

being produced by photosynthesis. At greater depth the respiration processes of the marine organisms as well as of decomposition dominate and oxygen levels fall. Eventually, at depths between 500 m and 1000 m, oxygen minima develop. The oxygen levels at these minima may be so low that the water is described as **anoxic**. At even greater depths the oxygen levels rise again due to deep, cold ocean currents bringing in dense oxygenated water from the polar seas. Figure 30.18 shows a typical oxygen profile with depth.

In summary, we can see that the concentration of gases in the oceans is lower than their concentration in the atmosphere. In the oceans the concentration of gases is measured in parts per million (Table 30.2). The proportion of carbon dioxide in sea water, however, is much higher than the proportion of oxygen or nitrogen due to chemical, physical and biological effects as previously discussed.

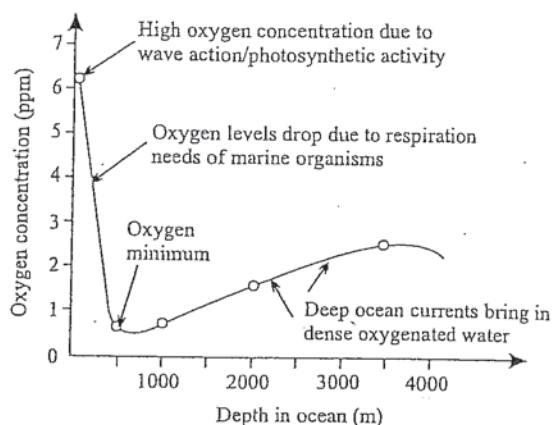


Figure 30.18 Oxygen concentration with depth

Table 30.2 Comparison of gas concentrations in the atmosphere (troposphere) and the oceans

Gas	% v/v in troposphere	Relative % in sea water	Concentration range in sea water (ppm)
Nitrogen	78	48	10–18
Oxygen	21	36	1–13
Carbon dioxide	0.036*	15	60–110

* value rising due to the combustion of fossil fuels

Corrosion of the *Titanic*

The physical and chemical environment on ocean floors is highly variable. Ships that sink in deep oceans come to rest in a dark saline world of low temperatures and low oxygen concentrations. From our knowledge of reaction kinetics, we would predict that the rate of metal corrosion would be quite slow under such conditions. The pH of sea water (pH ~8) should also slow the corrosion process of steel. Thus, steel ships like the *Titanic*, which came to rest in the deep frigid waters of the north Atlantic in April 1912, would be expected to exhibit very little rusting.

On 1 September 1985 the wreck of the *Titanic* was discovered in 3700 m of water. The ship had broken into two main sections with a debris field between the two. In 1986 video cameras showed that despite the frigid, low oxygen conditions the steel components had rusted to produce long flows and strands of rust ('rusticles'). Chemically, the cores of these rusticles consist of iron(III) oxide hydroxide ($\text{FeO}(\text{OH})$).

Anaerobic bacterial corrosion

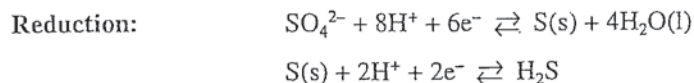
Not all species of bacteria rely on oxygen to obtain energy from organic nutrients by cellular respiration. Examination of the rusticles from the *Titanic* wreck showed that they were produced by the activity of anaerobic bacteria. Sulfate-reducing bacteria, such as *Sporovibrio desulfuricans*, are present in both terrestrial and marine environments and obtain their energy via oxidation–reduction reactions involving the reduction of sulfate ions to hydrogen sulfide. In waterlogged clay soils these

bacteria are responsible for the corrosion of steel pipes. In sea water up to 60% of the corrosion of steel pipes can be attributed to sulfate-reducing bacteria. Pipes that are covered with concretions will continue to rust due to the activities of these anaerobic microbes.

Sulfate-reducing bacteria are active in salt water due to the abundance of sulfate ions. Sulfate ions represent 7.7% by weight of total solutes. Many artefacts from the *Titanic* wreck were often stained black due to the activity of the anaerobic bacteria on the steel and other metal objects. These black stains were metallic sulfides produced by the reaction of cations with hydrogen sulfide produced by the reduction of the sulfate ions.

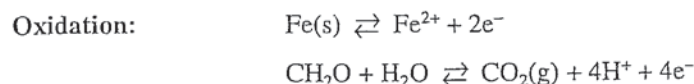
Apart from the sulfate-reducing bacteria, other types of bacteria are present and contribute to the corrosion of a wreck. Slime-forming bacteria produce slimy material that creates anaerobic environments for sulfate-reducing bacteria. Iron-oxidising bacteria can utilise the iron(II) ions released by other bacteria and convert them to insoluble iron(III) hydroxide. Finally, sulfur-oxidising bacteria utilise the sulfur that is an intermediate metabolic product of the activities of the sulfate-reducing bacteria and convert it to sulfuric acid.

The reduction of sulfate ions to hydrogen sulfide by sulfate-reducing bacteria can be considered as a two-step process:



The intermediate formation of sulfur is important for sulfur-oxidising bacteria which can oxidise it back to sulfate ions (i.e. the reverse of the first half-equation).

Electrons required for this sulfate reduction are derived from the oxidation of organic debris (e.g. carbohydrate CH_2O) and the oxidation of the iron.

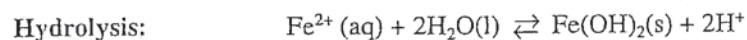


The hydrogen sulfide released by the reduction half-reaction precipitates cations such as iron(II) ions with the formation of black iron(II) sulfide.



Acidic microclimate

Analysis of silt attached to artefacts from the *Titanic* showed it to be acidic (pH 4.2). This acidic microenvironment around the rusting wreck is caused by the hydrolysis of the hydrated iron(II) ion as well as by the precipitation of iron(II) ions by hydrogen sulfide.



Depending on the oxygen concentration of various local microclimates, the iron(II) hydroxide may be oxidised to form a variety of intermediates such as hydrated magnetite as well as hydrated iron(III) hydroxide (rust).

Oxidation of iron(II) hydroxide:

