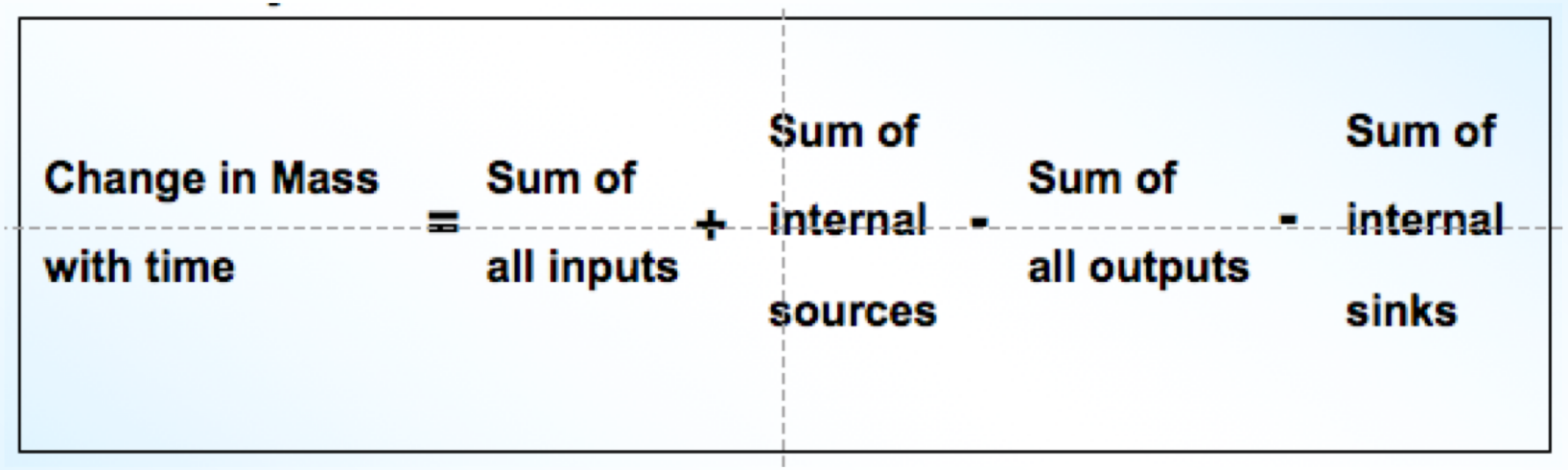
Describe how differentiation of the Earth provides for distinct geochemical reservoirs

•4/24/18 – Reservoirs, Fluxes

Apply concepts of steady state, residence time, and mass balance equations to biogeochemical problems

- 4/24/18 – Reservoirs, Fluxes



•4/24/18 – Reservoirs, Fluxes

Geochemical Reservoirs, Transfer Processes, and Mass Balance

An integrated look at how elemental feedback cycles control seawater composition

OCN 623 - 2018

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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Summary of Significant Events in Earth History (Ga = billion years before present)

Dr. M.J. Mottl, Dept. of Oceanography, University of Hawaii

4.567 Ga	± 0.001 Ga = Age of Solar System based on meteorites (CAI's)
4.56 Ga	Origin of Earth by infall of planetesimals: most of mass within 10 Ma
4.54 Ga	Accretion, core formation on Earth and formation of the Moon are largely complete. 80% of atmosphere outgassed.
4.45 Ga	Age of Lunar highlands
4.4-4.2 Ga	Oldest known minerals on Earth (zircons from NW Australia)
4.00 Ga	Oldest known rocks on Earth (Acasta gneiss, NW Canada)
3.85 Ga	End of major bolide impacts on the Moon and inner planets (the "Lunar Cataclysm"). Oldest known evidence for life on Earth: carbon isotope systematics Continents begin to grow rapidly, till 2.5 Ga.
3.5 Ga	Oldest fossils of life on Earth (bacteria and stromatolites, NW Australia)
2.5 Ga	End of Archean Eon; beginning of the Proterozoic Eon. Continental growth slows.
2.45-2.32 Ga	Beginning of the rise of free O_2 in Earth's atmosphere (*Nature* **427**:117)
2.2 Ga	Oldest known continental glaciation (Gowganda tillite, Canada)
2.1-1.9 Ga	Rise of atmospheric O_2 to about 1% of present level (?)
1.8 Ga	Oldest known fossils of eukaryotic cells (i.e., those with a nucleus) (but these may have evolved much earlier, ≥2.7 Ga)
1.4 Ga	Oldest multicellular eukaryotes (seaweed)
800-700 Ma	Varangian glaciation, pole to tropics ("Snowball Earth"?)
580 Ma	Ediacaran fauna of soft-bodied metazoans
	Increase of atmospheric O_2 to a large fraction of present level?
560 Ma	End of Proterozoic; beginning of the Phanerozoic ("visible life") Eon and the Cambrian Period (caused by rise of O_2?)
430 Ma	First land plants (Silurian Period)
360 Ma	First land vertebrates (end of Devonian Period)

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

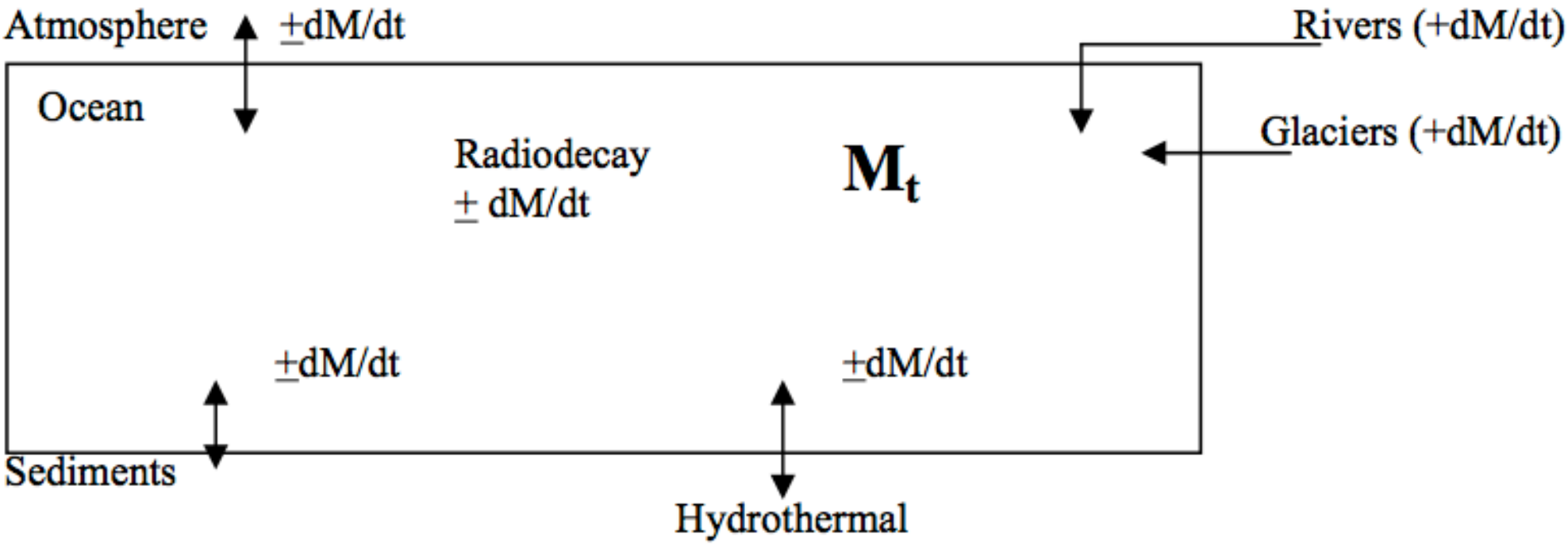
Change in Mass with time	=	Sum of all inputs	+	Sum of internal sources	-	Sum of all outputs	-	Sum of internal sinks

