

## Oxidation-Reduction Processes in Natural Waters

### A. Introduction

#### General considerations

Chemical and biochemical transformations that result in transfer of electrons are redox reactions. In oxidation-reduction reactions the compound that gives up an electron is oxidized, and the compound that accepts an electron is reduced. Photosynthesis and respiration can be described in these terms. The carbon in carbon dioxide is reduced in photosynthesis when it accepts an electron from water to form carbohydrates.

In fact, the fundamental chemical processes of life can be expressed as redox reactions shown below. Or, stated another way, if there is energy to be extracted from a reaction there an organism has evolved to exploit that energy source.

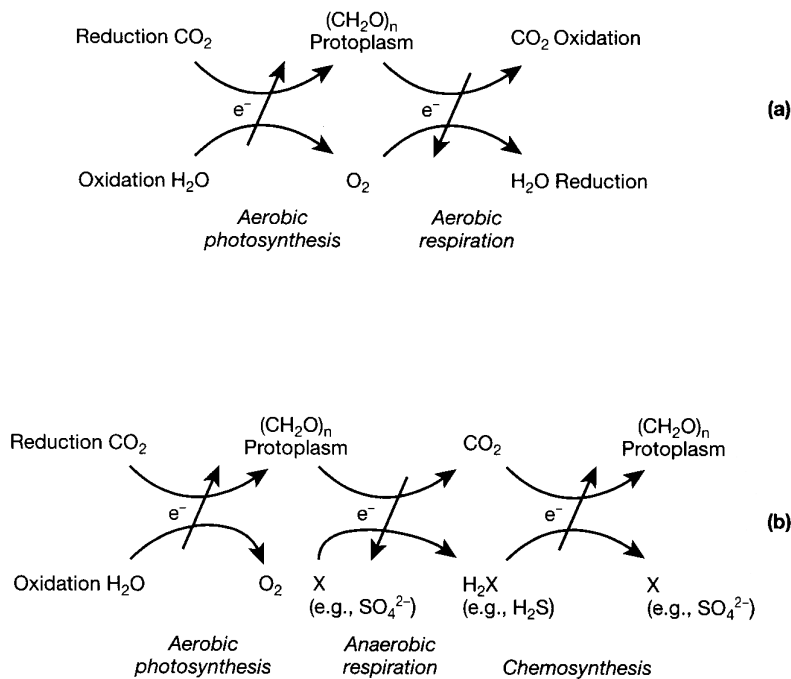
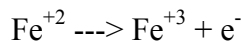


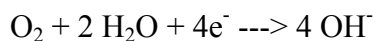
Figure 16-1 Oxidation-reduction reactions, showing (a) photosynthesis-respiration reactions under aerobic conditions; and (b) reactions in oxic and anoxic systems. The transfer of electrons ( $e^-$ ) is indicated by arrows. (Modified after Kortmann and Rich 1994.)

Many chemicals dissolved in water are subject to oxidation or reduction in coupled oxidation-reduction reactions (or in short, redox reactions).

If a chemical undergoes **oxidation**, it **increases in valence and loses electrons**. (Mnemonic: **S**ubstance **O**xidized **I**ncreases in valence and **L**oses electrons, or “SOIL”) For example, dissolved ferrous iron,  $Fe^{+2}$  may be oxidized to ferric iron,  $Fe^{+3}$ :



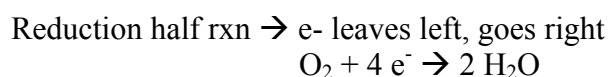
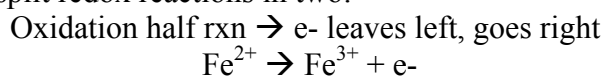
In contrast, a chemical which undergoes **reduction decreases in valence and gains electrons**. For example, oxygen may be reduced:



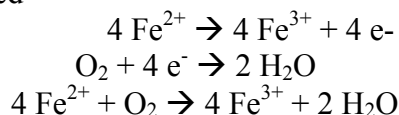
Electrons cannot float around unattached, and redox reactions occurring in natural waters (i.e. without the presence of chemists using platinum electrodes and voltmeters) always occur in linked reactions in which one substance is reduced while another is simultaneously oxidized. Hence, the two examples above are not possible unless combined with each other or with other similar “half reactions”.

For such a redox reaction, the number of electrons involved must be the same for both parts of the paired reaction. Accordingly, the two half reactions given as an example can combine as:

Often split redox reactions in two:



Sum of ox and red



In effect, the electron has been transferred from the iron to the oxygen.

This combined redox reaction is possible if there is a surplus of  $\text{Fe}^{+2}$  and oxygen simultaneously. The iron serves as the *reducing agent*, and is itself oxidized. The oxygen serves as the *oxidizing agent* and is itself reduced.

Redox reactions may produce or consume protons ( $\text{H}^+$ ), and therefore are influenced by the prevailing pH.

The chemical species which are stable in a particular environment depend on the redox potential. Historically, redox potential was usually reported as Eh, in units of volts. Currently, the use of pE ( $\text{pE} = -\log_{10} [\text{e}^-]$ , in analogy to  $\text{pH} = -\log_{10} [\text{H}^+]$ ) has become more popular.

