

The Sulfur Cycle

The essential steps of the **sulfur cycle** are:

- Mineralization of organic sulfur to the inorganic form, hydrogen sulfide, H_2S .
- Oxidation of sulfide and elemental sulfur (S) and related compounds to sulfate, SO_4^{2-} .
- Reduction of sulfate to sulfide.
- Microbial immobilization of the sulfur compounds and subsequent incorporation into the organic form of sulfur.

The Sulfur Cycle

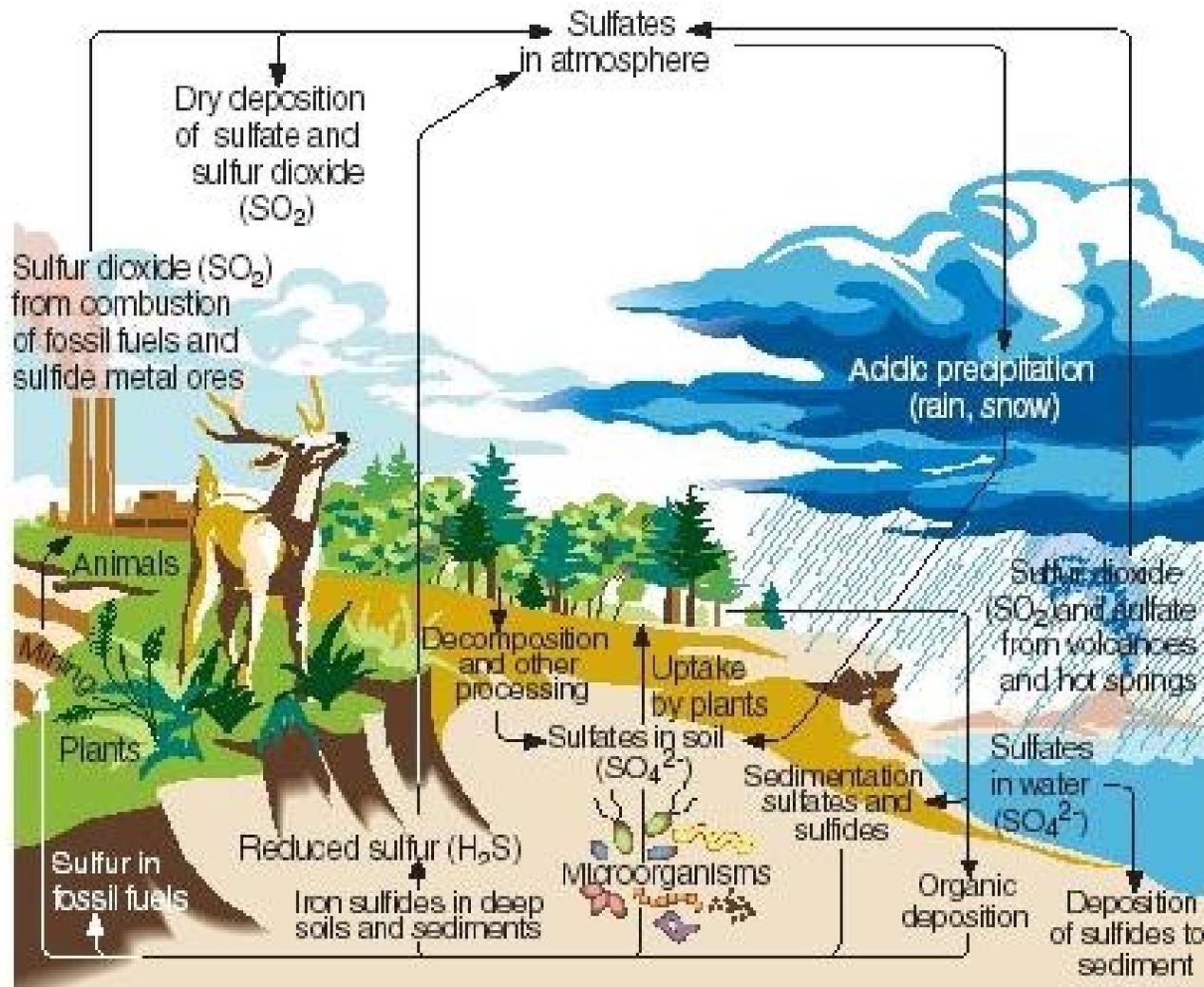
These are often termed as follows:

Assimilative sulfate reduction (sulfur assimilation) in which sulfate (SO_4^{2-}) is reduced to organic sulfhydryl groups (R–SH) by plants, fungi and prokaryotes. The oxidation states of sulfur are +6 in sulfate and –2 in R–SH.

Desulfuration and *Dissimilative sulfur reduction* in which organic molecules containing sulfur can be desulfurated, producing H_2S . Note the similarity to deamination.

Oxidation of hydrogen sulfide produces elemental sulfur (S^0), oxidation state = 0. This reaction is done by the photosynthetic green and purple sulfur bacteria and some chemolithotrophs. Further *oxidation of elemental sulfur* produces sulfate.

The Sulfur Cycle



Sulfur Reservoirs in Nature

Reservoirs of sulfur atoms:

- The largest physical reservoir is the Earth's crust where sulfur is found in gypsum (CaSO_4) and pyrite (FeS_2).
- The largest reservoir of biologically useful sulfur is found in the ocean as sulfate anions (2.6 g/L), dissolved hydrogen sulfide gas, and elemental sulfur.
- Other reservoirs include:
 - Freshwater - contains sulfate, hydrogen sulfide and elemental sulfur
 - Land - contains sulfate
 - Atmosphere - contains sulfur oxide (SO_2) and methane sulfonic acid (CH_3SO_3^-); volcanic activity releases some hydrogen sulfide into the air.

Sulfur in Fossil Fuels

Human impact on the sulfur cycle is primarily in the production of sulfur dioxide (SO_2) from industry (e.g. burning coal) and the internal combustion engine. Sulfur dioxide can precipitate onto surfaces where it can be oxidized to sulfate in the soil (it is also toxic to some plants), reduced to sulfide in the atmosphere, or oxidized to sulfate in the atmosphere as sulfuric acid, a principal component of acid rain.

