Stable Isotope Geochemistry

http://eps.mcgill.ca/~courses/c220/

Structure of the atom

Inner electron shell

Outer electron shell

Nucleus

10^{-8} cm

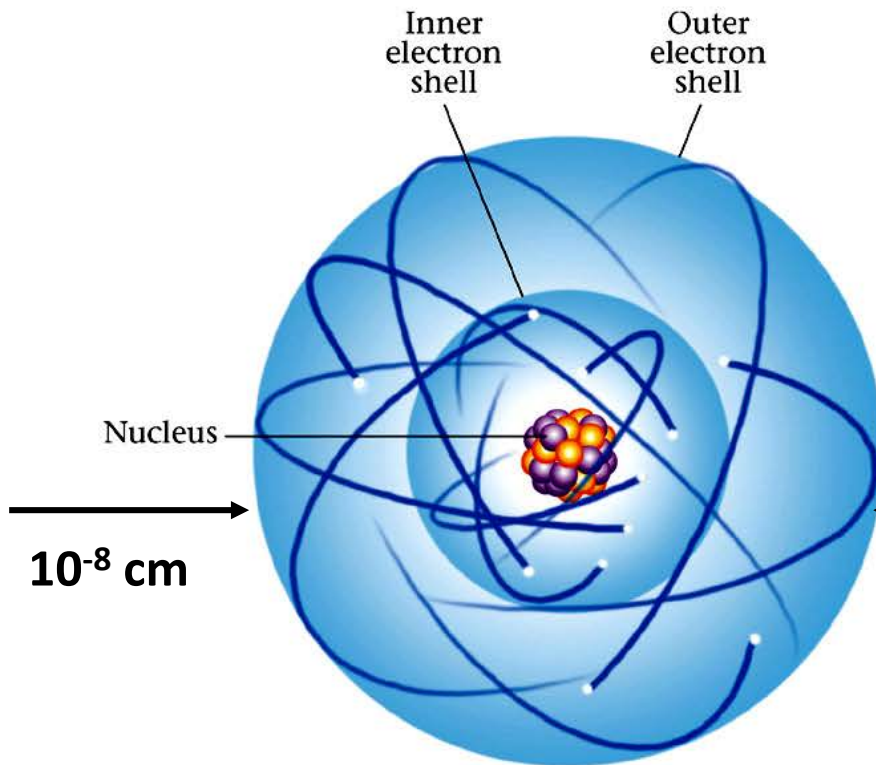Electron — negatively-charged particle
Proton — positively-charged particle
Neutron — neutral particle (no charge)

(b)

(c)

A neutrally-charged atom will have an equal number of electrons and protons, n = p

protons = atomic number (nature of the atom)
protons + # neutrons = atomic mass

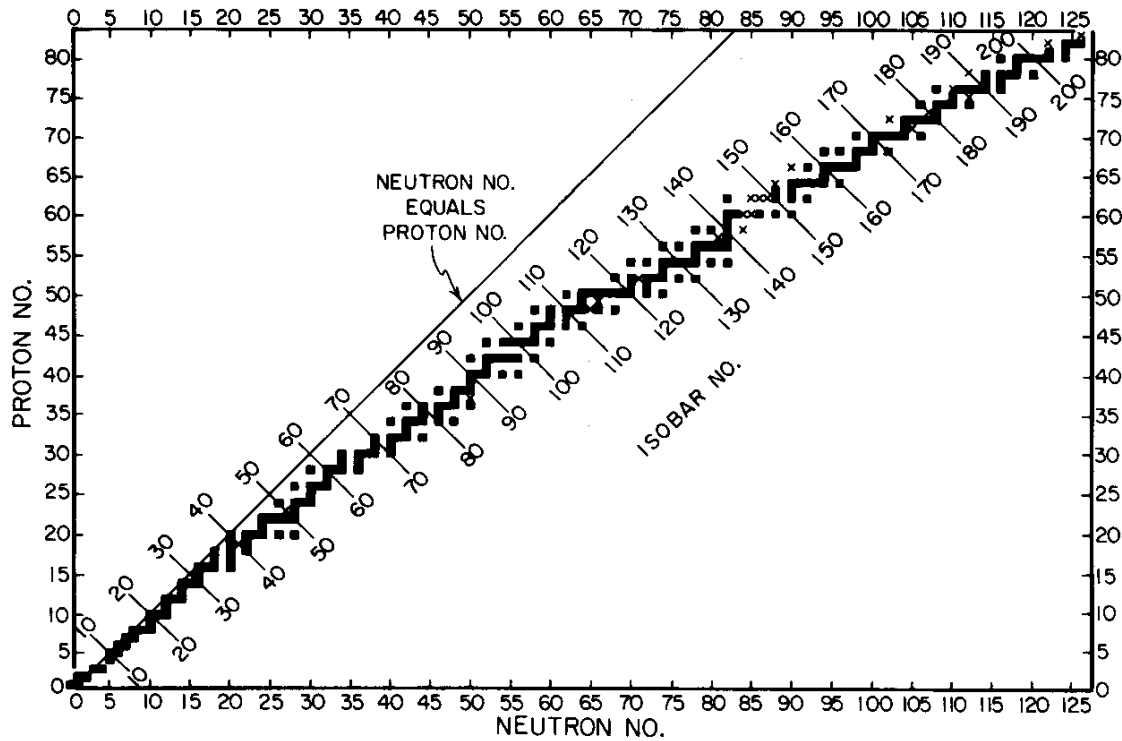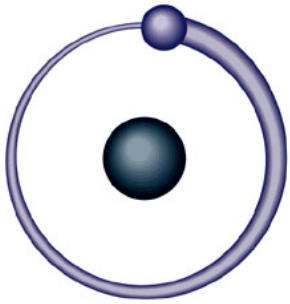(protons and neutrons are ~1800 times heavier than electrons)

Figure 2-2. Stable nuclide configurations: The squares represent stable combinations of neutrons and protons. The x's represent radioactive nuclides whose half-lives are so long that they survive billions of years after their formation in stars. All the remaining combinations are radioactive with half-lives sufficiently short that they are no longer present in the solar system. Nuclides lying along the same horizontal line (i.e., those with the same proton number) are referred to as isotopes. Those falling along the same vertical line (i.e., those with the same number of neutrons) are referred to as isotones. Those falling along the same diagonal line (i.e., those with the same number of nuclear particles) are called isobars. The diagram terminates with the heaviest stable nuclide (^{209}Bi).

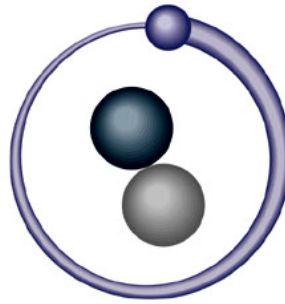**From: W.S. Broecker (1985) How to build a habitable planet**

The three isotopes of hydrogen

1 p	(Atomic	1 p	(Atomic	1 p	(Atomic
0 n	weight = 1)	1 n	weight = 2)	2 n	weight = 3)

Regular hydrogen

Deuterium
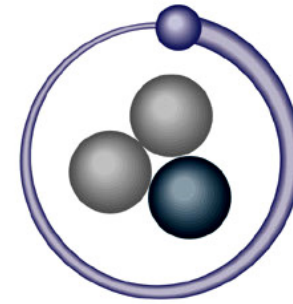
Tritium

(Protium)

Isotopes of the same element have the same number of protons but different numbers of neutrons in their nucleus, hence different mass.

Radio-isotopes have an unstable combination of protons and neutrons in the nucleus and undergo **radioactive decay**

Abundances and mass of stable isotopes of light elements

Element	Stable isotopes	Mass, amu	Average abundance, %	Mass[a] difference, %
Hydrogen	^1_1H	1.007 825	99.985	99.8
	^2_1H (D)[b]	2.0140	0.015	
Carbon	$^{12}_6C$	12.000 000	98.90	8.36
	$^{13}_6C$	13.003 355	1.10	
Nitrogen	$^{14}_7N$	14.003 074	99.63	7.12
	$^{15}_7N$	15.000 108	0.37	
Oxygen	$^{16}_8O$	15.994 915	99.762	12.5
	$^{17}_8O$	16.999 131	0.038	
	$^{18}_8O$	17.999 160	0.200	
Sulfur	$^{32}_{16}S$	31.972 070	95.02	6.24 ($^{34}S - ^{32}S$)
	$^{33}_{16}S$	32.971 456	0.75	
	$^{34}_{16}S$	33.967 866	4.21	
	$^{36}_{16}S$	35.967 080	0.02	

[a] The mass difference is expressed as $(m_H - m_L)/m_L \times 10^2$, where m_H and m_L are the masses of molecules containing the heavy and light isotopes, respectively.
[b] Deuterium symbolized by D.

High Resolution Mass Spectrometry
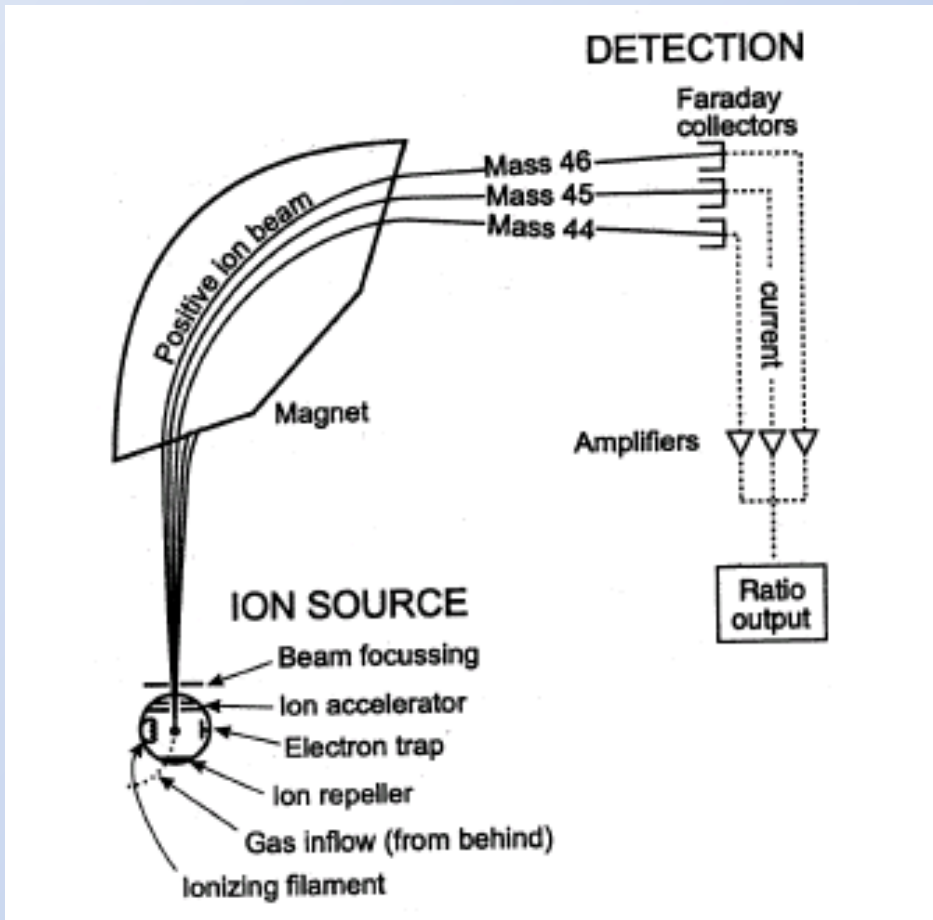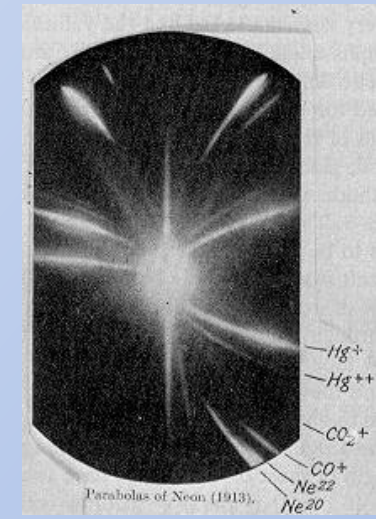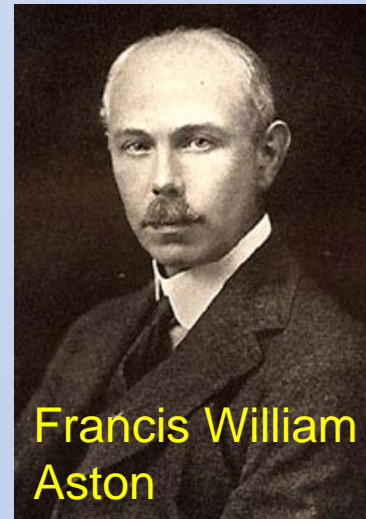
Gas source isotope ratio mass spectrometer

Harold Clayton Urey (1893-1981)

- Discovered Deuterium in 1932
- Nobel Prize in Chemistry, 1934
- Manhattan project during WWII (separation of U-235 and U-238)
- Pioneering work on O-18 & paleoclimatic research.

