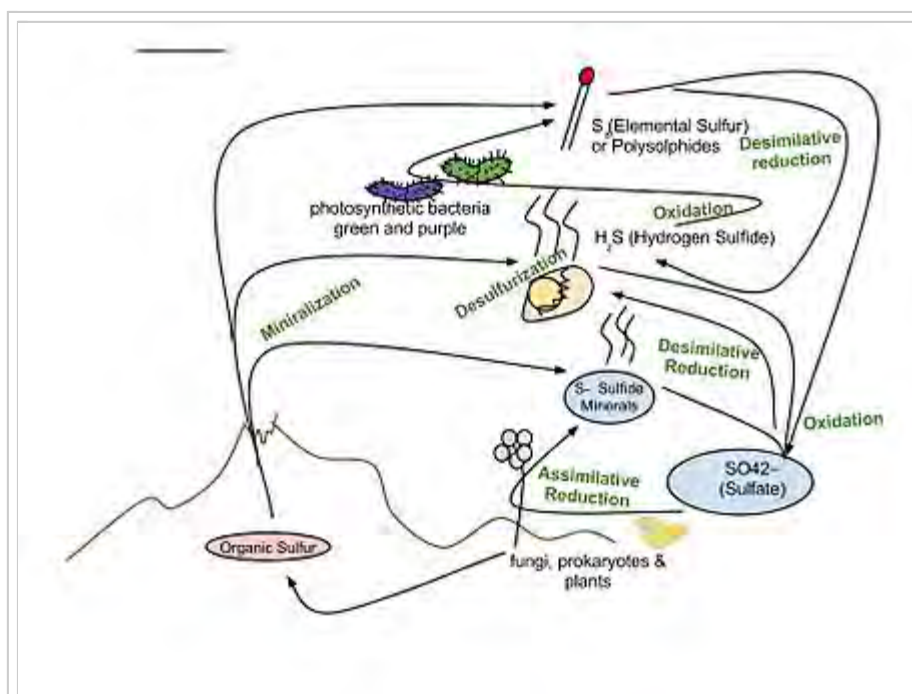# Sulfur cycle

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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. Biochemical cycles are also important for life because sulfur is an essential element, being a constituent of many proteins and cofactors.[1]

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).

The Sulfur cycle (in general)

These are often termed as follows:

Assimilative sulfate reduction (see also sulfur assimilation) 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.
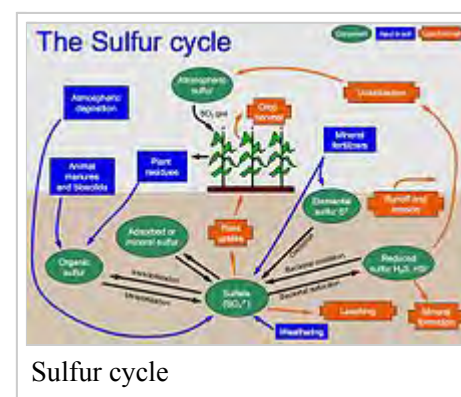
Desulfurization in which organic molecules containing sulfur can be desulfurized, producing hydrogen sulfide gas (H_2S, oxidation state = –2). An analogous process for organic nitrogen compounds is deamination.

Sulfur cycle

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.

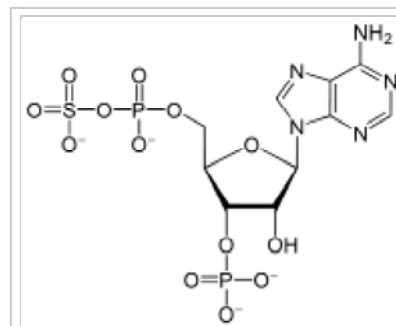*Dissimilative sulfur reduction* in which elemental sulfur can be reduced to hydrogen sulfide.

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

Contents

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

Sulfur sources and sinks

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 SO_4^{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:[3]

1. input from rivers
2. sulfate reduction and sulfide re-oxidation 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,[4] 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 [$(CH_3)_2S$ 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.[1]

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. Dissimilarity sulfate reduction has two different definitions:[5]

> 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.[6] 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 H_2S 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.[7]

The main difference between these two reactions is obvious, one is organically driven and the other is chemically driven. Therefore, the temperature for thermochemical sulfate reduction is much higher due to the activation energy required to reduce sulfate. Bacterial sulfate reductions requires lower temperatures because the sulfur reducing bacteria can only live at relatively low temperature (below 60 °C). BSR also requires a relatively open system; otherwise the bacteria will poison themselves when the sulfate levels rise above 5–10%.