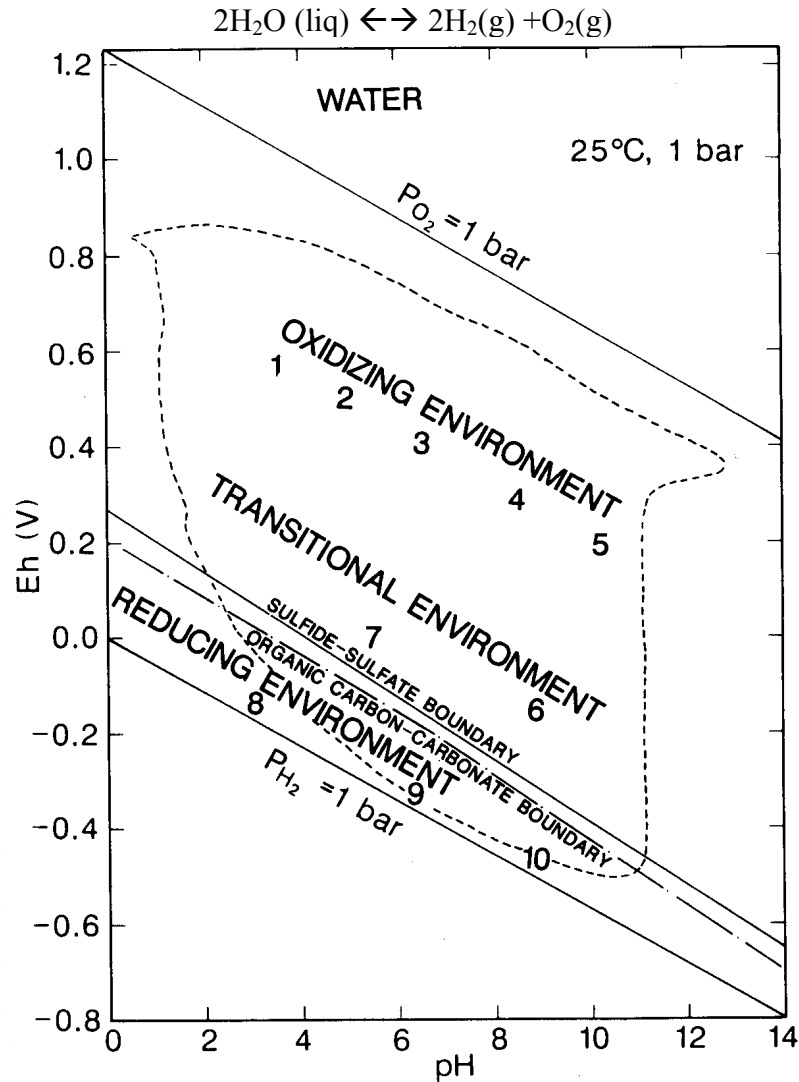
$$\text{pE} = (F/2.3RT)\text{Eh}$$

where: F= Faraday’s constant  
R= gas constant  
T= absolute temperature

Use of pE provides a reasonable analogy for the expected dominant redox species. Just as a low pH in the water would imply that most of the  $\text{C}_T$  would be present in the form of  $\text{H}_2\text{CO}_3^*$ , so too

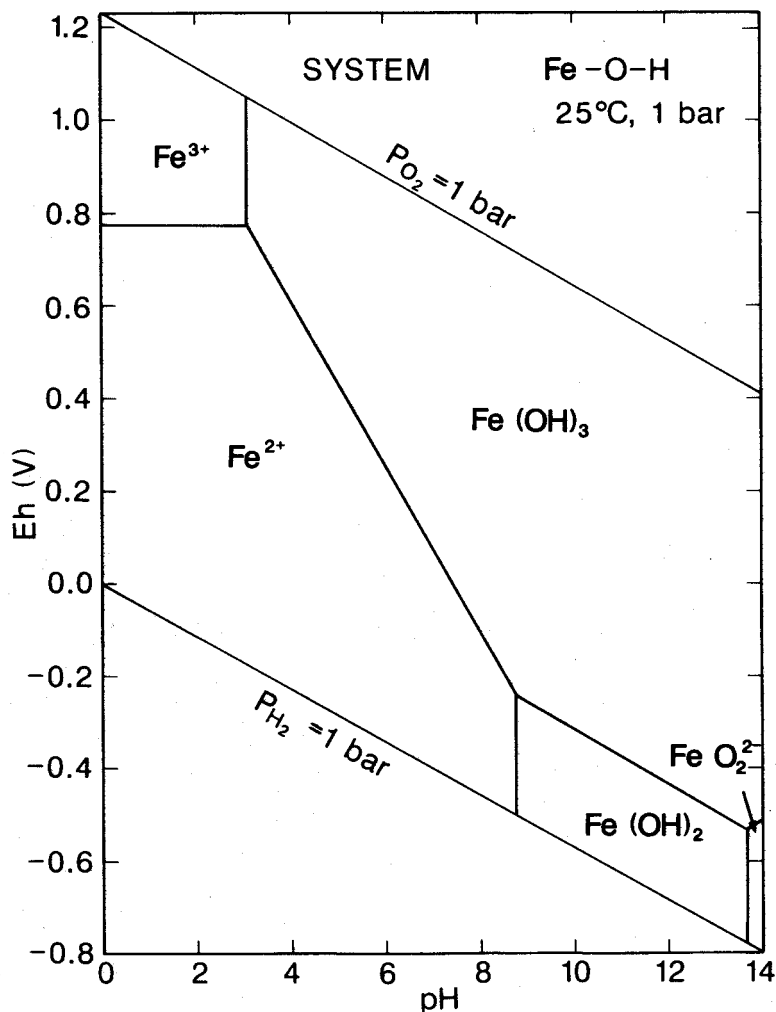
can we anticipate that at low pE (i.e. lots of electrons about),  $\text{Fe}^{+2}$  is a more common form of Fe than is  $\text{Fe}^{+3}$ .

Diagrams of the stable forms of various participants involved in redox reactions can be constructed which simultaneously take pH and pE into account. Below is a general description of the effect of pH and redox on the redox environment. Note that there are stability limits for water, which is also subject to oxidation and reduction under appropriate pE/pH conditions.



**Fig. 1.** Generic Eh-pH diagram for water showing several features. The upper and lower stability limits of water are given where  $P_{\text{O}_2}$  and  $P_{\text{H}_2} = 1$  bar, respectively. The *dotted line* represents the range of natural Eh-pH water measurements reported by Baas Becking et al. (1960). The *solid line* marked sulfide-sulfate boundary separates oxidizing, sulfate-bearing waters above this boundary to reducing, sulfide (as  $\text{HHS}^-$ )-bearing waters below. The *dash-dot* boundary separates organic carbon (boundary) from carbonate species (above boundary). Oxidizing, transitional, and reducing environments are indicated. Specific environments are (*numbers on figure*): 1 mine water; 2 rain; 3 streams; 4 normal ocean water; 5 aerated saline water residues; 6 groundwater; 7 bog waters; 8 water-logged soils; 9 euxenic marine waters; 10 organic-rich, saline water. See text for discussion

An example based on iron is shown below. Note that this is again a log-log plot (c.f. the carbonate system), but the axis are pH (abscissa) and pE (ordinate). The lines represent the boundaries between the regions in which particular redox species of iron are expected to be dominant. Note that at higher redox potential,  $\text{Fe(OH)}_3$  is the stable form, except at very low pH. At lower pH,  $\text{Fe}^{2+}$  is the more stable form, except at higher pH, where  $\text{Fe(OH)}_2$  or  $\text{Fe}_3(\text{OH})_8$  are the more stable form. Because  $\text{Fe(OH)}_3$  precipitates,  $\text{Fe}^{+2}$  is a much more soluble species than is  $\text{Fe}^{+3}$ . It is therefore not surprising that  $\text{Fe}_T$  is higher in anoxic hypolimnia than in oxidized hypolimnia (or in the epilimnion). The upper and lower boundaries in the diagram are the limits of stability of water itself, which is also subject to oxidation or reduction under.



