6 Benthic Cycling of Oxygen, Nitrogen and Phosphorus

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6.1 Introduction

All particles settling at the sea floor continuously undergo diagenetic alteration due to physical and chemical processes in the sediment (e.g. particle mixing, compaction, redox reactions). Marine sediments are the primary long-term repository of organic matter and the systematic analysis of the control mechanisms and processes modifying the original input signal is of key importance for the understanding and the reconstruction of biogeochemical cycles in the ocean. This chapter mainly focuses on processes occurring at the transition zone between sediments and bottom water where fresh, bio-available organic material is subject to intense bacterially mediated oxidation. Oxygen and nitrate are treated together because they are thermodynamically the most favorable electron acceptors in the diagenetic sequence of organic matter decomposition and their pathways are coupled through oxidation of reduced nitrogen species (nitrification) in oxic systems (cf. Section 3.2.3). Generally, their involvement in the biogeochemical cycles of the ocean is much more complex than only seen from this point of view and therefore, the combined examination of both parameters is for reasons of convenience and follows the general concept of this book. Both oxygen and nitrate pathways are very important and inherent for the understanding of the oceanic carbon cycle. Oxygen is introduced into surface waters by photosynthesis and, even more important, by exchange with the atmosphere. Conversely, it is consumed in the course of the degradation of organic matter. The latter occurs throughout the water column and in the sediments resulting in the release of carbon dioxide, nitrate, and phosphate. Nitrate itself is then used as the "next" suitable electron acceptor for organic matter degradation in environments where oxygen availability is limited, such as oxygen minimum zones or below the oxygen penetration depth in the sediments. Nitrate and phosphate are the most important limiting nutrients for driving primary productivity in the surface water. There is, however, a still ongoing debate on whether one or the other is the limiting nutrient on different time and spatial scales. The arguments are often called the "biologist's view" (nitrogen limitation) and the "geochemist's view" (phosphorus regulation), because they implicate two different perspectives on looking at the oceanic biogeochemical cycles. The typical geochemist would argue that over long time scales nitrogen fixers (converting N_2 to organic nitrogen) may be able to balance the nitrate deficit by using the huge reservoir of dissolved N_2 and allowing certain levels of productivity even if nitrate becomes exhausted relative to phosphorus. The supply of phosphorus depends solely on the riverine input and the remineralisation in the water column and in the sediments. Once it is exhausted, there is no other means of replenishing the reservoir. The view of the biologist might be supported by the fact that in certain areas of the global ocean small residues of phosphorus exist while nitrate is undetectable and the inorganic dissolved N:P ratio of the global ocean is often below 16:1. A sort of compromising theory has been proposed by Tyrrell (1999), which differentiates between nitrogen as the "proximate limiting nutrient" (with regard to immediate growth rates) and phosphate as the "ultimate limiting nutrient" (with regard to the whole system productivity over long timescales). However, since this is not the final conclusion and a more

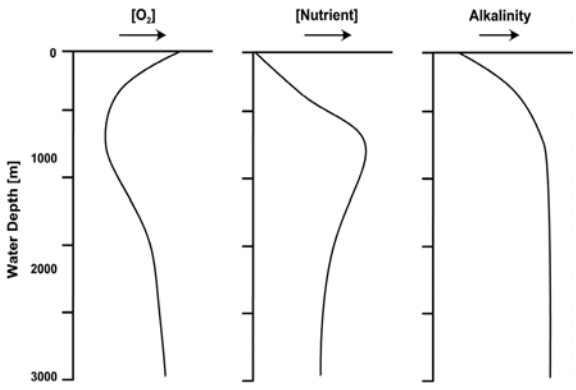

Fig. 6.1 Idealized vertical sections of dissolved oxygen, nutrients and alkalinity through the water column. The nutrients are completely consumed in surface waters. With increasing depth nutrients and CO_2 are produced while oxygen is consumed during organic matter decomposition.

detailed discussion is beyond the scope of this chapter we would like refer to general compilations of this topic (i.e. Falkowski 1997; Tyrrell 1999; Wallmann 2003; Mills et al. 2004).

Phosphate, in contrast to nitrate, does not change between different redox states. Phosphate is released into the pore water from degrading organic material and by polyphosphate accumulating bacteria, and may either diffuse into the overlaying water, adsorb to iron minerals (see Section 7.4.4.3), or precipitate as phosphate bearing minerals like apatite.

In the following sections, we will first give a short overview concerning the distribution and the geochemistry of oxygen nitrate in the modern oceans followed by a more detailed description of the relevant geochemical processes in marine sediments.

6.2 Distribution of Oxygen, Nitrate and Phosphate in Seawater

The distribution of dissolved oxygen in seawater results from the interaction of different factors. Those are (a) the input of oxygen across the atmosphere-ocean interface and the oxygen production by phytoplankton, (b) the microbially catalyzed degradation of organic matter and oxidation of other reduced substances, and (c) physical transport and mixing processes in the ocean. Theoretically, the oxygen concentration in seawater is limited by its solubility, but in fact the saturation concentration is only reached in surface waters. At some places, surface waters are even supersaturated with respect to oxygen,

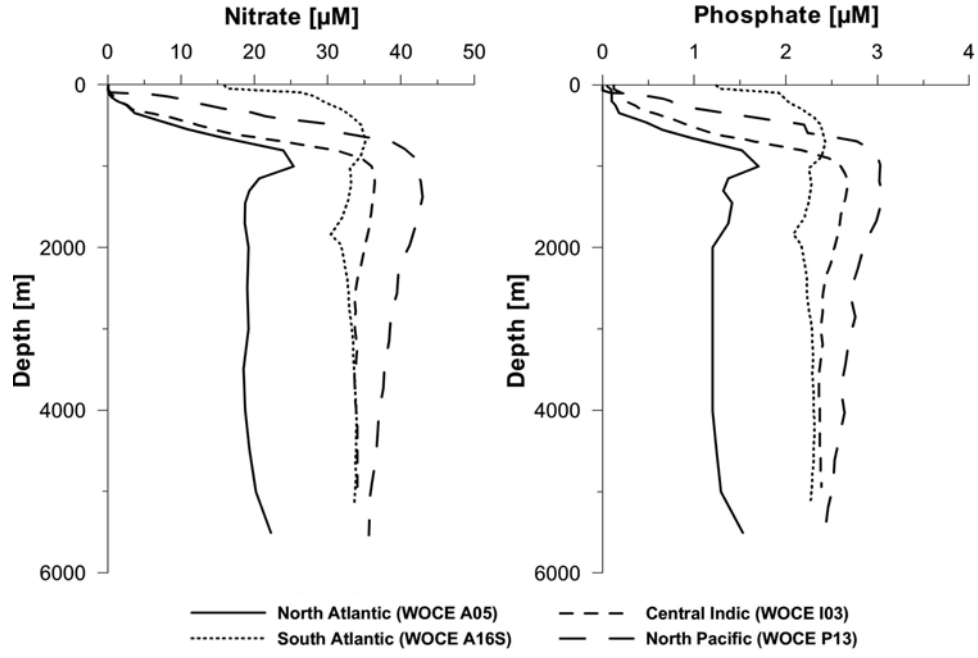

Fig. 6.2 Vertical sections of nitrate and phosphate in different ocean basins. Older water masses in the Pacific and Indian Ocean are generally more enriched in nitrate and phosphate (data from WOCE-sections A05, A16S, I03, and P13; WOCE 2002).

which is thought to be caused by entrapment of air bubbles (cf. Chester 1990). Below the productive mixed layer oxygen is depleted by bacterial respiration processes. Numerous studies show that this process is most intense within the upper 1,000 m of the water column, which marks approximately the lower end of the permanent thermocline. As a consequence significant oxygen minimum zones can be observed in areas with high surface water productivity (see Fig. 4.2). Such areas exist where upwelling water masses significantly enhance the supply of nutrients, mainly at the west coasts of the continents (trade wind belts of America and Africa), but also along the equatorial divergence zones and related to the Polar Fronts (e.g. Antoine et al. 1996; Behrenfeld and Falkowski 1997; see Fig. 12.5). Generally, the distribution of oxygen in the water column is dependent on how much the oxygen depletion exceeds the supply by vertical and lateral advection and diffusion at a certain depth. Since carbon oxidation is the main reason for oxygen depletion, a syngenetical increase of dissolved nutrients (nitrate and phosphate) and a decrease of particulate organic carbon with increasing water depth is the typical feature. Figure 6.1 shows idealized depth profiles of oxygen, a typical nutrient (like phosphate or nitrate), and alkalinity. Alkalinity, in this case, has to be understood as a sum parameter for dissolved carbon species which increase with depth due to the continued decay of organic material. These patterns, however, may deviate between the ocean basins depending on the oceanographic setting (currents, mixing of water masses), the particle-transport through the water column, and the composition of mineralized organic matter. Figure 6.2 shows some examples of the nitrate distribution in different ocean basins. The deep waters of the Pacific and the Indian Ocean are enriched in nitrate relative to the North Atlantic due to deep-water transport through the ocean basins (see below). As pointed out above, both nutrients are depleted in the surface water.

The investigation of the key processes has largely benefited from the invention of sediment traps measuring the particle flux through the water column over long periods of time. A number of researchers have attempted to quantify export fluxes of organic carbon from surface waters and their transition to the bottom by empirical formulations (cf. Section 4.2; e.g. Betzer et al. 1984; Berger et al. 1987; Martin et al. 1987). Generally, these are exponential and power equations predicting about 90% of the remineralization within the upper hundreds of meters of the water column (cf. Fig 12.1). To illustrate this process Figure 6.3 shows the application of three different equations to predict the vertical (transit) carbon flux. In all cases a surface primary productivity of 250 gC $m^{-2}yr^{-1}$ is assumed. At a depth horizon of 1,000 m only less than 5% of primarily produced organic carbon remain.

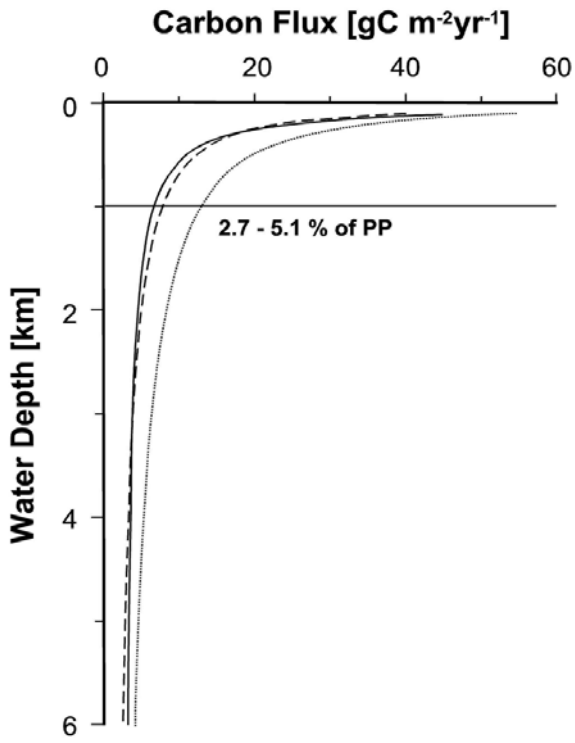

Fig. 6.3 Example calculations for the transit flux of organic carbon after empirical equations assuming a surface primary productivity of 250 gC m^{-2} yr^{-1}. More than 95% of the organic carbon is oxidized above the 1,000 m horizon.

Solid line: J_{Corg} [gC m^{-2} yr^{-1}] = 17 PP/z + PP/100 (Berger et al. 1987)
Broken line: J_{Corg} [gC m^{-2} yr^{-1}] = 9 PP/z + 0.7 $PP/z^{0.5}$ (Berger et al. 1987)
Dotted line: J_{Corg} [gC m^{-2} yr^{-1}] = 0.409 $PP^{1.41}/z^{0.628}$ (Betzer et al. 1984)

Comparative studies of the relation between primary productivity and benthic mineralization processes (Jahnke et al. 1990; Rowe et al. 1994; Hensen et al. 2000) show, however, that these empirical formulations are restricted to a limited, regional use (cf. Section 12.3). A further important factor in this regard is the reaction stoichiometry of organic matter degradation, since it determines the proportional release of CO_2, NO_3 and PO_4. Based on planktonic decomposition studies,

Redfield et al. (1963) suggested an overall C/N/P/O_2 ratio of 106/16/1/138 (see Eq. 6.1, cf. Fig 3.11). However, although widely used, subsequent investigations have put this formulation into question. Deviating ratios were formulated as 140/16/1/172 (Takahashi et al. 1985) or 117/16/1/170 (Anderson and Sarmiento 1994) implying that there is still debate on the general validity of the use of one "Redfield ratio" for all ocean basins and all water depths. Instead, C/N/P ratios seem to be subject to regional variation.

Oxygen depth profiles show an opposite trend to alkalinity and nitrate resulting from low mineralization rates in the deep ocean waters and input of oxygen-rich water masses by advective transport. Figure 6.4 shows a meridional transect of oxygen concentration through the Atlantic Ocean compiled by Reid (1994). The most prominent pattern is the southward flow of oxygen-rich North Atlantic Deep Water raising the oxygen concentration along its flow path into the equatorial South Atlantic at water depths of 3,000 – 4,000 m. Less prominent, but still significant, is also the northward flow of oxygen-rich Antarctic Intermediate Water which is marked by elevated oxygen concentrations on a south-north path (50°S – 20°S) between 0 – 1,000 m water depth. The distribution of oxygen in ocean water is therefore strongly dependent on large-scale circulation patterns. The same is valid for the distribution of nutrients: Vertical concentration profiles are always a mixture of *in situ* decomposition and advective transport processes. The global deep-water circulation pattern shows a general flow path from the North Atlantic to the North Pacific and Indian Oceans. As a result, "older" deep waters in the Pacific and Indian Oceans are depleted of oxygen and enriched in nutrients (Fig. 6.2) and CO_2 (Broecker and Peng 1982; Kennett 1982; Chester 1990; see Chapter 9).

When studying the early diagenesis of deep-sea sediments, it is very important to consider all features of the oceanic environment and consequently of the composition of the overlying deep-ocean water, since it determines the availability of any solute, i.e. oxygen or nitrate, as possible oxidants for organic carbon mineralization. As a consequence of intense deep water mixing and limited supply of degradable material to the sediments within the big central gyres, oxidant limitation is the exceptional case, which has, however, not always been the case in earth history (cf. Section 4.1).

6.3 The Role of Oxygen, Nitrogen and Phosphorus in Marine Sediments

To estimate the role of oxygen and nitrate we have to describe the general processes occurring close to the sediment water interface, the methods how to measure concentrations, fluxes, and consumption rates, and how to relate them to organic matter degradation and other processes. Subsequently, we will show examples from case studies to characterize the magnitude of fluxes and different environments in deep-sea sediments. The early diagenetic processes at the sediment-water interface are of special interest in global biogeochemical cycles because it is decided at this separation line between ocean water and sediment if any substance is recycled or buried for a long period of time in a geological sense.

