Formation and respiration of organic matter

DINutrients $\Rightarrow$ POM
Primary Producers
Autotrophs

Mostly photosynthesizers (they use light energy) called phytoplankton
phyto = light
plankton = small drifting organisms

Some chemotrophs (don’t need light)
live in unusual environments like
hydrothermal vents, anoxic environments

C, H, O, N, P, S + trace elements
Oceanic reservoirs of N, P are small
Production and destruction biogeochemistry

*Redfield-Richards Equation:*

\[
\text{CO}_2 + N + P + \text{H}_2\text{O} \xrightarrow{\frac{p}{r}} \text{Organic matter} + \text{O}_2
\]

We will look first at the so-called “*inorganic nutrients*”:

N, P and Si

They are also called “*biolimiting elements*” -- Why?

1. Small reservoir size in oceans
2. Fast turnover time
3. Required for many kinds of biological activity

**Controls on Atmospheric CO\(_2\)**

Remarkable consistency for glacial/interglacial concentrations of CO\(_2\)**
### Chemical Composition of Biological Particulate Material

#### Hard Parts - Shells

<table>
<thead>
<tr>
<th>Plants</th>
<th>Name</th>
<th>Mineral</th>
<th>Size (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Coccoliths</td>
<td>CaCO$_3$</td>
<td>Calcite</td>
</tr>
<tr>
<td></td>
<td>Diatoms</td>
<td>SiO$_2$</td>
<td>Opal</td>
</tr>
<tr>
<td></td>
<td>Silicoflagellates</td>
<td>SiO$_2$</td>
<td>Opal</td>
</tr>
<tr>
<td>Animals</td>
<td>Foraminifera</td>
<td>CaCO$_3$</td>
<td>Calcite</td>
</tr>
<tr>
<td></td>
<td>Radiolaria</td>
<td>SiO$_2$</td>
<td>Opal</td>
</tr>
<tr>
<td></td>
<td>Pteropods</td>
<td>CaCO$_3$</td>
<td>Aragonite</td>
</tr>
<tr>
<td></td>
<td>Acantharia</td>
<td>SrSO$_4$</td>
<td>Celestite</td>
</tr>
</tbody>
</table>
Soft Parts - protoplasm

The Redfield or "RKR" Equation (A Model)
The mean elemental ratio of marine organic particles is given as:

\[ \frac{P}{N} : C = 1:16:106 \]

The average ocean photosynthesis (forward)
and aerobic (\( O_2 \)) respiration (reverse) is written as:

\[ 106 \, CO_2 + 16 \, HNO_3 + H_3PO_4 + 122 \, H_2O + \text{trace elements (e.g. Fe, Zn, Mn...)} \]

\[ \text{light (h \( \nu \))} \downarrow \]

\[ (C_{106}H_{263}O_{110}N_{16}P) + 138 \, O_2 \]

or

\[ (CH_2O)_{106}(NH_3)_{16}(H_3PO_4) \]

Algal Protoplasm

The actual chemical species assimilated during this reaction are:

\[ \text{HCO}_3^- \quad \text{NO}_3^- \quad \text{PO}_4^{3-} \]

\[ \text{NO}_2^- \quad \text{NH}_4^+ \]
1. This is an **organic oxidation-reduction reaction** - during photosynthesis C and N are reduced and O is oxidized. During respiration the reverse occurs. There are no changes in the oxidation state of P. 
We assume C has an oxidation state of 0 which is the value of C in formaldehyde (CH\textsubscript{2}O), that N has an oxidation state of -III and that H and P do not change oxidation states.

2. Photosynthesis is **endothermic**. This means is requires energy from an outside source. In this case the energy source is the sun. Essentially plants convert the photo energy from the sun into high energy C - C bonds. This conversion happens in the plants photosystems.
Respiration is **exothermic**. This means it could occur spontaneously and release energy. In actuality it is always mediated by bacteria which use the reactions to obtain their energy for life.

