Change in Mass with time = Sum of all inputs + Sum of internal sources - Sum of all outputs - Sum of internal sinks

•4/13/17 – Reservoirs, Fluxes

Geochemical Reservoirs, Transfer Processes, and Mass Balance

An integrated look at how elemental feedback cycles control seawater composition

OCN 623 - 2017

Most slides are from Mike Mottl

Three Fundamental Questions

…and hundreds of specific ones…

1. **Why does Earth have oceans?**

2. **Why does Earth have dry land?**

3. **Why are the oceans salty?**

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INVITED REVIEW

Water and astrobiology

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Earth's Reservoirs

Products of differentiation of the Earth

Reservoir: a largely isolated part of a larger system, which is relatively homogeneous internally and distinct from adjoining reservoirs based on its composition and/or physical properties

crust, mantle, outer core, inner core

Earth's Reservoirs

flux: rate at which a given material moves between reservoirs per unit of time

steady state: when sources & sinks are balanced and don't change over time

residence or turnover time: ratio of the content of a reservoir divided by the sum of its sources or sinks

$$\tau = M/\Sigma Q \quad \text{or} \quad \tau = M/\Sigma S$$

Mass Balance, "the cornerstone of chemical oceanography" -- James Murray

chemical distributions on the earth and in the ocean reflect transport and transformation processes, many of which are cyclic

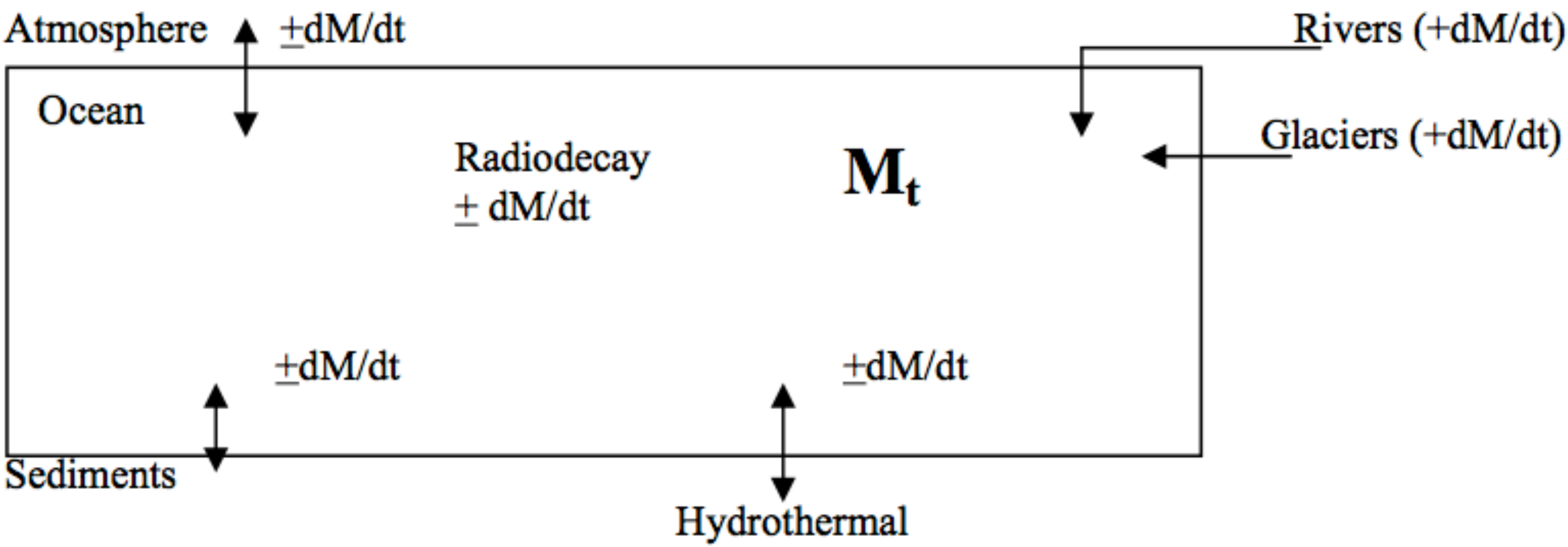
Change in Mass with time	**=**	**Sum of all inputs**	**+**	**Sum of internal sources**	**-**	**Sum of all outputs**	**-**	**Sum of internal sinks**

Such box models are used to determine the rates of transfer between reservoirs and transformation within a reservoir

But remember, the fundamental concept of Conservation of Mass:

THINGS HAVE TO ADD UP!