70 Tg(S) per year in the form of SO_2 comes from fossil fuel combustion and industry

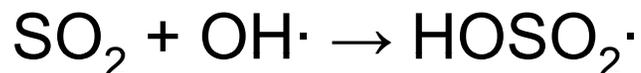
2.8 Tg(S) from wildfires

8 Tg(S) per year from volcanoes

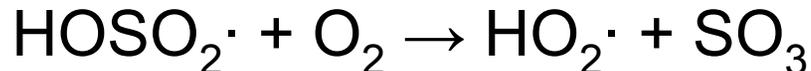
Acid Rain

Formation of sulfuric acid by radical chemistry

In the gas phase sulfur dioxide is oxidized by reaction with the hydroxyl radical via an intermolecular reaction:



which is followed by:



In the presence of water sulfur trioxide (SO_3) is converted rapidly to sulfuric acid:



http://www.epa.gov/acidrain/effects/surface_water.html

Chemistry in Cloud Droplets

When clouds are present the loss rate of SO_2 is faster than can be explained by gas phase chemistry alone. This is due to reactions in the liquid water droplets

Hydrolysis

Sulphur dioxide dissolves in water and then, like carbon dioxide, hydrolyses in a series of equilibrium reactions:



Oxidation

There are a large number of aqueous reactions that oxidize sulfur from S(IV) to S(VI), leading to the formation of sulphuric acid. The most important oxidation reactions are with ozone, hydrogen peroxide and oxygen (reactions with oxygen are catalysed by iron and manganese in the cloud droplets).

Environmental Effects: Water

Both the lower pH and higher aluminum concentrations in surface water that occur as a result of acid rain can cause damage to fish and other aquatic animals. At pHs lower than 5 most fish eggs will not hatch and lower pHs can kill adult fish. As lakes become more acidic biodiversity is reduced. Acid rain has eliminated insect life and some fish species, including the brook trout in some Appalachian streams and creeks. However, there has been some debate on the extent to which acid rain contributes to lake acidity (i.e., that many acid lakes may result primarily from characteristics of the surrounding watershed, and not the rain itself). The EPA's website states: *"Of the lakes and streams surveyed, acid rain caused acidity in 75 percent of the acidic lakes and about 50 percent of the acidic streams"*.

Environmental Effects: Soil

Soil biology can be seriously damaged by acid rain. Some tropical microbes can quickly consume acids but other microbes are unable to tolerate low pHs and are killed. The enzymes of these microbes are denatured (changed in shape so they no longer function) by the acid. The hydronium ions of acid rain also mobilize toxins and leach away essential nutrients and Minerals. Acid rain can slow the growth of vulnerable forests and cause leaves and needles to turn brown and fall off.

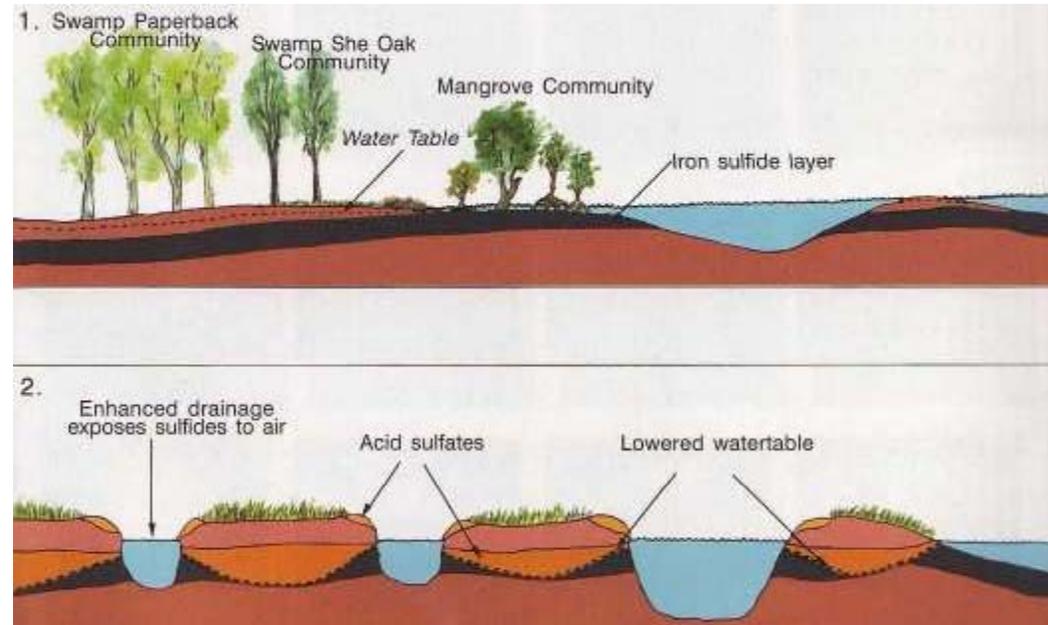
High altitude forests are especially vulnerable as they are often surrounded by clouds and fog which are more acidic than rain. Other plants can also be damaged by acid rain but the effect on food crops is minimized by the application of fertilizers to replace lost nutrients. In cultivated areas, limestone may also be added to increase the ability of the soil to keep the pH stable, but this tactic is largely unusable in the case of wilderness lands.



Effect of acid rain on a forest, Jizera Mountains, Czech Republic

Acid Sulfate Soils

Acid sulfate soil is the name given to soils that contain iron di-sulfate. Most acid sulphate soils were formed 6000 to 10000 years ago during the last major sea level rise. When the polar ice melted, new coastal landscapes were formed through rapid sedimentation. Bacteria living in the rich sedimentary mud converted sulfate from tidal waters and iron from organic sediments to form iron disulfate – most commonly pyrite.