3. **Stoichiometry breakdown of oxygen production**

\[
\begin{align*}
\text{CO}_2 + \text{H}_2\text{O} & \rightarrow (\text{CH}_2\text{O}) + \text{O}_2 & \text{C : O}_2 & \rightarrow 1 : 1 \\
\text{H}^+ + \text{NO}_3^- + \text{H}_2\text{O} & \rightarrow (\text{NH}_3) + 2\text{O}_2 & \text{N : O}_2 & \rightarrow 1 : 2
\end{align*}
\]

**Total oxygen production**: \( 106 \text{ C} + 16 \text{ N} \times 2 = 138 \text{ O}_2 \)

4. If **ammonia** is available it is preferentially taken up by phytoplankton.

If NH\textsubscript{3} is used as the N source then less O\textsubscript{2} is produced during photosynthesis

\[
\begin{align*}
106 \text{ CO}_2 + 16 \text{ NH}_3 + \text{H}_3\text{PO}_4 + 122 \text{ H}_2\text{O} & \text{trace elements} & \text{light (hν)} & \downarrow \\
(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}(\text{H}_3\text{PO}_4) & + & 106 \text{ O}_2
\end{align*}
\]

The relationship between O\textsubscript{2} and NO\textsubscript{3}/NH\textsubscript{4} is 2:1 (as shown in point #3)

\[
16 \text{ HNO}_3 + 16 \text{ H}_2\text{O} = 16 \text{ NH}_3 + 32 \text{ O}_2
\]
Inorganic Nutrients

1. Physical Speciation (operational definitions!)

   A. Dissolved -- pass thru a specified filter
   
   B. Particulate -- retained by a specified filter
   
   C. Colloidal -- pass thru conventional filters, but are not dissolved

2. Chemical Speciation
   
   A. Phosphorus
      
      i. Dissolved Inorganic Phosphorus (DIP)
         
         a. pH-dependent speciation of Orthophosphate:
            
            $\text{H}_3\text{PO}_4$
            $\text{H}_2\text{PO}_4^-$
            $\text{HPO}_4^{2-}$ (most important at sw pH)
            $\text{PO}_4^{3-}$
            
         b. Polyphosphate – linked phosphate polymers

   Dissolved Organic Phosphorus (DOP) – e.g., Phospholipids, ATP, ADP
THE GLOBAL PHOSPHORUS CYCLE

TERRESTRIAL
- Erosion: Biotites, soils, and sediments
- Chemical Weathering: Dissolved P

MARINE
- Phytoplankton, P uptake
- Detrital input
- Decomposition
- Diagenesis

SLOPE SEDIMENTS
- Benthic P inputs
- Respiration
- Detritus

ARCTICAL SEDIMENTS
- Respiration
- Detritus

Characteristic deep-sea dissolved phosphate profiles for three ocean basins

SEDEX Scheme for Different Forms of Phosphorus in Marine Sediments

<table>
<thead>
<tr>
<th>Step</th>
<th>Extractant</th>
<th>Extracted</th>
</tr>
</thead>
<tbody>
<tr>
<td>I-A</td>
<td>MgCl₂ (pH 8)</td>
<td>Locally sorbed P</td>
</tr>
<tr>
<td>I-B</td>
<td>MgCl₂ (pH)</td>
<td>Residual</td>
</tr>
<tr>
<td>I-C</td>
<td>H₂O wash</td>
<td>Residual</td>
</tr>
<tr>
<td>I-D</td>
<td>H₂O wash</td>
<td>Residual</td>
</tr>
<tr>
<td>II-A</td>
<td>CDB (pH 7.6)</td>
<td>Fe-bound P</td>
</tr>
<tr>
<td>II-B</td>
<td>MgCl₂ (pH)</td>
<td>Residual</td>
</tr>
<tr>
<td>II-C</td>
<td>H₂O wash</td>
<td>Residual</td>
</tr>
<tr>
<td>III-A</td>
<td>Acetate Bathill (pH 4.6)</td>
<td>Authigenic Apatite</td>
</tr>
<tr>
<td>III-B</td>
<td>MgCl₂ (pH)</td>
<td>Biogenic Apatite</td>
</tr>
<tr>
<td>III-C</td>
<td>H₂O wash</td>
<td>CaCO₃-bound P</td>
</tr>
<tr>
<td>III-D</td>
<td>Residual</td>
<td>Detrital Apatite</td>
</tr>
<tr>
<td>IV</td>
<td>M HCl</td>
<td>Organic P</td>
</tr>
<tr>
<td>V</td>
<td>Ethanol 55% 92% M HCl</td>
<td>3 h, 25°C</td>
</tr>
</tbody>
</table>

Ruttenberg
Seasonal P variations

Sedimentation of particulate phosphorus (org P dep)

Release of DIP from seds

B. Nitrogen

Redox-dependent speciation of dissolved forms:

<table>
<thead>
<tr>
<th>Species</th>
<th>Oxid State</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{NO}_3^-$ (nitrate)</td>
<td>+V</td>
</tr>
<tr>
<td>$\text{NO}_2^-$ (nitrite)</td>
<td>+III</td>
</tr>
<tr>
<td>$\text{N}_2\text{O}$ (nitrous oxide)</td>
<td>+I</td>
</tr>
<tr>
<td>$\text{N}_2$ (dinitrogen)</td>
<td>0</td>
</tr>
<tr>
<td>$\text{NH}_4^+$ (ammonium ion)</td>
<td>-III</td>
</tr>
<tr>
<td>Organic-N (e.g., Urea $\text{H}_2\text{N-CO-NH}_2$)</td>
<td>-III</td>
</tr>
</tbody>
</table>

Dissolved Inorganic Nitrogen (DIN)

Dissolved Organic Nitrogen (DON)

Ammonia $\text{NH}_3$:

- $\text{NH}_4^+$ (ammonium ion)
- $\text{NH}_3$ (ammonia)
Main Ocean Source of N
Nitrogen Fixation
Enzyme catalyzed reduction of N₂

\[ \text{N}_2 + 8\text{H}^+ + 8\text{e}^- + 16 \text{ATP} \rightarrow 2\text{NH}_3 + \text{H}_2 + 16\text{ADP} + 16\text{P}_i \]

Mediated by a two protein (Fe and Fe-Mo) complex called nitrogenase

Inactivated when exposed to O₂

Main Ocean Sink of N
Fixed Nitrogen (NO₃⁻, NO₂⁻, NH₄⁺) is converted to N₂ in low oxygen zones of the ocean

Two Pathways
Denitrification (<2 to 10 mM O₂):

2 NO₃⁻ + organic matter \rightarrow N₂

Anammox (<2 mM O₂)

\[ \text{NH}_4^+ + \text{NO}_2^- \rightarrow \text{N}_2 + \text{H}_2\text{O} \]

Aquatic microbial N cycling

A) nitrogen fixation  
B) NOx assimilation  
C) ammonification  
D) NH₄⁺ assimilation  
E) NH₄⁺ oxidation  
F) NO₂⁻ oxidation  
G) NO₃⁻ ammonification  
H) Denitrification  
I) anammox

a, burial  
b, downward diffusion  
c, upward diffusion  
d, NH₄⁺ adsorption  
e, NH₄⁺ desorption

Canfield Fig. 11.10
C. Silica

Soluble forms:

- $H_2SiO_3$ (95% of total dissolved silica – over a broad pH range)
- $HSiO_3^-$ (5% of total dissolved silica)
- $SiO_3^{2-}$ (<1% of total dissolved silica)

![Silica solubility diagram]

Nutrient Regeneration and AOU

**The Redfield-Richards equation:**

$$106 \text{CO}_2 + 16 \text{HNO}_3 + 1 \text{H}_2\text{PO}_4 + 122 \text{H}_2\text{O} \rightarrow (\text{CH}_2\text{O})_{106} (\text{NH}_3)_{16} (\text{H}_2\text{PO}_4) + 138 \text{O}_2$$

The forward reaction is Photosynthesis
The reverse reaction is Respiration

The elemental changes during respiration:

<table>
<thead>
<tr>
<th>Species</th>
<th>$\Delta C$</th>
<th>$\Delta N$</th>
<th>$\Delta P$</th>
<th>$\Delta O$</th>
<th>$\Delta O_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(dissolved species)</td>
<td>+106</td>
<td>+16</td>
<td>+1</td>
<td>-276</td>
<td>-138</td>
</tr>
</tbody>
</table>

- $\Delta P$ = Oxidative Phosphate = $P_{\text{oxid}}$ = P released during respiration
- $\Delta O_2$ = Apparent Oxygen Utilization (AOU)

Detrital POM + lateral water mass movement + aerobic respiration = O$_2$ consumption

AOU = Normal Atmospheric Equilibrium Conc − [O$_2$]$_{\text{in situ}}$
**Food Web Structure**

**Different N Sources**

**New Production** - NO$_3$ - as N source (from diffusion/upwelling from below and from the atmosphere via nitrogen fixation and nitrification)

**Regenerated Production** - NH$_4^+$ and urea as N source

**New/Net/Export Flux**

The $f$-ratio:

$$f = \frac{\text{NO}_3 \text{ uptake}}{\text{NO}_3 + \text{NH}_4 \text{ uptake}}$$

