Lecture 16. Chemical Tracers - Stable Isotopes

Stable isotopes ≡ non-radioactive atoms of the same element that differ from each other only in the number of neutrons in their nucleus. See an example to the right for the three stable isotopes (and one radioisotope) of oxygen.

Isotope	#Protons Z=atomic#	#Neutrons N=neutron#	Atomic wt A=mass#	Atom%
^{16}O	8	8	16	99.8
^{17}O	8	9	17	0.04
^{18}O	8	10	18	0.2
^{19}O	8	11	19	0*

*T½ = 29.4 sec

Stable isotopes

1. Carry "embedded" geographic information for discriminating sources, such as:
    a. Different ocean water masses
    b. Marine versus terrestrially-derived organic matter
    c. Clay minerals and organic matter from different regions within drainage basins.
2. Provide information within fossils about the temperatures, geographic settings, transport mechanisms and ecology of ancient environments.
3. Integrate the cumulative results of processes occurring over time or to varying extents (e.g. diet, climate change, marine productivity, and the formation and melting of continental glaciers).

Measuring Stable Isotopic Abundances:

The key is to be able to measure the relative abundances of stable isotopes very precisely:
Lighter (Z<50) isotopes are usually measured in gaseous molecules that:

a. Contain the element in question as a major component.
b. Are chemically non-reactive and not "sticky" to surfaces (e.g. H_2O is a bad actor).
c. Can be easily formed, purified and moved in a gas line.

The **ratio mass spectrometer**: Operates as a continuous ion separator:

a. Molecules are ionized by an electron beam in the ion source and the resulting cations are repelled down the analyzer tube into the magnetic sector.
b. The stream of mixed ions is "resolved" into two components (based on their different masses and focused onto separate detectors ("collectors").
c. The gas source is continuously alternated between sample and standard inputs.

The isotope composition of the sample is measured as the per mil (‰) relative deviation, δ, of its isotope ratio from the ratio of a standard material:

$$\delta H = \left[\frac{(H/L)_{spl} - (H/L)_{std}}{(H/L)_{std}} \right] x\ 1000 \qquad \textbf{(1)}$$

where H & L = "heavy" & "light" isotopes of the targeted element in the sample.

All bioactive elements, except phosphorous, have multiple stable isotopes, and hence offer the possibility for tracer/process studies.
Change in the isotope ratios of different components occurs due to isotopic fractionation.

Element	Isotope	atom%	Standard
Hydrogen	^{1}H	99.99	SMOW*
	^{2}H	0.01	
Carbon	^{12}C	98.9	PDB $CaCO_3$
	^{13}C	1.1	
Nitrogen	^{14}N	99.6	Air
	^{15}N	0.4	
Oxygen	^{16}O	99.8	SMOW*
	^{17}O	0.04	
	^{18}O	0.2	
Sulfur	^{32}S	95.0	Canyon Diablo triolite (FeS)
	^{33}S	0.8	
	^{34}S	4.2	
	^{36}S	0.02	

*SMOW = Standard Mean Ocean Water

Isotope fractionation occurs either because:

a. Molecules of the same type with different isotopic components have slightly different free energies (an **equilibrium isotope effect**).
b. Molecules of the same type have a bond linking different isotopes of the same element that break at different rates (a **kinetic isotope effect**).

Isotope effects often lead to unequal distributions of heavy and light isotopes among otherwise identical molecules. Kinetic isotope effects are pronounced only for atoms directly involved in the bond that is being formed or broken.

Equilibrium Isotope Effects:

A carbonate buffer system example:

$$^{13}CO_{2(g)} + H^{12}CO_3^-{}_{(aq)} \Leftrightarrow {}^{12}CO_{2(g)} + H^{13}CO_3^-{}_{(aq)}$$

If this isotope exchange reaction (which involves no chemical changes) comes to equilibrium, the resulting isotopic fractionation can be described by an equilibrium constant, that is a function of temperature and pressure:

$$K = \frac{[^{12}CO_{2(g)}][H^{13}CO_{3(aq)}]}{[^{13}CO_{2(g)}][H^{12}CO_{3(aq)}]}$$

Temp (°C)	K
0	1.0092
30	1.0068

a. In this (and most other) equilibrium isotope effects, the heavier isotope ends up concentrated in the chemical compound which has the strongest (or most numerous) bond to its atom (in this example, within $H^{13}CO_3^-{}_{(aq)}$).
b. In general, equilibrium (and kinetic) isotope effects decrease as system temperature increases (see above carbonate example).

