Isotope Geochemistry I
Applications of Stable Isotopes

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Examples of applications

To establish an isotopic “profile” for a material, the ratios of the stable isotopes of a number of elements such us $^{2}H/^{1}H$, $^{13}C/^{12}C$, $^{15}N/^{14}N$ and $^{18}O/^{16}O$ can be measured. The isotopic abundances of these elements were fixed when Earth was formed and, on a global scale, have not changed since. Subtle variations in the isotopic composition may be introduced during biological, chemical and physical processes.

The technique:

Isotope Ratio Mass Spectrometry (IRMS) is used to measure the relative abundance of isotopes in different materials

Examples of applications

- Geosciences
  - Geochemistry and geology
    - Extent and temperature of post-burial alteration of rocks
    - Provenancing of clasts
    - Identifying the source of water smples

  - Palaeoclimatology
  - Paleoecology

Examples of applications

- Biological sciences
  - ➢ Ecology
    - Photosynthetic pathways
    - Food webs
    - Ecohydrology
    - Nutrient cycling
  - ➢ Human provenancing
  - ➢ Metabolic studies
  - ➢ Sports medecine
  - ➢ Toxicology
    - Distinguishing endogenous vs exogenous bio-chemicals

Examples of applications

- Forensic sciences
  - ➢Environmental forensics and monitoring
    - Identifying the source of poluutants (eg. Oil spills)
    - Monitoring atmospheric gases to distiguish between natural – anthropogenic sources
    - Climate studies
    - Water cycle research
  - ➢ Food authenticity and traceability
    - Identifying adulteration of foods with cheaper foodstuffs

Isotopes

- Isotopes have different ## of neutrons, and thus a different mass
- Affect on reactions in small, but real, and provides another measurement of reactions – affected by similar physicochemical parameters!
- Also a critical tracer – the isotopes can be used to track molecules in a reaction!

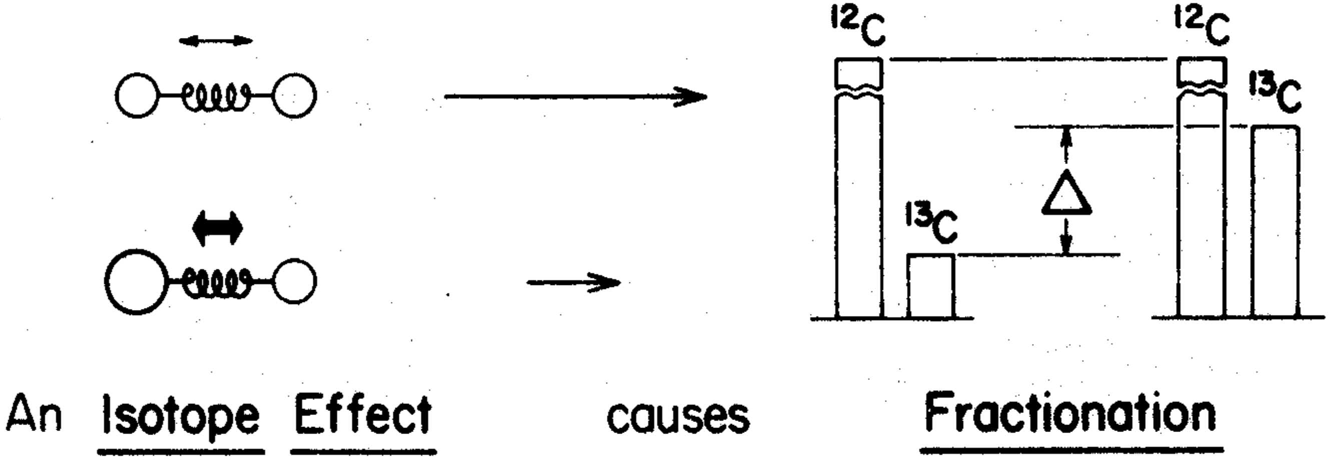
Table 1.2 Atomic Weights and Abundances of the Stable H, C, N, and O Isotopes

Element	Isotope	Atomic Weight (amu)	Abundance (atom %)
Hydrogen ($Z = 1$)		**1.0079**	
	^{1}H (Protium)	1.007825	99.985
	^{2}H (D or Deuterium)	2.014102	0.015
Carbon ($Z = 6$)		**12.011**	
	^{12}C	12.00000	98.90
	^{13}C	13.00335	1.10
Nitrogen ($Z = 7$)		**14.0067**	
	^{14}N	14.003074	99.63
	^{15}N	15.000109	0.37
Oxygen ($Z = 8$)		**15.9994**	
	^{16}O	15.994915	99.76
	^{17}O	16.999131	0.04
	^{18}O	17.999160	0.20

Source: Walker et al., 1989.

Fractionation

- A reaction or process which selects for one of the stable isotopes of a particular element
- If the process selects for the heavier isotope, the reaction product is ‘heavy’, the reactant remaining is ‘light’



Fractionation Factor, α

- R is the ratio of heavy to light isotopes
- α, or fractionation factor, is the ratio between reactant and product

$$\alpha = \frac{R_{reac\tan ts}}{R_{products}}$$

$$H_2O_{water} \longleftrightarrow H_2O_{vapor}$$

$$\alpha^{18}O_{water\text{-}vapor} = \frac{(^{18}O/^{16}O)_{water}}{(^{18}O/^{16}O)_{vapor}}$$

Why a ratio???

- Differences between 2 isotopes of one element is VERY small – to measure them individually with enough precision is difficult to impossible for most isotope systems
- By comparing a sample ratio to a standard ratio, the difference between these two can be determined much more precisely!!

Isotope Standards

- VSMOW – Vienna Standard Mean Ocean Water – bunch of ocean water kept in Austria – O and H standard
- PDB – Pee Dee Belemnite – fossil of a belemnite from the Pee Dee formation in Canada – C and O
- CDT – Canyon Diablo Troilite –meteorite fragment from meteor crater in Arizona, contains FeS mineral Troilite – S
- AIR – Atmospheric air - N

Measuring Isotopes

- While different, isotopes of the same element exist in certain fractions corresponding to their natural abundance (adjusted by fractionation)

$$\alpha_b^a = \frac{R_a}{R_b}$$

Where R_a is the ratio of heavy/light isotope and α is the fractionation factor

- We measure isotopes as a ratio of the isotope vs. a standard material (per mille ‰)

$$\delta^{18}O = \left(\frac{R_{sample} - R_{\text{standard}}}{R_{\text{standard}}} \right) \times 10^3$$

‰

$$10^3 \ln \alpha_b^a \approx \delta_a - \delta_b = \Delta_b^a$$

δ is “delta”, and is the isotope ratio of a particular thing (molecule, mineral, gas) relative to a standard times 1000. sometimes called ‘del’

$$\delta^{18}O = \left(\frac{R_{sample} - R_{\mathrm{standard}}}{R_{\mathrm{standard}}} \right) \times 10^{3}$$

Δ is “delta” and is the difference between two different isotope ratios in a reaction:

$$\Delta_{A-B} = \delta_{A} - \delta_{B}$$

Many isotopers are very sensitive about misuses of isotope terminology. Harmon Craig’s immortal limerick says it all:

There was was a young man from Cornell
Who pronounced every "delta" as "del"
But the spirit of Urey
Returned in a fury
And transferred that fellow to hell

Equilibrium Fractionation

- For an exchange reaction:

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

- Write the equilibrium:

$$K = \frac{(C^{18}O_2)^{\frac{1}{2}}(H^{16}{}_2O)}{(C^{16}O_2)^{\frac{1}{2}}(H^{18}{}_2O)}$$

- Where activity coefficients effectively cancel out
- For isotope reactions, K is always small, usually 1.0xx (this K is 1.047 for example)

WHY IS K DIFFERENT FROM 1.0?

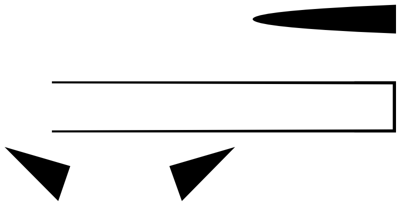
Because ^{18}O forms a stronger covalent bond with C than does ^{16}O.

The vibrational energy of a molecule is given by the equations:

$$\boxed{E_{vibrational} = \tfrac{1}{2} h\nu}$$

$$\boxed{\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}}}$$

$$\boxed{F = -kx}$$



Thus, the frequency of vibration depends on the mass of the atoms, so the energy of a molecule depends on its mass.

- The heavy isotope forms a lower energy bond; it does not vibrate as violently. Therefore, it forms a stronger bond in the compound.
- The Rule of Bigeleisen (1965) - The heavy isotope goes preferentially into the compound with the strongest bonds.

Temperature effects on fractionation

- The fractionation factors, α, are affected by T (recall that this affects E_A) and defined empirically:

$$10^3 \ln \alpha_b^a = \frac{A \times 10^6}{T^2} + B$$

Where A and B are constants determined for particular reactions and T is temp. in Kelvins

- Then,

$$\boxed{10^3 \ln \alpha_b^a \approx \delta_a - \delta_b = \Delta_b^a}$$

- As T increases, Δ decreases – at high T Δ goes to zero

FRACTIONATION DURING PHYSICAL PROCESSES

- Mass differences also give rise to fractionation during physical processes (diffusion, evaporation, freezing, etc.).
- Fractionation during physical process is a result of differences in the velocities of isotopic molecules of the same compound.
- Consider molecules in a gas. All molecules have the same average kinetic energy, which is a function of temperature.

$$E_{kinetic} = {}^{1}\!/_{2}\, mv^2$$

Using isotopes to get information on physical and chemical processes

- Fractionation is due to some reaction, different isotopes can have different fractionation for the same reaction, and different reactions have different fractionations, as well as being different at different temperatures and pressures
- Use this to understand physical-chemical processes, mass transfer, temperature changes, and other things…

