A Primer on the Concepts and Uses of Stable Isotope Geochemistry

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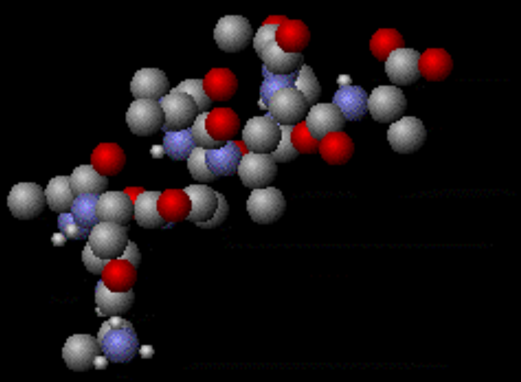
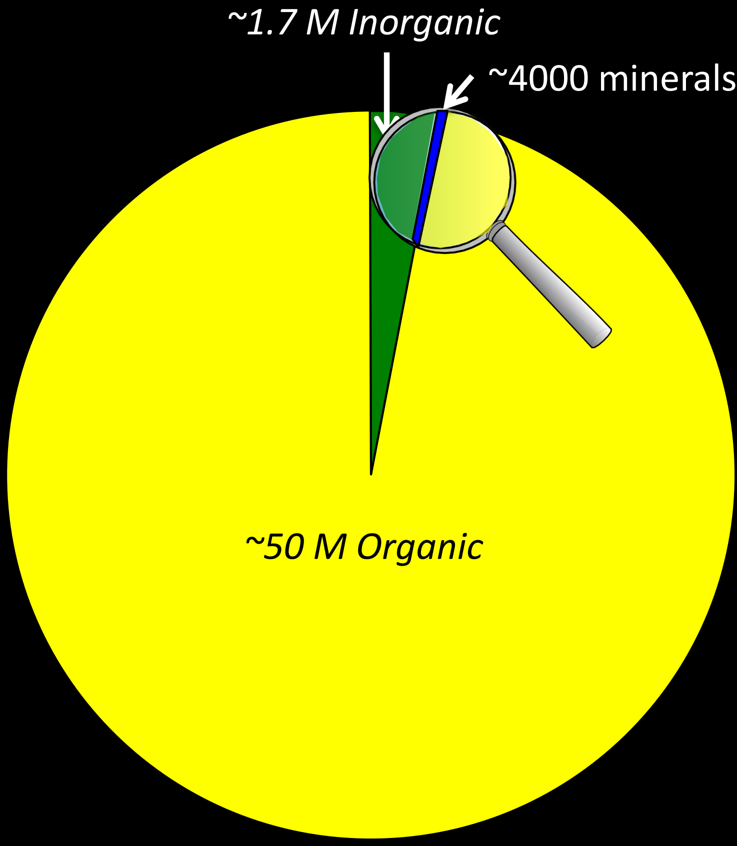
“I have lived much of my life among molecules. They are good company.”
— George Wald



Protein enlarged by a factor of ~10^9 and slowed by a factor of ~10^{12}

The ~52 million known compounds

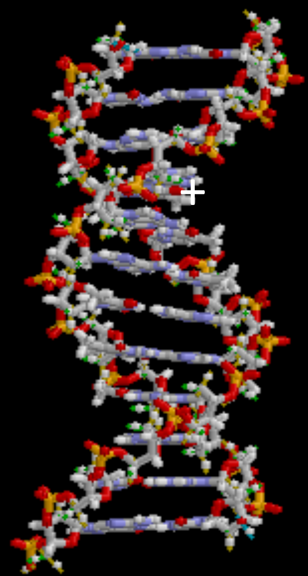


Chemists, physicists and most other scientists and engineers approach molecules, minerals and other materials like small machines, asking questions about their structure, dynamics, behaviors and uses

Geoscientists and other natural scientists ask other sorts of questions, motivated by a need to know the unique history of each sample

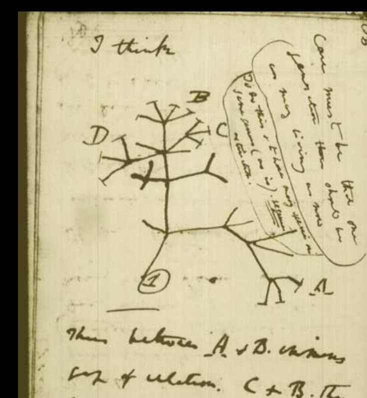
- From *what* was it made?
    - *How* was it made?
        - *When* was it made?
            - *Where* have it's travels brought it?
                - What *conditions* has it experienced ? (T, P, pH, etc.)
                    - What *processes* has it experienced after formation?
                        - To *whom* does it belong?

DNA is a familiar case where chemical structure alone answers many of these sorts of questions



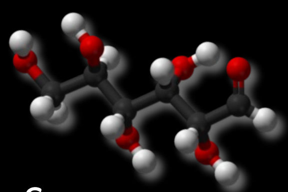
- Tremendous structural complexity and diversity

- Individualized through mutation and inheritance



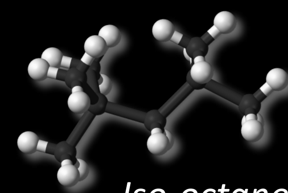
- Analyzable through gene sequencing → Forensics, Diagnosis, Treatment, Engineering

But most of the rest of the chemical world seems anonymous by comparison

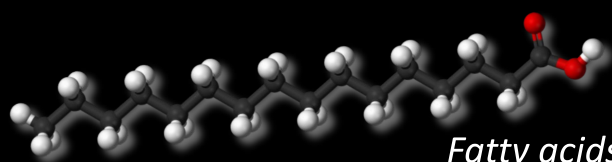


Sugars

- Also serve essential functions

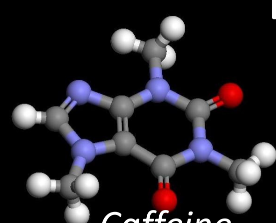


Iso-octane

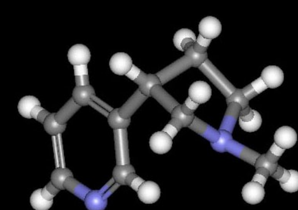


Fatty acids

- But most are structurally simple
- More importantly, they are uniform. Everyone's sugar molecules seem the same



Caffeine

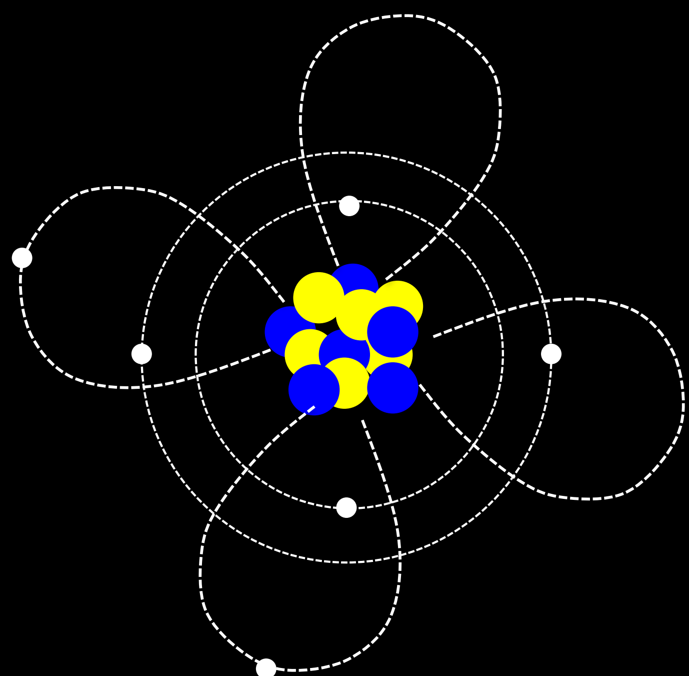


Nicotine

Or are they...

Atoms

"Look closely. The beautiful may be small."
Immanuel Kant



Carbon

Proton – positive charge, heavy

Neutron – uncharged, heavy

Electron – negative charge, light

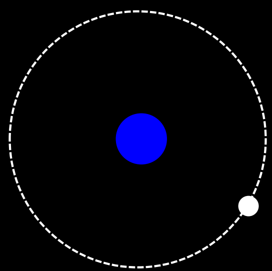
Electron orbital 'path'

Number of Protons → electronic structure → chemical properties

Isotopes: 'At the same place'

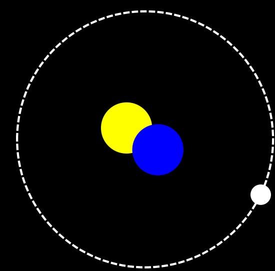
i.e., two (or more) nuclear species that occupy the same space on the periodic table of elements

Hydrogen



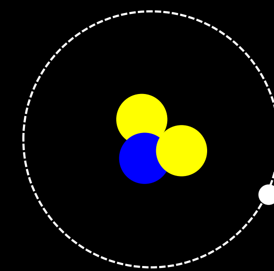
- 99.99 % of natural hydrogen

Deuterium

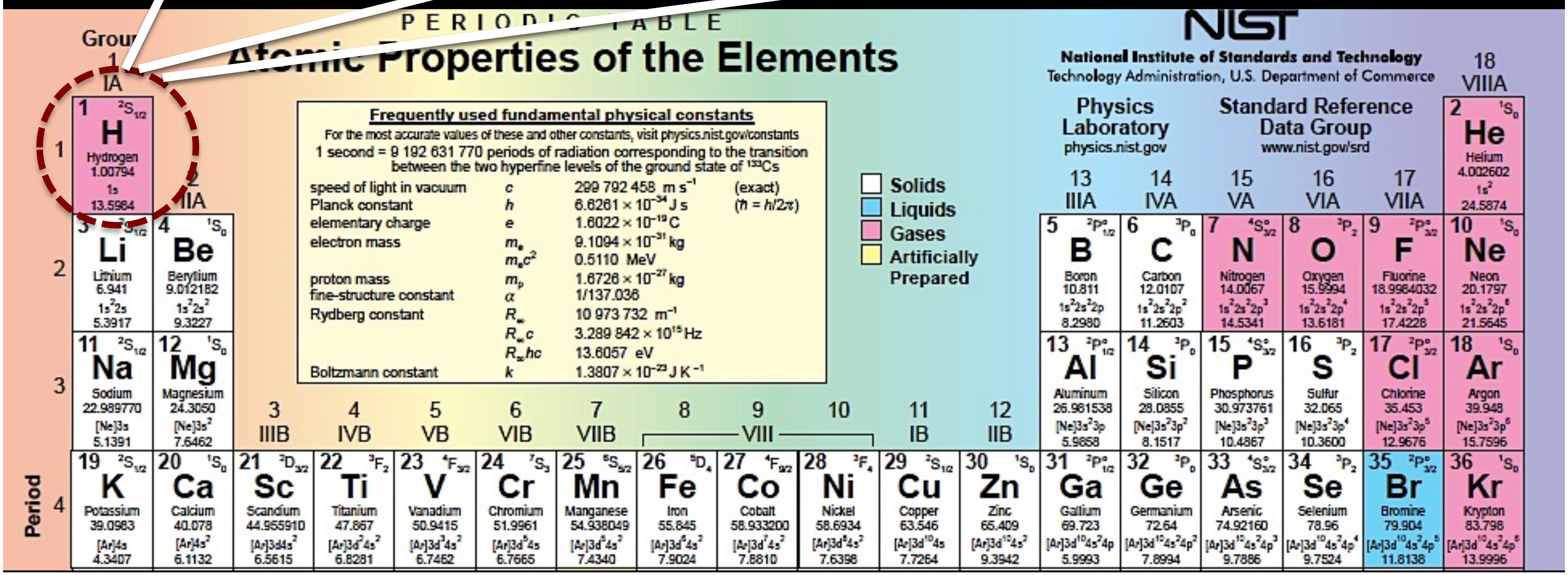


- 0.01 % of natural hydrogen
  Stable

Tritium

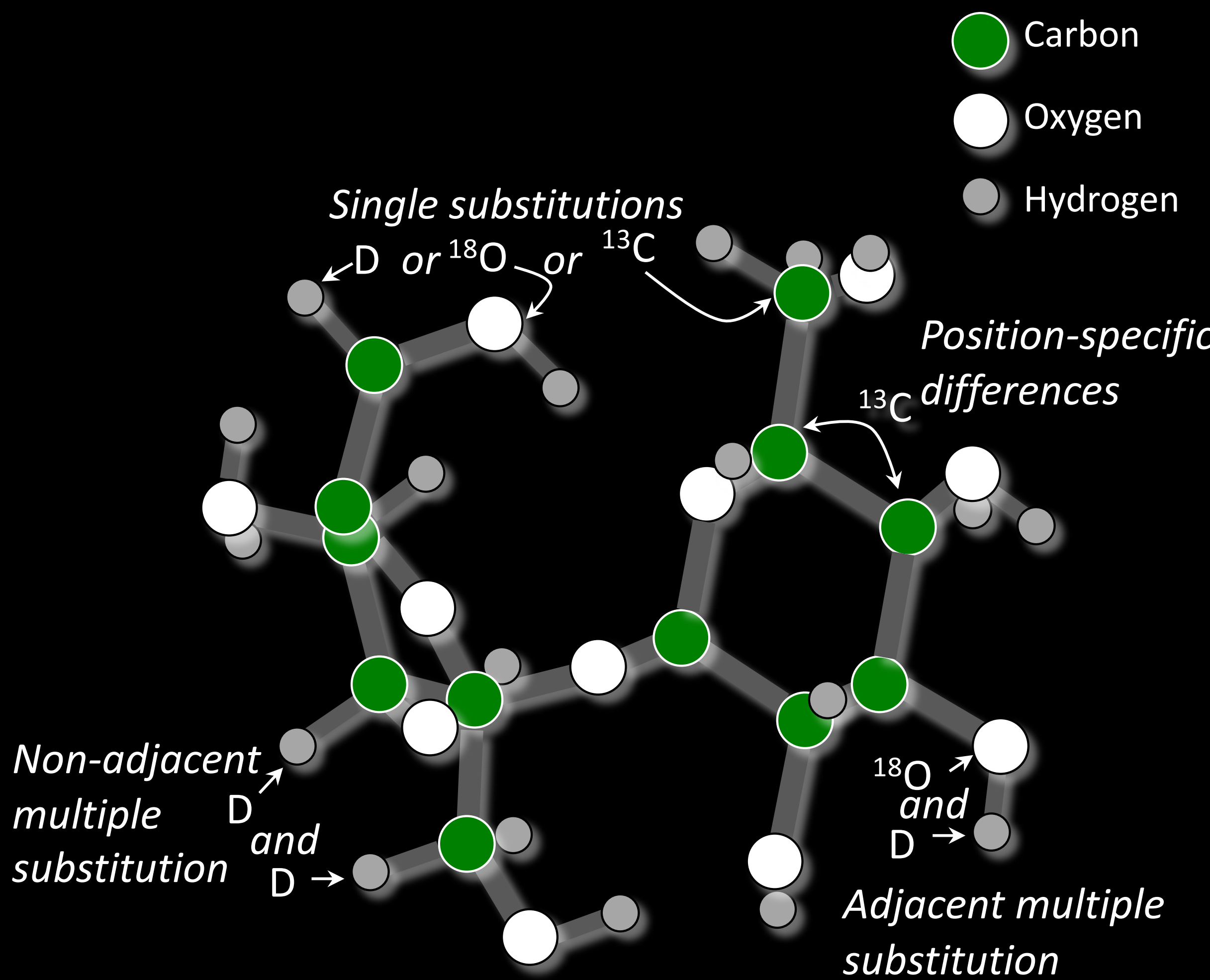


- 1 part in 10^{18} of natural hydrogen
  Radioactive



Isotopes turn molecules into nearly infinitely complex records of process, history and forensic identity

Consider Sucrose (table sugar)



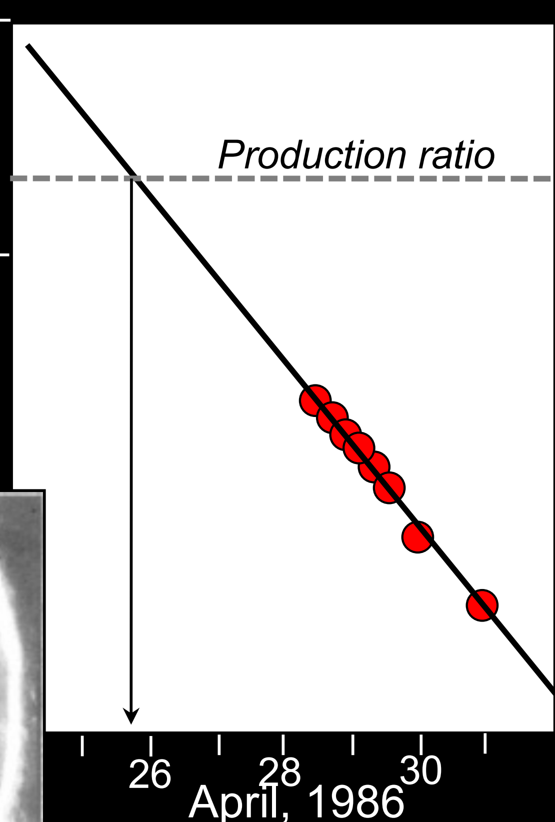
~ $3x10^{15}$ different versions

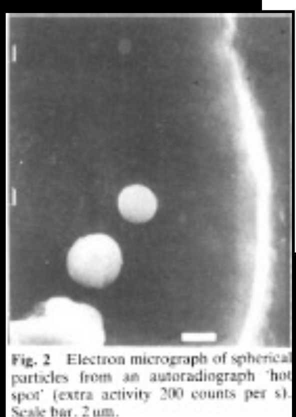
The human genome has ~25,000 genes

Our galaxy contains ~ $3x10^{11}$ stars

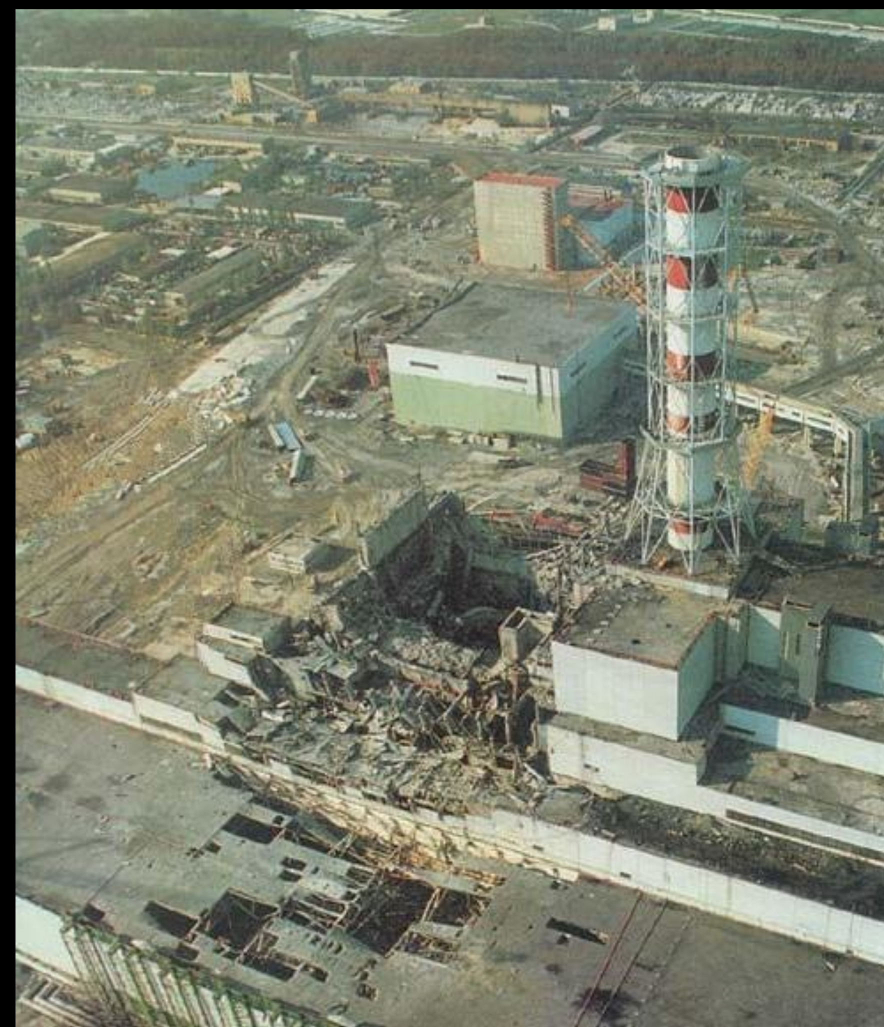
Radioactive decay is one source of isotopic ‘signals’

