

Traditionally and non traditionally used stable isotopes

- Elements that have more than one non-radiogenic isotope, for which the mass difference between isotopes is a significant fraction of the atomic mass, and which have enough interesting chemistry to fractionate the isotopes

IA	IIA	IIIB	IVB	VB	VIB	VIB	VIIIB	IB	IIIB	IIIA	IVIA	VIA	VIIA	VIIIA	
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	
1	Be	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Al	Si	P	2 He
2	Mg	Ca	40	41	42	43	44	45	46	47	48	49	50	51	3 Ne
3	Na	19	22	23	24	25	26	27	28	29	30	31	32	33	17 F
4	K	Ca	39	40	41	42	43	44	45	46	47	48	49	50	18 Ne
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	53 Cl
6	Cs	Ba	72	73	74	75	76	77	78	79	80	81	82	83	36 Ar
7	Fr	Ra	104	105	106	107	108	109	110	111	112	113	114	115	54 Br
			57	58	59	60	61	62	63	64	65	66	67	68	56 Kr
			Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	55 Xe
			59	90	91	92	93	94	95	96	97	98	99	100	54 Rn
			Actinides												
			143	140	141	142	143	144	145	146	147	148	149	150	142 At
			147	148	149	150	151	152	153	154	155	156	157	158	159 Lu
			151	152	153	154	155	156	157	158	159	160	161	162	163 Lr

- Traditional stable isotope chemistry focuses entirely on the light elements (H, Li, B, C, N, O)
- More recently analytical tools have become precise enough to enable work on the small anomalies in heavier metals

Element	# isotopes	$\Delta m/m$	Abundances (%)
H	2	1	99.985, 0.015
Li	2	1/6	7.5, 92.5
B	2	1/10	19.9, 80.1
C	2	1/12	98.89, 1.11
N	2	1/14	99.634, 0.366
O	3	2/16	99.762, 0.038, 0.2
Mg	3	2/24	78.99, 10.0, 11.01
Si	3	2/28	92.23, 4.67, 3.10
S	4	4/32	95.02, 0.75, 4.21, 0.02
Cl	2	2/35	75.77, 24.23
Fe	4	4/54	5.85, 91.75, 2.12, 0.28

Elements suitable for stable isotope study

- They have low atomic mass
- The relative mass difference between the isotopes is large
- They form bonds with a high degree of covalent character or
- The elements exist in more than one oxidation state (C, N, and S), form a wide variety of compounds (O), or are important constituents of naturally-occurring solids and fluids
- The abundance of the rare isotope is sufficiently high (generally at least tenths of a percent) to facilitate analysis

Isotope fractionation

- Fractionation refers to the partial separation of two isotopes of the same element during physico-chemical processes, producing reservoirs with different ratios of the isotopes
- These differences are called isotope anomalies/effects
- Physical properties of an element determined by its nucleus
- According to classical mechanics, chemical properties of an element depends on its electronic configuration
- All isotopes of an element have the same electronic structure. All isotopes of an element should therefore have the same chemical properties
- **Why do then two isotopes of the same element get fractionated from each other?**

Types of isotope fractionation

(1) Mass dependent isotope fractionation

- Depend only on the mass of the isotope; will fractionate, say $^{18}\text{O}/^{16}\text{O}$ about twice as much as $^{17}\text{O}/^{16}\text{O}$

Two basic mechanisms

Equilibrium isotope fractionation

- Due to differences in bond energies of isotopes in compounds

Kinetic isotope fractionation

- Due to differences in average velocity or reaction rates or diffusion rates of different isotopes

(2) Mass independent isotope fractionation

- Mechanisms remains uncertain
- One proposed mechanism is photo-dissociation of molecules by UV radiation (isotope-specific wavelengths) and is thought perhaps to have been relevant in the solar nebula

Equilibrium Isotope Fractionation

- A quantum-mechanical phenomenon, driven mainly by differences in the vibrational energies of molecules and crystals containing atoms of differing masses

What did all that mean?

