

Lecture 5

Introduction to Stable Isotopes

Stable Isotope Geochemistry

Primarily concerned with the isotope ratios of H, C, N, O, and S – Si and B often included and new instrumentation has opened up others such as Mg, Fe, Cu, Se, Sn, Mo, Tl etc.

Common Properties

1. Low atomic mass
2. Large relative mass difference e.g. D-H 100%
3. They form highly covalent chemical bonds e.g. ^{40}Ca - ^{48}Ca shows little range
4. More than one oxidation state (C, N, S), form many compounds (O) and are important constituents of common solids and liquids
5. Rare isotopes are sufficiently abundant to allow precise measurements

In terrestrial materials, stable isotope geochemistry deals only with isotopic variations that arise from:

- (1) Isotope exchange reactions, (equilibrium isotope distribution) or**
- (2) Kinetic effects - mass-dependent fractionations that accompany physical and chemical processes and are dependant on differences in reaction rates**

We are used to elemental properties being controlled by electronic configuration.

1 H			
3 Li	4 Be		
11 Na	12 Mg		
19 K	20 Ca	21 Sc	22 Ti
37 Rb	38 Sr	39 Y	40 Zr
55 Cs	56 Ba	57 La	72 Hf
87 Fr	88 Ra	89 Ac	104 Rf

Shell	K	L	M	N	O
Orbital	1s	2s 2p	3s 3p 3d	4s 4p 4d 4f	
Li	2	1			
Na	2	2 6	1		
K	2	2 6	2 6	1	
Rb	2	2 6	2 6 10	2 6	1

58 Ce	59 Pr
90 Th	91 Pa

e.g. Group 1A alkali metals all have a single electron in their outer electron shell

So, different isotopes of an element will have similar properties

However, small differences in mass between isotopes of an element in a molecule can change the physical properties of the molecule e.g. H_2^{16}O b.p. 100°C c.f. D_2^{16}O b.p. 101.42°C

These differences can cause separation of the different isotopes during chemical reactions i.e. **isotope fractionation** – the partitioning of isotopes between 2 substances or 2 phases of the same substance with different isotope ratios.

The **fractionation factor** between two substances **A** and **B** ($\alpha_{\text{A-B}}$) simply

$$\alpha_{\text{A-B}} = \frac{R_{\text{A}}}{R_{\text{B}}} \text{ where } R \text{ is an isotope ratio e.g. } ^{12}\text{C}/^{13}\text{C}$$

At equilibrium α is related to the thermodynamic equilibrium constant K , such that:

$$\alpha = K^{1/n}$$

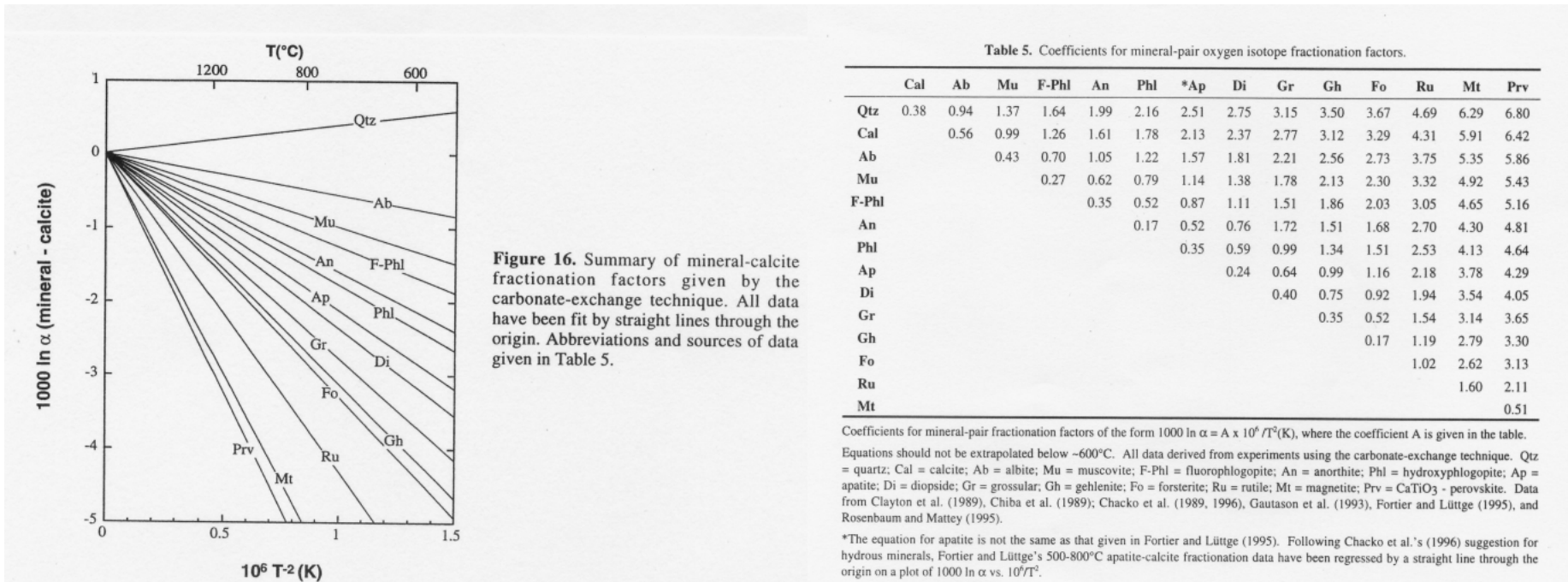
where n is the number of atoms exchanged in the reaction and subject to the (good) approximation that isotopes are randomly distributed among all possible sites in the molecule.