Dating the Chernobyl reactor disaster using radioactive iodine



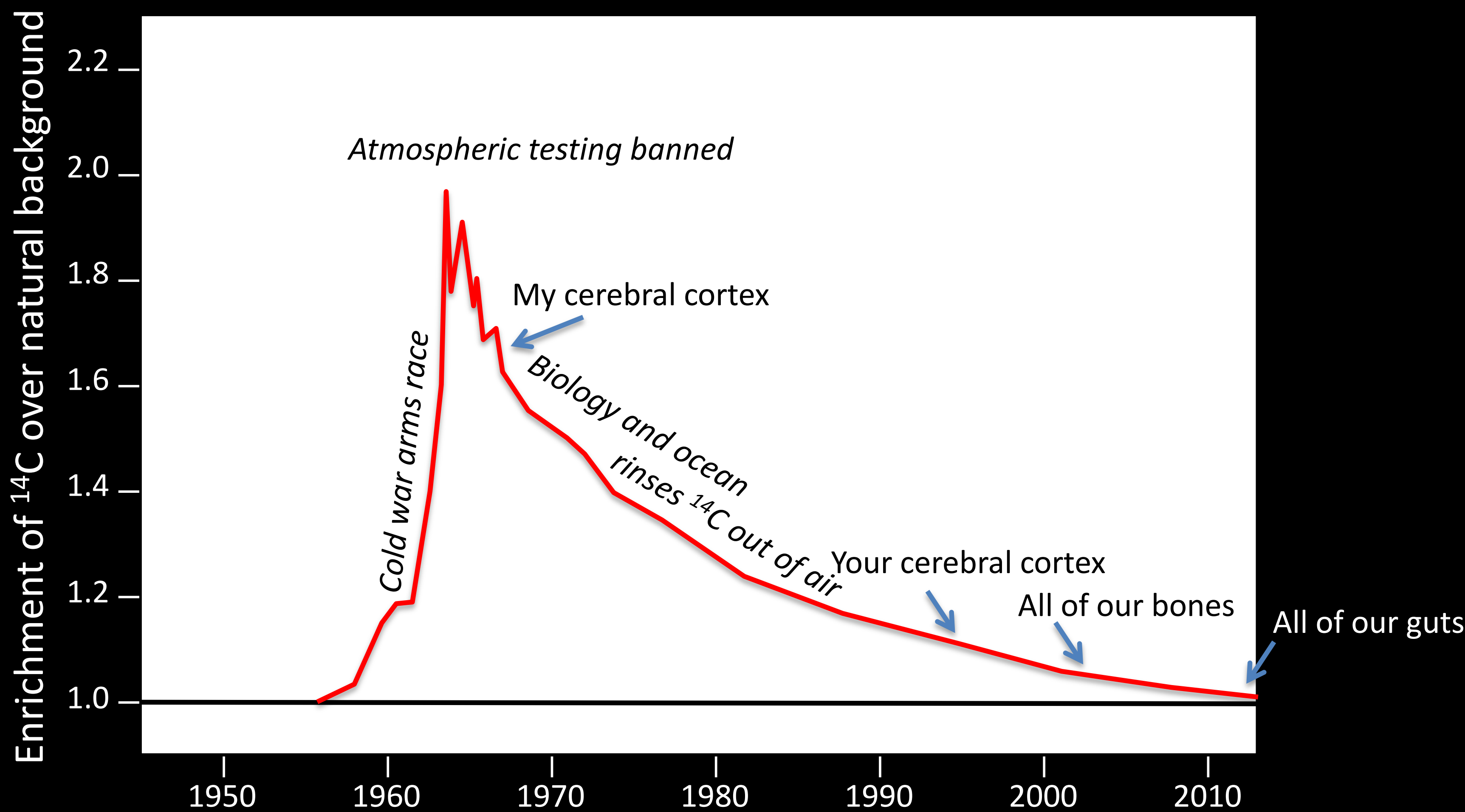


Nature, 1986, v. 321



Dilution of radioactive isotopes through natural chemical cycles is another source of isotopic variation

We date the DNA in your cells using radioactive ^{14}C from cold-war era atom bombs



Taken from the Wikimedia Commons

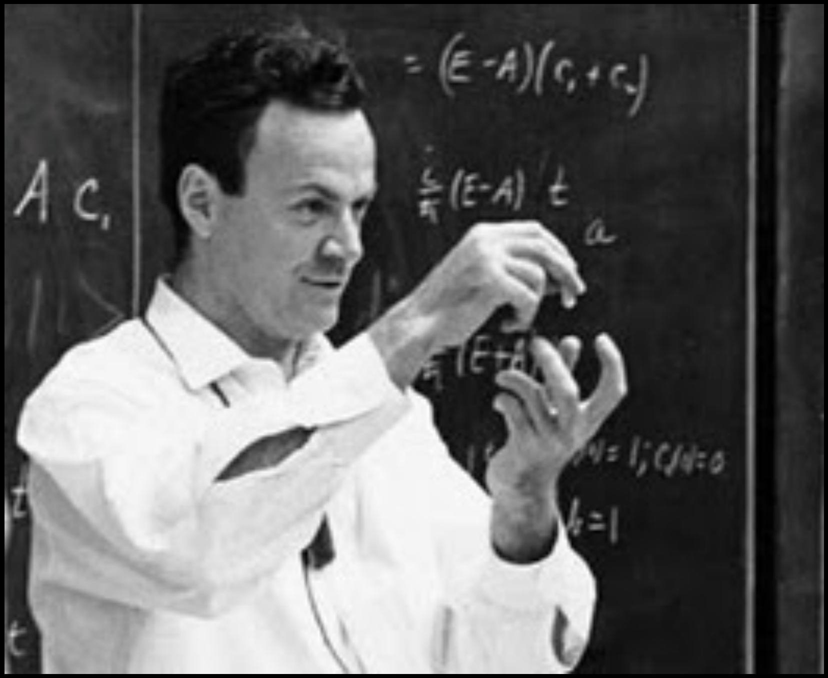
Chemical physics, especially quantum mechanics, leads to more subtle, but complex and ubiquitous natural isotopic variations

"Because atomic behavior is so unlike ordinary experience,

it is difficult to get used to, and it appears peculiar and mysterious to everyone

– both to the novice and to the experienced physicist."

Richard Feynman (1963)

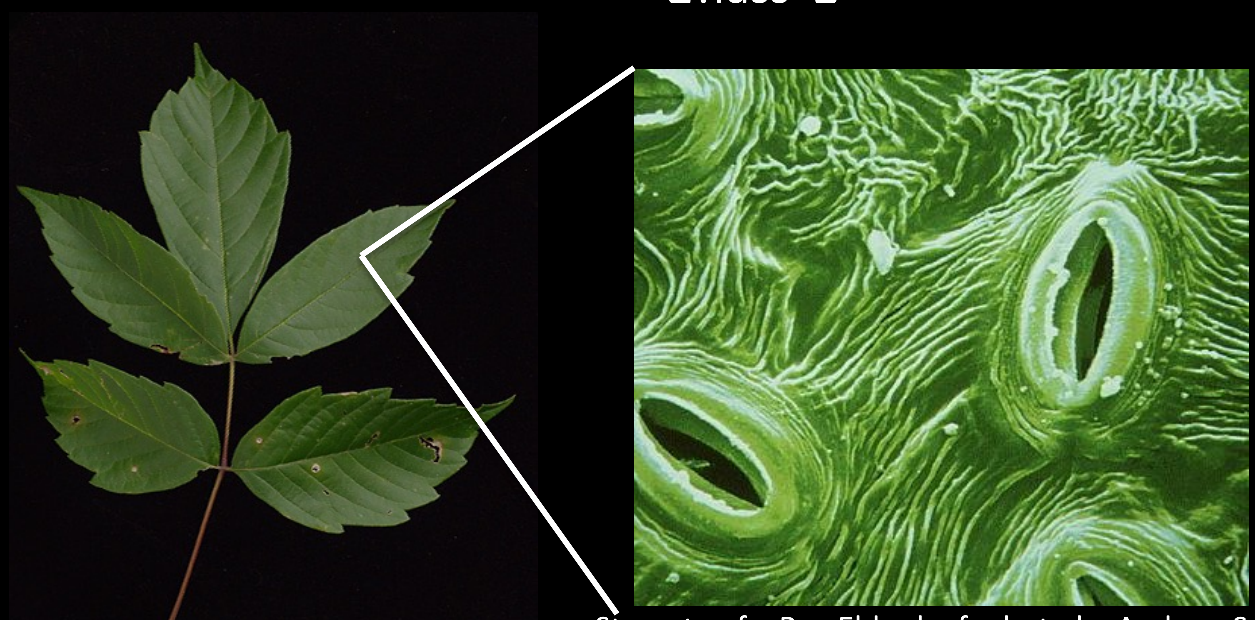


Richard Feynman, preparing to levitate a student using only his mind

Diffusion of gas through pores or tubes can separate isotopes

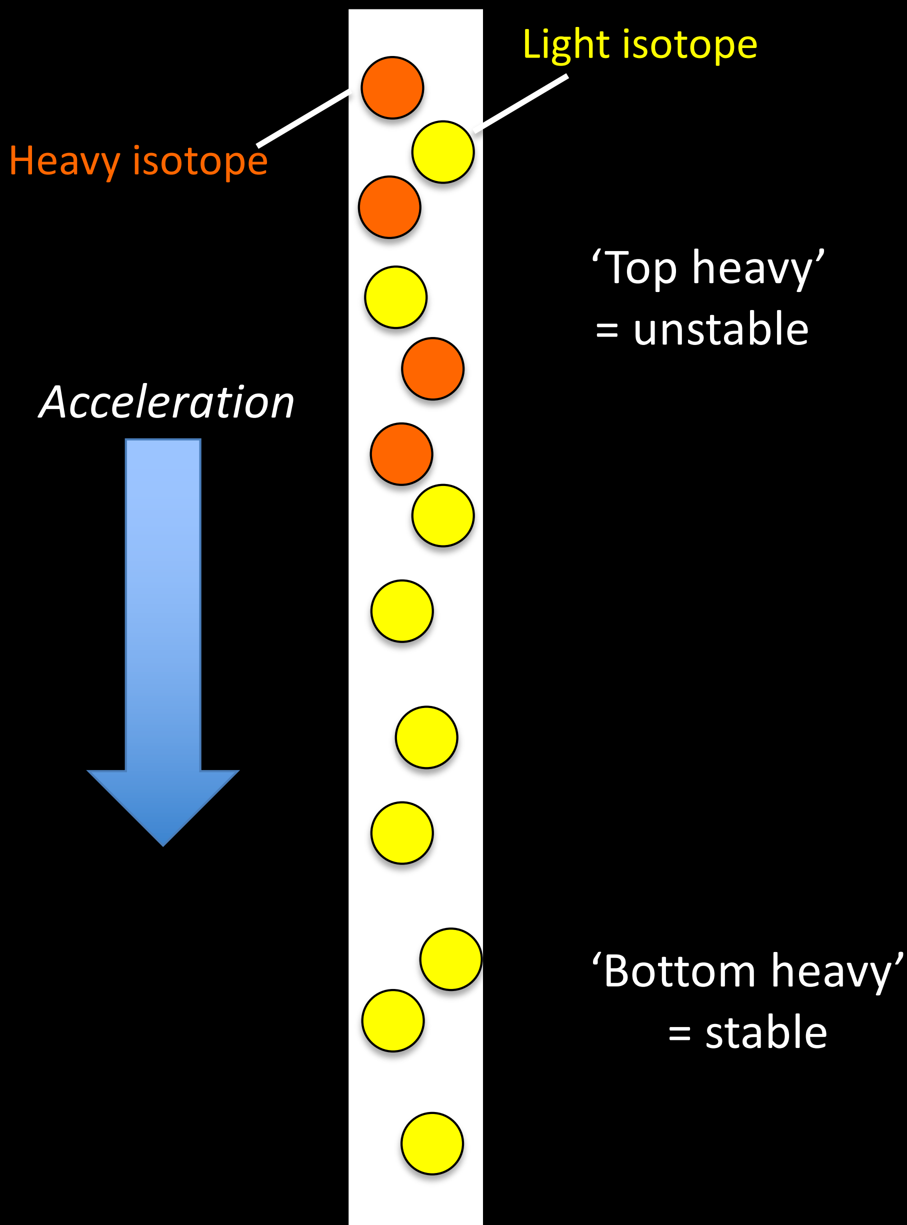
Kinetic energy (E) is proportional to temperature

$$\text{Velocity} = \left[\frac{2xE}{\text{Mass}}\right]^{1/2}$$



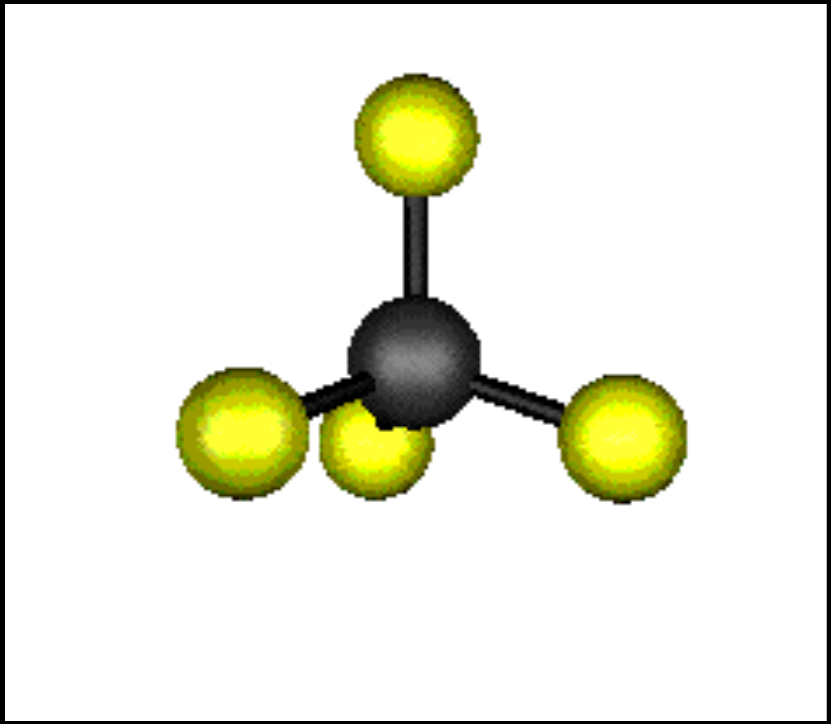
Stomata of a Box Elder leaf; photo by Andrew Syred

Gravitational ‘settling’



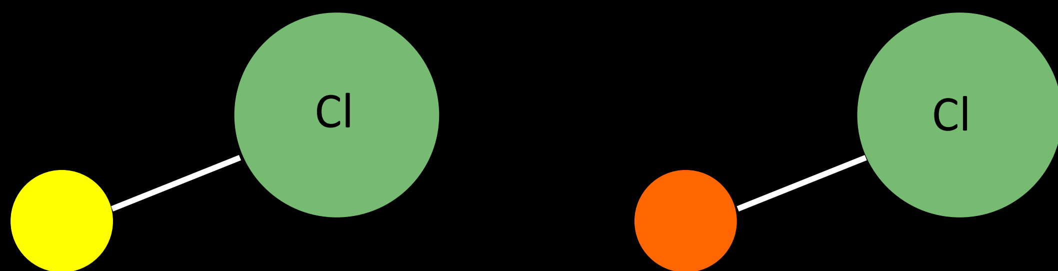
Glacial firn, Weissmiesgletscher Switzerland
Photo by J. Alean