Fractionation of stable isotopes occurs because of differences in the vibrational energy of isotopically different molecules

This is because vibrational energy is quantised and given by

$$E = (n+1/2)\hbar\nu$$

Therefore at absolute zero ($n=0$) the vibrational energy of a molecule is a finite distance above zero equal to $1/2\hbar\nu$, where \hbar is Planck's constant and ν the vibrational frequency.

This is called the ZERO POINT ENERGY (ZPE)

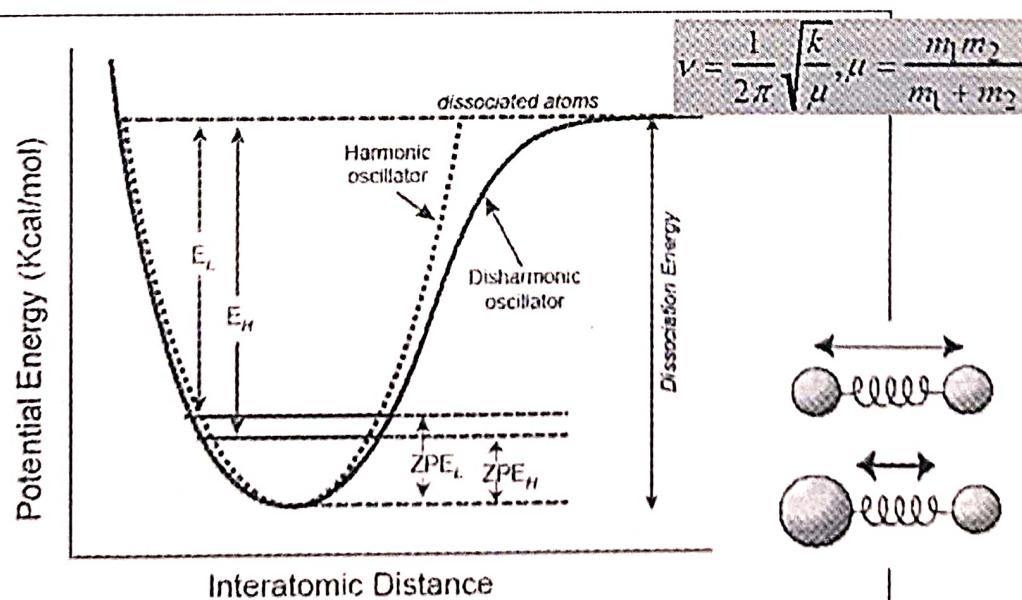
Mechanism of equilibrium isotope fractionation

Molecules containing the heavy isotope have a lower ZPE than molecules containing the light isotope

Molecules containing the heavy isotope are more stable than molecules containing the light isotope

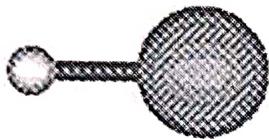
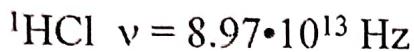
At very low temperatures the vibration of an isotopic molecule is harmonic. However with increasing temperatures, the vibrations of all molecules becomes increasingly disharmonic and the spacings between energy levels becomes increasingly smaller until dissociation occurs.

Mechanism of equilibrium isotope fractionation

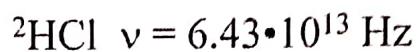


Isotopes distribute themselves among compounds in a way that minimizes the energy of the system. The sensitivity to mass comes in through the vibrational modes of inter-atomic bonds

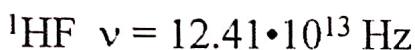
Zero point energies



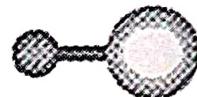
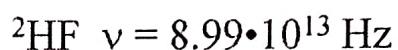
$$E(\text{vib}) = 1/2 \cdot h\nu \\ \approx 17,900 \text{ J/mol}$$



$$E(\text{vib}) = 1/2 \cdot h\nu \\ \approx 12,800 \text{ J/mol}$$



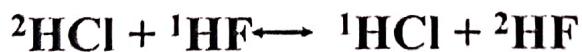
$$E(\text{vib}) = 1/2 \cdot h\nu \\ \approx 24,800 \text{ J/mol}$$



