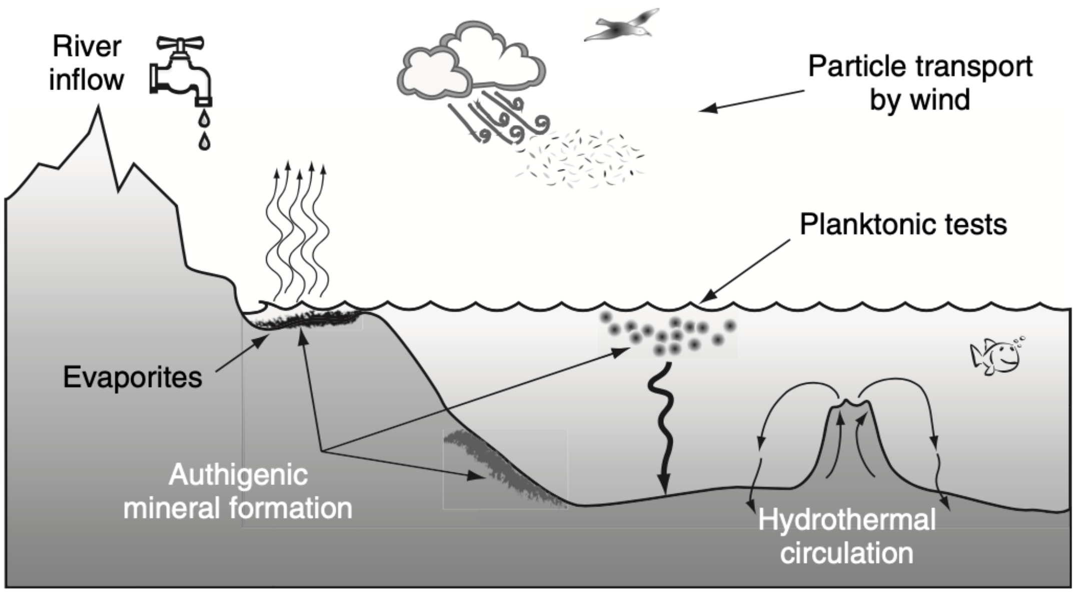
Balance of ocean constituents



Major ocean transports / fluxes / balances

- Geologic – balance between river inflow and sediment / hydrothermal loss
  - Steady state, long-term changes
- Surface / deep ocean – production and consumption of organic matter
  - Respiration in water / sediment column
- Air-sea exchange

E&H Fig. 2.2

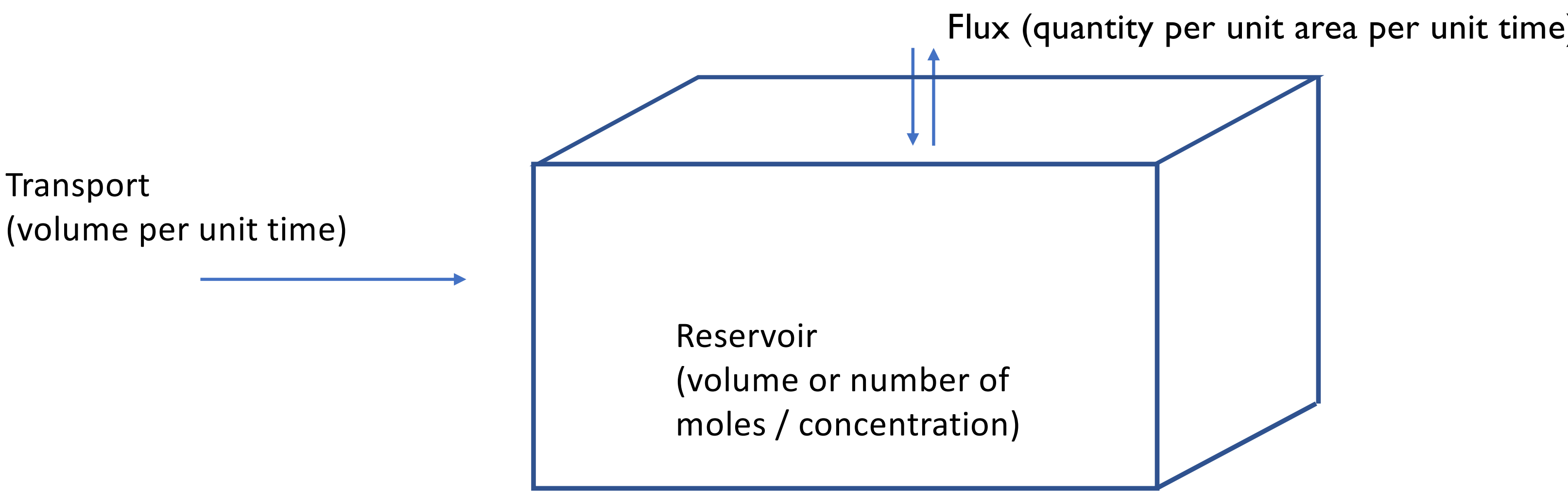
Geochemical Mass Balance

Two types:

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

2. Geochemical cycles and the balancing of inputs with outputs from various reservoirs: ex. seawater

Terminology: Fluxes, transports, reservoirs/ volumes

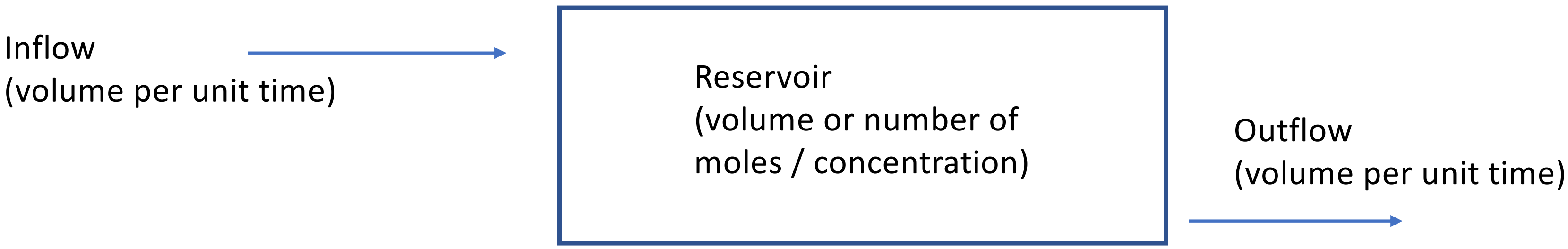


Examples:

- Concentration: mol O_2 kg^{-1} or mol O_2 m^{-3}
- Flux: mol O_2 m^{-2} d^{-1}
- Transport: m d^{-1} or mol d^{-1}
- Reservoir: mol O_2

v2025

Geochemical Mass Balance

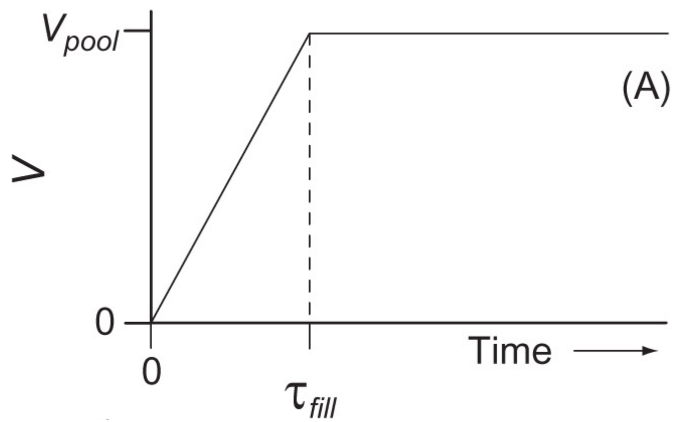


Geochemical Mass Balance

Inflow
(volume per unit time)

Reservoir
(volume or number of moles / concentration)

Outflow
(volume per unit time)



Residence / fill time of a volume, defined as:

$$\tau_{fill} = \frac{inventory\ (vol)}{inflow\ (\frac{vol}{time})} = \frac{V}{f}$$

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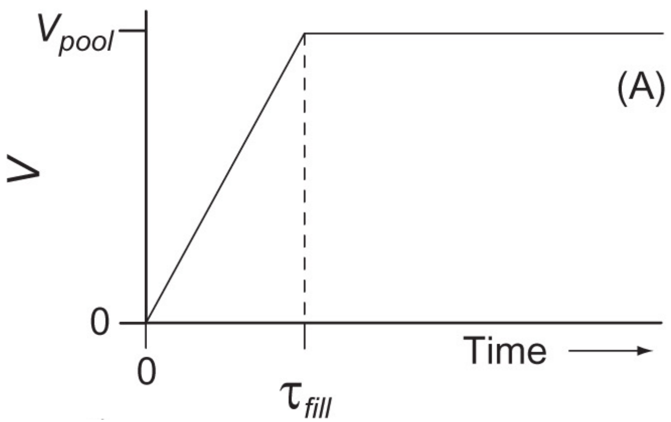

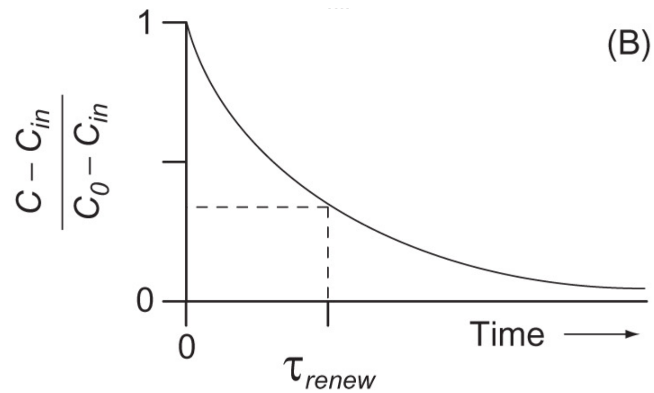

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Residence time of a tracer:

$$\tau = \frac{inventory\ (mol\ or\ vol)}{inflow\ (\frac{mol\ or\ vol}{time})} = \frac{[C]V}{f}$$

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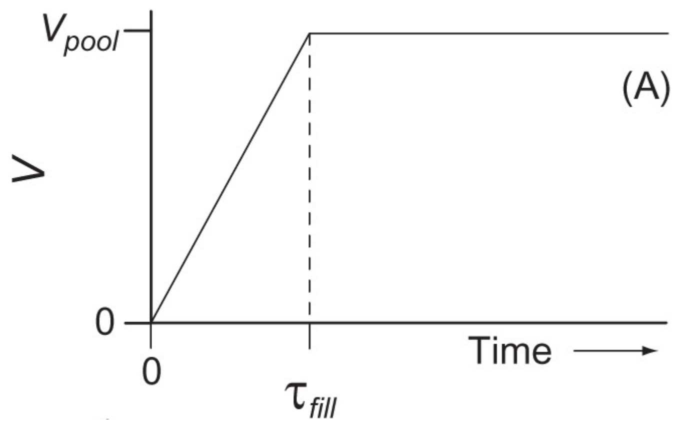