Stable isotope compositions

Because absolute measurements of individual isotope concentrations are extremely difficult, isotopic abundances are generally expressed as a ratio of the different isotopes of a same element. The isotopic ratio, R, is generally defined in terms of the proportion of a rare isotope with respect to the most abundant:

$$R = I_r/I_a \text{ , } (^2H/^1H, {}^{13}C/{}^{12}C, {}^{15}N/{}^{14}N, {}^{18}O/{}^{16}O, {}^{34}S/{}^{32}S)$$

High resolution mass spectrometers are used to measure the difference between the isotopic ratio of a sample relative to a standard of know isotopic composition and this difference is reported in what is called the delta (δ) notation:

$$\delta_{sample/STD} = ((R_{sample} - R_{STD})/R_{STD}) \times 1000$$
$$= ((R_{sample}/R_{STD}) - 1) \times 1000$$

The delta notation is reported in ‰ or per mil.
It refers to the relative difference, in parts per thousand, of the isotopic ratios of a sample and of a reference standard.

Stable isotope standards

Oxygen

SMOW (Standard Mean Ocean Water) and the PDB (rostrum of a Cretaceous belemnite from the Peedee Formation in South Carolina) are most commonly used. SMOW has recently run out and has been replaced by V-SMOW (Vienna-SMOW).

$$SMOW \ ^{18}O/^{16}O = 1993.4(\pm 2.5) \times 10^{-6}$$
$$V\text{-}SMOW \ ^{18}O/^{16}O = 2005.2(\pm 0.45) \times 10^{-6}$$
$$\delta^{18}O_{SMOW} = 1.03086 \ \delta^{18}O_{PDB} + 30.86$$

The Vienna agency also distributes a lighter standard called SLAP (Standard Light Arctic Precipitation) for which

$$\delta^{18}O_{SLAP/V\text{-}SMOW} = -55.5 \ ‰$$

Hydrogen

As in the case of oxygen, V-SMOW is the most common standard for hydrogen.
$$V\text{-}SMOW \ ^{2}H/^{1}H = 157.6 \ (\pm 0.3) \times 10^{-6}$$

for water samples that are poor in heavy isotope, SLAP is occasionally used
$$SLAP \ \ ^{2}H/^{1}H = 89.02 \ (\pm 0.05) \times 10^{-6}$$
or
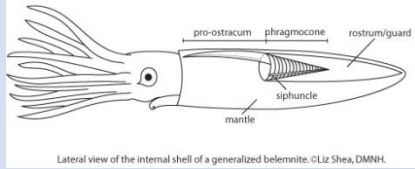$$\delta^{2}H_{SLAP/V\text{-}SMOW} = -435.2 \ ‰$$

Stable isotope standards

Carbon

With the exception of a few NIST standards of limited use (NBS-20 & 21), the PDB (Pee Dee Belemnite) standard is the one used in all cases.

Lateral view of the internal shell of a generalized belemnite. ©Liz Shea, DMNH.

PDB $^{13}C/^{12}C = 1237.2 \, (\pm \, 0.5) \times 10^{-6}$

Nitrogen

The reference standard for nitrogen is the atmospheric nitrogen reservoir which, with respect to its size and its mixing rate, is considered to be homogeneous.

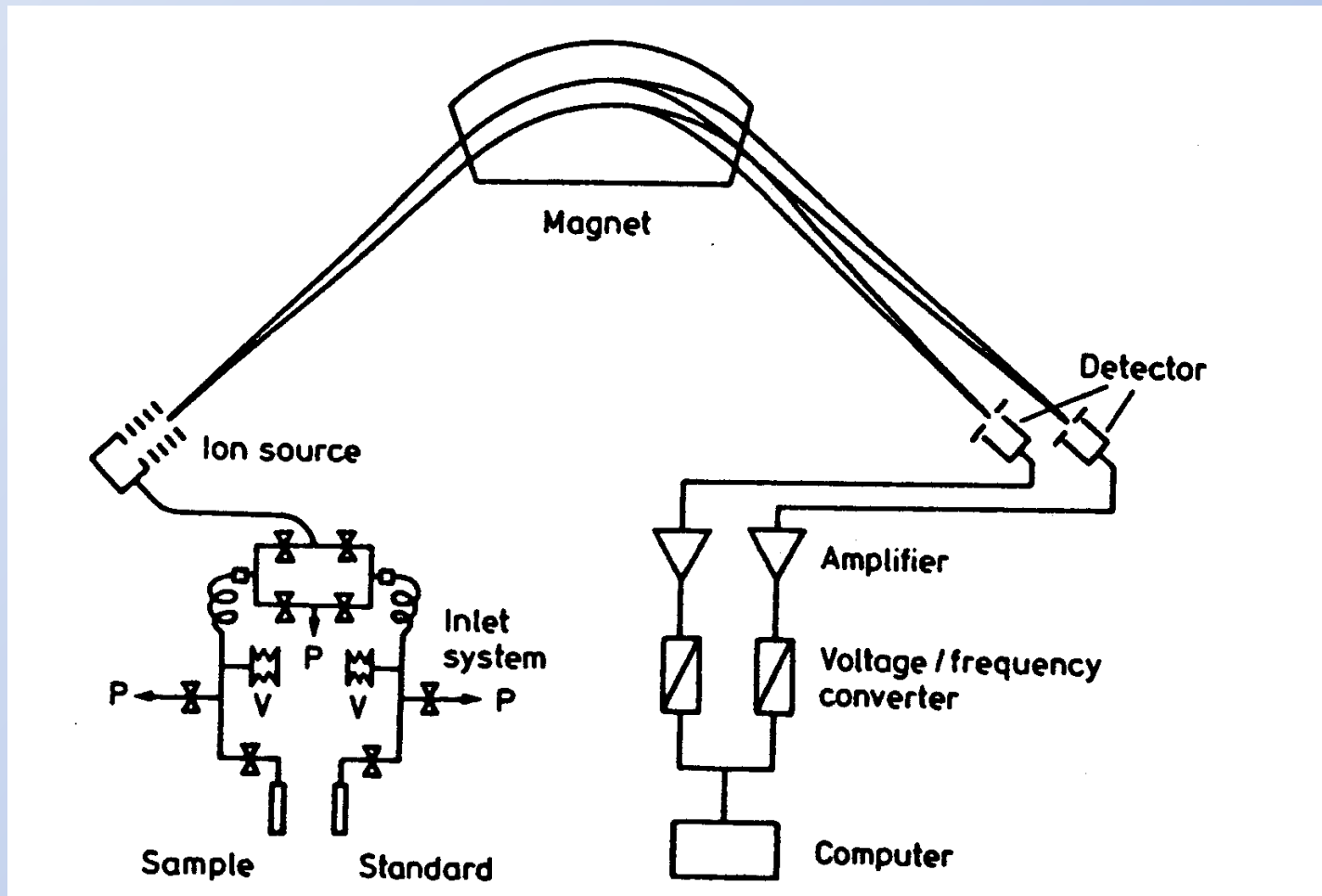Air $^{15}N/^{14}N = 3676.5 \, (\pm \, 0.1) \times 10^{-6}$

Sulfur

The reference standard most often used for sulfur is a troilite (iron monosufide, FeS) of the iron meteorite Canyon Diablo recovered from the Meteor Crater in Arizona. [The isotopic composition of S is determined by analyzing SO_2 gas prepared from the samples.]

$^{34}S/^{32}S = 0.045004 \pm 0.00005$

Double-inlet gas mass spectrometer

Isotopic fractionation and fractionation factors

The term "isotopic fractionation" refers to the partial separation/ discrimination of isotopes which can occur during physical or chemical processes.
**This separation/discrimination results from small differences in the physico-chemical properties of the isotopes of the same element.**

The two main phenomena that lead to isotopic fractionation are:

1) isotopic exchange reactions, an equilibrium fractionation processes resulting from differences in the thermodynamic properties of isotopically-substituted species/compounds.

2) kinetic processes, resulting from differences in the rates of chemical reactions or physical processes (e.g., evaporation) of molecules made up of different isotopes of the same element.
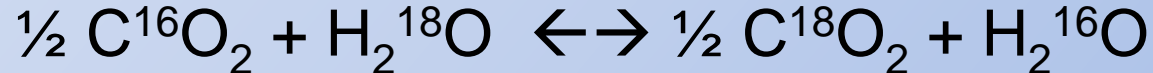
Isotopic fractionation and fractionation factors

Let's consider the following exchange reaction:

$$aA_1 + bB_2 \longleftrightarrow aA_2 + bB_1$$
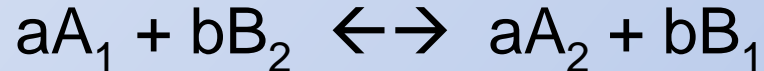
where the subscript indicate that species A and B contain either the light (1) or the heavy (2) isotope.

More familiar, would be a reaction such as:

$$\tfrac{1}{2}\ C^{16}O_2 + H_2^{18}O \longleftrightarrow \tfrac{1}{2}\ C^{18}O_2 + H_2^{16}O$$

At equilibrium, the mass action law applies and thus:

$$K = (C^{18}O_2)^{\frac{1}{2}}\ (H_2^{16}O) / (C^{16}O_2)^{\frac{1}{2}}\ (H_2^{18}O)$$
$$= (C^{18}O_2/C^{16}O_2)^{\frac{1}{2}}/(H_2^{18}O/H_2^{16}O)$$

$$K = (A_2^a\ B_1^b)/(A_1^a\ B_2^b) = (A_2/A_1)^a/(B_2/B_1)^b$$

Equilibrium fractionation

The different vibrational energy levels in identical molecules composed of two isotopes of the same element are responsible for isotopic fractionation.

The lowest vibrational energy level of a molecule is equal to:

$$E_0 = \tfrac{1}{2}\, h\, \upsilon_0 = \tfrac{1}{2}\, h\, /(2\pi\, (k/\mu)^{\frac{1}{2}})$$

where k is the binding constant (spring constant in the mechanical analog) and μ is the reduced mass.

μ = reduced mass = $m_1\, m_2/(m_1 + m_2) = m_1/(1 + (m_1/m_2))$
where m_1 and m_2 are the mass of the atoms involved in the bond.

For two molecules, one containing the heavy (H) isotope and the other the light (L) isotope of the same element.

**μ(H) > μ(L) and , υ_0(H) < υ_0(L) and E_0(H) < E_0(L)
meaning that the binding energy of the molecule containing the heavy isotope is stronger than that of the light isotope.**
Consequently, heavy isotopes will favor situations leading to stronger binding sites whether it is a chemical reaction or a change in phase (i.e., solid>liquid>gas).
The greater the difference in reduced mass between the molecules, the greater the difference in binding energy and the larger the discrimination.
Ex: Si-^{1}H and Si-^{2}H, μ(H)/μ(L) = 1.933
        Si-^{16}O and Si-^{18}O, μ(H)/μ(L) = 1.076
        Si-^{235}U and Si-^{234}U, μ(H)/μ(L) = 1.00045

Isotopic fractionation and fractionation factors

Geologists rarely discuss isotopic fractionation in terms of equilibrium constants but characterize it by a **fractionation factor, α,** where:

$\alpha = \Sigma\, \alpha_i$ or the sum of all elementary fractionations resulting from physical and chemical factors.

ex: $CO_2(g) \xrightarrow{\alpha_1} CO_2(sol'n) \xrightarrow{\alpha_2} HCO_3^- \xrightarrow{\alpha_3} CO_3^{2-} \xrightarrow{\alpha_4} CaCO_3$
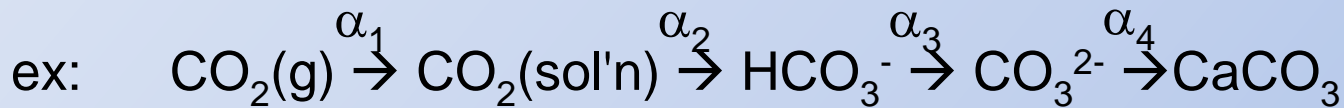
Under equilibrium conditions, the fractionation factor between two components or phases A and B is given by the ratio of the relative abundance of the two isotopes in component A divided by the corresponding ratio in component B:

$\alpha_{A-B} = R_A/R_B = (I_r/I_a)_A/(I_r/I_a)_B$ and if $I_r << I_a$, $\alpha_{A-B} = Ir_A/Ir_B$

where α_{A-B} is a constant for a given temperature and pressure.