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



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

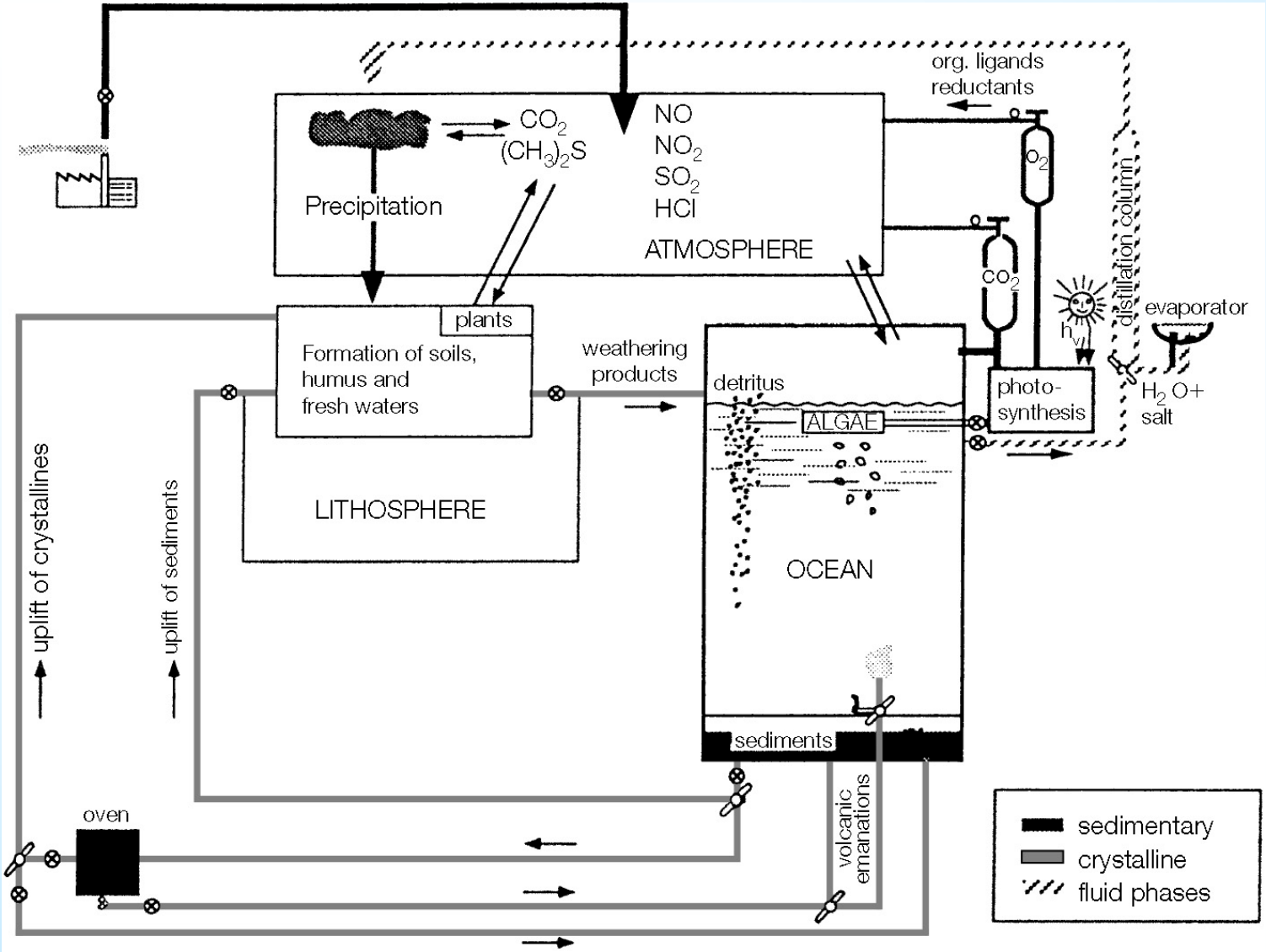
$$(dM/dt)_{ocn} = F_{atm} + F_{rivers} - F_{seds} + F_{hydrothermal}$$

Is this steady state?

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

The crustal-ocean-atmosphere "factory"

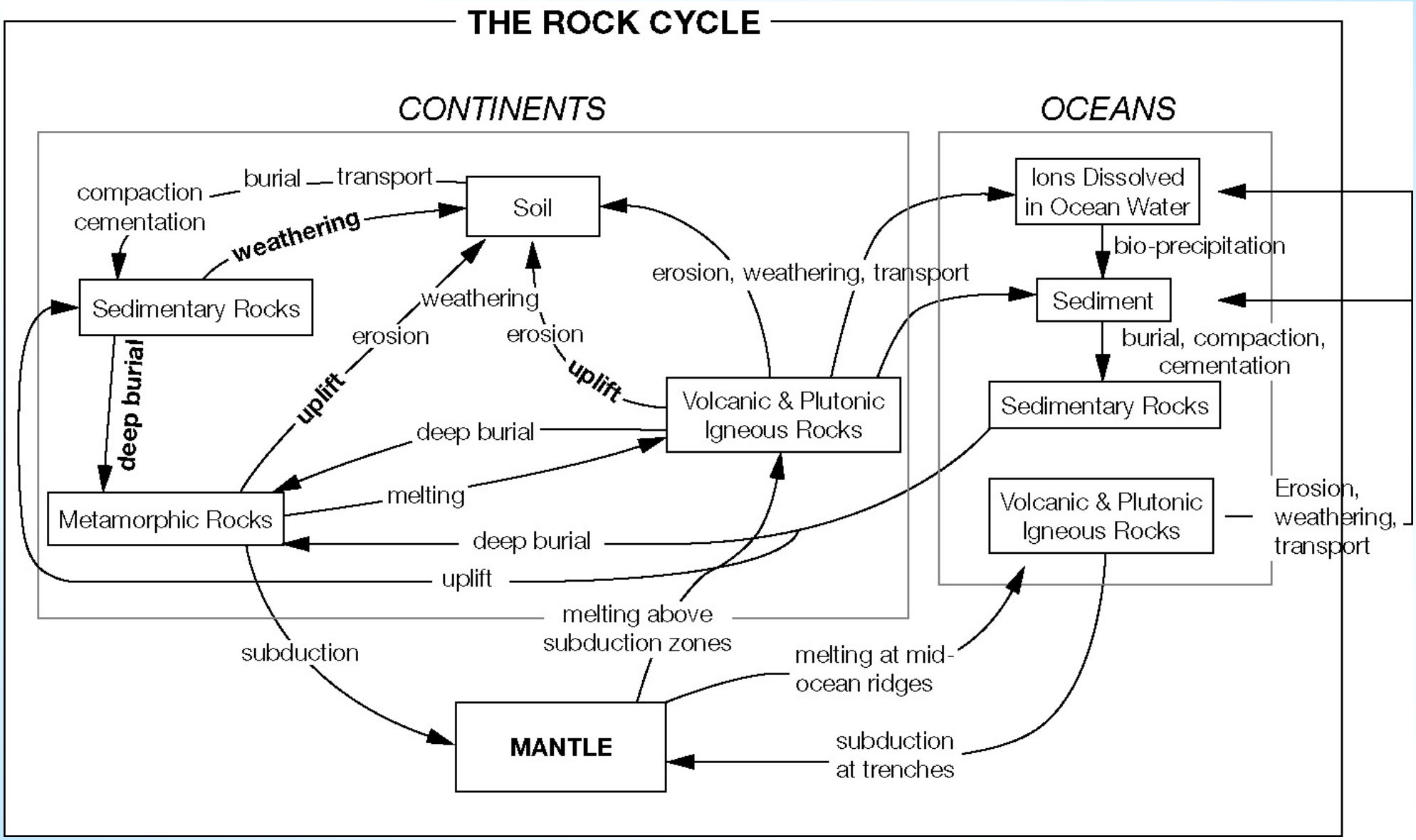
Mobility of chemicals is strongly affected by partitioning at interfaces



energy flows, material cycles

Libes Fig. 1.1

The global rock cycle box model

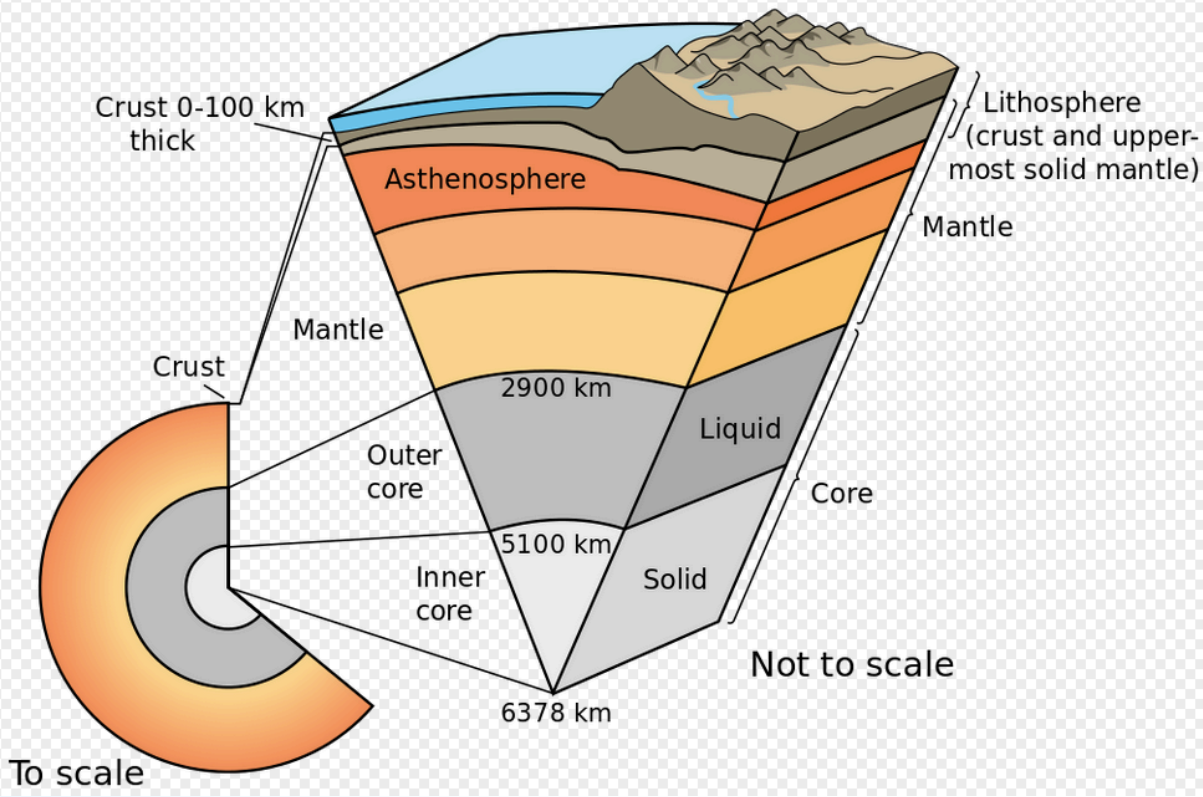


e.g., What's the turnover time for marine sediment *wrt* river input of solid particles?

