

Environmental Geochemistry

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Syllabus: 0365481

- Time: 8:00–9:00
- Day: Sunday, Tuesday, Thursday
- Room: GEO106
- Hours Credit: 3
- Textbook: Nelson Eby (2004):
Principles of Environmental
Geochemistry

Environmental geochemistry

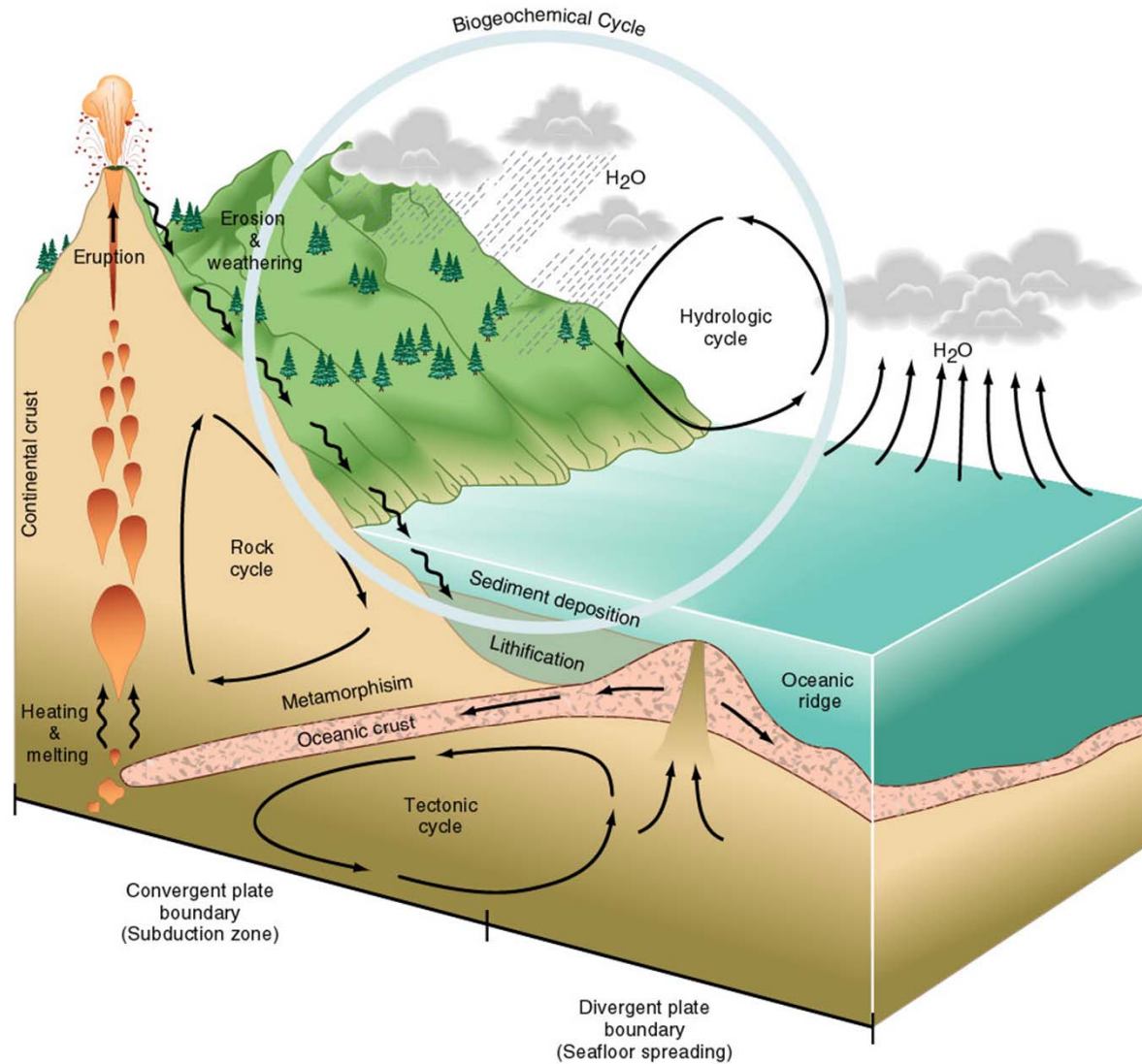
- Is the application of chemical principles to predicting the fate of organic and inorganic pollutants at the earth's surface and in the atmosphere

Fig 4.5 Periodic table of the elements.

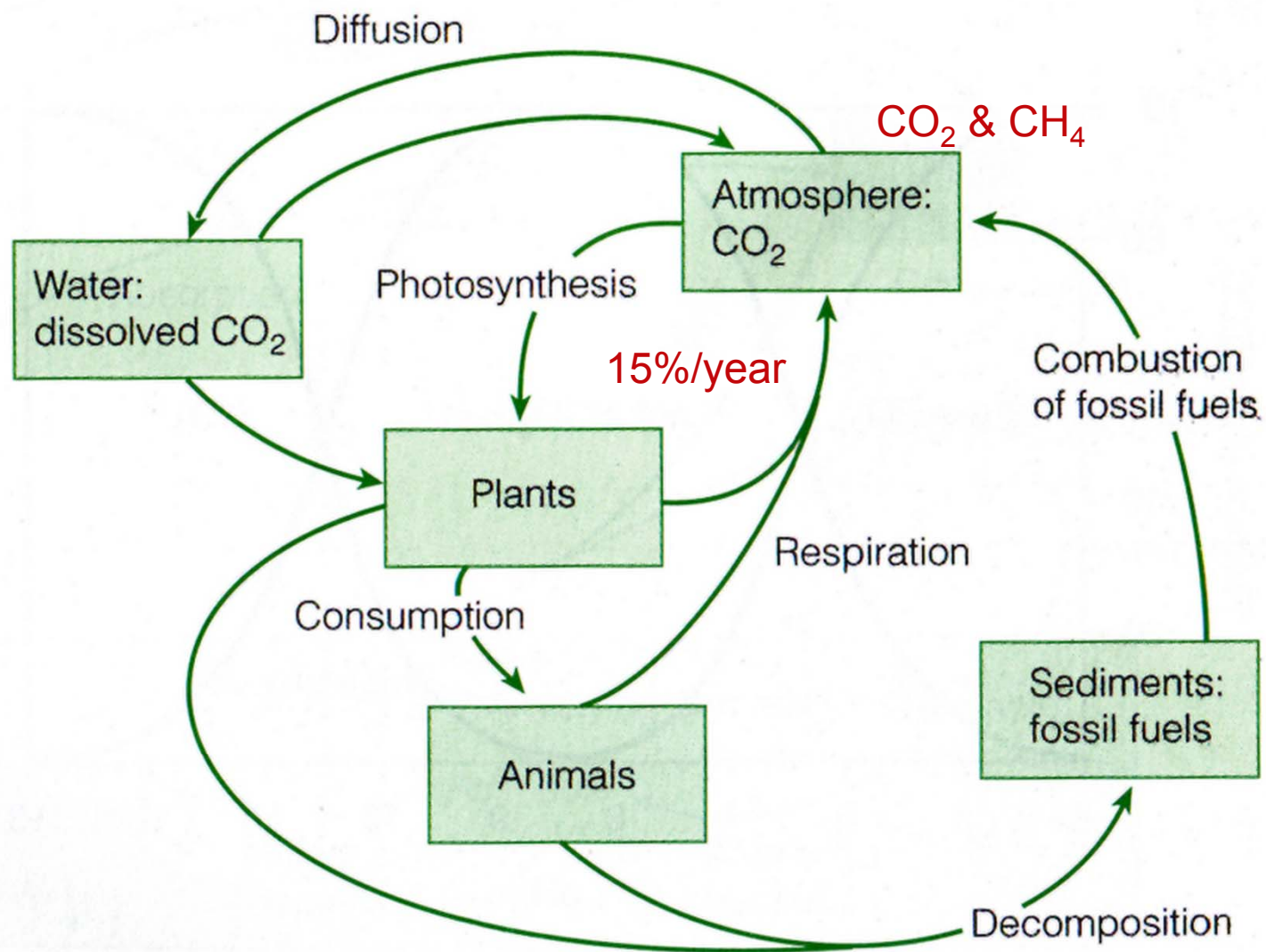
1 H Hydrogen																	2 He Helium					
3 Li Lithium	4 Be Beryllium																	10 Ne Neon				
11 Na Sodium	12 Mg Magnesium																	18 Ar Argon				
19 K Potassium	20 Ca Calcium	21 Sc Scandium	22 Ti Titanium	23 V Vanadium	24 Cr Chromium	25 Mn Manganese	26 Fe Iron	27 Co Cobalt	28 Ni Nickel	29 Cu Copper	30 Zn Zinc	31 Ga Gallium	32 Ge Germanium	33 As Arsenic	34 Se Selenium	35 Br Bromine	36 Kr Krypton					
37 Rb Rubidium	38 Sr Strontium	39 Y Yttrium	40 Zr Zirconium	41 Nb Niobium	42 Mo Molybdenum	43 Tc Technetium	44 Ru Ruthenium	45 Rh Rhodium	46 Pd Palladium	47 Ag Silver	48 Cd Cadmium	49 In Indium	50 Sn Tin	51 Sb Antimony	52 Te Tellurium	53 I Iodine	54 Xe Xenon					
55 Cs Cesium	56 Ba Barium	57 La Lanthanum	72 Hf Hafnium	73 Ta Tantalum	74 W Tungsten	75 Re Rhenium	76 Os Osmium	77 Ir Iridium	78 Pt Platinum	79 Au Gold	80 Hg Mercury	81 Tl Thallium	82 Pb Lead	83 Bi Bismuth	84 Po Polonium	85 At Astatine	86 Rn Radon					
87 Fr Francium	88 Ra Radium	89 Ac Actinium	104 Rf Rutherfordium	105 Db Dubnium	106 Sg Seaborgium	107 Bh Bohrium	108 Hs Hassium	109 Mt Meitnerium														
									58 Ce Cerium	59 Pr Praseodymium	60 Nd Neodymium	61 Pm Promethium	62 Sm Samarium	63 Eu Europium	64 Gd Gadolinium	65 Tb Terbium	66 Dy Dysprosium	67 Ho Holmium	68 Er Erbium	69 Tm Thulium	70 Yb Ytterbium	71 Lu Lutetium
									90 Th Thorium	91 Pa Protactinium	92 U Uranium	93 Np Neptunium	94 Pu Plutonium	95 Am Americium	96 Cm Curium	97 Bk Berkelium	98 Cf Californium	99 Es Einsteinium	100 Fm Fermium	101 Md Mendelevium	102 No Nobelium	103 Lw Lawrencium

= Required for all life
 = Required for some life-forms
 = Moderately toxic: either slightly toxic to all life or highly toxic to a few forms
X = Highly toxic to all organisms, even in low concentrations

Atomic number → 20
 Element relatively abundant in the Earth's crust → ★
 Element symbol → **Ca**
 Environmentally important trace elements → □ □
 Name → Calcium



Idealized diagram of the geologic cycle, which includes the tectonic, hydrologic, rock and biogeochemical cycles.



The global carbon cycle.

Modified from D. T. Krohne, General Ecology

Fig 4.14 The Carbon Cycle.

