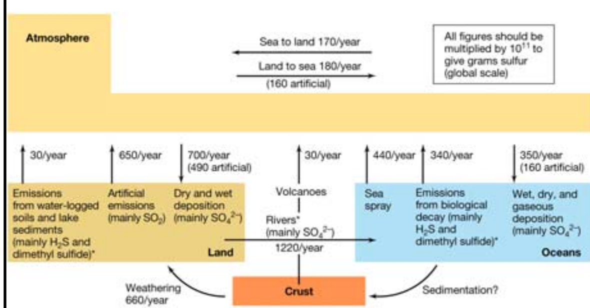
ESM 219

Nov 5th: S, Fe, Hg cycles and microbes

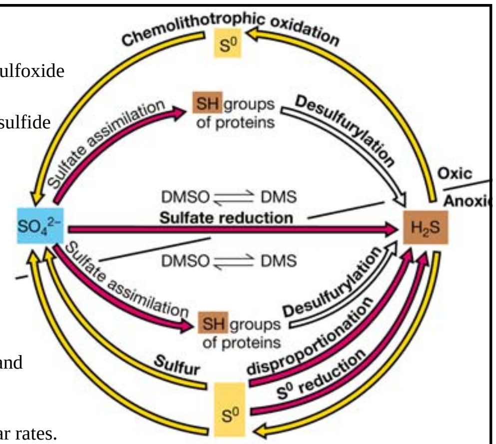
Microbes in the S cycle

The global balance of sulfur. Artificial emissions are derived from human activities. An asterisk indicates a process that is partially or solely due to microbial action.



DMSO= dimethyl sulfoxide

DMS = dimethyl sulfide



NOTE: Biological and chemical S cycling are at similar rates.

Key Processes and Prokaryotes in the Sulfur Cycle

Process	Organisms
Sulfide/sulfur oxidation ($H_2S \rightarrow S^0 \rightarrow SO_4^{2-}$)	
Aerobic	Sulfur chemolithotrophs (*Thiobacillus*, *Beggiatoa*, many others)
Anaerobic	Purple and green phototrophic bacteria, some chemolithotrophs
Sulfate reduction (anaerobic) ($SO_4^{2-} \rightarrow H_2S$)	*Desulfovibrio*, *Desulfobacter*,
Sulfur reduction (anaerobic) ($S^0 \rightarrow H_2S$)	*Desulfuromonas*, many hyperthermophilic *Archaea*
Sulfur disproportionation ($S_2O_3^{2-} \rightarrow H_2S + SO_4^{2-}$)	*Desulfovibrio*, and others
Organic sulfur compound oxidation or reduction ($CH_3SH \rightarrow CO_2 + H_2S$) (DMSO → DMS)	
Desulfurylation (organic-S → H_2S)	Many organisms can do this

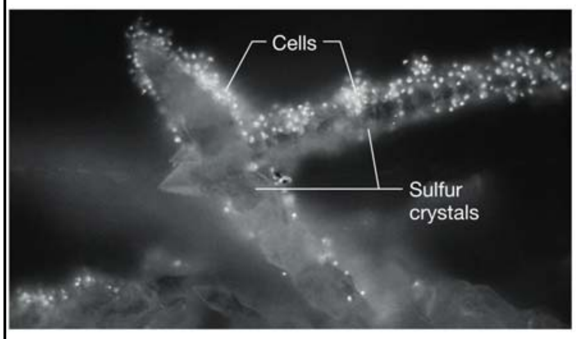
Sulfur and sulfide oxidation

- sulfur oxidation (autrophic or heterotrophic)
- Lowers pH
- *Thiobacillus* are everywhere
- *Beggiatoa*
  - mixotroph: organic cmpd for C, H_2S for energy
- Oxidation reactions (can involve NO_3^-)
  - $S^o + 3/2\ O_2 + H_2O \rightarrow H_2SO_4$ -587 kJ/rxn
  - $H_2S + 2O_2 \rightarrow SO_4^{2-} + 2H^+$ -798.2 kJ/rxn
  - $HS- + ½\ O_2 + H^+ \rightarrow S^o + H_2O$ -209.4 kJ/rxn
  - $S_2O_3^{2-}+H_2O+2O_2 \rightarrow 2SO_4^{2-}+2H^+$ -822.6 kJ/rxn

Fates of DMS

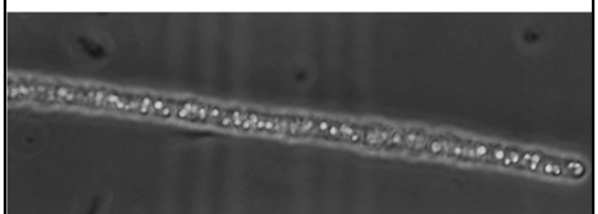
- atmosphere release then photochemical oxidation
- in anoxic sys. is a substrate for methanogens
- e^- donor to phototrophs yielding DMSO
- e^- donor for chemolithotrophs or autotrophs

Attachment of the sulfur-oxidizing archaeon Sulfolobus acidocaldarius to a crystal of elemental sulfur. Cells are visualized by fluorescence microscopy after staining the cells with the dye acridine orange. The sulfur crystal does not fluoresce.