For example, the fractionation factor for the following global reaction:

$$^{13}CO_2(g) + Ca^{12}CO_3 \longleftrightarrow {}^{12}CO_2(g) + Ca^{13}CO_3$$
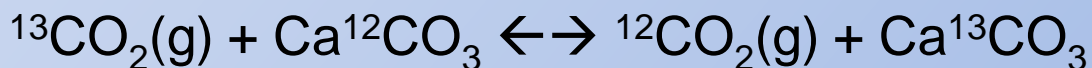
is given by $\alpha(CaCO_3-CO_2) = (^{13}C/^{12}C)_{CaCO3}/(^{13}C/^{12}C)_{CO2} = 1.010$ at 25^oC

Fractionation factors

Since α is usually close to a value of 1, isotope fractionations are often given in terms of ε (epsilon) values:

$$\varepsilon = (\alpha-1)10^3$$

If α varies from unity only in the third decimal (i.e., $\alpha = 1.00x$), the following approximation is also often used:

$$\varepsilon \approx 10^3 \ln \alpha \text{ since } 10^3 \ln 1.00x \approx x$$

Since the isotopic composition of two components X and Y are measured in the laboratory are reported in δ-values:

$$\delta_X = ((R_X/R_{STD})-1)10^3 \text{ and } \delta_Y = ((R_Y/R_{STD})-1)10^3$$
$$R_X = ((\delta_X/10^3)+1)R_{STD} \text{ and } R_Y = ((\delta_Y/10^3)+1)R_{STD}$$
$$\alpha_{X-Y} = R_X/R_Y = (10^3 + \delta_X)/(10^3 + \delta_Y)$$
$$\varepsilon = (((10^3 + \delta_X)/(10^3 + \delta_Y))-1)10^3$$
$$\varepsilon = ((\delta_X - \delta_Y)/(\delta_Y + 10^3))10^3$$
$$\varepsilon \approx \delta_X - \delta_Y \text{ if } \delta_Y << 10^3,$$

since δ_Y rarely exceeds 100:

$$\varepsilon_{X-Y} \approx \delta_X - \delta_Y \approx (\alpha_{X-Y} - 1)10^3 \approx 10^3 \ln \alpha_{X-Y}$$
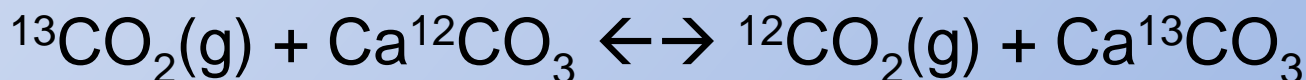
Fractionation factors

Table 3. Comparison between Δ, a, and $10^3 \ln a$

δ_A	δ_B	Δ_{A-B}	a_{A-B}	$10^3 \ln a_{A-B}$
1.00	0	1	1.001	0.9995
10.00	0	10	1.01	9.95
20.00	0	20	1.02	19.80
10.00	5.00	4.98	1.00498	4.96
20.00	15.00	4.93	1.00493	4.91
30.00	20.00	9.80	1.00980	9.76
30.00	10.00	19.80	1.01980	19.61

Thermodependence of the fractionation factors

$$10^3 \ln \alpha = a + b/T + c/T^2$$

$$^{13}CO_2(g) + Ca^{12}CO_3 \longleftrightarrow ^{12}CO_2(g) + Ca^{13}CO_3$$

$$10^3 \ln \alpha_{(CaCO_3-CO_2)} = 1.194 \times 10^6/T^2 - 3.63$$

Isotopic fractionation and fractionation factors

The second phenomenon producing fractionations is related to the kinetics of the processes, or the rate at which chemical or physical processes take place.

The rate at which a molecule can react is proportional to the probability that this molecule will encounter or collide with another molecule and that this collision will be energetic enough to result in a reaction. Simplistically, probability that two molecules will collide is a direct function of their motion (translation) in the system.

The translation energy of a molecule is in a simplistic way related to its kinetic energy. The kinetic energy of a molecule is proportional to the temperature and is identical for all molecules in an ideal system:

$$\tfrac{1}{2}\, mv^2 = f(T)$$

Isotopic fractionation and fractionation factors

If we have two molecules or atoms A and B at the same temperature, they must have the same kinetic energy, and we can write:

$$\tfrac{1}{2}\, m_A v_A^2 = \tfrac{1}{2}\, m_B v_B^2$$

from which we can derive the following relationship:

$$(v_A/v_B)^2 = m_B/m_A$$

the squared ratio of the rate of translation (diffusion or reaction) is inversely proportional to the ratio of masses. In other words, a light molecule will have a faster rate of translation than a heavier particle and hence will diffuse and probably react faster than heavier molecules leading to the depletion of the heavy isotope in the end-product of the reaction.

For example, the velocity of $^{12}C^{16}O$ is 1.0177 times greater than that of $^{13}C^{16}O$ regardless of the temperature.

$$v_L/v_H = (28.99827/27.994915)^{1/2} = 1.0177$$

For this reason, during the evaporation of water, $H_2{}^{16}O$ molecules escape into the vapour more rapidly than $H_2{}^{18}O$ and thus enrich the vapour in ^{16}O leaving the remaining water enriched in ^{18}O. This process enhances the isotopic fractionation that takes place when liquid water and water vapour are in equilibrium.
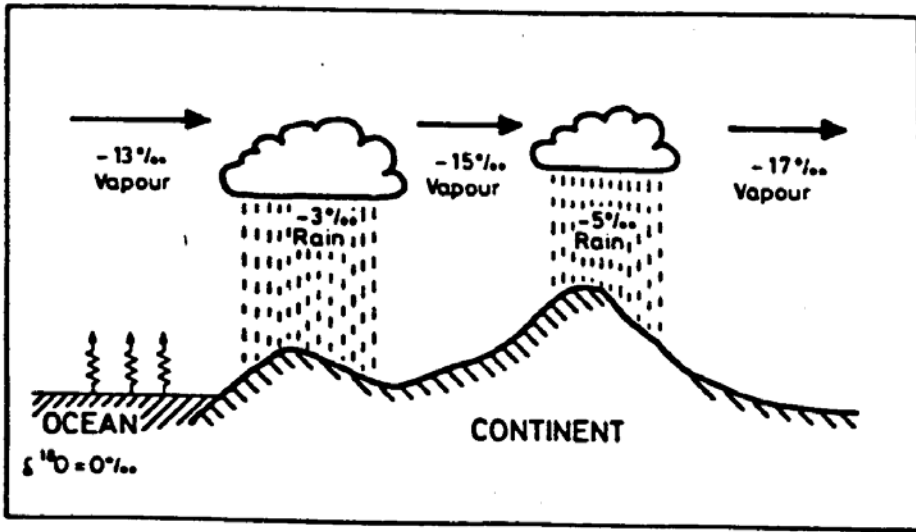
The water cycle

Fig. 4. $\delta^{18}O$ in a cloud vapor and condensate plotted as a function of the fraction of remaining vapor in the cloud for a Rayleigh process. The temperature of the cloud is shown on the lower axis. The increase in fractionation with decreasing temperature is taken into account. (After Dansgaard 1964)
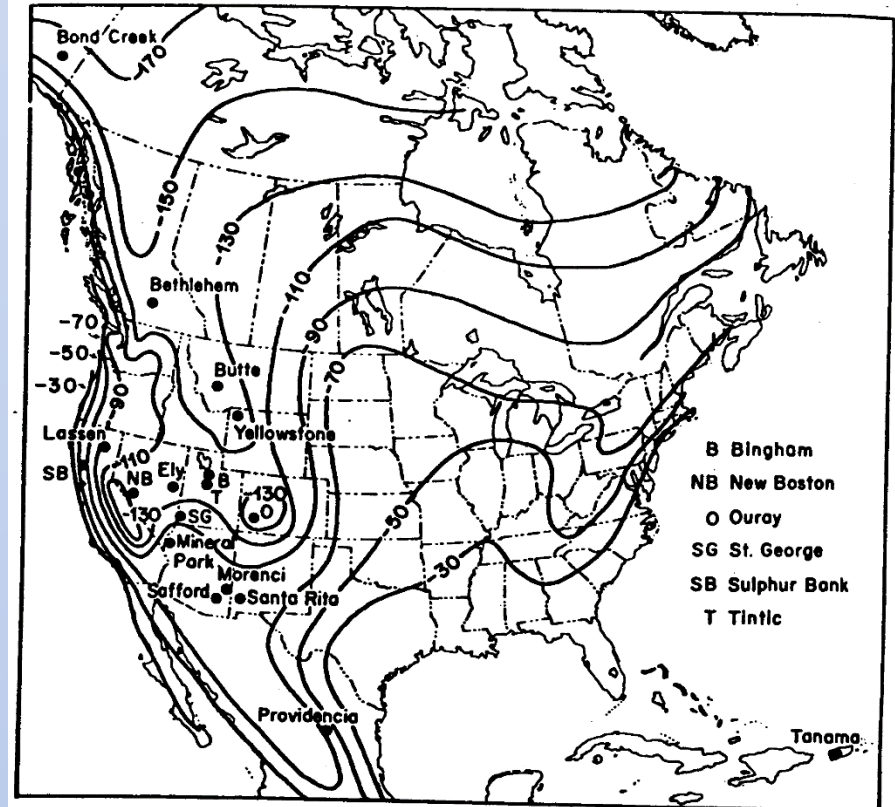
B   Bingham
NB New Boston
O   Ouray
SG St. George
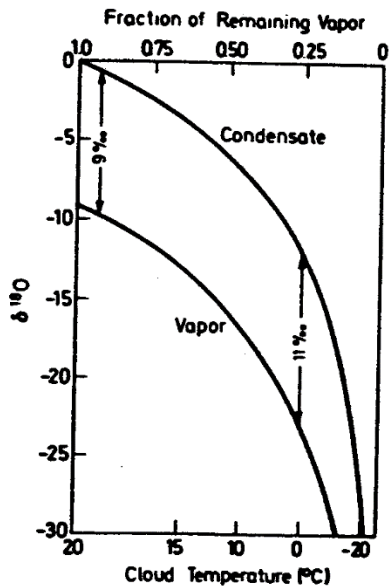SB Sulphur Bank
T   Tintic

FIG. 4. Map of North America showing locations of mineral deposits studied in this work. The contours indicate how the D/H ratios of meteoric lake, stream, river, and spring waters vary over the land surface (generalized from data by Friedman et al., 1964; Craig, 1963; Dansgaard, 1964).

The water cycle

$$\delta^{18}O_L = \alpha_V^L (\delta^{18}O_V + 10^3) - 10^3 \text{ and}$$
$$\delta D_L = \alpha_V^L (\delta D_V + 10^3) - 10^3$$

The latitudinal effect on the isotopic composition of meteoric water is caused by:

1) progressive isotopic fractionation of water vapour by condensation and removal of the water droplets with rain
2) the increased fractionation factors caused by decreasing temperatures
3) reevaporation of meteoric water from the surface of the Earth
4) evapotranspiration of water by plants.

Since H and O occur together in water molecules and both experience the same sequence of events during the migration of air masses, the δD and $\delta^{18}O$ values of meteoric water are strongly correlated and yield the **meteoric water line**. The equation describing this line is:

$$\delta D = 8\delta^{18}O + 10$$

The slope of this line is equal to the ratio of their isotopic fractionation factors of H and O :

$$(\alpha_V^L(H) - 1)/(\alpha_V^L(O) - 1) = 8.0$$

The Meteoric water line
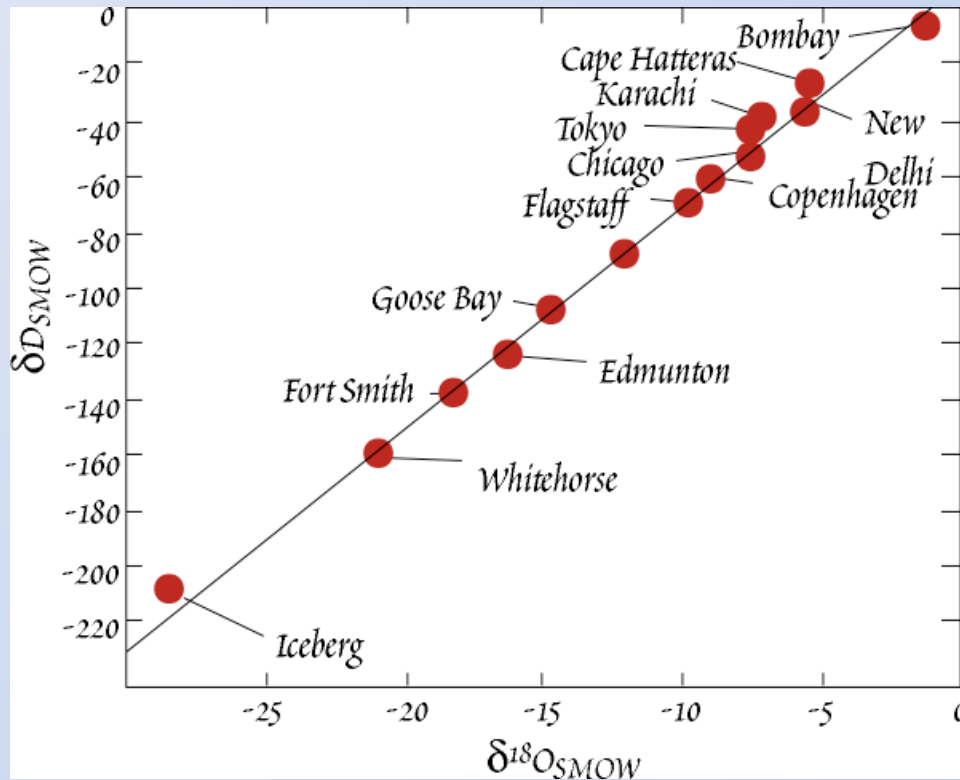
Northern hemisphere variation in δD and $\delta^{18}O$ in precipitation and meteoric waters.
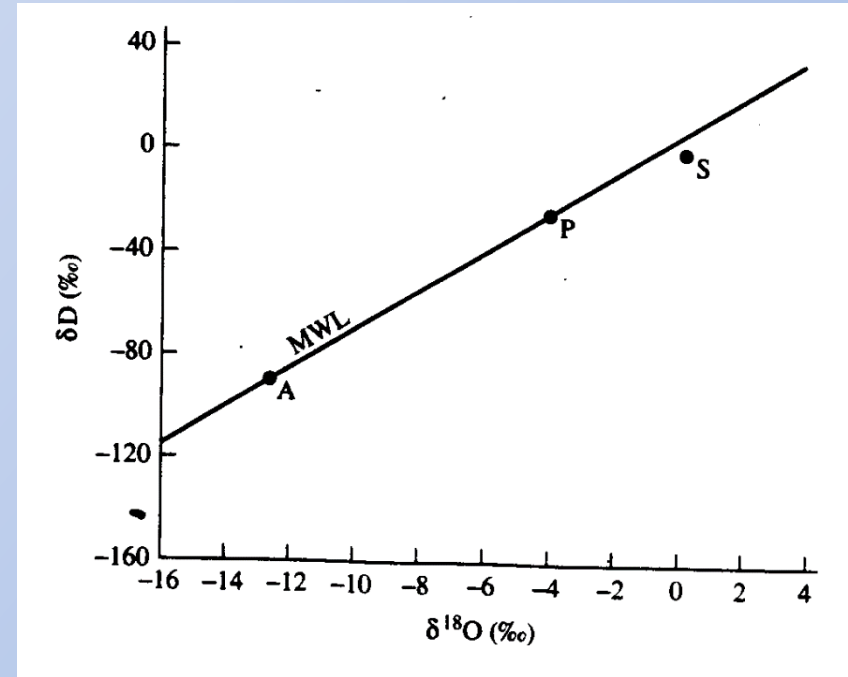The relationship between δD and $\delta^{18}O$ is approximately $\delta D = 8 \times \delta^{18}O + 10$.