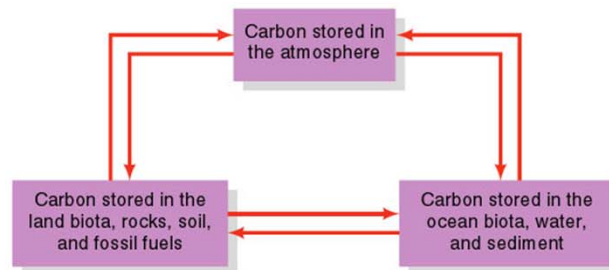
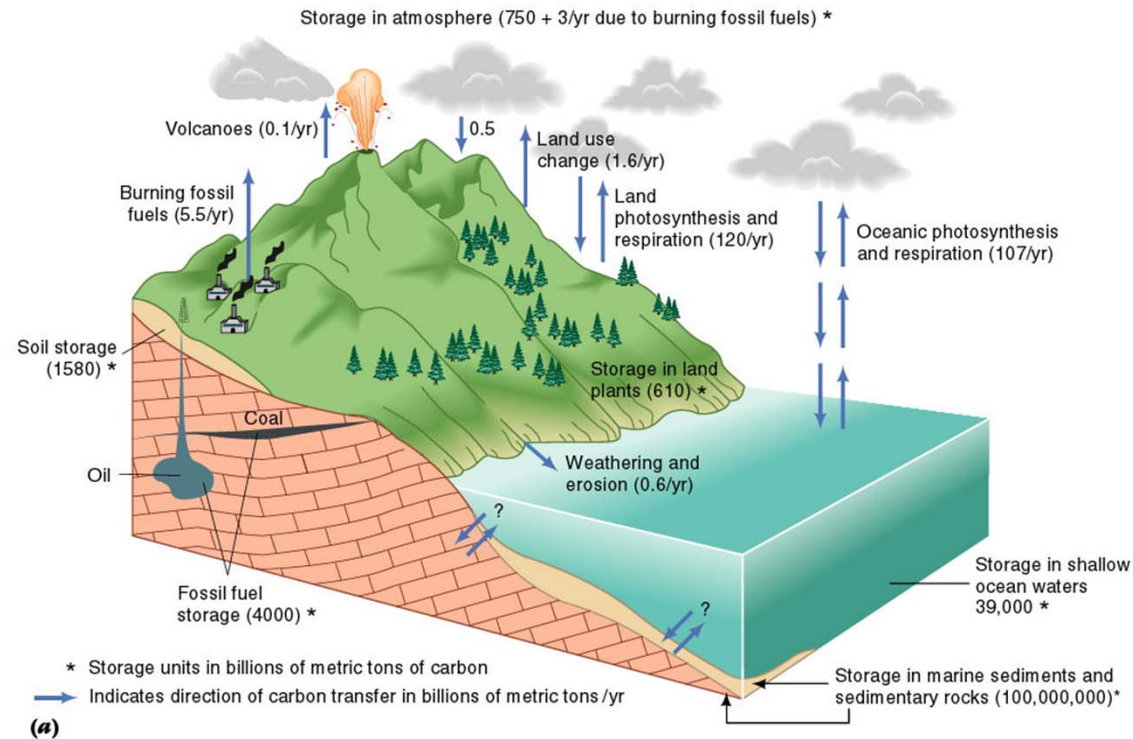
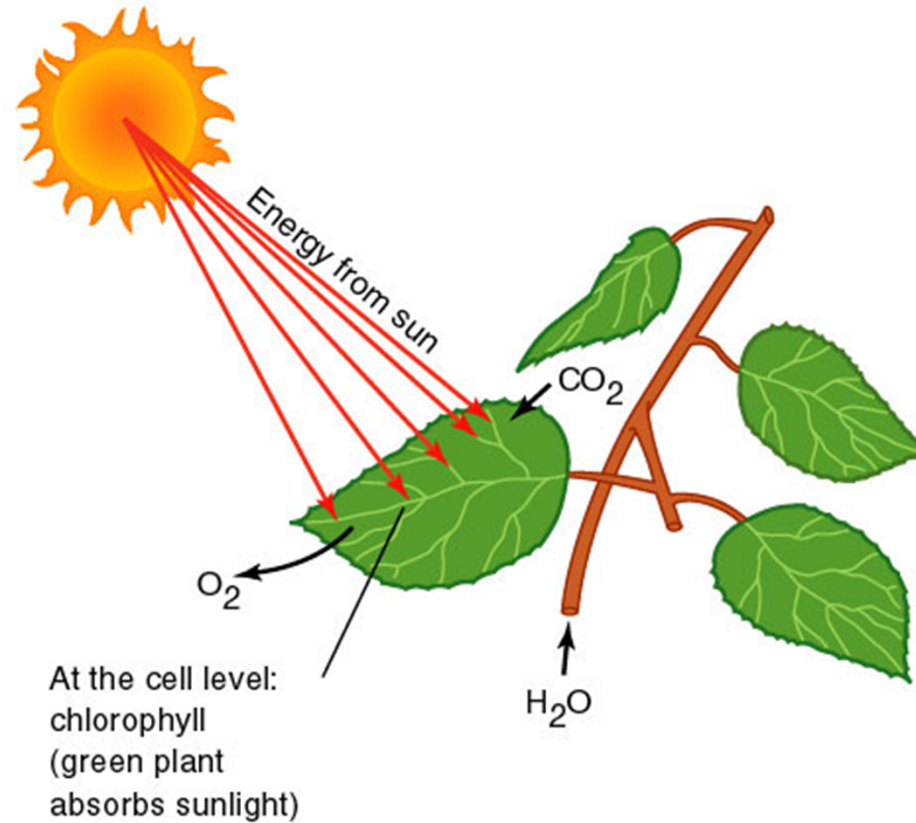


Fig 4.15 Idealized diagram illustrating photosynthesis for a green plant (tree) and generalized reaction.



General Photosynthesis: chemical reaction

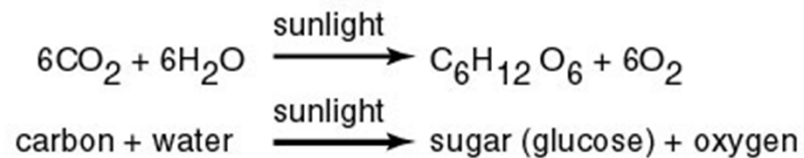
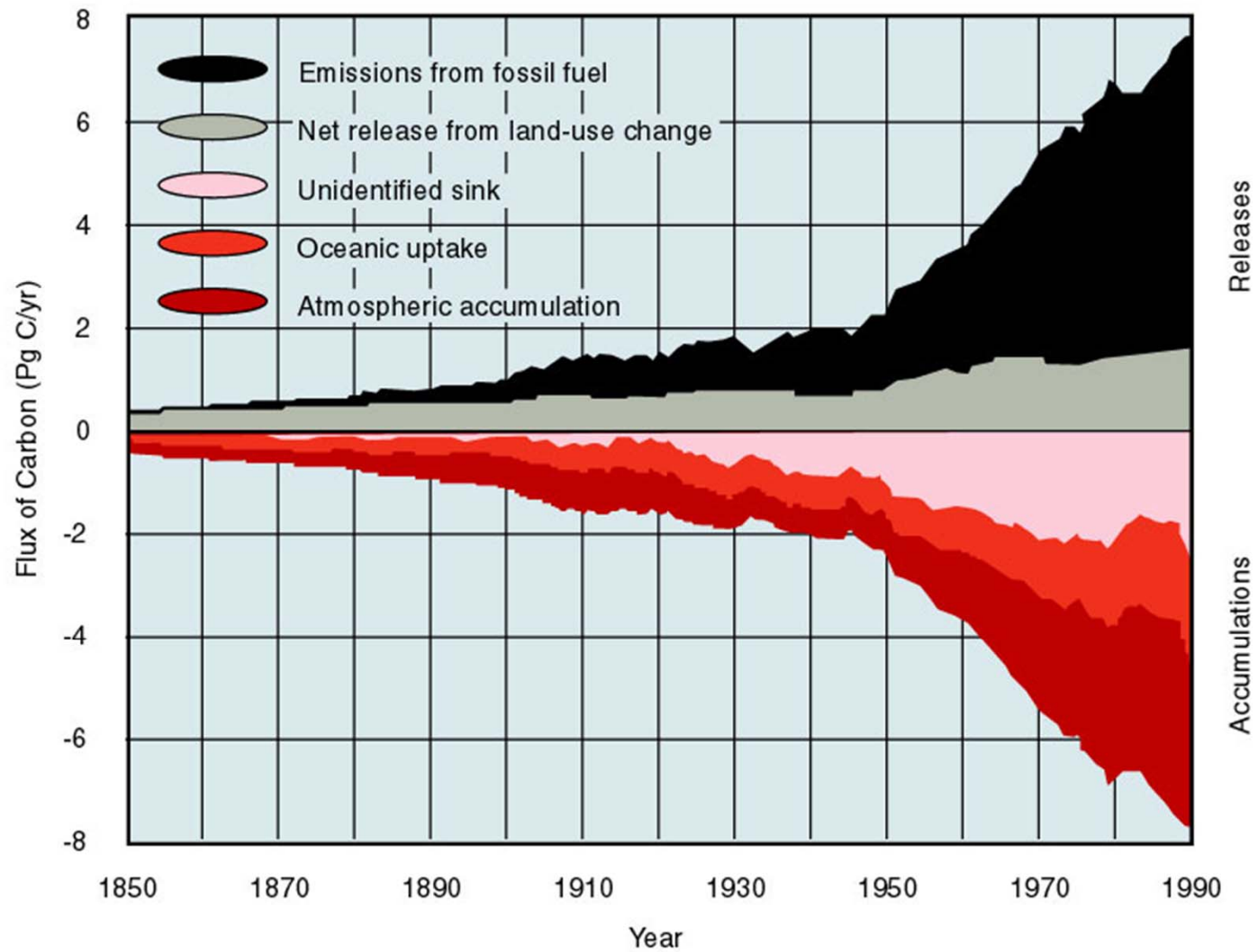
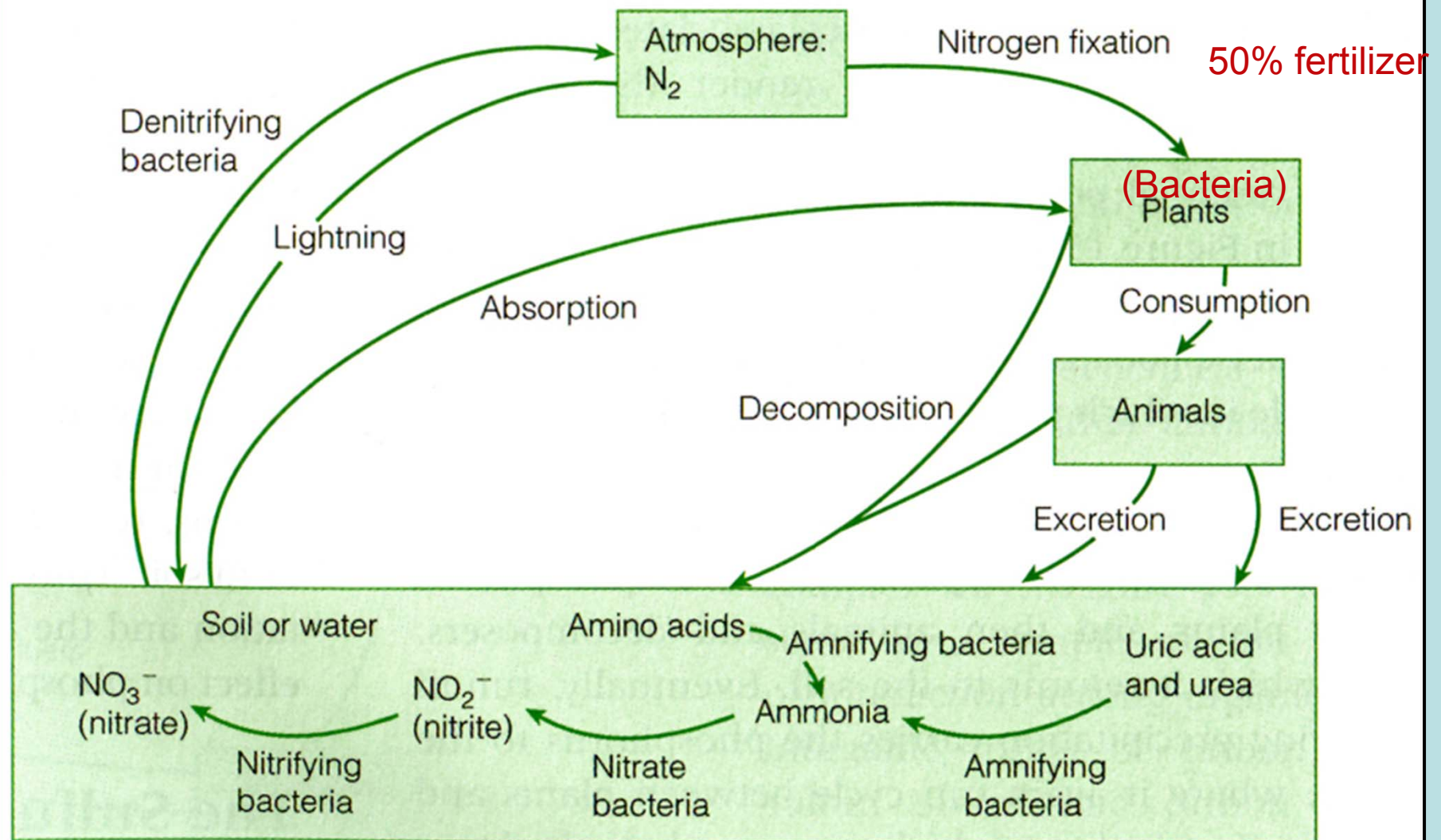


Fig 4.17 Global flux of carbon, 1850-1990.