Chemical bonds are (sort of) like springs



Chemical isotope effects

HCl DCl

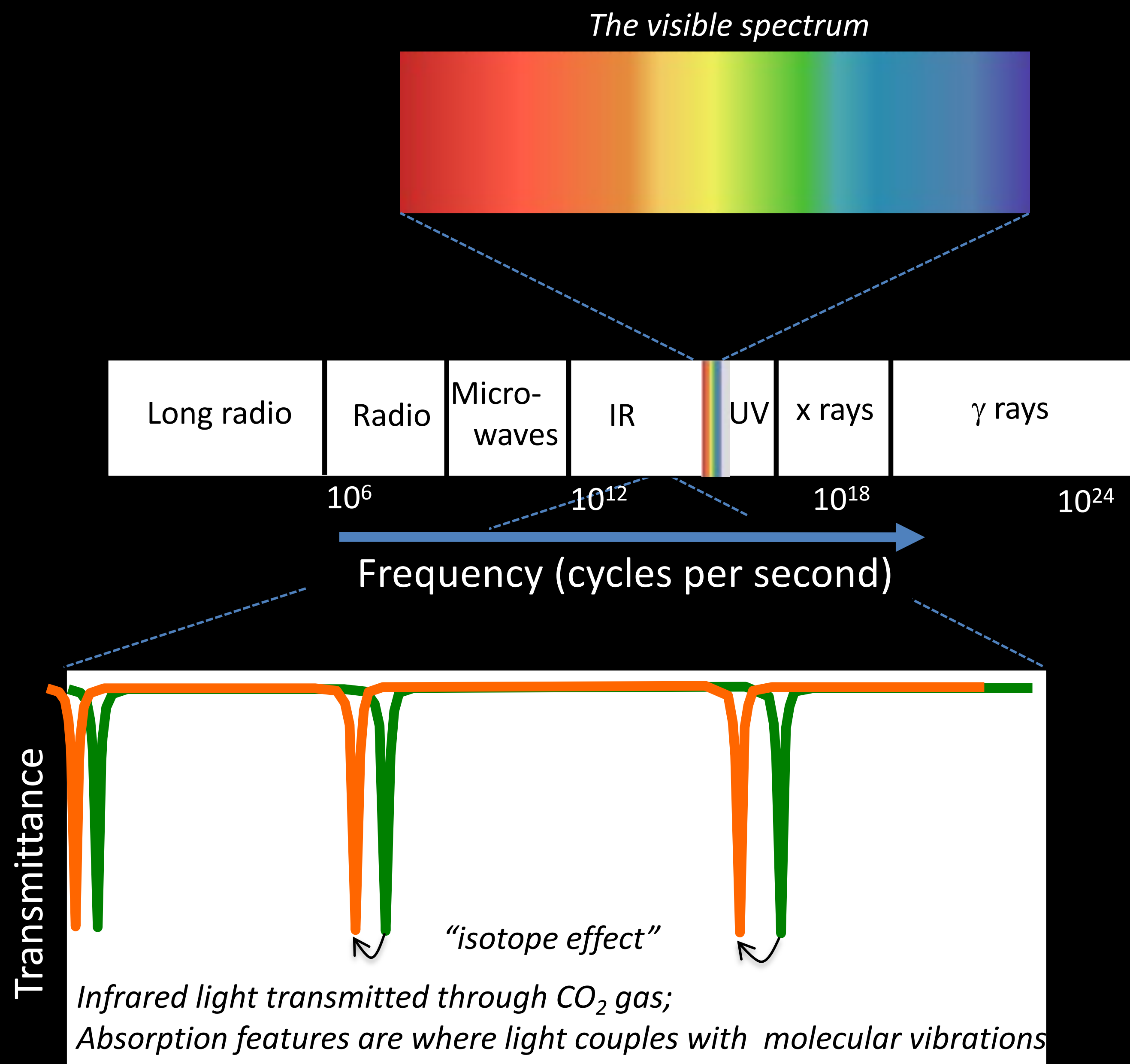


Higher mass = lower frequency

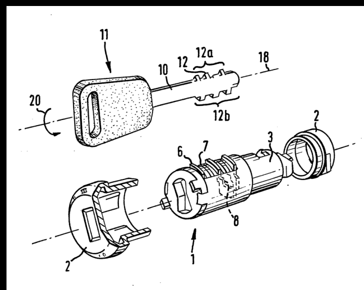
Energy ∝ frequency, thus…

Higher mass = lower frequency = lower energy = more stable

Absorption spectra of molecules changes with isotopic substitution

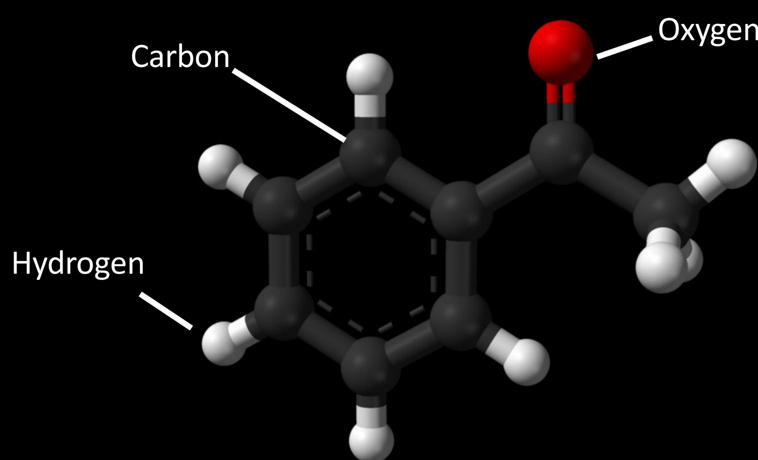


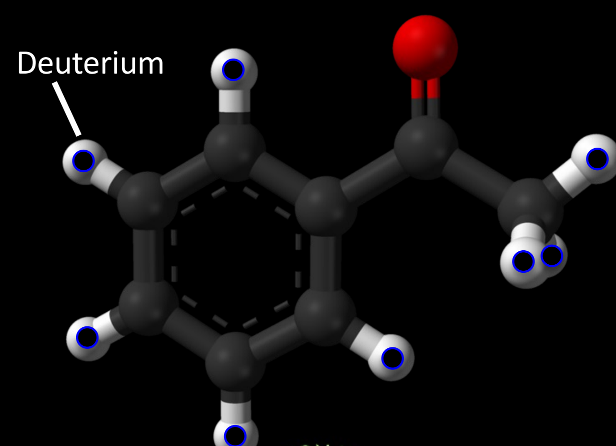
The effect of isotopic mass on bond vibrations can change how something smells (at least, to a fly)



It is widely believed that our sense of smell depends on molecular shape matching a sensor site – like a key to a lock

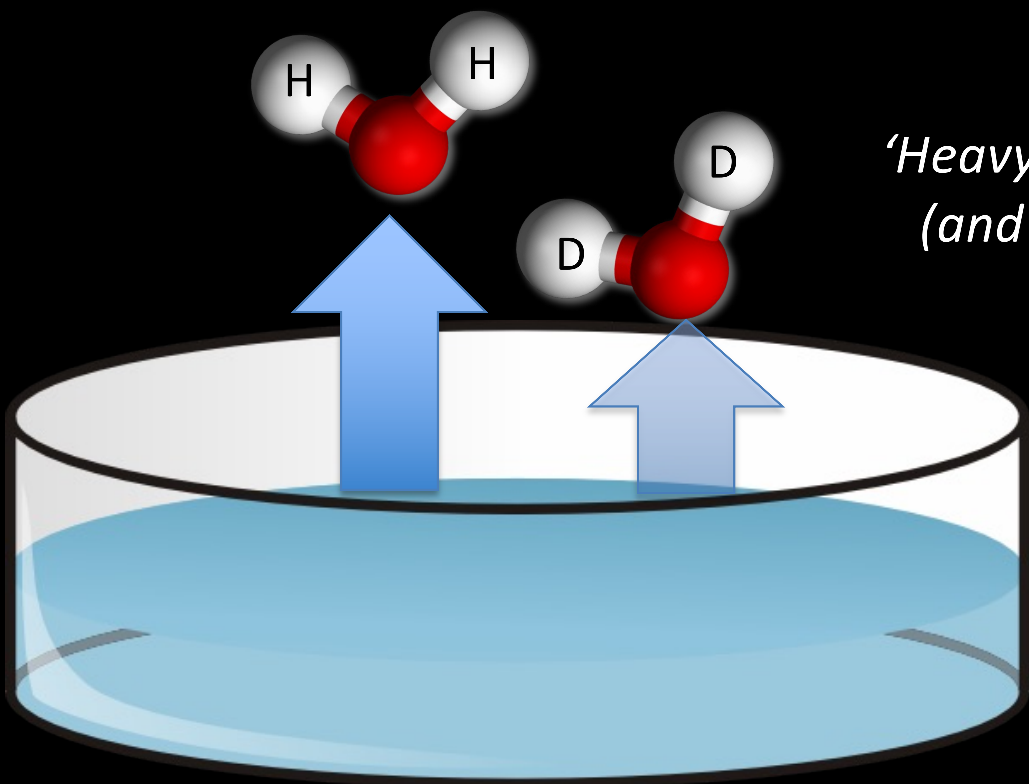
But flies exposed to an odorant they normally love (e.g., Acetophenone) will avoid it if its molecular vibration frequencies are changed through isotopic substitution





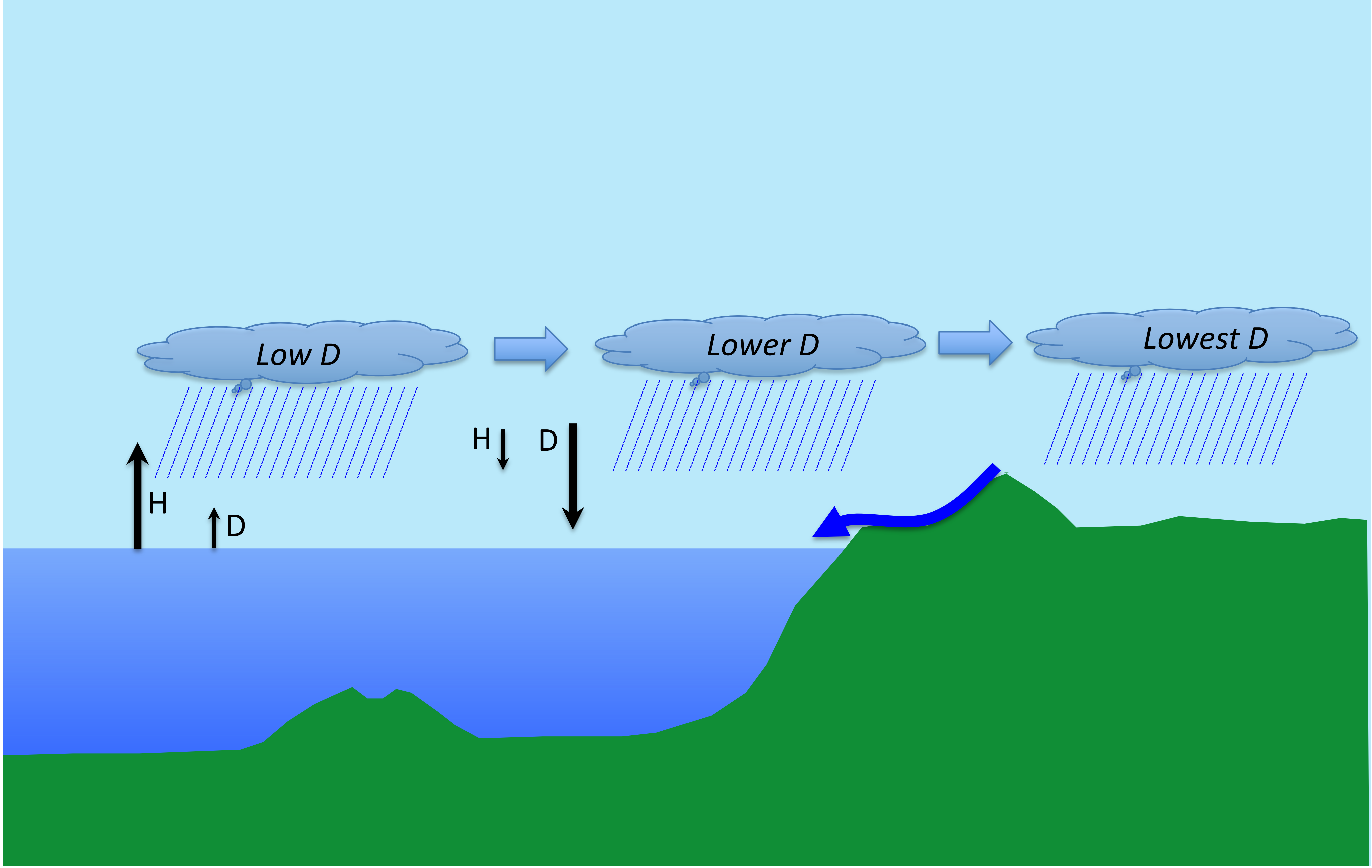
Franco et al., 2011

Chemical isotope effects

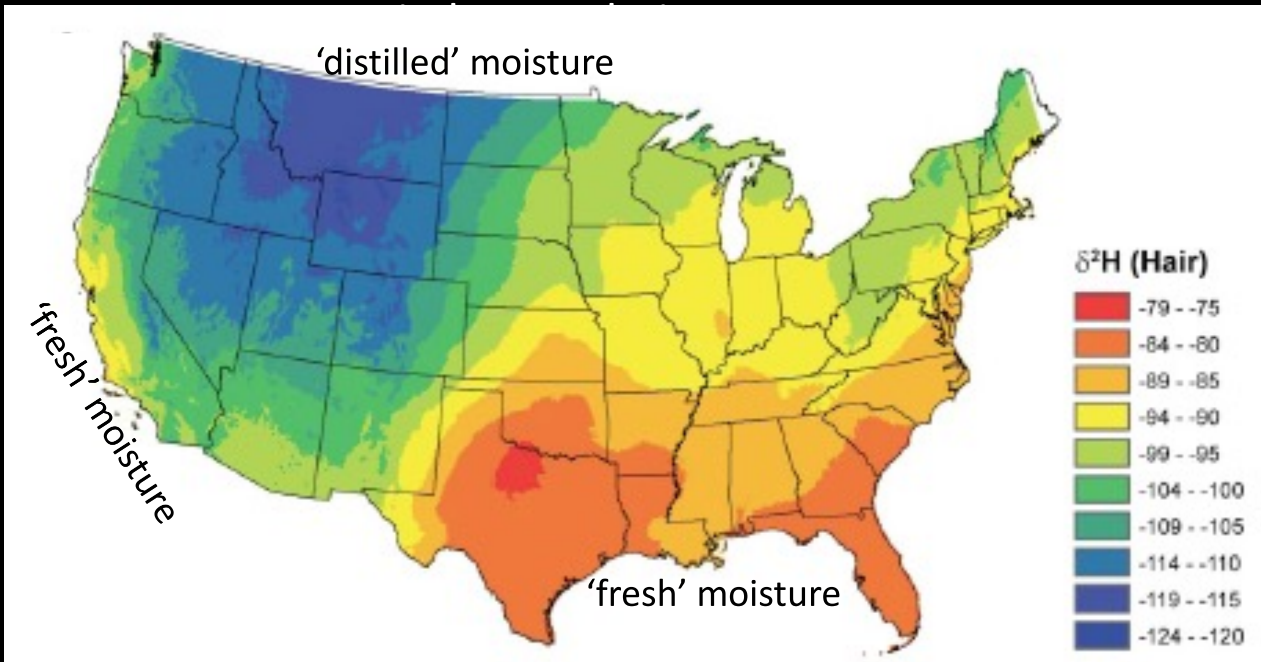


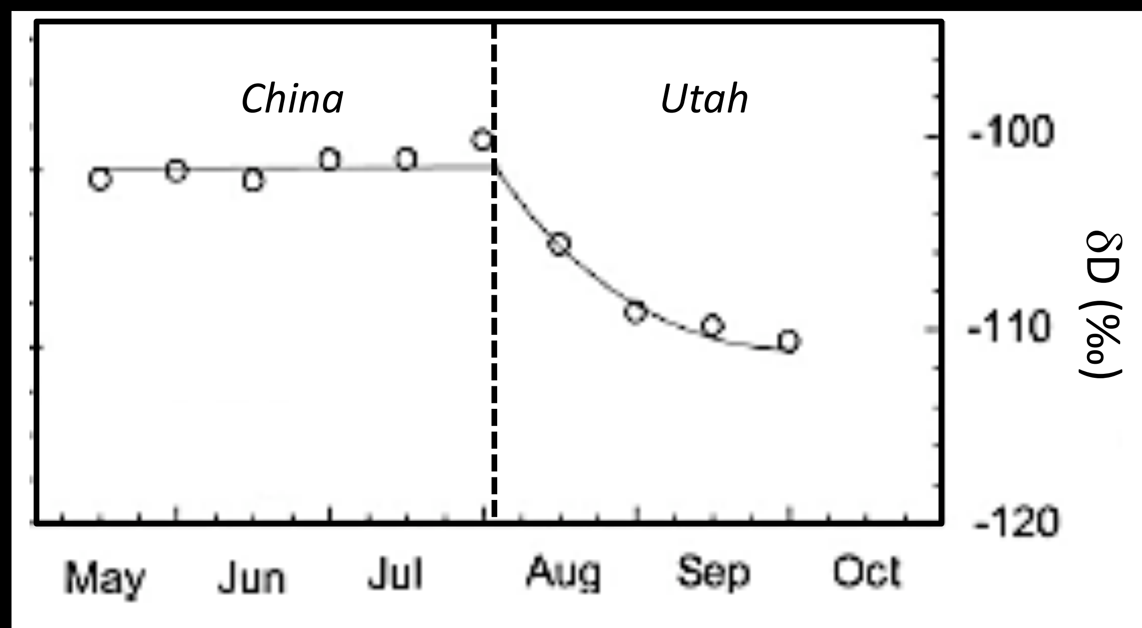
'Heavy' water boils at 101.4 ˚C, not 100 ˚C
(and it is poisonous!)