Figure 2-15 Variation in δD and $\delta^{18}O$ in the hydrologic cycle. MWL = meteoric water line; S = surface ocean water; P = mean precipitation over the oceans; A = mean atmospheric water vapor over the oceans. Evaporation of seawater produces vapor depleted in D and ^{18}O (point A). Condensation of the vapor produces precipitation enriched in ^{18}O and D (point P). After Welhan (1987).

Glacial cycles
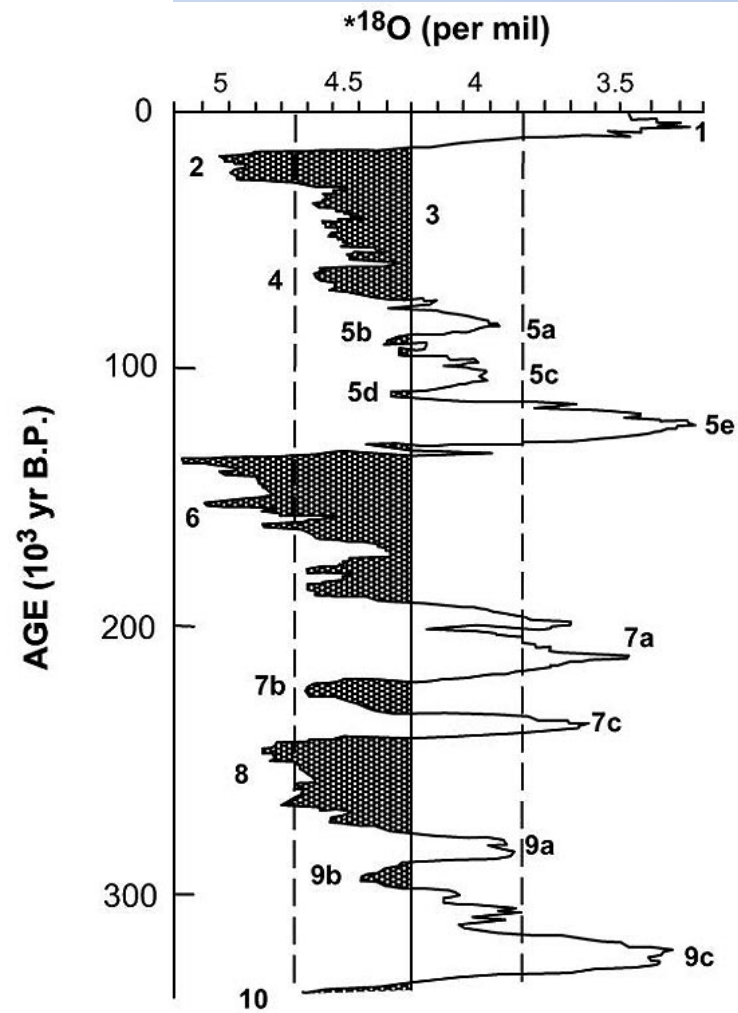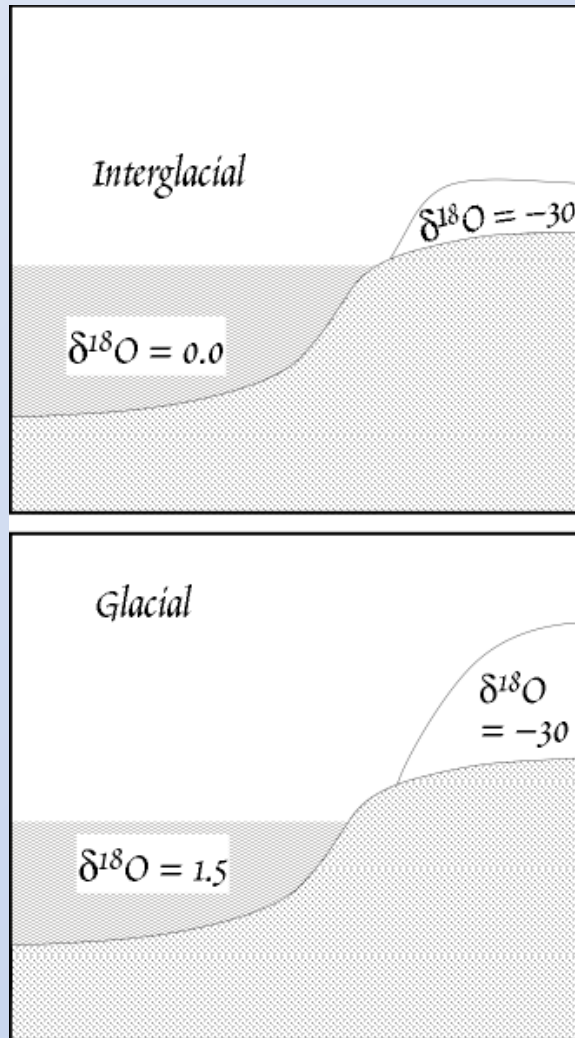
Marine oxygen isotope record

Geothermometers

Thermodependence of the fractionation factors
$$10^3 \ln \alpha = A/T^2 + B$$

Table 17.3 Temperature Dependence of the O-Isotope Fractionation Factor Between Minerals and Water in the Form $10^3 \ln \alpha = A \times 10^6/T^2 + B$[a]

Mineral	A	B
Clay Minerals		
Kaolinite	2.5	−2.87
Illite	2.43	−4.82
Smectite	2.67	−4.82
Chlorite	1.56	−4.70
Other Minerals		
Quartz	3.38	−3.40
Calcite	2.78	−2.89[b]
Dolomite	3.14	−2.0
Anhydrite	3.21	−4.72

[a] Compiled from the literature and recalculated by Anderson and Arthur (1983) to be consistent with Friedman and O'Neil (1977).
[b] From Friedman and O'Neil (1977).

From: Faure (1991)
Inorganic Geochemistry

Geothermometers

Table 17.5 Sulfur Isotope Fractionation Between Sulfide Minerals That Equilibrated Sulfur with the Same Reservoir at Elevated Temperatures in Kelvins

	Reference[a]
Pyrite–galena	
$10^3 \ln \alpha = (1.1 \times 10^6)/T^2$	(1)
Pyrite–sphalerite (or pyrrhotite)	
$10^3 \ln \alpha = (3.0 \times 10^5)/T^2$	(1)
Pyrite–chalcopyrite	
$10^3 \ln \alpha = (4.5 \times 10^5)/T^2$	(1)
Chalcopyrite–galena	
$10^3 \ln \alpha = (6.5 \times 10^5)/T^2$	(1)
Sphalerite–chalcopyrite and pyrrhotite–chalcopyrite	
$10^3 \ln \alpha = (1.5 \times 10^5)/T^2$	(1)
Sphalerite–galena	
$10^3 \ln \alpha = (8.9 \times 10^5)/T^2 - 0.57$	(2)
$10^3 \ln \alpha = (8.0 \times 10^5)/T^2$	(1)
$10^3 \ln \alpha = (7.0 \times 10^5)/T^2$	(3)
$10^3 \ln \alpha = (6.6 \times 10^5)/T^2 - 0.1$	(4)
Molybdenite–galena (experimental)	
$10^3 \ln \alpha = (1.3 \times 10^6)/T^2 - 0.80$	(5)
Molybdenite–sphalerite (experimental)	
$10^3 \ln \alpha = (0.71 \times 10^6)/T^2 - 0.15$	(5)
Molybdenite–pyrite (calculated, 400–750 °C)	
$10^3 \ln \alpha = (0.48 \times 10^6)/T^2 - 0.75$	(5)
Molybdenite–chalcopyrite (calculated, 400–750 °C)	
$10^3 \ln \alpha = (0.72 \times 10^6)/T^2 - 0.70$	(5)
Molybdenite–pyrrhotite (calculated, 400–750 °C)	
$10^3 \ln \alpha = (0.65 \times 10^6)/T^2 - 1.65$	(5)
$SO_2(g)$–$H_2S(g)$ (287–1000 °C)	
$10^3 \ln \alpha = (4.54 \times 10^6)/T^2 - 0.30$ (experimental)	(6)
$10^3 \ln \alpha = (3.65 \times 10^6)/T^2$ (calculated)	(6)
$HSO_4^-(aq)$–$H_2S(g)$ (200–320 °C)	
$10^3 \ln \alpha = (5.1 \times 10^6)/T^2 + 6.3$	(7)
Sphalerite–$HS^-(aq)$ (50–340 °C)	
$10^3 \ln \alpha = (1.11 \times 10^5)/T^2 + 1.36$	(2)
Galena–$HS^-(aq)$ (50–340 °C)	
$10^3 \ln \alpha = (7.82 \times 10^5)/T^2 + 1.7$	(2)

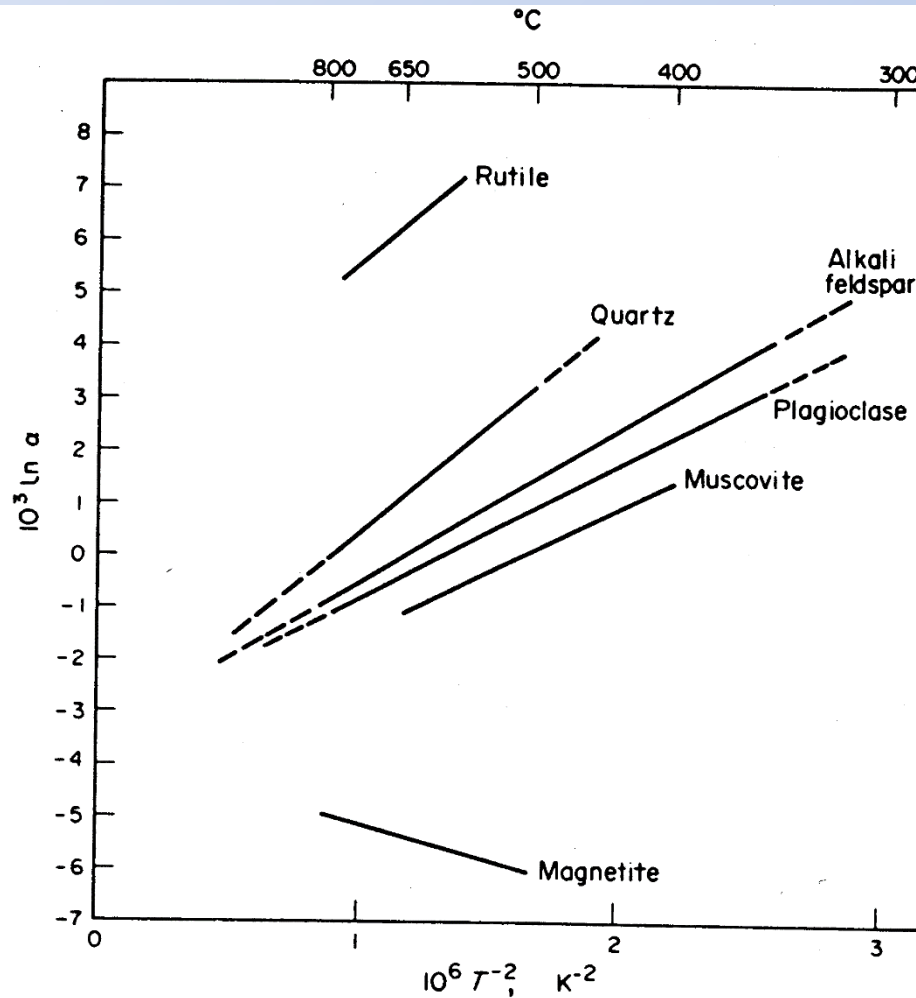From: Faure (1991)
Inorganic Geochemistry

Geothermometers

FIG. 9.3. Mineral-water fractionations for oxygen isotopes as a function of temperature. (The fractionation factor, α, is defined by equation (9.9).) (Data mainly from Friedman and O'Neil, 1977)

