EPSS C113/213 Biological and Environmental Chemistry
January 8-12, 2018

Lecture 1: Biogeochemical cycles and origins of the major geochemical reservoirs.
Reading: Chapter 1 and 2 of Schlesinger & Bernhardt.

Ch. 1: Geochemical cycles

To first order, it is common to think of surface geochemical reservoirs as being near a steady state, and look at changing fluxes into and out of these reservoirs as perturbations. Ubiquitous and/or inert chemicals (i.e., $H_2O$, Ar) are considered implicitly. The longer the geologic time of interest, and the larger the perturbation, the less accurate the steady-state assumption becomes. However, the oceanic and atmospheric reservoirs of many important elements like C and S, as we will learn, are much smaller than geological reservoirs. Over time, fluxes of these elements into and out of geological reservoirs should nearly balance unless the Earth is gaining or losing them to space.

Berner feedback:

| | |
|---|---|
| Weathering | $CaSiO_3 + 2CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^- + SiO_2$ |
| Shell builders | $Ca^{2+} + 2\,HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O$ |
| *Net reaction:* | $CaSiO_3 + CO_2 \rightarrow CaCO_3 + SiO_2$ *(this is the Urey reaction)* |

More weathering – $CO_2$ drops, water has less carbonic acid – less weathering. The system tends to restore itself after perturbation, a simple (and simplistic) example of negative feedback.

Deep-earth processes complete the loop:

Metamorphism $CaCO_3 + SiO_2 \rightarrow CaSiO_3 + CO_2$ *(Urey backwards)*

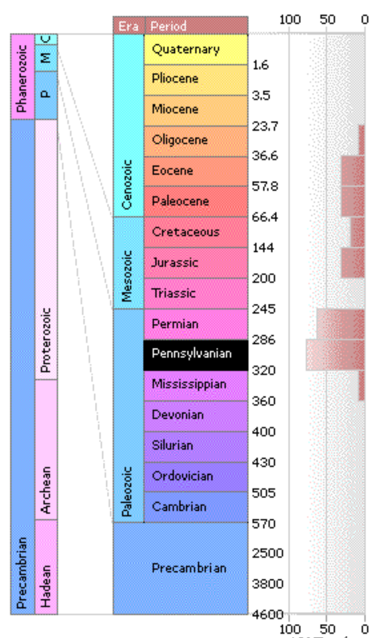
Garrels and Lerman web (Schlesinger Fig. 1.1) Numbers are “fluxes”, $dX_{box1\rightarrow box2}/d(time)$. A flux arrow pointing at the ocean or atmosphere is a “source”. A flux arrow pointing away is a “sink”. The ocean & atmosphere are assumed to be at steady state.

This assumption, and the relationships in an updated paper (Garrels and Lerman 1984), lead to the following reaction:

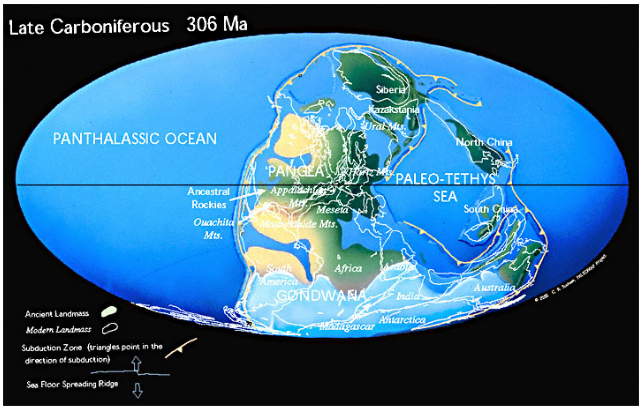
$$4FeS_2 + CaCO_3 + 7CaMg(CO_3)_2 + 7SiO_2 + 15H_2O \rightleftarrows 15CH_2O + 8CaSO_4 + 2Fe_2O_3 + 7MgSiO_3$$

Example: Pennsylvanian coal deposition.

Extensive coal deposits in swamps (large flux to organic matter box) must be balanced by input of carbon to oceanic reservoir.




N. Am. Coal deposition vs. Time




Implies weathering of $CaCO_3$ +/- $MgCO_3$. These add $Ca^{2+}$ and $Mg^{2+}$ as well as carbon, so the non-carbonate sinks of $Ca^{2+}$ and $Mg^{2+}$ must increase ($CaSO_4$ deposition in evaporates +/- $MgSiO_3$ deposition in altered oceanic crust).

Biogeochemical Cycles: repetitive perturbation of the geochemical reservoirs.

