are they really old plants: coal, oil?

What about recently decaying plants, trees cut and burned, garbage burned, other recent releases of CO_2?

- For this we turn to another isotope of carbon, ^{14}C.

Two scenarios

1. Recent burning

415 ppm	**280 ppm**	**135 ppm**

$^{12+13+14}CO_2$(observed) = $^{12+13+14}CO_2$(before homo) + $^{12+13}CO_2$(recent)

Measure the ^{14}C fraction — should have ^{14}C — should have ^{14}C

Expect ^{14}C in atmosphere to be constant

2. Burning ancient hydrocarbons

415 ppm	**280 ppm**	**135 ppm**

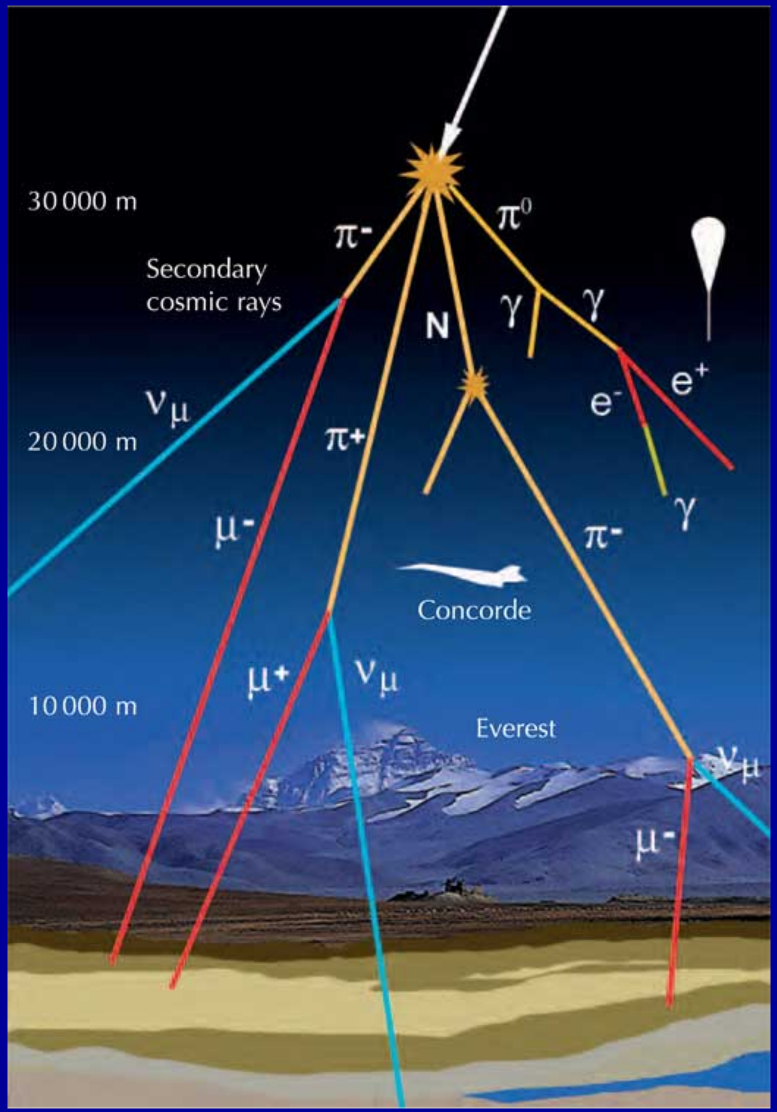
$^{12+13+14}CO_2$(observed) = $^{12+13+14}CO_2$(before homo) + $^{12+13}CO_2$(fossil)