Libes Fig. 1.2

Earth's Reservoirs

Products of differentiation of the Earth



crust, mantle, outer core, inner core

lithosphere, asthenosphere, mesosphere

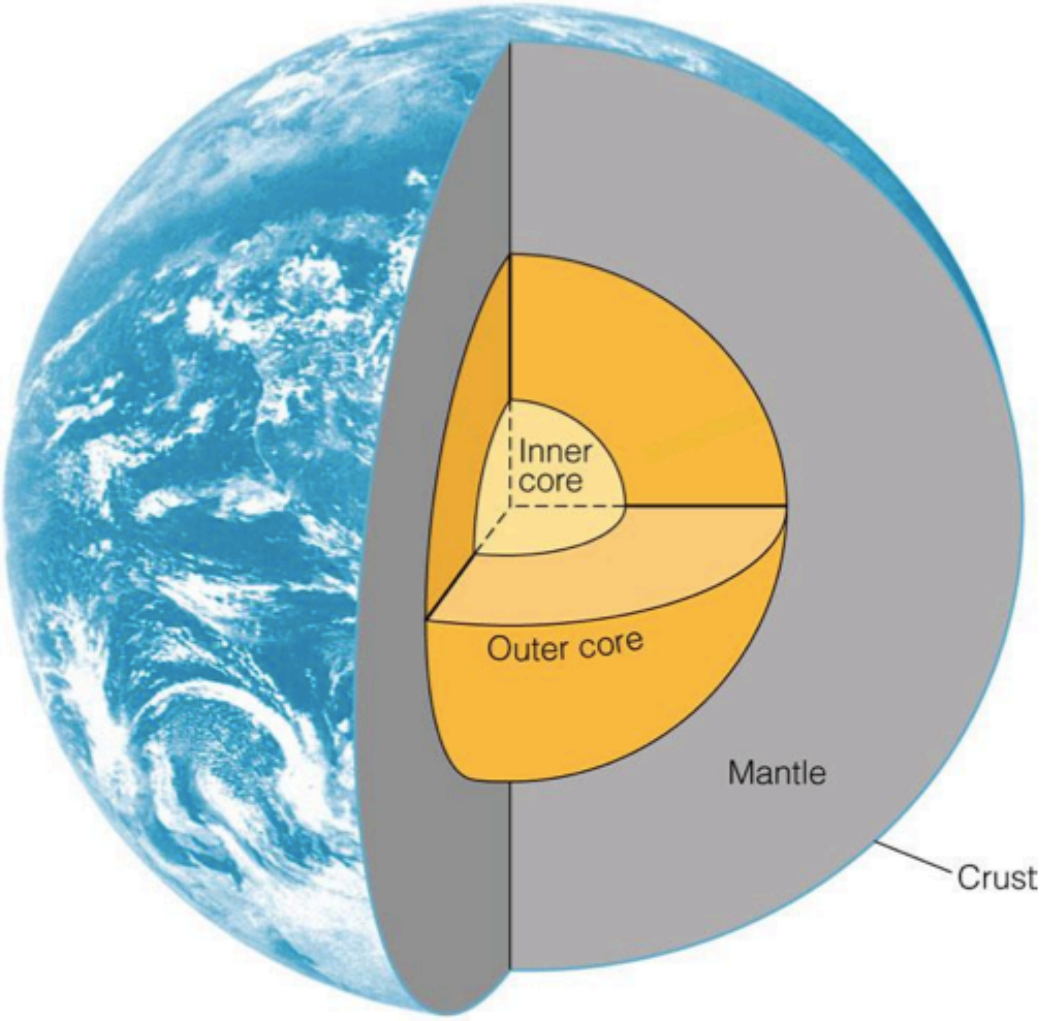
lithosphere, hydrosphere, atmosphere, biosphere

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.



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Bulk Composition of Earth

• Fe	32.0 wt%	• Ni	1.8
• O	29.7	• Ca	1.7
• Si	16.1	• Al	1.6
• Mg	15.4	• 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?

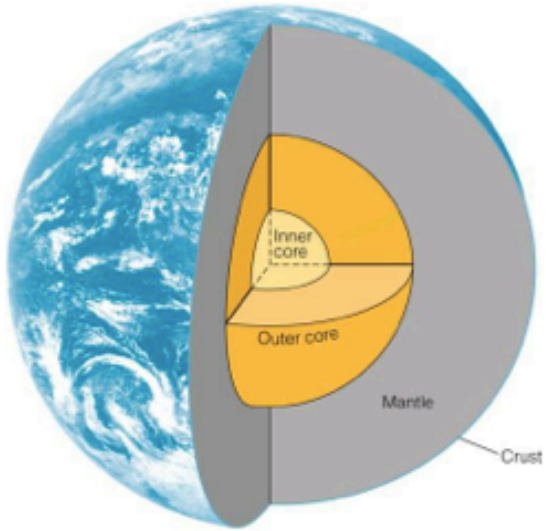
1) Hydrodynamic escape
2) Rayleigh distillation as, e.g., during Jeans escape
3) Impact erosion
4) Dissolution from the atmosphere into a magma ocean
5) Subduction and outgassing.

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 ($\times 10^{-6}$)
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 ($x10^{-6}$)
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

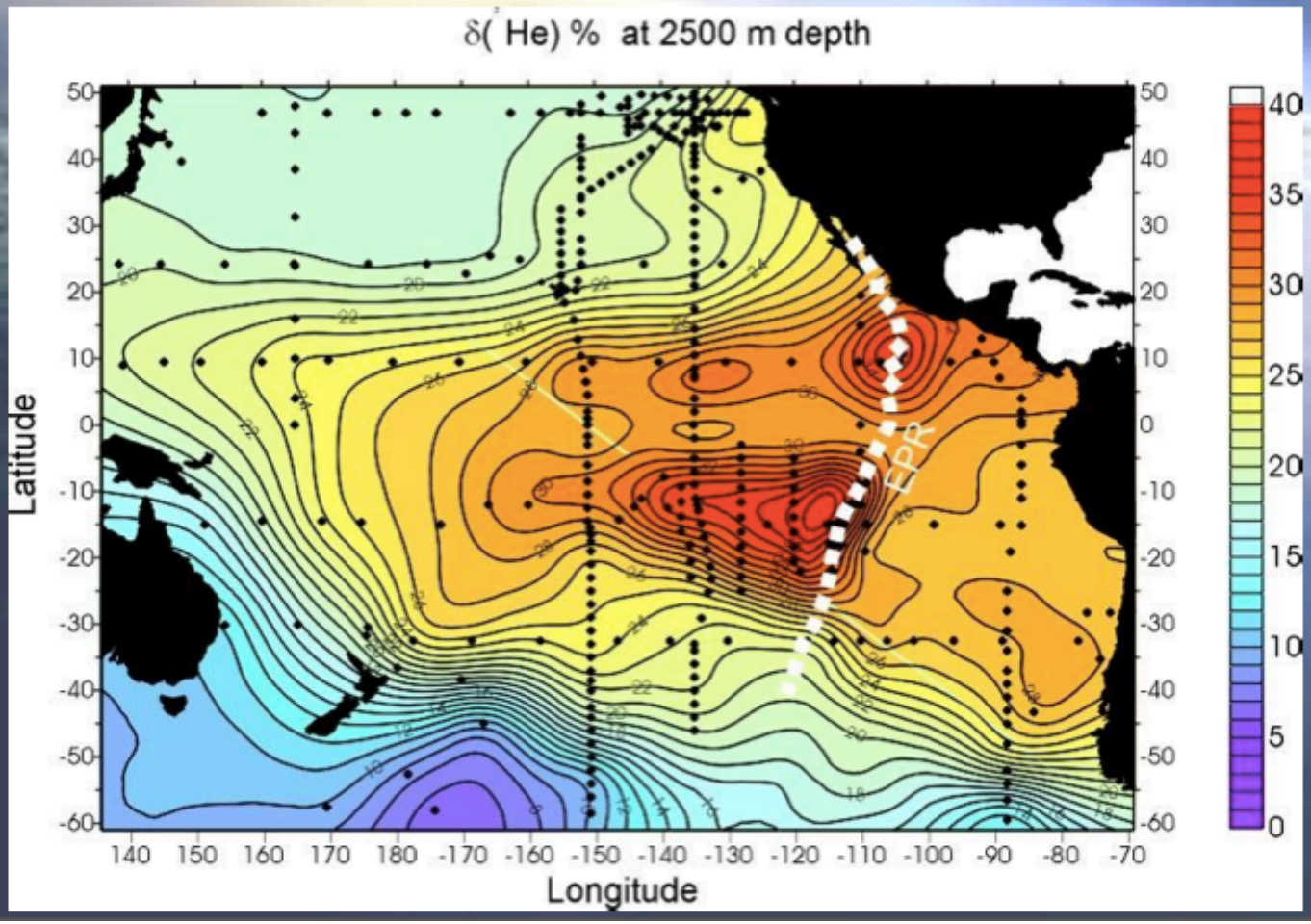
Conclusion

- 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.

