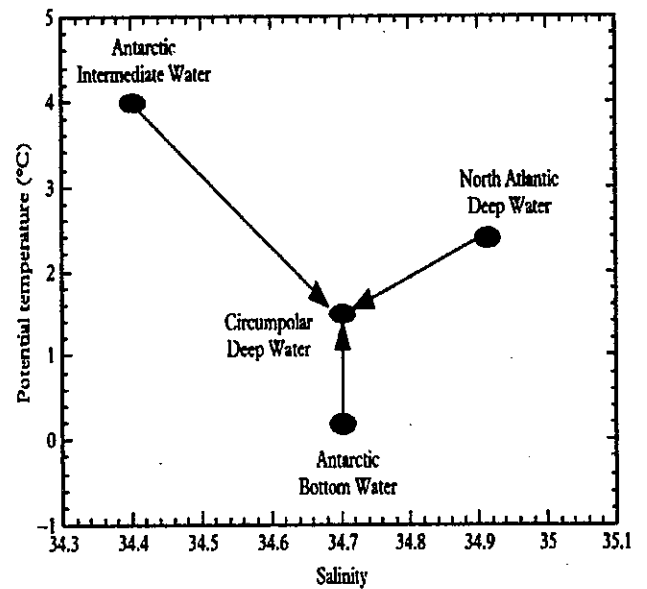


1. Ocean mixing and the Circumpolar Deep Water (9 points)

The Circumpolar Deep Water (CDW) is derived from a mixture of different water masses in the Southern Ocean, mainly including the North Atlantic Deep Water (NADW), the Antarctic Bottom Water (AABW) and the Antarctic Intermediate Water (AAIW). Use the data in Table 1 to calculate the fractions (%) of NADW, AABW and AAIW in the formation of CDW.

Table 1. Potential temperature and salinity characteristics of the main water masses

Water Mass	$\theta$ (°C)	S
North Atlantic Deep Water (NADW)	2.4	34.9
Antarctic Intermediate Water (AAIW)	4	34.4
Antarctic Bottom Water (AABW)	0.2	34.7
Circumpolar Deep Water (CDW)	1.45	34.7



2. Residence time of Na in the ocean (8 points, 4 points each question)

The main source of sodium (Na) in the ocean is the dissolved Na transported by rivers. The flux of river water to the ocean is of the order of  $10^6 \text{ m}^3 \text{ s}^{-1}$ . The average Na concentration is  $0.49 \text{ mol kg}^{-1}$  in seawater and  $2.3 \times 10^{-4} \text{ mol kg}^{-1}$  in river water. The volume of the ocean is approximately  $1.36 \times 10^{18} \text{ m}^3$ .

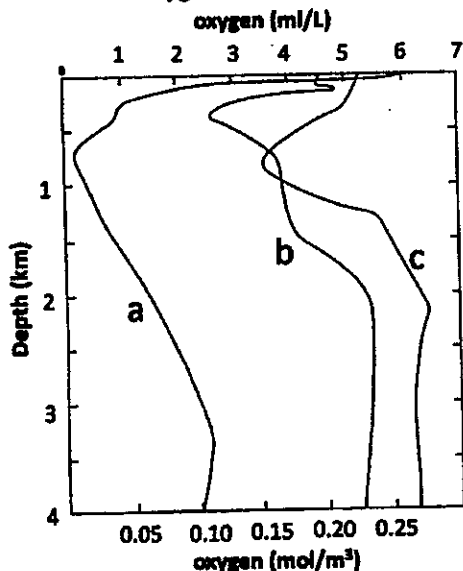
(1) Calculate the residence time of Na in the ocean. (2) Compare this time to the ocean mixing time. What can you conclude about the distribution of Na in the ocean?

3. Ionic strength of seawater and river water (16 points, 4 points each question)

The ionic strength of water increases with salinity and influences the activity of dissolved ions. Table 2 summarizes the concentrations of some major ions in seawater and river water. Use the equation for ionic strength  $I = 0.5 \times (\sum M_i \times Z_i^2)$  ( $M_i$ : moles;  $Z_i$ : charges of the ions) and the data in Table 2 to calculate the ionic strength of (1) seawater when only considering sodium and chlorine, (2) seawater, and (3) river water when considering all the ions listed in Table 2. (4) Compare the values of ionic strength between seawater and river water and explain their impact on the element reactivity during the mixing of seawater and river water.

