

SULFUR CYCLE:-

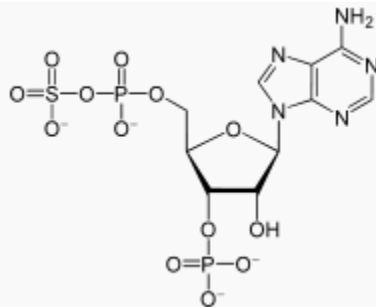
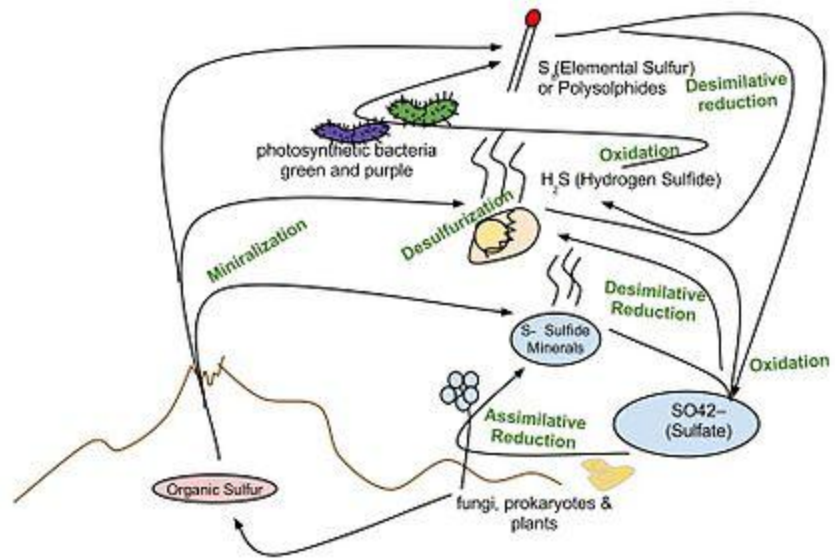
The **sulfur cycle** is the collection of processes by which sulfur moves to and from minerals (including the waterways) and living systems. Such **biogeochemical cycles** are important in **geology** because they affect many minerals. Biogeochemical cycles are also important for life because **sulfur** is an **essential element**, being a constituent of many **proteins** and **cofactors**

The Sulfur cycle (in general)

Sulfur cycle

Steps of the **sulfur cycle** are:

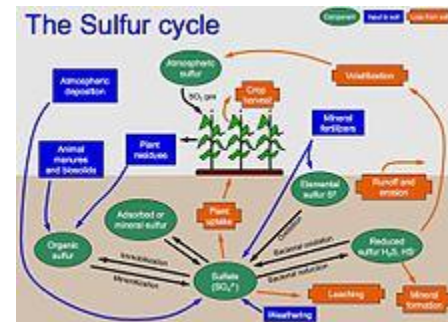
- Mineralization of **organic sulfur** into inorganic forms, such as **hydrogen sulfide** (H_2S), elemental sulfur, as well as **sulfide minerals**.
- Oxidation of **hydrogen sulfide**, **sulfide**, and elemental sulfur (S) to **sulfate** (SO_4^{2-}).
- Reduction of sulfate to sulfide.
- Incorporation of sulfide into organic compounds (including metal-containing derivatives).



Structure of **3'-phosphoadenosine-5'-phosphosulfate**, a key intermediate in the sulfur cycle.

These are often termed as follows:

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



Desulfurization in which organic molecules containing sulfur can be desulfurized, producing hydrogen sulfide gas (H_2S , oxidation state = -2). An analogous process for organic nitrogen compounds is deamination.

Oxidation of hydrogen sulfide produces elemental sulfur (S_8), oxidation state = 0. This reaction occurs in the **photosynthetic green and purple sulfur bacteria** and some **chemolithotrophs**. Often the elemental sulfur is stored as **polysulfides**.

Oxidation of elemental sulfur by sulfur oxidizers produces sulfate.

Dissimilative sulfur reduction in which elemental sulfur can be reduced to hydrogen sulfide.

Dissimilative sulfate reduction in which **sulfate reducers** generate hydrogen sulfide from sulfate.