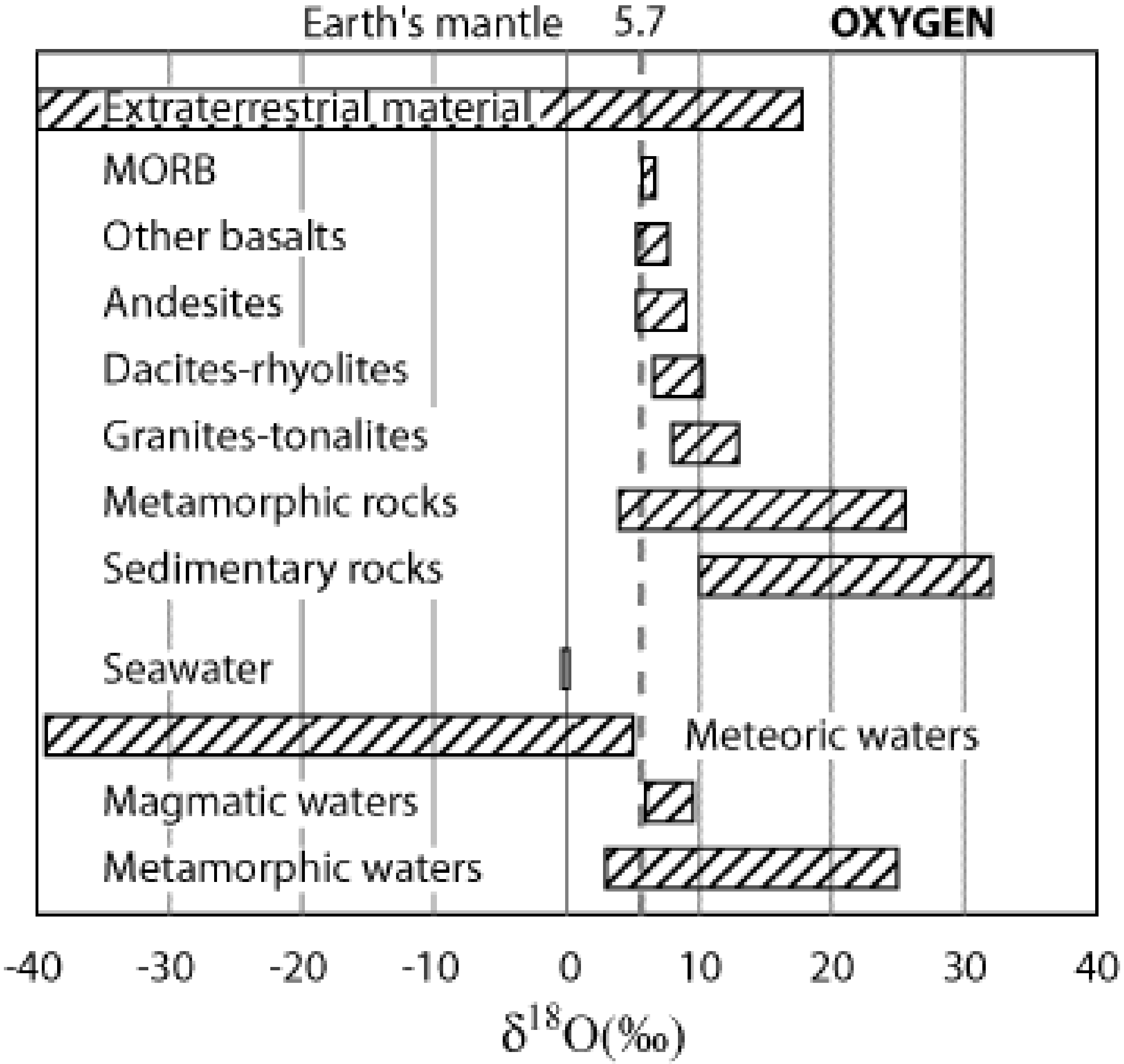


Figure 2. Typical oxygen isotopic composition of selected natural materials. Dashed line represents the earth's mantle. Modified from Hoefs (1997) and Best (2003). Igneous rock values exclude hydrothermally altered rocks.

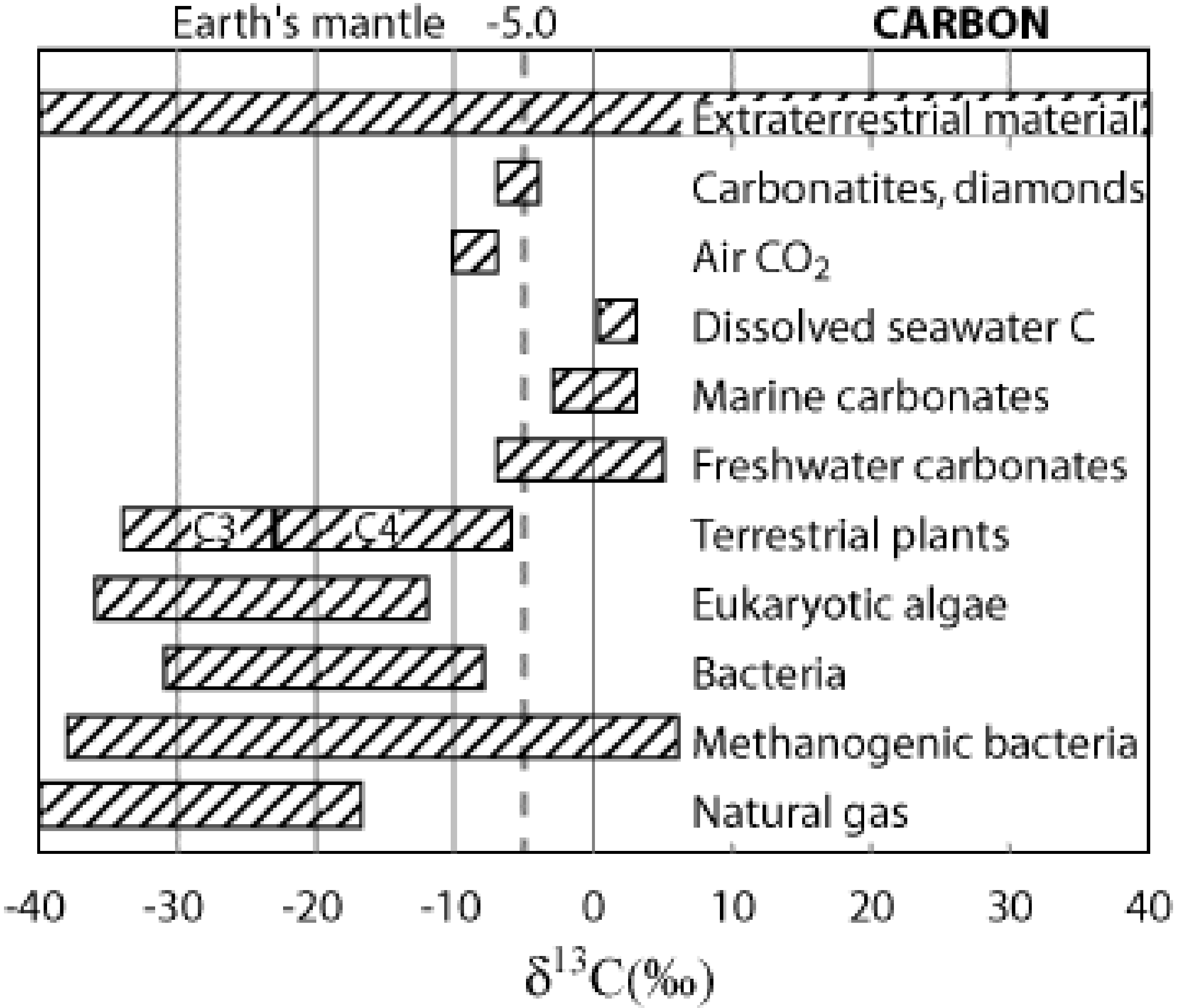


Figure 3. Typical carbon isotopic composition of selected natural materials. Dashed line represents the earth's mantle. Modified from Hoefs (1997). Terrestrial plants include ranges for C3 and C4 plants that use different photosynthetic pathways.

Equilibrium Fractionation II

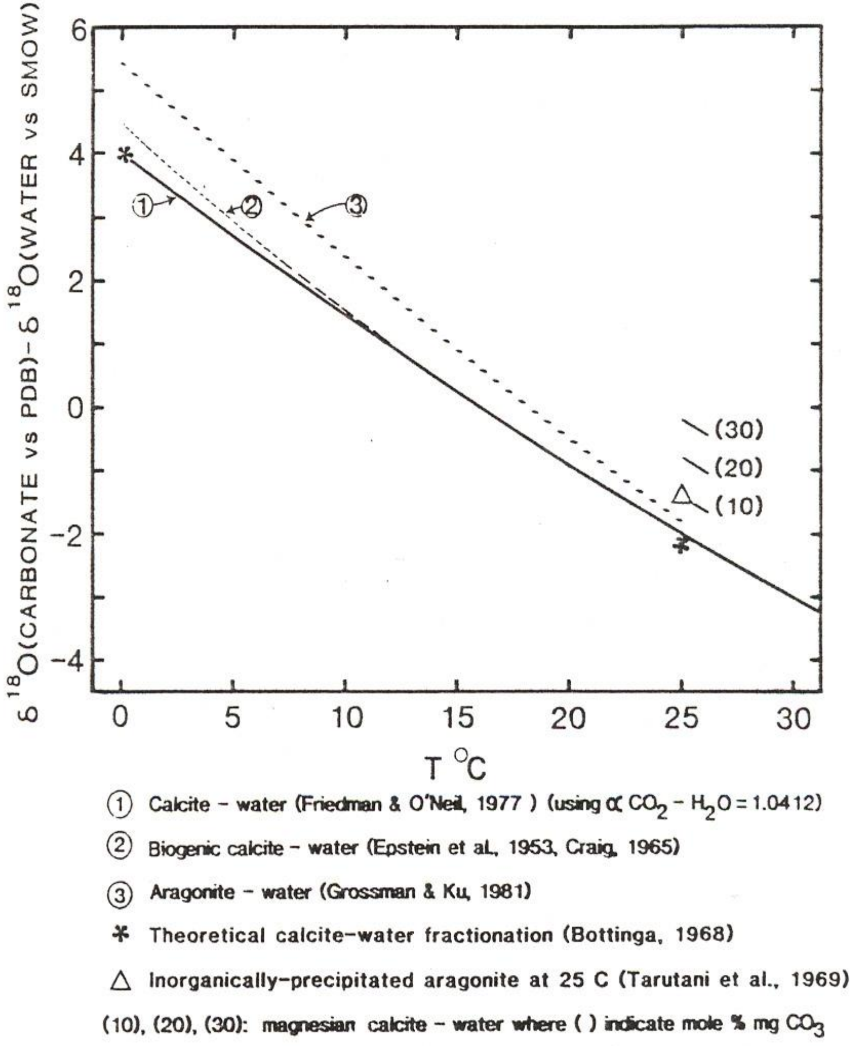
- For a mass-dependent reaction:
- $Ca^{2+} + C^{18}O_3^{2-} \rightarrow CaC^{18}O_3$
- $Ca^{2+} + C^{16}O_3^{2-} \rightarrow CaC^{16}O_3$
- Measure $\delta^{18}O$ in calcite ($\delta^{18}O_{cc}$) and water ($\delta^{18}O_{sw}$)
- Assumes $^{18}O/^{16}O$ between H_2O and CO_3^{2-} at some equilibrium

$$\mathbf{T\ ^{o}C = 16.998 - 4.52\ (\delta^{18}O_{cc} - \delta^{18}O_{sw}) + 0.028\ (\delta^{18}O_{cc} - \delta^{18}O_{sw})^2}$$

Empirical Relationship between Temp. & Oxygen Isotope Ratios in Carbonates

At lower temperatures, calcite crystallization tends to incorporate a relatively larger proportion of ^{18}O because the energy level (vibration) of ions containing this heavier isotope decreases by a greater amount than ions containing ^{16}O.