**Fig. 36.** Eh-pH diagram for part of the system Fe-O-H assuming  $\text{Fe(OH)}_3$  as stable Fe(III) phase. Assumed activity of dissolved Fe =  $10^{-6}$ . See text for discussion

SURPLUS ORGANIC MATTER HETEROTROPHIC ORGANISMS	Kcal/mole CH <sub>2</sub> O ΔG	SURPLUS OXYGEN AUTOTROPHIC ORGANISMS	Kcal/mole O <sub>2</sub> ΔG
CH <sub>2</sub> O+O <sub>2</sub> --> CO <sub>2</sub> +H <sub>2</sub> O	-121.89	CO <sub>2</sub> +H <sub>2</sub> O--> CH <sub>2</sub> O+O <sub>2</sub>	+121.89
2CH <sub>2</sub> O+NO <sub>3</sub> <sup>-</sup> +2H <sup>+</sup> --> 2CO <sub>2</sub> +NH <sub>4</sub> <sup>+</sup> +H <sub>2</sub> O	-85.88	NH <sub>4</sub> <sup>+</sup> +2O <sub>2</sub> -->NO <sub>3</sub> <sup>-</sup> +2H <sup>+</sup> +H <sub>2</sub> O	-36.01
CH <sub>2</sub> O+4Fe <sup>+3</sup> +H <sub>2</sub> O-->CO <sub>2</sub> +4Fe <sup>+2</sup> +4H <sup>+</sup>	-75.68	4Fe <sup>+2</sup> +4H <sup>+</sup> +O <sub>2</sub> --> 4Fe <sup>+3</sup> +2H <sub>2</sub> O	-46.21
2CH <sub>2</sub> O+SO <sub>4</sub> <sup>-2</sup> +2H <sup>+</sup> -->2CO <sub>2</sub> +H <sub>2</sub> S+2H <sub>2</sub> O	-32.54	H <sub>2</sub> S+2O <sub>2</sub> --> SO <sub>4</sub> <sup>-2</sup> +2H <sup>+</sup>	-89.35
CH <sub>2</sub> O+CH <sub>2</sub> O --> CO <sub>2</sub> +CH <sub>4</sub>	-19.24	CH <sub>4</sub> +2O <sub>2</sub> --> CO <sub>2</sub> +2H <sub>2</sub> O	-102.65
CH <sub>2</sub> O+H <sub>2</sub> O --> CO <sub>2</sub> +2H <sub>2</sub>	+3.90	2H <sub>2</sub> +O <sub>2</sub> -->2H <sub>2</sub> O	-125.79

**Organisms catalyze all significant redox reaction in natural waters.** As illustrated in the table, with the exception of photosynthesis and hydrogen generation, all of the reactions in the table are thermodynamically favorable as written. That is, the reactions as written have a negative free energy. (If light energy were included in photosynthesis, it too would of course be favorable as written. Also, hydrogen generation does occur under extremely reducing conditions because the concentrations of the reactants greatly exceed the concentration of products. As written in the table, the reactants and products are assumed to be present in equal concentration.)

In spite of the reactions being favored as written, they do not occur to any appreciable extent in the absence of organisms because of **slow kinetics**. (An exception is the oxidation of Fe<sup>+2</sup> to Fe<sup>+3</sup>, which will occur spontaneously by chemical means alone.) Because of the combination of slow chemical kinetics and favorable thermodynamic conditions, opportunistic microbes catalyze all the important redox reactions as a means of obtaining metabolic energy.

The table includes most of the significant redox reactions in natural waters. **Other redox reactions might be added.** For example, manganese follows a redox cycle very similar to iron. Many other trace metals might also be included in the table as well. However, the table includes the most important redox processes, and other reactions follow the same general pattern.

Note that the reactions are written in **idealized form** to draw attention to the overall pattern of the redox processes. Actual reactions will differ somewhat: for example, the reduced carbon compounds subject to anaerobic respiration using oxidized species of iron, nitrogen, or sulfur, includes many fatty acids, proteins, carbohydrates, etc. and not just the simple organic compound (CH<sub>2</sub>O) included in the table. In the discussion of the redox cycle of each of the elements which follows, some of the alternative compounds are included to illustrate the diversity of actual compounds involved. The advantage of using the idealized reactions is that they better reveal the overall pattern and therefor give a better understanding of the general nature of redox processes in natural water.

As indicated in the table, the important redox processes are based on:

**surplus organic matter** being oxidized by oxidized species of iron, nitrogen, sulfur, or by organic carbon itself in methane fermentation (the left-hand column of reactions), or

the presence of **reduced species** of iron, nitrogen, sulfur or methane being oxidized by **oxygen** (the right-hand column of reactions).

The two types of reactions *do not occur in the same place* or under the same redox conditions, but may very well occur at different depths in the same stratified lake. For example, it is likely that nitrate ( $\text{NO}_3^-$ ) might be reduced in the hypolimnion of a lake with a clinograde oxygen curve, producing ammonia ( $\text{NH}_4\text{OH}$ ). Should the ammonia subsequently be transported to the epilimnion ( $\text{O}_2$  present), the ammonia will be oxidized back to nitrate. In general, the first type of reaction (left hand column) will take place under more reducing conditions, and the second type (right hand column) will occur under more oxidizing conditions and in the presence of oxygen.

The reactions occur as a **hierarchy**: in general, nitrate and ferric iron will be reduced before any reduction of sulfate occurs. Similarly, sulfate reduction will proceed to nearly total consumption of sulfate before methane fermentation occurs.

The pH/pE circumstances under which each of the reactions may be expected to occur can be anticipated based on the hierarchy of reactions.

