8 Sulfur Cycling and Methane Oxidation

Bo Barker Jørgensen and Sabine Kasten

This chapter deals with the biogeochemical transformations of sulfur and methane in marine sediments during early diagenesis. The term 'early diagenesis' refers to the whole range of post-depositional processes that take place in aquatic sediments and are coupled either directly or indirectly to the degradation of organic matter. We focus on the processes that drive sulfate reduction together with the manifold associated biotic and abiotic reactions that make up the sedimentary sulfur cycle – including the various pathways of sulfide oxidation. Furthermore, we give an overview of the quantitative significance of microbial sulfate reduction for the mineralization of organic matter and oxidation of methane in different depositional environments and discuss the different approaches to quantify sulfate reduction through radiotracer measurements or modeling of pore-water concentration profiles. As sedimentary pyrite represents the most important sink for seawater sulfate, the mechanisms of pyrite formation are discussed. The sulfidization of sediment organic matter is another sink for sulfur in the modern ocean, but will not be discussed here. For an overview of the processes and pathways involved in the incorporation of sulfur into organic matter, we refer to Orr and White (1990), Krein and Aizenshtat (1995), Schouten et al. (1995), and Werne et al. (2004).

Due to the profound alteration of the primary sediment geochemistry across and below the sulfate/methane transition (SMT, also called the sulfate/methane interface), where the process of anaerobic oxidation of methane (AOM) takes place, we also dedicate a part of this chapter to the processes of mineral dissolution and precipitation occurring at and below the SMT. We will demonstrate that sulfate reduction driven by AOM significantly alters primary mineral associations accompanied by strong perturbations of mineralogical, isotopic and rock magnetic signatures. These diagenetic processes have a profound impact on the preservation of numerous paleoceanographic proxy variables and are therefore relevant for the interpretation of the geological record.

Reviews of the sulfur cycle from a biogeochemical or microbiological perspective have recently been presented, e.g. by Amend et al. (2004) and Canfield et al. (2005). The latter authors describe the relationship between the different microorganisms metabolizing sulfur compounds and their environment and emphasize the organisms as well as the biogeochemical processes.

8.1 Introduction

With $1.3 \cdot 10^9$ Tg (teragram = megaton = 10^{12} g) of sulfur present as sulfate, the oceans represent one of the largest sulfur pools on earth (Vairavamurthy et al. 1995). The main influx of sulfur to the oceans occurs via river water carrying the products of mechanical and chemical weathering of continental rocks. Relative to this fluvial input, the atmospheric transport of sulfur is of minor importance. It mainly consists of recycled oceanic sulfate from seaspray, volcanic sulfur gases, H_2S released by sulfate-reducing bacteria, organic S-bearing compounds released into seawater and subsequently into the atmosphere by phytoplankton, and anthropogenic emissions of sulfur dioxide. Due to the oxic conditions that prevail in the world's oceans, the dominant sulfur species in seawater is by far the sulfate ion (SO_4^{2-}). Sulfate is the second most abundant anion next to chloride and has a concentration of 29 mM (2.71 g/kg) in ocean water.

Marine sediments are the main sink for seawater sulfate which demonstrates that the sedimentary sulfur cycle is a major component of the global sulfur cycle. The most important mechanisms for removing sulfate from the oceans to the

sediments are (1) the bacterial reduction of sulfate to hydrogen sulfide, which subsequently reacts with iron to form sulfide minerals, particularly pyrite (FeS_2), (2) the formation of organic sulfur, i.e. the incorporation of sulfur into sedimentary organic matter during early diagenesis, and (3) the precipitation of calcium sulfate minerals in evaporites (Vairavamurthy et al. 1995). With respect to the relative importance of each pathway, Vairavamurthy et al. (1995) point out that although marine evaporites were important sinks for sulfate from the Late Precambrian to the late Tertiary, their rate of formation in today's oceans, over the last few million years, is quantitatively insignificant. Thus, they conclude that the burial of sulfide minerals and, to a less extent, of organic sulfur represents the major sink for oceanic sulfur in the modern ocean.

8.2 Sulfate Reduction and the Degradation of Organic Matter

Throughout the water column of the ocean, ten billion tons of organic particles derived from plankton production in the photic surface layer steadily sink towards the sea floor. The annual deposition of organic material on the sea floor is also about ten billion tons, i.e. of the same magnitude as the total organic particle pool in the ocean. As the particles sink through the water column, the organic material is gradually degraded and respired back to CO_2 and nutrients by zooplankton and by microorganisms. Thus, with increasing distance from the coast and with increasing water depth, a gradually decreasing fraction of the sinking particles remains to ultimately land on the sea floor. On the shallow continental shelves this fraction is generally in the range of 20-50% of the phytoplankton productivity in the overlying water (Jørgensen 1983). In the deep sea the fraction is only 1-2% (Jahnke 1996). Deep sea sediments, therefore, play only a minor quantitative role in the oceanic carbon and nutrient cycles, as the following discussion will show.

As the particulate organic matter is deposited on the sea floor it is immediately attacked by a broad range of organisms that all contribute to its degradation and gradual mineralization. At the sediment surface, macrofauna plays a particular role by mechanically disintegrating the detritus and by mixing of the upper sediment layer through their burrowing and feeding activity (bioturbation), whereby the organic material becomes repeatedly exposed to oxygen. The benthic fauna also irrigates the burrows in order to transport oxygen down for

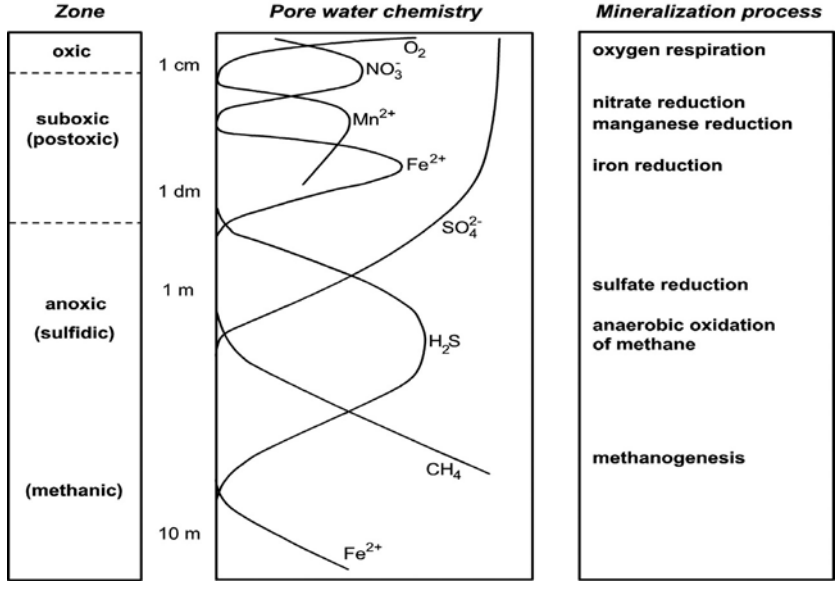

Fig. 8.1 Schematic representation of the biogeochemical zonation in marine sediments. The names of the main zones were proposed by Froelich et al. (1979) and Berner (1981, in parenthesis). The depth scale is quasi-logarithmic; the exact depths, however, vary strongly and increase from the shelf to the deep sea. The pore water chemistry shows relevant dissolved species. Peak heights and concentration scales are arbitrary. The chemical profiles reflect the depth sequence of the dominant mineralization processes through which organic matter is oxidized to CO_2 (Modified from Froelich et al. 1979).

respiration, and possibly food particles, and thereby extend the oxic zone (i.e. the zone containing O_2) deeper down into the sediment. Due to this macrofaunal activity, an extended surface layer of sediment remains oxidized (i.e. with positive redox potential and with many chemical species such as iron or manganese in their oxidized state). The macrofauna thus has a critical influence on the early diagenesis in sediments and affects both the pathways and the rates of many processes.

8.2.1 Geochemical Zonation

Apart from the heterogeneous chemical structure caused by faunal activity, marine sediments have a distinct biogeochemical zonation of the main aerobic and anaerobic mineralization processes. Fig. 8.1 shows how the dominant oxidants for mineralization change with depth, regulated partly by their concentration in sea water and partly by the energy yield of the process by which they are consumed (cf. Chapter 5). Many microorganisms gain energy from the oxidation of organic matter with an external oxidant (electron acceptor). Thermodynamically, oxygen is the most favorable electron acceptor. The supply of oxygen from seawater to the sediment is, however, highly transport-limited. In coastal marine sediments or in ocean areas of high productivity, e.g. upwelling regions, a high organic matter flux or low oxygen content of the bottom water reduces the thickness of the oxic surface layer of the sediment to only a few mm or cm. In deep sea sediments the depth of oxygen penetration may be a dm or a m or even more (Chapter 6).

Where oxygen has been consumed by aerobic respiration, the sediment is anoxic, i.e. O_2-free, and microorganisms utilize other terminal electron acceptors for the mineralization of organic matter. Listed in an order of decreasing energy gain these are: nitrate (NO_3^-), manganese oxides (represented by Mn(IV)), iron oxides (represented by Fe(III)), and sulfate (SO_4^{2-}) (Fig. 8.1). The sediment layer where NO_3^-, Mn(IV) and Fe(III) reduction predominate has been termed the suboxic zone (Froelich et al. 1979). Although these electron acceptors are energetically more favorable than sulfate, they are usually less important biogeochemically because of their limited supply to the sediments. The processes of O_2, NO_3^- and Fe(III) reduction are discussed in detail in Chapter 6 and 7.

Below the suboxic zone, sulfate reduction is the main pathway of organic carbon oxidation and it generally extends many meters down into the sediment. The high concentration of sulfate in seawater makes it a dominant electron acceptor (Henrichs and Reeburgh 1987). With an average concentration of about 29 mmol/l (Vairavamurthy et al. 1995), sulfate concentrations in seawater are more than two orders of magnitude higher than in freshwater (about 0.1 mmol/l) (Bowen 1979). The mineralization of organic material by sulfate in marine sediments is, therefore, much more important than in freshwater.

In the even deeper subsurface sediment, where also sulfate is exhausted, there is little net oxidation of the organic carbon but rather a degradation to CH_4 and CO_2. As a stable end product of carbon degradation in the absence of oxidants, methane tends to accumulate in deep sub-surface sediments from where it slowly diffuses up towards the sulfate zone. Upon entry into the lower sulfate zone, however, also methane becomes oxidized completely to CO_2. The organic material initially deposited on the sediment surface thus undergoes an efficient progressing degradation as it becomes buried deeper and deeper down through this sequence of diagenetic processes. Only a small fraction escapes mineralization and remains after thousands or millions of years to contribute to the great pool of fossil organic carbon in marine sediments.

The main degradation of organic material takes place as it gradually becomes buried down through the oxic and suboxic zones. The fraction that still remains once it reaches the sulfate reduction zone therefore depends on how deep oxygen, nitrate, manganese and iron reduction predominate. In coastal sediments with high organic sedimentation these oxidants are rapidly depleted and the main sulfate reduction zone starts already a few cm below the sediment surface. Although it is not so apparent from the chemical zonation, sulfate reduction also occurs in suboxic and even in oxic sediment where the produced sulfide is rapidly reoxidized (Jørgensen and Bak 1991). In the deep sea, the metal oxides may be exhausted only several meters below the surface and little organic material is available once it becomes buried down into the sulfate reduction zone. The overall sulfate reduction in sediments is therefore very sensitive to the organic deposition rate and is geographically strongly shifted towards the continental margins and shelf sediments. In fact, a large part of the deep sea floor lies under low-productivity ocean regions where

the organic sedimentation is so scanty that sulfate reduction is hardly detectable throughout the entire sediment column. Fig. 8.2 shows such an example, with data taken from an expedition of the Ocean Drilling Program in the eastern tropical Pacific Ocean.

Fig. 8.2 shows some of the main chemical changes with depth in the 320 m thick deposit overlying old ocean crust of Miocene age. The mineralization of organic carbon and organic nitrogen is apparent from the increase in pore water concentration of total CO_2 and ammonium. It is striking that these concentrations drop back towards sea water values at the bottom of the sediment column. This is due to a slow advection of sea water through the porous ocean crust which removes these products of mineralization and thereby influences the entire chemistry of the sea bed and its exchange with sea water in this part of the Pacific Ocean. Surprisingly, the microbial activity at the bottom of the sediment column is so low that even nitrate (and possibly oxygen) remains in the crustal fluid and provides an additional source of oxidant from below (Fig. 8.2, middle frame). The Mn^{2+} gradient in the upper 100 m and its slight increase at 200-300 mbsf show the importance of manganese reduction throughout this deep sea sediment. Consequently, sulfate reduction is inhibited by electron acceptors with higher energy yield, and even a sediment layer of 320 m thickness generates only a marginal drop in sulfate concentration (Fig. 8.2, right frame). Methane producing microorganisms are even more strongly inhibited and, although present throughout the entire sediment deposit, methane does not exceed a trace concentration of 0.2 µM.

8.2.2 Dissimilatory Sulfate Reduction

Two types of sulfate reduction can be distinguished: (1) assimilatory sulfate reduction which serves the biosynthesis of sulfur-containing organic compounds that are part of the cell biomass, and (2) dissimilatory sulfate reduction from which microorganisms conserve energy and release H_2S to the environment. With respect to the mineralization of organic matter and the main source of H_2S in sediments, only dissimilatory sulfate reduction plays a role and is the process referred to when we discuss microbial sulfate reduction. The sulfate reducing bacteria use sulfate as the terminal electron acceptor for their anaerobic respiration (see Chapter 5). As energy and carbon source they use mostly short-chain fatty acids (acetate, formate, propionate, butyrate) and other small organic molecules that are produced from the degradation and fermentation of sediment organic matter. H_2 is also a product of fermentation and serves as an important energy source for sulfate reduction in marine sediments.