By convention, the magnitude of an equilibrium isotope effect is expressed as a **fractionation factor** (α), with the reaction written to form a heavy product (so that $\alpha > 1$). By definition:

$$\alpha_{H/L} = \frac{(H/L)_{strong}}{(H/L)_{weak}} = \frac{(^{13}C/^{12}C)_{HCO_3^-}}{(^{13}C/^{12}C)_{CO_2}} \qquad \textbf{(2)}$$

For this example (with stoichiometric coefficients of 1), $\alpha = K$.

A related expression is the "**difference fractionation factor**" (Δ), that is a simple difference between the δ values of a product and its precursor (the reactant), thus for carbon:

$$\Delta^{13}C = \delta^{13}C_{product} - \delta^{13}C_{reactant} \qquad \textbf{(3)}$$

note that:

$$\Delta \approx 1000 \ln\alpha \approx 1000 (\alpha-1) \qquad \textbf{(4)}$$

The paleotemperature ^{18}O method is a method for determining the temperature of an ancient aqueous environment from the $\delta^{18}O$ of a carbonate shell preserved from it, and is based on the equilibrium temperature dependence of the reaction:

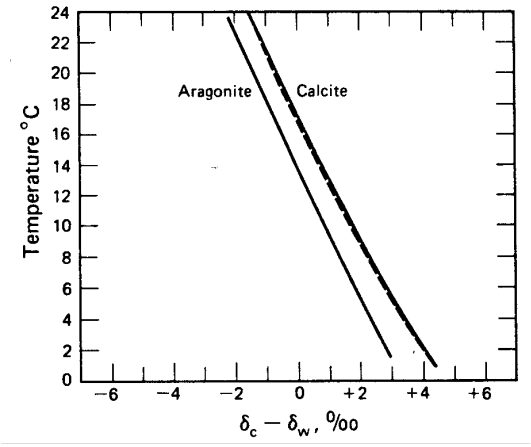
$$CO_3^{2-} + H_2{}^{18}O \Leftrightarrow C^{18}O_3^{2-} + H_2O \qquad \textbf{(5)}$$

Assumptions:

a. The organism precipitated $CaCO_{3\,(s)}$ (calcite or aragonite) in isotopic equilibrium with dissolved CO_3^{2-} (and water) in the water where it lived (no "**vital effect**").
b. The $\delta^{18}O$ of that original water is known, or can be accurately estimated.
c. The $\delta^{18}O$ of the shell has not changed since the time it was formed by the organism.

The procedure for determining the paleotemperature of a sample environment, or for generating an $\delta^{18}O$ vs temperature calibration curve is as follows:

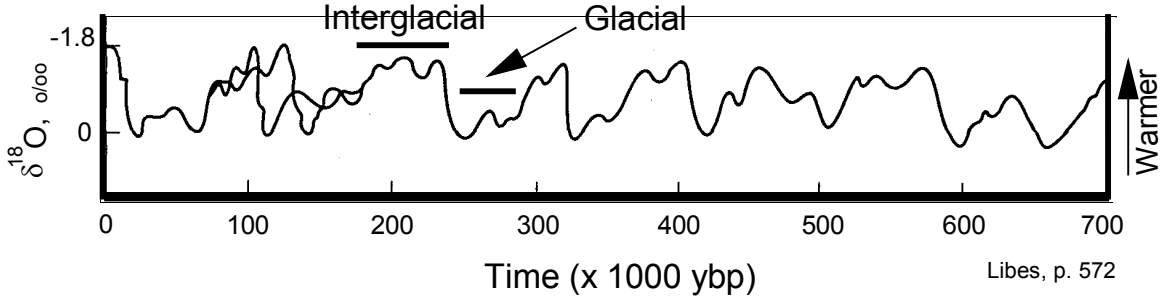
1. Measure the $\delta^{18}O$ of CO_2 released (without isotope exchange) by reacting H_3PO_4 with $CaCO_{3(s)}$ to get (δ_c).
2. For a calibration, measure the $\delta^{18}O$ of CO_2 gas equilibrated with water (at a known temperature) in which the organisms grew - over a range of constant known temperatures to get (δ_w).
3. Generate a calibration curve and/or use δ_c with an assumed δ_w to calculate a paleotemperature:



$°C_{aragonite} = 13.85 - 4.54(\delta_c-\delta_w) + 0.04(\delta_c-\delta_w)^2$.

$°C_{calcite} = 17.04 - 4.34(\delta_c-\delta_w) + 0.16(\delta_c-\delta_w)^2$.

Using oxygen isotopes for identifying glacial/interglacial periods:



Two factors contribute toward "heavy" $\delta^{18}O$ values during glacial times:

1. Lower water temperatures.
2. Storage of "light" water ($\delta^{18}O \approx -30‰$) in continental ice caps during glacial time. If 4% of the ocean volume were stored in glacial ice, then the $\delta^{18}O$ of the ocean would be 1.2 ‰ heavier and about ¾ of the measured 1.8‰ offset would result from a change in water storage.

If we know one component, e.g. the temperature of the water mass or the isotopic composition of seawater, we could derive the other. The curve could be used for dating and correlation regardless of this knowledge, since the bulk seawater oxygen isotopic composition at any given time is homogenous.

Kinetic Isotope Effects

Kinetic isotope effects occur under non-equilibrium conditions for one of two reasons:

- First, molecules of the same compound, but containing different stable isotopes, move at different rates (due to unequal masses).
    - For example: $^{12}CO_2$ vs. $^{13}CO_2$, both the light ($M_{wt} = 44$) and heavy ($M_{wt} = 45$) molecules must have the same kinetic energy at the same temperature. Thus:

      $\frac{1}{2} M_{44} V_{44}^2 = \frac{1}{2} M_{45} V_{45}^2$ and $\therefore \quad V_{44}/V_{45} = \frac{\sqrt{45}}{\sqrt{44}} = \frac{6.708}{6.633} = 1.012$

      Therefore, $^{12}CO_2$ travels 1.2% faster than $^{13}CO_2$ and will tend to lead a "pack" of diffusing carbon dioxide molecules.

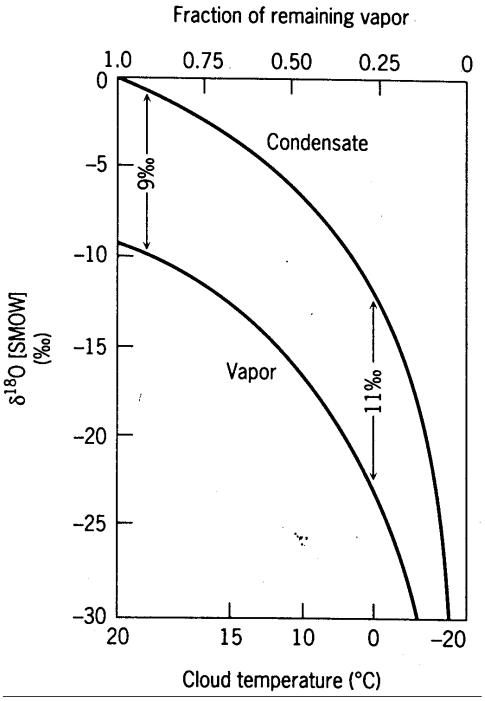
- Second, molecules of the same compound, but containing different stable isotopes, *react* at different rates (due to unequal inter-atomic bond energies).

- In general, the lighter of two molecules of the same compound will move and react faster.