As temperatures drop, the energy level of ^{18}O declines progressively by an amount that this disproportionately greater than that of the lighter ^{16}O.



ISOTOPE FRACTIONATION IN THE HYDROSPHERE

Evaporation of surface water in equatorial regions causes formation of air masses with H_2O vapor depleted in ^{18}O and D compared to seawater.

This moist air is forced into more northerly, cooler air in the northern hemisphere, where water condenses, and this condensate is enriched in ^{18}O and D compared to the remaining vapor.

The relationship between the isotopic composition of liquid and vapor is:

$$\delta^{18}O_l = \alpha_v^l\left(\delta^{18}O_v + 10^3\right) - 10^3$$

Assuming that $\delta^{18}O_v$ = -13.1‰ and $\alpha_v^l(O)$ = 1.0092 at 25°C, then

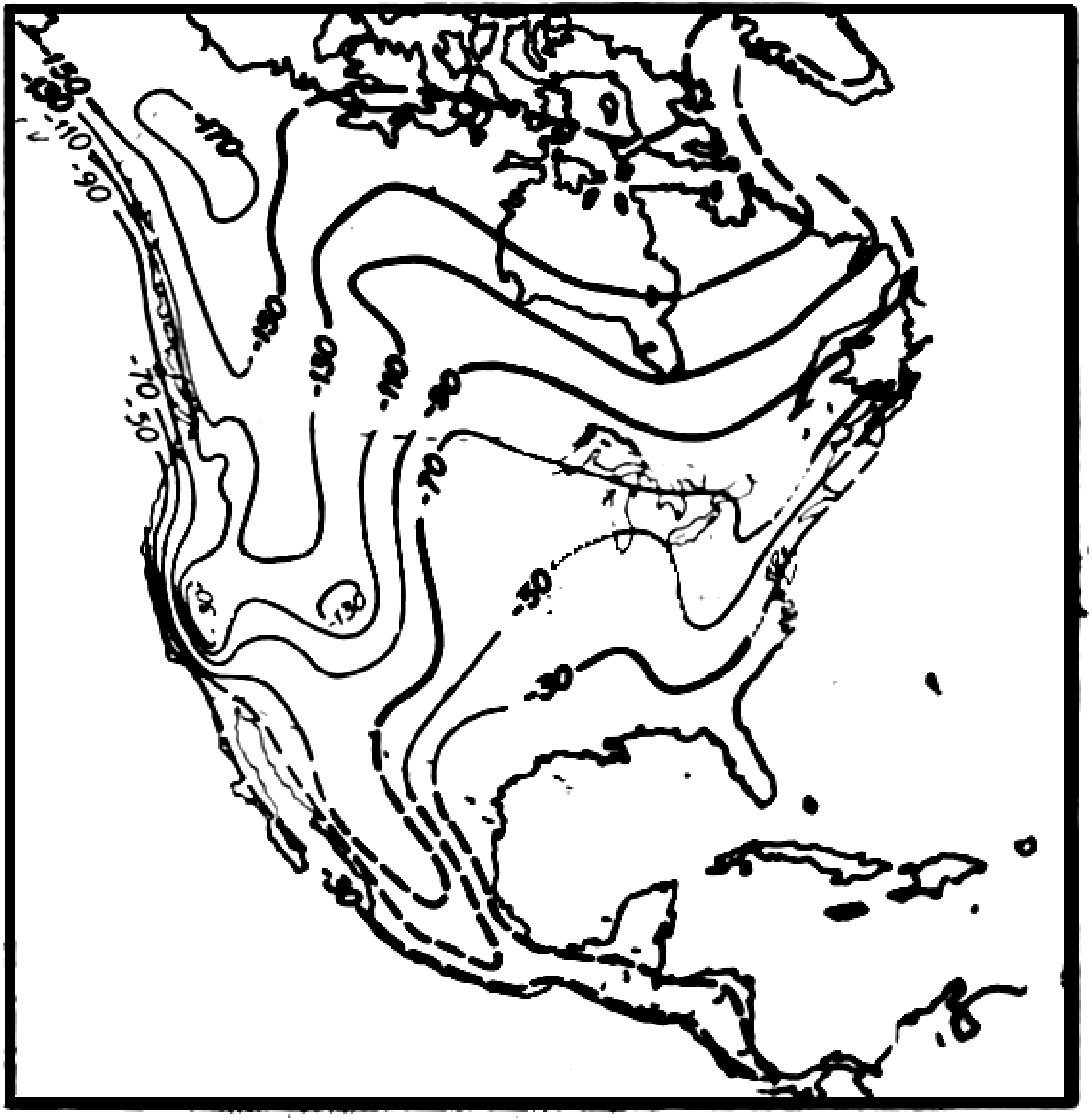
$$\delta^{18}O_l = 1.0092\left(-13.1 + 10^3\right) - 10^3 = -4.0\text{‰}$$

and assuming δD_v = -94.8‰ and $\alpha_v^l(H)$ = 1.074 at 25°C, then

$$\delta D_l = 1.074\left(-94.8 + 10^3\right) - 10^3 = -27.8\text{‰}$$

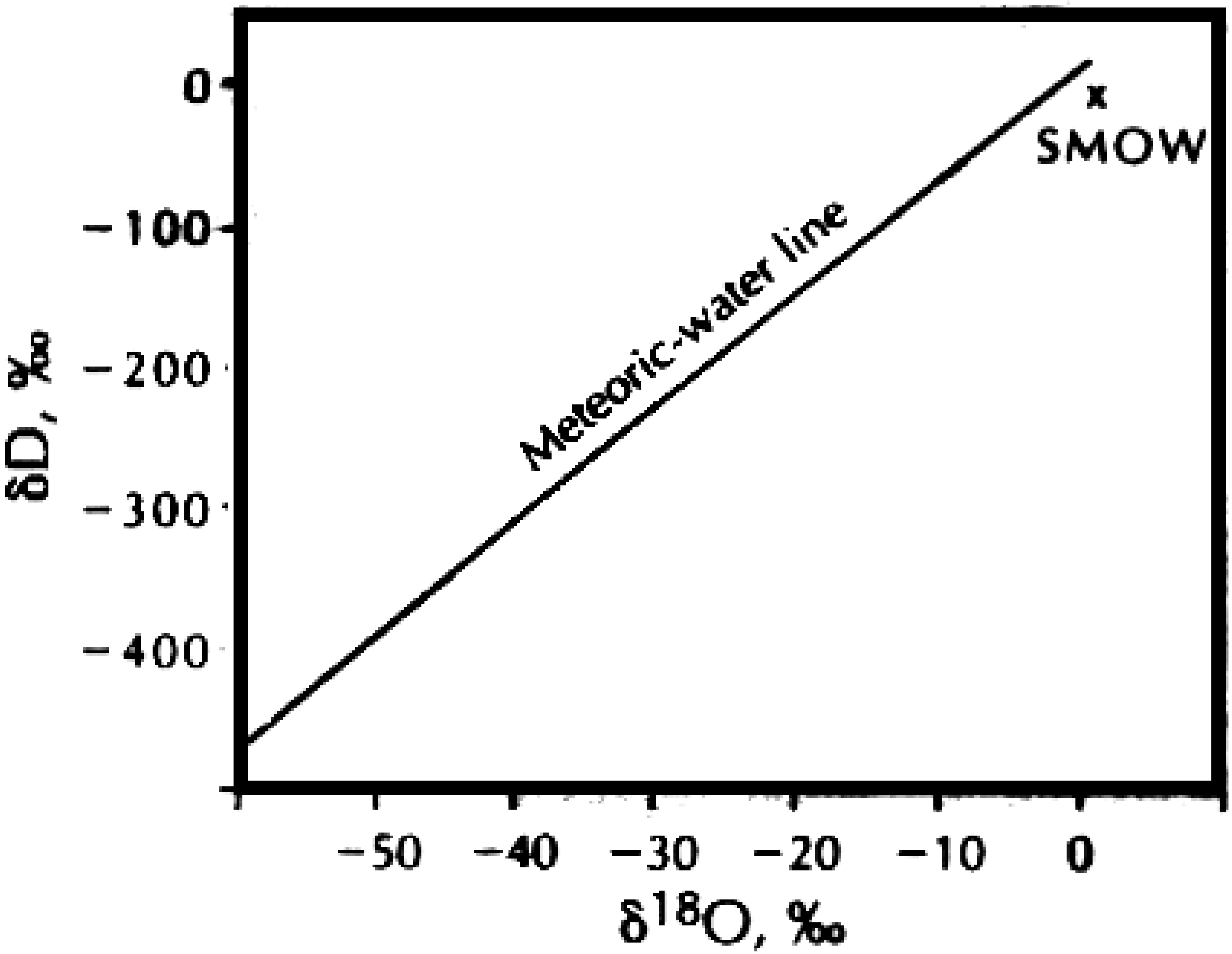
These equations give the isotopic composition of the first bit of precipitation. As ^{18}O and D are removed from the vapor, the remaining vapor becomes more and more depleted.

Thus, $\delta^{18}O$ and δD values become increasingly negative with increasing geographic latititude (and altitude.



Map of North America showing contours of the approximate average δD values of meteoric surface waters.

Because both H and O occur together in water, $\delta^{18}O$ and δD are highly correlated, yielding the meteoric water line (MWL): $\delta D \approx 8\delta^{18}O + 10$

