Definitions and Isotopic Fractionation

Elemental Ecology

Week One

Chemistry Refresher

What's an isotope?

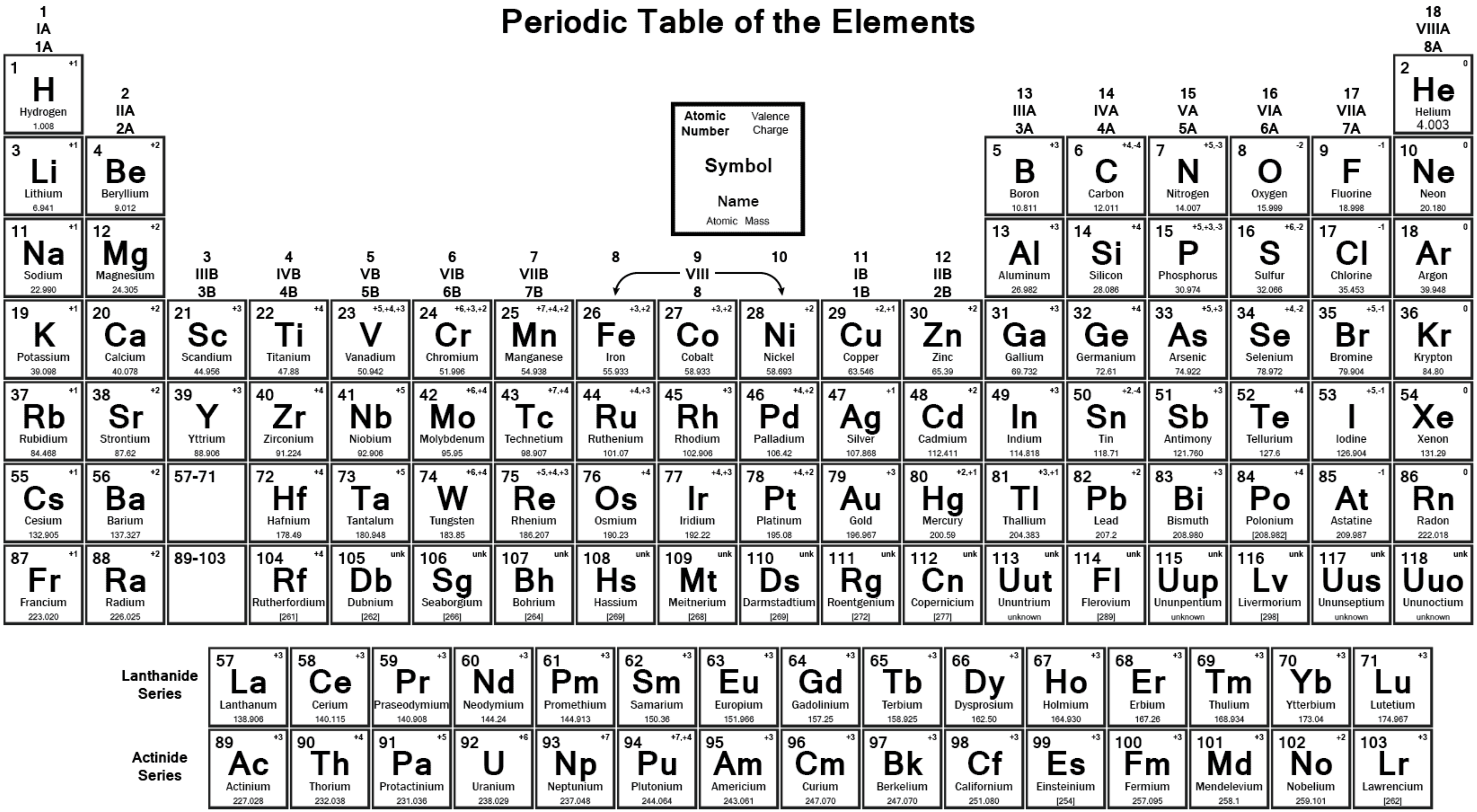
Units and Definitions

Measuring and reporting isotopic data

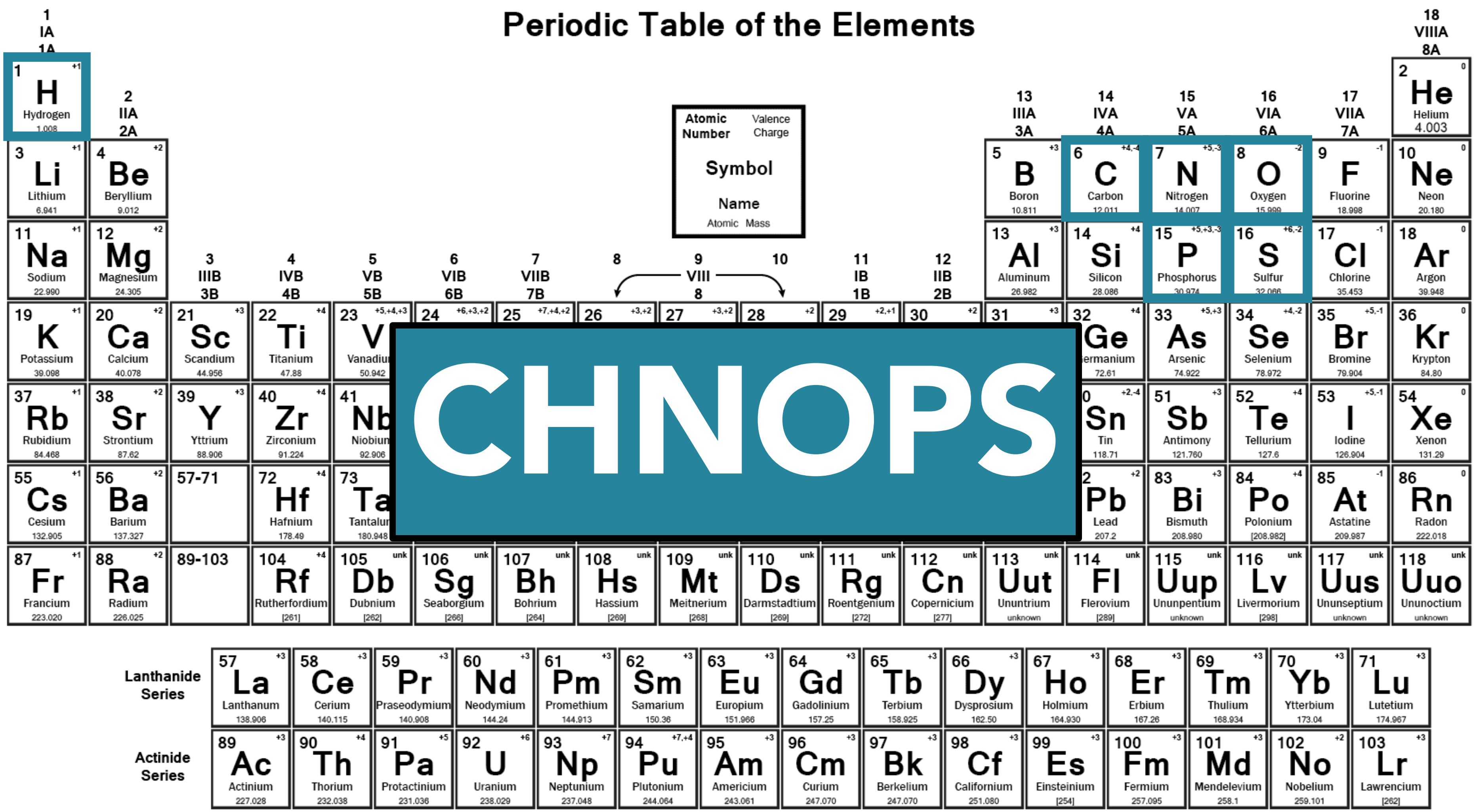
Isotopic Fractionation

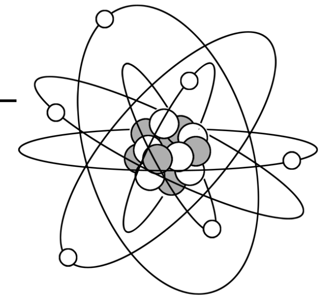
Why are isotopes useful?

What are the six main elements found in living organisms?



What are the six main elements found in living organisms?





6

C

Carbon

12.011

What makes up an atom?

Proton (Z): Subatomic particle with a positive charge found in the nucleus.

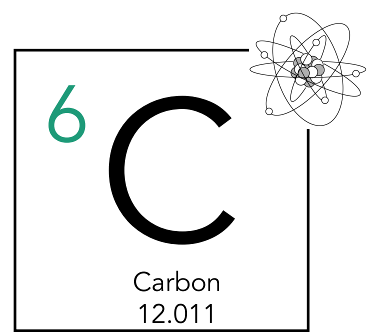
1.67262×10^{-27} kg

Neutron (N): Subatomic particle with no charge found in the nucleus.

1.67493×10^{-27} kg

Electron: Subatomic particle with a negative charge found orbiting the nucleus.

9.10938×10^{-31} kg



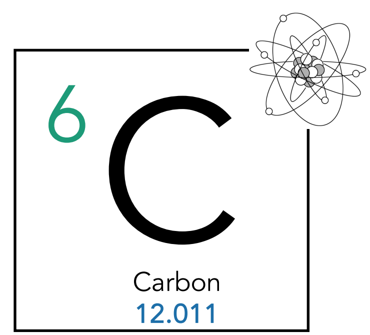
Terms & definitions for nuclides

Atomic Number (Z): Integer that expresses the number of protons in a nucleus.

Mass Number (A): Total number of protons and neutrons in a nucleus. $A = N + Z$.

Atomic Mass: Average of the masses of all naturally occurring ***isotopes*** of an element weighted by their abundances.

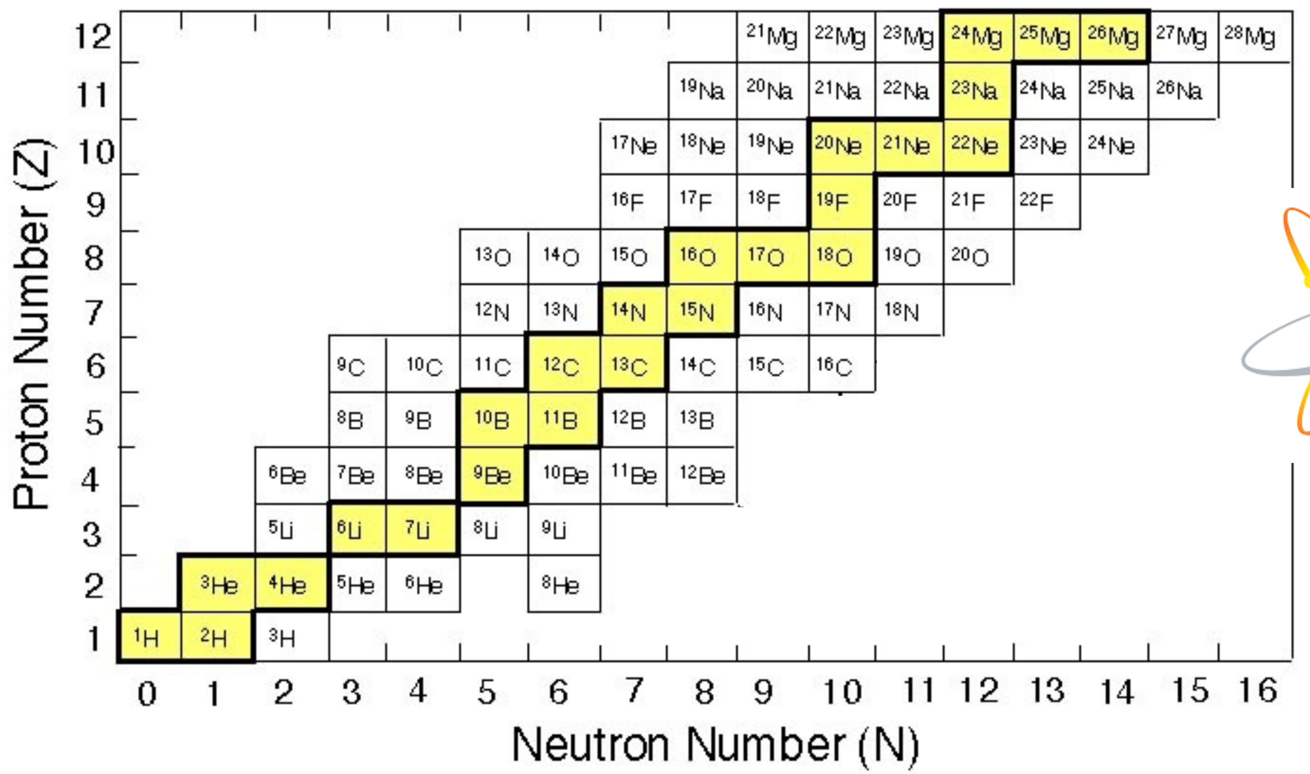
Atomic Mass Unit (AMU): A mass equal to exactly 1/12th the mass of a ^{12}C atom.



So, what's an isotope?

Isotope: A particular form of an element defined by a specific number of neutrons.