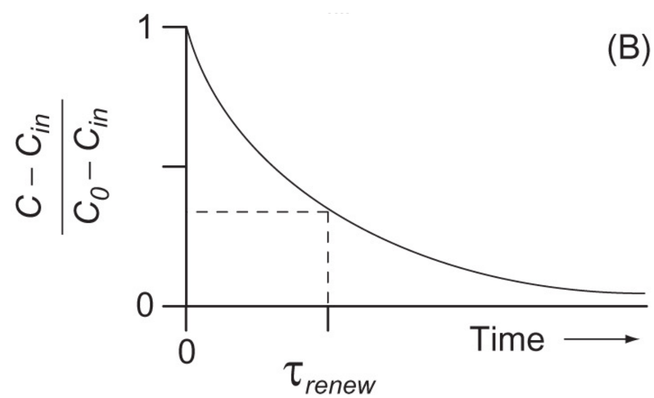

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General equation for calculating concentration at time t:

$$C_t - C_{inflow} = (C_0 - C_{inflow})e^{-(\frac{f}{V}t)}$$

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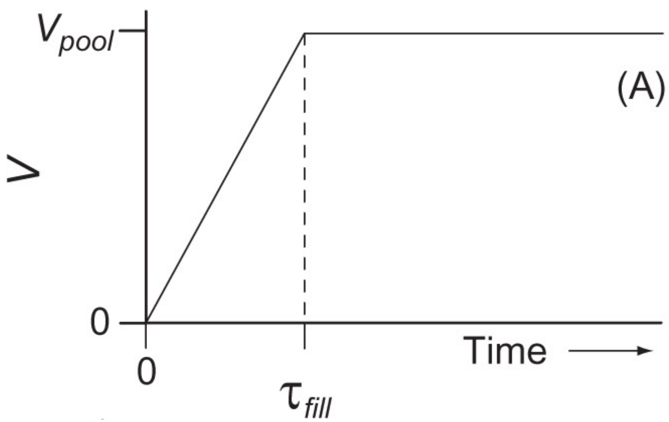

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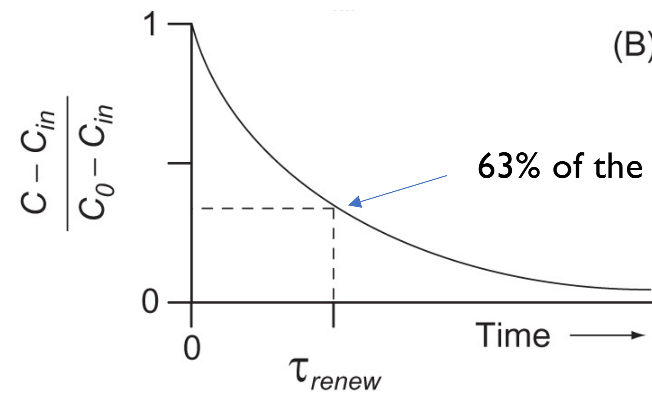

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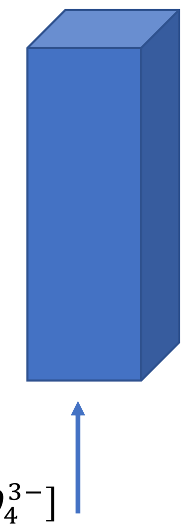
Geochemical Mass Balance

1 m x 1 m column



h = 100m

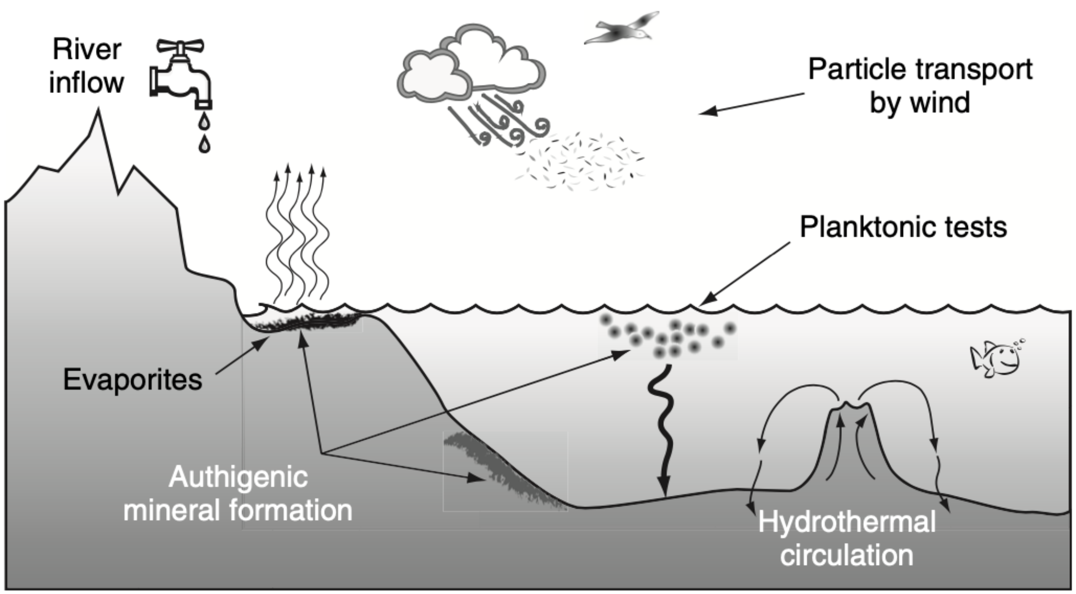
f_{in} = 5 m/d
C_{in} = 2 µmol kg^{-1} $[PO_4^{3-}]$

Consider a water column with a 100 m wintertime mixed layer depth, initially at steady state:

What is the residence time of water in the system?