(b)

Deposition of internal sulfur granules by *Beggiatoa*.



(a)

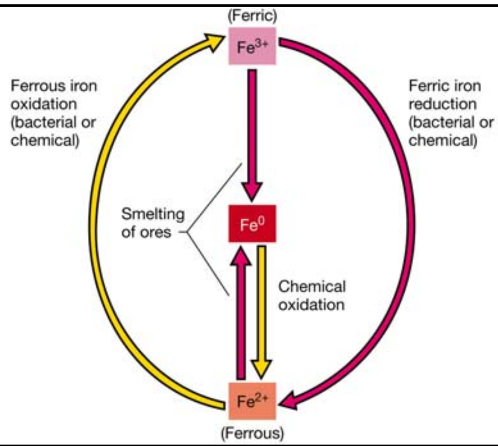
Sulfur and sulfate reduction

- Elemental sulfur can be reduced (*Archaeal*)
- Sulfate reduction to hydrogen sulfide
  - $SO_4^{2-} + 8H \rightarrow H_2S + 2H_2O + 2OH^-$
  - Organic C oxidized, sulfate = e^- acceptor
  - Some can oxidize H_2 and acetate
    - K_s for H_2
      - 6.6 µM for methanogens
      - 1.3 µM for sulfate reducers
    - K_s for acetate
      - 3 mM for methanogens
      - 0.2 mM for sulfate reducers

Mineralization of Organic S

- Organic S
  - dimethyl sulfide: $H_3C\text{-}S\text{-}CH_3$ produced in marine sys. fr. dimethyl sulfonium priopionate; most abundant organic S form
  - Methanethiol: CH_3SH
  - Dimethyl disulfide: $H_3C\text{-}S\text{-}S\text{-}CH_3$
  - Carbon disulfide: CS_2

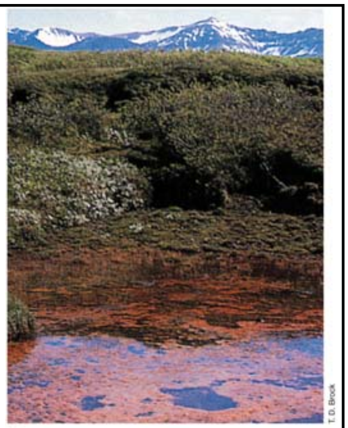
Microbes in the Fe cycle



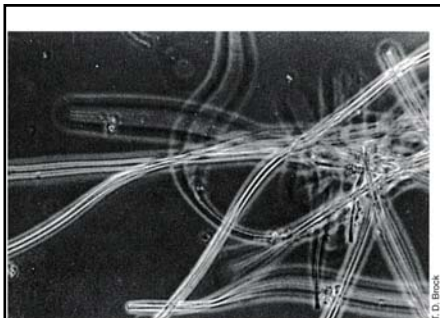
Ferric Iron reduction

- Fe^{3+} used as e^- acceptor
- Fe^{3+} reduction occurs in anoxic environs (water-logged soils, bogs, etc.) Fe^{2+} re-oxidizes spontaneously in oxic environs:
  - $Fe^{2+} + \frac{1}{4} O_2 + H^+ \rightarrow Fe^{3+} + \frac{1}{2} H_2O$
  - $Fe^{3+} + 3 H_2O \rightarrow Fe(OH)_3 + 3H^+$
  - $Fe^{2+} + \frac{1}{4} O_2 + 2\frac{1}{2} H_2O \rightarrow Fe(OH)_3 + 2H^+$

Iron oxidizing (Fe^{2+} to Fe^{3+}) bacteria *Gallionella* and *Leptothrix* contribute to the formation of ferric hydroxide in nonacidic environs, but it also happens spontaneously.



(c)



Sphaerotilus **also oxidizes iron to gain energy and, like the other bacteria in anoxic environments, thrives at the oxic/anoxic interface.**

Acid Mine Drainage

AMD = very acidic, metal-rich drainage from deep mines

In acidic environments, ferrous iron oxidation is by *Thiobacillus ferrooxidans*

Overall Reaction:

$4 FeS_2 + 15 O_2 + 14 H_2O \rightarrow 4 Fe(OH)_3 \downarrow + 8 H_2SO_4$

Pyrite + Oxygen + Water → "Yellowboy" + Sulfuric Acid

Acid Mine Drainage

Step 1: Pyrite is exposed to oxygen as a result of mining, and pyrite is oxidized.