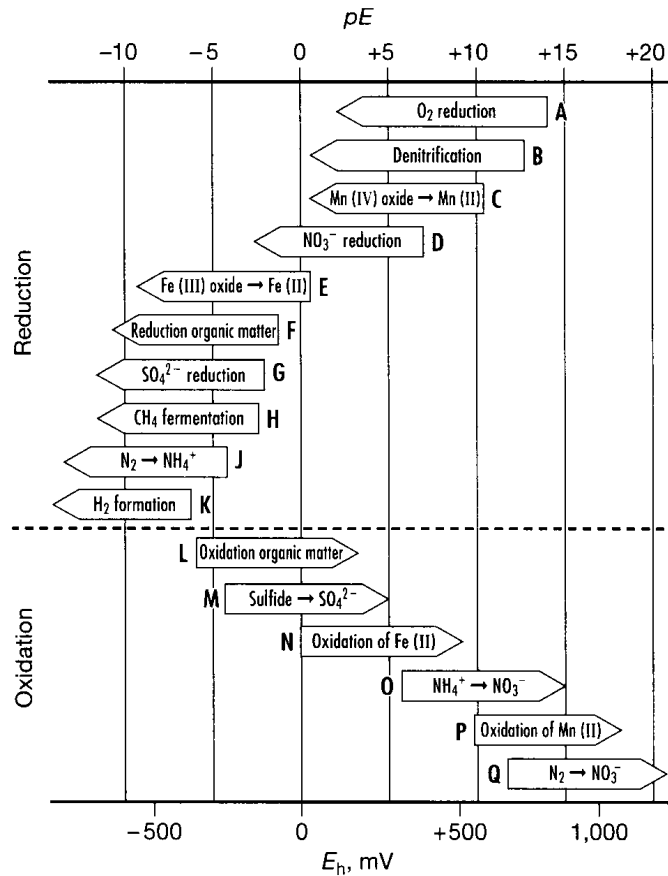


Figure 16-2 Biologically mediated redox processes (calculated for pH = 7) in the oxidation of organic matter (A-K, and L), nitrogen fixation (J and L), and the oxidation of reduced elements in the presence of oxygen (M-Q), which yields energy for the reduction of  $\text{CO}_2$  in chemosynthetic processes. Overlapping  $E_h$  or  $pE$  ranges indicate that several redox systems operate at the same time. (After Stumm and Baccini 1978.)

## **Assimilatory vs. dissimilatory metabolism.:**

**assimilatory metabolism:** Organisms assimilate many elements to serve as structural components of growth. For example, organisms may assimilate  $\text{SO}_4^{-2}$  and use it to fashion methionine for protein.

**dissimilatory metabolism:** Certain organisms can utilize inorganic chemicals as oxidizing or reducing agents to fuel their energy needs. For example, in the presence of oxygen, *Thiobacillus* will assimilate  $\text{S}^{-2}$ , oxidize it to  $\text{SO}_4^{-2}$  while capturing the energy released, and then release the  $\text{SO}_4^{-2}$ . Hence, the process is said to be dissimilatory sulfur metabolism.

Some other nomenclature of interest.

Microbiologists categorize microbes according to their source of energy and their source of carbon.

**lithotrophs or chemolithotrophs:** organisms that use inorganic chemicals as energy sources.

**chemoautotrophs:** organisms which use  $\text{CO}_2$  as a source of carbon, and inorganic chemicals such as  $\text{H}_2\text{S}$  as energy sources.

**photoautotrophs:** organisms which use  $\text{CO}_2$  as a source of carbon and light as a source of energy.

**photoheterotrophs:** organisms which obtain at least some energy from light and use organic carbon compounds as a source of carbon.

**heterotrophs or chemoheterotrophs:** organisms which use organic compounds as their source of energy and carbon.

## **The carbon cycle**

**Photosynthesis by photoautotrophs is the ultimate origin of nearly all of the organic carbon and energy available in natural ecosystems.** This is true even if there are chemoautotrophic bacteria present which grow by oxidizing inorganic chemicals (such as  $\text{H}_2\text{S}$ ) and assimilating inorganic C as a carbon source. Such organisms are said to be autotrophs, but do not contribute any new energy to the food chain since the inorganic chemicals they depend on owe their presence to the anaerobic respiration of organic matter produced by photosynthesis. (A possible exception could be geothermal sources of reduced sulfur or other elements.)

In oxygenated water, the organic compounds created by photoautotrophs are oxidized by the autotrophs themselves or the heterotrophs which eat them, using  $\text{O}_2$  as an oxidizing agent to release energy for their metabolism (aerobic respiration).

If no oxygen is available, as might be expected in the hypolimnion of a eutrophic lake or the monimolimnion of a meromictic lake, other inorganic species such as  $\text{NO}_3^{-1}$  or  $\text{SO}_4^{-2}$  will serve as oxidizing agents, or “electron acceptors” (anaerobic respiration). If oxygen is the oxidizing

agent, the process is said to be **aerobic respiration**. If an oxidizing agent other than oxygen is used, the process is said to be **anaerobic respiration**.

### **Photosynthesis and respiration.**

Without the availability of light energy, photosynthesis as written would be a very unfavorable reaction (see table). Ultimately, the energy available in natural ecosystems stems from solar energy captured by photosynthesis. The table is constructed based on the production of organic matter, "CH<sub>2</sub>O", by photosynthesis, followed by the oxidation of the organic matter by respiration (aerobic based on O<sub>2</sub> as oxidizing agent) or anaerobic (based on NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>-</sup>, etc. as oxidizing agent). Aerobic respiration is expected in oxygenated water, but respiration will shift to anaerobic respiration deeper in the water column or in the sediment if oxygen is lacking.

### **The nitrogen cycle.**

Assimilation: NH<sub>4</sub> preferred over NO<sub>3</sub>

Nitrification: (aerobic) ammonia is oxidized to nitrite and then nitrate

Denitrification: (anaerobic or anoxic) nitrate is reduced to nitrogen gas, which is lost to the atmosphere

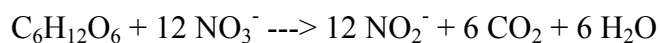
Ammonification: Organic N → NH<sub>4</sub><sup>+</sup>

Fixation: N<sub>2</sub> fixed into NH<sub>4</sub> by bacteria (Azobacter, Clostridium) and cyanobacteria (Nostoc, Anabaena, Gleotrichia, Aphanizomenon). N-fixation can be a major source of N in lakes. N-fixation increases when NO<sub>3</sub> and NH<sub>4</sub> are depleted. The ability of some species to fix N has important consequences for phytoplankton succession.

Nitrogen reduction.