Fractionation Factors

To apply stable isotopes we need to know the size and temperature dependence of isotopic fractionation factors for the minerals and fluids studied.

Fractionation factors are determined in three ways:

1. Semi-empirical calculations from spectroscopic data using statistical mechanics
2. Laboratory calibration studies
3. Measurements of natural samples whose formation conditions are known.



The Delta Value (δ)

Most commonly stable isotope ratios e.g. $^{18}\text{O}/^{16}\text{O}$ are expressed as delta values e.g. $\delta^{18}\text{O}$. where δ is the measured ratio divided by some standard and multiplied by 1000

$$\text{i.e. } \delta = \frac{R_{(\text{SAMPLE})} - R_{\text{STANDARD}}}{R_{\text{STANDARD}}} \times 1000 (\text{‰})$$

Two compounds A and B have been analysed.

$$\delta_A = (R_A/R_{\text{STD}} - 1) \times 1000$$

$$\delta_B = (R_B/R_{\text{STD}} - 1) \times 1000$$

$$\delta_A - \delta_B = \Delta_{A-B} (\text{"big delta"}) \approx 10^3 \ln \alpha_{A-B}$$

STANDARDS

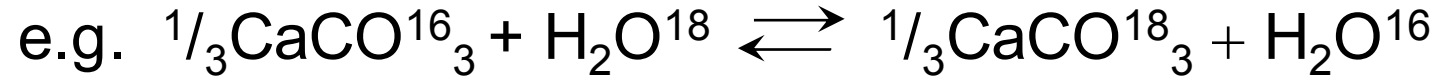
δD	D/H	Standard Mean Ocean Water	Vienna - SMOW
$\delta^{13}C$	$^{13}C/^{12}C$	Cretaceous Belemnite, Peedee Formation, South Carolina	PDB
$\delta^{15}N$	$^{15}N/^{14}N$	Atmospheric nitrogen	Air
$\delta^{18}O$	$^{18}O/^{16}O$	Standard Mean Ocean Water	V-SMOW
$\delta^{34}S$	$^{34}S/^{32}S$	Troilite (PbS) from Canyon Diablo iron meteorite	CDT

Sometimes, particularly in palaeoclimate studies of carbonates $\delta^{18}O_{PDB}$ are presented:

$$\delta^{18}O_{PDB} = 0.97002 \delta^{18}O_{SMOW} - 29.98$$

$$\delta^{18}O_{SMOW} = 1.03091 \delta^{18}O_{PDB} - 30.91$$

Isotope Exchange



We can write an equilibrium constant (K) for this reaction:

$$K = \frac{[\text{CaCO}^{18}_3]^{1/3} / [\text{CaCO}^{16}_3]^{1/3}}{[\text{H}_2\text{O}^{18}] / [\text{H}_2\text{O}^{16}]}$$

so, K is the ratio of $^{18}\text{O}/^{16}\text{O}$ in carbonate divided by $^{18}\text{O}/^{16}\text{O}$ in water

$$K = R_c / R_w = \alpha$$

fractionation factor (α) at $25^\circ\text{C} = 1.0286$

so carbonate deposited from seawater at 25°C has $^{18}\text{O}/^{16}\text{O}$ of $1.0286 \times$ seawater.

Since V-SMOW has $\delta^{18}\text{O} = 0\text{‰}$, carbonate precipitated from water at 25°C will have $\delta^{18}\text{O} = +28.6\text{‰}$

Kinetic Isotope Effects

Associated with fast, incomplete or unidirectional processes e.g. evaporation, diffusion and dissociation reactions.

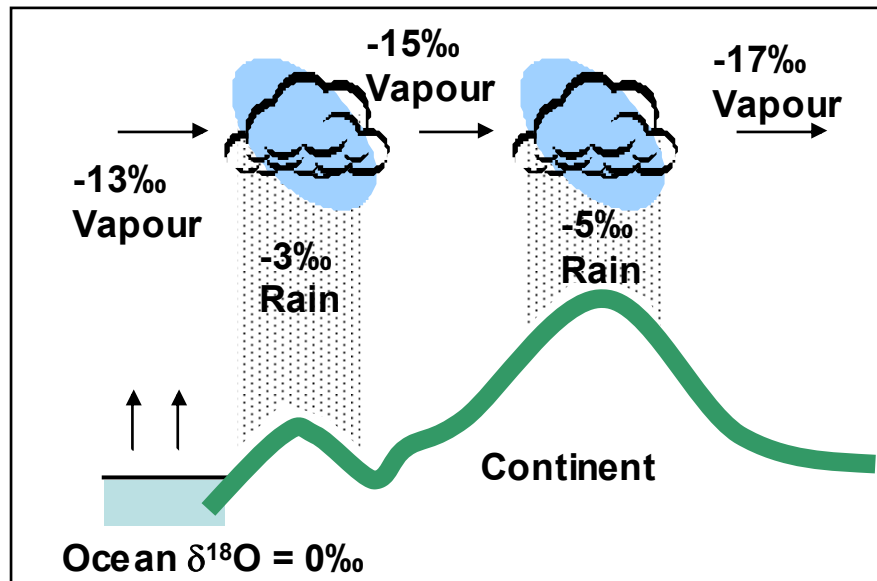
The average kinetic energy (K.E.) per molecule is the same for all ideal gases at a given temperature. Consider the molecules $^{12}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{18}\text{O}$ with masses 28 and 30

$\text{K.E.} = \frac{1}{2}mv^2$ so, if K.E. is equal, but mass is different, velocity must also be different by $(30/28)^{1/2} = 1.035$ i.e. At all temperatures the average velocity of $^{12}\text{C}^{16}\text{O}$ is 3.5% higher than $^{12}\text{C}^{18}\text{O}$ in the same system. This causes isotopic fractionation because e.g. in a diffusive system, the light molecules will leave more quickly, leaving the system enriched in the heavy isotope.

