

12.742: Lecture 1

History of Oceanography

A Timeline

1. HMS Challenger Expedition: 1872-1876
 - A global expedition that was the first of its kind to study of the ocean
 - Produced the first map of sea surface density
2. Establishment of WHOI: 1930
3. World War II: 1939-1945
 - The dawn of modern oceanography
 - Produced high resolution maps of the ocean, from bathymetry to currents
4. Geochemical Ocean Sections Study (GEOSECS): 1970s
5. U.S. Joint Global Ocean Flux Study (U.S. JGOFS): Late 1980s
6. World Ocean Circulation Experiment (WOCE): 1990s
7. Climate and Ocean Variability, Predictability, and Change (CLIVAR): 2000s
8. Global Ocean Ship-based Hydrographic Investigations Programs (GOSHIP): 2010s
9. An International Study of the Marine Biogeochemical Cycles of Trace Elements and Isotopes (GEOTRACES): 2010s
10. SeaWiFS: 1997 - 2010
11. MODIS: 2010s - Now
12. (Bio)-Argo: 2010s - Now
13. TARA Oceans: 2010s

Geo-context

We also put this history of oceanography within the context of enslaved peoples within the U.S.'s history. Modern oceanography developed, as seen in the timeline above, as a discipline in the 19th century with ocean depth sounding and charting of surface currents. Understanding of these currents and trade winds (note the name) were motivated by improving commercial trade ship navigation. On these ships between 18010 and 1860 over 3.5 million enslaved peoples across the Atlantic.

The Innovators

Before this section, I would like to note that the list given was all men. This is not indicative of current and past ocean science. As an addendum to the presentation given, I would like to highlight:

1. Maria Mitchell: the first woman to work for the U.S. Coast Survey
2. Marie Tharp: discovered the Mid-Atlantic Ridge and proved the validity of continental drift
3. Sylvia Earle: pioneering deep water explorer
4. Cindy Lee Van Diver: first and only woman to pilot Alvin

Some others (as given in the lecture):

1. Max Blumer: WHOI scientist who started the field of quantitative oil spill science
 2. Ed Carpenter: WHOI scientist who had the first paper on microplastics in the oceans
 3. Clair Patterson: Caltech scientist who used lead and its isotopes in remote environments to help pass the Clean Air Act
 4. Glen Shen and Ed Boyle: MIT scientists who demonstrated the decreases in contaminating lead using corals
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12.742: Lecture 2

Composition of seawater, mass balance, and box models

Major ocean inputs and outputs

There are a few hypotheses as to why we have salt in the ocean. The first of these is the **accumulation hypothesis**, which says there are rocks on land that are salts (i.e., have a cation and anion), there is weathering, which brings salts into the oceans, and then there is a hydrological cycle in which there is evaporation and precipitation. However, we note that in this model there is only an input, no output. This then means that we would constantly accumulate the salts, which isn't realistic. Let's look at the inputs and the outputs:

1. Inputs
 - Land weathering
 - Gas exchange
 - Vents
2. Outputs
 - Burial
 - Biological processes (processes that take place away from the sediment in the water column)
 - Authigenesis (the process whereby a mineral or sedimentary rock deposit is generated where it is found or observed)
 - Gas exchange
 - Vents
 - Evaporation

Now, to first order, we can forget all of these except for **weathering and burial**, as our important inputs and outputs.

1 Box model

The diagram of this model is given in Fig. 1.

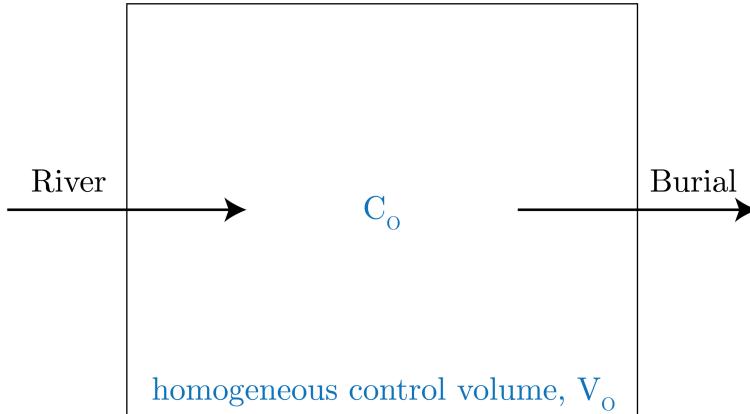


Fig. 1: A diagram of our 1-box model.

We start with, to get a rate of change of **mol s⁻¹**, we start with:

$$V_o \frac{dC_o}{dt} = \text{sources} - \text{sinks}.$$

Then, from above we know that we can ascribe the following **first-order reaction** to these inputs and outputs:

$$\begin{aligned} \text{sources} &= \text{rivers} = C_R Q_R, \\ \text{sinks} &= \text{burial} = V_o k C_o. \end{aligned}$$

Therefore, we get, for a **steady-state** assumption:

$$C_R Q_R = V_o k C_o.$$

We can then solve for the concentration to get:

$$C_o = \frac{C_R Q_R}{V_o k},$$

or the residence time:

$$\tau_R = \frac{1}{k} = \frac{C_O V_O}{C_R Q_R}.$$

If we do not assume steady-state, we consider the following first-order reaction solution.

Definition (First-order Reaction). We say that the solution to an equation of the form:

$$\frac{dC}{dt} = -kC,$$

is given by:

$$C(t) = C_0 \exp[-kt].$$

This is exponential decay with time.

Proof. We proceed with separation of variables:

$$\int \frac{dC'}{C} = -k \int dt,$$

which gives:

$$\log[C] = -kt + \text{const},$$

implying the solution, for the boundary condition $C(0) = C_0 \Rightarrow \exp[\text{const}] = C_0$:

$$C(t) = C_0 \exp[-kt].$$

We can see that this constant k , and more generally just the order and rate of reactions, for the elements within the ocean system are drastically, over 15 order of magnitude! That's alot. As an example, we can get the residence of the chlorine ion:

$$\tau_R^{\text{Cl}^-} = \frac{559 \cdot 1.34 \times 10^{18}}{0.23 \cdot 3.73 \times 10^{15}} \simeq 90 \text{ [My].}$$

However, we note that the 1-Box model is less accurate for complicated dynamics. As a general rule, the model is as good as the assumptions and set-up. For instance, if we try to get the residence time of water in the ocean with the above model we would get:

$$\tau_{\text{H}_2\text{O}} = \frac{V_0}{Q_R} \simeq 40 \text{ [Kyr].}$$

However, this is not correct as there is only an input here, no outputs. To add this in, we consider the output as evaporation and an input as precipitation. Therefore, we get:

$$\frac{dV_O}{dt} = R + P - E \simeq 4 \text{ [Kyr].}$$

Composition of the ocean

The most important part of the ocean composition of anions and cations, as this contributes to the charge of the ocean. The charge of the ocean is 0, that is it is net neutral. Therefore, in our mass balances, we really care about the charge of the ocean. We can look at profiles of these ions in Fig. 2

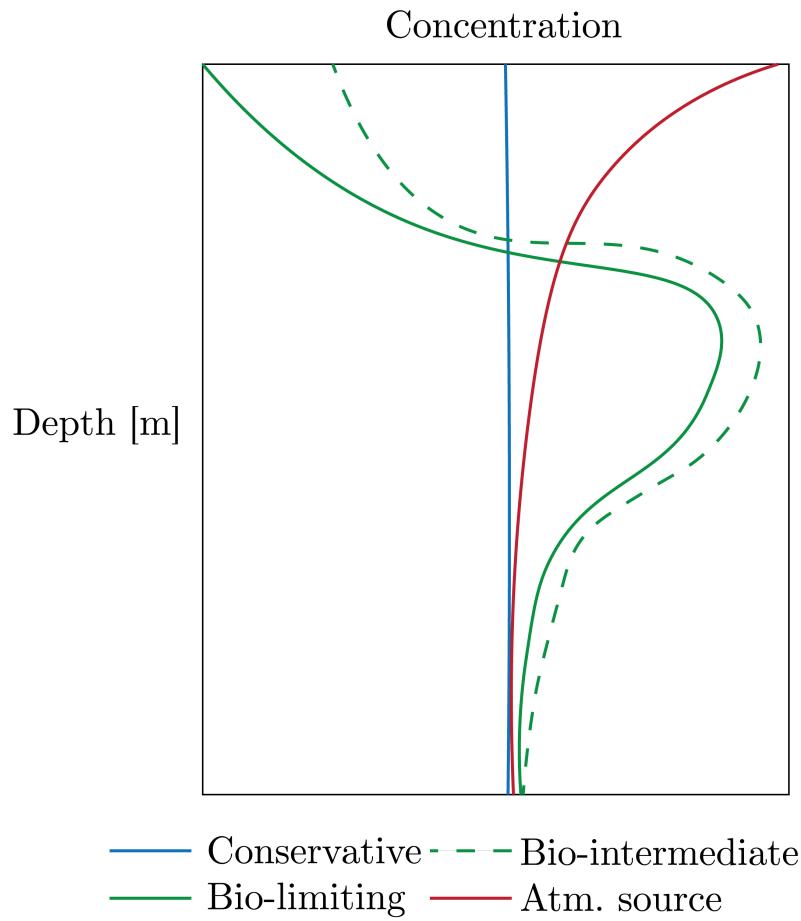


Fig. 2: Profiles of different forms of chemical constituents of the ocean.

2 Box Model

Now, we consider a two box model, in which there is a surface ocean box and a deep ocean box, shown in Fig. 3.

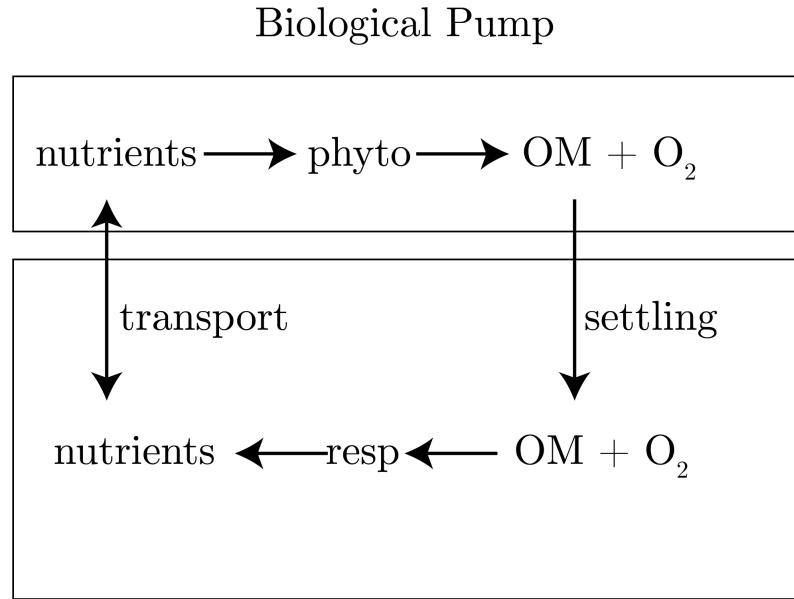


Fig. 3: The 2-box model we consider, which is known to represent the "biological pump".

The equations that we consider are for sinking, with ϕ denoted by ϕ , and transport v as the major movements of the chemical constituents. We write for the deep ocean:

$$V_d \frac{dC_d}{dt} = \phi + C_s v - C_d v,$$

which we can solve at steady state as:

$$\phi = v(C_d - C_s).$$

12.742: Lecture 3

Climate, circulation, and water masses

2-Box Model

We recall our 2-box model from last time as:

$$V_d \frac{dC_d}{dt} = v(C_s - C_d) + \phi = 0,$$

which gives:

$$\phi = v(C_d - C_s),$$

which importantly we note is linearly related to the exchange rate, so if this is off so is our estimate $\mathcal{O}(1)$.

Phosphate Example

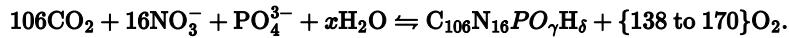
We can plug in numbers for phosphate PO_4^{3-} , a commonly used tracer for models like these, to get:

$$\phi^p = (1.2 \times 10^{15})(2.1 - 0) \simeq 2.5 \times 10^{12} [\text{mol P y}^{-1}].$$

This is a large number that is hard to really grasp. Therefore, we introduce the following concept.

Redfield Ratio

We have the following relationship between respiration and photosynthesis:



This then gives a Redfield ratio C:N:P:O₂ of:

$$106 : 16 : 1 : \{-138 \text{ to } 170\}.$$

A Cautionary Tale

We can use this box model to get the concentration of O₂ in the deep box, noting:

$$\phi^{O_2} = -150\phi^p = -150v(C_d^p - C_s^p),$$

which then gives:

$$C_d^{O_2} = C_s^{O_2} + \frac{\phi^{O_2}}{v} \simeq 234 - 150(2.1) = -81 [\mu\text{M}].$$

Clearly, this is wrong. Where did we go wrong? It is in the assumptions of our model, as our math here is clear and correct. So, this shows that we need to be very careful in what we assume when modelling. In the case of phosphate, we note that the Southern Ocean has disproportionately large values of phosphate, which ventilate the deep ocean.

3 Box Model

The set-up is presented in Fig. 1 for this model.

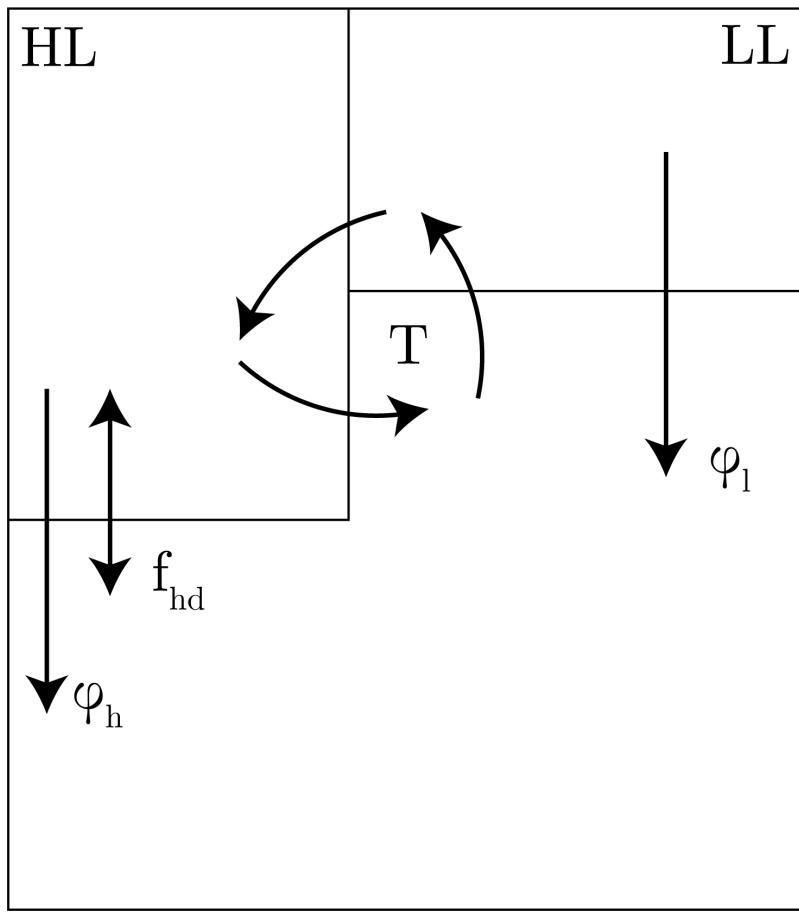


Fig. 1: The 3-box model.

We can write the equations for this model as:

$$V_d \frac{dC_d}{dt} = (T + f_{hd}) (C_h - C_d) + (\phi_l + \phi_h).$$

Density

In freshwater, we get:

$$\rho_{\text{fresh}} \simeq 10^3 \text{ [kg m}^{-3}\text{].}$$

In seawater, we get:

$$\rho_{\text{seawater}} \sim \rho(T, S, p).$$

We note that we can decompose this into:

$$\rho = \rho_0 + \sigma.$$

We define this anomaly as:

$$\sigma = \left(\frac{\rho}{\rho_0} - 1 \right) \times 10^3.$$

We note that this is nondimensional, and we often take $\rho_0 = 10^3$ [kg m⁻³].

Potential Temperature

We use potential temperature, Θ , as the temperature that a water parcel would be if it was at the surface.

Units

We define:

- Molarity = mol vol⁻¹
- Molality = mol mass⁻¹

We also define a Sverdrup as 10^6 [$\text{m}^3 \text{s}^{-1}$].

Mixing

We introduce the idea of mixing, in which we note that salinity and temperature are conservatively mixed, i.e. mixing proportional to the relative contributions of the endmembers. However, this is not the case in density, in which we have "cabelling", which we present in Fig. 2.

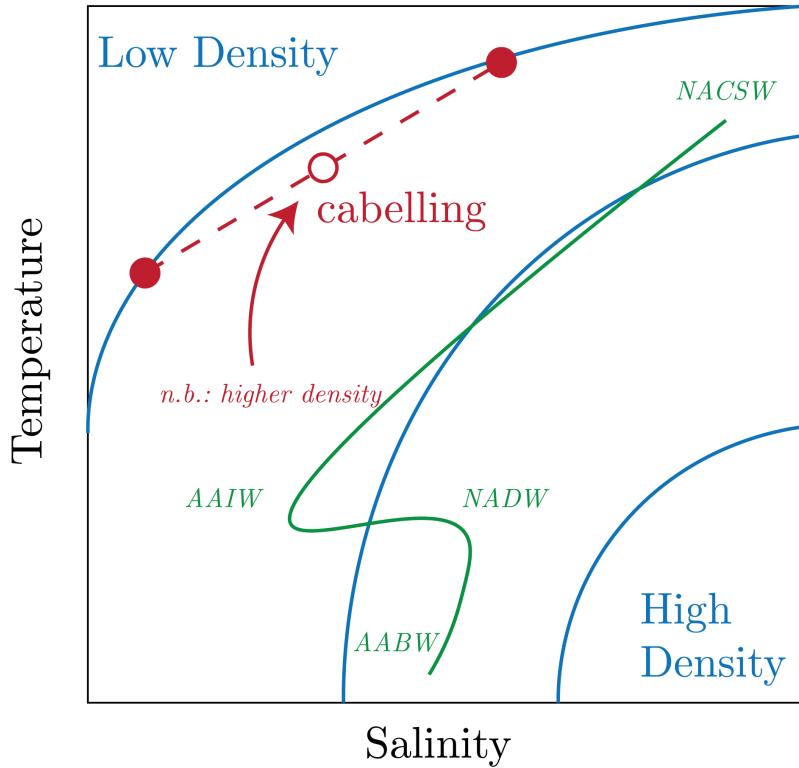


Fig. 2: Mixing and the effect on density from cabelling. We also provide a basic relation of different water masses

In addition, we provide a basic description of the different water masses in the T-S- ρ plot.

Heat Transport

We have transport of heat across the surface ocean, which is important for the formation of different water mass characteristics in our study in this class. We present a schematic of this heat input and output, as well as transport via atmospheric circulation, in Fig. 3.

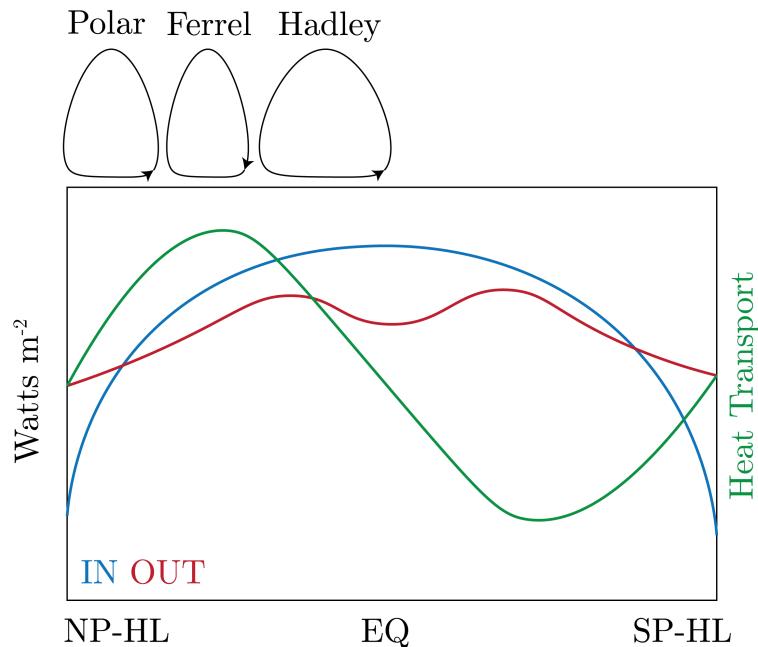


Fig. 3: Heat transports across the surface ocean globally.

12.742: Lecture 4

Surface boundary conditions

Pressure Gradient Force

We derive and show the pressure gradient force in Fig. 1.

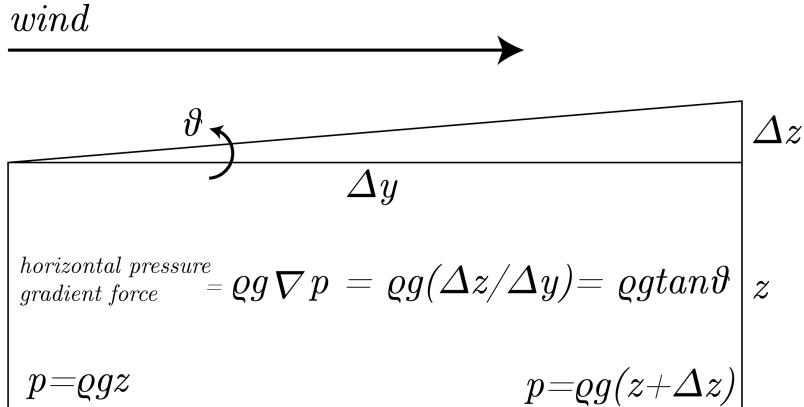


Fig. 1: An intuitive derivation of the pressure gradient force in the ocean.