Isotopes have same Z, different N, thus different A



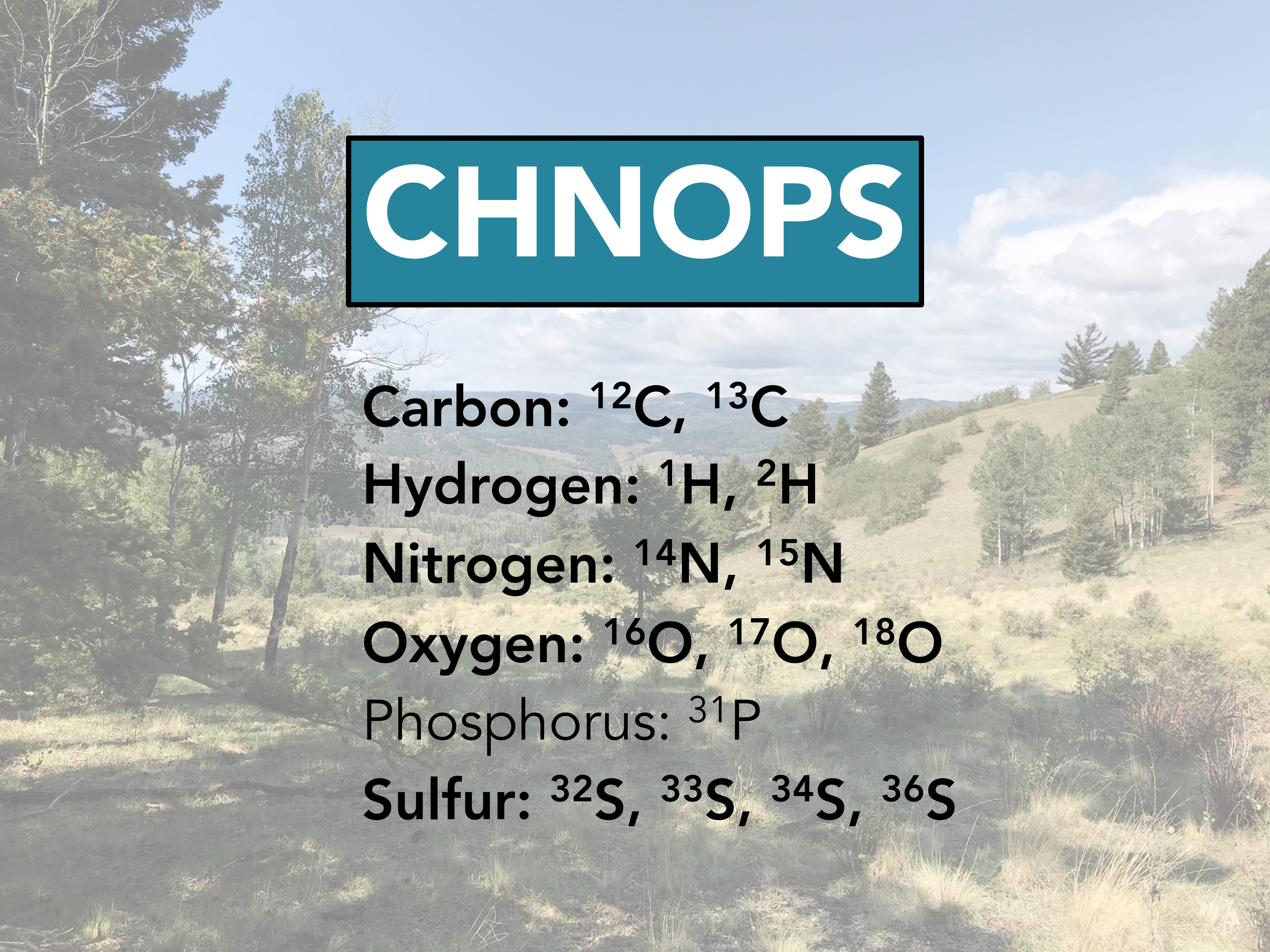
So, what's an isotope?

Isotope: A particular form of an element defined by a specific number of neutrons.

Radioactive Isotopes: Unstable nuclei that spontaneously decay emitting alpha/beta particles, or gamma rays and forming a new (radiogenic) element in the process.

Stable Isotopes: Nuclei that do not radioactively decay*, although they may be radiogenic.

Typically, the heavier stable isotopes of an element are less abundant than the lighter stable isotopes of the same element.

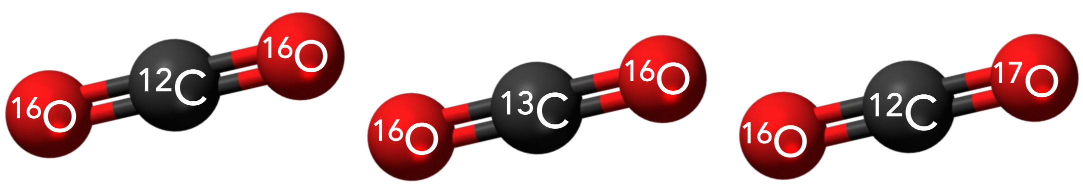

CHNOPS
Carbon: ^{12}C, ^{13}C
Hydrogen: ^{1}H, ^{2}H
Nitrogen: ^{14}N, ^{15}N
Oxygen: ^{16}O, ^{17}O, ^{18}O
Phosphorus: ^{31}P
Sulfur: ^{32}S, ^{33}S, ^{34}S, ^{36}S

Other Iso-Terms

Isotopologues: Molecules that differ from one another only in isotopic composition. May have the same, or different masses.

CO_2 has 12 isotopologues!

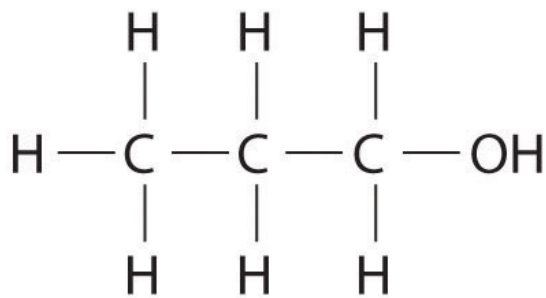
$^{12}C^{16}O^{16}O$, $^{12}C^{16}O^{17}O$, $^{12}C^{16}O^{18}O$, $^{12}C^{17}O^{17}O$, $^{12}C^{17}O^{18}O$, $^{12}C^{18}O^{18}O$,
$^{13}C^{16}O^{16}O$, $^{13}C^{16}O^{17}O$, $^{13}C^{16}O^{18}O$, $^{13}C^{17}O^{17}O$, $^{13}C^{17}O^{18}O$, $^{13}C^{18}O^{18}O$



No such thing as "CO_2 isotopes", or "H_2O isotopes"

Other Iso-Terms

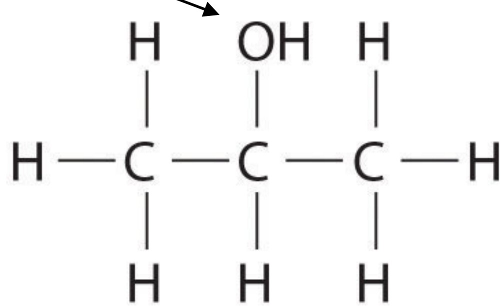
Isomers: molecules with the same chemical formula, but different structures



The hydroxyl group is attached to the terminal C atom

1-Propanol (*n*-propanol)

The hydroxyl group is attached to the middle C atom

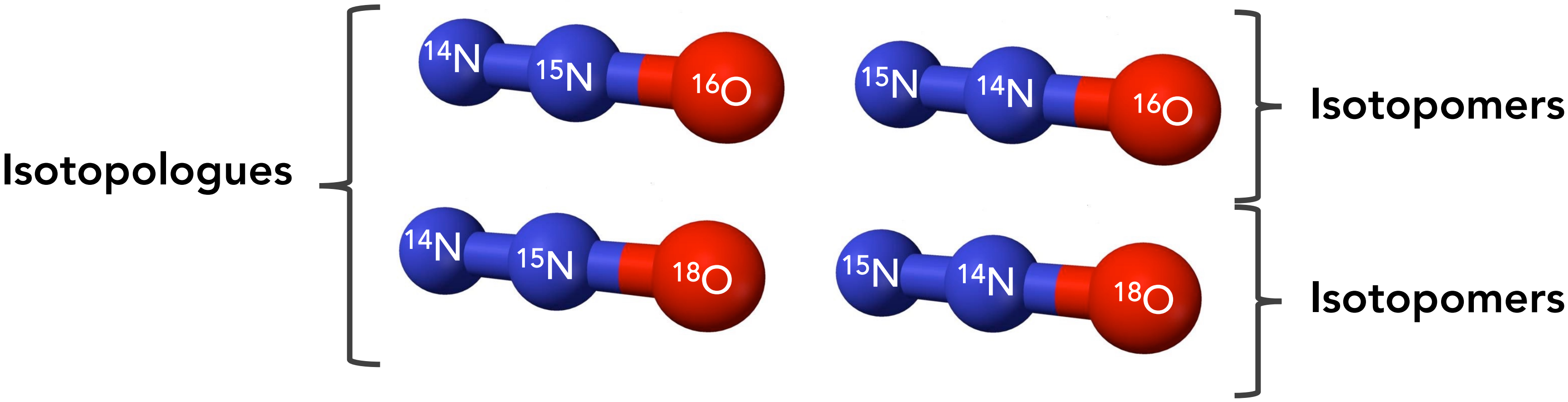


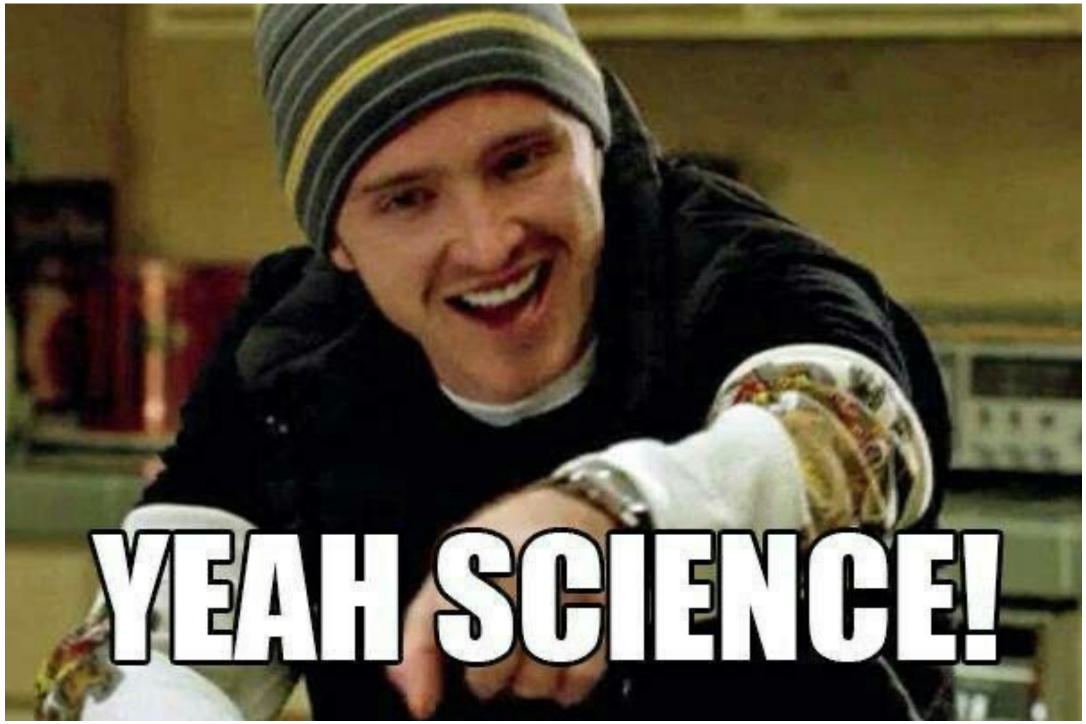
2-Propanol (isopropanol)

Other Iso-Terms

Isotopomers (Isotopic Isomers): isotopologues that differ from one another in the positions or locations of the isotopic elements. Have the **same** mass.

N_2O (laughing gas)





To be continued on Thursday…

So far as I personally am concerned, this has resulted in a great clarification of my ideas, and it may be helpful to others, though no doubt there is little originality in it. The same algebraic sum of the positive and negative charges in the nucleus, when the arithmetical sum is different, gives what I call "isotopes" or "isotopic elements," because they occupy the same place in the periodic table. They are chemically identical, and save only as regards the relatively few physical properties which depend upon atomic mass directly, physically identical also. Unit changes of this nuclear charge, so reckoned algebraically, give the successive places in the periodic table. For any one "place," or any one nuclear charge, more than one number of electrons in the outer-ring system may exist, and in such a case the element exhibits variable valency. But such changes of number, or of valency, concern only the ring and its external environment. There is no in- and out-going of electrons between ring and nucleus.

FREDERICK SODDY.

Physical Chemistry Laboratory,
University of Glasgow.

(1913) Nature **92**, 399–400

THE WORD "ISOTOPE"

SIR,—This word, now so familiar, was introduced in Glasgow about 1912 by a medical woman—Margaret Todd, who was also a novelist writing under the name Graham Travers—to fit the concept of elements occupying the same place in the periodic table. The occasion was a social gathering at 11, University Gardens, then the home of Sir George Beilby (the father-in-law of the late Frederick Soddy, who originated the concept of isotopes and other achievements in radiochemistry including the first approach to atomic numbers). Having been obliged to use awkward periphrases to express his "isotopic" ideas, Soddy said he needed a word for the concept; Dr. Todd immediately suggested *isotope*—*iso*, the same, *topos*, place. The word had indeed been published a few years before in a context of organic chemistry; but there is no reason to suppose that Dr. Todd was aware of that.

Purists may like to note that *homotope* would be more exact; Soddy, however, gratefully adopted the suggestion of isotope, and its use in its now accepted sense was first published by him in 1913.

To commemorate the coining of the radiochemical word, the Glasgow and West of Scotland section of the Royal Institute of Chemistry is making arrangements to affix a plain lettered plaque bearing the names of Soddy and Dr. Todd to the house concerned. This house is now the property of the University of Glasgow, and the arrangements are being made with the consent and support of the University authorities. No public appeal for funds is being made.

West of Scotland
Agricultural College,
Glasgow, C.2.