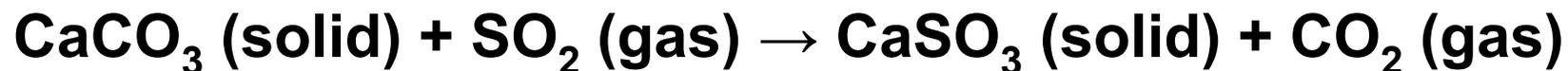


Technical Solutions

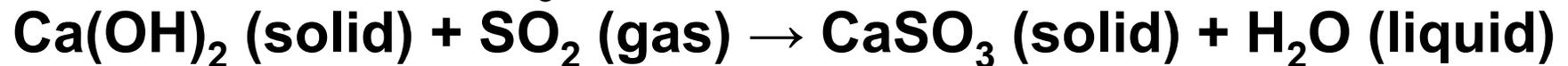
In the United States, many coal-burning power plants use Flue gas desulfurization (FGD) to remove sulphur-containing gases from their stack gases. An example of FGD is the wet scrubber which is commonly used in the U.S. and many other countries. A wet scrubber is basically a reaction tower equipped with a fan that extracts hot smoke stack gases from a power plant into the tower. Lime or limestone in slurry form is also injected into the tower to mix with the stack gases and combine with the sulphur dioxide present. The calcium carbonate of the limestone produces pH-neutral calcium sulfate that is physically removed from the scrubber. That is, the scrubber turns sulfur pollution into industrial sulfates. In some areas the sulfates are sold to chemical companies as gypsum when the purity of calcium sulfate is high. In others, they are placed in landfill.

Scrubbing with base solution

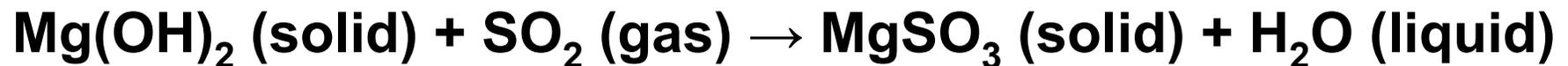
SO₂ is an acid gas and thus the typical sorbent slurries or other materials used to remove the SO₂ from the flue gases are alkaline. The reaction taking place in wet scrubbing using a CaCO₃ (limestone) slurry produces CaSO₃ (calcium sulfite) and can be expressed as:



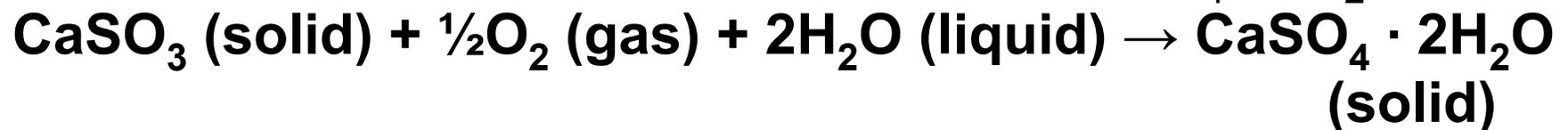
When wet scrubbing with a Ca(OH)₂ (lime) slurry, the reaction also produces CaSO₃ (calcium sulphite):



A similar process is possible with magnesium hydroxide:



Some FGD systems go a step further and oxidize the CaSO₃ (calcium sulphite) to produce marketable CaSO₄ · 2H₂O (gypsum),

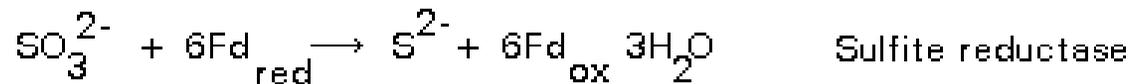
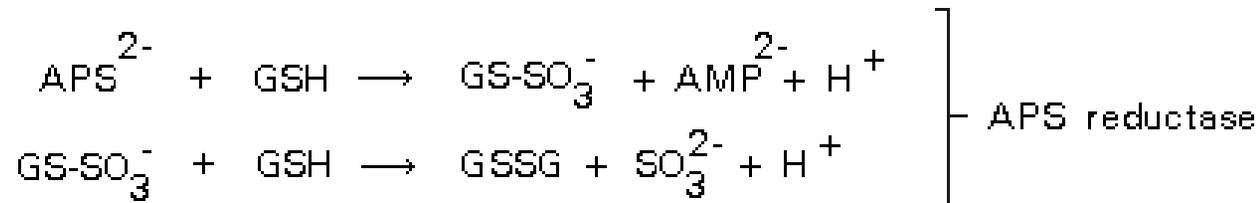
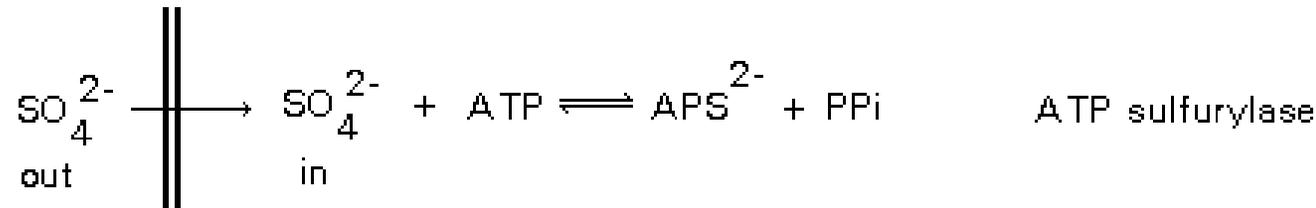