Coriolis Force

We know that the Coriolis force, for a rotating reference frame, is given by $2\Omega \times \underline{u}_R$, where Ω is the rotation of the earth and \underline{u}_R is the fluid flow in the reference frame R . See [12.801 notes for Lecture 1](#) for a complete derivation of this equation. We can think of this intuitively of the Earth having a large angular momentum at the Equator and a small angular momentum at the poles, given by $\underline{r} \sim \cos \phi$ and $\underline{L} = \underline{r} \times \underline{p}$, for ϕ latitude and $\underline{p} = m\underline{u}_R$ is the momentum. (We note that here we have not moved to infinitesimal fluid parcels for the sake of clarity, in which case we would divide by the density and not deal with momentum rather velocity). Therefore, as the radius gets smaller, we get that the angular momentum gets smaller. Thus, by the Conversation of Angular Momentum, we see the Coriolis force in action, by which it needs to curve in order to conserve the momentum it had in the trajectory closer to the Equator. Of use to use, we can define the Coriolis Parameter:

$$f = 2\Omega \sin \phi.$$

Geostrophic Balance

We can imagine a scenario in which, by Coriolis we have that in the NH the force is acting to the right (by the Right Hand Rule) and in a gyre we have a balanced pressure gradient force (fluid piles up in the center creating more pressure). Therefore, we get that the pressure gradient force, under some assumptions, balances the Coriolis force. This is the definition of Geostrophic Balance. Please see [12.801 notes](#) for more information on this derivation.

Ekman Transport

We also have Ekman transport via the Ekman spiral, for which the net integrated flow is to the right, in the NH. We know that Ekman transport is defined as:

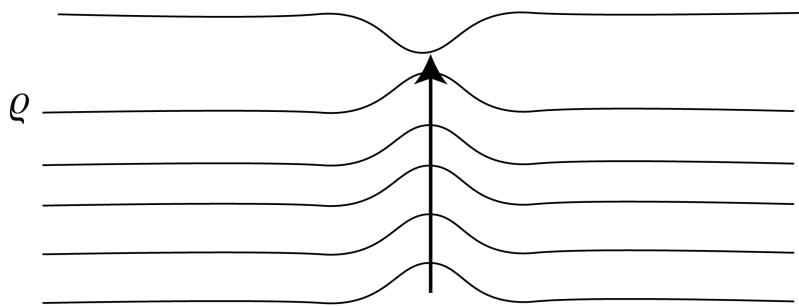
$$\underline{w}_{Ek} = \nabla \times \underline{\tau}_w,$$

which demonstrates this effect.

Transport in Chemical Species

Why do we care about all of this? Well, this is affect the distributions of chemical species in the ocean. There is a balance between the surface ocean having light and the deep ocean having nutrients. N.B.: light decays exponentially with depth. Now, one way to get an exchange between these is to have upwelling driven by winds that cause a transport of nutrients to the surface ocean. One place that this occurs is along the coast, such as in Peru or Namibia. We can also see that there is Equatorial Upwelling, at which point there is a divergence given the gyre circulation. Then, by mass continuity $\nabla \cdot \underline{u} = 0$ we know that upwelling must occur. This is different than subtropical convergence, where the gyre circulation is the same causing downwelling. We can see this in Fig. 2.

Upwelling (Cyclonic)



Downwelling (Anticyclonic)

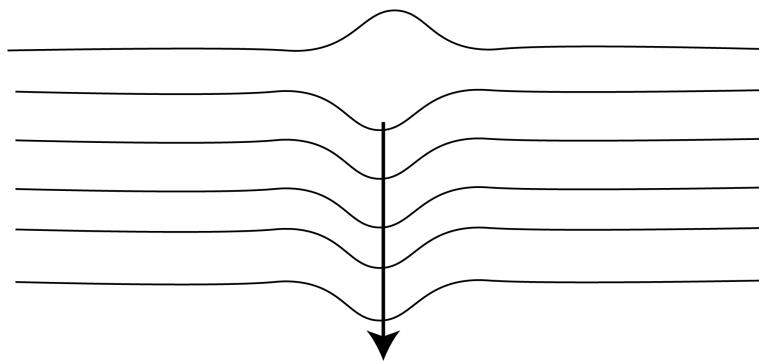


Fig. 2: A comparison of -welling scenarios.

In addition to large-scale circulation, eddies can also cause transport. These are $\mathcal{O}(10^5)$ [m] in size and last a few months. One example of this is Agulhas retroflection, which causes upwelling and an increases in productivity.

Mixed Layer Depths

One thing that this transport can do is change the homogeneous depth of the surface ocean, or the Mixed Layer Depth. We show this in Fig. 3.

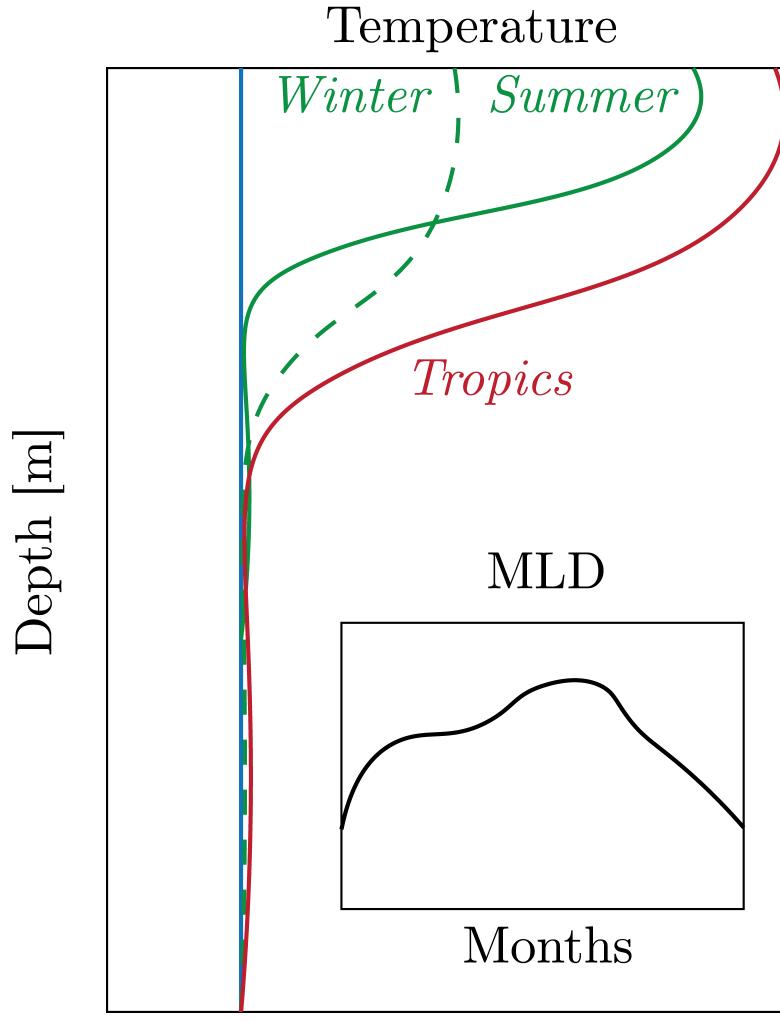


Fig. 3: Mixed Layer Depths.

Air-Sea Interaction

Thermodynamics

There are also important interactions with the atmosphere. We define Henry's Law for a gas \mathbf{X} as:

$$K_H = \frac{C_X}{p_x},$$

for p_x the partial pressure of \mathbf{X} . We can calculate the solubility functions for these gases from observation and get that they decrease with temperature, therefore warm water holds less gas. Additionally, salty water holds less gas, as the ions contract the water molecules, which make less space for the gas to be "fit" in. This does not have anything to do with time.

Kinetics

Kinetics deal with time. We define:

$$\phi = k_w (C_a - C_X),$$

where k_w is the gas transfer velocity or the piston velocity which is proportional to wind, for C_a the concentration of gas in the air.

12.742: Lecture 5

Primary Production I

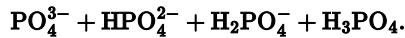
What is Primary Production?

We define primary production as the production of primary carbon, an autotrophic process. This is opposed to secondary and nth-dary production, which converts from this or the (n-1)st-dary production to that level. We care about this because it is fundamental to the nutrient cycle and is central to the carbon cycle (uptake and sequestration). As we discussed in the last lecture, we note that there is more food in the surface ocean.

Nutrients

We go over important nutrients no:

- Nitrogen
 - N₂: Nitrogen gas, which is mostly in the atmosphere (75%) with an oxidation state of 0. We note that there is a triple bond here, so it is super hard to break.
 - NO₃⁻: Nitrate, which has an oxidation state of +5, therefore the most oxidized state of N, which means it is the most abundant form in the ocean as the ocean is well oxygenated.
 - NH₄⁺ ⇌ NH₃: Ammonium and Ammonia, for which the equilibrium is driven by pH and in the ocean the dominant form is Ammonium, which has an oxidation state of +3. It is the most favoured of the N compounds.
- Iron
 - Fe²⁺: Much more soluble in Fe³⁺. The balance between these two (soluble and oxidized) and a major balance in the ocean, which organisms like siderophores help balance out.
 - Fe³⁺: As iron oxidation is very quick, this is the major constituent in the ocean.
- Phosphorous
 - PO₄³⁻: Phosphate. Here, really what we are talking about is the equilibrium of the following species, which is pH dependent:



- Carbon:
 - CO₂: fixed by RuBisCo, which turns carbon dioxide into carbonate. Very little in the ocean, given equilibrium.
 - HCO₃⁻: Bicarbonate, about 90% of the ocean DIC
 - CO₃²⁻: Carbonate ion, about 10% of the ocean DIC

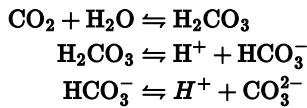
Important things to note here is that when we say phosphate, we mean the sum of all protonated forms, as this is a simple acid-base reaction that is pH dependent (as stated before). This means that the relative abundances are all the same order. However, in the case of iron and nitrogen (DIN), it is a set of redox reactions which are more complicated and therefore there are orders of magnitude differences between all these form which cause us to separate out their relative abundances.

Oxidation States

The oxidation state is the hypothetical charge of an atom if all of its bonds to different atoms were fully ionic (transfer of valence electron causing opposite charge attraction). It describes the degree of oxidation (the loss of electrons) of an atom in a chemical compound. The most favoured oxidation state for the nutrients discussed above is that which has the same oxidation state as that needed for the creation of organic material.

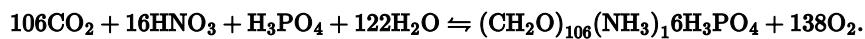
Carbonate Speciation

The following set of equations govern carbonate equilibrium:

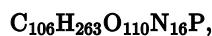


Redfield Ratio

We have the following equation governing the equilibrium of photosynthesis:



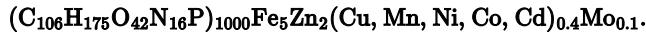
Summing all of this, we get something like:



however the exact values for H and O are highly underconstrained. The currently preferred ratio is:



This is the Anderson (1995) formulation. We can add in the micronutrients:



These metals are important because they can act as co-factors in enzymatic reactions, such as Zn for carbonic anhydrase (which modulates the carbonate equilibrium) and Ni is used for cleaving the nitrogen out of urea to form ammonium. This is an idealized ratio. This is all for "soft tissue", but for "hard tissue", we need:

- Si: diatoms
- CaCO_3 : coccolithophores

We can look at this between N:P in Fig. 1.

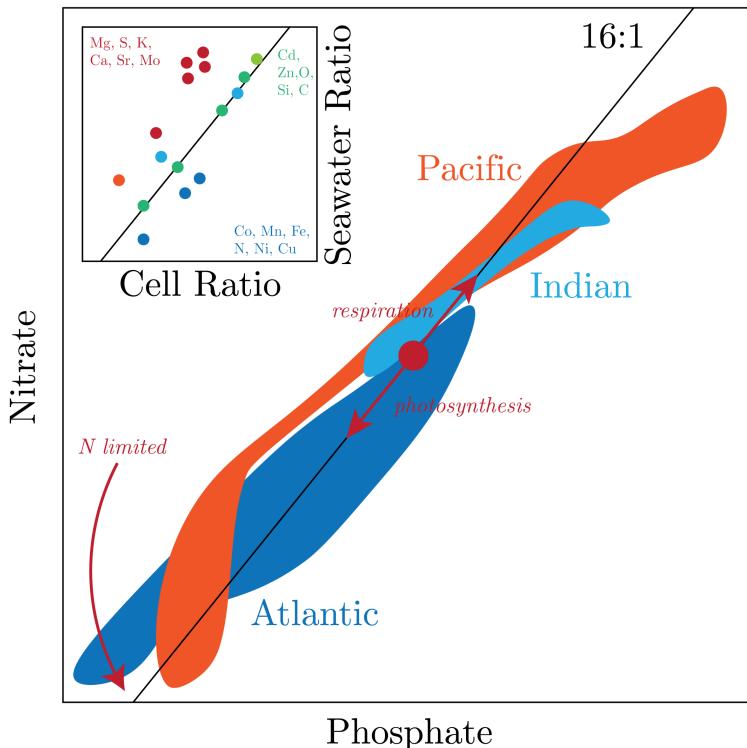


Fig. 1: An example of the Redfield Ration with N:P, where we note that it is an N limited regime. The colorbar of the inset is for residence time, with red being a 10,000 [kyr] residence time. It is also a log-log plot.

There are a few fundamental things we can draw from this figure. First, we note that this is generally "you are what you eat". Second, this is not the line of best fit, the 16:1 line and if you were to use RMA or another orthogonal, non-least squares fit (as you should for all data in which the independent variable has inherent uncertainty), you would get a slope between 14 and 15. However, the line of best fit does not represent just the composition of the OM, which we care about, but also other processes. Third, we note that this shows we are in a N limiting environment, given that the *y*-intercept is negative. Fourth, we note the vectors along the line, with the upward movement to be respiration and the downward movement to be photosynthesis. This is because of how we consume N and P with our governing equation above.

We note that the source of phosphates into the ocean is from weathering, the dissolution appetites. The general source of nitrogen in the ocean is nitrogen fixation, which is from the atmosphere. We note that this is a decoupling of the sources. Therefore, we can say that the reason we have the amount of the N in the ocean is from biology and the amount of P is from geology. So, this is a very dynamic system based on numerous factors, this is to say that biology affects geology and vice versa, on timescales long enough. This then gets to the fundamental fact that organisms today were optimized through evolution for the environments in which they were evolved. Therefore, remnants from the past are still here within the cellular framework, despite the fact that what is available has changed.

In the inset of Fig. 1, we see that all trace elements are pretty well constrained in log-log space to the N:P ratio. The deviations from this line in favour the cells has to do with the evolution of the organism, that is that the environment in which they were evolved had different compositions than the modern ocean. Originally, the ocean did not have as much oxygen as it has now, rather Fe was more relatively abundant. So, organisms evolved to use that Fe, and then the conditions of the ocean changed by the physiology of the organisms did not. We can see this in RuBisCo, which is not greater at fixing carbon dioxide when there is oxygen but when oxygen is around it has a higher affinity for the O_2 than the CO_2 , given that it only evolved once. This is why carbonic anhydrase is so important so as to concentrate the carbon for biological processes to take place. We can see that the major constituents of seawater, which are semi-conservative, are not needed as much for the cells, given the conditions in which these cells evolved.

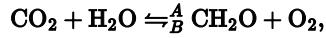
We can list the top % constituents of cell mass:

1. Protein: 30 to 65%
2. Lipids: 10 to 50%
3. Carbohydrates: 5 to 45%
4. Phosphoglycerides: 5 to 15%
5. RNA: 3 to 15%
6. DNA: 0.5 to 3%
7. Chlorophyll: 0.2 to 5%

These ratios change for growth, for cell types (pro- vs eu-karyotes).

The Photo-Respiration Balance

We can represent the exchange between photosynthesis and respiration as:



where we have simplified our OM from before to CH_2O , which is not perfect but not a terrible approximation. This basically assumes that everything in OM is sugar. We have the following definitions of productivity:

- Gross Primary Productivity: A
- Net Primary Production: $A - B$
- Net Community Production: $A - (B + C)$, where C is the pathway between CH_2O to CO_2 .
- Export: D , the amount of CH_2O that is exported to the deep ocean, below the euphotic zone.

From this, at steady state, we have to that $(A)\text{NCP} = \text{Export}$, as everything that isn't used up in the surface ocean has to be exported, by mass conservation.

Limitation

We have the following definitions:

- Bottom-Up
 - Nutrients
 - Light
 - Temperature
 - CO_2 ? (Think of a bloom)
 - Top-Down
 - Zooplankton. This is a linear, first-order reaction, as it is dependent on just how many nutrients the organism comes into contact with.
 - Viruses (Think of a bloom, again...). This is a quadratic, second-order reaction, as it depends on (1) getting the virus and (2) having the infected organism meet another organism.
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12.742: Lecture 6

Primary Production II

Regional Distributions

NPP and Chlorophyll maps show a 1:1 correspondence for the majority of the ocean (where we note here that maps we often see are annual averages, i.e., the Arctic has low Chlorophyll as there is no sunlight...). One glaring divergence from this rule is the Southern Ocean, whether or not this is true is up for debate (that is, we don't really have measurements for that region as it is hard to get the measurements). There are two particular regions that have high chlorophyll: the North Pacific and North Atlantic (Nordic Seas). These are the regions in which there is a deep ocean mixed layer that stimulates a bloom in the Spring, as nutrients are entrained given the deep mixing. We can also see coastal regions with appropriate winds having high chlorophyll, given the coastal upwelling. Also, in the pacific gyres, we can see the result of convergence (low productivity) and divergence (high productivity) given corresponding upwelling.

Limitations on Production

We have the following definitions of limitation regimes:

- Bottom-Up
 - (Macro-)Nutrients*
 - Light*
 - Temperature
 - CO₂? (Think of a bloom)
- Top-Down
 - Zooplankton. This is a linear, first-order reaction, as it is dependent on just how many nutrients the organism comes into contact with.
 - Viruses (Think of a bloom, again...). This is a quadratic, second-order reaction, as it depends on (1) getting the virus and (2) having the infected organism meet another organism.

There are some regions in which we have high nutrients and low chlorophyll (HNLC) regions. We can write all of these as a functional form of:

$$\text{SMS(Phyto)} = f(T, h\nu, \text{nutrients}, \dots).$$

Light

We can write the irradiance as:

$$I = I_0 \exp[-k(\lambda)z],$$

where we define the:

$$k(\lambda) = \underbrace{k_w}_{\text{H}_2\text{O}} + \underbrace{k_x}_{\text{CDOM}} + \underbrace{k_p \cdot P}_{\text{Phytoplankton}},$$

as a parameter that modulates how much "stuff" takes up the light. Oftentimes we can write the average:

$$\langle k_p \cdot P \rangle = \int_{-z}^0 dz k_p \cdot P.$$

Of course, for primary production not all wavelengths are created equal. Specifically, photosynthesis, and the photoreceptors in chloroplasts, have evolved to preferentially take-up blue and red wavelengths (simply: the plant is green, so it reflects that colour and does not absorb it). This is not necessarily the case for ancillary pigments, which have a wider range of colours. One important parameter is PAR: photosynthetically-active radiation. It is normally considered that PAR is about 40% of the incident light on the surface ocean. We can look at the relative penetration depths of wavelengths in Fig. 1.

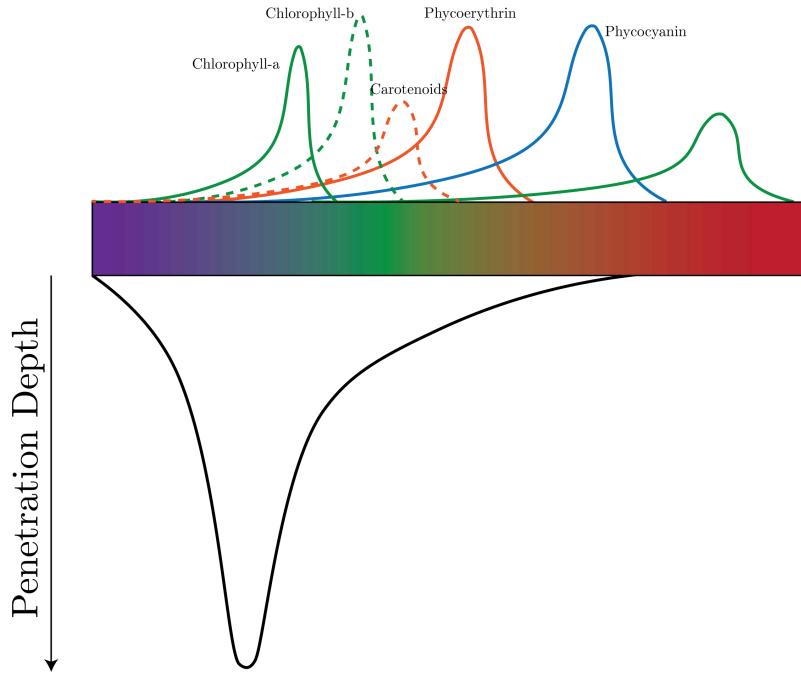


Fig. 1: The relative depths of penetration for different wavelengths.

Fig. 1 also demonstrates where different pigments absorb and their relative abundances of absorbance. PAR is often defined as the depth at which I falls to 1% of its surface value. We can sum up all of our discussions of photosynthesis with Fig. 2.

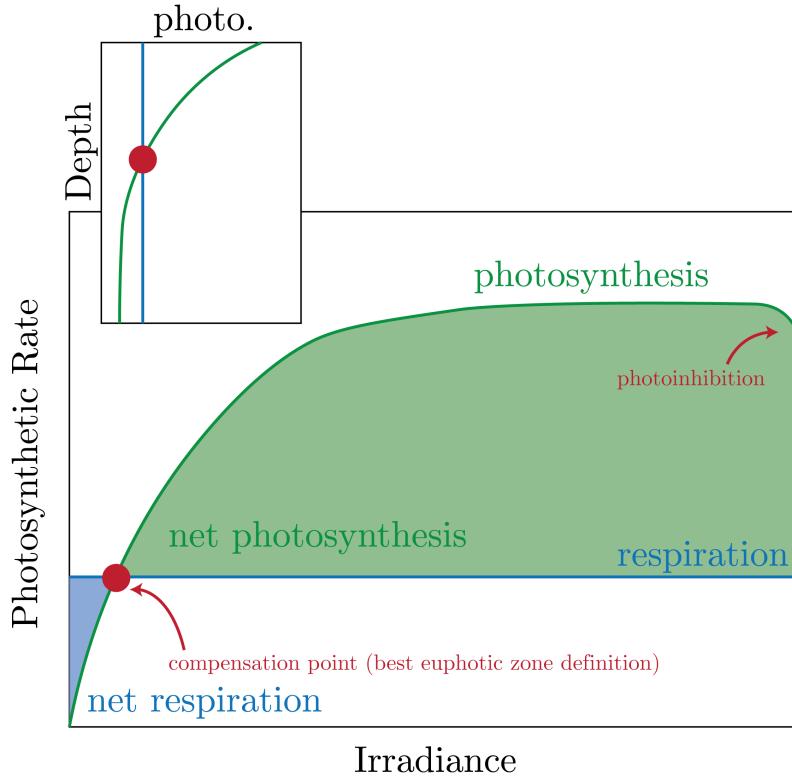


Fig. 2: The dynamics of photosynthesis and respiration and the corresponding characteristics.

Michaelis-Menten

We can write the max growth rate assuming Michaelis-Menten dynamics as:

$$\mu_{\max}(T) = \mu_{\max} \cdot Q^{(T-10^\circ)/10^\circ}.$$

Furthermore, we have the generic rate:

$$v = v_{\max} \frac{C}{C + K_S},$$

for a concentration C . A lower K_s represents a higher substrate affinity, which are species dependent. Therefore, the species (green and blue in Fig. 3) with the higher K_s can consume the nutrient faster. This, of course, drives evolution for species to fill their niche (bringing back Darwin).

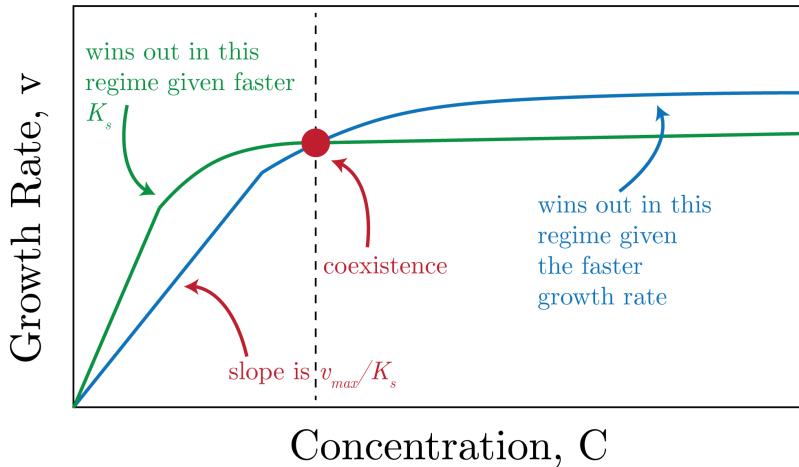


Fig. 3: Michaelis-Menten dynamics for two species, blue and green, which win out in different regimes.

An example: N Cycle

We remember the following nitrogen species in order of decreasing preferability: NH_4^+ , NO_3^- , N_2 . Then, we have a modification of the above equation of the form:

$$v = v_{\max} \left(\frac{C_{\text{NO}_3^-}}{K_{\text{NO}_3^-} + C_{\text{NO}_3^-}} \exp[-\psi C_{\text{NO}_3^-}] \right).$$

This ψ is experimentally defined, which is our inhibition parameter.

Co-limitation

In this case, we define:

$$v = v_{\max} \cdot \left(\frac{C_{\text{NO}_3^-}}{K_{\text{NO}_3^-} + C_{\text{NO}_3^-}} \{+ \text{ or } \times\} \frac{C_{\text{PO}_4^{3-}}}{K_{\text{PO}_4^{3-}} + C_{\text{PO}_4^{3-}}} \right),$$

Here, the difference is if we have a linear dependence or a **log** dependence. We also introduce the following:

Claim (Liebig Law of the Minimum). For co-limitation, we can make the simplification:

$$v = v_{\max} \cdot \min \left(\frac{C_{\text{NO}_3^-}}{K_{\text{NO}_3^-} + C_{\text{NO}_3^-}}, \frac{C_{\text{PO}_4^{3-}}}{K_{\text{PO}_4^{3-}} + C_{\text{PO}_4^{3-}}} \right),$$

High Nutrient Low Chlorophyll (HNLC)

One way to think about this is in the surface area to volume ratio of a sphere, which we assume our cells are:

$$\frac{\text{SA}}{\text{V}} = \frac{3}{r},$$

where we note the important thing here is that it is inversely proportional to the radius r , which shows that we are in the diffusive regime. Simply, is faster to diffuse across a small area. In low nutrient conditions, we therefore have small r , i.e., small cells. This is the opposite in high nutrient conditions. The canonical example of an HNLC is the Southern Ocean. Here, the major limitation is Fe. In the Atlantic, it is N limited. There are three major prokaryotic species we consider in the N limited regions, mostly cyanobacteria:

- Prochlorococcus
- Synechococcus
- Trichodesmium

There are also diatom-diazotroph and UCYN-A, the most common of them all. For eukaryotic cells, which make carbonate shells:

- Diatoms (need silica)
- Coccolithophores
- Dinoflagellates (good at changing environmental conditions)

This leads us to categorize the ocean by all of these conditions, from physical to chemical to biological conditions within the water masses.

12.742: Lecture 7

Export (and top-down controls)

Phytoplankton Dynamics

N-P Model: Bottom Up Limitation

We can write a model of the form:

$$\frac{dP}{dt} = P \cdot \left(v_{\max} \frac{N}{K_N + N} - \lambda_P \right) = ss 0,$$

where λ_P is the death rate. We can imagine this is a **growth – death** scenario. Therefore, we can get:

$$\lambda_P = \frac{v_{\max} N}{K_N + N}.$$

We can rearrange to get the nutrient, as a constant:

$$N = \frac{\lambda_P K_N}{v_{\max} - \lambda_P}.$$

We define the total nutrient as: $N_T = N + P$. We note that in this steady-state model, N is a constant, as it is a function of constants. Therefore, we can think of our system as having some total N , N_T , for which there is constant offset by N that gives us P . We can define two regimes here. The first is when N is very low such that the growth rate from photosynthesis is smaller than the death rate. Therefore, we would eventually get that $P \rightarrow 0$. However, we have that N is large enough, then P is supported and we reach a new steady state under the conditions of the system. If advection and diffusion come into play, then we need to consider more N to make up for this transport. We can think of this solution, lastly, as the maximum value of N that the system will hold, after which all additional N goes into the production of P .

N-P-Z Model: Top Down Limitation

We can also consider the effect of having top down limitation, i.e. zooplankton eat both N and P . Therefore, this removes the total amount of N within the system. We present all of this in Fig. 1. We can continue this to have multiple size classes, which is shown for two size classes for P and Z in the dashed lines in the right panel of Fig. 1.

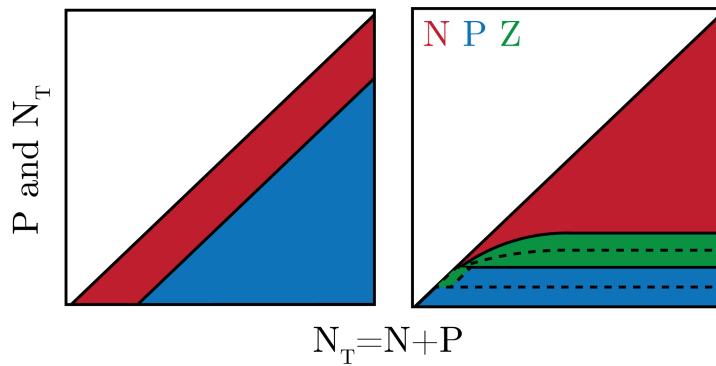


Fig. 1: Both top-down (right) and bottom-up (left) limitation models discussed thus far. The dashed lines in the TD control represent two sizes classes.

Sverdrup's Critical Depth Hypothesis

Sverdrup posits that the critical MLD is that where the integration of net photosynthesis and net respiration are equal, the compensation depth we discussed previously. In this case, we could get that there is enough nutrients from the deep MLD and enough light to have a bloom, which is why we have lots of primary productivity in regions of deep MLD (North Atlantic).

Photosynthesis

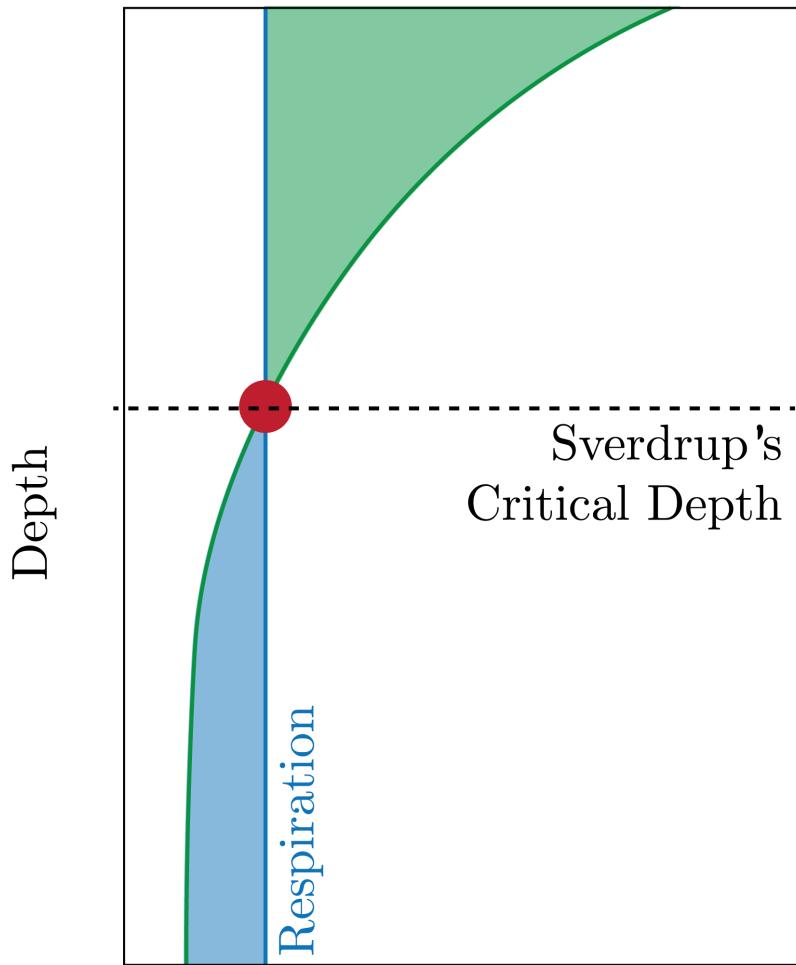


Fig. 2: Sverdrup's critical depth hypothesis.

Regional Distributions of Export

If you look at POC export maps and NPP maps, we see that there is high export in the high latitudes, at the equator (equatorial upwelling), and on the coasts (coastal upwelling). These are places that are known for high productivity, which is composed of larger cells and animals, i.e., not the diffusive limit. Larger cells sink faster, therefore there is a correlation between high PP and high POC export. We can also look at inorganic solids – such as CaCO_3 and opal – which come from coccolithophores and forams and diatoms. We mostly see the diatoms in the Southern Ocean and the Sub-arctic North Pacific, as there is high silica concentrations here. Silica is heavy, therefore there is large export (ballast). We see CaCO_3 export dominated in the other regions of high productivity. In areas of low productivity, we have these regions dominated by bacteria (i.e., small cells).

Nitrogen Cycle

We have three major nitrogen sources, in order of preference given oxidation state:

1. DON
2. NH_4^+ (Ammonium)
3. NO_3^- (Nitrate)
4. N_2

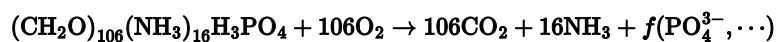
All of these lead to biomass assimilation. We can also consider dissimilation by considering nitrification:



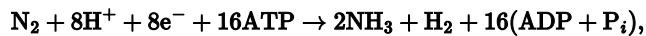
Next, we have nitrite oxidation:



We can relate all of this to our well-known respiration equation:



Therefore, there is competition for the ammonium, for which the phytoplankton will win. Next, we can consider nitrogen gas diazotrophy, or nitrogen fixation:



in which the triply bond of N_2 is cleaved off and to form ammonia. In these compounds, we see that they are enriched in N compared to C and P of Redfield, i.e. 150:25:1. Nitrogenase takes a lot of energy in order to cleave the N off of N_2 , so it is not preferable to go to this process, and also requires 38 Fe and is inhibited by O_2 . As the ocean is well oxygenated, this can become a problem. We often see nitrogen fixation in regions of high dust deposition, such as the North Atlantic, which is Fe rich. Instead, these cells will want to use Nitrate and Ammonium first as this processes is clearly prohibitive. We can therefore develop a model using nitrate as a tracer for export, as at steady state the upwelling from nitrification nitrate has to equal the export from production. We present this in Fig. 3.

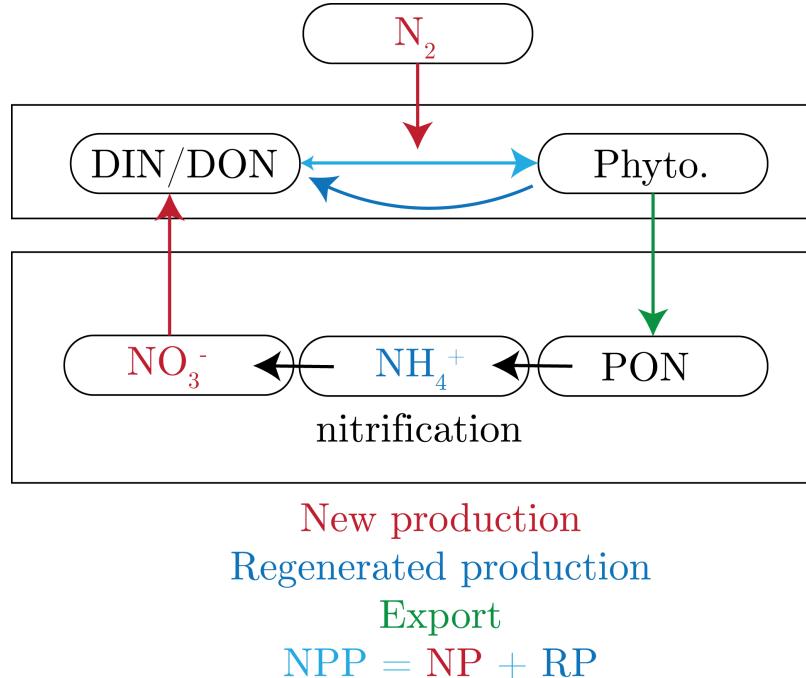


Fig. 3: The N cycle in the ocean.

We define a few terms here:

- New production = $NO_3^- + N_2$ (uptake)
- Regenerate production = NH_4^+ (uptake)
- Total production = NP + RP
- $NPP = TP$ at a theoretical steady state, however this is not always the case.

We correspondingly define:

$$\begin{aligned} e\text{-ratio} &= \frac{\text{Export}}{NPP}, \\ f\text{-ratio} &= \frac{NP}{TP}. \end{aligned}$$

Therefore, we should have that **e-ratio = f-ratio**. There is an assumption here that all nitrification is happening in the deep ocean. If there is any in the surface, then we have to decouple the export from the New Production. If there is any nitrification in the surface, then we would get a lower **f-ratio**. Regenerated production is a combination of things:

1. Leakage
2. Exudation
3. Cell death (by viruses)
4. Literally sloppy eating

where 2-50% of RP is from leakage. We can define all of this as the **microbial loop**, which describes the production equilibrium of POC into DOC. There are many ways that this happens (which is a two-way street). We can see a range in the -ratios from above, ranging from oligotrophic ranges of 15% to eutrophic ranges of 40%.

12.742: Lecture 8

Remineralization I

A diversion into decibars

We start with hydrostatic balance:

$$\partial_z p = -\rho g.$$

Then, we can integrate over some depth $[-h, 0]$ to get:

$$p = -\rho gh.$$

We can then get plugging in some numbers that $1 \text{ [m]} = 1 \text{ [dbar]}$. As we go down into the ocean, we can see that there is a large change in the processes that drive distributions of passive tracers in the ocean. This then means that [dbar] is a good way to viewing the ocean, at least one that shows the surfaces (i.e., isobars) that really dictate the distributions in the ocean over Cartesian coordinates.

Oxygen Utilization

We recall our 3-box model and have an equation for solution in the deep box of:

$$C_d^{O_2} = C_s^{O_2} - r_{O_2:P} (C_d^{PO_4^{3-}} - C_s^{PO_4^{3-}}).$$

This then means that we can view this as some partition between the initial concentration plus a change in that concentration through ventilation. Therefore, we define:

$$C_{\text{observed}} = C_{\text{preformed}} + \Delta C_{\text{remin}},$$

where we have defined $\Delta C_{\text{remin}} \simeq C_d^{PO_4^{3-}} - C_s^{PO_4^{3-}}$ and $C_{\text{preformed}} \simeq C_s^{O_2}$. This allows us to see the effect of remineralization globally. We can rearrange, and use oxygen gas as our tracer, to get:

$$\Delta O_2^{\text{remin}} = O_2^{\text{obs}} - O_2^{\text{pre}}.$$

The nice thing about gases is that the preformed gases exchange with atmosphere at a rate that is fast enough that we consider it at equilibrium with the surface ocean:

$$O_2^{\text{pre}} \simeq O_2^{\text{surf}} \simeq O_2^{\text{EQ or sat}}.$$

We then define this remineralization of oxygen as the consumed oxygen in biological processes, which we define as:

$$\text{Apparent } O_2 \text{ Utilization (AOU)} = -\Delta O_2^{\text{remin}} = O_2^{\text{sat}} - O_2^{\text{obs}} = f(\Theta, S) - \text{measurement},$$

where we note that the negative sign is due to the fact that the Redfield Ratio is negative for oxygen, as it is produced from photosynthesis while C, N, and P are consumed. This does make an assumption that we know what the solubility function at the surface is, i.e., what the surface ocean conditions were at the ventilation region. Additionally, there is a biology that complicates how much oxygen is consumed or produced. Also, the winds that cause bubble injection at different rates, etc. (As an aside: we note that this connection is the primary reason that we use $O_2:\text{Ar}$ ratios, in addition that the solubility curves are nearly identical). We next defined the **O₂ Utilization rate (OUR)**, defined as:

$$\text{OUR} = \frac{d\text{AOU}}{dt}.$$

Note that this is not commonly used as the rate with respect to time is hard to estimate accurately. To loop physical processes back in from previous lectures, we recall that it is really the winter MLD that drives the depth and depth at which the deep ocean is ventilated. The way that we can trace these processes is using CFCs (as we have a good atmospheric record with a slow decay rate) and tritium (from bombs, and we use the ratio with He). Canonical profiles of this look like the ones presented in Fig. 1.

OUR

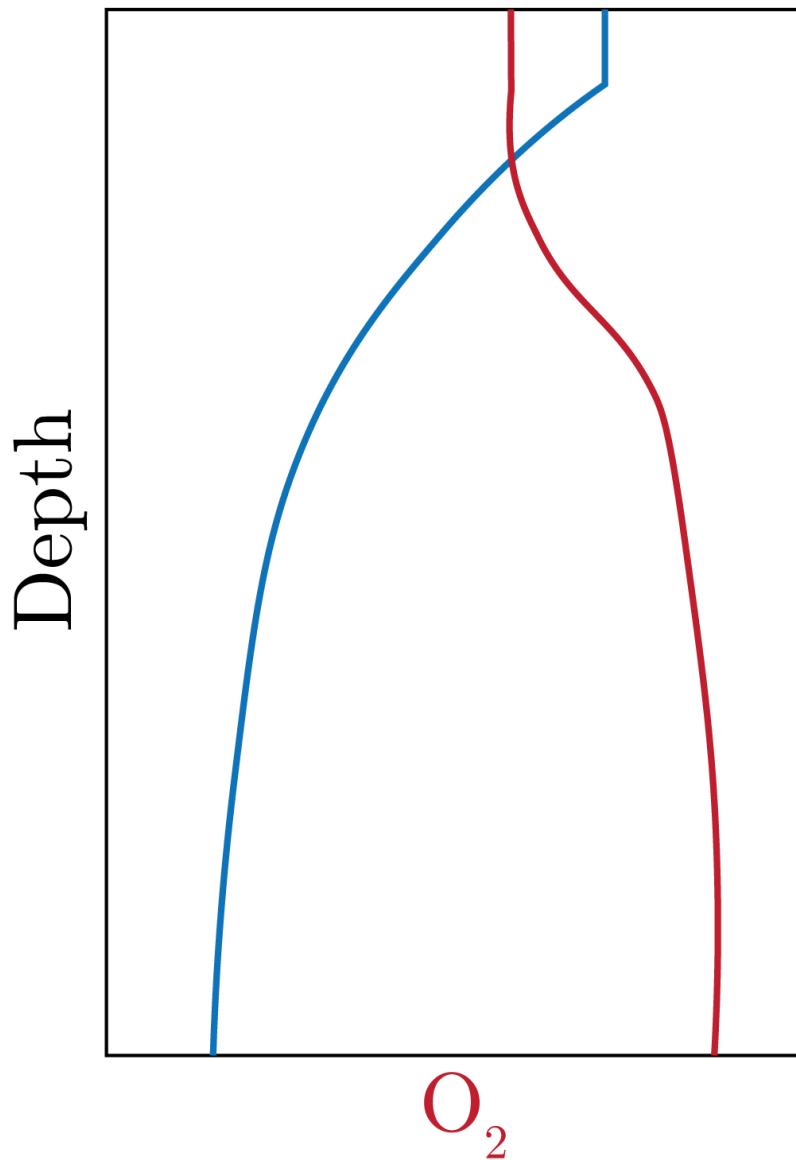


Fig. 1: Profiles of OUR and Oxygen.

Important here to note is the decrease in OUR with depth, which is due to the fact that there is less biology going on as you go deeper. The second thing to get from this is that in the oxygen profiles we have that increase with depth because there it is ventilated from the Southern Ocean, which is the primary region of ventilation for the deep ocean globally. Specifically, this ventilation (i.e., the physical transport of the nutrient) outways the drawdown by the biology, as it has been drawn down to such a level that biology does not really persist, and is therefore replenished at depth. This is the same reasoning for our remineralized values of nutrients in the deep ocean.

