Introduction

Sulfur is found in valence states ranging from $+6$ in $\text{SO}_4^{2-}$ to $-2$ in sulfides

Original pool on Earth was in igneous rocks, mainly igneous pyrite (FeS$_2$)
- Degassing and weathering of crust under O$_2$ transferred large amounts of S to oceans, where it is now found primarily as $\text{SO}_4^{2-}$

**TABLE 13.1**

When $\text{SO}_4^{2-}$ assimilated by organisms, it is reduced and converted to organic sulfur
- Essential component of protein
  - BUT VERY LITTLE SULFUR RESIDES IN THE BIOSPHERE
  - Major global pools are found in:
    - Sedimentary pyrite
    - Seawater
    - Evaporates derived from ocean water

Microbial transformations between valence states drive the global S cycle
- Under anaerobic conditions, $\text{SO}_4$ is substrate for sulfate reduction
- May lead to release of reduced gases to atmosphere and deposition of sedimentary pyrite

**Sulfate Reduction:**

Dissimilatory sulfate reduction in anaerobic soils analogous to denitrification
- $\text{SO}_4^{2-}$ acts as alternative electron acceptor during oxidation of organic matter by bacteria
  - Primarily *Desulfovibrio* sp. and *Desulfotomaculum* sp.

\[
e.g., 2\text{H}^+ + \text{SO}_4^{2-} + 2(\text{CH}_2\text{O}) \rightarrow 2\text{CO}_2 + \text{H}_2\text{S} + 2\text{H}_2\text{O}
\]

These bacteria produce a variety of sulfur gases, including:
• Hydrogen sulfide (H₂S)
• Dimethylsulfide [(CH₃)₂S]
• Carbonyl sulfide (COS)

Prior to human industrialization, wetlands soils was dominant source of biogenic sulfur gases in the atmosphere

• Escape of H₂S from wetlands much less than rates of sulfate reduction at depth, because of reactions between H₂S and other soil constituents
  o E.g., only 0.3% of sulfate added to peatlands was recovered as H₂S
  o H₂S can react with Fe²⁺ to precipitate FeS
    • FeS can then be converted to pyrite (FeS₂):
      • FeS + H₂S → FeS₂ + 2H⁺ + 2e⁻
  • When H₂S diffuses through zone of Fe³⁺, pyrite is precipitated:
    o 2Fe(OH)₃ + 2H₂S + 2H⁺ → FeS₂ + 6H₂O + Fe²⁺

• Therefore not all reduced iron in wetland soils is formed directly by iron-reducing bacteria

Iron content limits accumulation of iron sulfides in many wetland sediments

• However, iron sulfides effective traps for H₂S that might escape to atmosphere
  o During periods of low water, specialized bacteria may reoxidize iron sulfides, releasing SO₄²⁻ than can diffuse to zone of sulfate-reducing bacteria.

H₂S also reacts with organic matter to form carbon-bonded sulfur that accumulates in peat and lake sediments

• Carbon-bonded sulfur accounts for large fraction of sulfur in many coals, and current release to the atmosphere due to industrialization

SO₄²⁻ in soil solution exists in equilibrium with sulfate adsorbed on soil minerals.

Plant uptake of SO₄²⁻ is followed by assimilatory reduction and incorporation of carbon-bonded sulfur into the amino acids cysteine and methionine

• The molecular structure of S-reducing protein contains Fe as a cofactor
  o When soil sulfate concentrations are high, plants may accumulate SO₄ in leaf tissue

In most soils, majority of S pool held in organic forms

• Decomposition of plant tissues accompanied by microbial immobilizations

However, despite predominance of organic S forms, the pool of SO₄²⁻ in most soils is not insignificant

To maintain charge balance, plant uptake and reduction of SO₄²⁻ consumes H⁺ from the soil, whereas mineralization of organic sulfur returns H⁺ to soil solution, producing no net increase in acidity
• In contrast, reduced inorganic sulfur is found in association with some rock minerals (e.g., pyrite)
  o Oxidative weathering of reduced sulfide minerals accounts for highly acidic solutions draining mine tailings

