

Notes 12. Stable Isotopes

I. Fractionation of stable isotopes

A. Equilibrium

B. Kinetic

II. Nomenclature

III. Oxygen (and Hydrogen) isotope fractionation at the Earth's surface

IV. Carbon isotope fractionation and life

Isotopes of an element have identical chemical properties - same # of protons in the nucleus, and the same electronic configuration (same charge, same ionic radius); hence, same "chemical properties".

But isotopes do differ in their mass. What properties might be affected by this? Physical properties:

Properties related to potential energy - bond strength, vibrational energy of molecular bonds (responsible for equilibrium fractionation). In general the heavy isotope fractionates into the site with the strongest bond. Equilibrium fractionation is independent of reaction rate (forward rate = reverse rate) or reaction mechanism, normally an exchange reaction. Examples: $2\text{Si}^{18}\text{O}_2 + \text{Fe}_3^{16}\text{O}_4 = 2\text{Si}^{16}\text{O}_2 + \text{Fe}_3^{18}\text{O}_4$ and $\text{H}_2^{16}\text{O} (\text{l}) + \text{H}_2^{18}\text{O} (\text{v}) = \text{H}_2^{18}\text{O} (\text{l}) + \text{H}_2^{16}\text{O} (\text{v})$. Much like elemental exchange reactions, isotopic exchange reactions are temperature dependent, with K's approaching 1 with higher temperature. One can make the same argument as with elemental exchange reactions, i.e. this represents a state of higher disorder at higher temperature and qualitatively could have been predicted from a basic knowledge of thermodynamics. Unlike elemental exchange reactions, isotopic exchange reactions have K's very close to one, even at temperatures as low as surface temperatures. The presence of water essential causes many of the low temperature reactions on earth. Low temperature reactions have K's that are most different from 1 (on the order of 1.01 for oxygen isotopes). Thus, the range of materials with different oxygen isotopic compositions on earth, is largely due to the presence of water. Moon rocks, for example, which formed at high temperatures and have not been affected by low temperature reactions have a very narrow range of oxygen isotopic compositions.

Properties related to kinetic energy - rates of chemical reaction, translational energy of molecules (evaporation, diffusion of gas, solids, liquids, or of gas in porous medium, responsible for kinetic fractionation). Kinetic effect - due to differences in translational velocity or reaction rates of isotopes – generally non-equilibrium processes. Example: water evaporating from the surface ocean when water vapor pressure is less than saturation (less than 100% relative humidity).

$$\frac{\text{H}_2^{16}\text{O}}{\text{H}_2^{18}\text{O}} : \frac{v_{\text{H}_2^{16}\text{O}}}{v_{\text{H}_2^{18}\text{O}}} = 1.054, \text{H}_2^{16}\text{O} \text{ is } 5.4 \% \text{ faster}$$

With either kinetic or equilibrium fractionation, one would expect that the bigger the fractional (or percentage) difference in mass, the larger the fractionation. For example one

would expect (all other factors being equal) that the degree of fractionation would decrease for the following sequence: $^2\text{H}/^1\text{H} = 2$ (100% mass difference), $^{18}\text{O}/^{16}\text{O} = 1.13$ (13% mass difference), and $^{88}\text{Sr}/^{84}\text{Sr} = 1.05$ (5% mass difference).

Example of macroscopic properties affected by isotopic composition (not appreciable in nature):

	H_2^{16}O	H_2^{18}O
ρ (20°C)	0.9979	1.1106
T of greatest ρ	3.98°C	4.30°C
1 atm M.P.	0.00°C	0.28°C
1 atm B.P.	100.00°C	100.14°C

Nomenclature

δ - notation

relative difference in isotope ratios, not absolute ratios

$$\delta (\text{‰}) = \left(\frac{R_{\text{sample}}}{R_{\text{std}}} - 1 \right) \cdot 10^3, \quad R = ^{18}\text{O}/^{16}\text{O}, ^{13}\text{C}/^{12}\text{C}, \text{D}/\text{H}, \text{etc.},$$

For oxygen, the δ notation would be $\delta^{18}\text{O}$; the convention is to put the mass of minor isotope after the symbol δ .

Standards

1. Hydrogen

VSMOW (Vienna Standard Mean Ocean Water)

$$\delta^2\text{H} (\text{VSMOW}) \equiv 0.000 \text{‰} \quad \text{D}/\text{H} = (155.95 \pm 0.08) 10^{-6}$$

$$\delta^2\text{H} (\text{SLAP})_{\text{VSMOW}} \equiv -428.0 \text{‰}. \quad \text{D}/\text{H} = (89.12 \pm 0.07) 10^{-6}$$

2. Oxygen

VSMOW or VPDB (PeeDee belemnite)

$$^{18}\text{O}/^{16}\text{O} (\text{V.SMOW}) = (2005.20 \pm 0.45) 10^{-6} \quad \text{or } \sim 0.2 \text{‰ } ^{18}\text{O}$$

Conversion of delta values from VSMOW standard to VPDB and vice versa use these formulae:

$$\delta^{18}\text{O}_{\text{VSMOW}} = 1.03086 \delta^{18}\text{O}_{\text{VPDB}} + 30.86$$

$$\delta^{18}\text{O}_{\text{VPDB}} = 0.97006 \delta^{18}\text{O}_{\text{VSMOW}} - 29.94$$

VSMOW standard is typically used for minerals and water, and VPDB standard is used for carbonates (same standard for both oxygen and carbon), but some people use VSMOW for carbonates.

3. Carbon

VPDB

4. Nitrogen

atmospheric nitrogen

5. Sulfur

VCDT (Cañon Diablo troilite, FeS)