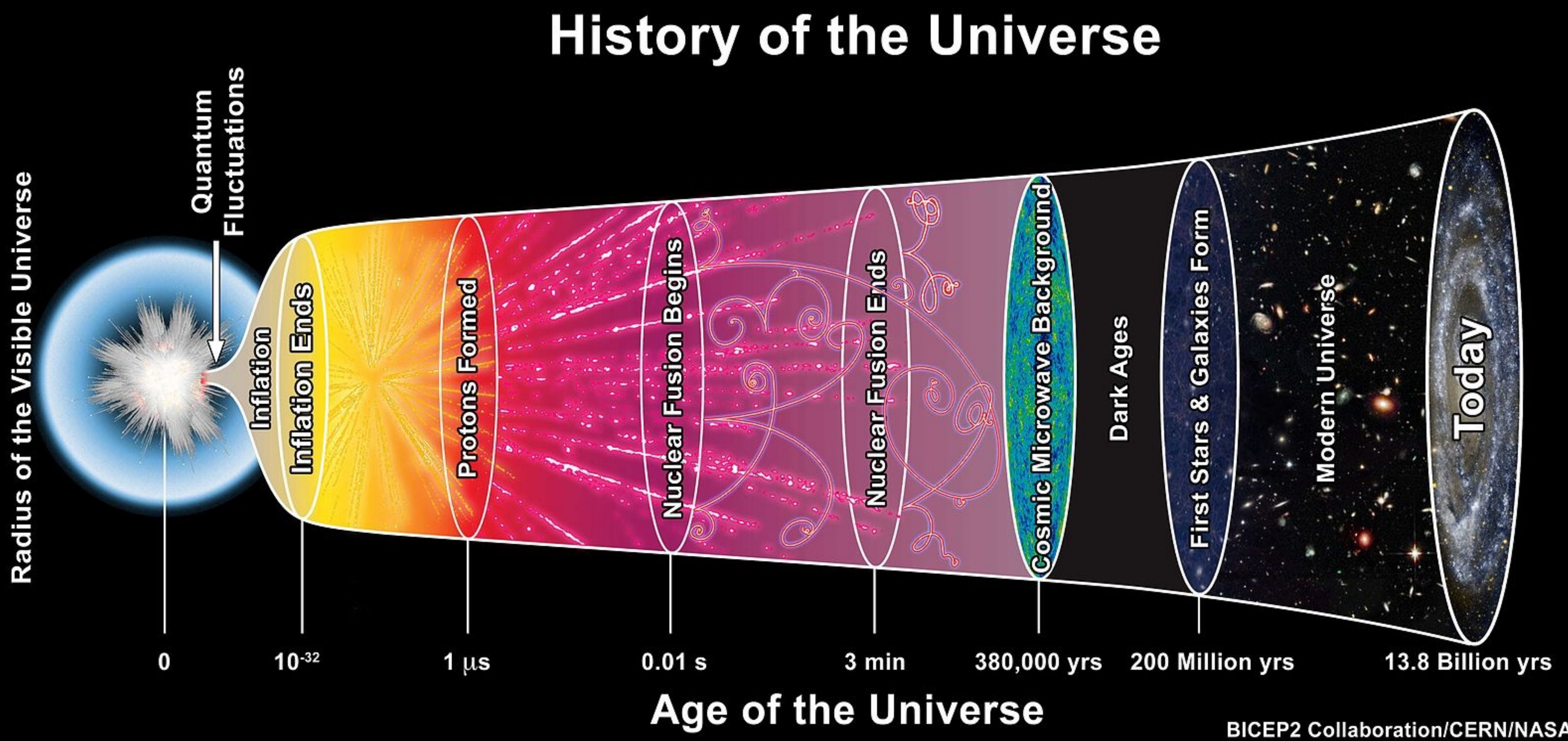
HUGH NICOL
Chairman, Glasgow and
West of Scotland section,
Royal Institute of Chemistry.

Nicol, H (1957). The word 'isotope'. *The Lancet* 269: 1358–59.

Nagel, MC (1982). Frederick Soddy: From alchemy to isotopes. *Journal of Chemical Education*, *59*(9), 739.

How were the elements and their isotopes formed?

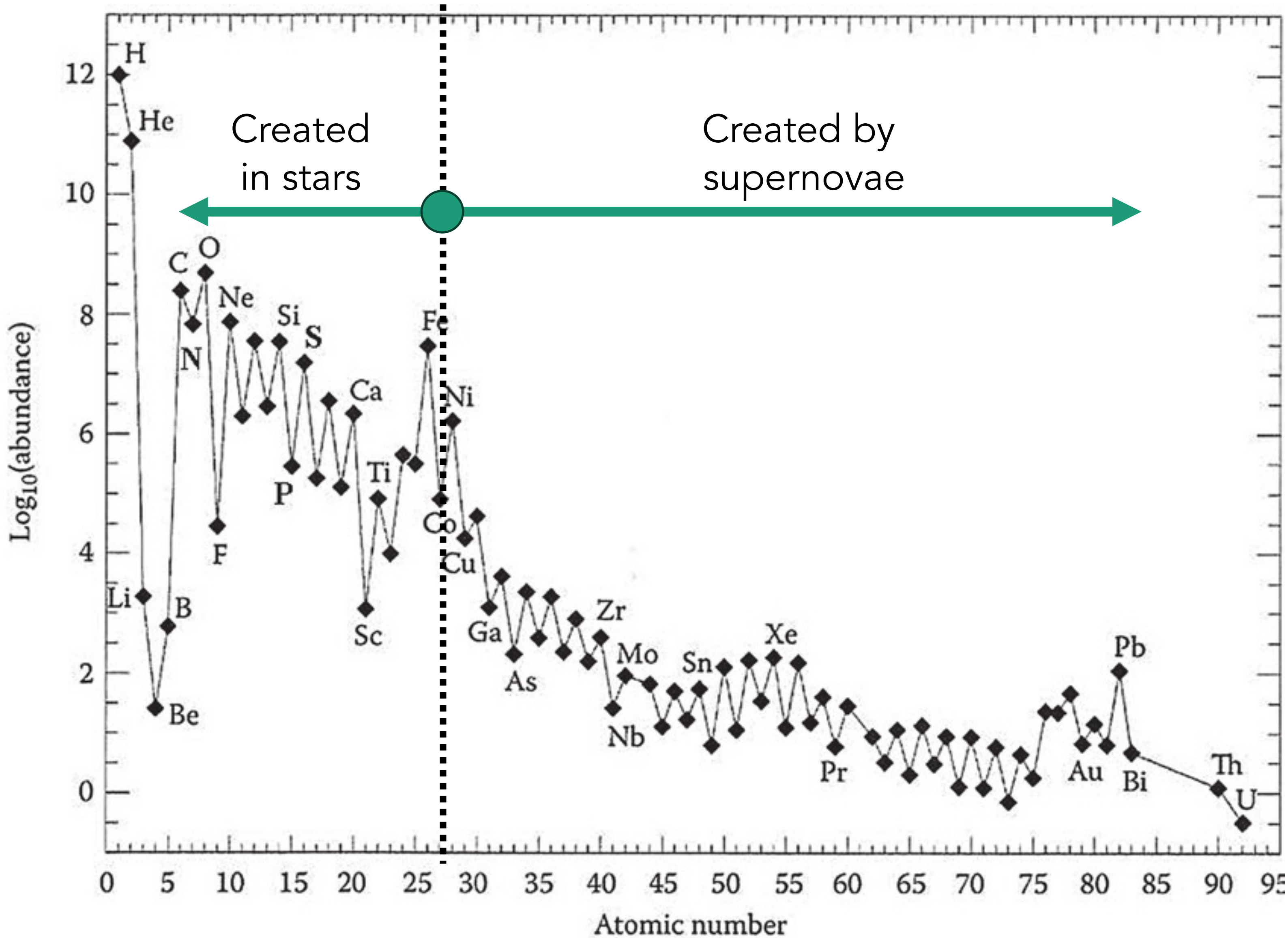
NUCLEOSYNTHESIS



Formation of H, ^{2}H, ^{3}He, ^{4}He, ^{7}Li

Formation of everything else

Abundance of elements in our solar system



Isotope abundances on Earth

Isotope	Mass (amu)	Abundance (% of Total Element)
^{1}H	1.007825	99.985
^{2}H	2.0140	0.015
^{12}C	12	98.89
^{13}C	13.00335	1.11
^{14}N	14.00307	99.63
^{15}N	15.00011	0.37
^{16}O	15.99491	99.759
^{17}O	16.99914	0.037
^{18}O	17.99916	0.204
^{32}S	31.97207	95.0
^{33}S	32.97146	0.76
^{34}S	33.96786	4.22
^{36}S	35.96709	0.014

Sharp, Z (2019). Principles of Stable Isotope Geochemistry

How do we report stable isotope values?
delta (δ) notation

Means of expressing the *relative* abundance of the heavier stable isotope in a mixture

$$\delta = \left(\frac{R_{sample}}{R_{standard}} - 1 \right) \times 1000$$

R = ratio of the abundance of the heavy to light isotope

Reported in units of **parts per thousand**,
aka **per mil (‰)**

International Isotopic Standards

Acronym	Standard Name	Isotopes	$R_{heavy/light}$
V-SMOW	Vienna Standard Mean Ocean Water	$^{2}H/^{1}H$	0.00015576
V-SMOW	Vienna Standard Mean Ocean Water	$^{18}O/^{16}O$	0.00200520
V-PDB	Vienna Pee Dee Belemnite	$^{13}C/^{12}C$	0.0112372
V-PDB	Vienna Pee Dee Belemnite	$^{18}O/^{16}O$	0.0020672
Air	Atmospheric Air	$^{15}N/^{14}N$	0.0036765
Air	Atmospheric Air	$^{3}He/^{4}He$	1.38×10^{-6}
CDT	Canyon Diablo Troilite	$^{34}S/^{32}S$	0.04500451

In-house reference materials (internal lab standards) must be calibrated to the appropriate international reference standards.

V-PDB

Calcium carbonate marine fossil from the PeeDee Formation in South Carolina

Late Cretaceous (66–72 mya)

Collected by Heinz Lowenstam and analyzed by Harold Urey

BULLETIN OF THE GEOLOGICAL SOCIETY OF AMERICA
VOL. 62, PP. 399-416, 1 FIG., 1 PL. APRIL 1951

MEASUREMENT OF PALEOTEMPERATURES AND TEMPERATURES OF THE UPPER CRETACEOUS OF ENGLAND, DENMARK, AND THE SOUTHEASTERN UNITED STATES

BY H. C. UREY, H. A. LOWENSTAM, S. EPSTEIN, AND C. R. MCKINNEY

Let's try calculating a $\delta^{13}C$ value!

$[^{13}C/^{12}C]_{leaf} = 0.0109338$

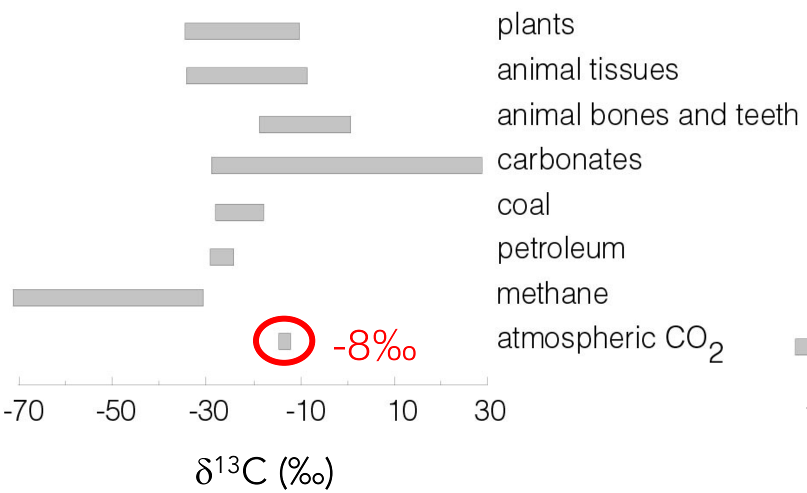
$\delta^{13}C = ??$

Important notes about δ

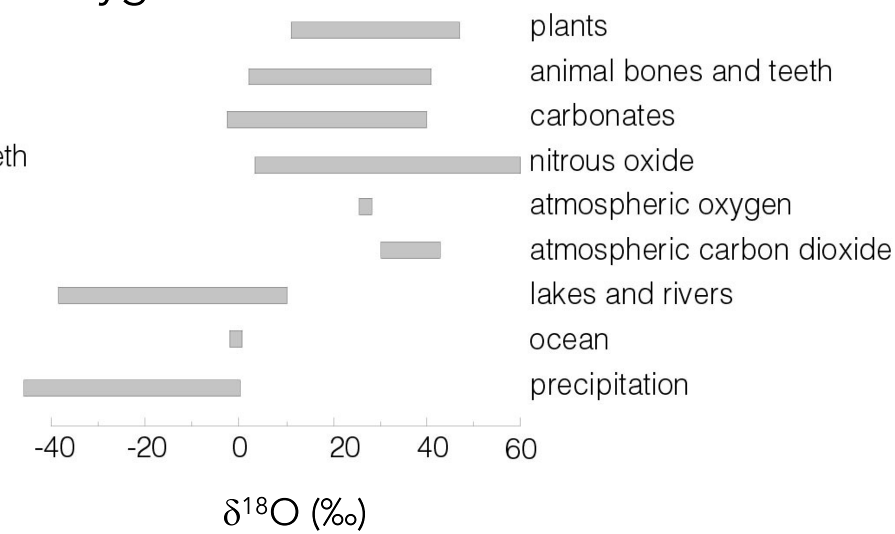
- δ values do not represent absolute atomic concentrations. They are **ratios**, reported in parts per thousand.
- Because δ values are measured relative to a standard, they are often negative.
- δ values must be calculated using the same international standard to be comparable.
- Many mathematical calculations should be made by converting δ values to a concentration unit (e.g., atom percent).

