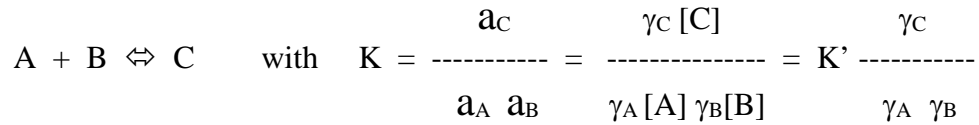


(10) 1. List and explain five (5) reasons for studying trace metal speciation or the speciation of any element or chemical constituent found in the ocean.

(10) 2. Given the following hypothetical equilibrium reaction between three ions in water



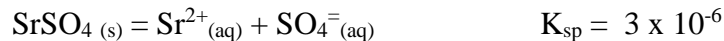
When going from freshwater (e.g., the river end member) to saltwater (e.g., the coastal ocean end member), the species A, B and C experience the ionic or electrostatic influence from the various seawater salts present. Assuming that none of these background salt species directly react with A, B or C, but rather provide nonspecific ionic interactions, explain briefly the following:

(a) Do A and B react with each other to a greater extent in freshwater or saltwater? Why?

(b) Is K larger at a low ionic strength as found in freshwater or for an ionic strength as found in seawater at a salinity of 35? What about K'?

(10) 3. Briefly define the following terms: carbon capture, ocean sequestration, hydrate, dense plume, CO<sub>2</sub> lake

(10) 4. Acantharin protozoa use strontium to form celestite, SrSO<sub>4(s)</sub>, skeletons. The solubility of celestite is written as:



(a) Set up the solubility product expression (i.e. equation for K) and calculate the solubility of SrSO<sub>4</sub> in distilled water.

(b) Using the Davies equation given below, do the same calculation for the ionic strength of seawater at a salinity of 35.

$$\log \gamma = -AZ^2 \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2I \right)$$

where A = 0.51

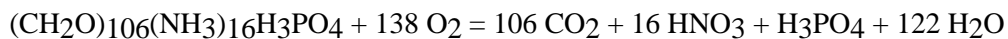
(c) If seawater has a [SO<sub>4</sub><sup>2-</sup>] = 28.93 mmol/L, calculate the expected free strontium concentration, [Sr<sup>2+</sup>], using the solubility product expression, the K<sub>sp</sub> and the sulfate concentration. Be sure to correct for ionic strength.

(10) 5. In class and in the book, depth profiles (depth vs. concentration) were given and discussed for species (e.g. trace metals) that are found distributed in at least six different, yet well characterized ways. A conservative profile was the simplest of these behaviors. Name and draw examples of four (4) other profiles (not including conservative behavior) and explain what might give rise to the observed distribution. Give an example of each.

(10) 6. What are the equilibrium expressions that define the carbonate system in natural waters? Define each parameter and variable used in these equations. Sketch a plot showing the effect of pH on the relative proportions of the major carbonate species. How does this plot reflect

the equilibrium expressions? Also referencing this plot, what is meant by ocean acidification and what are its environmental implications?

- (10) 7. (a) What is the critical depth hypothesis and how does it account for the onset of the canonical spring phytoplankton bloom? What is the equation used to calculate the penetration of light into the ocean and its significance to the critical depth hypothesis. What is the value of the extinction coefficient if 1% of surface light intensity is found at 80 m. Sketch as a function of depth the relative changes in light and primary production. What factors cause a spring bloom to 'crash'?
- (10) 8. Discuss the major components of the marine N cycle with respect to sources and sinks as well as internal cycling as a function of redox state. Include a description of the oceanographic settings which favor different processes. What is the importance of the N cycle to other major marine biogeochemical cycles? How is the residence time for oceanic N estimated? How can the ocean's N cycle influence global climate?
- (10) 9. Robots of varying kinds (floats, gliders) are starting to do most oceanographic data collection. Imagine one initially deployed near-surface in the subduction zone for AAIW. It collects data at sampling point #1, and then sinks and moves along the flow path for AAIW by tracking an isopycnal surface. Below are the data for point #1 and O<sub>2</sub> data for 2 subsequent collection points. If Redfield stoichiometry held, predict the values for the empty boxes. Assume release of DIC from CaCO<sub>3</sub> dissolution equally important as from organic matter decomposition. What could cause deviations in Redfield stoichiometry, giving a specific example? What would happen if O<sub>2</sub> reached values < 5 μmol/kg?

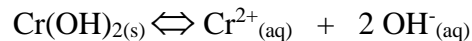


Sampling #	O <sub>2</sub> (μM)	O <sub>2</sub> sat. (μM)	AOU (μM)	NO <sub>3</sub> <sup>-</sup> (μM)	PO <sub>4</sub> <sup>-3</sup> (μM)	TCO <sub>2</sub> (μM)	Alk (μM)
1	300	300		16.0	1.0	2200	2350
2	200	300					
3	150	300					
4	50	100					

- (10) 10. (a) <sup>238</sup>U has a half life of 4.47 billion years. Why is it a 'primordial' radioisotope? If somehow you obtained a sample of <sup>238</sup>U with an activity of 10,000 Bq, how long would your descendants have to wait before they are left with 9,999 Bq. Assuming secular equilibrium, what is the activity of the daughter <sup>234</sup>Th (half life ~ 24.1 days) and the mode of decay? If you chemically isolated the <sup>234</sup>Th, what would the activity be after 48.2 days and why? Briefly, why is this parent-daughter pair well suited for measuring particle fluxes in the ocean?
- (b) You are trying to date several depth layers in a sediment core and determine its average sedimentation rate using <sup>14</sup>C (half life ~ 5730 years). At the core top you observe the organic C has the same <sup>14</sup>C content as expected for modern carbon (100%). At 10 cm depth in the core, organic C has 67% of the modern <sup>14</sup>C content, at 20 cm 45% of the modern content, and at 30 cm 30 % of the modern content. What are apparent ages for each of these four depth layers and the average sedimentation rate in cm/thousand years? What assumptions did you need to make? Ignore atom bomb <sup>14</sup>C.

- (8) 1. (a) List and explain four (4) reasons for studying trace metal speciation or the speciation of any element or chemical constituent found in the ocean.
- (2) (b) Describe a speciation methodology discussed in class giving a general outline of how it works, what measurements are made, what type of data is produced, etc.
- (1) 2. (a) Accurately state the Rule of Constant Proportions (a.k.a., Marcet Principle or Constancy of Composition).
- (5) (b) List five (5) major ions in seawater that it applies to.
- (4) (c) Describe four (4) of the several exceptions to the Rule of Constant Proportions that were described in class.
- (10) 3. Briefly define the following terms: carbon capture, ocean sequestration, hydrate, dense plume, CO<sub>2</sub> lake.

- (10) 4. A marine biologist would like to conduct a bioaccumulation experiment involving the exposure of the mussel, *Mytilus edulis*, to chromium (II) ion (Cr<sup>2+</sup>) in filtered Boston Harbor seawater using aquaria in the laboratory. The marine biologist comes to you because of your vast knowledge of ionic equilibria and to determine how much free chromium (II) ion will be present in full strength seawater at a salinity of 35. You find out that the experiment calls for a total chromium concentration of 5.0 x 10<sup>-6</sup> moles/kg. Under certain pH conditions, Cr<sup>2+</sup> reacts with OH<sup>-</sup> (i.e., it hydrolyzes) to form the insoluble Cr(OH)<sub>2</sub> precipitate described by the single step reaction



and the solubility expression is

$$K_{sp} = a_{\text{Cr}} (a_{\text{OH}})^2$$

Calculate the amount of free Cr<sup>2+</sup> that would be soluble in the seawater for mussel exposures at pH 8.2 typical of the open ocean and pH 7.4 which is common for estuaries like Boston Harbor. In other words, calculate the solubility of Cr(OH)<sub>2</sub> in SW at both pH 8.2 and 7.4. Be sure to correct for the ionic strength by selecting an appropriate value and using the Davies equation given below.

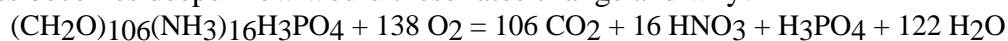
$$\ln \gamma = -1.17 Z^2 \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right)$$

The K<sub>sp</sub> for Cr(OH)<sub>2</sub> at 25°C is 4.75 x 10<sup>-18</sup>. Express your answer as the concentration of free Cr<sup>2+</sup> ion in moles/kg that remains dissolved. (Hint: The solubility expression has only 3 terms, one is given and another can be calculated from the pH.)