6.3.1 Respiration and Redox Processes

6.3.1.1 Nitrification and Denitrification

In principle, the sequence of oxidants is determined by the energy yield for the microorganisms. When oxygen and nitrate are depleted reduction of Mn and Fe (oxo)hydroxides and sulfate as well as methane fermentation follow in the sequence with decreasing yield of energy (Froelich et al. 1979; cf. Section 3.2.5 and subsequent chapters). This sequence is generally valid, even though numerous studies have identified an overlap of carbon oxidation pathways within the sediment resulting from competition between microbial populations (Canfield 1993) and the presence of microenvironments (e.g. Jørgensen 1977; cf. Chapters 7, 8, 12).

The general equations of coupled oxic respiration and nitrification (6.1) and denitrification (6.2) describing the "top" of the diagenetic sequence are given as:

Oxic respiration and nitrification

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 138\ O_2 \rightarrow 106\ CO_2 + 16\ HNO_3 + H_3PO_4 + 122\ H_2O$$
$$\Delta G^0 = -3190\ kJ\ mol^{-1} \qquad (6.1)$$

Denitrification

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 94.4\ HNO_3 \rightarrow 106\ CO_2 + 55.2\ N_2 + H_3PO_4 + 177.2\ H_2O$$
$$\Delta G^0 = -3030\ kJ\ mol^{-1} \qquad (6.2)$$

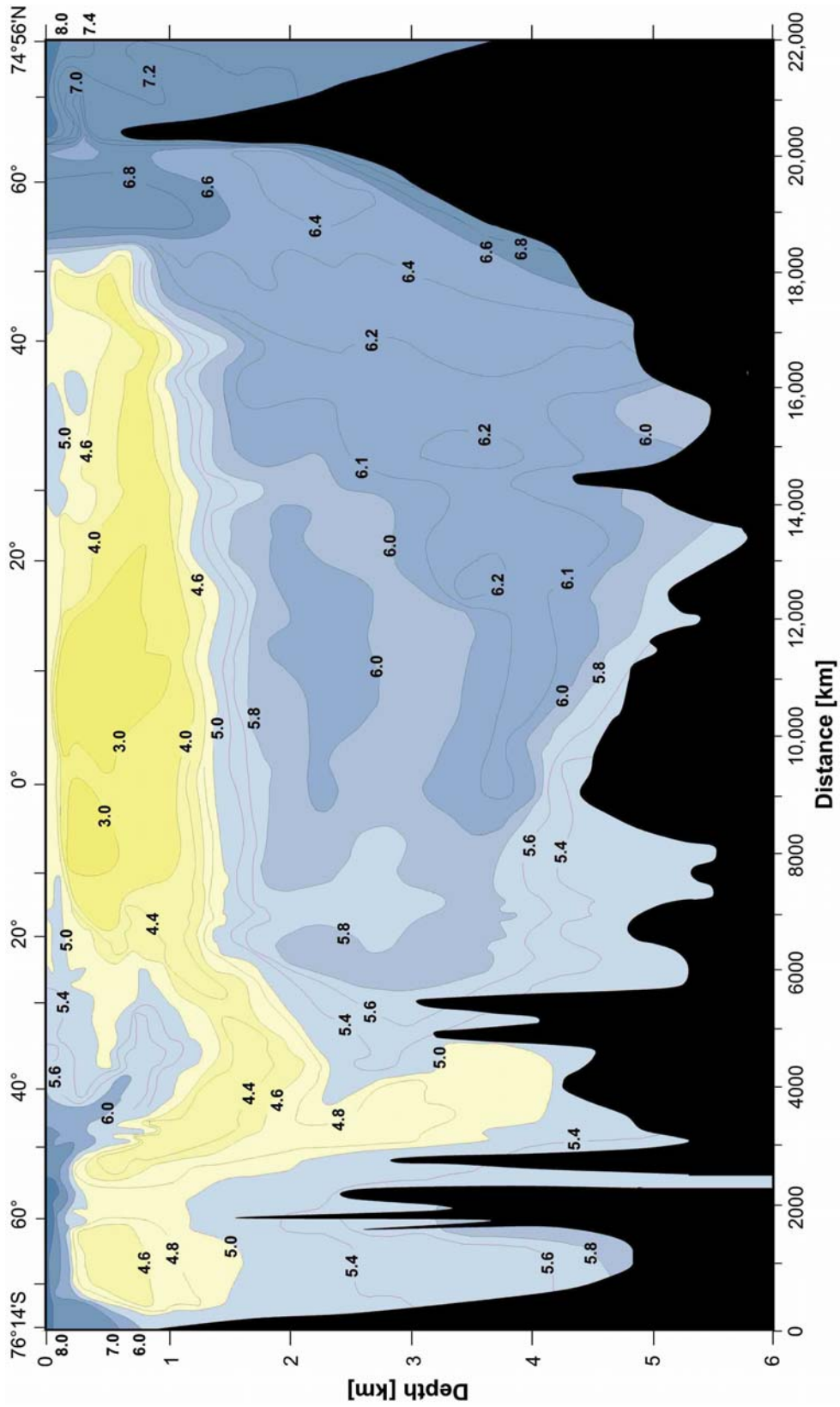

Fig. 6.4 North-South section of dissolved oxygen (ml/l) across the Atlantic Ocean (after Reid 1994). See text for explanation.

The ΔG^0-values indicate the higher energy yield for using oxygen rather than nitrate as the terminal electron acceptor. In these equations, it is assumed that organic matter with a C/N/P ratio of 106/16/1 is oxidized. Equation (6.1) requires that ammonia released during oxic respiration is quantitatively oxidized to nitrate. The process of nitrification is, however, more complex than described above and is known as a stepwise oxidation of nitrogen species by different microbes. Those can be grouped into ammonia oxidizers, generally with a genus name starting with the prefix Nitroso- and nitrite oxidizers, starting with the prefix Nitro-. Although ammonia and nitrite oxidizing bacteria are physiologically depending on each other and usually occur in close proximity, they are phylogenetically two distinct groups of bacteria, which are not closely related (Bock and Wagner 2001). The oxidation of ammonia to nitrite is also a two step process in which hydroxylamine is formed as an intermediate product (Eq. 6.3). The second step yields the biogeochemically useful energy (Eq. 6.4):

$$2\ NH_3 + O_2 \rightarrow 2\ NH_2OH \qquad (6.3)$$

$$NH_2OH + O_2 \rightarrow NO_2^- + H_2O + H^+ \qquad (6.4)$$

In the following step nitrite is oxidized by lithotrophs like *Nrobacter* or *Nrococcus* to nitrate (Eq. 6.5):

$$NO_2^- + \tfrac{1}{2}\ O_2 \rightarrow NO_3^- \qquad (6.5)$$

In summary, nitrifying bacteria are considered to be strictly aerobic and therefore depend on adequate oxygen supply for their energy gain (Painter 1970). Experimental results of Henriksen et al. (1981) on control factors of nitrification rates in shallow water sediments from Denmark revealed that nitrification is strongly dependent on temperature, oxygen availability (oxygen penetration depth), ammonia supply and the number of nitrifying bacteria. These complex interactions are more thoroughly discussed in comprehensive reviews on nitrification in coastal marine environments by Kaplan (1983) and Henriksen and Kemp (1988).

Denitrification starts when oxygen is almost depleted (below the oxygen penetration depth) by inducing an enzymatic system of nitrate reductase and nitrite reductase by facultative aerobic bacteria, which can only use nitrogenous oxides if oxygen is - nearly - absent. Measurements carried out with a combined microsensor for O_2 and N_2O indicated that denitrification is restricted to a thin anoxic layer below the oxic zone (Christensen et al. 1989). Denitrification is the only biological process that produces free nitrogen. It removes fixed nitrogen compounds and, therefore, exerts a negative feedback on eutrophication making it a crucial process for the preservation of life on earth. For example, denitrification in rivers and coastal environments reduces the supply of fixed nitrogen from the continents by about 40%. (Seitzinger 1988).

The reduction of nitrate to dinitrogen occurs first as a reduction of nitrate to nitrite (Eq. 6.6) and then a stepwise reduction to nitrogen oxide, dinitrogen oxide (Eq. 6.7) and dinitrogen (Eq. 6.8):

$$NO_3^- + 2\ H^+ + 2\ e^- \rightarrow NO_2^- + H_2O \qquad (6.6)$$

$$2\ NO_2^- + 6\ H^+ + 4\ e^- \rightarrow N_2O + 3\ H_2O \qquad (6.7)$$

$$N_2O + 2\ H^+ + 2\ e^- \rightarrow N_2 + H_2O \qquad (6.8)$$

The last reduction step from nitrous oxide to dinitrogen (Eq. 6.8) is not always completed so that the final product of denitrification is not necessarily dinitrogen. Nitrous oxide may therefore be produced or consumed during denitrification. A compilation of Seitzinger (1998) for coastal marine environments shows, however, that in most cases the net ratios between N_2O:N_2 production rates are usually very small (between 0.0002-0.06). The total amount of dinitrogen produced obviously depends on the partial pressure of oxygen (higher oxygen contents seem to be suitable for the production of N_2O; Jørgensen et al. 1984), the pH, and the presence of H_2S.

The major prerequisite for denitrification is the availability of nitrate (including nitrite). In marine sediments the dominant sources of nitrate are the production during nitrification and the supply from overlying bottom water by means of bioturbation, bioirrigation, and diffusion (see Section 6.3.2). Furthermore, denitrification is strongly dependent on temperature, but also on the oxygen concentration and the availability of organic matter are limiting for the process (Middelburg et al. 1996a). There is also evidence that denitrification may be reduced at high sulfate reduction rates, because low sulfide concentrations completely inhibit nitrification which in turn is necessary for denitrification (Seitzinger 1988). Generally, most suitable conditions for denitrification are obtained

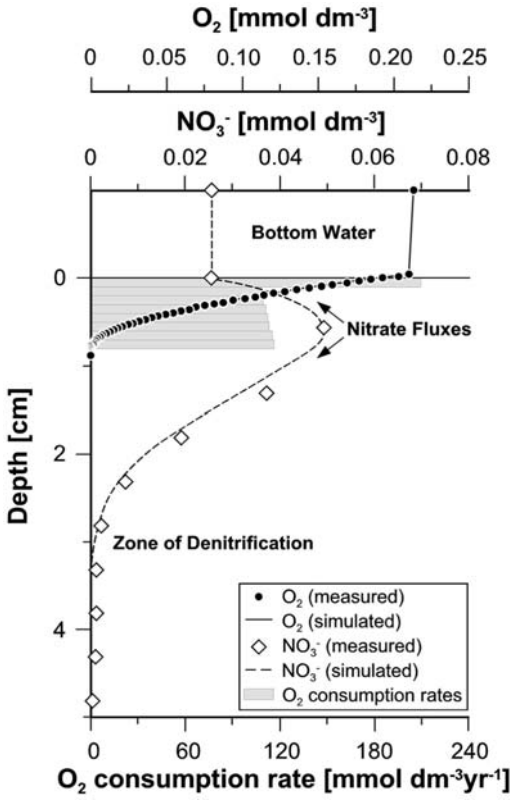

Fig. 6.5 Measured and simulated profiles of oxygen and nitrate of station GeoB 1711 from the continental slope off Namibia at a water depth of approximately 2000 m. Degradation of organic matter with a C/N ration of 3.7 was assumed for simulation. Bars indicate oxygen consumption rates required for model fit (after Hensen et al. 1997).

at intermediate carbon availability levels when carbon is not limiting for oxic respiration, but sulfate reduction is still low or absent. Studies of Jørgensen and Sørensen (1985) along a salinity gradient in a Danish estuary revealed evidence that denitrification and nitrate reduction (Eq. 6.9) became a more important pathway as sulfate became limited due to increased freshwater input close to the river outlet.

Many bacteria are able to reduce nitrate to ammonia in order to use nitrate as a nitrogen source for the build up of biomass (assimilation). Also the dissimilatoty nitrate reduction to ammonia (DNRA), where nitrate is respired to ammonia, is a widespread physiological ability among bacteria. Nevertheless, until recently it was thought to have small ecological significance, because the potential energy gain of nitrate reduction to nitrogen is higher (compare Fig. 5.9). The ability of some bacteria to reduce nitrite further to ammonia (Jørgensen and Sørensen 1985; Sørensen 1987) can be expressed by the following equation:

$$NO_2^- + 8\ H^+ + 6\ e^- \rightarrow NH_4^+ + 2\ H_2O \qquad (6.9)$$

Figure 6.5 shows typical pore water profiles of oxygen and nitrate measured in organic rich sediments off Namibia summing up the net reactions described above. Due to nitrification, the highest nitrate concentrations are reached approximately at the oxygen penetration depth. At about 3 cm depth, nitrate is consumed in the process of denitrification. The nitrate profile indicates an upward flux into the bottom water and a downward flux to the zone of denitrification. Both profiles are verified by the application of Equations 6.1 and 6.2 within the computer model CoTAM/CoTReM (cf. Chapter 15) as indicated by the solid and dashed lines.

It could be shown that the processes described above are of key importance for the distribution of oxygen and nitrate in the sediment column and can directly be related to the degradation of organic matter. The reduction by any other reduced species (e.g. H_2S, Fe^{2+}, Mn^{2+}) can, however, also be an important pathway (see below and cf. Chapters 7, 8). Generally, most of these processes are microbially mediated (cf. Chapter 5; e.g. Chapelle 1993; Stumm and Morgan 1996). This also includes the (re-oxidation) of upward diffusing reduced nitrogen species (mainly ammonia) during oxic respiration. In the example of Figure 6.5 the C/N ratio of decomposed organic matter had to be decreased to a factor of 3.7 (instead of 6.625; cf. Eq. 6.1) to reproduce the measured nitrate concentration profile. This is a reasonable explanation because fresh organic matter (with a high fraction of N-rich amino acids) could be supplied in this specific marine environment (cf. Section 4.4), but the oxidation of upward diffusing reduced nitrogen species and/or artificially increased nitrate concentrations (see Section 6.3.2) have to be considered for interpretation.