Measure the ^{14}C fraction — should have ^{14}C — should have no ^{14}C

Expect ^{14}C in atmosphere to be going down

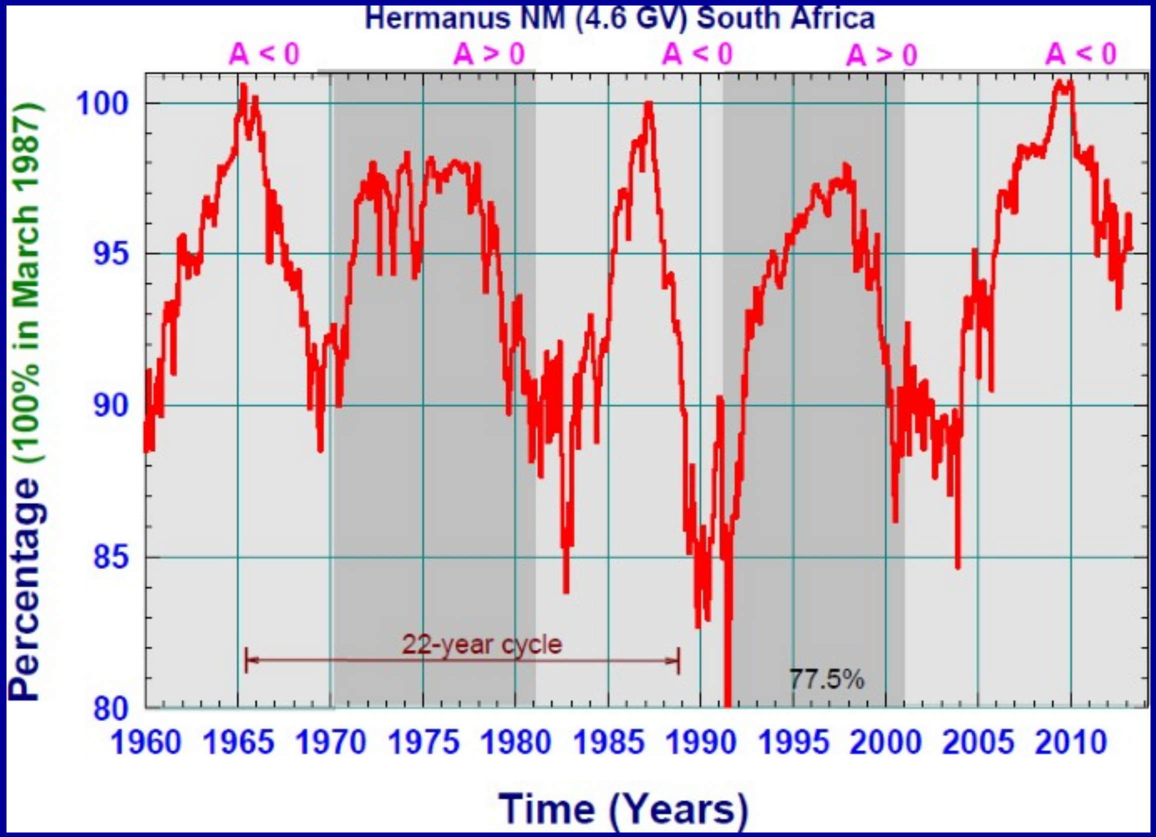
To decide between these scenarios, we need to digress to show that ^{14}C is produced continuously.

What is a cosmic ray?

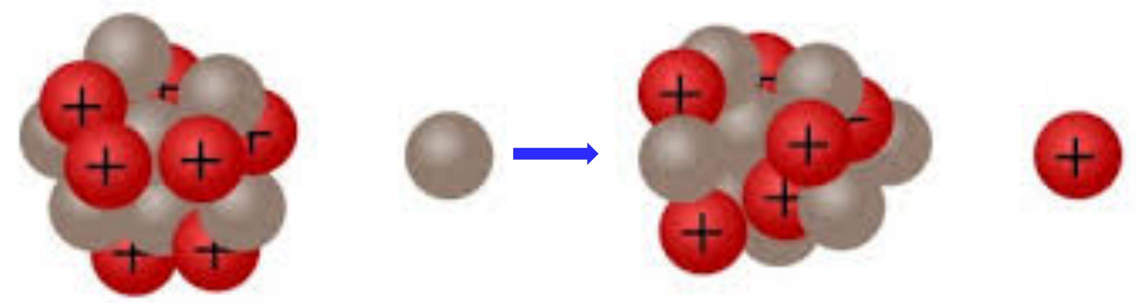


- A bare nucleus of an atom (mostly protons) flying around the galaxy
  - With energies like those produced in big Earth based accelerators (SLAC, CERN or Fermilab)
  - Charged particles, nuclei; the electrons are stripped away
- Produce neutrons from interactions with atoms in the air

- Cosmic rays are believed to have been constant (within +/-50%) in intensity for 100s of thousands years.
  - There is a modulation of intensity on a 22 yr cycle of the sun’s magnetic fields.