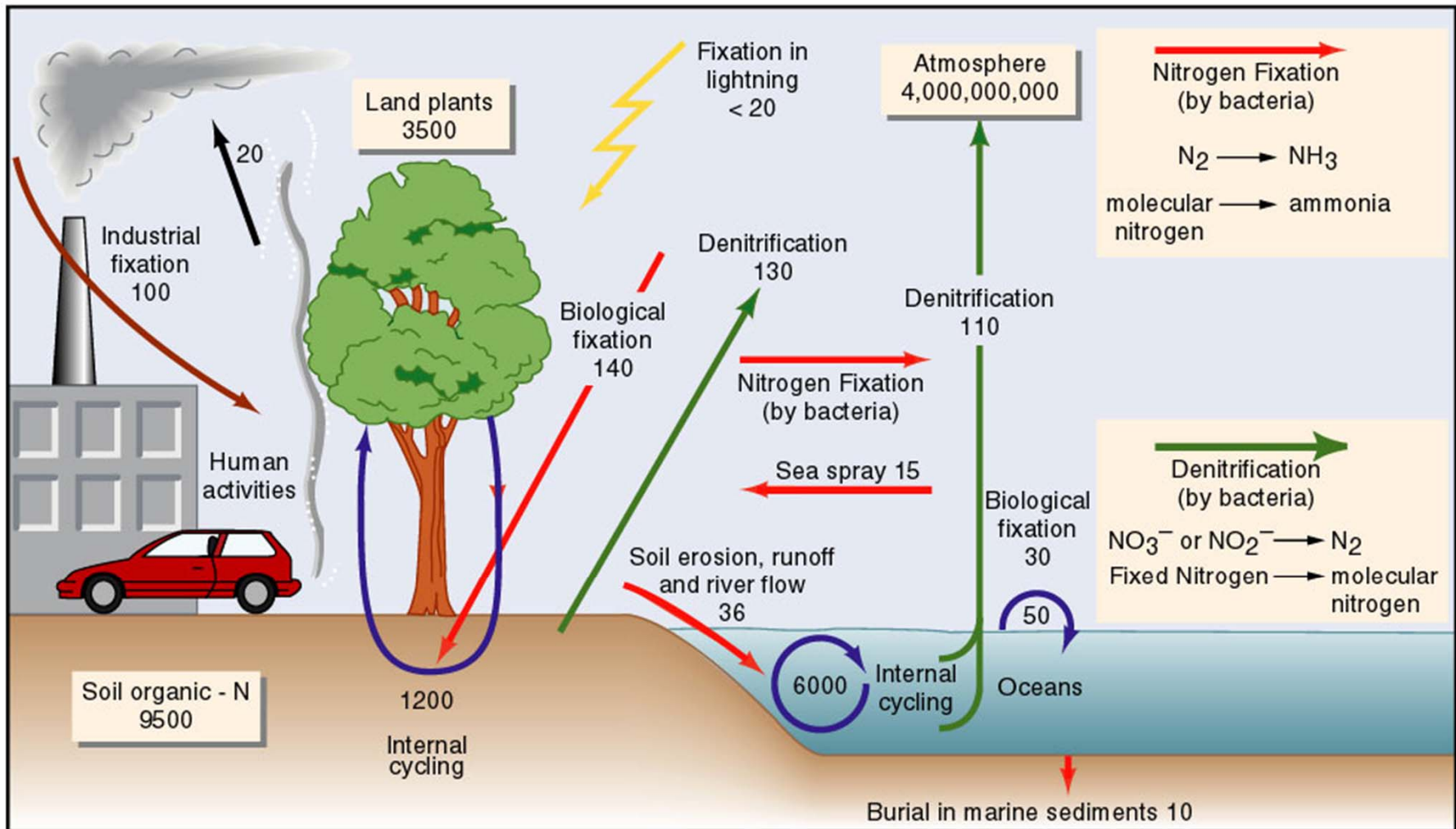




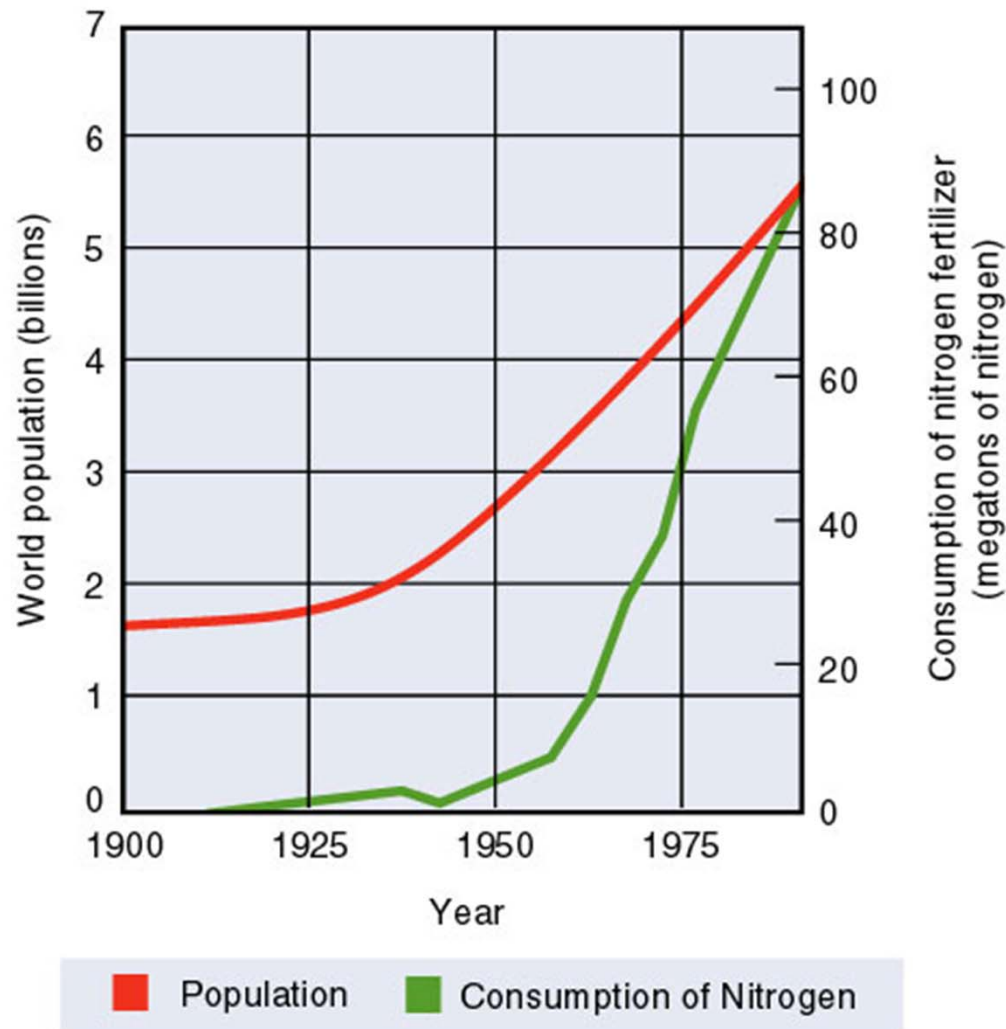
The global nitrogen cycle.

Modified from D. T. Krohne, General Ecology

Fig 4.19 The global nitrogen cycle.



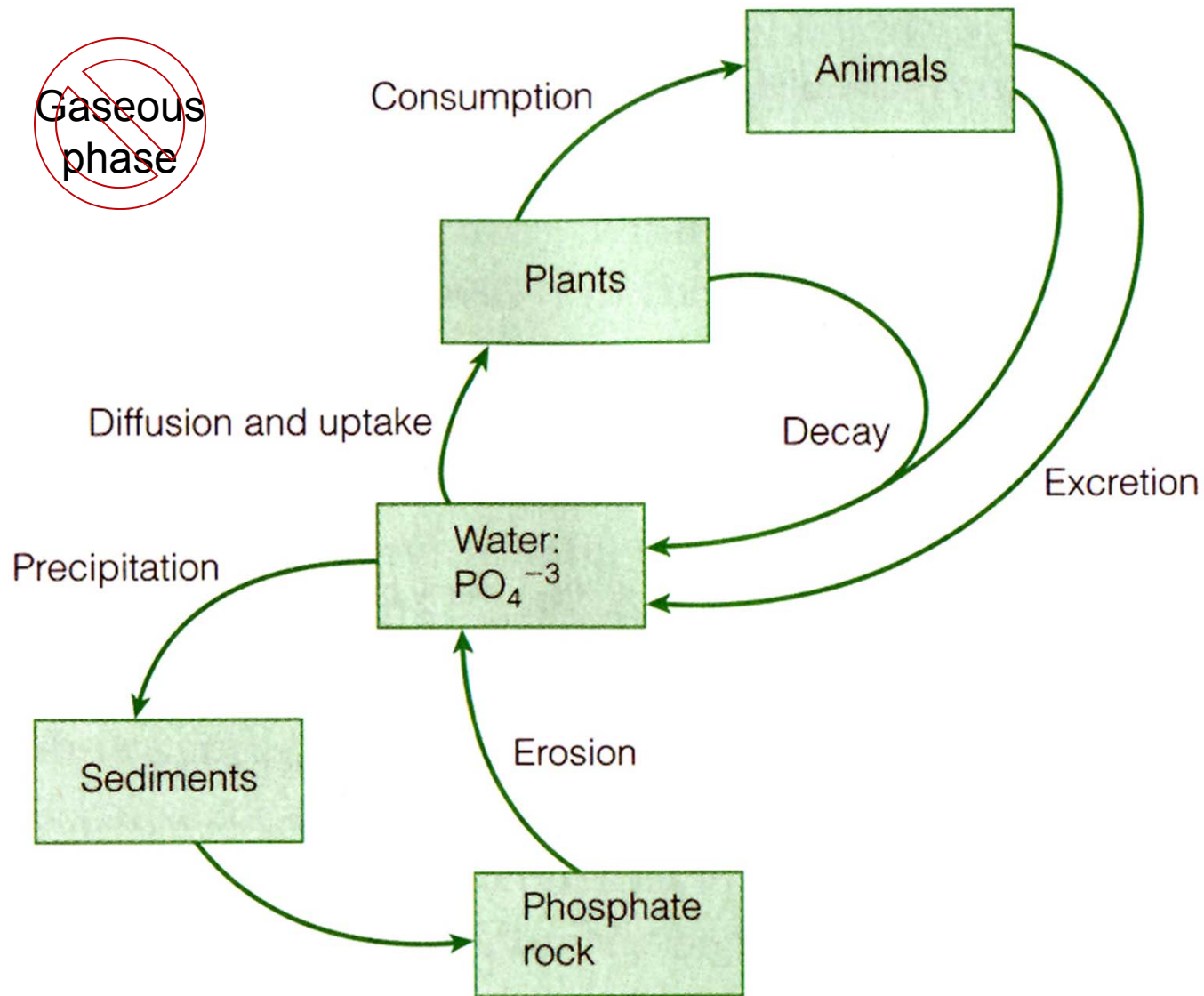
Critical Thinking Issue – How are Human Activities Affecting the Nitrogen Cycle?



Effects of increased use of nitrogen fertilizer:

- Increased nitric acid in soil:
 - Leaching of magnesium and potassium
 - Increased aluminum levels
 - Plant root damage
 - Changes in microbe communities
 - Fish kills
- Eutrophication of water bodies
- Nitrates in drinking water
- Global effects on plant based CO₂ uptake

~~Gaseous
phase~~



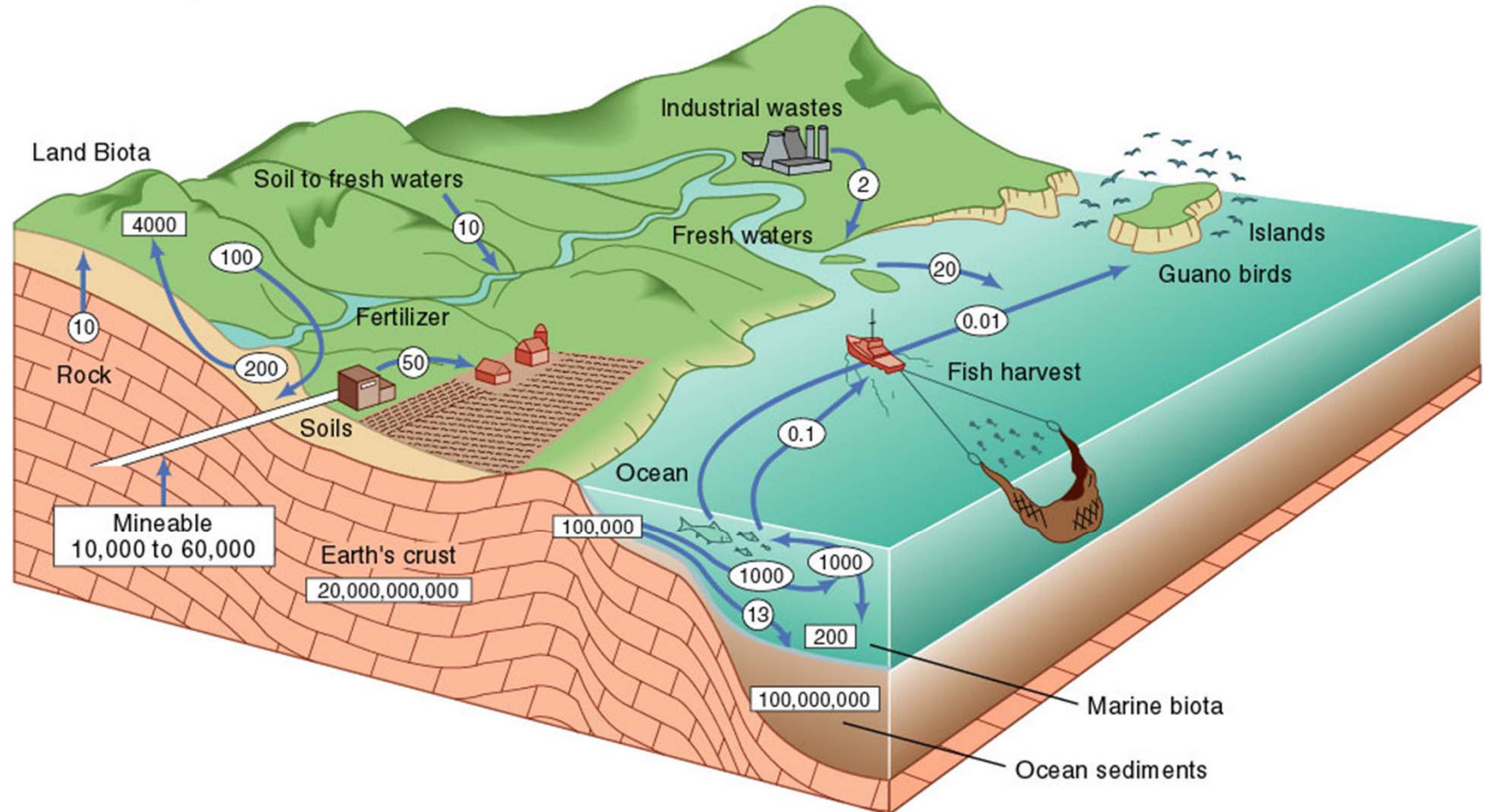
The global phosphorus cycle.