$$E(\text{vib}) = 1/2 \cdot h\nu \\ \approx 17,900 \text{ J/mol}$$

Theory of equilibrium isotopic fractionation

At Equilibrium, for H-isotope exchange between HF and HCl:



$$\Delta G_0 \approx \Delta E(\text{vib}) = E(\text{vib})_{\text{products}} - E(\text{vib})_{\text{reactants}}$$

$$E(\text{vib})_{\text{products}} = 17,900 \text{ J/mol} (^1\text{HCl}) + 17,900 \text{ J/mol} (^2\text{HF})$$

$$E(\text{vib})_{\text{reactants}} = 12,800 \text{ J/mol} (^2\text{HCl}) + 24,800 \text{ J/mol} (^1\text{HF})$$

$\Delta E(\text{vib}) = -1,800 \text{ J/mol}$, driving the reaction to the right and concentrating ^2H in HF (by a factor of 2 at 25 °C)!

- Need to consider all energy levels, not just ground state (Boltzmann statistics), as well as entropy terms, both of which give *smaller fractionations at high temperature*

Delta notation

- Stable isotope ratios are almost always expressed in δ -notation:

$$\delta = \left(\frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{Standard}}} \right) \times 1000$$

e.g., $\delta^{18}\text{O} = \left[\frac{(^{18}\text{O}/^{16}\text{O})_{\text{sam}} - (^{18}\text{O}/^{16}\text{O})_{\text{SMOW}}}{(^{18}\text{O}/^{16}\text{O})_{\text{SMOW}}} \right] \times 10^3$

The $\times 1000$ implies that the units on δ are parts per thousand, permil, or ‰

Table 9.1. ISOTOPE RATIOS OF STABLE ISOTOPES

Element	Notation	Ratio	Standard	Absolute Ratio
Hydrogen	δD	$\text{D}/\text{H} (^2\text{H}/^1\text{H})$	SMOW	1.557×10^{-4}
Lithium	$\delta^{7}\text{Li}$	$^{7}\text{Li}/^{6}\text{Li}$	NBS L-SVEC	12.02
Boron	$\delta^{11}\text{B}$	$^{11}\text{B}/^{10}\text{B}$	NBS 951	4.044
Carbon	$\delta^{13}\text{C}$	$^{13}\text{C}/^{12}\text{C}$	PDB	1.122×10^{-2}
Nitrogen	$\delta^{15}\text{N}$	$^{15}\text{N}/^{14}\text{N}$	atmosphere	3.613×10^{-3}
Oxygen	$\delta^{18}\text{O}$	$^{18}\text{O}/^{16}\text{O}$	SMOW, PDB	2.0052×10^{-3}
	$\delta^{17}\text{O}$	$^{17}\text{O}/^{16}\text{O}$	SMOW	3.76×10^{-4}
Sulfur	$\delta^{34}\text{S}$	$^{34}\text{S}/^{32}\text{S}$	CDT	4.43×10^{-2}

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Fractionation factor

The Fractionation Factor

The Fractionation factor (α) is the ratio of the heavy to the light isotope in molecule A, divided by the ratio of the heavy to the light isotope in molecule B

$$\alpha_{A-B} = R_A / R_B \text{ where } R_A \text{ is } (^{18}\text{O}/^{16}\text{O})_A, (^{13}\text{C}/^{12}\text{C})_A \text{ etc.}$$

At equilibrium α is related to the equilibrium constant K by the expression:

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

where n = the number of atoms exchanged. By convention, isotope exchange reactions are written such that only one atom is exchanged and thus $\alpha = K$.