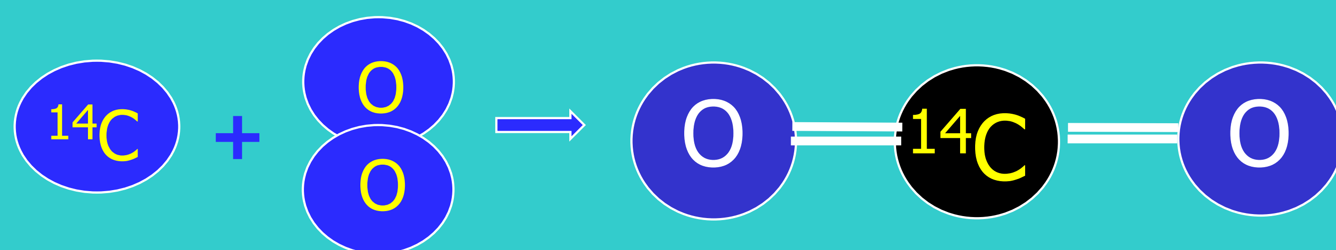
Making a $^{14}CO_2$



8 neutrons →
7 protons →

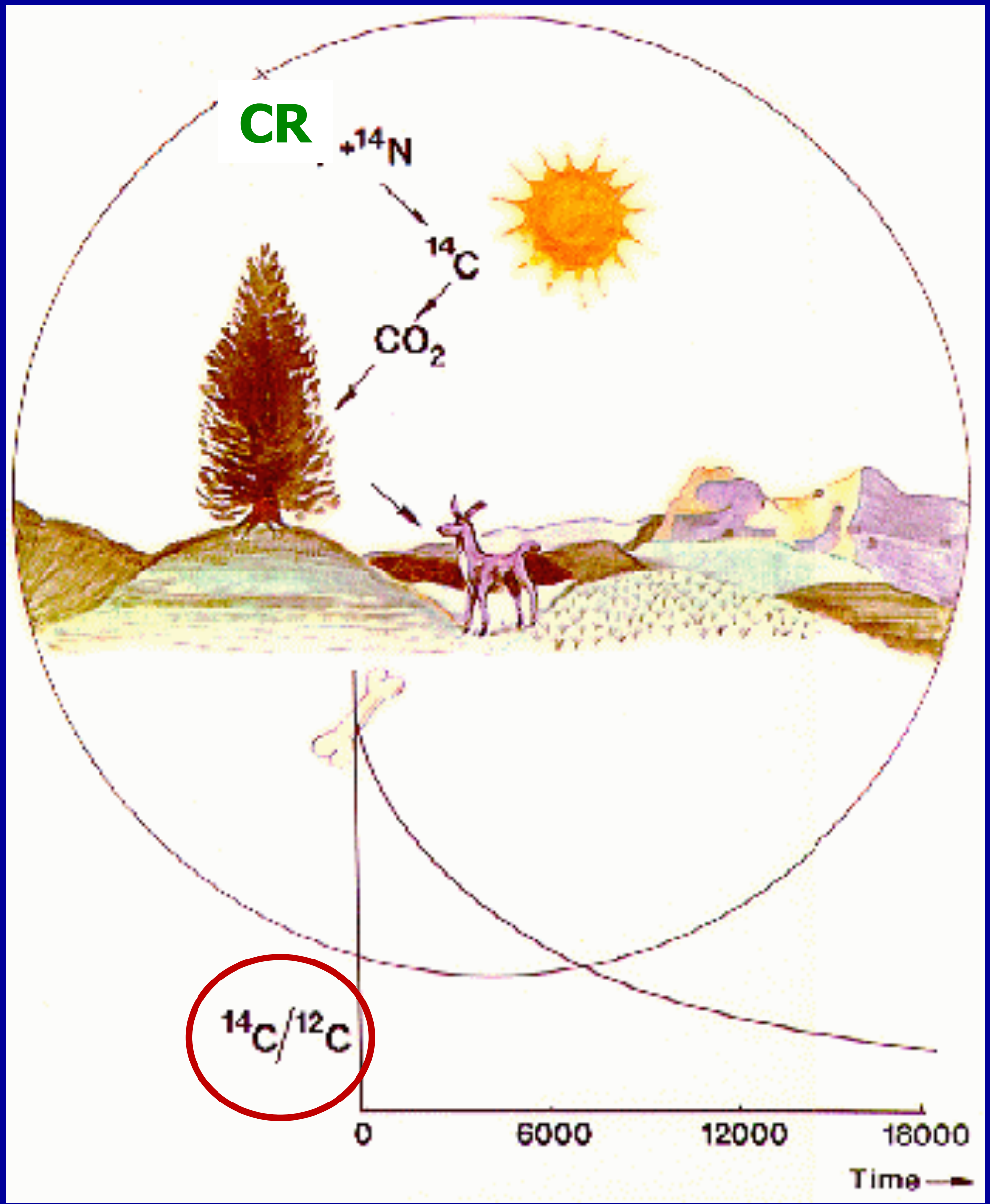
$$^{14}_{7}N + ^{1}_{0}n \rightarrow ^{14}_{6}C + ^{1}_{1}p$$