Isotope Effects During the Hydrologic Cycle:

An example is shown to the right for ^{18}O fractionation during different stages of evaporation from seawater and precipitation from the resulting vapor:

1. A cloud formed by evaporation from the surface of a warm ocean (20 °C) will have the $\delta^{18}O$ composition shown for "vapor" on the left side of this plot.
2. "Heavy" water molecules (primarily DHO and $HH^{18}O$) will concentrate in the condensate, versus the parent vapor, because these molecules are larger, slower, and hence have a lower vapor pressure.
3. The $\delta^{18}O$ of the water molecule mixture falling at any point will reflect both the ~+10‰, fractionation factor between the vapor and condensate, plus the cumulative depletion ("lightening") over time of the remnant vapor in molecules containing ^{18}O.

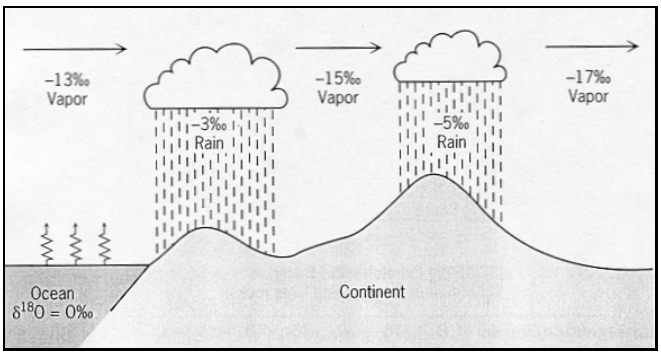


The **Rayleigh distillation** equation relates the initial (R_o) and transient (R_t) stable isotope ratios of a reservoir to the fraction (f) of the initial material that <u>remains</u> (often equivalent to C_t/C_o) when product is removed with a constant fractionation factor (α):

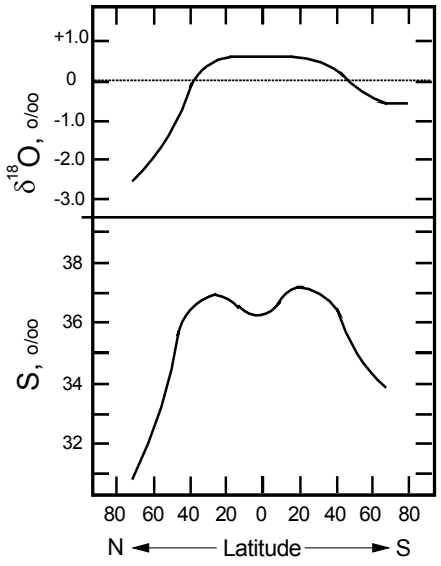
$$\frac{R_t}{R_o} = f^{(\alpha-1)} = \left(\frac{C_t}{C_o}\right)^{(\alpha-1)} \qquad \textbf{(1)}$$

for $\delta^{18}O$, equation **(1)** can be recast as:

$$\delta^{18}O_t = [(\delta^{18}O_o + 1000)\, f^{(\alpha-1)} - 1000] \quad \textbf{(2)}$$



The concentration of "heavy water" at the surface of ocean regions subject to net evaporation leads to parallel elevations in $\delta^{18}O$ (and δD) versus salinity



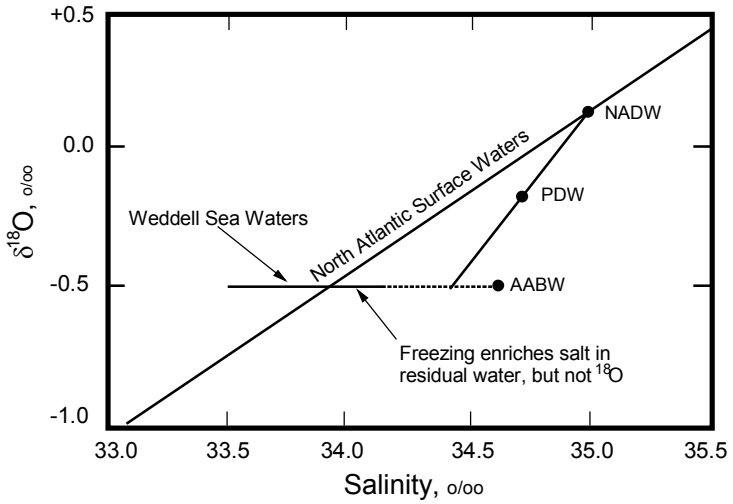
Hydrogen isotopes in water undergo proportional fractionation to O isotopes during the hydrologic cycle.