Most of the known dissimilatory sulfate reducers are bacteria, but also some thermophilic archaea belong to this group (Rabus et al. 2004; Stetter et al. 1993). For an overview of the most

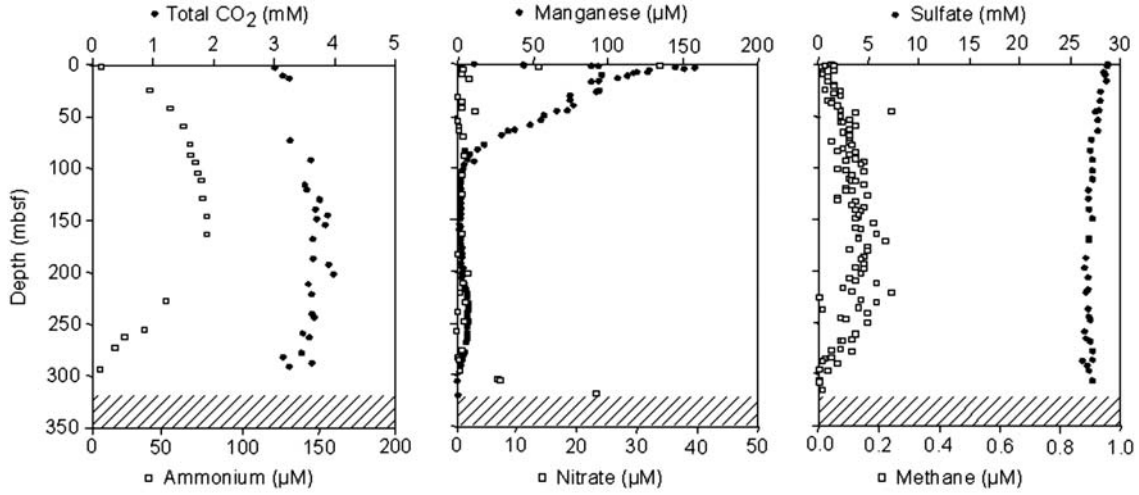

Fig. 8.2 Pore water chemistry of a deep sea sediment from the eastern tropical Pacific Ocean (ODP Site 1225). The core was obtained during Leg 201 of the Ocean Drilling Program and spans the entire sediment deposit, from the sediment surface at 3760 m water depth down to the 11 million years old basaltic crust (hatched) at 320 mbsf (meter below sea floor). Data from D'Hondt et al. (2003).

Table 8.1 Mineralization of deposited organic carbon (C_{org}) in marine sediments and the role of sulfate reduction. Data range from the shelf to the deep sea and are listed according to decreasing significance of sulfate reduction. The Black Sea is included at the end as an example of an anoxic basin totally dominated by sulfate reduction. The data are based on radiotracer measurements of sulfate reduction rates (* represents a modeled rate).

Location	Water depth	Rate of C_{org} degradation	C_{org} mineralized by sulfate reduction	Reference
	[m]	[mmol m^{-2} d^{-1}]		
Cape Lookout Bight	9	114	72%	Crill and Martens (1987)
Chilean shelf	34-122	10	56-79%	Thamdrup and Canfield (1996)
Baltic Sea	16	9.8	44%	Jørgensen (1996)
Gulf of Maine	50-300	10.7	43%	Christensen (1989)
St. Lawrence Estuary	335	10	26%	Edenborn et al. (1987)
E. South Atlantic	850-3000	0.28-3.1	9-40%	Ferdelman et al. (1999)
Eastern tropical Pacific	3760	0.5	0.05%*	D'Hondt et al. (2004) Jahnke (1996)
Black Sea, anoxic	130-1176	1.30-2.86	~100%	Jørgensen et al. (2004)

common sulfate-reducing bacteria in marine sediments we refer to Widdel (1988). Besides sulfate there are also other oxidized sulfur compounds, e.g. thiosulfate ($S_2O_3^{2-}$) and elemental sulfur (S^0), that can serve as the terminal electron acceptor (Ehrlich 1996). They are, however, not of similar quantitative importance as sulfate.

Dissimilatory sulfate reduction can be described by the following net equation:

$$2\,[CH_2O] + SO_4^{2-} \rightarrow 2\,HCO_3^- + H_2S \qquad (8.1)$$

where $[CH_2O]$ simply represents organic material. When the sulfate reducing bacteria are growing, a part of the $[CH_2O]$ will be assimilated to produce cell material. Hydrogen, in contrast, is used only as an energy source and the cell assimilates CO_2 or an organic subtrate:

$$4\,H_2 + SO_4^{2-} + 2\,H^+ \rightarrow 4\,H_2O + H_2S \qquad (8.2)$$

8.2.3 Sulfate Reduction and Organic Carbon Mineralization

Continental margin sediments play a major role for the overall budget of the global carbon cycle in the modern ocean. Most burial of organic carbon takes place on the continental shelf, in particular in deltaic and other coastal sediments (Berner 1982; Hedges and Keil 1995). Thus, 82% of the buried organic carbon is stored in shelf sediments and 16% in continental slope sediments (Wollast 1998). Only 2% of the marine organic carbon burial takes place in deep sea sediments. It is important to note, however, that during glaciations the sea level has in the past dropped by more than 100 m and thereby exposed vast shelf areas to erosion and transport of stored material into deeper water. The current burial of organic material in shelf sediments is, therefore, in a geological perspective a transient state that may undergo major reallocation during a future glaciation. On the other hand, in case of a long-term global warming the sea level would rise and the area and sediment accumulation on the continental shelves would increase.

The aerobic and anaerobic mineralization of organic material is also strongly focused towards the ocean margins. Table 8.1 presents examples of the areal rates of organic carbon degradation in a number of representative sediments, ranging from coastal embayments to the deep sea. The table also shows the fraction of the overall organic carbon mineralization that takes place by sulfate reduction. Sulfate reduction predominates especially in sediments underlying highly productive and/or oxygen-depleted coastal waters, e.g. in the Black Sea, Cape Lookout Bight, or the upwelling areas of the Chilean shelf. In other shelf sediments sulfate reduction generally accounts for 25-50% of the mineralization (Jørgensen 1982). The relative importance of sulfate reduction drops to <1% as we move down the continental slope and it

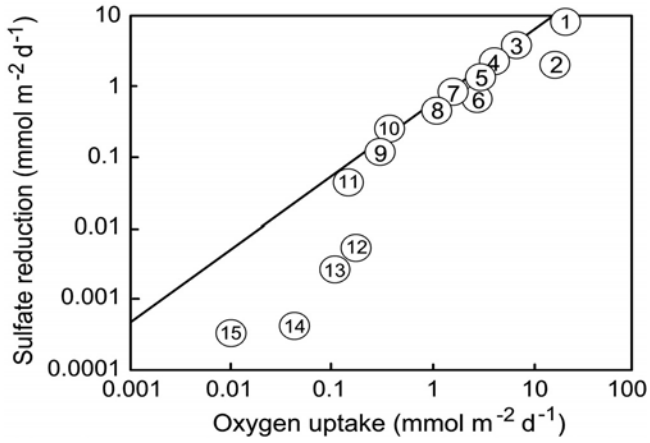

Fig. 8.3 Sulfate reduction versus oxygen uptake rates in marine sediments grouped according to ocean margin type and water depth: (1) Salt marsh; (2) mangrove; (3) shallow, high deposition; (4) seagras beds; (5) intertidal; (6) estuaries and embayments; (7) upwelling; (8) shelf - depositional; (9) shelf - non depositional; (10) upper slope (200-1000 m); (11) lower slope (1000-2000 m); (12) rise (2000-3000 m); (13) abyss (3000-4000 m); (14) abyss (4000-5000 m); (15) abyss (>5000 m). The line indicates equimolar mineralization rates of organic carbon by oxygen consumption and by sulfate reduction. The double-logarithmic plot is based on data compiled by Canfield (1993) and Canfield et al. (2005).

is insignificant in vast regions of the deep sea. The additional source of H_2S from the anaerobic degradation of organic sulfur plays a minor role relative to this dissimilatory sulfate reduction.

Radiotracer measurements of sulfate reduction rates have mainly been carried out in shallower waters, so that the data base for sediments below 500 m water depth is very limited. A detailed study was done by Ferdelman et al. (1999) between 855 and 4766 m water depth on the continental margin of southwest Africa. This area forms part of the Benguela upwelling system. The authors demonstrated that the depth-integrated sulfate reduction rates over the upper 20 cm of the sediment strongly correlated with the concentrations of organic carbon in the surface sediments. They further estimated that sulfate reduction at for example 3700 m water depth accounts for 3 to 16 % (Table 8.1) of total oxygen consumption. Thus, even on the lower continental slope in this region, a small but significant fraction of organic matter is degraded anaerobically through sulfate reduction.

Canfield (1993) and Canfield et al. (2005) have compiled published data on oxygen uptake and sulfate reduction in marine sediments and grouped these into different coastal types and into different depth regions of the ocean. Based on their data, Fig. 8.3 presents the relationship between aerobic mineralization and sulfate-based anaerobic mineralization in sediment types comprising the entire ocean floor. The sulfate reduction rates were determined experimentally by the radiotracer method in shelf and slope sediments whereas they were modeled from pore water sulfate profiles in deep sea sediments (see Section 8.6). It is striking that shelf and slope sediments generally fall along or slightly below a line of equimolar carbon mineralization by oxygen and by sulfate, thus confirming that sulfate reduction in ocean margin sediments accounts for 25-50% of the entire organic carbon mineralization. Mangrove sediments provide an exception as they have predominant aerobic mineralization, perhaps due to an efficient oxygen transport by the mangrove aerial roots down into the root zone where most degradation of organic material takes place. Below 2000 m depth in the ocean sulfate reduction clearly looses importance relative to oxygen respiration and to suboxic processes such as nitrate, manganese or iron reduction.

This trend is illustrated in Fig. 8.4 where the 15 sediment types presented in Fig. 8.3 have been grouped into five depth zones of the global ocean. The graph shows how strongly the mineralization of organic matter in the sea bed is shifted towards ocean margin and shelf sediments. The continental shelf out to 200 m water depth comprises only 8% of the global ocean area of $3.6 \cdot 10^8$ km^2. Yet, 61% of the entire benthic oxygen uptake and 68% of the sulfate reduction take place here. If we include also the continental slope down to 1000 m water depth, this upper ocean margin includes

even 70% of the oxygen uptake and 96% of the sulfate reduction. In other words, according to the data compiled by Canfield et al. (2005) only 30% of the global oxygen uptake of the sea floor and 4% of the sulfate reduction take place at depths below 1000 m, covering 87% of the ocean. Although a larger fraction of oxygen respiration than sulfate reduction occurs in deep sea sediments below 1000 m, still ca. 40% of the aerobic mineralization below 1000 m ocean depth occurs along the continental margins (Jahnke 1996).

The accuracy of such global estimates is clearly limited by the available data from which they were calculated. Other estimates of the total global mineralization rates in the sea bed vary by at least two-fold. Thus, the estimate of $23 \cdot 10^{13}$ mol yr^{-1} by Canfield et al. (2005) is slightly higher than the $19 \cdot 10^{13}$ mol yr^{-1} estimated by Jørgensen (1983) and close to the $22 \cdot 10^{13}$ mol yr^{-1} estimated by Smith and Hollibaugh (1993). Middelburg et al. (1997) calculated a range of $15\text{-}26 \cdot 10^{13}$ mol yr^{-1}, depending on whether the geometric or the arithmetric mean value of each depth interval was used. The low contribution of deep sea sediments to the global benthic oxygen respiration is consistent with the earlier budget calculations of Jørgensen (1983). Middelburg et al. (1997) estimated that 28% of the global sea floor mineralization and 7% of the sulfate reduction take place below 2000 m water depth. It should be noted that the low contribution of sulfate reduction in deep sea sediments may be affected by the method of sulfate reduction rate determination. In sediments of the shelf and upper slope this is primarily by radiotracer experiments whereas in the deep sea rates were modeled. The modeling approach provides net rates rather than gross rates as obtained by the radiotracer method and thereby tends to underestimate the total rates, in particular in the near-surface sediment layer (see Section 8.6).

Since methane formation is shifted at least as strongly as sulfate reduction towards sediments with high organic deposition, an equally small fraction of the global biogenic methane production presumably takes place in the deep sea below 1000 m.