H^+ ion



$$^{14}C + O_2 \text{ -> } ^{14}CO_2$$

Production of ^{14}C



high energy cosmic rays interact with nuclei in the atmosphere & produce slow moving neutrons

CR + A > p′ + A′ + *neutrons*

^{14}N nucleus has 7p & 7n
^{14}C nucleus has 6p & 8n

The neutrons exchange charge with a ^{14}N to make a ^{14}C

$$n + {}^{14}N \rightarrow {}^{14}C + p$$

^{14}C decays naturally back to ^{14}N

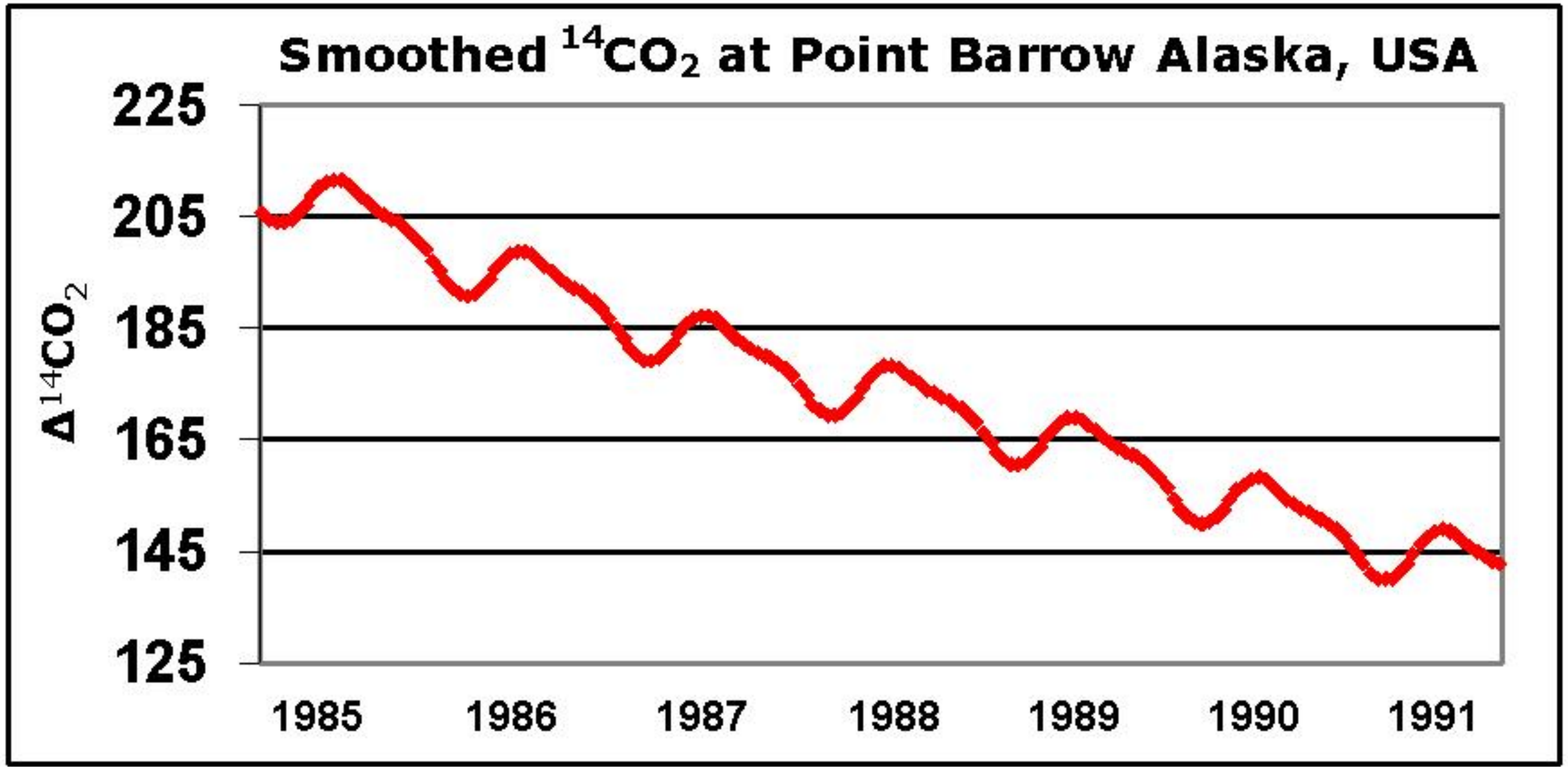