Power plant in New Mexico before installation of flue gas scrubber

Biological Sulfur Pathways

Uptake by Plants



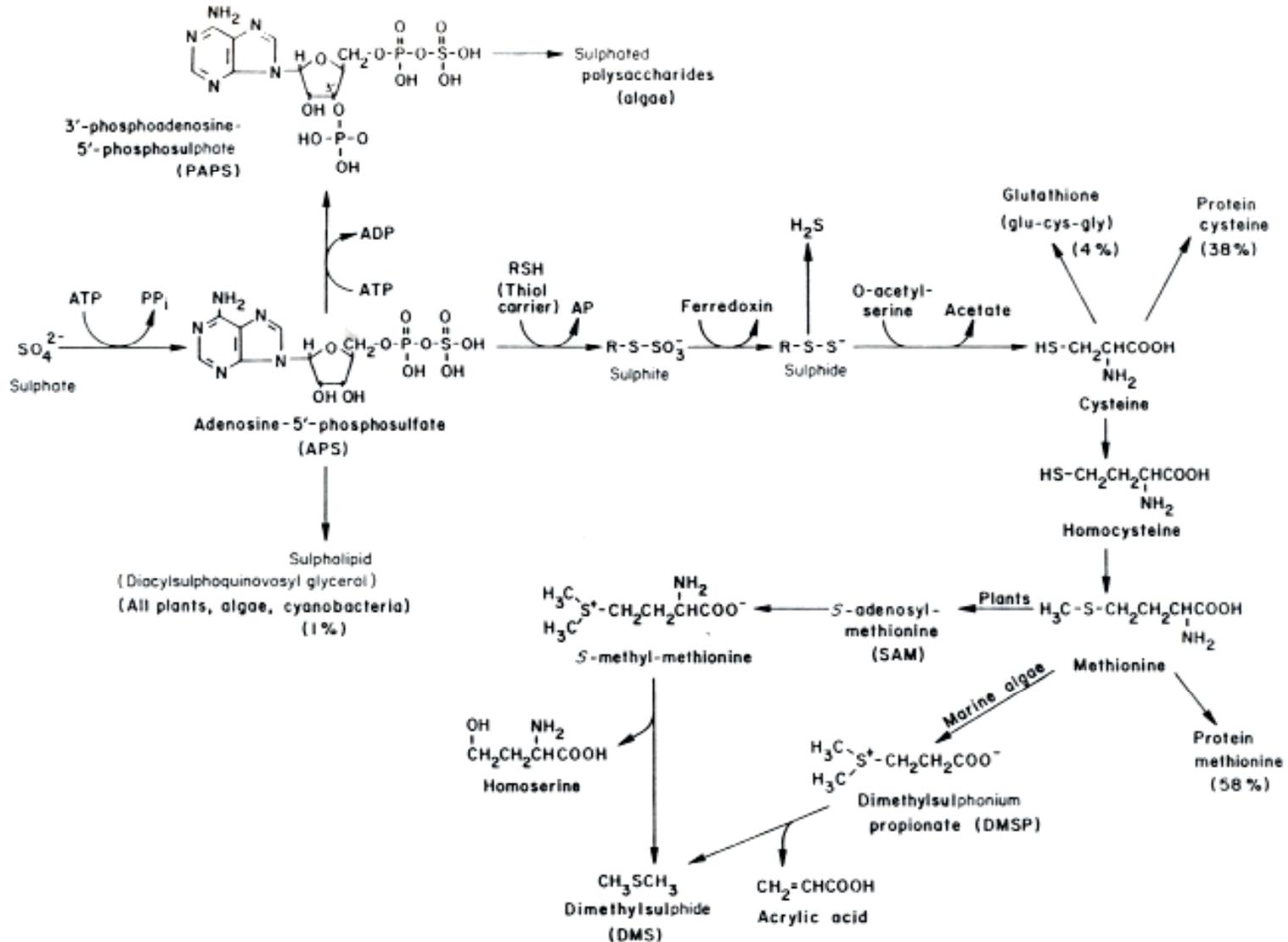
Uptake by Plants

The prevailing evidence is that in plants the sulfate assimilation pathway differs from that in other sulfate assimilating organisms; the main pathway of sulfate reduction in plants appears to be via APS rather than PAPS (i.e. APS can be utilized directly, without activation to PAPS, as an intermediary substrate in reductive sulfate assimilation). Sulfite is formed from APS by the action of a glutathione-dependent APS reductase which possesses APS sulfo-transferase activity.

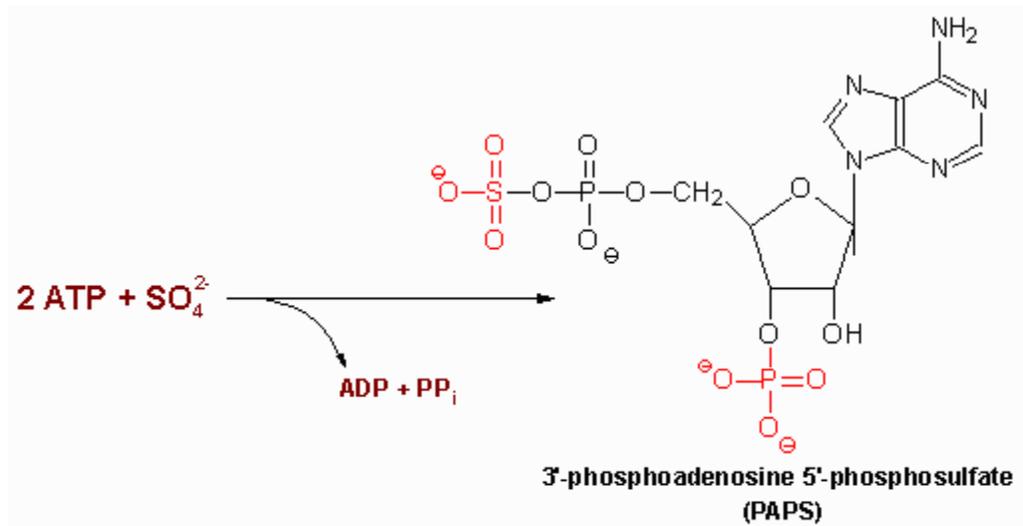
Sulfite generated by the catalytic action of APS reductase is reduced to free sulfide by sulfite reductase [EC 1.8.7.1].