Given an initial concentration of 0.1 µmol kg-1, what would the concentration be after 10 days?

Balance of ocean constituents



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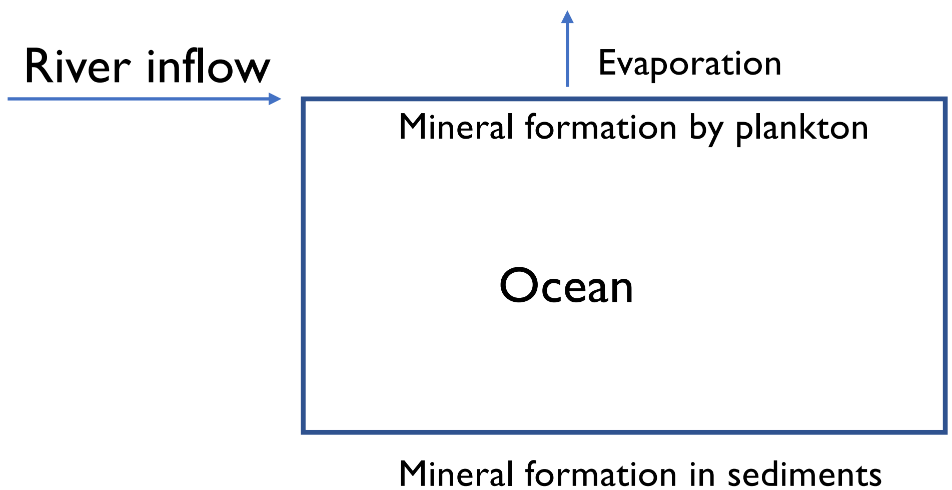
E&H Fig. 2.2

Balance of ocean constituents



- Does $[C]_{river\ inflow}$ match $[C]_{ocean}$?

- Major ocean transports / fluxes / balances
  - Geologic – balance between river inflow and sediment / hydrothermal loss
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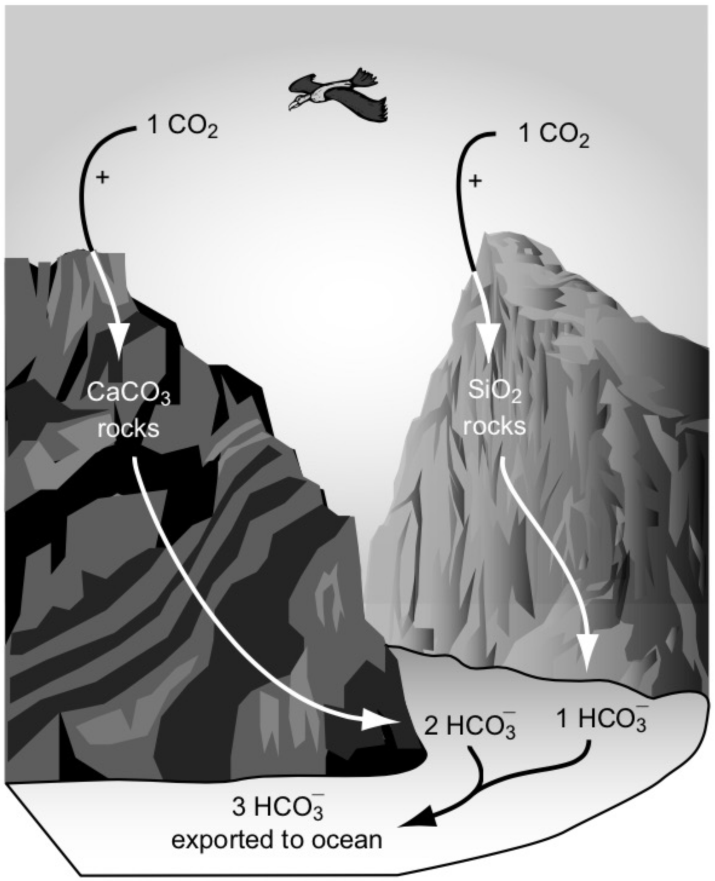
* Authigenesis – in situ formation of minerals (authigenic minerals)

E&H Fig. 2.2

Chemical weathering – supply of minerals to the ocean



- Carbon dioxide reacts with rocks to form the dissolved composition of rivers

Chemical weathering

- Basic idea: Carbon dioxide reacting with water to form H^+ that breaks down minerals to release ions

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(a) CO_2 in soils reacts with water to form H^+ that dissolves $CaCO_3$ according to the net reaction (iii):

i $\quad CO_2 + H_2O \rightleftarrows HCO_3^- + H^+$

ii $\quad CaCO_3(s) + H^+ \rightleftarrows HCO_3^- + Ca^{2+}$

iii $\quad \underset{\textit{carbonate rocks}}{CaCO_3(s) + CO_2 + H_2O} \rightleftarrows \underset{\textit{dissolved ions}}{2HCO_3^- + Ca^{2+}}$