The "**meteoric water line**" has the equation:

$$\delta D = 8\ \delta^{18}O + 10 \qquad \textbf{(3)}$$

Thus, isotopic fractionation is 8 times larger for hydrogen than for oxygen isotopes.

The different δD and $\delta^{18}O$ values of water masses can be used to distinguish the origins and volume percentages of derivative mixtures. Thus, salinity and $\delta^{18}O$ compositions can be used to determine that Pacific Deep Water (PDW) is a mixture of North Atlantic Deep Water (NADW) and water that compositionally resembles Antarctic Bottom Water (AABW). This figure is from Broecker, 1974.



Carbon Isotope Effects:

Inorganic carbon undergoes relatively fast equilibrium isotope fractionation:

Atmospheric CO_2 is –7‰, versus +1‰ for HCO_3^- and +2‰ for marine $CaCO_{3(s)}$.

Organic carbon is "lighter" than the inorganic carbon from which it photosynthesized. Most land plants (and all trees) are C3 types, having $\delta^{13}C$ values near -26‰. Fewer land plants are of the C4 type (e.g. corn, bamboo, and many grasses) and are considerably heavier ($\delta^{13}C$ ~

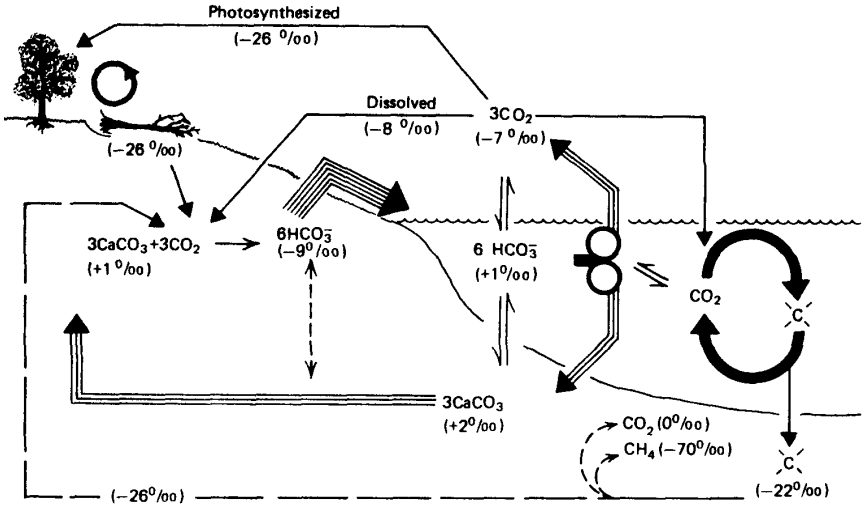
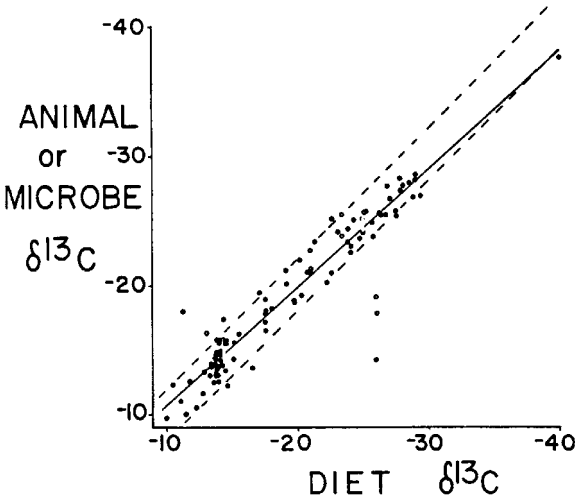


Fig. 14. Schematic depiction of the oxidized and reduced carbon cycles and their isotopic interactions. δC^{13} values in parentheses. Heavy circles denote rapid cycling in the biosphere. Two-way arrows indicate isotopic exchange leading toward isotopic equilibrium. Based on data compiled by Degens (1969) and Schwarcz (1969).

