

## Lecture 25

# Stable Isotopes: applications to the Carbon Cycle and Earth's Climate

*Reading:* White Ch 9.1 to 9.7.1 (or digital p370-400)

*Today*

1. Stable Isotopes for hydrologic and climate applications

*Next week*

2. Paleoclimate records
3. Future near term Climate

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### Stable Isotope Systematics:

The **chemical properties** of an element are defined by the number of **protons** in their nucleus.

Different **isotopes** of an element have different numbers of neutrons, and therefore different atomic masses.

Different isotopes are chemically equivalent but behave slightly differently in chemical reactions because of mass difference causes variations in molecular kinetic energy and in vibrational energy contained in chemical bonds.

### Isotope fractionation

- ❖ refers to a slight separation of one isotope from another.
- ❖ Results from processes in which different isotopes of an element behave differently.
- ❖ causes easy to detect abundance variations among the isotopes of the lighter elements in natural materials of **hundredths of a percent to a few percent**.
- ❖ differences can be measured using a *mass spectrometer*, a sensitive instrument that accelerates charged particles into a strong magnetic or electric field and then takes advantage of the mass-dependent trajectories of ions moving through the field to separate individual isotopes into distinct ion beams.

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### Stable Isotope Systematics:

**Isotope fractionation** differences are relatively small in magnitude compared to other chemical phenomena we have been discussing this semester.

However, they can be exploited to understand the details of how natural processes occur today and how they have differed in the past.

**Fractionation** arises from mass dependent energy differences between isotopes. Thus, the lighter the element, the more dramatic the isotopic fractionation during a given process or chemical reaction.

#### Consider the isotopes of H, C and O:

element	isotope (common name)	mass (amu)
H	$^1_1\text{H}$ (hydrogen)	~1
	$^2_1\text{H}$ (deuterium = "D")	~2
	$^3_1\text{H}$ (tritium = "T")	~3
C	$^{12}_6\text{C}$	12
	$^{13}_6\text{C}$	13
	$^{14}_6\text{C}$ (radiocarbon)	14
O	$^{16}_8\text{O}$	16
	$^{17}_8\text{O}$	17
	$^{18}_8\text{O}$	18

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### Stable Isotope Systematics:

- a deuterium atom is twice as massive as a hydrogen atom
- $^{13}_6\text{C}$  is 1/12 or ~ 8% heavier than  $^{12}_6\text{C}$
- $^{18}_8\text{O}$  is 2/16 or ~ 12% heavier than  $^{16}_8\text{O}$ .

We therefore expect (and generally find) that:

H and D fractionation  $\gg$  O-16 and O-18 fractionation  $>$  C-12 and C-13 fractionation

However, we can find examples where the general  $\text{H} > \text{O} > \text{C}$  order of isotopic heterogeneity *does not hold* (e.g., where C is more heterogeneous than O).

*Note: Many other elements* have multiple isotopes that are used for stable isotope studies, such as N, S, Li, B, Mg, Ca, Fe...

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## Stable Isotope Systematics:

Isotopic fractionation is temperature dependent.

higher temperature = lesser effect (usually)

**Why?** Because the system is *more energetic overall* at higher T, so that the energy differences arising from the isotope mass differences are often a *smaller proportion* of the whole.

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## The 3 Types of Isotope Fractionation Effects:

- Those due to overall molecular mass in compounds containing different isotopes of the same elements
- Those due to mass-dependent bond energy differences
- kinetic effects arising from either of the above.

**Type "a" effects:** Water molecules with 5 different molecular masses are possible using the common isotopes of H and O (H, D,  $^{16}\text{O}$  and  $^{18}\text{O}$ ).

molecule:	<i>lightest</i> H- $^{16}\text{O}$ -H	H- $^{16}\text{O}$ -D	D- $^{16}\text{O}$ -D
mass:	18	19	20
molecule:	H- $^{18}\text{O}$ -H	H- $^{18}\text{O}$ -D	D- $^{18}\text{O}$ -D
mass:	20	21	22 <i>heaviest</i>

The heaviest species,  $^{18}\text{OD}_2$ , is 4/18 or ~ 22% heavier than the lightest,  $^{16}\text{OH}_2$ .

Note: D makes up only ~ 0.015% of the hydrogen on earth and  $^{18}\text{O}$  makes up only ~0.2%. Thus, the molecular mass 18 water molecules (H- $^{16}\text{O}$ -H) are by far the most abundant.

