

Lecture 12 – Global Biogeochemical Cycles

(1) If rivers are the chief source of the dissolved salts in seawater, why is seawater not simply a concentrated version of average composition of all rivers?

The answer lies in the chemical behavior of dissolved constituents as they circulate through the hydrological cycle. Some are more soluble than others.

(2) Would you expect rainwater to be more similar to seawater or river water (a) in its total salt content? (b) In the relative composition of dissolved elements in the solution?

(a) Rain water will be more similar to river in its salt content (less total salts) (b) and to seawater in the relative composition of salts since most dissolved salts in rain water are from sea salt spray

(3) Which of the following relative cation and anion abundances patterns apply to river water (corrected for cyclic salts) and which for seawater?

- (a) Na > Mg > Ca
- (b) Ca > Mg > Na
- (c) HCO₃⁻ > SO₄²⁻ > Cl⁻
- (d) Cl⁻ > SO₄²⁻ > HCO₃⁻

B and C for River and A and D for seawater

(4) Give an example of important reactions that are responsible for the composition of river water.

Rock weathering: $\text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{HCO}_3^-$
 $2\text{NaAlSi}_3\text{O}_8 + 2\text{H}_2\text{CO}_3 + 8\text{H}_2\text{O} \rightleftharpoons \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 2\text{Na}^+ + 2\text{HCO}_3^- + 4\text{H}_2\text{SiO}_3$

(5) If the only source of Na to seawater is weathering how many grams of rock must be weathered to supply the Na for 1 liter of seawater?

Assume: ~11 g of Na in 1 liter of seawater
~ 2.4% Na in continental rocks
~ 75% of the Na in rocks is “leached” during weathering reactions.

Would weathering of the same weight of rock explain the of Zn, and Br in 1 liter of seawater? The Zn, and Br rock contents are 0.007%, and 0.00025% respectively and their concentrations in seawater 10⁻⁷ g/l and 0.067 g/l. What may that imply?

$0.024 \times X \times 0.75 = 11$; $X \approx 600$ g We need to weather 600 g of rock!

For Zn: The amount of Zn in 600 g rock is: $0.00007 \times 600 = 0.042$ g; In 1 liter seawater we only have 10⁻⁷ g Zn, less than expected. This suggests that Zn does not readily go into solution

For Br: The amount on 600 g rock is: $0.0000025 \times 600 = 0.0015$ g; In 1 liter seawater we have 0.067 g, this is more than in the 600g of rock implying an additional source for Br, e.g. volcanic source.

(9) Estimate the CO₂ consumed (neutralized) by silicate and carbonate weathering using the following simple model. Assume that on average silicate minerals produce one HCO₃⁻ from each CO₂ consumed while releasing 2H₄SiO₄ (e.g. silicate + CO₂ + H₂O = HCO₃⁻ + 2H₄SiO₄). Each CO₂ consumed by carbonate minerals produces two HCO₃⁻. Below is a table with the limestone and silica derived HCO₃⁻ as measured in rivers from various continents. Limestone HCO₃⁻ was calculated from Ca²⁺ + Mg²⁺ - SO₄²⁻ in rivers; Silica HCO₃⁻ was calculated as ½ moles SiO₂ in rivers.

Continent	Limestone HCO ₃ ⁻	CO ₂ consumed By limestone	Silica HCO ₃ ⁻	CO ₂ consumed By silicates
Europe	1.49	0.75	0.06	0.06
Asia	1.1	0.55	0.10	0.10
North America	1.06	0.53	0.07	0.07
Africa	0.65	0.33	0.20	0.20
South America	0.38	0.19	0.10	0.10
World Average	0.85	0.42	0.11	0.11

* Unites are in mmol/liter

Calculate the percent that is neutralized by silicate weathering from total weathering (for the world average).

0.11/0.53 = 0.20; 20% of the CO₂ consumed by weathering is from silicate weathering

Why is the % CO₂ consumed by silicate or carbonate weathering so different in the different continents ranging?