In the absence of O<sub>2</sub>, NO<sub>3</sub><sup>-</sup> will serve as oxidizing agent (see table). In this case, the process is described as anaerobic respiration because it is based on nitrate as oxidizing agent rather than oxygen as oxidizing agent. Most of the organisms capable of using nitrate as the oxidizing agent can also use oxygen, and hence are described as **facultative anaerobes**.

Organic matter is not all CH<sub>2</sub>O by any means, but anaerobic respiration can be illustrated by:

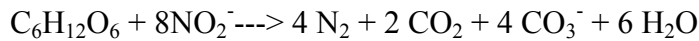


The overall nature of the reaction is the same for other organic compounds, and the actual pathways and chemical species involved are more diverse than implied by the table. Organisms capable of anaerobic respiration using nitrate as electron acceptor include *Pseudomonas*, *Achromobacter*, *Escherichia*, *Bacillus* and other genera.

There are two special cases of nitrogen reduction which are commonly singled out for special treatment: **denitrification** and **nitrogen fixation**.



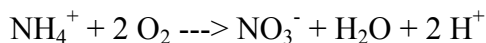
**Denitrification** leads to the loss of fixed nitrogen from an ecosystem as  $N_2$  under anaerobic conditions. The reaction may be illustrated as:



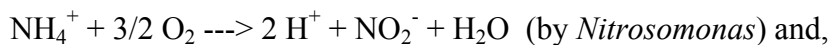
In contrast, **nitrogen fixation** is the conversion of atmospheric nitrogen to fixed nitrogen (usually in the form of ammonia). A select group of organisms may use  $N_2$  as a source of nitrogen for *assimilatory* nitrogen requirements. The best known organisms capable of fixing atmospheric nitrogen are symbiotic prokaryotes living in association with particular higher plants such as legumes, alders, and Scotch broom. Some free-living aquatic bacteria (**Azotobacter**, **Clostridium**, etc.) also fix  $N_2$ . In aquatic ecosystems, most nitrogen fixation is carried out by bluegreen "algae", or more properly, cyanophytes. In contrast to the other reactions discussed here, nitrogen fixation requires the **input of energy**, and is usually coupled indirectly to photosynthesis.

### Nitrogen oxidation processes.

In the presence of oxygen, several microorganisms are capable of acquiring metabolic energy by the dissimilatory oxidation of ammonia and other reduced species of nitrogen. The overall process, which converts ammonia to nitrate, is called **nitrification**. The overall reaction may be illustrated by (see table):



However, the reaction actually proceeds in two distinct steps catalyzed in each case by a particular genus of bacteria.



Because these organisms obtain their energy from the oxidation of inorganic compounds (ammonia and nitrite), they are called "**chemoautotrophs**" or "**chemolithotrophs**". They are described as "autotrophs" because they use inorganic  $CO_2$  as a source of carbon. However, with the possible exception of geothermal sources, nitrifiers do not capture any new energy for the ecosystem. *Rather they are simply part of an alternate pathway by which the organic matter originally produced by photosynthesis is eventually respired.* Note in particular that the sum of energy released by anaerobic respiration based on nitrate reduction plus the energy released by the subsequent nitrification of the ammonia is exactly equal to the energy released by aerobic respiration. At the same time, the *net chemical reaction* is also the same. That is, the consumption and production of  $NO_3^-$  and  $NH_4^+$  cancel when the two processes are summed.

The potential impact of nitrification on oxygen concentration is obvious: **nitrification consumes oxygen**. Therefore, ammonium discharges into a river or stream can lead to anoxic conditions if nitrification is intense.

Where would you expect to find  $NH_4$  in a lake?

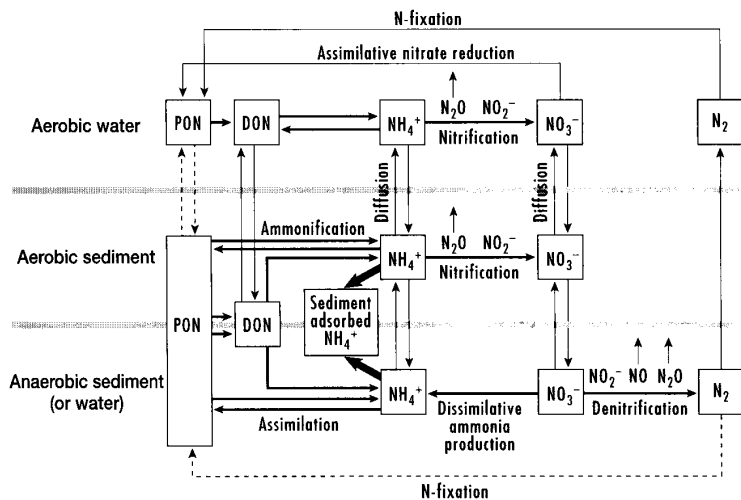


Figure 18-2 Nitrogen transformations near the sediment-water interface. Not shown are inputs from the land and atmosphere or stream outflows. Minor pathways are also not shown. (Modified from Kamp-Nielsen and Anderson 1977.)

Representative profiles on inorganic N in a stratified lake

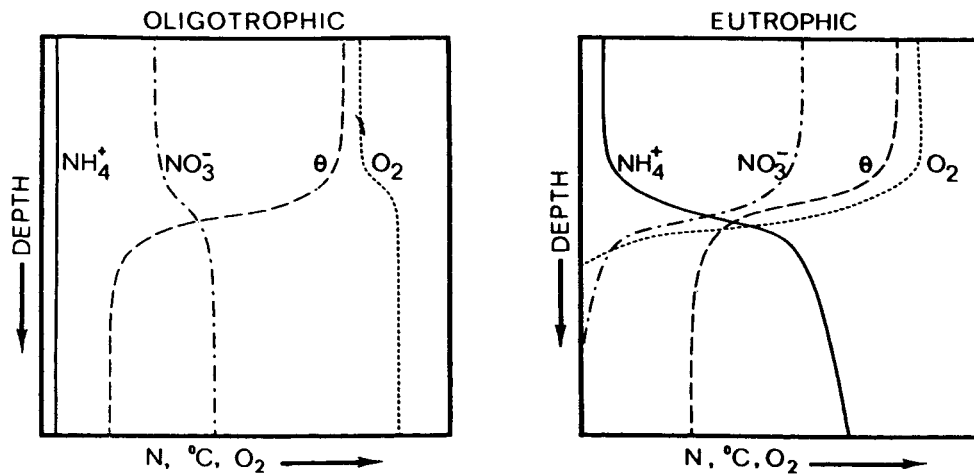


FIGURE 12-4 Generalized vertical distribution of ammonia and nitrate nitrogen in stratified lakes of very low and high productivity.