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### Type "a" effects: molecular mass differences

Bulk mass differences affect the way water molecules move about. For instance, the mean molecular velocity of a gas is given by:

$$v = \left( \frac{8kT}{\pi m} \right)^{1/2}, \quad \text{where } T = \text{temperature, } m = \text{mass, and } k = \text{the boltzman constant.}$$

$v$  is inversely proportional to the square root of mass

Water molecules of different mass due to different isotopic compositions have different mean velocities as a function of temperature. Lighter molecules move faster.

For two  $H_2$  molecules of mass 2 and 4 ( $H_2$  and  $D_2$ ), we can use the equation above to show that :

$$v_1/v_2 = (m_2/m_1)^{1/2} = (4/2)^{1/2} = 1.414$$

For two water molecules of mass 18 and mass 22, we can use the equation above to show that

$$v_1/v_2 = (m_2/m_1)^{1/2} = (22/18)^{1/2} = 1.106$$

The lighter hydrogen molecule moves 41% faster and the lighter water molecule moves almost 11% faster than their respective heavier counterparts.

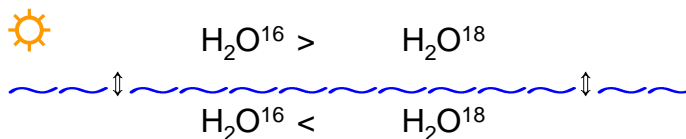
Thus, a process like diffusion would allow isotopic fractionation due to molecular velocity differences.

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### type "c" effects: kinetics

Kinetic effect can enhance fractionation arising from "a".

Consider the evaporation to the gas phase of water composed for simplicity of only the two most common forms,  $H_2O^{16}$  and  $H_2O^{18}$ . At chemical equilibrium we would predict:



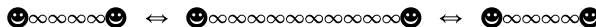
Yet, because  $H_2O^{16}$  moves *faster* than  $H_2O^{18}$ , it can attain equilibrium *faster*, thereby enhancing the level of  $H_2O^{16}$  enrichment during evaporation of water to a moving parcel of atmosphere over a body of water.

This process occurs on Earth as  $H_2O$  evaporates from the oceans, since the atmosphere is rarely saturated with respect to  $H_2O$ . The opposite process occurs during condensation of  $H_2O$  liquid or solid from the atmosphere.

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### type "b" effects - chemical bonding

Chemical bonds are like springs, vibrating in proportion to their contained energy and the bonded atoms' masses .



Each chemical bond has a "spring" constant that describes how hard or easy it is to stretch and compress. The energy condition due to spring vibration can be put into the Schroedinger equation to derive the energy states of this bond (modeled as a spring). The lowest energy state gives a measure of bond strength at absolute zero (0° K).

$$E = \frac{1}{2} \frac{(h) (k)}{2\pi (m)}^{1/2}$$

where h is Plank's constant (6.63 x10<sup>-34</sup> J/sec) and k is the spring constant.

Equating with

E = hv (energy as a function of wavelength), one derives...

$$v = \frac{1}{4\pi} \frac{(k)^{1/2}}{(m)}$$

which is the bond vibration frequency at 0° K.

Both E and v are inversely proportional to the square root of mass

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### type "b" effects - chemical bonding

The spring constant k is mostly determined by the chemical properties of the bonded elements (e.g., valence electronic configuration).

*Nuclear properties (e.g., neutron number) play almost no role in bond "springiness".*

k is the same for two different isotopes of the same element involved in the same type of chemical bond with another element, so the higher isotope mass has lower bond vibration v, and vice versa.

At 0° K the energy at this particular v is known as the zero-point energy, zpe.

The relative zpe of bonds involving a heavy and light isotope of the same element to another (e.g., <sup>1</sup>H-X and <sup>2</sup>H-X) are depicted below:

$$v_{\text{heavy bond}} < v_{\text{light bond}} \text{ so } E_{\text{heavy bond}} < E_{\text{light bond}}$$

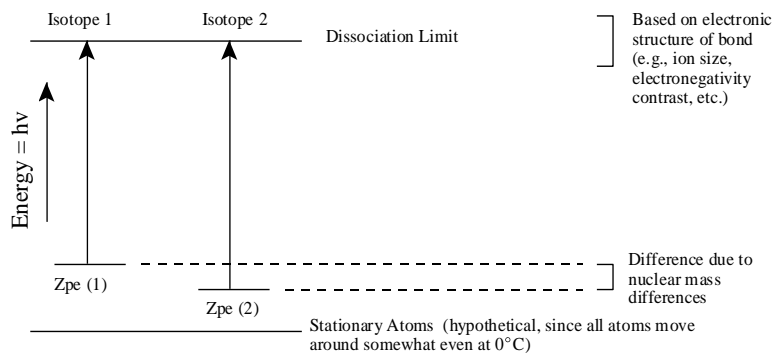
at 0°K the heavier isotope makes the stronger (lower v) bond.