In evaporation, the higher velocities of the light molecules allow them to break through the liquid surface preferentially. For example the $\delta^{18}\text{O}$ of water vapour above the ocean is about $-13\text{‰}_{\text{SMOW}}$ but the equilibrium fractionation factor predicts -9‰ , **the difference is the kinetic effect.**

Heavy isotope molecules are more stable and it is easier to break e.g. $^{32}\text{S-O}$ than $^{34}\text{S-O}$ bonds. Dissociation and bacterial reactions can produce large fractionations, predominantly in **low temperature processes.**

Evaporation - Precipitation



During evaporation, water vapour is enriched in ^{16}O because H_2^{16}O has a higher vapour pressure than other combinations of isotopes.

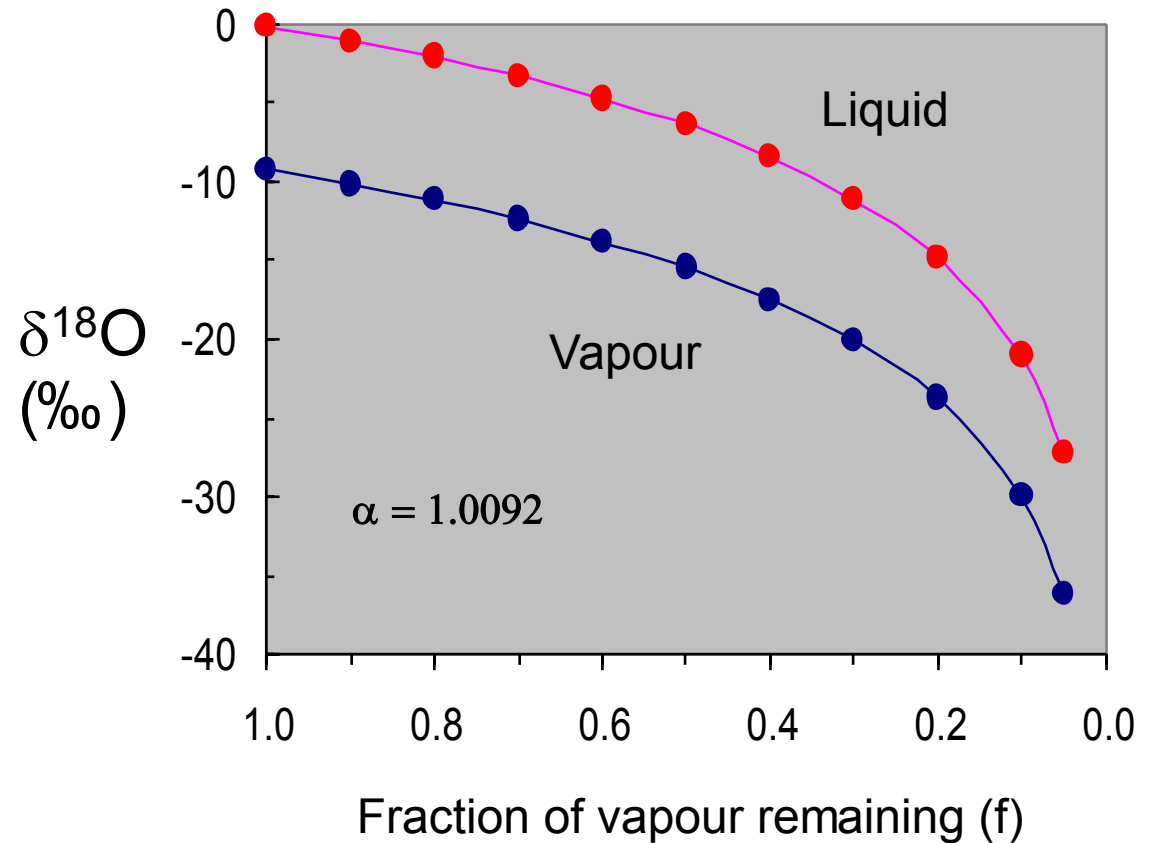
Rain drops and snow are enriched in ^{18}O .

Thus, an air mass evolves lower $\delta^{18}\text{O}$ as precipitation is removed from it.