### Pool concentrations

Nitrate: ranges from trace concentrations when plant assimilation is high to 1 mg/L during periods of minimal assimilation

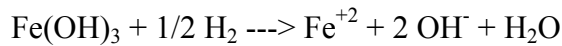
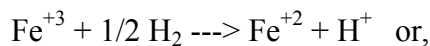
Nitrite: only trace amounts common

Ammonia: reduced form preferred by plants, abundant in oxygenated water only in polluted and highly productive systems, abundant in hypolimnion of eutrophic lakes. Present primarily as  $\text{NH}_4^+$  (ammonium ion) and  $\text{NH}_4\text{OH}$ .  $\text{NH}_4\text{OH}$  is toxic to fish.  $\text{NH}_4\text{OH}$  increases in abundance with pH and temperature. Ammonia toxicity is possible to fish at high pH and temperature.

### The iron cycle.

Iron reduction. [See the diagram above for the iron cycle.]

Iron reduction has not been discussed as much as iron oxidation. A number of organisms use ferric iron as an electron acceptor. Many of these organisms also reduce nitrate, and since they are facultative anaerobes, they can also use O<sub>2</sub>. The following reactions have been suggested:



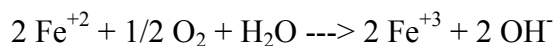
Organisms capable of catalyzing this reaction belong to *Micrococcus*, *Bacillus*, or *Desulfovibrio*.

The reduction of iron at the sediment water interface allows the **release of phosphorus** from the sediment and may accordingly have a strong influence on lake fertility. This is because oxidized iron, Fe<sup>+3</sup>, precipitates as Fe(OH)<sub>3</sub> and related compounds which readily adsorb PO<sub>4</sub><sup>-3</sup>. Several species of Fe/P minerals, such as FePO<sub>4</sub>, may also precipitate. In effect, the presence of Fe<sup>+3</sup> will lower the availability of PO<sub>4</sub><sup>-3</sup>. In particular, a surface layer of oxidized sediment, which inevitably contains Fe<sup>+3</sup>, will serve as a barrier for the recycling of sediment bound P.

As might be expected, if iron is reduced to the more soluble Fe<sup>+2</sup>, sediment P can be more effectively recycled to the overlying water column. If a lake becomes sufficiently eutrophic that it develops a clinograde oxygen curve, it may become "self-fertilizing" because of the recycling of sediment bound P.

### Iron oxidation

Iron oxidation can be expected where the water contains both reduced iron and oxygen. The reaction may be represented as:

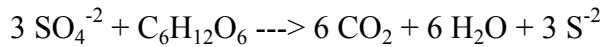


Several organisms are capable of oxidizing reduced iron and generating energy in the process. Sample genera are: *Leptothrix*, *Gallionella*, *Ferrobacillus ferrooxidans*. These organisms appear only where there are steep gradients of oxygen and ferrous iron. A "plate" of precipitated ferric hydroxide [Fe(OH)<sub>3</sub>] is likely to develop at the interface between the iron and oxygen gradients. The organisms must compete with the abiotic oxidation of iron because the purely chemical oxidation of ferrous iron occurs relatively rapidly. Because very little energy is generated in the oxidation of ferrous to ferric iron, these bacteria must oxidize large amounts of iron in order to grow.

### The Sulfur cycle

Sulfur reduction reactions.

There are two genera of bacteria that are said to carry out dissimilatory sulfate reduction, in that they reduce sulfate in connection with the production of energy. [This is in contrast to assimilatory sulfate reduction, which is very widespread, among organisms which assimilate sulfate as a source of sulfur for biosynthesis.] Sulfate reduction may be represented as:



The organisms capable of catalyzing this reaction and extracting energy belong to *Desulfovibrio* and *Desulfotomaculum*. In effect, these organisms utilize sulfate as a terminal electron acceptor in the oxidation of organic matter. This is an example of anaerobic respiration. In contrast with the iron and nitrate reducers, however, **sulfate reducers are obligate anaerobes.**

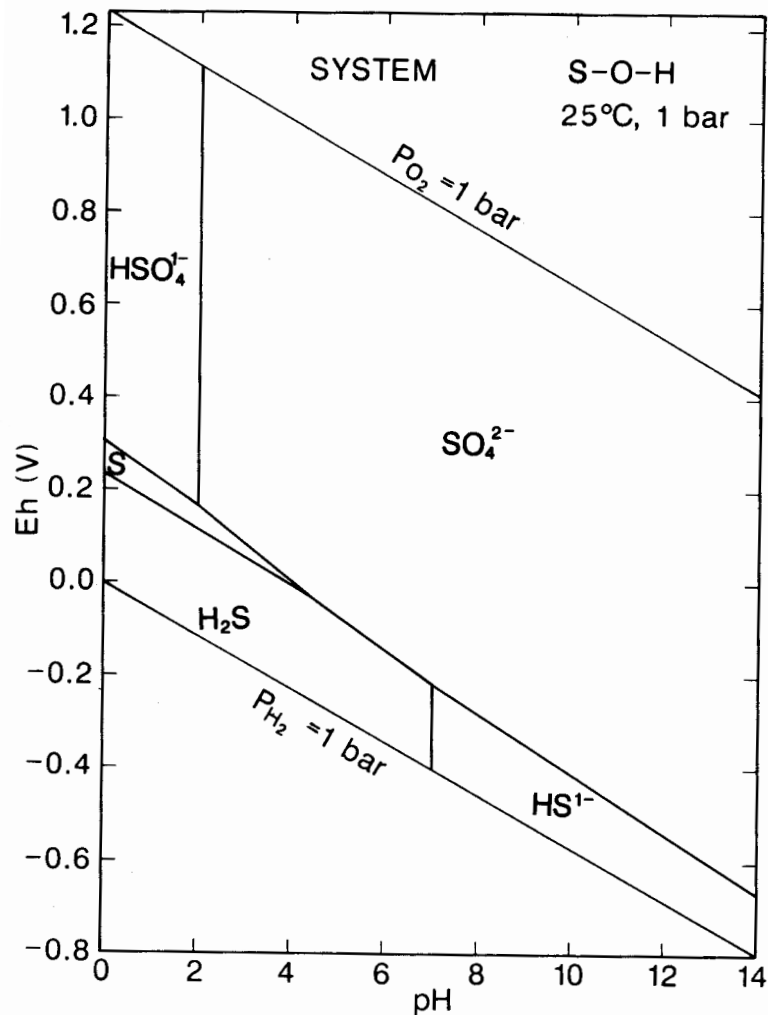
Accordingly, they are found only in anoxic sediment and anoxic water. The sulfide ( $\text{S}^{2-}$ ) produced may precipitate metal sulfides and give sediment a characteristic black color (and bad smell if disturbed!). Because of the abundance of  $\text{SO}_4^{2-}$  in seawater, marine sediments and isolated basins may produce large amounts of  $\text{H}_2\text{S}$  (e.g. the Black Sea).

