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This Problem Set is designed to be open book and open notes, but you are expected to work individually to obtain your answers. This will constitute approximately 10 % of your overall grade. You have 2 weeks to complete this assignment (due 4/29/21) and submit it to me and Prof. Altabet by email. Some of the material covered by these questions will be introduced in the next few lectures, so please be patient. Please email us concerning any specific questions so as not to use valuable class time on this. Please submit your answers with file names consistent with the protocol Lastname, Firstname – PS#4.doc.

Ryan questions

1) Five classes of geochemical species for metal ions where 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

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) a brief, 1 or 2 sentence description of its relevant chemical behavior
c) what or how the metal reacts (this might be covered in b above)
d) approximate total concentration of metal (order of magnitude 10^{-6} or 10^{-9} M)
e) approximate percentage that might take part in the behavior being described.

All the information needed to answer this question is from class material or the posted chapter from Millero (2006), chapter 3.

2) In Emerson & Hedges chapter 8 and Libes chapters 22 and 23 (provided on the class website) as well as in the lecture slides many classes of organic compounds and organic functional groups are identified as being components of marine organic material. In theory any or all of these can be incorporated into humic material becoming part of their structure or functionality.

In the attached PowerPoint diagrams circle one example of each of the following structural entities:

Figure 1 - aromatic ring, aliphatic carboxylic acid group, methyl group, alcoholic group (aliphatic), saturated hydrocarbon chain, unsaturated hydrocarbon chain, fatty acid, carbonyl group, peroxide group, glycerine backbone.

Figure 2 - aromatic carboxylic acid group, aliphatic carboxylic acid group, phenolic group, amine group, amino acid, metal complex, hydrogen bond, quinone, polysaccharide, alumino-silicate clay, ether, ester, aldehyde, ketone, amide.

The functional groups can be circled using the circles provided on the right side of each of the PowerPoint slides. Just open the file in PowerPoint and position your cursor over the border of a circle. Click and hold the left mouse button and the circle will go into edit mode. With the mouse button still depressed you can move the circle to the desired location on the PowerPoint slide to highlight a structural feature. While in the edit mode the circles can be stretched to make ovals and resized to <u>accurately</u> encircle the structural feature of interest. Identify the features with a key for the circle color (provided).

Altabet questions

1) **(a)** Organic matter is produced in the surface ocean by phytoplankton with a consistent depletion in ^{13}C relative to ^{12}C of about 22‰. Explain in a short essay why there is a consistent positive relationship between PO_4 concentration and the δ^{13}C of DIC throughout the deep ocean. Estimate the slope of that relationship.

   (b) Explain in a short essay how and why the down core variation in ▯^{18}O of benthic foraminifera records past sea level. How does sea level reflect the Earth's climate state over the last 120 thousand years. Include a description of the ^{18}O isotope effects occurring during the hydrological cycle and how the ▯^{18}O of foraminiferal calcite reflect the ▯^{18}O of ocean water. Estimate the change in sea level corresponding to a 1.5‰ increase in ▯^{18}O assuming glacial ice is formed with a ▯^{18}O 40‰ lower than seawater.

2) **(a)** ^{238}U has a half life of 4.47 billion years. Why is it a' primordial' radioisotope? If somehow you obtained a sample of ^{238}U with an activity of 981.00 Bq, how long would your descendants have to wait before they are left with 980.95 Bq. Assuming secular equilibrium, what is the activity of the daughter ^{234}Th (half life ~ 24.1 days) and the mode of decay? If you chemically isolated the ^{234}Th, what would the activity be after 72.3 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 ^{14}C (half life ~ 5730 years). At the core top you observe the organic C has the same ^{14}C content as expected for modern carbon (100%). At 15 cm depth in the core, organic C has 67% of the modern ^{14}C content, at 30 cm 45% of the modern content, and at 45 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 that could in practice lead to errors? Ignore atom bomb ^{14}C.