A schematic view of earth's water cycle



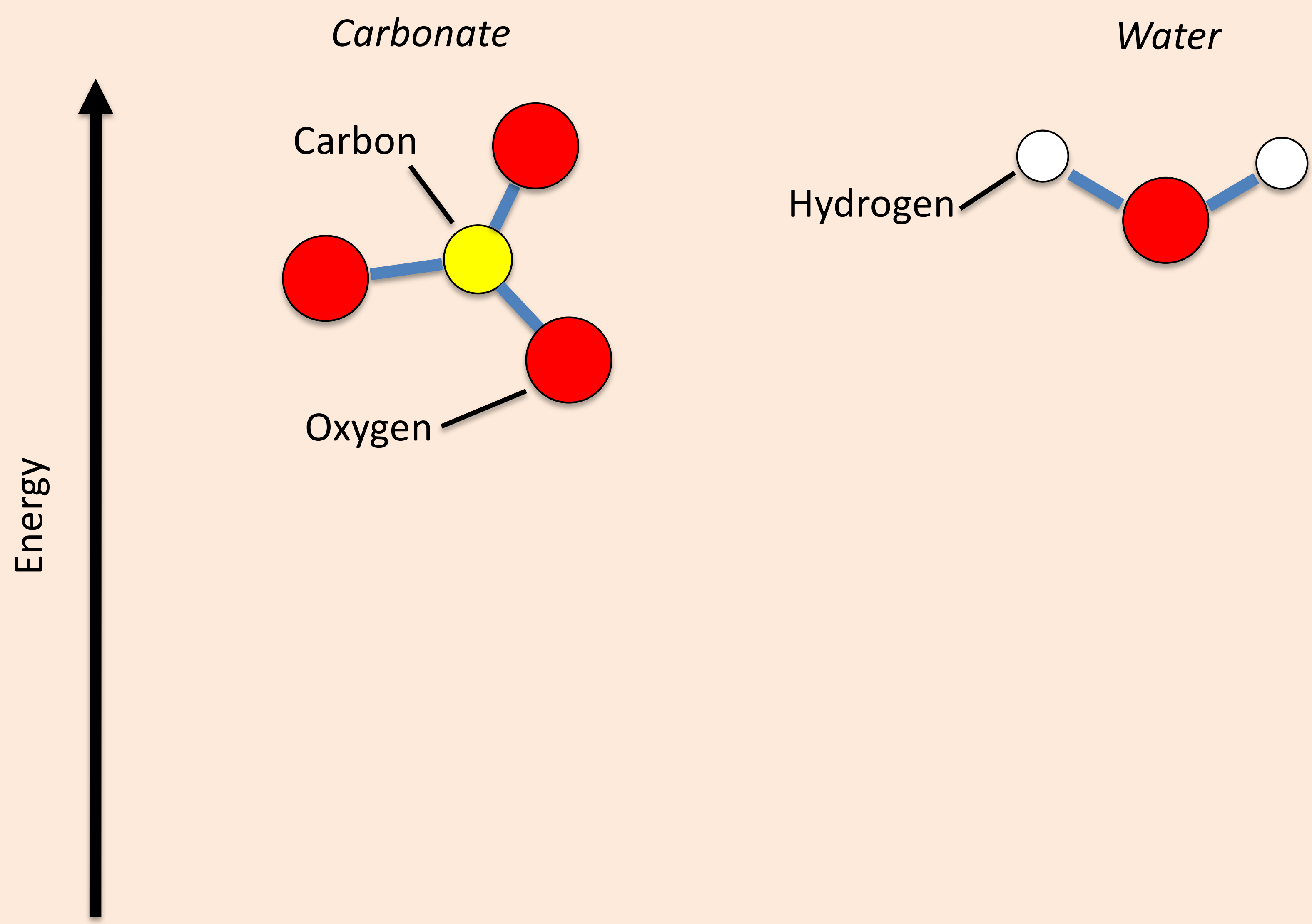
Tracking the locations of migratory graduate students



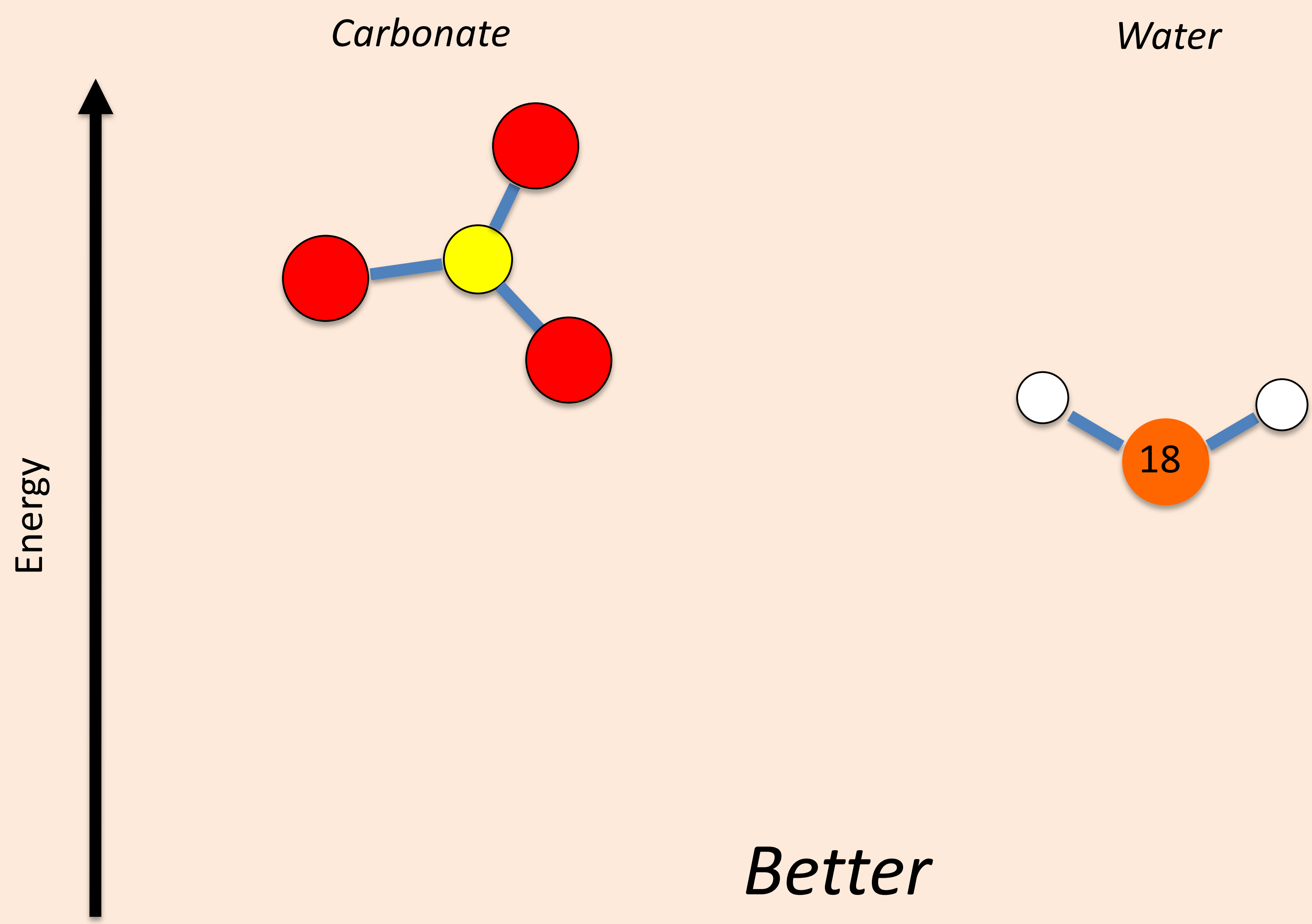


Ehleringer et al., 2008

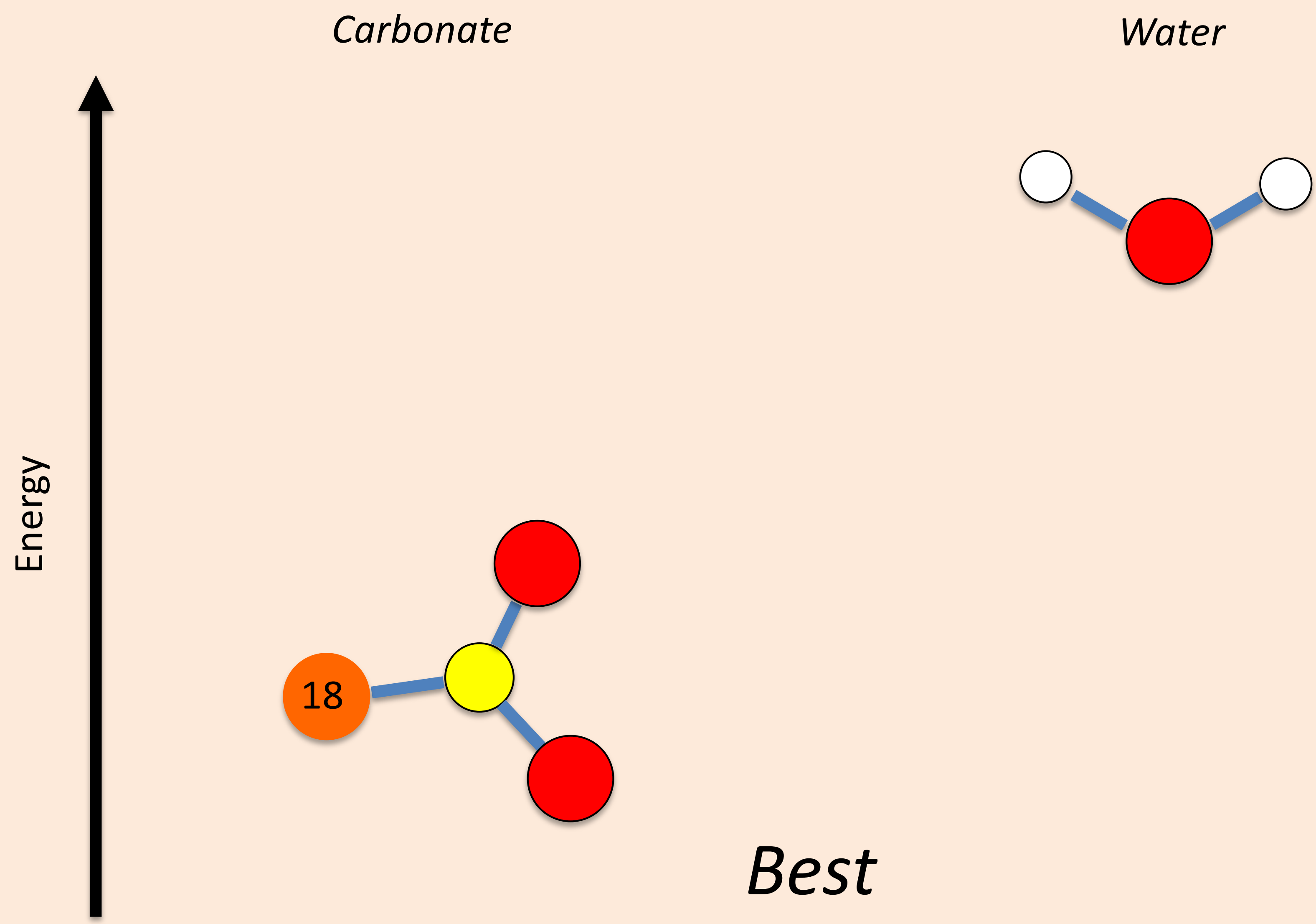
Isotope effect on a heterogeneous reaction



Isotope effect on a heterogeneous reaction



Isotope effect on a heterogeneous reaction

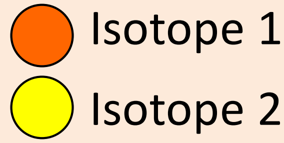


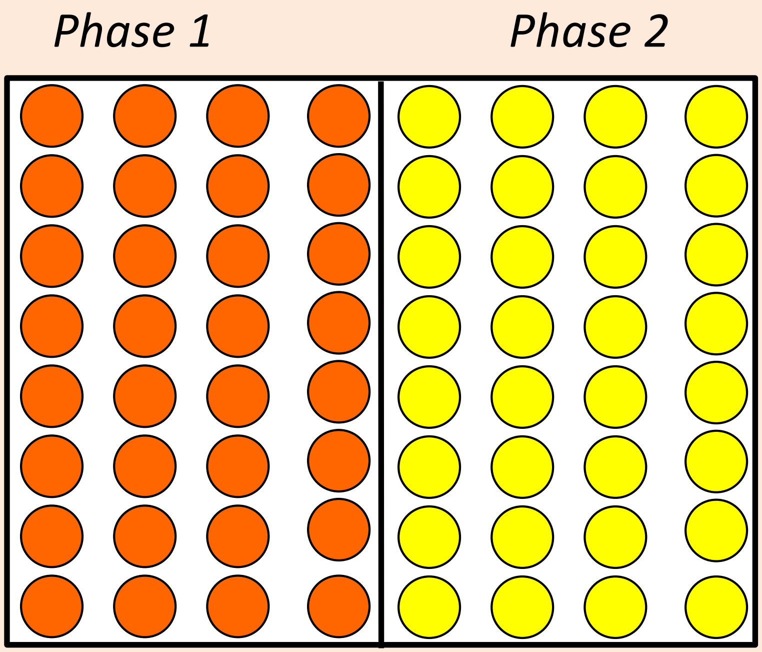
Best

So, some types of chemical bonds 'steal' rare, heavy isotopes from other types of bonds

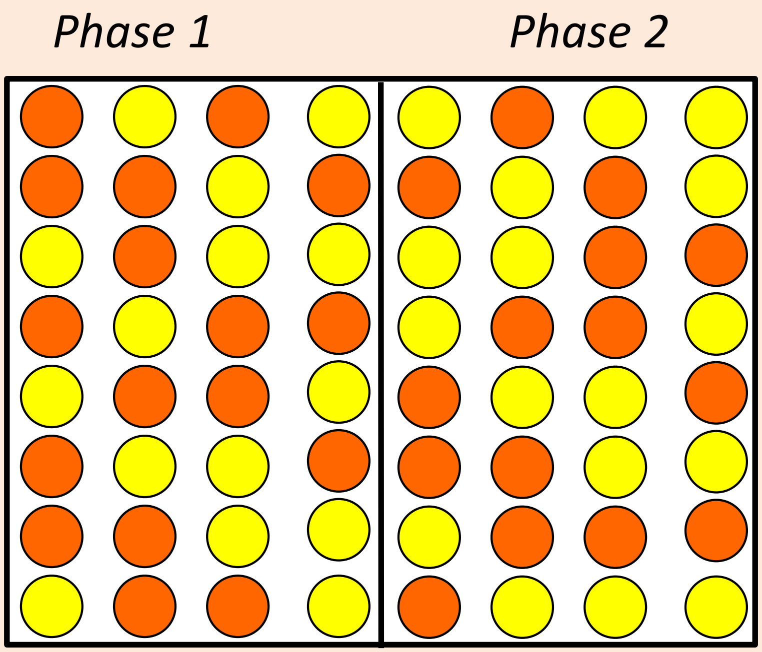
Another simple but important term

The entropy (or ‘randomness’) of isotopic distribution





- Very few ways atoms can be arranged that ‘look’ different
- A low entropy state



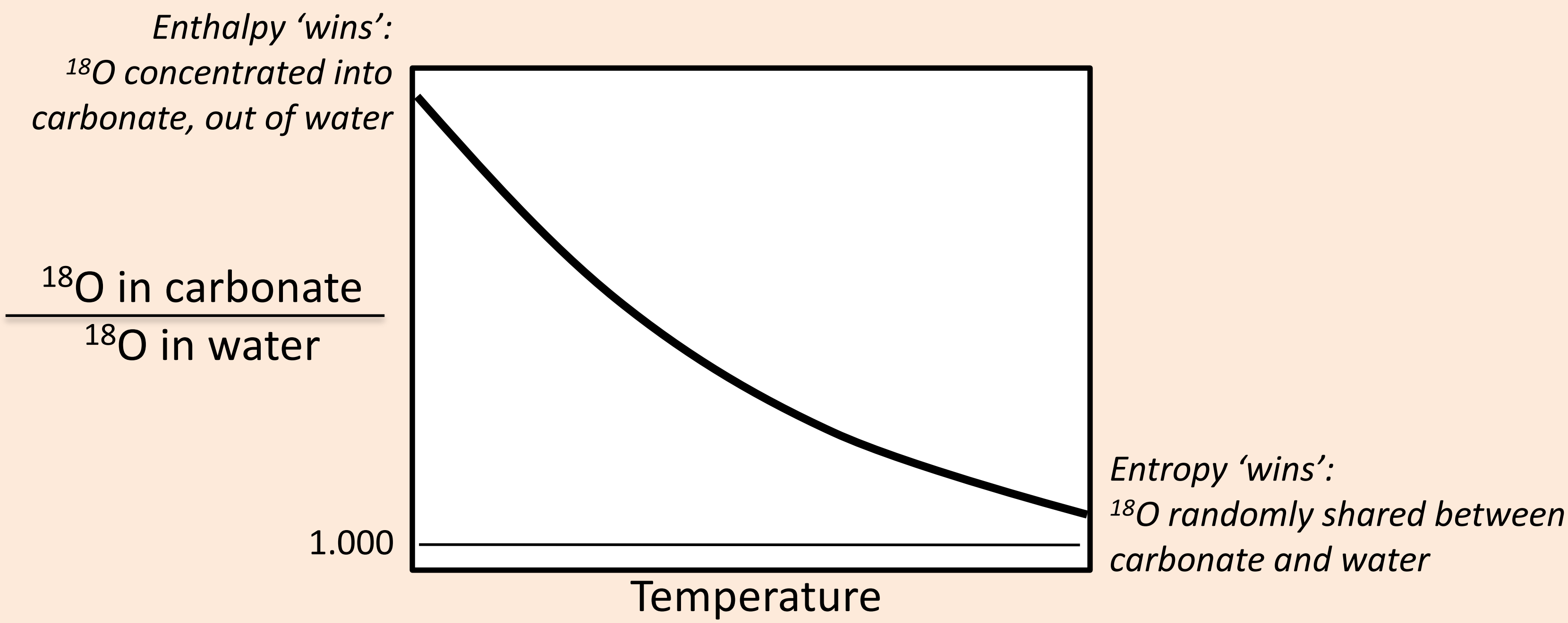
- Very many ways atoms can be arranged that ‘look’ different
- A high entropy state

Temperature dependence of isotope exchange reactions

Easiest to understand through classical thermodynamics

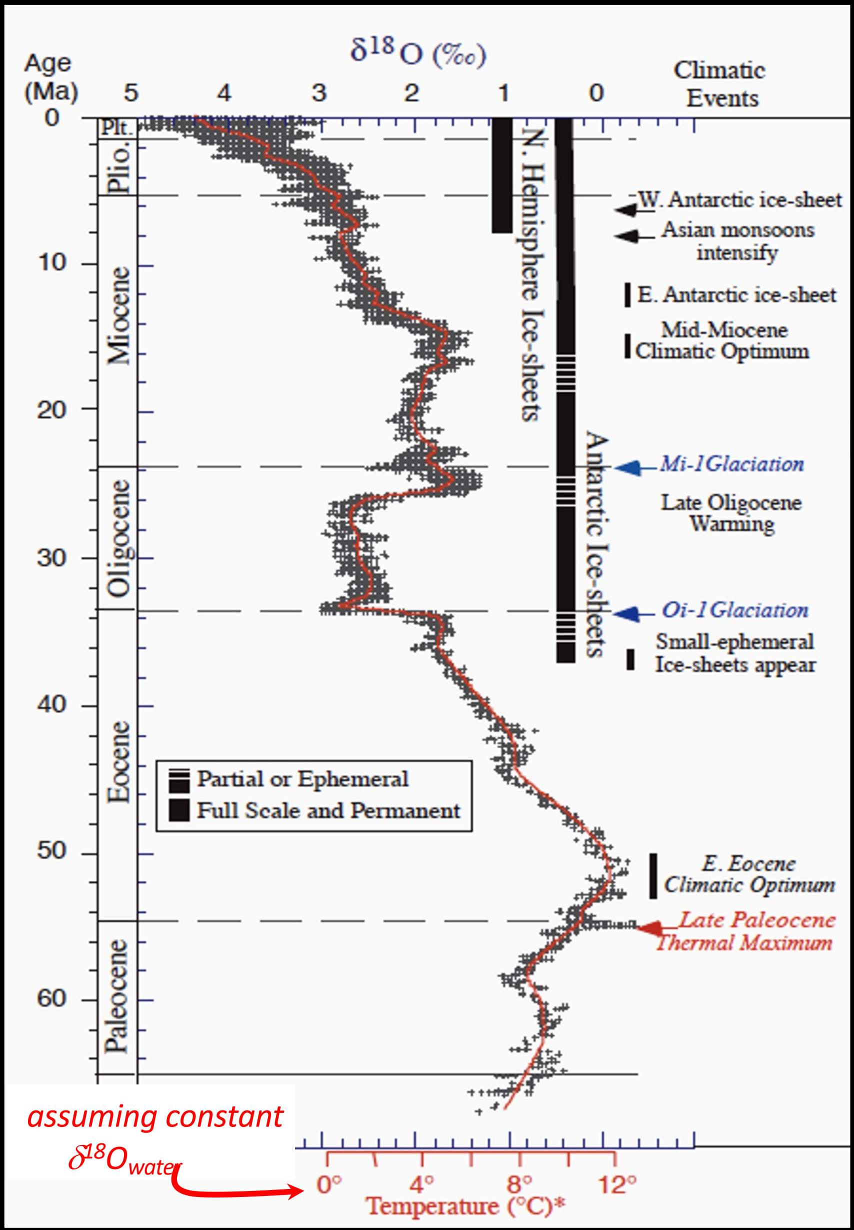
$$\Delta G = \Delta H - T\Delta S$$

- ΔG: Total energy change of reaction (negative is better)
- ΔH: Enthalpy of reaction; like frequency effect on vibration energy
- $T\Delta S$: Entropy of reaction; random states have high entropy