- (10) 5. In class and in the textbook, depth profiles (depth vs. concentration) were given and discussed for species (e.g. trace metals) that are found distributed in at least six different, yet well characterized ways. A conservative profile was the simplest of these behaviors. Name and draw examples of four (4) other profiles (not including conservative behavior) and explain what might give rise to the observed distribution. Give one (1) chemical constituent of seawater as an example of each.
- (10) 6. What are the equilibrium expressions that define the carbonate system in natural waters? Define each parameter and variable used in these equations. Sketch a plot showing the effect of pH on the relative proportions of the major carbonate species. How are these proportions altered by changing pH from 8 to 6? When organic matter degrades in the deep ocean, how do the carbonate system parameters change and why? Reference this plot in your answer. Accordingly, what are the relative changes in carbonate system parameters expected as a water mass ages in the deep ocean. Also referencing this plot, what is the cause of ocean acidification and what are its environmental implications?

- (5) 7. (a) What is the critical depth hypothesis and how does it account for the onset of the canonical spring phytoplankton bloom? What is the equation used to calculate the penetration of light into the ocean and what is its significance to the critical depth hypothesis? Define each parameter in the equation. What is the value of the extinction coefficient if 1% of surface light intensity is found at 70 m?
- (5) (b) What are HNLC regions and where are they found? What is thought to limit productivity in these regions and what is the evidence for it citing specific examples? How do HNLC conditions lead to preformed nutrients in the deep ocean?
- (10) 8. Discuss the major microbial pathways for the marine N cycle with respect to sources and sinks as well as internal cycling. How does the wide range of redox states for nitrogen favor these pathways? What are the oceanographic settings that promote different processes? Why is the N cycle important to other major marine biogeochemical cycles and how can we detect past changes in the ocean nitrogen cycling (cite a specific example)?
- (10) 9. Robots of varying kinds (floats, gliders) are starting to do most oceanographic data collection. Imagine one initially deployed in the subduction zone for AAIW. It collects data at sampling point #1 which is near-surface, and then sinks and moves along the flow path for AAIW by tracking an isopycnal surface. Below are the data for point #1 and O<sub>2</sub> data for 3 subsequent collection points. If Redfield stoichiometry held, predict the values for the empty boxes. Assume that CaCO<sub>3</sub> dissolution is not occurring.

What data would you need to calculate rates of C, N and P remineralization? As the water mass becomes deeper how would these rates change and why?

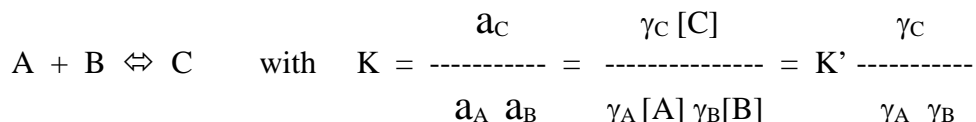


Sampling #	O <sub>2</sub> (μM)	O <sub>2</sub> sat. (μM)	AOU (μM)	NO <sub>3</sub> <sup>-</sup> (μM)	PO <sub>4</sub> <sup>-3</sup> (μM)	TCO <sub>2</sub> (μM)	Carbonate Alk (μM)
1	250	250		16.0	1.0	2200	2350
2	150	250					
3	100	250					
4	50	250					

- (5) 10. (a) <sup>238</sup>U has a half life of 4.47 billion years. Why is it a 'primordial' radioisotope? If somehow you obtained a sample of <sup>238</sup>U with an activity of 97 Bq, how long would your descendants have to wait before they are left with 96.9 Bq? Assuming secular equilibrium, what is the activity of the daughter <sup>234</sup>Th (half life ~ 24.1 days) and the mode of decay? If you chemically isolated the <sup>234</sup>Th, what would the activity be after 96.4 days and why? Briefly, why is this parent-daughter pair well suited for measuring particle fluxes in the ocean? Illustrate with a schematic of depth distribution of <sup>234</sup>Th and <sup>238</sup>U in the near-surface ocean.
- (5) (b) You are trying to date several depth layers in a sediment core and determine its average sedimentation rate using <sup>14</sup>C (half life ~ 5730 years). At the core top you observe the organic C has the same <sup>14</sup>C content as expected for modern carbon (100%). At 40 cm depth in the core, organic C has 67% of the modern <sup>14</sup>C content, at 80 cm 45% of the modern content, and at 120 cm 30 % of the modern content. What are <sup>14</sup>C (radiocarbon) ages for each of these four depth layers and the average sedimentation rate in cm/thousand years? What assumptions did you need to make? Ignore atom bomb <sup>14</sup>C. You measure the same <sup>14</sup>C content at 4 depths in the upper 10 cm. Why is that?

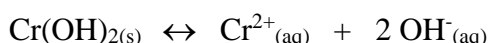
- (10) 1. (a) State the Rule of Constant Proportions (a.k.a., Marcet Principle or Constancy of Composition).  
 (b) List five (5) major ions in seawater that it applies to.  
 (c) Describe four (4) of the several exceptions to the Rule of Constant Proportions that were described in class.

- (10) 2. Given the following hypothetical equilibrium reaction between three ions in water



When going from freshwater (e.g., the river end member) to saltwater (e.g., the coastal ocean end member), the species A, B and C experience the ionic or electrostatic influence from the various seawater salts present. Assuming that none of these background salt species directly react with A, B or C, but rather provide nonspecific ionic interactions, explain briefly the following:

- (a) Do A and B react with each other to a greater extent in freshwater or saltwater? Why?
- (b) Is K larger at a low ionic strength as found in freshwater or for an ionic strength as found in seawater at a salinity of 35? What about K'?
- (10) 3. Briefly define the following terms as they apply to the transformation of organic materials in marine systems: humification, decarboxylation, dehydration, demethanation, early diagenesis, carbonization, condensation, polymerization, aggregation, maturation.
- (10) 4. A marine biologist would like to conduct a bioaccumulation experiment involving the exposure of the mussel, *Mytilus edulis*, to chromium (II) ion ( $\text{Cr}^{2+}$ ) in filtered Boston Harbor seawater using aquaria in the laboratory. The marine biologist comes to you because of your vast knowledge of ionic equilibria and to determine how much free chromium (II) ion will be present in full strength seawater at a salinity of 35. You find out that the experiment calls for a total chromium concentration of  $5.0 \times 10^{-6}$  moles/kg. Under certain pH conditions,  $\text{Cr}^{2+}$  reacts with  $\text{OH}^-$  (i.e., it hydrolyzes) to form the insoluble  $\text{Cr}(\text{OH})_2$  precipitate described by the single step reaction



and the solubility expression is

$$K_{sp} = a_{\text{Cr}} (a_{\text{OH}})^2$$

Calculate the amount of free  $\text{Cr}^{2+}$  that would be soluble in the seawater for mussel exposures at pH 8.0 being sure to correct for the ionic strength using the Davies equation given below. In other words, calculate the solubility of  $\text{Cr}(\text{OH})_2$  in SW at pH 8.0.

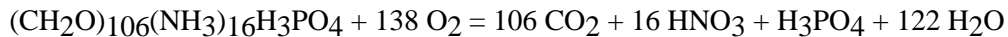
$$\ln \gamma = -1.17 Z^2 \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3 I \right)$$

The  $K_{sp}$  for  $\text{Cr}(\text{OH})_2$  at  $25^\circ\text{C}$  is  $4.75 \times 10^{-18}$ . Express your answer as the concentration of free  $\text{Cr}^{2+}$  ion in moles/kg that remains dissolved. (Hint: The solubility expression has only 3 terms, one is given and another can be calculated from the pH.)

- (10) 5. In class and in the book, depth profiles (depth vs. concentration) were given and discussed for species (e.g. trace metals) that are found distributed in at least six different, yet well

characterized ways. A conservative profile was the simplest of these behaviors. Name and draw examples of four (4) other profiles (not including conservative behavior) and explain what might give rise to the observed distribution. Give an example of each.

- (10) 6. What are the equilibrium expressions that define the carbonate system in natural waters? Define each parameter and variable used in these equations. Sketch a plot showing the effect of pH on the relative proportions of the major carbonate species. How does this plot reflect the equilibrium expressions? Also referencing this plot, what is meant by ocean acidification and what are its environmental implications?
- (10) 7. (a) What is the critical depth hypothesis and how does it account for the onset of the canonical spring phytoplankton bloom? What is the equation used to calculate the penetration of light into the ocean and its significance to the critical depth hypothesis. What is the value of the extinction coefficient if 1% of surface light intensity is found at 100 m. Sketch as a function of depth the relative changes in light and primary production
- (10) 8. Discuss the major components of the marine N cycle with respect to sources and sinks as well as internal cycling as a function of redox state. Include a description of the oceanographic settings which favor different processes. What is the importance of the N cycle to other major marine biogeochemical cycles? How is the residence time for oceanic N estimated? What does the magnitude of the N residence time imply regarding the marine N cycle's ability to respond to environmental changes occurring on time scales < 10,000 years?
- (10) 9. In the future, robots may do most oceanographic data collection. Imagine one initially deployed near-surface in the subduction zone for NADW. It collects data at sampling point#1, and then sinks and moves along the flow path for NADW by tracking an isopycnal surface. Below are the data for point #1 and O<sub>2</sub> data for 2 subsequent collection points. If Redfield stoichiometry held, predict the values for the empty boxes. Assume release of DIC from CaCO<sub>3</sub> dissolution equally important as from organic matter decomposition. What would cause deviations in Redfield stoichiometric, giving specific examples?