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### type "b" effects - chemical bonding

The *dissociation limit* is the maximum  $\nu$  ( $\nu_{\max}$ ) at which a bond can exist.

At  $\nu > \nu_{\max}$ , the bond breaks.



If nuclei were stationary in the ground state of a molecule, different isotopes would have the same bond dissociation energy. Differences in the dissociation energy occur at the zero-point vibrational energy (zpe) associated with motions between the bonded atoms

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### type "b" effects - chemical bonding

Bond energy at  $\nu_m$  is also property of the electronic structures of the atoms involved so it is independent of isotope mass:

i.e.,  $\nu_m$  is the same for the heavy and light isotope bonds

Thus, the **lighter isotope bond is closer in energy to the E of dissociation** than the heavier isotope bond and at 0 K the **heavier isotope makes the stronger (lower  $\nu$ ) bond**.

The same is qualitatively true at other temperatures too.

It is therefore easier to break bonds involving lighter isotopes of elements than heavier ones.

**We see this effect in many natural processes.**

#### magnitude of the effect

This is strongly dependent on the material involved, because the spring constant  $k$  is different for different bonds and different substances.

In **isotope-exchange reactions**, the proportions of isotopes we find in the products and reactants depend on the **relative energies of all** of the bonds formed/broken for that given element.

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### Quantifying Isotopic Fractionation

Isotopic composition of the light stable isotopes are usually expressed as ratios of minor to major isotope.

For H, C and O, this corresponds to a ratio of heavy/light isotope (e.g., D/H,  $^{13}\text{C}/^{12}\text{C}$ ,  $^{18}\text{O}/^{16}\text{O}$ ). In the discussion that follows, I use the generic "R" for ratios of this sort.

We constrain the relative extent of isotopic fractionation between materials A and B (that are related by a chemical/physical process) by comparing their isotopic compositions ( $R_A$  and  $R_B$ ).

Often, geochemists refer to the *fractionation factor*  $\alpha_B^A$ , which is  $R_A/R_B$ .

In the following reaction:



$$K_{\text{eq}} = \frac{a_{\text{HDO}} \cdot P_{\text{H}_2}}{a_{\text{H}_2\text{O}} \cdot P_{\text{HD}}}$$

We can substitute  $R_{\text{H}_2\text{O}} \sim a_{\text{HDO}}/a_{\text{H}_2\text{O}}$  and  $R_{\text{H}_2} \sim P_{\text{HD}}/P_{\text{H}_2}$  into the  $K_{\text{eq}}$  equation to get

$$K_{\text{eq}} \sim R_{\text{H}_2\text{O}}/R_{\text{H}_2} = \alpha_{\text{H}_2}^{\text{H}_2\text{O}}$$

(where R is the D/H ratio in the water and molecular hydrogen, and we are ignoring the very minor amount of  $\text{D}_2\text{O}$  and  $\text{D}_2$  that is also formed to keep things simple)

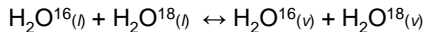
So,  $K_{\text{eq}} \sim \alpha$  at equilibrium

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### Quantifying Isotopic Fractionation

Isotopic composition of the light stable isotopes are usually expressed as ratios of minor to major isotope.

Similar equations can be written for exchange during phase changes:



$$R_l/R_v = \alpha_{l/v} = 1.0092 \text{ (coexisting liquid is } \sim 1\% \text{ heavier than vapor, at } 25^\circ\text{C)}$$

As geologists, we're often more interested in what the isotopic composition of a natural material tells us about the conditions that existed in the system when the material formed.

In this case, we use the relative fractional difference in its isotopic composition relative to a standard reference material:

$$\frac{R_A}{R_{\text{STD}}} - 1 \text{ or } \frac{R_A - R_{\text{STD}}}{R_{\text{STD}}}$$

This quantity is 0 at  $R_A = R_{\text{STD}}$ .