Fractionation factor is T dependent

Equilibrium constant can be written as a ratio of partition functions of heavy and light isotopes (statistical mechanics)

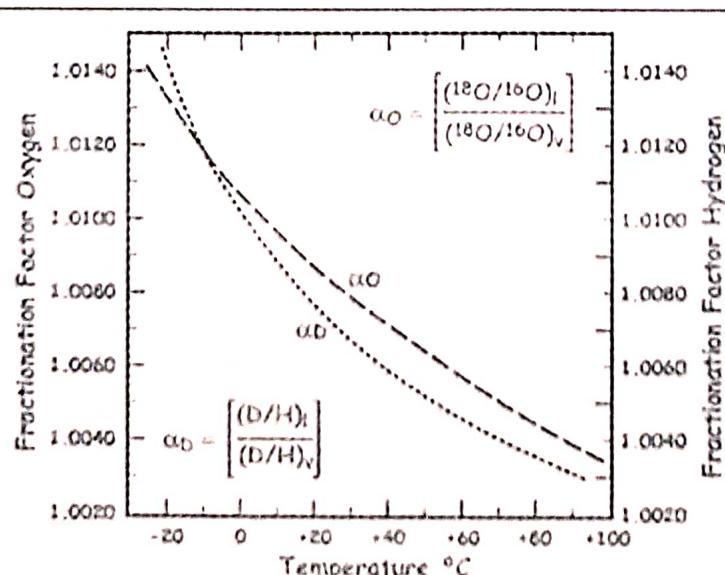
$$\alpha = K = \frac{[Q_H]}{[Q_L]} \propto \frac{-e^{-U_H/2}}{-e^{-U_L/2}} \frac{1 - e^{-U_L}}{1 - e^{-U_H}}$$

where $U = hv/kT$, then taking the natural log of the above shows us that

$$\ln \alpha = 1/T^2$$

where T is in Kelvin and K is a constant

Fractionation Factors and Temperature



Temperature variation of isotope fractionation factors for evaporation of water

Relationship Between δ and α

The Fractionation factor

$$\alpha_{a-b} = R_a / R_b$$

The Delta Value

$$\delta_b = \frac{[R_b - R_{smow}]}{[R_{smow}]} \times 1000$$

Therefore δ and α are related by the expression

$$\alpha_{a-b} = \frac{[\delta_a + 1000]}{[\delta_b + 1000]}$$

Since α is of the form 1.00XX we can make the approximation

$$1000 \ln 1.00XX \approx X \cdot X \approx \delta_a - \delta_b \approx \Delta_{a-b}$$

So if $\alpha_{water-vapour}$ is 1.0098 then $\delta^{18}O_{water}$ is 9.8‰ heavier or higher than $\delta^{18}O_{vapour}$

Note that the above approximation only holds for low values of X

Experimental results show that $1000 \ln \alpha$ is often a smooth function of $1/T^2$ for mineral-mineral and mineral-fluid pairs

Isotope Thermometry

The relationship

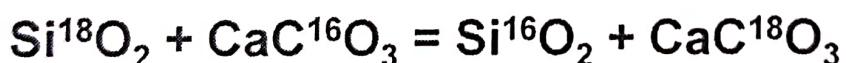
$$1000 \ln \alpha_{a-b} = \frac{X}{T^2} + Y = \delta_a - \delta_b = \Delta_{a-b}$$

is useful for two reasons

1. we can measure δ_a and δ_b and use them to determine T
2. we can measure δ_a and δ_b and using our knowledge of T from other methods assess the degree of equilibrium with respect to the isotopic system

Values of α_{a-b} are normally determined experimentally using (a) mineral-water pairs and (b) mineral-calcite pairs

Isotope Thermometry



In general minerals exchange more readily with a free water phase than with each other

EXAMPLE $1000 \ln \alpha_{\text{qtz}-\text{H}_2\text{O}} = 3.38 \times 10^6 / T^2 - 2.90$
 $1000 \ln \alpha_{\text{cc}-\text{H}_2\text{O}} = 2.78 \times 10^6 / T^2 - 2.89$