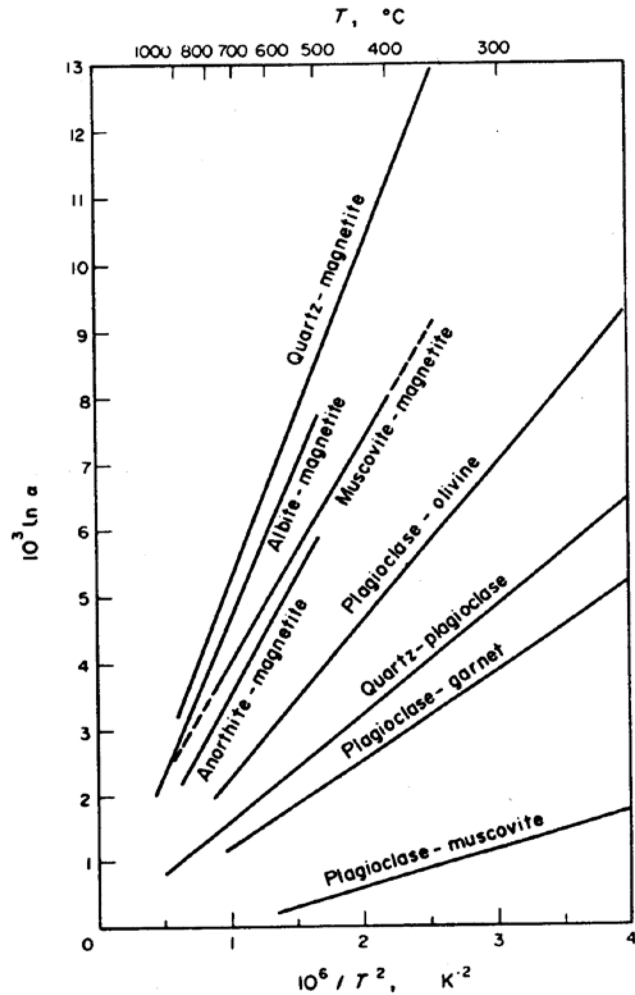From: Henderson (1982) Inorganic Geochemistry

Geothermometers

FIG. 9.4. Oxygen isotope fractionation for mineral pairs as a function of temperature. (Data from Friedman and O'Neil, 1977)
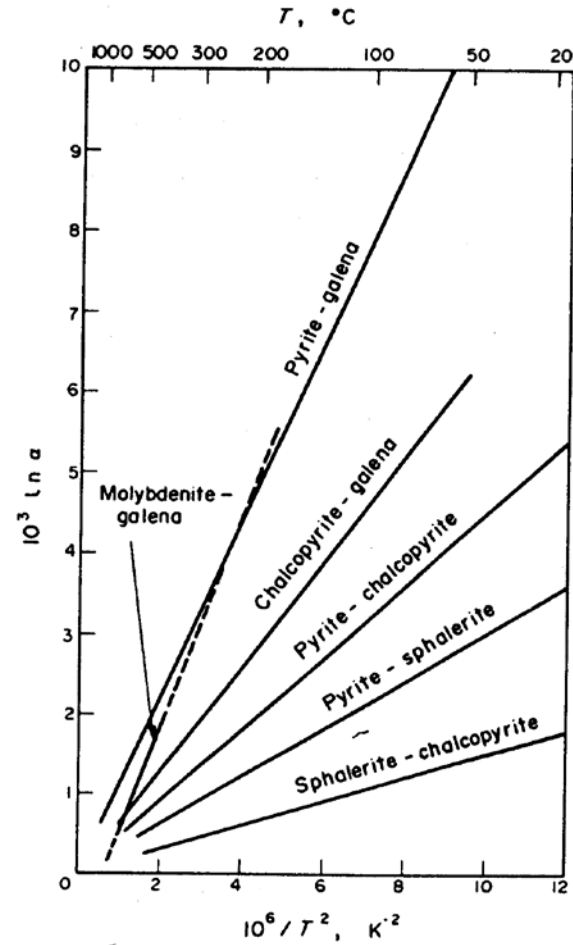
FIG. 9.5. Sulphur isotope fractionation for selected mineral pairs as a function of temperature. (Data from Friedman and O'Neil, 1977)

From: Henderson (1982) Inorganic Geochemistry

Isotopic fractionation in biological systems

Large fractionations of both carbon and nitrogen isotopes occur during primary production. The most important of these processes is photosynthesis. Photosynthetic fractionation of carbon isotopes is primarily kinetic.
For terrestrial plants (those utilizing atmospheric CO_2), the first step is diffusion of CO_2 into the boundary layer surrounding the leaf, through the stomata, and internally in the leaf. On theoretical grounds, a fractionation of $-4.4‰$ is expected. Marine algae and aquatic plants can utilize either dissolved CO_2 or HCO_3^- for photosynthesis:

$$CO_2(g) \rightarrow CO_2(aq) + H_2O \rightarrow H_2CO_3 \rightarrow H^+ + HCO_3^-$$
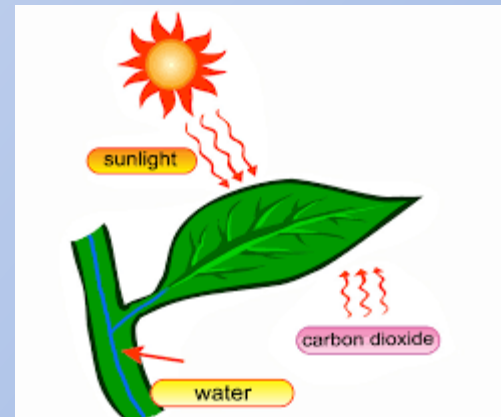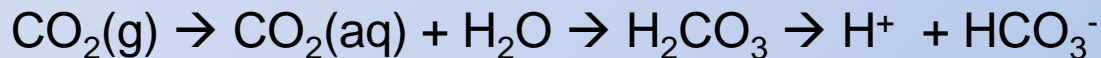
An equilibrium fractionation of $+0.9‰$ is associated with dissolution ($^{13}CO_2$ will dissolve more readily), and an equilibrium $+7.0$ to $+8‰$ fractionation occurs during hydration and dissociation of CO_2 (i.e., steps 2 and 3 in the reaction above).

Isotopic fractionation during photosynthesis

Most plants use an enzyme called *ribulose bisphosphate carboxylase oxygenase* (RUBISCO) to catalyze a reaction to produce a compound containing 3 carbon atoms, in a process called *carboxylation.*

These plants are called C3 plants, and this process is called the Benson-Calvin Cycle, or simply the Calvin Cycle. C3 plants constitute about 90% of all plants today and include algae and autotrophic bacteria and comprise the majority of cultivated plants, including wheat, rice, and nuts.

In addition to the fractionation associated the dissolution, hydration and dissociation of CO_2 (previous slide), there is a kinetic fractionation associated with this process that has been determined by several methods to be $-29.4‰$ in higher terrestrial plants. Bacterial carboxylation has different reaction mechanisms and a smaller fractionation of about $-20‰$. Thus, for terrestrial plants a fractionation of about $-34‰$ is expected from the sum of the individual fractionations. The actual observed total fractionation is in the range of -20 to $-30‰$.

Isotopic fractionation during photosynthesis

The other photosynthetic pathway is the Hatch-Slack cycle, used by the C4 plants that include hot region grasses and related crops such as maize (corn) and sugarcane. These plants use *phosphenol pyruvate carboxylase* (PEP) to fix the carbon initially and form oxaloacetate, a compound that contains 4 carbons.
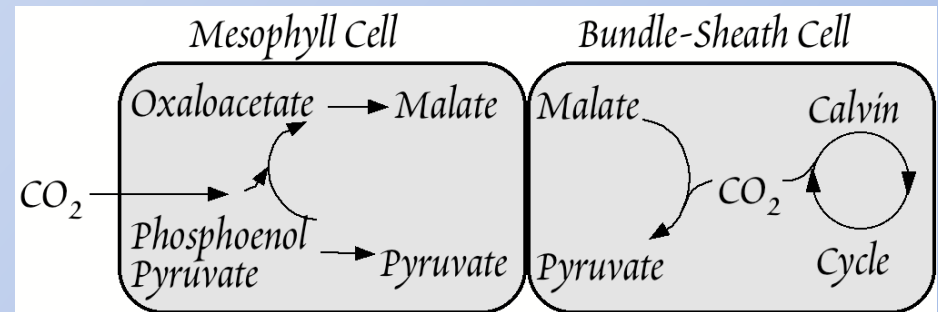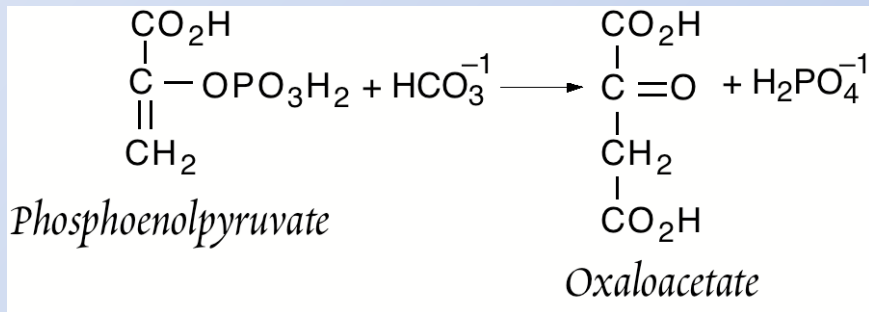
The photosynthetic environment is almost a closed system, so that virtually all the carbon carried there is refixed and there is little fractionation during this step. Thus, C4 plants have average $\delta^{13}C$ of -13‰,

A third group of plants, the CAM plants, has a unique metabolism called the *Crassulacean acid metabolism*. These plants generally use the C4 pathway, but can use the C3 pathway under certain conditions. These plants are generally succulents adapted to arid environments and include pineapple and many cacti; they have $\delta^{13}C$ intermediate between C3 and C4 plants.

Isotopic fractionation during photosynthesis

Comparison of C_3, C_4, and CAM plants

C3 plants	C4 plants	CAM plants
Most plants	Tropical grasses like corn, sugarcane	Succulents, pineapple, agave
Fix carbon in Calvin cycle - attach CO_2 to RuBP	Fix carbon in cytoplasm - attach CO_2 to PEP	Fix carbon at night only, fix it to organic molecules
Enzyme - Rubisco	Enzyme – PEP-ase	Enzyme – PEP-ase
Most energy efficient method	1/2 way between these two	Best water conservation
Loses water through photorespiration	Loses less water	Loses least water

Isotopic fractionation during photosynthesis

Terrestrial plants, which utilize CO_2 from the atmosphere, generally produce greater fractionations than marine and aquatic plants, which utilize dissolved CO_2 and HCO_3^-, together referred to as *dissolved inorganic carbon* or DIC. There is about a +8‰ equilibrium fractionation between dissolved CO_2 and HCO_3^-. Since HCO_3^- is about 2 orders of magnitude more abundant in seawater than dissolved CO_2, marine algae utilize this species, and hence tend to show a lower net fractionation between dissolved carbonate and organic carbon during photosynthesis.
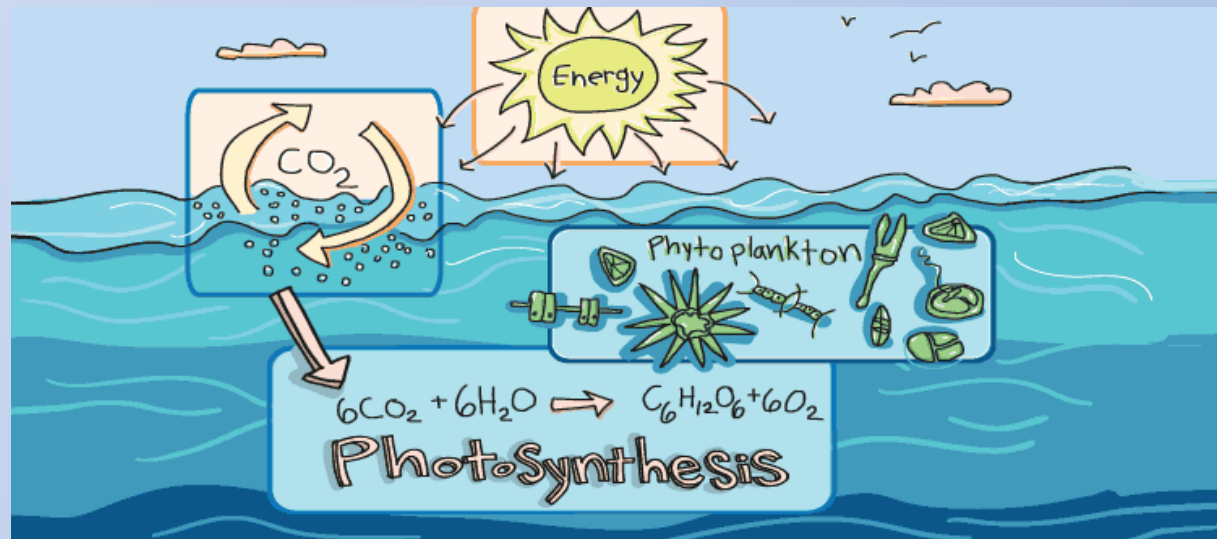
Calypso (51.6 m) piston core recovered on the R/V Marion Dufresne II
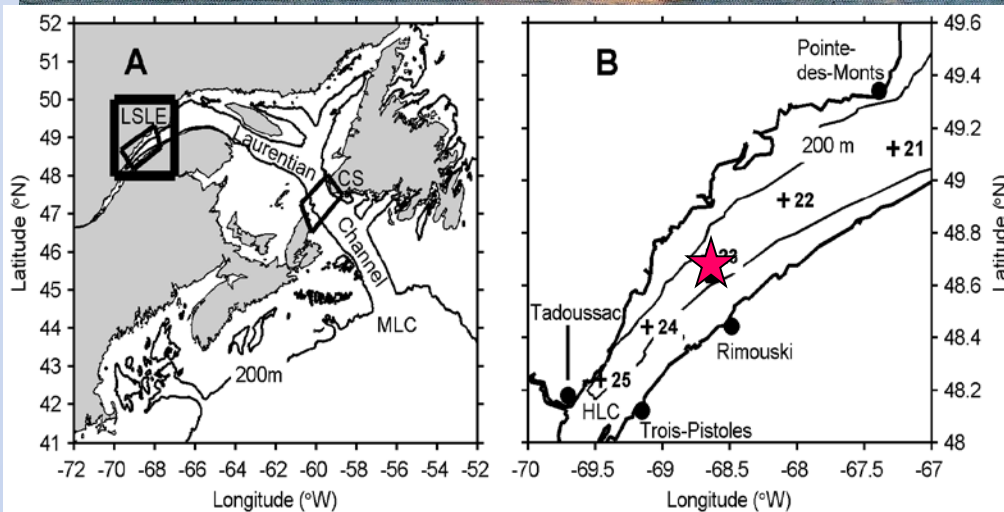
Box-corer (~51 cm long) and recovered, undisturbed interface

Organic carbon content and $\delta^{13}C$ in a composite sequence (box core AH and upper part of MD99-2220)

Terrestrial ← → Marine

Corg.(%) δ^{13}Corg.