Rayleigh Distillation

$$R/R_0 = f^{(\alpha - 1)}$$

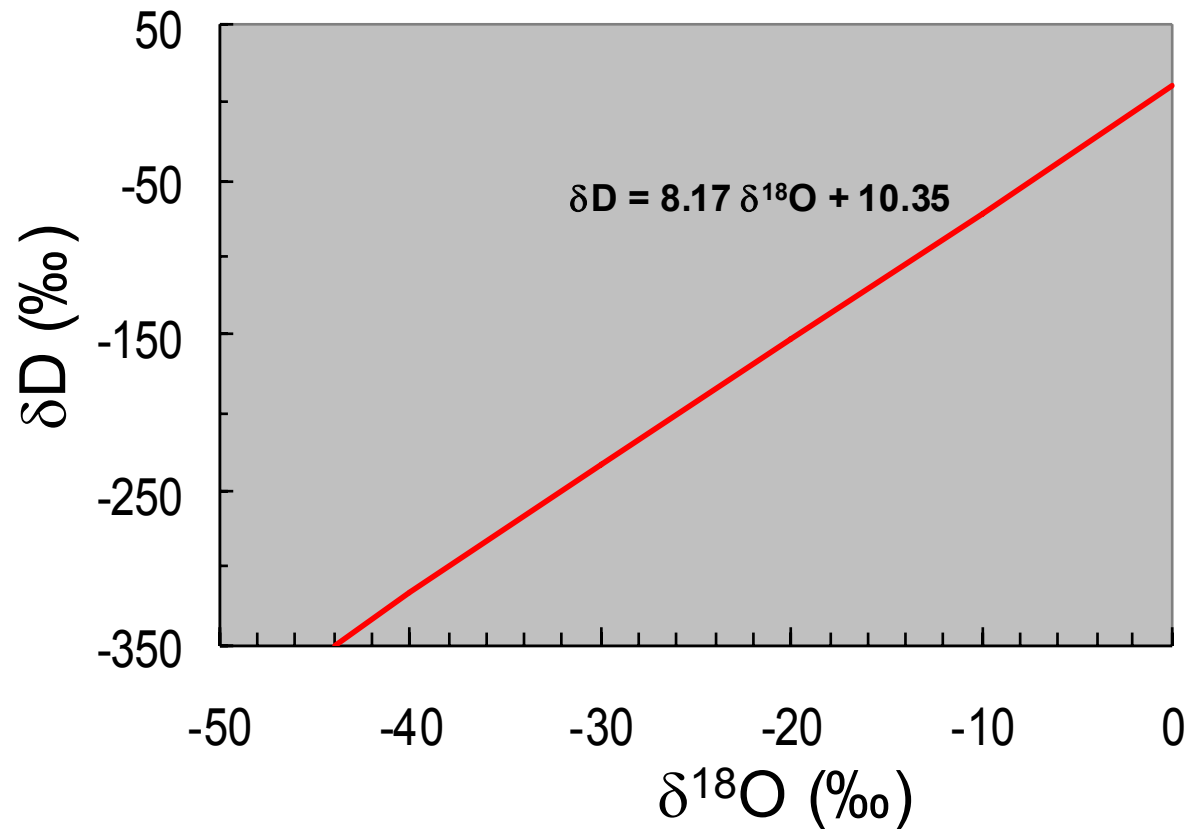
R – $^{18}\text{O}/^{16}\text{O}$ of vapour
R₀ – initial $^{18}\text{O}/^{16}\text{O}$
f - fraction of vapour left
 α - fractionation factor

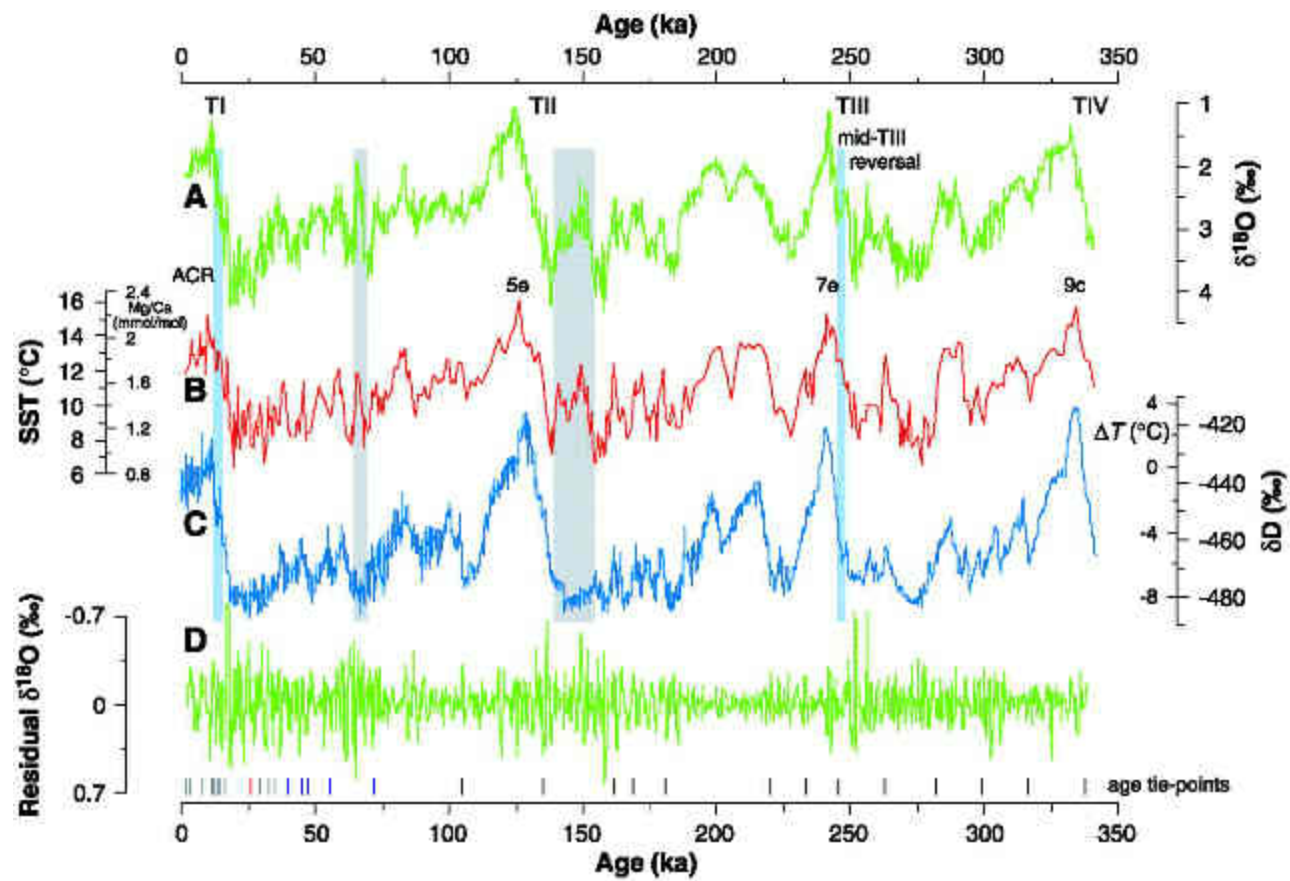


Global Meteoric Water Curve

In all evaporation – condensation processes H isotopes are fractionated in proportion to O isotopes because a corresponding difference in vapour pressure exists between H_2O - HDO and H_2^{16}O - H_2^{18}O . Therefore, δD and $\delta^{18}\text{O}$ in meteoric waters are always correlated.