The general reaction principle and the coupling of all processes described in this section is illustrated in Figure 6.6. All dissolved species created during nitrification and denitrification may either escape into the bottom water, mainly by diffusion, or are involved in subsequent redox processes. Ammonium is generally re-oxidized in

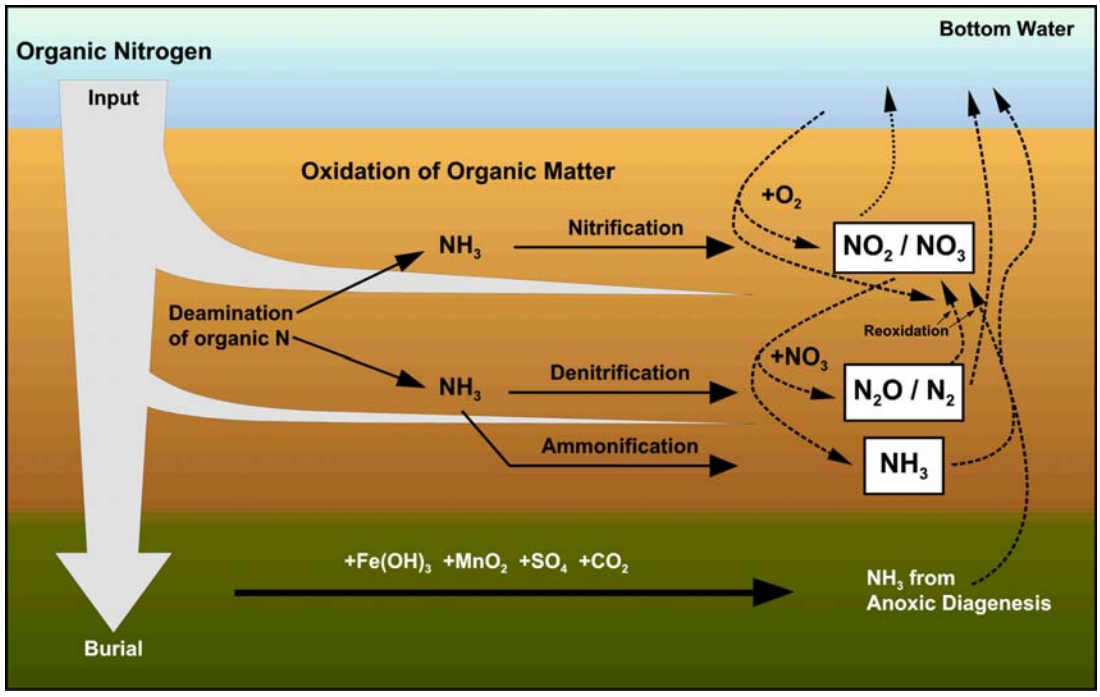

Fig. 6.6 Pathways of nitrogen in marine surface sediments. Arrows: black, organic matter degradation; gray, particulate organic nitrogen; dotted, diffusion of solutes.

oxygenated sediments (cf. Section 6.3.1.3), but it may also diffuse into the bottom water, if oxygen or other suitable oxidants are either limited or absent.

Nitrate as terminal electron acceptor is especially important for the oxidation of ferrous iron (Straub et al. 1996) or hydrogen sulfide. Particularly among the sulfide oxidizing bacteria a unique adaptation for the use of nitrate as electron acceptor has evolved: a central vacuole used for the storage of nitrate (Fossing et al. 1995). The vacuolated sulfur bacteria contain nitrate in concentrations ranging from several tens to hundreds of mmolar, which is up to five orders of magnitude higher than the ambient environmental concentrations (Fossing et al. 1995). High internal nitrate concentrations are found in three genera of sulfur bacteria (Fig. 6.7) called *Beggiatoa* (McHatton et al. 1996), *Thioploca* (Fossing et al. 1995) and *Thiomargarita* (Schulz et al. 1999). All of these bacteria are also storing the electron donor sulfide in the form of sulfur globules. The vacuolated sulfur bacteria can be unusually large (up to several 100 µm diameter), because the volume of the vacuole is not metabolically active. Their sulfur inclusions scatter the light giving these bacteria a bright white appearance, which makes it possible to see them with the naked eye.

Beggiatoa and *Thioploca* are filamentous bacteria, meaning that the cells occur in a row and are connected with each other. The filaments are motile by gliding. *Thioploca* filaments are found as very dense mats in sediments of the upwelling areas off Chile and Peru. The filaments live as bundles in vertical sheaths reaching up to 20 cm into the sediment (Fig. 6.7). In the sheaths they glide between the surface of the sediment, where they take up nitrate, and deeper parts of the sediment, where sulfide produced by sulfate reducing bacteria is available (Fossing et al. 1995). The larger nitrate storing forms of *Beggiatoa* are frequently encountered in areas with locally enhanced sulfide flux, such as hydrothermal vents and seeps or methane hydrates. In contrast to *Thioploca* the filaments are not forming bundles. They are usually found as white or more seldom orange mats at the sediment surface (Fig. 6.7). In the Benguela upwelling region, a large area of the seafloor covered with loose diatome ooze, is populated by *Thiomargarita* cells (Schulz et al. 1999). In contrast to their close relatives *Beggiatoa* and *Thioploca* these sulfur bacteria are not

motile and do not form true filaments. The individual, spherical cells are hold together in strings by a slime sheath (Fig. 6.7). They are the largest bacteria known so far (>700 µm diameter) and may survive up to several years in sulfidic sediments without getting into contact with nitrate or oxygen. Instead of actively gliding in between different sediment horizons they seem to rely on getting passively transported into nitrate containing water by sediment suspension.

Even though it is quite obvious that the nitrate storing sulfur bacteria use nitrate as electron acceptor for the oxidation of sulfide, it is still not completely clear, whether the end product of nitrate respiration is ammonia or nitrogen. As this group of bacteria cannot be grown in pure cultures yet, all conclusions on their metabolism are drawn from indirect evidences and remain to some degree speculative. Earlier reports on denitrification in *Beggiatoa* (Sweerts et al. 1990) have been doubted since Otte et al. (1999) could show ammonia production in cleaned *Thioploca* filaments. At first glance, it seems more likely to assume denitrification, as the energy yield per mole sulfide oxidized with nitrate is much higher if nitrate is reduced to nitrogen (-714.7 kJ mol^{-1}) and not to ammonia (-436.2 kJ mol^{-1}) (Jørgensen and Nelson 2004). Nevertheless, per mole nitrate the energy yields of both processes are quite comparable with -446.7 kJ mol^{-1} for denitrification and 436.2 kJ mol^{-1} for dissimilatory reduction of nitrate to ammonia (DRNA). Furthermore, the last step of denitrification is easily blocked by sulfide, which suggests that DNRA might be a more efficient way of anaerobic sulfide oxidation than denitrification (Jørgensen and Nelson 2004).

6.3.1.2 Coupling of Oxygen and Nitrate to other Redox Pathways

Below the oxygenated zone anoxic diagenesis is stimulated, if biodegradable organic matter is still sufficiently available. Anoxic mineralization processes result in a release of reduced species, like ammonia (Fig. 6.6), into pore water which might be re-oxidized again as they diffuse back to the surface layers. Stimulation of anoxic diagenesis requires high input of organic matter to the sediment surface which is usually combined with high sediment advection restricted to coastal and high

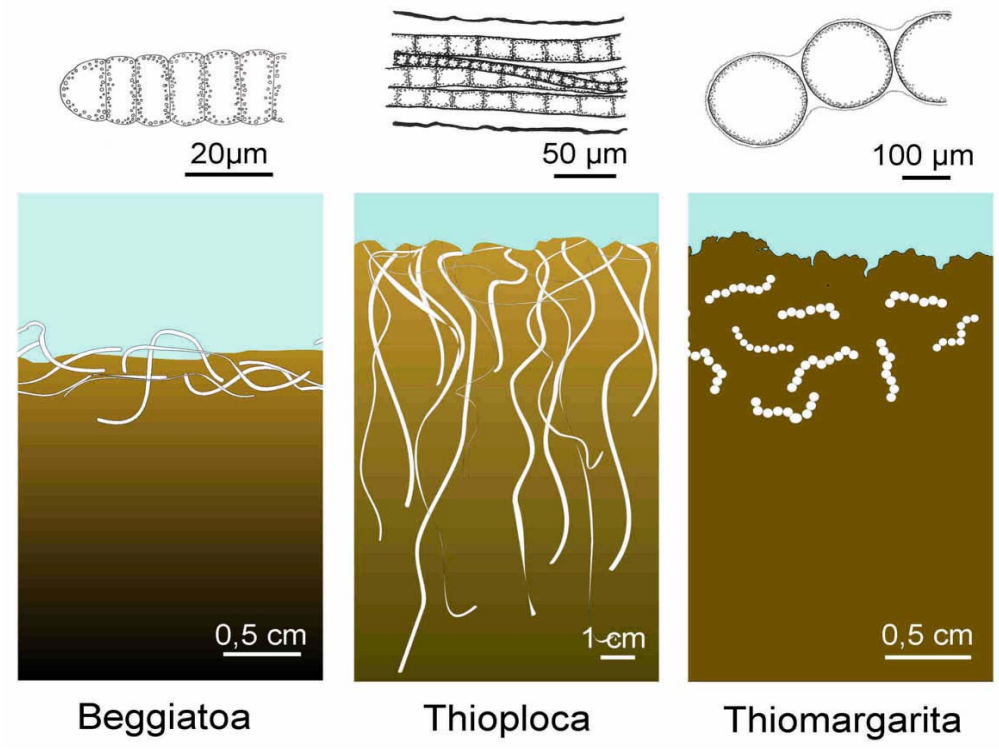

Fig. 6.7 Morphology of the three genera of nitrate storing sulfur bacteria. Above: appearance in the light microscope. Below: distribution in the sediment.

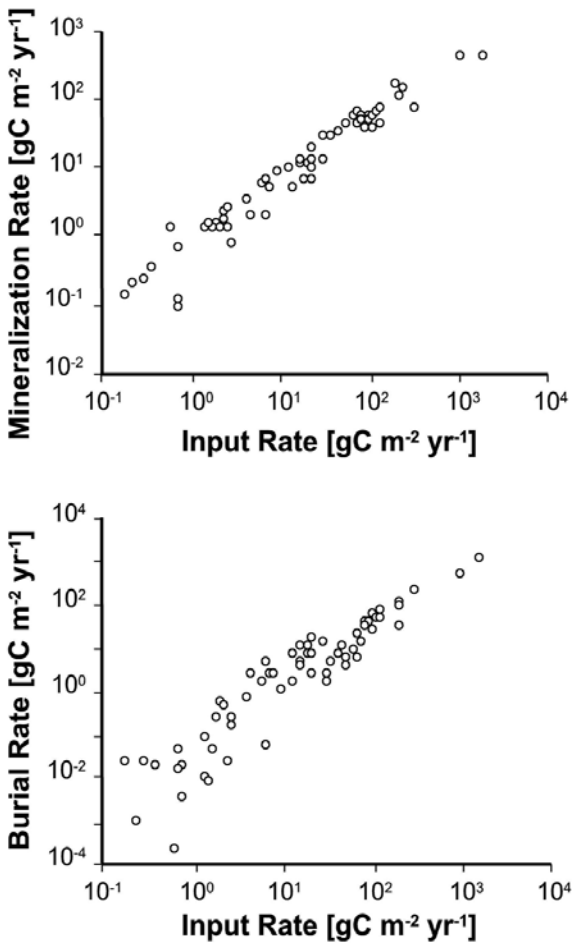

Fig. 6.8 Input rates of organic carbon plotted against carbon mineralization and carbon burial from different data sources (after Henrichs 1992).

production areas adjacent to continental margins. The general coupling between sediment advection, deposition (burial) and mineralization of organic matter is depicted in Figure 6.8 and has been documented in numerous studies (cf. Sections 4.2, 4.3; e.g. Henrichs and Reeburgh 1987; Henrichs 1992; van Cappellen et al. 1993; Tromp et al. 1995).

The amount of fresh organic matter arriving at the sediment surface also constitutes a control parameter for the population density of benthic macrofauna responsible for the biological mixing of the sediment. Biological mixing is known to be much more important for the transport of labile organic particles to deeper sediment layers than sedimentation (cf. Section 7.4.4). The strong correlation between sedimentation rate and particle mixing was recently compiled by Tromp et al. (1995) and is shown in Figure 3.28. Based on this compilation Tromp et al. (1995) derived the following regression equation:

$$\log D_{bio} = 1.63 + 0.85 \log \varpi \qquad (6.10)$$

where D_{bio} is the bioturbation coefficient ($cm^2\ yr^{-1}$) and ϖ is the sedimentation rate ($cm\ yr^{-1}$). A closer look at the data shown in Figure 3.28 and Equation 6.10 makes clear that there is a difference between both parameters of up to three orders of magnitude. The correlation is, however, only applicable when other environmental factors, like bottom water anoxia, extreme sedimentation rates, or current action, are not effective. Bottom water deficiency of oxygen (below 20% sat.) has been shown to seriously decrease the bioturbation intensity (Rhoads and Morse 1971) and below an oxygen saturation of about 5% nearly no macrofauna will survive (Baden et al. 1990).

For some practical reasons, oxygen is often used as a measure for total respiration of a sediment, mainly in the marine environment (cf. Jahnke et al. 1996; Seiter et al. 2005; Section 12.5.2; Figs. 12.17 - 12.19). Because of all subsequent mineralization processes occurring below, this is of course not strictly correct. Rather a complete net-reoxidation of all reduced species produced during anoxic diagenesis is required – ultimately by means of oxygen (Pamatmat 1971).

Any fixation and burial of reduced species (e.g. the formation of sulfides or carbonates; pyrite, siderite,...) or the escape of reduced solutes across the sediment-water interface (e.g. CH_4, NH_4; N_2O, N_2, Mn^{2+}, Fe^{2+}; Bartlett et al. 1987; Seitzinger 1988; Devol 1991; Tebo et al. 1991; Johnson et al. 1992; Thamdrup and Canfield 1996; Wenzhöfer et al. 2002) results in an underestimation of the total respiration. The evaluation whether a reoxidation is complete is generally very difficult and is limited by the availability of measurements of all key species. The main questions are: (1) How big is the contribution of each pathway compared to the total mineralization? (2) To which amount and by which processes are these pathways interrelated? Since in most studies a lack of information on certain parameters remains, or different methods are applied to determine one pathway (e.g. differences resulting from *in situ / ex situ* determination of a species, or different methods to determine for example denitrification and sulfate reduction rates; see Section 6.4), the conclusion remains at least to some extent arbitrary. Reimers et al.

(1992) calculated for rapidly accumulating sediments on the continental margin off California that aerobic respiration is the major pathway of organic matter oxidation and more than 90% of the oxygen flux into the sediments is used for organic carbon oxidation. Since respiration by anoxic processes is estimated to exceed 30% of the total mineralization in the sediment this indicates an incomplete reoxidation cycle. Results of Canfield et al. (1993 a,b) and Wenzhöfer et al. (2002) from continental shelf sediments of the Baltic Sea indicate that oxygen consumption by reoxidation processes is quantitatively more important than aerobic respiration. In these environments sulfate reduction seems to be the dominant respiration process (Wenzhöfer et al. 2002; Thamdrup et al. 1994), although metal oxides can also play a significant role in particular cases. Canfield et al. (1993 a,b) have shown that the importance of metal oxides in the diagenetic sequence is strongly dependent on bioturbation activity. Mineralization rates simply derived from pore water gradients might underestimate the true rates by one order of magnitude (Haese 1997). Such complex interactions between different pathways of organic matter decomposition and redox reactions are restricted to coastal marine environments and highly accumulating upwelling regions. In oligotrophic regions of the deep sea, 100 to 1,000-times more organic carbon is oxidized by oxygen than by sulfate reduction and other pathways (Canfield 1989). For the major part of the world oceans the oxygen flux into the sediment provides a good approximation to the total rate of organic carbon oxidation.