Table 2	Molarity (M)	
	Seawater	River water
Na(1+)	0.49	0.0002
Mg(2+)	0.053	0.00014
Ca(2+)	0.01	0.00022
K(1+)	0.01	0.00003
Cl(1-)	0.57	0.00009
SO <sub>4</sub> (2-)	0.028	0.0001
HCO <sub>3</sub> (1-)	0.002	0.0008

4. Dissolved oxygen in the oceans (15 points)

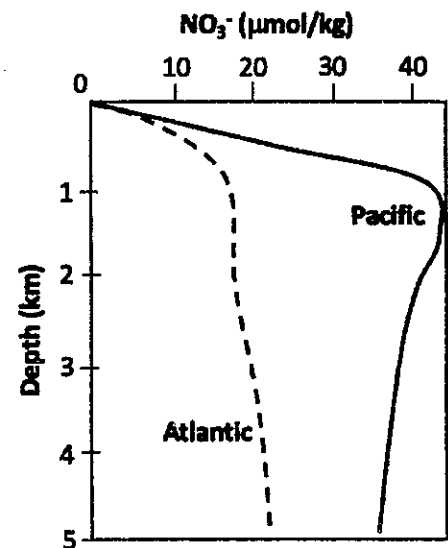


The figure in this section shows three depth profiles of dissolved oxygen from the South of California, the Eastern part of the South Atlantic and the Gulf Stream. (1) Identify where are the a, b, and c profiles each from (6 points). (2) What determines the values of minimum dissolved oxygen around 1km depth (4 points)? (3) If the offset of oxygen between profiles a and c is purely driven by the respiration of particulate organic matter, how much phosphate is regenerated according to the Redfield model (PO<sub>4</sub> unit: mol/m<sup>3</sup>) (5 points)?

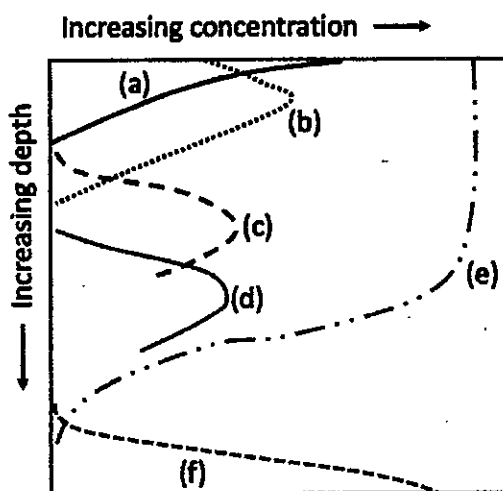
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5. Seawater nutrient and elemental distribution (20 points)

The distributions of seawater nutrients and elements can vary differently between depths and ocean basins. For example, the figure in this section shows the depth profiles of nitrate in the Atlantic and Pacific. (1) Draw similar depth profiles for Ca, PO<sub>4</sub>, Si and Pb in the Atlantic and Pacific, and briefly explain their sources and reasons for variations in these profiles (16 points). (2) In these profiles, does PO<sub>4</sub> reach a maximum at a shallower or deeper depth than Si, and why (4 points)?



6. Redox processes in marine sediments (16 points)

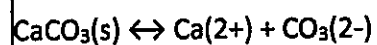


Oxidation reactions of sedimentary organic matter require electron acceptors, and hence some reactants and products follow a particular sequence in marine sediments due to the availability of electron acceptors. In the transition from oxygenic to anoxic environments, the depth profiles of several contents in the sediment pore fluids reflect this sequence and the change of oxidation reactions. For instance, the figure in this section shows 6 unknown profiles (labelled a-f), which relate to oxygen, iron, manganese, nitrate, sulfate, and methane. (1) Identify the contents in each of these profiles (a-f) (12 points). (2) Based on your understanding of the Gibbs free energy between these reactions, briefly explain why these profiles follow a particular sequence (4 points).

7. Calcium carbonate in seawater (16 points, 4 points each question)

Calcium carbonate minerals are an important building block for the skeletons and shells of many marine organisms. Their solubility is controlled by the concentration of carbonate and hence the pH value in seawater. Due to the increasing concentration of carbon dioxide in the atmosphere and enhanced ocean acidification, the change of calcium carbonate solubility has become one of the important issues in chemical oceanography research.

The reaction of calcium carbonate dissolution can be written as:



The values of standard free energy of formation ( $\Delta G_f^\circ$ ) for each species are listed below:

CaCO<sub>3</sub>(s): -1128.79 kJ/mol

Ca<sup>2+</sup>: -553.58 kJ/mol

CO<sub>3</sub><sup>2-</sup>: -527.81 kJ/mol

(1) Calculate the standard Gibbs free energy of reaction.

$$\Delta G_r = \sum \Delta G_{f, \text{products}} - \sum \Delta G_{f, \text{reactants}}$$

(2) Calculate the equilibrium constant (K) of the solubility reaction at 25°C ( $\log K = -\Delta G_r / 5.708$ ).

(3) In surface seawater (T=25°C), [CO<sub>3</sub><sup>2-</sup>] is approximately 220 μM and [Ca<sup>2+</sup>] is approximately 10 mM. Is the surface water at saturation with respect to CaCO<sub>3</sub> (demonstrate using a calculation)?

(4) According to the model prediction, the atmospheric CO<sub>2</sub> level may increase up to 750 ppm by the year 2100 if business carries on as usual, which may enhance ocean acidification by increasing [CO<sub>2</sub>] and reducing pH and [CO<sub>3</sub><sup>2-</sup>] in seawater. The figure in this section shows the projection of surface seawater pH, [CO<sub>2</sub>] and [CO<sub>3</sub><sup>2-</sup>] from the pre-industrial time to the year 2100. Will the surface seawater still be at saturation with respect to CaCO<sub>3</sub> in the year 2100 (demonstrate using a calculation)?