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## Quantifying Isotopic Fractionation

### Common isotope standards ( $R_{STD}$ )

Element	Standard	Isotopes	per mil isotopic variation	
			rocks/minerals	natural waters
H	Standard Mean Ocean Water (SMOW)	$^2\text{H}/^1\text{H}$ (D/H)	-180 to +20	-410 to +50
C	Calcite PD Belemnite (PDB)	$^{13}\text{C}/^{12}\text{C}$	-35 to +5	
O	SMOW, or PDB	$^{18}\text{O}/^{16}\text{O}$	-2 to + 36, or -32 to +5	-50 to +15, or -78 to -15

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## Quantifying Isotopic Fractionation

Isotope Standards are useful for more than just referencing the isotopic composition of a material to a common baseline.

They also provide a means for cross-calibrating isotopic compositions measured by different labs (where small differences in analytical procedures can introduce biases).

Say five labs each analyze SMOW multiple times and get slightly different mean values.

A correction factor can be applied to adjust the raw value measured for each sample in each lab (unknown) to a single reference-standard value.

Or, in cases of  $\delta\text{O}^{18}$  using  $R_{SMOW} \text{O}^{18} = R_{STD}$ , the biases between labs come out automatically, assuming  $R_{unknown}$  and  $R_{STD}$  are being biased the same way.

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## Quantifying Isotopic Fractionation

Since light isotope fractionation is typically observed at the ‰ to ‰ range, we can take the two equivalent quantities above and multiply by 1000, to express fractionation with a quantity known as "delta":  $\delta$  ( $\delta$  is in units of ‰ (ppt)).

$$1000 \times \left( \frac{R_A}{R_{STD}} - 1 \right) \quad \text{or} \quad 1000 \times \left( \frac{R_A - R_{STD}}{R_{STD}} \right)$$

**Please, Please, Please** don't ever refer to  $\delta$  as "del", for instance as in "del O-18". You often hear people making this nomenclature mistake but it is a meaningless term. Proper pronunciation of  $\delta^{18}\text{O}$  is an easy way to distinguish a geochemist (who will rightly say "delta O-18") from the less-informed geologist (who will wrongly say "del O-18").

A few additional mathematical relationships are:

$$\alpha^1_2 = \frac{1 + \delta_1/1000}{1 + \delta_2/1000} = \frac{\delta_1 + 1000}{\delta_2 + 1000}$$

$$\alpha^1_2 \sim 1 + (\delta_1 - \delta_2)/1000$$

$$\delta_1 - \delta_2 = \Delta^1_2 \sim 1000 \ln \alpha^1_2$$

The conversion between  $\delta^{18}\text{O}_{(\text{SMOW})}$  and  $\delta^{18}\text{O}_{(\text{PDB})}$  is:

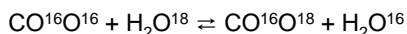
$$\delta^{18}\text{O}_{(\text{SMOW})} = 1.03086 \delta^{18}\text{O}_{(\text{PDB})} + 30.86$$

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## Isotopic Exchange as Monitors of Paleo-conditions

Consider the formation of  $\text{CaCO}_3$  from sea water containing DIC in equilibrium with atmospheric  $\text{CO}_2$ . The isotopic composition of the DIC will reflect equilibrium with the atmosphere for both C and O isotopes and with the  $\text{H}_2\text{O}$  for O isotopes.

For instance, the DIC- $\text{H}_2\text{O}$  exchange reaction is:



The  $\delta^{18}\text{O}$  of the DIC affects the  $\delta^{18}\text{O}$  of the  $\text{CaCO}_3$  by



These two can be combined into one reaction



We can use  $R(\text{O}^{18}/\text{O}^{16})$  that we measure in the  $\text{CaCO}_3$  to say something about the R values in the  $\text{H}_2\text{O}$  and the  $\text{CO}_2$  from which the  $\text{CaCO}_3$  formed  $\rightarrow$  and therefore about the *conditions* at the time it formed.

How we do this will become clearer after the next couple of topics.

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### Temperature dependence of fractionation

Just as chemical equilibria are temperature dependent, so are isotopic fractionation reactions, as predicted by

$$\left(\frac{\partial \log K}{\partial T}\right)_P = \frac{\Delta H^\circ}{2.303RT^2}, \quad \text{or} \quad \left(\frac{\partial \log \alpha}{\partial T}\right) = \frac{\Delta H^\circ}{2.303R} \left(\frac{1}{T^2}\right)$$

So that **fractionation is inversely proportional to temperature**.