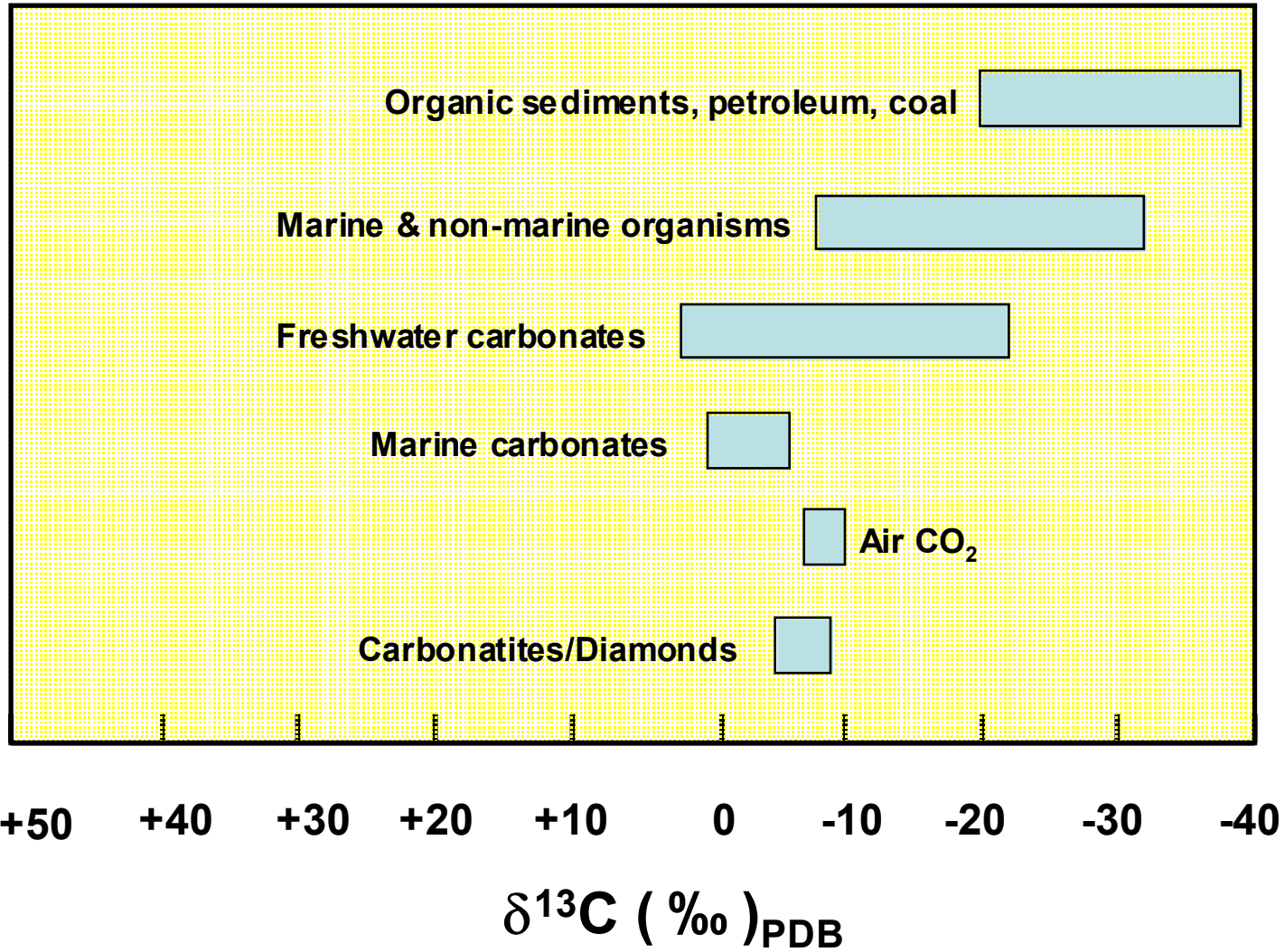
In detail there are non equilibrium effects which impose local variations but the curve is a good approximation





Pahnke et al. (2003) *Science* 301, 5635, 948-952.