Since $\alpha_{a-c} = \alpha_{a-b} - \alpha_{c-b}$

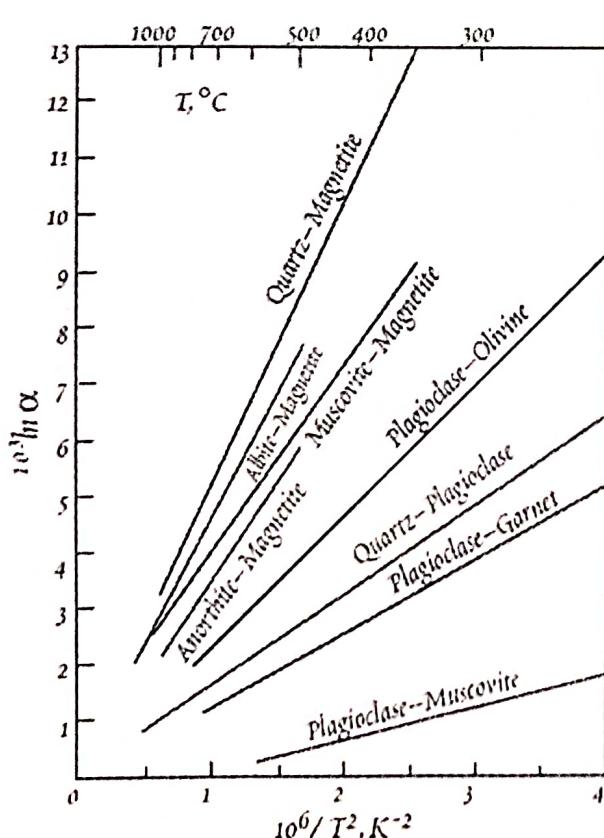
Then $\alpha_{\text{qtz}-\text{cc}} = \alpha_{\text{qtz}-\text{H}_2\text{O}} - \alpha_{\text{cc}-\text{H}_2\text{O}}$

$$1000 \ln \alpha_{\text{qtz}-\text{cc}} = (3.38 - 2.78) \times 10^6 / T^2 + 0.01$$

Isotope Geothermometry

Sequence of minerals in order of their increasing tendency to concentrate ^{18}O

	$\delta^{18}\text{O}$
1. Quartz	15.0
2. Dolomite	14.2
3. K-feldspar, albite	13.0
4. Calcite	12.8
5. Na-rich plagioclase	12.5
6. Ca-rich plagioclase	11.5
7. Muscovite, paragonite	11.3
8. Augite, orthopyroxene, diopside (kyanite)	10.5
9. Hornblende (titanite, lawsonite)	10.0
10. Olivine, garnet (zircon, apatite)	9.5
11. Biotite	8.5
12. Chlorite	8.0
13. Ilmenite	5.5
14. Magnetite, hematite	4.5



Stable isotope thermometry

- Measurements of isotope fractionation between coexisting phases presumed to have equilibrated with one another define the temperature at which they equilibrated
- Several common mineral pairs have been calibrated by laboratory exchange experiments
- The general problem is that equilibrium is most readily achieved at high temperature but the isotope thermometers are most sensitive at low temperature!

Figure 9.6. Oxygen isotope fractionation for several mineral pairs as a function of temperature.

Kinetic Isotope Fractionation

Isotope fractionations are basically caused by either

- Kinetic Effects
- Equilibrium Isotope Exchange

Kinetic Effects

Kinetic isotope effects are associated with processes such as evaporation, diffusion and dissociation reactions. These types of processes are unidirectional and relatively rapid. They fractionate isotopes because

1. The velocities of isotopic molecules are different
2. The velocity of a molecule is inversely proportional to its mass