"A number of economically important mineral deposits have been formed as a result of bacterial sulfate reduction. Biogenic sulfide mineral deposits are characteristically found in thin layers (stratiform) in association with other sedimentary rocks (e.g. shales)." Brock, p439.

Much of the S contained in oil and coal probably originated with the same process after the original organic matter was buried. As can be seen in the table, sulfate reduction produces alkalinity (i.e. consumes  $\text{H}^+$ ). It should not be surprising then that when the oil or coal are later oxidized at the surface, whether by acid mine drainage or by burning, this "acid debt" will reappear.

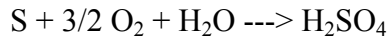
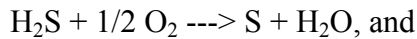
### Sulfur oxidation

There are two distinct groups which oxidize reduced sulfur: the colorless oxidizing bacteria (thiobacilli) and photosynthetic (green and purple) sulfur bacteria.

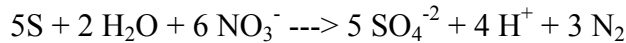


## Colorless bacteria

The oxidation of sulfur by colorless bacteria may be represented by:

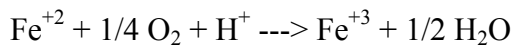
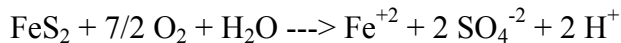


Organisms which catalyze these reactions include *Beggiatoa*, *Thiothrix*, *Thiobacillus thiooxidans*, and *Thiobacillus thioparus*. Of particular interest is the anaerobic oxidation of sulfur by *Thiobacillus denitrificans*:



Note the link of nitrate reduction, in place of oxygen as electron donor.

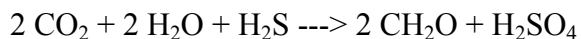
Several thiobacilli (most famous is *Thiobacillus thiooxidans*) can oxidize pyrite, causing acid mine drainage.



An important result of these reactions is the production of  $\text{H}^+$ . (In effect, the oxidation of the reduced S contained in oil and coal and other old buried organic matter returns the acid consumed by sulfate reduction at the time of burial.) Such waters can become quite acid (pH < 1.0). Because some species are very tolerant of acid conditions and others are tolerant of alkaline conditions, the group as a whole is very widespread in terms of its pE-pH characteristics.

## Photosynthetic bacteria

There are two groups of organisms which oxidize  $\text{H}_2\text{S}$  photosynthetically: the green sulfur bacteria (Chlorobacteriaceae, e.g. *Chlorobium*) and the purple sulfur bacteria (Thiorhodaceae, e.g. *Chromatium*). Some of these organisms also oxidize other reduced sulfur species. Sample reaction:

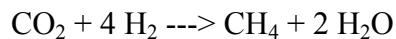
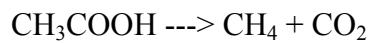


An important distinction between these photosynthetic bacteria and the thiobacteria is their **source of energy**. The photosynthetic sulfur bacteria require light as an energy source. The photosynthetic bacteria use light as an energy source and  $\text{H}_2\text{S}$  as an electron source in the photosynthetic reduction of  $\text{CO}_2$ . They are therefore considered to be photolithotrophs along with green plants. In contrast to other photosynthetic organisms, the photosynthetic sulfur bacteria are strict anaerobes. Accordingly, they can be expected to occur only where  $\text{O}_2$  is absent, and light and  $\text{H}_2\text{S}$  are present. Examples might be: in the metalimnion of a hypereutrophic lake or the chemocline of a meromictic lake.

## Methane

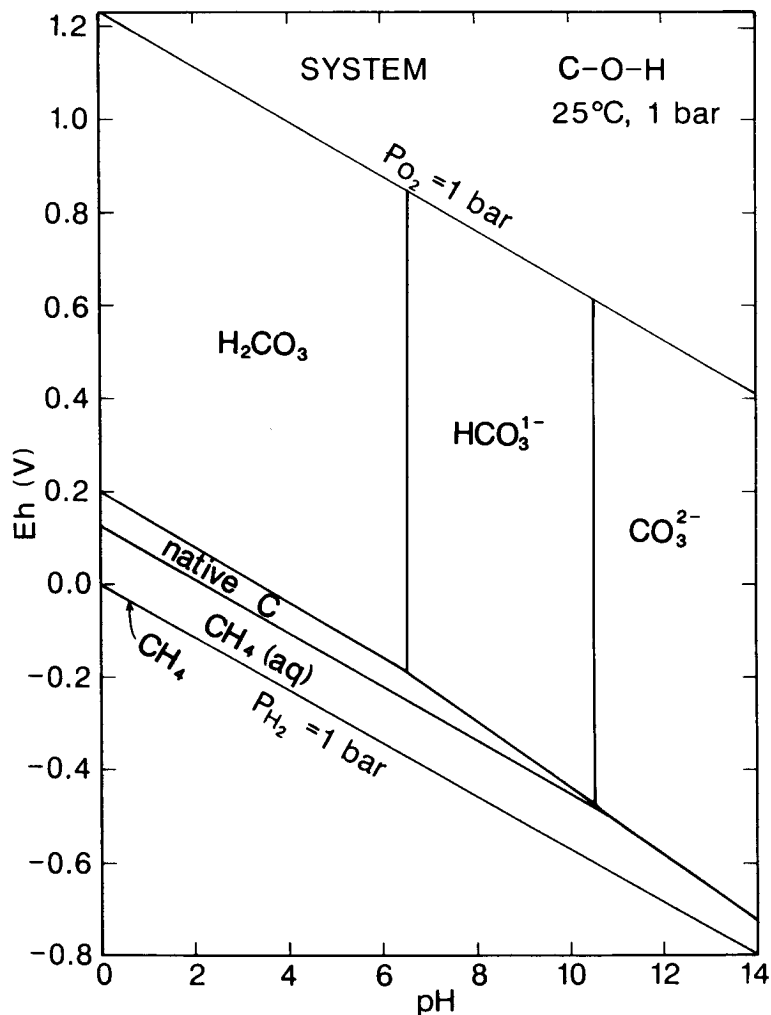
Methanogenesis.