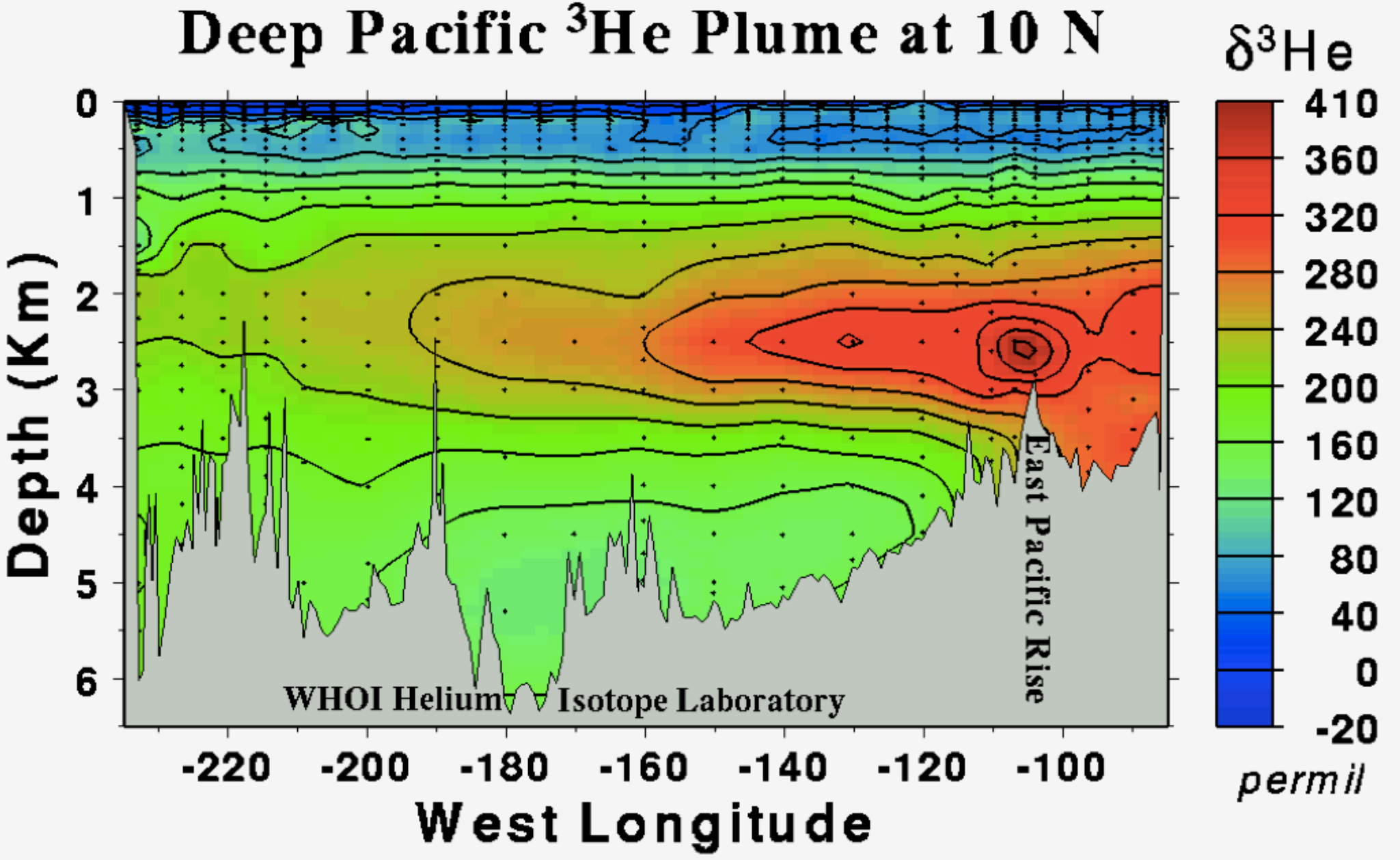
Origin of Oceans/Atmosphere

- 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):

$H_2O + CO_2 +$ "$CaSiO_3$" → $CaCO_3 + SiO_2 + H_2O$

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	ice
		(1 ocean in 30-300 million years)	
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.

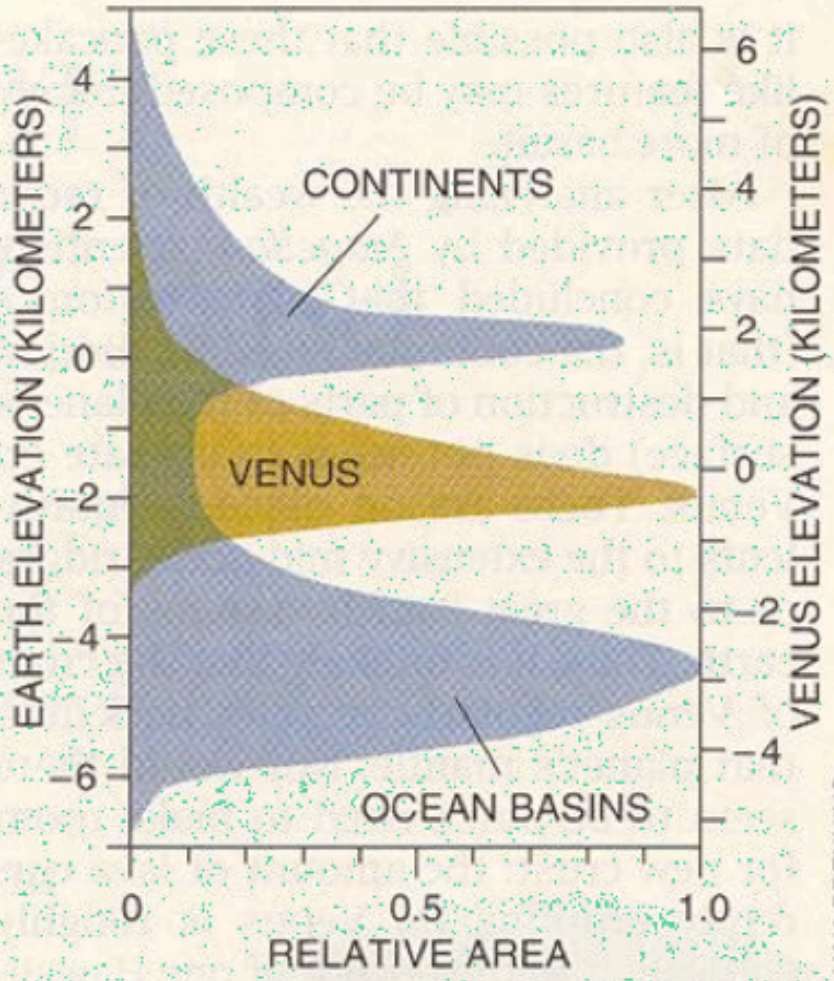
-- $CO_2 + H_2O = CH_2O + O_2$ **Photosynthesis** →

(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

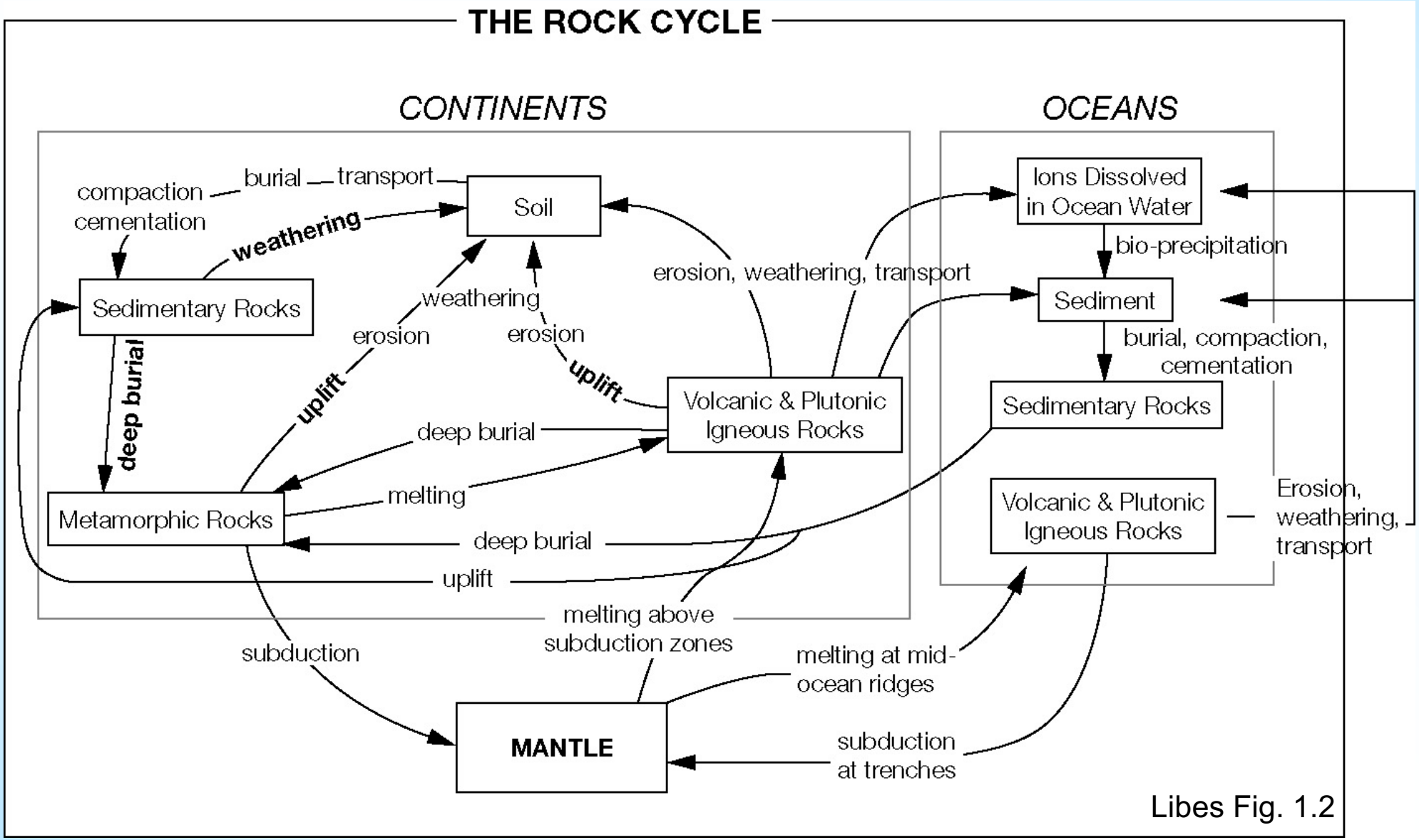
To understand how the Earth works as a chemical system, i.e.,

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	

[c] ... somewhat different from those in Table 21.8

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).