Modified from D. T. Krohne, General Ecology

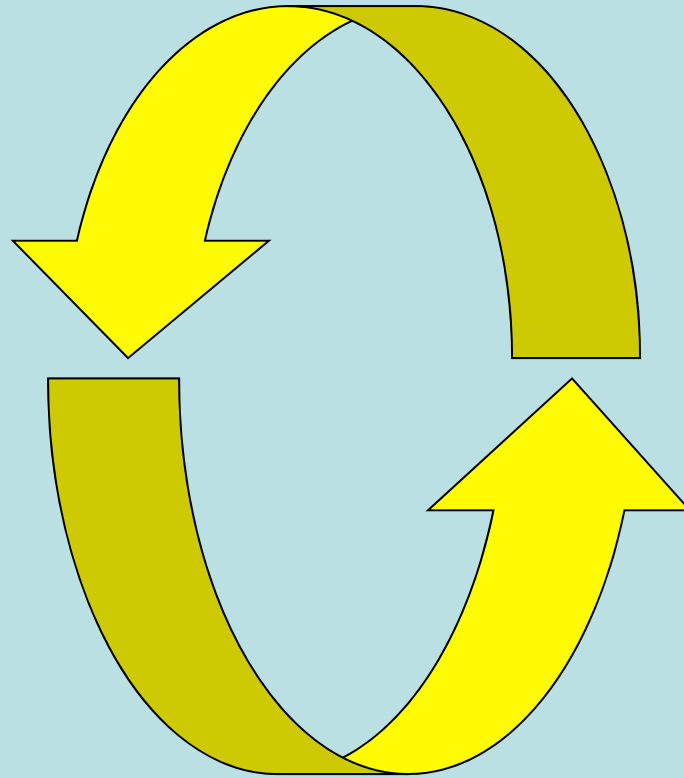
Fig 4.20 The global phosphorus cycle.

Numbers in represent stored amounts in millions of metric tons (10^{12} g)

Numbers in represent flows in millions of metric tons (10^{12} g) per year



Ecosystems and the Gaia Hypothesis



Ecosystem defined: a community of organisms and its corresponding abiotic environment through which matter cycles and energy flows

- Wide variation in ecosystems
- Borders can be well defined or vague
- Can be natural or artificial, managed or wild
- Wide range in scale
- Common to all ecosystems: energy flow and cycling of matter

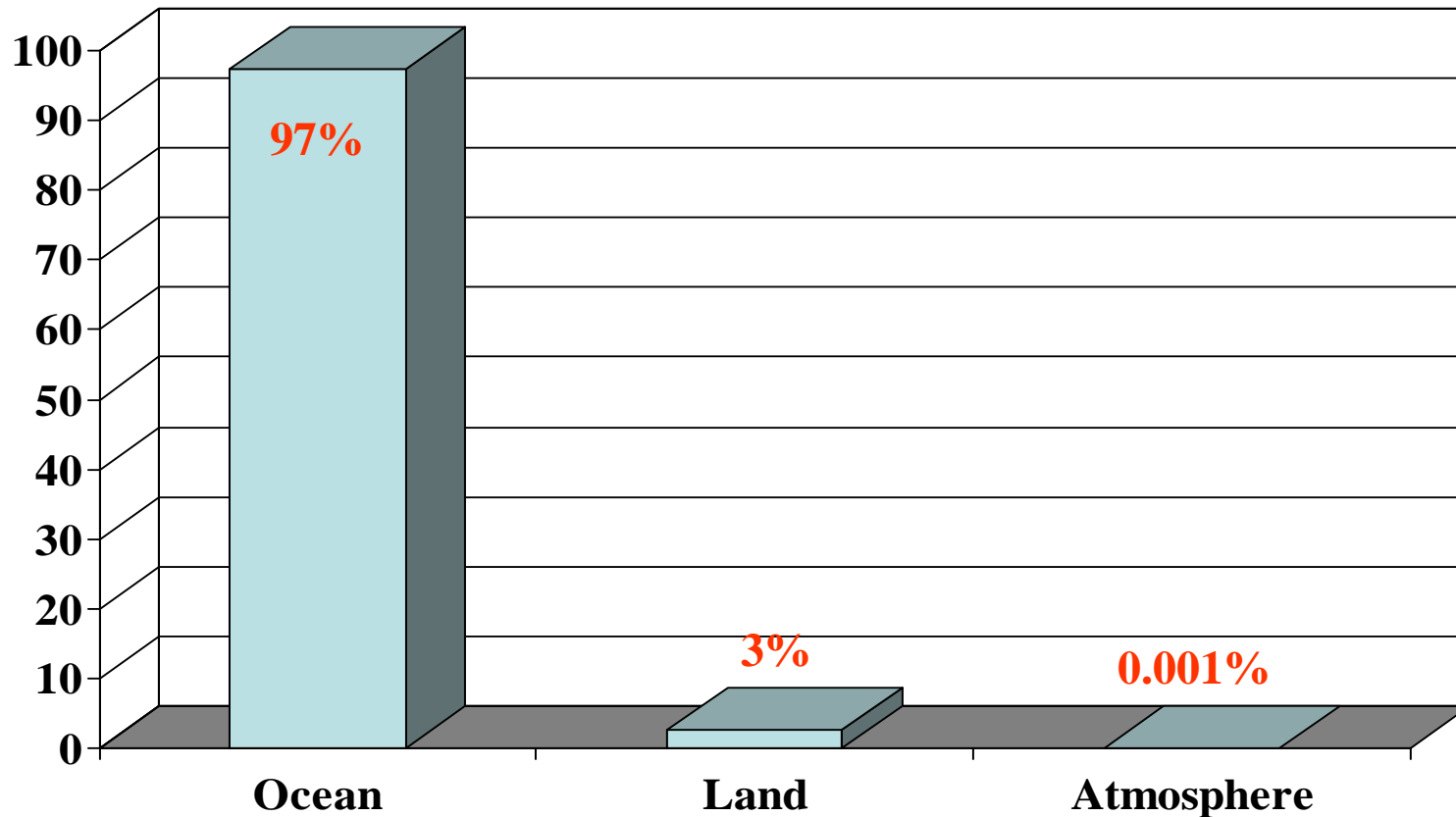
Lecture Overview

- Properties of Water
 - Physical
 - Chemical

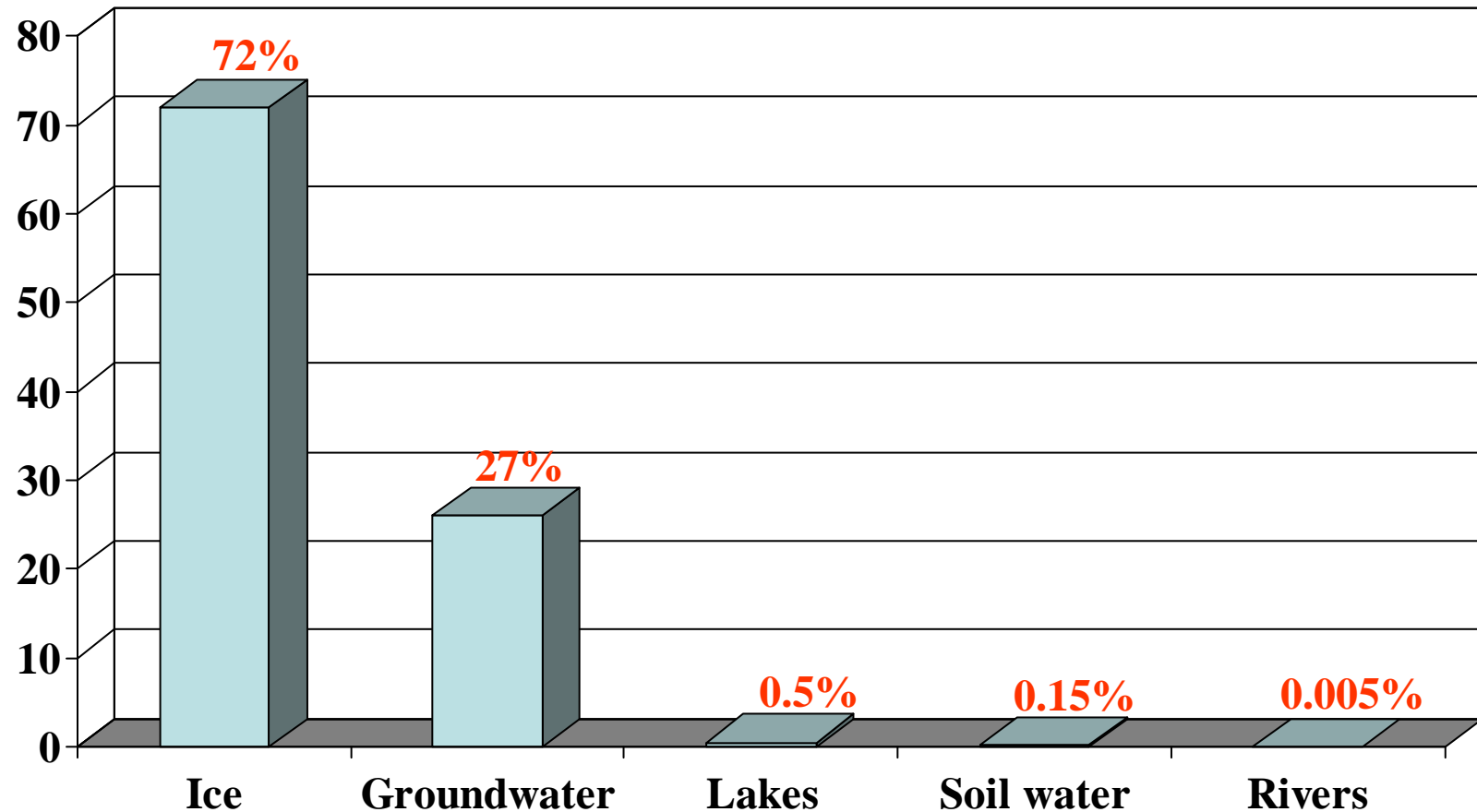
Did you know...

- ❑ The earth is the only planet in the solar system where water occurs in all three phases (solid, liquid, gas)
- ❑ Water covers 70% of the earth's surface
- ❑ The amount of water (1.4 billion km³) in the earth system is constant
- ❑ The oceans accounts for over 97% of the earth's water
- ❑ Water is in constant movement in a circulation called the hydrologic cycle
- ❑ 60-75% of the human body is water

Occurrence of water on the earth



Occurrence of non-oceanic water



Classification of Waters

- **Meteoric** - recently derived from the atmosphere as rain or snow
- **Formation** - pore water in deep sedimentary rocks
- **Metamorphic** - from dehydration reactions
- **Juvenile** - from the mantle

Table 1-7. Properties of water

Property	Comparison to other substances
Heat capacity	Highest of all common liquids (except ammonia) and solids
Latent heat of fusion	Highest of all common liquids (except ammonia) and most solids
Latent heat of vaporization	Highest of all common substances
Dissolving ability	Dissolves more substances (particularly ionic compounds), and in greater quantity than any other common liquid.
Transparency	Relatively high for visible light
Physical state	Water is the only substance that occurs naturally in all three states at the earth's surface
Surface tension	Highest of all common liquids
Conduction of heat	Highest of all common liquids (Hg is higher)
Viscosity	Relatively low viscosity for a liquid

METALS VS. NON-METALS

- Ionization potential (IP) - The energy required to remove an electron from a neutral atom to an infinite distance from the nucleus.
- Electron affinity (EA) - The tendency of a neutral atom to attract electrons.
- Metal - An element with a low IP and a low EA; it tends to lose electrons and form a cation.
- Nonmetal - An element with a high IP and high EA; it tends to gain electrons and form an anion.

IONIC BONDS

- Ionic bonds - bonds formed via the electrostatic attraction between oppositely charged ions.

- Coulomb's law

$$F = \frac{Z_+ Z_-}{4\pi\epsilon_0 r^2}$$

ϵ_0 = permittivity of free space = 8.84×10^{-9} farads m^{-1}

1 farad = 1 coulomb volt⁻¹

F = force of attraction; Z_+ and Z_- are the charges of the cation and anion respectively; r is the cation-anion distance.

COVALENT BONDS

- Covalent bonds - bonds formed by sharing of electrons.
- Many gaseous species and organic compounds contain covalent bonds, e.g., N_2 .
- A few minerals, such as diamond and graphite, contain covalent bonds.
- Sharing may not be equal. That is, covalent bonds may have some ionic character, and vice versa.

MEASURE OF IONIC/COVALENT CHARACTER

- Electronegativity (χ) - measures the ability of an atom in a compound to attract electrons to itself.
- Metals have low χ values and non-metals have high χ values (see Table 1-2 in Kehew for electronegativity values of the elements).
- We use differences in electronegativity to determine degree of ionic character of a bond.
- Example: CsF $\chi_{\text{Cs}} = 0.7; \chi_{\text{F}} = 4.0$
 $\chi_{\text{F}} - \chi_{\text{Cs}} = 3.3$
 > 92% ionic; < 8% covalent

TABLE 1-2 Electronegativity values of the elements.