Flux ~ 100gC/m².a

Flux ~ 25gC/m².a

~ 1970 AD

~ 1940 AD

580 ± 50 BP
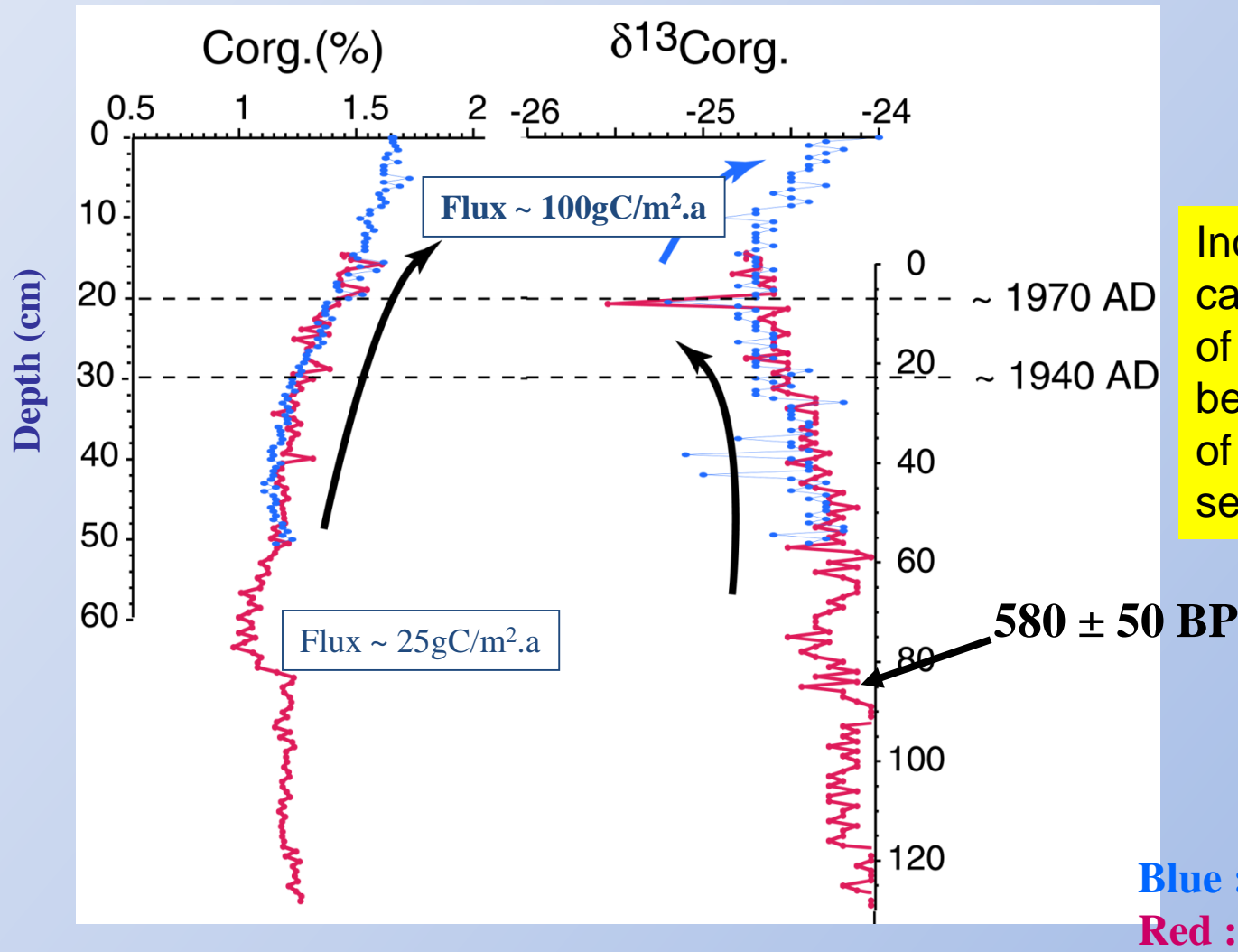
Increase in organic carbon content (C_{ORG}) of the sediment beginning at the time of European settlement

Blue : Box core (50 cm)
Red : Calypso core (~35 m)

Thibodeau, de Vernal and Mucci (2006; Mar. Geol. 231: 37-50)

"You are what you eat"
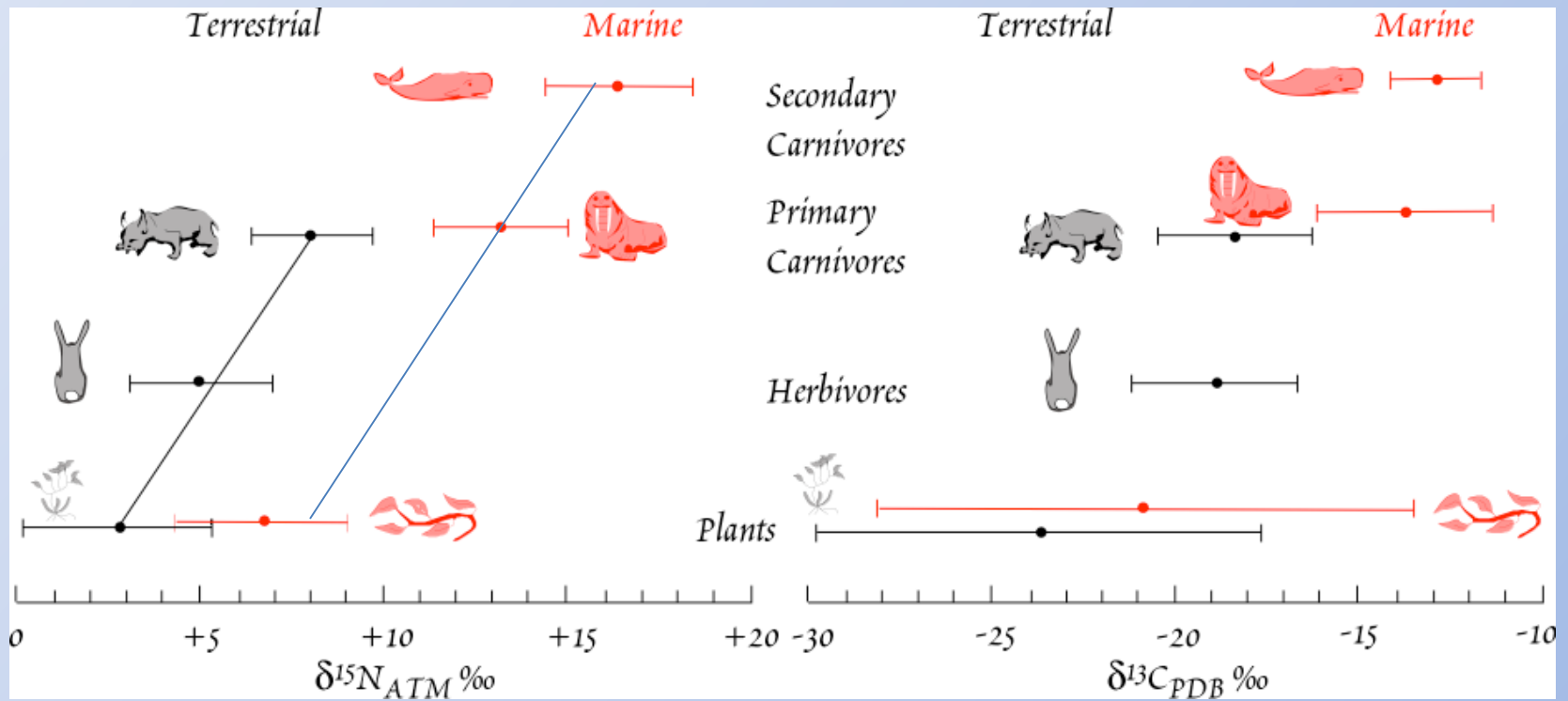
Values of $\delta^{13}C$ and $\delta^{15}N$ in various marine and terrestrial organisms.

Sulfate reduction and diagenesis
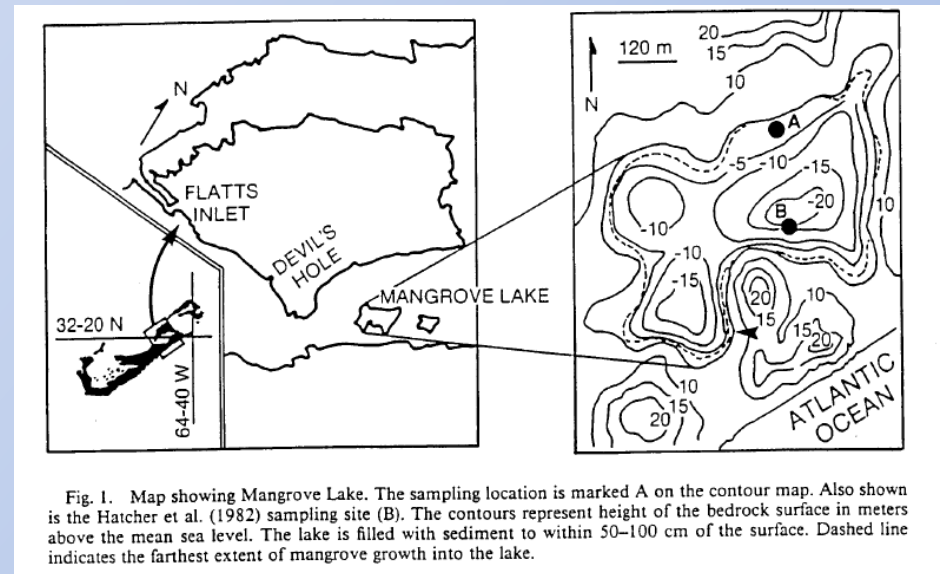
Fig. 1. Map showing Mangrove Lake. The sampling location is marked A on the contour map. Also shown is the Hatcher et al. (1982) sampling site (B). The contours represent height of the bedrock surface in meters above the mean sea level. The lake is filled with sediment to within 50–100 cm of the surface. Dashed line indicates the farthest extent of mangrove growth into the lake.

Sulfur, in the form of sulfate, can act as an electron acceptor or oxidant, and is utilized as such by sulfur-reducing bacteria. This process, in which H_2S is liberated, is called *dissimilatory sulfate reduction* and plays an important role in biogeochemical cycles, both as a sink for sulfur and source for atmospheric oxygen.

Sulfate reduction and diagenesis

$$(CH_2O)_X(NH_3)_Y(H_3PO_4)_Z + X/2\ SO_4^{2-} \rightarrow X HCO_3^- + X/2\ H_2S + Y\ NH_3 + Z\ H_3PO_4$$
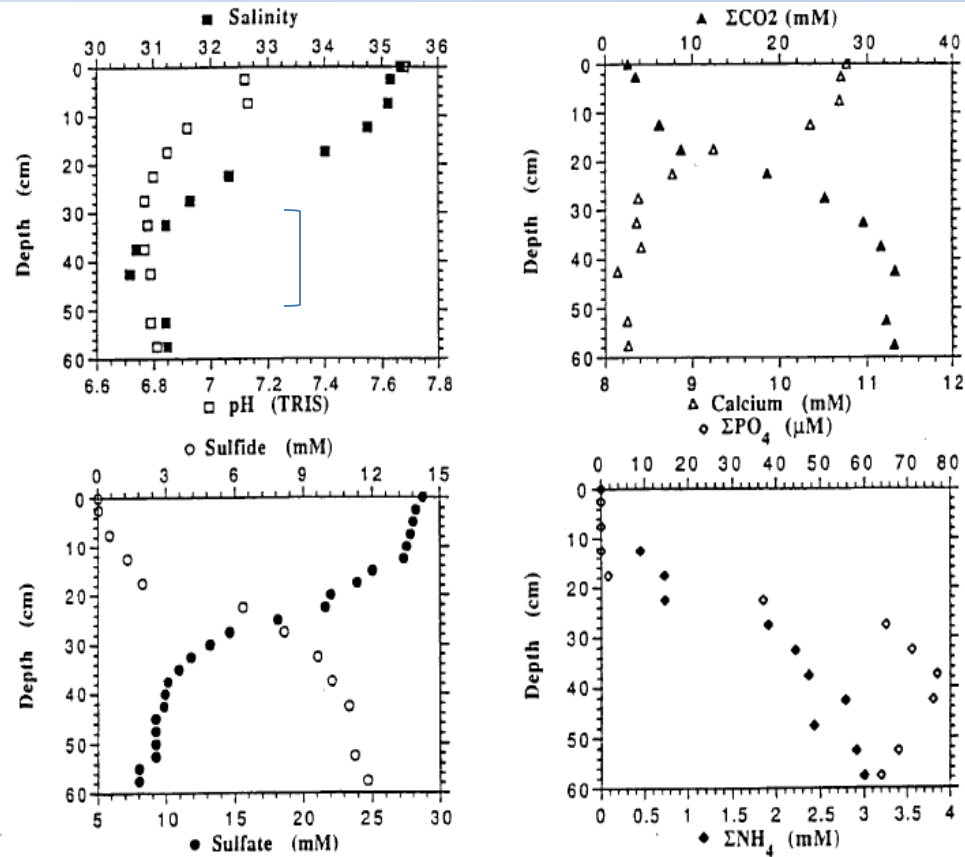
Fig. 2. Depth profiles of the major pore-water species in the sediments of Mangrove Lake. The surface pH value is nearly hidden underneath the surface salinity point (upper left). With regard to the sulfate profile, the second data point (at 2.5 cm) and every other sample thereafter was analyzed by the method of Mucci (1991). The intervening data were obtained by the more traditional method described in the text.

From: Boudreau, Canfield and Mucci (1992) Limnol. Oceanogr. **37:** 1738-1753.

Sulfate reduction and diagenesis

$$(CH_2O)_X(NH_3)_Y(H_3PO_4)_Z + X/2\ SO_4^{2-} \rightarrow X\ HCO_3^- + X/2\ H_2S + Y\ NH_3 + Z\ H_3PO_4$$
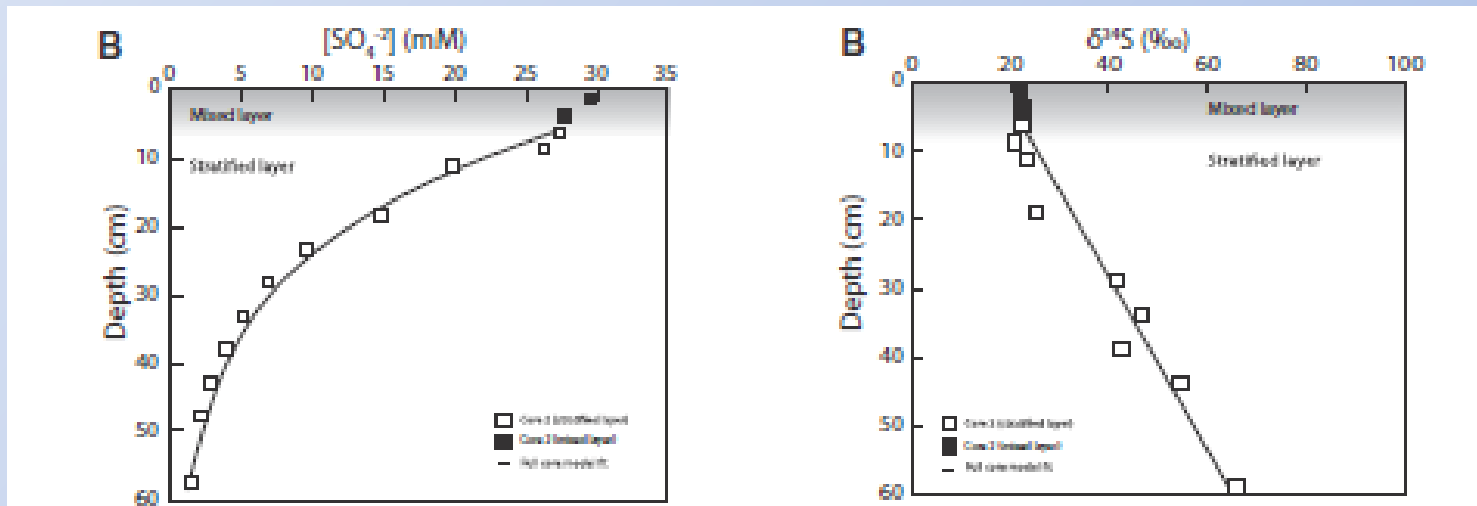
A large fractionation of +5 to –46‰ is associated with this process.

Sulfate reduction and diagenesis

The water cycle

Fig. 4. $\delta^{18}O$ in a cloud vapor and condensate plotted as a function of the fraction of remaining vapor in the cloud for a Rayleigh process. The temperature of the cloud is shown on the lower axis. The increase in fractionation with decreasing temperature is taken into account. (After Dansgaard 1964)

B Bingham
NB New Boston
O Ouray
SG St. George
SB Sulphur Bank
T Tintic

FIG. 4. Map of North America showing locations of mineral deposits studied in this work. The contours indicate how the D/H ratios of meteoric lake, stream, river, and spring waters vary over the land surface (generalized from data by Friedman et al., 1964; Craig, 1963; Dansgaard, 1964).

Rayleigh Distillation

Rayleigh Distillation

If, $R_0 = A_0{}^{18}O/A_0{}^{16}O$, the initial isotopic ratio, $^{18}O/^{16}O$, of the reservoir of water and $R = A^{18}O/A^{16}O$, the isotopic composition of the remaining water at time t.
At anytime, the ice crystals being formed will have an isotopic composition determined by the fractionation factor α(ice-water):

$$\alpha\text{(ice-water)} = R_{ice}/R_{water} = (A^{18}O/A^{16}O)_{ice}/(A^{18}O/A^{16}O)_{water}$$
$$= (dA^{18}O/dA^{16}O)_{ice}/(A^{18}O/A^{16}O)_{water}$$

$$\text{or } dA^{18}O/A^{18}O = \alpha\, dA^{16}O/A^{16}O$$

where $dA^{18}O$ and $dA^{16}O$ are the respective infinitesimal quantity of the two isotopes taken up by the ice crystals.
If we integrate from 0 to a time t:

$$\int_0^t dA^{18}O/A^{18}O = \int_0^t \alpha\, dA^{16}O/A^{16}O$$

and since α is a constant under isothermal conditions, we obtain:

$$\ln (A^{18}O/A_0{}^{18}O) = \alpha \ln (A^{16}O/A_0{}^{16}O), \quad \text{or}$$
$$A^{18}O/A_0{}^{18}O = (A^{16}O/A_0{}^{16}O)^{\alpha} = (A^{16}O/A_0{}^{16}O)(A^{16}O/A_0{}^{16}O)^{\alpha-1}$$

Rayleigh Distillation

Rearranging,

$$A^{18}O/A^{16}O = (A_0^{18}O/A_0^{16}O)(A^{16}O/A_0^{16}O)^{\alpha-1}$$
$$\text{or } R = R_0 (A^{16}O/A_0^{16}O)^{\alpha-1}$$

Since, in practice, $A^{16}O \gg A^{18}O$,

$$f = \text{fraction of residual water} = A^{16}O/A_0^{16}O$$
$$R = R_0 \, f^{(\alpha-1)} \text{ or } R/R_0 = f^{(\alpha-1)}$$
$$\text{or } \ln R/R_0 = (\alpha-1) \ln f \text{ (the Rayleigh equation)}$$

Since $R/R_0 \approx 1$

$$\ln R/R_0 \approx (R/R_0) - 1 \quad \text{since for } R/R_0 = 1.0x, \quad \ln R/R_0 \approx 0.0x$$

and

$$(R/R_0) - 1 \approx (\alpha - 1) \ln f$$

Rayleigh Distillation

in δ notation,

$$\delta_0 = (R_0 - R_{STD}/R_{STD})10^3 \text{ and } \delta = (R - R_{STD}/R_{STD})10^3$$

and $R_{STD} = A^{18}O/A^{16}O$ of the standard,

$$\delta - \delta_0 = (R - R_0/R_{STD})10^3$$

since isotopic ratios only change in the third or fourth significant figure, $R-R_0 \ll R_{STD}$ or $R_0 \approx R_{STD}$, then:

$$(R-R_0)/R_{STD} \approx (R-R_0)/R_0 \approx (R/R_0)-1 \approx (\delta - \delta_0)/10^3$$

$$10^3 [(R/R_0)-1] = \delta - \delta_0 \approx 10^3 (\alpha-1) \ln f$$

for most isotopes and for the particular process considered here,

$$\delta - \delta_0 \approx \varepsilon_{(ice-water)} \ln f$$

where δ = isotopic composition of the reservoir at a time t
and δ_0 = isotopic composition of the initial reservoir at t=0

Rayleigh fractionation with variable T
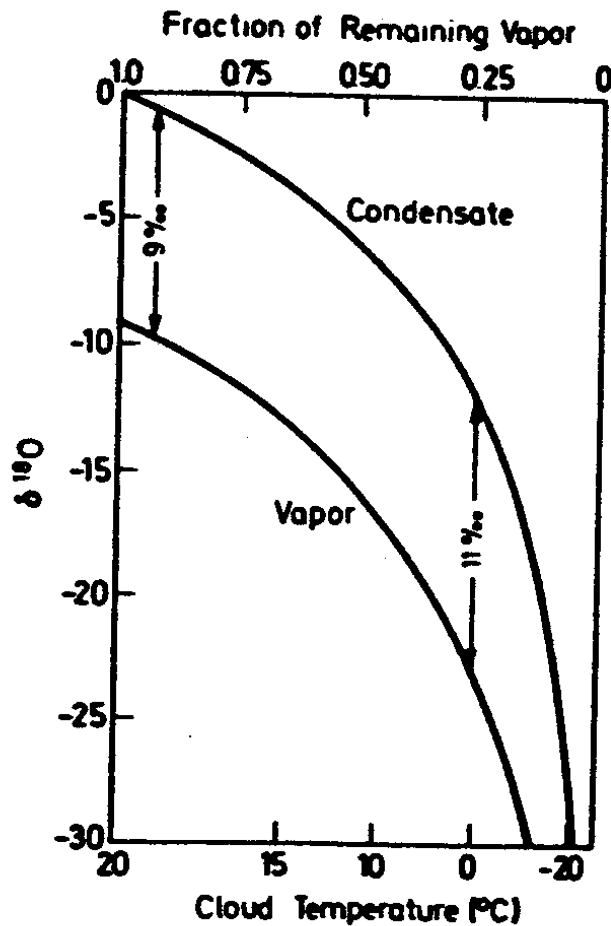
Fig. 4. $\delta^{18}O$ in a cloud vapor and condensate plotted as a function of the fraction of remaining vapor in the cloud for a Rayleigh process. The temperature of the cloud is shown on the lower axis. The increase in fractionation with decreasing temperature is taken into account. (After Dansgaard 1964)

Sulfur isotopes and ore deposits

There are two major reservoirs of sulfur on the Earth that have uniform sulfur isotopic compositions: the mantle, which has $\delta^{34}S$ of ~0 and in which sulfur is primarily present in reduced form, and seawater, which has $\delta^{34}S$ of +20 and in which sulfur is present as SO_4^{2-}.
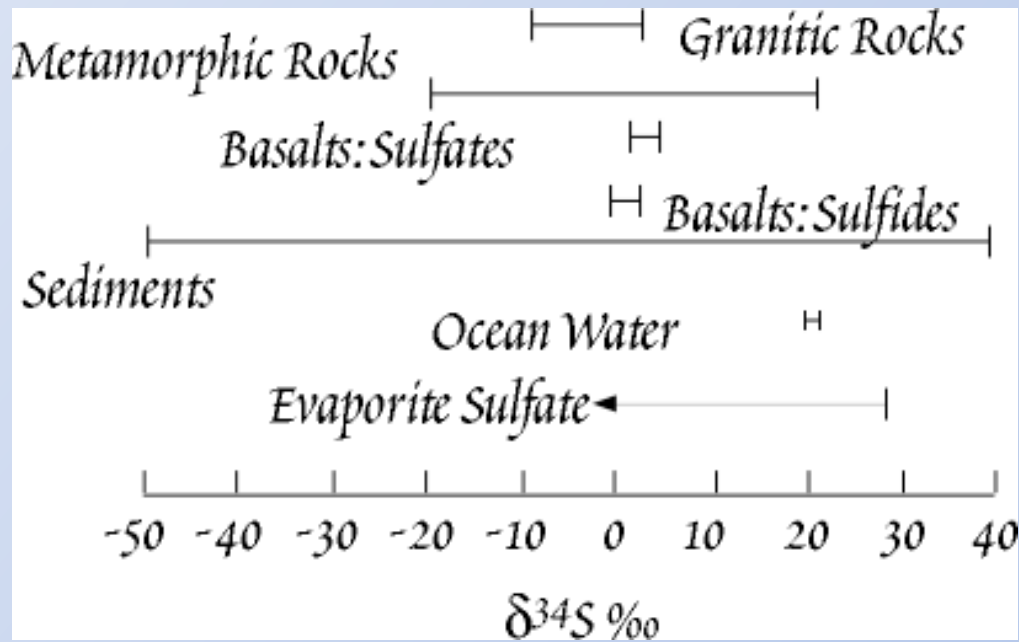
$\delta^{34}S_{CDT}$ in various geologic materials
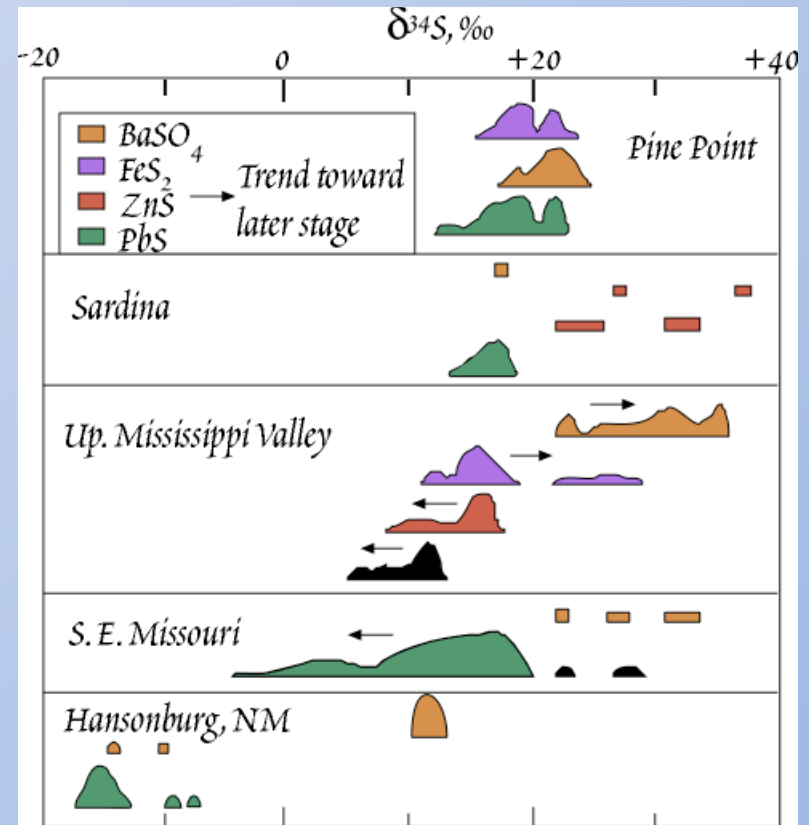
Sulfur isotope ratios in some Mississippi Valley-type Pb and Zn deposits.

