

1. a) The boundary between where  $O_2$  and  $NO_3^-$  are used as electron acceptors occurs at the point of inflection in the  $NO_3^-$  profile. Above this point the curvature of the profile indicates  $NO_3^-$  production, beneath it the curvature indicates consumption. We could solve for this mathematically – the point of inflection will be where the second derivative is zero. We do not have an equation for the line, but we could compute the slope based on the data given, then the change in the slope with depth (the second derivative). However, we can also eyeball it – and that is much easier to do. Based on the first method, the boundary is at about 6.5 cm (see excel sheet  $\Delta\Delta NO_3^-$ ).

b) The diffusive flux of  $NO_3^-$  is calculated by Fick's first law of diffusion:

$$F = -\phi D_{sed}(dC/dz)$$

So to calculate the flux across the sediment water interface we need to use the gradient closest to the interface, the porosity and the diffusivity of  $NO_3^-$  in sediments at that point. If we use values that are too far apart (more than 2 or 3 points, a cm is a huge difference) we are missing the extent of the flux. This is because the profile is significantly curved, and the steepest slopes are closest to the interfaces. No deductions were taken for choice of points, however, because this concept was never addressed. To calculate the flux of nitrate into the anoxic zone we do the same thing at 6.5 cm. Because of the sign convention of Fick's first law a negative number means a flux OUT (up) of the sediments and a positive number means a flux IN (down) to the sediments.

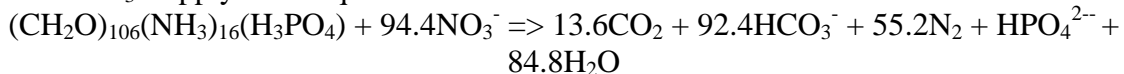
Sed/Water interface:

$$F = -0.84 * 233(\text{cm}^2/\text{y}) * 1.643\text{E}-2(\mu\text{mol cm}^{-4}) = -3.21 \mu\text{mol cm}^{-2} \text{y}^{-1}$$

Oxic/Anoxic Boundary:

$$F = -.7021 * 163(\text{cm}^2/\text{y}) * -3.385\text{E}-3(\mu\text{mol cm}^{-4}) = 0.387 \mu\text{mol cm}^{-2} \text{y}^{-1}$$

c) At steady state the rate of  $N_2$  production must be (stoichiometrically) equal to the rate of  $NO_3^-$  supply. The equation is:



$$\begin{aligned} \text{N}_2 \text{ production rate} &= (55.2/94.4) * \text{Flux of } \text{NO}_3^- \text{ into anoxic zone} \\ &= 0.585(\text{mol N}_2/\text{mol NO}_3^-) * 0.387 \mu\text{mol NO}_3^- \text{ cm}^{-2} \text{y}^{-1} \\ &= 0.226 \mu\text{mol N}_2 \text{ cm}^{-2} \text{y}^{-1} \end{aligned}$$

The rate of OM oxidation by  $O_2$  must (stoichiometrically) equal the rate of production of  $NO_3^-$ . The production of  $NO_3^-$  must equal the total flux out of the oxic sediments at steady state.

$$\text{Total Flux} = \text{Flux up} + \text{Flux down} = 3.21 + 0.387 = 3.60 \mu\text{mol cm}^{-2} \text{y}^{-1}$$



$$\begin{aligned} \text{OM oxidation rate} &= (106/16\text{NO}_3^-) * \text{NO}_3^- \text{ production rate} = (1/16) * \text{NO}_3^- \text{ total flux} \\ \text{OM oxidation rate} &= 0.0625 * 3.60 = 0.225 \mu\text{mol OM oxidized cm}^{-2} \text{y}^{-1} \end{aligned}$$

ALTERNATIVELY: OC instead of OM

$$\text{OC ox. rate by O}_2 = (106/16) * 3.60 = 23.85 \mu\text{mol C}_{\text{org}} \text{ oxidized by O}_2/\text{cm}^2\text{y}$$

The rate of OM oxidation by  $\text{NO}_3^-$  must be stoichiometrically equal to the flux of  $\text{NO}_3^-$  into the anoxic zone of the sediments:

$$\begin{aligned} \text{OM ox. rate by NO}_3^- &= (1\text{OM}/94.4\text{NO}_3^-) * \text{Flux of NO}_3^- \\ &= (1/94.4) * 0.387 = 0.0041 \mu\text{mol OM cm}^{-2} \text{ y}^{-1} \text{ oxidized by NO}_3^- \end{aligned}$$