A simple 1-box ocean



$$(dM/dt)_{ocn} = \Sigma dM_i / dt$$

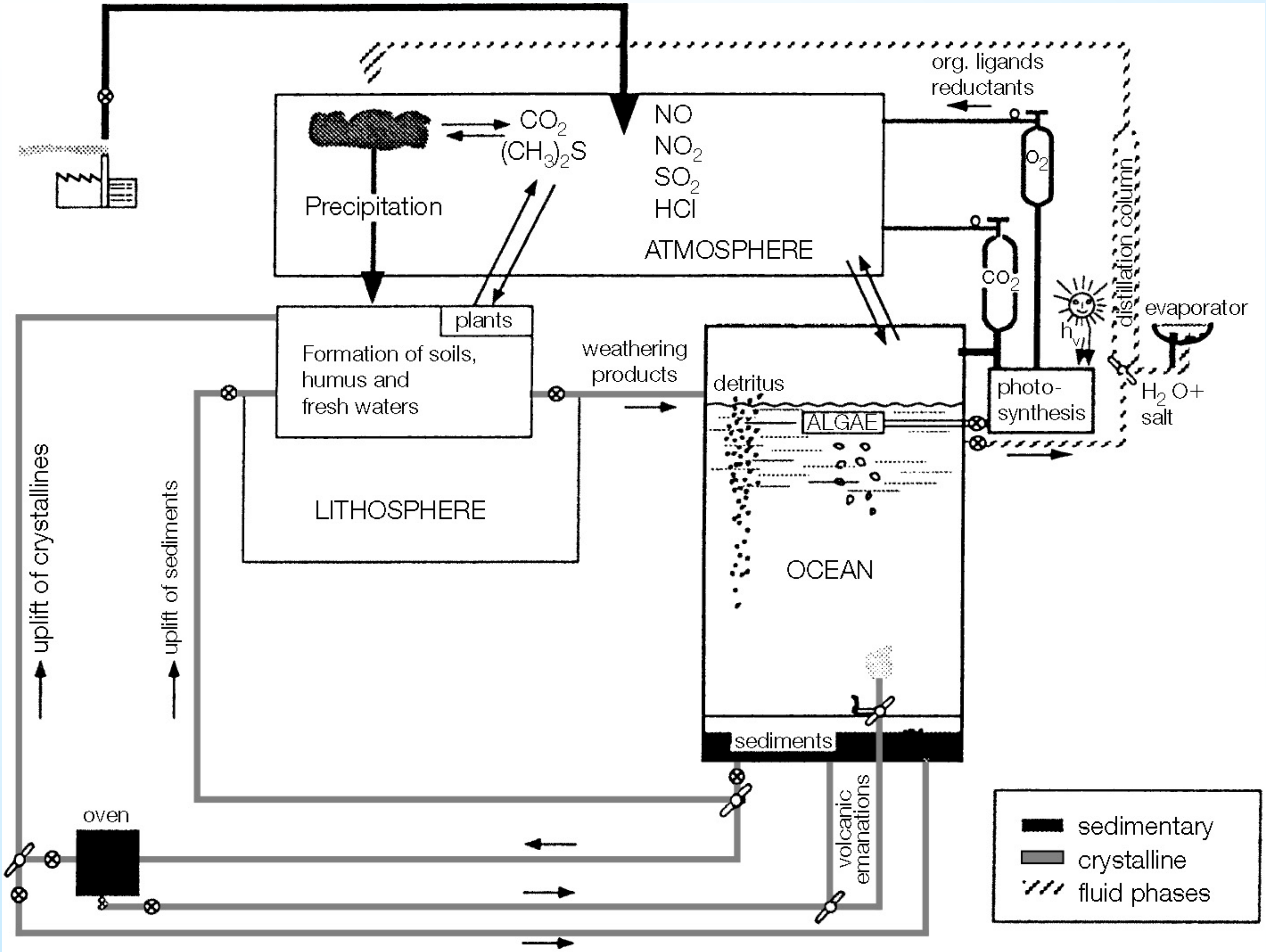
$$(dM/dt)_{ocn} = F_{atm} + F_{rivers} - F_{seds} + F_{hydrothermal}$$

$$F_{rivers} = F_{sediment} + F_{hydrothermal}$$

Is this steady state?

The crustal-ocean-atmosphere "factory"

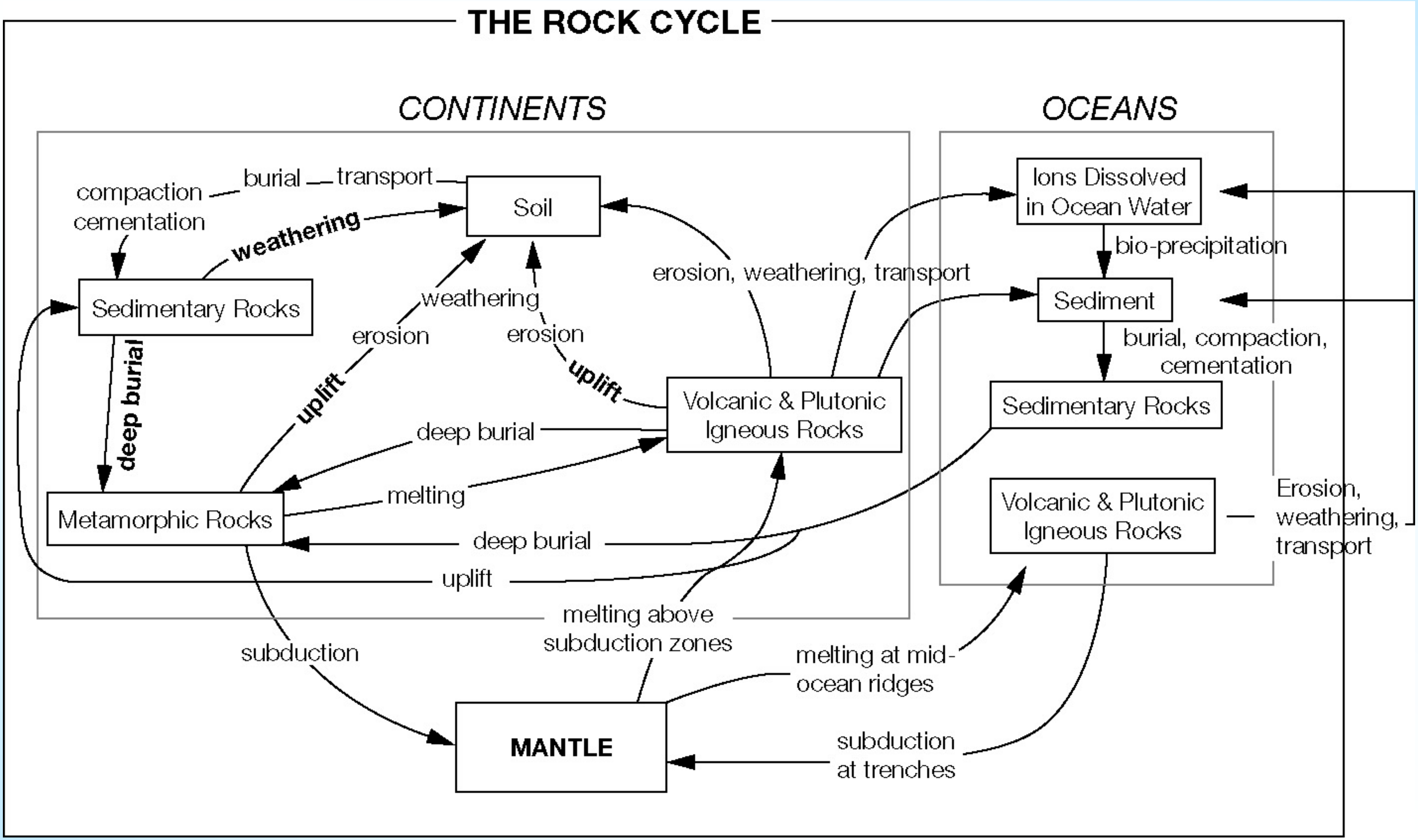
Mobility of chemicals is strongly affected by partitioning at interfaces