The organic reactants involved in BSR are organic acids which are distinctive from the organic reactants needed for TSR. In both cases sulfate is usually derived from the dissolution of gypsum or taken directly out of the seawater. The factors that control whether BSR or TSR will occur are temperature, which is generally a product of depth, with BSR occurring in shallower levels than TSR. Both can occur within the oil window. Their solid products are similar but can be distinguished from one another petrographically, due to their differing crystal sizes, shapes and reflectivity.[7]

$\delta^{34}S$

Although 25 isotopes are known for sulfur, only four are stable and of geochemical importance. Of those four, two (^{32}S, light and ^{34}S, heavy) comprise (99.22%) of S on Earth. The vast majority (95.02%) of S occurs as ^{32}S with only 4.21% in ^{34}S. The ratio of these two isotopes is fixed in our solar system and has been since its formation. The bulk Earth sulfur isotopic ratio is thought to be the same as the ratio of

22.22 measured from the Canyon Diablo troilite (CDT), a meteorite.[8] That ratio is accepted as the international standard and is therefore set at δ0.00. Deviation from 0.00 is expressed as the $\delta^{34}S$ which is a ratio in per mill (‰). Positive values correlate to increased levels of ^{34}S, whereas negative values correlate with greater ^{32}S in a sample.

Formation of sulfur minerals through non-biogenic processes does not substantially differentiate between the light and heavy isotopes, therefore sulfur values in gypsum or baryte should be the same as the overall ratio in the water column at their time of precipitation. Sulfate reduction through biologic activity strongly differentiates between the two isotopes because of the more rapid enzymic reaction with ^{32}S.[8] Sulfate metabolism results in an isotopic depletion of -18‰, and repeated cycles of oxidation and reduction can result in values up to -50 ‰. Average present day seawater values of $\delta^{34}S$ are on the order of +21‰.

Throughout geologic history the sulfur cycle and the isotopic ratios have coevolved with the biosphere becoming overall more negative with the increases in biologically driven sulfate reduction, but also show substantial positive excursion. In general positive excursions in the sulfur isotopes mean that there is an excess of pyrite deposition rather than oxidation of sulfide minerals exposed on land.[8]

Evolution of the sulfur cycle

The isotopic composition of sedimentary sulfides provides primary information on the evolution of the sulfur cycle.

The total inventory of sulfur compounds on the surface of the Earth (nearly 10^{22} g S) represents the total outgassing of sulfur through geologic time.[8] Rocks analyzed for sulfur content are generally organic-rich shales meaning they are likely controlled by biogenic sulfur reduction. Average seawater curves are generated from evaporites deposited throughout geologic time because again, since they do not discriminate between the heavy and light sulfur isotopes, they should mimic the ocean composition at the time of deposition.

4.6 billion years ago (Ga) the Earth formed and had a theoretical $\delta^{34}S$ value of 0. Since there was no biologic activity on early Earth there would be no isotopic fractionation. All sulfur in the atmosphere would be released during volcanic eruptions. When the oceans condensed on Earth, the atmosphere was essentially swept clean of sulfur gases, owing to their high solubility in water. Throughout the majority of the Archean (4.6–2.5 Ga) most systems appeared to be sulfate-limited. Some small Archean evaporite deposits require that at least locally elevated concentrations (possibly due to local volcanic activity) of sulfate existed in order for them to be supersaturated and precipitate out of solution.[9]

3.8–3.6 Ga marks the beginning of the exposed geologic record because this is the age of the oldest rocks on Earth. Metasedimentary rocks from this time still have an isotopic value of 0 because the biosphere was not developed enough (possibly at all) to fractionate sulfur.[10]

3.5 Ga anoxyogenic photosynthesis is established and provides a weak source of sulfate to the global ocean with sulfate concentrations incredibly low the δ^{34}S is still basically 0.[9] Shortly after, at 3.4 Ga the first evidence for minimal fractionation in evaporitic sulfate in association with magmatically derived sulfides can be seen in the rock record. This fractionation shows possible evidence for anoxygenic phototrophic bacteria.