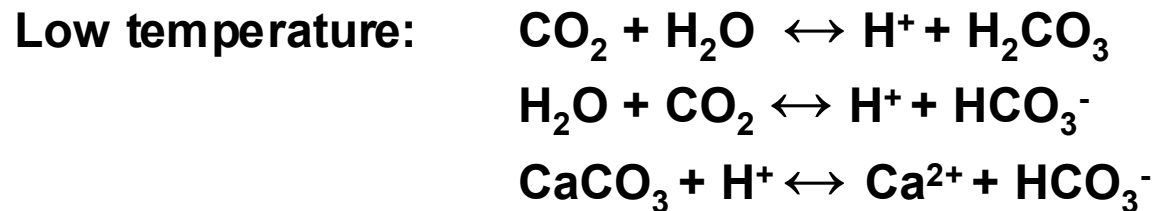
Carbon – important reservoirs



Carbon

Fractionation mechanisms

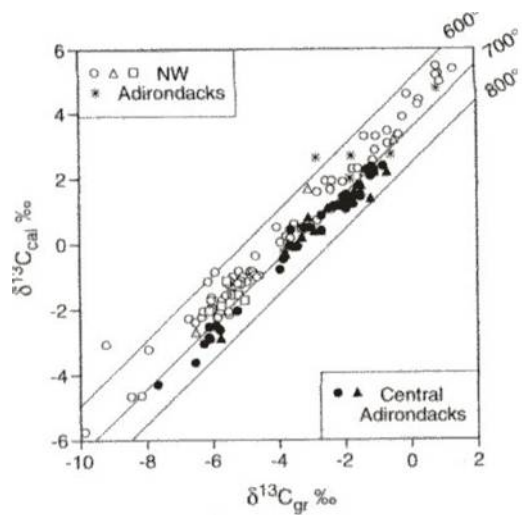
1. Isotopic equilibrium exchange reactions within inorganic C system



Each of these equilibria involves a temperature dependent isotope fractionation. Calcite enriched in ^{13}C relative to CO_2 by c. 10‰ at 20°C

At high temperature equilibrium isotope exchange within the system CO_2 – Carbonate – graphite – CH_4 . In particular, the calcite – graphite fractionation yields a useful geothermometer.

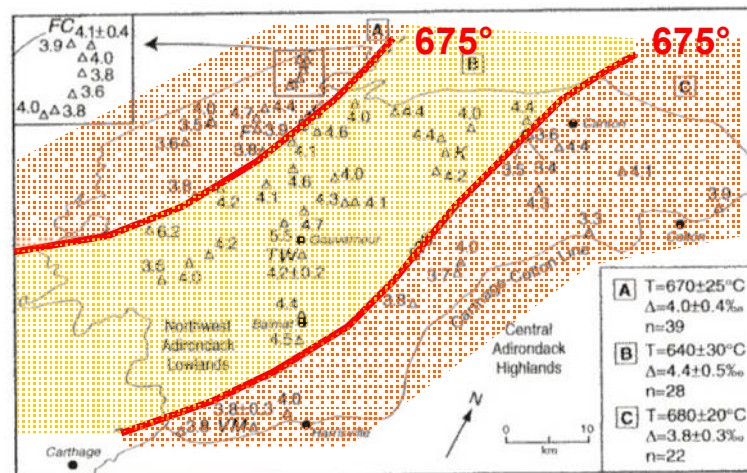
Calcite
 $\delta^{13}\text{C}$



Calcite-Graphite
C-Isotope Geothermometry

Adirondacks Marbles

Graphite $\delta^{13}\text{C}$



After: Kitchen & Valley (1995)
J. Metamor. Geol. 12, 7577-594

Carbon

Fractionation mechanisms

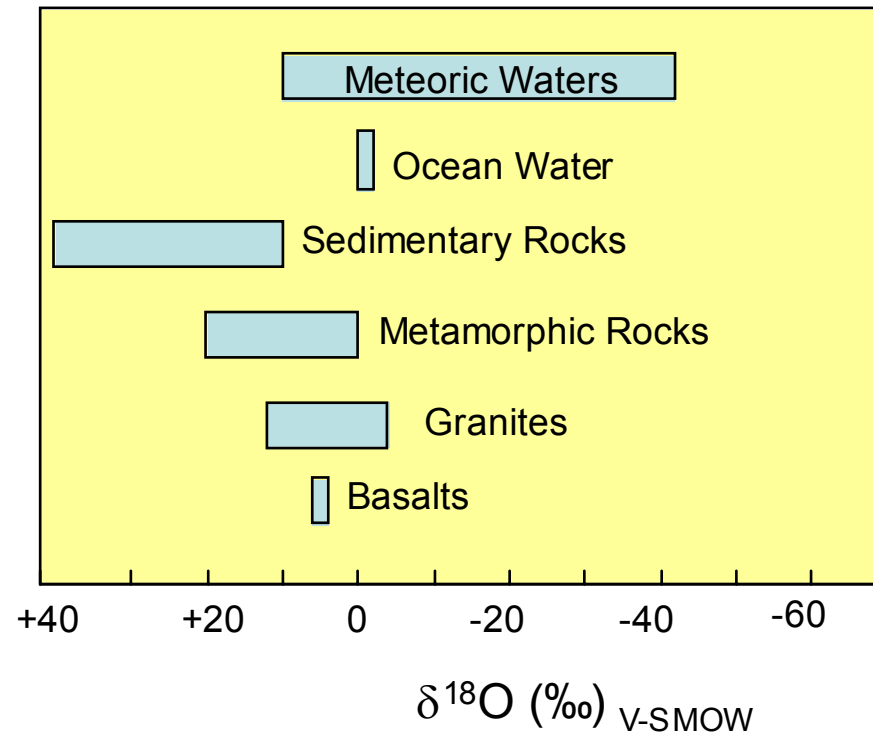
2. Kinetic effects during photosynthesis concentrate ^{12}C in synthesized organic matter.

So-called C3 and C4 plants vary in the mechanisms used to fix C and synthesize plant tissue. C3 plants are less efficient at C fixation and induce a large isotope fractionation. C4 plants are more efficient and induce less isotope fractionation.