energy flows, material cycles

Libes Fig. 1.1

The global rock cycle box model

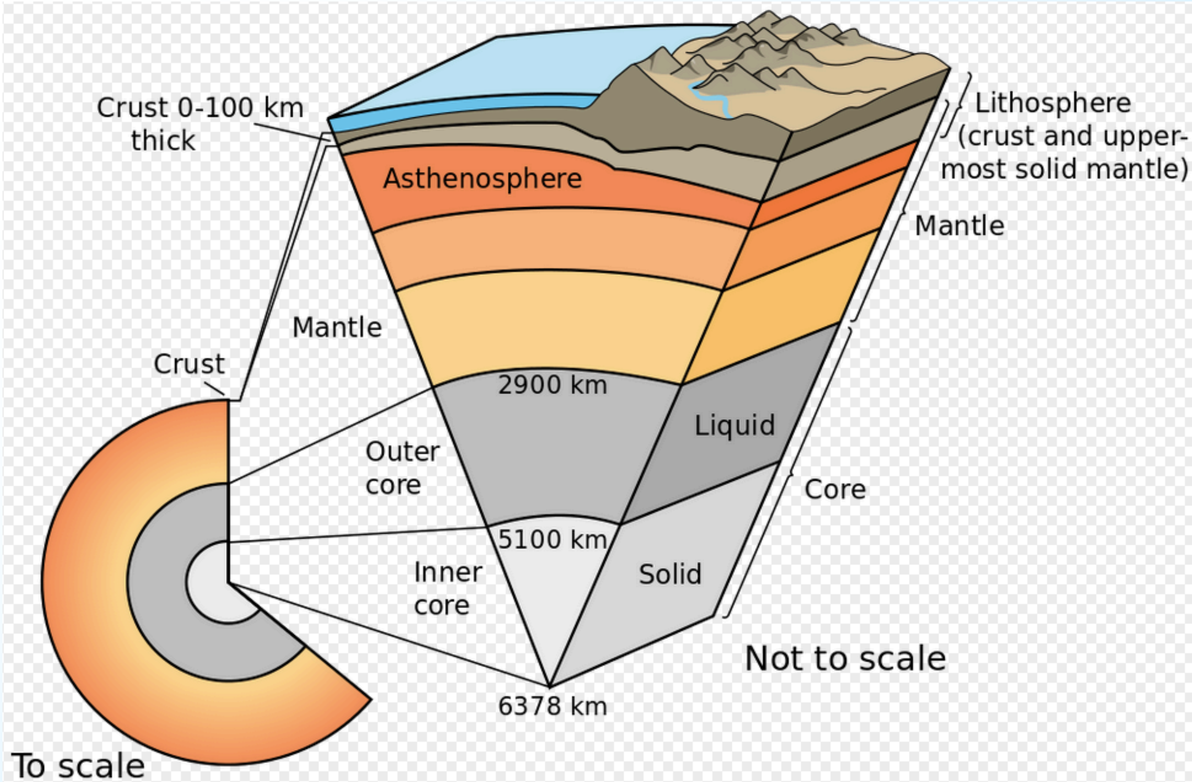


e.g., What's the turnover time for marine sediment *wrt* river input of solid particles?

Libes Fig. 1.2

Earth's Reservoirs

Products of differentiation of the Earth



crust, mantle, outer core, inner core

lithosphere, asthenosphere, mesosphere

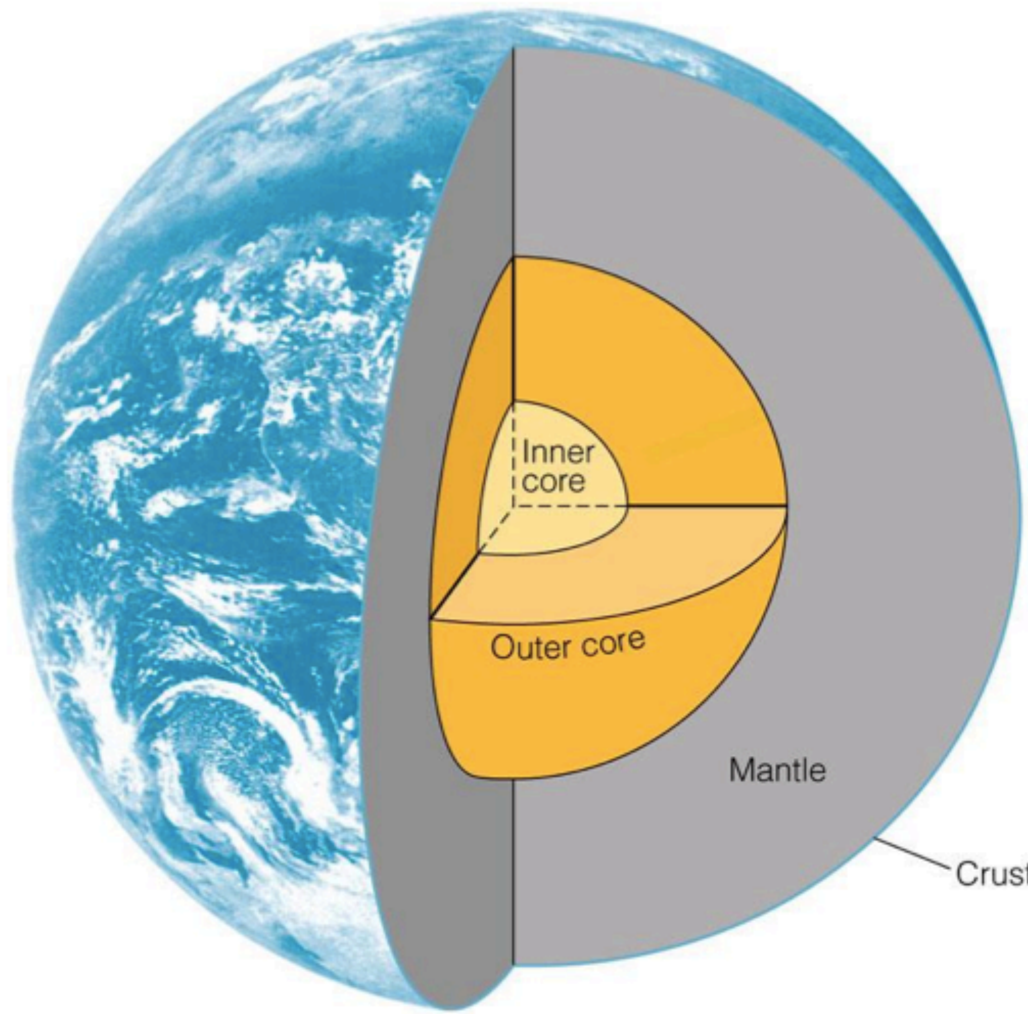
lithosphere, hydrosphere, atmosphere, biosphere