A cDNA termed *sir* has been isolated from *Arabidopsis thaliana* le

Biological sulfur transformations

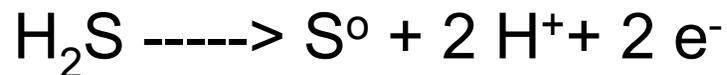


PAPS



Photosynthetic sulfur oxidation

The light-induced oxidation of hydrogen sulfide for harvesting electrons during photosynthesis uses the following process:



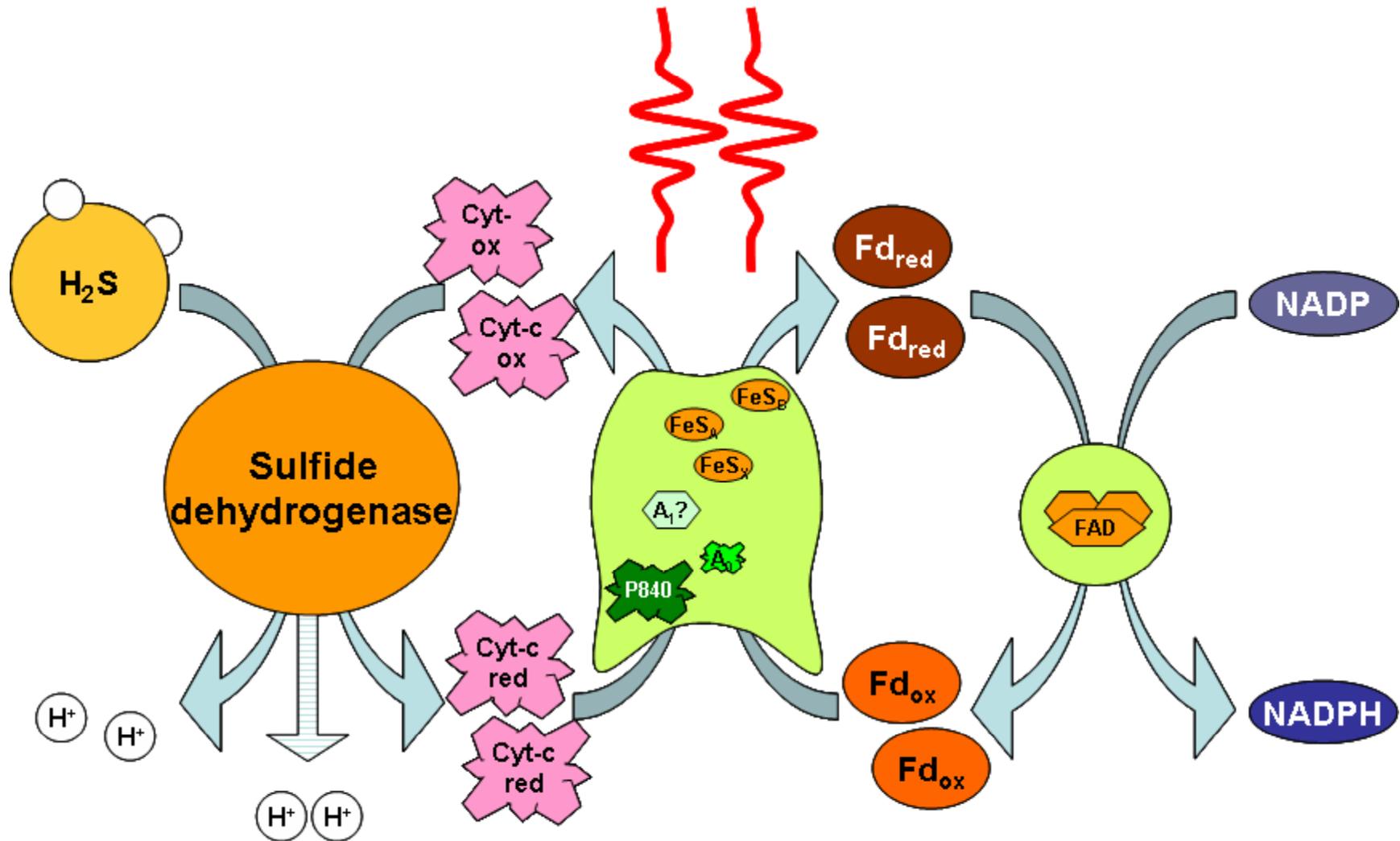
Green and purple sulfur bacteria (photosynthetic).

Must live in the light. Cannot exist deep in the deep oceans.

Environment must contain a source of hydrogen sulfide, usually arising from desulfuration of decaying organic material or from sulfate reduction.

These organisms are often found in waters "one level" above decaying organics or sulfate reducers where they acquire hydrogen sulfide bubbling up from below and are simultaneously illuminated by the sunlight.

Green sulfur bacteria



Green sulfur bacteria

The purple sulfur bacteria chanced upon another way. All cells already c

Chemolithotrophs

Oxidation of hydrogen sulfide generates energy:

a. Hydrogen sulfide can be oxidized to elemental sulfur:



b. Elemental sulfur in turn can be oxidized to sulfate:



Bacteria that oxidize sulfur-containing materials occur in *both* oxic and anoxic environments. Those that live in oxic environments perform the reactions shown above. A different electron acceptor, such as nitrate, is utilized in anoxic environments since the "favorite" acceptor, oxygen, is unavailable. The oxidation of sulfur in oxic habitats produces sulfuric acid ($\text{SO}_4^{2-} + 2 \text{H}^+ = \text{H}_2\text{SO}_4$). Oxic chemolithotrophs must be acidophiles that can tolerate acidic habitats.

Chemolithotrophs

What is the source of hydrogen sulfide?