Reading for Thursday

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY B

Phil. Trans. R. Soc. B (2008) **363**, 2705–2716
doi:10.1098/rstb.2008.0054
Published online 16 May 2008

Review

Electrons, life and the evolution of Earth's oxygen cycle

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The biogeochemical cycles of H, C, N, O and S are coupled via biologically catalysed electron transfer (redox) reactions. The metabolic processes responsible for maintaining these cycles evolved over the first *ca* 2.3 Ga of Earth's history in prokaryotes and, through a sequence of events, led to the production of oxygen via the photobiologically catalysed oxidation of water. However, geochemical evidence suggests that there was a delay of several hundred million years before oxygen accumulated in Earth's atmosphere related to changes in the burial efficiency of organic matter and fundamental alterations in the nitrogen cycle. In the latter case, the presence of free molecular oxygen allowed ammonium to be oxidized to nitrate and subsequently denitrified. The interaction between the oxygen and nitrogen cycles in particular led to a negative feedback, in which increased production of oxygen led to decreased fixed inorganic nitrogen in the oceans. This feedback, which is supported by isotopic analyses of fixed nitrogen in sedimentary rocks from the Late Archaean, continues to the present. However, once sufficient oxygen accumulated in Earth's atmosphere to allow nitrification to out-compete denitrification, a new stable electron 'market' emerged in which oxygenic photosynthesis and aerobic respiration ultimately spread via endosymbiotic events and massive lateral gene transfer to eukaryotic host cells, allowing the evolution of complex (i.e. animal) life forms. The resulting network of electron transfers led a gas composition of Earth's atmosphere that is far from thermodynamic equilibrium (i.e. it is an emergent property), yet is relatively stable on geological time scales. The early coevolution of the C, N and O cycles, and the resulting non-equilibrium gaseous by-products can be used as a guide to search for the presence of life on terrestrial planets outside of our Solar System.

Keywords: biogeochemical cycles; nitrogen isotopes; Archaean ocean; Wilson cycle; oxygenic photosynthesis

Revisiting Hydrothermal Processes

Hydrothermal regeneration of CO_2

$$\underset{\text{anorthite}}{CaAl_2Si_2O_8} + 2H^+ + H_2O \rightarrow Ca^{2+} + \underset{\text{kaolinite}}{Al_2Si_2O_5(OH)_4} \quad (21.3)$$

$$\frac{1}{2}\underset{\text{kaolinite}}{Al_2Si_2O_5(OH)_4} + \left(Na^+,K^+\right) + 2SiO_2 \rightarrow \left(Na^+,K^+\right)\underset{\text{albite}}{AlSi_3O_8} + \frac{1}{2}H_2O + H^+ \quad (21.4)$$

$$Mg^{2+} + \frac{1}{5}\underset{\text{kaolinite}}{Al_2Si_2O_5(OH)_4} + \frac{1}{5}SiO_2 + \frac{7}{5}H_2O \rightarrow \frac{1}{5}\underset{\text{chlorite}}{Mg_5Al_2Si_3O_{10}(OH)_8} + 2H^+ \quad (21.5)$$

$$SO_4^{2-} + 2H^+ + \frac{11}{2}\underset{\text{iron silicate}}{Fe_2SiO_4} \rightarrow \frac{1}{2}\underset{\text{pyrite}}{FeS_2} + \frac{7}{2}\underset{\text{magnetite}}{Fe_3O_4} + \frac{11}{2}SiO_2 + H_2O \quad (21.6)$$

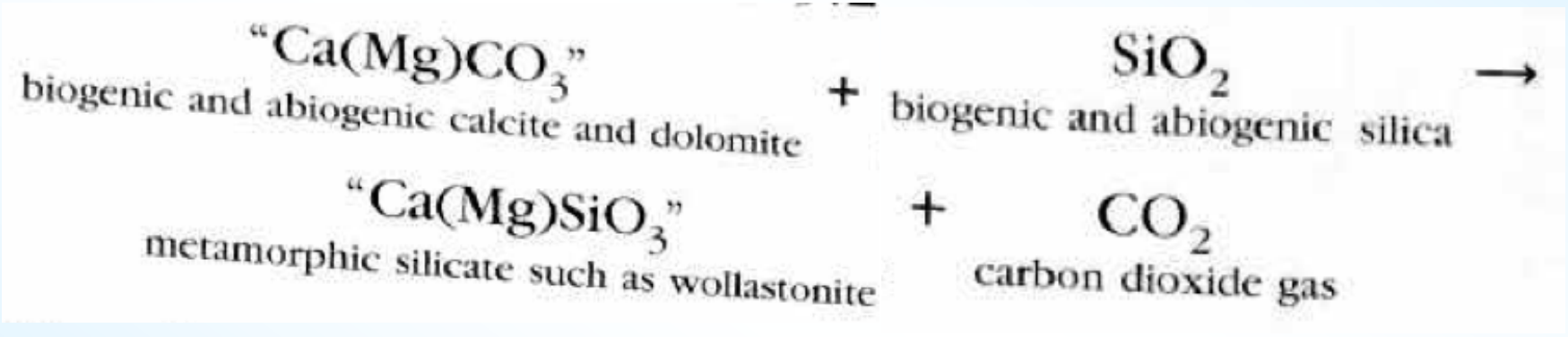
$$\underset{\text{alkalinity}}{Ca^{2+} + 2HCO_3^-} \rightarrow \underset{\text{calcite}}{CaCO_3} + CO_2 + H_2O \quad (21.7)$$

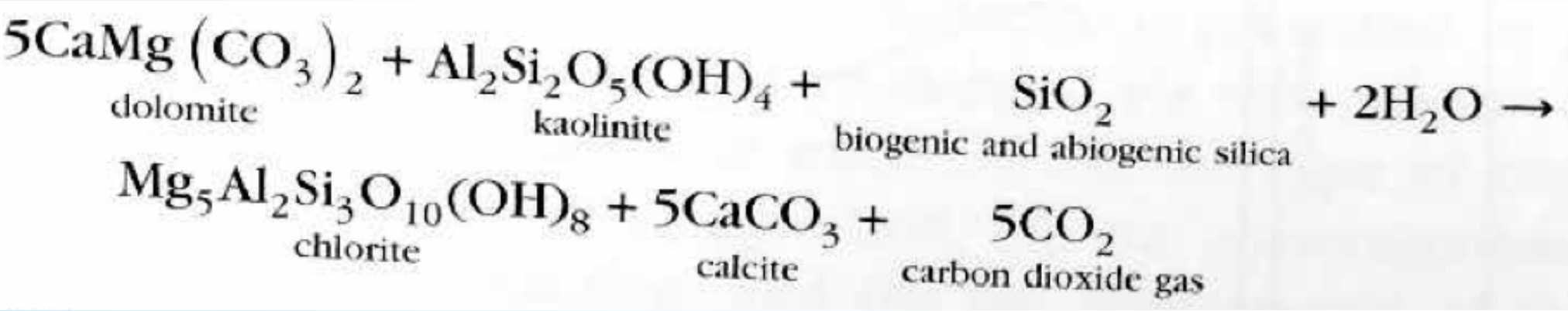
Calcium has two fates: (i) calcite or (ii) Ca^{2+} in SW