H 2.1																	He ...
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne ...
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar ...
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr ...
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe ...
Cs 0.7	Ba 0.9	La-Lu 1.1-1.2	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn ...
Fr 0.7	Ra 0.9	Ac-Lr 1.1															

PERCENT IONIC CHARACTER

Electronegativity difference	% Ionic character	Electronegativity difference	% Ionic character	Electronegativity difference	% Ionic character
0.1	0.5	1.2	30	2.3	74
0.2	1	1.3	34	2.4	76
0.3	2	1.4	39	2.5	79
0.4	4	1.5	43	2.6	82
0.5	6	1.6	47	2.7	84
0.6	9	1.7	51	2.8	86
0.7	12	1.8	55	2.9	88
0.8	15	1.9	59	3.0	89
0.9	19	2.0	63	3.1	91
1.0	22	2.1	67	3.2	92
1.1	26	2.2	70	>3.2	>92

10

WHY DO WE CARE IF A BOND IS IONIC OR COVALENT?

- All physical and chemical properties of a compound depend on the character of the bonds.
- Example: Solubility in water

A general rule is that, like dissolves like. As we will see, water is a polar covalent solvent.

Ionically bonded compounds have high aqueous solubilities

e.g., NaCl $\chi_{\text{Cl}} - \chi_{\text{Na}} = 3.0 - 0.9 = 2.1$

67% ionic, relatively soluble in water

C(diamond) $\chi_{\text{C}} - \chi_{\text{C}} = 0$

0% ionic, nearly insoluble in water

RULES TO DETERMINE OXIDATION STATES

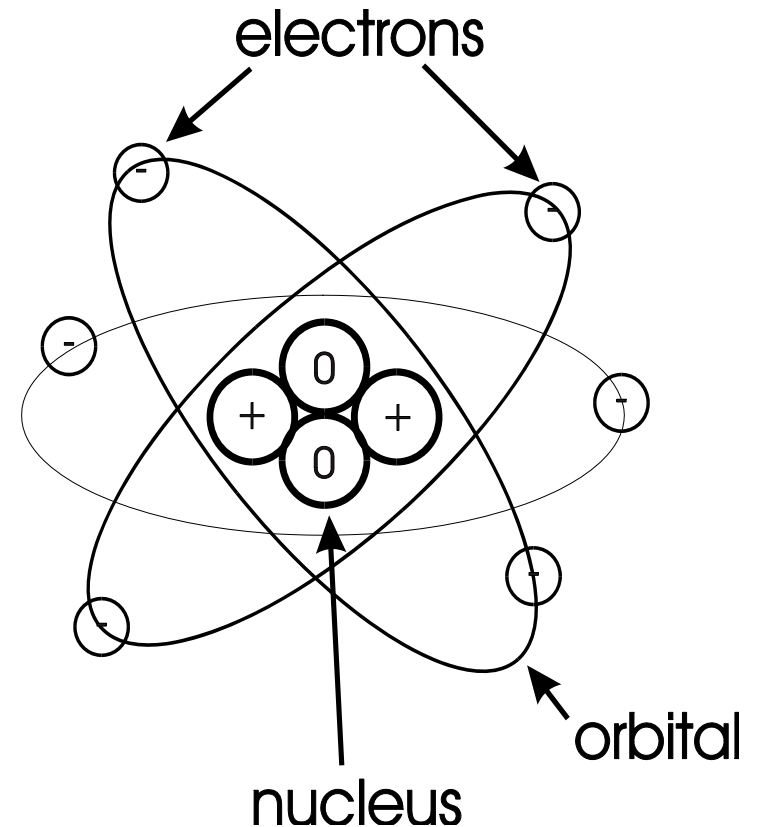
- 1) The oxidation state of all pure elements is zero.
- 2) The oxidation state of H is +1, except in hydrides (e.g., LiH, PdH₂), where it is -1.
- 3) The oxidation state of O is -2, except in peroxides (e.g., H₂O₂), where it is -1.
- 4) The algebraic sum of oxidation state must equal zero for a neutral molecule or the charge on a complex ion.

ELEMENTS WITH VARIABLE OXIDATION STATES

- Sulfur: SO_4^{2-} (+6), SO_3^{2-} (+4), $\text{S}(0)$, FeS_2 (-1), H_2S (-2)
- Carbon: CO_2 (+4), $\text{C}(0)$, CH_4 (-4)
- Nitrogen: NO_3^- (+5), NO_2^- (+3), NO (+2), N_2O (+1), $\text{N}_2(0)$, NH_3 (-3)
- Iron: Fe_2O_3 (+3), FeO (+2), $\text{Fe}(0)$
- Manganese: MnO_4^- (+7), MnO_2 (+4), Mn_2O_3 (+3), MnO (+2), $\text{Mn}(0)$
- Copper: CuO (+2), Cu_2O (+1), $\text{Cu}(0)$
- Tin: SnO_2 (+4), Sn^{2+} (+2), $\text{Sn}(0)$
- Uranium: UO_2^{2+} (+6), UO_2 (+4), $\text{U}(0)$
- Arsenic: H_3AsO_4^0 (+5), H_3AsO_3^0 (+3), $\text{As}(0)$, AsH_3 (-1)
- Chromium: CrO_4^{2-} (+6), Cr_2O_3 (+3), $\text{Cr}(0)$
- Gold: AuCl_4^- (+3), $\text{Au}(\text{CN})_2^-$ (+1), $\text{Au}(0)$

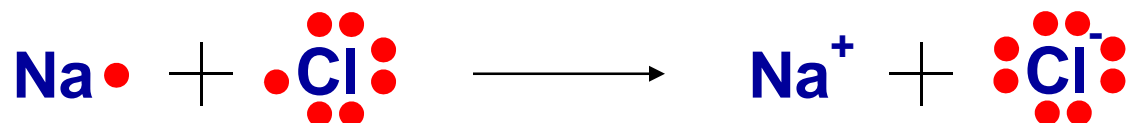
ATOMIC STRUCTURE

- Each atom of an element is composed of a **nucleus** surrounded by **electrons** in various **orbitals**.
- Nucleus - a central concentration of mass consisting of **protons** and **neutrons**.
- Electrons - negatively charged particles of relatively low mass.
- Protons - positively charged particles of relatively high mass.
- Neutrons - particles with no charge but mass similar to that of protons.



CHEMICAL BONDING

- **Ionic bonds** - bonds formed via the electrostatic attraction between oppositely charged ions.

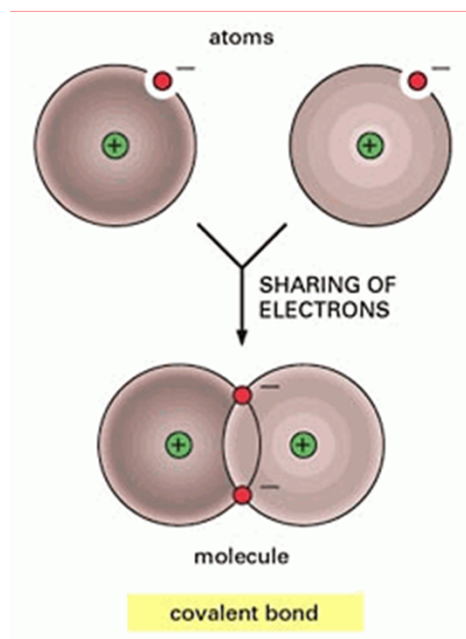


Na contributes electron, leaving it with a closed shell
Cl gains electron, leaving it with a closed shell

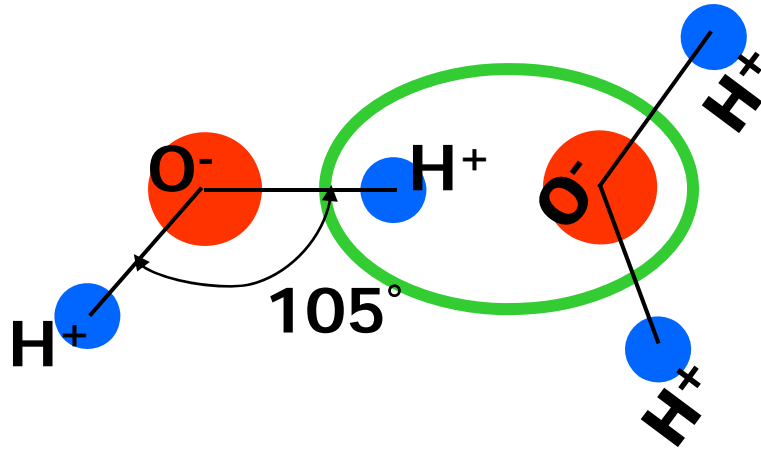
- **Covalent bonds** - bonds formed by sharing of electrons.



- **Polar Covalent bonds** - the sharing of the electron pair is unequal. There is a charge separation with one atom being slightly more positive and the other more negative.

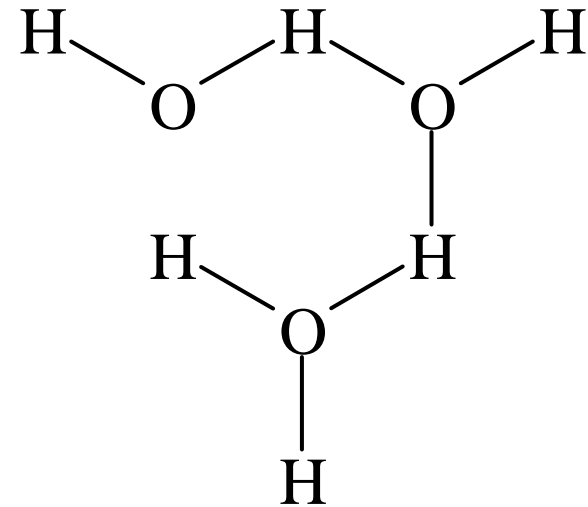


PROPERTIES OF WATER

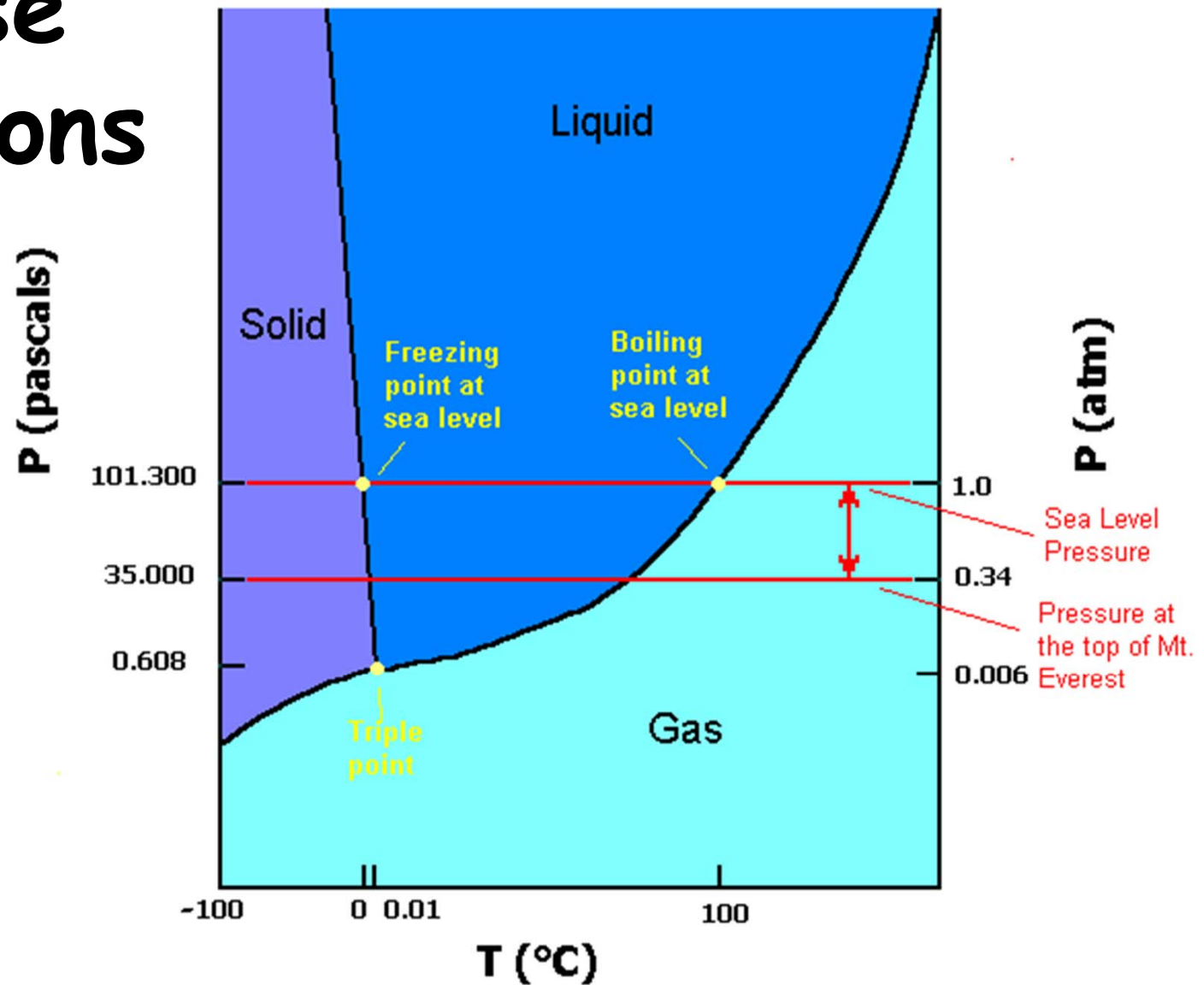


Because each water molecule has a positive and a negative end, these can attract one another to form a *hydrogen bond*.

