

Sulfur Cycle

I. Cycle operates on different time scales

A. geologic cycle and a short-term cycle

1. short term cycle linked to climate and also affected by anthropogenic activity

B. major components

1. dissolved sulfate – oceans
2. sedimentary components
 - a. pyrite (FeS_2), gypsum ($\text{Ca}_5\text{O}_4 \cdot 2\text{H}_2\text{O}$) and S in organic matter
3. reduced S gasses
 - a. DMS, H_2S , COS and SO_2
4. other atmos compounds - sulfate aerosols

II. Geological cycle

Fig. 13-1

A. balance between weathering (sulfate input to oceans) and removal from the oceans

B. removal processes

1. pyrite ppt.
 - a. pyrite ppt. mediated by sulfate reducing bacteria
2. sulfate removal at hydrothermal vents
 - a. predominantly involves high temp. sulfate reduction (sulfide formation)
3. gypsum ppt. (CaSO_4)
 - a. results from evaporite formation
 - b. not apparently important in the present ocean

B. sulfate/sulfide buried in marine sediments is eventually brought to continents

1. sulfides re-oxidized back to sulfate
2. gypsum dissolves
3. another type of weathering rxn.

C. balance between pyrite burial in sediments and pyrite oxidation on land plays a role in affecting the redox balance of the earth's surface.

1. this process also requires OM as an intermediate to catalyze sulfate reduction at earth sfc. conditions
2. similar to burial of reduced OM and the release of O_2 to atm.
3. leads to a balance/coupling between pyrite and OM burial in sediments and kerogen/pyrite oxidation on land
 - a. varies over time

D. $\delta^{34}\text{S}$ curve

show curves

1. indicates changes in the rel. size of the sulfate reservoir in seawater
2. positive excursions - sulfate reduction and pyrite burial predominates
 - a. sulfate reservoir depleted
 - b. sulfate reduction uses light sulfate - makes residual sulfate heavier
 - c. produces light pyrite
 - d. 'balanced' by equal and opposite changes in carbon burial
 - i. avoid fluctuations in atmospheric O_2
3. negative excursions
 - a. oxidation of these light sulfides
 - b. again balanced by changes in carbon burial

III. The short-term S cycle

Fig. 5.15a

- A. atmos. cycling important
- B. dominated by emissions of several different reduced sulfur gasses
 - 1. oceanic gas emissions dominated by DMS
 - a. some OCS, CS₂ and H₂S
 - b. DMS produced by marine algae - more later
- C. natural terr emissions dominated by H₂S - sulfate reduction in freshwater wetlands
- D. volcanic emissions - mostly SO₂ and H₂S
 - 1. episodic inputs that can have major impacts on global climate
- E. this pre-industrial cycle suggests a small land to ocean S flux
- F. flux enhanced by man's activities
 - 1. much larger atmos. -> ocean flux
- G. all of these reduced S gasses are fairly reactive in the atmos.
 - 1. oxidized rapidly to sulfate
 - a. deposited as non-sea salt sulfate
- H. atmospheric component of the S cycle
 - 1. remote marine areas: DMS → SO₂ → sulfate
 - 2. urban land areas: SO₂ → sulfate

Fig. 5.16

IV. anthropogenic cycle

Fig. 5.15b

- A. man's effects on the S cycle is clearly important
- B. dominated by SO₂ emissions due to fossil fuel burning
- C. depositional fluxes from atmos to oceans and land have both increased
 - 1. on land this contributes to problems associated with acid rain
- D. increases the net flow of atmos S from continents to oceans
- E. riverine S input to the oceans has also increased (104 ⇒ 213)
 - 1. likely has a very small effect on sulfate concs in seawater
 - 2. the same for enhanced atmos deposition

V. SO₂ and climate

- A. SO₂ in the atmos (regardless of source) is eventually oxidized to sulfate **Fig. 5.16**
 - 1. contributes to acid rain
 - 2. this oxidation process also forms cloud condensation nuclei in the form of sulfate aerosols
- B. sulfate aerosols can have a cooling effect
 - 1. aerosols increase albedo (reflectivity) of atmos.
 - 2. CCN's also lead to cloud formation that can cool
 - 3. these sulfate aerosols are important in discussions about possible global warming
- C. depends on where in the atmos SO₂ is input
 - 1. residence time of aerosols in troposphere (lower atmos.) is ~5 d
 - a. leads to a local effect
- D. SO₂ input from volcanos are input to stratosphere **show figure w/painting**
 - 1. here sulfate aerosols here can persist for several years
 - 2. episodic inputs that can have major impacts on global climate
 - 3. short-term cooling of earth due to production of sulfate aerosols from SO₂
 - a. dust and debris added to stratosphere also important

- b. Mt. Pinbatubo in 1991
- 4. eruption of Mt. Tambora (Indonesia), April 1815
 - a. led to “year without summer” in 1816
 - b. massive crop failures
 - c. cold waves and frosts every month in New England
 - d. snow falls were brown, blue and red

VI. DMS and climate control

- A. DMS from marine plankton can also be a source for SO_2 **Fig. 5.16**
- B. interest in recent years in the role of sulfur cycling in controlling climate
- C. look at in terms of the pos and neg feedback systems discussed in the Gaia hypothesis

VII. CLAW Hypothesis

show original figure

- A. based on the observation that marine algae emit large amounts of DMS
- B. IF increasing temp and low albedo increases algae growth
- C. then incr. temp increases DMS prdn.
- D. increased DMS $\rightarrow$ incr. CCN nuclei $\rightarrow$ incr. cloud cover
 - 1. leads to lowers temp and higher albedo
- E. this would then lead to decr. DMS prdn. (plankton growth)
 - 1. such a negative feedback system might tend to stabilize temp.
- F. one of the first attempts to prove/examine the Gaia hypothesis

VIII. several problems with CLAW

Fig. 3

- A. unsure of whether the relationships were indeed negative feedback ones
- B. negative feedback of DMS on climate not entirely consistent with anthropogenic SO_2 emissions
 - 1. no strong evidence (except immediately adjacent to the coast) that anthropogenic SO_2 emissions affect cloud albedo
 - 2. may be related to short lifetime of aerosols in troposphere

IX. Evidence that most high prod. regions in the oceans are at high latitudes

- A. cold not warm water **NASA image**
- B. plankton in the ocean grow best at temps. 8-10°C lower than optimal growth temps in lab cultures
- C. appears to be related to ocean physics
 - 1. appears to be related to ocean physics and nutrient availability
 - 2. if oceans are too warm the surface layer stratifies
 - a. limits nutrient exchange from the deep via either upwelling or deep wind driven mixing
 - b. increasing turbulence and upward mixing of nutrients
- D. may explain why prod. is generally highest at low latitudes
 - 1. compromise between colder temperatures and nutrient availability

X. Ice core records

Fig. 14-18

- A. nss-sulfate and MSA deposition higher during glacial times in the Antarctic
- B. both are DMS oxidation products
- C. suggests that oceanic DMS prodn. may actually have a positive feedback on climate

D. based on the assumption here that cooling leads to incr. primary prod./DMS emission

1. incr. DMS prdn -> incr. CCN -> incr. albedo -> lower temp.

Fig. 14-19

and Fig. 3b

XI. Brings up questions about glacial/interglacial systems

A. Lovelock stated “Gaia may like it cold”

B. look at Quaternary climates

1. 90% of this time the Earth is in a cold glacial period

C. warm inter-glacials are generally short lived phenomena

1. seems more desirable to us

D. Do the present-day climate regulating mechanisms work best at the lower glacial temps?