CO<sub>2</sub> is used by a small group of bacteria as their final electron acceptor, the reduction product being methane. These are the "methane bacteria" or methanogens. All species are strict anaerobes and have proven difficult to study. The substrates used by the methanogens include: fatty acids, alcohols, and H<sub>2</sub>. Sample reactions are:



These reactions, and other similar reactions, are carried out by species of *Methanobacterium*, *Methanobacillus*, *Methanococcus*, and *Methanosarcina*. It might be argued that these organisms straddle the definition of respiration vs. fermentation. In the second reaction above, CO<sub>2</sub> is serving as electron acceptor, and this is, by definition, a case of respiration, whereas for the first reaction, it might be proper to label the reaction fermentation.

Brock (p422)... "Methane formation occurs during the decomposition of such diverse substrates as cellulose, starch and sugars, proteins and amino acids, fats and fatty acids, alcohols, benzoic acid and a variety of other substrates. ...methane formation from these materials requires the participation of other anaerobic bacteria. These other bacteria then ferment the substances to either acetate or hydrogen and CO<sub>2</sub>, which are then used by the methanogenic bacteria. Thus,



**Fig. 13.** Eh-pH diagram for part of the system C-O-H. The assumed activity of dissolved C = 10<sup>-3</sup>. See text for discussion

*methanogenesis from organic carbon is virtually always a process carried out by a mixture of bacteria, none of which can perform the complete process by itself...the methanogenic bacteria are generally limited by the availability of H<sub>2</sub>. As soon as any H<sub>2</sub> is formed by a fermentative microorganism, it is quickly consumed by a methanogen. The only situation in which H<sub>2</sub> ever accumulates in nature are when methanogenesis is inhibited in some way." ..."sulfate, a major anion in seawater, strongly inhibits methanogenesis. The sulfate-reducing bacteria also use H<sub>2</sub> as a major electron donor. ... Only after sulfate is depleted...can methanogenesis proliferate."*

## Methane oxidation

Certain bacteria can oxidize methane in the presence of oxygen. For example:



Some organisms which can oxidize methane are *Methanomonas methanica* and *Methanomonas methanooxidans*. As expected, these organisms are abundant where there is a supply of both methane and oxygen. In some cases, (Rudd and Hamilton, 1975, Arch. Hydrobiol.) these organisms do not tolerate more than 1 ppm O<sub>2</sub> ("microaerophils") and accordingly are confined to a thin layer in the thermocline of a eutrophic lake.

## Unusual conditions.

The redox environment can be very different in unusual circumstances. For example, in the presence of acid mine drainage, conditions can be very reducing and very acidic (lower left of the figure). In the monimolimnion of a meromictic lake, redox potential can be very low. Sediments rich in organic matter are also commonly very reducing. Ground water is also often very reducing, as is sometimes evident from the brown stains that develop in a house served by well water (because the Fe<sup>+2</sup> is oxidized to insoluble Fe<sup>+3</sup> upon contact with the air.)

## Glossary:

assimilatory sulfate reduction	the reduction of sulfate in the process of acquiring S required for biosynthesis.
autotroph	an organism which is able to use CO <sub>2</sub> as a sole carbon source for growth.
chemoheterotrophs heterotrophs	organisms which obtain energy and carbon from reduced carbon compounds.
chemolithotrophs chemoautotrophs	organisms which use inorganic compounds as both electron donors (e.g. NH <sub>3</sub> ) and electron acceptors (e.g. O <sub>2</sub> ) to generate metabolic energy.
denitrification	the conversion of fixed nitrogen (e.g. NO <sub>3</sub> <sup>-</sup> ) to nitrogen gas (N <sub>2</sub> ).
dissimilatory sulfate reduction production of	the reduction of sulfate in connection with the energy.
facultative anaerobes	organisms which can use either oxygen (O <sub>2</sub> ) or some other inorganic compound (NO <sub>3</sub> <sup>-</sup> ) as a terminal electron acceptor.
fermentation	a metabolic process in which organic compounds serve as both electron acceptors and electron donors in the generation of energy.
nitrification	the oxidation of reduced nitrogen, NH <sub>3</sub> and NO <sub>2</sub> <sup>-</sup> , to nitrate, NO <sub>3</sub> <sup>-</sup> .
nitrogen fixation	the use of N <sub>2</sub> to meet nutritional requirements for nitrogen.
photolithotrophs photoautotrophs	organisms which derive energy from light and use inorganic compounds as electron donors.
respiration, aerobic	the process of producing metabolic energy from the oxidation of organic compounds using oxygen (O <sub>2</sub> ) as the terminal electron acceptor.
respiration, anaerobic	the process of producing metabolic energy from the oxidation of organic compounds using an inorganic compound (e.g. NO <sub>3</sub> <sup>-</sup> or SO <sub>4</sub> <sup>-2</sup> ) other than oxygen as the terminal electron acceptor.
strict or obligate anaerobes	organisms which cannot tolerate the presence of oxygen (O <sub>2</sub> ) and obtain energy and carbon from reduced carbon



compounds using an inorganic compound other than oxygen as the terminal electron acceptor.

### Groups of chemoautotrophs

Group	oxidizable substrate	oxidized product	terminal electron acceptor
nitrifying bacteria	NH <sub>3</sub> NO <sub>2</sub> <sup>-</sup>	NO <sub>2</sub> <sup>-</sup> NO <sub>3</sub> <sup>-</sup>	O <sub>2</sub> O <sub>2</sub>
sulfur oxidizers	H <sub>2</sub> S, S <sup>0</sup> , S <sub>2</sub> O <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>-2</sup>	O <sub>2</sub> , sometimes NO <sub>3</sub> <sup>-</sup>
iron bacteria	Fe+2	Fe+3	O <sub>2</sub>
hydrogen bacteria	H <sub>2</sub>	H <sub>2</sub> O	O <sub>2</sub> , sometimes SO <sub>4</sub> <sup>-2</sup> or NO <sub>3</sub> <sup>-</sup>