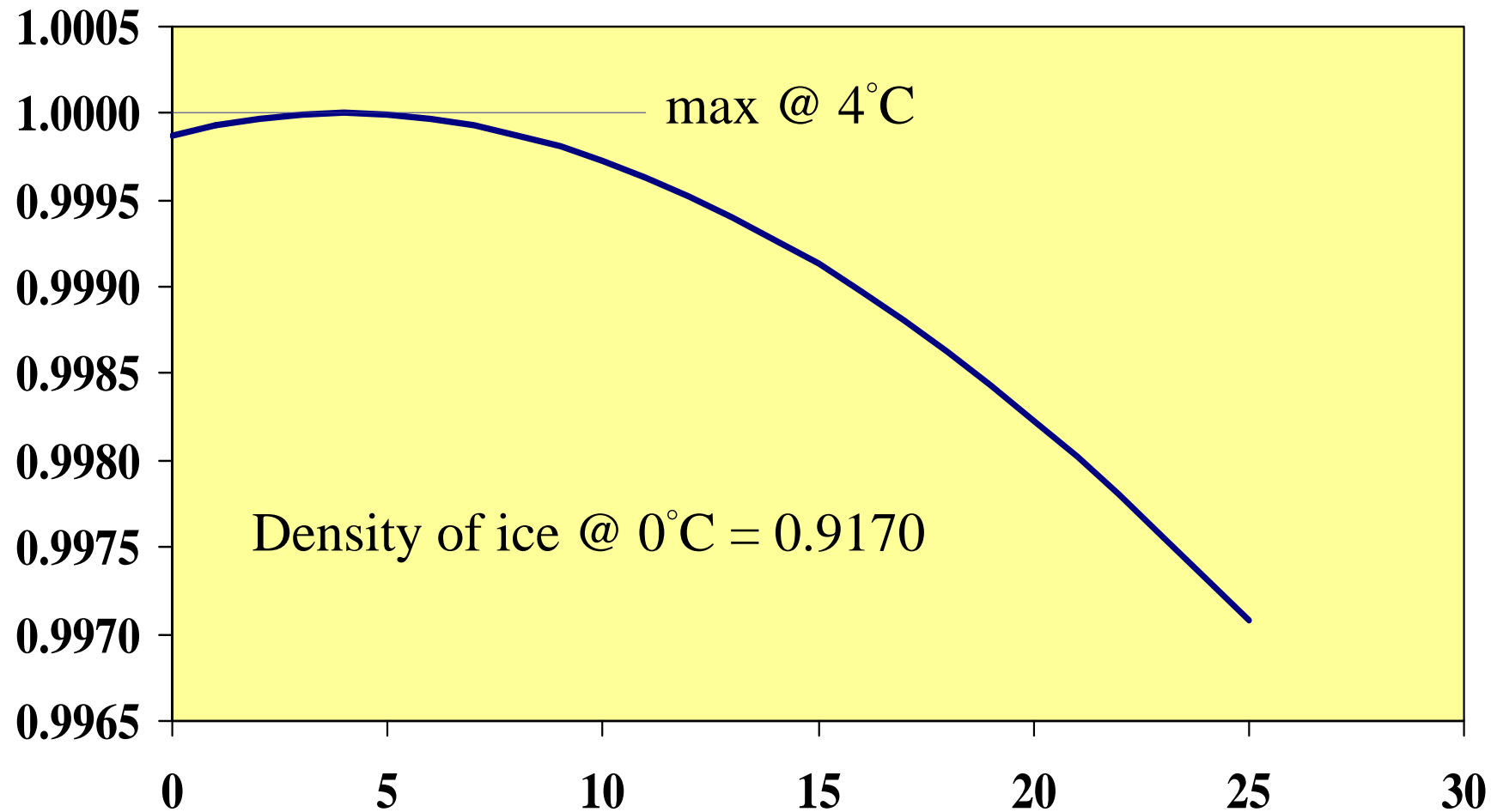
- The hydrogen bonding of water is responsible for many anomalous properties of water.
 - high boiling point & melting point
 - The maximum density is at 4C.
 - Ice is less dense than the liquid water.



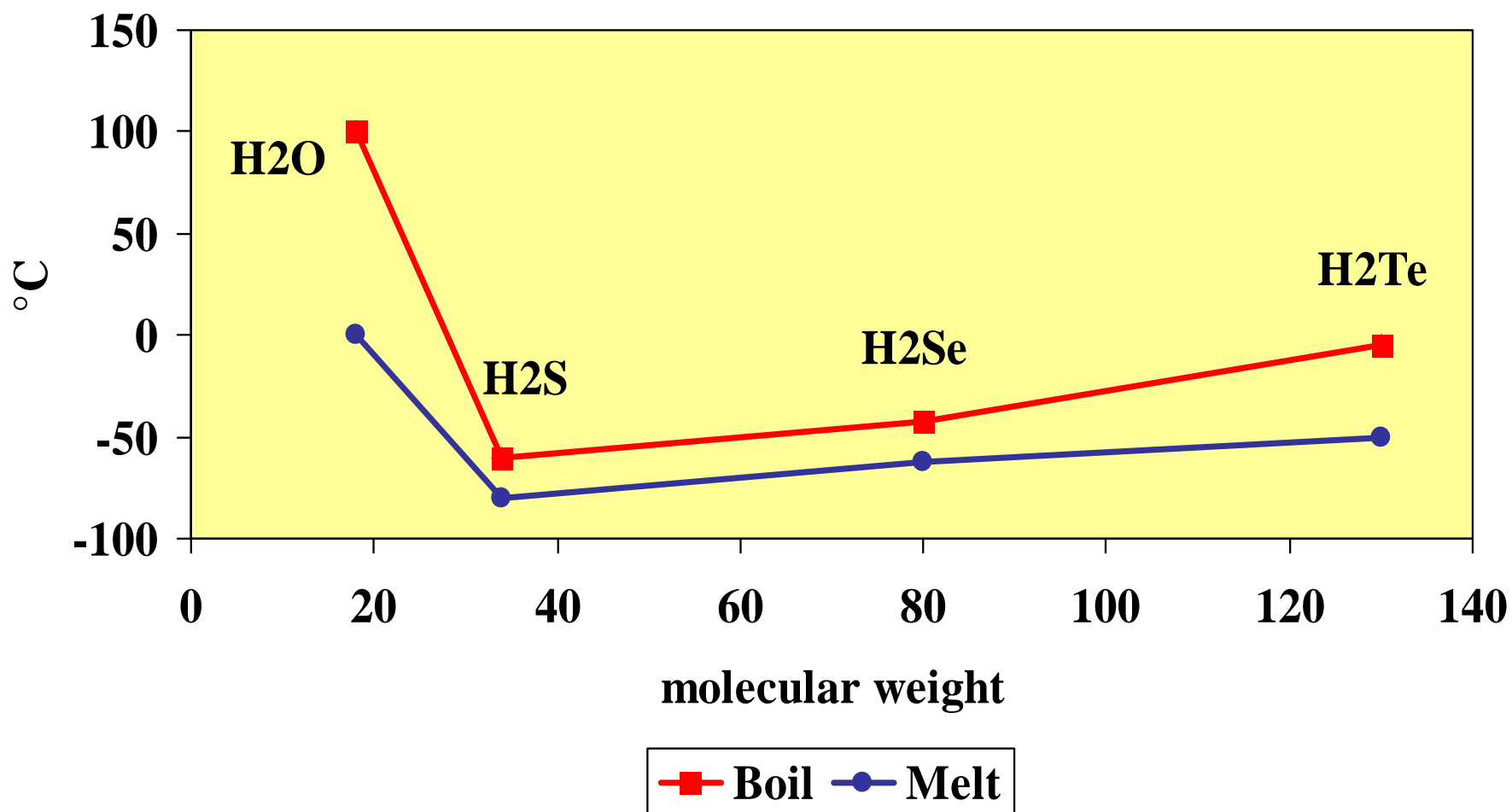
Phase Relations



Density of Water



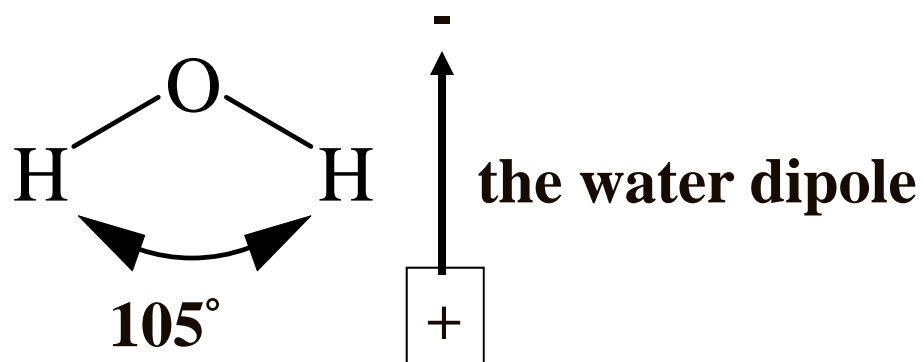
Boiling & Melting Points



WHY DO WE CARE IF A BOND IS IONIC OR COVALENT?

- All physical and chemical properties of a compound depend on the character of the bonds.
- **Solubility in water** (general rule - like dissolves like)

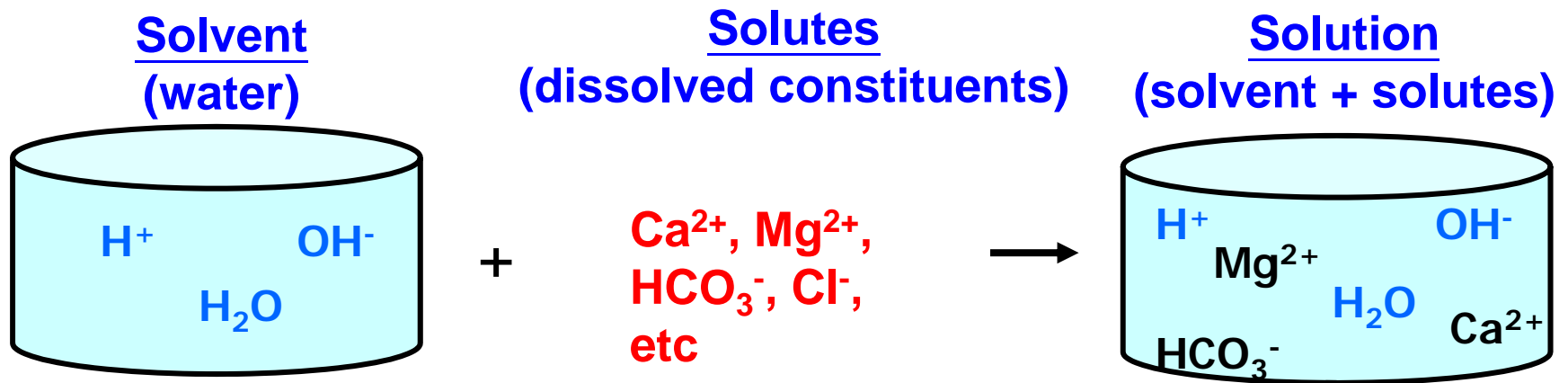
Water is a polar covalent **solvent** - 39% ionic & 61% covalent - meaning there is a positive and a negative pole to the molecule.



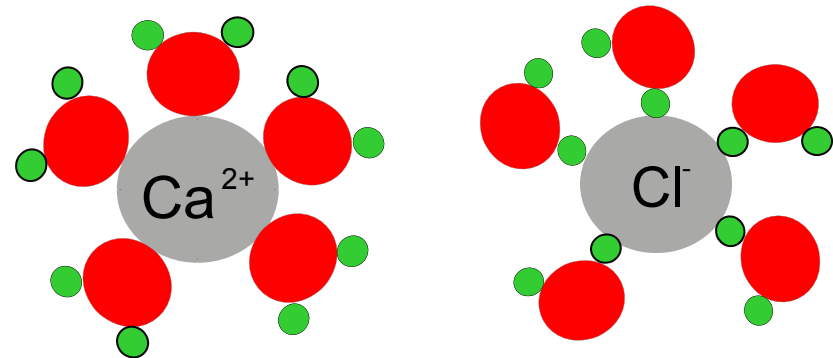
Water dissolves ionic solids (e.g., NaCl, K₂SO₄) very well. On the other hand, polar water is a very poor solvent for many organic compounds, e.g., toxic benzene (C₆H₆).

PROPERTIES OF WATER

- **Solvent** : Water dissolves some amount of virtually every solid or gas.



- Also because of the polar nature of water, ions will be surrounded by water dipoles (hydrated) in solution.
- Hydration isolates the ions from their neighbors and neutralizes the attractive forces that hold minerals together.



UNITS OF EXPRESSION

Mass Concentration – we use many units of concentration.