Overall, then Ca^{2+} is inverse with Mg^{2+}

Revisiting Hydrothermal Processes

Subduction decarbonation





CO_2 returned via volcanoes or diffusion

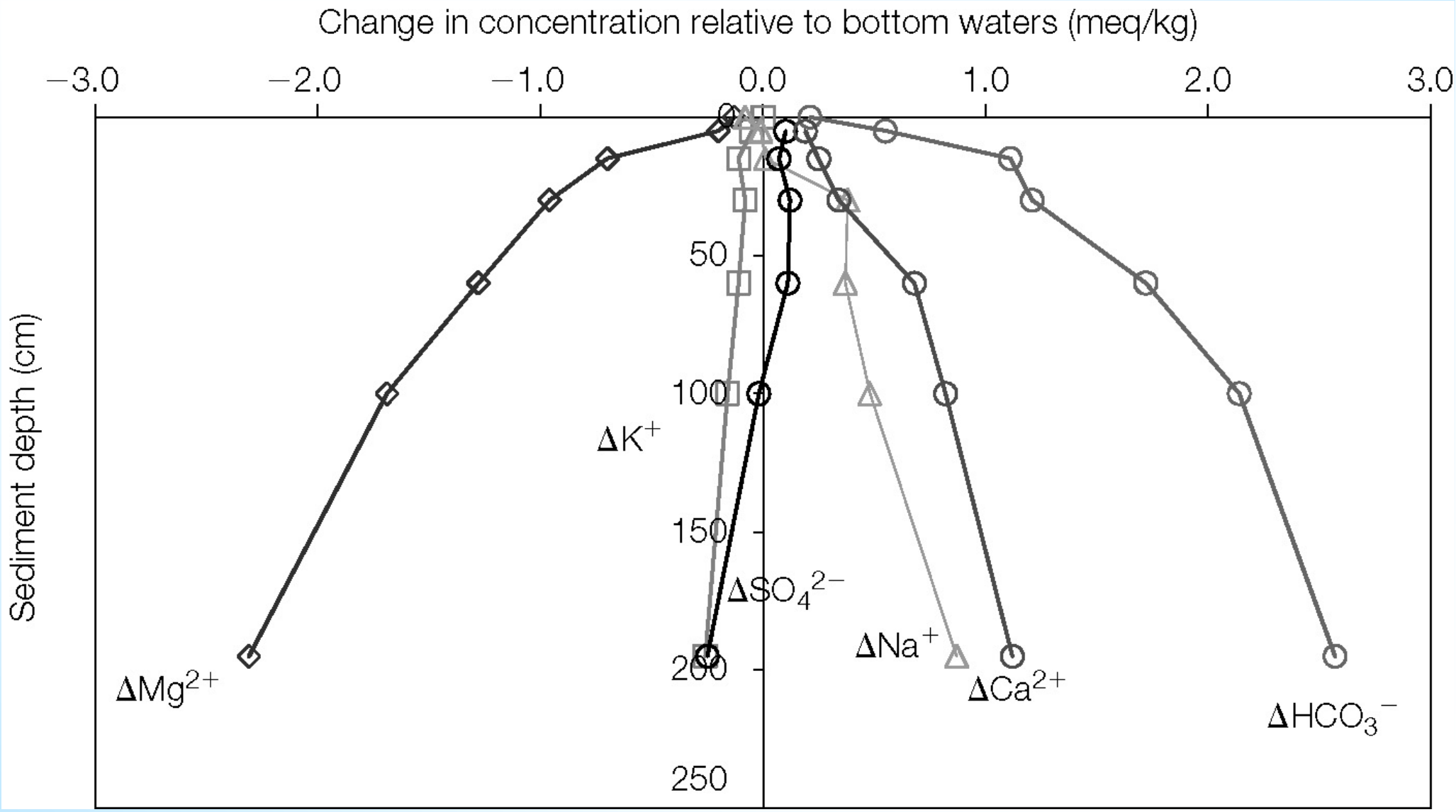
Revisiting Hydrothermal Processes

Abiogenic redox reactions in methane cycling

$$\underset{\text{magnetite}}{2Fe_3O_4} + 3SiO_2 + 2H_2S + CO_2 \rightarrow \underset{\text{iron silicate}}{3Fe_2SiO_4} + CH_4 + 2SO_2 \qquad (21.10)$$

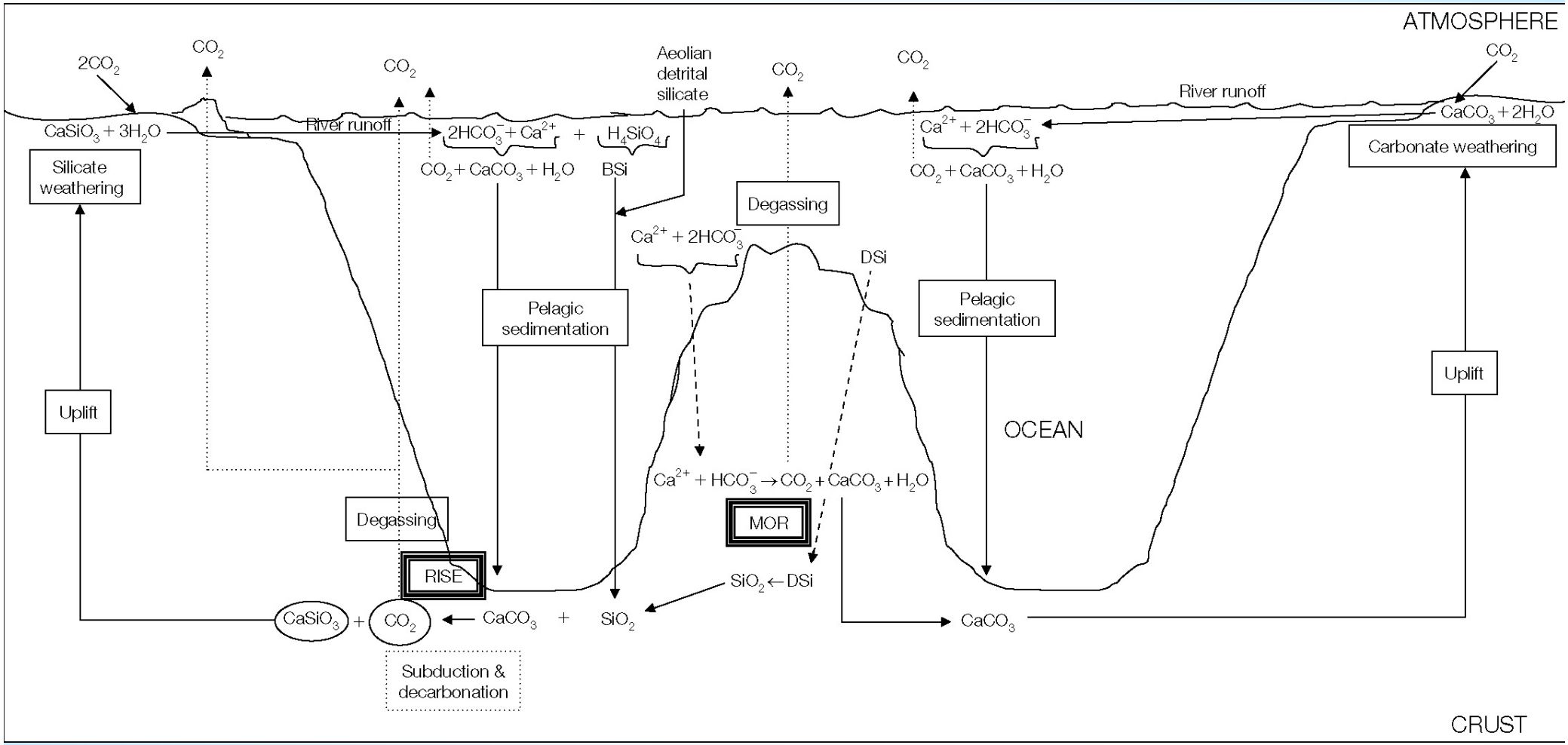
$$\underset{\text{calcite}}{CaCO_3} + CH_4 + H_2S + 5H_2O \rightarrow \underset{\text{anhydrite}}{CaSO_4} + 2CO_2 + 8H_2 \qquad (21.11)$$

Revisiting Reverse Weathering



Downcore gradients in porewater K & Mg^{2+}

Linking Global Rock Cycle to Carbon Cycle



Integrated Models

Equilibrium Models

Table 21.10 Results and Components in Kramer's Ocean Model.

Observed Concentration (M) at 25°C and 35‰	Equilibrium Concentration (M)	Aqueous Phase	Solids Controlling Concentrations
0.48	0.45	Na^+	Na-mont (cation exchange)
1.0×10^{-2}	9.7×10^{-3}	K^+	K-illite (cation exchange)
0.56	0.55 (defined)	Cl^-	0.55 (assumed)
2.9×10^{-2}	3.4×10^{-2}	SO_4^{2-}	$SrCO_3$, $SrSO_4$
1.1×10^{-2}	6.1×10^{-3}	Ca^{2+}	Phillipsite
5.4×10^{-2}	6.7×10^{-2}	Mg^{2+}	Chlorite
Variable	2.7×10^{-6}	PO_4^{3-}	OH-apatite
—	(1.7×10^{-3} atm)	CO_2	Calcite
7.0×10^{-5}	2.4×10^{-5}	F^-	F-CO_3-apatite
7.9×10^{-9}	4.7×10^{-9}	H^+	Given by electroneutrality

Integrated Models

Steady-State Mass Balance Models

Table 21.11 Mass Balance Calculation for the Removal of River-Derived Constituents from the Ocean.