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(b) CO_2 in soils reacts with water to form H^+ that reacts with potassium feldspar to form the clay mineral (kaolinite) according to the net reaction (vi)

iv $2CO_2 + 2H_2O \rightleftarrows 2HCO_3^- + 2H^+$

v $2KAlSi_3O_8(s) + 2H^+ + 9H_2O \rightarrow Al_2Si_2O_5(OH)_4(s) + 2K^+ + 4H_4SiO_4$

vi $\underbrace{2KAlSi_3O_8(s)}_{\text{K-feldspar}} + 2CO_2 + 11H_2O \rightarrow \underbrace{Al_2Si_2O_5(OH)_4(s)}_{\text{kaolinite}} + \underbrace{2K^+ + 2HCO_3^- + 4H_4SiO_4}_{\text{dissolved ions}}$

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(c) CO_2 in soils reacts with water to form H^+ that reacts with phlogopite mica to form the clay mineral (kaolinite) according to the net reaction (ix)

vii $14CO_2 + 14H_2O \rightleftarrows 14HCO_3^- + 14H^+$

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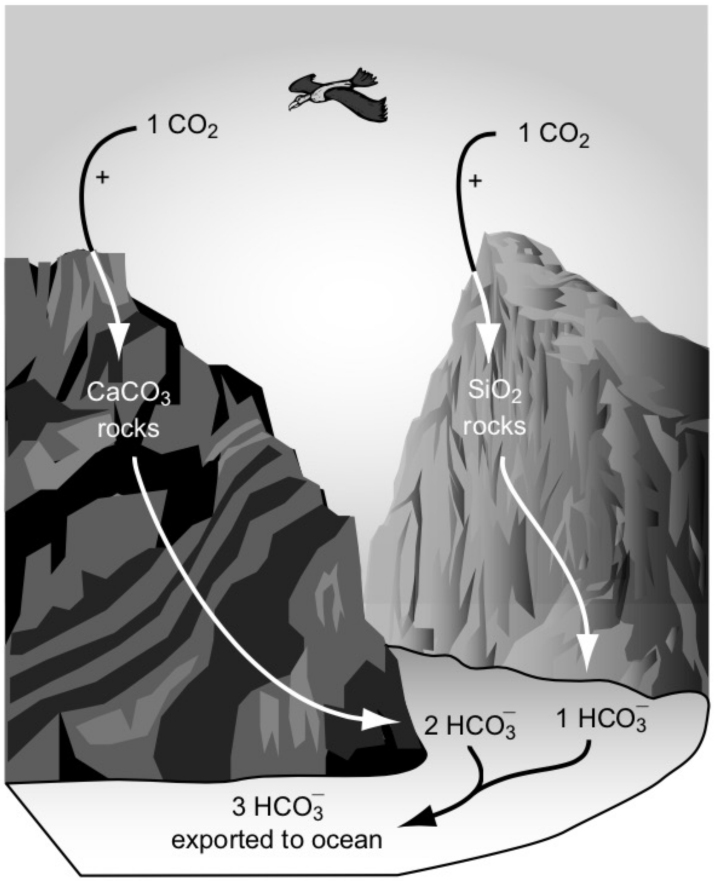
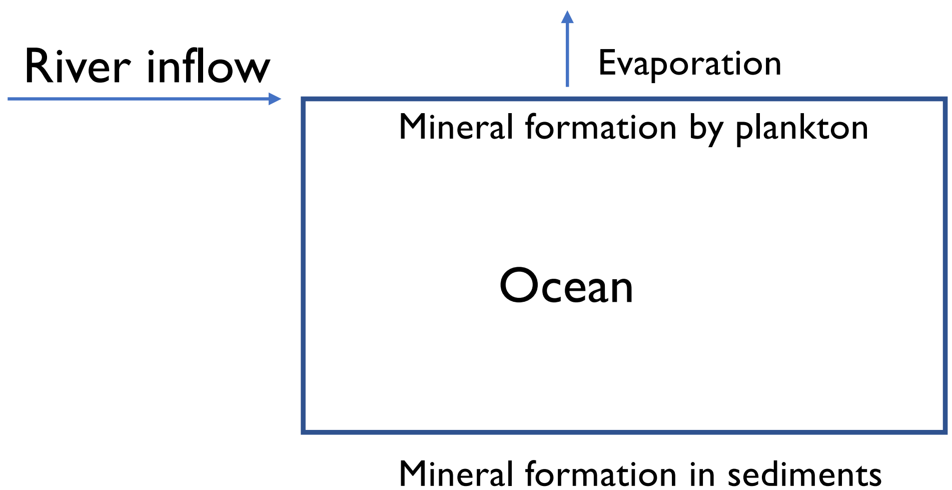


- Carbon dioxide reacts with rocks to form the dissolved composition of rivers
- Approximate equal weathering of $CaCO_3$ and SiO_2 rocks gives correct ratio of atmospheric to rock sources of HCO_3^-
- Do known river inputs match best estimates for formation of sediments on the ocean floor?