Kinetic Isotope Fractionation

Therefore
$$\frac{v_L}{v_H} = \left[\frac{M_H}{M_L} \right]^{1/2}$$

Example

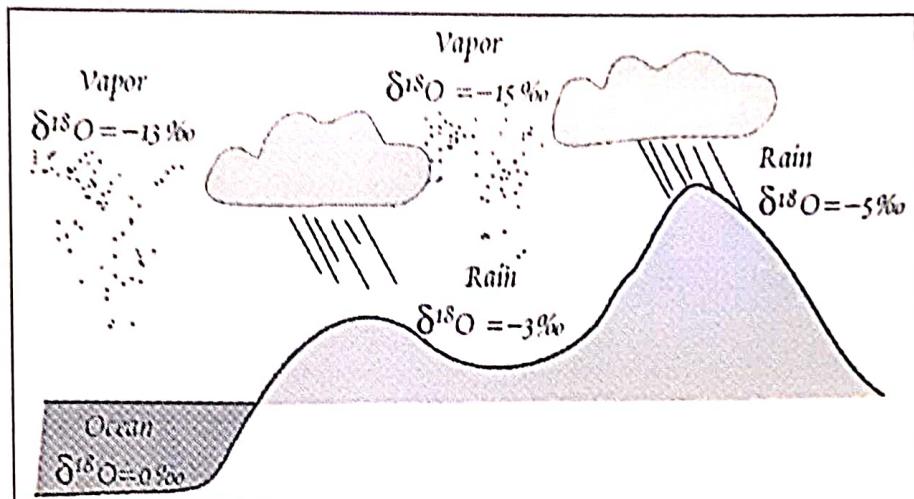
Carbon dioxide molecules $^{12}\text{C}^{16}\text{O}_2$ and $^{13}\text{C}^{16}\text{O}_2$, the ratio of the velocities is

$$\left[\frac{45}{44} \right]^{1/2} = 1.0113$$

The velocity of the light isotope is 1.011 times faster than that of the heavy isotope and leads to a fractionation of 11‰

Stable isotopes and the Hydrologic Cycle

- There is fractionation of oxygen (and hydrogen) isotopes by the hydrologic cycle
 - These are mostly kinetic factors, since evaporation and precipitation of water vapor, rain, and snow are nearly Rayleigh processes



Evaporation and condensation can be described by the Rayleigh distillation equation: $R/R_0 = f^{(\alpha-1)}$

Stable isotopes and Hydrologic Cycle

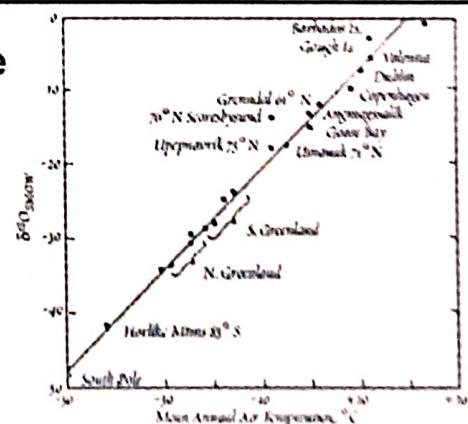
- The more rain you pull out of a cloud, the lighter the isotopes in the cloud become and the lighter the next increment of rain gets
- Since low temperature lowers solubility, air that reaches cold places has become very dry and very light
- Since water vapor originates in the ocean, by the time clouds get far inland they become very light

Linear relationship between $\delta^{18}\text{O}$ of average annual precipitation and average annual air T