Natural ranges of isotopic values

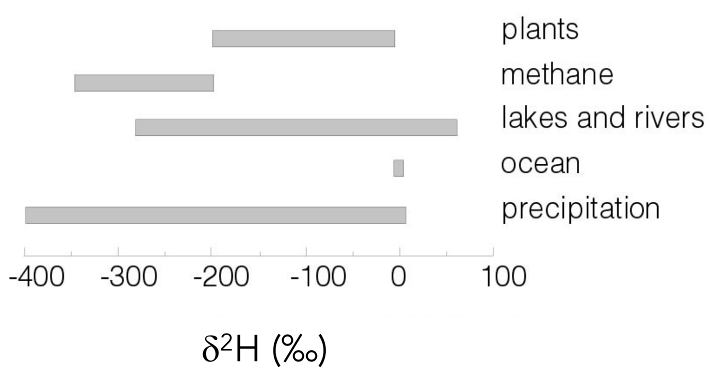
Carbon



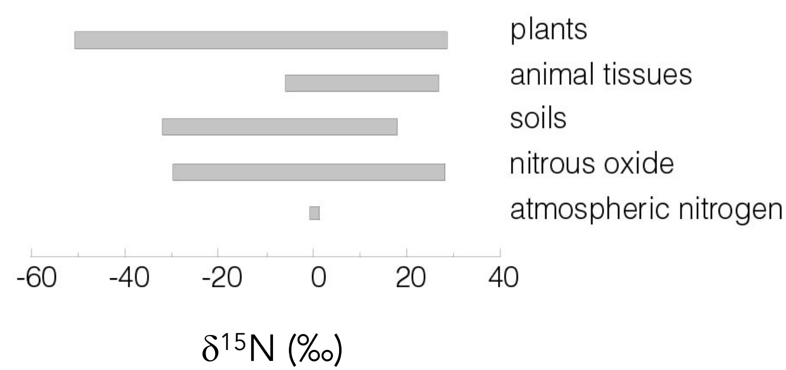
Oxygen



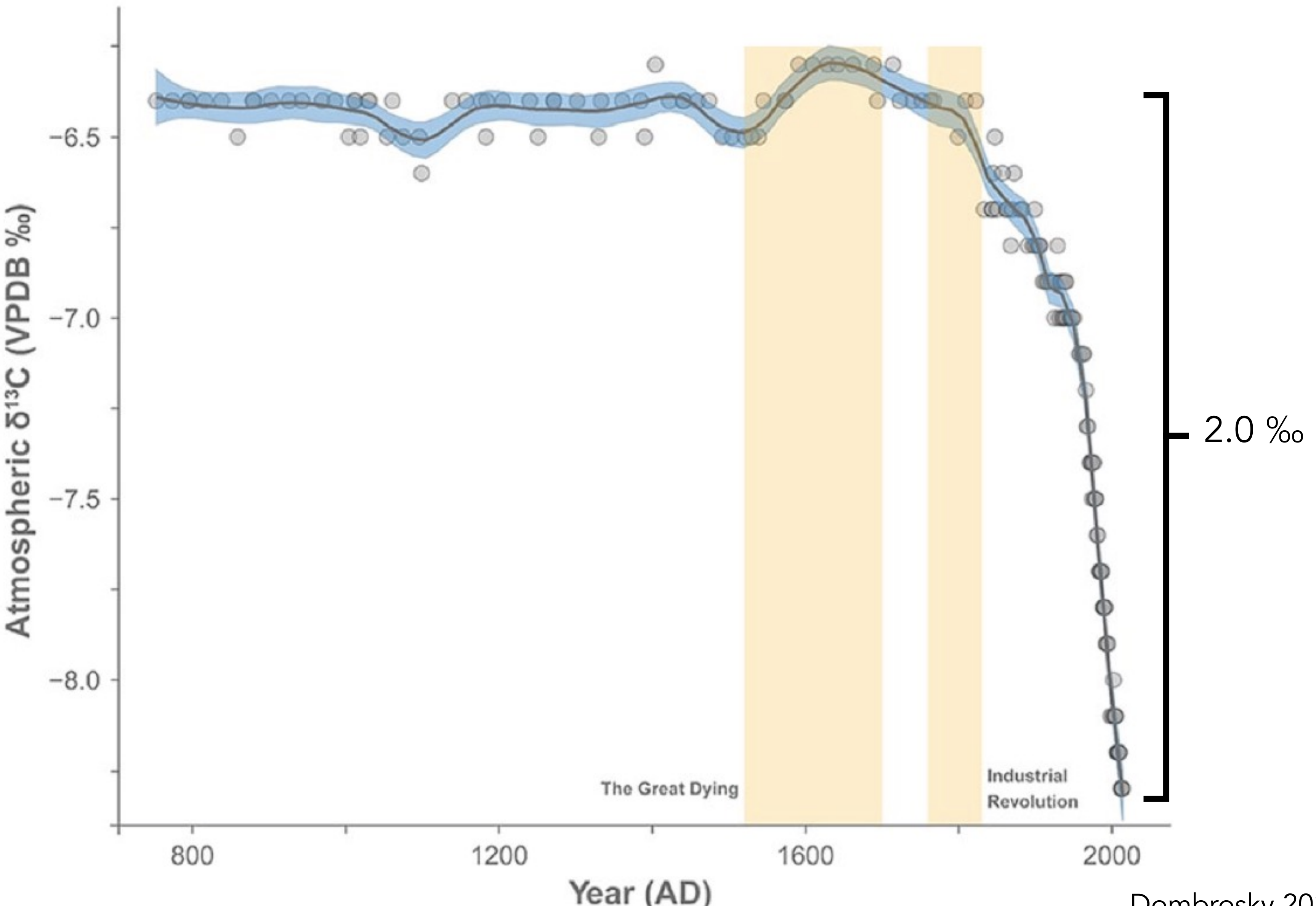
Hydrogen



Nitrogen

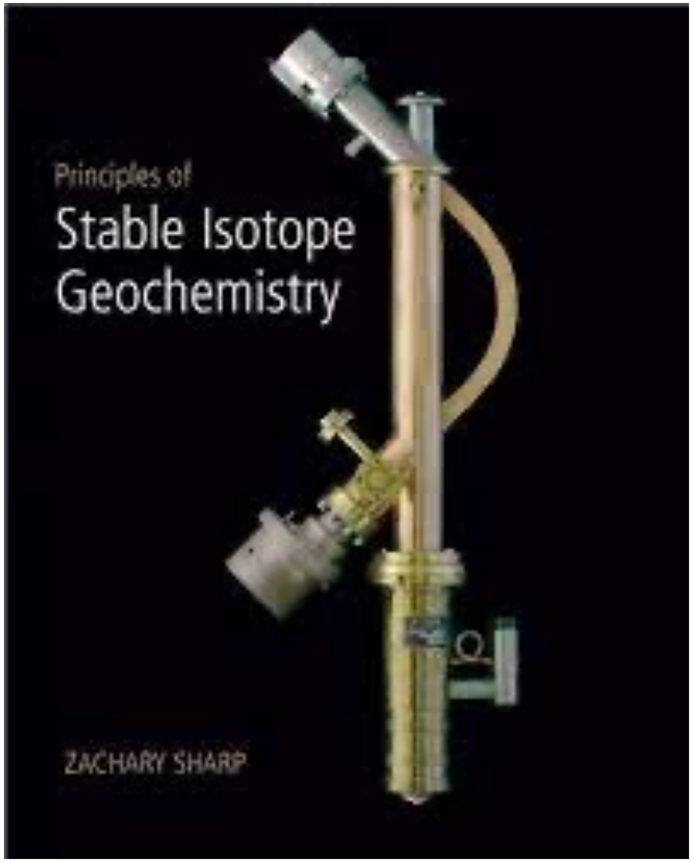


The 'Seuss Effect'



Dombrosky 2020

Isotopic fractionation: the basics

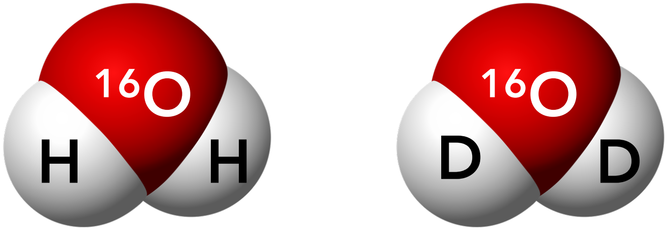


In any **multiphase** system, there may be fractionation of isotopes, with one phase **preferentially incorporating**

the heavy (or light) isotope relative to other coexisting phases.

Isotopic fractionation: the basics

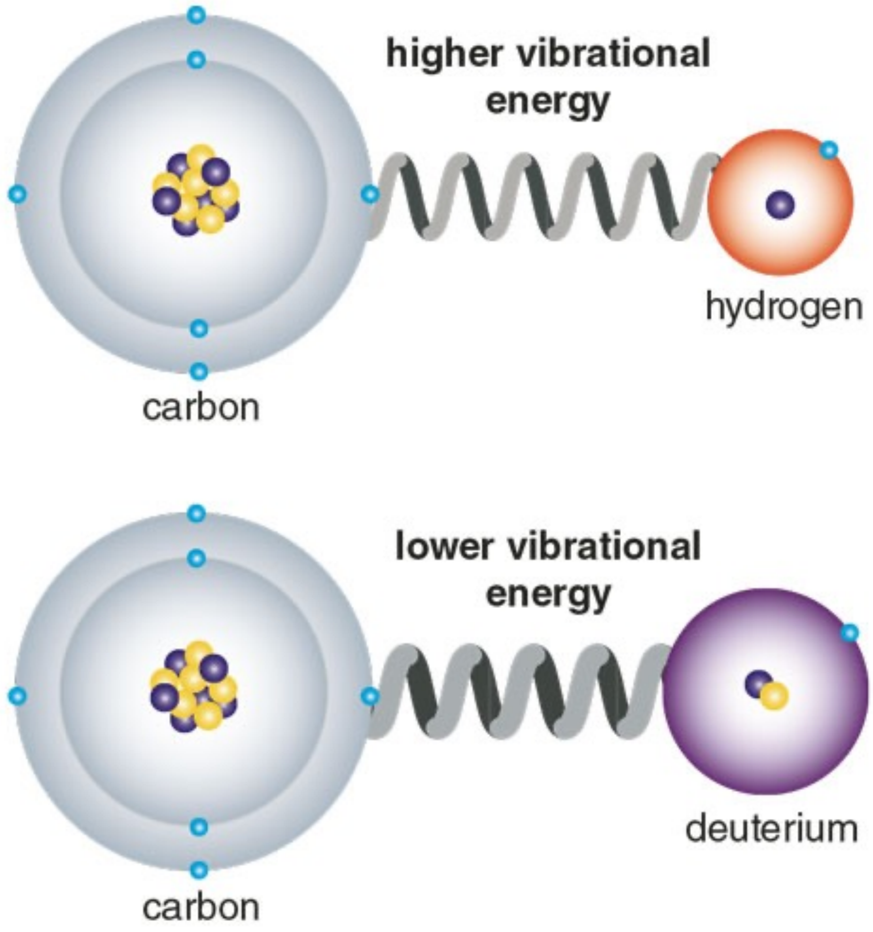
Isotopes have different **thermodynamic properties**.



	Freezing Point (°C)	Boiling Point (°C)
Heavy Water (D_2O)	3.82	101.42
Natural Water (H_2O)	0.00	100.00

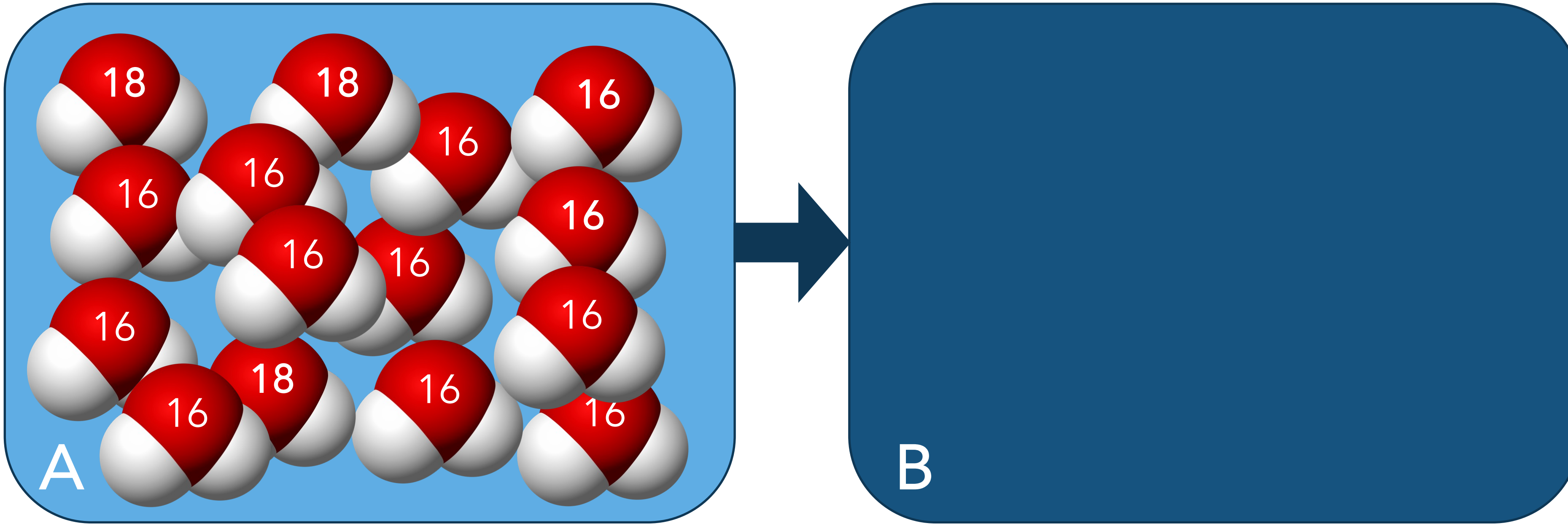
Thus, isotopes react at different rates in chemical reactions.