Desulfuration of decaying organic material

Sulfate reducers

Volcanic activity

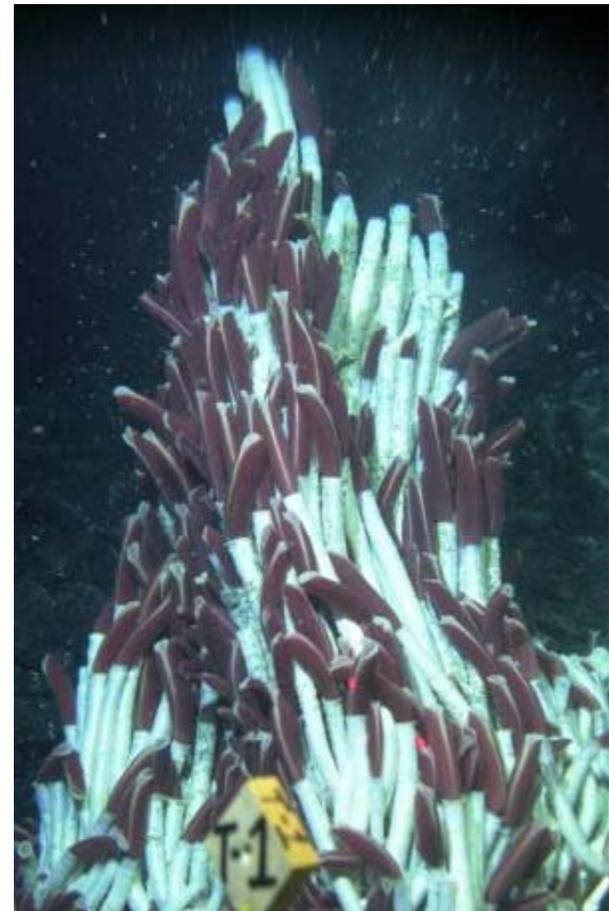
For example, chemolithotrophs near thermal vents in the deep sea harvest the energy from this source. Thus they form the foundation of whole communities in the deep sea where light cannot penetrate.

When is elemental sulfur (S^0) oxidized?

Organisms will oxidize hydrogen sulfide (H_2S) until it runs out and then begin utilizing elemental sulfur. This is logical, since more energy can be acquired from oxidizing hydrogen sulfide compared to elemental sulfur. Use of an alternate substrate requires the expression of genes not previously expressed.

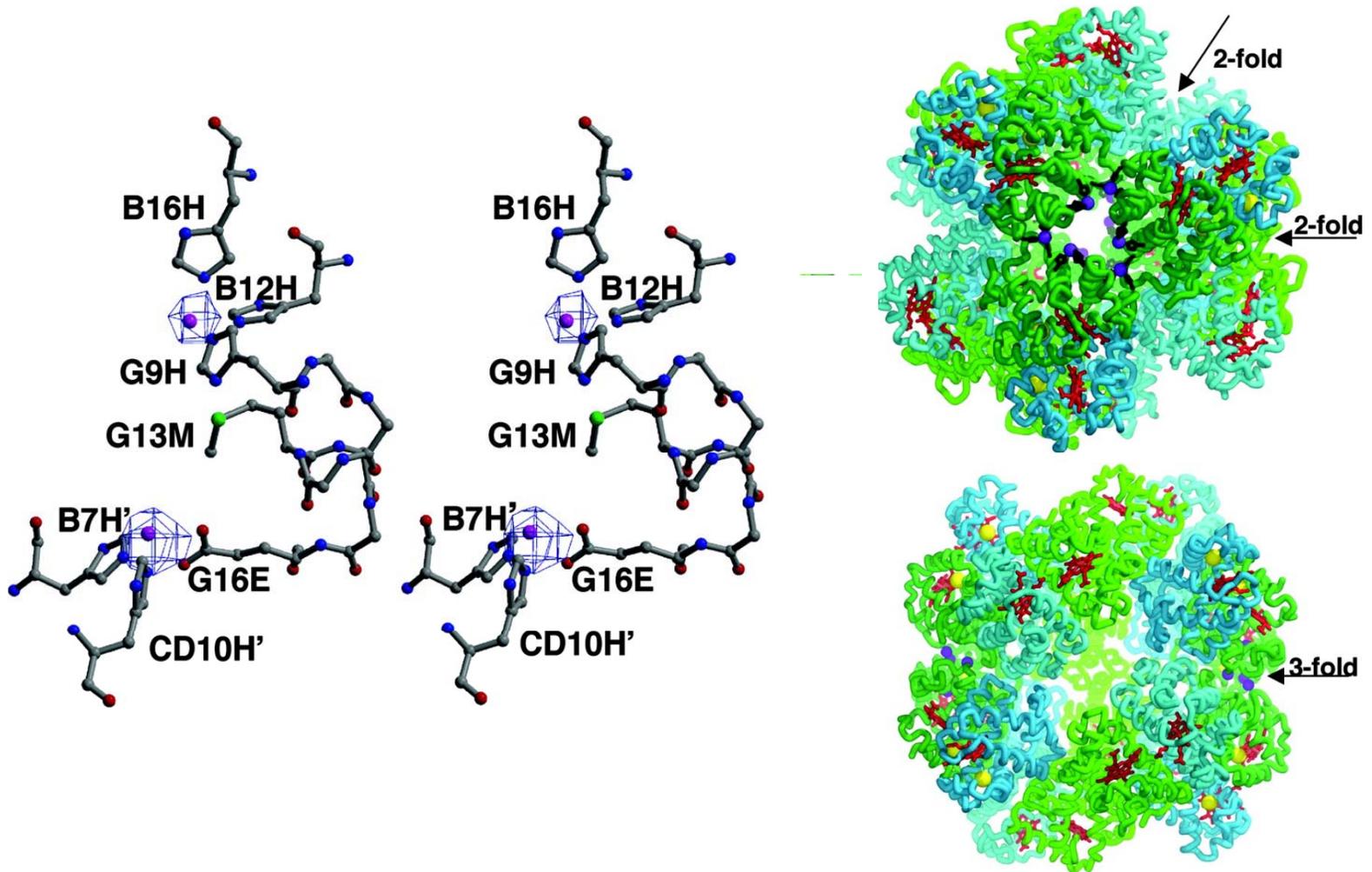
Chemolithotrophic organisms

(iii) The *Thiovulum/Riftia* symbiosis - *Riftia* is a tube worm, ~ 2 meters long, found near thermal vents in the deep sea. *Riftia* contains an organ called a trophosome that harbours *Thiovulum* and several other prokaryotic genera (~ 4×10^9 cells/gram). The worm contains a unique hemoglobin that binds the hydrogen sulfide generated by volcanic activity and delivers it to the bacterial symbiont. Bacterial oxidation of the hydrogen sulfide generates the energy that is required to fix carbon. The worm receives the fixed carbon from the bacteria.