Globally, upland soils are only a small source of sulfur gases to the atmosphere, since highly reducing, anaerobic conditions are required

Anoxic environments also support sulfur-based photosynthesis (thought to be one of first forms of photosynthesis on Earth)

In presence of O₂, reduced sulfur compounds oxidized by microbes
  • Oxidation usually coupled to reduction of CO₂, in reactions of S-based chemosynthesis

The Global Sulfur Cycle

No sulfur gas is a long-lived or major constituent of the atmosphere
  • Therefore must model global S cycle by explaining the fate of the large anthropogenic input of sulfur compounds to the atmosphere
    o Short mean residence time for atmospheric sulfur compounds as a result of their oxidation to SO₄

If Cl⁻ in rainfall is derived from the ocean, then seaspray should carry SO₄ roughly in proportion to the ratio of SO₄²⁻ to Cl⁻ in seawater
  • Therefore calculated that 4 X 10¹² g S/yr deposited on land should come from oceans
    o However, they were finding about 73 X 10¹² g S/yr
    o In U.S. found SO₄ abundant in rainfall of industrial regions and in areas downstream of deserts
      • Desert soils source of gypsum (CaSO₄·2H₂O)
      • Burning fossil fuels source of SO₂

IN ACTUALITY: our understanding of the global S cycle is primitive, with considerable uncertainty with most estimates

Episodic events (volcanic eruptions, dust storms) contribute to global cycling of S

Volcanic eruptions:
  • Using SO₄ in Antarctic ice pack, estimated impacts of volcanoes:
    o Tambora 1815 eruption was largest, releasing 50 X 10¹² g S to atmosphere
    o Typically, though, eruptions like Mt Pinatubo release 5-10 X 10¹² g S each
  • Average annual flux from volcanoes is about 10 X 10¹² g S/yr
    o About 70% of this leaked passively from volcanoes, the rest comes from major explosive events

Soil dusts:
  • Episodic and poorly understood
• Large particles usually deposited locally, whereas small particles can be transported long distances
  o e.g., dust from deserts of Middle East contributes to SO$_4$ in northwest Indian Ocean
• Average annual flux from dust transport in troposphere is about $8 \times 10^{12}$ g S/yr
  o About 10% of this from fossil fuel release

Estimates of flux of biogenic sulfur gases from land differ by factor of 10
• Again, dominant S gas emitted from wetlands and anoxic soils is H$_2$S
  o Emissions from plants poorly understood
• Estimates now think flux of biogenic S gases from land $< 1 \times 10^{12}$ g S/yr
  o Forest fires emit an additional $3 \times 10^{12}$ g S/yr

Direct emissions from human industrial activities largest source of S gases to atmosphere
• Estimates have ranged between 50-100 $\times 10^{12}$ g S/yr
  o Slightly lower values recently due to pollution abatement
• Owing to reactivity of S gases in atmosphere, most of anthropogenic SO$_2$ emissions deposited locally in precipitation and dryfall
  o Total deposition may be as high as $120 \times 10^{12}$ g S/yr, but only $90 \times 10^{12}$ g S/yr needed to balance global S cycle
  o Deposition in dryfall and the direct absorption of SO$_2$ poorly understood

Human activities also affect transport of S in rivers
• e.g., one study suggests about 28% of SO$_4$ content of rivers derived from air pollution, mining, erosion and other human activities
• another study suggests that current river transport of $131 \times 10^{12}$ g S/yr is roughly double pre-industrial conditions
• some estimates say that flux from rivers is currently $200 \times 10^{12}$ g S/yr
  o Small fraction of river load is derived from rainfall including cyclic salts carried from oceans ($4 \times 10^{12}$ g S/yr)