6.3.1.3 Anaerobic Oxidation of Ammonium with Nitrate (Anammox)

The usual way of transferring biological bound nitrogen to dinitrogen is a series of microbial activities starting with the release of ammonia from degraded organic material (ammonification), the oxidation of ammonia with oxygen to nitrate (nitrification) and the reduction of nitrate to dinitrogen, when nitrate is used as electron acceptor for the oxidation of organic material (Fig. 6.9, cf. Section 6.3.1.1). The last step, denitrification, was until recently thought to be the most important microbial process releasing gaseous nitrogen and thereby counteracting eutrophication. Nevertheless, an anaerobic microbial process removing ammonia has been proposed early on, because in the absence of oxygen, ammonia is not accumulating in rates corresponding to the break down of organic material (Richards et al. 1965) and thermodynamical calculations suggest that it would be possible for bacteria to gain energy by the oxidation of ammonia with nitrate or nitrite (Broda 1977). The first direct evidence for the occurrence of anaerobic ammonia oxidation derived from wastewater bioreactors, where bacterial populations oxidizing ammonia with nitrite and producing dinitrogen could be grown in enrichment cultures (Mulder et al. 1995; van de Graaf et al. 1995).

Until now none of the bacteria carrying out the anammox reaction could be isolated into pure culture, but much information could be gained from enrichment cultures. All anammox bacteria

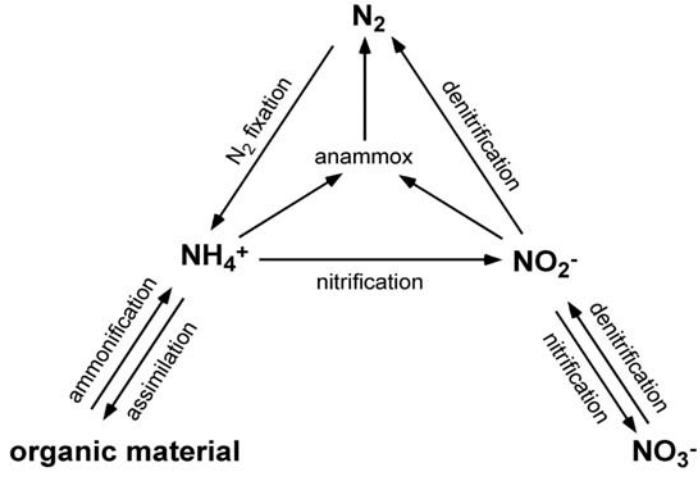

Fig. 6.9 Schematic nitrogen cycle (modified after Shapleigh 2000).

known so far seem to belong to the *Planctomycales* (Strous et al. 1999) a group of bacteria, which harbors relatively few isolated pure cultures, but seems to be quite abundant in marine environments. The process of anammox depends on nitrite, which occurs as an intermediate product during nitrification and denitrification (Fig. 6.9). Thus, anammox should not be seen as an alternative process to denitrification, but rather as a short cut in the nitrogen cycle, which still depends on the production of nitrite from denitrification. During the oxidation of ammonia with nitrite the highly toxic gas hydrazine (N_2H_4) is formed as an intermediate. To avoid a toxification of the cells with hydrazine the oxidation of ammonia to dinitrogen is restricted to a special cell compartment called anammoxosome. In the membrane of the anammoxosome a very unusual type of lipids called ladderanes is found that seem to be typical for anammox bacteria.

Rates of anaerobic ammonia oxidation in the environment can be determined by anaerobic incubation of samples with ^{15}N-labelled ammonia and recording the formation of labeled dinitrogen over time. For detection of anammox bacteria in the environment the ladderane lipids can be used as biomarkers for the detection of anammox bacteria. As all anammox bacteria known so far are phylogenetically closely related, it is also possible to search for anammox bacteria with molecular techniques such as fluorescent in situ hybridization. Although anammox bacteria were first described from wastewater reactors they were now also detected in various marine environments like the Skagerrak (Thamdrup and Dalsgaard 2002), the Black Sea (Kuypers et al. 2003), the Golfo Dulce (Dalsgaard et al. 2003) and the Benguela upwelling area (Kuypers et al. 2005). Thus, we have to assume that a considerable part of the total bacterial production of dinitrogen is carried out by anaerobic ammonia oxidation.

6.3.1.4 Nitrogen Isotopes in Marine Sediments

The stable isotope composition of sedimentary organic matter has widely been used to describe the state of the oceanic nitrogen cycle as it allows conclusions on nitrogen sources and transformation processes (i.e. assimilation or denitrification), which are subject to isotopic fractionation (i.e. Francois et al. 1992; Altabet and Francois 1994; Altabet et al. 1999; Thunell et al. 2004). We will briefly discuss this issue because early diagenesis

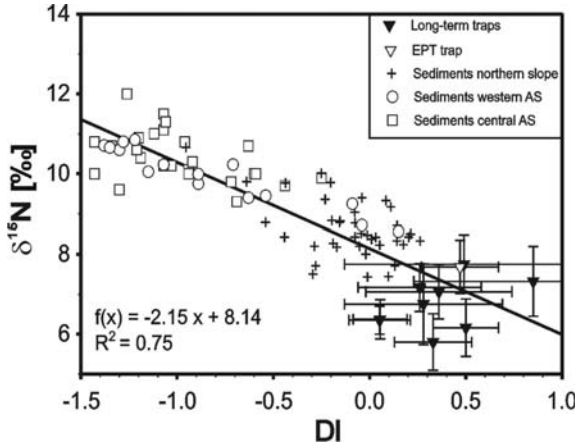

Fig. 6.10 δ^{15}N-values of sediment trap and surface sediment samples (Arabian Sea) plotted vs. the degradation index (DI). The correlation indicates isotopic fractionation in the course of organic matter degradation (Gaye-Haake et al. 2005).

plays a certain, but still somewhat unconstrained role affecting the isotopic composition of organic nitrogen compounds. Stable nitrogen isotope ratios are usually expressed as

$$\delta^{15}N = \left[\left(\frac{^{15}N/^{14}N_{sample}}{^{15}N/^{14}N_{standard}} \right) - 1 \right] \cdot 1000 \qquad (6.11)$$

where the standard, atmospheric nitrogen, has a δ^{15}N of 0‰.

Deep water nitrate seems to have a fairly constant δ^{15}N-level of about 5‰ (Sigman et al. 2000), which must be the result of almost balanced inputs and losses. The major input of nitrate is via nitrogen fixation – the ability of certain prokaryotes to transform dinitrogen to ammonia – which is then incorporated into new biomass. Although the controls are not completely understood, the process is of utmost significance in ocean biogeochemistry, because it may enable certain levels of primary productivity, even in nitrate-starved regions of the surface ocean. Since nitrogen fixation is considered to cause only little fractionation it produces fixed nitrogen with about the same δ^{15}N as atmospheric nitrogen (i.e. Codispoti et al. 2001). At present, we have to assume that the major losses of nitrate are caused by denitrification in the water column and the sediments. Due to the preferential use of the light isotope in the course of mineralization processes deep water nitrate becomes more enriched in ^{15}N. In suboxic zones of the water column the total nitrate pool is usually not depleted considerably by denitrification,

which allows a significant fractionation and $\delta^{15}N$-enrichment of the residual nitrate of up to 20‰ (Brandes et al. 1998). On annual time scales, the uptake of nitrate in the euphotic zone is generally believed to be complete (Thunell et al. 2004), so that upwelling of ^{15}N-enriched water masses causes the production of relatively ^{15}N-rich organic material. This process is believed to be particularly enhanced during interglacial rather than glacial times and gave rise to the use of $\delta^{15}N$ values of sedimentary material as a recorder of nutrient utilization and paleoproductivity (Altabet et al. 1995; Thunell and Kepple 2004). The applicability of this proxy has, however, been disputed, because of potential alterations of the primary signal during nitrification and denitrification in the sediments. Variations in the $\delta^{15}N$-record are considered to be dependent on the preservation of the organic material, hence burial potential controlled by the sedimentation rate and the oxygenation of the water column (cf. Sections 6.3.1.2 and 6.5.2). Whereas in regions characterized by high particle fluxes and low bottom water oxygen levels $\delta^{15}N$-values are indistinguishable from sediment trap material, poor preservation of organic matter may lead to increased $^{15}N/^{14}N$-ratios of up to 5‰ (i.e. Altabet et al. 1994; 1999; Thunell et al. 2004). The shift to higher $\delta^{15}N$-values is mainly attributed to the decomposition of amino acids, which are the main carriers of nitrogen in fresh marine detritus and more susceptible to degradation. Based on the observation that amino acids are rapidly consumed in surface sediments Dauwe et al. (1999) developed the so-called degradation index (DI), which has recently been used by Gaye-Haake et al. (2005) in order to demonstrate the dependence of the nitrogen isotope composition on the degradation of the sediments. Their data from the Arabian Sea clearly show the shift from lower (sediment traps) to higher $\delta^{15}N$-values (sediments) with increasing degradation (Fig. 6.10).

6.3.2 Input and Redistribution of Phosphate in Marine Sediments

6.3.2.1 P-Species and Forms of Bonding

Particulate phosphorus reaches marine sediments in various portions of inorganic and organic fractions. In a recent study Faul et al. (2005) have investigated the phosphorus distribution in sinking oceanic particulate matter from a wide range of oceanic regimes. Correspondingly, the P flux to the sediment is typically dominated by reactive P components including organic P (~40%), authigenic P (~25%), and labile P and/or phases which are associated with iron oxyhydroxides (~21%). With only about 13%, the non-reactive detrital fraction seems to be less important. While the most important carrier of inorganic P are iron oxyhydroxides, which mostly

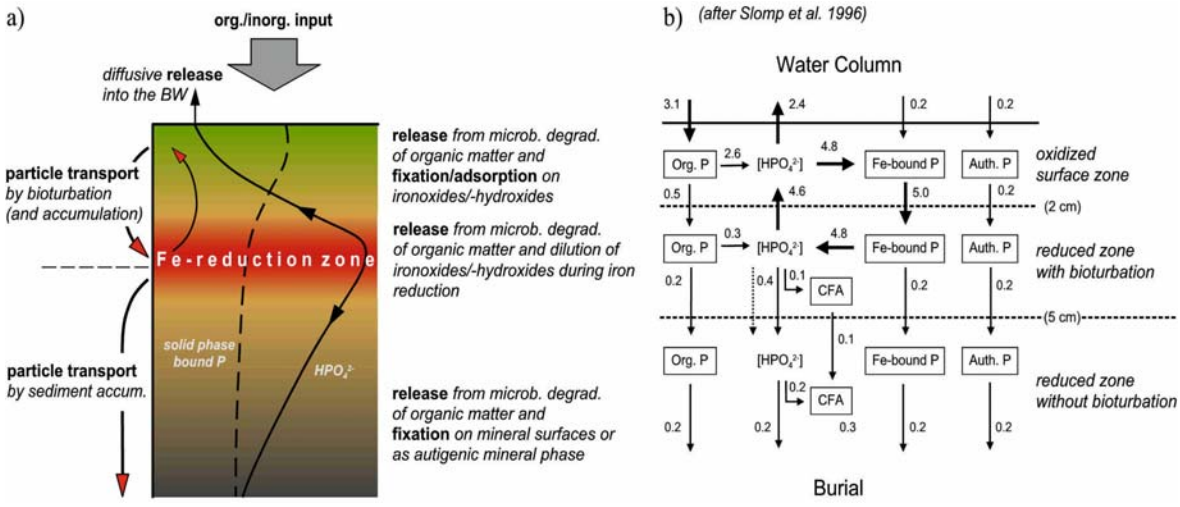

Fig. 6.11 The benthic phosphorus cycle in deep-sea sediments. a) generalized processes of particulate transport, release and fixation; b) example of fluxes of P (in 10^{-4} µmol $cm^{-2}d^{-1}$) between the pore water and the sediment P reservoirs as calculated with a model for a deep-water location at the western European continental platform Goban Spur (after Slomp et al. 1996).

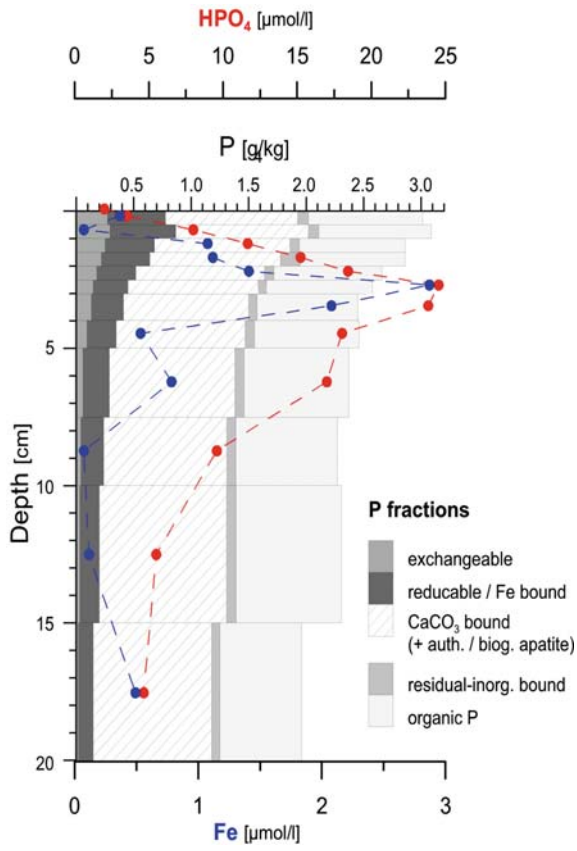

Fig. 6.12 Reservoirs of phosphorus in surface sediments and accompanying pore water profile of iron and phosphate. An example from the continental margin off Namibia (Zabel unpubl. data).

occur in form of aggregated colloidal suspensions or coating surfaces around suspended clay particles (e.g. Krom and Berner 1980; Froelich 1988), the organic fraction consists of organic matter and fish debris. After their accumulation on the sediment surface, the primary phases undergo an intensive redistribution due to early diagenetic modification, which is mainly affected by the close coupling of the P-cycling with the geochemistry of redox-sensitive iron phases (e.g. Froelich et al. 1982; Ruttenberg and Berner 1993; Slomp et al. 1996, 2002, 2004; Filippelli 1997, 2001; Schenau and de Lange 2001). A simplified illustration of most relevant processes in the generalised benthic P cycle is given in Figure 6.11.