Balance of ocean constituents



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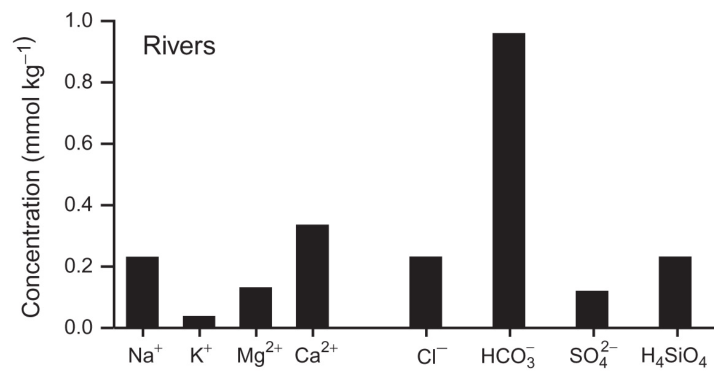
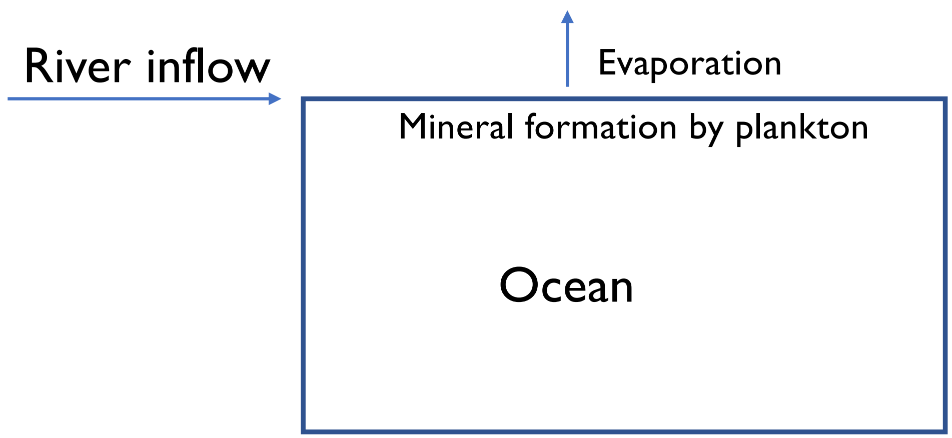


E & Hamme Fig. 2.3

Balance of ocean constituents



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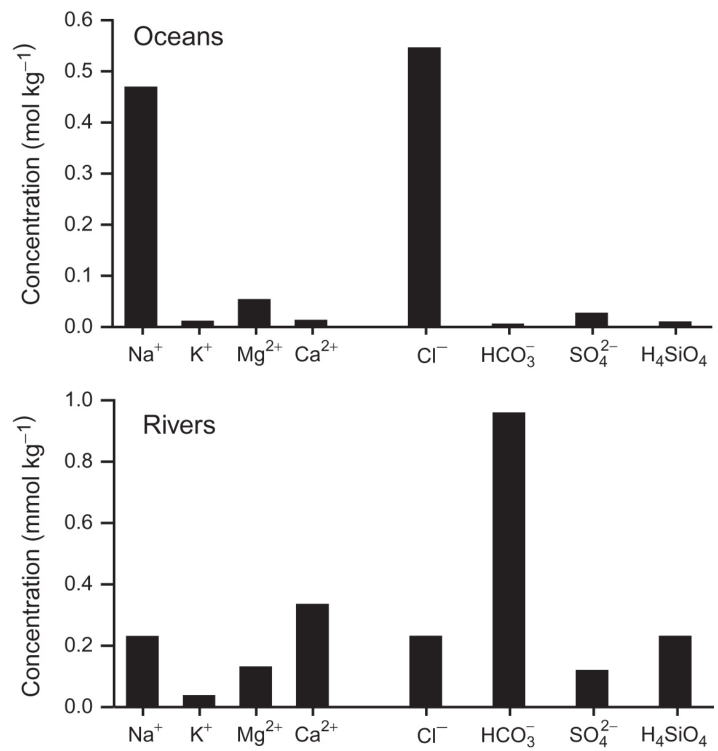


Concentration ratios

	Na^+/K^+	Mg^{2+}/Ca^{2+}	Na^+/Ca^{2+}	$(Mg^{2+}+Ca^{2+})/HCO_3^-$
Oceans	46	5.1	46	27
Rivers	6.0	0.39	0.70	0.48