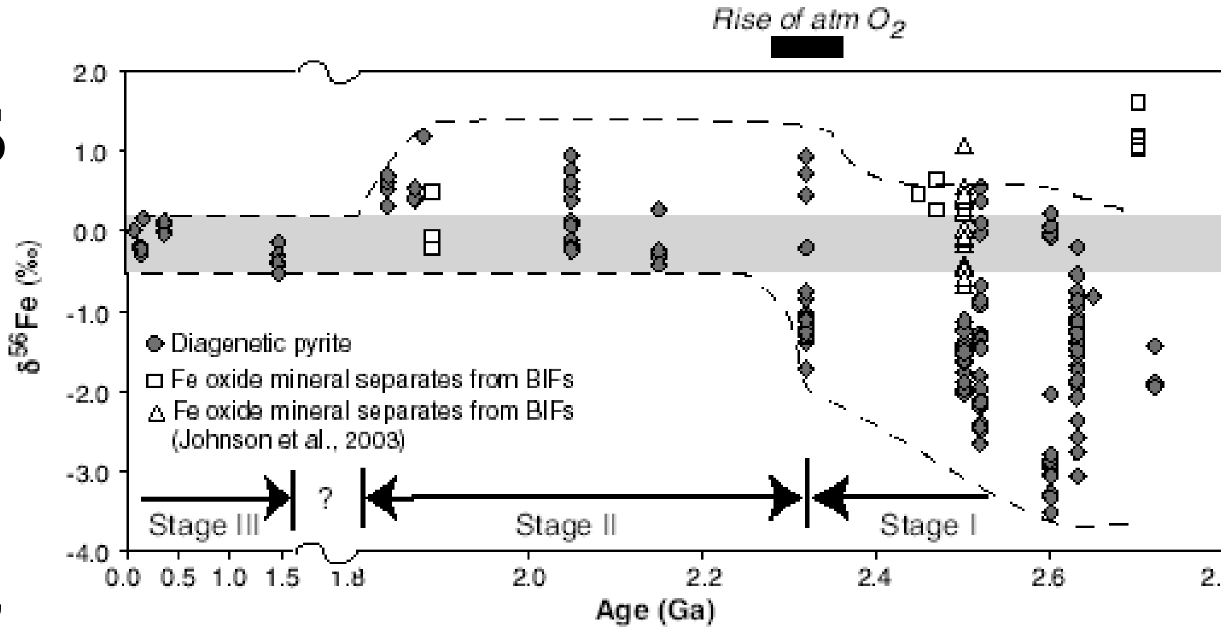


Deviation from MWL

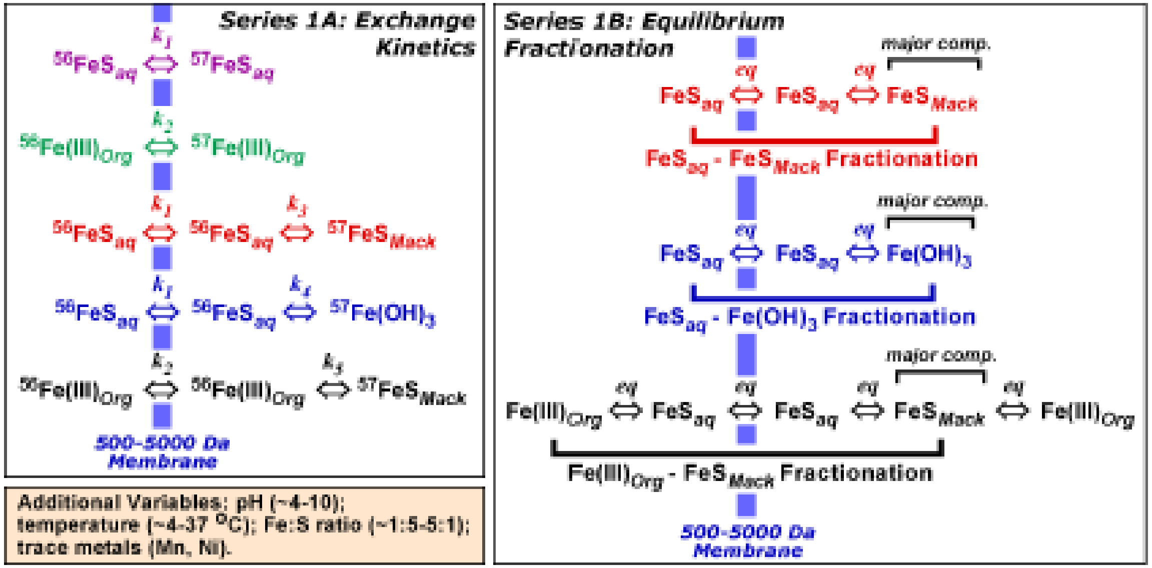
- Any additional fractionation process which affects O and D differently, or one to the exclusion of the other will skew a water away from the MWL plot
- These effects include:
  - Elevation effects - (δD -8‰/1000m, -4‰/ºC)
  - Temperature (α different!)
  - Evapotranspiration and steam loss
  - Water/rock interaction (little H in most rocks)

Iron Isotopes

Earth’s Oceans 3 Ga had no oxygen and lots of Fe^{2+}, cyanobacteria evolved, produced O_2 which oxidized the iron to form BIFs – in time the Fe^{2+} was more depleted and the oceans were stratified, then later become oxic as they are today



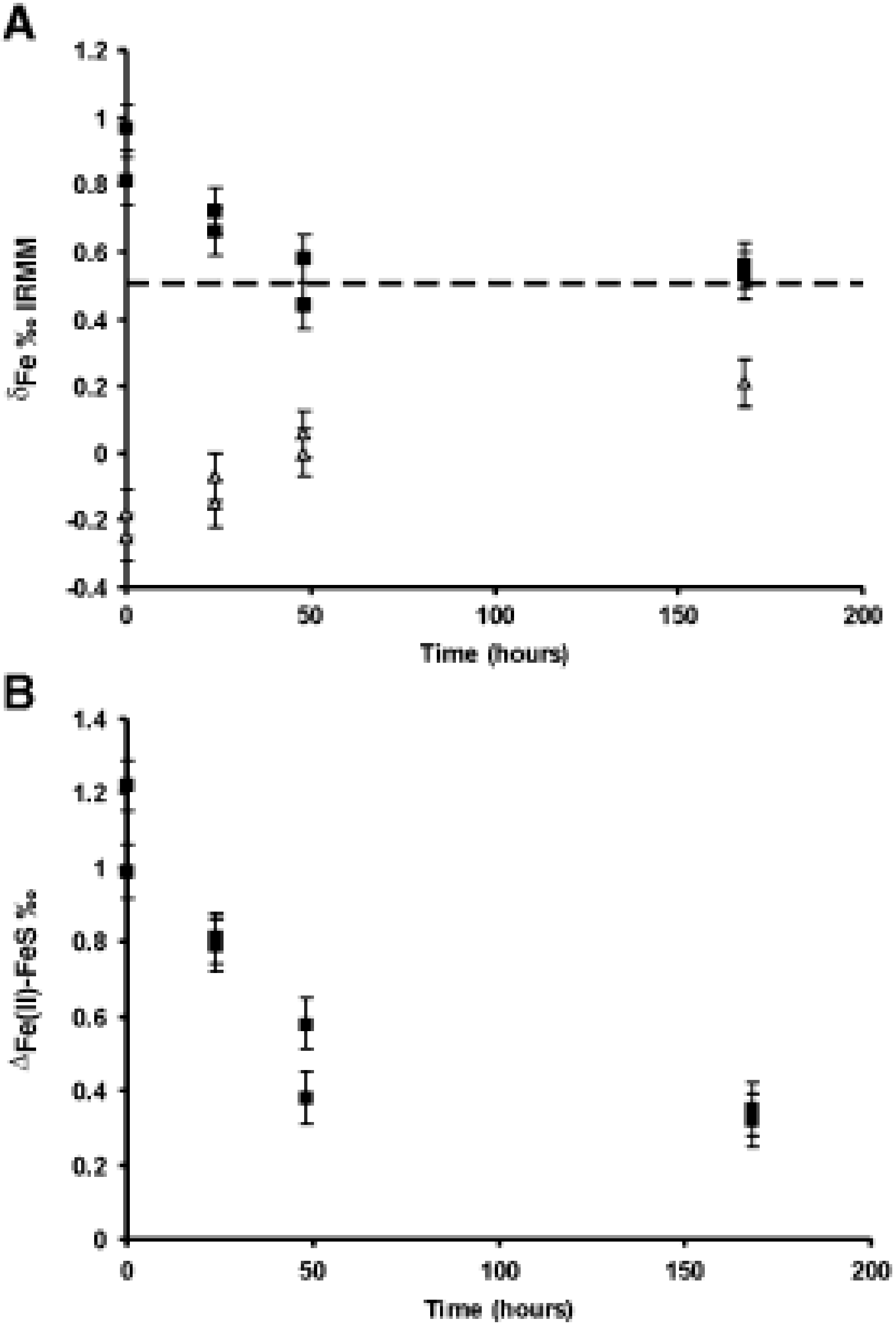
This interpretation is largely based on iron isotopes in iron oxides and sulfide minerals deposited at those times (Rouxel et al., 2005)



Additional Variables: pH (~4-10); temperature (~4-37 °C); Fe:S ratio (~1:5-5:1); trace metals (Mn, Ni).

Experiments

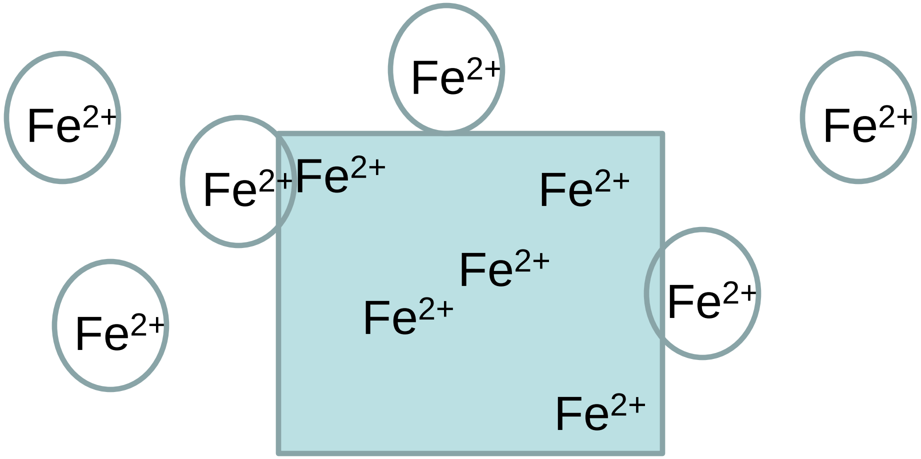
- Fe^{2+} and $FeS_{mackinawite}$ at equilibrium, separate physically (filter) and measure each component:

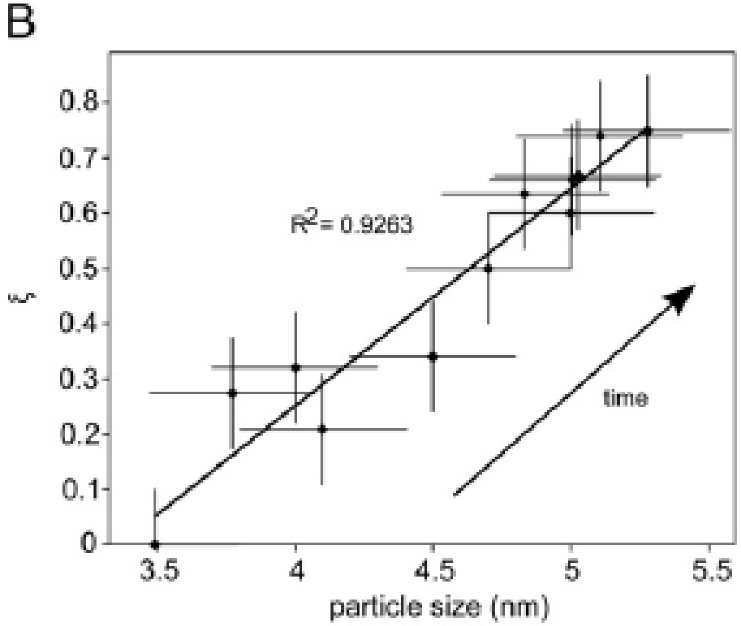


From Butler et al., 2005 EPSL 236 430-442

Fe –isotope exchange with a particle

- Particles coarsen via Ostwald ripening or topotactic alignment – how fast can isotopes exchange with Fe in a xstal actively getting bigger?
- At certain size internal Fe^{2+} does not exchange…