- **weight/weight units – ppm, ppb** $\text{ppm} = \frac{\text{mass of solute (mg)}}{\text{mass of solution (kg)}}$
- **weight/volume units – mg/L, g/L** $\text{mg/l} = \frac{\text{mass of solute (mg)}}{\text{volume of solution (l)}}$

The conversion factor between mg/L and ppm is:

$$\text{ppm (parts per million)} = \frac{1\text{g}}{10^6\text{g}} = \frac{1\text{mg}}{1\text{kg}} = \frac{1\text{mg}}{\text{L}} \text{ (in natural water)}$$

$$\frac{\text{mg}}{\text{kg}} = \frac{\text{mg}}{\text{L}} \times \boxed{\frac{1}{\rho}}$$

Because the density of many natural waters is near 1 kg/L, it is often a sufficiently good approximation that mg/L and ppm are numerically equal.

$$\text{ppm (parts per million)} = \frac{1\text{g}}{10^6\text{g}} \times \frac{10^3\text{mg}}{1\text{g}} \times \frac{10^3\text{g}}{1\text{kg}} = \frac{1\text{mg}}{1\text{kg}}$$

Molar Concentration - In almost all geochemical calculations, it is necessary to use molar concentrations rather than mass concentrations.

♣ Moles (1 mole = 6.023×10^{23} atoms or molecules)

$$\bullet \text{ Molality (m)} = \frac{\text{moles of solutes, mol}}{\text{mass of solvent, kg}}$$

$$\bullet \text{ Molarity (M)} = \frac{\text{moles of solutes, mol}}{\text{volume of solution, L}}$$

♣ Molarity is the most common concentration unit involved in calculations dealing with volumetric stoichiometry.

♣ Conversion from mol/L (*M*) to mg/L is accomplished using the formula:

$$\frac{\text{mg}}{\text{L}} = \frac{\text{mol}}{\text{L}} \times \text{molar mass} \left(\frac{\text{g}}{\text{mol}} \right) \times \frac{1000 \text{ mg}}{\text{g}}$$

Example. What's the molar mass for 1 mole of HCl?

1 H Hydrogen 1.00794	2 He Helium 4.002602						
3 Li Lithium 6.941	4 Be Beryllium 9.012182	5 B Boron 10.811	6 C Carbon 12.0107	7 N Nitrogen 14.00674	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.179
11 Na Sodium 22.989770	12 Mg Magnesium 24.3050	13 Al Aluminum 26.981538	14 Si Silicon 28.0855	15 P Phosphorus 30.973761	16 S Sulfur 32.066	17 Cl Chlorine 35.4527	18 Ar Argon 39.948
19 K Potassium 39.0983	20 Ca Calcium 40.078	31 Ga Gallium 69.723	32 Ge Germanium 72.61	33 As Arsenic 74.92160	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.80
37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.760	52 Te Tellurium 127.60	53 I Iodine 126.90447	54 Xe Xenon 131.29
55 Cs Cesium 132.90545	56 Ba Barium 137.327	81 Tl Thallium 204.3833	82 Pb Lead 207.2	83 Bi Bismuth 208.98038	84 Po Polonium (209)	85 At Astatine (210)	86 Rn Radon (222)

Average Atomic Mass

H: 1g (atomic mass) x 1 = 1g
Cl: 35.5g (atomic mass) x 1 = 35.5g \longrightarrow 1 + 35.5 = 36.5 g/mole

- **Mole fraction (X)** - another form of molar concentration

$$X_{\text{Solute}} = \frac{\text{moles of solute}}{\text{total moles of all components}}$$

the *mole fraction (X)* is used for solid solutions, e.g., solid solutions between KAlSi_3O_8 and $\text{NaAlSi}_3\text{O}_8$. In such a solid solution, the mole fraction of KAlSi_3O_8 would be written as:

$$X_{\text{KAlSi}_3\text{O}_8} = \frac{\text{moles KAlSi}_3\text{O}_8}{\text{moles KAlSi}_3\text{O}_8 + \text{moles NaAlSi}_3\text{O}_8}$$

- **Percentage (%)** - the ratio of a solute to the solution

If a solution concentration is given as a percentage, you can generally assume it is a mass percentage unless otherwise stated.

Example. Suppose you are given a concentrated solution of HCl which is known to be 37.0% HCl and has a solution density of 1.19 g/mL. What is the Molarity of HCl?

(1) Begin with the assumption of 100 g of solution.

$$\frac{37\text{g of solutes}}{100\text{g of solution (37g of solutes + 63 g of solvent)}}$$

(2) To find molarity, we need to determine the moles of HCl (solute).

$$\text{moles (mol)} = \frac{\text{mass (g)}}{\text{molar mass (g/mol)}} = \frac{37\text{g}}{36.5\text{g/mol}} = 1.01\text{mol}$$

(3) Convert the known mass of solution, 100 g solution, to liters of solution, using the density of the solution:

$$\frac{100\text{ g}}{1.19\text{ g/mL}} \times \frac{1\text{L}}{1000\text{ mL}} = 0.084\text{ L solution}$$

(4) Calculate the molarity (M)

$$\frac{1.01\text{mol HCl}}{0.084\text{ L solution}} = 12.0\text{ mol/L}$$

UNITS OF EXPRESSION

Equivalents and Normality (N)- units : equivalents/liter

- ♣ Equivalents (eq) are similar to moles, but take into account the valence of an ion.

$$0.002 \text{ mol L}^{-1} \text{ of } \text{Ca}^{2+} = 0.004 \text{ eq L}^{-1} \text{ Ca}^{2+}$$

$$0.001 \text{ mol L}^{-1} \text{ of } \text{Na}^{+} = 0.001 \text{ eq L}^{-1} \text{ Na}^{+}$$

$$0.003 \text{ mol L}^{-1} \text{ Al}^{3+} = 0.009 \text{ eq L}^{-1} \text{ Al}^{3+}$$

- ♣ Normality (N) is another name for eq L⁻¹.
- ♣ Alkalinity is an important solution parameter that is expressed as eq L⁻¹ or meq L⁻¹. Hardness is another parameter expressed as eq L⁻¹.

Example. The laboratory reported the concentration of Ca²⁺ in a water sample as 92 mg/L. What is the normality of Ca²⁺ ? **Valence (charge)**

$$\frac{\text{Equivalent}}{\text{Liter}} = \text{Conc.} \left(\frac{\text{mg}}{\text{L}} \right) \times \frac{1 \text{ mole}}{\text{atomic or molecular wt.}} \times \left(\frac{\text{\# of equivalents}}{\text{mole}} \right)$$

$$92 \frac{\text{mg}}{\text{L}} \times \frac{1 \text{ mole}}{40.08 \text{g}} \times \frac{1 \text{g}}{1000 \text{mg}} \times \frac{2 \text{equiv}}{\text{mole}} = 4.6 \times 10^{-3} \frac{\text{equiv}}{\text{L}} = 4.6 \frac{\text{milliequiv}}{\text{L}}$$

Box Models and Geochemical Cycles

- Box models and the **steady-state assumption** are widely used in the environmental sciences to trace the passage of various constituents through the bio-geo-hydro-atom-spheres and to assess the impact of anthropogenic inputs on these natural cycles.
- *A box model consists* of several boxes showing the reservoirs for a particular substance and the rate at which material is transferred between the reservoirs.

- In steady-state system, the total amount of a substance in each reservoir remains constant, thus the rate of addition to, and removal of a material from a reservoir must be the same.
- The hydrologic cycle box is the simplest box model shown in the next slide.
- From the figure, we can calculate the residence time for water in the various reservoirs.
- **Residence time:** *is the average length of time a particular substance will reside in a reservoir.*

$$\text{Residence Time} = \frac{\text{Amt. of material in reservoir}}{\text{Rate of addition (removal)}}$$

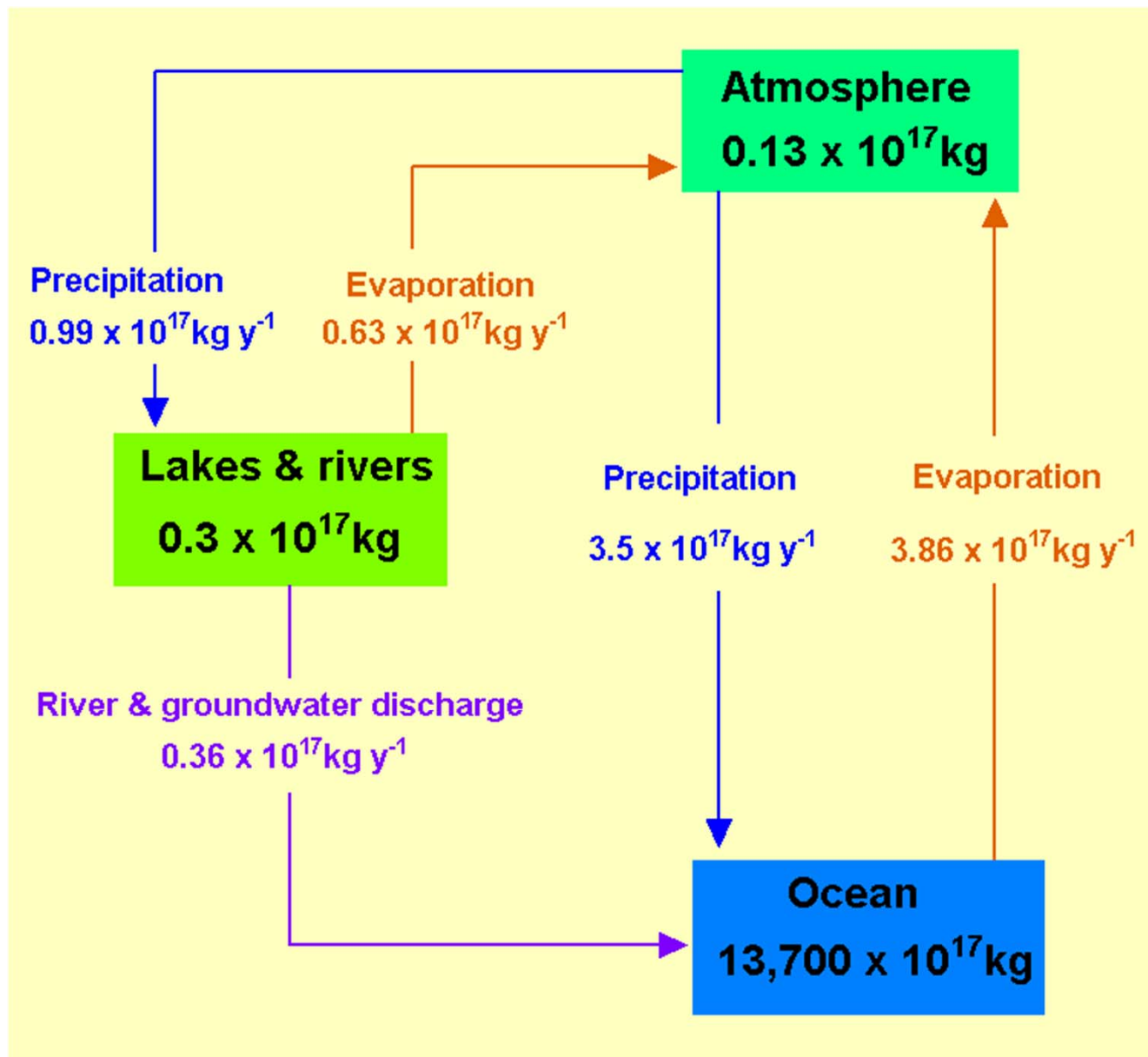


Figure 1-11. Simplified box model of the hydrologic cycle. Modified from Drever (1997).

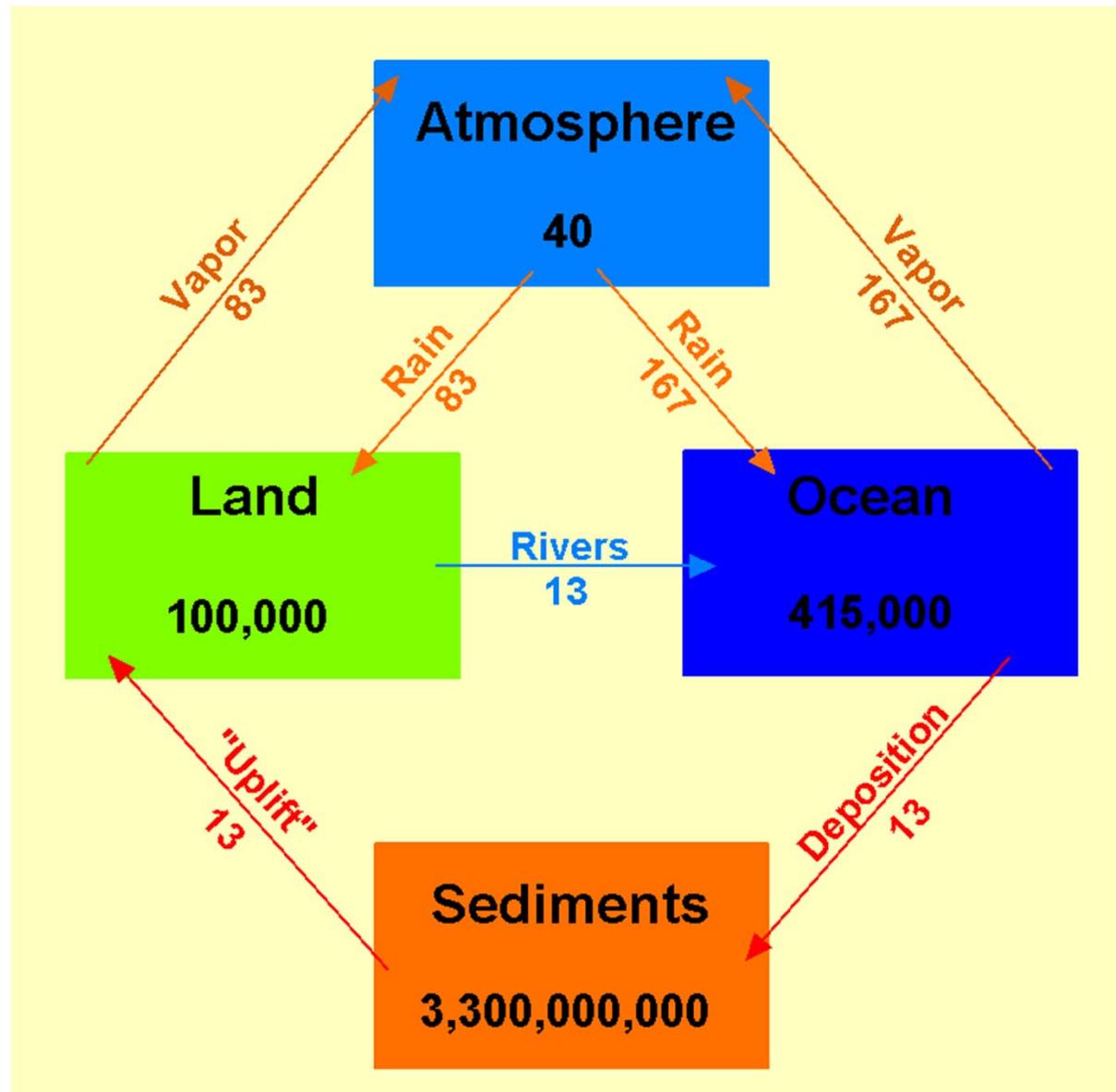


Figure 1-12. Prehuman cycle for mercury. Reservoir masses in units of 10^8 g . Fluxes in units of 10^8 g y^{-1} . From Garrels et al. (1975).