Isotopic fractionation: the basics



Differences in bond strengths among isotopologues results in fractionation during chemical reactions

A rudimentary example



$$\frac{^{18}O}{^{16}O} = \frac{3}{12} \longrightarrow \frac{^{18}O}{^{16}O} = \frac{2}{8}$$

$$\frac{^{18}O}{^{16}O} = \frac{1}{4}$$

Note the difference in isotopic abundances between the hypothetical ***phase A*** *and* ***phase B*** *pools.*

Large isotopic fractionations observed when…

1. Elements have relatively low atomic mass.
   - E.g., H, C, N, O, S.

2. The relative mass difference between isotopes is large.
   - Relative mass difference between ^{2}H (D) and ^{1}H is 100%
   - Relative mass difference between ^{87}Sr and ^{86}Sr only 1.2%

3. Elements form bonds of a high degree of covalent character (i.e., electrons are shared between atoms).
   - H_2O (covalent) vs. NaCl (ionic)

4. When elements undergo oxidation state change in a wide variety of compounds.
   - (+4) CO_2 vs. CH_4 (-4)

Types of isotopic fractionation

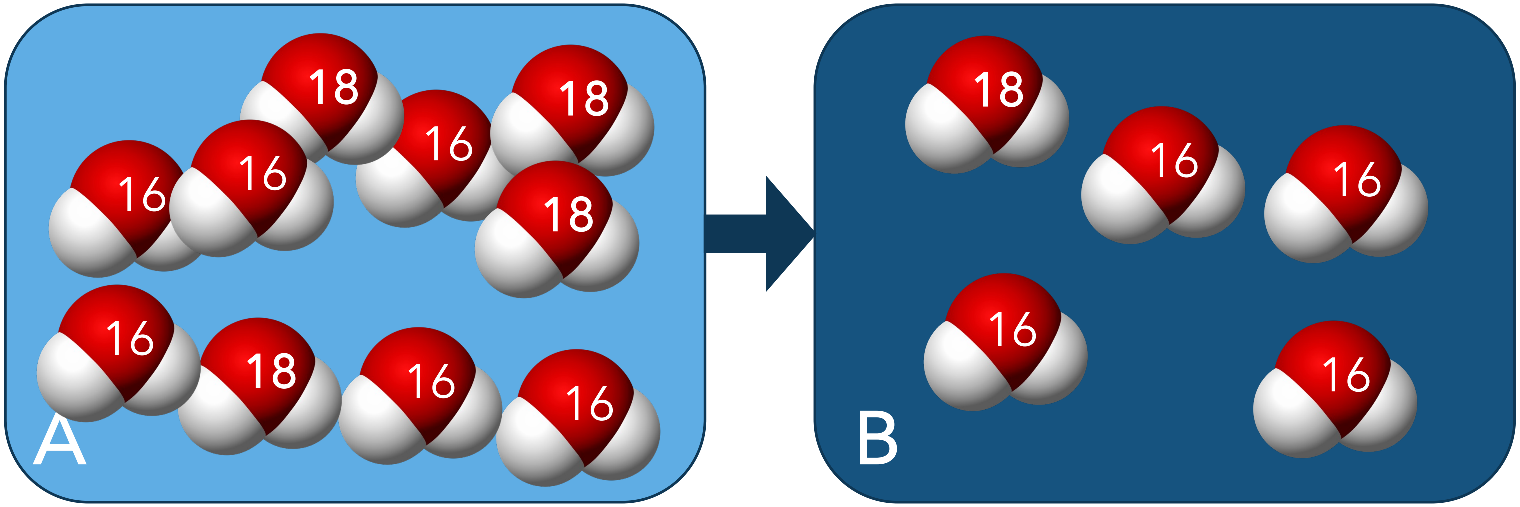
Equilibrium

- Forward and back reactions occur **at the same rate**.
- Products and reactants are offset by a constant fractionation factor (α) **at a given temperature**.
  - H_2O evaporation at 100% RH

Kinetic

- Associated with fast, **unidirectional processes**.
- Controlled by the **reaction rate** (kinetics).
  - Incorporation of CO_2 into plants during photosynthesis.
  - Diffusion of O_2 from lungs into blood.

Expressing the difference



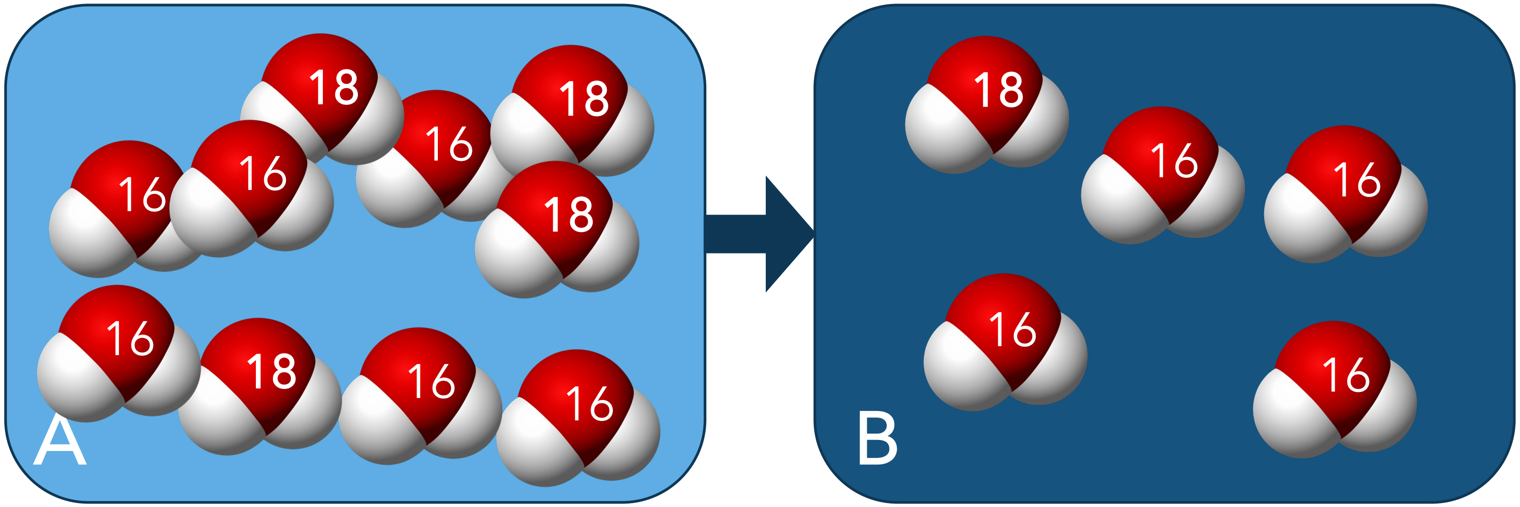
Isotopic Enrichment (ε)

$$\varepsilon_{A-B} = (\frac{R_A}{R_B} - 1)1000$$

Isotopic Discrimination (Δ)

$$\Delta_{A-B} = \delta_A - \delta_B$$

Expressing the difference



Fractionation Factor (α)

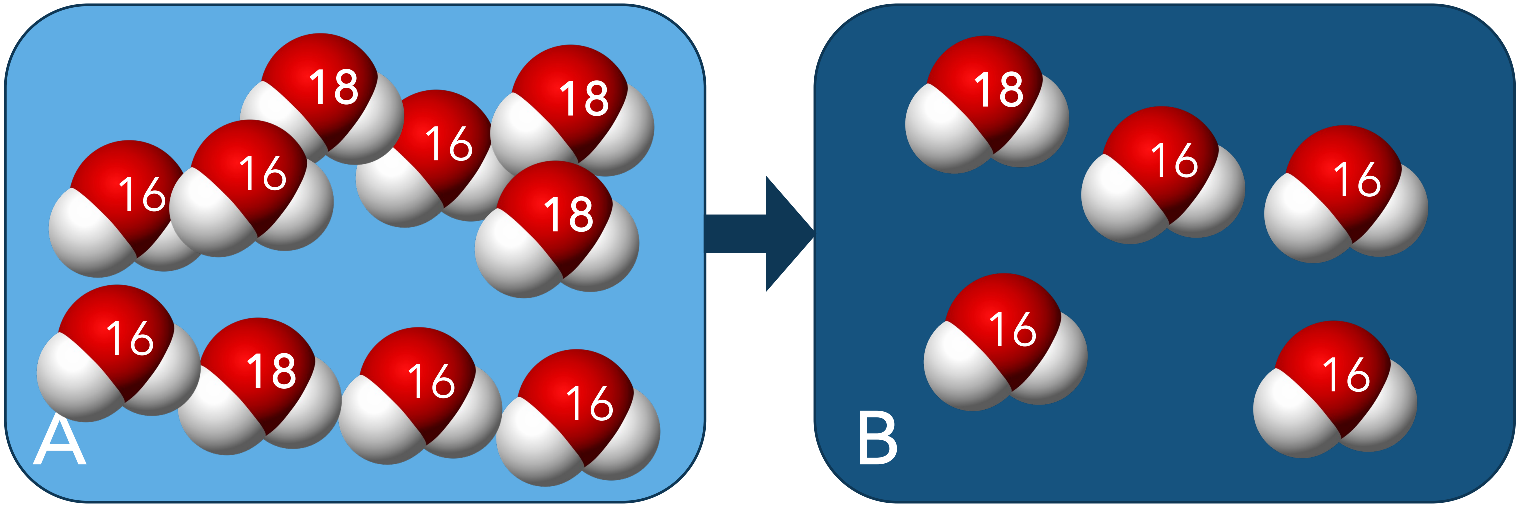
$$\alpha_{A\text{-}B} = \frac{R_A}{R_B}$$

Expressed in terms of R

$$1000\ln(\alpha_{A\text{-}B}) \approx \delta_A - \delta_B$$

Expressed in terms of δ

Expressing the difference



$$H_2O_{liquid} \leftrightarrow H_2O_{vapor}$$

$$\alpha^{18}O_{liquid\text{-}vapor} = 1.0093 \text{ (at } 25^{\circ}\text{C)}$$

$$1000\ln(\alpha) = 9.3 \text{ (at } 25^{\circ}\text{C)}$$

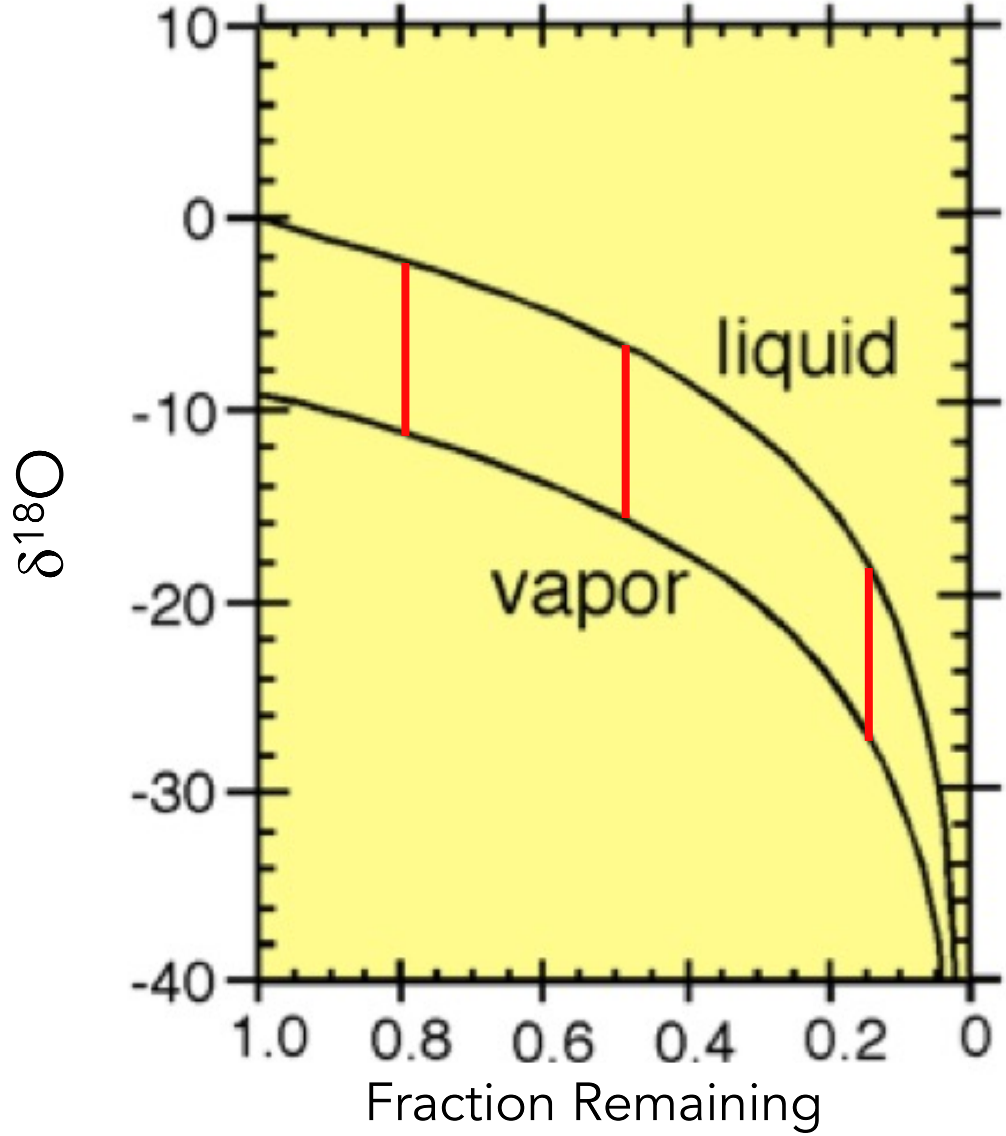
$$\delta_{liquid} - \delta_{vapor} \approx 9.3\ ‰$$

Rayleigh Fractionation

Evaporation

Vapor is formed from the liquid and the amount of original liquid remaining declines, as in an evaporating lake or beaker of water.