Endosphere vs. exosphere, surface vs. deep processes

(based on chemical and physical properties)

- **Inner Core**: 5100-6370 km, ***solid*** Fe + 6% Ni (16 g/cm^3)
- **Outer Core**: 2900-5100 km, ***liquid*** Fe-Ni (12 g/cm^3)
- Core is 32% of Earth mass, 16% of its volume
- **Mantle**: ~10-2900 km, solid Mg-Fe-silicates (4.5 g/cm^3), 68% of Earth mass, 83% of its volume
- **Crust:** the "skin" of Earth:

  0.4% of Earth mass and <1% of its volume.



Bulk Composition of Earth

• Fe	32.0 wt%	• Ni	1.8
• O	29.7	• Ca	1.7
• Si	16.1	• Al	1.6
• Mg	<u>15.4</u>	• S	0.6 wt%
	93.2		

Eight most abundant elements account for ~99% of total Earth mass.

Most Fe, Ni, and S are in core.
Mantle is mainly Mg, Si, O, with minor Ca, Al.
Crust is enriched in Ca, Al, Si relative to mantle.

Sun: *75% H and 23% He*

Origin of Earth's Oceans and Atmosphere

Where did the materials come from?

1) Solar nebular gas
2) comets
3) meteorites
4) cosmic dust.

How did the materials get here, and when?

1) condensation of the Solar nebula
2) accretion of planetary embryos during assembly of Earth
3) late impact of comets or meteorites.

How were the materials modified after arrival?

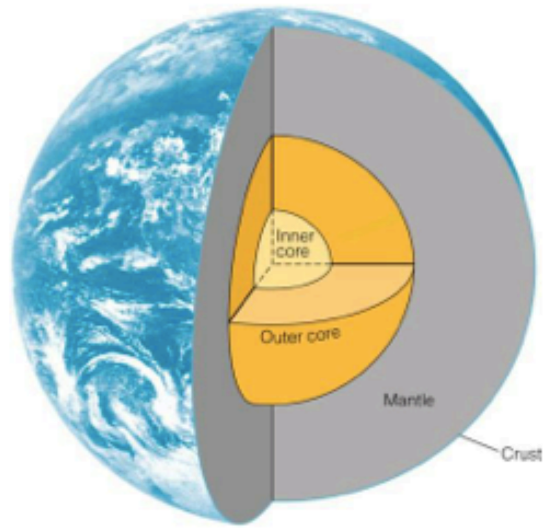
1) Hydrodynamic escape
2) Rayleigh distillation as, e.g., during Jeans escape
3) Impact erosion
4) Dissolution from the atmosphere into a magma ocean
5) Subduction and outgassing.

Bulk Composition of the Earth

(McDonough, 2005, *Treatise on Geochemistry*, ch. 2.15)

	Wt.%	Moles/100g	Mol%	% in core
Fe	32.0	0.573	15.12	86
O	29.7	1.856	48.99	0
Si	16.1	0.573	15.13	12
Mg	15.4	0.634	16.72	0
Subtotal	93.2	3.636	96.0	
Ni	1.8	0.031	0.82	93
Ca	1.7	0.043	1.13	0
Al	1.6	0.059	1.56	0
S	0.6	0.020	0.53	96
Subtotal	99.0	3.789	100.0	

Most of Earth's Fe, Ni, and S are in the core.
The mantle is mainly Mg (Fe) silicate/oxide.
Ca and Al are enriched in the crust.



Fe in core	0.490
Ni in core	0.029
Si in core	0.069
S in core	0.019
FeO	0.083
SiO_2	0.504
MgO	0.634
CaO	0.043
Al_2O_3	0.029

Bulk Silicate Earth = Mantle + Crust

Fe/(Fe+Ni+Si+S) in core = 0.808 — On a molar basis: Earth's core is 81 mol% Fe.

Fe/(Fe+FeO) in bulk Earth = 0.856 — 86% of Earth's Fe is in the core.

MgO/(MgO+FeO) in mantle = 0.885

8:1 Mg:Fe in mantle

Why do we have oceans?

Need **water**: lots of it, and liquid. Why does Earth have lots of water?

--Accretion of cold, icy, water-rich planetesimals, **rapidly**, allowing retention of H_2O on melting of ice

--Outgassing of Earth's interior, bringing water to surface

--Moderate distance from the Sun, allowing liquid water.

Do any other planets have oceans?

--**Mars** may have had oceans in the distant past.

--**Europa**, a moon of Jupiter, may have oceans under thick ice.

--**Titan**, the largest moon of Saturn, apparently has oceans of liquid hydrocarbons, and continents of rock and ice!