Because isotope fractionation factor increases with decreasing T

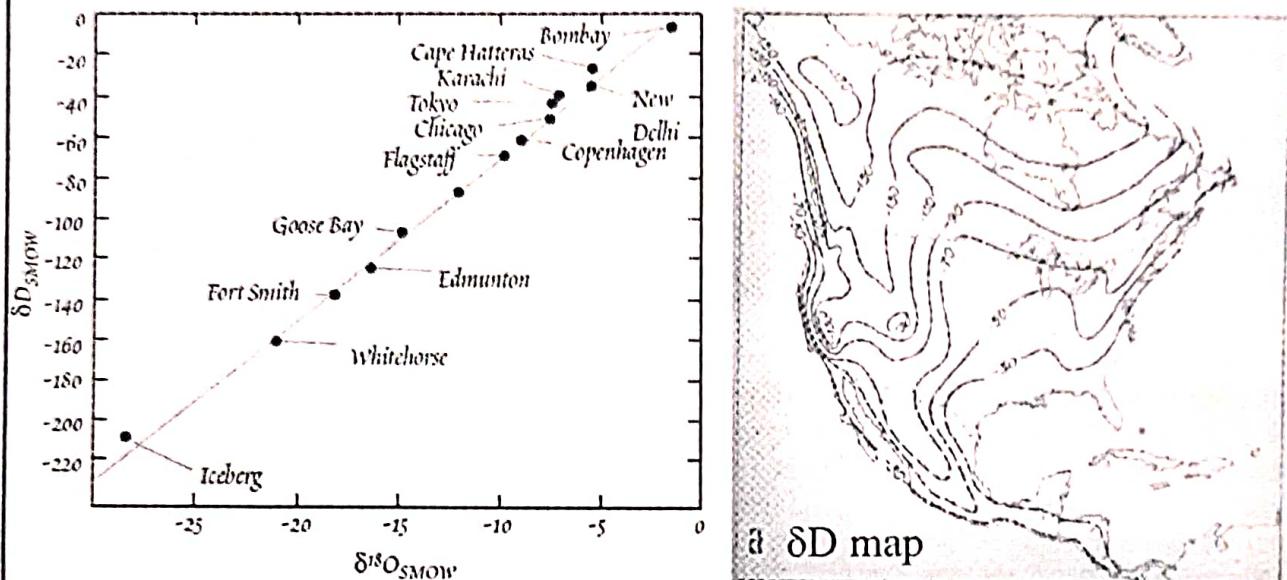
As moist air moves towards higher lat, $\delta^{18}\text{O}$ and δD of rain or snow from it becomes progressively more negative

There is a continental effect superimposed on a latitudinal gradient



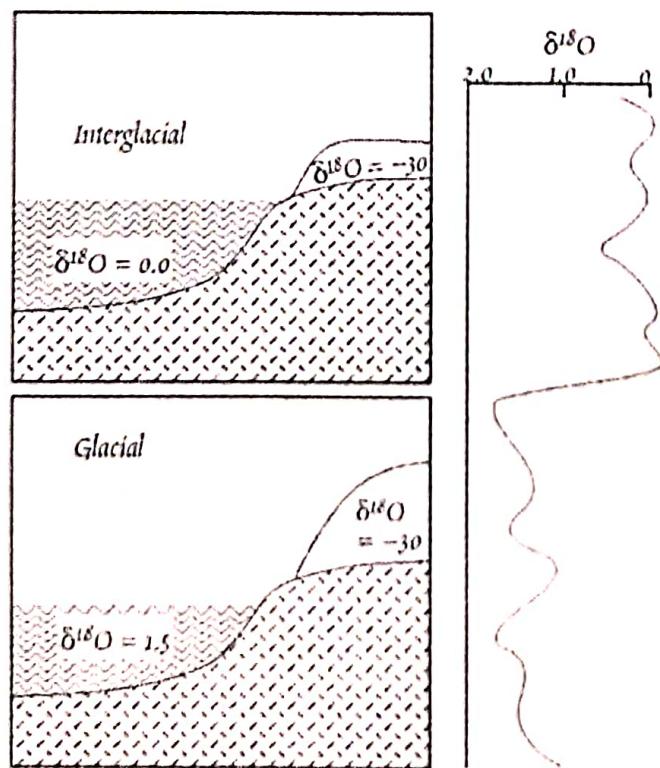
Stable isotopes and the Hydrologic Cycle

- Since hydrologic processes involve only mass fractionation, the **hydrogen** isotopes and **oxygen** isotopes co-vary quite closely, defining the *meteoric water line* $\delta D = 8 * \delta^{18}\text{O} + 10$



a δD map

Oxygen isotopes and paleo-T



Sediment-core records of the isotopic composition of biogenic calcite are available at various resolutions and record lengths covering the last 70 Ma

The biogenic calcite can be used to determine the $\delta^{18}\text{O}$ of sea water.

Why does seawater $\delta^{18}\text{O}$ change?
Because of the growth and decay of ice sheets... also T...and salinity variations

$$T (\text{°C}) = 16.9 - 4.2 * (\delta_c - \delta_w) + 0.13 * (\delta_c - \delta_w)^2$$

Figure 9.22 Cartoon illustrating how $\delta^{18}\text{O}$ of the ocean changes between glacial and interglacial periods.