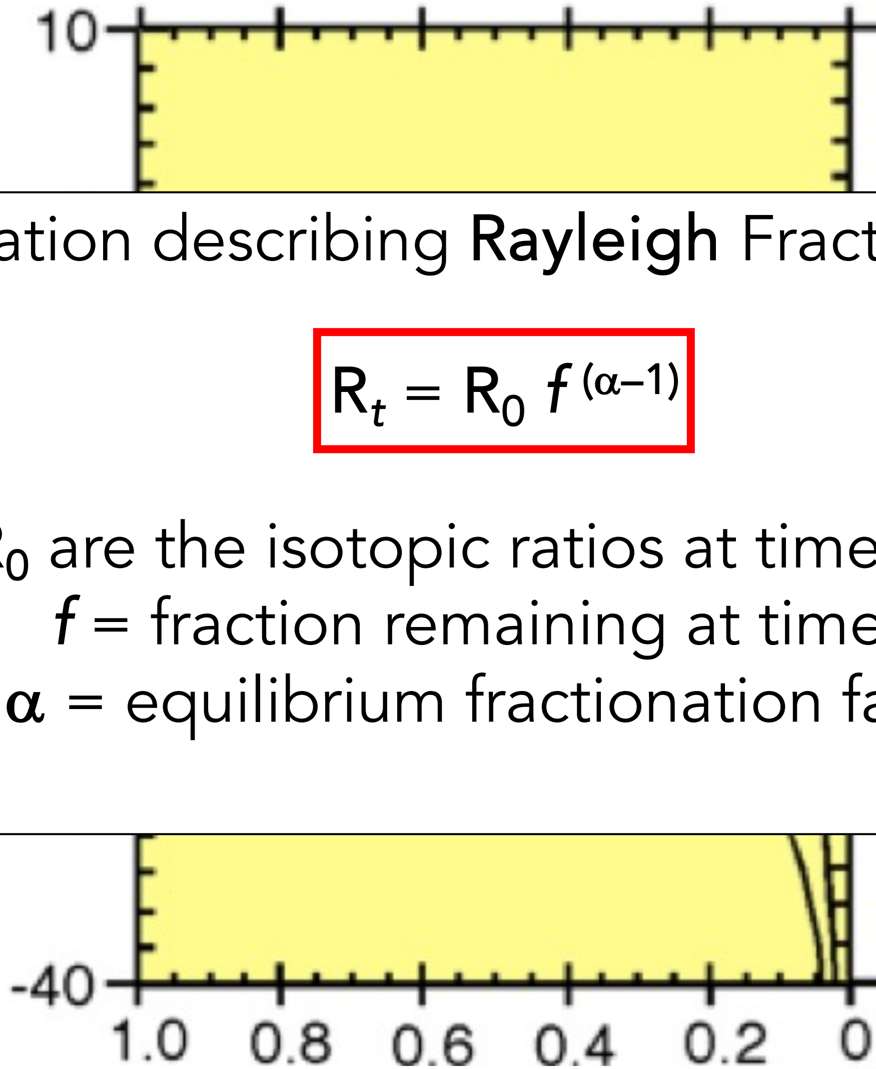
Rayleigh Fractionation



$\alpha = 1.0093$

9.3‰ at 25°C

Rayleigh Fractionation



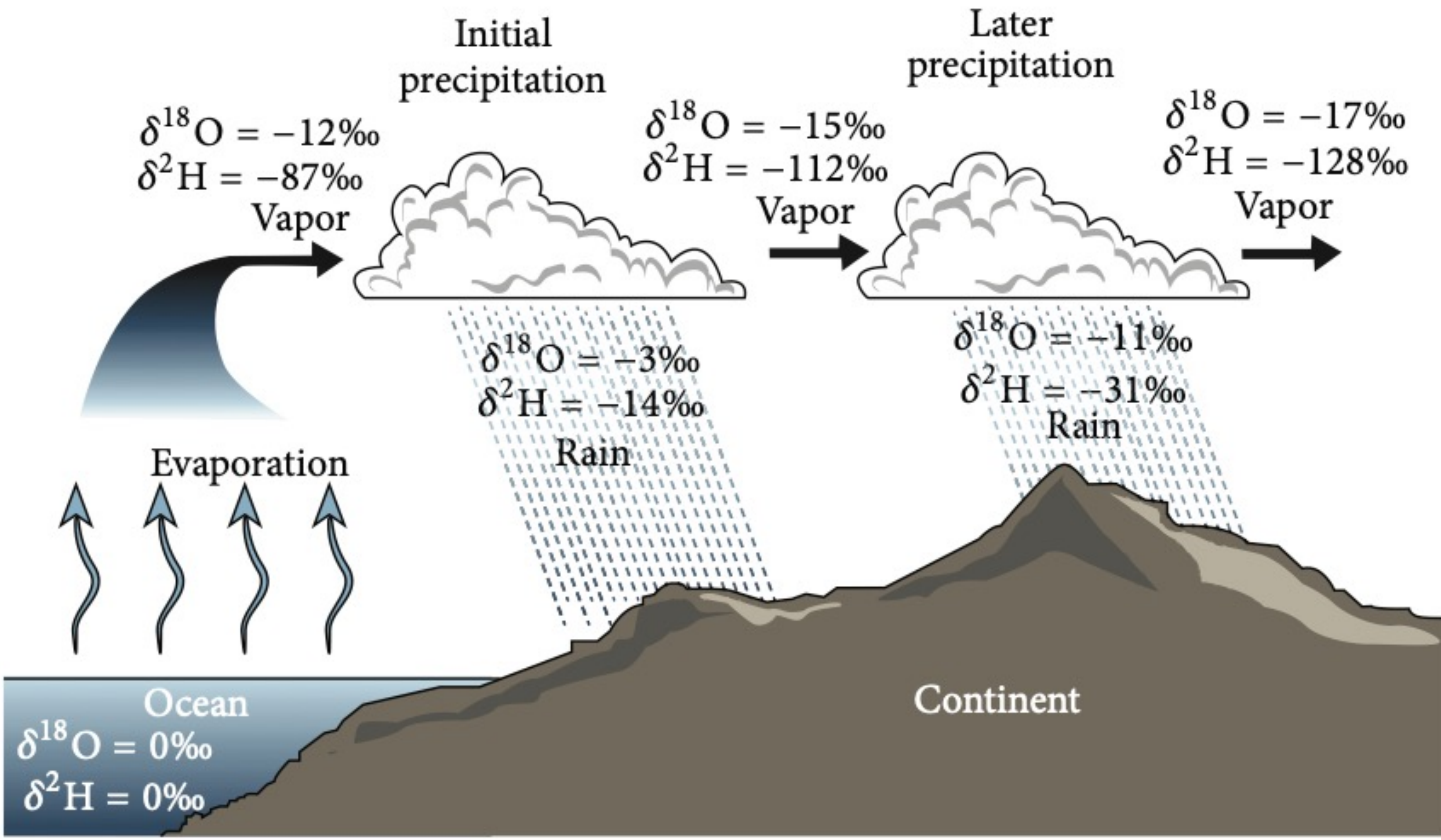
Equation describing **Rayleigh** Fractionation:

$$R_t = R_0 \, f^{(\alpha - 1)}$$

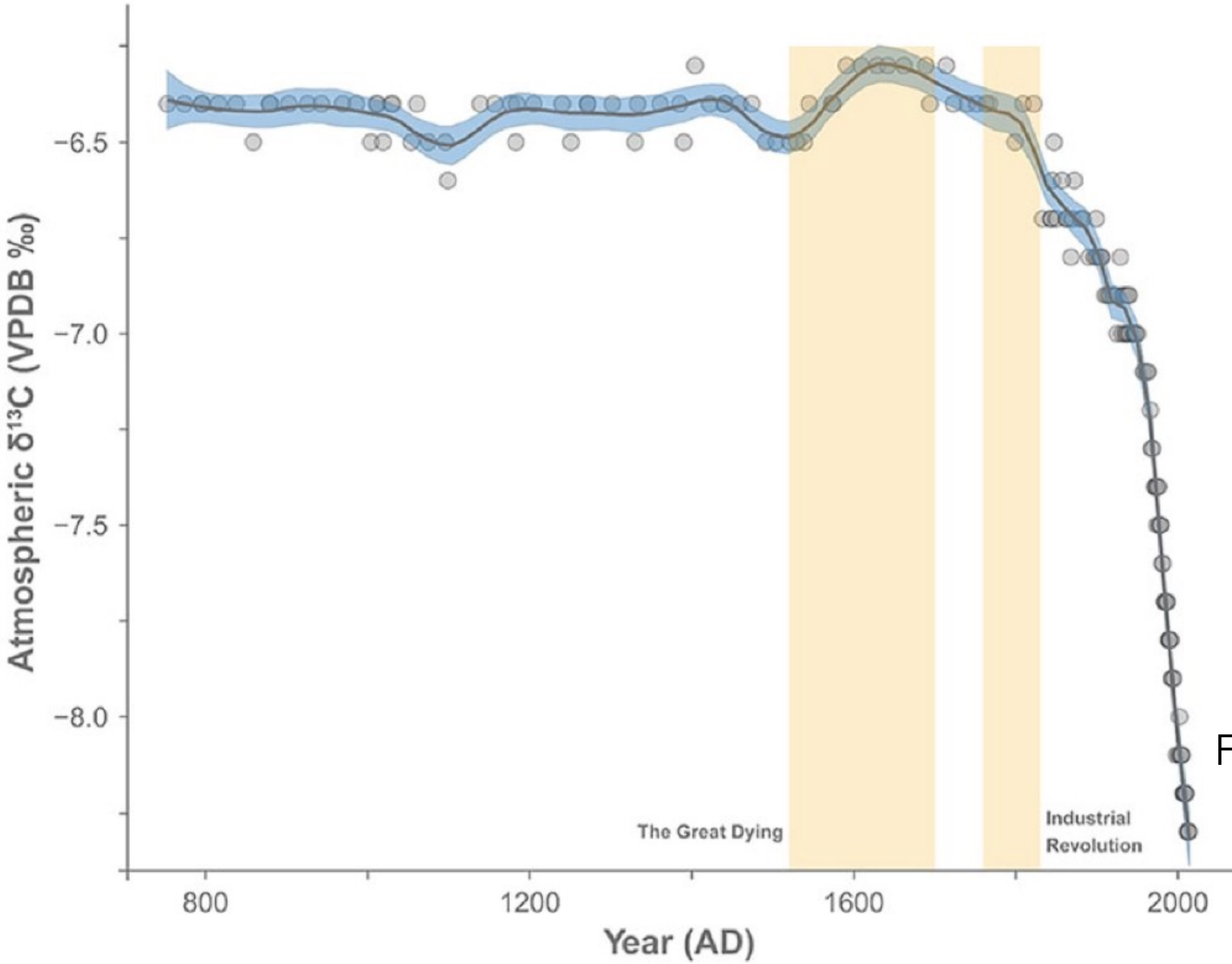
R_t and R_0 are the isotopic ratios at time ***t*** and at ***t*=0**

f = fraction remaining at time (**t**)

α = equilibrium fractionation factor


Initial
precipitation
Later
precipitation
δ18O = −12‰
δ2H = −87‰
Vapor
δ18O = −15‰
δ2H = −112‰
Vapor
δ18O = −17‰
δ2H = −128‰
Vapor
δ18O = −3‰
δ2H = −14‰
Rain
δ18O = −11‰
δ2H = −31‰
Rain
Evaporation
Ocean
δ18O = 0‰
δ2H = 0‰
Continent