Earth's Water

	Mass of H_2O (10^{18} kg)	ppm H in BSE	δD (o/oo)	D/H ($x10^{-6}$)
Oceans	**1371**	**38**	0	156
Marine sed. porewater	**180**	**5**	-1	156
Mar. basement fm. water	26	1	-1	156
Ice	27.8	1	-350	101
Continental groundwater	15.3	0	-10	154
Lakes, rivers, soils	0.192	0	-10	154
Total hydrosphere	**1621**	**44**	**-6**	**155**

= 1.2 oceans

Lecuyer et al. (1998) *EPSL* **145**:249; Mottl et al. (2007) *Chemie der Erde* **67**:253

Earth's Water

	Mass of H_2O (10^{18} kg)	ppm H in BSE	δD (o/oo)	D/H ($\times 10^{-6}$)
Shales	**221**	**6**	-80	143
Continental carbonates	2.56	0	-60	146
Evaporites	0.42	0	-5	155
Marine clays	7.56	0	-50	148
Marine carbonates	0.504	0	-30	151
Total sedimentary rocks	232	6	-79	144
Organic matter	1.36	0	-100	140
Cont. metamorphic rocks	36	1	-80	143
Oceanic (igneous) crust	40.6	1		
Hydrosphere	**1621**	**44**	**-6**	**155**
TOTAL Exosphere	**1931**	**53**	**-17**	**153**

= 1.4 oceans

Lecuyer et al. (1998) *EPSL* **145**:249; Mottl et al. (2007) *Chemie der Erde* **67**:253

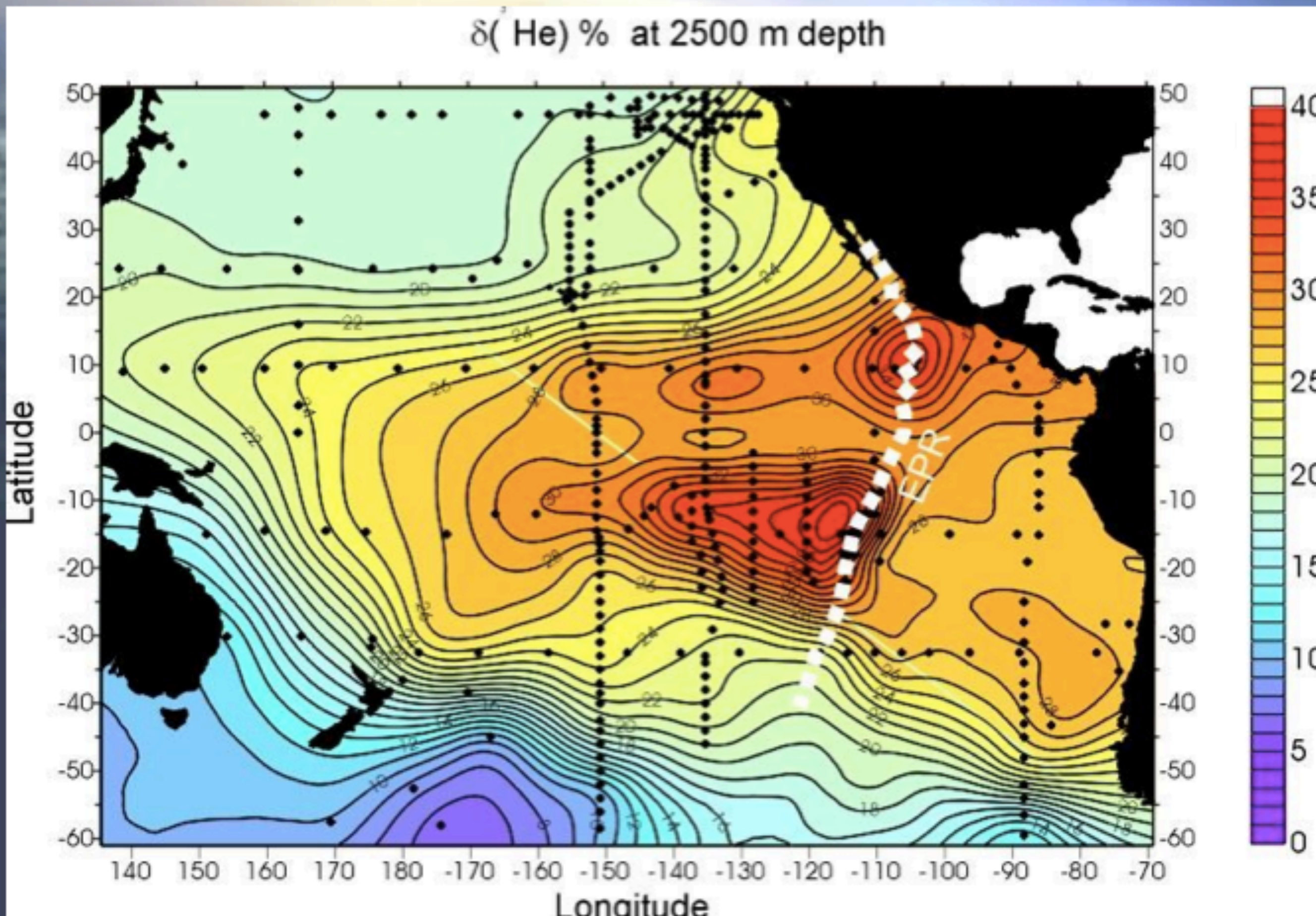
Conclusion

- H is a *trace element* in the bulk silicate Earth: 60-120 ppm (500-1100 ppm H_2O)!
- The Bulk Silicate Earth probably contains 1.5-3.2 oceans worth of water.
- Although this amount of water is small, it nonetheless plays a critical role in Earth tectonics, by lowering the viscosity of the mantle enough to allow for plate tectonics, deep recycling of oceanic crust and upper mantle, and formation of continental crust and hence dry land on Earth.