C3 $\delta^{13}\text{C} = -18 \text{ ‰}$

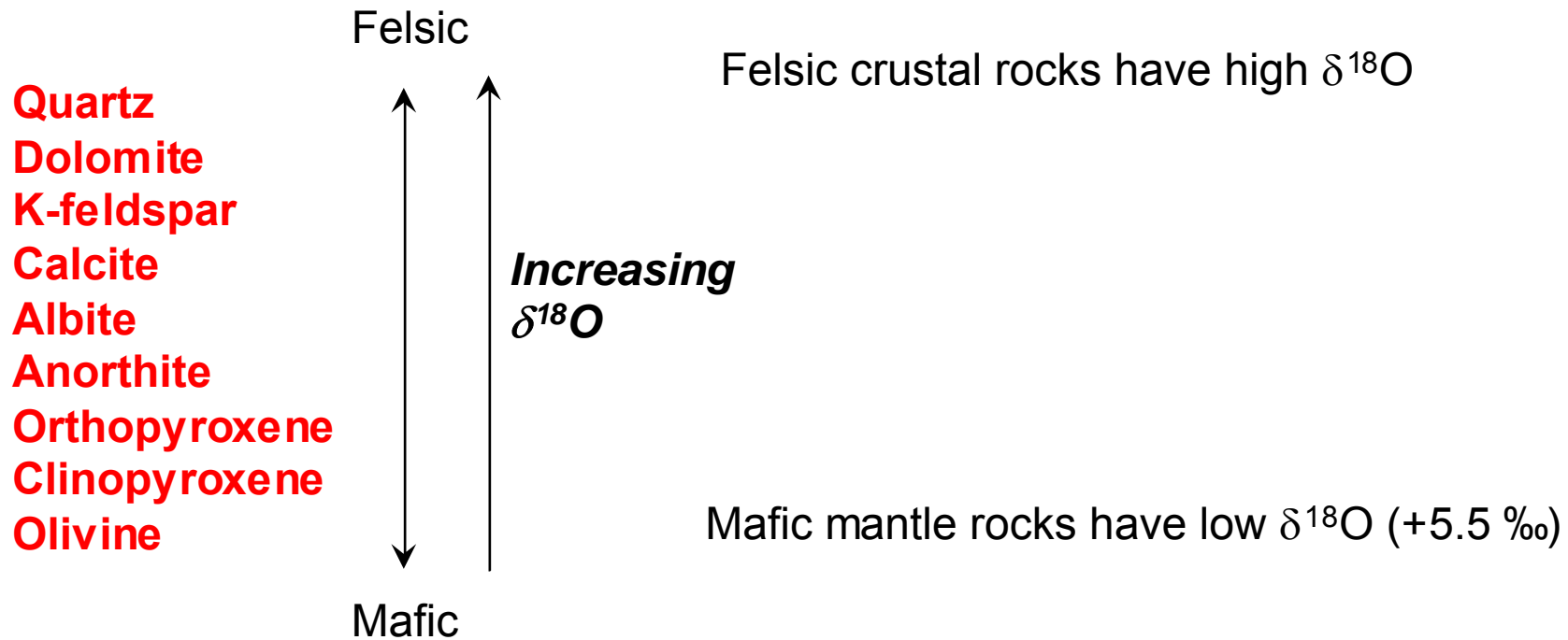
C4 $\delta^{13}\text{C} = -4 \text{ ‰}$ relative to atmospheric CO_2