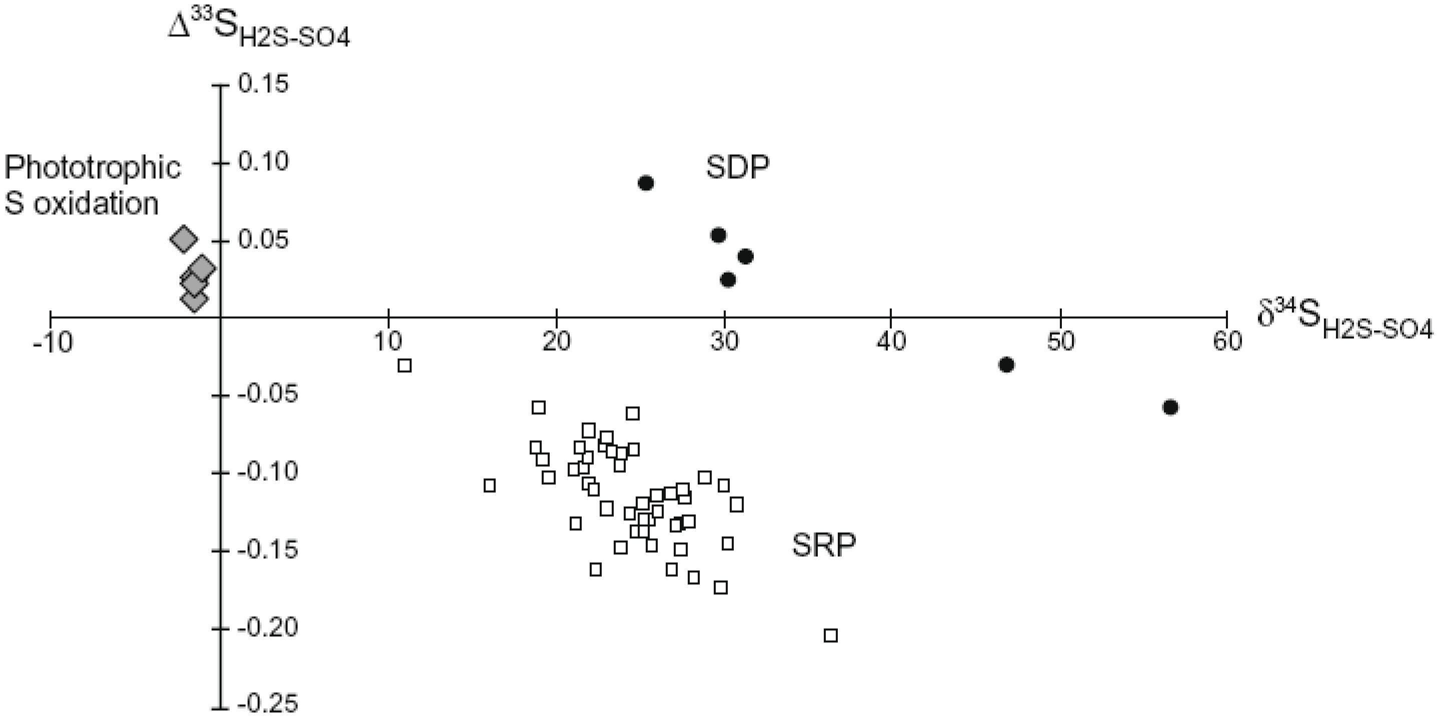


Guilbaud et al., 2010 EPSL 300 174-183

What can we get from using multiple isotopes?

- Many isotope systems have more than 2 stable isotopes – ^{56}Fe, ^{57}Fe, ^{58}Fe; ^{32}S, ^{33}S, ^{34}S, ^{36}S
- Looking at multiple isotopes can provide new insight on multiple processes, especially useful for complicated reaction pathways, also helps get at equilibrium v. kinetic processes, and mass-dependent v. independent processes…

- Tracing S-isotopic fractionation from different communities of organisms (Sulfate-reducers, sulfur disproportionation, phototrophic S oxid.)



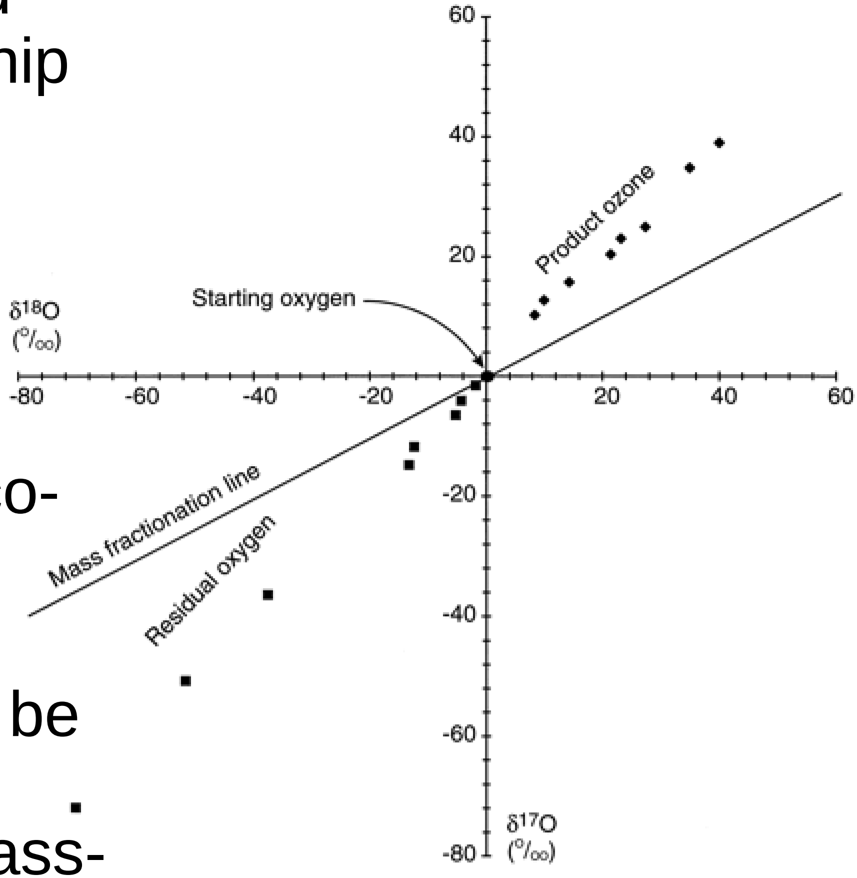
From Zerckle et al., 2009 GCA 73, 291-306

S isotopes and microbes

- The fractionation of H_2S formed from bacterial sulfate reduction (BSR) is affected by several processes:
  - Recycling and physical differentiation yields excessively depleted H_2S
  - Open systems – H_2S loss removes ^{34}S
  - Limited sulfate – governed by Rayleigh process, enriching ^{34}S
  - Different organisms and different organic substrates yield very different experimental $\delta^{34}S$
- Ends up as a poor indicator of BSR vs. TSR

Mass-independent fractionation

- Mass effects for 3 stable isotopes (such as ^{18}O, ^{17}O, and ^{16}O) should have a mass-dependent relationship between each for any process
- Deviation from this is mass-independent and thought to be indicative of a nuclear process (radiogenic, nucleosynthetic, spallation) as opposed to a physico-chemical process
- Found mainly associated with atmospheric chemistry, effect can be preserved as many geochemical reactions in water and rock are mass-dependent



S-isotopic evidence of Archaen atmosphere

- Farquar et al., 2001; Mojzsis et al., 2003 found MIF signal in S isotopes (^{32}S, ^{33}S, ^{34}S) preserved in archaen pyrites precipitated before 2.45 Ga
- Interpreted to be signal from the photolysis of SO_2 in that atmosphere – the reaction occurs at 190-220nm light, indicating low O_2 and O_3 (which very effficiently absorb that wavelength)

Volatilization

- calcite + quartz = wollastonite + carbon dioxide

  $CaCO_3 + SiO_2 = CaSiO_3 + CO_2$
- As the CO_2 is produced, it is likely to be expelled

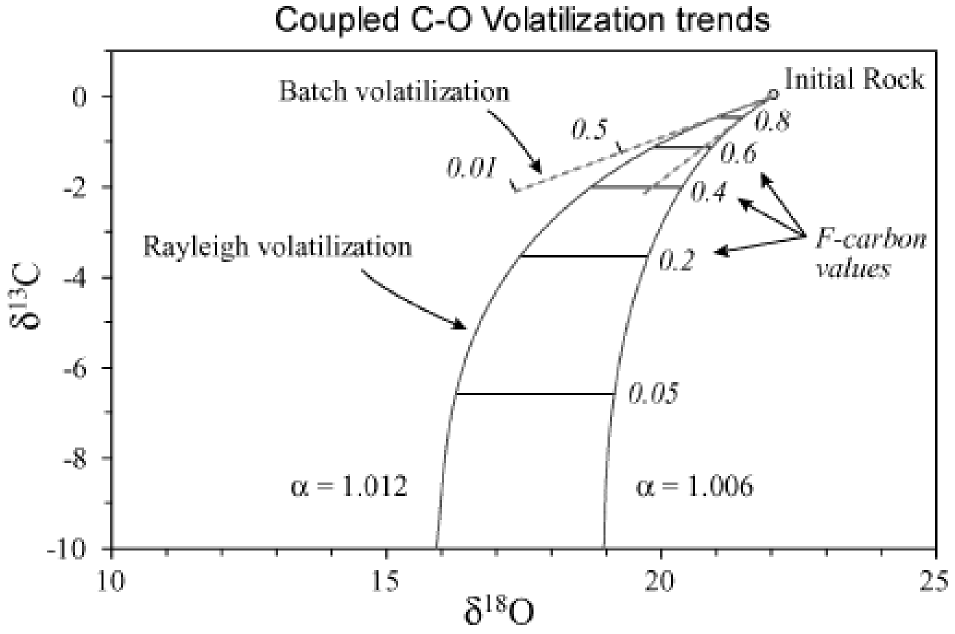
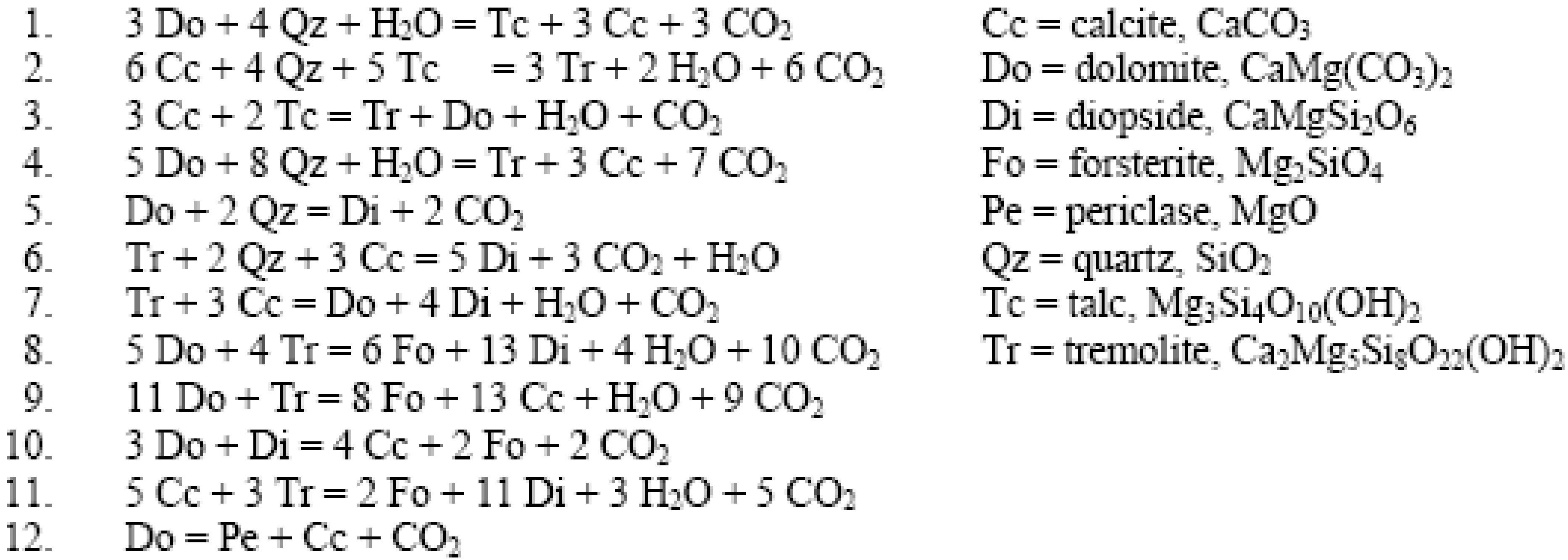