Step no.	Reaction (balanced in terms of mmol of constituents used)	Constituent balance ($\times 10^{21}$ mmol)								HCO_3^-	CO_2	Products		
		SO_4^{2-}	Ca^{2+}	Cl^-	Na^+	Mg^{2+}	K^+	SiO_2	HCO_3^-	Consumed (−) Evolved (+)	Consumed (−) Evolved (+)	($\times 10^{21}$ mmol)		Total products formed (mol basis) (%)
	Amount of material to be removed from ocean in 10^8 years	382	1220	715	900	554	189	710	3118					
1.	95.5 $FeAl_6Si_6O_{20}(OH)_4$ + 191 SO_4^{2-} + 47.8 CO_2 + 55.7 $C_6H_{12}O_6$ + 238.8 H_2O = 286.5 $Al_2Si_2O_5(OH)_4$ + 95.5 FeS_2 + 382 HCO_3^-	191	1220	715	900	554	189	710	3500	+382	−48	96 287	Pyrite Kaolinite	3 8
2.	191 Ca^{2+} + 191 SO_4^{2-} = 191 $CaSO_4$	0	1029	715	900	554	189	710	3500			191	$CaSO_4$	5
3.	52 Mg^{2+} + 104 HCO_3^- = 52 $MgCO_3$ + 52 CO_2 + 52 H_2O	0	1029	715	900	502	189	710	3396	−104	+52	52	$MgCO_3$ in magnesium calcite	2
4.	1029 Ca^{2+} + 2058 HCO_3^- = 1029 $CaCO_3$ + 1029 CO_2 + 1029 H_2O	0	0	715	900	502	189	710	1338	−2058	+1029	1029	Calcite and/or aragonite	29
5.	715 Na^+ + 715 Cl^- = 715 NaCl	0	0	0	185	502	189	710	1338			715	NaCl	20
6.	71 H_4SiO_4 = 71 $SiO_2(s)$ + 142 H_2O	0	0	0	185	502	189	639	1338			71	Free silica	2

Integrated Models

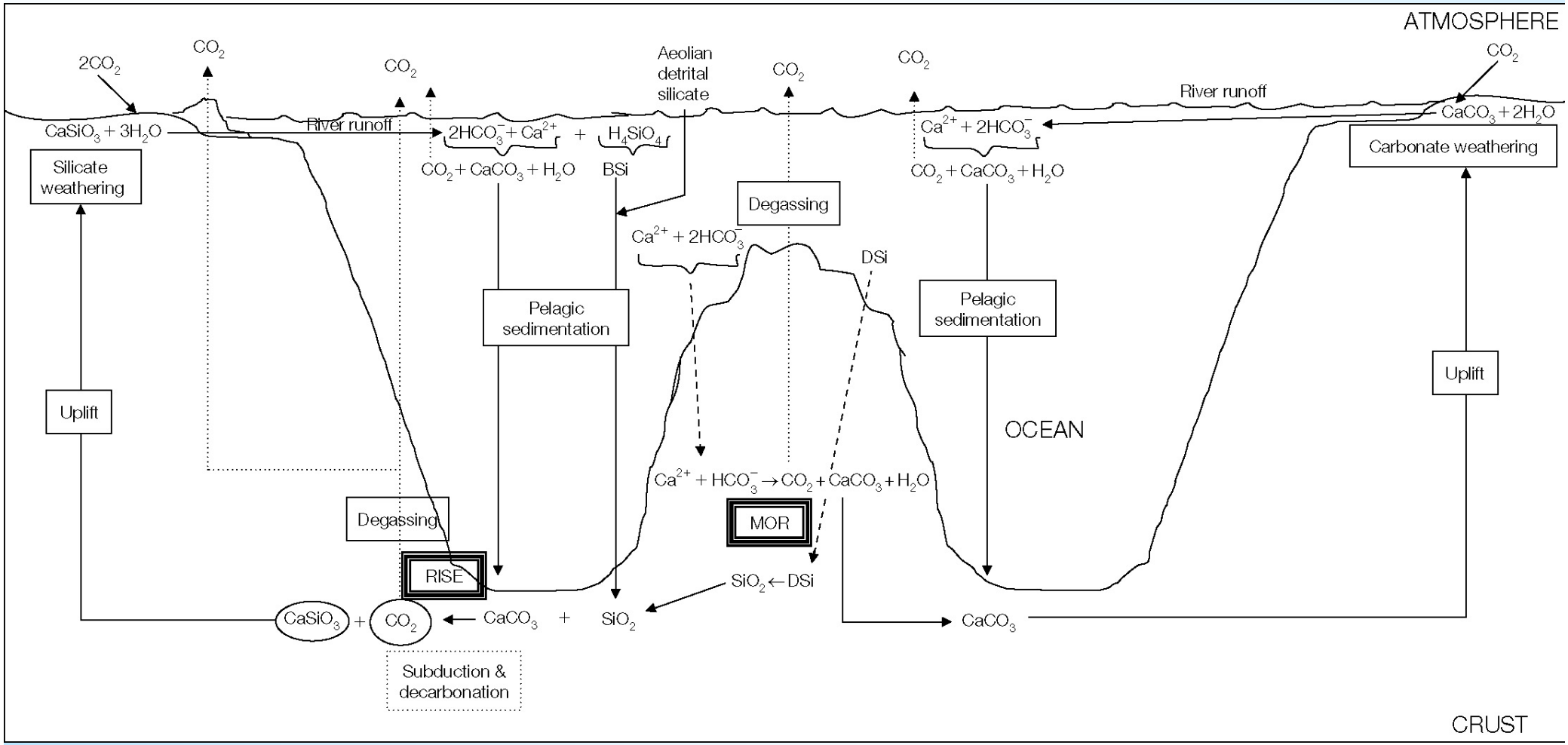
Steady-State Mass Balance Models

7.	138 $Ca_{0.17}Al_{2.33}Si_{3.67}O_{10}(OH)_2$ + 46 Na^+ = 138 $Na_{0.33}Al_{2.33}$ $Si_{3.67}O_{10}(OH)_2$ + 23.5 Ca^{2+}	0	24	0	139	502	189	639	1338			138	Sodic montmorillonite	4
8.	24 Ca^{2+} + 48 HCO_3^- = 24 $CaCO_3$ + 24 CO_2 + 24 H_2O	0	0	0	139	502	189	639	1200	−48	+24	24	Calcite and/or aragonite	1
9.	486.5 $Al_2Si_{2.4}O_{5.8}(OH)_4$ + 139 Na^+ + 361.4 SiO_2 + 139 HCO_3^- = 417 $Na_{0.33}Al_{2.33}$ $Si_{3.67}O_{10}(OH)_2$ + 139 CO_2 + 625.5 H_2O	0	0	0	0	502	189	278	1151	−139	+139	417	Sodic montmorillonite	12
10.	100.4 $Al_2Si_{2.4}O_{5.8}(OH)_4$ + 502 Mg^{2+} + 60.2 SiO_2 + 1004 HCO_3^- = 100.4 Mg_5Al_2 $Si_3O_{10}(OH)_8$ + 1004 CO_2 + 301.2 H_2O	0	0	0	0	0	189	218	147	−1004	+1004	100	Chlorite	3
11.	472.5 $Al_2Si_{2.4}O_{5.8}(OH)_4$ + 189 K^+ + 189 SiO_2 + 189 HCO_3^- = 378 $K_{0.5}Al_{2.5}$ $Si_{3.5}O_{10}(OH)_2$ + 189 CO_2 + 661.5 H_2O	0	0	0	0	0	0	29	−42	−189	+189	378	Illite	11

Source: *After Mackenzie, F. T., and R. M. Garrels (1966).* American Journal of Science *264, 507–525.*

Integrated Models

Dynamical Models



Mean Oceanic Residence Times & Reactivity

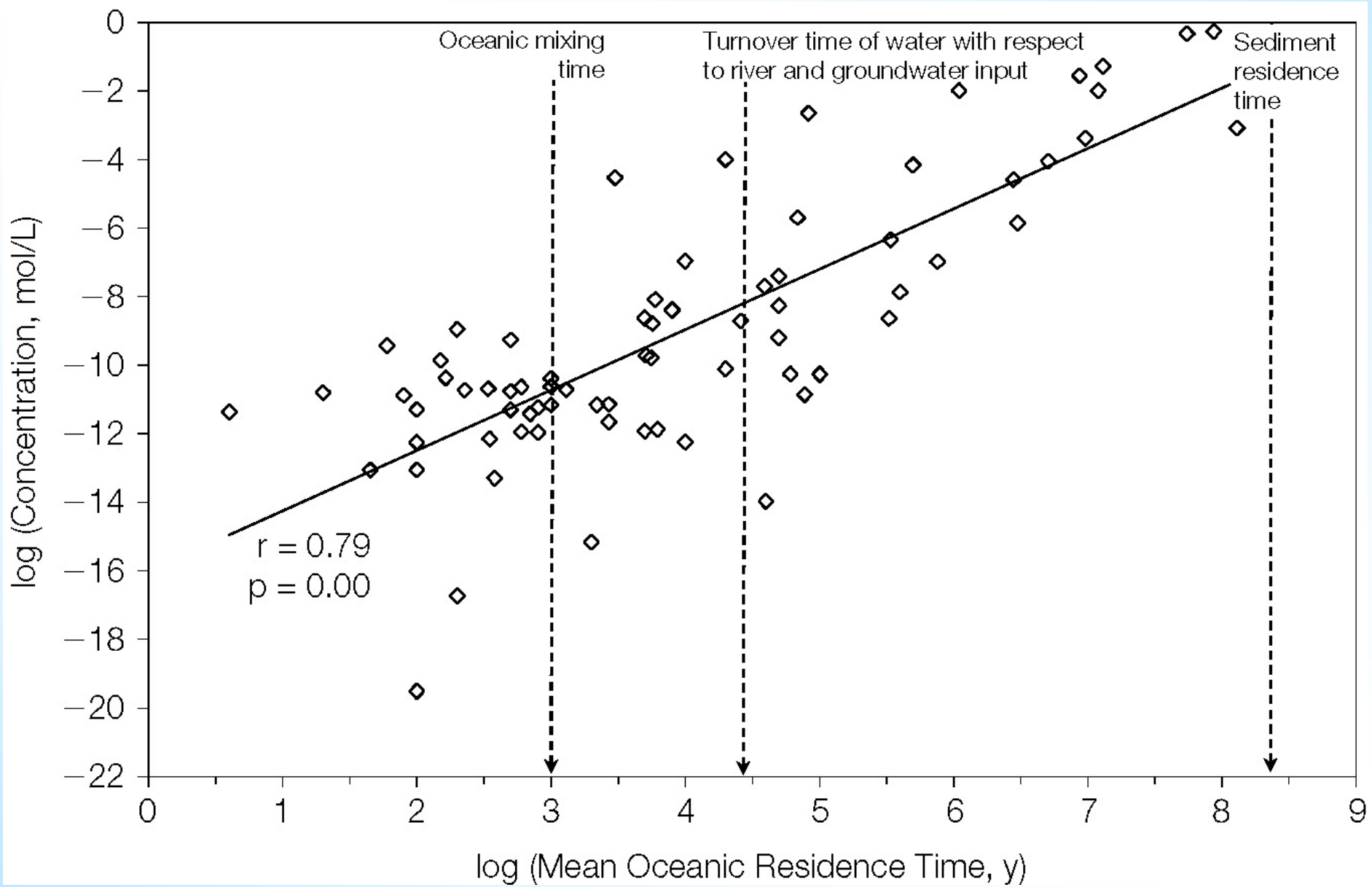
$$\frac{dM_A}{dt} = V\frac{dC_A}{dt} = J_{A\,in} - J_{A\,out}$$