Garlick, 1975

-12‰). Marine plankton contain organic carbon with an intermediate $\delta^{13}C$ (near –20 to -23‰).



Heterotrophism causes minimal fractionation of stable carbon isotopes. Therefore, the biomass carbon of heterotrophs (herbivores and/or carnivores) parallels the $\delta^{13}C$ of their diet "You are what you eat." The $\delta^{13}C$ of residual organic matter in soils, seawater and marine sediments closely resemble that of the source. In the case of mixed dietary substrates or source, the $\delta^{13}C$ of the mixture can be used to determine the fractions (f) of the sources. For a binary mixture of source 1 and 2, the fraction of source 1 (f_1) in the mixture can be determined algebraically as:

$$f_1 = \frac{{}^{13}C_{mix} - {}^{13}C_2}{{}^{13}C_1 - {}^{13}C_2} \qquad \textbf{(4)}$$

Thus for a typical coastal marine sediment of $\delta^{13} = -22.2‰$, formed from marine and terrestrial organic carbon with $\delta^{13}C$ values of –20.0‰ and –26.0‰, respectively:

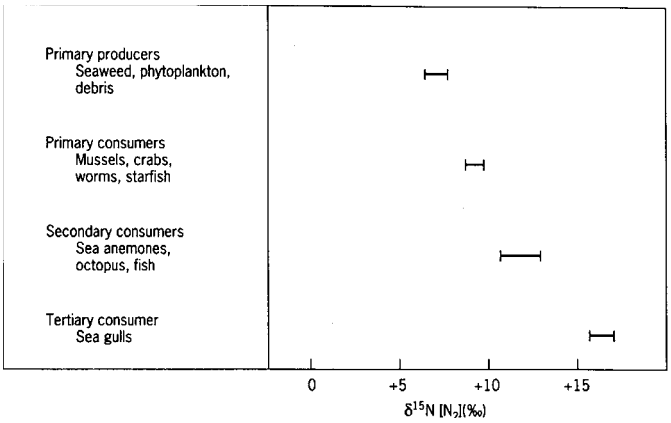
$$f_{ter} = \frac{-22.2-(-20.0)}{-26.0-(-20.0)} = \frac{-2.2}{-6.0} = 0.37$$

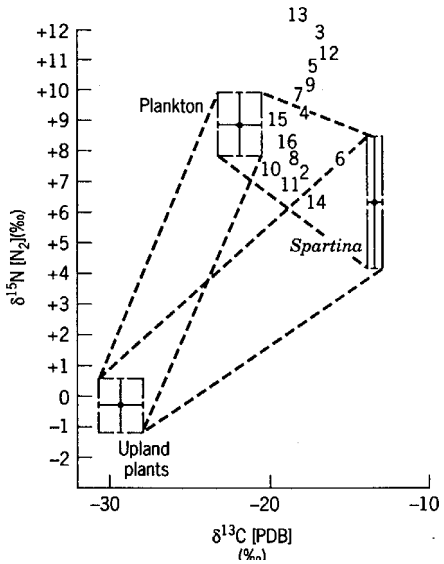
Stable Nitrogen Isotopes:

The chemical forms and stable nitrogen isotope compositions ($\delta^{15}N$) of marine organic matter are diverse, as are fractionation factors for processes of nitrogen conversion. These systematics allow numerous applications of $\delta^{15}N$ in tracer and process studies. Of the many process applications, two are particularly useful:

Assessment of nitrogen sources and availability in marine systems:
Nitrogen-fixers (e.g. cyanobacteria) take up dissolved N_2 with essentially no fractionation ($\Delta \approx 0$), the biomass of these organisms has a $\delta^{15}N$ near +1‰. Non-N_2-fixing phytoplankton (most types) preferentially take up ^{14}N versus ^{15}N from the nitrate and ammonia pools ($\delta^{15}N$ of nitrate and ammonia ranges from +5‰ to +10‰). If there is surplus of fixed N available, their biomass N will be lighter (+2‰ to +5‰) than the source. Since light NO_3^- and NH_4^+ are preferentially removed, the remnant nutrient becomes heavier. Since there is less total nutrient available, discrimination among the isotopic forms of the small remnant is small. The net result is that nitrogen in the biomass of phytoplankton becomes progressively heavy when the nitrogen source is limited (utilization > availability), hence reflecting increasing nutrient limitation (the heavier the $\delta^{15}N$ of organic matter the more nutrient limiting are the conditions).