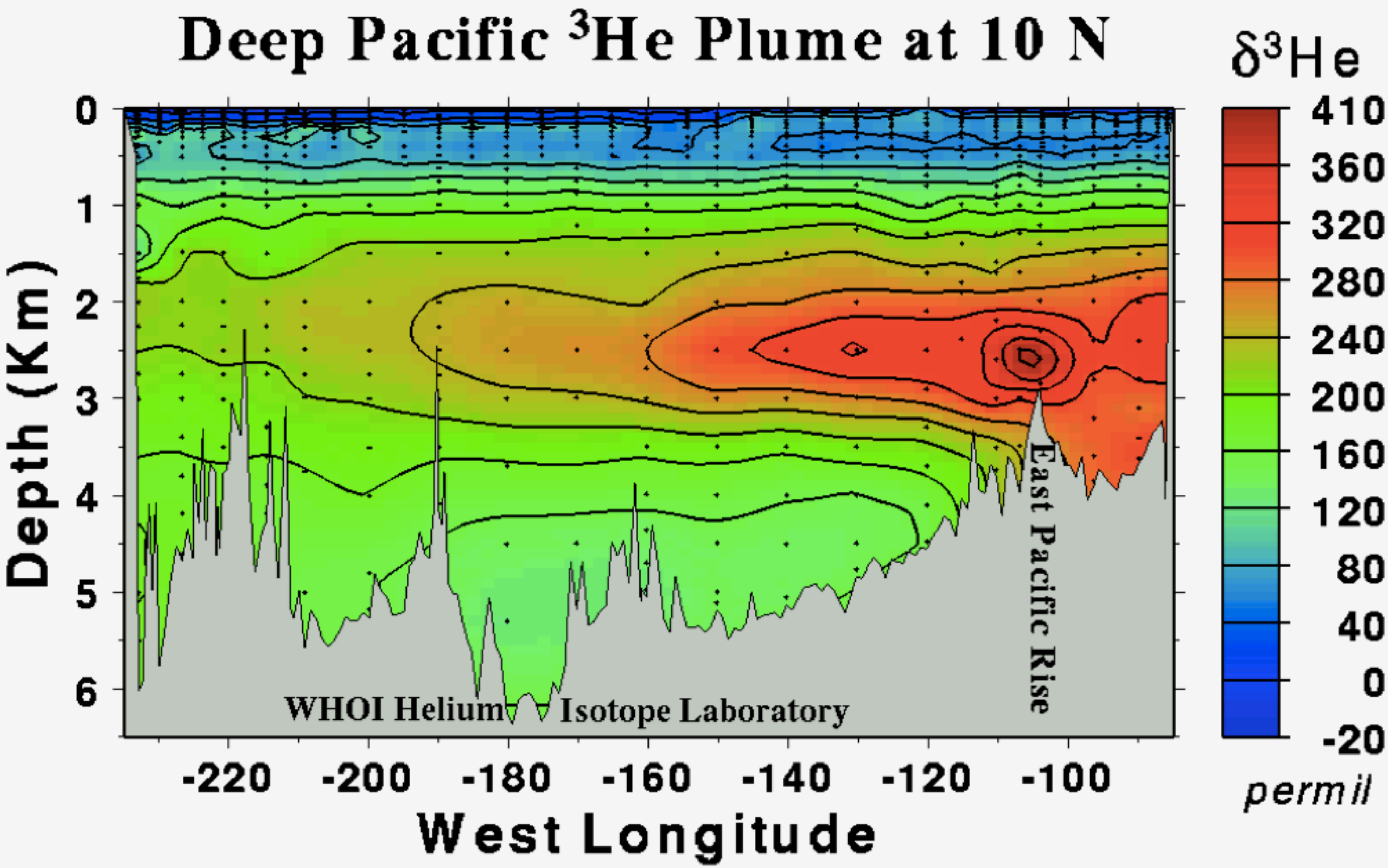
Origin of Oceans/Atmosphere

- Outgassing of Earth continues today.

  Evidence: ^{3}He detected in ocean, released from interior of Earth by volcanic processes



^{3}He in Pacific Ocean



Composition of Volcanic Gases

TODAY….

- 80% H_2O
- 10% CO_2
- 6% SO_2
- 1% H_2
- Trace of N_2, HCl

- Major gases are in oxidized form now.
- Early volcanic gases were likely in more reduced form:

  H_2, CH_4, H_2S, NH_3.

Early atmosphere: Free O2 would have been absent.
CO_2 and CH_4 were probably abundant.

The CO_2 would have eventually reacted with rocks (in water):

$$H_2O + CO_2 + \text{“}CaSiO_3\text{”} \rightarrow CaCO_3 + SiO_2 + H_2O$$

Solar luminosity has increased by ~30% over 4.5 b.y.:
"faint early Sun paradox": why didn't oceans freeze?

Urey reaction: $H_2O + CO_2 + CaSiO_3 = CaCO_3 + SiO_2 + H_2O$

Actual reactions

(for which the Urey reaction is shorthand):

Weathering of feldspar (most abundant mineral group in crust):

$$CaAl_2Si_2O_8 + 3H_2O + 2CO_2 = Al_2Si_2O_5(OH)_4 + Ca^{2+} + 2HCO_3^-$$

plagioclase feldspar; kaolinite = clay mineral = shale

Precipitation of calcium carbonate (limestone):

$$Ca^{2+} + 2HCO_3^- = CaCO_3 + H_2O + CO_2$$

calcite or aragonite

produces alkalinity, by cations kicked out into Si clays

SUMMARY:

Fate of Planetary Gases (volatile compounds)

	Earth	**Venus**	**Mars**
H_2O	oceans	H—space O—rocks (1 ocean in 30-300 million years)	ice
CO_2	**rocks**	**atmosphere**	**ice**
N_2	atmosphere	atmosphere	space (1 atm in 4.5 billion years)
O_2	atmosphere	none	none

Why didn't Earth end up like Venus?

EVOLUTION OF THE OCEAN-ATMOSPHERE SYSTEM:

THE RISE OF FREE OXYGEN (O_2)

--Earth is chemically ***reducing*** (lots of metallic Fe).

--Must separate reduced from oxidized: core formation.

-- $2\ H_2O\ =\ 2\ H_2 + O_2$ **Photodissociation**

followed by loss of hydrogen to space.