The 'Zachos curve' — A record of Cenozoic ocean temperature*

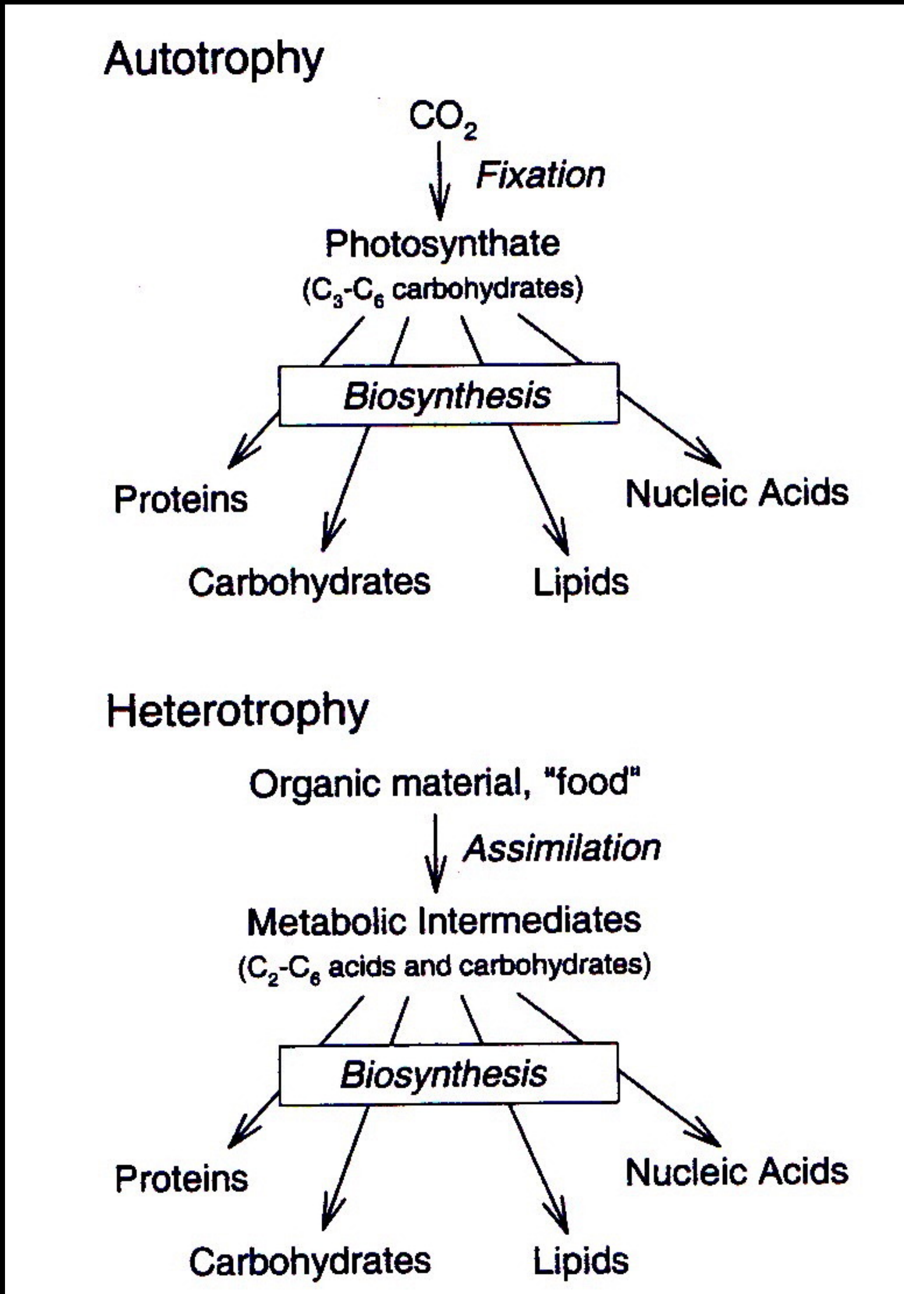
(Assuming you know how much ^{18}O is in sea water!)*



Benthic Foraminifera

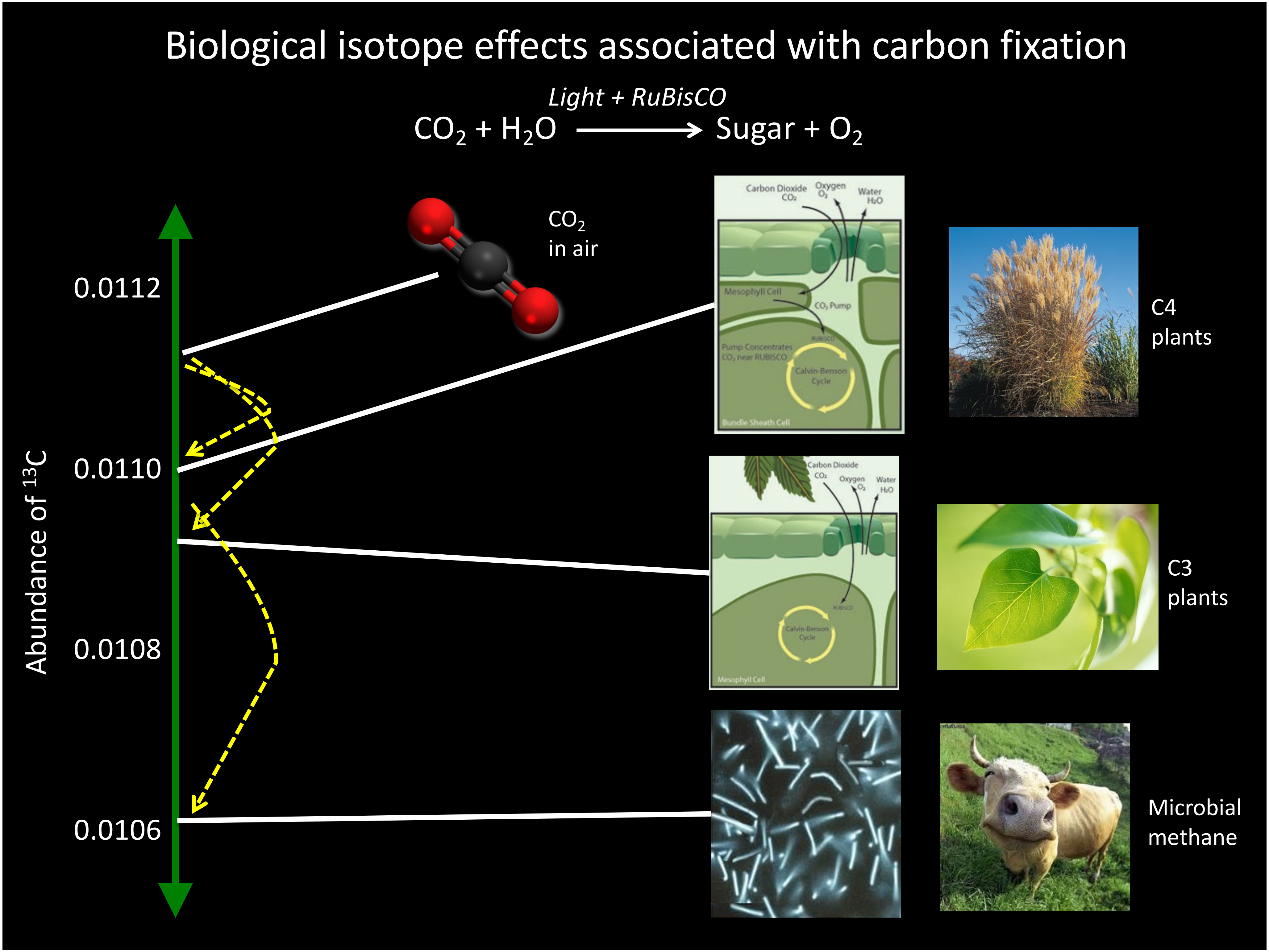
Zachos, 2001

The broadest overview of organismal-scale biosynthetic isotopic fractionation



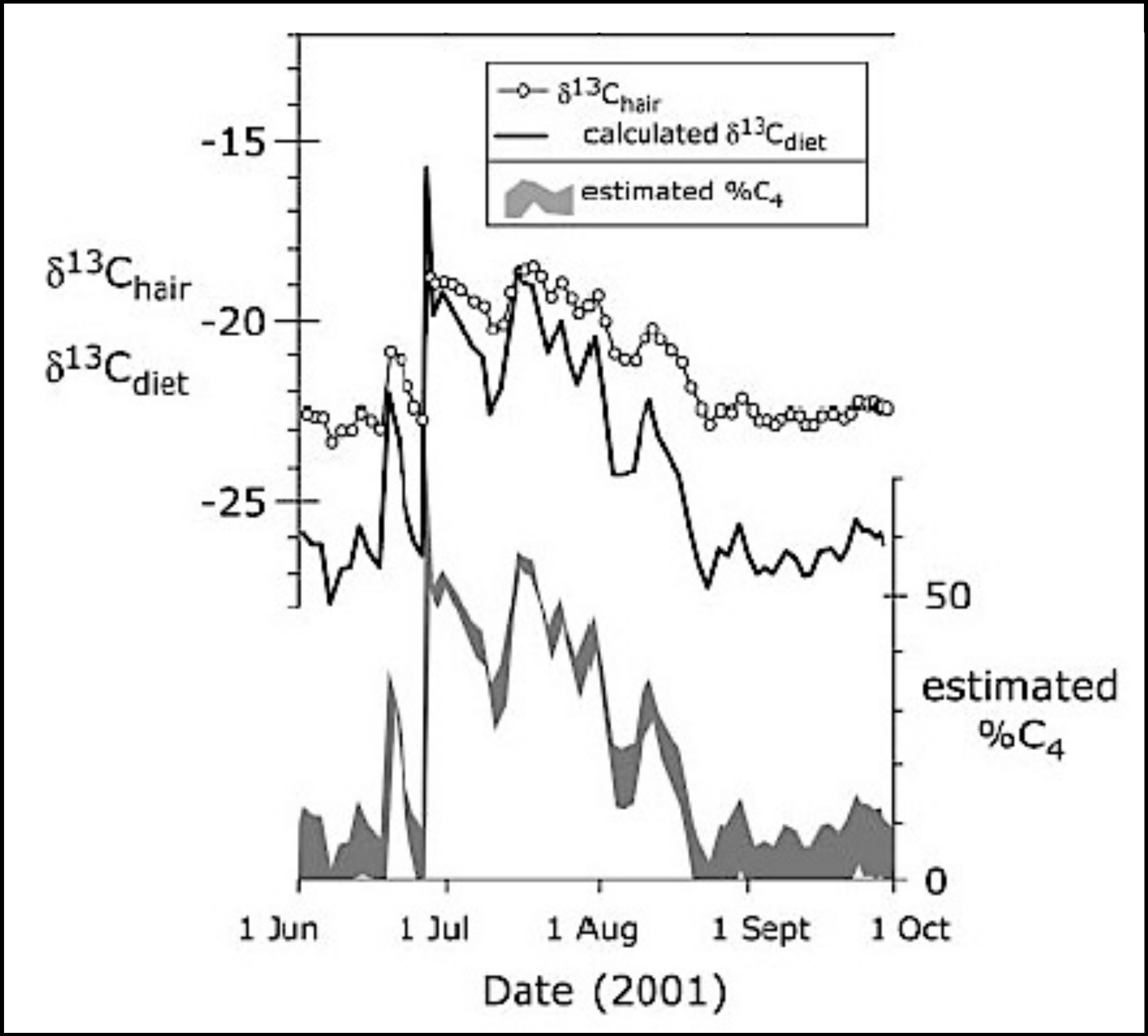
These sorts of reactions involve reduction of inorganic carbon (or analogous changes in oxidation state and bonding environment of H, N, S, etc.) and are generally very effective at separating isotopes

"You are what you eat" principle: *Bulk* living biomass of heterotrophs is similar in ^{13}C content to their food; i.e., if you 'shuffle' reduced carbon instead of reducing oxidized carbon, there is little overall isotopic discrimination (though possibly molecule- and site-specific effects)


Biological isotope effects associated with carbon fixation
Light + RuBisCO
$CO_2 + H_2O \rightarrow Sugar + O_2$
CO_2 in air
Abundance of ^{13}C
0.0112
0.0110
0.0108
0.0106
Carbon Dioxide CO_2
Oxygen O_2
Water H_2O
Mesophyll Cell
CO_2 Pump
RUBISCO
Pump Concentrates CO_2 near RUBISCO
Calvin-Benson Cycle
Bundle Sheath Cell
C4 plants
Carbon Dioxide CO_2
Oxygen O_2
Water H_2O
RUBISCO
Calvin-Benson Cycle
Mesophyll Cell
C3 plants
Microbial methane

Carbon isotope ecology based on differences in ^{13}C content between C3 and C4 plants

Tracking the diets of migratory elephants

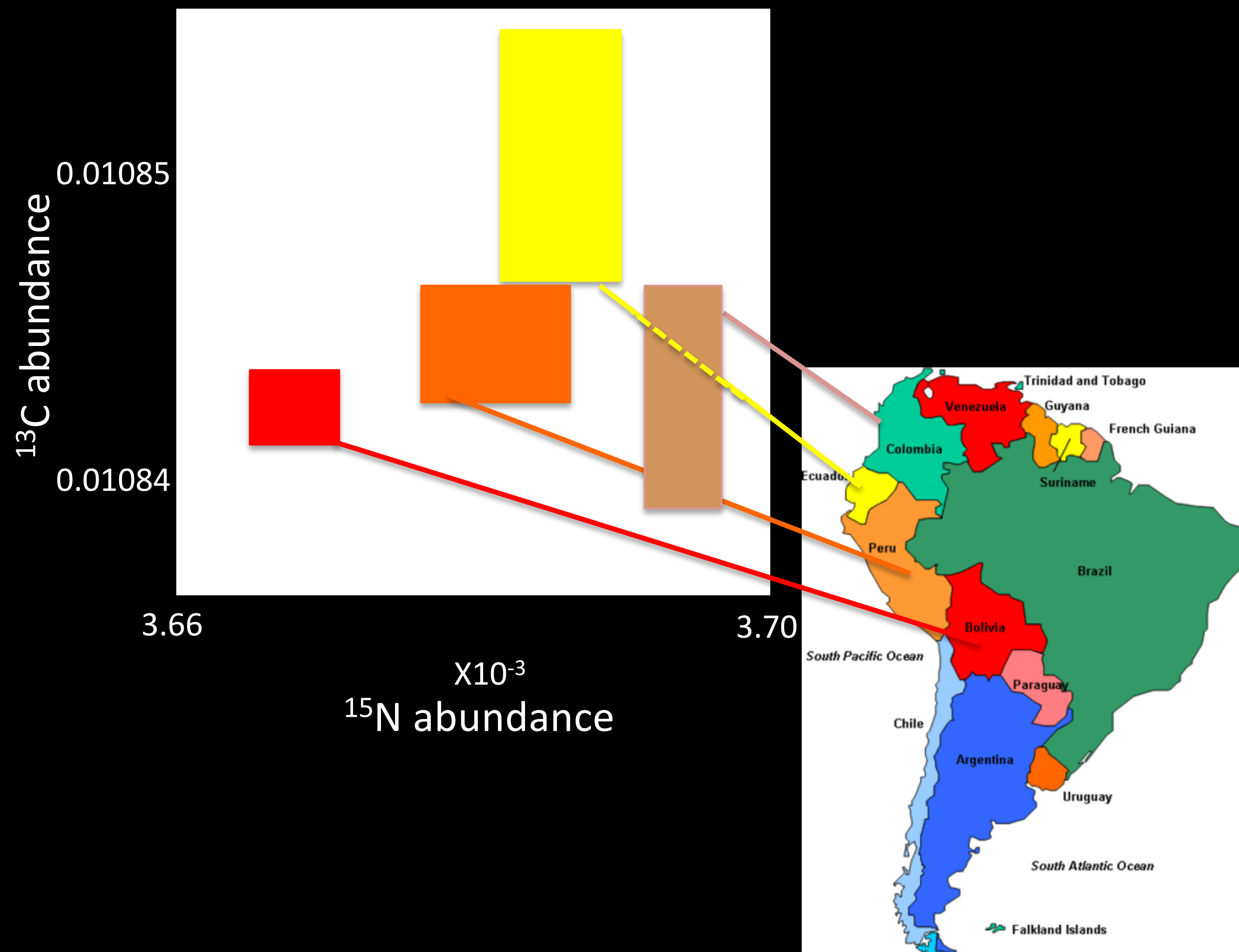


Cerling et al., 2006

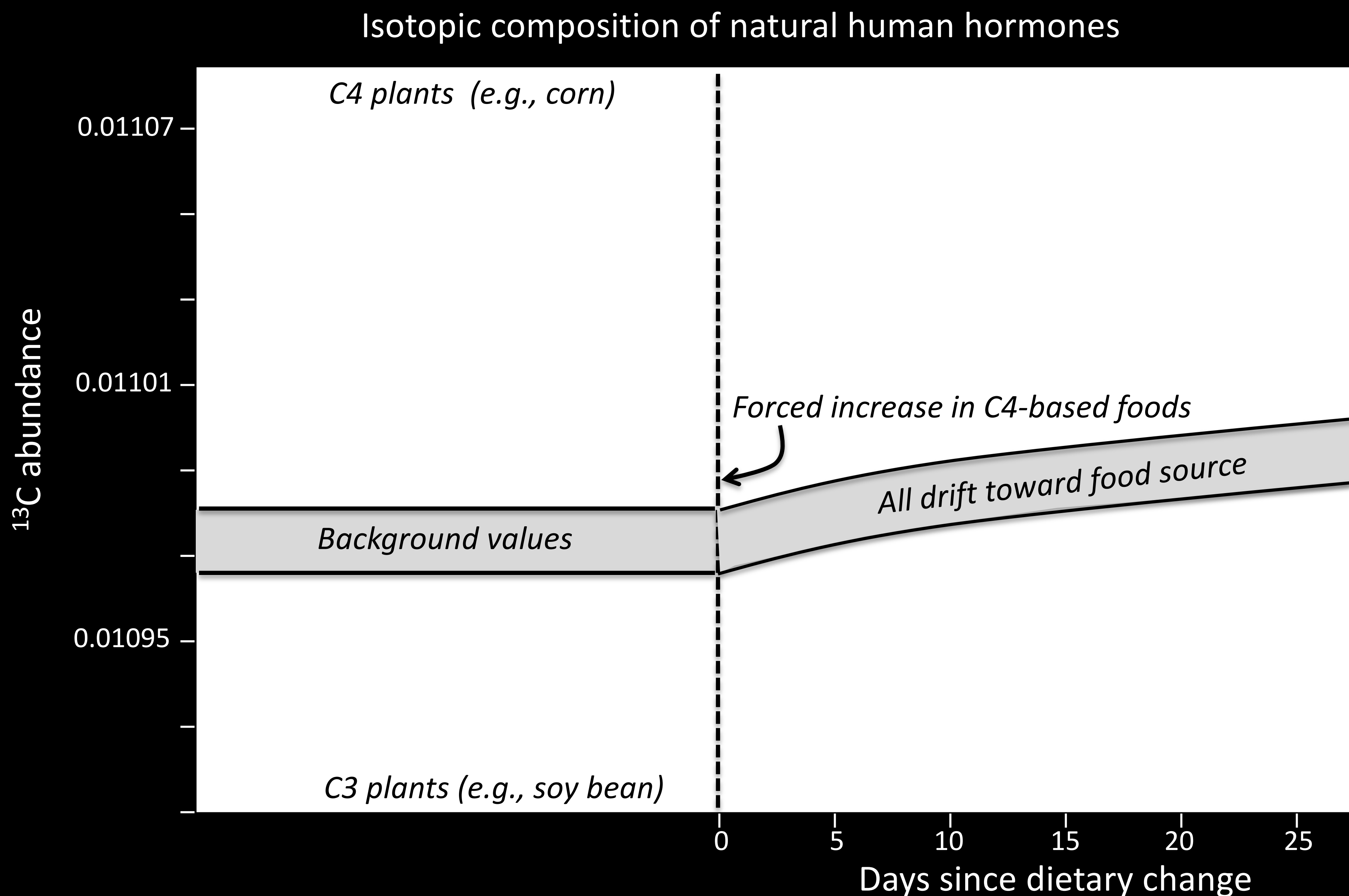
Criminal forensics of plant products

- Isotopic signatures of plants depend on growth conditions (humidity, soil type, etc.)
- This imparts a poorly understood but observable 'provinciality'
- Used for many purposes, including rolling up drug trafficking organizations