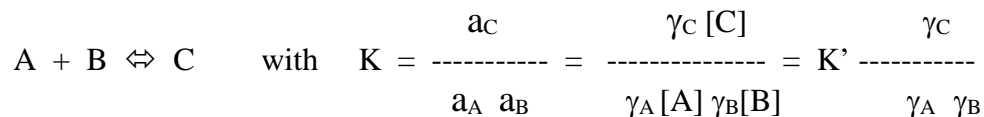


Sampling #	O <sub>2</sub> (μM)	O <sub>2</sub> sat. (μM)	AOU (μM)	NO <sub>3</sub> <sup>-</sup> (μM)	PO <sub>4</sub> <sup>-3</sup> (μM)	TCO <sub>2</sub> (μM)	Alk (μM)
1	300	300		8.0	0.5	2100	2300
2	200	300					
3	150	300					

- (10) 10. (a) <sup>14</sup>C has a half life of 5730 years. Why can't it be a 'primordial' radioisotope? How is it produced in the atmosphere and how could natural variations in atmospheric <sup>14</sup>C/C occur? With each decay, what is the nature of the radiation given off and the nuclide produced? If somehow you obtained 10 mg of pure <sup>14</sup>C, how long would your descendants have to wait before they are left with 8 mg. Discuss one assumption made for radiocarbon dating of deep sea sediments and the conditions under which this assumption fails.
- (b) In the absence of particle scavenging, why are the activities of <sup>238</sup>U and <sup>234</sup>Th in the ocean equal? Explain using appropriate equations. How does particle scavenging affect the ratio of these activities and how is this ratio related to biological production in the upper ocean? Why is the half life of <sup>234</sup>Th (24.1 days) convenient in this respect?

- (10) 1. In seawater  $\text{Cd}^{2+}$  binds with  $\text{Cl}^-$  ion in a series of reactions resulting in products that contain  $\text{Cd}^{2+}$  and one  $\text{Cl}^-$  ion (i.e.,  $\text{CdCl}^+$ ) all the way up to  $\text{Cd}^{2+}$  with four  $\text{Cl}^-$  ions (i.e.,  $\text{CdCl}_4^{2-}$ ). Write out the four stepwise reactions for  $\text{Cd}^{2+}$  with  $\text{Cl}^-$  (giving appropriate charges for the species) and the equilibrium constant expressions (products over reactants in square brackets) for each of the  $K$ 's,  $K_1$  through  $K_4$ . For the same four cadmium chloride products, write out the four overall reactions and the  $\beta$  expressions that describe them (products over reactants in square brackets). Given the following values for the  $\log \beta$ 's, calculate the numerical values of  $K_1$  through  $K_4$  ( $\log \beta_1 = 2.0$ ;  $\log \beta_2 = 2.6$ ;  $\log \beta_3 = 2.4$ ;  $\log \beta_4 = 1.7$ ).

- (10) 2. Given the following hypothetical equilibrium between three ions in water



Where  $a_X$  is activity of species X (A, B or C) and  $\gamma_X$  is the activity coefficient of X. When going from freshwater (e.g., the river end member) to saltwater (e.g., the coastal ocean end member), the species A, B and C experience ionic or electrostatic influence from the various seawater salts present. Assuming that none of these background salt species directly react with A, B or C, but rather provide nonspecific ionic interactions, explain briefly the following:

- (a) Do A and B react with each other to a greater extent in freshwater or saltwater? Why?  
 (b) Are  $K$  and  $K'$  larger at a low ionic strength as found in freshwater or for an ionic strength as found in seawater at a salinity of 35?

- (10) 3. Briefly define the following terms: carbon capture, ocean sequestration, dense plume,  $\text{CO}_2$  lake, rising plume, particle stabilized emulsion.

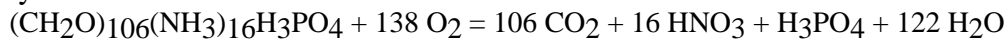
- (10) 4. Describe the sequence of processes that influence the various transformations of organic matter starting after its generation during photosynthesis and ending with the formation of fossil fuels (i.e., give a step by step account of what happens to the biomolecules produced). In your discussion, use the terms listed below, describing what they mean, when they occur in the overall scheme, whether they are predominantly aerobic or anaerobic and whether they are more likely to occur in a terrestrial or marine setting.

Terms: fossilization, carbonification, humification, decarboxylation, dehydration, demethanation, diagenesis, early diagenesis, catagenesis, metagenesis, carbonization, remineralization, regeneration, decomposition, degradation, condensation, polymerization, oxidation, aggregation, maturation.

- (10) 5. What are the equilibrium expressions that define the carbonate system in natural waters? Define each parameter and variable used in these equations. Sketch a plot showing the effect of pH on the relative proportions of the major carbonate species. How and why are these proportions altered when  $\text{CaCO}_3$  dissolves? When organic matter degrades in the deep ocean, how and why do the carbonate system parameters change? Reference this plot in your answer. What set(s) of observations can be made to calculate carbonate system speciation? Which of these can be used to estimate the relative importance of  $\text{CaCO}_3$  dissolution and organic matter remineralization to changes in the carbonate system of the deep ocean. Explain using a sketch of a relevant graph.

- (10) 6. There are large variations in the CaCO<sub>3</sub> content of deep ocean sediments. These variations are largely controlled by the chemistry of the overlying water. What are the calcite (or aragonite) saturation, carbonate compensation, and lysocline depths, giving examples? How is the calcite and aragonite saturation state determined for these depths; illustrate with pertinent equation(s) and graph(s) of vertical variations. Why do differences in saturation, compensation, and lysocline depths occur between the deep North Atlantic and deep N. Pacific and what is the consequence of these differences? Explain why about 30% of anthropogenic CO<sub>2</sub> released to the atmosphere is dissolving into the ocean. Why and how is this ocean uptake of CO<sub>2</sub> likely to change both calcite production in surface waters and its preservation in the sediments.
- (5) 7. (a) What is the critical depth hypothesis and how can it account for the onset of the canonical spring phytoplankton bloom? What is the equation used to calculate the penetration of light into the ocean and what is its significance to the critical depth hypothesis? Define each parameter in the equation. What is the value of the extinction coefficient if 1% of surface light intensity is found at 80 m?
- (5) (b) What are HNLC regions and where are they found? What is thought to limit productivity in these regions and what is the evidence for it citing specific examples? How do HNLC conditions lead to preformed nutrients in the deep ocean?
- (10) 8. Discuss the major microbial pathways for the marine N cycle distinguishing sources and sinks to the ocean as well as internal cycling. How does the wide range of redox states for nitrogen favor these pathways, citing specific examples? What are the oceanographic settings that promote different processes for nitrogen input and output to the ocean? If there is plenty of nitrogen in the form of dissolved N<sub>2</sub> gas in the ocean why is there nitrogen limitation of surface biological productivity over most of the ocean?
- (10) 9. Robots of varying kinds (floats, gliders) are starting to do most oceanographic data collection. Imagine one initially deployed in the subduction zone for AAIW. It collects data at sampling point#1 at the sea surface, and then sinks and moves along the flow path for AAIW by tracking an isopycnal surface. Below are the data for point #1 and O<sub>2</sub> data for 3 subsequent collection points. If Redfield stoichiometry held, predict the values for the empty boxes for AOU, NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>-3</sup>, and TCO<sub>2</sub>. Assume that CaCO<sub>3</sub> dissolution is not occurring.

Your instrumentation is particularly advanced and can measure CFC concentration of the water mass. How can the water mass ages (CFC age) shown in the table derived from CFC concentrations? Calculate O<sub>2</sub> utilization rates (OUR) for sampling points #2 to 4 and fill in the boxes. As the water mass becomes deeper how are these rates changing and why?