Temperature dependence is parameterized (fit to observations) in one of two ways:

$$\begin{aligned} \Delta^1_2 &= \delta^{18}\text{O}_1 - \delta^{18}\text{O}_2 \approx 1000 \ln \alpha^1_2 \\ &= A \times 10^6 + \frac{B}{T^2} \quad \text{or} \quad \frac{C}{T^2} \end{aligned}$$

The constants A, B, and C for these equations are specific to the phases (e.g., minerals) involved.

These constants are determined experimentally.

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### Temperature dependence of fractionation

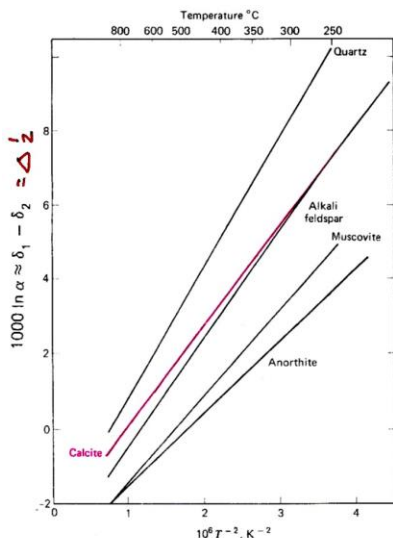


Figure 7.2 Experimentally determined oxygen isotope fractionation curves for selected mineral-H<sub>2</sub>O systems.

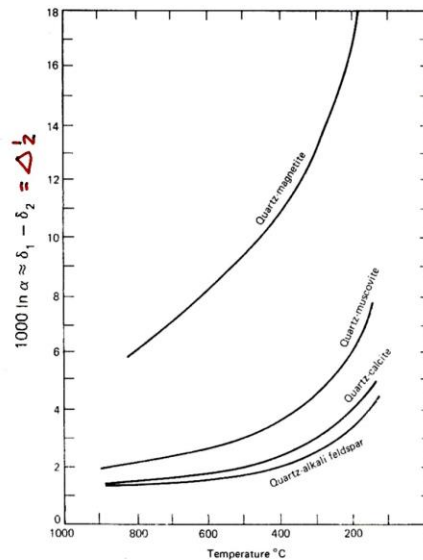


Figure 7.3 Oxygen isotope calibration curves for quartz-mineral systems.

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### Temperature dependence of fractionation

We can use the thermal dependence of mineral-mineral and mineral-water equilibria to constrain the temperatures of processes occurring today and in the past.

For instance, in the formation of  $\text{CaCO}_3$  from sea water containing DIC in equilibrium with atmospheric  $\text{CO}_2$  following the above exchange reactions...

two different samples of  $\text{CaCO}_3$  formed from a homogenous reservoir of  $\text{H}_2\text{O} + \text{DIC}$  with different  $\delta\text{O}^{18}$  will very likely be due to differences in formation temperatures.

We can use the data in the preceding plots to determine how much temperature difference is implied by the  $\delta\text{O}^{18}$  of the two materials.

This equation can be expressed for measurements relative to SMOW or PDB:

$$T = 16.9 - 4.20 (\delta_C - \delta_W) + 0.13(\delta_C - \delta_W)^2 \quad [\text{for } \delta_C \text{ SMOW}]$$

$$T = 16.0 - 4.14 (\delta_C - \delta_W) + 0.13(\delta_C - \delta_W)^2 \quad [\text{for } \delta_C \text{ PDB}]$$

$\delta_C$  = the oxygen isotopic composition of the calcite

$\delta_W$  = the oxygen isotopic composition of the water.

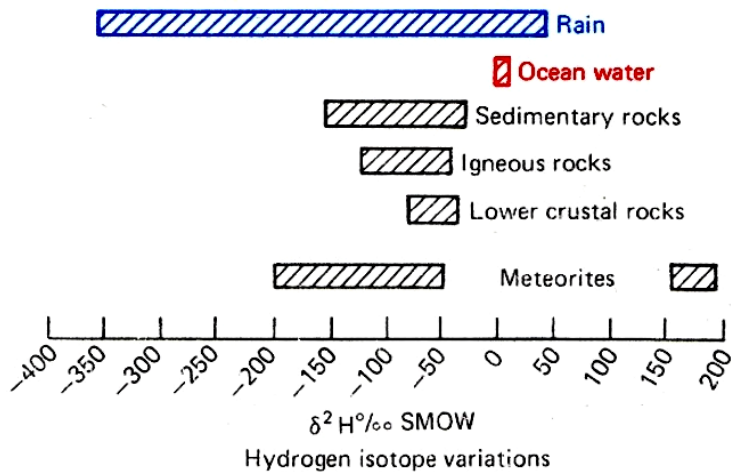
$\delta_W$  is relative to SMOW in both cases.