Figure 4. $\delta^{18}O$ versus $\delta^{13}C$ for volatilization (CO_2-loss) of a rock with initial $\delta^{18}O = 22‰$ and $\delta^{13}C = 0‰$. Two values of α for oxygen (CO_2-rock) are shown for both Rayleigh (solid lines) and batch (dashed lines) processes, $\alpha_{carbon} = 1.0022$. F values shown are for carbon. The F values for oxygen are related by $F_{oxygen} = 0.4F_{carbon} + 0.6$, which is the calc-silicate limit discussed in the text. (modified from Valley, 1986)

- Other volatilization reaction examples…



1. $3\ Do + 4\ Qz + H_2O = Tc + 3\ Cc + 3\ CO_2$
2. $6\ Cc + 4\ Qz + 5\ Tc = 3\ Tr + 2\ H_2O + 6\ CO_2$
3. $3\ Cc + 2\ Tc = Tr + Do + H_2O + CO_2$
4. $5\ Do + 8\ Qz + H_2O = Tr + 3\ Cc + 7\ CO_2$
5. $Do + 2\ Qz = Di + 2\ CO_2$
6. $Tr + 2\ Qz + 3\ Cc = 5\ Di + 3\ CO_2 + H_2O$
7. $Tr + 3\ Cc = Do + 4\ Di + H_2O + CO_2$
8. $5\ Do + 4\ Tr = 6\ Fo + 13\ Di + 4\ H_2O + 10\ CO_2$
9. $11\ Do + Tr = 8\ Fo + 13\ Cc + H_2O + 9\ CO_2$
10. $3\ Do + Di = 4\ Cc + 2\ Fo + 2\ CO_2$
11. $5\ Cc + 3\ Tr = 2\ Fo + 11\ Di + 3\ H_2O + 5\ CO_2$
12. $Do = Pe + Cc + CO_2$

Cc = calcite, $CaCO_3$
Do = dolomite, $CaMg(CO_3)_2$
Di = diopside, $CaMgSi_2O_6$
Fo = forsterite, Mg_2SiO_4
Pe = periclase, MgO
Qz = quartz, SiO_2
Tc = talc, $Mg_3Si_4O_{10}(OH)_2$
Tr = tremolite, $Ca_2Mg_5Si_8O_{22}(OH)_2$

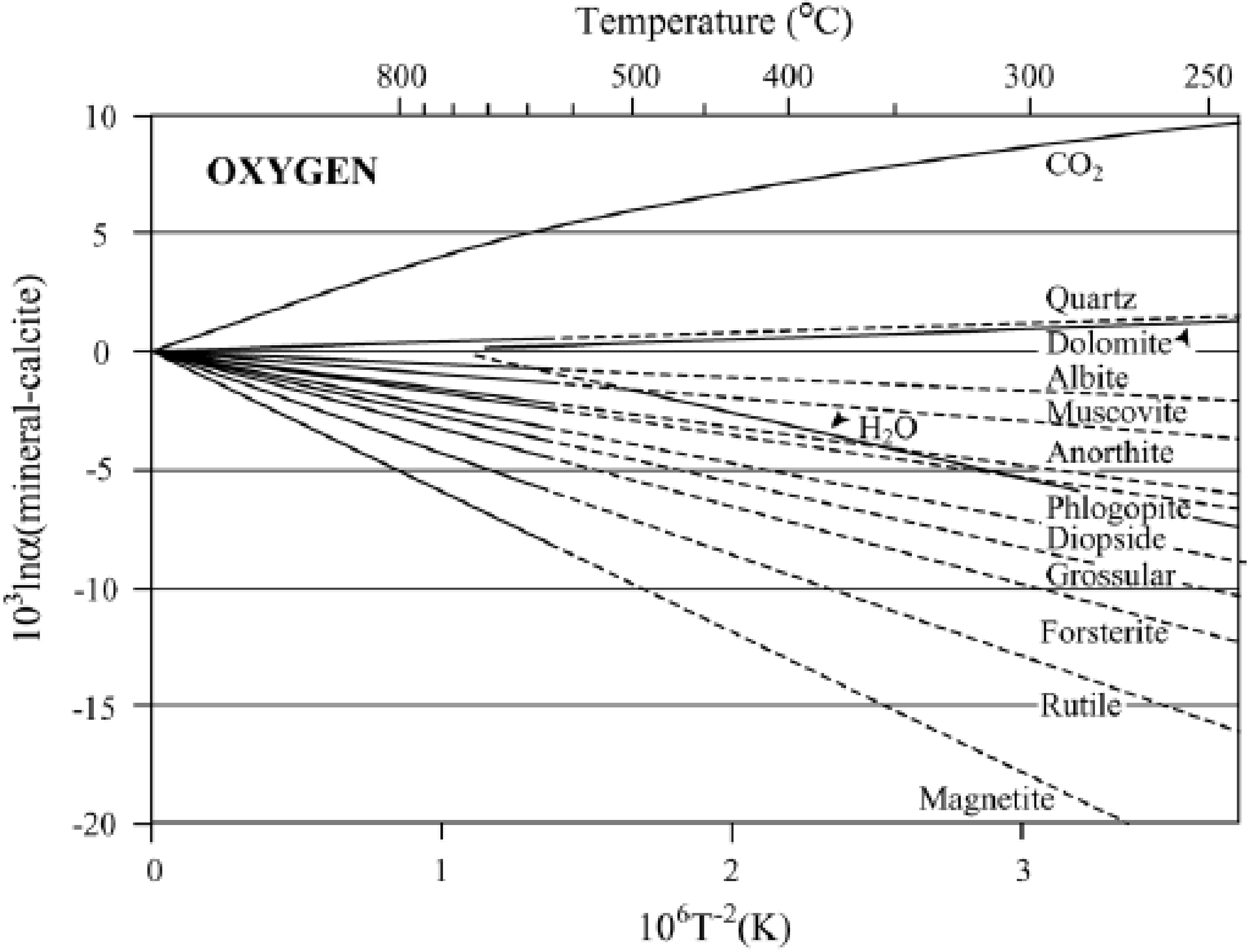


Figure 5. Fractionation of oxygen isotopes between selected minerals (and volatiles) and calcite. $10^3\ln\alpha$ between solids is normally assumed to be linear with $1/T^2$ as shown. Dashed lines are projected outside their experimental temperature range. Fractionation factors used are from various studies summarized in Chacko et al., 2001. H_2O-calcite is from O'Neil et al. (1969), updated by Friedman and O'Neil (1977), dolomite-calcite is from Sheppard & Schwarz (1970).

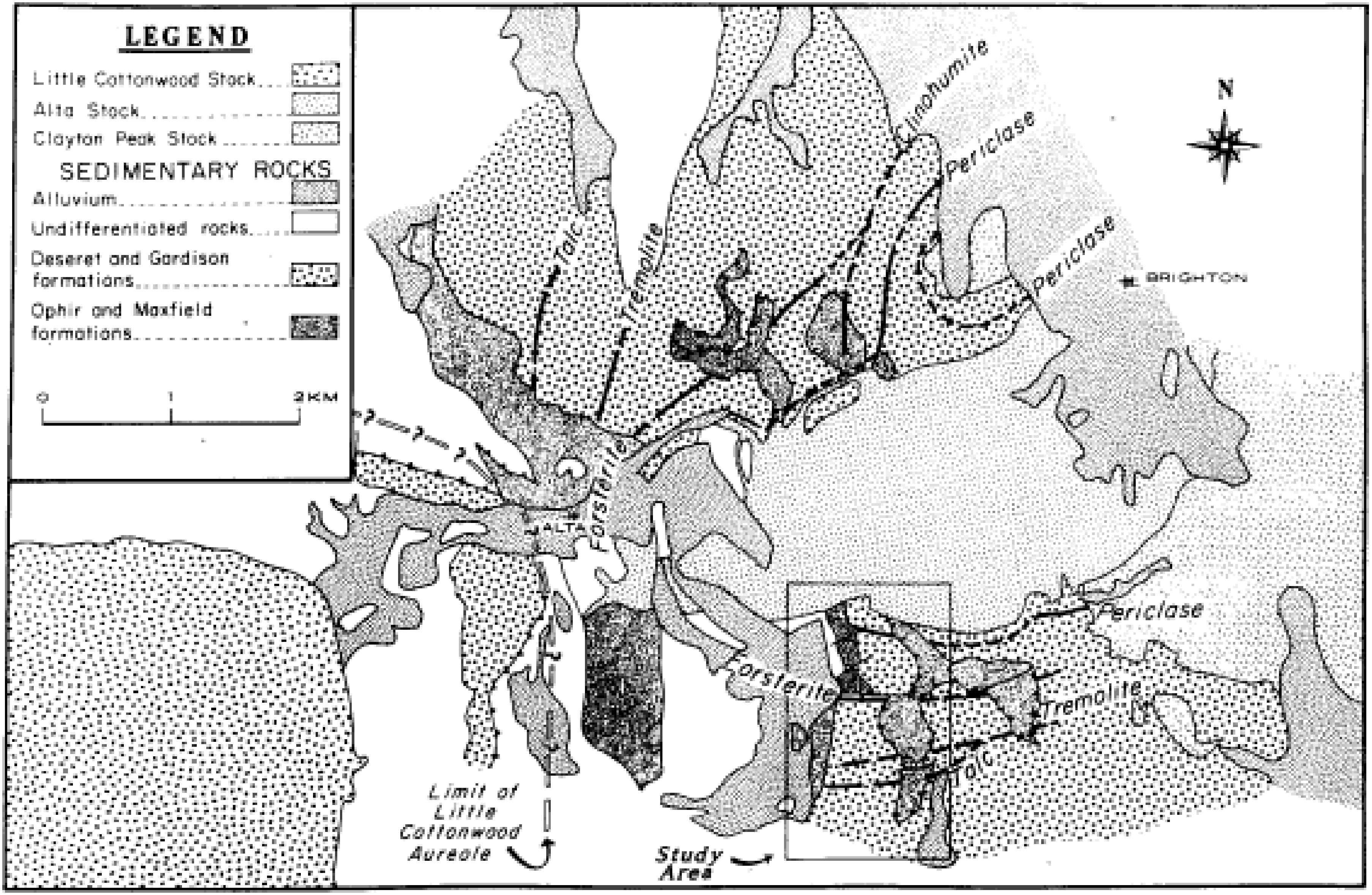


Figure 9. Geologic map of the Alta area, Utah (from Moore and Kerrick, 1976). Mineral reaction isograds surround the Alta stock within siliceous dolomites of the Mississippian Deseret and Gardison formations. The study area within the southern contact aureole is from Bowman et al. (1994).