Extension to Phosphate

From our definitions above, we can get that:

$$C_{\text{PO}_4^{3-}}^{\text{remin}} = -r_{\text{P:O}_2} \text{AOU}.$$

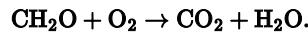
Therefore, we get that:

$$C_{\text{PO}_4^{3-}}^{\text{pre}} = C_{\text{PO}_4^{3-}}^{\text{obs}} + r_{\text{P:O}_2} \text{AOU} = C_{\text{PO}_4^{3-}}^{\text{obs}} - \frac{1}{150} \text{AOU}.$$

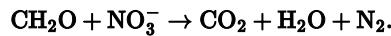
Now, we can also extend this to nitrate using the same procedure with the Redfield Ratio. However, the results globally are different. We discuss why now. The first is that phosphate is only consumed by photosynthesis and produced by respiration. The second is that nitrate additionally can be produced by nitrogen fixation and consumed by denitrification. This changes the global distribution differently for both nutrients. We can see this in our 16:1 N:P line, where in the upper ranges of phosphate we have a flattening in the N versus P in the Pacific and the Indian oceans. This is due to the decoupling of the anaerobic respiration in these regions.

Denitrification

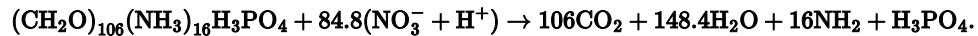
We start with our governing equation:



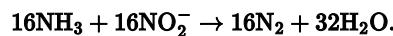
In the absence of oxygen, the next best electron receptor is nitrate, which is called denitrification (n.b. I'm about to not balance this equation because I am lazy but the gist is the same):



Therefore, denitrification only occurs when oxygen is sufficiently consumed, and it is these organisms (heterotrophs) can prefer the oxygen processes but have evolved to \frac{switch}{} Now, if we write down our equation for respiration with nitrate, we get:



We note here that in this equation, if there is no oxygen, then we are not able to perform nitrification, we we say was crucial to our new production in the N cycle in the deep ocean earlier. To be explicit, so the enzyme anammox performs this denitrification following:



This is the predominant processes for respiration in **Oxygen Deficient Zones**, such as off the coast of Mexico and Peru in the Eastern Tropical Pacific We can represent all of these processes as in Fig. 2.

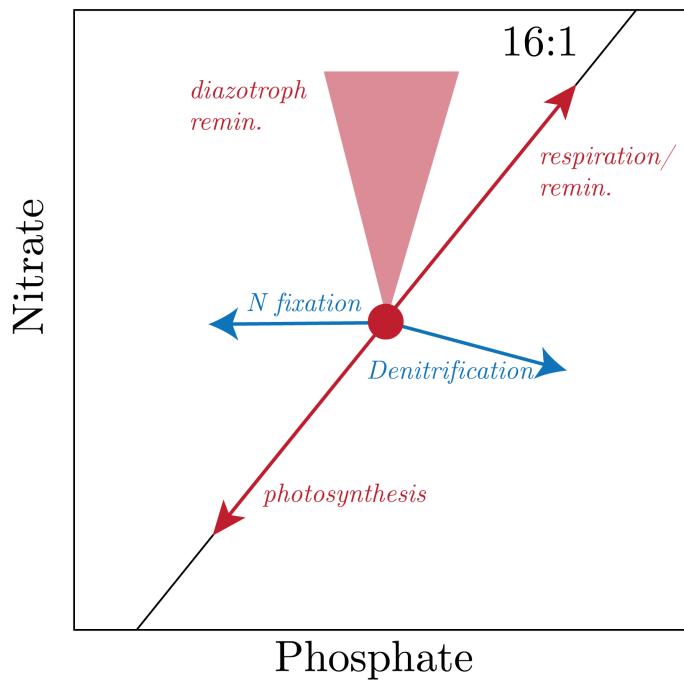


Fig. 2: Multiple N processes and their vectors on the N:P graph.

We note that N fixation removes phosphate with at a rate proportional to the Redfield Ratio but does not affect nitrate given that N_2 is the product. Correspondingly, we define the excess of N from the 16:1 line to identify areas of denitrification:

$$N^* = C_{\text{NO}_3^-} - 16C_{\text{PO}_4^{3-}} + 2.1 [\mu\text{mol kg}^{-1}],$$

where we add the scalar at the end to make the global average 0. This then means that N^* is a semi-conservative tracer, which the largest being in the Eastern Tropical North Pacific.

12.742: Lecture 9

Remineralization II

The Nitrogen Cycle, revisited

We have the following balances:

- Inputs
 - N₂ fixation*
 - Atmospheric deposition
 - River
- Outputs
 - Denitrification*
 - Burial

Therefore, we really have the denitrification has to equal N₂ fixation at steady state in the global ocean. We have the following pathway: More N through fixation and / or deposition → More biology → More export → Less oxygen at depth → Greater OMZ regions → More denitrification. This last step provides the stabilization to perturbations in the N cycle. Now, if there is more N to begin with, then we do not need as much N fixation and then the cascade above will reverse.

Particulate Carbon Fluxes

We start our study with the canonical Martin Curve, presented in Fig. 1.

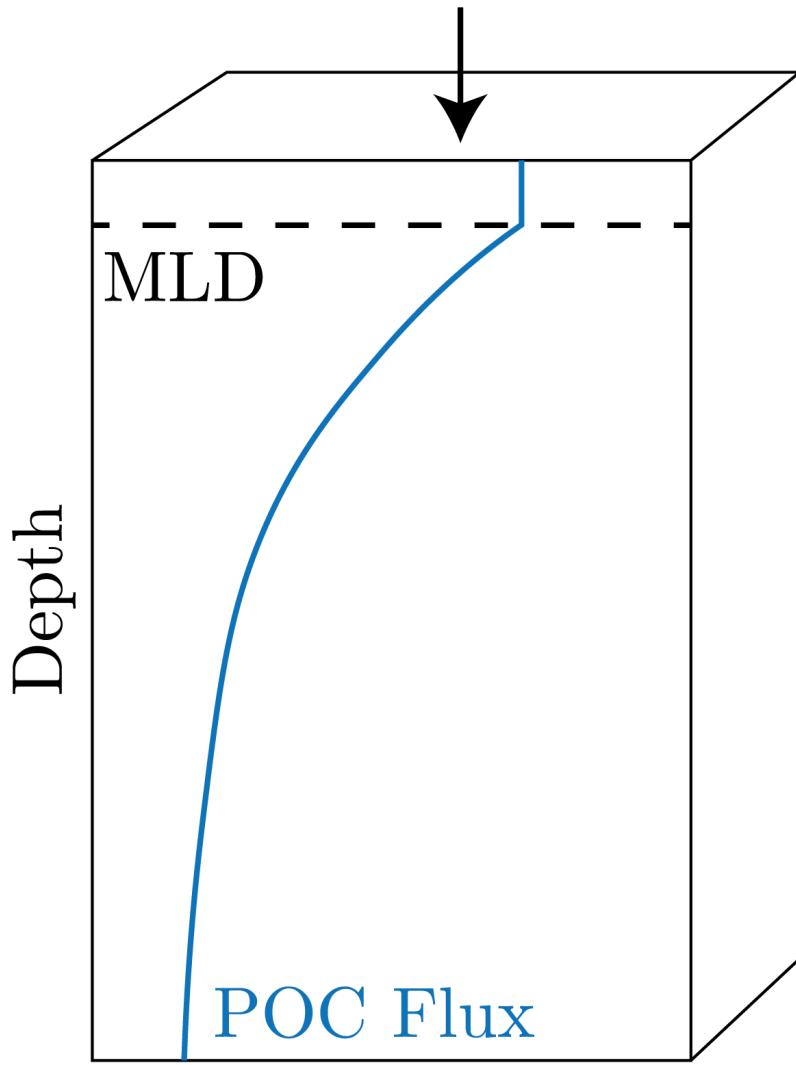


Fig. 1: The canonical Martin curve.

We can describe this as:

$$\phi(z) = \phi(z_0) \left(\frac{z}{z_0} \right)^{-b},$$

which is a power law. We can then say that this resembles our OUR as it is the utilization of oxygen by the particles described by the Martin curve. As the water mass ages, we get that in the surface ocean the AOU goes up as O₂ goes down at the same depth in the ocean in steady state. In the deep ocean we have that the AOU is lower and then given the transport oxygen will go up again (the regimes discussed in the previous lectures).

Drivers of Sinking Particles

Fundamentally, we have that the buoyancy force is less than the gravitational force. We can write this down in terms of densities in [kg m⁻³]:

$$\begin{aligned}\rho_{\text{org}} &\sim 1060 \\ \rho_{\text{CaCO}_3} &\sim 2710 \\ \rho_{\text{litho}} &\sim 2710 \\ \rho_{\text{opal}} &\sim 2710.\end{aligned}$$

The last three are so dense that we call those particles **ballast**. Therefore, the composition of the particles in these types is going to change the density and therefore the buoyancy.

Definition (Stokes' Law). *The terminal velocity experienced by a spherical particle in a fluid is given by:*

$$w_{\text{sink}} = \frac{2}{9} \frac{gr^2}{\mu} (\rho_{\text{part}} - \rho_{\text{sw}}),$$

for low **Re** numbers (that is, in a laminar flow), defined in this case as:

$$\text{Re} = \frac{wD}{\nu} = \frac{wD\rho_{\text{sw}}}{\mu},$$

for ν and μ the kinematic and dynamic viscosities.

Proof. We now give a proof sketch now by first assuming that the drag for a sphere is:

$$F_d = \frac{1}{2} \rho_{\text{sw}} v^2 C_d A.$$

At low **Re** we know that $C_d = 24/\text{Re}$. We can then substitute this all in, we get:

$$F_d = \frac{1}{2} \rho_{\text{sw}} v^2 \frac{24\mu}{v^2 r \rho_{\text{sw}}} \pi r^2 = 6\pi\mu r v.$$

We then define the buoyancy net force as:

$$F'_g = \frac{4}{3} \pi r^3 g (\rho_{\text{part}} - \rho_{\text{sw}}).$$

Then, at terminal velocities we have that these forces are equal, and then get:

$$6\pi\mu r w_{\text{sink}} = \frac{4}{3} \pi r^3 g (\rho_{\text{part}} - \rho_{\text{sw}}).$$

Solving for w_{sink} we get our answer.

We can say that the faster the sinking velocity, the better the record is preserved.

12.742: Lecture 10

The Carbon Cycle and OMZs

Particles

In the Martin curve, there is an important tuned parameter b , which as a global average is about $b = 0.86$. We can derive this equation by assuming $\partial_z w_{\text{sink}} = kz$, and then solve the DE. This b we get from this solution really changes based on the composition of the particle, with that being more energetically favourable being the most important characteristic. From Stokes' Law we say that really it is the density that drives the b .

We can also look at the size classes of particles, and see a nearly linear decrease over nearly 10 orders of magnitude in both size and number, showing that the smaller the particle the more likely it is in the ocean. We can also see that this is the case through the water column as well. Surely we see that there is an order of magnitude greater value of DOC in the ocean than POC, which we can see comparing POC to TOC plots of the ocean. However, we note that this DOC is not energetically preferable to the organisms compared to the POC, i.e., the "beer and broccoli" analogy. This divides labile (favourable) to refractory/recalcitrant (non-favourable) carbon particles.

One exciting new idea is "chemotaxis", that is that there is a "trail" of nutrients behind particles that organisms can follow. We could call this as a "chemi-attractant".

Elemental Cycles

We can see the relation of all of these cycles together in Fig. 1.

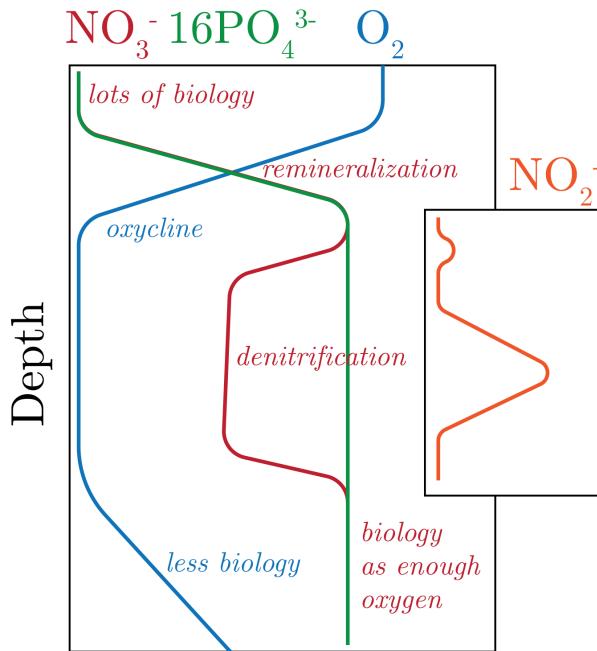


Fig. 1: A profile of three important nutrients.

Oxygen

OMZs mostly occur in the ETNP, ETSP, and the Arabian Sea. These are caused by high productivity and low transport.

Nitrogen

Of interest to us is why we do not see the amount of denitrification due to anammox (which is about 30%), rather a larger number. This is from nitrite. We can see in the inset plot of Fig. 1 above that the first maximum is due to chlorophyll whereas the second one is due to anoxic environments, such as in OMZs. Nitrous Oxide, N₂O, correlates 1:-1 with oxygen, as when you consume oxygen you produce nitrous oxide. N has a 3 [kyr] residence time.

Fe

Mostly supplied by the semi-arid Sahel dust. This is massively limiting nutrient and is a driver for N fixation, as well as a cofactor for many enzymatic reactions, which generally increase productivity. We have "the iron hypothesis", in which more Fe in the high latitudes leads to more productivity that sinks and therefore the concentration of carbon dioxide goes down. This is supported by ²³²Th records and is really driven by the

dust flux and wind conditions, though you have to be careful with the vapour pressure, as this will affect the rainout and it's respective distribution. Organisms have an ability to regulate how much iron they use, when, and where.

P

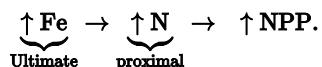
Similar to Fe, P is supplied by dust to the ocean with a 50 [kyr] residence time.

ENSO

During ENSO, we have a deeper thermocline and thus more stratification, which means that there will be less nutrient transport and less productivity. This is contrasted against La Nina, which is a wind intensification and we see the opposite effect.

Limitation

There is a difference between proximal and ultimate limitation:



We could also say that instead of Fe we have P. The ultimate definition is timescale dependent. For instance, many geochemists do not consider N to be limiting, as it has an atmospheric reservoir. However, biologists will consider it limiting because on short timescales it does matter, though on longer timescales this is not the case given the equilibration with the atmosphere.

12.742: Lecture 11

ODV

There is no content for this lecture, as we were introduced to Ocean Data View (ODV).

12.742: Lecture 12

Thermodynamics in Seawater

Gibbs Free Energy

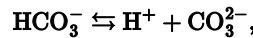
For chemical reactions, we can define:

$$\Delta G = \sum G_{prof} - \sum G_{react} = \sum_i v_i \mu_i,$$

where v_i is the stoichiometric coefficient and μ_i the chemical potential. This is the change in free energy or the chemical work that is being done in the system.

An Example

As an example, we can take:



then we have that:

$$\Delta G^0 = \mu_{\text{H}} + \mu_{\text{CO}_3^{2-}} + \mu_{\text{HCO}_3^-}.$$

The factors that contribute to our potential are:

1. concentrations
2. chemical nature ($G^0, \Delta G^0, \mu^0$)
3. interactions between species, such as non-ideal (like seawater)

We can define:

$$\mu_i = \mu_i^0 + \underbrace{RT \log [i]}_{\text{concentration}} = \mu_i^0 + RT \log a_i,$$

where we define the activity as:

$$a_i = \gamma_i [i] = \{i\},$$

for γ_i the activity coefficient.

$$\Delta G = \mu_{\text{H}} + \mu_{\text{CO}_3^{2-}} + \mu_{\text{HCO}_3^-} + RT \log \left[\frac{a_{\text{H}} a_{\text{CO}_3^{2-}}}{a_{\text{HCO}_3^-}} \right] = \Delta G^0 + RT \log Q,$$

where we note that Q is the ratio of reactants over products. Now, at equilibrium, we know that $\Delta G = 0$ (i.e., we are at a steady state). Therefore, we can rearrange to get:

$$Q = \exp [-\Delta G^0 / RT] = K_{eq},$$

which, at our equilibrium, is our reaction coefficient. Now, to tackle the activity coefficients, we note that:

$$\mu_i = \mu_i^0 + RT (\log \gamma_i + \log [i]).$$

These are super significant as they drive reactions in seawater, as there are myriad reactions going on. In seawater, the major driving force is the ionic strength of seawater. Typically, we can relate:

$$\log \gamma_i \propto \sqrt{I},$$

for I the ionic strength defined as:

$$I = \frac{1}{2} \sum_i [i] z_i^2,$$

for z_i the charge of i . As some examples, we know:

1. 1.0 M NaCl: $I = 1$
2. 1.0 M MgCl₂: $I = 3$

3. SW: $I \sim 0.7$

There are few things that we now recall:

1. Debye-Hückel: $\log \gamma_i = -Az_i^2 \sqrt{I}$, for $I < 0.01$ M
2. Davies (ion-ion): $\log \gamma_{\pm} = -Az_+ z_- \left(\frac{\sqrt{I}}{1+\sqrt{I}} \right) - bI$, for $I < 0.5$ M
3. Pitzer: super complicated, but the gold standard for $I <$ saturation

Now, we are going to define the thermodynamic equilibrium constant:

$$K_{thermo} = \frac{a_H a_{CO_3^{2-}}}{a_{HCO_3^-}} = \frac{\gamma_{H^+} [H^+] \gamma_{CO_3^{2-}} [CO_3^{2-}]}{\gamma_{HCO_3^-} [HCO_3^-]}.$$

Then, we can define the concentration equilibrium constant as:

$$K_{conc} = \frac{[H^+] [CO_3^{2-}]}{[HCO_3^-]},$$

which allows us to define:

$$K_{thermo} = \frac{\gamma_{H^+} \gamma_{CO_3^{2-}}}{\gamma_{HCO_3^-}} K_{conc}.$$

Now, the issue here is that electrodes, which is what we use to measure things in the lab, measure the activity not the concentration of H^+ ions. To combat this, we define the "mixed acidity constant" for freshwater as:

$$K' = \frac{a_{H^+} [CO_3^{2-}]}{[HCO_3^-]} = K_{thermo} \frac{\gamma_{CO_3^{2-}}}{\gamma_{HCO_3^-}}.$$

What we note is that we have only treated these as individual and not as species that are able to form ion-ion pairs. There are a few kinds of bonds:

1. Direct ion pair: coulombic ion pair, such as for Na^+ and Cl^-
2. Hydration sphere contact: localized hydrolysis, which is a water separated ion pair
3. Shared hydration sphere: water-like sharing

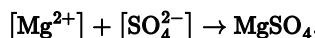
Ion Pairing

Magnesium Ion

Let's take an ion:

$$[Mg^{2+}]_T = [Mg^{2+}] + [MgOH^+] + [MgCO_2] + \dots$$

This then means that $[Mg^{2+}] \neq [Mg^{2+}]_T$. As an example:



Then, we can say that:

$$K_{MgSO_4} = \frac{\{MgSO_4\}}{\{Mg^{2+}\} \{SO_4^{2-}\}} \simeq 12.9.$$

Therefore, apply our definition of the equilibrium constant from above, we get that:

$$\{MgSO_4\} \simeq 12.9 \{Mg^{2+}\} \{SO_4^{2-}\}.$$

In order to get these values from the 1960s, there was a large minimization problem following:

1. Assume (wrongly) that $[Mg^{2+}]_T = [Mg^{2+}]$, the free species
2. Then, to correct this, form $[MgSO_4]$ and add this back into $[Mg^{2+}]_T$, which was not larger than the observed value
3. Next, adjust the free ion until
4. Convergence was reached for all species

The free species activities are what drive much of the chemistry within the ocean. Additionally, we see that Magnesium itself, given that the free species is at 87% abundance in the ocean, is a major catalyst for ionic interactions in the ocean. Importantly, over time, we note that these are not at steady state and very much change over time, such as between the LGM and now.

Carbonate Ion

We can start by defining:

$$\{\text{CO}_3^{2-}\} = \gamma_{\text{CO}_3^{2-}}^T [\text{CO}_3^{2-}]_T,$$

from which we can get:

$$\gamma_{\text{CO}_3^{2-}}^T = \gamma_{\text{CO}_3^{2-}} \frac{[\text{CO}_3^{2-}]}{[\text{CO}_3^{2-}]_T} \simeq 0.02.$$

Comparing to Seawater

We again define for freshwater:

$$K'_{a_2} = \frac{\{\text{H}^+\} [\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = K_{\text{thermo}} \frac{\gamma_{\text{CO}_3^{2-}}}{\gamma_{\text{HCO}_3^-}}.$$

Now, we set for seawater:

$$K_{a_2}^{\text{app}} = K_{a_2}^* = \frac{\{\text{H}^+\} [\text{CO}_3^{2-}]_T}{[\text{CO}_3^-]_T} = K'_{a_2} \frac{\gamma_{\text{CO}_3^{2-}}^T}{\gamma_{\text{HCO}_3^-}^T} \simeq 10^{-8.88}.$$

Contrast this with: $K'_{a_2} \simeq 10^{-10.33}$. That's more than an order of magnitude difference! We can then compare:

$$\frac{[\text{CO}_3^{2-}]_T}{[\text{HCO}_3^-]_T},$$

which shows us that at pH = 8, we have that freshwater is better at buffering than seawater as in seawater we are already more saturated in carbonate ion than freshwater.

12.742: Lecture 13

Carbonate System I

The Carbon Budget

The following are important reservoirs of carbon in the Earth system in [GT]:

1. Deep ocean: 37100
2. Fossil fuels: 3700
3. Terrestrial: 2300
4. Upper ocean: 900
5. Atmosphere: 597
6. Surface sediments: 150
7. Marine biota: 3

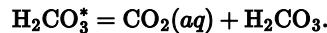
Despite the small biota contribution that is cycling, the actual fluxes are massive.