Reaction:

$2 FeS_2 + 7 O_2 + 2 H_2O \rightarrow 2 Fe^{2+} + 4 SO_4^{2-} + 4 H^+$

Pyrite + Oxygen + Water → Ferrous Iron + Sulfate + Acidity

(b)

Pyrite is exposed in coal mines.

Pyrite is also exposed in copper mines.

(c)

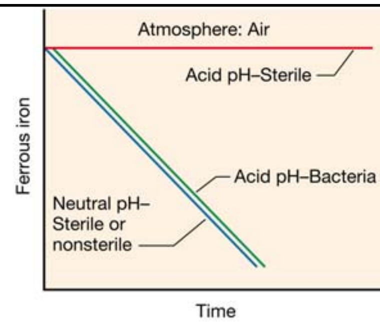
Acid Mine Drainage

Step 2: Ferrous iron is oxidized to ferric iron; this is fast by bacteria. This step is rate-limiting.

Reaction:

$4\ Fe^{2+} + O_2 + 4\ H^+ \rightarrow 4\ Fe^{3+} + 2\ H_2O$

Ferrous Iron + Oxygen + Acidity → Ferric Iron + Water



Iron oxidizing bacteria *Thiobacillus ferrooxidans* oxidizes ferrous iron under acidic conditions. If no bacteria are present, ferrous iron is stable at low pH.

Acid Mine Drainage

Step 3: Iron is hydrolyzed and a solid precipitate forms at pH's above 3.5 (the pH range also favorable to microbes in Step 2).

Reaction:

$4\ Fe^{3+} + 12\ H_2O \rightarrow 4\ Fe(OH)_3 \downarrow + 12\ H^+$

Ferric Iron + Water → Ferric Hydroxide (yellowboy) + Acidity

Acid Mine Drainage

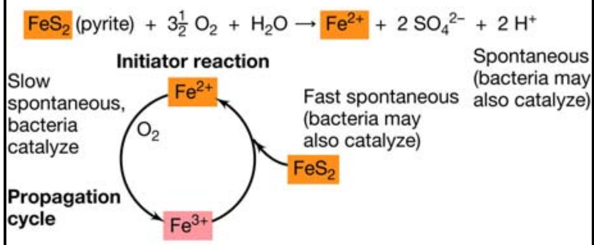
Step 4: The cycle is perpetuated because ferric iron produced in the first 2 steps react with pyrite to make more ferrous iron. This is a rapid, abiotic process.

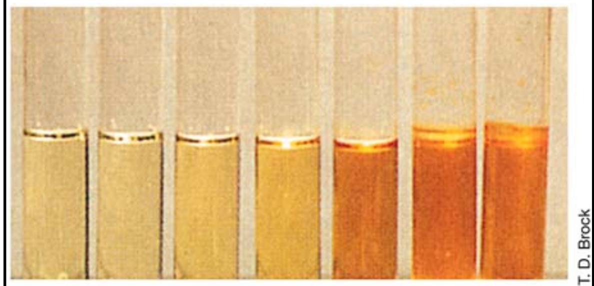
Reaction:

$FeS_2 + 14\ Fe^{3+} + 8\ H_2O \rightarrow 15\ Fe^{2+} + 2\ SO_4^{2-} + 16\ H^+$

Pyrite + Ferric Iron + Water → Ferrous Iron + Sulfate + Acidity

Iron cycle in acid mine drainage.





(b) *Thiobacillus ferrooxidans* oxidizes Fe^{2+} to Fe^{3+} which forms a yellow-orange iron hydroxide. Like *Leptospirillum*, this organism can grow autotrophically.

Microbially Influenced Corrosion

(MIC)

MIC under anaerobic conditions

- For example, under biofilms (which form in pipes), cathodic reactions could be

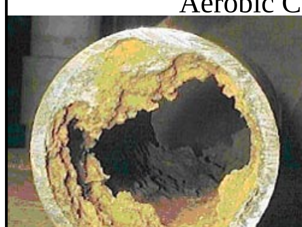
$$2H^+ + 2e^- \rightarrow 2H \rightarrow H_2$$

$$2H_2S + 2e^- \rightarrow 2HS^- + H_2$$

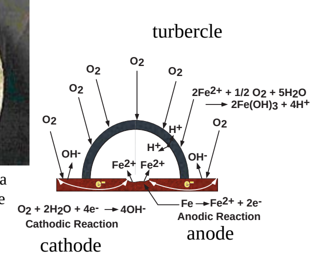
If hydrogen sulfide is present, the latter could occur.