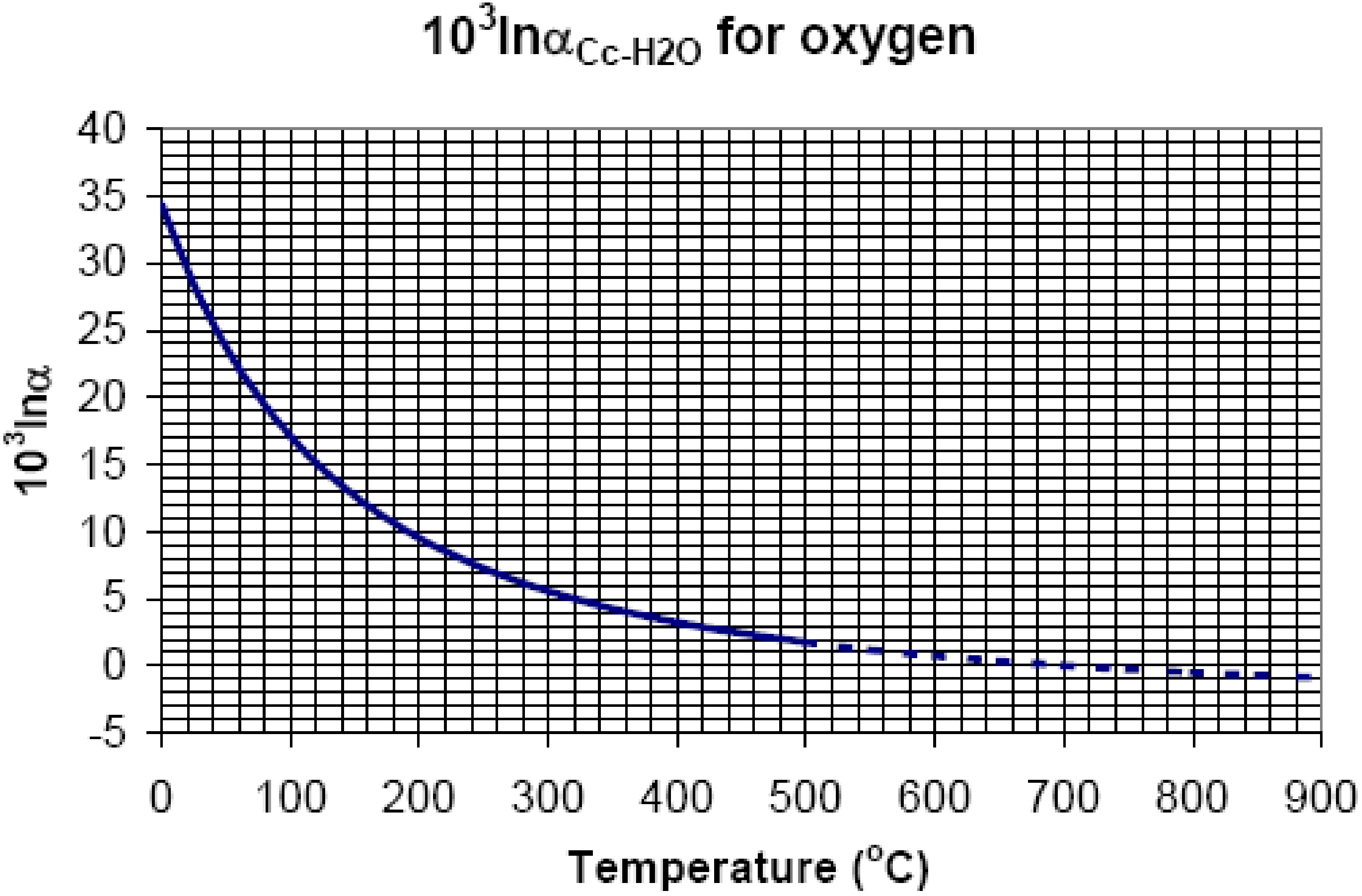


Figure 1. Fractionation of oxygen isotopes between calcite and water as a function of temperature(0-500°C). From O'Neil et al. (1969), updated by Friedman and O'Neil (1977), $10^3\ln\alpha_{Cc\text{-}H_2O} = 2.78(10^6T^{-2})-2.89$, T in Kelvin in this equation.

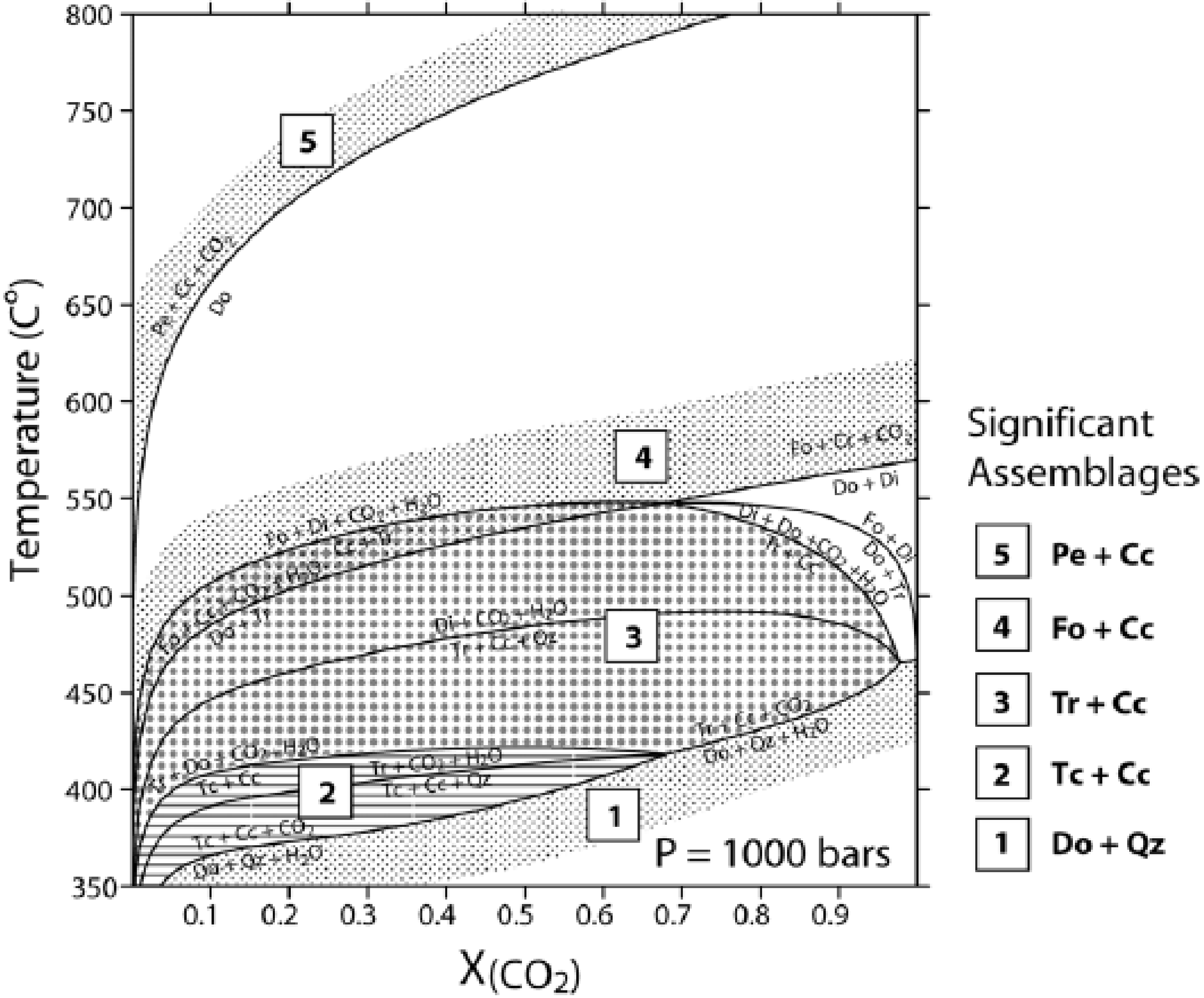


Figure 11. T-X_{CO_2} diagram for selected reactions with significant mineral assemblages highlighted. The sequence of mineral reactions seen approaching the Alta stock contact are consistent with increasing temperature. Geothermometry yields peak temperatures of 600°C in the periclase zone, which requires H_2O-rich fluid conditions.