-- $CO_2 + H_2O\ =\ CH_2O + O_2$ **Photosynthesis** ⟶

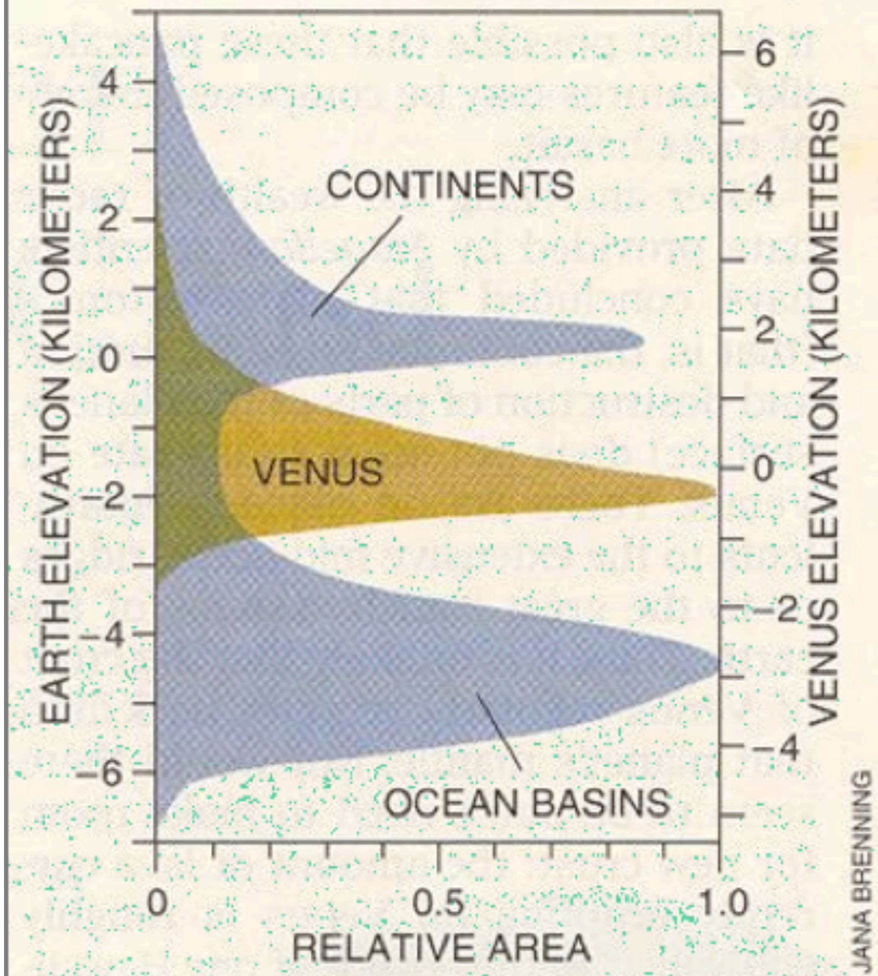
(Respiration and Decay ⟵)

followed by burial of organic carbon.

--Free oxygen arose about 2.4 Ga,

and reached near-present levels about 0.8 Ga.

This allowed development of multicellular organisms and their migration onto land.



SURFACE ELEVATIONS are distributed quite differently on the earth (*blue*) and on Venus (*gold*). Most places on the earth stand near one of two prevailing levels. In contrast, a single height characterizes most of the surface of Venus. (Elevation on Venus is given with respect to the planet's mean radius.)

Earth's solid surface has two levels representing ***oceanic*** and ***continental*** crust.

Venus's has only one!

Loss of H_2O probably prevented ***plate tectonics*** on Venus, including formation of continents!

Earth has dry land *because it has oceans!*

Geochemical Mass Balances

Two types:

1. Balance between reactants (igneous rocks and volcanic gases) and products (sediments, sedimentary rock, and seawater).

   These early attempts neglected to consider ***cyclical*** processes adequately: e.g., conversion of sediments into high-grade metamorphic and, ultimately, igneous rocks by melting. Na^+ in seawater thus represents only the "standing crop" of sediments and sedimentary rocks.

2. Geochemical cycles and the balancing of inputs with outputs from various reservoirs, esp. **seawater**.

Cycling of material among Earth reservoirs throughout Geologic time

Goal of Geochemistry

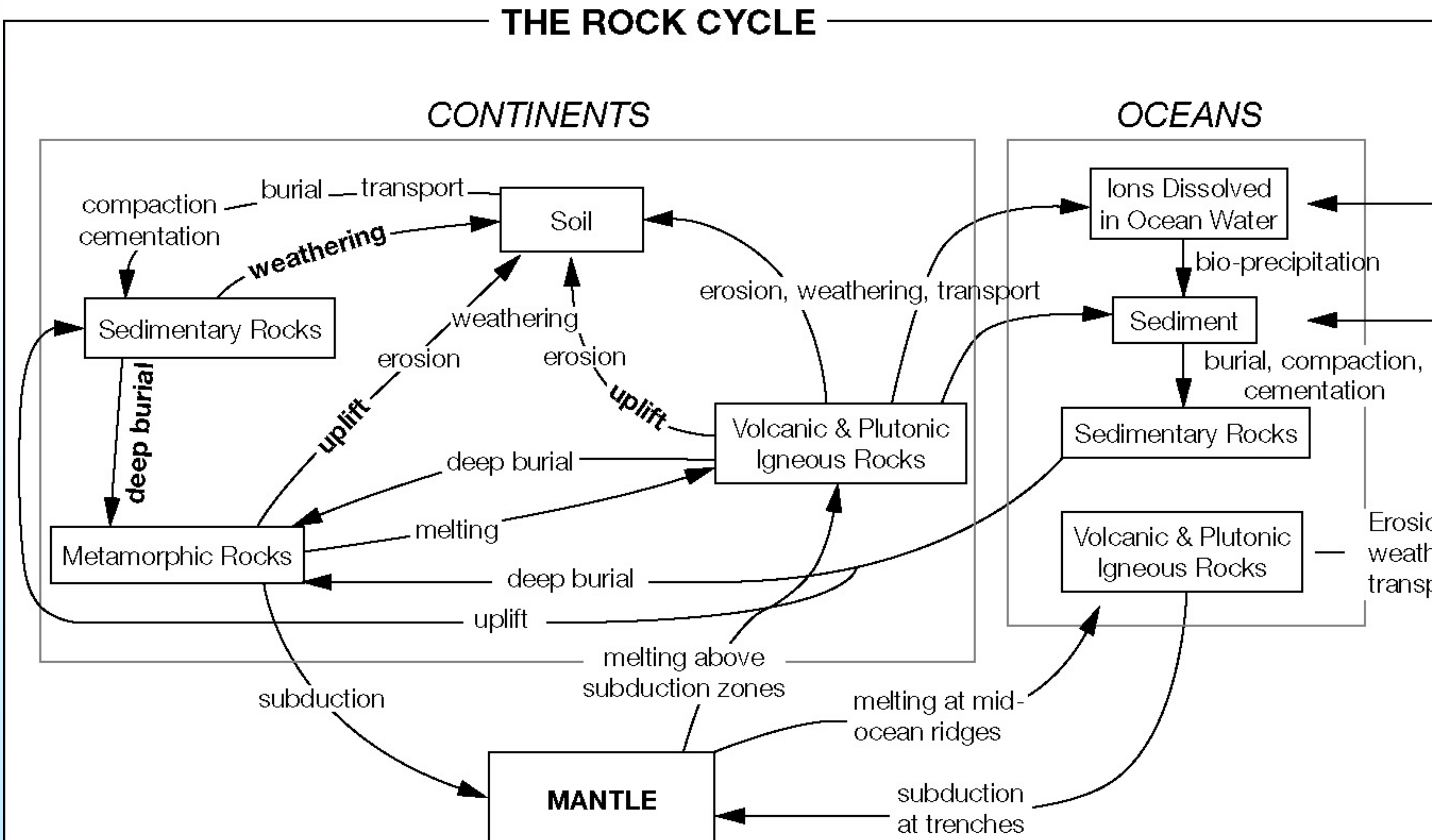
To understand how the Earth works as a chemical system, i.e.,