The major species of dissolved phosphorus in the marine environment is HPO_4^{2-}. Phosphate is mainly released to the (pore) water either during microbial degradation of organic matter and/or concomitant with the reduction of ferric iron. Since phosphate cannot be used as an electron acceptor (cf. next section) under most environmental conditions, the only processes consuming phosphate are 1) the biological uptake for the formation of new biomass, 2) the adsorbtion onto particle surfaces or co-precipitation with in-situ-formed minerals and 3) the formation of authigenic carbonate fluorapatite (CFA). To examine the different processes of the P-cycle and to quantify the transfer and flux rates, Ruttenberg (1992) developed a selective leaching procedure which allows the speciation of solid-phase P into five reservoirs on the basis of their chemical reactivity. This established analytical scheme, known as the SEDEX method, was slightly modified several times to get more detailed information about specific phosphorus-containing phases (e.g. Slomp et al. 1996; Eijsink et al. 1997; Schenau and de Lange 2000). However, the following solid phases could be identified as the quantitatively most important P-reservoirs in marine sediments: 1) exchangeable or loosely sorbed P, 2) P bound to ferric oxides and oxyhydroxides, 3) fish debris, 4) CFA + biogenic hydroxyapatite + $CaCO_3$-bound P, 5) detrital apatite of igneous or metamorphic origin, and 6) organic P. Figure 6.12 shows an example for the distribution of these reservoirs in surface sediments from the upwelling area off Namibia. The main release of both ferrous iron and phosphate occurs in the suboxic zone at about 2-3 cm (oxygen penetration depth was determined at 1.5 cm). This indicates that the main source of both constituents are iron oxyhydroxides being reduced at this depth. Based on the pore water profiles, diffusive fluxes are directed upward into the oxidized surface layer and downward into the anoxic zone. At the redoxinterface ferrous iron is oxidized back to oxyhydroxides and phosphate is adsorbed. The internal P-cycle is closed by downward bioturbation of mainly in-situ-formed Fe-bound phosphorus. These processes are clearly reflected particularly by the distribution of the exchangeable and reducible P-fractions. In this specific example the P-sink in the deeper part of the sediment could not be identified, but may be related to the authigenic formation of CFA. Assuming steady state conditions, quantitative budgeting of flux rates with reservoirs gives indication that P has to run several hundred times through this internal cycle across the redox interface until it is buried. A very impressive

hypothetical calculation showing the important role of iron oxyhydroxides for the P-cycle is given in Section 7.4.3.3. By studying the single P-reservoirs in marine sediments, Ruttenberg (1993) calculated the total burial flux of reactive/ bio-available P in the range of $8 – 18.5 \cdot 10^{10}$ mol yr^{-1}, which results in a reassessment of the average residence time of oceanic phos-phate as 16-38 kyr.

Finally, it is obvious that the processes described above have a strong impact on the sedimentary ratio between organic carbon and phosphorus (either as organic P also or as "reactive" P, which means the sum of authigenic, oxide-associated and organic P). While the initial organic matter can be approximated with a ratio close to Redfield (106:1), analysis on CFA gave values as low as 4:1 (Ruttenberg 1993). Therefore, several studies have discussed variations in the different types of C/P ratios as indicating temporal changes in the preservation efficiency of deposited organic matter (e.g. Ingall and Van Cappellen 1990; cf. Section 12.3.3), in the intensity of phosphorus regeneration relative to carbon (e.g. Slomp et al. 2004), or as a generally useful approach to describe the geochemical behavior of sedimentary P (Anderson et al. 2001).

6.3.2.2 Authigenic Formation of Phosphorites

There is no consistent definition for the use of the term phosphorites. Suggestions reach from a limiting P content of 6 wt.% (van Cappellen and Berner 1988) to a threshold value of 18 wt.% P_2O_5, as representative for authigenic and biogenic phosphate minerals (Jarvis et al. 1994). However, the formation of secondary P phases from initially more labile-P in marine sediments (see above) is one major sink for phosphorus on Earth, because this general process results in sequestration of P from the nutrient cycle in the water column (e.g. Compton et al. 2000).

Research on the benthic phosphorus cycle and phosphorites formation in particular was intensified especially in the seventies to early nineties of the last century (e.g. Burnet 1977; Burnett and Froelich 1988; Burnett and Riggs 1990; Nolton and Jarvis 1990; Föllmi 1996; Glenn et al. 2000). All present result clearly substantiate that the process of phosphogenesis (= the authigenic formation of carbonate fluorapatite - CFA) is highly complex and not completely understood. However, hydroxy-apatite may be the primary authigenic P-mineral phase. This initial apatite is forming intermediately under reducing conditions within the uppermost few centimeters of sediment. Following a recent study, the metabolic cycle of large sulfur bacteria may play a key role for this process (Schulz and Schulz 2005; cf. next Section). Subsequent dissolution-re-precipitation processes are thought to be responsible for the transfer into the more stable and complex carbonate-fluoride variety francolite, which is most common in phosphate-rich sediments and rocks (e.g. McClellan 1980; Kolodny and Luz 1992). The chemical composition of francolite is very complex and variable (Jarvis et al. 1994). Based on radiocarbon dating of phosphatic pellets from the Peru shelf, their formation can be very quick, on time scales of only a few years (Burnett and Froelich 1988). To investigate the different stages of phosphogenesis, many interdisciplinary studies have been performed, which include the sequential extractions mentioned before, the formation kinetics of special apatite crystals (e.g. Van Cappellen and Berner 1991), or the stable isotopic composition of sedimentary apatite reflecting the variability of environmental conditions (e.g. summarized in Kolodny and Luz 1992). Nevertheless, control factors of phosphogenesis in different environments are still under debate, particularly with regard to the overall benthic C-cycle.

Because CFA is forming at the expense of organic P, high productive areas or at least organic-rich sediments favor phosphogenesis. Therefore, it is not surprising that sites of present-day phosphorite formation are found along continental margins where the organic detrital input is sufficient for intense microbial activity and suboxic to anoxic conditions close to the sediment surface. This is particularly the case in regions of intense coastal upwelling and below permanent oxygen minimum zones (Fig. 6.13).

6.3.2.3 Release of Phosphate by Bacterial Activity

In contrast to the different sulfur and nitrogen species, phosphorus in marine environments occurs almost exclusively in the oxidation state +5. Thus, with few exceptions (Schink and Friedrich 2000), bacteria cannot gain energy by the oxidation of reduced phosphorus species and cannot use phosphate as an electron acceptor. Nevertheless, phosphorylation, the addition of a phosphate group to another compound, plays a major

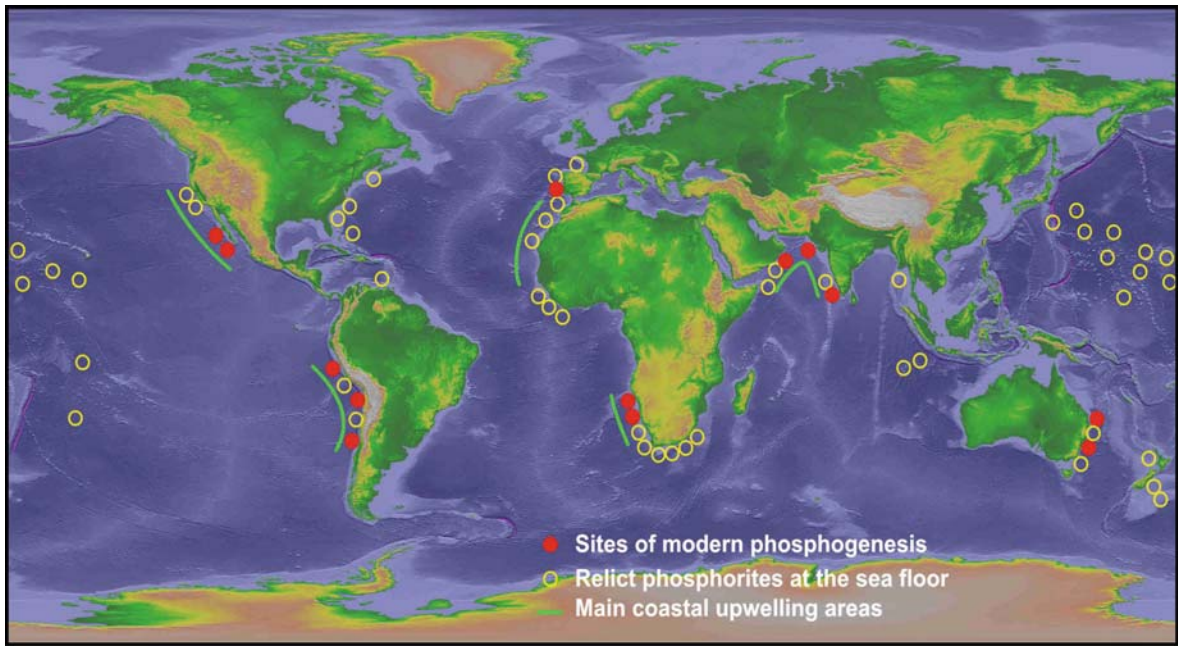

Fig. 6.13 Locations of present-day phosphorite formation, relic phosphorites at the sea-floor, and zones of coastal upwelling (modified after Baturin (1982) and Föllmi (1996)).

role in the biological energy transfer (e.g. in the formation of ATP by the phosphorylation of ADP). Alternatively, energy can be conserved in linear polymers of phosphate called polyphosphates. The build-up of polyphosphates requires energy, whereas ATP is formed in the breakdown. Although all living organisms contain polyphosphates, only some microorganisms accumulate polyphosphates in larger amounts, visible as compact inclusions (e.g. Kornberg 1995).

Bacterial phosphate accumulation and release has been studied most thoroughly in wastewater treatment plants, where polyphosphate accumulating bacteria are used since decades to remove phosphate. To induce polyphosphate accumulation in bacteria an anoxic phase has to be introduced followed by an oxic phase. During the anoxic phase end products of fermentation such as acetate accumulate in the wastewater. The bacteria take up acetate and store it, e.g. as PHA (polyhydroxyalkanoate) inclusions. The energy for the storage of acetate is gained by the break down of polyphosphate, which is accompanied by a release of phosphate. In the following oxic phase the bacteria have a suitable electron acceptor, oxygen, to oxidize PHA and can gain large quantities of energy, which is partly conserved in the build-up of polyphosphate. Consequently, phosphate disappears from the water and the sludge containing polyphosphate can be removed (e.g. Mino 2000).

Analogous to wastewater it had been proposed that polyphosphate accumulating bacteria could also play a role in the phosphorus cycle of the ocean (Nathan 1993). Particularly, large sulfur bacteria (Fig. 6.7) have been suspected to play a role in the formation of phosphorite, as they occur in the same areas where recent and active phosphorite formation is observed and have been found as fossils in phosphorite deposits (Williams and Reimers 1983). Lately, these bacteria have been shown to accumulate polyphosphate. *Thiomargarita*, the largest sulfur bacterium thriving off the coast of Namibia, was observed to release phosphate into anoxic sediments leading to an over-saturation of the pore water with phosphate and rapid precipitation of hydroxyapatite. Laboratory experiments showed that the release of phosphate by *Thiomargarita* cells could be induced by the addition of acetate to the medium (Schulz and Schulz 2005). This might indicate that the processes of bacterial phosphate accumulation and release in eutrophic marine environments are similar to those observed in wastewater.

6.4 Determination of Consumption Rates and Benthic Fluxes

6.4.1 Fluxes and Concentration Profiles Determined by *In Situ* Devices

One reason for determining changes of oxidant concentrations or consumption / production rates in the pore water fraction of a sediment is to quantify the underlying respiration processes and to define the reactive horizons. Until today, however, there is no method to determine oxic respiration directly. Total oxic respiration has to be calculated from the difference between the oxygen demand of the sediment and the amount of oxygen consumed by oxidation of reduced species (see above). There are two main methods to determine diffusive or total oxygen uptake rates in deep-sea sediments. These are (1) the application of microelectrodes and optodes to obtain one- or even two-dimensional (planar optodes) depth profiles and (2) benthic chambers to reveal total areal uptake rates (cf. Section 12.2). Clark-type microelectrodes as they are commonly in use since more than two decades (e.g. Revsbech et al. 1980; Revsbech and Jørgensen 1986; Revsbech 1989; Gundersen and Jørgensen 1990) and the more recently invented optodes (Klimant et al. 1995) have become a driving force in performing measurements of oxygen consumption and penetration depths in any kind of soft sediment. Since a couple of years the two-dimensional oxygen distribution can be determined by so-called planar optodes (Glud et al. 1996) showing an excellent correlation with measurements performed with microelectrodes. For the general principles of microelectrodes and optodes and their application in the deep sea we refer to the description in Section 3.5 and the references above.

Within the past two decades benthic lander systems have been increasingly applied in the deep-sea (e.g. Berelson et al. 1987; Jahnke et al. 1997; Reimers et al. 1992; Wenzhöfer et al., 2001a) to avoid artefacts resulting from sediment recovery (see discussion below). Some results obtained by these devices have already been shown in Chapter 3. The microelectrodes or optodes provide information on the oxygen penetration depth and its depth-dependent distribution, whereas the benthic chambers measure total fluxes across the sediment water interface. There is generally good agreement of fluxes obtained by both methods (Jahnke et al. 1990; Fig. 12.10), but total fluxes might exceed calculated diffusive fluxes from oxygen profiles. While diffusive transport of pore water is the dominant process in the large area of the oligotrophic oceans where the input of degradable organic matter to the sea-floor is low (Sayles and Martin 1995), this is not the case adjacent to continental margins. Glud et al. (1994) found that the total oxygen uptake was always larger than the diffusive uptake in continental slope sediments off Southwest Africa. The results shown in Figure 6.14a indicate a good correlation between the dry weight of macrofauna and the total oxygen uptake. Subtracting the diffusive oxygen uptake - measured with microelectrodes -

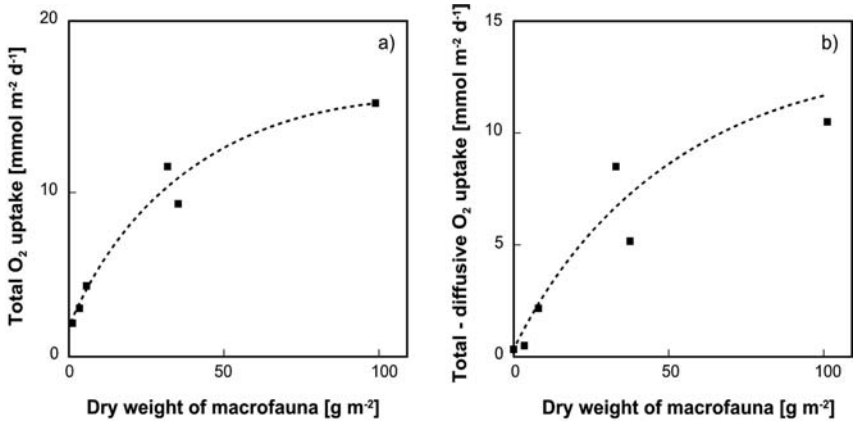

Fig. 6.14 Correlation of (a) total oxygen fluxes and (b) total-diffusive oxygen fluxes with the dry weight of organic macrofauna indicating the effect of macrobenthic activity for benthic respiration processes (adapted from Glud et al. 1994). Broken lines are fitted by eye.