(defined by Dugdale and Goering, 1969)

If we write $P =$ gross production and $R =$ respiration then we can also approximate $f$ as:

$$f = \frac{P - R}{P}$$

also called the ratio of **net to gross production**
**Nutrient Vertical Profiles**

*FIGURE 10.1. Vertical distribution of (a) nitrate, (b) phosphate, and (c) dissolved silicon in the Atlantic, Pacific, and Indian oceans. Note that 1 μg-atom/L is equivalent to 1 μM. Thus 1 μg-atom NO$_3^-$/L is equivalent to 1 μmol of dissolved nitrogen (in the form of NO$_3^-$) per liter of seawater.*
Mid-Ocean Nutrient Profiles - Phosphorus

Main processes controlling vertical distribution of nutrients:

- High consumption of inorganic nutrients; high production of organic nutrients
- Slow release of inorganic nutrients due to decomposition of falling particles; slow utilization of organic nutrients

Mid-Ocean Nutrient Profiles - Nitrogen

Denitrification (nitrate reduction):

\[ 2\text{NO}_3^- + \text{CH}_2\text{O} + 8\text{H}^+ + 6\text{e}^- \rightarrow \text{N}_2 + \text{CO}_2 + 5\text{H}_2\text{O} \]
Typically, nitrate and nitrite are measured together (reported as their sum). However, nitrite maxima can be observed:

Nitrite - An Indicator of “Suboxia”

Subsurface maximum (presumably due to suboxic zone in/on particles)

\( \text{O}_2 \)-minimum zone maximum

\( \text{NH}_4^+ \) profiles look similar (two maxima)

**Oxygen – Nutrient Diagrams**

Redfield-Richards Equation in Action – NW Pacific

**Fig. 4.** Oxygen-phosphate diagram. Comparison between winter and summer data. The numbers by the data points represent depth in meters. The position of the stations not given in the legend to Fig. 3 is: 116 (44°31.0’N, 174°37.0’W).

**Fig. 5.** Oxygen-nitrate diagram. Data presented as in Fig. 4.

Redfield: \( \text{AOU}/\Delta P = 138/1 = 138 \)

\( \text{AOU}/\Delta N = 138/16 = 9 \)

Actually, \( \text{NO}_2^- + \text{NO}_3^- \).

For simplicity, ignore \( \text{NH}_4^+ \).
Why Are Nutrient Concs Different in Each Ocean?

Look at Ocean Net Flow at 4000 m

Figure 1-12. Flow pattern at a depth of 4000 meters. The major inputs to this horizon are North Atlantic Deep Water (NADW) which enters at the northern end of the western basin of the Atlantic and Weddell Sea Bottom Water (WSBW) which enters from the margin of the Antarctic continent adjacent to the South Atlantic.

Dissolved Oxygen at 4000 m

Figure 1-11. The distribution of dissolved oxygen at 4000 meters depth in the world's major ocean basins. Based on results obtained during the GBSUSGOS program.
For biogeochemically regenerated elements in seawater, the Redfield-Richards Equation indicates:

\[
\text{[Measured]} = \text{[Preformed]} + \text{[Oxidative]}
\]

\text{[Oxidative]} = \text{Change in conc due to organic matter oxidation}
\[ 106 \text{CO}_2 + 16 \text{HNO}_3 + 1 \text{H}_3\text{PO}_4 + 122 \text{H}_2\text{O} \rightarrow [(\text{CH}_2\text{O})_{106} (\text{NH}_3)_{16} (\text{H}_3\text{PO}_4)] + 138 \text{O}_2 \]

The elemental changes during respiration:

\[
\begin{align*}
\Delta \text{C} & = +106 \\
\Delta \text{N} & = +16 \\
\Delta \text{P} & = +1 \\
\Delta \text{O} & = -276 \\
\Delta \text{O}_2 & = -138
\end{align*}
\]

\[ \text{[Measured]} = \text{[Preformed]} + \text{[Oxidative]} \]

**APPLICATION:**

Calculate organic matter oxidation rate in a given water mass using AOU.