2.8 Ga marks the first evidence for oxygen production through photosynthesis. This is important because there cannot be sulfur oxidation without oxygen in the atmosphere. This exemplifies the coevolution of the oxygen and sulfur cycles as well as the biosphere.

2.7–2.5 Ga is the age of the oldest sedimentary rocks to have a depleted δ^{34}S which provide the first compelling evidence for sulfate reduction.[9]

2.3 Ga sulfate increases to more than 1 mM; this increase in sulfate is coincident with the "Great Oxygenation Event", when redox conditions on Earth's surface are thought by most workers to have shifted fundamentally from reducing to oxidizing.[11] This shift would have led to an incredible increase in sulfate weathering which would have led to an increase in sulfate in the oceans. The large isotopic fractionations that would likely be associated with bacteria reduction are produced for the first time. Although there was a distinct rise in seawater sulfate at this time it was likely still only less than 5–15% of present-day levels.[11]

At 1.8 Ga, Banded iron formations (BIF) are common sedimentary rocks throughout the Archean and Paleoproterozoic; their disappearance marks a distinct shift in the chemistry of ocean water. BIFs have alternating layers of iron oxides and chert. BIFs only form if the water is be allowed to supersaturate in dissolved iron (Fe^{2+}) meaning there cannot be free oxygen or sulfur in the water column because it would form Fe^{3+} (rust) or pyrite and precipitate out of solution. Following this supersaturation, the water must become oxygenated in order for the ferric rich bands to precipitate it must still be sulfur poor otherwise pyrite would form instead of Fe^{3+}. It has been hypothesized that BIFs formed during to the initial evolution of photosynthetic organisms that had phases of population growth, causing over production of oxygen. Due to this over production they would poison themselves causing a mass die off, which would cut off the source of oxygen and produce a large amount of CO_2 through the decomposition of their bodies, allowing for another bacterial bloom. After 1.8 Ga sulfate concentrations were sufficient to increase rates of sulfate reduction to greater than the delivery flux of iron to the oceans.[9]

Along with the disappearance of BIF, the end of the Paleoproterozoic also marks the first large scale sedimentary exhalative deposits showing a link between mineralization and a likely increase in the amount of sulfate in sea water. In the Paleoproterozoic the sulfate in seawater had increased to an amount greater than in the Archean, but was still lower than present day values.[11] The sulfate levels in the Proterozoic also act as proxies for atmospheric oxygen because sulfate is produced mostly through weathering of the continents in the presence of oxygen. The low levels in the Proterozoic simply imply that levels of atmospheric oxygen fell between the abundances of the Phanerozoic and the deficiencies of the Archean.

750 million years ago (Ma) there is a renewed deposition of BIF which marks a significant change in ocean chemistry. This was likely due to snowball earth episodes where the entire globe including the oceans was covered in a layer of ice cutting off oxygenation.[12] In the late Neoproterozoic high carbon burial rates increased the atmospheric oxygen level to >10% of its present-day value. In the Latest Neoproterozoic another major oxidizing event occurred on Earth's surface that resulted in an oxic deep ocean and possibly allowed for the appearance of multicellular life.[13]

During the last 600 million years, seawater SO_4 has varied between +10 and +30‰ in $\delta^{34}S$, with an average value close to that of today. This coincides with atmospheric O levels reaching something close to modern values around the Precambrian–Cambrian boundary.

Over a shorter time scale (ten million years) changes in the sulfur cycle are easier to observe and can be even better constrained with oxygen isotopes. Oxygen is continually incorporated into the sulfur cycle through sulfate oxidation and then released when that sulfate is reduced once again.[3] Since different sulfate sources within the ocean have distinct oxygen isotopic values it may be possible to use oxygen to trace the sulfur cycle. Biological sulfate reduction preferentially selects lighter oxygen isotopes for the same reason that lighter sulfur isotopes are preferred. By studying oxygen isotopes in ocean sediments over the last 10 million years [14] were able to better constrain the sulfur concentrations in sea water through that same time. They found that the sea level changes due to Pliocene and Pleistocene glacial cycles changed the area of continental shelves which then disrupted the sulfur processing, lowering the concentration of sulfate in the sea water. This was a drastic change as compared to preglacial times before 2 million years ago.