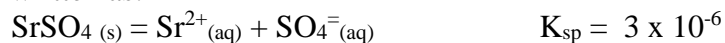
Sampling #	Depth (m)	O <sub>2</sub> (μM)	O <sub>2</sub> sat. (μM)	CFC age (yrs)	AOU (μM)	OUR (μM O <sub>2</sub> /yr)	NO <sub>3</sub> <sup>-</sup> (μM)	PO <sub>4</sub> <sup>-3</sup> (μM)	TCO <sub>2</sub> (μM)
1	0	220	220	0		Not relevant	16.0	1.0	2200
2	250	150	250	5					
3	500	100	275	15					
4	1000	50	300	30					



- (5) 10. (a)  $^{238}\text{U}$  has a half life of 4.47 billion years. Why is it a 'primordial' radioisotope? If somehow you obtained a sample of  $^{238}\text{U}$  with an activity of 98.00 Bq, how long would your descendants have to wait before they are left with 97.9 Bq? Assuming secular equilibrium, what is the activity of the daughter  $^{234}\text{Th}$  (half life ~ 24.1 days) and the mode of decay? If you chemically isolated the  $^{234}\text{Th}$ , what would the activity be after 96.4 days and why? Briefly, why is this parent-daughter pair well suited for measuring particle fluxes in the ocean? Illustrate with a schematic of depth distribution of  $^{234}\text{Th}$  and  $^{238}\text{U}$  in the near-surface ocean.
- (5) (b) You are trying to date several depth layers in a sediment core and determine its average sedimentation rate using  $^{14}\text{C}$  (half life ~ 5730 years). At the core top you observe the organic C has the same  $^{14}\text{C}$  content as expected for modern carbon (100%). At 40 cm depth in the core, organic C has 67% of the modern  $^{14}\text{C}$  content, at 80 cm 45% of the modern content, and at 120 cm 30 % of the modern content. What are  $^{14}\text{C}$  (radiocarbon) ages for each of these four depth layers and the average sedimentation rate in cm/thousand years? What assumptions did you need to make? Ignore atom bomb  $^{14}\text{C}$ . You measure  $^{14}\text{C}$  content at 4 depths in the upper 10 cm and each has the same value. Why is that?

(12) 1. More than a dozen anomalous properties of water were discussed in class. List 6 of them, without duplication, giving a brief description of each.

(9) 2. Acantharin protozoa use strontium to form celestite,  $\text{SrSO}_4(s)$ , skeletons. The solubility of celestite is written as:



(a) Set up the solubility product expression (i.e. equation for K) and calculate the solubility of  $\text{SrSO}_4$  in distilled water.

(b) Using the Davies equation given below, do the same calculation for the ionic strength of

$$\log \gamma = -AZ^2 \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2I \right)$$

seawater at a salinity of 35.

where  $A = 0.51$

(c) If seawater has a  $[\text{SO}_4^{2-}] = 28.93 \text{ mmol/L}$ , calculate the expected free strontium concentration,  $[\text{Sr}^{2+}]$ , using the solubility product expression, the  $K_{sp}$  and the sulfate concentration. Be sure to correct for ionic strength.

(9) 3. Describe the sequence of processes that influence the various transformations of organic matter starting after its generation during photosynthesis and ending with the formation of fossil fuels (i.e., give a step by step account of what happens to the biomolecules produced). In your discussion, use the terms listed below, describing what they mean, when they occur in the overall scheme, whether they are predominantly aerobic or anaerobic and whether they are more likely to occur in a terrestrial or marine setting.

Terms: fossilization, carbonification, humification, decarboxylation, dehydration, demethanation, diagenesis, early diagenesis, catagenesis, metagenesis, carbonization, remineralization, regeneration, decomposition, degradation, condensation, polymerization, oxidation, aggregation, maturation.

(10) 4. Five classes of geochemical species for metal ions were discussed in class:

- 1) Inorganic complex or Ion Pair
- 2) Organic Complex
- 3) Organometallic species
- 4) Redox species (i.e. an element that undergoes oxidation or reduction)
- 5) Colloid bound or particle adsorbed species (particle reactive)

For each of these classes give the following:

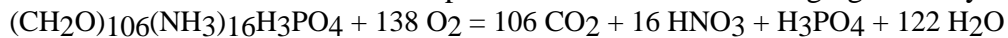
- a) a specific metal that belongs in that category (i.e. is an example of that class)
- b) briefly describe its relevant chemical behavior (i.e. chemical characteristics)
- c) what or how the metal reacts (this might be covered in b above)
- d) approximate total concentration of metal (is it major, minor or trace level)
- e) approximate percentage that might take part in the behavior being described.

(10) 5. Briefly define the following terms: carbon capture, ocean sequestration, hydrate, dense plume,  $\text{CO}_2$  lake.

(10) 6. What are the equilibrium expressions that define the carbonate system in natural waters? Define each parameter and variable used in these equations. Sketch a plot showing the effect of pH on the relative proportions of the major carbonate species. How and why are these proportions altered by changing pH from 8 to 6? When organic matter degrades in the deep ocean, how and why do the carbonate system parameters change? Reference this plot in your answer. Accordingly, what are the relative changes in carbonate system parameters expected

between the deep North Atlantic and deep N. Pacific. What is the role of the ‘ocean conveyor belt’ in this?

- (5) 7. (a) What is the critical depth hypothesis and how can it account for the onset of the canonical spring phytoplankton bloom? What is the equation used to calculate the penetration of light into the ocean and what is its significance to the critical depth hypothesis? Define each parameter in the equation. What is the value of the extinction coefficient if 1% of surface light intensity is found at 80 m?
- (5) (b) What are HNLC regions and where are they found? What is thought to limit productivity in these regions and what is the evidence for it citing specific examples? How do HNLC conditions lead to preformed nutrients in the deep ocean?
- (10) 8. Discuss the major microbial pathways for the marine N cycle distinguishing sources and sinks to the ocean as well as internal cycling. How does the wide range of redox states for nitrogen favor these pathways, citing specific examples? What are the oceanographic settings that promote different processes for nitrogen input and output to the ocean? If there is plenty of nitrogen in the form of dissolved N<sub>2</sub> gas in the ocean why is there nitrogen limitation of surface biological productivity over most of the ocean?
- (10) 9. Robots of varying kinds (floats, gliders) are starting to do most oceanographic data collection. Imagine one initially deployed in the subduction zone for AAIW. It collects data at sampling point #1 at the sea surface, and then sinks and moves along the flow path for AAIW by tracking an isopycnal surface. Below are the data for point #1 and O<sub>2</sub> data for 3 subsequent collection points. If Redfield stoichiometry held, predict the values for the empty boxes for AOU, NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>-3</sup>, and TCO<sub>2</sub>. Assume that CaCO<sub>3</sub> dissolution is not occurring. Your instrumentation is particularly advanced and can measure CFC concentration of the water mass. How can the water mass ages (CFC age) shown in the table derived from CFC concentrations? Calculate O<sub>2</sub> utilization rates (OUR) for sampling points #2 to 4 and fill in the boxes. As the water mass becomes deeper how are these rates changing and why?

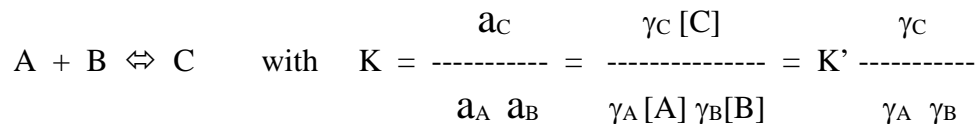


Sampling #	Depth (m)	O <sub>2</sub> (μM)	O <sub>2</sub> sat. (μM)	CFC age (yrs)	AOU (μM)	OUR (μM O <sub>2</sub> /yr)	NO <sub>3</sub> <sup>-</sup> (μM)	PO <sub>4</sub> <sup>-3</sup> (μM)	TCO <sub>2</sub> (μM)
1	0	250	250	0		Not relevant	16.0	1.0	2200
2	250	150	250	5					
3	500	100	250	15					
4	1000	50	250	30					

- (5) 10. (a) <sup>238</sup>U has a half life of 4.47 billion years. Why is it a ‘primordial’ radioisotope? If somehow you obtained a sample of <sup>238</sup>U with an activity of 97.00 Bq, how long would your descendants have to wait before they are left with 96.95 Bq? Assuming secular equilibrium, what is the activity of the daughter <sup>234</sup>Th (half life ~ 24.1 days) and the mode of decay? If you chemically isolated the <sup>234</sup>Th, what would the activity be after 96.4 days and why? Briefly, why is this parent-daughter pair well suited for measuring particle fluxes in the ocean? Illustrate with a schematic of depth distribution of <sup>234</sup>Th and <sup>238</sup>U in the near-surface ocean.
- (5) (b) You are trying to date several depth layers in a sediment core and determine its average sedimentation rate using <sup>14</sup>C (half life ~ 5730 years). At the core top you observe the organic C has the same <sup>14</sup>C content as expected for modern carbon (100%). At 32 cm depth in the core, organic C has 67% of the modern <sup>14</sup>C content, at 64 cm 45% of the modern content, and at 96 cm 30 % of the modern content. What are <sup>14</sup>C (radiocarbon) ages for each of these four depth layers and the average sedimentation rate in cm/thousand years? What assumptions did you need to make? Ignore atom bomb <sup>14</sup>C. You measure <sup>14</sup>C content at 4 depths in the upper 10 cm and each has the same value. Why is that?