ALTERNATIVELY: OC instead of OM

$$\text{OC ox. rate by NO}_3^- = (106/94.4) * 0.387 = 0.435 \mu\text{mol C}_{\text{org}} \text{ cm}^{-2} \text{ y}^{-1} \text{ oxidized by NO}_3^-$$

2.1) In August the temperature of the water is higher, and  $\text{O}_2$  concentration is about  $100 \mu\text{mol/L}$  lower. This is likely due to higher productivity in the surface waters overlying this region. In the summer increased temperature and light availability allow an increase in productivity. This increases the amount of OM that needs to be oxidized back to  $\text{CO}_2$  at depth, which uses up  $\text{O}_2$  in the water column. Due to the substantial change between March and August in the  $\text{O}_2$  concentrations I would suspect that these measurements were made in a fairly shallow area (and thus likely close to shore and nutrients). In fact, according to Bill Martin (a very reliable source) these measurements were made in Buzzards Bay – which substantiates the above hypothesis.

2.2) Possibilities: diffusion = straight line  
consumption = concave relative to the line of diffusion  
production = convex relative to the line of diffusion

$\text{O}_2$  is consumed between 0-0.8 cm in March and 0-0.4 cm in August.

$\text{Mn}^{2+}$  is produced between ~1-10 cm in March and ~0.2-2 cm in August, and consumed between 0-1 cm in March and 0-0.2 in August. It is a little hard to see what is going on in August, it appears to perhaps be consumed deeper in the sediments (~4 cm – but this is probably an artifact or bioirrigation). Either or both answers are fine.

$\text{Fe}^{2+}$  is produced between 2-8 cm in March and 0.2- 4 cm in August. It is consumed above 1 cm in March and between 0 and 0.2 cm in August.

In March the Oxygen Penetration Depth (OPD) is deeper, and prevents the formation and build up of  $\text{Mn}^{2+}$  and  $\text{Fe}^{2+}$  until the porewaters become anoxic which is about 1 cm. Not only are Mn and Fe not used as electron acceptors (EAs) until below this depth, but if they diffuse into the oxic sediments they are quickly removed by reaction to their insoluble, oxidized species, and/or they form oxides ( $\text{MnO}_2$ ,  $\text{Fe}_2\text{O}_3$ ). We see this in both the Mn and Fe profiles above 1 cm they are consumed. Mn appears to be produced directly below the oxic sediments, so it appears to switch directly from production to consumption at 1 cm. Fe, on the other hand, appears to diffuse upwards from 2 cm (top of production) to 1 cm (beginning of consumption). This is visible as a straight line in the depth profile. This means that  $\text{O}_2$  is not only used to oxidize organic matter (OM), but also to oxidize the reduced Mn and Fe species that anoxically oxidized OM more deeply in the sediments.

In August, bottom water O<sub>2</sub> concentrations drop, which decreases the OPD. This change allows Mn<sup>2+</sup> and Fe<sup>2+</sup> to be present in the water column all the way up to 0.2 cm of the sediment water interface, which is basically at the s/w interface on the scale of the Fe and Mn graphs. The consumption of both of these species will occur in the extremely thin boundary layer of 0-0.2 cm of oxic sediments.

From both months it appears that once the O<sub>2</sub> is used up, Mn is used as the EA, then Fe.

2.3.a) O<sub>2</sub> consumption rates will be equal to the diffusion across the sediment water interface if this system is at steady state. To calculate diffusion we do the same thing as for question 1 of this problem set, find the steepest slope (greatest  $\Delta C/\Delta t$ ) and multiply by the sediment porosity and the species- and temperature-specific D<sub>sed</sub>:

For March:

$$O_2 \text{ consumption rate} = F_{O_2} = -\phi D_{\text{sed}} \frac{\Delta C}{\Delta z}$$

$$O_2 \text{ consumption rate} = 0.8 \left( \frac{\text{cm}^3 \text{ water}}{\text{cm}^3 \text{ bulk sed.}} \right) * 270 \left( \frac{\text{cm}^2 \text{ bulk sed.}}{\text{y}} \right) * \frac{250 - 100 \mu\text{mol/L}}{0.4 - 0.2 \text{cm}}$$

$$O_2 \text{ consumption rate} = 1.62 \times 10^5 \left( \frac{\mu\text{mol} \cdot \text{cm}_{\text{bulk sed.}}}{\text{y} \cdot \text{L}} \right) \left( \frac{10^3 \text{ L}}{\text{m}^3} \right) \left( \frac{1 \text{ m}^3}{10^6 \text{ cm}^3} \right)$$

$$O_2 \text{ consumption rate} = 162 \frac{\mu\text{mol}}{\text{cm}^2 \cdot \text{y}}$$