The Carbonate System in Seawater

We define the total carbon as:

$$C_T = T_{\text{CO}_2} = \sum \text{CO}_2 = \text{DIC} = [\text{H}_2\text{CO}_2^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}],$$

where we define carbonic acid as:



The equilibrium is given by:



We get that, for the conditions of seawater (i.e., pH and carbonic anhydrase) only about 0.15% of H_2CO_3^* is actually H_2CO_3 . Therefore, this term only contributes carbon dioxide. We can then define the activity coefficients as:

$$K_{a_1}^* = K'_{a_1} \frac{\gamma_{\text{H}_2\text{CO}_3}^T}{\gamma_{\text{HCO}_3^-}^T} \quad \text{and} \quad K_{a_1}^* = K'_{a_1} \frac{\gamma_{\text{HCO}_3^-}^T}{\gamma_{\text{CO}_3^{2-}}^T},$$

where we have that the primes represent the freshwater activity coefficients. We next remember our concentration equilibrium constants as:

$$K_{a_1} = \frac{[\text{H}^+] [\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3^*]} \quad \text{and} \quad K_{a_2} = \frac{[\text{H}^+] [\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}.$$

We can put some numbers on these as:

$$\begin{aligned} pK_{a_1} &: 6.3, 6.0 \\ pK_{a_2} &: 10.3, 8.9 \end{aligned}$$

for freshwater, saltwater. We define:

$$pK_a = -\log K_a,$$

which goes like pH with acidity, and as a refresher:

$$pH = -\log [\text{H}^+].$$

The DIC System in $\log [C]$ -pH Space

The result is presented in Fig. 1.

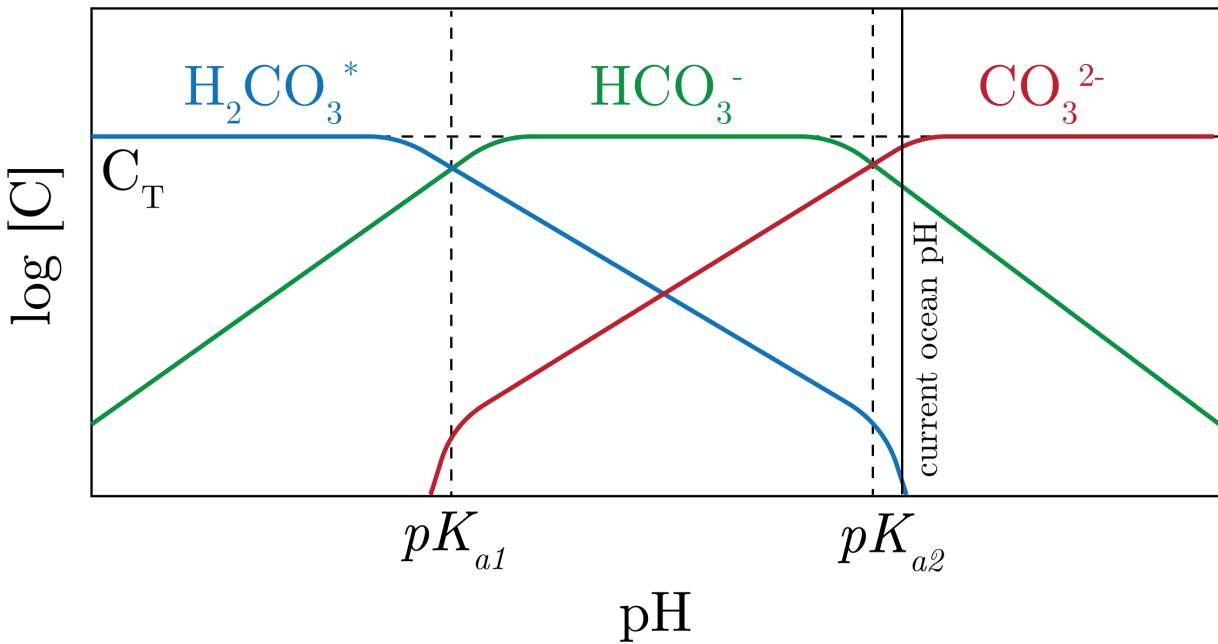


Fig. 1: The DIC system in $\log [C]$ -pH space.

We can start to design this as follows:

$$\begin{aligned}
 pH = pK_{a_1} : pH - pK_{a_1} = 0 &\Rightarrow \frac{K_{a_1}}{[H^+]} = \frac{[HCO_3^-]}{[H_2CO_3^*]} = 1 \\
 pH < pK_{a_1} : pH - pK_{a_1} < 0 &\Rightarrow \frac{[HCO_3^-]}{[H_2CO_3^*]} \ll 1 \Rightarrow C_T \simeq [H_2CO_3^*] \\
 pH = pK_{a_2} : pK_{a_2} - pH = 0 &\Rightarrow \frac{K_{a_2}}{[H^+]} = \frac{[CO_3^{2-}]}{[HCO_3^-]} = 1 \\
 pH > pK_{a_2} : C_T &\simeq [CO_3^{2-}]
 \end{aligned}$$

Then, for $[HCO_3^-]$, we have that for $pH < pK_{a_1}$, where we assume the second equation from above substituted into the first:

$$\frac{K_{a_2} C_T}{[H^+]} = [HCO_3^-],$$

and taking the log of both sides gives:

$$\log [HCO_3^-] = \log [K_{a_1} C_T] + pH$$

Therefore, we get that $[HCO_3^-]$ in this regime has a slope of 1 with pH . We can do this for $[CO_3^{2-}]$ for $pH \in [pK_{a_1}, pK_{a_2}]$ and get the same 1:1 relationship with pH . For $[CO_3^{2-}]$ at $pH < pK_{a_1}$, we get, using our definition of pK_{a_2} and substituting in our value for $[HCO_3^-]$ from above:

$$\frac{C_T K_{a_1} K_{a_2}}{[H^+]^2} = [CO_3^{2-}].$$

Taking the log we then get:

$$\log [CO_3^{2-}] = \log [C_T K_{a_1} K_{a_2}] + 2pH,$$

which is a slope of 2 with pH . Now, we can do this for $[H_2CO_3^*]$ for $pK_{a_1} < pH < pK_{a_2}$ to get:

$$\log [H_2CO_3^*] = \log [H^+] + \log \left[\frac{C_T}{K_{a_1}} \right],$$

which is a slope of -1 with pH . We can do this for all configurations to get corresponding slopes of ± 1 and ± 2 . An important note is how low the carbon dioxide/carbonic acid is at the current ocean pH , therefore we have that small changes in the pH of the ocean have a large change in atmospheric composition of carbon dioxide, as well as the ocean's.

Alkalinity

Alkalinity, for a geologic perspective, is the ocean's ability to balance the discrepancy in charge of the major ocean ion compositions. This is to say that alkalinity is the ocean's charge balance. This isn't always the best way of thinking of alkalinity. There are a few acid-base pairs that matter for

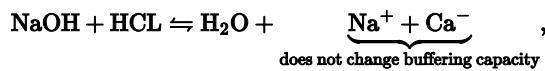
seawater, that is where the concentration is high and the K_a 's are near the pH of seawater:

1. $[\text{HCO}_3^-]$ and $[\text{H}_2\text{CO}_3^*]$
2. $[\text{B}(\text{OH})_4^-]$

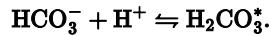
Some that don't work are:

1. H_2SO_4 , as the K_a 's are too low
2. NH_4^+ as the concentration is too low (though OMZ's might be high enough)
3. H_4SiO_4 as the K_a 's are too low
4. H_3PO_4 as the concentration is too low
5. H_2S as the concentration is too low (but might care about in porewaters)

Another way of thinking about this is by looking at plots like for the carbonate system above for these species. For seawater carbonate equivalence points of $pH \in [2, 5]$, we look at the dominant ion for each species. Therefore, the most number of H^+ protons that can be accepted by each is, at most, the deficit from this dominant species to any other species in that regime. This is why we cannot think of alkalinity as the total number of protons that the ocean can accept, rather the total number of ions that the ocean can accept given the pH and dominant specie-dynamics. Alkalinity is always relative to the carbonate / CO_2 equivalence point in seawater (as it is the carbonate system that is our reference). We can use the phosphate system as an example of this, in which the neutral species is not the dominant species at the CO_2 equivalence point and therefore protons added is not relative to that neutral point. We care about the equivalence point in natural waters, which we determine from titration as the inflection point of the pH with the volume of the acid added. Here, this is where the acid added is equal to the extra base in the solution. For example:



The sodium and chloride ions do not change the buffering capacity of the water because of our definition of pH . To relate this to seawater, we have that HCO_3^- is about 90% of all DIC in seawater, so we care about designing our understanding of alkalinity around this instead of water, given by:



At the equivalence point here, we get that $[\text{HCO}_3^-] = [\text{H}^+]$. For natural waters, we have that it is nearly impossible to have a neutral pH , which only occurs in a strong acid-base system. In general, we define alkalinity to some reference, which in seawater we have defined as the carbonate system.

An Important Note

We can see in our example above that adding sodium and chloride to our system does not change the buffering capacity, the same thing is for H_2CO_3^* . Therefore, this is why adding or removing carbon dioxide does not change the ocean's alkalinity.

Total Alkalinity

We define this as:

$$TA = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] + [\text{B}(\text{OH})_4^-] + [\text{HS}^-] + 2[\text{S}^{2-}] - [\text{H}_3\text{PO}_4] + [\text{HPO}_4^{2-}] + 2[\text{PO}_3^{2-}].$$

In reality, we really are interested in the carbonate-borate system, given that these are the most dominant species in sea water from our discussion above. The pros of alkalinity:

1. It is linearly mixable
2. It is measurable by titration
3. It adds another constraint to the ocean system

The most rigorous definition is the amount of bicarbonate ion such that its concentration is equal to the amount of H^+ ion.

12.742: Lecture 14

Carbonate System II

Governing Equations

We define the total carbon in our system (inorganic) as:

$$DIC = C_T = [\text{H}_2\text{CO}_3^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}].$$

Then, to relate these things together we define the equilibrium constants, or the disassociation constants:

$$K_{a_1} = \frac{[\text{H}^+] [\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3^*]} \quad \text{and} \quad K_{a_2} = \frac{[\text{H}^+] [\text{CO}_3^{2-}]}{[\text{HCO}_3^-]},$$

and we additionally define the disassociation constant for water:

$$K_w = [\text{H}^+] [\text{OH}^-].$$

This is an underdetermined system, as there are 4 equations and 5 unknowns. Therefore, we define alkalinity to solve this:

$$TA = [\text{HCO}_3^-] + 2 [\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+],$$

which then gives a determined system. We can do the same thing for the borate system:

$$B_T = [\text{B(OH)}_3] + [\text{B(OH)}_4^-] \sim f(S),$$
$$K_B = \frac{[\text{B(OH)}_4^-]}{[\text{H}^+] [\text{B(OH)}_3]}.$$

where we have stated that borate scales with salinity, i.e., it is conservative in seawater (which breaks down near freshwater inputs). This is again a determined system. Therefore, as long as we solve for total alkalinity, total carbon, and salinity, we can solve our system of equations. So, we can continue to expand our definition, but we need to have some knowledge of the constants in order to solve our equation. This all breaks down with organic acids, as we do not know a good handle on these constants. Importantly, we note that:

$$[\text{H}_2\text{CO}_3^*] = K_H p\text{CO}_2,$$

where we assume, as before, that $[\text{H}_2\text{CO}_3^*] \simeq [\text{CO}_2]$.

Now, we can think of this as only having to measure two of the following to solve for the rest:

$$C_T, A_T, pH, p\text{CO}_2.$$

This then implies that it can really be the total alkalinity and inorganic carbon that drives the carbon dioxide concentrations in the surface ocean, and thus the atmosphere.

A note on notation is that μ_{eq} is equal to the charge equivalent at carbon dioxide equivalence point.

Contouring Solutions

When comparing our contoured solutions of C_T and A_T against pH and $p\text{CO}_2$, we note a few things. First, the system is shifted toward A_T , that is there is more alkalinity than there is total carbon (which we can get from the definitions of these quantities above). Second, we can see that we can increase C_T via the addition of CO_2 , which increases pH but alkalinity remains the same. This is ocean acidification, as the dissociation of CO_2 forms H^+ but forms equal amounts of H^+ ions to their receptors, H_2CO_3^* and CO_3^{2-} , which "cancels" out the contribution, keeping alkalinity constant. Additionally, we note that if we bring a parcel of water from the deep into contact with the equilibrium values in the surface ocean, then it will have to equilibrate correspondingly (lose or gain based on values relative to the equilibrium value). We can look at the different processes that drive us moving around on these contours as in Fig. 1.

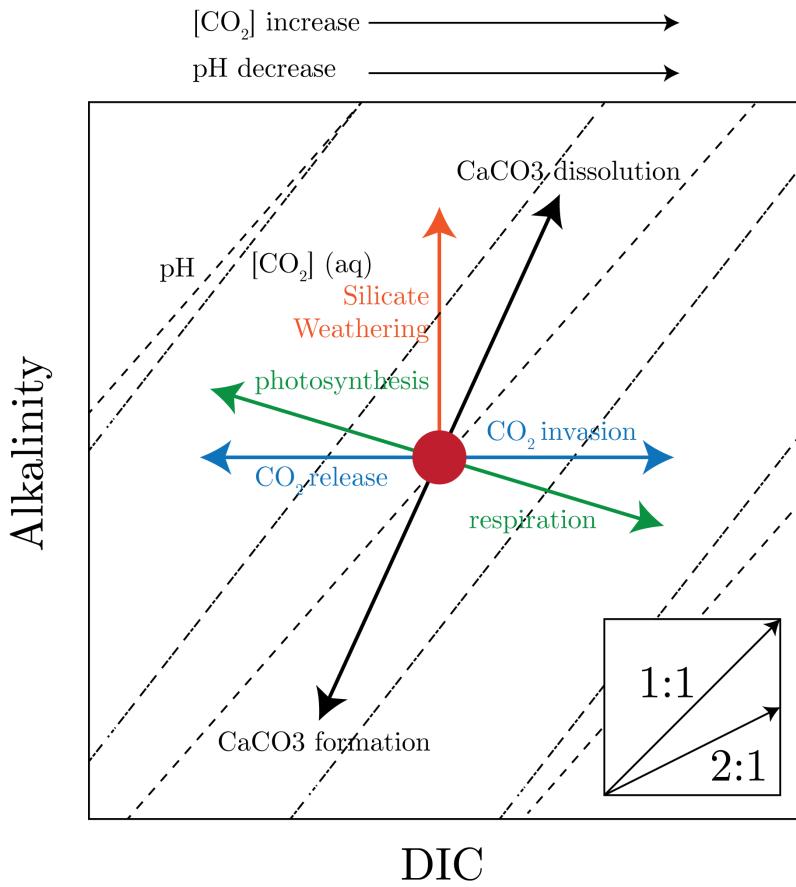


Fig. 1: Vectors representing different processes that move us around contoured solutions of C_T and A_T .

We note a few things here. First, we can increase DIC with increasing ocean acidification, which leaves alkalinity unchanged and reduces pH . Second, photosynthesis removes CO_2 , thus changing DIC, with the slope having to do with the oxidation and reduction of nitrogen in the formation of organic compounds from nitrate which consumes protons (increasing alkalinity). The opposite is the case for respiration, in which the production of nitrate via the oxidation of organic nitrogen produces protons, which decreases alkalinity and increases DIC. The slope here is also dependent on the Redfield ratio. Third, we note the different slope of the calcium carbonate vectors, the most important application being that increasing coral coverage (and thereby increasing CaCO_3 formation) will increase $p\text{CO}_2$ by increasing $[\text{CO}_2]$ concentrations and decreasing pH . The way to actually decrease $p\text{CO}_2$, we have to add alkalinity to decrease these vectors, which is CaCO_3 dissolution. We derive these slopes now.

Processes that affect Alkalinity and DIC

We list the processes and their slopes now:

| Process | ΔA_T | ΔC_T |
|---|-------------------|--------------|
| CO_2 solition | 0 | +1 |
| CO_2 degassing | 0 | -1 |
| Photosynthesis: $\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_2\text{O} + \text{O}_2$ | $r_{\text{N:C}}$ | -1 |
| Respiration | $-r_{\text{N:C}}$ | +1 |
| Calcification: $\text{Ca}^{2+} + \text{CO}_3^{2-} \rightarrow \text{CaCO}_3$ | -2 | -1 |
| CaCO_3 Dissolution | +2 | +1 |
| Silicate Weathering: $\text{H}_2\text{O} + 2\text{CaSiO}_3 + 2\text{CO}_2 \rightarrow 2\text{Ca}^{2+} + 2\text{HCO}_3^- + \text{SiO}_2$ | +2 | 0 |

We note for calcification that it is an important processes for the oceans, as many organisms such as coccolithophores use it to produce shells, and about 80% of surface carbon is calcium carbonate and 20% is organic carbon. Silicate weathering is extremely important for alkalinity enhancement which then means that we can take up more CO_2 , and drives a cooling feedback. Now, we can map all of this onto the oceans, as we have done in Fig. 2.

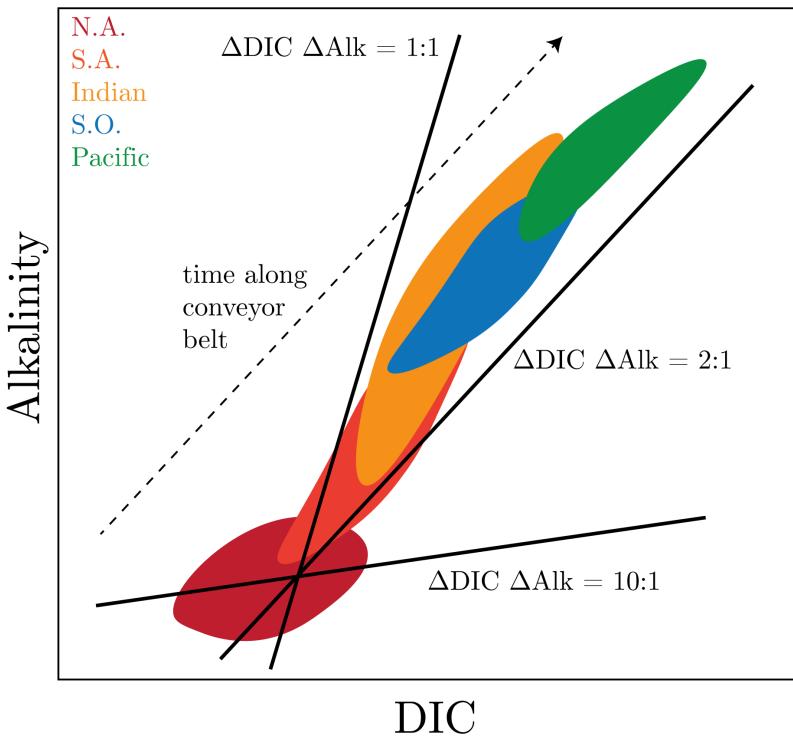


Fig. 2: How we can map the global oceans, and the time along the global conveyor belt, into this space of C_T and A_T .

We explain this chart now. We start in the North Atlantic, the beginning of the conveyor belt. The lowest DIC and Alkalinity in the ocean. As the water subducts, organic material in the surface rains down and gets remineralized, increasing nitrate, phosphate, and DIC concentrations. In so doing, alkalinity will be changed, especially if there are calcium carbonate shells being remineralized. As we move along the conveyor belt, we are increasing the dissolved calcium carbonate concentrations in the water in carbon units. We can see that the addition of alkalinity and DIC to seawater mostly falls in the 1:1 and 2:1 in the global ocean, which means that there is more organic material being remineralized than calcium carbonate (i.e., organic matter goes into DIC at a greater rate than alkalinity). Next, we can look at these ratios in our Fig. 1 plot. This means that as we move along the conveyor belt, we are remineralizing more organic matter, so that we are pushed along the 2:1 line, which means that we are pushed into lower pH and higher pCO_2 regimes, as the water accumulates that carbon. In the 1:1 case, we are much closer to constant contours of pH and pCO_2 , however there is still a slight increase. These vectors can be decomposed into respiration and CaCO_3 vectors shown:



and



This is to say that it is the dissolution of CaCO_3 in the ocean that reduces the impact of respiration, and is thereby the major stabilizing feedback that allows the ocean to moderate a near constant pH through time. The 1:1 ratio comes up in organic carbon flux to CaCO_3 and opal (inorganic), showing that this dissolution is really a predominate factor in the ocean.

Global Distribution

We note that one reason the ocean is able to store so much CO_2 is because of the stratification between the deep ocean and the surface ocean, such as through the thermocline. We can see that we have degassing in regions of upwelling, which breaks down this stratification. The result is that the ocean has been able to take up about 25% of all anthropogenic CO_2 emissions. The distributions of this is in regions of low upwelling, so that that water is not equilibrated with the surface oceans and atmosphere. This can be seen in transport studies, in which we can artificially impose sequestration at different depths, with the greatest sequestration times occurring at deep (stratified) depths.

The Biology

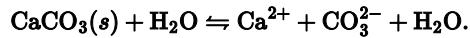
There are a few important organisms that make CaCO_3 :

1. Coccolithophors: calcite
2. Foraminifera: calcite
3. Pteropods: aragonite

There is a 5:1 ratio of Mg to Ca ions in the ocean, both of which can form with carbonate. This all has to do with the dynamics of the system, from which we can see that CaCO_3 is the most stable (with, given the different structures, calcite being more stable than aragonite), despite the fact that it is less abundant therefore it is preferred to be incorporated by biology.

Calcium Carbonate Dynamics

We consider the reaction:



We can define the solubility product as:

$$K_{sp}^* = \frac{k_f}{k_r} = \frac{([\text{Ca}^{2+}] [\text{CO}_3^{2-}])_{eq}}{\{\text{CaCO}_3\}},$$

where we define: $\{\text{CaCO}_3\} = 1$. We can then define:

$$\Omega = \frac{[\text{Ca}^{2+}] [\text{CO}_3^{2-}]}{K_{sp}^*}.$$

Greater, equal, and less than 1 defined as supersaturated, equilibrium, and undersaturated. Dissolutions moves in whatever direction to get to equilibrium (oversaturated means dissolution toward equilibrium). As $[\text{Ca}^{2+}]$ is basically conservative in seawater, we can define:

$$\Omega \simeq \frac{[\text{CO}_3^{2-}]}{[\text{CO}_3^{2-}]_{sat}},$$

which allows us to define:

$$\Delta\text{CO}_3 = [\text{CO}_3^{2-}] - [\text{CO}_3^{2-}]_{sat},$$

where we can similarly define greater than 0 as supersaturated and less than 0 as undersaturated. Some profiles are presented in Fig. 3.