E & Hamme Fig. 2.3

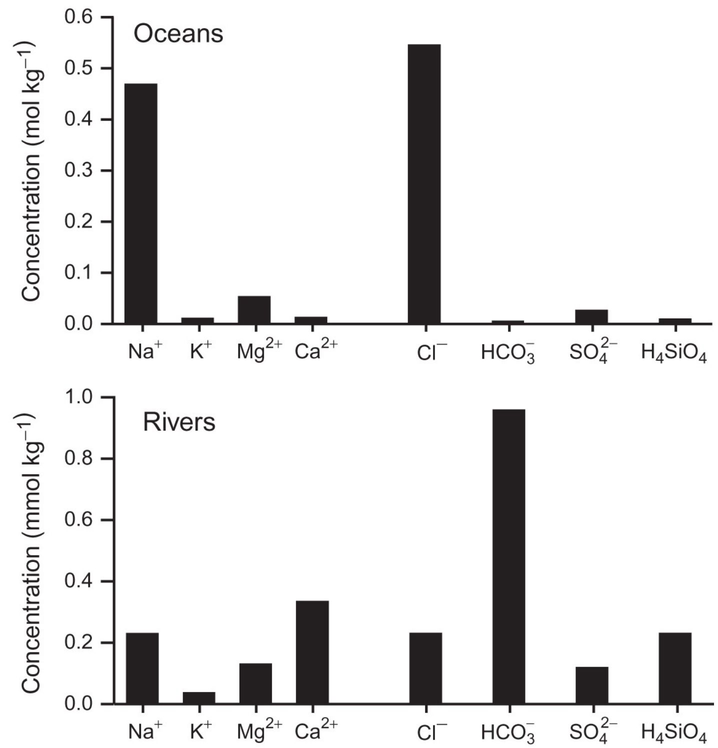
Balance of ocean constituents

Constituent	Seawater concentration (mmol kg^{-1})	Inventory[a] (10^{18} mol)	River water concentration (μmol kg^{-1})	River inflow[b] (10^{12} mol y^{-1})	τ (10^6 y)
H_2O					0.04
Na^+	469.1	647	231	8.6	75
Mg^{2+}	52.8	72.9	128	4.8	15
Ca^{2+}	10.3	14.2	332	12.4	1.1
K^+	10.2	14.1	38.4	1.4	10
Cl^-	545.9	753	220	8.2	92
SO_4^{2-}	28.2	38.9	115	4.3	9.0
DIC[c]	2.3	3.2	958	35.7	0.1
H_4SiO_4	0–0.2	0.1[d]	158[d]	5.9	0.01

$$\tau = \frac{inventory\ (mol)}{river\ inflow\ flux\ (mol\ yr^{-1})}$$

- Residence time of ocean water: 40,000 yrs (circulation time is ~1000 yrs)
- Most reactive ion: HCO_3^-
- Least reactive ion: Cl^-

E & Hamme Fig. 2.3



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Mackenzie and Garrels 1966

Major ion		SO_4^{2-}	Ca^{2+}	Cl^-	Na^+	Mg^{2+}	K^+	H_4SiO_4	HCO_3^-
Mass removed in 10^8 *y* (10^{18} *mol*)		429	1238	821	861	477	143	589	3573
Mineral formed	Moles Removed	*Amount of ion remaining after reaction*							

River input that needs to be balanced by mineral formation

Mackenzie and Garrels 1966

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Pyrite, FeS_2	215[a]	214	1238	821	861	477	143	589	3573

[a] Assume half of the SO_4 is removed by pyrite formation and half by $CaSO_4$ formation
[b] The biogenic opal (SiO_2) burial is taken from Tregeur and DeLaRocha, 2013

(b) Formation reactions:

Pyrite: $SO_4^{2-} + 2CH_2O(s) \rightleftarrows S^{2-} + 2CO_2 + H_2O$ followed by $Fe^{2+} + S^{2-} + S^0 \rightleftarrows FeS_2$

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Sodium Chloride, NaCl	821			0	40	477	143	589	1525
Opal, SiO_2	630[b]				40	477	143	0	1525

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Sodium Chloride: $Na^+ + Cl^- \rightleftarrows NaCl(s)$

Opal: $H_4SiO_4 \rightleftarrows SiO_2(s) + 2H_2O$

Possible additional sinks: Reverse weathering

Dissolution reactions in reverse – proposed as a way to remove excess ions from the ocean

- Deposited clay minerals on the ocean seafloor react with seawater, using up Mg^{+}, K^{+}, HCO_3^{-}

vi $$2KAlSi_3O_8 + 2\ CO_2 + 11H_2O \rightarrow Al_2Si_2O_5(OH)_4(s) + 2K^+ + 2HCO_3^- + 4H_4SiO_4$$

K-feldspar *kaolinite* *dissolved ions*

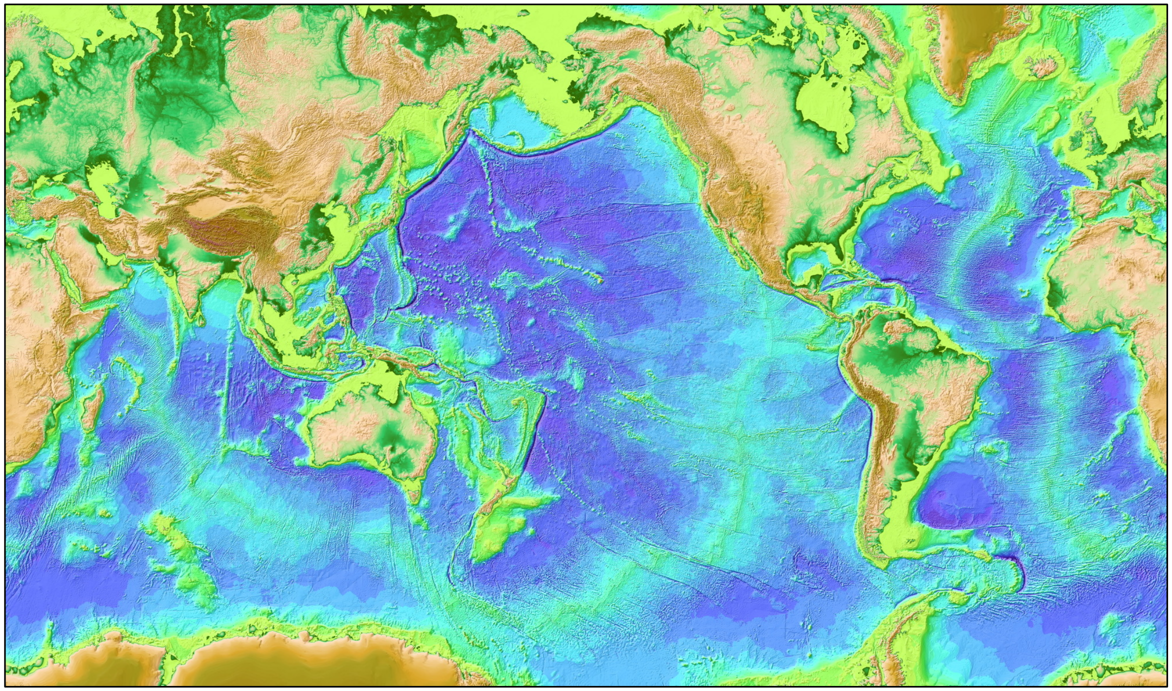
ix $$2KMg_3AlSi_3O_{10}(OH)_2(s) + 14CO_2 + 15H_2O \rightarrow Al_2Si_2O_5(OH)_4(s) + 2K^+ + 6Mg^{2+} + 14HCO_3^- + 4H_4SiO_4$$