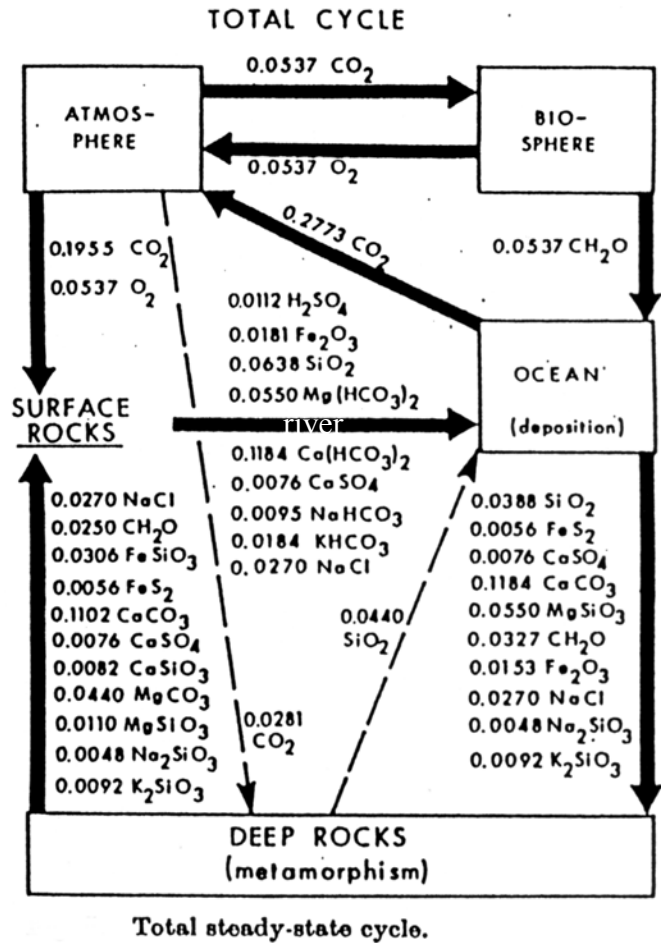
Different continents have different types of rocks exposed to weathering and different weatherability (how much rock is weathered and added to 1 liter of water)

(10) Following is a representation of global biogeochemical cycles from Garrels and Perry (Vol. 5 The Sea) all fluxes are in units of 10^{14} moles/year.

Follow the Mg cycle describe how Mg moves from surface rocks through the cycle. What is the major sink of Mg in the ocean?

The casual observer might surmise that McKenzie and Garrels could have obtained any result they wanted in their calculation of the fractions of riverine ions that can be removed by precipitating major authigenic phases such as pyrite, anhydrite, calcium carbonates, halite and opal. There are in fact at least three quantitative constraints that limit the possible outcome of their balance.

Which of the following is **not** a major constraint on Mackenzie and Garrels' model for chemical mass balance between rivers and oceans?



1. The authigenic mineral products formed must be realistic part of the marine sedimentary record.
2. The ocean is assumed to be at steady state, such that all introduced ions should be removed.
3. Authigenic mineral formation can be allowed to proceed until all ions of a given type are completely removed to form authigenic minerals.
4. The reactions for authigenic mineral formation must follow strict stoichiometries.
5. The ionic composition of rivers is assumed to have been the same as present day global average for the last 10^8 years.

0.044×10^{14} moles/year MgCO₃ and 0.011×10^{14} moles/year MgSiO₃ are weathered from the rocks and thus 0.055×10^{14} moles/year Mg(HCO₃)₂ is the river input to the ocean. This is deposited in the ocean as MgSiO₃ into the deep rock reservoir and eventually through metamorphism and uplift becomes part of the surface rocks. Note the deposition in the sediments through "reversed weathering" reactions this has not been shown to be a significant sink (the model was published before hydrothermal vents were discovered).

(11) Which of the following aspects of the proposed model for the control of atmospheric O₂ concentrations over geologic time is/are **not true**?

1. Extensive weathering of organic matter relative to burial will result in O₂ uptake from the atmosphere during rock weathering
2. O₂ solubility in seawater may provide a feedback, during lower atmospheric oxygen less oxygen will be delivered to the deep ocean resulting in increased organic matter preservation and burial thus restoring atmospheric oxygen.
3. During periods with extensive pyrite burial less organic C would be buried
4. Extensive losses of sedimentary organic matter must occur concurrently with losses of sedimentary pyrite.
5. Substantial increases and decreases in atmospheric O₂ concentrations are possible on time scales of 500,000 years and can have major effects for living organisms.
6. A negative correlation between $\delta^{13}\text{C}$ of carbonates and $\delta^{34}\text{S}$ of sulfates is expected.

(12) Evaporite sequences were used to constrain the possible range of change in major dissolved salts in seawater on geological time scales: Which of the following aspects in **NOT** true in accord with this model:

1. evaporite sequences suggest that Ca >> than SO₄
2. HCO₃⁻ must be < 2 X Ca
3. NaCl always precipitates in seawater before KCl and MgSO₄
4. Ca in the ocean could not have been more than 3X its present value
5. Mg concentrations have possibly varied with time but did not exceed MgCO₃ saturation

(13)

Which of these sequences of events provide a negative feedback to increased/decreased atmospheric pCO₂ that result from changes in spreading rate and which is a positive feedback?

High spreading rate – sea level rise – reduction in continental area – reduced weathering – lower PP

High spreading rate (SR) – increased temperature – increased weathering – increased PP

High SR – sea level rise – increased continental slope – increased organic C burial at fast sed. rates

Low SR – sea level drops – shelves exposed – increased nutrient input from shelves-

increased PP

The sequence in 1 and 4 provide a positive feedback while 2 and 3 provide a negative feedback.