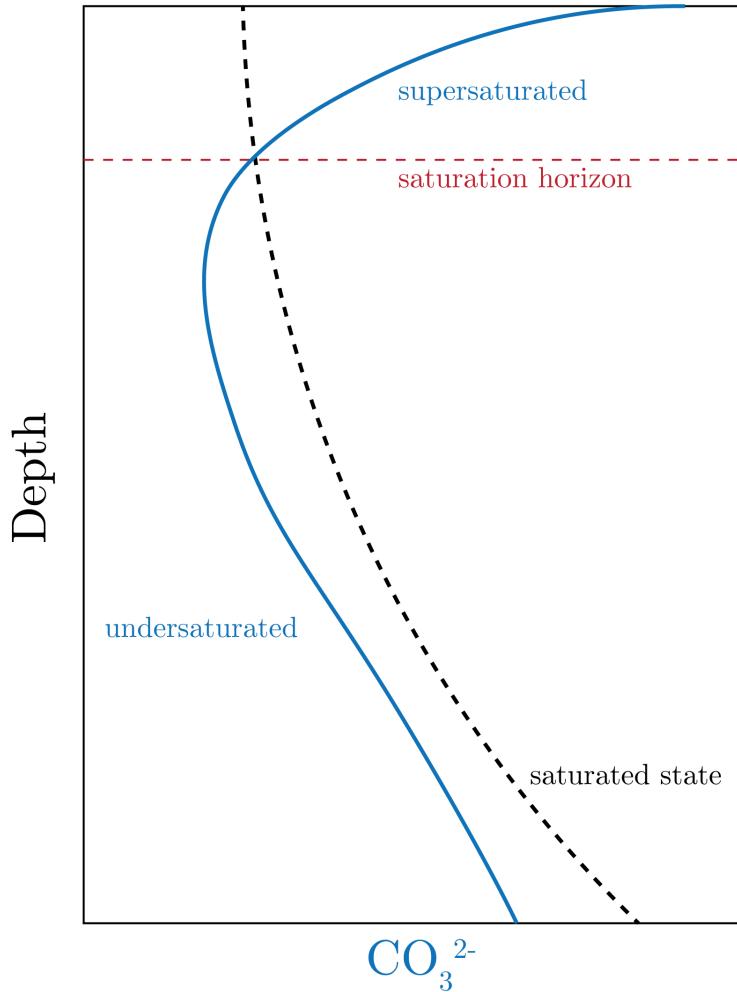


Fig. 3: Profiles of CO_3^{2-} in different regimes of saturation for calcite.

We can see from Fig. 3 most of the surface ocean is supersaturated for calcite. This is where we see most of the calcification, at the ocean surface, which thermodynamically makes sense to reach equilibrium (as discussed previously). As we go deeper, we see the carbonate ion going down, which is the biological carbon pump which respires organic matter, producing CO_2 . We then are pushed toward equilibrium with depth. Note that calcite becomes more soluble with depth, which is the pressure effect in play, that causes the saturation curves to be non-linear. The saturation horizon is much lower along the conveyor belt, as there is more carbonate ion in the water given the accumulation of the respire organic matter. We

note that aragonite has a higher saturation state than calcite. We can look at sediment CaCO_3 maps and see that they look more than bathymetry more so than productivity. This comes from the fact that it is really depth that dictates how much CaCO_3 is in sediment, much like the snow line on a mountain (as calcium carbonate is a light mineral). We can make depths of sediment values and see that they show there is something else at play.

We define a few terms to understand this. First, we define the **lysocline** as the depth range over which % CaCO_3 decreases sharply (decrease from 80-90% to 5-10%). Next, we define the **calcite compensation depth** is the depth at which the calcite rain is balanced by dissolution of CaCO_3 out of the sediments, which can be locally or globally defined. We can then define this mathematically as:

$$F_{\text{burial}} = F_{\text{rain}} - F_{\text{dissolution}} = 0.$$

This term allows us to account for sedimentation of calcite globally, or we could have it as a reference to the N. Pacific, which is the end of the conveyor belt and therefore the most calcite/mineralized organic material.

Kinetics of CaCO_3

From our above equations for CaCO_3 dissolution, solubility product, and Ω , we can move away from thermodynamics to kinetics to get a rate:

$$R_{\text{diss}} = k_f[\text{CaCO}_3] - k_r [\text{Ca}^{2+}] [\text{CO}_3^{2-}] = 0,$$

assuming equilibrium. Then, assuming the solid CaCO_3 is 1, we get that:

$$R_{\text{diss}} = k_f(1 - \Omega),$$

which says that our dissolution rate is going to be linear with $(1 - \Omega)$. There are a number cool power laws that we can get from data, for instance putting highly polished calcite spheres in the ocean at different depths to get the dissolution rates. The result is a set of power laws of the form:

$$R_{\text{diss}} = k_f(1 - \Omega)^n,$$

for n the range of power laws. Recent work has shown that there are three regimes: homogeneous, defect-assisted, and step retreat, which are physical chemical terms to do with the matrix of CaCO_3 .

CaCO_3 Ocean Budget

We have that the shallow CaCO_3 dissolution is needed in order to balance the CaCO_3 budget in the ocean, largely driven by biology. As CaCO_3 is heavy, this sinks well, and it is therefore a good way of sequestering carbon in the deep ocean.

12.742: Lecture 15

MATLAB and CO2SYS

There is no content to this lecture as we covered MATLAB and CO2SYS basics.

12.742: Lecture 16

Gas Exchange

Air-Sea Gas Exchange

We can define the difference between the atmosphere and the ocean:

$$\Delta [O_2] = ([O_2]_{atm} - [O_2]_{oc}).$$

This gradient drives the passive diffusion of gases. We then define Henry's Law:

$$p_A = \chi_A P,$$

and solubility, S :

$$C_A = S_A p_A.$$

We can define the fugacity to capture the non-ideality of gases to get:

$$S_A \sim f_A = \phi_A p_A,$$

for ϕ_A acting like the activity coefficient γ we have encountered previously.

Stagnant Film Model

The setup is presented in Fig. 1

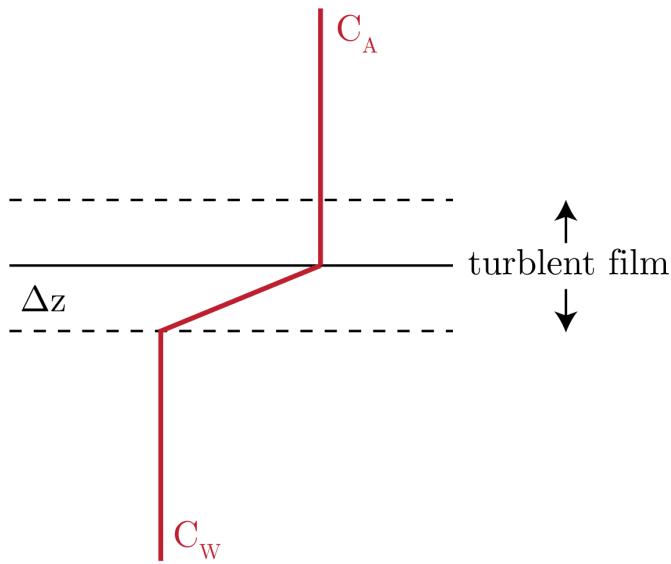


Fig. 1: The stagnant film model for gas exchange.

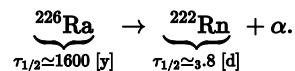
We start by defining Ficks' First Law:

$$F = D \partial_z C \simeq D \frac{C_A - C_W}{\Delta z} = k_w (C_A - C_w).$$

We define k_w as the piston velocity or the gas transfer velocity which we say is about $3 \text{ [m d}^{-1}]$ and D the diffusivity.

Estimation of Piston Velocities

We first want to estimate Δz , for which we use the:



Then, for this model we assume that the gas loss via gas transfer is balanced by radioactive production. We then use the model as follows:

$$^{222}\text{Rn flux} = \text{stagnant film flux},$$

which we then get as:

$$\text{MLD}(^{226}\text{A} - ^{222}\text{A}) = \frac{D_{\text{Rn}}}{\Delta z} ([^{222}\text{Rn}]_{\text{atm}} - [^{222}\text{Rn}]_{\text{oc}}).$$

Another way of thinking about this is that, as the parent-daughter relationship is not at equilibrium in the water column, this must be driven by some physical processes over the MLD, which we attribute solely to passive diffusion by Fick's First Law. The result from observational data is 40 [μm]... that is small! However, we note that there are a lot of things that can change this piston velocity:

1. wind speed
2. wave activity
3. T, S characteristics
4. surfactants

We need to balance:

1. diffusion of momentum, through the viscosity of seawater and the transport of new parcels of water to the surface
2. diffusion of gas in water

One way that we can understand all of these processes is through the Schmidt number, which we define as:

$$\text{Sc} = \frac{\nu}{D}.$$

From experiments, we know that:

$$k_w \sim \text{Sc}^{-n} u_{10}^m,$$

where we empirically derive n, m . Following this, we can see that we can get:

$$n = -\frac{\log [k_{w1}/k_{w2}]}{\log [\text{Sc}_1/\text{Sc}_2]},$$

where we define **1, 2** as two separate cases, with the reference **1** often being CO₂. For most of the ocean, we get that $n = 0.5$ and is constant across all ocean conditions. To get m , we just look at the transfer velocity as a function of windspeed in the ocean. To get the velocity, people have used bomb carbon as well as releasing tracers. Currently, people use an $m = 2$ quadratic dependency on wind speed. The equation we often use, to conclude, is:

$$k_w = 0.251 \langle u_{10} \rangle^2 \left(\frac{\text{Sc}}{660} \right)^{-1/2}.$$

However, these do not cover bubbles (which is what I conduct research on... guess it gives me a job, haha)!

Bubble Theory

There are two major kinds of bubble injection: complete and partial bubble dissolution. We can look at all of these processes within a vector diagram, as we do in Fig. 2

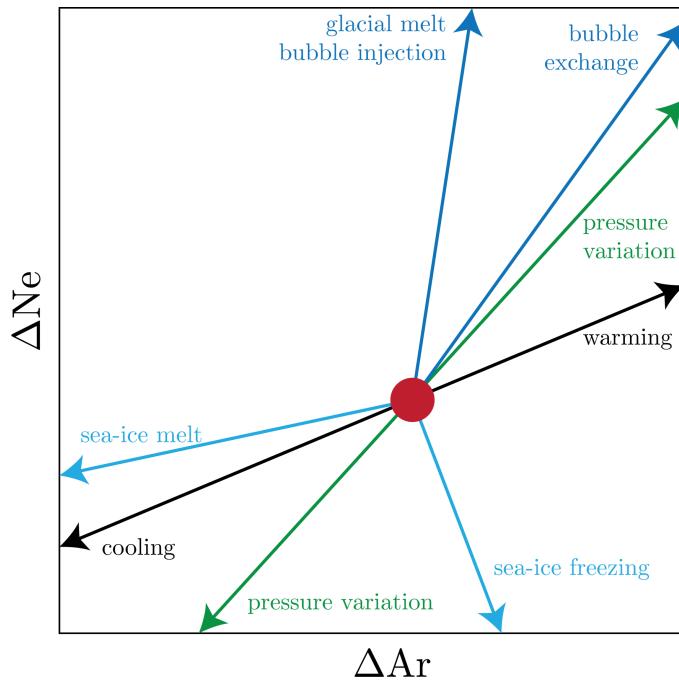


Fig. 2: Gas exchange processes and their effect on noble gas solubility anomalies.

Here, we define the solubility anomaly as:

$$\Delta C = \frac{C_{\text{meas}}}{C_{\text{eq}}} - 1.$$

Mixed Layer Dynamics

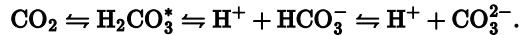
Now, we can calculate:

$$k_w = \frac{D}{\Delta z} \simeq \frac{10^{-5} [\text{cm}^2 \text{s}^{-1}]}{40 [\mu\text{m}]} = 3 [\text{m d}^{-1}].$$

Then, for the ML the residence time is:

$$\tau = \frac{50}{3} \simeq 2 [\text{weeks}],$$

for τ the residency time, or the time that it takes the concentration to get to $1/e$. This number is true for more ideal gases, and those that do not deal with the carbonate system. However, for CO_2 , we get that we have the carbonate system to deal with. Therefore, we have:



Now, we CO_2 , we define something called the Revelle Factor, which.

$$\text{RF} = \frac{\partial p\text{CO}_2}{\partial \text{DIC}} \frac{\text{DIC}}{p\text{CO}_2} \simeq \frac{\Delta p\text{CO}_2/p\text{CO}_2}{\Delta \text{DIC}/\text{DIC}} \sim 9 \text{ to } 10,$$

therefore we get that for the carbonate system that:

$$\tau^* = \text{RF} \tau \sim 5 [\text{months}].$$

We can plot the RF against carbonate ion and get that it decreases nonlinearly with carbonate ion concentration. We see that the RF increases with latitude, as there is more carbonate ion at lower latitudes on the coast of the US given that the high temperatures have more evaporation leads to greater alkalinity to DIC ratio, and thus a larger buffering capacity.

Carbonate System Residencies

We can calculate the residence time as:

$$\tau = \frac{\text{Inventory}}{\text{Flux}} \simeq 10 [\text{y}].$$

That is huge! We can look at the $\Delta^{14}\text{C}$ if different ocean water as a function of latitude, and we get a similar inverse relationship between water mass age and $\Delta^{14}\text{C}$, that is we get atmospheric deposition in the younger (Atlantic) waters and then the radioactive decay reduces the values as the water

masses are transported and get older. Another way that we can get these residence times is from CFCs, given the well known record we have in the atmosphere, and what we get is the best record we have for accumulation of anthropogenic carbon into the ocean. What we get is the younger water has more DIC in it, from the anthropogenic carbon!

12.742: Lecture 17

Isotope Geochemistry

Terminology

Isotopes are a difference in the number of neutrons in the nucleus, and this changes the relative abundances of each isotope. These behave singularly for every kind of element, that is C isotopes behave mostly similarly (i.e., C isotope doesn't function like N).

Notation

We define the ratio as:

$$R^{\text{heavy}} = \frac{\text{heavy } C}{\text{reference } C},$$

and the fractional abundance:

$$f^{\text{heavy}} = \frac{\text{heavy } C}{\text{heavy } C + \text{light } C}.$$

Next, we can define our δ -notation:

$$\delta^{\text{heavy}} C = \left(\frac{R_{\text{meas}}^{\text{heavy}} - R_{\text{std}}^{\text{heavy}}}{R_{\text{std}}^{\text{heavy}}} \right) \times 10^3.$$

We also might care about mixing equation:

$$n_T \delta_T = n_A \delta_A + n_B \delta_B + \dots,$$

but this is not necessarily the case for large δ 's, where we have that $n_T = n_A + n_B$ for n the number of each isotope. The better way of doing this is with fractional abundances:

$$n_T f_T = n_A f_A + n_B f_B + \dots.$$

We can also define the fractionation factor as:

$$\alpha_{A/B} = \frac{R_B}{R_A},$$

for a process $A \rightarrow B$, where we note that α is products over reactants. We can also define the enrichment factors:

$$\epsilon_{A/B} = (\alpha_{A/B} - 1) \times 10^3 \simeq \delta_A - \delta_B.$$

Vibrational Modes

We can think about a molecule that has a vibrational model with a spring constant k and the frequency of vibration ν can be defined:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}},$$

for μ our reduced mass. Therefore, our Zero Point Energy is going to change for different isotopes, with the heavier isotope having lower ZPE and thus will take more energy to dissociate. This is the basis of isotope fractionation, which happens as work is applied to system. We see that this ZPE is going to dictate which isotope dissociates first given this applied work on the system, and therefore the chemistry that stems from this work will be dependent ultimately on this mass differences and the associated ZPE differences.

Fractionation Effect

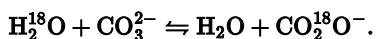
We have two kinds of fractionation:

1. Equilibrium
2. Kinetic

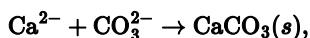
Equilibrium

We imagine a beaker with liquid and vapour phases, with isotopic composition δ_L and δ_V , respectively. If we take the species to be water, the vapour phase will preferentially prefer the lighter isotopes as it is a gas are more energetic (^{16}O over ^{18}O or ^1H over ^2H). Therefore, we can get that $\delta_V < \delta_L$ which then means that we can define $\epsilon_{V/L} = \delta_V - \delta_L < 0 \sim f(T)$.

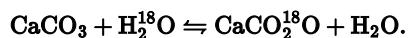
Another example would be in marine carbonates, specifically the formation of heavy carbonate ion:



and the formation of calcium carbonate:



which gives, overall:



We can define an equilibrium constant as:

$$K_{eq} \propto \frac{^{18/16}\text{O}_{solid}}{^{18/16}\text{O}_{water}} \sim f(T).$$

Therefore, we have a thermometer, which experimentally we know this relation is linear. So if we measure the ratio in water and we know the equilibrium constant, and we measure the solid in the water, we can tease our the temperature.

Kinetic

We are talking about the pathway of getting from one product to another. Let's consider the formation of Methanol from Methane, in Fig. 1.

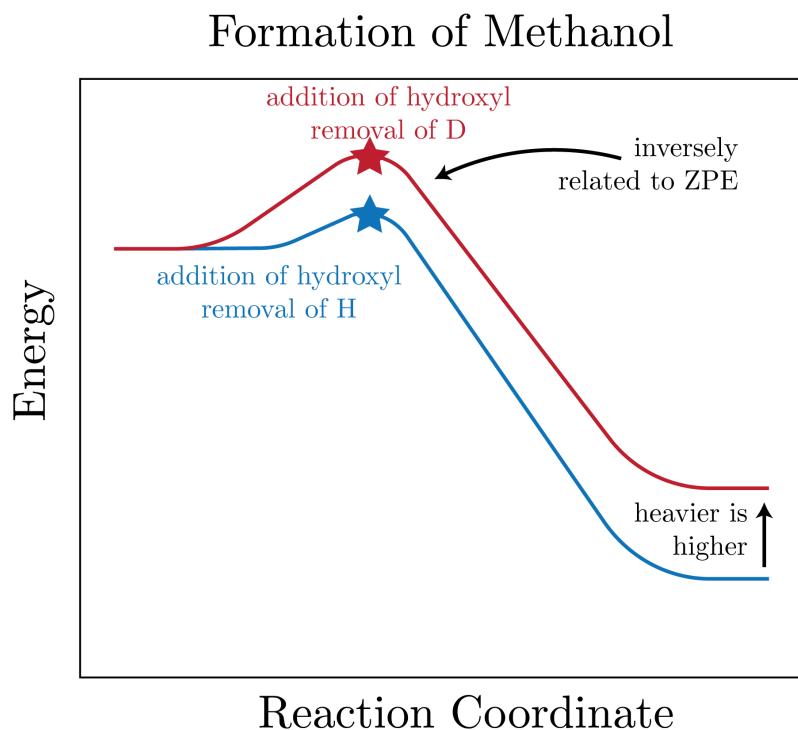


Fig. 1: The formation of Methanol from Methane in reaction coordinate-energy space.

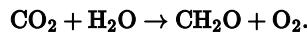
Import to note here is that the lower the ZPE, the higher the energy required to pull off the hydrogen (or deuterium) and add on the hydroxyl group. The fractionation factor is defined as:

$$\alpha_{\text{CH}_4/\text{CH}_3\text{OH}} = \frac{R_{\text{MeOH}}}{R_{\text{CH}_4}}.$$

The key is to:

1. Find where the reaction is irreversible
2. Identify dependent reactions on the pathway, such as:
 - o Enzymes
 - o Intermediates
 - o Temperature

One great example of this is photosynthesis:



One important thing to note here that C₃ photosynthesis, from plants and algae, has a fractionation factor of around 10 to 20, whereas C₄ plants, such as dry/land grasses, have an order of magnitude less. Therefore, we can see this in the $\delta^{13}\text{C}$ record, especially in recent years when C₄ plants expand. We can also see the effect on oxygen, as these isotopes tell us about the hydrological cycle and how much water is stored in ice versus in water.

Modelling with Isotopes

Global Carbonate System

We can think of the world as a single box of carbon, which we present in Fig. 2.

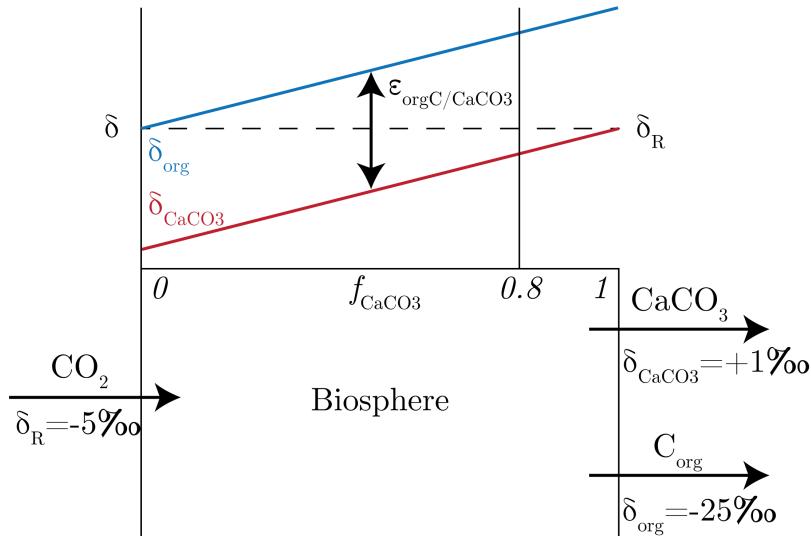


Fig. 2: Modelling the global carbonate system with carbonate isotopes.

At steady-state, we can define the inputs equal to the outputs, giving:

$$f_R \delta_R = f_{\text{CaCO}_3} \delta_{\text{CaCO}_3} + f_{\text{org}} \delta_{\text{org}}$$

We can see that as the fraction of calcium carbonate increases, we have the corresponding isotope fractionation ϵ , which is the difference between the two, increase. For most of earth's history, we have that $f_{\text{CaCO}_3} = 0.8$, so that most of the fractionation that was occurring was given by the calcium carbonate.

Expanding to multiple species

We can expand our model above to include the reaction itself, i.e. assuming some reaction of the form:

$$R \rightleftharpoons P,$$

which has an isotope fractionation of $\epsilon_{R/P}$. We can consider the above plot of δ as having that $\delta_{\text{org}} \sim \delta_P$ and $\delta_{\text{CaCO}_3} \sim \delta_R$. Therefore, speciation matters in isotope fractionation. An interesting exception is that aqueous CO₂ has heavier isotope signatures than gaseous, which is counter-intuitive. We can then use this speciation to get at the age of water and the influence of anthropogenic emissions by relating CFCs and $\delta^{13}\text{C}$, which is lighter in isotopic composition in DIC. Combined with CFC measurements, increasing CFC shows increasing $\delta^{13}\text{C}$ in DIC, the slope of which gives the rate of accumulation. This is similar to the global conveyor belt accumulation we saw earlier, in that the older waters accumulate more of the carbon as time goes on.