phlogopite *kaolinite* *dissolved ions*

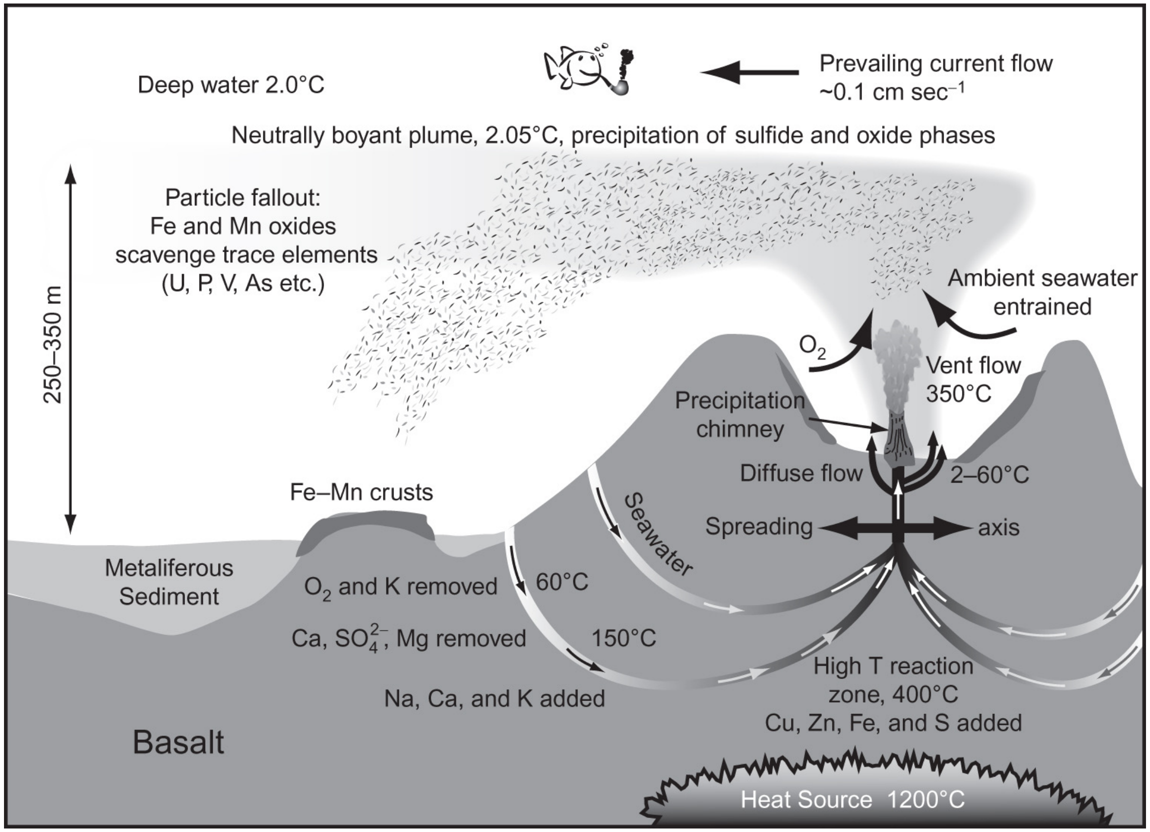
However, there's a problem! It is unclear how much these reactions actually occur.

What else are we missing from our picture of the ocean and inflows / outflows?

Possible additional sinks: Hydrothermal circulation

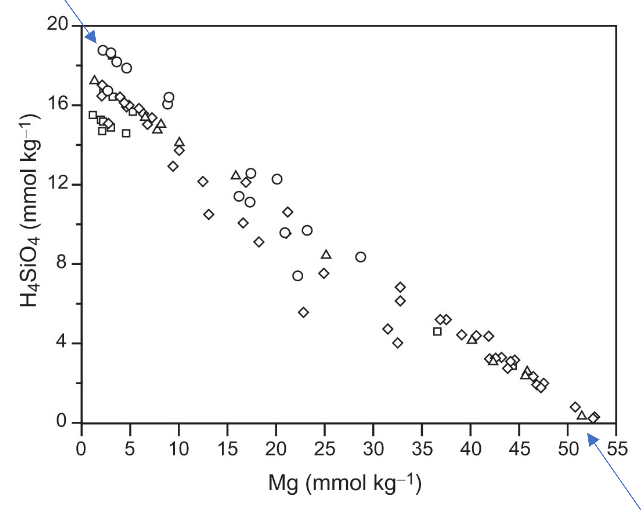


Possible additional sinks: Hydrothermal circulation



Emerson and Hamme, 2021

Hydrothermal end member



Seawater end member

In actuality, both reverse weathering and hydrothermal vents are responsible for removing excess ions, though magnitudes are unclear

Nick Hawco will cover hydrothermal vents later in the semester