The global mineralization of sediment organic matter by oxygen was estimated in Fig. 8.4 to be $23 \cdot 10^{13}$ mol O_2 yr^{-1} while the global sulfate reduction was $7.5 \cdot 10^{13}$ mol SO_4^{2-} yr^{-1}. According to simple stoichiometries of oxygen respiration and sulfate reduction, one mol of oxygen oxidizes one mol of organic carbon to CO_2 whereas one mol of sulfate oxidizes two mol of organic carbon (Chapter 5):

$$[CH_2O] + O_2 \rightarrow CO_2 + H_2O \quad (8.3)$$

$$2\,[CH_2O] + SO_4^{2-} + 2\,H^+ \rightarrow 2\,CO_2 + H_2S + 2\,H_2O \quad (8.4)$$

This means that the global estimate of sulfate reduction should be multiplied by two in order to convert it to carbon equivalents. Thus, sulfate

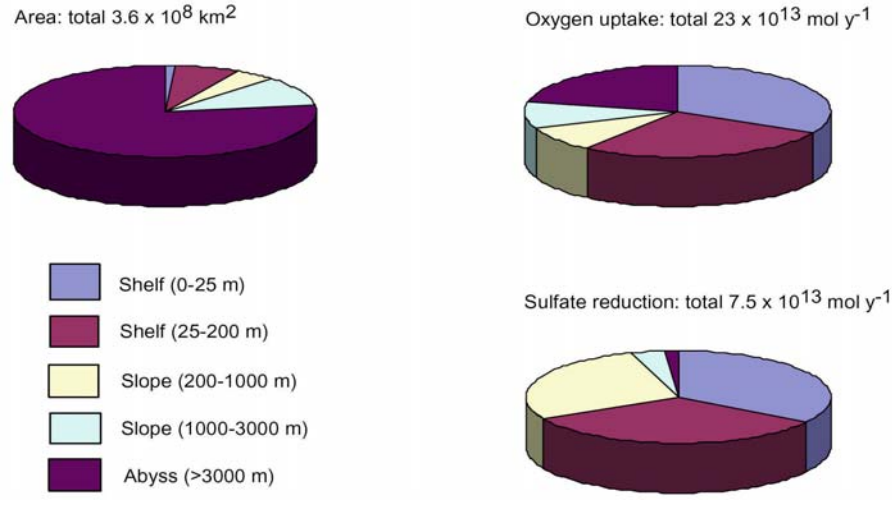

Fig. 8.4 Relative distributions of total ocean area and of global ocean oxygen uptake or sulfate reduction, grouped into five depth zones of the ocean. Based on data compiled by Canfield (1993) and Canfield et al. (2005).

oxidizes $15 \cdot 10^{13}$ mol organic carbon per year. This is equivalent to 65% of the global sediment oxygen uptake. The major part of the sulfide produced from sulfate reduction, around 90% in many shelf sediments, does not become buried in the sediment but is directly or indirectly reoxidized back to sulfate (see Section 8.5). The complex process of sulfide oxidation will thereby ultimately consume oxygen corresponding to the net equation:

$$H_2S + 2\,O_2 \rightarrow SO_4^{2-} + 2\,H^+ \qquad (8.5)$$

It is a striking consequence of these simple calculations that about half of the entire oxygen uptake in shelf sediments, where most sulfate reduction takes place, is used for the reoxidation of sulfide or of reduced metals originally reduced by reaction with sulfide (cf. Jørgensen 1977). Thus, if 90 % of $15 \cdot 10^{13}$ mol O_2 yr^{-1} is consumed in this process, it means that 13 out of 23 mol O_2 yr^{-1} or 56% of the oxygen is somehow involved in the reoxidation of sulfide (see Section 8.5). Only the remaining half of the oxygen is therefore available for all the animals and heterotrophic microorganisms that oxidize organic matter directly through their aerobic respiration.

8.3 Anaerobic Oxidation of Methane (AOM)

Below the sulfate zone, methanogenesis is the main terminal pathway of organic carbon mineralization. Methane is produced exclusively by anaerobic archaea that utilize a narrow spectrum of substrates for the process (Whitman et al. 1999). Methanogenic bacteria or eukaryotes are not known to exist. The primary sources of methane formation in marine sediments are from the splitting of acetate (CH_3COO^-) and from the reduction of CO_2 by hydrogen (Eq. 8.6 and 8.7):

$$CH_3COO^- + H^+ + \rightarrow CH_4 + CO_2 \qquad (8.6)$$

$$CO_2 + 4\,H_2 \rightarrow CH_4 + 2\,H_2O \qquad (8.7)$$

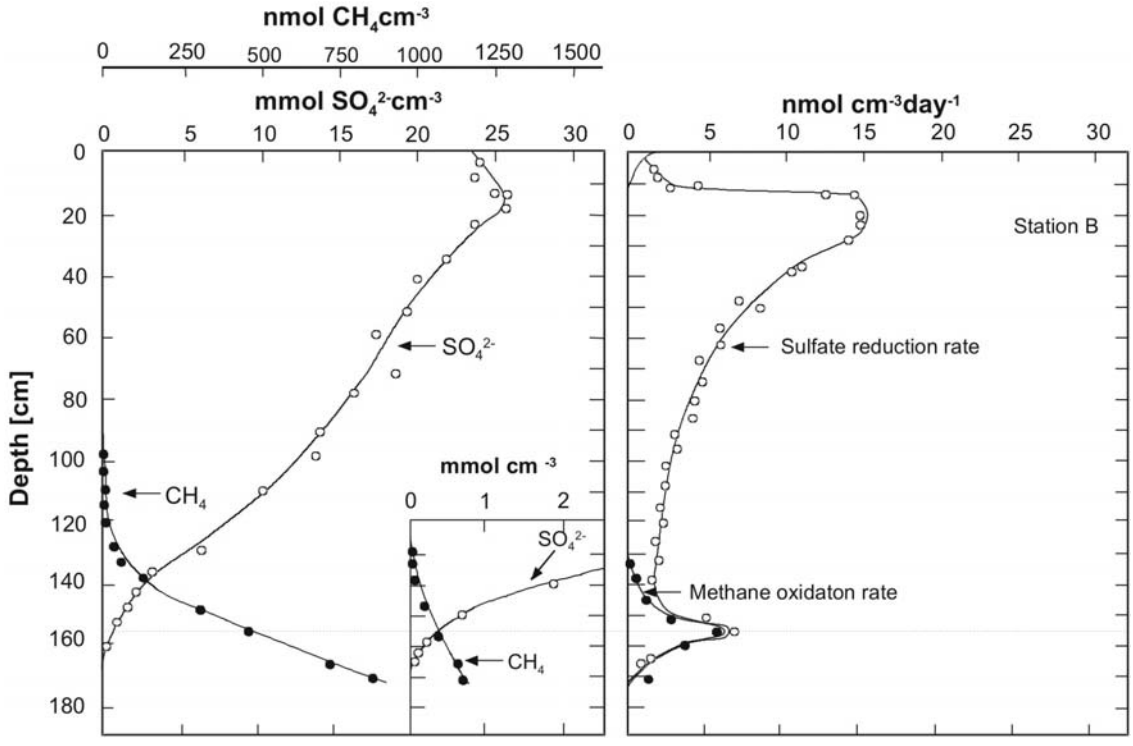

Fig. 8.5 Profiles of pore-water sulfate and methane concentrations and of rates of sulfate reduction and methane oxidation for a sediment core recovered from the Kattegat (Station B; 65 m water depth). The broken horizontal line denotes the depth where sulfate and methane were at equimolar concentrations - indicating the peak of the sulfate/methane transition. From Iversen and Jørgensen (1985).

As minor sources, also methanol, formaldehyde, and some methylated compounds such as methyl amines and methyl mercaptans may be used for methanogenesis. The energy yields by these terminal steps in organic degradation are lower than by anaerobic respiration, e.g. with nitrate, metal oxides or sulfate. Sulfate reducing bacteria therefore compete effectively with the methanogenic archaea for substrates which both groups of organisms can utilize, primarily acetate and H_2. As a result, methane is not produced as the main end product in marine sediments until sulfate has been largely depleted by sulfate reducing bacteria and electron acceptors for a respiratory oxidation of the organic matter are therefore no longer available (Martens and Berner 1974). Only small amounts of methane may still be generated in the sulfate zone from non-competitive methylated substrates. This is a major difference from the degradation of organic matter in freshwater sediments where sulfate is highly limited and methane is the main end product of anaerobic mineralization.

Methane is a chemically unreactive molecule that requires microbiological catalysis for the activation and oxidation to CO_2 at environmental temperatures. Aerobic bacteria that oxidize methane with O_2 are well known from diverse environments, including sea water and marine sediments, and have been studied in pure culture in the laboratory (Bowman 2000). These earlier physiological and biochemical studies indicated that biological methane oxidation requires molecular oxygen. Anaerobic oxidation of methane (AOM) was recognized by geochemists already in the 1970'ies, however, as a key process in marine sediments (Reeburgh 1969, 1976; Martens and Berner 1974; Barnes and Goldberg 1976). A large number of studies based on reaction-transport modeling, radiotracer experiments, inhibition techniques, and stable isotope data have since then firmly established that methane is oxidized biologically in the absence of O_2 at the transition between sulfate and methane. The microorganisms responsible for the process remained elusive, however, and even today it has not been possible to bring anaerobic methane oxidizers into pure culture for detailed laboratory study. In spite of this, the identity of the organisms has now been discovered and research on the biogeochemistry of anaerobic oxidation of methane has made significant progress in recent years (see reviews by Valentine and Reeburgh 2000; Hinrichs and Boetius 2002).

8.3.1 The AOM Zone in Marine Sediments

Most of the methane produced in the sulfate depleted sub-surface sediment diffuses upwards along a steep methane gradient until it reaches the lower sulfate zone and becomes oxidized. Within this reaction zone, referred to as the "sulfate-methane transition" (SMT), pore-water methane and sulfate are both consumed to depletion. This distinct zone is typically located one to several meters below the sediment surface in continental margin sediments and plays a key role in the biogeochemistry of the sea bed. In this zone most of the energy and reducing power of organic carbon mineralized to CO_2 and CH_4 below the sulfate zone comes into contact with an efficient electron acceptor, sulfate, and is finally oxidized to CO_2. Since this methane flux comprises most of the subsurface methanogenesis, the anaerobic oxidation of methane integrates the degradation of buried organic carbon from the lower boundary of the sulfate zone to very deep sediment layers which were deposited many thousands to millions of years ago. The coupled sulfate-methane reaction has been proposed to proceed according to the following net equation, assuming a one to one stoichiometry between methane and sulfate (e.g. Murray et al. 1978; Devol and Ahmed 1981):

$$CH_4 + SO_4^{2-} \rightarrow HCO_3^- + HS^- + H_2O \qquad (8.8)$$

Figure 8.5 shows an example of the sulfate-methane transition zone in a continental shelf sediment from Kattegat (Denmark) at the transition between the Baltic Sea and the North Sea. The sediment was characterized by a high sedimentation rate (0.16 cm yr^{-1}) and consisted of fine-grained silt and clay with an average organic matter content of 12% (Iversen and Jørgensen 1985). Sulfate diffused downwards to become depleted by sulfate reduction at 160 cm sediment depth while methane diffused upwards and penetrated ca. 40 cm into the lower sulfate zone to ca. 120 cm depth. In order to determine anaerobic methane oxidation rates in the sulfate-methane transition zone, Iversen and Jørgensen (1985) carried out radiotracer measurements of sulfate reduction using $^{35}SO_4^{2-}$ and of methane oxidation using $^{14}CH_4$. Fig. 8.5 (right frame) shows that the rates of sulfate reduction were high, starting from below the 10-15 cm deep suboxic sediment, and gradually dropped with increasing depth and age in the sediment. In the SMT, the rates increased

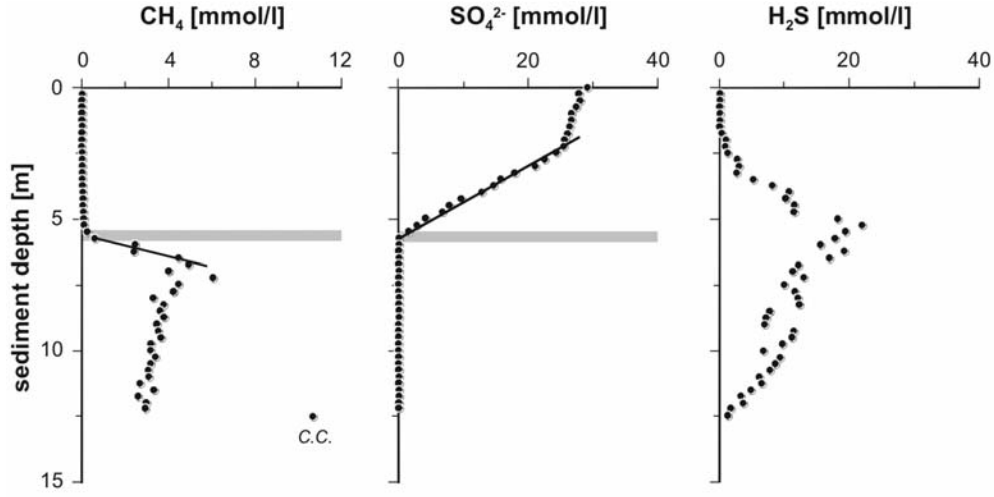

Fig. 8.6 Pore-water concentration profiles from gravity core GeoB 3714-9 from the Benguela upwelling area (2060 m water depth), South Atlantic. The shaded bar marks the sulfate-methane transition zone. The methane sample labeled C.C. was taken from the core catcher immediately after core recovery. From Niewöhner et al. (1998).

again with a peak just where sulfate and methane reached the same molar concentrations (small insert in Fig. 8.5). At that depth also the anaerobic oxidation of methane peaked with similar rates as the sulfate reduction. The integrated rates of methane oxidation in the transition zone accounted for 89 % of sulfate reduction at this depth. This example illustrates how bacterial sulfate reduction changes from organiclastic (based on the degradation of organic material) to methanotrophic (based on the oxidation of methane) down through the sediment column.