(10) 1. List and explain five (5) reasons for studying trace metal speciation or the speciation of any element or chemical constituent found in the ocean.

(10) 2. Given the following hypothetical equilibrium reaction between three ions in water



When going from freshwater (e.g., the river end member) to saltwater (e.g., the coastal ocean end member), the species A, B and C experience the ionic or electrostatic influence from the various seawater salts present. Assuming that none of these background salt species directly react with A, B or C, but rather provide nonspecific ionic interactions, explain briefly the following:

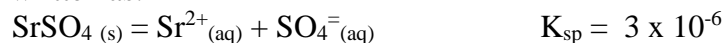
(a) Do A and B react with each other to a greater extent in freshwater or saltwater?

Why?

(b) Is K larger at a low ionic strength as found in freshwater or for an ionic strength as found in seawater at a salinity of 35? What about K'?

(10) 3. Briefly define the following terms: carbon capture, ocean sequestration, hydrate, dense plume, CO<sub>2</sub> lake

(10) 4. Acantharin protozoa use strontium to form celestite, SrSO<sub>4(s)</sub>, skeletons. The solubility of celestite is written as:



(a) Set up the solubility product expression (i.e. equation for K) and calculate the solubility of SrSO<sub>4</sub> in distilled water.

(b) Using the Davies equation given below, do the same calculation for the ionic strength

$$\log \gamma = -AZ^2 \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2I \right)$$

of seawater at a salinity of 35.

where A = 0.51

(c) If seawater has a [SO<sub>4</sub><sup>2-</sup>] = 28.93 mmol/L, calculate the expected free strontium concentration, [Sr<sup>2+</sup>], using the solubility product expression, the K<sub>sp</sub> and the sulfate concentration. Be sure to correct for ionic strength.

(10) 5. In class and in the book, depth profiles (depth vs. concentration) were given and discussed for species (e.g. trace metals) that are found distributed in at least six different, yet well characterized ways. A conservative profile was the simplest of these behaviors. Name and draw examples of four (4) other profiles (not including conservative behavior) and explain what might give rise to the observed distribution. Give an example of each.

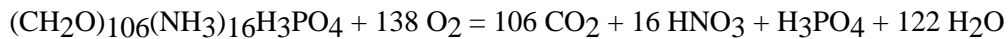
(10) 6. What are the equilibrium expressions that define the carbonate system in natural waters? In practice, what parameters should be measured in order to calculate the concentration of all relevant species. Compare/contrast the influence organic matter decay vs CaCO<sub>3</sub> dissolution on these parameters? Sketch a plot showing the effect of pH on the relative proportions of the major carbonate species. What is the significance of the crossover points?

(10) 7. (a) What is the critical depth hypothesis and how does it account for the onset of the canonical spring phytoplankton bloom? What is the equation used to calculate the penetration of light into the ocean and its significance to the critical depth hypothesis. How are its parameters likely to vary between winter and summer at a northern temperate latitude?.

(b) Describe HNLC conditions and where they are found. What is the current thinking as to their cause? Briefly cite supporting evidence. What has been proposed to do in these regions to ameliorate rising CO<sub>2</sub> in the atmosphere? Do you think this is a good or bad idea?

(10) 8. Compare/contrast the oceanic N and P cycles with respect to sources and sinks. Include descriptions of the environmental settings which favor different processes. What is the importance of these cycles to other major marine biogeochemical cycles? How are their residence times estimated and how do they generally compare? What was Redfield's logic for concluding that P was the ultimate limiting nutrient? Is their evidence to the contrary?

(10) 9. In the future, robots may do most oceanographic data collection. Imagine one initially deployed near-surface in the subduction zone for AAIW. It collects data at sampling point #1, and then sinks and moves along the flow path for AAIW by tracking an isopycnal surface. Below is the data for point #1 and O<sub>2</sub> data for 2 subsequent collection points. If Redfield stoichiometry held, predict the values for the empty boxes. Assume release of DIC from CaCO<sub>3</sub> dissolution equally important as from organic matter decomposition.



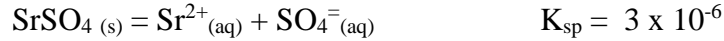
Sampling #	O <sub>2</sub> (μM)	O <sub>2</sub> sat. (μM)	AOU (μM)	NO <sub>3</sub> <sup>-</sup> (μM)	PO <sub>4</sub> <sup>-3</sup> (μM)	TCO <sub>2</sub> (μM)	Alk (μM)
1	220	220		20	1.25	2200	2400
2	140	220					
3	60	220					

(10) 10. (a) <sup>14</sup>C has a half life of 5730 years. Why can't it be a 'primordial' radioisotope? How is it produced in the atmosphere and how could natural variations in atmospheric <sup>14</sup>C/C occur? With each decay, what is the nature of the radiation given off and the nuclide produced? If somehow you obtained 10 mg of pure <sup>14</sup>C, what would its activity be (remember to give it in proper units).

(b) You are trying to date several depth layers in a sediment core and determine its average sedimentation rate. At the core top you observe the organic C has the same <sup>14</sup>C content (<sup>14</sup>C/C) as expected for modern carbon (100%). At 20 cm depth in the core, organic C has 67% of the modern <sup>14</sup>C content, at 40 cm 45% of the modern content, and at 60 cm 30 % of the modern content. What are the <sup>14</sup>C ages for each of these four depth layers and the average sedimentation rate in cm/thousand years? What are assumptions did you need to make? Ignore atom bomb <sup>14</sup>C.

(9) 1. More than a dozen anomalous properties of water were discussed in class. List 6 of them, without duplication, giving a brief description of each.

(12) 2. Acantharin protozoa use strontium to form celestite,  $\text{SrSO}_4$  (s), skeletons. The solubility of celestite is written as:



- (a) Set up the solubility product expression (i.e. equation for K) and calculate the solubility of  $\text{SrSO}_4$  in distilled water.
- (b) Using the Davies equation given below, do the same calculation for the ionic strength of seawater at a salinity of 35. where  $A = 0.51$

$$\log \gamma = -AZ^2 \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2I \right)$$

- (c) If seawater has a  $[\text{SO}_4^{2-}] = 28.93 \text{ mmol/L}$ , calculate the expected free strontium concentration,  $[\text{Sr}^{2+}]$ , using the solubility product expression, the  $K_{\text{sp}}$  and the sulfate concentration. Be sure to correct for ionic strength. (Common ion effect)

(9) 3. Briefly define the following terms: carbon capture, ocean sequestration, dense plume,  $\text{CO}_2$  lake, rising plume, particle stabilized emulsion.

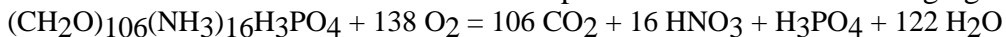
(10) 4. Describe the sequence of processes that influence the various transformations of organic matter starting after its generation during photosynthesis and ending with the formation of fossil fuels (i.e., give a step by step account of what happens to the biomolecules produced). In your discussion, use the terms listed below, describing what they mean, when they occur in the overall scheme, whether they are predominantly aerobic or anaerobic and whether they are more likely to occur in a terrestrial or marine setting. Terms: fossilization, carbonification, humification, decarboxylation, dehydration, demethanation, diagenesis, early diagenesis, catagenesis, metagenesis, carbonization, remineralization, regeneration, decomposition, degradation, condensation, polymerization, oxidation, aggregation, maturation.

(10) 5. What are the equilibrium expressions that define the carbonate system in natural waters? Define each parameter and variable used in these equations. Sketch a plot showing the effect of pH on the relative proportions of the major carbonate species. How and why are these proportions altered when  $\text{CaCO}_3$  dissolves? When organic matter degrades in the deep ocean, how and why do the carbonate system parameters change? Reference this plot in your answer. What set(s) of observations can be made to calculate carbonate system speciation? Which of these can be used to estimate the relative importance of  $\text{CaCO}_3$  dissolution and organic matter remineralization to changes in the carbonate system of the deep ocean. Explain using a sketch of a relevant graph.

(10) 6. There are large variations in the  $\text{CaCO}_3$  content of deep ocean sediments. These variations are largely controlled by the chemistry of the overlying water. What are the calcite (or aragonite) saturation, carbonate compensation, and lysocline depths, giving examples? How is the calcite and aragonite saturation state determined for these depths; illustrate with pertinent equation(s) and graph(s) of vertical variations. Why do differences in saturation, compensation, and lysocline depths occur between the deep

North Atlantic and deep N. Pacific and what is the consequence of these differences? What is ocean acidification and how is it likely to change both CaCO<sub>3</sub> production in surface waters and its preservation in the sediments.

