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Suboxic sediments (1206/640)

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Definition

The suboxic zone lies between the oxic and anoxic zones, where the concentrations of both dissolved oxygen and sulfide are low. Sediment pore waters are generally driven to suboxic conditions via microbial degradation of organic matter, and these intermediate waters commonly host the biogeochemical cycling of nitrogen, manganese and iron. Suboxic pore waters modify the chemistry and mineralogy of sediments between their deposition and eventual burial, and represent an important component of early diagenesis.

Keywords: Oxygen, redox, diagenesis, organic carbon, microbes, respiration, pore waters.

History

A classification scheme for suboxic sediments was originally outlined by Froelich et al. (1979), based on chemical profiles of pore waters within marine sediments. These sediments were deposited below oxygenated bottom waters, but contained sufficient organic carbon to consume oxygen (via aerobic respiration) from pore waters. Froelich et al. (1979) defined suboxic sediments as those which support the reduction of nitrate, manganese and iron before the onset of sulfate reduction and methanogenesis (Figure 1). A later classification scheme outlined by Berner (1981) proposed the term 'post-oxic' as an alternative to suboxic, and this equivalent term is sometimes seen in the literature.

The term suboxic has since become popular among biogeochemists, but is often applied rather randomly, with different intended meanings. For example, the term suboxic is sometimes used to imply low, but significant, oxygen levels (e.g. 1-10 µM, Oakley et al., 2007). However, the concentration of O_2 at which nitrate, manganese and iron reduction occur is variable, and this O_2 range risks incorporating the process of aerobic respiration of organic matter (Christensen et al., 1989). Furthermore, iron reduction has historically been included as a suboxic process despite occurring under strictly anaerobic conditions. As such, suboxic conditions cannot be defined based on oxygen levels alone.

Another source of confusion has been the application of the term suboxic to describe sediments. This can variably refer to sediments deposited beneath suboxic bottom waters, or to suboxic pore waters within the sediment pile. It is important to distinguish between these two meanings, given that with a sufficient supply of organic matter pore waters are commonly driven to suboxic and anoxic conditions even below well-oxygenated bottom waters. This distinction may be clarified by using the terms ‘sediments deposited below suboxic waters’ or ‘suboxic pore waters’.

While geochemists use the term suboxic to refer to specific biogeochemical processes, sedimentologists commonly apply the term to describe palaeoenvironments on the basis of mineral assemblages in sedimentary rocks. For example, minerals such as glauconite can indicate that oxygen was present intermittently (Berner, 1981).

To ameliorate this confusion, a new scheme was outlined by Canfield and Thamdrup, (2009). They proposed that the nebulous term suboxic is, where possible, replaced with a description of the individual metabolic zone, identified by its chemical signature. However, the term suboxic has persisted in the literature, and can be useful when collectively referring to the biogeochemical cycling of nitrate, manganese and iron.