Mass-dependent and mass-independent fractionation of sulfur isotopes

In the modern Earth, variations in sulfur isotope ratios are almost always mass dependent and $\delta^{33}S$ and $\delta^{36}S$ are related to variations in $\delta^{34}S$ as:

$$\delta^{33}S = 0.515 \times \delta^{34}S \text{ and } \delta^{36}S = 1.90 \times \delta^{34}S$$

Farquhar et al. (2000) found that the relationships do not hold for sulfur in many Archean sediments and ore deposits.
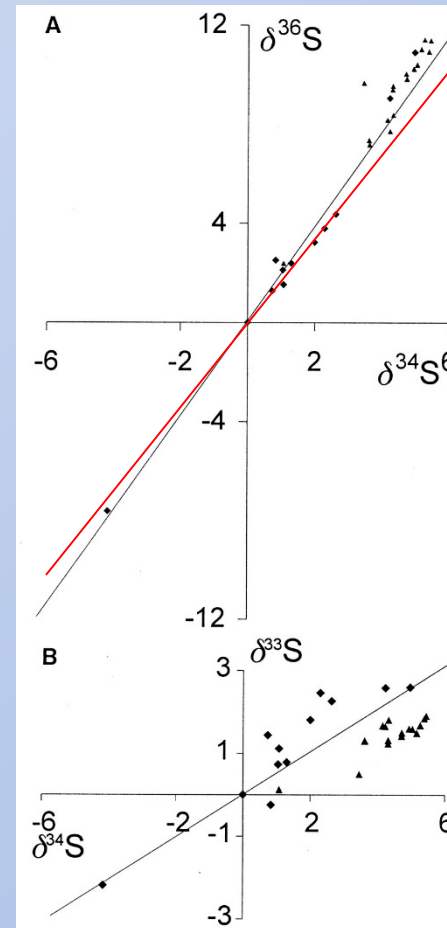He found:
$$\delta^{36}S = 2.17 \times \delta^{34}S$$
and that $\delta^{33}S$ scatters all around the mass-dependent relationship.

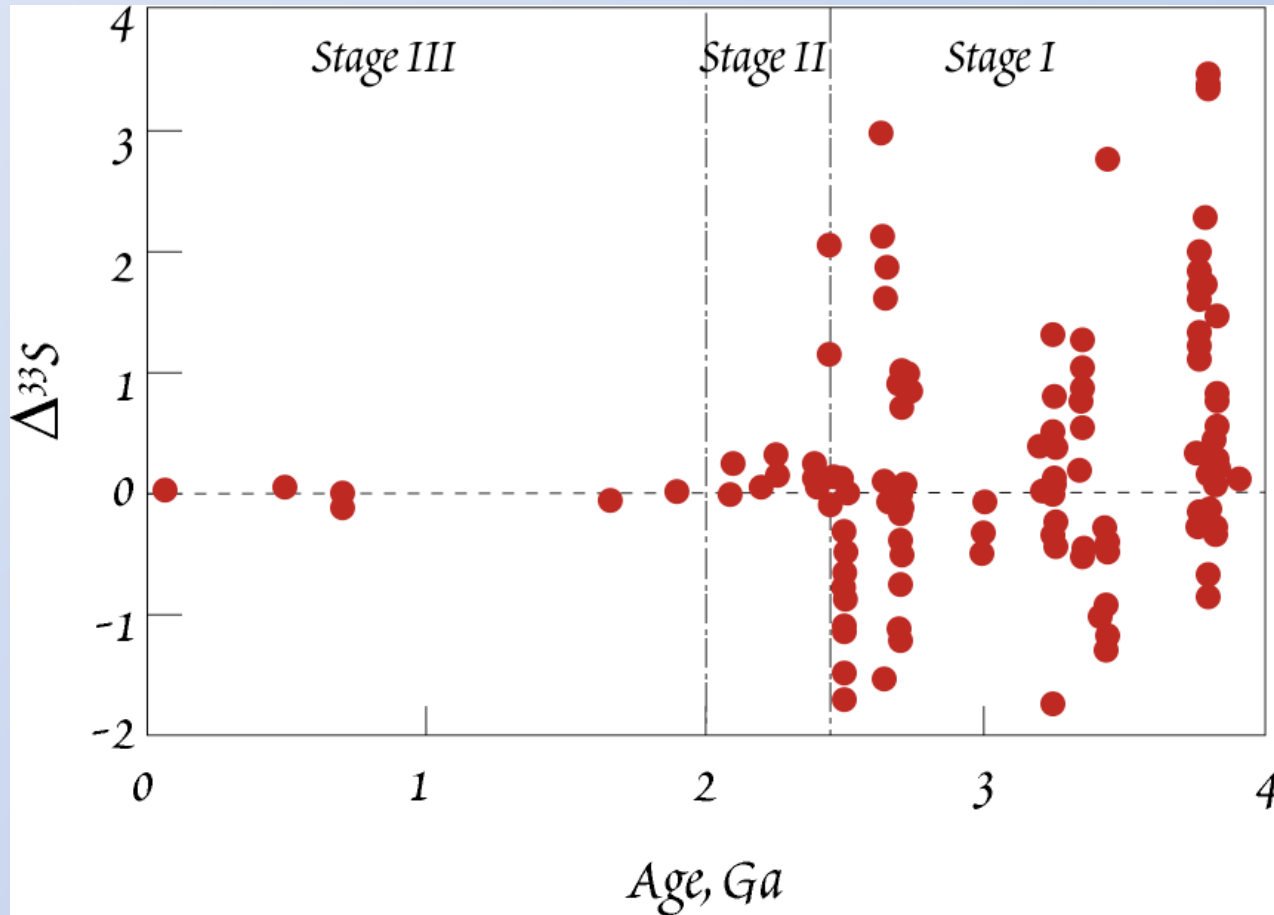Deviations from the relationships above are given by $\Delta^{33}S$ and $\Delta^{36}S$:

$$\Delta^{33}S = \delta^{33}S - 0.515 \times \delta^{34}S$$
and
$$\Delta^{36}S = \delta^{36}S - 1.90 \times \delta^{36}S$$
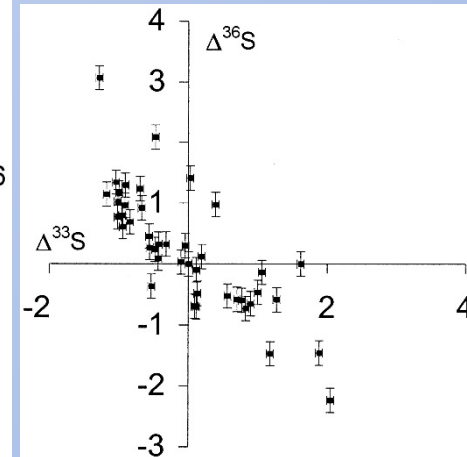
$\Delta^{33}S$ in sulfur through time. During Stage 1 (prior to 2.45 Ga), extensive mass independent fractionation occurred as evidenced by $\Delta^{33}S$ up to 3.5‰, indicating the lack of atmospheric oxygen. During Stage 2 (2.45 to 2.0 Ga), limited amounts of atmospheric oxygen (up to 1% of present levels) absorbed most UV radiation and limited mass independent fractionation to <0.5‰. High levels of atmospheric oxygen in Stage 3 (since 2.0 Ga) effectively eliminate UV radiation and mass independent fractionation.

The Great Oxidation Event
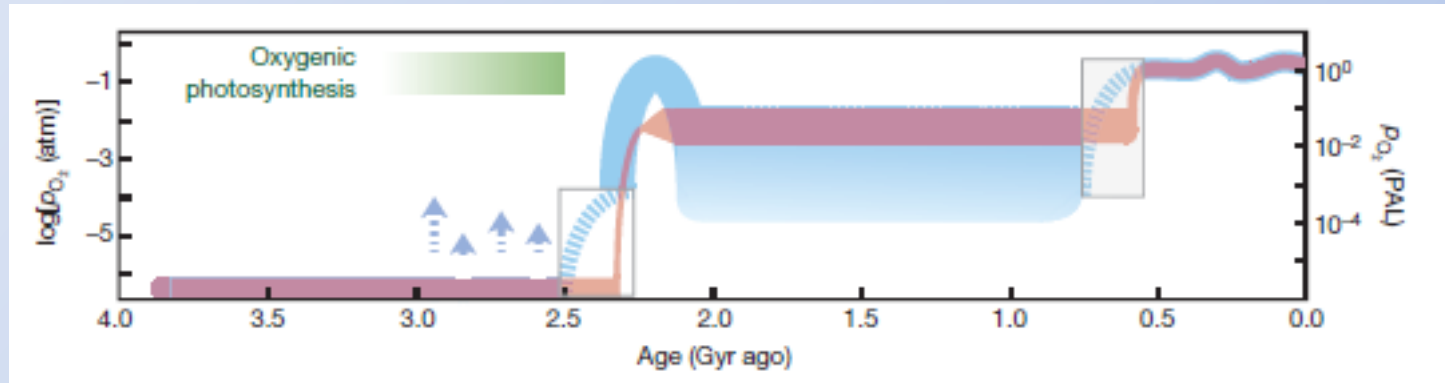
Evolution of Earth's atmospheric oxygen content through time – Faded red curve is the "classical, two-step" view of atmospheric evolution. PO2 relative to present-day level (PAL).
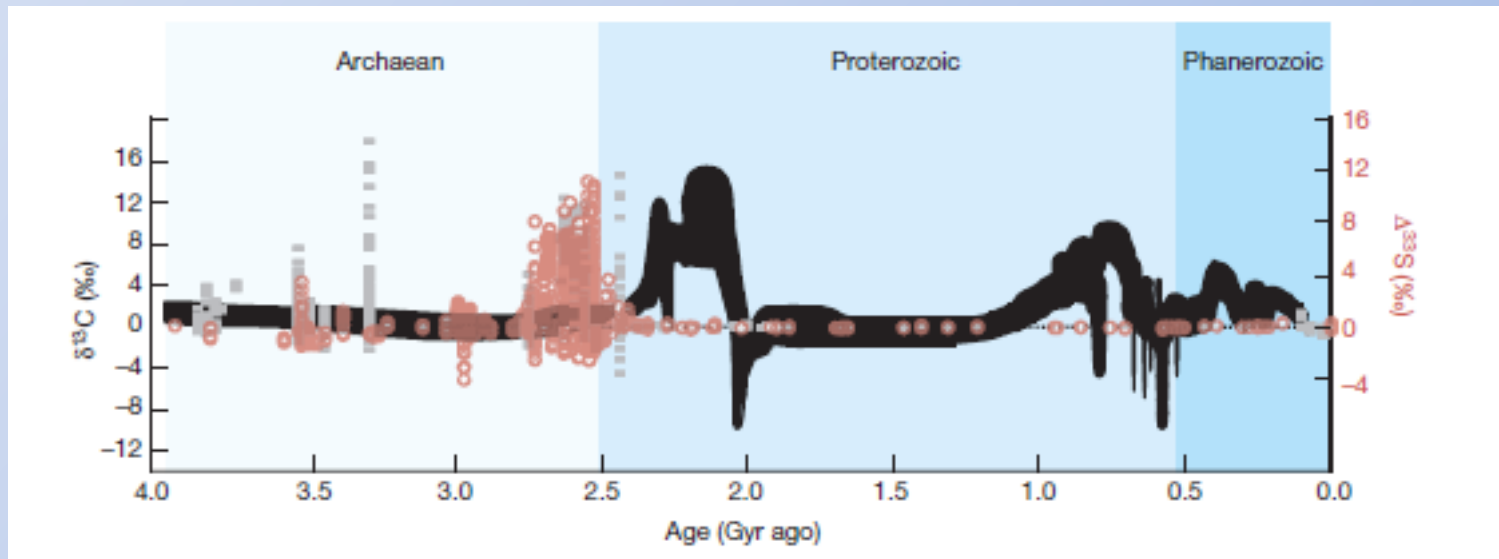
Summary of carbon (black) and sulfur (red and grey) isotope data through Earth's history

From: Lyons et al. (Nature, 2014)

The fate of carbon in sediments