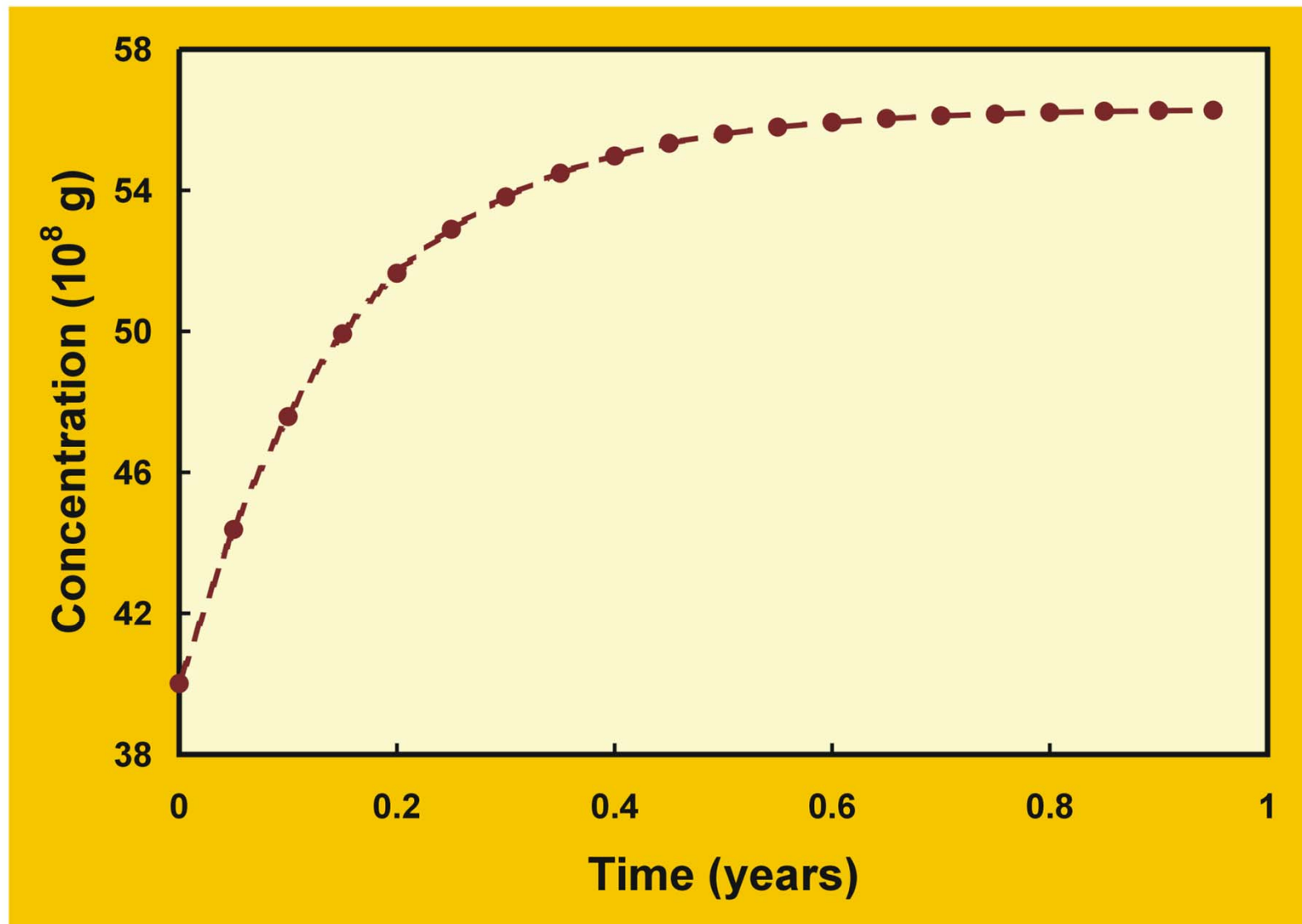


Figure 1-13. Variation in mercury content of the atmosphere as a function of time.

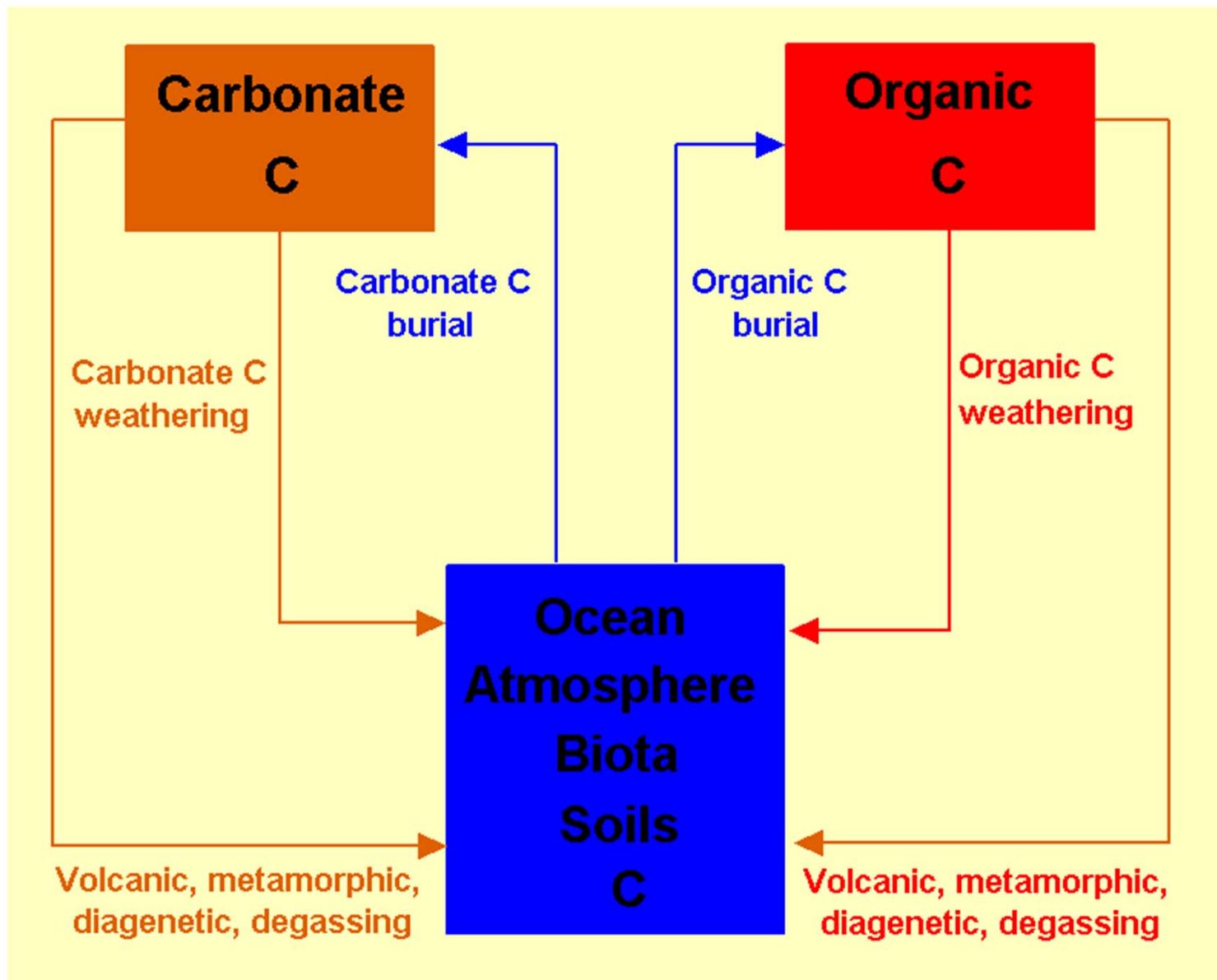


Figure 1-14b. The long term carbon cycle. After Berner (1999).

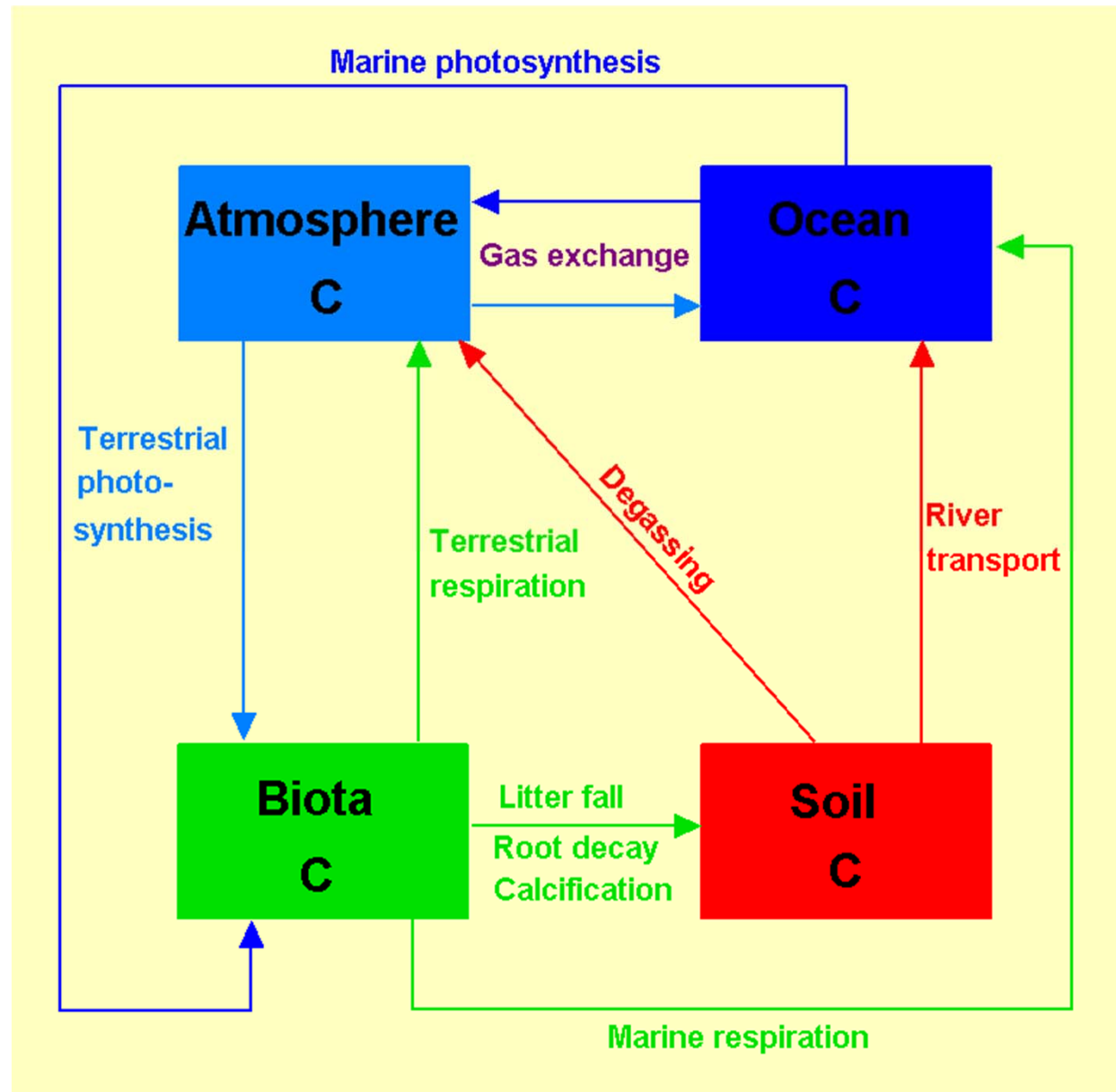


Figure 1-14a. The short-term carbon cycle, excluding anthropogenic inputs. After Berner (1999).