Sulfur sources and sink

Sulfur is found in **oxidation states** ranging from $+6$ in SO_4^{2-} to -2 in **sulfides**. Thus elemental sulfur can either give or receive electrons depending on its environment. Minerals such as **pyrite** (FeS_2) comprise the original pool of sulfur on earth. Owing to the sulfur cycle, the amount of mobile sulfur has been continuously increasing through **volcanic activity** as well as **weathering** of the **crust** in an oxygenated atmosphere.^[1] Earth's main sulfur sink is the oceans as SO_2 , where it is the major **oxidizing agent**.^[2]

When SO_4^{2-} is assimilated by organisms, it is reduced and converted to organic sulfur, which is an essential component of **proteins**. However, the **biosphere** does not act as a major sink for sulfur, instead the majority of sulfur is found in **seawater** or **sedimentary rocks** especially pyrite rich **shales** and **evaporite rocks** (**anhydrite** and **baryte**). The amount of **sulfate** in the oceans is controlled by three major processes

1. input from rivers
2. sulfate reduction and sulfide reoxidation on continental shelves and slopes
3. burial of anhydrite and pyrite in the oceanic crust.

There is no significant amount of sulfur held in the atmosphere with all of it coming from either sea spray or windblown sulfur rich dust, neither of which is long lived in the atmosphere. In recent times the large annual input of sulfur from the burning of **coal** and other **fossil fuels** adds a substantial amount SO_2 which acts as an **air pollutant**. In the geologic past, **igneous intrusions** into **coal measures** have caused large scale burning of these measures, and consequential release of sulfur to the atmosphere. This has led to substantial disruption to the climate system, and is one of the proposed causes of the **great dying**.

Dimethylsulfide [(CH₃)₂S or DMS] is produced by the decomposition of **dimethylsulfoniopropionate** (DMSP) from dying **phytoplankton** cells in the shallow levels of the ocean, and is the major biogenic gas emitted from the sea, where it is responsible for the distinctive “smell of the sea” along coastlines. DMS is the largest natural source of sulfur gas, but still only has a residence time of about one day in the atmosphere and a majority of it is redeposited in the oceans rather than making it to land. However, it is a significant factor in the climate system, as it is involved in the formation of clouds.

Biologically and thermochemically driven sulfate reduction

Sulfur can be reduced both biologically and thermochemically. Dissimilatory sulfate reduction has two different definitions:

1. the microbial process that converts sulfate to sulfide for energy gain, and
2. a set of forward and reverse pathways that progress from the uptake and release of sulfate by the cell to its conversion to various sulfur intermediates, and ultimately to sulfide which is released from the cell.

Sulfide and thiosulfate are the most abundant reduced inorganic sulfur species in the environments and are converted to sulfate, primarily by bacterial action, in the oxidative half of the sulfur cycle. Bacterial sulfate reduction (BSR) can only occur at temperature from 0 up to 60–80 °C because above that temperature almost all sulfate-reducing microbes can no longer metabolize. Few microbes can form H₂S at higher temperatures but appear to be very rare and do not metabolize in settings where normal bacterial sulfate reduction is occurring. BSR is geologically instantaneous happening on the order of hundreds to thousands of years. Thermochemical sulfate reduction (TSR) occurs at much higher temperatures (160–180 °C) and over longer time intervals, several tens of thousands to a few million years.

Economic importance

Sulfur is intimately involved in production of **fossil fuels** and a majority of metal deposits because of its ability to act as an oxidizing or reducing agent. The vast majority of the major mineral deposits on Earth contain a substantial amount of sulfur including, but not limited to: **sedimentary exhalative deposits**(SEDEX), Mississippi Valley-Type (MVT) and copper porphyry deposits. Iron sulfides, **galena** and **sphalerite** will form as by-products of **hydrogen sulfide** generation, as long as the respective transition or base metals are present or transported to a sulfate reduction site.^[7] If the system runs out of reactive hydrocarbons economically viable elemental sulfur deposits may form. Sulfur also acts as a reducing agent in many natural gas reservoirs and generally ore forming fluids have a close relationship with ancient hydrocarbon seeps or vents