$t_{1/2}$ = 5730 years

Live plants take up some $^{14}CO_2$

- Give confirmation of tree ring dates.
- Date archeological sites
  - e.g. construction beams and fire pits
- Burning recently grown plants (<2000 years old) will have $^{14}CO_2$.
- Ancient hydrocarbons have no remaining ^{14}C. It has all long since decayed.

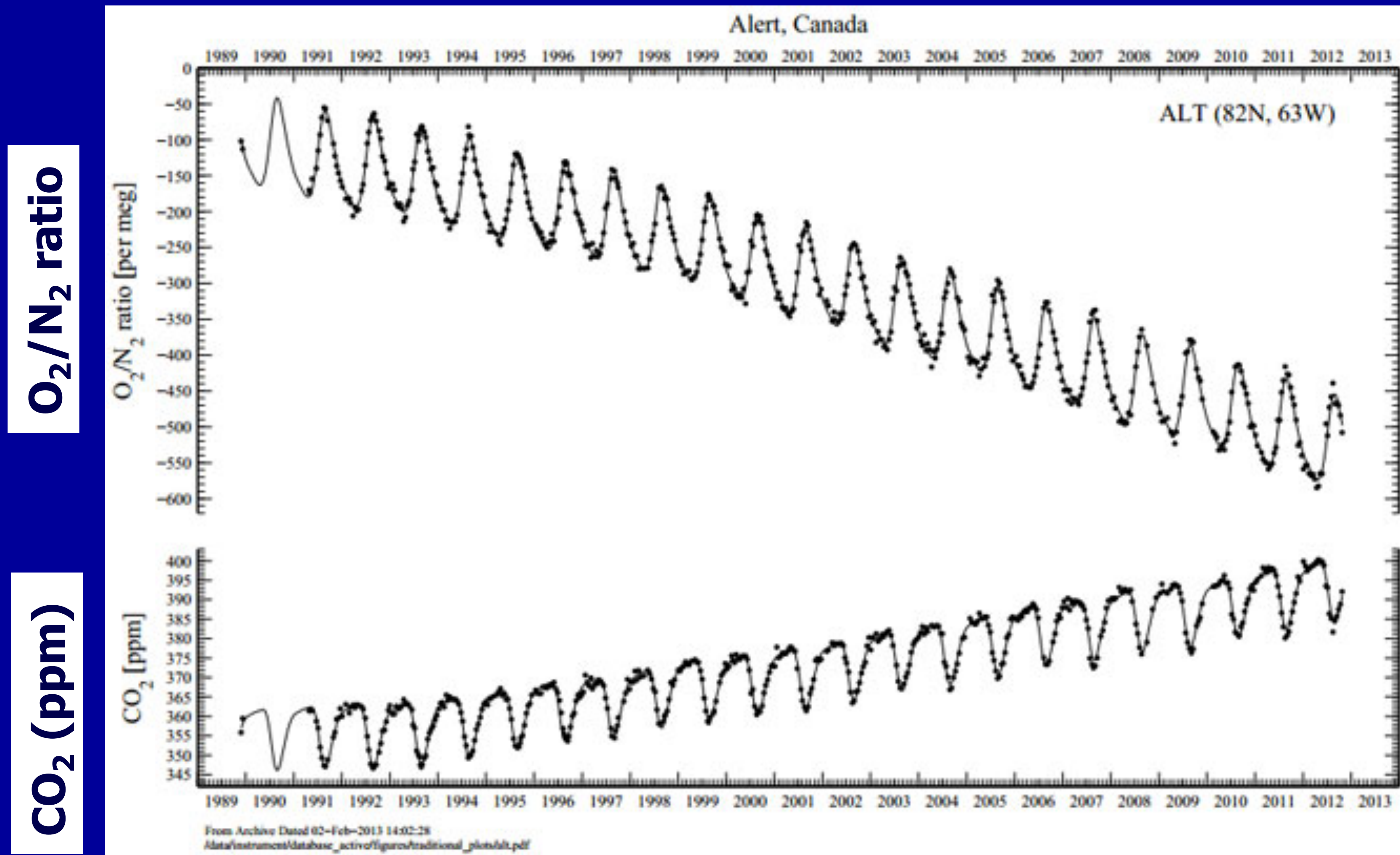
Ancient hydrocarbons have no $^{14}CO_2$

