1) Box Models of Nitrogen Cycling
Nitrogen fixation has become the latest "hot topic". Lets assess its importance. Construct a two-box ocean model for nitrogen as nitrate. Include river inflow, atmospheric deposition of NO₃, nitrogen fixation, upwelling, downwelling, denitrification in the deep box and a biological flux of organic N (B). The removal rate to the sediments (S) is expressed as \( S = f \times B \). Assume for today that denitrification is a sink process that removes nitrate by converting it to \( \text{N}_2 \) gas that escapes back to the atmosphere. Nitrogen fixation is a source process whereby organisms ultimately convert atm \( \text{N}_2 \) to nitrate.

From the literature we find some information that we may (or may not) need:

- Global ocean denitrification = 175 TgN y⁻¹
- River Input = 76 TgN y⁻¹
- Atmospheric Deposition = 30 TgN y⁻¹
- Sediment Burial = 25 TgN y⁻¹
- Upwelling rate \( V = 300 \text{ cm y}^{-1} \)

\[ f = 0.01 \]
\[ \text{Area} = 3.61 \times 10^8 \text{ km}^2 \]

a) Draw the Broecker style two-box model for this problem and label the fluxes (including transport terms \( V_m \) and biological fluxes \( B \) and the fluxes listed above). (5 pts).

b) Write the mass balance equations for nitrate the surface and deep boxes. You can assume that the N buried in the sediments \( fB \) equals the river flux \( VrCr \). Derive an expression for the B flux from the surface box to deep box. Use the mass balance for nitrate in the deep box explain what controls the nitrate concentration. (10 pts)
2) Ocean Carbonate System
Imagine you have a sample of surface seawater in the lab. Indicate what will happen to
the following properties when you perform the operations listed on the left by inserting
an up arrow (↑), down arrow (↓), or horizontal line (if it remains unchanged). No
explanation is necessary. (21 pts)

<table>
<thead>
<tr>
<th>Operation</th>
<th>[CO₂] + [H₂CO₃]</th>
<th>[HCO₃⁻]</th>
<th>[CO₃²⁻]</th>
<th>pH</th>
<th>DIC</th>
<th>Alk</th>
<th>δ¹³C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bubble with N₂ gas</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Respire OM to DIC</td>
<td></td>
<td></td>
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<tr>
<td>Dissolve CaCO₃(s)</td>
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</tr>
</tbody>
</table>

3) Radioactive Decay
A shortened version of the ²³⁸U decay chain is shown below. The activities of the two isotopes of
U and Th in the deep sea are also given.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>dpm 100kg⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>²³⁸U</td>
<td>240</td>
</tr>
<tr>
<td>²³⁴Th</td>
<td>240</td>
</tr>
<tr>
<td>²³⁴U</td>
<td>280</td>
</tr>
<tr>
<td>²³⁰Th</td>
<td>0.15</td>
</tr>
</tbody>
</table>

a) U is a conservative element in seawater but the activities of ²³⁸U and ²³⁴U are different.
Which isotope has the higher molar concentration (you don’t need to calculate the concentration)
and explain why? (10 pts)

b) Are ²³⁸U and ²³⁴Th in secular equilibrium in the deep ocean? Explain what conditions are
required for secular equilibrium and what this means.(10 pts)

c) Explain in a few short sentences and/or equations why the activities of ²³⁴Th and ²³⁰Th in the
deep ocean are so different.(5 pts)
4) **CaCO₃ versus organic carbon**

We know from ice core records that atmospheric CO₂ varied from high values of about 280 ppm during interglacials to 180 ppm during glacial periods. The regular variation of P₇CO₂ over many glacial cycles has been one of the major unexplained puzzles in marine geochemistry.

During the last glacial period organic matter degradation took place deeper in the ocean causing the deep water to have a lower pH and be more corrosive to CaCO₃. If everything else was the same as now, except that a lot more CaCO₃ dissolution took place in ocean sediments over a period of about 10 kyr,

a) How would the present day plot of DIC vs Alk (from Emerson and Hedges Plate 2) change? Draw the qualitative new trend and explain. (10 pts)

b) How would the new Alk vs DIC, which after time would be mixed into the surface ocean, affect the P₇CO₂ of the atmosphere. Support your answer with carbonate system justification. Is this in the right direction to explain the glacial/interglacial changes? (10 pts)
5. **Biological stoichiometry**

Nitrate and oxygen have been measured as a time series in the subarctic North Pacific at Station P (Whitney et al., 2007, Progress in Oceanography, 75, 179-199). The rates of change in integrated concentrations between 100m to 600m between 1994 and 2003 (see lines in the Figure) were +0.26 mol NO$_3$ m$^{-2}$ y$^{-1}$ and -2.4 mol O$_2$ m$^{-2}$ y$^{-1}$.

a) What is the magnitude of the relative change in O$_2$ to NO$_3$? Is this consistent with the Redfield equation for the stoichiometry of biological respiration? Explain what the data suggest. (10 pts)

![Graph showing changes in oxygen (O2) and nitrate (NO3) concentrations over time.]

b) Explain how these trends could be explained by changes in ocean new production or rate of thermocline ventilation. (10 pts)

c) These changes could also result in a natural ocean acidification. What would you predict to be the rate of addition of CO$_2$ to these waters from this change in respiration (5 pts).