For August:

$$O_2 \text{ consumption rate} = F_{O_2} = -\phi D_{\text{sed}} \frac{\Delta C}{\Delta z}$$

$$O_2 \text{ consumption rate} = 0.8 \left( \frac{\text{cm}^3 \text{ water}}{\text{cm}^3 \text{ bulk sed.}} \right) * 355 \left( \frac{\text{cm}^2 \text{ bulk sed.}}{\text{y}} \right) * \frac{225 - 100 \mu\text{mol/L}}{0.1 - 0 \text{cm}} * \left( \frac{1 \text{ L}}{10^3 \text{ cm}^3} \right)$$

$$O_2 \text{ consumption rate} = 355 \frac{\mu\text{mol}}{\text{cm}^2 \cdot \text{y}}$$

2.3.b) Assuming that the sedimentary organic carbon is “Redfieldian” we can calculate the rate of organic carbon oxidation for each month:

$$\text{OC oxidation rate} = \text{O}_2 \text{ consumption rate} * \left( \frac{C_{\text{org}}}{\text{O}_2} \right)_{\text{Redfield}}$$

$$\text{March OC oxidation rate} = 162 \frac{\mu\text{mol}}{\text{cm}^2 \cdot \text{y}} * \left( \frac{106}{138} \right)_{\text{Redfield}}$$

$$\text{March OC oxidation rate} \approx 124 \frac{\mu\text{mol}}{\text{cm}^2 \cdot \text{y}}$$

$$\text{August OC oxidation rate} = 355 \frac{\mu\text{mol}}{\text{cm}^2 \cdot \text{y}} * \left( \frac{106}{138} \right)_{\text{Redfield}}$$

$$\text{August OC oxidation rate} \approx 273 \frac{\mu\text{mol}}{\text{cm}^2 \cdot \text{y}}$$

2.4.a) There is net removal of U from 1-2 cm in March, and from 0-4 cm in August.

2.4.b) U is removed insoluble in anoxic water and soluble in oxic water (basically, the opposite of Fe, in terms of solubility). So, U is diffusing into the sediments across the sediment water interface, being reduced to its insoluble form and removed from pore waters. The same basic idea: “the rate of diffusion must equal the rate of consumption” applies to U, just as it applies to the other species.

For August:

$$\text{U removal rate} = F_U = -\phi D_{\text{sed}} \frac{\Delta C}{\Delta z}$$

$$\text{U removal rate} = 0.8 \left( \frac{\text{cm}^3 \text{ water}}{\text{cm}^3 \text{ bulk sed.}} \right) * 150 \left( \frac{\text{cm}^2 \text{ bulk sed.}}{\text{y}} \right) * \frac{8 - 0.5 \text{ nmol/L}}{4 - 0 \text{ cm}} * \left( \frac{1 \text{ L}}{10^3 \text{ cm}^3} \right)$$

$$\text{U removal rate} = 0.225 \frac{\text{nmol}}{\text{cm}^2 \cdot \text{y}}$$

2.4.c) We can calculate the expected concentration of authigenic U using the U removal (precipitation) rate and the sedimentation rate of these sediments. This assumes that the sediments are at steady state, and there are no artifacts of bioirrigation, etc.

$$[U]_{\text{authigenic}} = \frac{\text{U removal rate}}{\text{sedimentation rate}}$$

$$[U]_{\text{authigenic}} = \frac{0.225 \text{ nmol/cm}^2 \cdot \text{y}}{0.03 \text{ cm/y}}$$

$$[U]_{\text{authigenic}} = 7.5 \text{ nmol/cm}^3 \text{ (bulk sediment)}$$

2.4.d) By comparing the U profiles for each month with the OPD for each month we can see that when the OPD decreases by 75% the U profile barely changes. In March U

diffuses about 1 cm before removal commences, and in August removal seems to begin right at the s/w interface. In each case U is present in porewaters to about the same depth. However, the flux of U, and hence its accumulation rate, may change as the  $D_{sed}$  changes (T dependant), despite the similarity of the profiles. From the information and profiles we have, it does not seem like U is a great indicator of changes in the OPD, although it certainly does indicate the presence of anoxia.

Some of your answers made the very valid point that the rates of diffusion, flux, and accumulation will change between March and August, and thus the concentration of U in the sediment would change, giving the expected relationship with the OPD. This is absolutely true. However, generally these proxies are used for paleowork, and it is difficult to separate the sediments by season – sedimentation rates are such (0.3 mm/y) that bioturbation will easily mix away any differences.