Extra slides



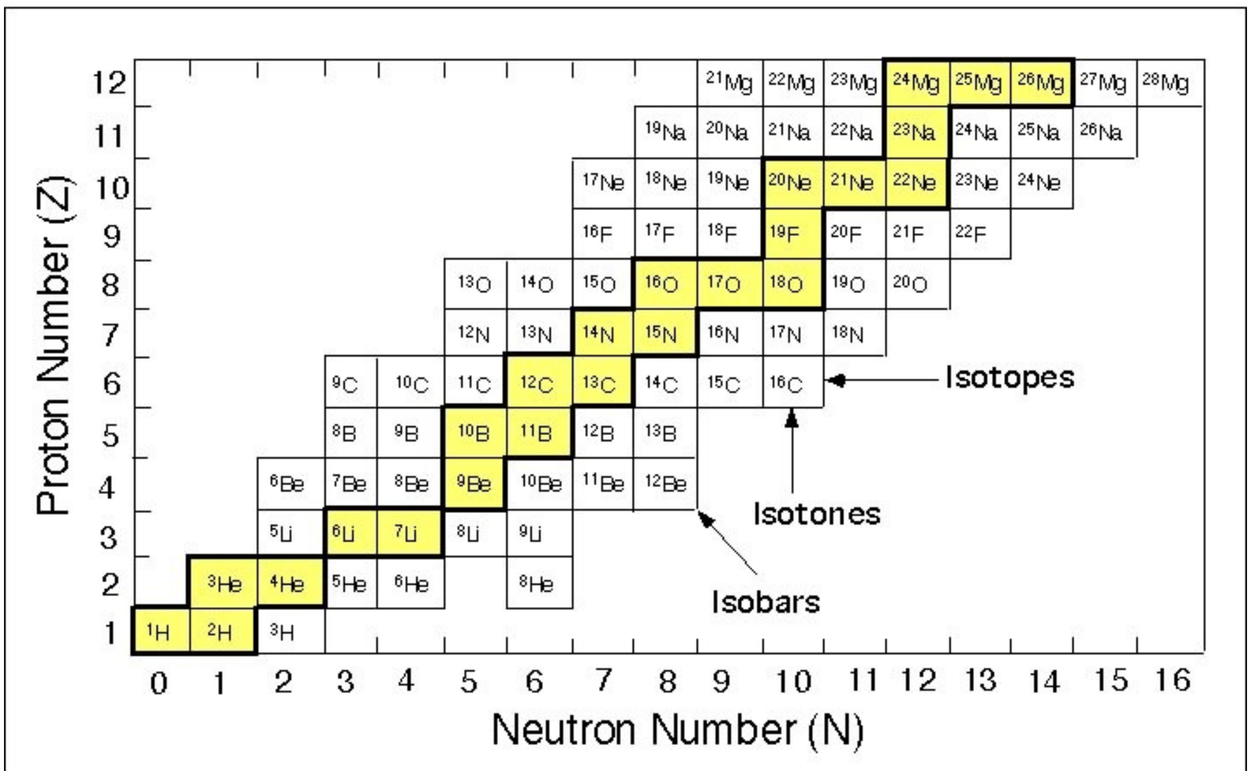
Fossil fuels
-23‰

Dombrosky 2020

Other Iso-Terms

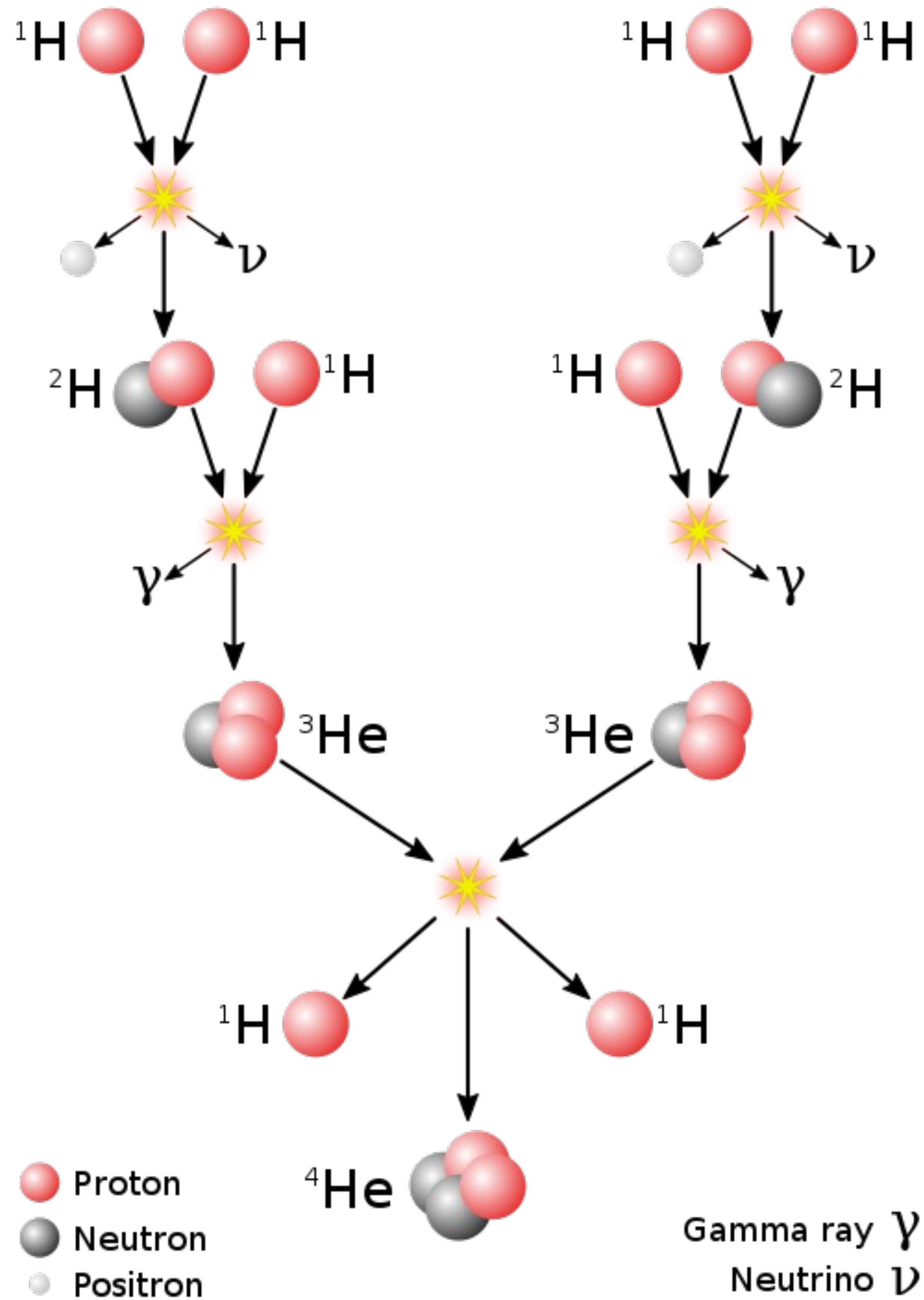
Isotones: nuclides with the same number of neutrons, but different numbers of protons.

Isobars: different elements with the same atomic mass



Proton-Proton Chain (Hydrogen Burning)

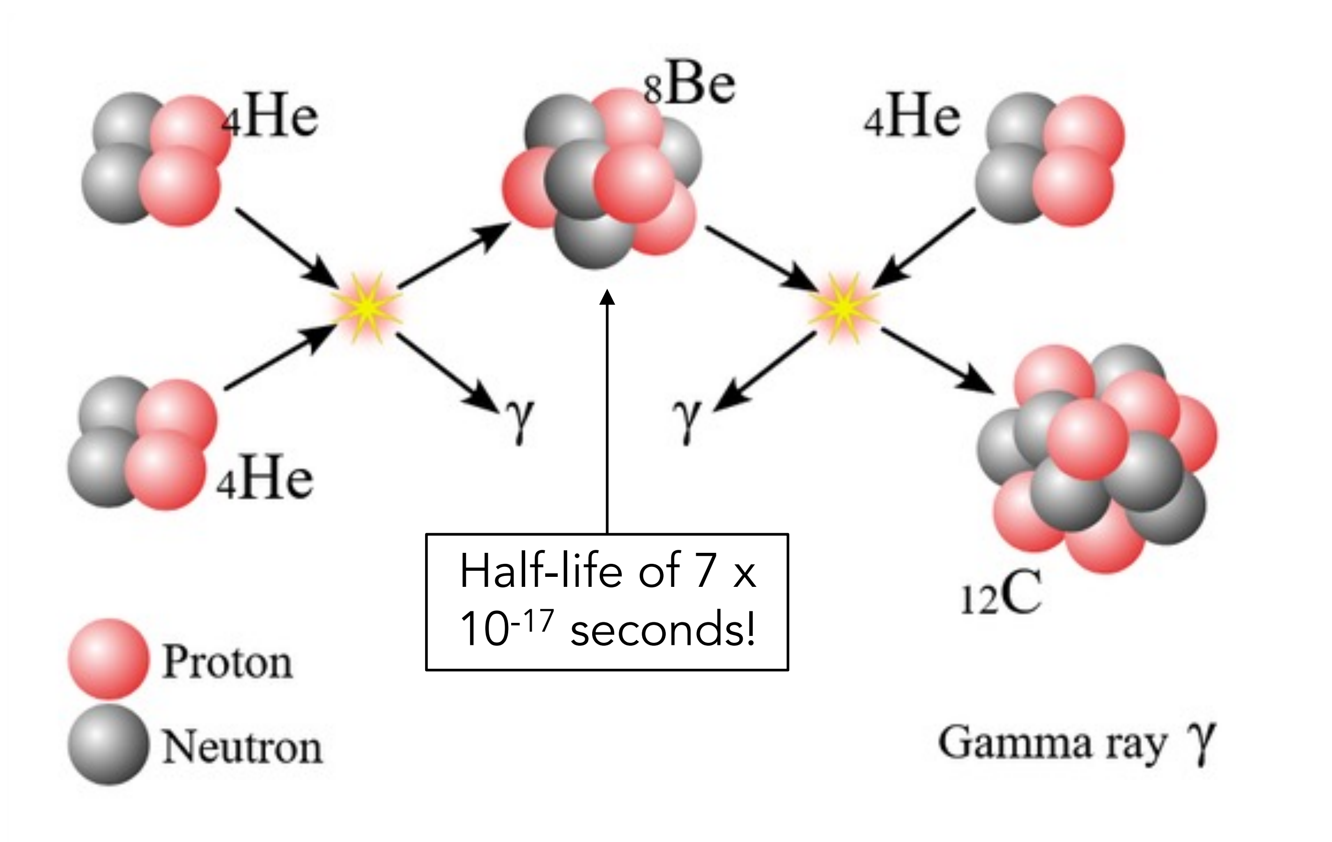
Produces Deuterium (^2H) and Helium



Triple-α Process (Helium Burning)

Produces ^{12}C

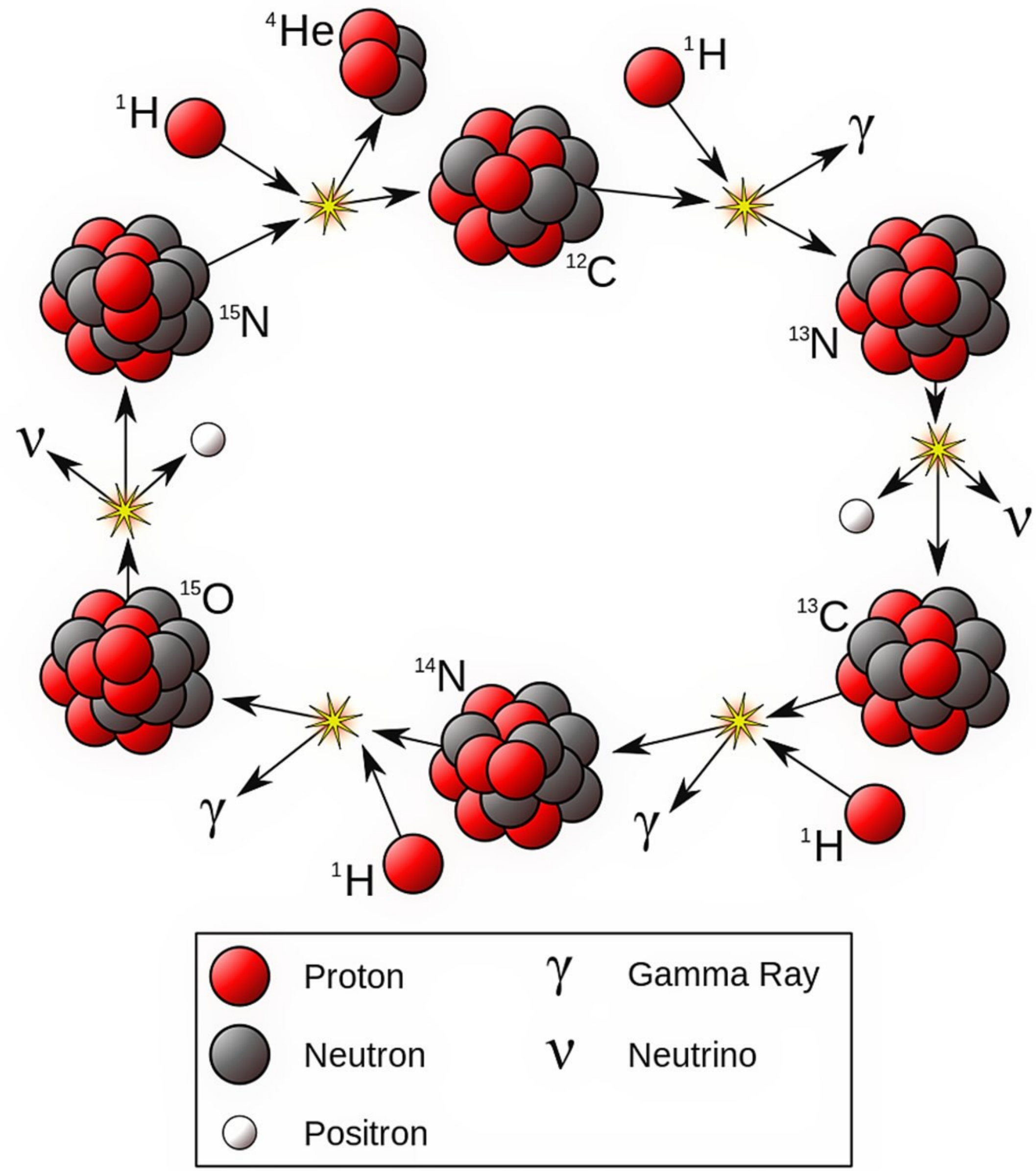
Necessary for the synthesis of elements with a $Z \geq 6$



CNO Cycle

Produces Helium (^4He)

^{12}C is a catalyst



Synthesis of Elements with Z > 6

Occurs by fusion of nuclei with Z of 6, 8, and 10, and by capture of α-particles (i.e., ^{4}He), protons, and neutrons