**Note: When organisms carry out the production of  $\text{CaCO}_3$ , each species creates shells with slightly different temperature relationships, due to "vital" effects.**

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### The range of isotopic compositions of H, C and O on the earth

$\delta\text{D}$  ( $\delta^2\text{H}$ ) shows the greatest range, as expected from the large D-H mass difference.



**Figure 7.7** Hydrogen isotope variations.

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## The range of isotopic compositions of H, C and O on Earth

$\delta^{18}\text{O}$  in rocks *decreases* overall with *increasing* formation temperature of the rock.

(Oxygen in Si-O-Si bonds, as in chert, is more enriched in  $^{18}\text{O}$  than in Si-O-Al or Si-O-Mg bonds.)

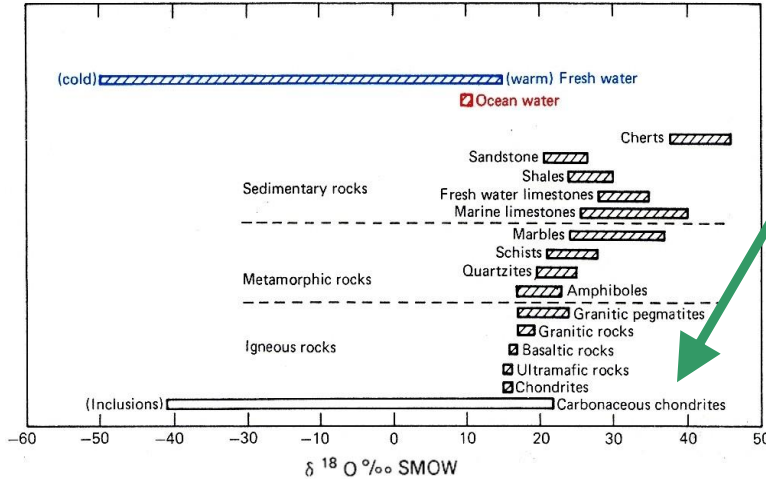


Figure 7.1 Oxygen isotope variation in common rocks, minerals, and waters.

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## The range of isotopic compositions of H, C and O on Earth

inorganic materials have *heavier* C than organic ones.

Organic matter is isotopically light because biotic metabolisms are highly tuned to chemical reaction energetics. The energy difference in  $^{12}\text{C-X}$  and  $^{13}\text{C-X}$  bonds is great enough that they prefer breaking the higher energy (easier to break)  $^{12}\text{C-X}$  bonds.

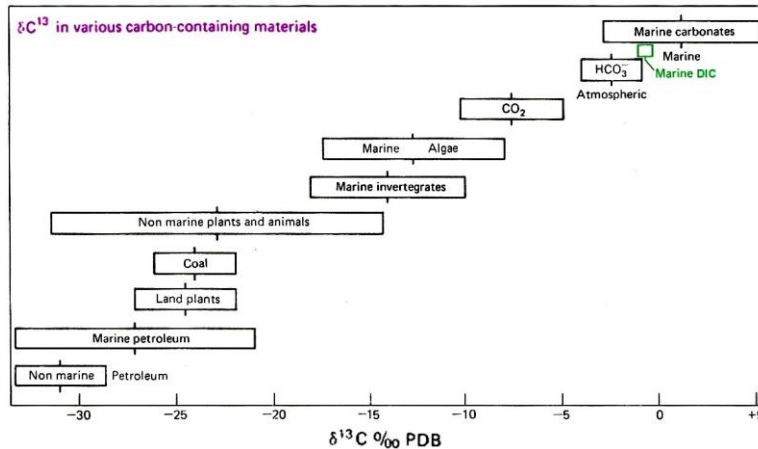


Figure 7.5 Carbon isotope variation in natural carbon-containing materials.