- (5) 7. (a) What is the critical depth hypothesis and how can it account for the onset of the canonical spring phytoplankton bloom? What is the equation used to calculate the penetration of light into the ocean and what is its significance to the critical depth hypothesis? Define each parameter in the equation. What is the value of the extinction coefficient if 1% of surface light intensity is found at 80 m?
- (5) (b) What are HNLC regions and where are they found? What is thought to limit productivity in these regions and what is the evidence for it citing specific examples? How do HNLC conditions lead to preformed nutrients in the deep ocean?
- (10) 8. Discuss the major microbial pathways for the marine N cycle distinguishing sources and sinks to the ocean as well as internal cycling. How does the wide range of redox states for nitrogen favor these pathways, citing specific examples? What are the oceanographic settings that promote different processes for nitrogen input and output to the ocean? If there is plenty of nitrogen in the form of dissolved N<sub>2</sub> gas in the ocean why is there nitrogen limitation of surface biological productivity over most of the ocean?
- (10) 9. Robots of varying kinds (floats, gliders) are starting to do most oceanographic data collection. Imagine one initially deployed in the subduction zone for AAIW. It collects data at sampling point#1 at the sea surface, and then sinks and moves along the flow path for AAIW by tracking an isopycnal surface. Below are the data for point #1 and O<sub>2</sub> data for 3 subsequent collection points. If Redfield stoichiometry held, predict the values for the empty boxes for AOU, NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>-3</sup>, and TCO<sub>2</sub>. Assume that CaCO<sub>3</sub> dissolution is not occurring.  
Your instrumentation is particularly advanced and can measure CFC concentration of the water mass. Shown in the table are water mass ages (yrs) derived from CFC concentrations. Why would ages derived from radiocarbon (<sup>14</sup>C) not be appropriate for this water mass? Calculate O<sub>2</sub> utilization rates (OUR) for sampling points #2 to 4 and fill in the boxes. As the water mass becomes deeper how are these rates changing and why?



Sampling #	Depth (m)	O <sub>2</sub> (μM)	O <sub>2</sub> sat. (μM)	CFC age (yrs)	AOU (μM)	OUR (μM O <sub>2</sub> /yr)	NO <sub>3</sub> <sup>-</sup> (μM)	PO <sub>4</sub> <sup>-3</sup> (μM)	TCO <sub>2</sub> (μM)
1	0	225	225	0		Not relevant	14.0	0.8	2300
2	250	155	255	5					
3	500	105	280	15					
4	1000	55	305	30					

- (5) 10. (a) <sup>238</sup>U has a half life of 4.47 billion years. Why is it a ‘primordial’ radioisotope? If somehow you obtained a sample of <sup>238</sup>U with an activity of 98.00 Bq, how long would your descendants have to wait before they are left with 97.95 Bq? Assuming secular equilibrium, what is the activity of the daughter <sup>234</sup>Th (half life ~ 24.1 days) and the mode of decay? If you chemically isolated the <sup>234</sup>Th, what would the activity be after 96.4 days and why? Briefly, why is this parent-daughter pair well suited for measuring

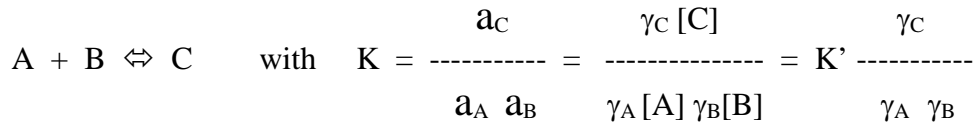
particle fluxes in the ocean? Illustrate with a schematic of depth distribution of  $^{234}\text{Th}$  and  $^{238}\text{U}$  in the near-surface ocean.

- (5) (b) You are trying to date several depth layers in a sediment core and determine its average sedimentation rate using  $^{14}\text{C}$  (half life  $\sim 5730$  years). At the core top you observe the organic C has the same  $^{14}\text{C}$  content as expected for modern carbon (100%). At 40 cm depth in the core, organic C has 67% of the modern  $^{14}\text{C}$  content, at 80 cm 45% of the modern content, and at 120 cm 30 % of the modern content. What are  $^{14}\text{C}$  (radiocarbon) ages for each of these four depth layers and the average sedimentation rate in cm/thousand years? What assumptions did you need to make? Ignore atom bomb  $^{14}\text{C}$ .



- (10) 1. (a) State the Rule of Constant Proportions (a.k.a., Marcet Principle or Constancy of Composition).  
 (b) List five (5) major ions in seawater that it applies to.  
 (c) Describe four (4) of the several exceptions to the Rule of Constant Proportions that were described in class.

- (10) 2. Given the following hypothetical equilibrium reaction between three ions in water

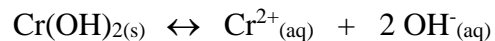


When going from freshwater (e.g., the river end member) to saltwater (e.g., the coastal ocean end member), the species A, B and C experience the ionic or electrostatic influence from the various seawater salts present. Assuming that none of these background salt species directly react with A, B or C, but rather provide nonspecific ionic interactions, explain briefly the following:

- (a) Do A and B react with each other to a greater extent in freshwater or saltwater? Why?  
 (b) Is K larger at a low ionic strength as found in freshwater or for an ionic strength as found in seawater at a salinity of 35? What about K'?

- (10) 3. Briefly define the following terms: carbon capture, ocean sequestration, hydrate, dense plume, CO<sub>2</sub> lake,

- (10) 4. A marine biologist would like to conduct a bioaccumulation experiment involving the exposure of the mussel, *Mytilus edulis*, to chromium (II) ion (Cr<sup>2+</sup>) in filtered Boston Harbor seawater using aquaria in the laboratory. The marine biologist comes to you because of your vast knowledge of ionic equilibria and to determine how much free chromium (II) ion will be present in full strength seawater at a salinity of 35. You find out that the experiment calls for a total chromium concentration of 5.0 x 10<sup>-6</sup> moles/kg. Under certain pH conditions, Cr<sup>2+</sup> reacts with OH<sup>-</sup> (i.e., it hydrolyzes) to form the insoluble Cr(OH)<sub>2</sub> precipitate described by the single step reaction



and the solubility expression is

$$K_{sp} = a_{Cr} (a_{OH})^2$$

Calculate the amount of free Cr<sup>2+</sup> that would be soluble in the seawater for mussel exposures at pH 8.2 typical of the open ocean and pH 7.4 which is common for estuaries like Boston Harbor. In other words, calculate the solubility of Cr(OH)<sub>2</sub> in SW at both pH 8.2 and 7.4. Be sure to correct for the ionic strength by selecting an appropriate value and using the Davies equation given below.

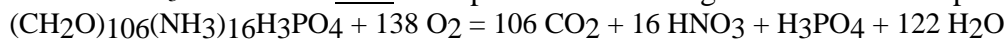
$$\ln \gamma = -1.17Z^2 \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right)$$

The K<sub>sp</sub> for Cr(OH)<sub>2</sub> at 25°C is 4.75 x 10<sup>-18</sup>. Express your answer as the concentration of free Cr<sup>2+</sup> ion in moles/kg that remains dissolved. (Hint: The solubility expression has only 3 terms, one is given and another can be calculated from the pH.)

- (10) 5. In class and in the book, depth profiles (depth vs. concentration) were given and discussed for species (e.g. trace metals) that are found distributed in at least six different, yet well characterized ways. A conservative profile was the simplest of these behaviors. Name and draw examples of four (4) other profiles (not including conservative behavior) and explain what might give rise to the observed distribution. Give an example of each.

- (10) 6. What are the equilibrium expressions that define the carbonate system in natural waters? Define each parameter and variable used in these equations. Sketch a plot showing the effect of pH on the relative proportions of the major carbonate species. When organic matter degrades in the deep ocean, how do the carbonate system parameters change and why, referencing this plot. When CaCO<sub>3</sub> dissolves in the deep ocean, how do the carbonate system parameters change and why, referencing this plot. Also referencing this plot, what is the cause of ocean acidification and what are its environmental implications?
- (10) 7. (a) What is the critical depth hypothesis and how does it account for the onset of the canonical spring phytoplankton bloom? What is the equation used to calculate the penetration of light into the ocean and its significance to the critical depth hypothesis. Define each parameter. What is the value of the extinction coefficient if 1% of surface light intensity is found at 70 m. Sketch as a function of depth the relative changes in light and primary production. How and why does I<sub>0</sub> vary from winter to spring in at northern temperate latitudes?
- (10) 8. Discuss the major microbial pathways for the marine N cycle with respect to sources and sinks as well as internal cycling as a function of redox state. Include a description of the oceanographic settings which favor different processes. Why is the N cycle important to other major marine biogeochemical cycles? How is the residence time for oceanic N estimated? How can we detect past changes in the ocean nitrogen cycling citing a specific example?
- (10) 9. Robots of varying kinds (floats, gliders) are starting to do most oceanographic data collection. Imagine one initially deployed in the subduction zone for AAIW. It collects data at sampling point#1 which is near-surface, and then sinks and moves along the flow path for AAIW by tracking an isopycnal surface. Below are the data for point #1 and O<sub>2</sub> data for 3 subsequent collection points. Why are the non-zero NO<sub>3</sub><sup>-</sup> and PO<sub>4</sub><sup>-3</sup> concentrations observed at point#1 referred to as preformed nutrients. What is the likely cause for incomplete nutrient utilization near-surface in this area and why is it referred to as an HNLC region.