Giant zinc binding hemoglobin

Riftia pachytila C1 Hb structure

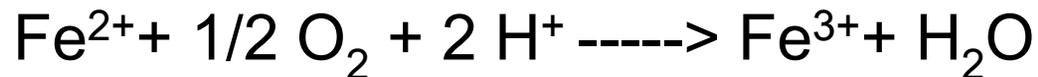


Flores, Jason F. et al. (2005) Proc. Natl. Acad. Sci. USA 102, 2713-2718

Chemolithotrophic organisms

(i) *Beggiatoa* - historically important because it was the first chemolithotroph identified.

(ii) *Thiobacillus* - an obligate acidophile, very tolerant of low pH; in addition to oxidizing hydrogen sulfide, this organism can extract iron from solid pyrite (FeS_2) in a two-step process in which sulfur atoms are oxidized. First, the organism catalyzes the oxidation of ferrous iron, generating ferric iron



Secondly, the ferric iron produced spontaneously reacts with pyrite



Note: The reaction is self-supporting, since the ferrous iron produced in the second reaction can be fed back into the first reaction.

Dissimilative sulfur reduction

Dissimilative sulfate reduction involves using sulfate as a terminal electron acceptor during the energy-generating oxidation of various materials. A specific example of sulfate reduction involves the oxidation of molecular hydrogen (H₂) that occurs in several steps:

1. Sulfate, which is fairly stable, is activated by reaction with ATP, forming adenosine phosphosulfate (APS):



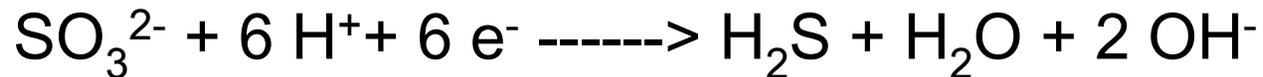
2. A hydrogenase splits molecular hydrogen, and the electrons contained therein are used to reduce the sulfur atom of APS, releasing sulfite (SO₃²⁻).



This reaction involves an intermediate electron carrier, cytochrome c3, that is diagnostic for dissimilative sulfate reducers.

Dissimilative sulfur reduction

3. Using more electrons derived from molecular hydrogen, sulfite is reduced, producing hydrogen sulfide:



Two additional points:

- a. Sulfite is toxic to most organisms, so it is reduced as soon as it is produced, i.e. organisms do not wait until sulfate is exhausted to begin utilizing sulfite. The hydrogen sulfide product is also toxic, but it is a gas that escapes into the atmosphere as it is generated.
- b. The reaction generates hydroxide ions that elevate the pH and thus aid in de-acidification.

Characteristics of dissimilative organisms

The dissimilative sulfate reducers live in anoxic environments. Sulfate reducers occur in aquatic habitats, where sulfate is generally abundant. Some occur in the anoxic layers of soils where a lesser amount of sulfate resides.

The dissimilative sulfate reducers are mostly organotrophs. Because of sulfate's low reduction potential, its reduction generates little energy. In other words, sulfate is a poor electron acceptor. Thus, it is not practical to fix carbon using sulfate reduction as an energy source. As a rule, dissimilative sulfate reducers require a carbon source, commonly acetate.

Note - Some organisms can use a variety of electron acceptors. They exhaust the preferred acceptor first and then switch to the next best acceptor, etc.

Rank of electron acceptors: $O_2 > NO_3^- > SO_4^{2-}$

Sulfite oxidase function

Sulfite oxidase is a biologically important enzyme found in all liv

Sulfite oxidase structure

Sulfite oxidase contains two identical subunits.

The N-terminal domain has a heme cofactor with three adjacent antiparallel beta sheets and five alpha helices.

The C-terminal domain hosts a molybdopterin cofactor that is surrounded by thirteen beta sheets and three alpha helices.