The pore water gradients of sulfate and methane and the depth of the AOM zone may vary strongly among sediments, depending on water depth, organic flux and other factors. Fig. 8.6 shows an example from the continental slope of the Benguela upwelling area in the southern Atlantic. The sulfate profile here shows little depletion in the top 0-2 m below which sulfate dropped almost linearly down to the sulfate-methane transition located at 5-6 m depth below sea floor. The concentration of H_2S peaked right at the SMT from where the H_2S concentration decreased both upwards towards the sediment surface and downwards (discussed below in Section 8.5). Based on pore-water concentration profiles, Niewöhner et al. (1998) calculated the diffusive flux of sulfate and methane into the transition zone in the sediment. Their calculations showed that anaerobic methane oxidation accounted for 100% of the deep sulfate reduction within the sulfate-methane transition zone, i.e. it could consume the total diffusive sulfate flux. These findings demonstrate that methane can be the primary electron donor for sulfate reduction in the sulfate-methane transition zone.

The methane profile in Fig. 8.6 shows that below the steep gradient at the top of the methane zone the methane concentrations gradually drop again. This is an artifact due to degassing of methane immediately upon core retrieval. Due to the relatively low solubility of methane and the large pressure difference between *in situ* depth and sea surface, methane is highly supersaturated in the pore water upon recovery of sediment cores and escapes as bubbles before sampling on board ship. For this reason, true methane concentration gradients above atmospheric pressure are difficult to determine and only recently have pressurized core barrels been introduced (Dickens et al. 2003).

8.3.2 Energy Constraints and Pathway of AOM

Microorganisms able to perform anaerobic oxidation of methane were only recently discovered through intensive studies, not of the "normal" subsurface SMT, but of unique marine environments in which AOM dominates the carbon and sulfur cycles, such as sediments associated with gas hydrates and methane seeps. (Gas hydrates are ice-like solids - generally composed of water and methane - which occur

naturally in sediments under conditions of high pressure, low temperature and high methane concentrations; see also Chapter 14). In such sediments from the Hydrate Ridge at 700 m water depth off the Oregon coast, conspicuous microbial aggregates, apparently responsible for the anaerobic oxidation of methane, were first observed (Boetius et al. 2000). The 3-5 µm large aggregates were stained with fluorescent molecular probes and studied under the fluorescence microscope. They were all found to consist of a central colony of archaea overgrown by sulfate reducing bacteria. In the AOM zone of the sediment, the biomass of these aggregates exceeded the biomass of all other microorganisms by an order of magnitude, thus indicating that they were indeed responsible for the methane oxidation with sulfate. Since then, similar aggregates have been found world-wide in diverse methane enriched surface sediments (Orphan et al. 2001, 2002; Michaelis et al. 2002; Knittel et al. 2005).

Further evidence for the identity of the anaerobic methane oxidizers had come from isotope analyses of specific lipid biomarkers in sediments with high rates of AOM. Relative to marine organic carbon or bicarbonate, methane is highly enriched in the lighter carbon isotope, ^{12}C, over the heavier carbon isotope, ^{13}C, with $\delta^{13}C$ values ranging from -50 to -90‰ (Whiticar 1999; see also Chapter 10). The archaeal biomarkers in these sediments were strongly enriched in ^{12}C, which indicated that methane served as the main carbon source for the microorganisms (Hinrichs et al. 1999; Elvert et al. 2000; Thiel et al. 2001). Also biomarkers derived from bacteria showed extreme ^{12}C enrichment and indicated that the associated sulfate reducers were also involved in the AOM process (Hinrichs et al. 2000; Elvert et al. 2000; Pancost et al. 2000). Final evidence that the aggregates carried out anaerobic oxidation of methane was provided by a recently developed SIMS technique (secondary ion mass spectrometry) by which carbon isotopic analysis could be done on individual microscopic AOM aggregates and thereby confirm that their cell material contained the ^{12}C depleted isotope signal of methane (Orphan et al. 2001).

Equation 8.8 above proposed a net equation for anaerobic oxidation of methane by sulfate that is based on modeled pore water profiles and laboratory experiments with sediment enrichments. No single microorganism is yet known, however, that is able to carry out such a complete oxidation of methane to bicarbonate and it remains an open question whether such organisms exist. Instead, the process may proceed in two steps involving an intermediate electron carrier that is transferred from the archaea to the sulfate reducers within the AOM aggregates. Hoehler et al. (1994) first suggested that AOM is carried out by a consortium of archaea and sulfate reducing bacteria and that hydrogen might serve as such an intermediate that is transferred from the methane oxidizers to the sulfate reducers in a two-step reaction (Fig. 8.7):

$$\text{I.}\quad CH_4 + 2\,H_2O \rightarrow CO_2 + 4\,H_2 \qquad (8.9)$$

$$\text{II.}\quad SO_4^{2-} + 4\,H_2 + H^+ \rightarrow HS^- + 4\,H_2O \qquad (8.10)$$

Sum of Eq. 8.9 and 8.10 = Eq. 8.8

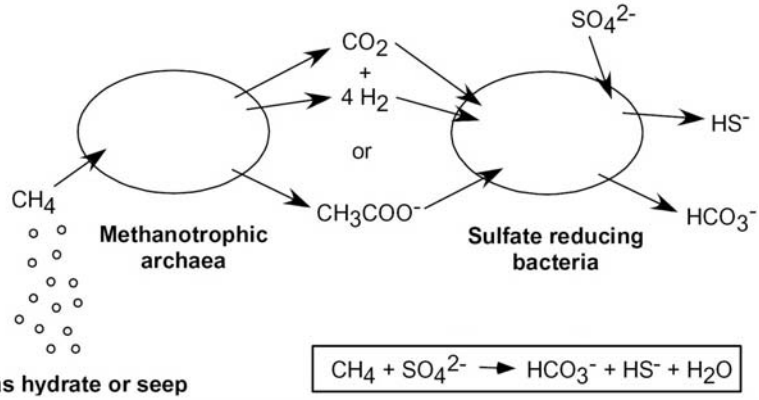

Fig. 8.7 Schematic of AOM aggregate with a syntrophic metabolism among two members that only in combination can catalyze the complete oxidization of methane with sulfate. A transfer of H_2 or acetate (CH_3COO^-) from methanotrophic archaea to sulfate reducing bacteria has been proposed as an intermediate in the net process. Such an interspecies transfer of hydrogen or organic carbon is still hypothetical and has not been directly demonstrated.

The first step in this reaction (Eq. 8.9) is obviously a reversal of methanogenesis from CO_2 and H_2 shown in Eq. 8.7. How can a metabolic process run in two opposite directions and yet yield energy for both types of archaea? Hoehler et al. (1994, 1998) showed that the energy yield is highly dependent on the H_2 concentration which, in turn, is regulated by the predominant process of mineralization. In the deep methanogenic zone the H_2 concentration is relatively high, about 10 nM, so that methanogenesis (Eq. 8.7) is an exergonic, energy yielding process. In the sulfate zone, the sulfate reducing bacteria maintain such a low H_2 concentration, about, 1 nM, that it falls below the concentration required for an exergonic methanogenesis. On the contrary, the reversal of methanogenesis (Eq. 8.9) becomes exergonic and AOM may proceed. This strong dependence on H_2 concentration could explain why the methane oxidizing archaea grow in aggregates together with the sulfate reducing bacteria. Only when the sulfate reducers efficiently scavenge H_2 as it is produced by the archaea are these able to continue oxidizing methane.

Although this idea of a syntrophic association based on inter-species hydrogen transfer is very appealing, it explains only a part of the observations on AOM. Since both the methanotrophic archaea and the sulfate reducing bacteria carry the light carbon isotopic signal of methane, it is a question how also carbon is transferred in this syntrophic association. An alternative pathway could therefore be the conversion of methane to acetate and the subsequent oxidation of acetate (CH_3COO^-) by the sulfate reducers with a concurrent incorporation of part of the acetate into their cell biomass:

$$CH_4 + HCO_3^- \rightarrow CH_3COO^- + H_2O \qquad (8.11)$$

$$SO_4^{2-} + CH_3COO^- \rightarrow HS^- + 2\,HCO_3^- \qquad (8.12)$$

Further possibilities exist, such as a combined transfer of acetate and hydrogen or a transfer of formate, both of which may explain the $\delta^{13}C$ observations and be more compatible with the energetic constraints on AOM (Valentine and Reeburgh 2000; Sørensen et al. 2001). Further research is required to understand the basic mechanism and regulation of this key process in the methane cycle.

Although AOM provides an almost complete barrier to methane escape from the sea floor in sediments with diffusive methane flux, the process is surprisingly sluggish and takes place over a sediment horizon and a time scale that highly exceed that of most other microbial processes in gradient environments. Thus, the life-time of methane upon diffusion up into the sulfate zone is generally on the order of months to years (Jørgensen et al. 2004). This is a reason why we prefer the term "sulfate-methane transition" rather than "sulfate-methane interface". A reason for the slow turnover may be that the methane oxidizing community is operating near the theoretical minimum in energy yield required for microbial growth. The estimated energy yield of AOM in a number of sedimentary environments is -20 to -25 kJ per mol of methane consumed (Hoehler et al. 1994) which is less than the energy required for the formation of ATP (see Chapter 5). If the process does indeed involve a two-step reaction such as suggested in Eq. 8.9-8.10 or 8.11-8.12, then this energy even has to be shared among two partners. This may explain why the growth of AOM aggregates is exceedingly slow and requires many months for a doubling of the biomass in laboratory incubations (Nauhaus et al. 2002). It may also explain why anaerobic methane oxidizing microorganisms have not yet been isolated in pure culture in the laboratory. They simply grow so slow that isolation may take many years. These observations demonstrate, however, that processes catalyzed by microbial communities in the environment can be highly efficient in energy conservation and operate close to the theoretical thermodynamic limits (Schink 1997; Hoehler et al. 2001; Jackson and McInerney 2002).

By the use of molecular methods based on sequence information from 16S rRNA genes, a broad diversity of archaea that all belong to the *Euryarchaeota* (Orphan et al. 2002; Knittel et al. 2005) and sulfate reducing bacteria mostly belonging to the *Desulfosarcina-Desulfococcus* branch of the *Delta-proteobacteria* (Boetius et al. 2000; Orphan et al. 2001) has been consistently found to be associated with anaerobic oxidation of methane. Although the genetic identity of AOM microorganisms is now revealed, the physiology and biochemistry of AOM are still incompletely understood. A recent clue came from the discovery that the terminal key enzyme of methanogenesis, methyl coenzyme M reductase, and its encoding gene seem also to be involved in the process of AOM in a slightly modified form, thus indicating that AOM may partly be a reversal of

Table 8.2 Role of methane as a carbon source for sulfate reduction in marine sediments. The compiled data show cumulative sulfate reduction rates measured by radiotracer technique, either over the entire sulfate zone, or in the upper 0-15 cm combined with modeling below that depth. The contribution of methane was calculated from the diffusion flux of methane up into the lower sulfate zone. In other data sets where sulfate reduction rates are determined only by modeling, or where also methane oxidation was measured by radiotracer technique, the calculated % of SRR from CH_4 is higher than shown here. (SRR = sulfate reduction rate).

Location	Water depth [m]	SRR [mmol m^{-2} d^{-1}]	CH_4 flux, % of SRR	References
Skan Bay, Alaska	65	19	8%	Alperin and Reeburgh (1988)
Århus Bay, Baltic Sea	18	2.90	3%	Thode-Andersen and Jørgensen (1989)
				Knab and Fossing (unpubl.)
Kattegat-Skagerrak	65-200	4.8-5.6	4-6%	Iversen and Jørgensen (1985)
Saanich Inlet	225	17	9%	Devol et al. (1984)
Namibian slope	1372-2060	1.25-2.22	10-12%	Fossing et al. (2000)
Chilean slope	799-2744	0.53-0.82	8-24%	Treude et al. (2005)
Cape Lookout Bight	9	24-27	40%	Crill and Martens (1983, 1986)
				Chanton (1985)
Black Sea, anoxic zone	130-1176	0.65-1.43	7-18%	Jørgensen et al. (2001)

methanogenesis in certain archaea (Krüger et al. 2003; Hallam et al. 2003). In this respect, microbiological and biogeochemical research is currently providing mutually supporting evidence for the nature of AOM.

8.3.3 Quantitative Role of AOM

Since methane formation is largely restricted to sediment layers below the depth of sulfate penetration, there is relatively little organic carbon with low reactivity left to fuel methanogenesis. When integrated through the sediment column, the amount of organic carbon mineralized with the formation of methane is generally only 5-20% of that mineralized by sulfate reduction (Canfield 1993; Canfield et al. 2005; Table 8.2), with 10% possibly representing a mean value. Since sulfate reduction typically accounts for half of the organic mineralization in ocean margin sediments, it should only be about 5% of the total mineralized organic carbon that is ultimately degraded to methane. In deep sea sediments the fraction is presumably lower but relevant data to confirm this are lacking. In some coastal environments with very high organic loading, such as Cape Lookout Bight on the Atlantic coast of North America, much more of the organic carbon may be buried below the sulfate zone and be degraded to methane (Crill and Martens 1986). Also in ocean margin sediments where the methane flux is enhanced due to subduction or is focused in association with methane seeps or surficial gas hydrate accumulations, methane may provide the main carbon source for the entire sulfate reduction (e.g. Boetius and Suess 2004). Table 8.2 provides selected examples of the contribution of methane as a carbon and energy source for sulfate reduction in ocean margin sediments.