Helium Burning: produces ^{12}C, ^{16}O, ^{18}O, ^{22}Ne, ^{25}Mg

Carbon Burning: produces ^{20}Ne, ^{23}Na, ^{24}Mg

Oxygen Burning: produces ^{28}Si, ^{31}P, ^{32}S

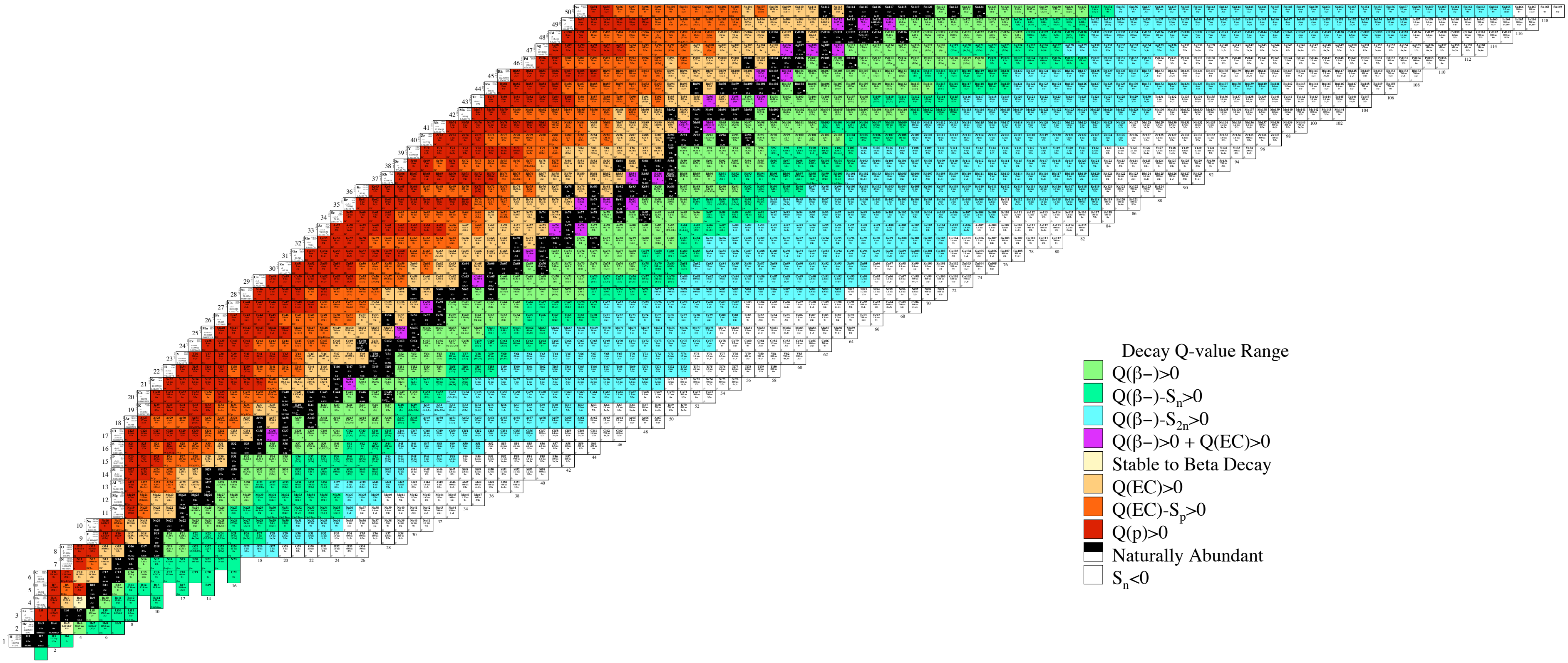
Neon Burning: produces ^{16}O, ^{24}Mg

TABLE 1. Principal burning stages in hydrostatic stellar evolution.

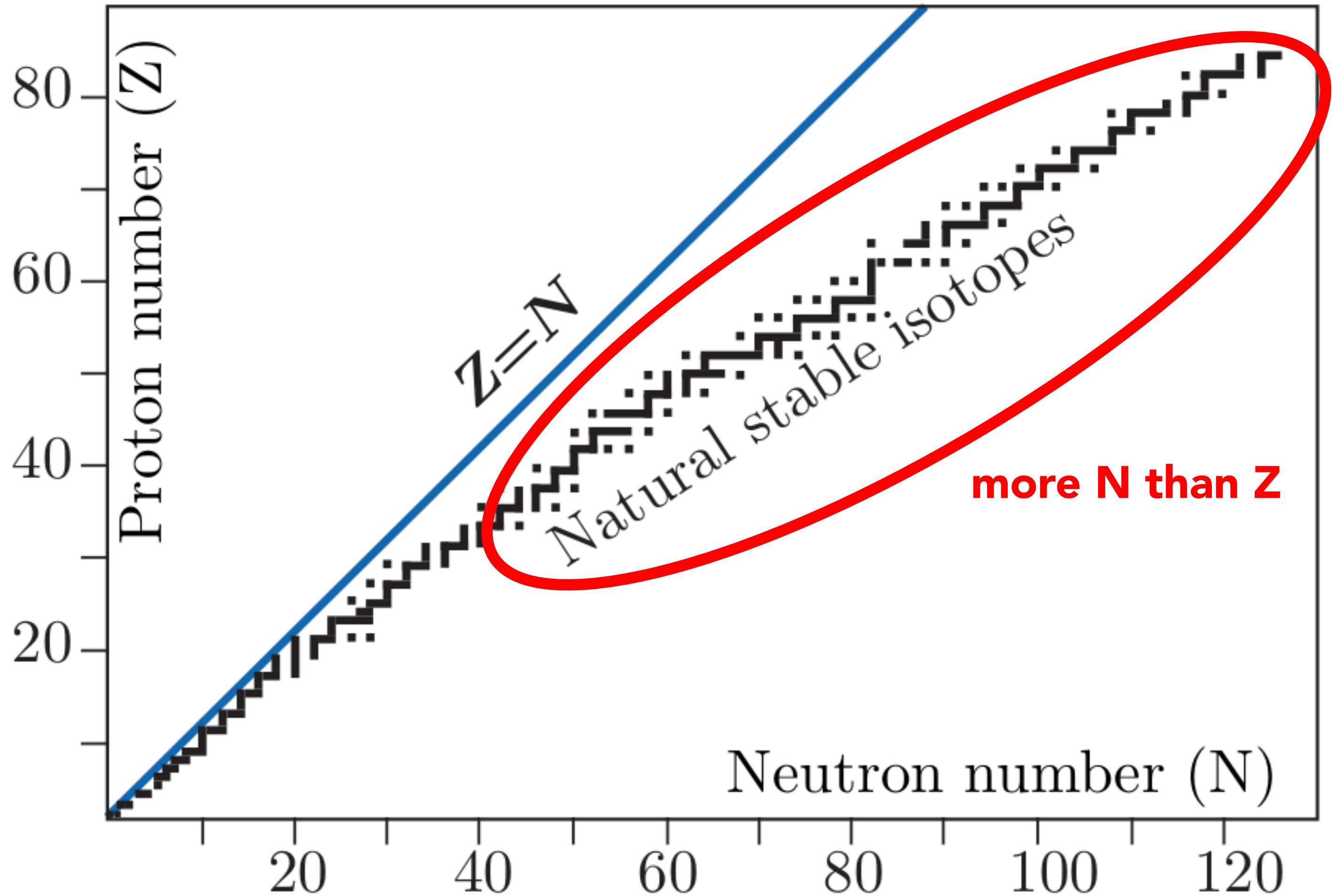
Stage	Key Reactions	Important Products	Notes
Hydrogen	PPI: $^1H + ^1H \rightarrow ^2H + \gamma$ $^2H + ^1H \rightarrow ^3He + \gamma$ $^3He + ^3He \rightarrow ^4He + 2^1H$	^4He	In the solar interior, PP chain percentages are PPI (85%), PPII (15%), PPIII (0.02%). The percentages are expected to be somewhat different in other stars.
	PPII: $^3He + ^4He \rightarrow ^7Be + \gamma$ $^7Be + e^- \rightarrow ^7Li + \nu$ $^7Li + ^1H \rightarrow ^4He + ^4He$	^4He	
	PPIII: $^3He + ^4He \rightarrow ^7Be + \gamma$ $^7Be + ^1H \rightarrow ^8B + \gamma$ $^8B \rightarrow 2^4He + e^+ + \nu$	^4He	
	CN cycle: $^{12}C + ^1H \rightarrow ^{13}N + \gamma$ $^{13}N \rightarrow ^{13}C + e^+ + \nu$ $^{13}C + ^1H \rightarrow ^{14}N + \gamma$ $^{14}N + ^1H \rightarrow ^{15}O + \gamma$ $^{15}O \rightarrow ^{15}N + e^+ + \nu$ $^{15}N + ^1H \rightarrow ^{12}C + ^4He$	^4He, ^{14}N, ^{26}Al	Together, the CN and NO cycles comprise the CNO bicycle. During shell burning of H in the CN and NO cycles temperatures are high enough to produce ^{26}Al via $^{25}Mg + ^1H \rightarrow ^{26}Al + \gamma$
	NO cycle: $^{15}N + ^1H \rightarrow ^{16}O + \gamma$ $^{16}O + ^1H \rightarrow ^{17}F + \gamma$ $^{17}F \rightarrow ^{17}O + e^+ + \nu$ $^{17}O + ^1H \rightarrow ^{15}N + ^4He$	^4He, ^{14}N, ^{17}O, ^{26}Al	The NO cycle operates at higher temperature than the CN cycle and provides a leakage out of the CN cycle.
Helium	$^4He + ^4He + ^4He \rightarrow ^{12}C + \gamma$ $^{12}C + ^4He \rightarrow ^{16}O + ^4He$ $^{14}N + ^4He \rightarrow ^{18}F + \gamma$ $^{18}F \rightarrow ^{18}O + e^+ + \nu$ $^{18}O + ^4He \rightarrow ^{22}Ne + \gamma$ $^{22}Ne + ^4He \rightarrow ^{25}Mg + n$	^{12}C, ^{16}O, ^{18}O, ^{22}Ne ^{25}Mg, s-process isotopes	End burning stage of stars under 8 $M_\odot$.
Carbon	$^{12}C + ^{12}C \rightarrow ^{24}Mg^*$ $^{24}Mg^* \rightarrow ^{20}Ne + ^4He$ $\rightarrow ^{23}Na + ^1H$ $\rightarrow ^{24}Mg + \gamma$	^{20}Ne, ^{23}Na, ^{24}Mg	End burning stage of stars in mass range 8–10 $M_\odot$.
Neon	$^{20}Ne + \gamma \rightarrow ^{16}O + ^4He$ $^{20}Ne + ^4He \rightarrow ^{24}Mg + \gamma$	^{16}O, ^{24}Mg	
Oxygen	$^{16}O + ^{16}O \rightarrow ^{32}S^*$ $^{32}S^* \rightarrow ^{28}Si + ^4He$ $\rightarrow ^{31}P + ^1H$ $\rightarrow ^{32}S + \gamma$	^{28}Si, ^{31}P, ^{32}S	QSE clusters develop
Silicon	$^{28}Si + ^{28}Si \rightarrow ^{54}Fe + 2^1H$ $^{28}Si + ^{28}Si \rightarrow ^{56}Ni$ $^{56}Ni \rightarrow ^{56}Co + e^+ + \nu$ $^{56}Co \rightarrow ^{56}Fe + e^+ + \nu$	Fe-peak isotopes ^{56}Fe, ^{54}Fe	$^{28}Si + ^{28}Si$ are effective reactions. The true character of silicon burning is a QSE shift from ^{28}Si to iron isotopes.

Meyer and Zinner

Table of Isotopes (1996) Z=0-50

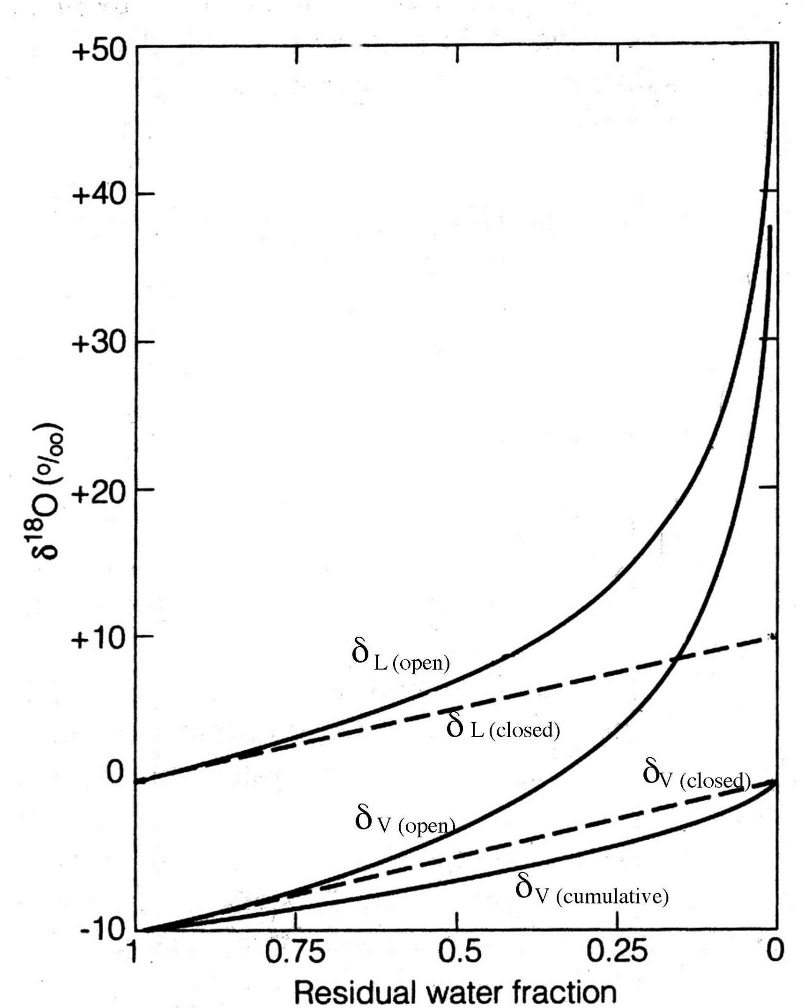


The Valley of Stability: https://www.youtube.com/watch?v=UTOp_2ZVZmM



Larger nuclei have more proton-proton repulsions and require more neutrons to compensate and hold the nucleus together

Rayleigh Fractionation

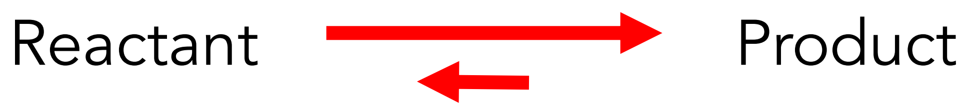


What about open vs. closed system?

Rayleigh fractionation can also describe the process of isotope fractionation as a vapor mass condenses (e.g., rainfall)

Kinetic Reactions

The forward reaction rate is accelerated relative to the backward reaction and the opportunity for backward mixing diminishes.



Most Biological (Enzyme) Reactions

light isotope rate constant

fractionation factor $$\alpha = \frac{k_1}{k_2}$$

heavy isotope rate constant

For ***unidirectional reactions*** (e.g., enzyme reactions), the ratio of reaction rate constants (*k*) determines the fractionation.