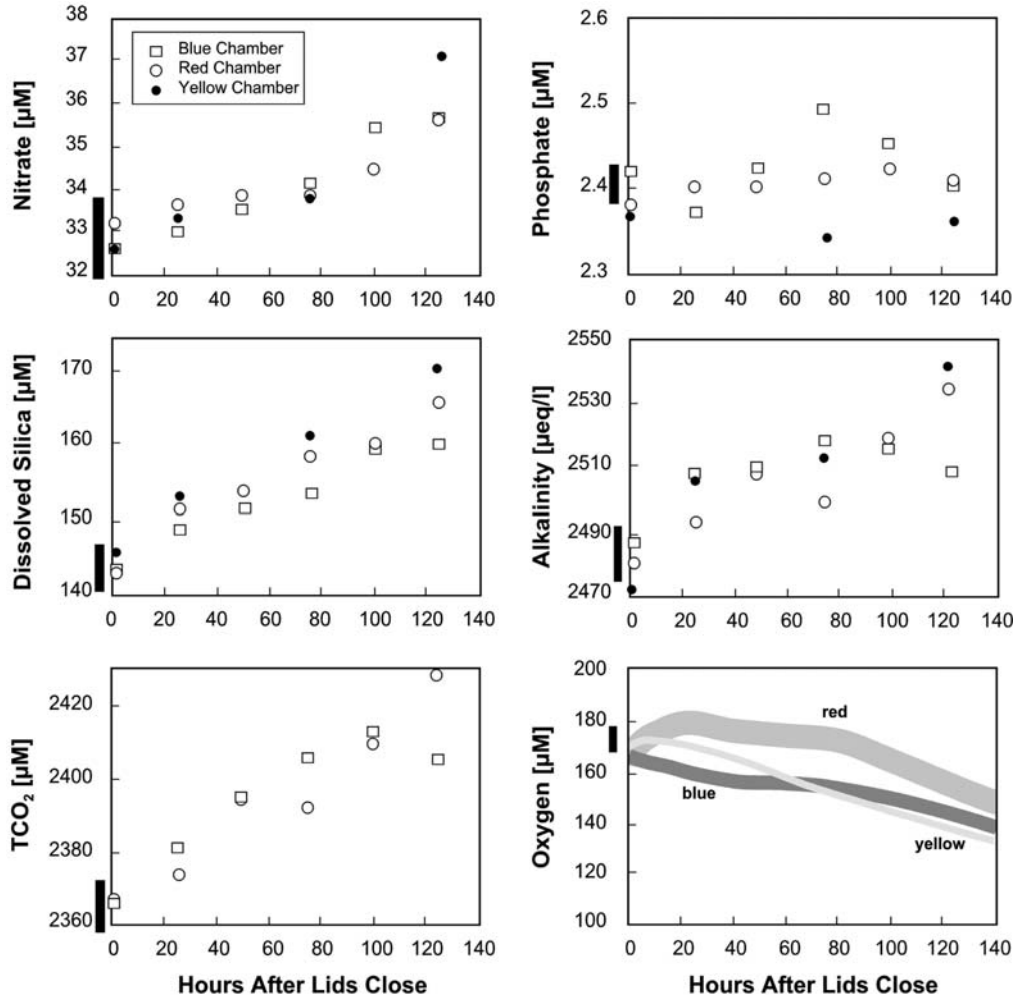

Fig. 6.15 Concentration versus time plots of different solutes measured with benthic chambers in the central equatorial Pacific (from Hammond et al. 1996). Black vertical bars indicate bottom water values.

from the total uptake rates reveals values close to zero for stations with a low dry weight of macrofauna obviously increasing with increasing population density (Fig. 6.14b). On one hand, the difference between both fluxes provides a measure of bioirrigation meaning that there is additional transport across the sediment-water interface due to active pumping of organisms and a higher oxygen demand due to an increased surface area at additional sites where oxygen is consumed (worm burrows etc.). On the other hand, the respiration by the macro- or meiofauna itself increases the oxygen consumption (Glud et al. 1994; Heip et al. 1995; Soetaert et al. 1997). Since the chamber system provides information on total mineralization rates and fluxes, and the profiling lander on the depth distribution of solutes and redox processes, the application of both lander systems is required to properly investigate the oxygen demand and the pathways of oxygen in the sediment.

The determination of *in-situ* fluxes of nitrate is comparatively limited. Although there are electrodes for the determination of micro-concentration profiles in form of biosensors (Larsen et al. 1996), they are not yet suitable to be used on lander systems in the deep sea. The measurement of total nitrate fluxes by benthic chambers in continental slope sediments off California is shown in Figure 3.24 (Jahnke and Christiansen 1989). At this site, nitrate fluxes are directed into the sediment indicating strong denitrification supported by very low oxygen concentrations in the overlying bottom water.

Under normal deep-sea oxygen conditions, the nitrate flux is generally directed out of the sediment due to nitrification and lower denitrification as shown by results reported by Hammond et al. (1996) from measurements in the central equatorial Pacific (Fig. 6.15). It is further indicated that fluxes of oxygen, silicate, or $\sum CO_2$ are easier to determine than nitrate or, particularly, phosphate, because of the magnitude of concentration change over time. Phosphate in Figure 6.15 shows large scatter and does not allow a reliable flux calculation. The differences in the order of magnitude result from the reaction stoichiometry of organic matter decomposition (Eq. 6.1). Additional processes, like the dissolution of biogenic opal and calcium carbonate in the sediments, is of further significance for the parameters silicate and alkalinity. Whereas silicate fluxes depend on the amount and the surface area of soluble opal, the degree of silica undersaturation in pore waters, and the content of terrigenous components (cf. Section 12.3.3), variations of alkalinity and $\sum CO_2$ fluxes are controlled by respiratory production of CO_2 and dissolution of calcium carbonate (cf. Section 9.3.2).

The result of the phosphate measurement shown in Figure 6.15 indicates that flux chamber measurements are restricted to a certain number of measurable parameters. Even more, this is true for profiling lander systems. Apart from oxygen, only pH-, pCO_2-, H_2S and Ca-electrodes have been successfully employed on *in situ* lander systems (Cai et al. 1995; Hales and Emerson 1997; Wenzhöfer et al. 2001a; de Beer et al. 2005). There is, however, another microelectrode technique described by Brendel and Luther (1995) which has, however, not yet been tested *in situ*. This voltammetric microelectrode technique allows the simultaneous determination of the most characteristic redox species: oxygen, manganese, iron and sulfide. Results from continental slope sediments of northeast Canada revealed clear and undisturbed vertical redox sequences, which is usually not the case when different methods are applied (Luther et al. 1997, 1998).

6.4.2 *Ex-Situ* Pore Water Data from Deep-Sea Sediments

Mostly, solutes are still determined *ex-situ* by extraction of pore water from multicorer or box corer samples (see Chapter 3). Additionally, numerous *ex-situ* measurements of oxygen and nitrate exist which were carried out by onboard core incubations or microelectrode measurements. Generally, the determination of a dissolved species in water samples does not pose a problem, if sampling is handled carefully and, in specific cases, contact with atmospheric oxygen is avoided. Manifold problems arise, however, when a sediment sample is retrieved from some thousand meters below the sea surface and subsequently during the extraction of pore water onboard a ship which leads to changes in pore water concentrations compared to *in situ* conditions. Such effects can be caused either by decompression and/or transient heating of a sample during its transport through the water column. These problems arise because of the large temperature difference between deep water and surface water in

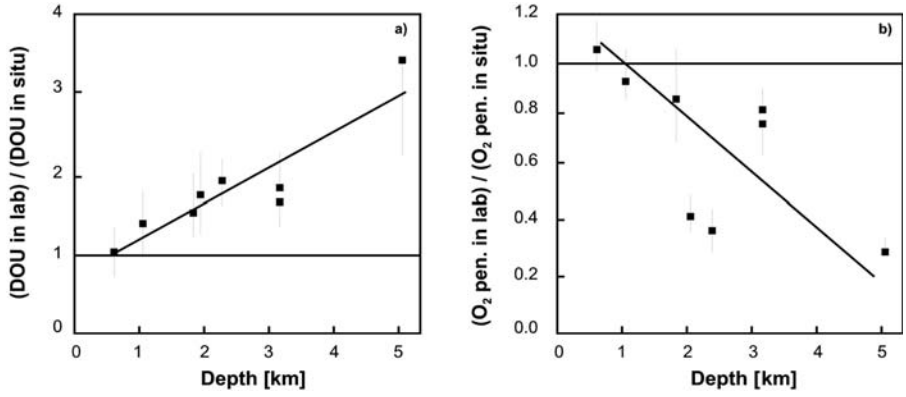

Fig. 6.16 Plots of (a) the ratio between diffusive oxygen uptake rates (DOU) *ex-situ* and *in-situ* and (b) oxygen penetration depth *ex-situ* and *in-situ* versus water depth from stations off the continental slope off Southwest Africa (from Glud et al. 1994). Solid lines indicate linear regressions. With increasing water depth fluxes appear to be overestimated and oxygen penetration underestimated when measured *ex-situ*.

most areas of the global ocean. With regard to oxygen a possible intensification of organic matter decay, triggered by the temperature increase or the lysis of cells, might result in a reduction of the oxygen penetration depth due to higher oxygen consumption. This effect has intensely been studied by Glud et al. (1994) and Wenzhöfer and Glud (2002) who could show that there might be significant discrepancies between *in-situ* and *ex-situ* measured fluxes and oxygen penetration depths. This effect is illustrated in Figure 6.16 and shows that the difference obviously increases with increasing water depth. At or above 1,000 m the sampling effect seems to be more or less negligible.

In analogy to oxygen, such artifacts are believed to exist also for nitrate profiles determined *ex-situ*. The occurrence of increased (compared to Redfield stoichiometry in Eq. 6.1) subsurface nitrate concentrations has been described in a number of studies (e.g. Hammond et al. 1996; Martin and Sayles 1996), but is mostly attributed to the centrifugation method in pore water extraction (see Section 3.3.2). Artificially increased subsurface nitrate concentration would consequently lead to an overestimation of benthic fluxes of nitrate. Berelson et al. (1990) and Hammond et al. (1996) found evidence for increased nitrate fluxes after pore water centrifugation compared to lander measurements, which were up to a factor of 3, but also agreement between both methods for quite a number of stations was found. However, the possibility of low C/N organic matter or oxidation of reduced nitrogen species (diffusing upwards from deeper layers) can be important natural factors increasing nitrate concentrations deviating from the general expected stoichiometry. Following results of Luther et al. (1997) the amount of subsurface nitrate production due to nitrification can also be regulated by the manganese oxide content of the sediment. As discussed in Section 6.3.2.3 high MnO_2 concentrations favor a catalytic reduction of nitrate to N_2 already in the oxic zone of the sediment so that nitrate peaks only occur when the solid-phase manganese content is low.

A further aspect of decompression that should be kept in mind is the degassing of CO_2 and the resulting precipitation of $CaCO_3$, which might affect pore water concentrations of phosphate by adsorption or co-precipitation (Jahnke et al. 1982). This effect can even imply negative fluxes as discussed below (see Section 6.5.1).

In general, fluxes, which are calculated on the basis of *ex-situ* data should be interpreted with caution; the overall result, however, in most cases reveals a reasonable approximation to real conditions (cf. Section 12.2).

6.4.3 Determination of Denitrification Rates

The downward flux of nitrate (e.g Fig. 6.5) indicates the depth of active denitrification, but is no measure for the total rate of denitrification. As mentioned above, denitrifying bacteria are facultative anaerobic and denitrification is generally located directly below the oxic zone (Christensen et al. 1989). The shape of a nitrate profile depends on the total rate of nitrification and the denitrification rate. Considering the example shown in Figure 6.5, the fit of the measured nitrate profile was achieved by determining an indirect nitrification rate (coupled oxidation and nitrification as described by Equation 6.1 and the C/N ratio) and denitrification occurring with a distinct rate at a depth of about 3 cm. A reduction of the denitrification rate would result in a greater nitrate penetration depth, i.e. not all the nitrate can be consumed in this depth zone. On the other hand, an increase of the denitrification rate would lead to a depression of the nitrate maximum and therefore reduce upward and downward fluxes, and finally induce a total nitrate flux from the bottom water into the sediment. To clarify these interactions we plotted three nitrate profiles from different regions of the South Atlantic in Figure 6.17. Two profiles indicate high respiration rates with a nitrate penetration depth of approximately 3 cm, but a distinct peak is visible only at one station. The station with the nearly linear gradient into the sediment is indicative for strong denitrification. The third profile shows a low gradient into the bottom water which is due to nitrification and remains nearly constant with depth indicating that denitrification does not occur close to the sediment surface.

Depletion of nitrate and the formation of dinitrogen are, however, not exclusively coupled to denitrification, since the microbially mediated reduction utilizing reduced species like Mn^{2+} or Fe^{2+} might occur. Based on field observations, a number of studies invoke the reduction of nitrate by Mn^{2+} to form N_2 instead of organic matter respiration (Aller 1990; Schulz et al. 1994; Luther et al. 1997,1998).

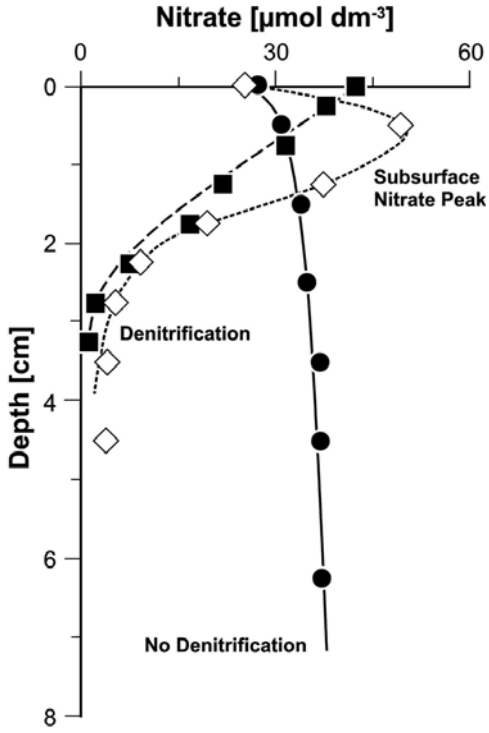

Fig. 6.17 Typical nitrate concentration profiles of surface sediments from different productivity regions in the South Atlantic Ocean. The profiles from the continental slope of the Argentine and the Cape Basin indicate denitrification at about 3 cm. The profile from an oligotrophic equatorial site shows no denitrification.

The direct determination of denitrification rates has been carried out by a number of different methods which all have certain advantages and restrictions. It is beyond the scope of this chapter to describe all of these methods in detail so that we will only give a short summary of the general principles. A more detailed overview of this subject can be found, for example, in Koike and Sørensen (1988); Seitzinger et al. (1993); and Kana et al. (1998).

The most important methods of measuring denitrification are (1) the detection of totally produced N_2 gas by incubation, (2) isotope-labeling methods with ^{15}N and ^{13}N, and (3) the acetylene (C_2H_2) inhibition technique.

(1) The first method aims at measuring the total production of N_2 as equal to the rate of denitrification (Eq. 6.6-6.8) by sediment incubation (Seitzinger et al. 1984; Devol 1991). At present, this is thought to be the best method to accurately determine rates of overall denitrification, although the contamination with atmospheric N_2 is possible during long incubation periods and thought to be the main restriction (Koike and Sørensen 1988; Seitzinger 1988). More recently, however, the technique of membrane inlet mass spectrometry, which is able to detect small changes of dissolved nitrogen with high temporal resolution and without perturbation of the sediment has been developed (Kana et al. 1994, 1998; Hartnett and Seitzinger 2003). Perturbations by atmospheric nitrogen are avoided by detecting changes of N_2/Ar ratio relative to seawater standards.