As discussed in Section 8.6, the sulfate reduction rates determined from modeling of sulfate profiles may underestimate the rates in the most active layers of near-surface sediment, and model comparisons of sulfate and methane fluxes therefore tend to indicate a greater role of methane for the entire sulfate reduction than data based on experimental rate measurements. From interstitial flux calculations, Reeburgh (1976, 1982) thus estimated that approximately 50 % of the net downward sulfate flux at a Cariaco Trench station - an anoxic basin - could be accounted for by methane oxidation. For Saanich Inlet sediments, 75 % of the downward sulfate flux was attributed to anaerobic methane oxidation according to simple box model calculations (Murray et al. 1978). Devol et al. (1984) obtained lower percentages of 23 to 40 % of the downward sulfate flux consumed by methane oxidation for these same sediments using a coupled reaction diffusion model. Iversen and Jørgensen (1985) reported that in Kattegat

and Skagerrak sediments methane oxidation accounted for only 10 % of the electron donor requirement for the depth integrated sulfate reduction. In this case sulfate reduction rates were measured by radiotracer technique throughout the entire sulfate zone.

The proportion of sulfate used for organic matter degradation in comparison to sulfate used for anaerobic methane oxidation may be calculated under molecular diffusion conditions from the shape of sulfate profiles. Borowski et al. (1996) inferred that the linear sulfate pore water concentration profiles found in Carolina Rise and Blake Ridge sediments imply that anaerobic methane oxidation is the dominant sulfate consuming process. They calculated the upward methane flux from measured sulfate pore water profiles assuming that the downward sulfate flux is stoichiometrically balanced by upward methane flux. In this way they used the sulfate concentration profiles to calculate the methane flux from the underlying methane gas hydrates which had been documented by seismic profiling. Niewöhner et al. (1998) found similar linear sulfate concentration profiles in sediments of the Benguela upwelling area (see Fig. 8.6) and concluded that anaerobic methane oxidation could account for the entire deep sulfate flux.

These studies demonstrate that the sulfate-consuming process occurring in the deeper sediments, i.e. AOM, is the dominant factor determining the shape of the sulfate pore water profiles, although oxidation of organic matter demonstrably occurs throughout the entire sulfate zone. Linear sulfate profiles can, therefore, be used to calculate the upward methane flux (e.g. Devol and Ahmed 1981; Borowski et al. 1996; Niewöhner et al. 1998) but they do not provide accurate sulfate reduction rates occurring in near-surface sediments. Concave-down pore water profiles may develop when methane dependent sulfate reduction in deeper sediment layers is less important as is schematically illustrated in Figure 8.8 or if transient conditions prevail in the pore water system (Hensen et al. 2003; Kasten et al. 2003).

Reeburgh et al. (1993) estimated the global methane flux in marine sediments to a mean value of 70 Tg yr^{-1} or $0.5 \cdot 10^{13}$ mol CH_4 yr^{-1}. This is equivalent to 2% of the entire organic carbon mineralization via oxygen respiration and about 7% of the global sulfate reduction. A more recent estimate by Hinrichs and Boetius (2002) of AOM in marine sediments yielded a four-fold higher number, 300 Tg yr^{-1} or about $2 \cdot 10^{13}$ mol CH_4 yr^{-1}. These calculations do not include hot-spots of methane fluxes from cold seeps, hot vents or surficial gas hydrates, since reliable estimates of the total areal distribution of such sites are not yet available. Methane seeps occur both at active and passive margins but are highly focused and often variable over time. Judd et al. (2002) made an estimate of the global flux of methane from the sea bed of 16-40 Tg yr^{-1}, i.e. much less than the estimated subsurface flux. Data compiled by Hinrichs and Boetius (2002) indicate that, even if the area affected by methane seepage at continental margins is below 1%, this might have

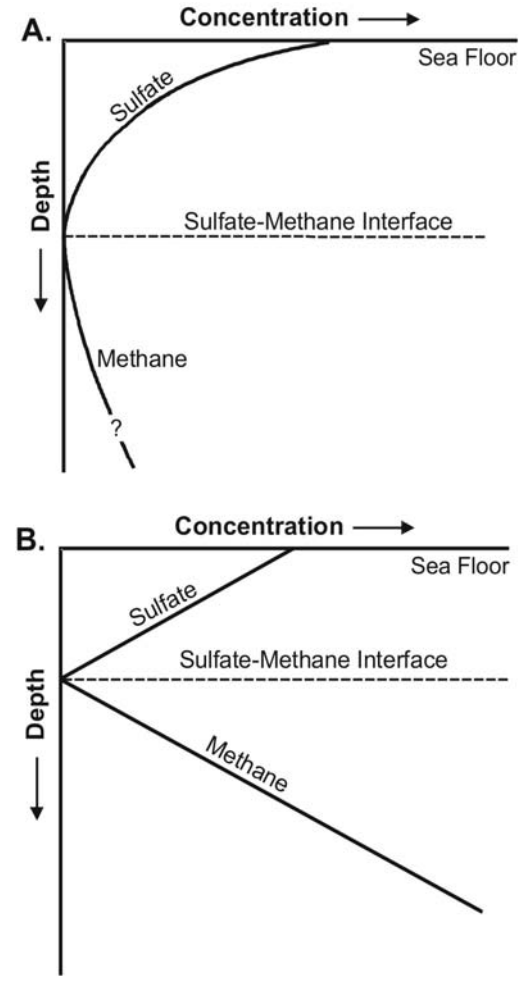

Fig. 8.8 Schematic profiles of sulfate and methane in marine sediments. A) In sediments with low methane flux, sulfate reduction based on oxidation of sediment organic matter predominates throughout the sulfate zone. B) In sediments with high methane flux, sulfate reduction based on anaerobic oxidation of methane tends to straighten out the sulfate profile.

Table 8.3 Reactivity of iron (oxyhydr)oxides towards sulfide. Half-lives ($t_{1/2}$) are given for reductive dissolution in seawater at pH 7.5 and at a sulfide concentration of 1000 µM. [a]data from Poulton et al. (2004); [b]data from Canfield et al. (1992) and Raiswell et al. (1994). (Adopted from Nüster, 2005).

Mineral	$t_{1/2}$[a]	$t_{1/2}$[b]
Freshly precipitated hydous ferric oxide	5 min.	
2-line ferrihydrite	12.3 hours	2.8 hours
Lepidocrocite	10.9 hours	< 3 days
Goethite	63 days	11.5 days
Magnetite	72 days	105 years
Hematite	182 days	< 31 days

a significant impact on the total methane budget. Therefore, a more extensive mapping of seepage areas, as well as a broader data base on diffusive methane fluxes, is needed for more accurate calculations of the methane cycling in the global sea bed (see also Chapter 14).

8.4 Effects of Sulfate Reduction on Sedimentary Solid Phases

Sulfate reduction, occurring either due to the oxidation of methane or the mineralization of organic material, can lead to a pronounced overprint or modification of the primary sediment composition by dissolution/reduction of minerals and precipitation of authigenic mineral phases. Since most of the minerals affected are also commonly used for paleoceanographic and paleoclimatologic reconstructions it is crucial to consider and assess the extent of diagenetic alteration of the sedimentary record driven by sulfate reduction.

8.4.1 Reactions with iron

Iron sulfides represent the most important minerals that form in association with both organoclastic and methanotrophic sulfate reduction, or - more precisely - as a result of the hydrogen sulfide produced by these processes. The different pathways of pyrite formation via intermediate iron sulfides will be described in more detail in Section 8.4.2. The first step in all pyrite forming sequences involves a reaction of hydrogen sulfide with either dissolved Fe^{2+} or solid-state iron (oxyhydr)oxides. The reactivity of oxidized iron minerals towards sulfide varies significantly as shown in Table 8.3. In their recent study, Poulton et al. (2004) demonstrated that minerals with a lower degree of crystal order react within minutes to hours, while more ordered minerals react on time scales of days to years (c.f. Chapter 7). The largest discrepancy in reactivity between the studies of Canfield et al. (1992) and Raiswell et al. (1994) on the one hand and Poulton et al. (2004) on the other hand exists for the mineral magnetite (105 years versus 72 days; Table 8.3). This difference was explained by the surface area of magnetite, which was taken into consideration in the study of Poulton et al. (2004).

Within or around the zone of anaerobic oxidation of methane, other important mineral precipitates comprise authigenic carbonates – such as Mg-calcite, aragonite and dolomite – which precipitate due to the high concentrations of HCO_3^- ions generated by AOM (c.f., Eq. 8.8; e.g., Greinert et al. 2002; Moore et al. 2004), as well as diagenetic barite (e.g., Brumsack 1986; Torres et al. 1996). Due to the high rates of AOM, the formation of carbonate precipitates is particularly pronounced in sedimentary settings influenced by venting and seepage of methane-rich fluids and/or the presence of gas hydrates. The formation of carbonates in such methane dominated environments, which are mostly driven by advective transport processes, is discussed in Chapters 13 and 14. The factors and conditions determining the dissolution and preservation of the different carbonate phases are the subject of Chapter 9.

8.4.2 Pyrite Formation

Iron-sulfide minerals are important sinks for iron and sulfur as well as for trace metals and play an important role in the global cycles of these elements. Over the past 30 years extensive studies –

both in the field and in the laboratory – have been performed to elucidate the mechanisms of pyrite formation and in particular to understand the main factors which control the formation of pyrite in natural environments. Although these studies have provided significant new insights, fundamental questions remain with respect to (a) the different reaction rates obtained on the basis of field studies and laboratory experiments, (b) the role of FeS surface reactions and the electron acceptor involved in the conversion to pyrite, and (c) the role of sulfate-reducing bacteria – in particular their cell walls - in directing and promoting the pyrite precipitation process. A comprehensive review of pyrite formation in sedimentary environments by Rickard et al. (1995) was recently updated by Schoonen (2004). Besides the detailed description of the different pathways and mechanisms of sedimentary pyrite formation, the review by Schoonen (2004) also discusses the synthesis of nanoscale pyrite, trace element incorporation, and the formation of electronic defects during the formation process.

All pyrite forming pathways identified so far involve several reaction steps. First, hydrogen sulfide, produced during sulfate reduction (Eq. 8.1, 8.2 and 8.8), reacts with dissolved iron or reactive (towards sulfide) iron minerals to form amorphous iron sulfides, such as mackinawite (FeS). The precipitated amorphous iron sulfide is highly unstable and rapidly transforms to metastable iron sulfide phases such as pyrrhotite ($Fe_{x-1}S$) or greigite (Fe_3S_4), both of which represent intermediates in the reaction pathways to pyrite (FeS_2). The conversion of amorphous FeS to pyrite requires an electron acceptor and a change in the molar Fe:S ratio from about 1:1 to 1:2. The electron acceptor is needed to oxidize the S(-II) component in FeS to the mean oxidation state of –I in FeS_2. Concurrently, the Fe:S ratio has to decrease either via the addition of sulfur or the loss of iron. Three general pathways have been reported to convert FeS to pyrite:

(1) Addition of sulfur with the sulfur species acting as electron acceptor (Berner 1970; Berner 1984; Luther 1991). This pathway has been termed the "polysulfide pathway".

$$FeS + S^0 \rightarrow FeS_2 \qquad (8.13)$$

(2) Reaction with hydrogen sulfide, i.e. addition of sulfur with a non-sulfur electron acceptor (Rickard and Luther 1997). This conversion mechanism is known as the "H_2S pathway".

$$FeS + H_2S \rightarrow FeS_2 + H_2 \qquad (8.14)$$

(3) Loss of iron, combined with an (additional) electron acceptor (Wilkin and Barnes 1996), known as the "iron-loss pathway".

$$2FeS + 2H^+ \rightarrow FeS_2 + Fe^{2+} + H_2 \qquad (8.15)$$

As reviewed in detail by Schoonen (2004) these different conversion mechanisms – and in particular the H_2S pathway – have received controversial discussion. However, field studies have shown that hydrogen sulfide can indeed sulfidize amorphous FeS and form pyrite. Rickard (1997) found that the H_2S process is by far the most rapid of the pyrite-forming reactions hitherto identified and suggested that it represents the dominant pyrite forming pathway in strictly anoxic systems. In addition, Morse (2002) discussed that the oxidation of FeS by hydrogen sulfide is the faster process compared with the oxidation by elemental sulfur. Berner (1970) suggested that, in the presence of zero-valent sulfur, a complete transformation of FeS to pyrite should be possible on a time scale of years. An incomplete conversion of FeS to pyrite, as often observed, e.g. in

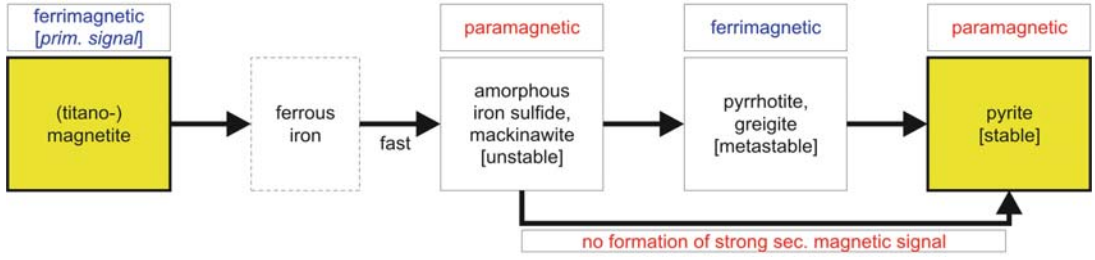

Fig. 8.9 Schematic representation of the major pathways of the transformation of iron oxides to iron sulfides in anoxic marine environments, in relation to the alteration of the magnetic record. From Riedinger (2005).