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## The range of isotopic compositions of H, C and O on the earth

1.  $\delta^{18}\text{O}$  values relative to SMOW and PDB are the way they are because of the processes that form them (e.g.,  $\delta^{18}\text{O}$  vapor < liquid < solid):

- a) **SMOW is liquid water**, so most minerals (solids) have positive  $\delta^{18}\text{O}$  relative to SMOW.
- b) **PDB is a shell (solid)**, which should have  $\delta^{18}\text{O}$  greater than the water from which it formed. Thus,  $\delta^{18}\text{O}$  values of natural waters are usually lighter (isotopically negative) relative to PDB.

2.  $\delta^{13}\text{C}$  values relative to PDB are the way they are because:

- c)  $\delta^{13}\text{C}$  of PDB (solid) should be greater than the DIC of the water in which it formed; the same is true for other shells, which have similar (slightly < or >) values compared to PDB.
- d) carbon in atmospheric  $\text{CO}_2$  (gas) is isotopically lighter than shell material and organic matter is lighter still.

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## H and O isotopic composition in Natural waters on Earth

The hydrologic cycle involves many phase changes (solid  $\leftrightarrow$  liquid  $\leftrightarrow$  vapor).

The **extent of isotopic fractionation** during liquid  $\leftrightarrow$  vapor exchange is a **strong function of temperature**.

Liquid-vapor exchange occurs over a wide temperature range. Thus substantial isotopic heterogeneity can occur in the hydrosphere without ever breaking any O-H bonds.

Evaporation of water favors the **lighter** isotopes at all temperatures, but more so at **lower** temperature.

Examples for O are shown to the left. H behaves similarly

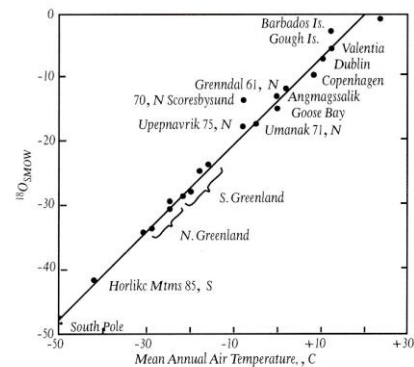


Figure 9.8. Variation in  $\delta^{18}\text{O}$  in precipitation as a function of mean annual temperature both figures from White, "Geochemistry"

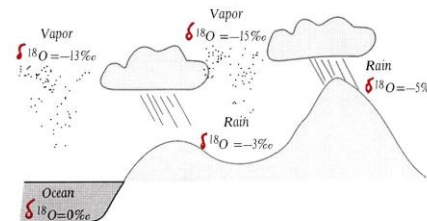


Figure 9.9. Cartoon illustrating the process of Rayleigh fractionation and the decreasing  $\delta^{18}\text{O}$  in rain as it moves inland.

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## H and O isotopic composition in waters on Earth

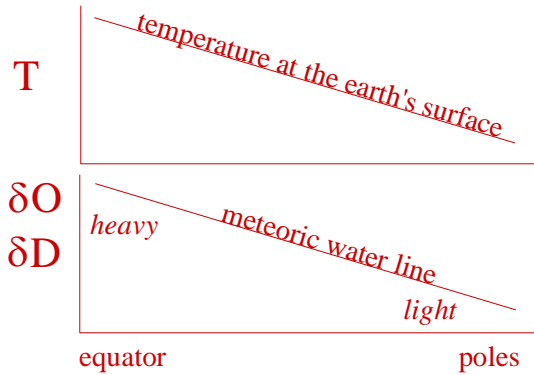
Temperatures are relatively cool at the poles, so evaporating water is relatively depleted in the heavy isotopes than at warmer equatorial locales (i.e., it is *more* fractionation from the liquid phase)

The magnitude of the effect is greater than would be predicted for chemical equilibrium

(from a homogeneous liquid water reservoir)

because kinetic effects enhance the fractionation and because the surface oceans also have water variable isotopic compositions reflecting local precipitation.

It is the temperature gradient from equator to poles that causes variations in both the isotopic ratios of surface ocean waters and of water vapor in the overlying atmosphere.



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## H and O isotopic composition in waters on the earth

Meteoric and atmospheric waters from around the world follow the  $\delta D$  vs.  $\delta^{18}O$  relationship shown here, which is known as the "meteoric water line":

$$\delta D_{SMOW} = 8 \delta^{18}O_{SMOW} + 10$$

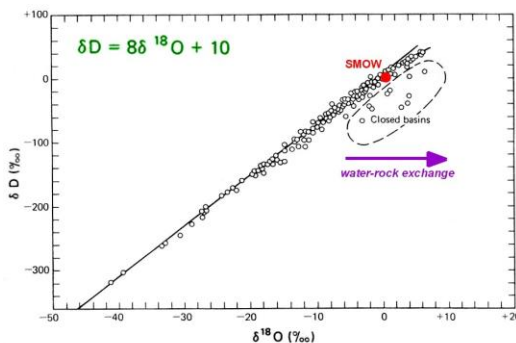


Figure 17-1 Deuterium and  $^{18}O$  variations in rivers, lakes, rain, and snow. (Craig, 1961. Copyright 1961 by the American Association of Science.)