(2) The intention of the isotope methods is to add $^{15}NO_3$ or $^{13}NO_3$ to the nitrate pool of the supernatant water during incubation and to measure the ^{15}N and ^{13}N content of the total amount of produced N_2. As the half-life of ^{13}N is 10 minutes, this method is only of limited use. The ^{15}N method already applied by Goering and Pamatmat (1970) to marine sediments off Peru is, in contrast, widely accepted and was used in a number of recent incubation studies of shallow marine and freshwater environments (e.g. Nielsen 1992; Rysgaard et al. 1994). This so-called ion-pairing method (Nielsen 1992) allows the determination of the total rate of denitrification and its dependence on the nitrate concentration in bottom water. Additionally, a number of authors (e.g. Nielsen 1992; Rysgaard et al. 1994; Sloth et al. 1995) believe that it also enables to distinguish between the source of nitrate, either as coming directly from the bottom water or from nitrification. This, however, has caused an intense discussion regarding the potential of the method and the benefits of its performance (Middelburg et al. 1996bc; Nielsen et al. 1996).

(3) At last, the C_2H_2 inhibition technique takes advantage of the property of acetylene to block the reduction of N_2O to N_2 after it is injected into the sediment. The total amount of N_2O produced is then the measure for the denitrification rate as it is easy to determine by gas chromatography (Andersen et al. 1984) or by microsensors (Christensen et al. 1989). The advantage of this method is that analyses can be carried out rapidly and sensitively. Problems are: (a) N_2O reduction is sometimes incomplete, (b) a homogenous distribution of C_2H_2 in the pore water is difficult to maintain, (c) C_2H_2 inhibits nitrification in the sediment meaning that the coupled system (nitrification / denitrification) might be seriously affected due to the applied method, and (d) might lose its inhibitory properties in the presence of hydrogensulfide (Sørensen et al. 1987;

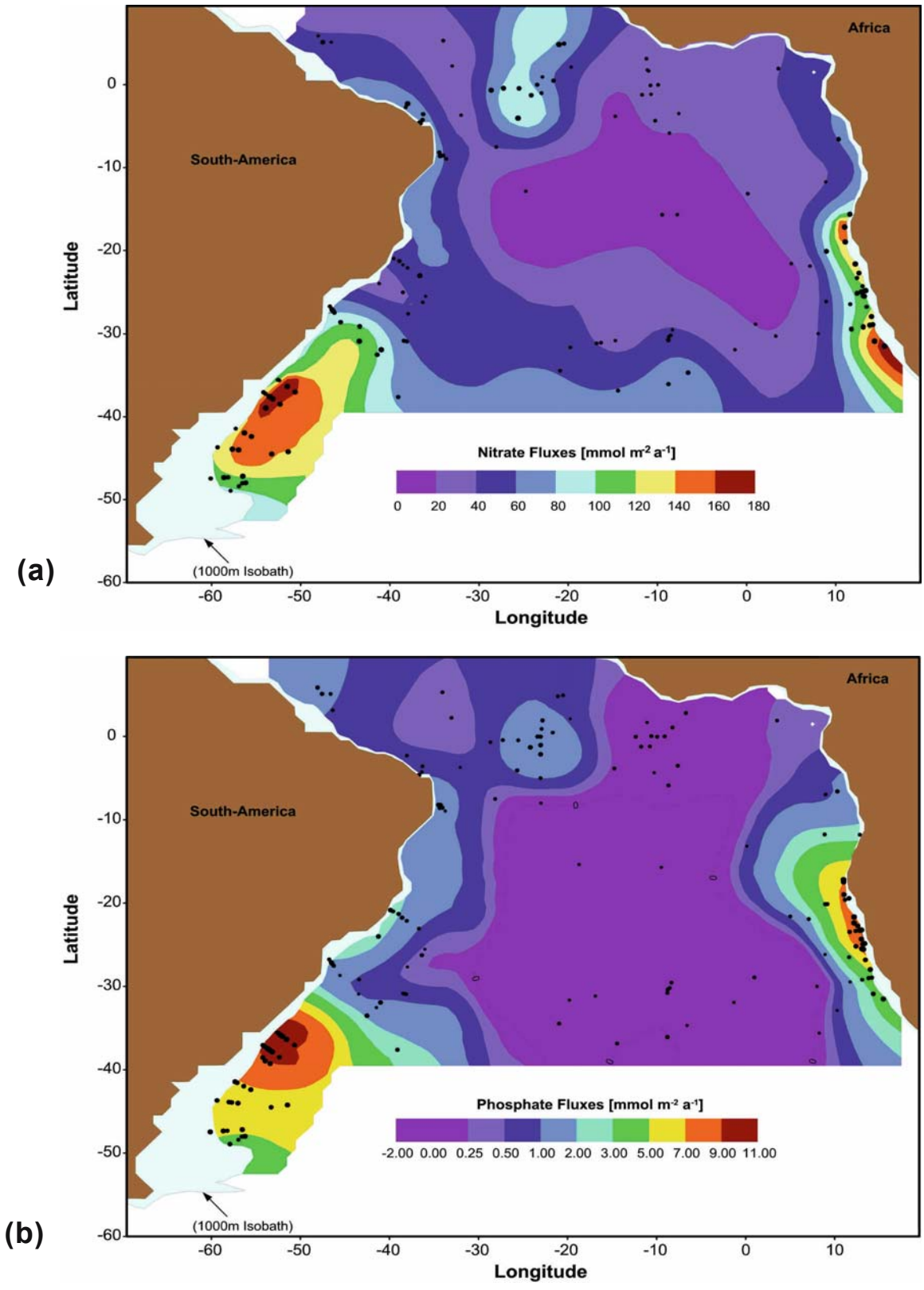

Fig. 6.18 Regional distribution of benthic nitrate (a) and phosphate (b) release rates in the South Atlantic below 1,000 m water depth (from Hensen et al. 1998).

Koike and Sørensen 1988; Hynes and Knowles 1978; Seitzinger 1988).

The application of acetylene and nitrogen labeling methods usually results in the determination of lower denitrification rates when compared to total nitrogen fluxes (Seitzinger et al. 1993; cf. Section 6.5). Apart from the above restrictions inherent to the methods themselves, the recently published concept of Luther et al. (1997) provides an additional explanation for the observed discrepancy. They tested the thermodynamic properties of several redox reactions and found evidence for a catalytic short circuit for the coupled process of nitrification-denitrification within the oxic zone (Eq. 6.12.). Organic nitrogen and ammonia released during oxic respiration are therefore oxidized to N_2 by MnO_2, instead of being further oxidized to NO_3.

$$2\ NH_3 + 3\ MnO_2 + 6\ H^+ \rightarrow 3\ Mn^{2+} + N_2 + 6\ H_2O \qquad (6.12)$$

This process may outweigh nitrification in manganese-rich surface sediments and circumvents denitrification. Elevated N_2 fluxes without increasing denitrification rates and even N_2 production in oxidized sediments as observed by Seitzinger (1988) may be explained by this process.

6.5 Significance and Quantitative Approaches

After the description of the general biogeochemical processes controlling the distribution of oxygen and nitrate in marine sediments, including the possibilities and limitations of determining these inorganic compounds in the deep-sea, the following section will give an overview of the dimensions of their fluxes and their distribution in different marine environments.

6.5.1 Estimation of Global Rates and Fluxes

The basic mechanism inducing microbial activity is the supply of organic matter to the seafloor and this is generally coupled to surface water productivity. Most of the highly productive areas in the global ocean are adjacent to the continents, so that we can expect a decrease of respiration intensity from the coastal marine environments over the continental shelves and slopes into the deep-sea. This becomes evident when we look at the data compiled by Middelburg et al. (1993) which indicate that 83% mineralization and 87% burial in marine sediments occurs in the coastal zone occupying only ~9% of the total ocean area. This means that the sediments with the highest respiration rates also have the highest burial efficiency in marine environments. For a more detailed discussion of this subject see also reviews by (Henrichs and Reeburgh 1987; Henrichs 1992; Canfield 1993). As shown in Figure 6.3 the organic matter supply is not only a function of productivity, but also of water depth generally amplifying this gradient between shallow and deep water environments.

Fluxes of oxygen and nitrate, therefore, vary over several orders of magnitude between oligotrophic open ocean areas and continental shelf and slope areas. This is about 50 to 6,000 mmol m^{-2} yr^{-1} for oxygen and -600 to 380 mmol m^{-2} yr^{-1} for nitrate (e.g. Devol and Christensen 1993; Glud et al. 1994; Berelson et al. 1994; Hammond et al. 1996; Luther et al. 1997; Hensen et al. 1998; Wenzhöfer and Glud 2002) where negative nitrate fluxes indicate fluxes into the sediment. The above minimum and maximum values do not permit differentiation between total and diffusive or *in situ* and *ex situ* fluxes. Figure 6.18 reveals the distribution of nitrate and phosphate fluxes released from sediments below 1,000 m water depth in the South Atlantic (Hensen et al. 1998) based on about 180 *ex-situ* concentration profiles. Averaged fluxes vary between 10 – 180 mmol m^{-2} yr^{-1} for nitrate and (-2)-11 mmol m^{-2} yr^{-1} for phosphate (where negative values are considered to be artifacts due to decompression and warming, cf. 6.3.2.2). Based on this compilation the total annual release for the whole area (about one tenth of the global deep ocean) is about 1.6 10^{12} mol NO_3 yr^{-1} and 3.5 10^{10} mol PO_4 yr^{-1}.

Global denitrification in marine sediments has been estimated by Middelburg et al. (1996a) to be about $1.64 – 2.03 \cdot 10^{13}$ mol N yr^{-1} with a contribution of $0.71 \cdot 10^{13}$ mol N yr^{-1} of shelf sediments. This model-based re-estimation produced values which are up to 3 to 20 times higher than those previously estimated by a number of authors in the mid-1980s. The predicted denitrification rates, however, are in the range of those derived from literature, and the total contribution to organic

matter mineralization (7-11%) is well within the range of current estimates (see compilation in Middelburg et al. 1996a). Even higher rates of $3.2 \cdot 10^{13}$ mol N yr^{-1} have been estimated more recently by Codispoti et al. (2001) who explained this upward correction mainly by the need of balancing the isotopic nitrate pool at $\delta^{15}N$ of about 5‰ (Sigman et al. 1999, 2000).

Total denitrification rates vary between 0.4 mmol $m^{-2}yr^{-1}$ in the deep-sea (Bender and Heggie 1984) and 1,200 mmol m^{-2} yr^{-1} (measured by the N_2 method) in continental margin sediments (Devol 1991) which is up to a factor of two higher than otherwise indicated by the highest fluxes of nitrate into the sediments. For estuarine and coastal areas Seitzinger et al. (1988) have summarized average rates between 440-2,200 mmol m^{-2} yr^{-1} with highest rates of up to 9,000 mmol m^{-2} yr^{-1}. However, considering the suggestions of Luther et al. (1997) a high amount of N_2 fluxes may be due to ammonia oxidation by MnO_2 in the oxic zone of the sediment bypassing denitrification and thus organic matter decay. If their estimate is correct that this process could contribute to up to 90% of N_2 production in continental margin sediments a careful evaluation and possibly a re-estimation of published denitrification rates for this environment is required.

6.5.2 Variation in Different Marine Environments: Case Studies

We already emphasized the importance of oxic respiration over other pathways in the deep-sea. Denitrification (or related processes) only account for a few percent of the carbon oxidation rate by oxic respiration, provided that oxygen is sufficiently available. In oxygen-depleted waters, the proportions can be dramatically shifted and denitrification might become an important pathway. Figure 6.19 represents data from different oceanic regions as compiled by Canfield (1993) where the ratio of carbon oxidation by oxygen and nitrate is plotted as a function of the oxygen concentration in bottom water. It clearly shows that denitrification becomes more important than oxic respiration below oxygen concentrations of about 20 µmol l^{-1}.

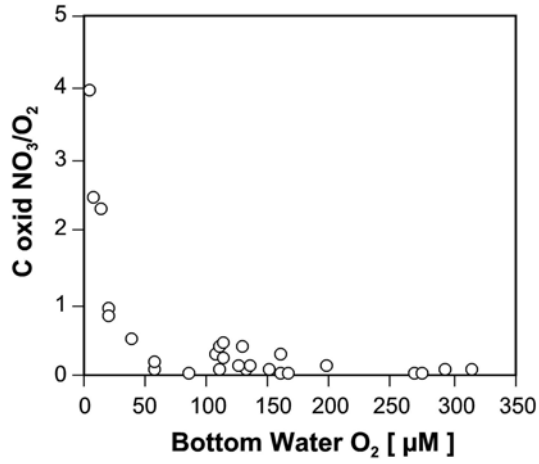

Fig. 6.19 Ratio of carbon oxidation by denitrification and oxic respiration as a function of bottom water oxygen content (after Canfield 1993).

To illustrate the general trend of decreasing respiration processes from the continental margin to the deep-sea, Figure 6.20 shows the results of *in situ* oxygen microelectrode measurements for

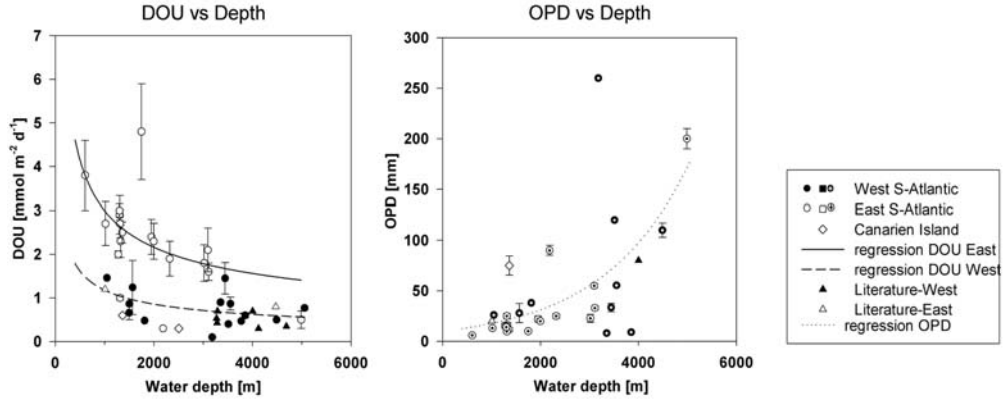

Fig. 6.20 Diffusive oxygen fluxes (a) and oxygen penetration depths (b) for a number of sites in the South Atlantic and the Canaries (from Wenzhöfer and Glud 2002). Oxic respiration decreases with increasing water depth resulting in higher oxygen penetration into the sediment.

the total South Atlantic as compiled by Wenzhöfer and Glud (2002). Both, the diffusive oxygen flux and the oxygen penetration depth at these stations can be clearly described as a function of water depth, even though scattering data points indicate some regional variability. The evident close correlation of diffusive oxygen flux and oxygen penetration depth is depicted in Figure 6.21.

Since microelectrode measurements are limited to a few centimeters of sediment depth, oxygen penetration depths have been difficult to obtain in strongly oligotrophic areas until the late 1990s. The invention of optode techniques, however, allows measurements up to several decimeters into the sediment (Fig. 6.22). The example is from a station located in the oligotrophic western equatorial Atlantic.