Oxygen – important reservoirs

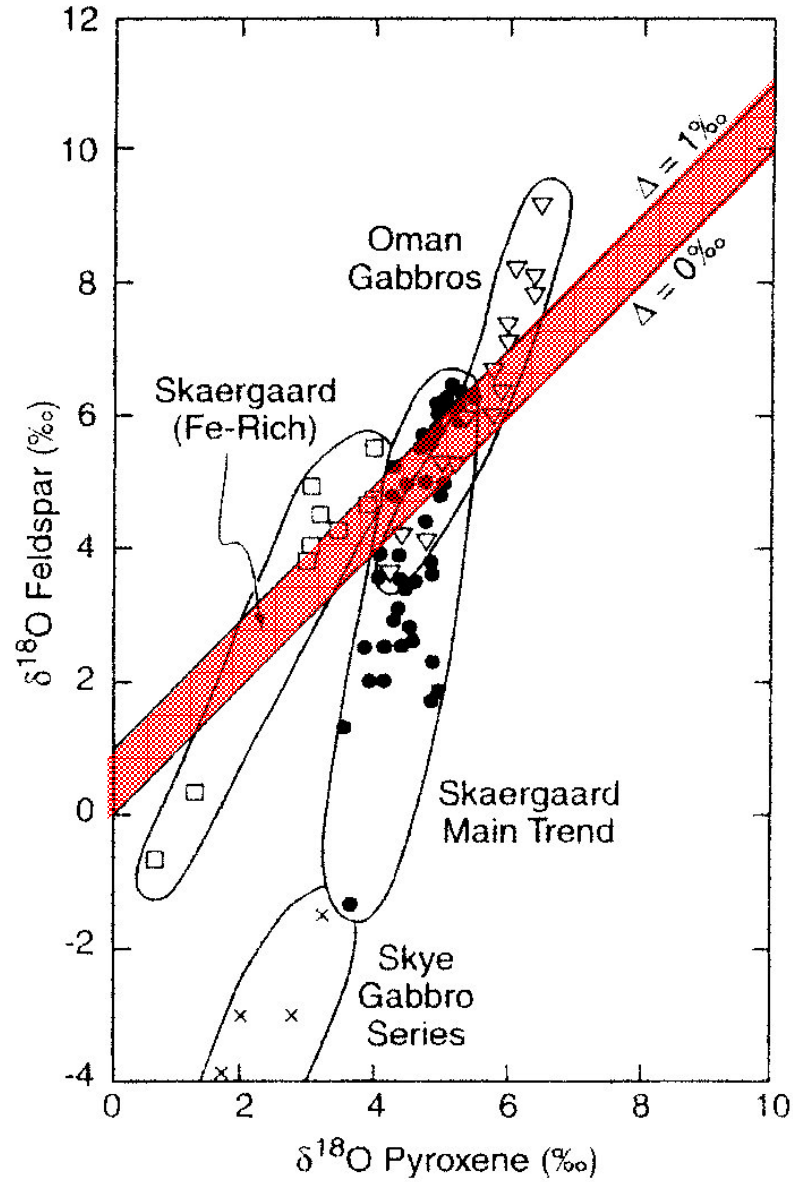


Oxygen

Minerals ranked in order of tendency to concentrate ^{18}O



Fluid – Rock Interaction



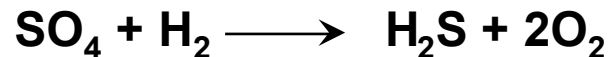
Equilibrium phases plot along straight line with slope = 1 and small Δ offset from 0.

After: Criss et al. (1987)
GCA 51, 1099-1108

Sulphur

Fractionation mechanisms:

1. Sulphate reduction by bacteria
e.g. *Desulfovibrio desulfuricans*

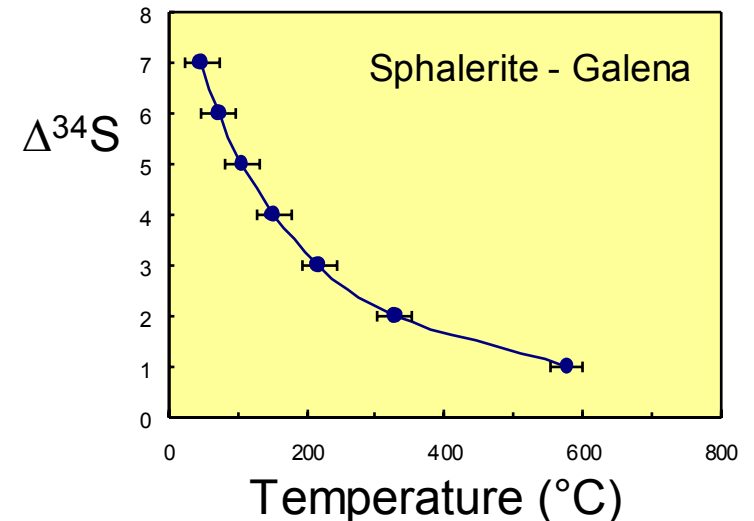


in which H_2S is enriched in ^{32}S cf SO_4
producing strongly negative $\delta^{34}\text{S}$ in reduced S.

2. Chemical exchange reactions between sulphate and sulphide and between sulphide minerals.

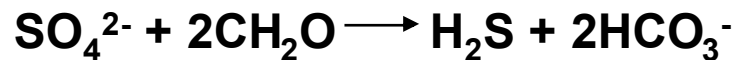
Pairs of sulphide minerals show different $\delta^{34}\text{S}$ with the difference being a function of formation temperature of the form:

$\Delta^{34}\text{S} = A/T^2$ - where A is a characteristic constant and T is absolute temperature (K)



Biogenic S fractionation

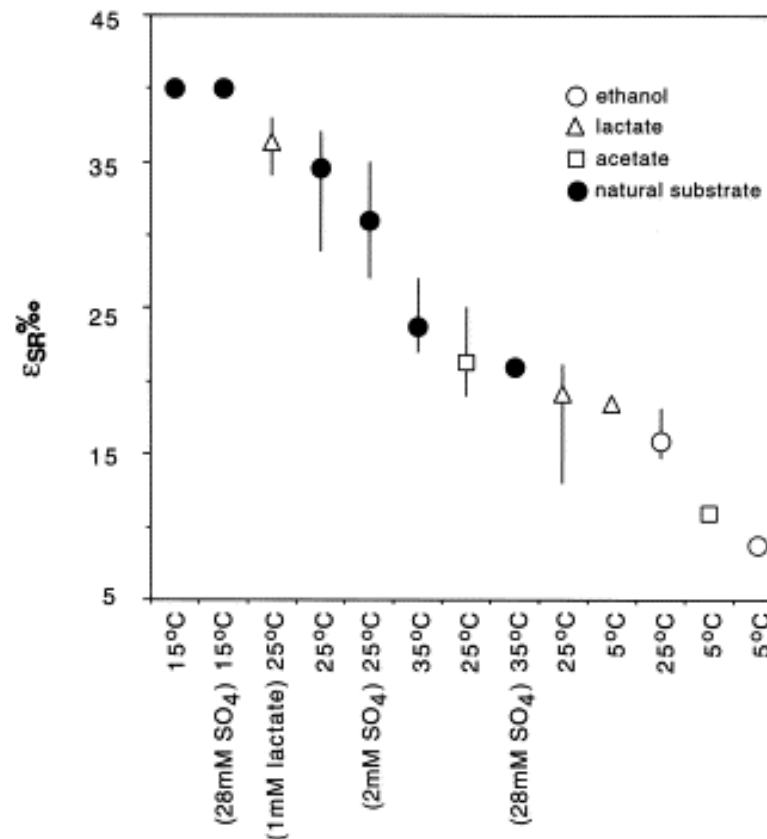
Over 100 organisms are known that gain energy through reduction of sulphate while oxidising organic C or H



In general the rate limiting step is the breaking of the first S-O bond as sulphate is reduced to sulphite.

Laboratory experiments using bacterial cultures gave mixed results with sulphite depleted in ^{34}S by 4-46 ‰.

Recent experiments on natural populations yield large fractionations.



Sulphur – important reservoirs