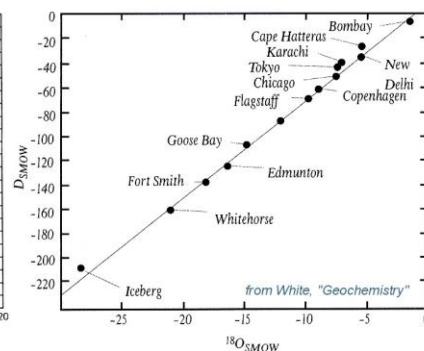


Figure 9.10. Northern hemisphere variation in  $\delta D$  and  $\delta^{18}O$  in precipitation and meteoric waters. The relationship between  $\delta D$  and  $\delta^{18}O$  is approximately  $\delta D = 8 \times \delta^{18}O + 10$ . After Dansgaard (1964).

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## H and O isotopic composition in waters on Earth

This contour map of the H and O isotopic composition of precipitation over North America illustrates both the **latitudinal (temperature) effect**, and the **“rain-out” effect**, which is similar to the loss of marine aerosols as a storm moves inland.

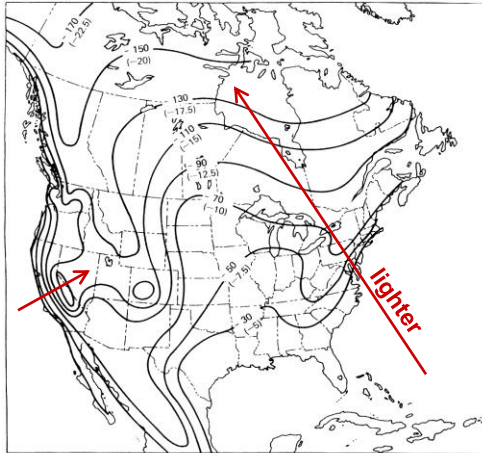


Figure 17-2 Distribution of  $\delta D$  and corresponding  $\delta^{18}O$  (in parentheses) in meteoric waters in North America (adapted from Sheppard et al., 1969).

The rain-out effect: precipitation is enriched in the heavy isotope, as we saw earlier, by:

$$\alpha_V^L = 1.0092 \text{ at } 25^\circ\text{C}.$$

Thus, as an air mass moves inland and produces more rain, water condenses from vapor that is continually growing lighter.

For this reason, the rain (and surface meteoric water) also gets isotopically lighter as we move inland from the coast, even at a single latitude.

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## H and O isotopic composition in waters on the earth

During **high-temperature (>50°C)** interaction of meteoric water with rocks, other types of fractionation effects occur between the water and minerals in the rock (water-rock reactions).

These have the effect of **shifting  $\delta^{18}O$  without much change in  $\delta D$**  (because rocks contain little exchangeable H).

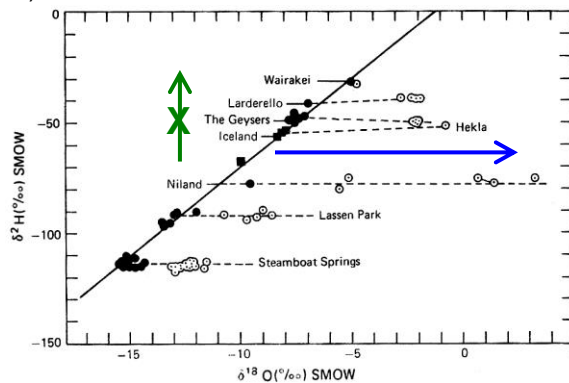


Figure 7.9 Isotopic variations in some geothermal waters and in geothermal steam. ■: local meteoric waters or slightly heated nearsurface ground waters; ●: hot springs or geothermal water; ○: high temperature, high pressure, geothermal steam. Niland = Salton Sea Geothermal Area. (After CRAIG, 1963. *Conf. on Nuclear Geology in Geothermal Areas*. Spoleto, Italy.)

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