

Please read each question carefully

1. In the following hypothetical situation, assume you are assisting a modern marine biologist who is using molecular biological and biochemical techniques to study the potential toxic or deleterious effects of Ag exposure on the health of an important baitfish minnow present in the salt marsh environs of northern Taiwan. This minnow (i.e. killifish) exhibits a high salinity tolerance and is found in fresh and salt waters. It is an important food for bluefish and striped bass, which are major commercial and recreational resources. The biologist is puzzled by the experimental results which indicate that the tolerance of the minnow to Ag decline dramatically with decreasing salinity. Indeed, it is observed that the production of an important digestive enzyme (found in the minnow's liver) is reduced by at least a factor 10 when the minnows are exposed to the same amount of Ag in fresh water (pH of 5.9) as compared to the seawater (pH of 8.1). Use your knowledge of marine biogeochemistry to help the marine biologist in formulating a reasoned hypothesis to explain the observation (see attached page in Appendix I for information necessary to provide supporting documentation). (20 pts)
2. Zinc can precipitate as the mineral hydrozincite which has the formula $Zn_5(CO_3)_2(OH)_6(s)$. Assume that the oceans can be characterized as seawater with the Garrels and Thompson major ion composition at 25 °C, 1 atmosphere and pH 8.1. Given your knowledge of Zn in seawater, demonstrate whether Zn in the model ocean is controlled by precipitation of hydrozincite. Are the results applicable to the "real" ocean? The logK for the formation of hydrozincite is 74 at 25 °C, 1 atmosphere. As in question 1, see attached page for useful information to provide supporting documentation for your answer. (20 pts)
3. According to the previous studies, (a) rivers deliver annually to the sea about 10^5 tons of dissolved Mn. Some $4-6 \times 10^6$ tons of Mn are removed annually to deep-sea sediments (including ferro-manganese nodules). Consider and discuss how a geochemist would use this information in a study of the cycling of Mn in the marine environment (10 pts);

(b) Rivers deliver 5 Tmol and hydrothermal inputs yield 0.2 Tmol annually to the sea of dissolved Si. The flux of opaline silica reaching the sea floor is 29 Tmol per year. How might a geochemist would use this information in a study of the cycling of Si in the marine environment? (A Tmol= 10^{12} mol) (10 pts)
4. Answer all parts briefly: (40 pts)
 - a) Write the equation for the generalized reaction leading to the production of Redfield ratio organic matter in seawater
 - b) Define non-conservative chemical distribution in the marine environment; provide an example (sketch) from two different oceanic regimes
 - c) Write the general equation for the chemical weathering of crustal rock.
 - d) Describe, explain and sketch briefly "Thermohaline circulation" and "Ventilation". How will the thermohaline circulation be changed under the scenario of global warming and what effects will be?
 - e) Could the formation of coral reef reduce the effect of global warming? Please describe and explain?

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Appendix I.

Equilibrium Constants for Ion Pairs and Complexes

		OH ⁻	CO ₃ ²⁻	SO ₄ ²⁻	Cl ⁻	Br ⁻	F ⁻	NH ₃ ⁻
Ag ⁺	AgL	2.0	Ag ₂ L(s) 11.1	AgL 1.3	AgL 3.3	AgL 4.7	AgL 0.4	AgL 3.3
	AgL ₂	4.0		Ag ₂ L(s) 4.8	AgL ₂ 5.3	AgL ₂ 6.9		AgL ₂ 7.2
	AgL(s)	7.7			AgL ₃ 6.4	AgL ₃ 8.7		
					AgL(s) 9.7	AgL ₄ 9.0		
						AgL(s) 13.3		

Distribution of species in seawater according to model by Garrels and Thompson

I. Major Dissolved Species in Seawater (19‰ chlorinity, 25°C, pH = 8.1)

Metal Ion, Me	Conc. Total, molal	Free Ion, %	MeSO ₄ (aq), %	MeHCO ₃ , %	MeCO ₃ (aq), %
Na(I)	0.48	99	1+	-	-
K(I)	0.01	99	1	-	-
Mg(II)	0.054	87	11	1	0.3
Ca(II)	0.01	91	8	1	0.2

Ligand, L	Conc. Total, molal	Free Ion, %	CaL, %	MgL, %	NaL, %	KL, %
SO ₄ ²⁻	0.028	54	3	22	21	0.5
HCO ₃ ⁻	0.0024	69	4	19	8	-
CO ₃ ²⁻	0.00027	9	7	67	17	-
Cl ⁻	0.56	100	-	-	-	-

The ligand concentrations (molal) for the DS river are:

CO ₃ ²⁻	SO ₄ ²⁻	Cl ⁻	Br ⁻	F ⁻	NH ₃ ⁻
10 ^{-6.3}	10 ^{-4.0}	10 ^{-3.7}	<10 ⁻⁶	10 ^{-6.0}	10 ^{-6.0}

Note: Appendix I. Equilibrium Formation Constant (given as the logarithm for the formation of complexes and solids from cations and ligands at I=0, 25 °C and one atmosphere). Activity coefficients for singly, doubly and triply charged solution species in seawater are 0.7, 0.3 and 0.1, respectively. Zero charged species have an activity coefficient of 1. Assume I=0 for fresh water.

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