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.[11]

Important sources of sulfur in ore deposits are generally deep-seated, but they can also come from local country rocks, sea water, or marine evaporites. The presence or absence of sulfur is one of the limiting factors on both the concentration of precious metals and its precipitation from solution. pH, temperature and especially redox states determine whether sulfides will precipitate. Most sulfide brines will remain in concentration until they reach reducing conditions, a higher pH or lower temperatures.

Ore fluids are generally linked to metal rich waters that have been heated within a sedimentary basin under the elevated thermal conditions typically in extensional tectonic settings. The redox conditions of the basin lithologies exert an important control on the redox state of the metal-transporting fluids and deposits can form from both oxidizing and reducing fluids.[11] Metal-rich ore fluids tend to be by

necessity comparatively sulfide deficient, so a substantial portion of the sulfide must be supplied from another source at the site of mineralization. Bacterial reduction of seawater sulfate or a euxinic (anoxic and H_2S-containing) water column is a necessary source of that sulfide. When present, the $\delta^{34}S$ values of barite are generally consistent with a seawater sulfate source, suggesting barite formation by reaction between hydrothermal barium and sulfate in ambient seawater.[11]

Once fossil fuels or precious metals are discovered and either burned or milled, the sulfur become a waste product which must be dealt with properly or it can become a pollutant. There has been a great increase in the amount of sulfur in our present day atmosphere because of the burning of fossil fuels. Sulfur acts as a pollutant and an economic resource at the same time.

Human impact

Human activities have a major effect on the global sulfur cycle. The burning of coal, natural gas, and other fossil fuels has greatly increased the amount of S in the atmosphere and ocean and depleted the sedimentary rock sink. Without human impact sulfur would stay tied up in rocks for millions of years until it was uplifted through tectonic events and then released through erosion and weathering processes. Instead it is being drilled, pumped and burned at a steadily increasing rate. Over the most polluted areas there has been a 30-fold increase in sulfate deposition.[15]

Although the sulfur curve shows shifts between net sulfur oxidation and net sulfur reduction in the geologic past, the magnitude of the current human impact is probably unprecedented in the geologic record. Human activities greatly increase the flux of sulfur to the atmosphere, some of which is transported globally. Humans are mining coal and extracting petroleum from the Earth's crust at a rate that mobilizes 150×10^{12} gS/yr, which is more than double the rate of 100 years ago.[16] The result of human impact on these processes is to increase the pool of oxidized sulfur (SO_4) in the global cycle, at the expense of the storage of reduced sulfur in the Earth's crust. Therefore, human activities do not cause a major change in the global pools of S, but they do produce massive changes in the annual flux of S through the atmosphere.[17]

When SO_2 is emitted as an air pollutant, it forms sulfuric acid through reactions with water in the atmosphere. Once the acid is completely dissociated in water the pH can drop to 4.3 or lower causing damage to both man-made and natural systems. According to the EPA, acid rain is a broad term referring to a mixture of wet and dry deposition (deposited material) from the atmosphere containing higher than normal amounts of nitric and sulfuric acids. Distilled water (water without any dissolved constituents), which contains no carbon dioxide, has a neutral pH of 7. Rain naturally has a slightly acidic pH of 5.6, because carbon dioxide and water in the air react together to form carbonic acid, a very weak acid. Around Washington, D.C., however, the average rain pH is between 4.2 and 4.4. Since pH is on a log scale dropping by 1 (the difference between normal rain water and acid rain) has a dramatic effect on the strength of the acid. In the United States, roughly 2/3 of all SO_2 and 1/4 of all NO_3 come from electric power generation that relies on burning fossil fuels, like coal.

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External links

- EPA (http://www.epa.gov/)

- Sulfur Oxidation from Soil Microbiology course at Virginia Tech University (http://filebox.vt.edu/users/chagedor/biol_4684/Cycles/Soxidat.html)
- Sulfur Cycle at Carnegie Mellon University (http://telstar.ote.cmu.edu/environ/m3/s4/cycleSulfur.shtml)
- Lenntech (http://www.lenntech.com/sulphur-cycle.htm)

See also

- Sulfur metabolism
- Microbial metabolism
- Sulfide intrusion

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