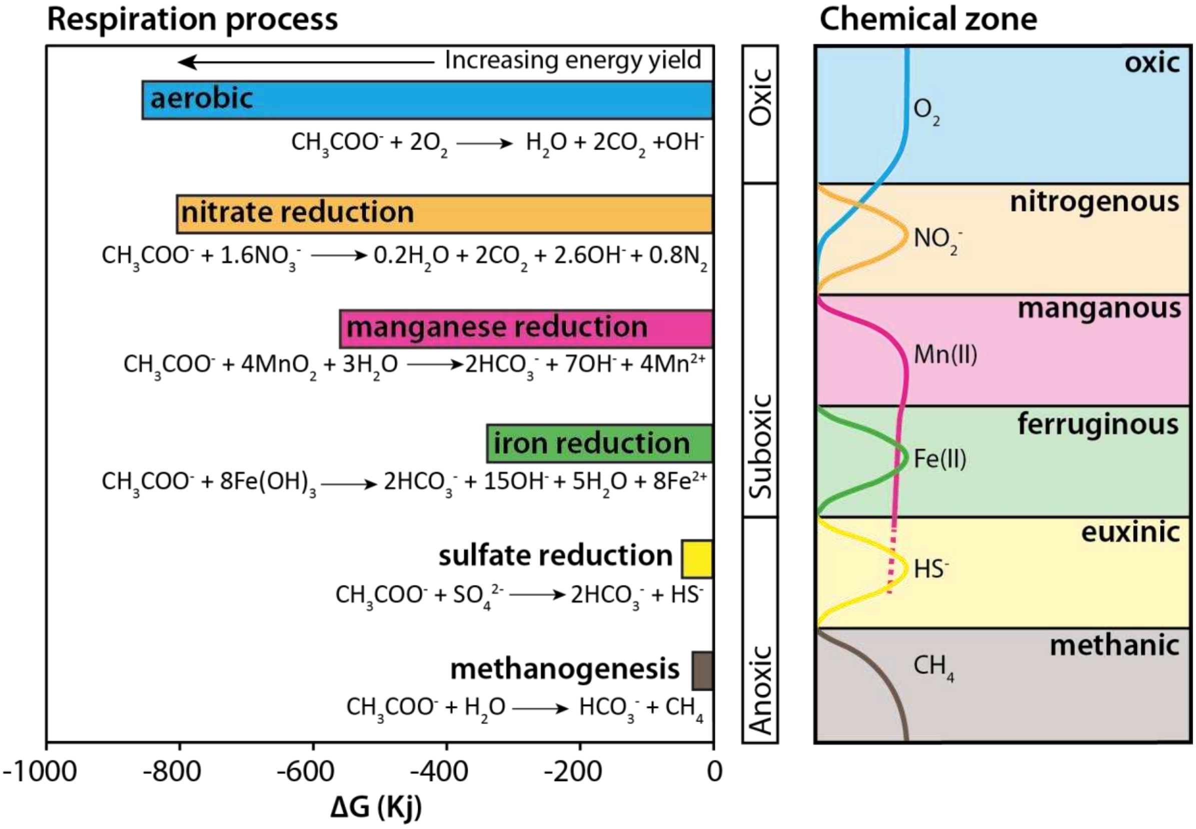

Figure 1: Generalised scheme showing the energy yield (ΔG) for each respiration processes (left) and the associated sedimentary chemical zone (right). Relative concentrations of oxidised species, such as oxygen (in blue), and reduced metabolic products, such as nitrite (orange), Mn^{2+} (pink), Fe^{2+} (green), sulfide (yellow) and methane (brown), are shown in cartoon form on the right. Adapted from Froelich et al. (1979).

Overview

The microbial oxidation of organic carbon can be coupled to the reduction of oxygen or to a series of alternative oxidised species with lower reduction potentials, each one liberating less energy than the last. In general, microbes do not begin to respire the next species in the hierarchy until the more desirable one has been significantly depleted. This is reflected in the sediments, where pore waters become stratified into distinct chemical zones with depth.

The first alternate metabolic zone is the nitrogenous zone, which hosts nitrate reduction (or denitrification). This involves the reduction of nitrate to nitrite, which is then converted to N_2 gas or ammonia. The nitrogenous zone can be detected by the associated nitrite peak in pore waters. The second alternate metabolic zone is the manganous zone, where Mn(IV) oxide minerals are reduced to aqueous Mn^{2+}. The onset of manganese reduction occurs below the nitrite peak, but commonly overlaps with the base of the nitrogenous zone. In sediments, the top of the manganous zone is often marked by a distinct layer of MnO_2, as upward diffusing Mn^{2+} encounters nitrate or O_2. In practice, the manganous zone is often insignificant due to the low abundance of Mn oxide minerals in most sedimentary systems (Calvert and Pedersen, 1996).

Below the manganous zone is the ferruginous zone, where Fe(III) oxide minerals are reduced to ferrous iron, Fe^{2+}. Iron reduction proceeds first with highly reactive ferric hydroxides, but as these become depleted, microbes utilise more crystalline phases such as hematite, goethite or magnetite. Some of the Fe^{2+} generated may diffuse upwards, and be re-oxidised via reactions with MnO_2, NO_3^- or O_2. As such, Fe^{2+} only accumulates under fully anoxic conditions.

The term suboxic is used to collectively refer to the nitrogenous, manganous and ferruginous zones. In practice, it is often easier to identify the metabolic zone by the impact it has on pore water chemistry, rather than by detecting the activity of the responsible microbes. As such, the zones are defined by the loss of reactants, such as sulfate, or the build-up of aqueous products, such as Mn^{2+} or Fe^{2+}. Where metabolic zones overlap, the zone should be assigned according to whichever metabolic product is most abundant (Canfield and Thamdrup, 2009).

The dominant microbial metabolisms and their chemical fingerprints do not always perfectly overlap. Firstly, chemical products may persist in the absence of active metabolic production. For example, Mn^{2+} removal is governed by the precipitation of Mn carbonate minerals, such as kutnohorite and rhodochrosite, and thus Mn^{2+} enriched pore waters may persist below the zone of active production and well into the anoxic zone. The manganous zone must therefore be defined by the accumulation of Mn^{2+} in the absence of other anaerobic metabolic products. Secondly, reactions other than anaerobic respiration may produce nitrite, Mn^{2+} or Fe^{2+} as a by-product. For example, chemolithoautotrophic bacteria may drive manganese reduction coupled to the oxidation of iron sulfide minerals. While the chemical fingerprint may be similar, Mn^{2+} build-up under these conditions is differentiated by context.

In contrast, chemical products may not be detectable despite active metabolic production. For example, sulfide produced through sulfate reduction can be rapidly oxidised by iron oxide minerals, pushing the top of the sulfidic zone to greater depths than the onset of active sulfate reduction (e.g. Canfield et al., 1992). In this case, active sulfate reduction may either be measured directly using radio-labelled $^{35}S\text{-}SO_4$, or indirectly indicated by the formation of iron sulfide minerals (e.g. pyrite, FeS_2). Thus these metabolic processes would often go undetected using traditional geochemical techniques, and yet they play an important role in energy fluxes and elemental cycling.

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