Rayleigh Distillation

We can imagine the scenario presented in Fig. 3.

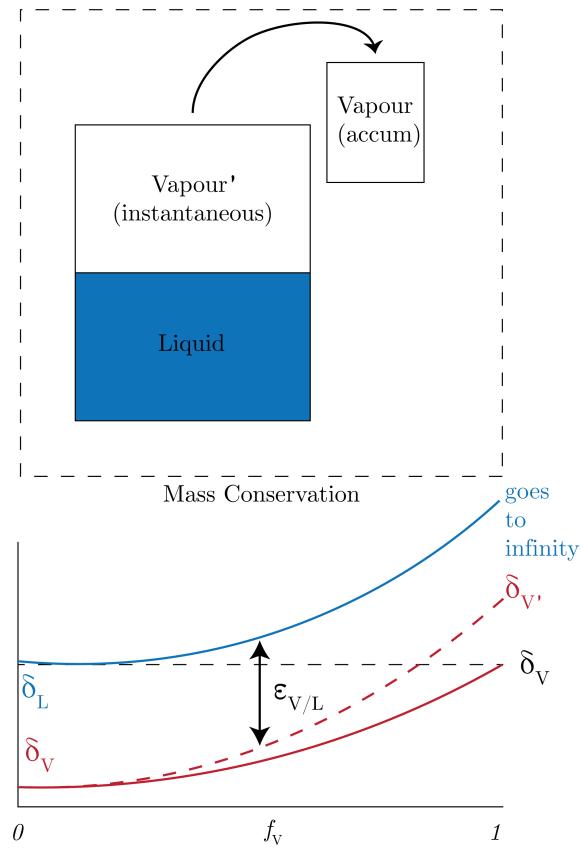


Fig. 3: Rayleigh distillation scenario.

We can write this out as:

$$R_L = R_L^0 f_v^{\alpha-1} \quad \text{and} \quad R_{V'} = R_L \alpha \quad \text{and} \quad R_V = R_L^0 \frac{(1-f_v)^\alpha}{1-f_v}.$$

In δ space, we can write these as (noting that there is error in these as they are approximations):

$$\delta_L = \epsilon_{L/V} \log [1 - f_V] + \delta_{L^0} \quad \text{and} \quad \delta_{V'} = \delta_L + \epsilon_{L/V} \quad \text{and} \quad \delta_V = \delta_{L^0} - \epsilon_{L/V} \frac{1-f}{f} \log [1-f].$$

We can think of this as oxygen in the hydrological system, i.e. evaporation and precipitation. After the vapour formation, we have that it is transported to the poles where it is rained out into the ice.

Radioactivity

We are interested in the Uranium-238 decay series, which decay from ^{238}U into stable lead, ^{207}Pb , through β and α decay. We can extrapolate to this to having that all radioactive elements always decay into stable isotopes, which we can see in the "Valley of Stability". Next, we have the decay equation:

$$\frac{dN}{dt} = -\lambda N,$$

for the BC that $N(0) = N_0$:

$$N = N_0 \exp [-\lambda t],$$

Next, we define the activity A as:

$$A = \lambda N \sim [\text{dpm m}^{-3}].$$

We can then assume a steady state of parent-daughter decay to get **secular equilibrium**:

$$\frac{dN_D}{dt} = N_P \lambda_P - N_D \lambda_D,$$

which means then that:

$$A_D = A_P.$$

We assume this steady state when doing most calculates, and it is secular because the steady state is only in one direction. One useful use of this is for POC flux with ^{238}U and ^{234}Th , starting with the dissolved D :

$$\frac{dA_{234}^D}{dt} = \lambda_{234} A_{238} - \lambda_{234} A_{234}^D - \psi_{234}^*.$$

and particulate P :

$$\frac{dA_{234}^P}{dt} = -A_{234}^P \lambda_{234} + \psi_{234}^* - J_{234}^*,$$

where we define ψ as the particle -sorption and J as the particle sinking flux, which causes the disequilibrium in the surface ocean. Therefore, at steady state we can get:

$$\frac{dA_{234}^D}{dt} + \frac{dA_{234}^P}{dt} = 0.$$

This then means that;

$$J_{234}^* = \lambda_{234} A_{238} - \lambda_{234} (A_{234}^P + A_{234}^D).$$

We need to integrate over space to get:

$$F_{234}^* = \int_{-D}^0 dz J_{234}^*.$$

Thus, if we can measure the activities of the particulate and dissolved phases, we can get the sinking flux. Something to think about is that this is integrated flux through the Euphotic Zone, whereas with sediment traps and pumps you have a timescale observation dependent measurement.

12.742: Lecture 18

Weathering, Estuaries, and Vents

Major Composition of Seawater

We have the following major constituents of seawater, in relative order of abundance:

| Cations | Anions (no proton exchange) | Anions (proton exchange) |
|------------------|-------------------------------|---------------------------------|
| Na ⁺ | Cl ⁻ | HCO ₃ ⁻ |
| Mg ²⁺ | SO ₄ ²⁻ | CO ₃ ²⁻ |
| Ca ²⁺ | Br ⁻ | B(OH) ₄ ⁻ |
| K ⁺ | F ⁻ | |
| Sr ²⁺ | | |
| Li ⁺ | | |

We note that the summation of the cations must equal the summation of the anions, and it is the anions with the significant proton exchange, i.e., the alkalinity, that make up that difference. Now, we are interested in what the inputs and outputs are to these important chemical constituents.

Inputs and Outputs

We have the following list:

| Inputs | Outputs |
|------------|--------------------------------------|
| Rivers | Evaporation |
| Atmosphere | Sediments (biological and inorganic) |
| Vents | Radioactive decay |
| | Vents |

We go over these now.

Weathering Reactions

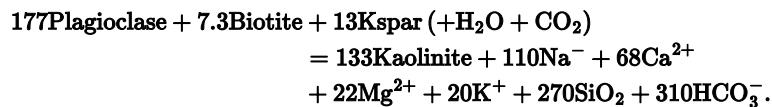
We have the general formulation of weather below:



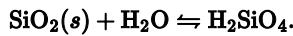
One of these inputs that is important is rocks, in order of rate of weathering / stability:

1. Iron Oxides (residue of weathering)
2. Al hydroxides (residue of weathering)
3. Quartz
4. Clay minerals (residue of weathering)
5. Pyroxene
6. Feldspar
7. Olivine
8. Calcite (complete dissolution: salt)
9. Halite (complete dissolution: salt)

How can we convolve these endmembers? Garrels and Mackenzie (1967) picked a number of known weathering equations and went to the Sierra Nevada's and looked at the mass balance of the dissolved minerals in the water from the mountains. The resultant mass balance gave the overall reaction:



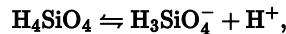
Now, the first thing that comes to mind is... what is kaolinite and why was this chosen as the end member out of all of the possibilities? To answer this, we start with quartz dissolution, given by:



The equilibrium constant is equal to:

$$K_{eq,1} = \frac{\{\text{H}_2\text{SiO}_4\}}{\{\text{H}_2\text{O}\}} = \{\text{H}_2\text{SiO}_4\} = K_{sp}.$$

Now, as the product is acidic, we can get:



where we have that:

$$K_{eq,2} = \frac{\{\text{H}^+\}\{\text{H}_3\text{SiO}_4^-\}}{\{\text{H}_4\text{SiO}_4\}}.$$

Now, we can substitute in our definition of K_{sp} from above, take the **log** and solve to get:

$$\log\{\text{H}_3\text{SiO}_4^-\} = -\log\{\text{H}^+\} + \log[K_{sp} K_{eq,2}].$$

Then, we can make a plot with respect to pH , which is the first term on the RHS above, and then the data, if the system is in equilibrium with quartz, would fall along the **log – log** space line described by this equation. Note that we would expect the same thing for the carbonate system, where the number of H^+ removed equalling the slope. We can do this until all protons are gone and then sum to get the total. If we do this and compare to amorphous silica equilibrium constants, we get opal is higher. Therefore, we need something to make up this difference but also note that if our concentration is lower than the equilibrium line, dissolution will occur and if the concentration is higher in the ocean, then precipitation will occur. Now, if we look at a plot of Silicate mineral in the ocean, we see that the ocean is everywhere undersaturated everywhere, with the lowest at the surface. But we still have diatoms/radiolarians producing silica everywhere in the ocean. How is this possible? Note that this shows how important biology is and that thermodynamics isn't everything. We can then make phase diagrams similar to the one for quartz and silica but for multiple phases. In so doing, we can trace out the stability relationships between mineral systems as a function acid concentration and protons. The slopes of the lines is related to the equilibrium constants and the solubilities. If we plot rivers and ocean, we get that the most stable (i.e., the one that is within the water) is kaolinite. Therefore, Garrels and Mackenzie chose this is the ultimate endmember, as seen in Fig. 1.

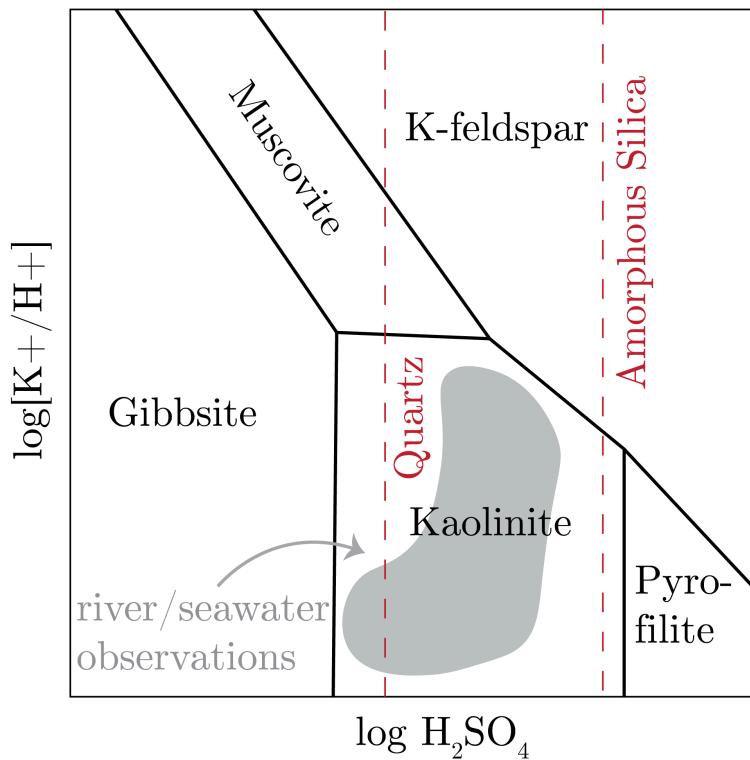


Fig. 1: Phase diagram of rivers and seawater in silicic acid and potassium to proton space.

Discharge-Solute Relationships

One thing to note is that this is not in equilibrium, therefore there are kinetics that are playing a role. We can start to see this in Fig. 2, in which we see different limitation regimes.

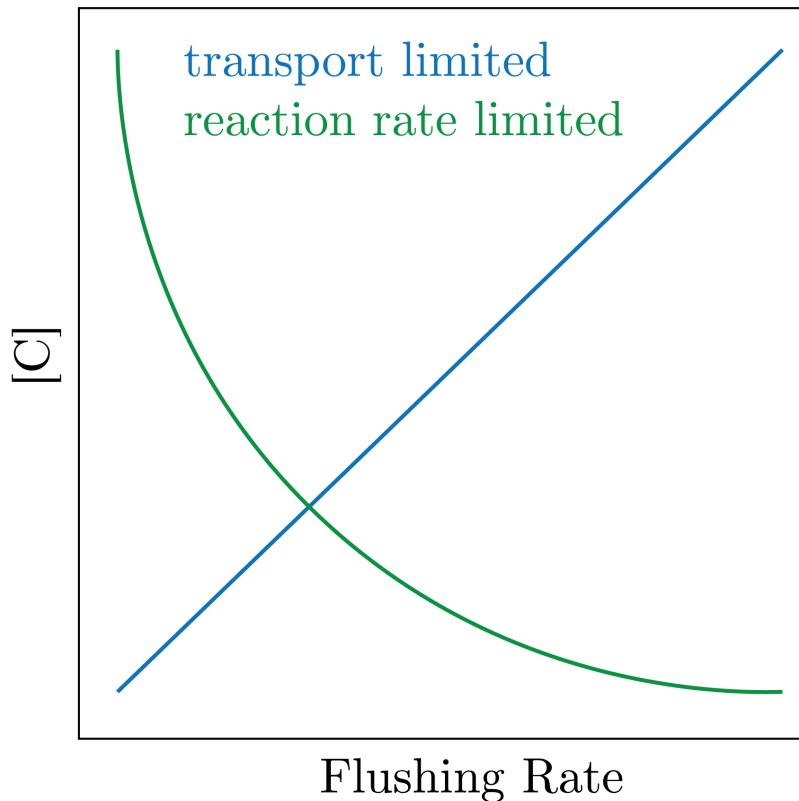
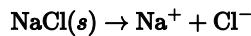


Fig. 2: Limitation regimes.

For example, we can take a transport limitation to be N and a reaction rate limitation to alkalinity (i.e., it takes time to build up). We can look at the dissolved and sediment transport loads from land, with large discharges being from rivers like the Amazon and the Brahmaputra and South East Asia/Oceania for carbonates. Now, Garrels and MacKenzie did pretty well, but their mass balance was missing a few things, as they took river discharge from the Sierra Nevada's which is a big granite reservoir. For instance, where are the salts, carbonates, and sulfides?

Salts and carbonates

We often think about salt weathering coming from evaporates, such as:



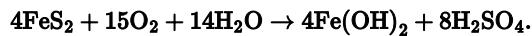
or for carbonates:



Important here is that timescale matters, as we note that there is no CO_2 in the sodium chloride dissolution versus the calcium carbonate. The Garrels and MacKenzie method was extended to include a larger suite of endmembers and was performed for 60 major rivers. The result was that the biggest influence on dissolved river composition was carbonates, silicates, and atmospheric deposition.

Sulfides

We can think of this weathering reaction as:



Therefore, the oxidation of sulfides produces a lot of alkalinity, and there is a lot of S in seawater. This then means that S is super important for the history of the Earth, as we have linked Fe to O and S. This is all to say that weathering is highly important to the long term stability of Earth's climate.

Rivers to Seawater

If we look at the absolute and relative magnitudes of the major constituents of river and seawater, we can see that there is a drastic difference. Reasons for this might be:

1. Biology
2. CaCO_3 precipitation
 - $[\text{Ca}^{2+}]$ is constant in the ocean
 - Ca: HCO_3^- should change in a 1:1 ratio but it does not between the seawater and the oceans
3. Estuaries

- Chemical filtering
- Big salt gradients due to activity changes and ion-pairing effects

Estuaries

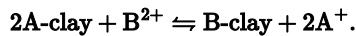
We note that there are a few stratification scenarios in estuaries that can change how these weathering products exchange with the ocean. There is a salt tongue, where surface freshwater floats atop colder salt water such as in the Mississippi, or a weakly stratified in the Chesapeake. There is also strongly stratified as in fjords or well-mixed as in Severn (in Annapolis). The transport of this dissolved load moves as follows:



The cut off between DP and CP is $0.2 \mu\text{m}$ and between CP and PP is 0.45 , which are empirically defined. It is really going to be the colloidal phase that contributes to clays. We can look at these clays, and see that they possess a kaolinite structure, which is known as a 1:1 clay that has balanced charge. This means that there are alternating layers of octohedral and tetrahedral structure of silicate and oxygen sheets, leading to the full balance (as equal number of layers). There are 2:1 clays, where there are missing layers where then can be vacancies that ions can fit into the balance the charge, during which time there are chemical reactions that are facilitated.

Clay Mineral Exchange of Cations

Consider a reaction between a clay mineral, A^+ and B^{2+} . To maintain charge balance, we get:



Assume that A and B are the only important cations in seawater so that:

$$\{\text{A}\} = \{\text{B}\} = 1.$$

Now we will define a chemical exchange capacity as:

$$\chi_A = \text{mole fraction of A-clay} \quad \text{and} \quad \chi_B = \text{mole fraction of B-clay},$$

such that:

$$\chi_A + \chi_B = 1.$$

We can define the equilibrium constant as:

$$K_{eq} = \frac{\{\text{B-clay}\}\{\text{A}^+\}^2}{\{\text{A-clay}\}^2\{\text{B}^{2+}\}}.$$

Using our chemical exchange capacities, we can get:

$$K_{eq} \simeq \frac{\chi_B\{\text{A}\}^2}{\chi_A^2\{\text{B}\}} = 1,$$

when then means, as the activities are the same, that:

$$\chi_A = 0.63 \quad \text{and} \quad \chi_B = 0.38,$$

which is that roughly 2 times more sites in the clay are occupied by A^+ than B^{2+} . This then means that there are doubly more 2 plus charged ions in the dissolved phase. If we dilute this by 10^3 , then we get that:

$$K_{eq} = 1 = \frac{\chi_B}{\chi_A} 10^{-3},$$

which gives that:

$$\chi_A = 0.03 \quad \text{and} \quad \chi_B = 0.97.$$

Therefore, with this simple dilution, we have totally flipped the preference of the clay. This is why seawater has a lot more Na^+ than Ca^{2+} , for these A and B, respectively in the example above. We can extrapolate this to seawater, in which ions start to interact with the ionic medium of the solution itself. This then means that particles will gain a charge, which ions absorb onto. Typically there is a primary layer of the particle, onto which ions are tightly bound and then a secondary, diffusive layer called the "gluey" layer. Then, we can get a clay colloids that are preferentially taking up 2-plus ions, as we just showed, then then interact with negatively charged particles that aggregate (and disaggregate) while sinking to the sediment. This then means that that the river water in the estuaries are relatively enriched in Na^+ which is exported into the ocean. We call this flocculation.

If we plot river discharge as a function of salinity, then the stratification changes will be removed and we can see a change from river (no salinity) to seawater (high salinity) and the change in different nutrients, such as Fe and Ba. We see that the data between the two endmembers for iron is not conservative as it is not a line between two the river and seawater endmembers. Instead the mixing line is concave up. Therefore, we get that we are preferentially removing Fe from the system through flocculation. This happens across all salinities. The opposite would be Ba, which is concave down, and therefore shows that we are preferentially adding Ba to the system, which happens at low salinities (nearer the river input).

Processes at Work

We have:

1. Physical transport and mixing
2. Chemical reactions

We would get that (1) from above would get that for linear mixing between endmembers A and B:

$$F_A + F_B = 1,$$

which means:

$$[A]F_A + [B]F_B = [A, B]_{mix}.$$

We can then solve for any of these parameters given the proper number of constrained measurements. We can then estimate the exact amount of nonlinear mixing as taking the difference between the linear mixing from the above equation and the curved observed line, we can take the integrated difference between the two to get the amount removed. This is shown in Fig. 3.

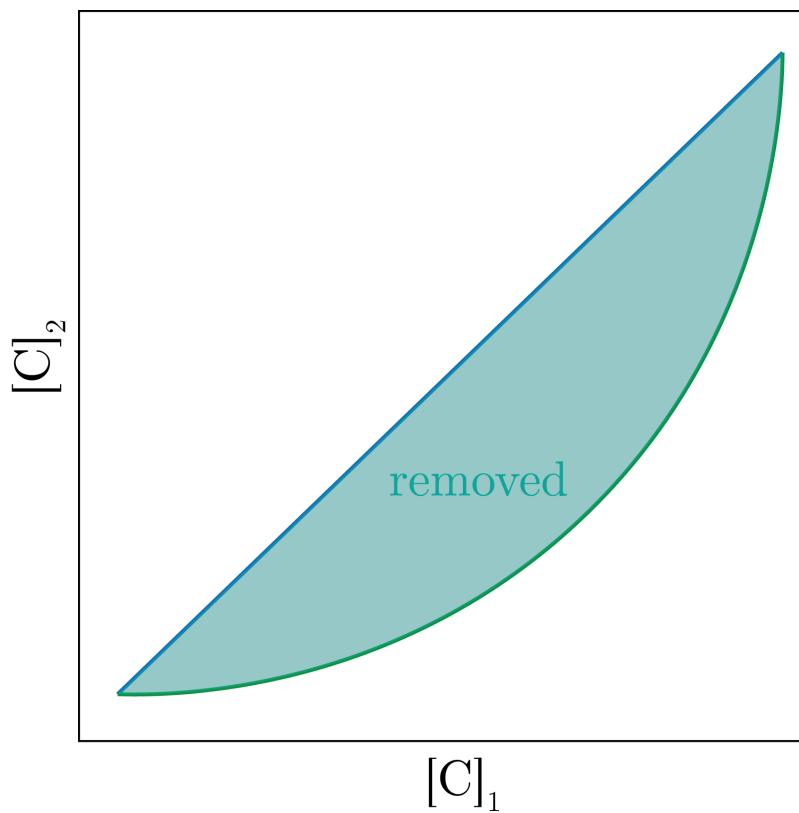


Fig. 3: A diagram showing nonlinear mixing and the amount removed.

Vents

New seafloor is being produced at the Mid Atlantic Ocean Ridge, which is new and hot. We also the East Pacific Rise. As this sea floor moves away and deeper, it cools and ages. The age of the Atlantic is about 180 million years. We can measure the heat flux that is coming out of the ocean floor. The result shows that a lot less heat is being transported via diffusive transport, which happens where the floor is produced. At this interface between the freshly floor seafloor and the water, we get a lot of interesting chemistry, which changes in pH , sulfate, silicate, and ions, all of which are major compositions of seawater.

Bischoff and Dickson Reactions

The first is anhydrate formation:



The next is basalitic glass forming clays:



where the glass is rich in Fe(II), K⁺, Mn(II), Al, and SiO₄. We also have quartz dissolution and precipitation, as the silica concentration is at saturation: Lastly, we have H⁺ production through the reaction:

1. Hydroxide clays
2. $2\text{HCO}_3^- + \text{Ca}^{2+} \rightleftharpoons \text{CaCO}_3 + \text{H}_2\text{CO}_3^*$
3. Reduced metal oxidation, such as Fe(II) to Fe(III) which produces protons that reduces fugacity

We can then use silica as a proxy for these processes, as we know that the ocean is globally undersaturated in silica. Therefore, we can use this as an endmember and get mass balances. We found that hydrothermal vents acted as sinks for:

1. Mg
2. SO_4^{2-}
3. Alk
4. P

With respect to rivers, we can see that hydrothermal inputs are more important for Mn and Fe whereas rivers are more important for Mg, Alk, and P. Hydrothermal vents are able to subsist because of the constant rain of carbon from above... Recent research has shown that both particulate and dissolved phases of Fe are important in the input of Fe to the ocean system.