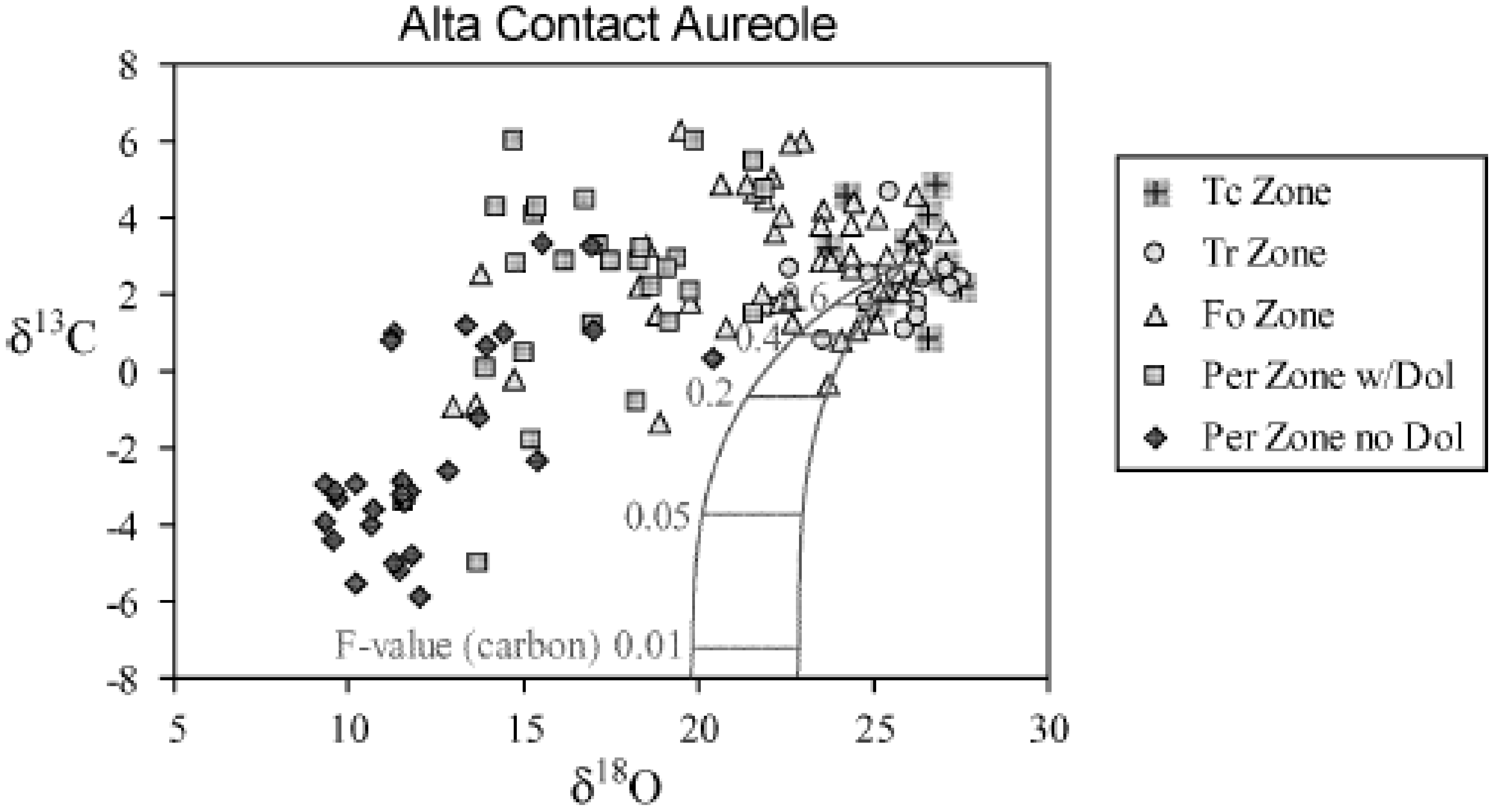


Figure 12. C-O isotopic trend for carbonates from the southern Alta aureole. The Rayleigh volatilization trend starts at the average of the talc zone samples, 26‰ and 3‰, and uses the same fractionation factors as Fig. 4. Data from Bowman et al., 1994, and additional unpublished data from J. R. Bowman.

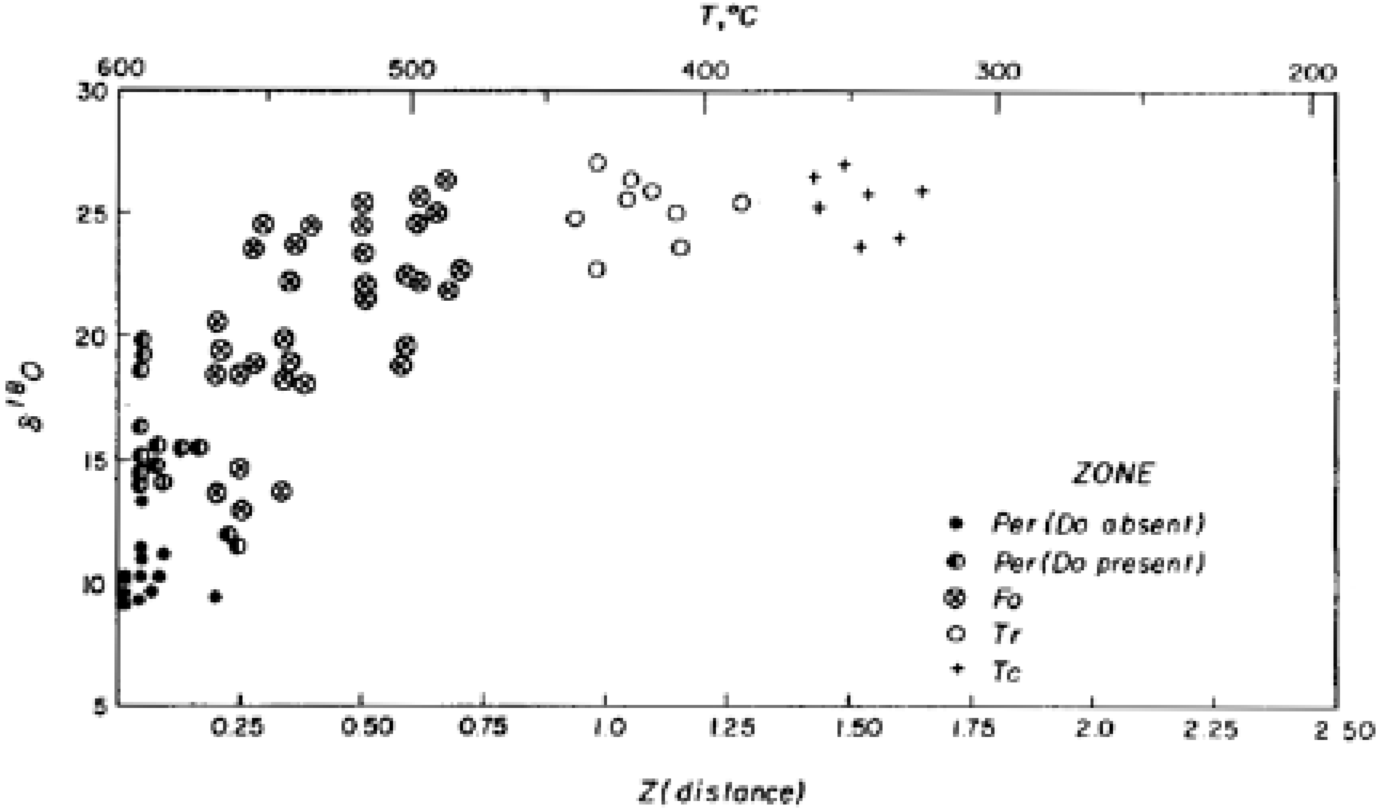


Figure 13. $\delta^{18}O$ versus distance (Z, in kilometers) from the contact of the Alta stock Temperatures are from Cook and Bowman (1994). Taken from Bowman et al. (1994).

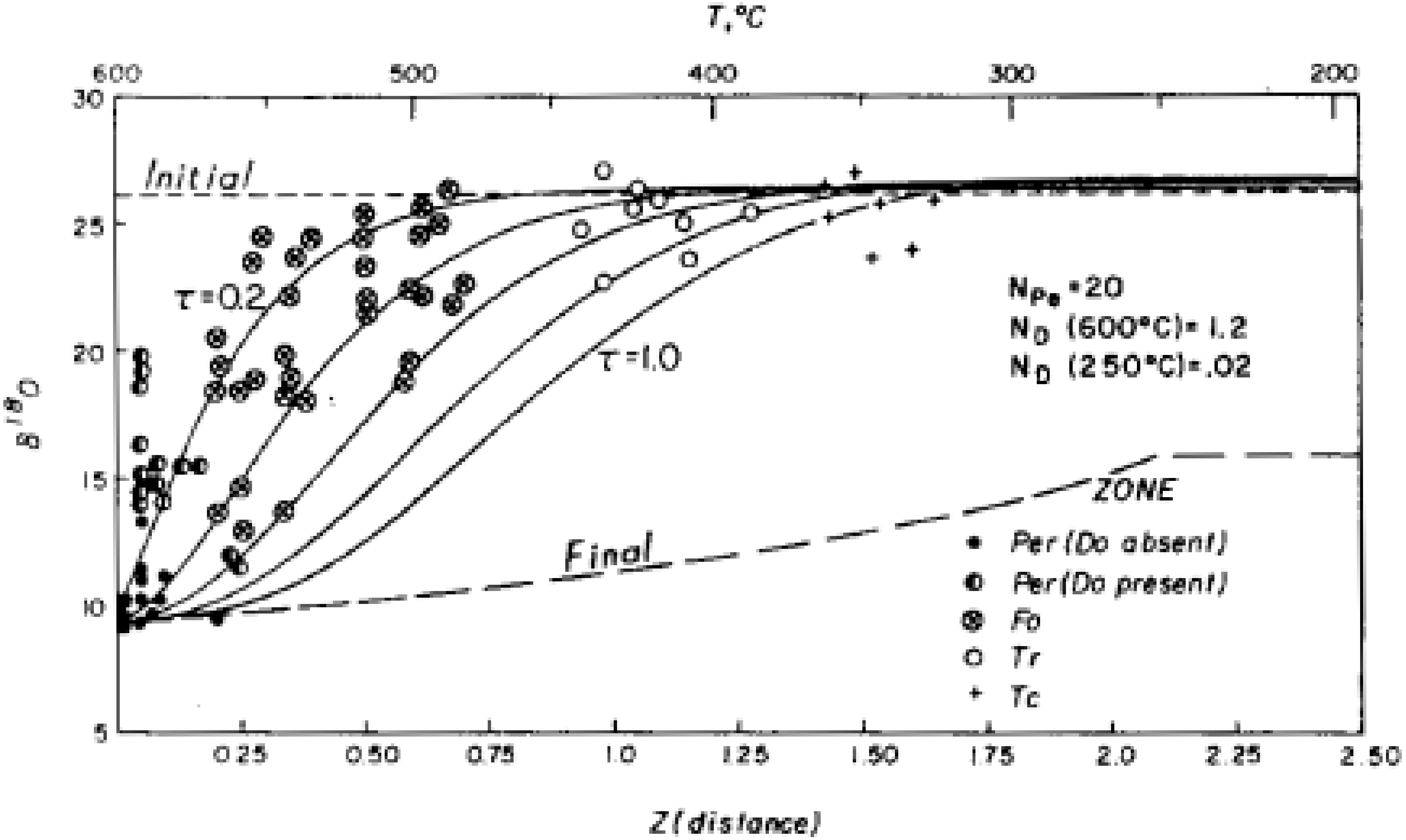


Figure 14. One dimensional fluid flow models superimposed on the Alta $\delta^{18}O$ data (figure taken from Bowman et al., 1994). Model inputs include initial rock at 26‰, fluid input at 8‰, temperature steady-state as indicated. Distance (Z) is in kilometers.