$$0 = V\frac{dC_A}{dt} = J_{A\,in} - kC_A$$

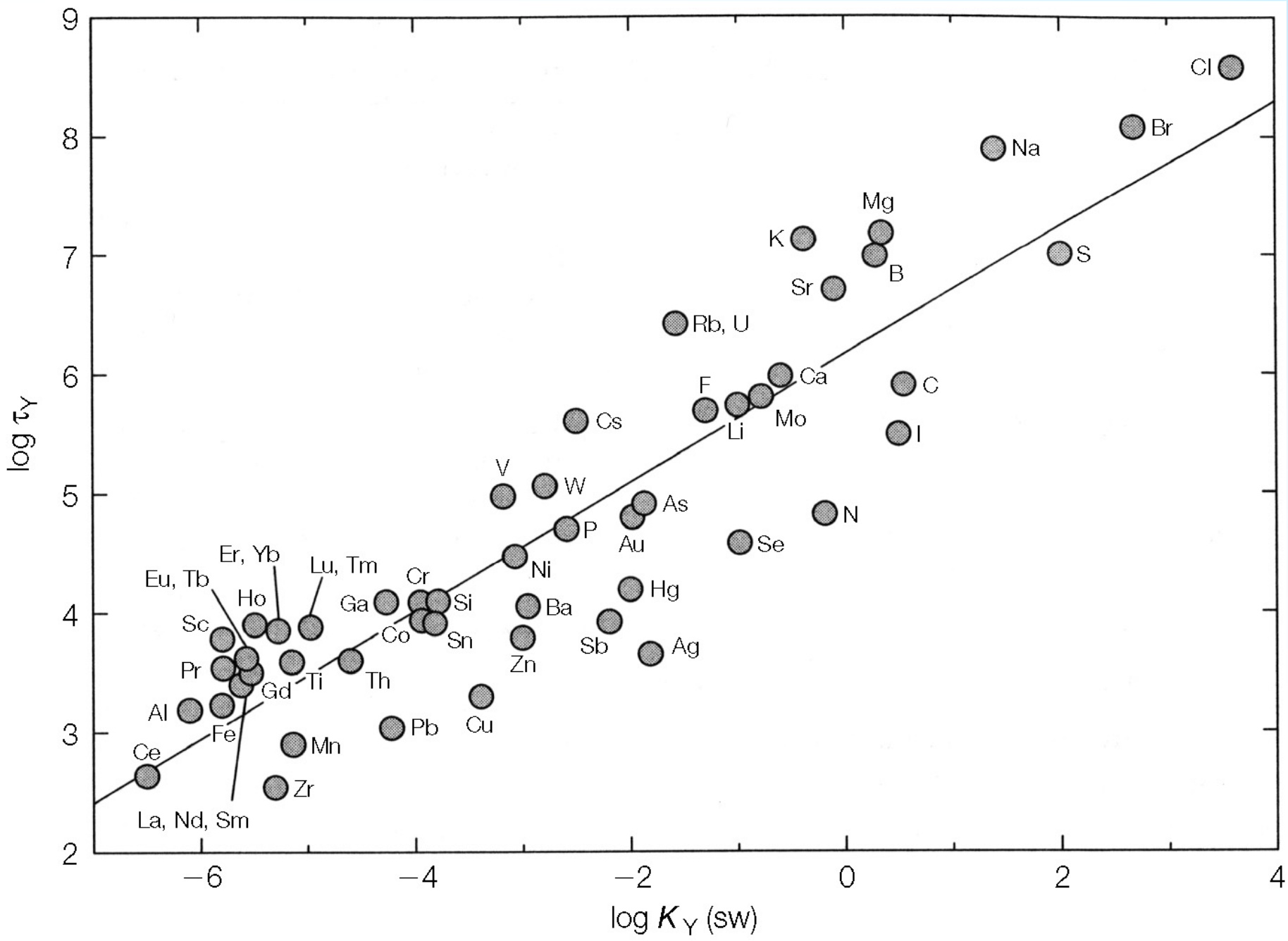
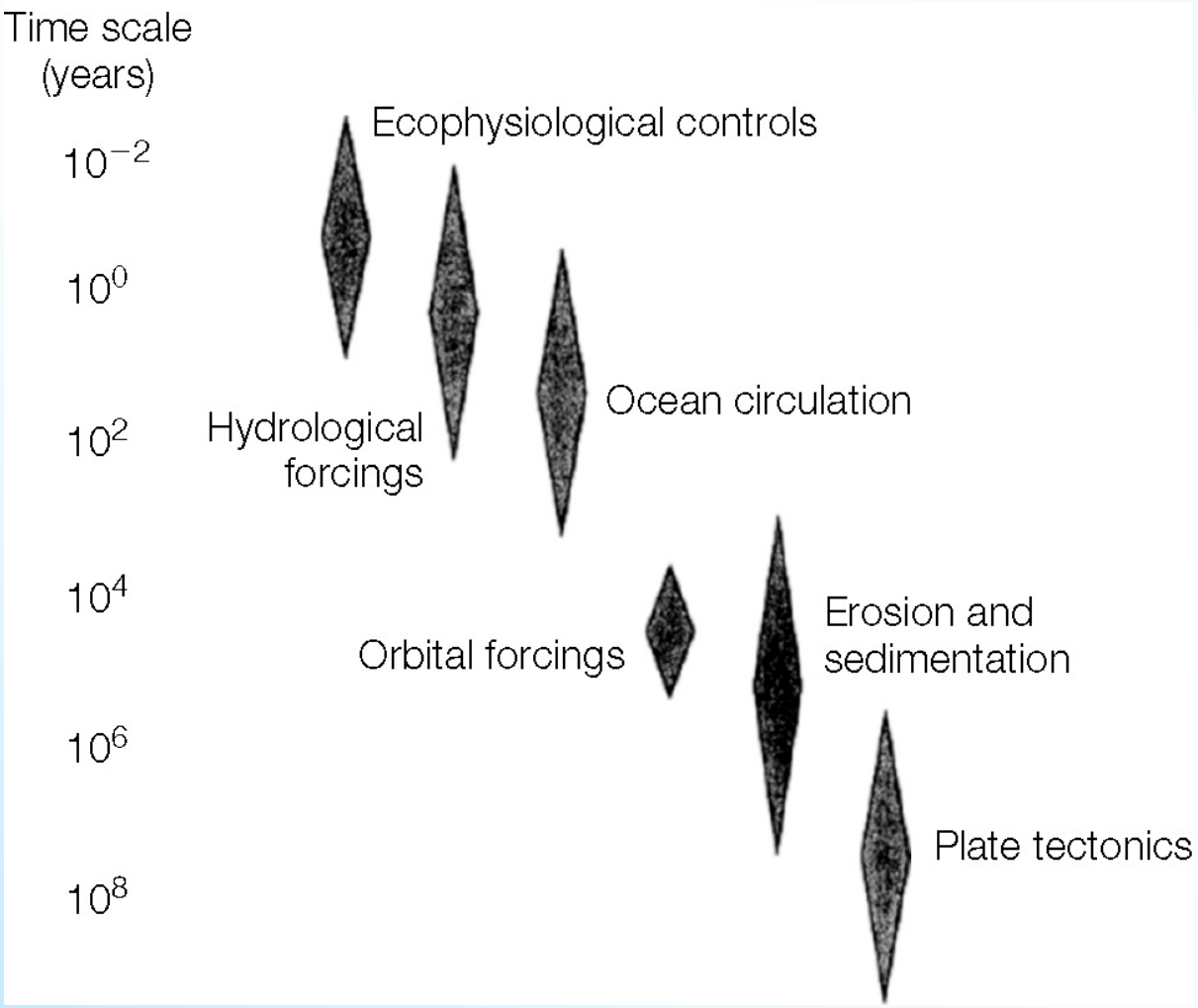
$$\frac{1}{k} = \frac{C_A}{J_{A\,in}} = \mathrm{MORT}_A$$

$$\frac{1}{\tau} = \sum_{i=1}^{i=n}\frac{1}{\tau_i} = \frac{1}{\tau_1} + \frac{1}{\tau_2} + \cdots \frac{1}{\tau_n}$$

Mean Oceanic Residence Times & Reactivity



Mean Oceanic Residence Times & Reactivity



Why is seawater ~35ppt?