If Redfield stoichiometry held, predict the values for the empty boxes. Assume release of DIC from CaCO<sub>3</sub> dissolution 50% as important as from organic matter decomposition.



Sampling #	O <sub>2</sub> (μM)	O <sub>2</sub> sat. (μM)	AOU (μM)	NO <sub>3</sub> <sup>-</sup> (μM)	PO <sub>4</sub> <sup>-3</sup> (μM)	TCO <sub>2</sub> (μM)	Carbonate Alk (μM)
1	300	300		16.0	1.0	2200	2350
2	200	300					
3	150	300					
4	50	300					

- (10) 10. (a) <sup>238</sup>U has a half life of 4.47 billion years. Why is it a 'primordial' radioisotope? If somehow you obtained a sample of <sup>238</sup>U with an activity of 980 Bq, how long would your descendants have to wait before they are left with 979.9 Bq. Assuming secular equilibrium, what is the activity of the daughter <sup>234</sup>Th (half life ~ 24.1 days) and the mode of decay? If you chemically isolated the <sup>234</sup>Th, what would the activity be after 96.4 days and why? Briefly, why is this parent-daughter pair well suited for measuring particle fluxes in the ocean? Illustrate with a schematic of depth distribution of <sup>234</sup>Th and <sup>238</sup>U in the near-surface ocean.

(b) You are trying to date several depth layers in a sediment core and determine its average sedimentation rate using  $^{14}\text{C}$  (half life  $\sim 5730$  years). At the core top you observe the organic C has the same  $^{14}\text{C}$  content as expected for modern carbon (100%). At 20 cm depth in the core, organic C has 67% of the modern  $^{14}\text{C}$  content, at 40 cm 45% of the modern content, and at 60 cm 30 % of the modern content. What are  $^{14}\text{C}$  (radiocarbon) ages for each of these four depth layers and the average sedimentation rate in cm/thousand years? What assumptions did you need to make? Ignore atom bomb  $^{14}\text{C}$ .

**EXTRA CREDIT – 5 pts Attempt this only after completing rest of test**

In an alternative reality, you are the first person to measure the  $\delta^{18}\text{O}$  of carbonate ( $\text{CaCO}_3$ ) microfossils produced by benthic foraminifera from the deep sea. You find out that forams from the last glacial period had  $\delta^{18}\text{O}$  values 1.3 higher than at present. How do you know that this reflects a change in the average  $\delta^{18}\text{O}$  of ocean water itself and not decreased temperature? What was the cause? Explain in a short paragraph.

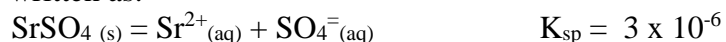
Since you also know that a) ice forming the glacial ice caps has an average  $\delta^{18}\text{O}$  of -40‰ relative to modern ocean water and b) the average ocean depth is 3700 m, you realize that you can calculate the reduction in sea level during the last glacial period. Make this calculation, showing your work. Hint: use change in ocean depth as a proxy for change in volume.

- (1) 1. (a) Accurately state the Rule of Constant Proportions (a.k.a., Marcet Principle or Constancy of Composition).  
 (5) (b) List five (5) major ions in seawater that it applies to.  
 (4) (c) Describe four (4) of the several exceptions to the Rule of Constant Proportions that were described in class.

- (9) 2. In seawater  $\text{Cd}^{2+}$  binds with  $\text{Cl}^-$  ion in a series of reactions resulting in products that contain  $\text{Cd}^{2+}$  and one  $\text{Cl}^-$  ion (i.e.,  $\text{CdCl}^+$ ) all the way up to  $\text{Cd}^{2+}$  with four  $\text{Cl}^-$  ions (i.e.,  $\text{CdCl}_4^{2-}$ ). Write out the four stepwise reactions for  $\text{Cd}^{2+}$  with  $\text{Cl}^-$  (giving appropriate charges for the species) and the equilibrium constant expressions (products over reactants in square brackets) for each of the  $K$ 's,  $K_1$  through  $K_4$ . For the same four cadmium chloride products, write out the four overall reactions and the  $\beta$  expressions that describe them (products over reactants in square brackets). Given the following values for the  $\log \beta$ 's, calculate the numerical values of  $K_1$  through  $K_4$  ( $\log \beta_1 = 2.0$ ;  $\log \beta_2 = 2.6$ ;  $\log \beta_3 = 2.4$ ;  $\log \beta_4 = 1.7$ ).

- (12) 3. Define each of the terms below using diagrams (for 2 points each):  
 Flickering cluster model, water pentamer, ice 1h, hydrogen bonding, secondary hydration shell, non-specific long-range interactions.

- (9) 4. Acantharin protozoa use strontium to form celestite,  $\text{SrSO}_4$  (s), skeletons. The solubility of celestite is written as:



- (a) Set up the solubility product expression (i.e. equation for  $K$ ) and calculate the solubility of  $\text{SrSO}_4$  in distilled water.

Using the Davies equation given below, do the same calculation for the ionic strength of seawater at a

$$\log \gamma = -AZ^2 \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2I \right)$$

salinity of 35.

where  $A = 0.51$

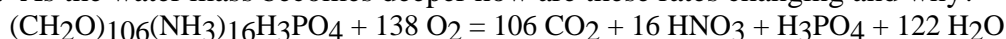
- (c) If seawater has a  $[\text{SO}_4^{2-}] = 28.93$  mmol/L, calculate the expected free strontium concentration,  $[\text{Sr}^{2+}]$ , using the solubility product expression, the  $K_{\text{sp}}$  and the sulfate concentration. Be sure to correct for ionic strength.

- (10) 5. What are the equilibrium expressions that define the carbonate system in natural waters? Define each parameter and variable used in these equations. Sketch a plot showing the effect of pH on the relative proportions of the major carbonate species. How and why are these proportions altered when  $\text{CaCO}_3$  dissolves? When organic matter degrades in the deep ocean, how and why do the carbonate system parameters change? Reference this plot in your answer. Accordingly, what are the relative changes in carbonate system parameters expected between the deep North Atlantic and deep N. Pacific. What is the likely reason for this difference? How and why does the calcite saturation depth and carbonate compensation depth (CCD) change between the N. Atlantic and N. Pacific?
- (5) 6. (a) What is the critical depth hypothesis and how can it account for the onset of the canonical spring phytoplankton bloom? What is the equation used to calculate the penetration of light into the ocean and what is its significance to the critical depth hypothesis? Define each parameter in the equation. What is the value of the extinction coefficient if 1% of surface light intensity is found at 80 m?
- (5) (b) What are HNLC regions and where are they found? What is thought to limit productivity in these regions and what is the evidence for it citing specific examples? How do HNLC conditions lead to preformed nutrients in the deep ocean?

(10) 7. Discuss the major microbial pathways for the marine N cycle distinguishing sources and sinks to the ocean as well as internal cycling. How does the wide range of redox states for nitrogen favor these pathways, citing specific examples? What are the oceanographic settings that promote different processes for nitrogen input and output to the ocean? If there is plenty of nitrogen in the form of dissolved N<sub>2</sub> gas in the ocean why is there nitrogen limitation of surface biological productivity over most of the ocean?

(10) 8. Robots of varying kinds (floats, gliders) are starting to do most oceanographic data collection. Imagine one initially deployed in the subduction zone for AAIW. It collects data at sampling point#1 at the sea surface, and then sinks and moves along the flow path for AAIW by tracking an isopycnal surface. Below are the data for point #1 and O<sub>2</sub> data for 3 subsequent collection points. If Redfield stoichiometry held, predict the values for the empty boxes for AOU, NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>-3</sup>, and TCO<sub>2</sub>. Assume that CaCO<sub>3</sub> dissolution is not occurring.

Your instrumentation is particularly advanced and can measure CFC concentration of the water mass. How can the water mass ages (CFC age) shown in the table derived from CFC concentrations? Calculate O<sub>2</sub> utilization rates (OUR) for sampling points #2 to 4 and fill in the boxes. As the water mass becomes deeper how are these rates changing and why?



