ESS C113/C213 Biological and Environmental Chemistry

Lecture 19: Global Sulfur cycle
Reading: Schlesinger "Global cycles of sulfur and mercury"

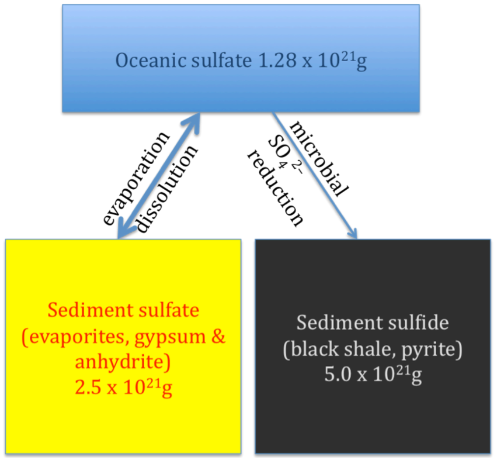
Ch. 13. The sulfur cycle

1. Fig. 13-1
    a. Major crustal pools
        i. $CaSO_4$ & $CaSO_4.2H_2O$ 2.5x10^21 g
        ii. Shale organics/sulfides 5.0x10^21 g
    b. Surface (active) pools
        i. *Atmosphere 2.8x10^12* g
        ii. Ocean 1.28x10^21 g MRT≈10^7 years!
        iii. Soil (organic) 1.5x10^16 g
        iv. Land Plants 8.5x10^15 g

2. Fluxes (~1990's)
    i. Sea-salt aerosols 1.4x10^14 g/yr (most falls back)
    ii. Fossil-fuel burning 9x10^13 g/yr (1990's estimate)
    iii. Biogenic gases ~2x10^13 g/yr (highly uncertain)
        1. H_2S, $(CH_3)_2S$, SCO (mostly sulfides)
    iv. Volcanoes ~1x10^13 g/yr (variable)
        1. H_2S, $SO_2 \rightarrow SO_4^{2-}$
    v. Dust ~8x10^12 g/yr (large uncertainty)

3. Unlike carbon, there is no long-lived atmospheric reservoir (most S-bearing gases quickly oxidize to sulfate, which nucleates aerosols/precipitation).
    a. S-pollution is mainly regional, not global, and typically reacts only to short-term forcings.
        i. Concentration of effects near sources: S from coal → acid rain
            1. perturbs weathering, can overcome normal neutralization capacity of soils
            2. leaching of Mg2+, Ca2+, K+
            3. may mobilize normally immobile elements to toxic levels (i.e., Al3+)
    b. Violent volcanic eruptions can inject sulfate to stratosphere – where it lasts longer than typical tropospheric aerosols
        i. sulfate aerosols typically light-colored, small: reflect lots of sunlight
        ii. ~year long climate effects

4. Simplified sulfur cycle (Schlesinger 13-2):



5. Ancient sulfur cycles
    a. Much like carbon, large geologic pools interact with more mobile surface pools of sulfur
    b. Also like carbon, isotopic signatures of oxidized & reduced phases can proxy for rates of sulfur "loss" and "gain" from these reservoirs.
        i. $\delta^{34}S$ -- $^{34}S/^{32}S$ relative to a standard (troilite, an FeS mineral from the Cañon Diablo meteorite), thought to be more-or-less like bulk Earth (and volcanic emissions)
            1. $\delta^{34}S = [(^{34}S/^{32}S)_{sample}/(^{34}S/^{32}S)_{standard} - 1] \times 1000$
        ii. Main isotope separation mechanism during the Phanerozoic: sulfate reduction (!)
            1. Sulfide (H_2S) typically has $\delta^{34}S$ ~25‰ lower than the reactant sulfate (SO_4^{2-})
                a. actually varies quite a bit (can be up to 60‰!)
            2. Seawater sulfate, precipitated evaporite minerals seem to have similar $\delta^{34}S$
        iii. Isotopic see-saw
            1. More sulfate reduction → loss of ^{32}S from surface reservoirs (ocean) → higher $\delta^{34}S$ in sulfate **and** sulfide relative to today.
            2. Less sulfate reduction → more ^{32}S in environment → lower $\delta^{34}S$ than today.
            3. ~10^7 residence time of sulfate in ocean (at least today), much slower than mixing of ocean water, suggests a global response
            4. Schlesinger fig. 13.3.
                a. Roughly equal balance between sulfide and sulfate today.
                b. Wide variations in past
                c. Anti-correlation with d13C
                Garrels and Lerman equation

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

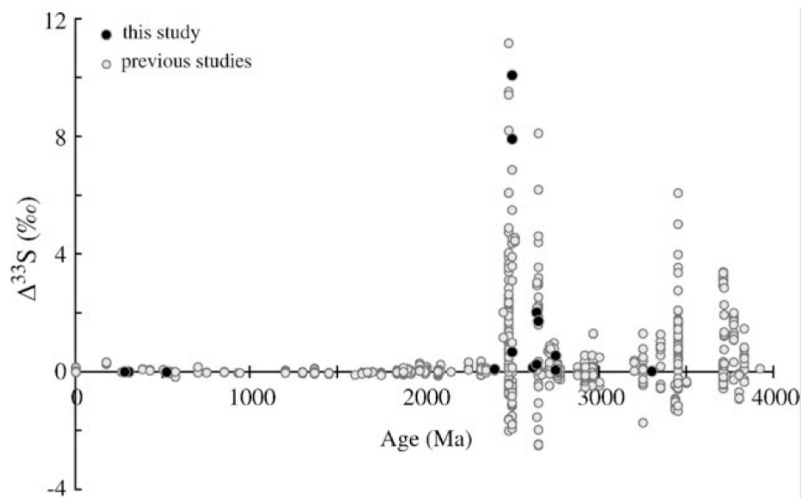
c. A weird discovery…

   i. James Farquhar and others measured not just 34/32, but also 33S/32S in ancient sulfide and sulfate samples.

   ii. They found that $\delta^{33}S$ wasn't always ½ as big as $\delta^{34}S$ – even though normal chemical and physical processes would be expected to separate ^{34}S from ^{32}S twice as efficiently as ^{33}S.

   iii. Difference between measured $\delta^{33}S$, and $\delta^{33}S$ expected from $\delta^{34}S$:

$$\Delta^{33}S \approx \delta^{33}S - 0.515 \times \delta^{34}S$$

   iv. 

(Summary fig from Domagal-Goldman et al., 2007, Science 317:1900)

   v. "Mass independent fractionation" before 2.5×10^9 years ago (the Archean)

   vi. Most likely explanation: UV photochemistry.

      1. Ozone does the same thing! (Though the details are probably different)
      2. But atmospheric sulfur species (the ones that are moving around in a UV-irradiated environment) are dominated by oceanic sulfate fluxes (out) and fossil fuel/ocean fluxes (in).

   vii. What if oceanic sulfate isn't the dominant mobile sulfur pool?

   viii. Anoxia – little sulfate present, Fe^{2+} more common in natural waters?

      1. Sulfides much less soluble, ocean pool much smaller.
      2. Atmosphere less dominated by sulfate aerosols
      3. Some sulfur leaves the atmosphere in reduced or intermediate oxidation states – depending on the photochemical pathway.
      4. Photochemistry of volcanic SO_2, reduced sulfur species more important.

5. Probably requires atmosphere with < 0.2 Pa O_2 (there's 20,000 Pa O_2 today!)