Table 8.4 Authigenic iron sulfides formed in marine sediments. Modified from Schinzel (1993).

Mineral	Composition	Crystal class	Magnetic properties
mackinawite	FeS	tetragonal	paramagnetic
pyrrhotite	$Fe_{1-x}S$	hexagonal or orthorhombic	ferrimagnetic, antiferrimagnetic
pyrite	FeS_2	cubic	paramagnetic
markasite	FeS_2	orthorhombic	diamagnetic
greigite	Fe_3S_4	cubic	ferrimagnetic

the anoxic sediments of Kau Bay, Indonesia, (Middelburg 1990) or the Amazon Fan (Kasten et al. 1998), can be due to a shortage of zero-valent sulfur during pyrite formation. Zero-valent sulfur may form as a result of the incomplete oxidation of H_2S or FeS by oxidants such as O_2, NO_3^-, MnO_2 or FeOOH. A limited transformation of FeS to pyrite can therefore be due to either (a) a limited amount of sulfide available to be oxidized to zero-valent sulfur or (b) a shortage in the amount of oxidants supplied by diffusion, bioturbation or burial.

Direct precipitation of pyrite without intermediate iron sulfide precursors was reported for salt marsh sediments, where pore waters were undersaturated with respect to amorphous FeS but oversaturated with respect to pyrite (Howarth 1979; Giblin and Howarth 1984). In these sediments, the oxidizing activity of the roots favored the formation of elemental sulfur and polysulfides which were thought to react directly with Fe^{2+}. The direct reaction pathway may proceed within hours, resulting in the formation of single small, euhedral pyrite crystals (Rickard 1975; Luther et al. 1982). Framboidal pyrite, apart from that formed by the mechanism presented by Rickard (1997), is formed slowly (over years) via intermediate iron sulfides (Sweeney and Kaplan 1973; Raiswell 1982).

Irrespective of the pyrite forming pathway the conversion of FeS into pyrite via intermediate iron sulfides goes along with a pronounced change in the rock magnetic properties of the particular iron sulfide phases (Fig. 8.9, Table 8.4). Amorphous FeS is paramagnetic and therefore has a low magnetic susceptibility and does not contribute to the remanent magnetization of sediments. In contrast, the metastable iron sulfides, pyrrhotite and greigite, which represent precursor phases of pyrite, are ferrimagnetic and thus have a significant magnetic potential. This becomes obvious from maxima in magnetic susceptibility located slightly above enrichments of amorphous FeS in the form of black bands in sediments of the Amazon Fan (see Fig. 8.11 below; Kasten et al. 1998) and in the Black Sea (Neretin et al. 2004). The presence of greigite and pyrrhotite – responsible for the peaks in magnetic susceptibility – document the progress in the sequence of conversion of FeS to pyrite. With a further progression in the conversion pathway and the formation of the stable pyrite the magnetic signal is lost again as pyrite is paramagnetic (Fig. 8.9, Table 8.4).

It is generally assumed and found that there is a gradual decrease in the amount of amorphous iron sulfides and a corresponding increase in the amount of pyrite – thus a drop in the AVS to pyrite ratio – upon burial with increasing sediment depth. The discussion and examples presented in the following sections will, however, show that this is not always the case. In particular in sedimentary sequences affected by sulfidization fronts the sequence of conversion of FeS into pyrite can be reversed with depth and the most immature and unstable Fe sulfides be found at greater depth coinciding with the current depth of the diffusional H_2S/Fe^{2+} boundary. Furthermore, iron sulfide formation often occurs at or along fixed geochemical boundaries or reaction fronts. Thus, the sequence of iron sulfide formation is often restricted to or even bound to certain depth horizons rather than occurring gradually with

increasing sediment depth. Mineral precipitation at sulfidization fronts can also occur cyclically within the sedimentary sequence – superimposed by episodic changes in depositional or other environmental conditions.

8.4.3 Magnetite and Barite

Besides the precipitation of mineral phases, dissolution of numerous minerals initially supplied to the seafloor can occur in sediments that experience sulfate reduction and/or sulfate-depleted conditions. Iron (oxyhydr)oxides and barite ($BaSO_4$) are two examples with particular relevance for paleoceanographic research.

Magnetic iron (oxyhydr)oxides, especially magnetite (Fe_3O_4), are the main carriers of remanent magnetization in sediments. Magnetostratigraphy of deep sea sediment cores is a valuable method of dating and comparing sedimentary records. Dissolution of the magnetic minerals under sulfate- and iron-reducing conditions and/or subsequent precipitation of authigenic iron minerals may, however, alter the initial remanent magnetization and seriously compromise the interpretation of the sedimentary geomagnetic record (e.g. Karlin and Levi 1983, 1985; Funk et al. 2003a, 2003b; Reitz et al. 2004). The effects of AOM-driven sulfate reduction on the transformation of iron minerals and the associated modification of rock magnetic properties will be demonstrated below using examples from the Amazon Fan and the western Argentine Basin.

A second sedimentary component important for paleoceanographic reconstructions, which is prone to dissolution under conditions of sulfate reduction – or more precisely in sulfate-depleted sediments - is the barium sulfate mineral, barite ($BaSO_4$). Since a correlation has been detected between barite deposition and the flux of organic matter through the water column, the concentration of barite in sediments has been proposed and applied as a geochemical tracer to reconstruct past changes in ocean productivity (e.g., Bishop

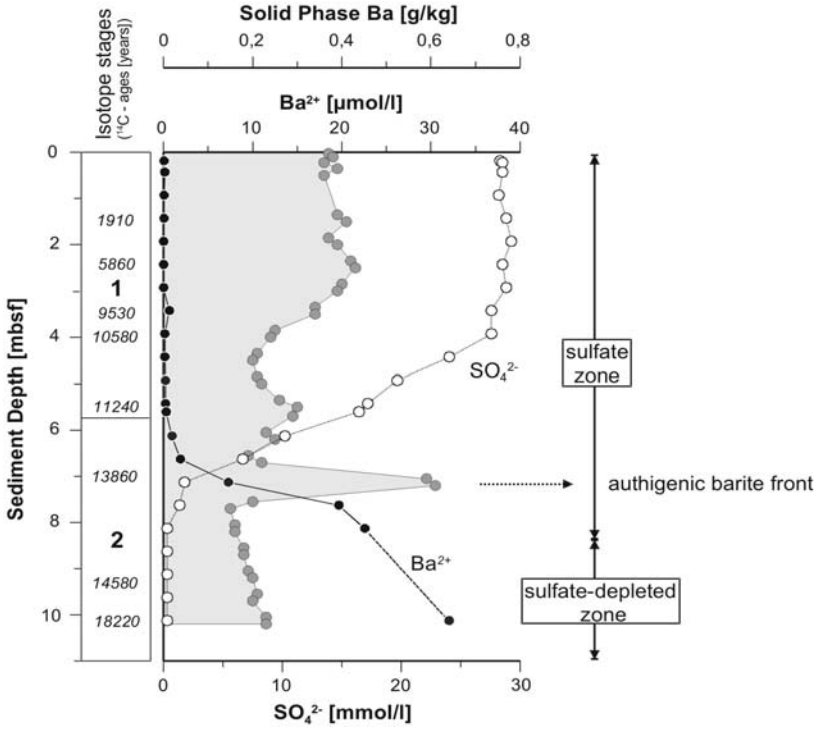

Fig. 8.10 Geochemical data for core GeoB 1023-4 recovered off north Angola (17°09.6'S, 10°59.9'E, 2047 m water depth). Barium and sulfate pore-water concentration profiles as well as the distribution of solid-phase barium indicate the precipitation of authigenic barite at a front slightly above the depth of complete sulfate consumption. Below the sulfate/methane transition barite becomes undersaturated and is thus subject to dissolution due to the total depletion of pore-water sulfate. Dissolved barium diffuses upwards into the sulfate zone where the mineral barite becomes supersaturated and so-called authigenic or diagenetic barite precipitates at a front at the base of the sulfate zone. Modified from Gingele et al. (1999), after Kölling (1991).

1988; Dehairs et al. 1991; Dymond et al. 1992; Gingele and Dahmke 1994; Paytan et al. 1996a). Sedimentary barite has also been used to reconstruct the strontium isotope composition of seawater over time (e.g., Paytan et al. 1993; Mearon et al. 2003), to determine the sulfur isotope ratio of marine sulfate (Cecile et al. 1983; Goodfellow and Jonasson 1984; Paytan et al. 1998), and to characterize Holocene sedimentation rates by using excess ^{226}Ra decay (Paytan et al. 1996b; van Beek and Reyss 2001; van Beek et al. 2002).

Although it is frequently stated that the process of sulfate reduction promotes barite dissolution it is, in fact, the *complete depletion* of interstitial sulfate which leads to an undersaturation of the pore water with respect to barite and to its subsequent dissolution (e.g., von Breymann et al. 1992; Torres et al. 1996; Gingele et al. 1999). This process is obvious from pore water Ba^{2+} concentrations which typically increase to micromolar concentrations with depth below the SMT. Dissolution of barite below the SMT and reprecipitation of diagenetic barite slightly above the sulfate penetration depth in so-called authigenic or diagenetic barite fronts can drastically obscure the primary barite record and thus lead to wrong paleoceanographic interpretations. The effect of barite dissolution in the zone of total sulfate depletion, and the subsequent reprecipitation of diagenetic barite at higher sediment levels is illustrated in Figure 8.10 for a sediment core recovered from the continental margin off Angola. The use of barite as a geochemical tracer or archive for paleoceanographic reconstructions is therefore limited – not to say precluded - in sediment intervals that are either currently sulfate-free or have been strongly sulfate depleted in the past (e.g. von Breymann et al. 1992; Gingele and Dahmke 1994; Torres et al. 1996; Gingele et al. 1999; Dickens 2001). While the current geochemical zonation of a sediment column can be determined from pore water sulfate data, a past migration of the SMT – and particularly a downward strike over time as a result of a transient decrease in methane flux from below – has also to be considered a possible cause that may alter the solid-phase Ba contents.

In a novel approach, Dickens (2001) used sedimentary Ba records to assess temporal changes during the Late Pleistocene in the upward flux of methane within sediments of the Blake Ridge that are rich in sub-surface gas hydrates. Due to a lack of Ba enrichment above the present depth of the barite front the author concluded that the upward methane flux from the underlying gas hydrate reservoir has not varied significantly across major changes in sea level and hydrostatic pressure. A possible means to identify the origin/source of barite enrichments is the analysis of the stable sulfur isotopic composition, $\delta^{34}S$, of the barite particles. As the sulfur isotopic composition of sulfate in the water column, where the productivity-related biogenic barite is assumed to be formed, is significantly lighter (around +21 ‰; Paytan et al. 2002) than that of pore water sulfate at the SMT, where diagenetic barite precipitates (around + 40 ‰; Torres et al. 1996), it is generally assumed that the $\delta^{34}S$ of barite should give insight into its formation mechanism or origin (Paytan et al. 2004).

8.4.4 Non-Steady State Diagenesis

A particularly pronounced alteration of the sedimentary solid phase by mineral dissolution and authigenic mineral precipitation can take place in connection with sulfate reduction during non-steady-state diagenesis, i.e. during phases of deposition by which sedimentary conditions are not constant over time and sediment geochemistry adjusts to the new situation. Non-steady-state diagenesis can be initiated by any changes in the fluxes of electron donors and acceptors and environmental conditions, for example by changes in type of depositing sediment, oxygen content of the bottom water, sedimentation rate, flux of organic matter to the seafloor, and upward flux of methane (e.g., Kasten et al. 2003). The non-steady-state processes that occur during the transition from one depositional situation to another, or at the interface between two sediment types, typically comprise the development of geochemical reaction fronts. These fronts can either be fixed at particular sediment horizons for a prolonged period of time or move downwards or upwards within the sediment column. During a fixation or a slow migration of reaction fronts or geochemical boundaries the diagenetic processes acting at these fronts can produce higher concentrations of the authigenic minerals formed at specific sediment levels than under steady-state conditions. On the other hand, a fast upward migration of a geochemical front may support the burial and thus the preservation of substantial amounts of metastable minerals (Riedinger et al. 2005, see below).