Sampling #	Depth (m)	O <sub>2</sub> (μM)	O <sub>2</sub> sat. (μM)	CFC age (yrs)	AOU (μM)	OUR (μM O <sub>2</sub> /yr)	NO <sub>3</sub> <sup>-</sup> (μM)	PO <sub>4</sub> <sup>-3</sup> (μM)	TCO <sub>2</sub> (μM)
1	0	220	220	0		Not relevant	16.0	1.0	2200
2	250	150	250	5					
3	500	100	275	15					
4	1000	50	300	30					

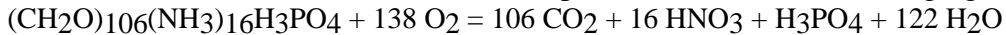
(5) 9. (a) <sup>238</sup>U has a half life of 4.47 billion years. Why is it a 'primordial' radioisotope? If somehow you obtained a sample of <sup>238</sup>U with an activity of 98.00 Bq, how long would your descendants have to wait before they are left with 97.9 Bq? Assuming secular equilibrium, what is the activity of the daughter <sup>234</sup>Th (half life ~ 24.1 days) and the mode of decay? If you chemically isolated the <sup>234</sup>Th, what would the activity be after 96.4 days and why? Briefly, why is this parent-daughter pair well suited for measuring particle fluxes in the ocean? Illustrate with a schematic of depth distribution of <sup>234</sup>Th and <sup>238</sup>U in the near-surface ocean.

(5) (b) You are trying to date several depth layers in a sediment core and determine its average sedimentation rate using <sup>14</sup>C (half life ~ 5730 years). At the core top you observe the organic C has the same <sup>14</sup>C content as expected for modern carbon (100%). At 40 cm depth in the core, organic C has 67% of the modern <sup>14</sup>C content, at 80 cm 45% of the modern content, and at 120 cm 30 % of the modern content. What are <sup>14</sup>C (radiocarbon) ages for each of these four depth layers and the average sedimentation rate in cm/thousand years? What assumptions did you need to make? Ignore atom bomb <sup>14</sup>C. You measure <sup>14</sup>C content at 4 depths in the upper 10 cm and each has the same value. Why is that?

- (8) 1. (a) List and explain four (4) reasons for studying trace metal speciation or the speciation of any element or chemical constituent found in the ocean. Give examples either real or hypothetical to justify and explain your reasons.
- (2) (b) Describe two approaches that would allow you determine or estimate trace metal speciation (1 sentence each).
- (15) 2. A biologist would like to conduct a series of bioaccumulation experiments involving the exposure of several different aquatic organisms to silver (I) ion ( $\text{Ag}^+$ ) using aquaria in the laboratory. Some of the organisms are freshwater species and others marine. The biologist comes to you because of your vast knowledge of ionic equilibria and to determine how much free silver (I) ion will be present in the freshwater tanks where essentially no chloride ion is present, and in aquaria containing full strength seawater at a salinity of 35. The experiment calls for a total silver concentration of  $1.5 \times 10^{-5}$  moles/kg. You know from Chemical Oceanography class that silver reacts with chloride to form the insoluble  $\text{AgCl}$  precipitate described by the single step reaction
- $$\text{AgCl}_{(s)} \rightarrow \text{Ag}^+_{(aq)} + \text{Cl}^-_{(aq)} \quad K_{sp} \text{ for AgCl at } 25^\circ\text{C is } 1.75 \times 10^{-10}$$
- (a) Set up the solubility product expression (i.e. equation for  $K$ ) and calculate the solubility of  $\text{AgCl}$  in a freshwater system assuming an ionic strength of zero ( $I = 0$ ). How much silver (I) ion will dissolve? Will the soluble silver ion be above or below the experimental protocol level of  $1.5 \times 10^{-5}$  moles/kg?
- (b) Using the Davies equation given below, do the same calculation for the ionic strength of seawater at a salinity of 35 (i.e. calculate the solubility of  $\text{AgCl}$  at an ionic strength appropriate for seawater). How much silver ion will dissolve now?
- $$\log \gamma = -AZ^2 \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2I \right) \quad \text{where } A = 0.51$$
- (c) If seawater has a  $[\text{Cl}^-] = 5.46 \times 10^{-2}$  moles/kg, calculate the expected free silver concentration,  $[\text{Ag}^+]$ , using the solubility product expression, the  $K_{sp}$  value and the chloride concentration. Be sure to correct for ionic strength. Note: This is a common ion effect problem.
- (10) 3. Briefly define the following terms: carbon capture, ocean sequestration, dense plume,  $\text{CO}_2$  lake, rising plume, particle stabilized emulsion.
- (10) 4. Describe the sequence of processes that influence the various transformations of organic matter starting after its generation during photosynthesis and ending with the formation of fossil fuels (i.e., give a step by step account of what happens to the biomolecules produced). In your discussion, use the terms listed below, describing what they mean, when they occur in the overall scheme, whether they are predominantly aerobic or anaerobic and whether they are more likely to occur in a terrestrial or marine setting. Terms: fossilization, carbonification, humification, decarboxylation, dehydration, demethanation, diagenesis, early diagenesis, catagenesis, metagenesis, carbonization, remineralization, regeneration, decomposition, degradation, condensation, polymerization, oxidation, aggregation, maturation.
- (10) 5. What are the equilibrium expressions that define the carbonate system in natural waters? Define each parameter and variable used in these equations. Sketch a plot showing the effect of pH on the relative proportions of the major carbonate species. How and why are these proportions altered when  $\text{CaCO}_3$  dissolves? When organic matter degrades in the deep ocean, how and why do the carbonate system parameters change? Reference this plot in your answer. What set(s) of observations can be made to calculate carbonate system speciation? Which of these can be used to estimate the relative importance of

CaCO<sub>3</sub> dissolution and organic matter remineralization to changes in the carbonate system of the deep ocean. Explain using a sketch of a relevant graph.

- (10) 6. There are large variations in the CaCO<sub>3</sub> content of deep ocean sediments. These variations are largely controlled by the chemistry of the overlying water. What are the calcite (or aragonite) saturation, carbonate compensation, and lysocline depths, giving examples? How is the calcite and aragonite saturation state determined for these depths; illustrate with pertinent equation(s) and graph(s) of vertical variations. Why do differences in saturation, compensation, and lysocline depths occur between the deep North Atlantic and deep N. Pacific and what is the consequence of these differences? What is ocean acidification and how is it likely to change both CaCO<sub>3</sub> production in surface waters and its preservation in the sediments.
- (10) 8. Discuss the major microbial pathways for the marine N cycle distinguishing sources and sinks to the ocean as well as internal cycling. How does the wide range of redox states for nitrogen favor these pathways, citing specific examples? What are the oceanographic settings that promote different processes for nitrogen input and output to the ocean? If there is plenty of nitrogen in the form of dissolved N<sub>2</sub> gas in the ocean why is there nitrogen limitation of surface biological productivity over most of the ocean?
- (15) 9. Robots of varying kinds (floats, gliders) are starting to do most oceanographic data collection. Imagine one initially deployed in the subduction zone for AAIW. It collects data at sampling point #1 at the sea surface, and then sinks and moves along the flow path for AAIW by tracking an isopycnal surface. Below are the data for point #1 and O<sub>2</sub> data for 3 subsequent collection points. If Redfield stoichiometry held, predict the values for the empty boxes for AOU, NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>-3</sup>, and TCO<sub>2</sub>. Assume that CaCO<sub>3</sub> dissolution is not occurring. Explain the processes acting to give the values for AOU and nutrients observed for #1 and contrast them with the processes acting subsurface that produce the values at the subsequent observation points.
- Your instrumentation is particularly advanced and can measure CFC concentration of the water mass. Shown in the table are water mass ages (yrs) derived from CFC concentrations. Why would ages derived from radiocarbon (<sup>14</sup>C) not be appropriate for this water mass? Calculate O<sub>2</sub> utilization rates (OUR) for sampling points #2 to 4 and fill in the boxes. As the water mass becomes deeper how are these rates changing and why?



Sampling #	Depth (m)	O <sub>2</sub> (μM)	O <sub>2</sub> sat. (μM)	CFC age (yrs)	AOU (μM)	OUR (μM O <sub>2</sub> /yr)	NO <sub>3</sub> <sup>-</sup> (μM)	PO <sub>4</sub> <sup>-3</sup> (μM)	TCO <sub>2</sub> (μM)
1	0	225	225	0		Not relevant	12.0	0.6	2200
2	250	155	255	5					
3	500	105	280	15					
4	1000	55	305	30					

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- (5) (b) You are trying to date several depth layers in a sediment core and determine its average sedimentation rate using  $^{14}\text{C}$  (half life  $\sim 5730$  years). At the core top you observe the organic C has the same  $^{14}\text{C}$  content as expected for modern carbon (100%). At 40 cm depth in the core, organic C has 67% of the modern  $^{14}\text{C}$  content, at 80 cm 45% of the modern content, and at 120 cm 30 % of the modern content. What are  $^{14}\text{C}$  (radiocarbon) ages for each of these four depth layers and the average sedimentation rate in cm/thousand years? What assumptions did you need to make? Ignore atom bomb  $^{14}\text{C}$ .