- After several half lives (e.g. 30,000 years) the ^{14}C has decayed; what's left is undetectable.
- There is no ^{14}C remaining in fossil fuel.
- Add CO_2 from ancient hydrocarbons to atmosphere, the fraction [$^{14}CO_2/CO_2$] will decrease.



Fossil fuels have no ^{14}C (half-life 5739 yrs).
Declining $^{14}CO_2$ indicates the recently added atmospheric CO_2 is from ancient material, not from plants that grew and died recently.
(Careful about bomb tests!)

Oxygen used by burning



The observed downward trend is 19 'per meg' per year. This corresponds to losing 19 O_2 molecules out of every 1 million O_2 molecules in the air/year.
http://scrippso2.ucsd.edu

∴CO_2 is increasing due to the burning of ancient hydrogen carbon fuels.

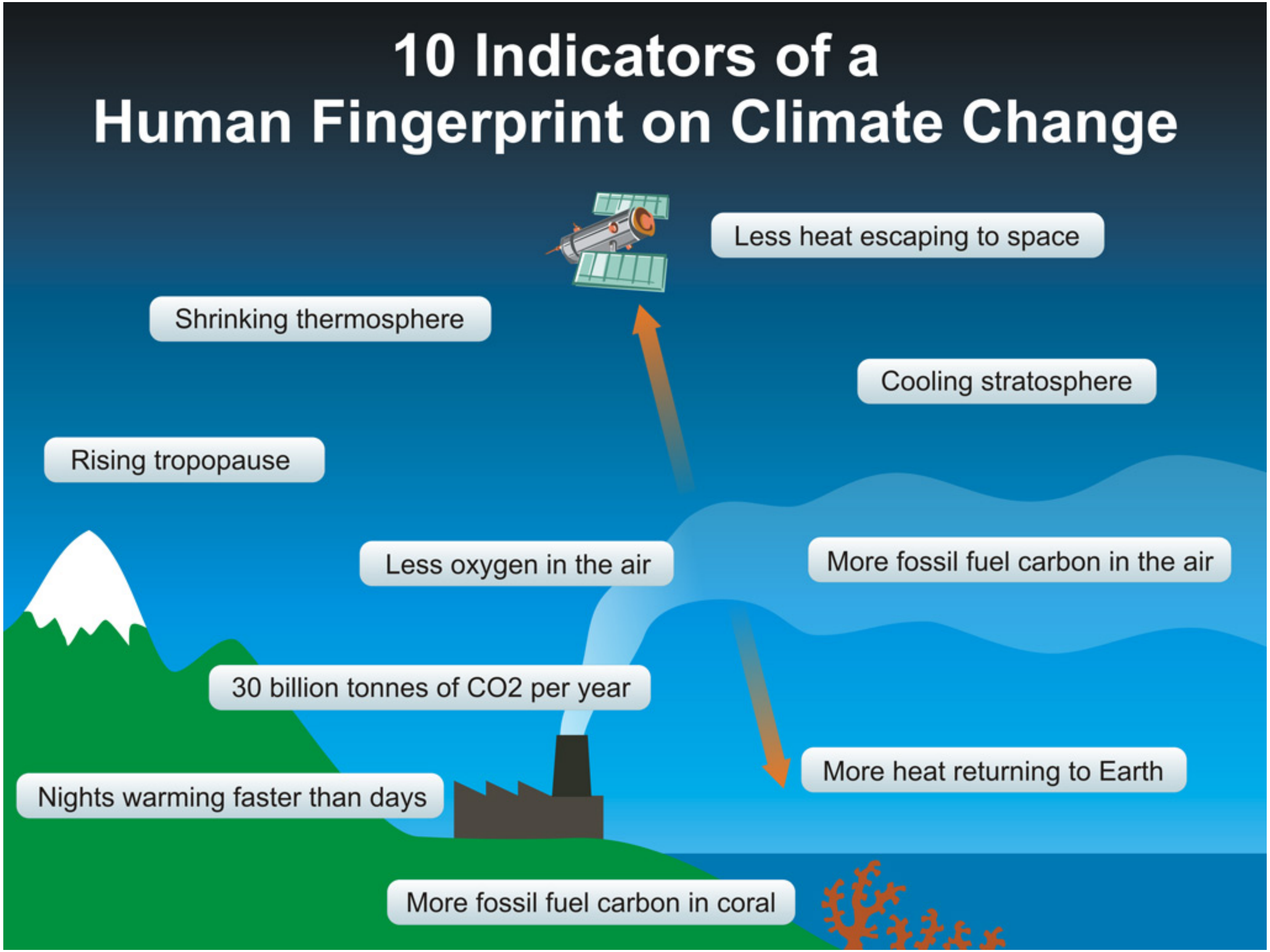
Alternative explanations??

I know of no other explanation for the simultaneous decreases in the ratios of [$^{13}CO_2/^{12}CO_2$] and [$^{14}CO_2/^{12}CO_2$] in the atmosphere and in corals (and decreasing O_2/N_2).

If you know of one, please inform the instructor.

Summary of Evidence for Anthropogenic changes

- Changes in the infrared spectrum from the sky (as seen from Earth) and from the Earth (as seen from space)
- Warming (and rising) troposphere and cooling stratosphere
- Nights warming faster than days and winters faster than summers (not the sun)