To identify and quantify those processes which transfer Earth materials from one reservoir to another:

1. Identify and characterize ***reservoirs***.
2. Identify ***mass transport processes*** and quantify their rates.
3. Identify and quantify relationships among transport processes and reservoir characteristics, i.e., ***feedback mechanisms***.

The crustal-ocean-atmosphere factory

storage reservoirs and removal mechanisms



Libes Fig. 1.2

How has the long-term subduction cycle altered chemical composition of mantle magma?

Cyclic Seawater Ions

Large annual production of seasalt spray, quickly returned

5×10^{12} kg/y

Table 21.6 Percentage of Cyclic Seawater Ions by Weight Relative to Their Total Weight in Rivers.

Element	Berner and Berner 1996[a]	Holland 1978[b]	Garrels and Mackenzie 1971[b]	Meybeck 1983[c]
Cl^-	13(18)	27	55	72
Na^+	8(11)	19	35	53
SO_4^{2-}	2(2)	39[d]	6	19
Mg^{2+}	2(2)	<3	7	15
K^+	1(1)	<14	15	14
Ca^{2+}	0.1(0.1)	1.3	0.7	2.5

~1% is deposited on coastal land

Input-Output Balance for Major Ions & Alkalinity

Other processes drive removal over longer time scales

Table 21.7 Input-Output Balance for the Major Ions and Alkalinity.

		Cl^-		Na^+		Mg^{2+}		SO_4^{2-}		K^+		Ca^{2+}		Alk	
		J	M	H[c]	M	H	M	H	M	H	M	H	M	H	M
Ocean inventory ($\times 10^{18}$ mol)[a]		765		658		74		40		14		14		3	
Rates ($\times 10^{12}$ mol/y)[a]															
Rivers (natural)			6.1	2.4	8.5	6.1	5.2	4.2	3.2	1.4	1.2	15.0	12.5	37.6	31.9
Volcanic gas		0.2 to 0.6													
Hydrothermal systems	On axis[b]			−1.1	−0.9	−2.0	−3.1	−1.0	−1.7	0.6	−0.6	0.9	2.0	−0.1	−0.4
	Off axis					−0.4				−0.4					
Clays	Ion exchange			−1.5	−1.9	−0.3	−1.2			−0.3	−0.4	1.0	2.6		0.5
	Reverse Weathering									−0.8	−0.1				
Carbonate	Dolomite deposition					−1.7	−0.6					−1.7		−6.8	
	Carbonate deposition											−15.7	−17.0	−31.4	−35.0
Silicate	BSi deposition														
Sulfides	Sulfate reduction													4.0	
	Pyrite deposition							−2.0	−1.2						2.4

Seawater magnesium, sulfate, sodium are close to steady state

Input-Output Balance for Major Ions & Alkalinity

Table 21.7 *(Continued)*

		Cl^-		Na^+		Mg^{2+}		SO_4^{2-}		K^+		Ca^{2+}		Alk	
		J	**M**	**H**[c]	**M**	**H**	**M**	**H**	**M**	**H**	**M**	**H**	**M**	**H**	**M**
Salts	Atmospheric seasalt cycling, pore water burial, evaporite deposition		−6.1	[c]	−5.7		−0.3		−0.3		−0.06		−0.1		
	Atmospheric seasalt cycling	−1.1 to −4.5													
	Pore water burial	0.1													
	Evaporite deposition							−0.2				−0.2			
Total inputs − Total outputs			0.0	−0.2	0.0	1.7	0.0	1.0	0.0	0.5	0.0	−0.7	0.0	3.3	−0.6
Increment (+)/Decrement (−) estimated from data[d]				0.0		1.7		1.0		?		−0.7			
Conclusions from Holland (2005)				Imbalance within uncertainty of data		Nonsteady state supported by data		Nonsteady state supported by data		Outputs likely under-estimated		Nonsteady state supported by data		Imbalance within uncertainty of data	

Revisiting River vs. Seawater Composition

River water is single largest source of major ions, concentrations are lower & ratios differ

Table 21.8 Comparison of River and Seawater Composition.

Ion	River Water			Seawater				
	Concentration (μmol/L)	Runoff ($\times 10^{12}$ mol/y)	% Contribution by Mass to Total Dissolved Solids	Concentration[a] (μmol/L)	Inventory[b] ($\times 10^{18}$ mol)	% Contribution by Mass to Total Dissolved Solids	[Seawater] / [Riverwater]	Replacement Time (Million Years)
Na^+	226	10	6.0%	479,955	658	30.8%	2,122	65
Mg^{2+}	140	6	3.9%	54,050	74	3.7%	386	12
Ca^{2+}	334	15	15.5%	10,522	14	1.2%	31	1
K^+	33	1	1.5%	10,446	14	1.1%	314	10
Cl^-	164	7	6.7%	558,626	765	55.2%	3,415	104
SO_4^{2-}	55	2	6.1%	28,897	40	7.7%	524	16
HCO_3^-	852	38	60.2%	1,904	3	0.3%	2	0.068

Residence time for water = few thousand yrs

In-class exercise

Element 'X' is at steady state in the contemporary ocean, with concentration = 1.0×10^{-3} mol L^{-1} (M)

The main input is from rivers and the main removal is by stripping of 'X' from seawater during hydrothermal circulation (concentration in vent fluid = 0).