Sulfate Reducing Bacteria (SRB) oxidize H_2, and reduce SO_4^{2-}, making S^{2-} which reacts with Fe^{2+} to make FeS.

Microbially Influenced Corrosion: Aerobic Conditions

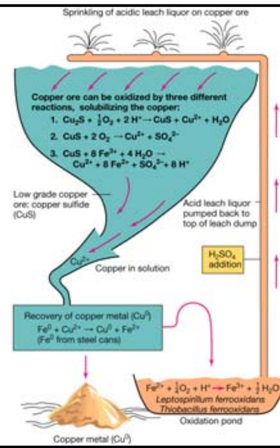


Microbes colonize the surface and form a biofilm.Under the biofilm, conditions are reduced. Electrons flow through the metal and react with oxygen at the cathode. Ferrous iron oxides and precipitates. If SRB are present, FeS will also form.

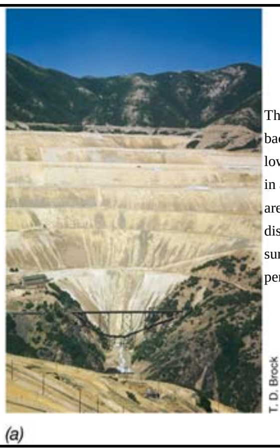


(Source: W. Allan Hamilton, 1995)

Microbes and Cu

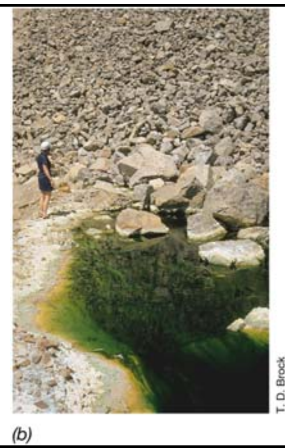


Arrangement of a leaching pile and reactions involved in the microbial leaching of copper sulfide minerals to yield Cu0 (copper metal). Reaction 1 is primarily bacterial, while Reaction 2 occurs both biologically and chemically. Reaction 3 is strictly chemical, but is probably the most important reaction in copper-leaching processes. Note how it is essential for Reaction 3 to proceed that the Fe^{2+} produced (from the oxidation of sulfide in CuS to sulfate) be oxidized back to Fe^{3+} by *Thiobacillus ferrooxidans* and *Leptospirillum ferrooxidans* (bottom of art).



The leaching of low-grade copper ores using bacteria. (a) A typical leaching dump. The low-grade ore has been crushed and dumped in a large pile in such a way that the surface area exposed is as high as possible. Pipes distribute the acidic leach water over the surface of the pile. The acidic water slowly percolates through the pile and exits at the bottom.

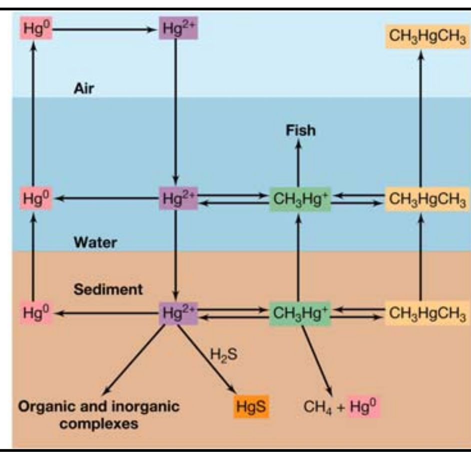
(a)



The leaching of low-grade copper ores using bacteria. (b) Effluent from a copper leaching dump. The acidic water is very rich in dissolved copper.

(b)

Microbes and Hg



Mercury transformations

- Microbes methylate Hg^{2+} in aquatic environments to CH_3Hg^+ then to CH_3HgCH_3
- CH_3Hg^+: toxic, bioaccumulates
- CH_3HgCH_3: volatile
- other reactions:
  - $H_2S + Hg^{2+} \rightarrow$ HgS (low solubility, reoxidized by *Thiobacilli*)
  - Demethylation: $CH_3Hg^+ \rightarrow CH_4 + Hg^o$

Other metals

- **Mn:** reduction of Mn^{4+} to Mn^{2+} occurs anoxically, Mn4+ is e^- acceptor
-
- **Se:** SeO_4^{2-} reduced to SeO_3^{2-} then to Se^o
- selenate selenite
- **As**: arsenate (AsO_4^{3-}) can serve as electron acceptor, arsenite (AsO_3^{3-}) formed