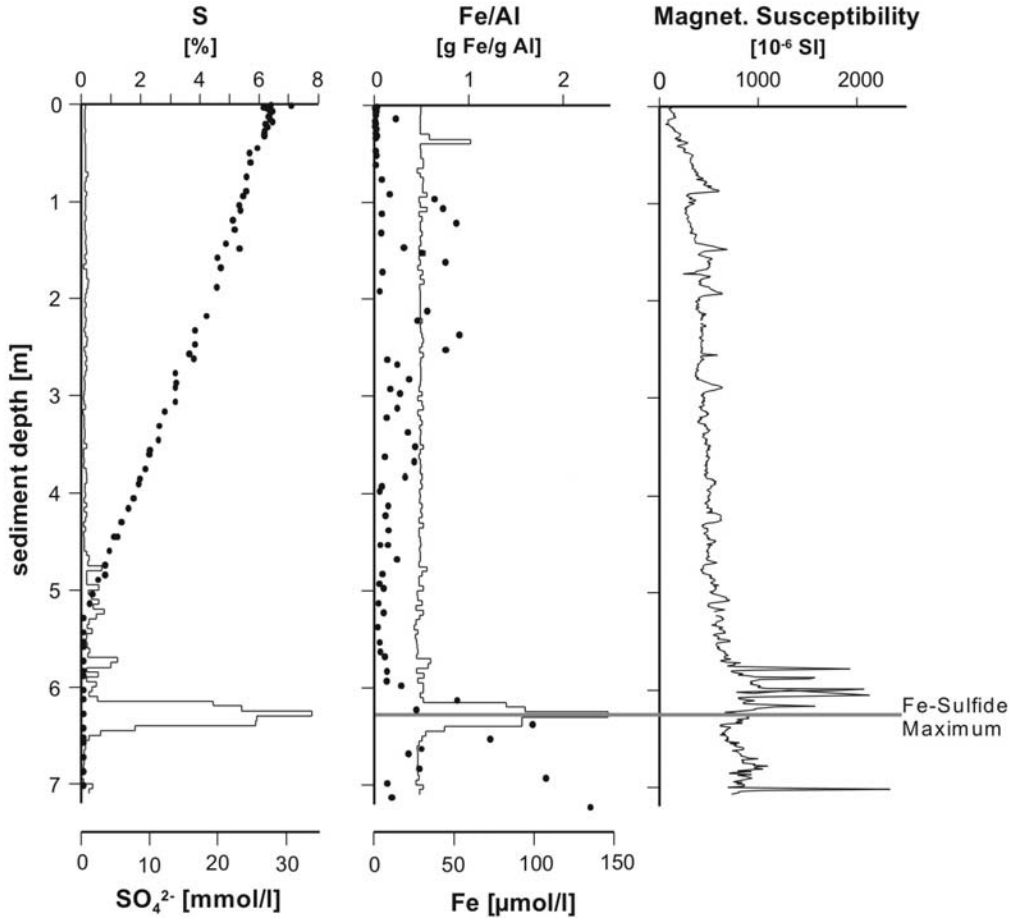

Fig. 8.11 Solid phase profiles of total sulfur and Al-normalized concentration of Fe from total digestion (solid lines), magnetic susceptibility (Funk, unpublished data), as well as pore-water concentration profiles of SO_4^{2-} and Fe^{2+} (solid circles) for core GeoB 1514-6 recovered from the Amazon deep-sea fan (3509 m water depth). The horizontal line demonstrates that the iron peak, which represents mainly iron sulfides, does not directly coincide with the peak in magnetic susceptibility. Modified from Kasten et al. (1998), after Schulz et al. (1994).

In the glacial sediments of the Amazon Fan, which were deposited during the Pleistocene sea level low-stand, Kasten et al. (1998) reported a pronounced enrichment of iron sulfides located several meters below the seafloor, near the present-day SMT (Fig. 8.11). They concluded that this iron sulfide enrichment formed during a period of non-steady state diagenesis, when the zone of anaerobic methane oxidation became fixed at this particular sediment level for an extended period. The condition that is likely to have initiated the non-steady state diagenetic situation was a pronounced decrease in sedimentation and organic carbon accumulation rate during the transition from the Pleistocene to the Holocene. Similar distinct enrichments of authigenic minerals due to a fixation of the SMT during non-steady state depositional conditions induced by decreases in sedimentation rate or even pauses in sedimentation have also been reported by Raiswell (1988), Torres et al. (1996) and Bréhéret and Brumsack (2000).

A second striking feature of the Amazon Fan sediments (gravity core GeoB 1514-6) is the occurrence of a pronounced maximum in magnetic susceptibility, located slightly above the zone of strong enrichment of iron sulfide minerals (Fig. 8.11). As the total iron sulfides did not display a local maximum at the depth of the susceptibility peak, Kasten et al. (1998) suggested the presence of a specific iron sulfide with a high magnetic potential. X-ray diffraction analyses performed on sediment samples from this depth revealed the presence of the magnetic iron sulfide mineral,

greigite (Fe_3S_4). These findings demonstrate that non-steady-state diagenesis does not only lead to a modification of the bulk sediment composition, but can also generate distinct magnetic signals of post-depositional origin within the sedimentary record.

The continental margin off Argentina and Uruguay is a highly dynamic sedimentary setting characterized by gravity driven mass-flow deposits and is therefore ideally suited to study diagenetic processes under shifting depositional conditions. As a typical feature of the deposits in this area, distinct minima in magnetic susceptibility are found a few meters below the sediment surface (c.f. Fig. 8.12). In order to reveal the origin of these susceptibility "gaps", Riedinger et al. (2005) carried out extensive geochemical and rock-magnetic investigations as well as numerical transport-reaction modeling using the program CoTReM (Chapter 16). Pore water data revealed that the conspicuous minima in susceptibility coincide with the current depth of the SMT (Fig. 8.12). The hydrogen sulfide generated by this process reacts with the abundant iron (oxyhydr)-oxides resulting in the precipitation of iron sulfides accompanied by a nearly complete loss of the magnetic signal. Below the sulfidic sediment interval, where the magnetic susceptibility had not significantly suffered from diagenetic overprint, high amounts of iron oxides were present. Numerical modeling of geochemical data suggests that these high amounts of preserved Fe(III) as well as the distinct and spatially restricted loss in susceptibility can only be produced by extremely high glacial sedimentation rates (≥100 cm/kyr) - shielding the Fe(III) minerals from complete

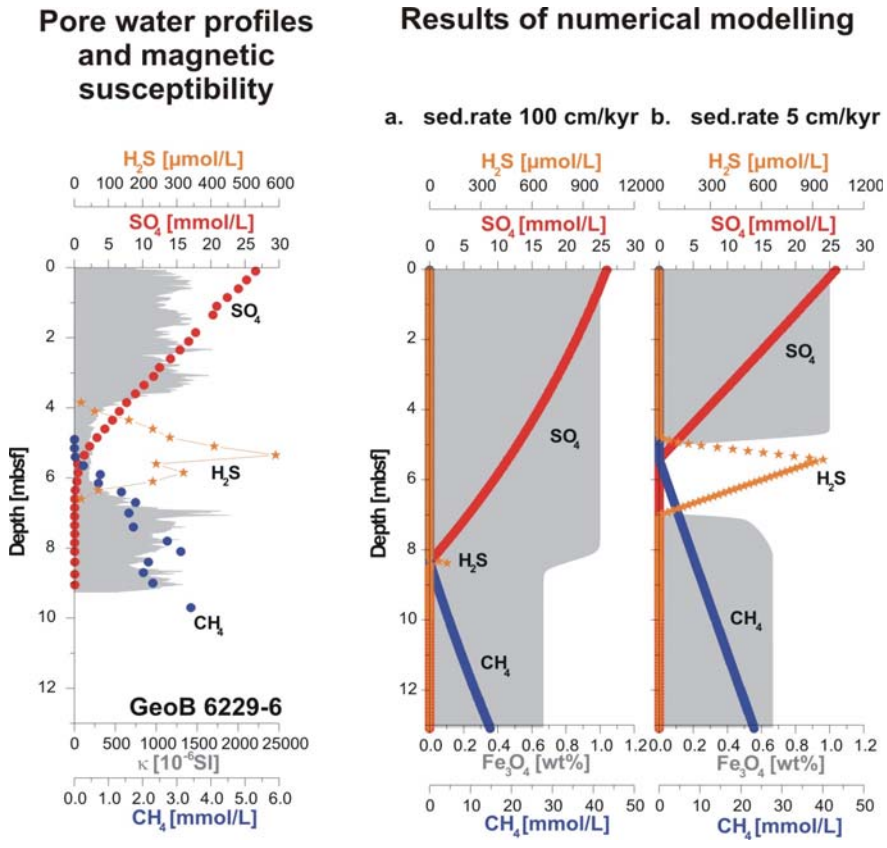

Fig. 8.12 *Left frame:* Sulfate (red circles), methane (blue circles), and sulfide (stars) pore water profiles for core GeoB 6229-6 (3446 m water depth) from the western Argentine Basin off the Rio de la Plata (sulfate data are from Hensen et al. 2003). The magnetic susceptibility is shown in grey. *Middle and right frame:* Results of numerical modeling of diagenetic alteration of magnetite to iron monosulfide with a major change of mean sedimentation rate (SR) for a sediment porosity of 75%. (a) A mean sedimentation rate of 100 cm kyr^{-1} leads to reduction of only about one third of the magnetite. (b) If the mean sedimentation rate is decreased to 5 cm kyr^{-1}, a time interval of ~9000 years is needed to reduce the total amount of magnetite initially contained within an interval of 2 m thickness. Modified from Riedinger et al. (2005).

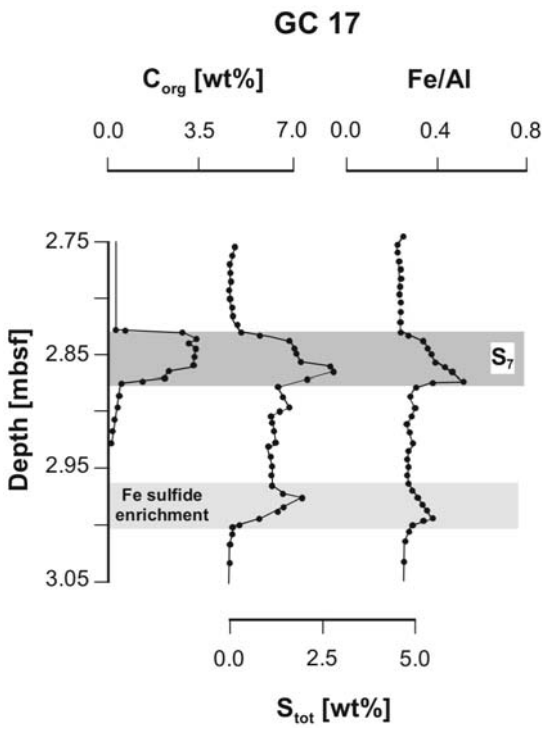

Fig. 8.13 Concentration versus depth profiles of organic carbon (C_{org}), total sulfur (S_{tot}) and Fe/Al ratio (mol/g Fe divided by mol/g Al) through sapropel S_7 in gravity core GC17 from the eastern Mediterranean. The upper dark-grey bar marks the stratigraphical position of the sapropel visible in the core. The lower light-grey bar marks the coincident peaks of S_{tot} and Fe/Al below the sapropel which represent a Fe-sulfide band formed by Liesegang phenomena. Modified from Passier et al. (1996).

reduction - and a subsequent drastic drop during the glacial/Holocene transition (Fig. 8.12). Similar to the conditions on the Amazon Fan the strong decrease in sedimentation rate encountered during the last climatic transition induced a fixation of the SMT and an enhanced overprint of rock magnetic and mineralogical properties at this particular sediment layer. To obtain the observed geochemical and magnetic patterns, the SMT must have remained at a fixed position for about 9000 years – a time span which closely corresponds to the time since the Pleistocene/Holocene transition.

Sulfate reduction can also occur within discrete, organic-rich layers which can lead to a distinct overprint of the primary sediment composition within the organic-rich layers or in the sediment above and below. The non-steady state diagenetic processes occurring in and below the organic-rich layers (sapropels) of the Eastern Mediterranean have been studied by Passier et al. (1996). They presented a model for the formation of distinct iron sulfide enrichments below the sapropels (Fig. 8.13) by the development of a downward moving sulfidization front, similar to Liesegang phenomena (formation of distinct iron sulfide bands) described by Berner (1969). A Liesegang situation exists in depositional systems that are characterized by intermediate contents of reactive (towards sulfide) iron, i.e. in systems that are neither iron nor sulfide dominated. Passier et al. (1996) concluded that excess hydrogen sulfide generated by dissimilatory sulfate reduction within the sapropel was able to migrate downwards (downward sulfidization). This resulted in the formation of pyrite below the sapropel by the reaction of hydrogen sulfide with solid-phase ferric iron and Fe^{2+} diffusing upwards from underlying sediments as schematically illustrated in Figure 8.14.

Downward progressing sulfidization fronts have also been reported to be initiated by transitions from limnic to brackish/marine conditions in the Baltic Sea (Böttcher and Lepland 2000; Neumann et al. 2005) and the Black Sea (Jørgensen et al. 2004; Neretin et al. 2004). In contrast to the example from the Eastern Mediterranean presented above, the sulfide driving the downward sulfidization in these sedimentary settings is derived primarily from AOM and from the increase in sulfate concentration in the water column during the Holocene. At the sites on the western continental slope of the Black Sea investigated by Jørgensen et al.

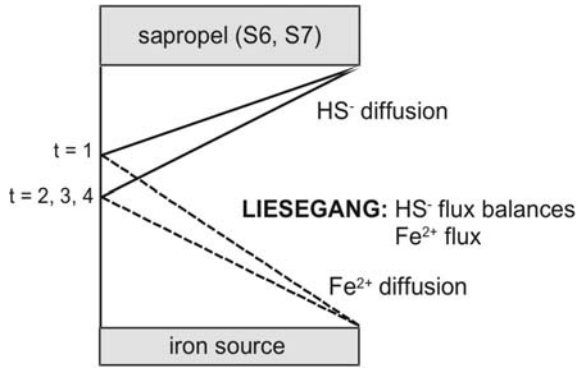

Fig. 8.14 Model for formation of iron sulfide bands below sapropels. The schematic depicted here represents a Liesegang situation (Berner 1969). The front at which downward diffusing hydrogen sulfide and upward diffusing iron react to form iron sulfides is fixed at particular levels below the sapropel for a prolonged period of time. Modified from Passier et al. (1996).