Trophic level studies:
Marine heterotrophs preferentially excrete light nitrogen, leaving biomass nitrogen enriched in ^{15}N. The average offset (Δ) is about +3‰ per trophic level. Multiple stable isotope compositions can be used together to distinguish sources and trophic levels.





References:

A. General:

Choppin G.R. and J. Rydberg (1980) Nuclear Chemistry: Theory and Applications. Pergamon Press, Oxford, 667.

Friedlander G., J.W. Kennedy and J.M. Miller (1964) Nuclear and Radiochemistry, second edition. Wiley, New York, 585pp.

Kruger P. (1971) Principles of Activation Analysis. Wiley-Interscience, New York, 522pp.

Overman R.T. and Clark H.M. (1960) Radioisotope Techniques. McGraw-Hill, New York, 476pp.

B. Raleigh Fractionation

Broecker W.S. and V.M. Oversby (1971) Chemical equilibria in the earth. McGraw-Hill, New York, 318pp.

Dansgaard, W. (1964) Stable isotopes in precipitation. Tellus, 16, 436.

C. Case Studies

Altabet M.A. (1988) Variations in nitrogen isotopic composition between sinking and suspended particles: implications for nitrogen cycling and particle transformation in the open ocean. Deep-Sea Res. 35, 535-554.

Altabet M.A. and L. F. Small (1990) Nitrogen isotopic ratios in fecal pellets produced by marine zooplankton. Geochim. Cosmochim. Acta 54, 155-163.

Berner R.A. (1987) Models for carbon and sulfur cycles and atmospheric oxygen: Application to Paleozoic geological history. Amer. J. Sci., 287, 177-196.

Berner R.A. (1989) Biogeochemical cycles of carbon and sulfur and their effect on atmospheric oxygen over Phanerozoic time. Palaoegraphy, Palaeoclimatalogy, Palaeoecology, 3, 97-122.

Canfield D.E. (1998) A new model for Proterozoic ocean chemistry. Nature, 396, 450-453.

Canfield D.E. and B. Thamdrup (1994) The production of 34 S-depleted sulfide during bacterial disproportionation of elemental sulfur. Science, 266, 1973-1975.
Cline J. and I.R. Kaplan (1975) Isotopic fractionation of dissolved nitrate during denitrification in the eastern tropical north Pacific Mar. Chem. 3, 271-299.
Degens E.T. (1968) Biogeochemistry of stable carbon isotopes. In: (Eqlinton and Murphy, eds.) Organic Geochemistry: Methods and Results. Springer, Berlin, 304-329.
Epstein S. and T. Mayeda (1953) Variation of 18 O content of waters from natural sources. Geochim. Cosmochim. Acta, 4, 213.
Fairbanks R.G. (1989) A 17,000-year glacio-eustatic sea level record: influence of glacial melting rates on the Younger Dryas event and deep-ocean circulation. Nature, 342, 637-642.
Fairbanks R.G. and R.K. Matthews (1978) Quat. Res. 10, 181-196.
Garrels R.A. and E.A. Perry, Jr. (1974) Cycling of carbon, sulfur and oxygen through geologic time. In:(E.D. Goldberg, ed) The Sea, v. 5, Wiley Interscience, New York, p. 303-336.
Garrels R.A. and A. Lerman (1984) Coupling of the sedimentary sulfur and carbon cycles –an improved model. Amer. J. Sci., 284, 989-1007.
Holland H.D. (1973) Systematics of the isotopic composition of sulfur in the oceans during the Phanerozoic and its implications for atmospheric oxygen. Geochim. Cosmochim. Acta., 37, 2605-2616.
Thode H.G., J. Macnamara and C.B. Collins (1949) Natural variations in the isotopic content of sulfur and their significance. Can J. Res. 27B, 361.