3.a) Carbonate ion anomalies ( $\Delta CO_3^{2-}$ ) is the difference between  $[CO_3^{2-}]_{meas.}$  and  $[CO_3^{2-}]_{sat.}$ , which is what the concentration of  $CO_3^{2-}$  would be at saturation with  $CaCO_{3(s)}$ . We can use just the  $\Delta CO_3^{2-}$  because  $Ca^{2+}$  concentrations are essentially constant throughout the ocean. Therefore,  $\Delta CO_3^{2-}$  changes with both changes in water column chemistry (which effect the measured  $CO_3^{2-}$ ) and the parameters that said the equilibrium constant for  $CaCO_3$ , such as temperature, salinity and pressure.

As a parcel of water moves along the ‘conveyor belt’ from the N. Atlantic to the N. Pacific it accumulates and oxidizes organic matter to  $CO_2$  and nutrients. This process essentially adds an acid to the water, resulting in a decrease in pH, and a corresponding decrease in the carbonate ion concentration, along the transect. The high latitudes are colder than the low latitudes, and this change in temperature changes the  $[CO_3^{2-}]_{sat.}$ , by changing the equilibrium constants.  $CaCO_3$  is more soluble in colder water than warm, so as the T decreases the  $[CO_3^{2-}]_{sat.}$  increases. Pressure has a similar effect,  $CaCO_3$  is more soluble at higher pressures and, thus,  $[CO_3^{2-}]_{sat.}$  increases with depth. Salinity also has thermodynamic effects on  $K_{sp}$  values, but these are small effects and there are only very small changes in salinity between different regions of the ocean. The combination of these effects means that for two parcel of waters at the same depth and latitude in the N. Pacific and the N. Atlantic (therefore having approximately the same K values – same T, S and P), the water in the N. Pacific has a lower  $\Delta CO_3^{2-}$  because it will have a lower pH because it has ‘seen’ more  $CO_2$  dissolved into it. The pH effect is accompanied by the fact that the N. Pacific is deeper than the N. Atlantic, and thus even if the basins had the same pH and  $K_{sp}$  profiles, the seafloor of the Pacific is deeper, and thus bottom water will have a lower  $\Delta CO_3^{2-}$  in the N. Pacific than the N. Atlantic. Both of these effects work together to make the N. Pacific deep water more corrosive to  $CaCO_3$  than the N. Atlantic.

3.b) This is a slightly strange question, and rather than specific depths or concentrations, I’m looking for a relative understanding of where these things occur, and how they change in the different basins. The key points are:

- All the horizons are deepest in the Atlantic and shallowest in the Pacific
- The lysocline is above the CCD
- The saturation horizons can be pulled off the graphs fairly accurately – so these should be close to my depiction

- The aragonite sat. hor. is shallower than the calcite sat. hor.
- The rain rate of  $\text{CaCO}_3$  is constant until the sat. horizon, then decreases quickly
- The burial rate is fairly constant until the lysocline, then decreases to 0 at the CCD

3.c) Aragonite is more soluble than calcite, so if all the organisms in the ocean that form  $\text{CaCO}_3$  all of a sudden started to form aragonite a lot more  $\text{CaCO}_3$  would dissolve before it hit the seafloor, increasing the alkalinity of the ocean (less  $\text{CO}_3^{2-}$  removed by  $\text{CaCO}_3$  burial). This, in turn, would increase the pH, and the aragonite saturation horizon would deepen. The CCD and the lysocline would still become shallower, because they were previously defined by calcite, which is so much more stable than aragonite. This transient response would decrease the amount of  $\text{CaCO}_3$  buried, but also allow more  $\text{CO}_2$  to dissolve in the ocean by shifting the distribution of the carbonate species towards carbonate (due to the change in alkalinity). The increasing alkalinity would allow  $\text{CO}_3^{2-}$  concentrations to increase such that the saturation horizon, lysocline and CCD would all eventually deepen and allow burial of  $\text{CaCO}_3$  to increase again. Eventually a steady state will be reached (incoming  $\text{CO}_2$  equals  $\text{CaCO}_3$  burial) where the oceans would have a higher concentration of DIC and the atmosphere would have less  $\text{CO}_2$ . There is an excellent discussion of this in Sarmiento and Gruber, p. 386 (they specify: 'a sudden decrease in  $\text{CaCO}_3(\text{s})$  flux', which is the same as switching from calcite to aragonite).