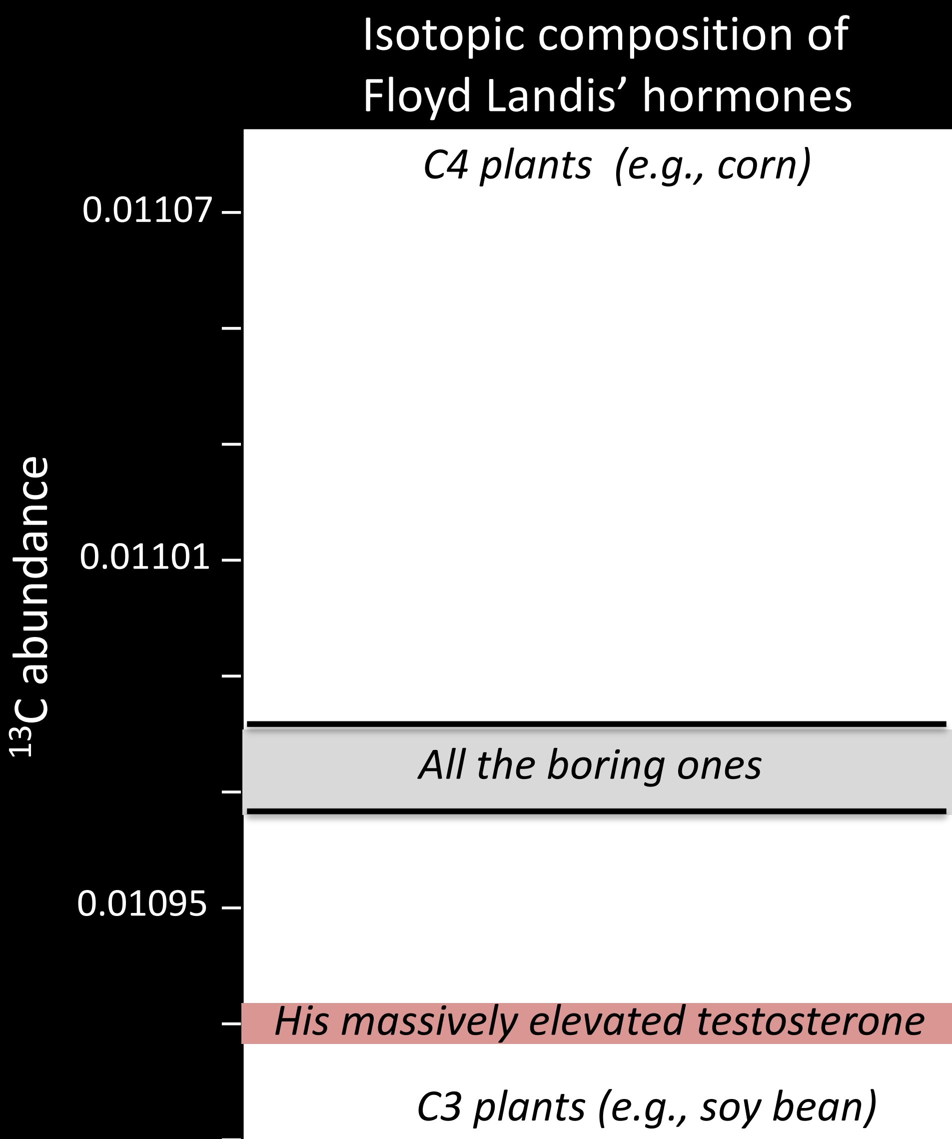
South American cocaine



Experimental evidence that you are what you eat



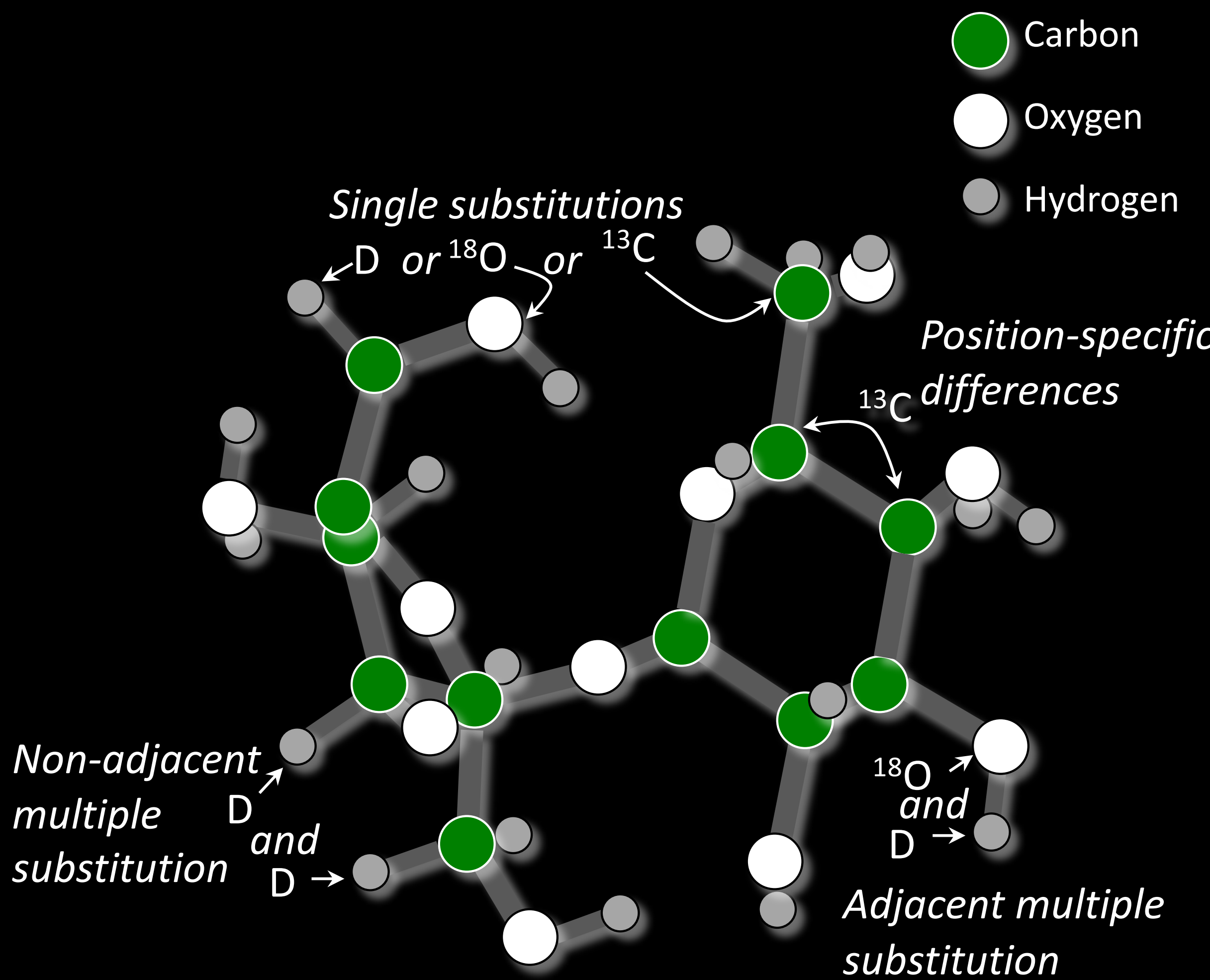
Isotopic proof that Floyd Landis is both a cheat and not very smart



Synthetic testosterone is usually made from phytosterol percursors, typically from soy

The preceding well-known applications are great, but what about all the other details molecular isotopic structure could record?

Consider Sucrose (table sugar)

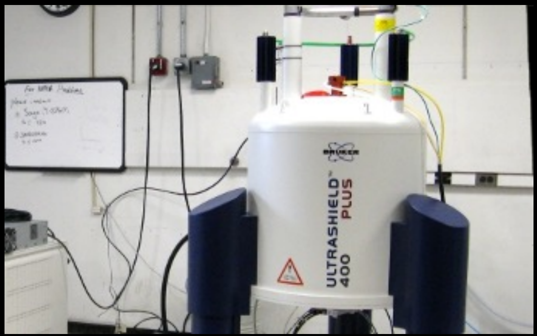


~ $3x10^{15}$ different versions

New technology is what turns ideas into action

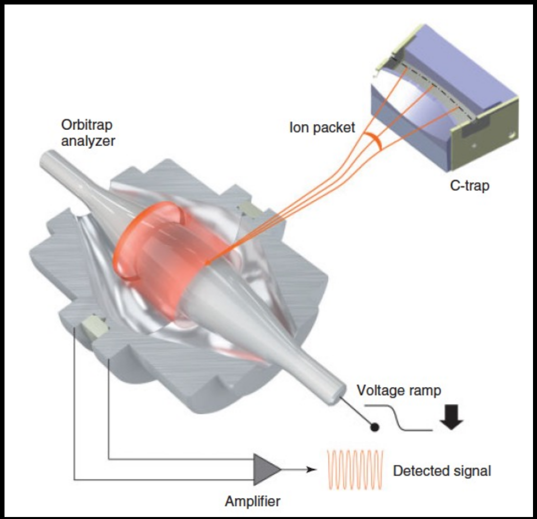
We must measure what is measurable and make measurable what cannot be measured.

—Galileo Galilei c. 1610

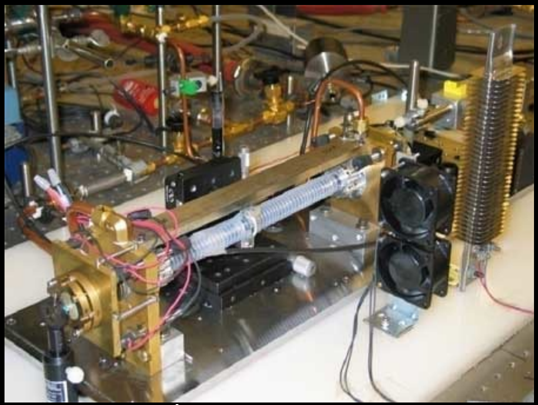


Nuclear magnetic resonance spectroscopy

High resolution sector mass spectrometry



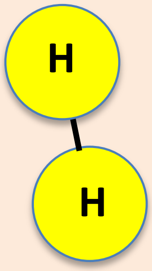
Fourier transform mass spec



Cavity ring down spectroscopy

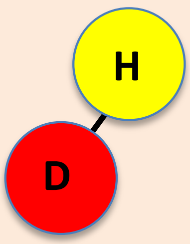
Ultra-high resolution sector MS

Multiple rare-isotope substitutions (isotope ‘clumping’) is a special, energetically favorable state of intramolecular rare-isotope ordering



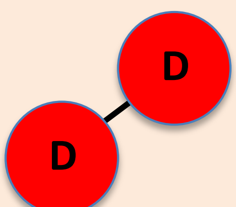
$$\nu = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{1/2}$$

$\mu = 1/2$, $\nu = 4395\ \text{cm}^{-1}$



$$\nu' = \frac{1}{2\pi}\left(\frac{k}{\mu'}\right)^{1/2}$$

$\mu' = 2/3$, $\nu' = 3806\ \text{cm}^{-1}$ $\Delta\nu = 589\ \text{cm}^{-1}$

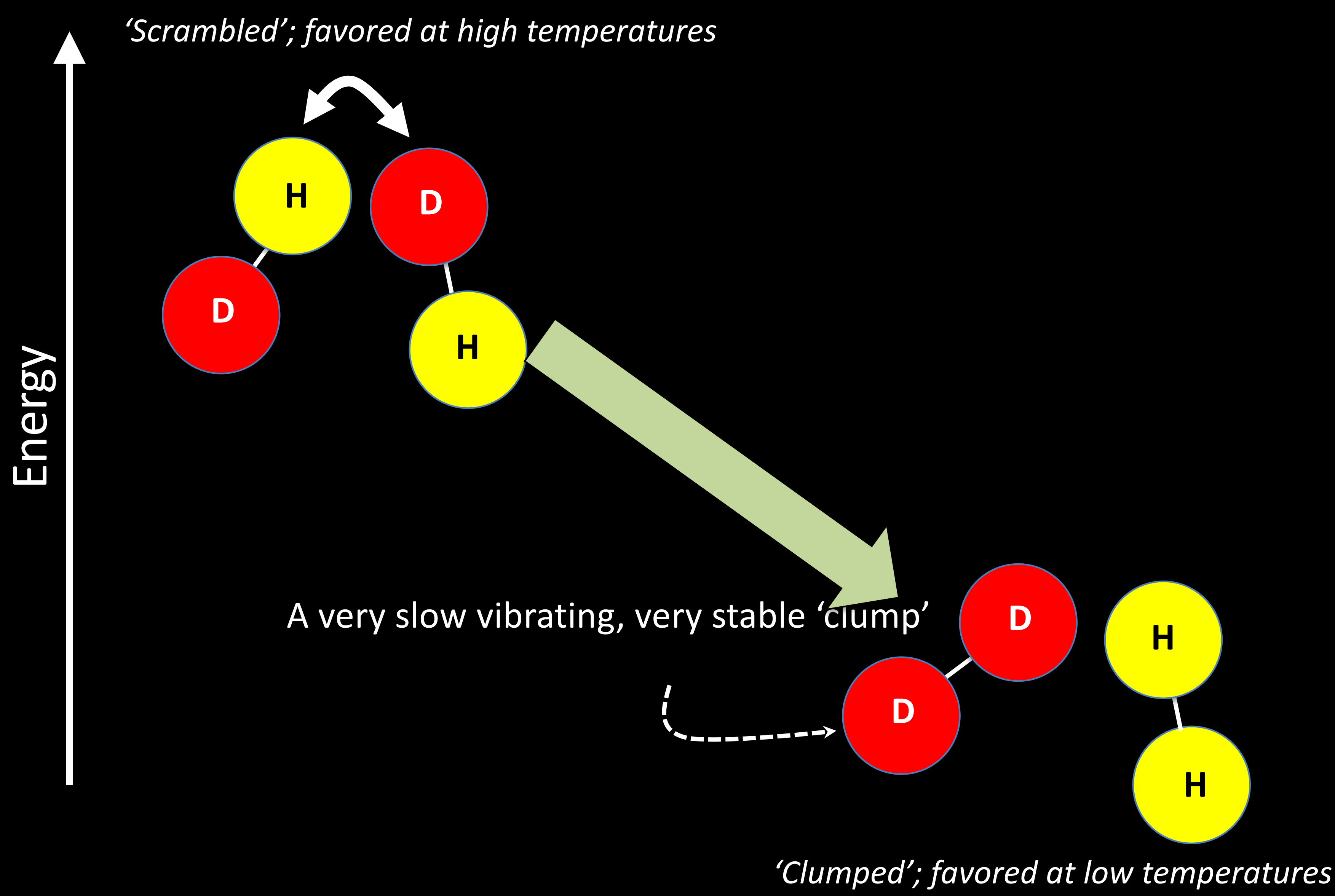


$$\nu'' = \frac{1}{2\pi}\left(\frac{k}{\mu''}\right)^{1/2}$$

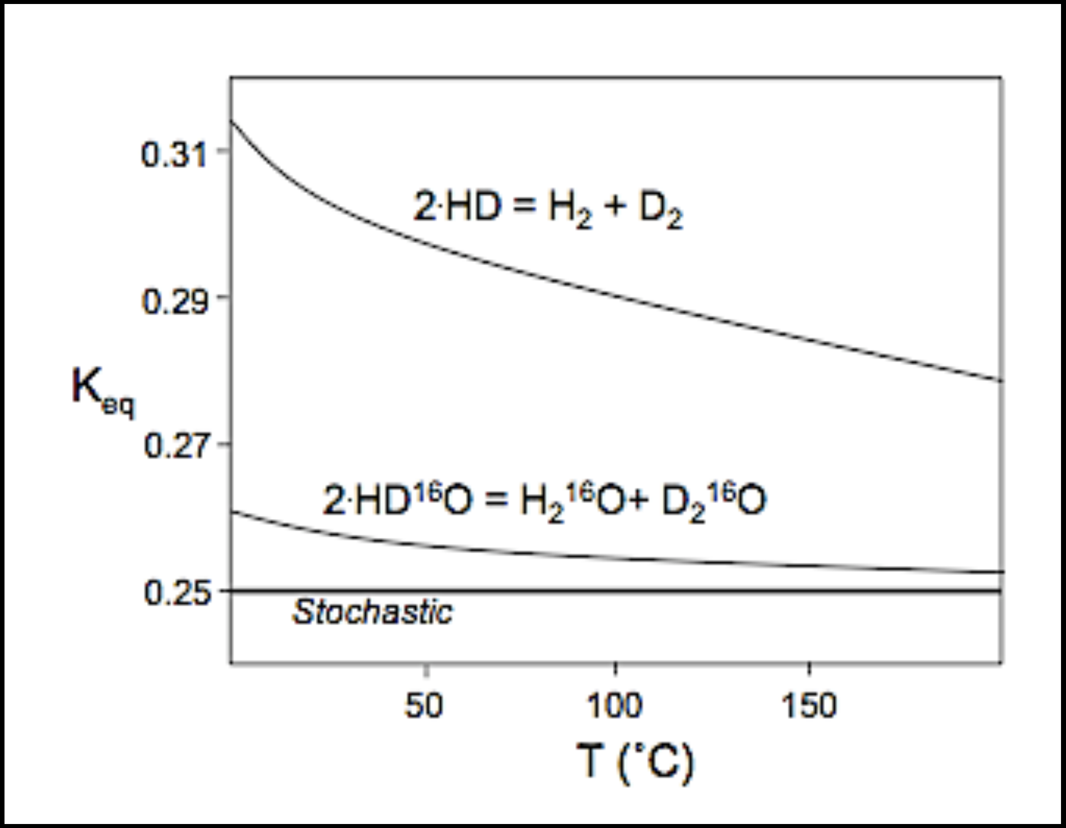
$\mu'' = 1$, $\nu'' = 3108\ \text{cm}^{-1}$ $\Delta\nu = 1287\ \text{cm}^{-1}$