There is a number of studies that confirm the trend indicated in Figure 6.20, but on a regional scale there is much more variability, so that a simple relation between oxygen or nitrate fluxes and water depth cannot be found. The problem of regional flux variability will be dealt with further in Chapter 12, but generally, there is a high degree of small-scale variability related to sediment surface topography and the inhomogeneous distribution of easily degradable organic matter. Such variability can be observed when several oxygen microprofiles are recorded on a given surface area of about 10 cm^2 (the area is determined by the construction of the device; cf. Fig. 3.24) during lander deployments. This often reveals conspicuous differences in the shape of the profiles as well as the oxygen penetration depth. A more sophisticated method used to determine vertical and lateral oxygen distribution in sediments on a millimeter scale is provided by planar optodes (Glud et al. 1996; Wenzhöfer and Glud 2004). Their data show an excellent resolution of oxygen distribution within the sediment and the diffusive boundary layer. Furthermore, it shows that variations are due to differences in the surface topography. Another reason might be that other pathways, like denitrification or sulfate reduction, become more important in areas characterized by high sediment accumulation rates which are associated with a large input of degradable organic matter.

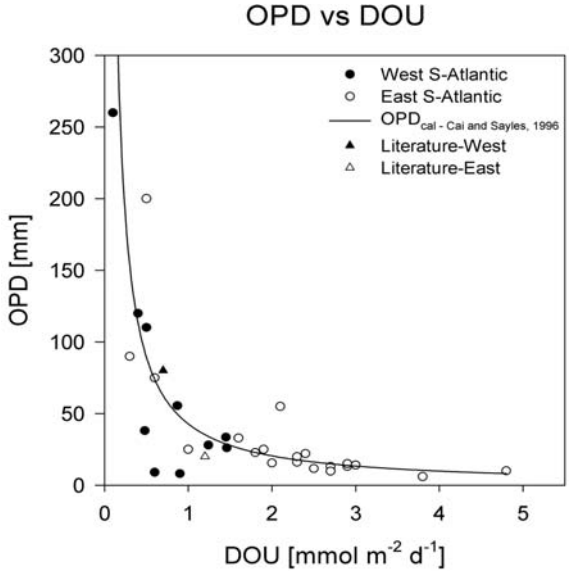

Fig. 6.21 Diffusive oxygen uptake vs. oxygen penetration depths for the same sites as shown in Fig. 6.20. The correlation follows the function found by Cai and Sayles (1996).

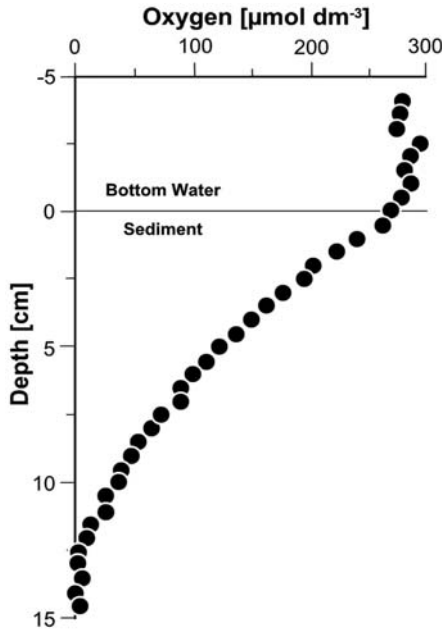

Fig. 6.22 Oxygen concentration profile measured with an *in situ* optode technique (after Wenzhöfer et. al. 2001b).

A general relation of the benthic oxygen flux to the availability of oxygen in the bottom water (as the limiting oxidant) and to the organic carbon content in the surface sediments (as limiting phase for respiration processes has been established by Cai and Reimers (1995). The highest oxygen fluxes across the continental margin of the Northeast Pacific were measured on the lower continental slope where the conditions for oxic respiration were optimal, because of the quanti-

tative ratio between oxidant and organic matter availability (Fig. 6.23). On the upper slope, organic matter is available in excess, but oxygen is the limiting phase and reduces the total oxygen uptake in this area. The opposite situation can be observed for the deep ocean. Cai and Reimers (1995) also developed an empirical equation representing this obvious relationship between oxygen flux on the one hand and oxygen bottom water concentration and surface organic carbon content on the other hand with:

$$FO_2 = \frac{\pi \cdot [TOC] \cdot [O_2]_{BW}}{(126 + [O_2]_{BW})} \qquad (6.13)$$

where FO_2 is the oxygen flux in mmol m^{-2} yr^{-1}, $[TOC]$ is the concentration of organic matter in wt.% (dry sediment) and $[O_2]_{BW}$ is the oxygen concentration in bottom water (in µM).

More recently Seiter et al (2005) refined this approach based on a much larger data set:

$$FO_2 = \frac{((\ln([TOC]+k_3)) \cdot k_1 + k_2)[O_2]_{BW}}{k_{ox} + [O_2]_{BW}} \qquad (6.14)$$

$$with k_{ox} > 0,\ k_1 > 0, [TOC] > [TOC]_{\lim}$$

where k_1, k_2 (both in mmol m^{-2} yr^{-1}), and k_3 (in wt%) are rate constants for the decay of organic matter and k_{ox} (in µM) is the saturation constant of oxygen in the bottom water.

Similarly, their approach considers depleted oxygen levels in the bottom water and the accumulation of organic matter above a certain threshold value $[TOC]_{\lim}$, which has a global mean of about 0.6 wt.% (Seiter et al. 2005).

In regions without limitation by bottom water oxygen depletion, as prevailing in large portions of the Southern and Northern Atlantic, Equation 6.14 can be simplified to

$$with\ k > 0, [TOC] < [TOC]_{\lim} \qquad (6.15)$$

Both relations given above have been successfully applied to data sets in the Northeast Pacific and the Atlantic (cf. Section 12.5.2 and Fig. 12.18).

Looking at the above situation, we need to emphasize that any confusion with the total rate of carbon oxidation – which is probably higher in the upper slope sediments – must be avoided. As

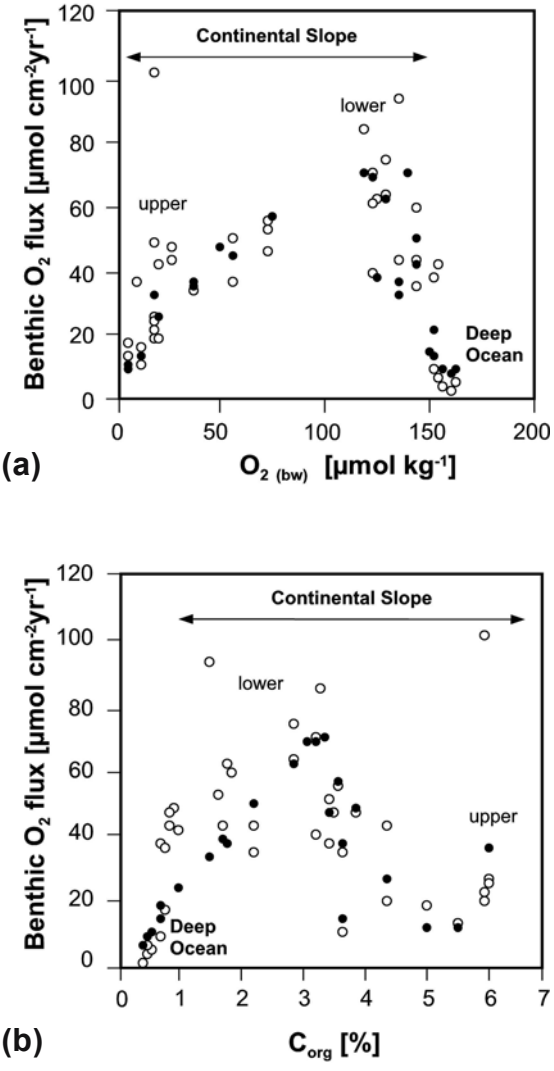

Fig. 6.23 Distribution of benthic oxygen fluxes across the continental slope in the Northeast Pacific related to (a) oxygen bottom water concentration and (b) organic carbon content in the surface sediments. Highest oxygen respiration occurs at the lower continental slope. Solid circles were calculated by applying Equation 6.12 (after Cai and Reimers, 1995).

stated previously, the mineralization rate and the burial rate are correlated to the input of organic carbon input, so that areas with the highest deposition of organic matter consequently have highest mineralization rates, but also the highest burial potential (Fig. 6.6). A further constraint for the standardization of empirical relations as given by Equation 6.12 or 6.13 is that temporal constancy, namely steady-state conditions, are required. The time dependent variability of early diagenetic proces-

ses, however, has been identified even in deep-sea sediments (e.g. Smith and Baldwin 1984). The important question in this regard is: How fast does oxic respiration react to the input of labile organic matter? If the reaction constant is high, organic matter will be quickly recycled at the sediment surface. If furthermore, the input of organic matter is episodic or seasonal, a highly variable oxygen flux at a given time interval might occur. Since organic particles are subject to burial, mixing, and other respiratory processes the surface content will always result in a more or less time-integrated value that does not necessarily reflect the oxygen flux at the time of a single measurement.

More recently, Soetaert et al. (1996) demonstrated the dependence of degradation rates of different mineralization pathways, as well as oxygen, nitrate, and other fluxes on seasonal variations in organic matter deposition and its reaction rate. Some of the model results compared to the measured carbon flux to the sediment and the oxygen uptake rates are plotted in Figure 6.24. The study was based on data derived from box corer and benthic chamber deployments in the abyssal Pacific and covered a time span of more than two years. The carbon flux function was derived from sediment trap data and sedimentation rates, whereas oxygen fluxes were obtained by the adaptation of total mineralization rates of organic material arriving at the sediment surface (and a number of other input parameters). A higher rate would account for variation as reflected by the carbon flux curve, whereas a low rate would continually reduce the seasonal variability.

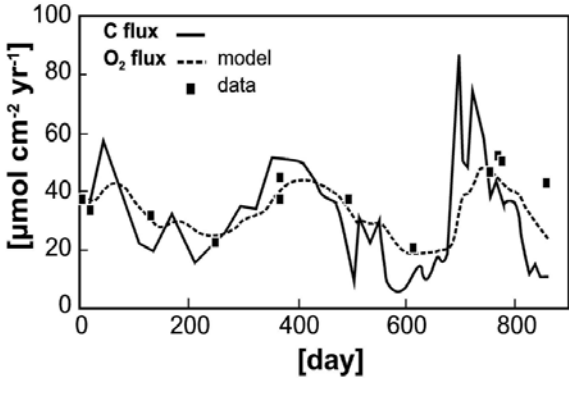

Fig. 6.24 Model results of Soetaert et al. (1996) for a site in the abyssal Pacific. The curve of mineralization rates (oxygen fluxes) is smoother and shows a slight shift compared to the sedimentary carbon flux caused by the effective reaction kinetics. Squares indicate oxygen fluxes determined on the basis of benthic chamber and box corer data.

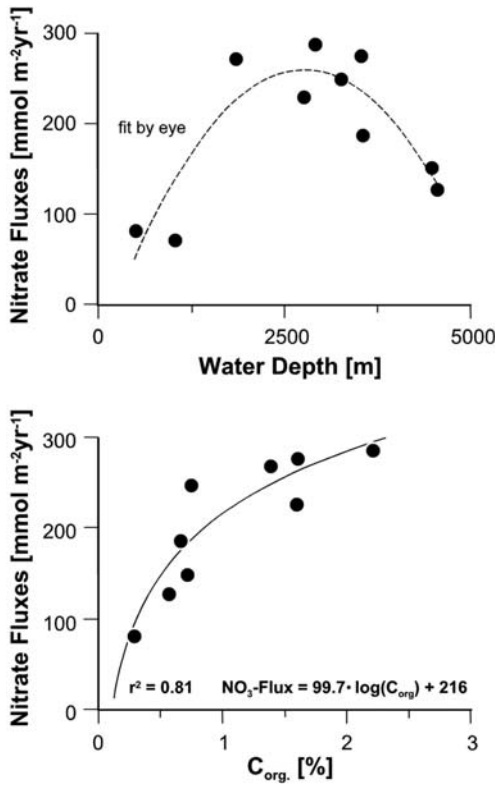

Fig. 6.25 Plot of diffusive benthic nitrate fluxes against (a) water depth and (b) organic carbon content in surface sediments off the Rio de la Plata mouth (Argentine Basin).

A situation different from that in the Northeast Pacific which does not comply to a general relationship can be found in the Argentine Basin. As shown in Figures 6.18 and 12.14, distribution maps of nutrient release from deep-sea sediments in the South Atlantic indicate high mineralization rates in this area. Figure 6.23a shows diffusive nitrate fluxes on several transects across the continental slope in front of the Rio de la Plata mouth. The highest release rates of nitrate were detected at intermediate and low depths of the slope. In contrast to the situation in the Northwest Pacific, there is no oxygen limitation in the bottom water of the Argentine Basin, suggesting that other processes must be responsible for the observed flux distribution. In this case, it is assumed that intense downslope transport processes deliver large amounts of sediments and organic matter to the lower slope where most of the degradable material is deposited, whereas the

upper slope surface sediments are partly depleted in organic carbon (Hensen et al. 2000; cf. section 12.3.2). This is indicated by the good correlation of nitrate fluxes with organic carbon content in the surface sediments (Fig. 6.25b).

The above examples have shown that there are large discrepancies between benthic biogeochemical processes in areas of high and low productivity, but there are no simple relationships or master variables to correlate benthic fluxes and mineralization rates with primary productivity or sediment parameters. However, the quantitative coupling between these processes will be a main objective of future research (cf. Chapter 12).

6.6 Summary

In this chapter we have summarized the general availability of oxygen, nitrate and phosphate in the oceans and aspects of their significance in the biogeochemical cycles of marine sediments. Oxic respiration is by far the most important pathway of organic carbon in deep-sea sediments and significantly determines the recycling of organic matter introduced onto the sediment surface. Even if some uncertainty remains, benthic oxygen fluxes reveal probably a reasonable approximation to the total carbon oxidation rate under deep-marine conditions. However, benthic fluxes vary considerably in the various ocean basins and the interactions between all parameters controlling benthic biogeochemical activities are not yet completely understood. Above, we showed some examples in which benthic activity deviates from the generally expected situation as suggested by export fluxes from the surface waters. We further elaborate these concepts in Chapter 12 where we summarize existent approaches for the regionalization of benthic fluxes and present methods how to access mineralization processes in surface sediments of the deep-sea globally and arrive at a definition of benthic biogeochemical provinces.

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6.7 Problems

Problem 1

Explain why oxygen consumption can be used as a measure for the sum of mineralization processes occurring in the sediment. Why is this - strictly speaking - not correct, but provides feasible results? In which areas of the seafloor would this method fail?

Problem 2

Explain the terms carbon limited and oxidant limited and give examples, where you would expect carbon- and oxidant-limited diagenesis.

Problem 3

Denitrification is a major pathway of carbon degradation in sediments of shallow-marine continental margin areas. Why is it so important for biogeochemical element cycles in the ocean, particularly in terms of regulation of nutrient levels and primary productivity?

Problem 4

Would you expect a higher (than Redfield) $C_{org.}/P_{org.}$ ratio in marine sediments under oxic or anoxic bottom water conditions?

Problem 5

Under which environmental conditions would you expect anammox (anaerobic ammonia oxidation) to be an important process?

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