1. Measure: \(T, S, [O_2_{\text{meas}}]\)

2. Calculate \([O_2_{\text{measured}}]\) from \(T\) and \(S\) data

3. Calculate: \(\text{AOU} = [O_2_{\text{measured}}] - [O_2_{\text{meas}}] \) (mol/L)

4. Calculate organic carbon oxidized in the water mass since its formation (\(\Delta C\)):
   \[
   \Delta C / \text{AOU} = 106 / 138 = 0.77 \quad \text{(Solve for } \Delta C)\]

5. Calculate average rate of organic matter oxidation:
   
   \[
   \text{Rate} = \Delta C / \text{time since "formation" of the water mass}
   \]

   \[
   \text{[E.g., obtain age of the water mass from } \Delta ^{14} \text{C, } \Delta \text{He}/\text{H data, or Freon-ratio data]}\]
Use appropriate local Redfield (C:P) ratio

\[ \text{Denitrification (nitrate reduction):} \]
\[ 2\text{NO}_3^- + \text{CH}_2\text{O} + 8\text{H}^+ + 6e^- \rightarrow \text{N}_2 + \text{CO}_2 + 5\text{H}_2\text{O} \]
Particle Composition

C : N : P ratio of sinking particulate matter will reflect:
1) The C : N : P ratio of the sources (plankton (with and without structural material), fecal pellets, eolian deposition, etc.)
2) Differential losses during sinking (biological activity, photo-decomposition, dissolution, etc.)
3) Differential inputs during sinking (adsorption, biosynthesis, etc.)

<table>
<thead>
<tr>
<th>Particle composition in surface seawater:</th>
<th>C : N : P</th>
<th>C : N</th>
</tr>
</thead>
<tbody>
<tr>
<td>North Pacific Gyre</td>
<td>152 : 18 : 1</td>
<td>8.4</td>
</tr>
<tr>
<td>Central North Pacific</td>
<td>410 : 29 : 1</td>
<td>14</td>
</tr>
<tr>
<td>Equatorial Atlantic</td>
<td>163 : 21 : 1</td>
<td>7.8</td>
</tr>
<tr>
<td>West. North Atlantic (Jan - winter)</td>
<td>59 : 5 : 1</td>
<td>11.8</td>
</tr>
<tr>
<td>West. North Atlantic (April - spring bloom)</td>
<td>68 : 13 : 1</td>
<td>5.2</td>
</tr>
</tbody>
</table>

Note: C : N varies by 3
C : P varies by 7

THUS, IF YOU PLAN TO USE THE “REDFIELD RATIO”,
YOU’LL NEED DATA FROM YOUR FIELD SITE!!

Homework Due: March 9

Annotated outline
(first draft due April 6)
Homework Due: March 9, 2010

Annotated outline

Topic Choice
The topic chosen is narrowed, specific, and appropriate for the length of the paper.

Purpose
The paper generates intellectual interest, suggesting a mature, realistic grasp of the material.

Audience
The author attends highly to the needs of the audience throughout, never talking down to or insulting the audience, and assumes that the audience is intelligent and interested.

Introduction
The introduction gains the reader’s attention legitimately, establishes the writer’s credibility, and forecasts the central thrust of the paper.

Paragraphing and Arrangement / Headings
Paragraphs are clearly focused, unified, and sensibly arranged. Transitions between and within paragraphs are thoughtfully chosen, and section headings—if included—are carefully worded and germane.

Conclusion
The conclusion is directly based on earlier parts of the paper and gives the reader new insight or reinforces the introduction’s hypothesis or thesis in a clear manner. The conclusion lends closure to the essay.

Content and Reasoning
Content is well-developed and thoughtfully selected; reasoning is in control of the subject’s complexity—i.e., examples are potent, relevant, concrete, and authoritative; generalizations are qualified and sensible; logic is sound.

Citation
Proper citation style is used, and sources are cited accurately and wisely. There is no hint of plagiarism.

Tables and Figures
Tables and figures are purposefully and professionally presented. Captions are well-worded and the accompanying interpretation of tables and figures is meaningful. Tables and figures work both independently and in context.

Sentence Structure / Wording / Usage
The paper exhibits ease with idioms. The writer shows facility with various sentence lengths and types so that the paper is highly readable. The writing includes concrete and exact nouns and adjectives, active interpretive verbs and adverbs, and an appropriate range of vocabulary and syntax. Usage—especially subject/verb agreement and pronoun/antecedent agreement—conforms to standard conventions of edited English.

Punctuation
There are few or no punctuation errors, especially errors such as comma splices, which hinder the reader’s understanding of the material. Punctuation is used to enhance both readability and comprehension.

Spelling and Proofreading
There are few or no spelling or typographical errors, especially in words key to the paper’s thrust.