The molybdopterin cofactor has a Mo(VI) center, which

is bonded

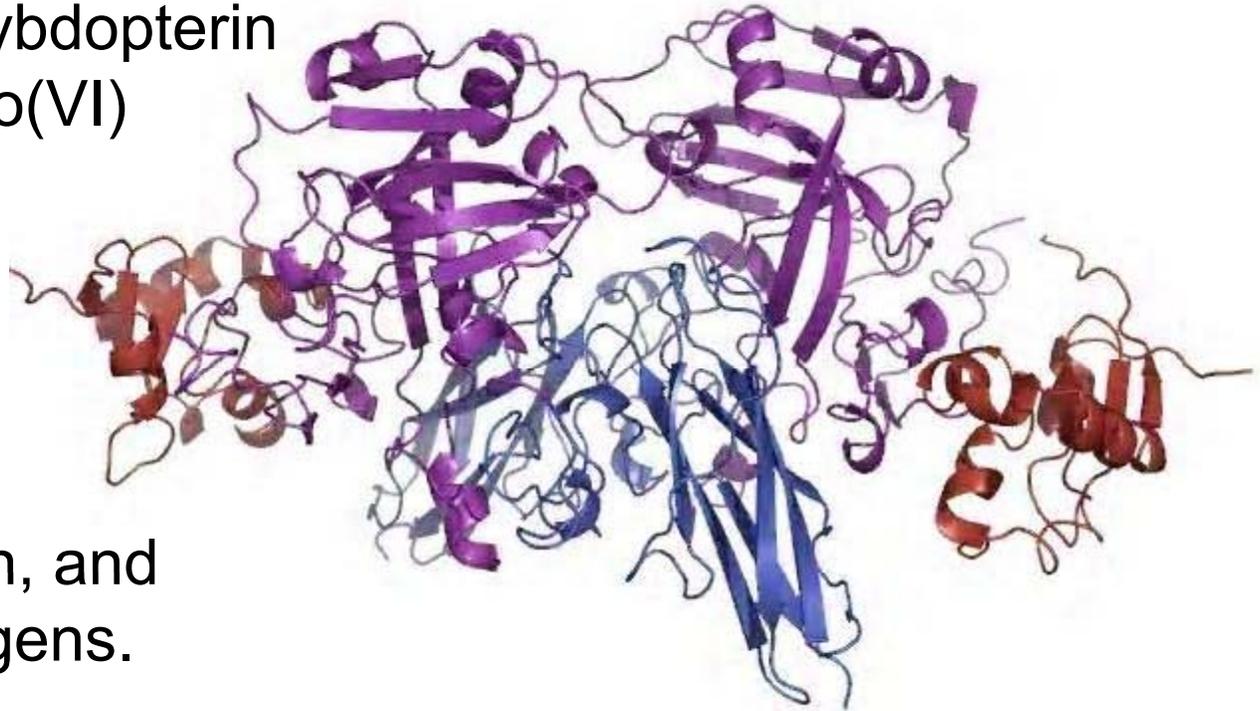
to a sulfur

from cysteine,

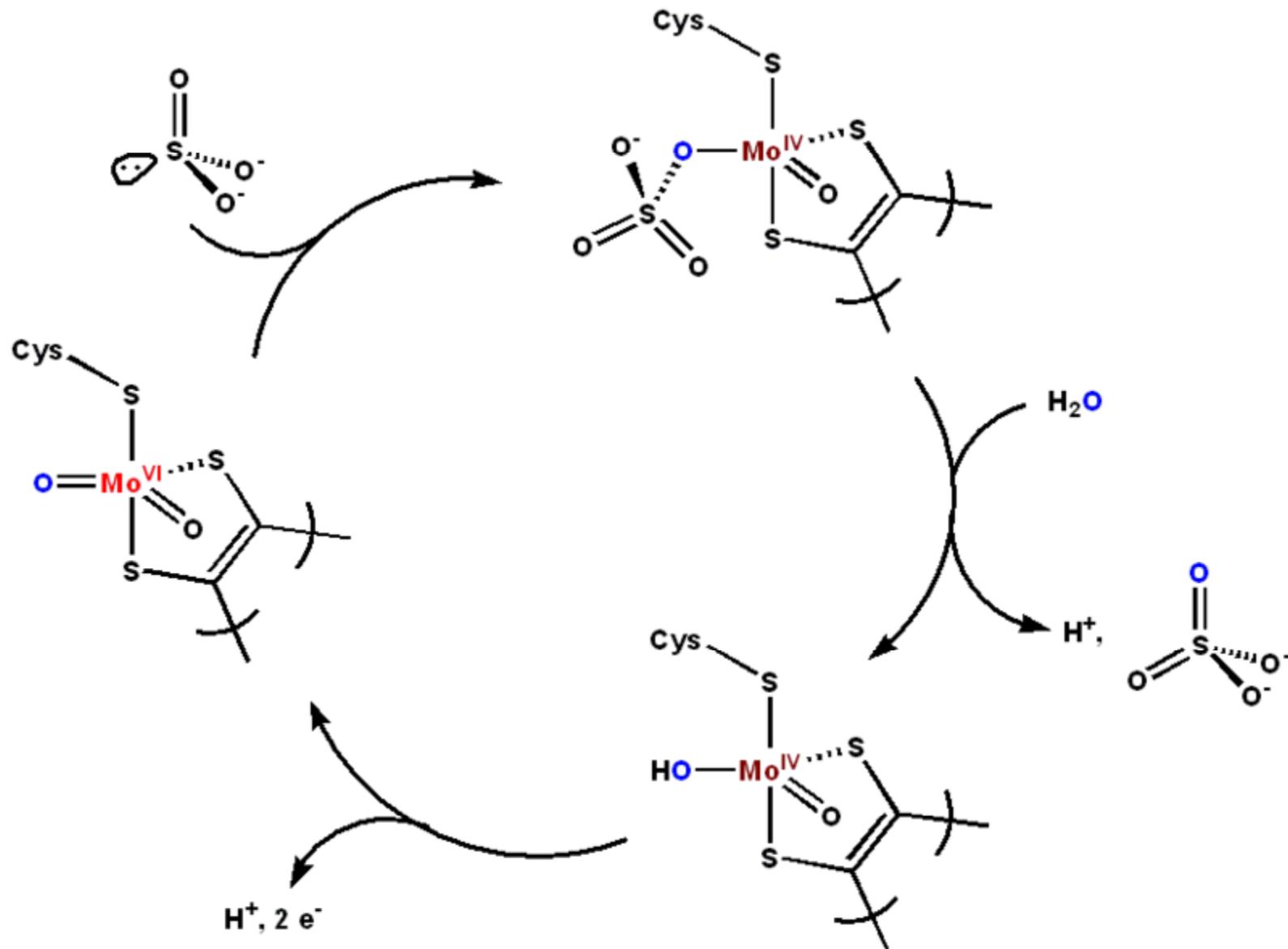
an ene-dithiolate

from pyranopterin, and

two terminal oxygens.



Sulfite oxidase mechanism



Acetoclastic methanogens consume molecular hydrogen and acetate, producing methane. Thus, a competition exists between the dissimilative sulfate reducers and methanogens. In aquatic environments, where sulfate is abundant, the methanogens lose the competition. An additional advantage of the dissimilative sulfate reducers over the methanogens is that the sulfate reducers have a greater affinity for H₂.

Some examples of sulfate reducers and their habitats:

Note that the prefix "*Desulfo*" indicates a sulfate reducer.

(i) *Desulfovibrio* - found in water-logged soils.

(ii) *Desulfotomaculum* - cause of the "sulfide stinker", a type of spoilage of canned foods. This is indicated by swelling of the can as hydrogen sulfide gas is produced and an unpleasant odor on opening the can.

(iii) *Desulfomonas* - found in intestines.

(iv) *Archaeoglobus* - a thermophilic *Archea* whose optimal growth temperature is 83°C.