Annual $CO_2$ abundance oscillation

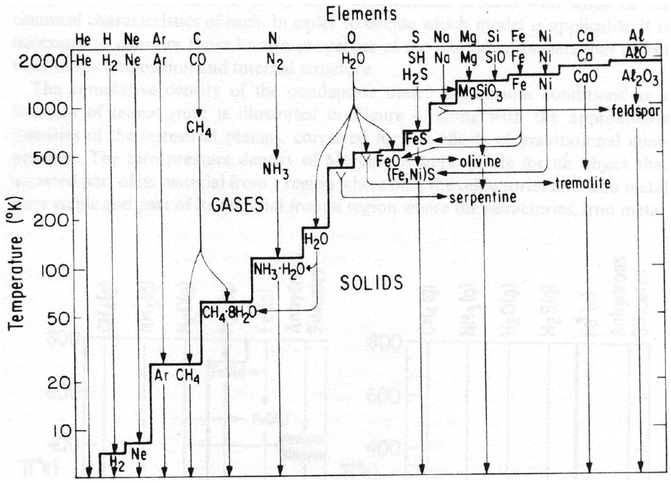
Milankovitch cycles

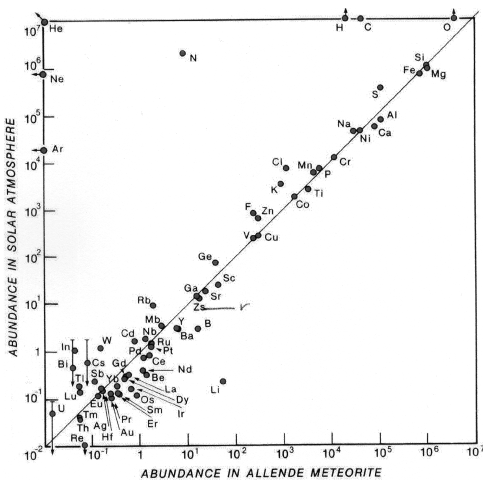
Monotonic perturbations: Anthropogenic greenhouse gas emission(?) Evolution of metabolic pathways(?)

Ch. 2: Origins of geochemical reservoirs

1. Nucleogenesis (Big Bang) {Photocopy of chart of nuclides}
   a. Energy captured in formation of hydrogen and helium
   b. $E=mc^2$ – stable atomic nuclei (low E) have low mass (low m).
      i. $^{1}H$ – 1.00782503 amu (1 amu ≈ $9x10^{10}$ KJ/mole)
      ii. $^{1}n$ – 1.00866491 amu (a free neutron will decay to $^{1}H$!)
      iii. $^{4}He$ – 4.00260323
         1. ($4x^{1}H = 4.0313 < {}^{4}He$ – $^{1}H$ spontaneously reacts to form $^{4}He$, but very slow unless Temp ~$10^{7}$K or more)
         2. Hot dense H "burns" to He
      iv. $^{8}Be$ – 8.0053051 > $^{4}He+^{4}He$ – difficult to burn $^{4}He$, so the short nucleogenesis stops at He + Li.
2. Nucleosynthesis (Stars)
   a. Main process is H -> He burning (mainly via a final $2x^{3}He \rightarrow {}^{4}He + 2x^{1}H$ step).
   b. Long timescale, high pressure, high temperatures ($10^{8}$K), build-up of $^{4}He$, allow creation of $^{12}C$ by triple-helium reaction (12.0 amu < $3x^{4}He$ = 12.00781 amu)
   c. Once $^{12}C$ is produced, heavier elements produced by successive $^{4}He$ capture and binary fusion ($^{12}C + {}^{4}He$ -> $^{16}O$, … $^{20}Ne + {}^{4}He$ -> $^{24}Mg$)
   d. ~$^{56}Fe$ is the most stable nucleus, end product of fusion
   e. Heavier elements formed by successive addition of $^{1}n$, rarely combined with photodissociation by $\gamma$-rays, acting on existing heavy nuclei.
3. Relevance to solar system geochemistry:
   a. H, He dominate solar system and universe.
   b. Even-numbered elements C -> Fe next most abundant
   c. Odd-numbered elements (N, P) less abundant
   d. Elements heavier than Fe progressively rarer

4. Formation of the Earth




a. Early Earth too small, hot to
retain full solar system abundance of gasses ($H_2$, He, CO, $CH_4$, $N_2$, $NH_3$)
b. Refractory (high vaporization temperature) elements concentrated (Fe, MgO, CaO, $Al_2O_3$, $SiO_2$).
c. Formation of the core removed most Fe, Ni, Zn, other alloy-loving elements.
d. Formation of the Earth's crust by melting & crystallization of lavas concentrated low-melting temperature elements (Na, K, P) at the Earth's surface – re-concentrates gasses at surface as well.