- Decreasing $^{13}CO_2$ points to fossil fuels (atmosphere and corals), ^{14}C is decreasing (not fresh growth)
- O_2 being depleted from burning fossil fuels
- Atmospheric warming and cooling vs. altitude as predicted by modeling
- Ocean warming patterns as predicted by modeling


10 Indicators of a
Human Fingerprint on Climate Change
Less heat escaping to space
Shrinking thermosphere
Cooling stratosphere
Rising tropopause
Less oxygen in the air
More fossil fuel carbon in the air
30 billion tonnes of CO2 per year
More heat returning to Earth
Nights warming faster than days
More fossil fuel carbon in coral

Conclusions

- The slow decline of the heavy isotopic versions of CO_2, $^{13}CO_2$ and $^{14}CO_2$, prove the CO_2 being added to the atmosphere is from burning ancient hydrocarbons.
- There are many other pieces of corroborating evidence that the CO_2 increase has an anthropogenic origin.
- The fraction of CO_2 from human activities is currently about 32%.

What drove climate over Earth's history

1. The bombardment of comets and meteorites
2. The solar intensity
3. Plate tectonics and motions
   - Volcanism
4. Greenhouse gases
5. Earth's orbit
   - eccentricity, precession and obliquity (tilt)
6. Internal variability
7. Human activities (Can we prove it?)

The end