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Sediments I

The Basics

Sediments composed of:

1. biological material
 - organic matter
 - shells/tests/frustals (opal, calcium carbonate)
2. clays
3. dust (volcanic rocks and minerals)
4. authigenic phases (formed in situ)
5. pore water

Specific mineral phases include, with max relative abundance:

1. Montmorillonite: 70%
2. Illite: 50%
3. Kaolinite: 50%
4. Chlorite: 30%

These are end of the line (generally) chemical species that are stable in seawater.

Distributions of Phases

Additionally, there are Manganese nodules at the bottom of the ocean (also called polymetallic nodules, given that they include numerous metals, including rare earth metals and Ni, Nd, etc.) In the Pacific Ocean we have a particularly abundant distribution. They take million of years to form, but it is unknown how they are formed but biology might play a role.

We can also look at the distribution of siliceous sediments, which looks very similar to surface ocean P. This is because diatoms take up silica in their shells, die, and then sink in these regions, depositing silica in the sediments. What is interesting is that the ocean is undersaturated Si everywhere and yet even with this dissolution there is silica burial.

Next, we can look at CaCO_3 distributions, which really gives maps of topography more so than chemistry. This is because calcium carbonate becomes more soluble with pressure, which then causes it to dissolve away. We can also compare the Pacific to the Atlantic waters. As the Pacific is older water (end of the global conveyor belt), we get there is more accumulated DIC and therefore a higher pH . This leads to the waters being more corrosive and thus CaCO_3 dissolves quicker, giving a steeper drop off with depth in the Pacific than the Atlantic. We can see this in Fig. 1.

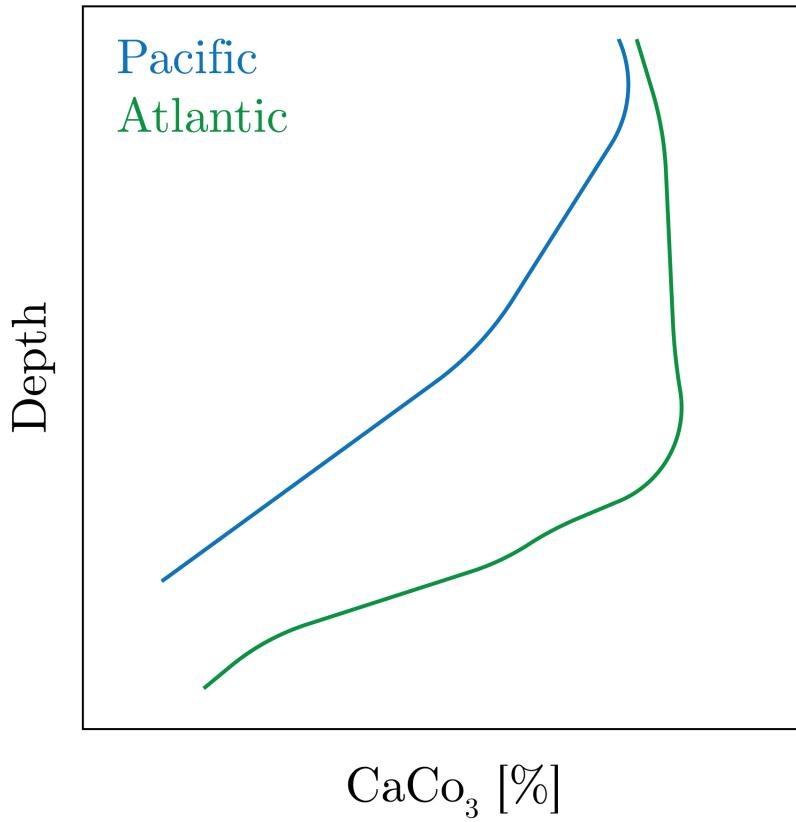


Fig. 1: Calcium carbonate as a function of depth between the Pacific and the Atlantic.

We can also look at sediment accumulation rates and it maps 1:1 onto the biological pump, which makes sense given that the biological pump forces downward flux. However, we can look at maps of total organic carbon and see that the only places of sediment (which are less than 10%) with TOC is along the coasts of the Pacific (off Peru). Clearly this is due to the fact that carbon is preferentially taken up in the water column, so it will not be in the water column by the depth at burial (we call this the attenuation of carbon). If we look at maps of TOC vs. POC, we see that there is an order of magnitude difference in favour of TOC. This does not translate into what is sinking, that is the particulate is fluxing but the dissolved is not. We can look at $\Delta^{14}\text{C}$ of these organic carbon phases, and see that it is the dissolved that is super replete in these radiocarbon values as it has decayed away (meaning that it is older), that is this is recalcitrant. This is contrasted against high $\Delta^{14}\text{C}$ in particulate matter, meaning that it is much younger. If we look at the f-ratio of POC, it is about 0.2 globally, with only about 5% being fluxed to the seafloor. Then, within the sediments we see that there is immense remineralization, leading to about only 0.5% being buried in sediments. Distribution wise, continental margins are over 90% of POC burial, which is due to the fact that the water column is less deep and there is more productivity here. This then means that the higher the accumulation rate, the more efficient the burial (less time and greater amount to preferentially take up).

Pore Waters

Here, in sediments we have that both solid and liquid phases are in close proximity, leading to high chemistry. One way to think of this is through porosity:

$$\phi = \frac{\text{volume of void spaces}}{\text{total volume}} = \frac{v_{\text{liq}}}{v_{\text{liq}} + v_{\text{solid}}}.$$

Correspondingly, we have the solid fraction as $1 - \phi$. In sediment, the porosity is greater than 0.8, and about 0.95 at the surface, inversely with depth, which is due to the pressure effect which compacts sediments to more solid phases.

Oxygen

We consider oxygen profiles in the water column and the sediment pore waters, which are affected by:

1. Biology
2. Advection
3. Diffusion
4. Chemical reactions

We can see these in play in Fig. 2.

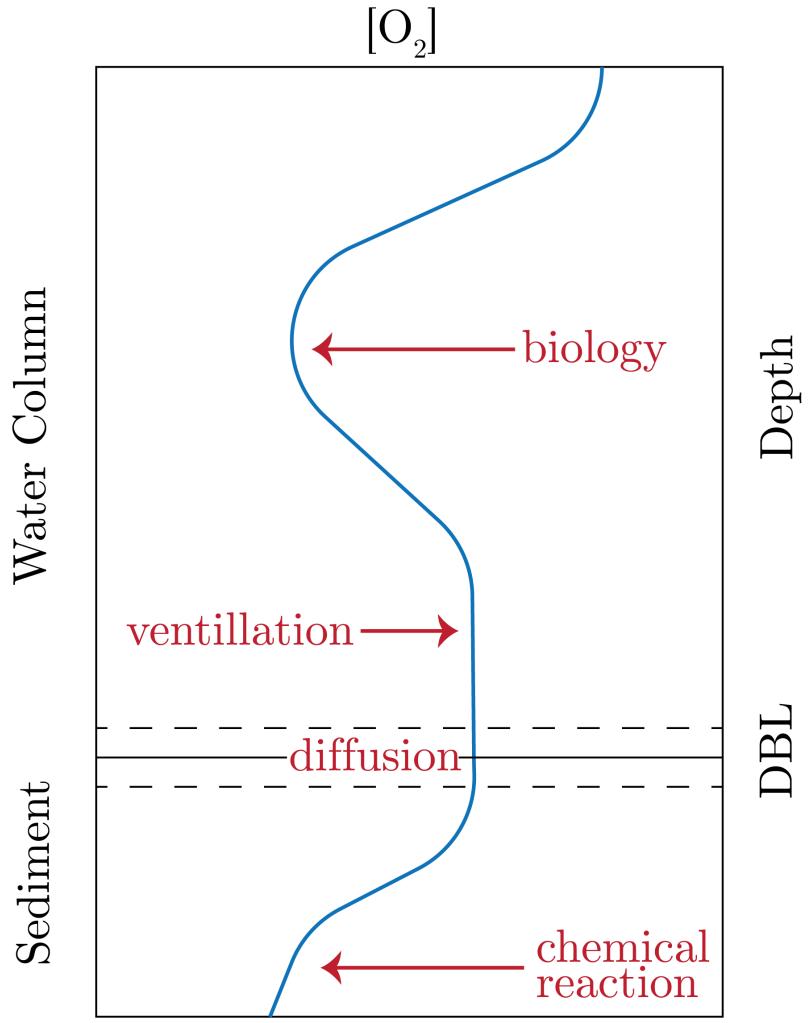


Fig. 2: A representative oxygen profile in the water column and sediment.

1-D Advection-Diffusion Reaction Equation

We start with the governing equation:

$$\partial_t C = \partial_z [\phi F \partial_z C] - \partial_z [\phi w C] + J.$$

Of immediate note is the sign convention. We can think about diffusion as smooth out gradients, i.e. it is acting in the opposite direction of advection. We can derive these as follows.

Advection

We imagine describing the water column into N many boxes, with equal thickness Δz . Then, we have some advection velocity w transporting material from one box to the next. Therefore, we can say that the flux from one box to the next is given by:

$$F = wC.$$

Then, we can say that:

$$\frac{\partial C}{\partial t} = \frac{F_{in} - F_{out}}{\Delta z} = \frac{wC_n - wC_{n+1}}{\Delta z} = w \frac{\Delta C}{\Delta z} \xrightarrow{\Delta z \rightarrow 0} \partial_z [wC].$$

Diffusion

We can use Fick's First law:

$$F = D \partial_z C.$$

Therefore, thinking about the change with respect to time, we get:

$$\partial_t C = \partial_z F = \partial_z [D \partial_z C].$$

Thus, we get that for diffusion we have that the term is proportional to the curvature of the system. We can then apply this to a linear profile that decreases with depth. Let's assume that this is a diffusion-dominated profile. Therefore, from above we know that the flux is proportional to the first derivative, therefore the flux is downwards. Now, we then know that the rate of change of the concentration is proportional the second derivative, which for a straight line is 0. Therefore, we are at steady state. Super useful!

We can think about D in terms of its vertical diffusion as well as its horizontal or eddy diffusivity. In sediments, we get that D can be caused by molecular diffusion, as well as bioturbation and bioirrigation, where we note that sediments are typically driven by molecular diffusion.

Time Scales of Diffusion Processes

We know that D has units of $[m^2 s]$. We can take the Root Mean Square diffusional displacement as:

$$D = \frac{1}{2} \frac{\Delta z^2}{\delta t}.$$

For most gases, we say that $D \approx 2 \times 10^{-9} [m^2 s^{-1}]$. Therefore, we get that it takes 8 years to move one year, as:

$$\Delta z = (0.5 D \Delta t)^{1/2}.$$

This then means that gradients in space determine the timescales of fluxes.

Sources and Sinks

At steady state with no advection, we can get that:

$$J = -D \partial_{zz} C.$$

Therefore, we can tease apart reaction rates are proportional to the curvature of the profile. Taking our linear example from before, we would therefore get that $J = 0$. For concave up (i.e., $\partial_{zz} > 0$) we get that $J < 0$ and for $\partial_{zz} < 0$ we get that $J > 0$. We show this in Fig. 3.

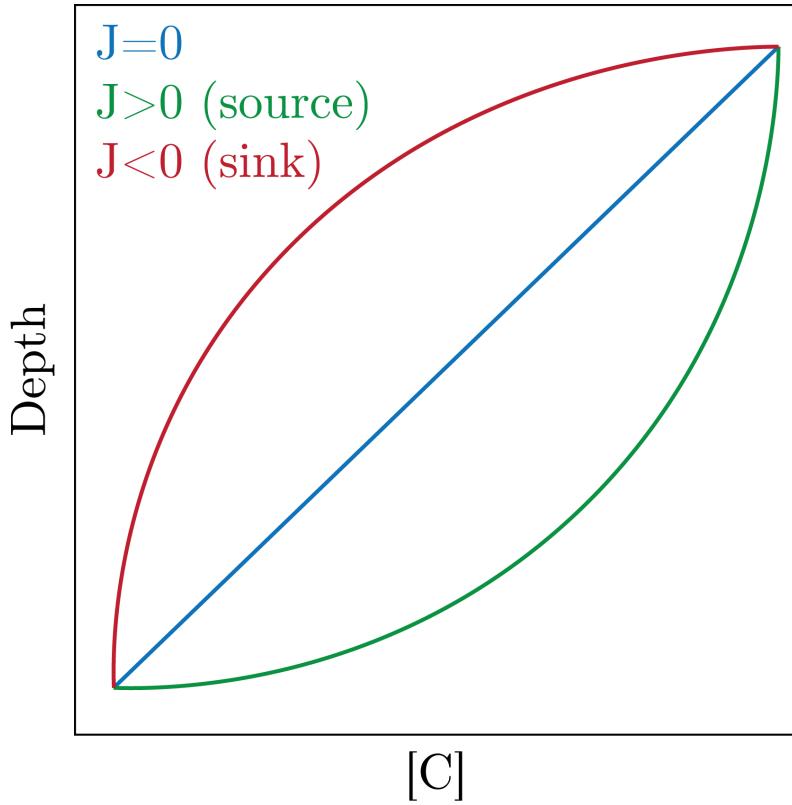


Fig. 3: Reaction given curvature of the profile.

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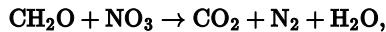
Sediments II

Anaerobic Metabolism

In these regions we have that they are oxygen limited, meaning that there is still enough carbon to perform respiration but not enough oxygen. Therefore, there needs to be other methods of metabolism.

Denitrification

One of these is denitrification, given by (unbalanced):



in which nitrate is being used as an electron acceptor for carbon reduction to form CO_2 , from which energy is gained to grow.

Free Energy

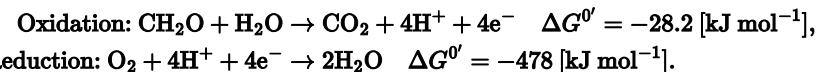
To quantify the energy yield, we use Gibbs Free Energy, the chemical energy to do work:

$$\Delta G^0 = \Delta G_{\text{products}}^0 - \Delta G_{\text{reactants}}^0 = 0,$$

at steady state. The "0" is a reference states of 0° , 1 [atm]. For natural chemistry, we then define "0'", in which we just include $pH = 7$ in the standard state.

An Example

Let's consider 2 redox half-reactions:



If we sum these up we get:



This is thermodynamics, of course, so this is really the theoretical maximum energy yield However, there can be:

1. losses to heat
2. intermediate formation along pathway
3. non-steady state conditions

Now, what are the energetics associated with the consumption of all of this oxygen? Froelich (1979) did out experiments on this consumption, using Redfield Ratio organic matter. For a range of electron acceptors, what Froelich found was, in $[\text{kg mol}^{-1}]$:

1. Oxygen, O_2 : $\Delta G^{0'} = -3190$, and producing acid in CO_2 and HNO_3
2. Manganese Dioxide, MnO_2 : $\Delta G^{0'} = -2920$ to -3090 , but consumes lots of protons
3. Nitric Acid, HNO_3 : $\Delta G^{0'} = -2750$ to -3030 , but consumes lots of protons

These are all nearly as much as oxygen! However, we get a decrease as soon as we get to:

1. Iron Oxide, Fe_2O_3 or FeOOH : $\Delta G^{0'} = -1330$ to 1410 , and consumes protons
2. Sulfate, SO_4^{2-} : $\Delta G^{0'} = -380$, and consumes protons

So what causes us to see the use of oxygen versus manganese dioxide or nitric acid? Well, the concentrations of these are incredibly small compared to sulfate or iron oxide, which are much more abundant than the more energetically favourable receptors. Additionally, we note that all but the electron acceptor of oxygen produce alkalinity! However, we note that this is all a little messy. The way to do DIC and alkalinity accounting is to:

1. balance reactions with species at the CO_2 equivalence point
2. balance the charge with H^+ ions

Redox Chains

From this study, we can get the redox chain reactions in the sediment, which show the favourability of each electron acceptor as those more favourable "above" it are used up. We present this chain in Fig. 1.

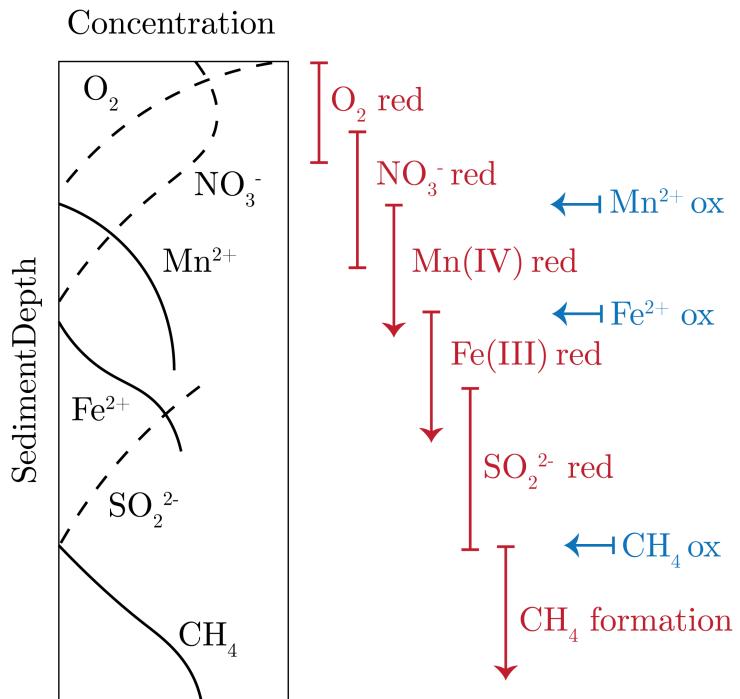


Fig. 1: Redox chains in the sediment.

Here, we can see that the most favourable electron acceptors are being used up first in the sediment as depth increases. Interestingly, we can see that it is the balance between reduced Mn diffusion up and the reduction from oxygen moving down in which we see that Mn nodules form in sediments. This is a direct connection between solid and liquid chemistry interfacing. We can look at the total remineralizing reaction as a function of electron acceptor, which mimics the results from above:

1. Aerobic respiration: 65%
2. Sulfate reduction: 17.9%
3. Methanogenesis: 9.8%
4. Denitrification: 6.5%
5. Mn reduction: 0.6%
6. Fe reduction: 0.3%

What we take away from this is really a balance between abundance and energetic favorability! One important thing to note is that nitrate has a greater contribution in the deeper ocean as it is used in the surface ocean. This is one of the few examples in which we see that thermodynamics are really driving the observations that we see. One reason for this is that we are really dealing with enzymes competing in these sediments, which are dictated by $\Delta G^0'$. We can determine the relative amount of OC being injected into the system by which core runs out of oxygen first in depth, as oxygen drives respiration.

Bioturbation

This is the mixing of sediments due to moving organisms in the sediments. We note that the timescales of bioirrigation, or the diffusion of chemical species through water, is on the order of minutes to even years, which is much less than that of bioturbation. We can write the advection-diffusion reaction equation again, this time corrected for bioirrigation, for dissolved species C :

$$\partial_t [\phi C] = \partial_z \left[\phi \underbrace{D_C}_{\text{molecular diffusion + bioirrigation}} \partial_z C \right] - \partial_z \left[\phi \underbrace{w}_{\text{sedimentation rate}} C \right] + J.$$

Now, for solids B , we have:

$$\partial_t [(1-\phi)B] = \partial_z \left[(1-\phi) \underbrace{D_B}_{\text{bioturbation}} \partial_z B \right] - \partial_z \left[(1-\phi) \underbrace{w}_{\text{sedimentation rate}} B \right] + \underbrace{J}_{\text{reactions creating or dissolving } B},$$

where the equations are coupled via J . From bioturbation, we essentially have a mixed layer in the surface of sediments, just like in the ocean. In order to get at the extent of bioturbation, we can use radioactive tracers, such as ^{210}Ob , which has a half-life of 22 [y] but that we see in depths greater than 10 [cm] in the sediment, long after it should be at negligible activities.

P Cycle

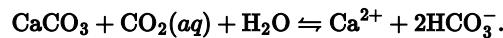
One important phase of phosphate is **apatite**. Importantly, Fe is able to aggregate with phosphate near vents, which are then sedimented, and therefore, this provides a path for deposition of phosphate from the water column. We can compare coastal and deep-sea dissolved phosphate in the

sediments and see that there are nearly no phosphate in sediments in the deep sea, unlike in the coastal regions. We note that Fe is far down the redox ladder, but it is still favourable. Therefore, we get that Fe (dioxide) is reduced to Fe(II), which then releases that phosphate which can diffuse back out into the ocean.

So, we can also note that bioturbation effects P removal, in which we would get that more Fe is perturbed to the surface, in which Fe(II) is oxidized and then more phosphate is absorbed onto the oxidized iron. This would then limit the phosphate in the ocean, which limits production, which then decreases oxygen production. This is one way to think of this as a main stabilizing feedback for why oxygen does not continually increase in the climate. Oxygen also spontaneously combust around high oxygen levels at which this feedback would occur (21%), so this could also be a feedback.

Ending with the C Cycle

Let's consider sediments receiving a constant rain of CaCO_3 and clay. Let's say that these sediments are receiving these in a 90:10 ratio. We can assume that there is a loss of calcium carbonate to dissolution. At 50% dissolution, we only get: $45/(45 + 10) \simeq 82\%$ of CaCO_3 in the sediment. Therefore, we get that percent abundance of calcium carbonate in the sediment is a poor way of getting at the dissolution of calcium carbonate in the water column. Now, we note that we have both DIC and DOC being rained onto the sediments. Therefore, we get respiration that implies dissolution of calcium carbonate due to increased CO_2 (production of alkalinity), which then means that we can go from super- to under-saturated in the upper column of the sediment by this dissolution. This then means that we have coupled two part of the carbon cycle together in the water column. This is the essence of the ocean's ability to buffer the carbon cycle. We can write this:



This calcium carbonate feedback is therefore the link between alkalinity and CO_2 . Powerful stuff...
