1. Acidity derived from the carbonic acid system is the most important control on the pH seawater and links many key processes. Use solubility and first and second acidity constants written below.

\[
\begin{align*}
\text{CO}_2(g) + \text{H}_2\text{O} &= \text{H}_2\text{CO}_3 \\
\text{H}_2\text{CO}_3 &= \text{H}^+ + \text{HCO}_3^- \\
\text{HCO}_3^- &= \text{H}^+ + \text{CO}_3^{2-}
\end{align*}
\]

- \( \log K'_{\text{H}} = -1.5 \)
- \( \log K'_{1} = -6.0 \)
- \( \log K'_{2} = -9.0 \)

a) The carbonate ion \( \text{CO}_3^{2-} \) and \( \text{P}_{\text{CO}_2} \) are observed to be inversely related in seawater. \textbf{Why is this the case? Qualitatively explain the controlling processes.} (5)

b) How does \( \text{P}_{\text{CO}_2} \) in the deep North Pacific compare with the deep North Atlantic? If they are different explain why. (5)

c) Write a balanced reaction of \( \text{P}_{\text{CO}_2} \) going to \( \text{CO}_3^{2-} \) (5)
d) What is the equilibrium constant for this reaction? (5)

e) Assume surface seawater is in equilibrium with the atmosphere \( P_{CO2} = 10^{-3.5} \) at pH 8.0 what is the concentration of \( CO_3^{2-} \)? Show your work. (10)

2. Weathering reactions are the main source for most ions in river water.
   True/False
   a) Clay minerals weather to make silicate minerals. (1)

   b) Calcite weathering produces two \( HCO_3^- \) for each \( CO_2 \) consumed. (1)

   c) In both seawater and river water \( Na^+ \) is the main cation
   and \( Cl^- \) is the main anion. (1)

   d) The composition of rivers differs between continents because of the variable proportions of carbonate and silicate rocks present on different continents. (1)
3. Potassium (K⁺) is one of the major ions in seawater. Some argue that K⁺ is conservative in seawater.

   How would you show this? What data would you need? (5)

4. Major ions in seawater (True/False)
   a) are all conservative in seawater (1)
   b) are all greater than 1 mg kg⁻¹ (1)
   c) are all added to the oceans from rivers (1)
   d) are all significantly removed from the ocean by ridge crest processes (1)
   e) have high concentrations because of evaporation of river water (1)

5. Oxygen is a chemical tracer for biological rates. Both photosynthesis and respiration take place in the photic zone. Explain how the balance between these processes influences the concentration of dissolved oxygen (O₂) in the water. Under what conditions would you find an excess of O₂ (5)
6. Respiration of organic matter
Consider 1) a sample from the Atlantic Ocean that has an apparent oxygen utilization (AOU) of 85 µmol kg⁻¹ and 2) the reaction listed below for the oxic respiration of particulate organic matter (POM).

\[
(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 138O_2 \rightleftharpoons 106CO_2 + 122H_2O + 16HNO_3 + H_3PO_4
\]

Equation 1

a) Calculate how many moles of carbon, moles of POM and milligrams of POM must have been completely oxidized in this sample according to the Redfield stoichiometry of POM shown in the above Equation 1? The molecular weight of this POM is 3553 g mol⁻¹. (10)

b) Define apparent oxygen utilization (AOU). How is AOU converted to an oxygen utilization rate (OUR)? What additional data and samples are needed? (5)
7. Arrigio (2005) described various processes of the nitrogen cycle in aquatic systems. Match the name in the first column with its proper chemical reaction from the second column by writing the appropriate letter in the blank space following the name. 
PON = Particulate Organic Nitrogen. (each correct answer is worth (1) point).

(i) ammonification _____ (a) PON ---> NH₄⁺
(ii) nitrification _____ (b) N₂ (g) ---> PON
(iii) denitrification _____ (c) NO₃⁻ ---> NO₂⁻ ---> N₂ (g)
(iv) nitrogen fixation _____ (d) NH₄⁺ + NO₂⁻ ---> N₂
(v) DIN assimilation _____ (e) NH₄⁺ ---> PON; NO₃----> PON
(vi) anammox _____ (f) NH₄⁺ ---> NO₂⁻ ---> NO₃⁻

8. Concentrations of organic matter in marine sediments vary by a factor of almost 100.

a) How do the concentrations of organic carbon (in units of weight %) vary from anoxic basins, coastal ocean and open ocean sediment? (S)

b) What types of environments have the highest concentrations of organic carbon? Why? In answering this question, consider what factors control the preservation of organic carbon in marine sediments that help explain the differences in carbon concentration in the environments listed in part (a)? (10)
9. Fresh organic matter in the ocean is made up of specific types of compounds.
   a) What major organic compound classes make up marine biomass? (2)
   
   b) Which would you expect to see preserved in ancient sediments. (1)

10. Calculate the oxygen exposure time (OET) in
    1) a typical coastal sediment with an oxic layer ~1mm thick and sedimentation rate of 1.0 cm/year. (5)
    2) an open ocean site with an oxic layer that is 10cm thick and a sedimentation rate of 1cm/1000years. (5)

   What do your calculations imply about the carbon burial efficiencies and organic carbon concentrations in these two environments? (5)

11. True of False: Assuming little sediment transport, medium order rivers should:
    a) Have a respiration: photosynthesis ratio greater than 1? (1).
    
    b) Contain more coarse particulate organic matter than low order rivers. (1)
    
    c) Be dominated by autochthonous inputs. (1)
12. Thiosulfate ($S_2O_3^{2-}$) is often found in near shore marine sediments.  
   a) What is the oxidation state of $S$ in $S_2O_3^{2-}$? (5) 

   b) Is thiosulfate oxidized or reduced relative to $SO_4^{2-}$? (2) 

13. The concentration of dissolved Mn in seawater (assumed to be $Mn^{2+}$) is about 20 nM (i.e. $10^{-8}$M). There is debate about whether the concentrations of $Mn^{2+}$ is in equilibrium with $MnO_2(s)$. $MnO_2$ is a major phase in marine sediments and manganese nodules.

   Two half reactions are given:
   
   \[ \frac{1}{4} O_2(g) + H^+ + e^- = \frac{1}{2} H_2O \quad \log K = 20.75 \]
   \[ \frac{1}{2} MnO_2(s) + 2H^+ + e^- = \frac{1}{2} Mn^{2+} + H_2O \quad \log K = 20.8 \]

   a) Write the balanced redox reaction of $Mn^{2+}$ being oxidized by $O_2$ (5)

   b) What is the value of the equilibrium constant for this reaction? (5)

   c) If $P_{O_2} = 0.2$ and pH = 8.0 what is the equilibrium concentration of $Mn^{2+}$. Compare this concentration with that observed. Is $Mn^{2+}$ in seawater in equilibrium with $MnO_2(s)$? (5)
14. Sarmiento and Gruber (2002) show the following carbon cycle. The black numbers show the reservoirs and fluxes before anthropogenic addition of CO₂. The red numbers are the increases.

a) Was atmospheric CO₂ at steady state before anthropogenic additions? Explain. (5)

b) Is atmospheric CO₂ currently at steady state? Explain. (5)

c) What is the residence time of C in marine biota? (5)