The ocean is large source of aerosols (seasalts) that contain SO$_4$
• Most of the $144 \times 10^{12}$ g S/yr flux in seasalt redeposited in oceans in precipitation and dryfall
• Dimethylsulfide [(CH$_3$)$_2$S or DMS] is major biogenic gas emitted from oceans
  o Currently estimated that biogenic flux from oceans about $16 \times 10^{12}$ g S/yr
  o Therefore DMS largest natural source of sulfur gases in atmosphere
  o Mean residence time of DMS in atmosphere is about 1 day because of oxidation to SO$_4$, and therefore most of DMS emissions fall back into oceans
• Current estimates of deposition of S to oceans suggests that they are sinks for SO$_4$ by over $10^{13}$ g S/yr
• Mean residence time of SO$_4$ in seawater is 10 million years with respect to current inputs from rivers!!!
The Marine Sulfur Cycle

Fig. 9.22

Sulfate abundant in oceans where it is found as $\text{SO}_4^{2-}$
- Metallic sulfides precipitated at hydrothermal vents and biogenic pyrite in sediments are major marine sinks

Oceans major source of DMS, which is produced during decomposition of dimethylsulfoiopropionate (DMSP) from dying phytoplankton cells
- Reaction mediated by enzyme dimethyl sulfoxide (DMSO) reductase
  - Grazing by zooplankton seems to be important to release of DMS to seawater
- Only small fraction of DMS lost to atmosphere
  - Remainder degraded by microbes in surface waters
- Mean residence time of DMS in seawater only about 2 days.

DMS is also important sulfur gas emitted from salt marshes
- Production of DMS increases as a function of increasing salinity, as river water mixes with seawater in estuaries

Oxidation of DMS to sulfate aerosols increases abundance of cloud condensation nuclei in atmosphere, leading to greater cloudiness
- Clouds over sea reflect incoming sunlight, leading to global cooling
  - Production of DMS related to growth of marine phytoplankton, so increase in marine NPP increases production of DMS
- If higher NPP is associated with warmer sea surface temperatures, then flux of DMS would have potential negative feedback on global warming.

Stratospheric Sulfur Compounds

Sulfate aerosols in stratosphere important to albedo of Earth
- Layer of sulfate aerosols (known as Junge layer) is found in stratosphere at about 20-25 km altitude
  - Origin of Junge layer two-fold:
    - Large volcanic eruptions can inject $\text{SO}_2$ into stratosphere where it is oxidized to sulfate
    - Large volcanic eruptions can increase stratospheric sulfate 100-fold where it persists for several years cooling the planet
    - Without volcanoes, dominant source of stratospheric sulfate is carbonyl sulfate (COS) that mixes up from troposphere
      - Once in stratosphere, COS is oxidized by photolysis forming sulfate aerosols that contribute to Junge layer
- Current increase in stratospheric sulfate may be due to increasing use of high-altitude aircraft and other anthropogenic perturbations of global S cycle.
COS most abundant sulfur gas in atmosphere (2.8 X 10^{12} g S) **Table 3.1**

- Based on global budget, mean residence time is about 5 years in atmosphere (**Table 13.3**)

Major source of COS appears to be ocean where it is produced by photochemical reaction with dissolved organic matter

- Other sources include:
  - Biomass burning
  - Fossil fuel combustion
  - Oxidation of CS$_2$ (largely produced by industry) by OH radicals in atmosphere

Some COS is oxidized in troposphere via OH radicals, but major tropospheric sink for COS appears to uptake by vegetation (between 55-89% of total annual destruction of COS globally)

**Acid rain**

When SO$_2$ is emitted as an air pollutant, it forms sulfuric acid through heterogeneous reactions with water in the atmosphere

- As a strong acid completely dissociated in water, H$_2$SO$_4$ suppresses disassociation of natural, weak acids in rainfall
  - e.g., dissolution of CO$_2$ in water will form weak solution of carbonic acid, and rainfall pH will be about 5.6:

\[
\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{HCO}_3^-
\]

- With strong acids that lower pH below 4.3, reaction moves to left and carbonic acid makes no contribution to free acidity

- In industrialized areas, free acidity in precipitation almost wholly determined by concentration of strong acid anions (SO$_4^{2-}$ and NO$_3^-$)
  - Rock weathering now driven by anthropogenic H$^+$, not carbonation

**Table 13.2**