1287 > 2 x 589

Isotopic ‘clumping’ reactions

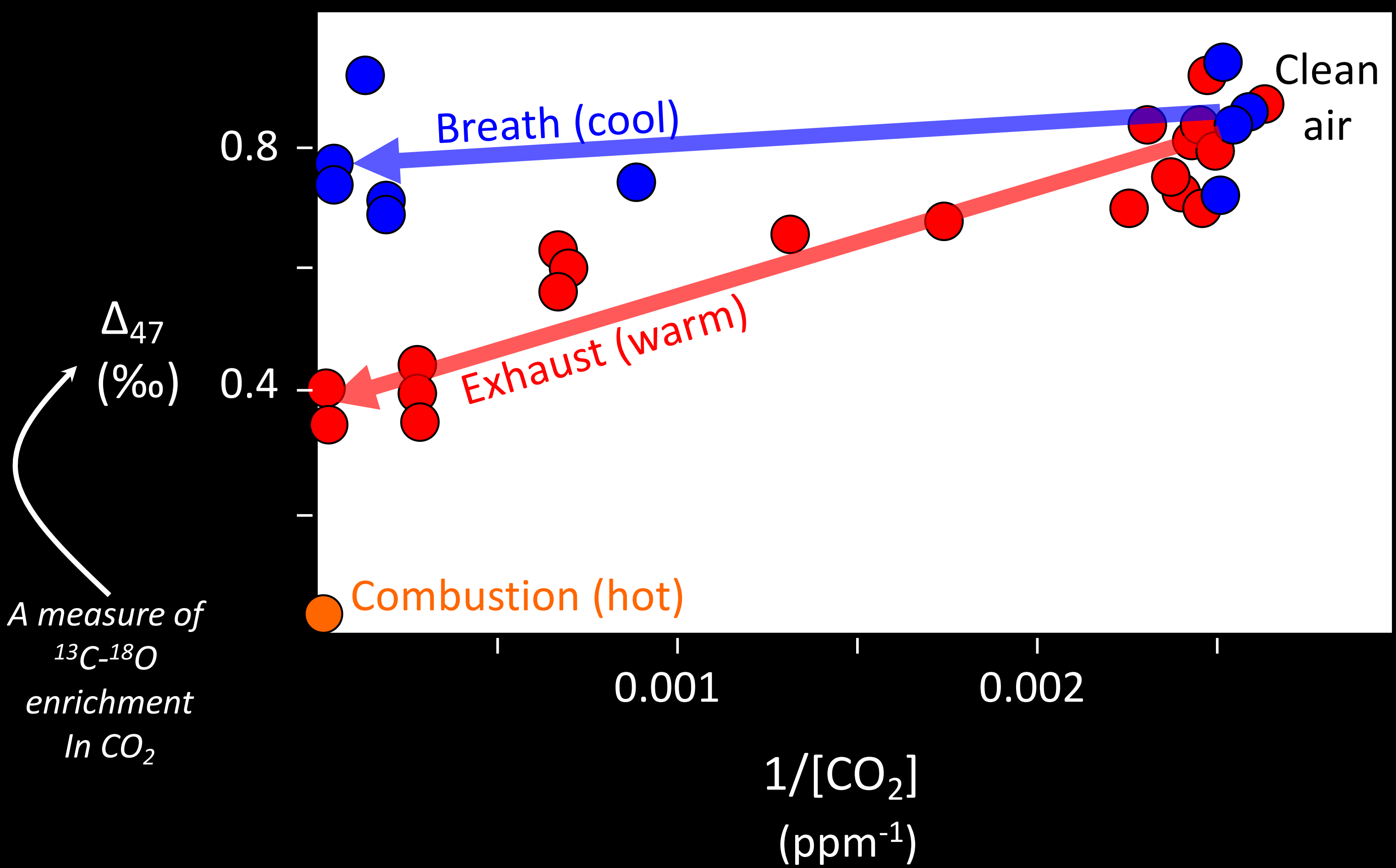


Just as for heterogenous reactions, the enthalpy and entropy terms compete, creating a temperature dependence



Determining the temperature of origin of anthropogenic CO_2

$$^{13}C^{16}O_2 + {}^{12}C^{18}O^{16}O = {}^{12}C^{16}O_2 + {}^{13}C^{18}O^{16}O$$

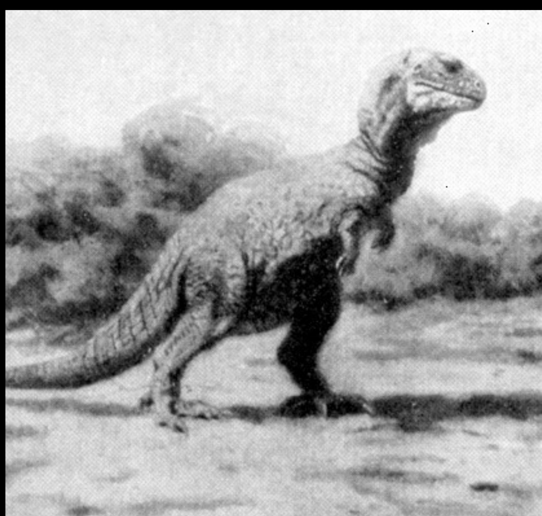


Affek and Eiler, 2006

Let’s try to solve something really tricky

— the body temperatures of dinosaurs

Did Dinosaurs more closely resemble modern lizards or modern birds?

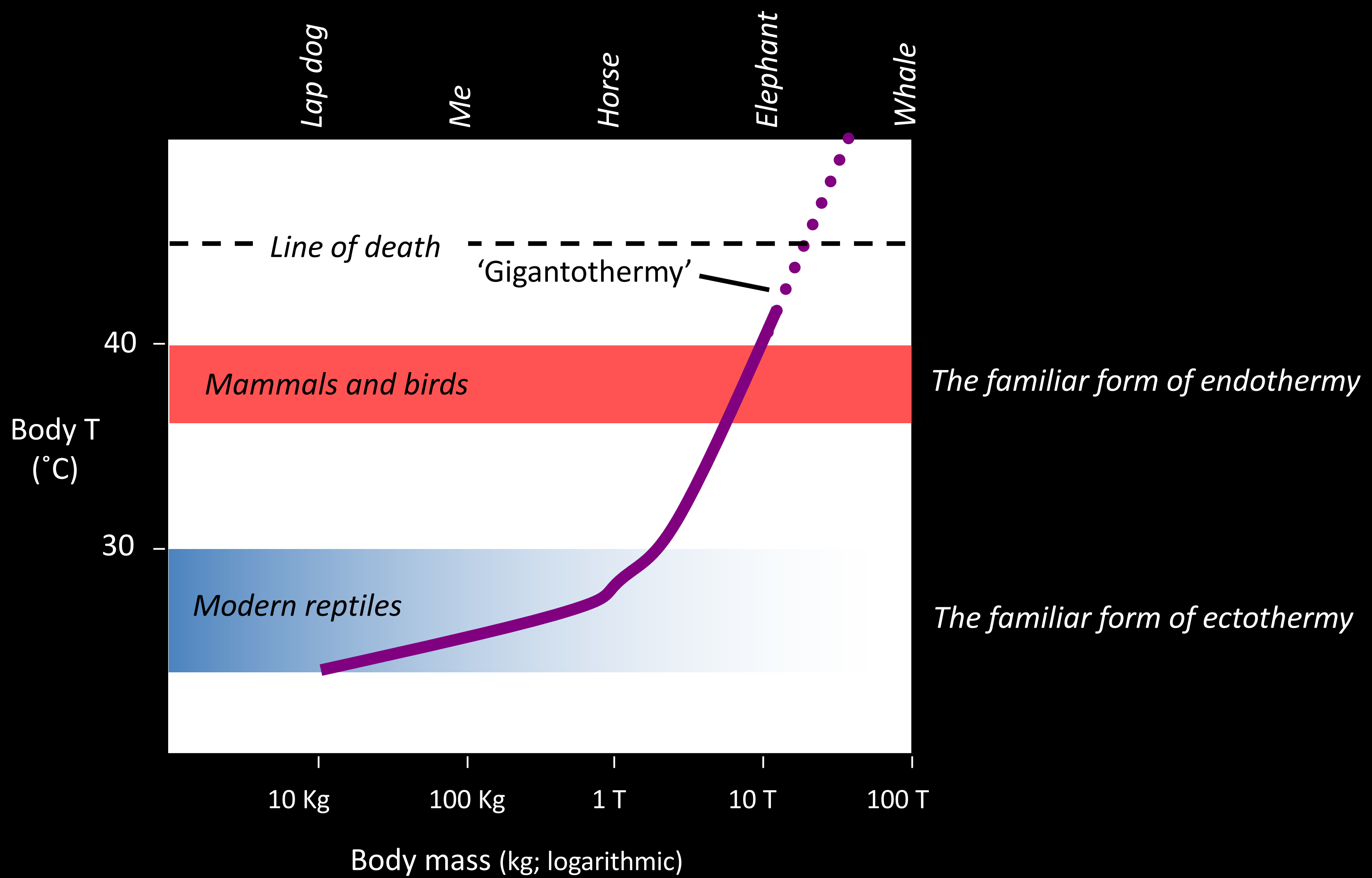


Slow, stupid, cold blooded T-Rex

Cold blooded ⟷	Warm blooded
Lethargic ⟷	Energetic
Awkward ⟷	Agile
Stupid ⟷	Less stupid

Fast, tricky, warm-blooded, Jeff-Goldbum-eating T-Rex

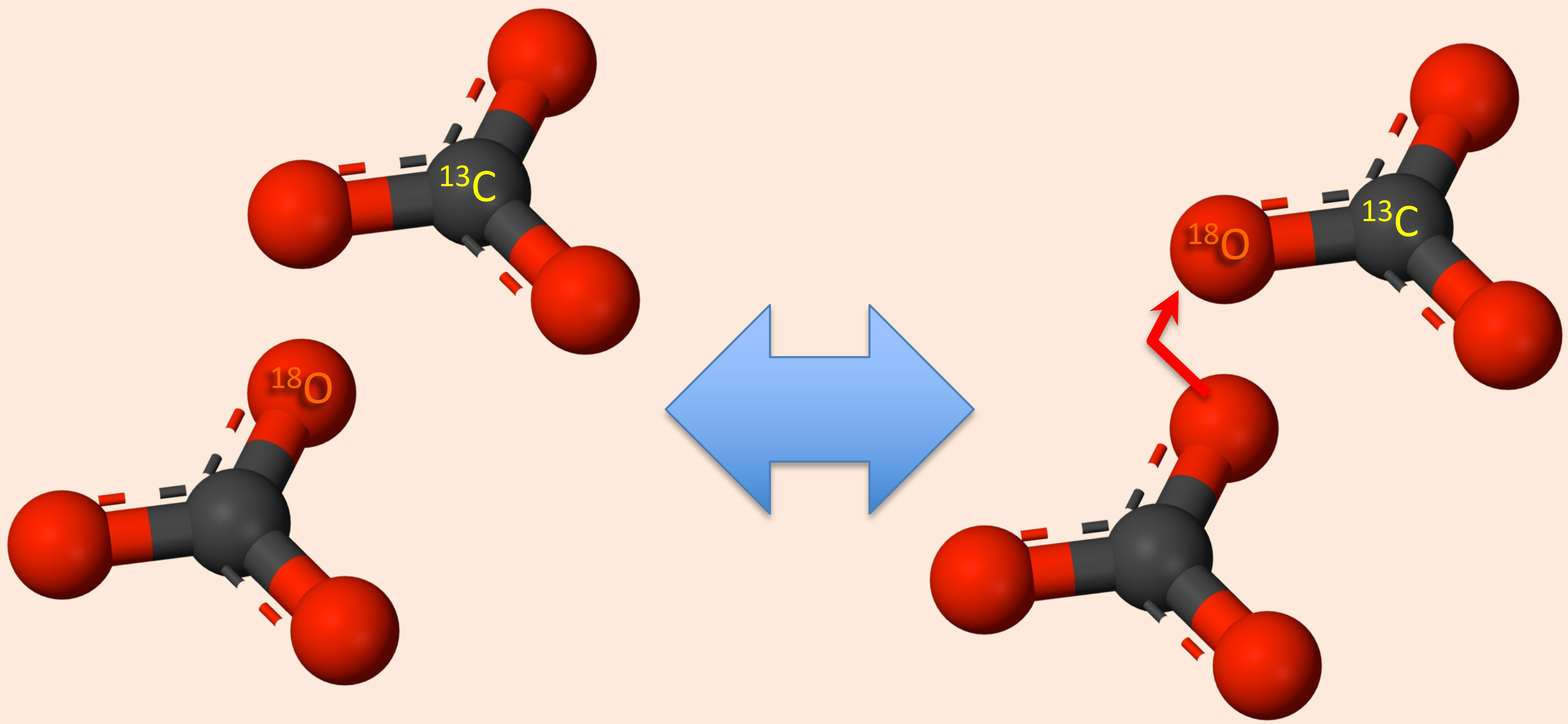
Predicting body temperatures for various hypotheses regarding Dinosaur metabolism



- And, ectotherms will vary with environment as well as size.
- Heterotherms might vary with ontogenetic age.

‘Clumping’ in the carbonate minerals

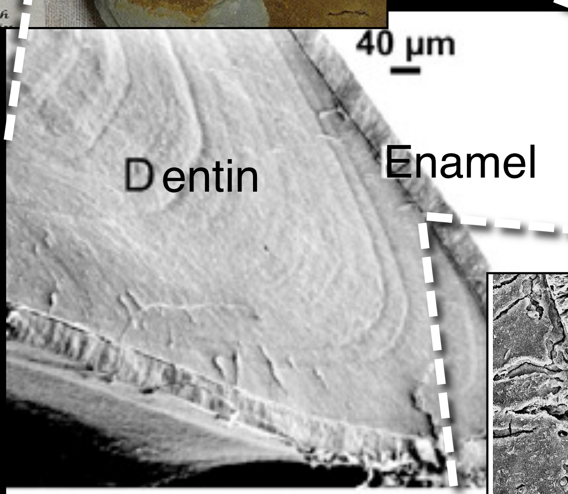
$$Ca^{13}C^{16}O_3 + Ca^{12}C^{18}O^{16}O_2 \longleftrightarrow Ca^{12}C^{16}O_3 + Ca^{13}C^{18}O^{16}O_2$$



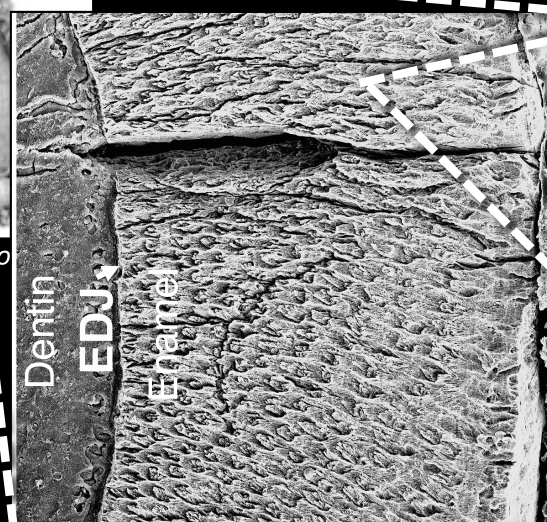
Disordered
Favored at high temperature

Ordered
Favored at low temperature

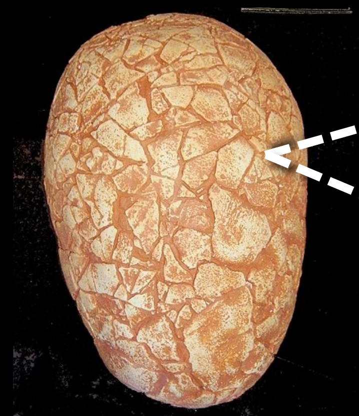
Isotopic 'clumping' in teeth and egg shells

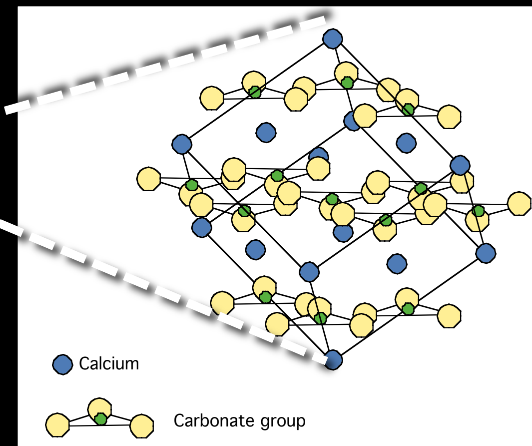


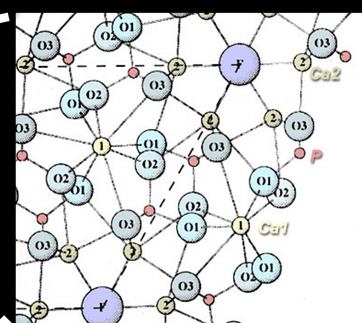
Cross-section of a modern Crocodile tooth



Close-up of a Cretaceous mammal tooth



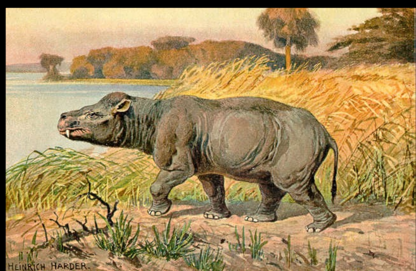


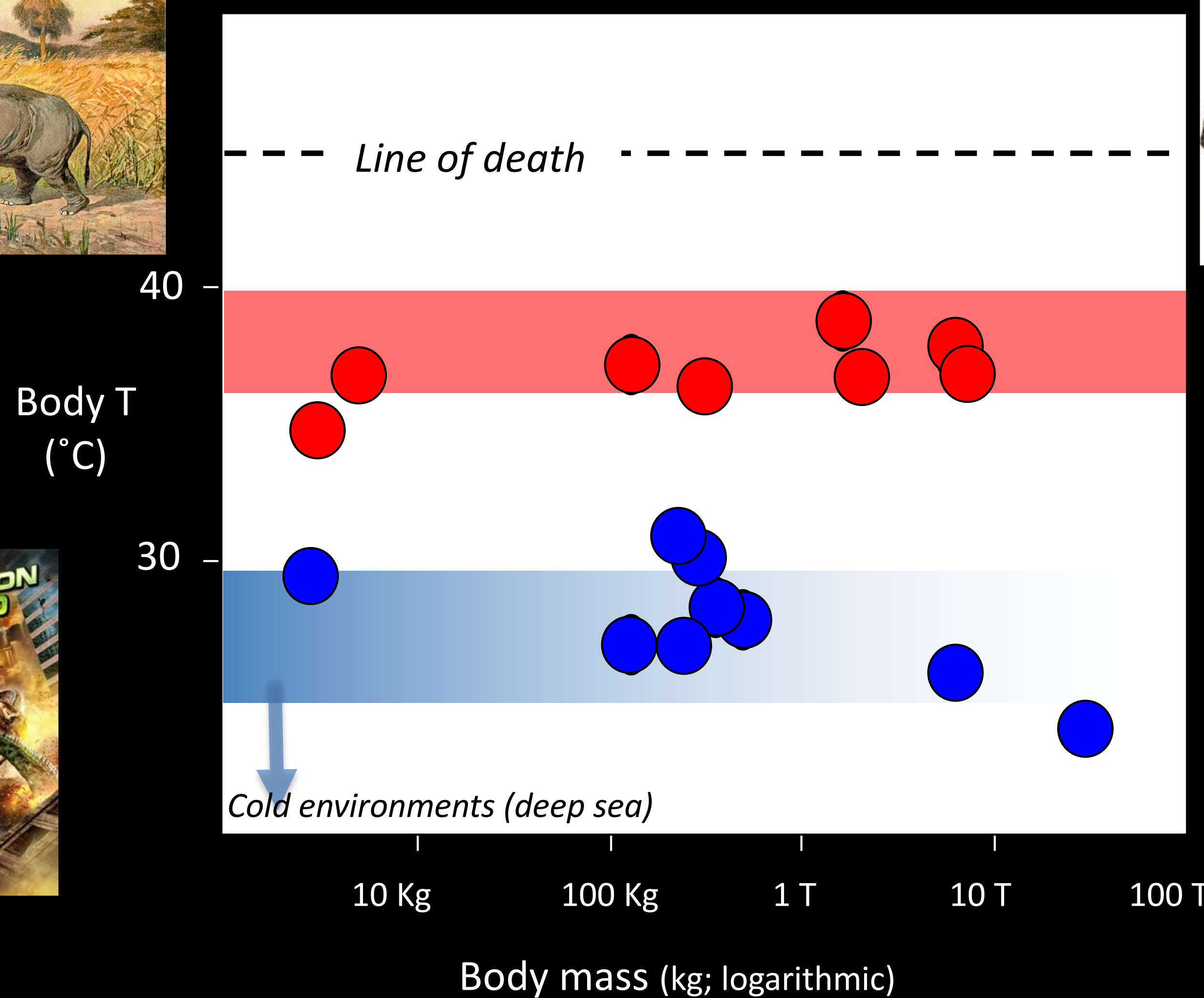


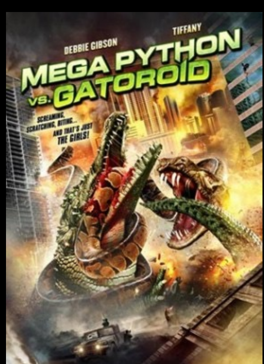
$CO_3^{-2} \leftrightarrow PO_4^{-3}$

$$^{13}C^{16}O_3 + {}^{12}C^{18}O^{16}O_2 = {}^{12}C^{16}O_3 + {}^{13}C^{18}O^{16}O_2$$

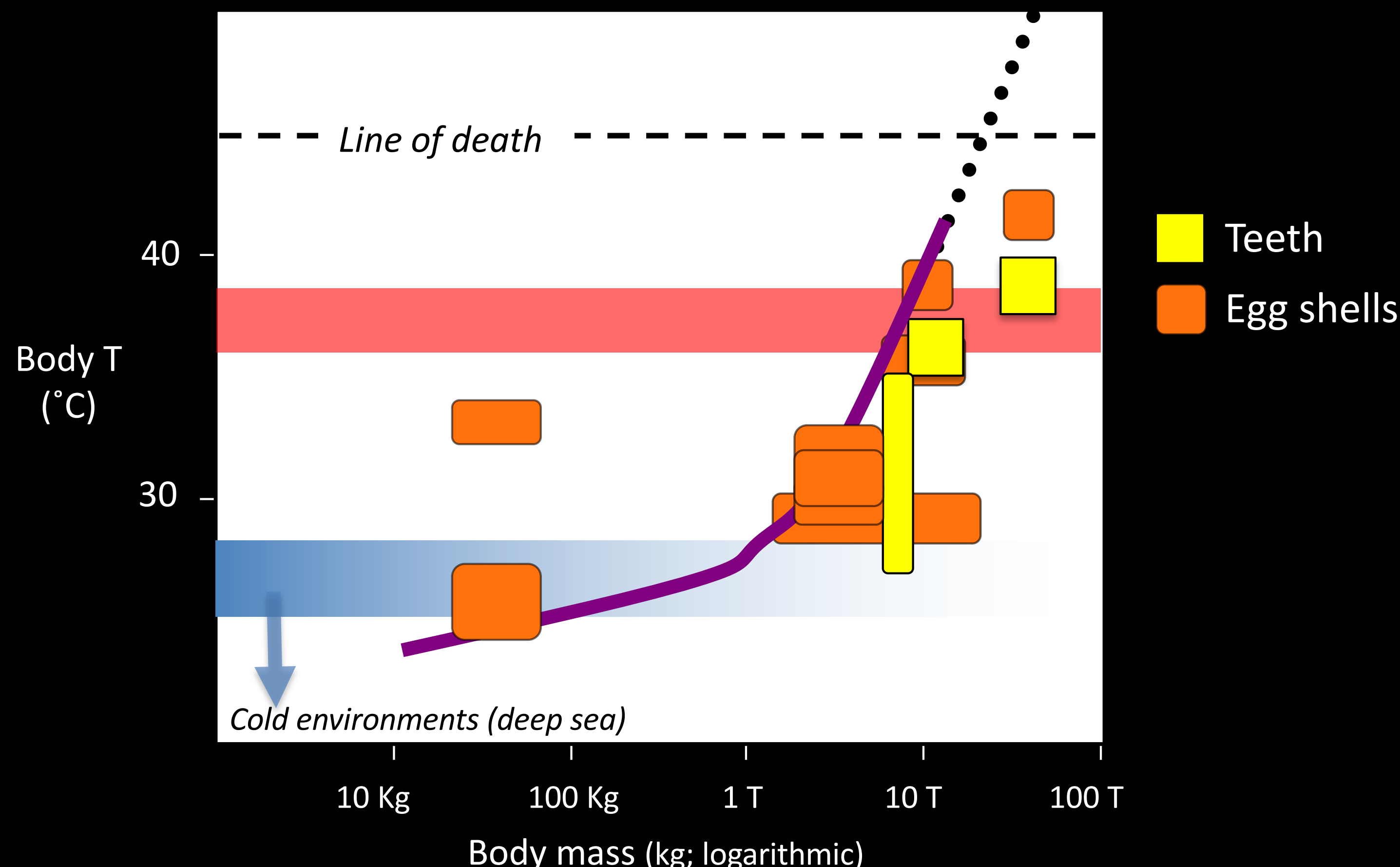
Taking our method for a spin with a variety of ‘known’ living and extinct animals







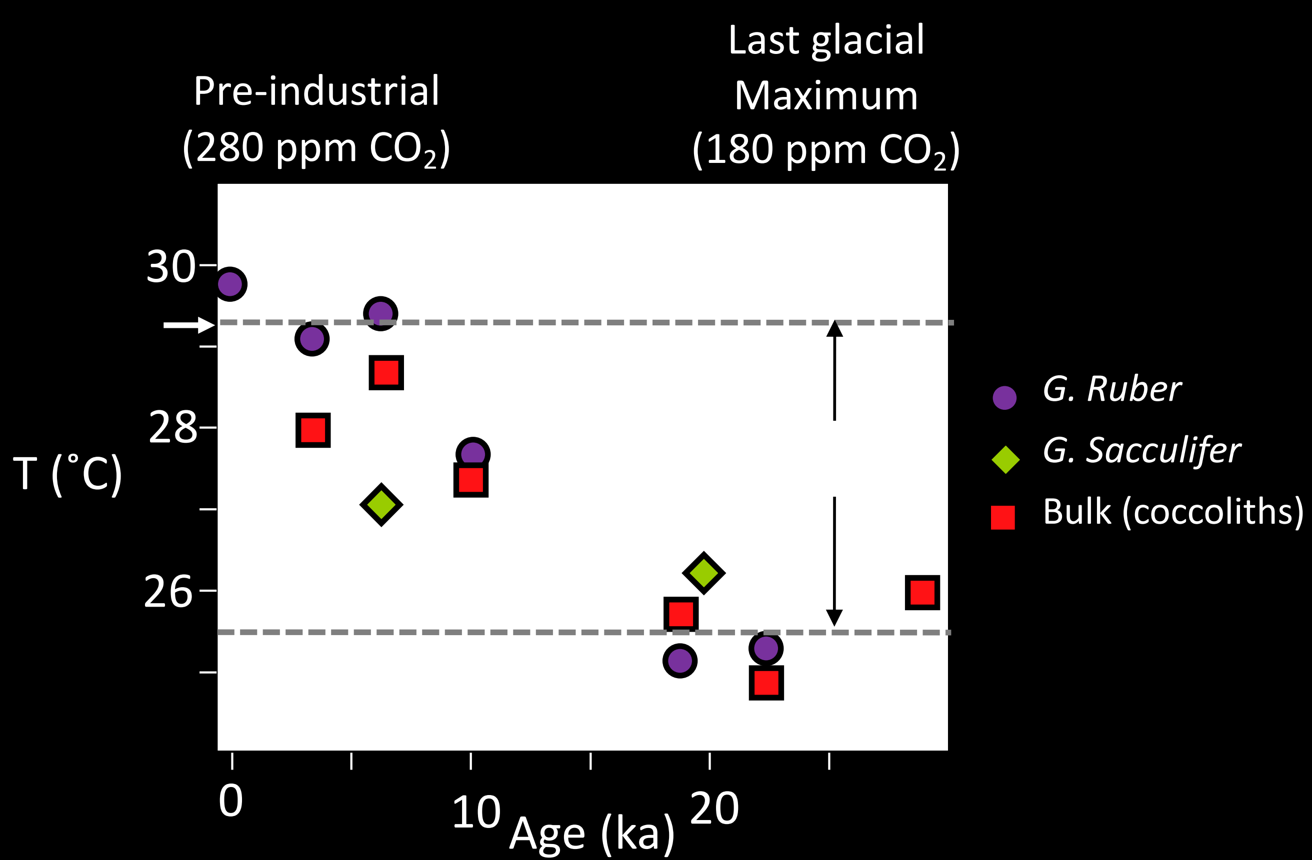
An overview of all data for dinosaurs



- Some are ‘warm blooded’ in a simple sense
- But overall too variable, and often too cold, to closely resemble birds and mammals
- ‘Gigantothermy’ is a plausible model for the animals studied to-date

This sort of measurement has opened new fronts on many challenging problems in earth history

Paleoclimate reconstructions

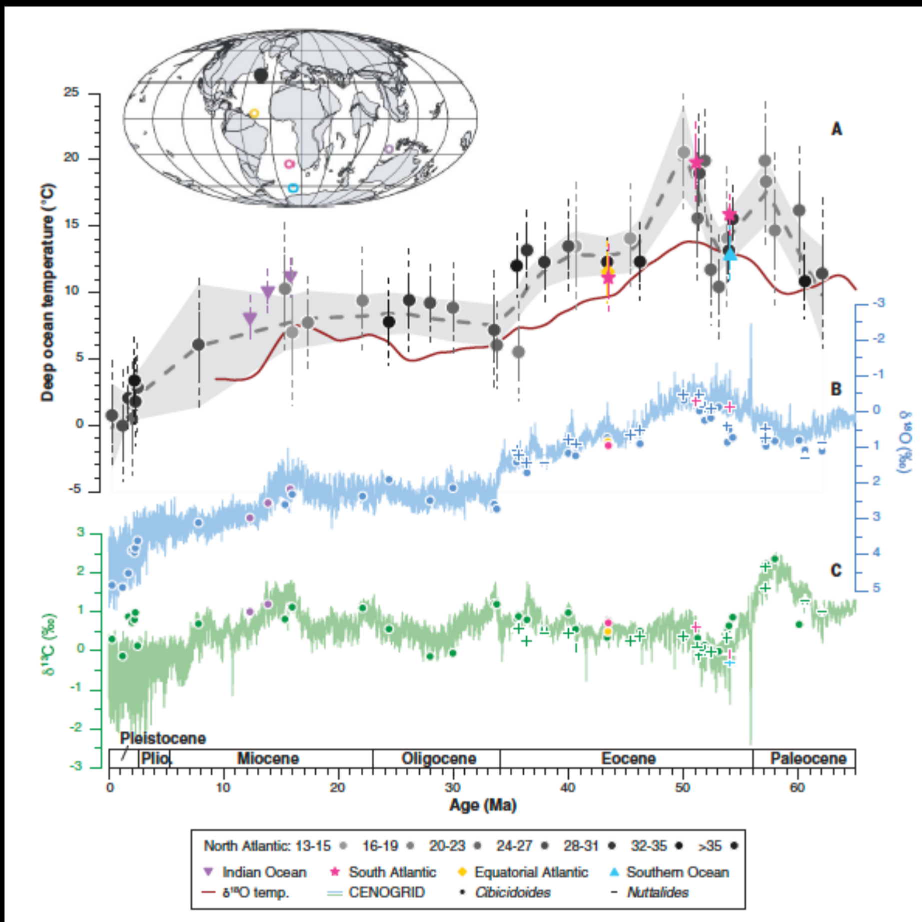


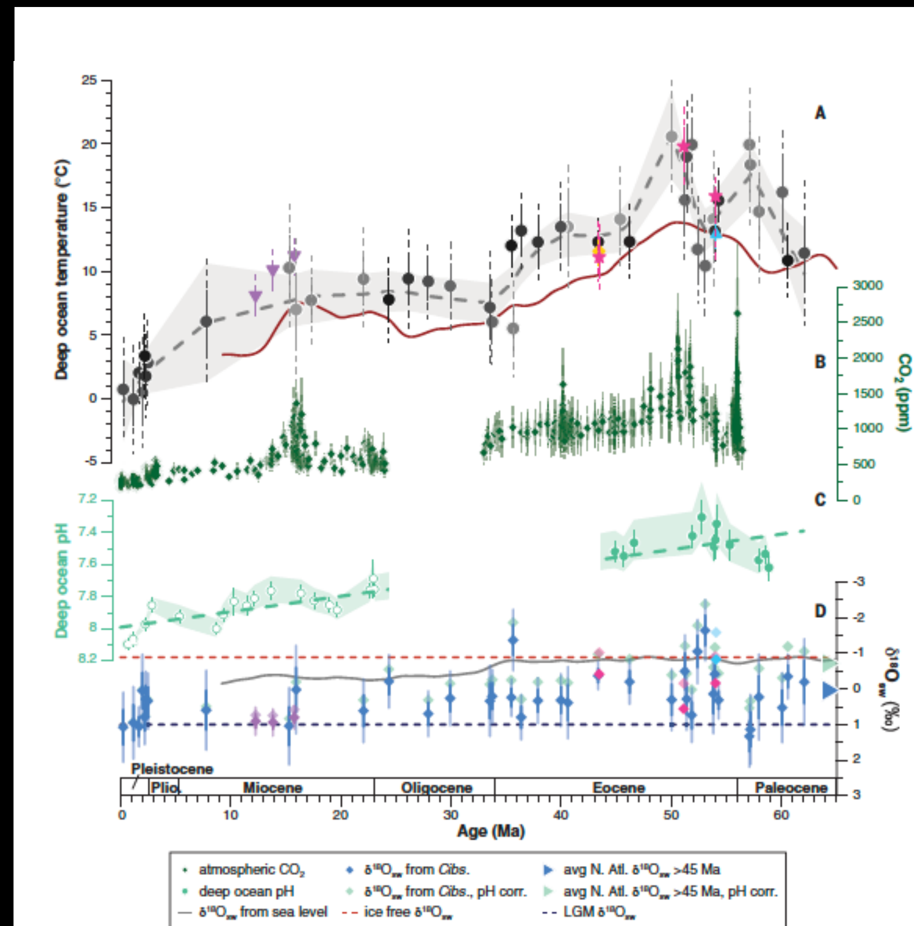
Work of Aradhna Tripati

A brand-new paper uses this method to re-examine the Cenozoic history of ocean temperatures

Cenozoic evolution of deep ocean temperature from clumped isotope thermometry

A. N. Meckler[1]*, P. F. Sexton[2], A. M. Piasecki[1]†, T. J. Leutert[1], J. Marquardt[1], M. Ziegler[3], T. Agterhuis[3], L. J. Lourens[3], J. W. B. Rae[4], J. Barnet[4], A. Tripati[5], S. M. Bernasconi[6]





Some take-aways

- The naturally-occurring, ‘stable’ isotopes are all around us, making up ~1%, on average, of all the atoms you encounter
- They combine in a dizzyingly complex variety of ways to create vast families of isotopically unique molecules
- The presence of isotopes changes properties, stabilities and rates of reaction for molecules, minerals and other materials
- Separation of isotopes through various physical and chemical processes imparts distinctive signatures that serve as records of natural conditions and processes
- Three iconic uses in the earth sciences are hydrology, ‘geothermometry’ and forensic fingerprinting of metabolisms in natural ecosystems
- Advances in analytical technology are making it possible to use molecular isotope structures as new, highly flexible tools for study of natural processes