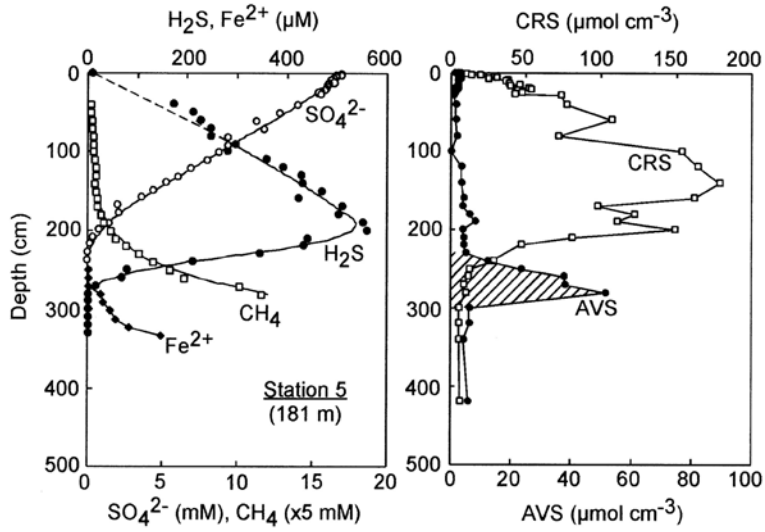

Fig. 8.15 Sulfur geochemistry of a 4-m deep sediment core from the upper slope of the western Black Sea. Left frame: SO_4^{2-}, H_2S, CH_4 and Fe^{2+} (notice scales) in the pore water. The smooth curves are model fits to the data based on the PROFILE model (Berg et al. 1998). Right frame: Chromium reducible sulfur (CRS) and acid volatile sulfide (AVS), the latter showing the black band of iron sulfide at 250-300 cm depth due to the downward progressing sulfidization front. From Jørgensen et al. (2004).

(2004) and Neretin et al. (2004) the sulfate-methane transition is typically located around 2 m sediment depth. Sulfide liberated into the pore water at this depth is diffusing up into the anoxic water column and is also drawn downward to a sulfidization front where it reacts with iron (oxyhydr)oxides and with Fe^{2+} diffusing up from the deeper iron-rich limnic deposits (Fig. 8.15). The current depth position of this HS^-/Fe^{2+} diffusion front is marked by a black band which mostly consists of amorphous iron sulfides termed AVS (acid volatile sulfide) in Fig. 8.15. These mineral phases are also responsible for the distinct black coloration of the sediment. Above (i.e., behind) this downward progressing sulfidization front the amorphous iron sulfides have been and are still converted into pyrite as seen from a distinct horizon of greigite and pyrite formation (c.f., CRS – chromium reducible sulfur representing pyrite; Fig. 8.15). Due to the unusual progression in the reaction sequence towards pyrite, the degree of pyritization (see Section 8.4.2) in this case decreases with increasing age of the deposits, i.e. the least mature or stable iron sulfides are found at greatest sediment depth.

The examples given above illustrate that sulfide produced by dissimilatory sulfate reduction, in particular in organic-rich layers or within the zone of AOM, can produce a profound diagenetic alteration of the sediment up to thousands or hundreds of thousands of years after initial deposition and thereby cause a delayed chemical, mineralogical, isotopic, and magnetic lock-in, i.e. a formation of a relatively stable sedimentary signal at a defined depth. As a consequence, the age of the particular authigenic mineral does not correspond to the age of the sediment layer, in which it is formed, but is much younger. Counterintuitive as it may seem, in the case of downward moving sulfidization fronts the age of the mineral precipitate becomes younger with increasing sediment depth. From these considerations it becomes obvious that the post-depositional alterations of mineral phases and element associations generated in this way complicate or even prevent interpretations of the geochemical environment during the time of original sediment deposition.

8.5 Pathways of Sulfide Oxidation

Vast amounts of sulfide, corresponding to 7 megaton of H_2S daily, are generated in marine sediments as the product of bacterial sulfate reduction. A small fraction of this sulfide is trapped within the sediment, mainly by reaction and precipitation with iron to form pyrite, or by the sulfidization of organic matter, and it thereby becomes buried in

the sea bed (Brüchert and Pratt 1996). In continental slope and deep sea sediments this provides a net burial of reducing power over geological time that contributes to maintain an oxidized surface of the earth and thus, together with the burial of organic carbon, to regulate the atmospheric oxygen level (Berner 1982, 1989). Berner and Raiswell (1983) found that organic carbon and reduced sulfur were buried in the present ocean bed at a mean ratio of ca. 2.8 (±1.5) on a weight basis. This corresponds to a C_{org}:S_{red} burial ratio of 7.4 on a molar basis. Since the complete oxidation of organic carbon to CO_2 represents a change of 4 oxidation steps while the complete oxidation of reduced sulfur (pyrite) to sulfate represents 7 oxidation steps, the burial ratio is 4.3 in terms of reducing equivalents. The latter ratio corresponds to the amount of oxygen that can potentially accumulate in the atmosphere due to the burial of organic carbon versus reduced sulfur. Thus, the reduced sulfur is equivalent to ca. 20% of the buried reducing equivalents in the sea bed.

In deltaic and shelf sediments, where most sulfide production takes place, the intensive sulfide burial during interglacial periods is interrupted during glaciations that bind ocean water in polar ice caps and thereby may lower the sea water level by 100 m. The glacial sea water low-stand causes erosion of accumulated shelf sediments and partly reoxidation of the exposed pyrite, thereby returning much of the accumulated sulfide into the oceanic sulfate pool. Berner (1982) estimated the current burial of pyrite in marine sediments to be 39 Mt S yr^{-1} or $0.12 \cdot 10^{13}$ mol S yr^{-1}. This is equivalent to the sulfide production over 5-6 days per year or to 1.6% of the total sulfate reduction in the global ocean floor (cf. Fig. 8.4). Thus, 98.4% of the produced sulfide is reoxidized back to sea water sulfate on a geological time scale (million years).

The short-term (years to thousand years) burial of sulfide in the form of pyrite in ocean margin sediments is more efficient and generally accounts for 5-20% of the entire sulfide production (Jørgensen et al. 1990; Lin and Morse 1991; Canfield and Teske 1996). This burial provides a sink in the dynamic cycling of sulfur that is limited by the availability of reactive iron to bind the large excess of sulfide. Raiswell and Canfield (1998) found that, of the total iron in marine sediments, on average only 25-28% is highly reactive, 23-31% is poorly reactive, and 41-42% is unreactive. In spite of the small fraction of net pyrite burial, a much larger fraction of the sulfur cycle, however, does go through pyrite and more labile iron sulfides, in particular in the surficial sediment. These metal-bound sulfides are recycled within the sediment together with the free sulfide so that 80-95% of the entire sulfide production is gradually oxidized back to sulfate. The reoxidation takes place at all depths of the sediment, most rapidly in the upper oxidized zone but also in the deeper and sulfidic part where the process is more difficult to detect.

The oxidation of organic material by sulfate reduction yields only a fraction of the energy that is available by aerobic respiration of the same organic compounds. Consequently, a large part of the potential chemical energy is still conserved in the product, H_2S, from sulfate reduction and this energy may become available to other microorganisms, provided a useful oxidant such as O_2 or NO_3^- is present. In coastal sediments where the organic deposition, and therefore the sulfate reduction, is particularly high, the reactive metal oxides may become completely reduced by sulfide. In this extreme case, H_2S may diffuse freely up to the sediment surface and reach the thin oxic skin of the surface sediment. A H_2S-O_2 interface thereby develops within the uppermost few mm of the sediment where the gradient-type of colorless sulfur bacteria may flourish on the chemical energy from H_2S. Such hotspots of sulfide oxidation may be recognizable from the dark coloration of the sediment surface due to black iron sulfide ("black spots"; Rusch et al. 1998). The sediments may also develop a distinct coating of filamentous sulfur bacteria, such as *Beggiatoa*, that store light refracting sulfur globules in their cells and thus provide the sediment with a distinct whitish appearence. Such white *Beggiatoa* mats are typical of the sediments around hydrothermal vents and cold seeps that bring H_2S from the subsurface in direct contact with oxygenated sea water (Jannasch et al. 1989). In extreme cases where the water column overlying the sediment is anoxic, e.g. in the permanently stratified Black Sea or during summer in some eutrophic coastal environments, sulfide is not retained at the sediment surface but penetrates directly up into the sea water (e.g., Roden and Tuttle 1992).

In oxic marine sediments, a brown layer rich in iron and manganese oxides generally separates O_2 and H_2S and thereby prevents a direct sulfide oxidation by oxygen (e.g. Thamdrup et al. 1994a). In this suboxic zone, neither O_2 nor H_2S is present

in detectable concentrations. The metal oxides constitute an efficient sulfide barrier by oxidizing and binding H_2S that diffuses up from the sulfidic sediment below. In this case, H_2S oxidation by oxygen is the exception and requires that the metal oxide layer is penetrated by advective transport, for example by bioirrigation by burrowing animals that pump oxic water for respiration directly down into the sulfidic sediment. Another advective mechanism may be current-induced advective pore water transport in porous sandy sediments (Huettel et al. 1998), or oxygen transport down into the root zone of sea grass beds (Ballbjerg et al. 1998). Through such oxygen penetration also pyrite may be oxidized with oxygen, a process that has been extensively studied (e.g. Lowson 1982; Luther 1987; Moses and Herman 1991; Morse 1991). Pyrite oxidation with O_2 is a rather fast process that may be purely abiotic, catalyzed by an electron shuttle between adsorbed Fe(II) and Fe(III) ions transferring electrons from pyrite to O_2. Sulfate is the end product of the sulfur oxidation and iron oxides often coat the surface of the oxidized pyrite grains.

Most sulfide oxidation in marine sediments is anoxic (i.e. takes place in the absence of oxygen) and generally involves the precipitation of iron sulfide and the subsequent oxidation of iron-sulfur minerals back to sulfate. Evidence for anoxic sulfide oxidation comes from studies of pore water chemistry, solid phase distributions of metal oxides and sulfides, mass balance calculations, and direct experiments. By the use of radiolabeled H_2S added to anoxic sediment cores or slurries, a rapid transfer of the label could be observed into sulfur fractions defined as acid volatile sulfide (mostly FeS), chromium reducible sulfide (mostly FeS_2), elemental sulfur (S^0), or sulfate (Fossing and Jørgensen 1990). The radiolabeled FeS and S^0 were readily oxidized to sulfate in the anoxic sediment. Pyrite, in contrast, is more stable and is oxidized only over longer incubations. Yet, pyrite comprises the main sulfur pool in marine sediments and undergoes slow transport and oxidation of critical importance for the sulfur cycle.

These processes are illustrated in Fig. 8.16. Sulfate that penetrates down into the sediment from the overlying sea water is reduced to H_2S by sulfate reducing bacteria that use the deposited organic material as their energy source. Also methane diffusing up from below feeds sulfate reduction in the lower sulfate zone. At depth in

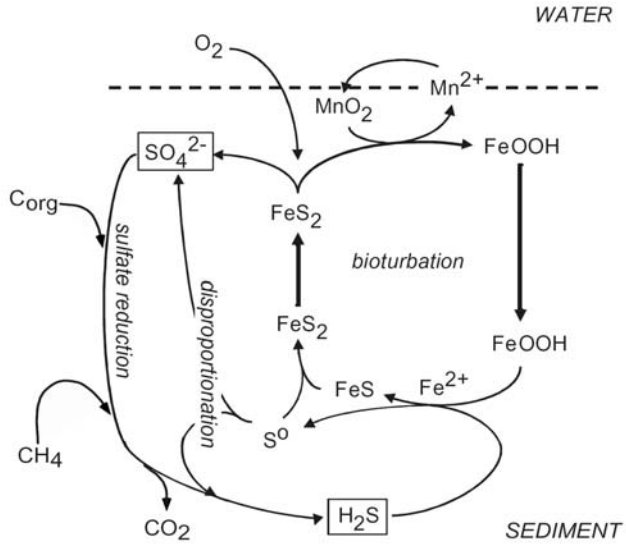

Fig. 8.16 The sulfur cycle in marine sediments. The cycle is energetically driven by deposited organic material and methane, both of which are used by sulfate reducing bacteria to produce H_2S. Much of the H_2S reacts chemically with iron (oxyhydr)oxides to form FeS and a range of intermediate oxidation states including S^0 and FeS_2. The further oxidation of these species back to sulfate is mediated by the vertical conveyer belt of bioturbation caused by burrowing macrofauna. Reoxidation of the solid phase sulfur species to sulfate at the sediment surface may be by oxygen, nitrate or manganese oxide. The same conveyer belt brings the oxidized iron back down towards the sulfide production zone where it reacts with further H_2S. A highly efficient recycling of sulfur is thereby achieved. (From Jørgensen and Nelson 2004).

marine sediments, the production of H_2S may exceed the availability of reactive metal oxides and H_2S accumulates in the pore water (see Fig. 8.6, 8.12, 8.13, and 8.17). The H_2S diffuses upwards along a concentration gradient that generally reaches zero at the bottom of the suboxic zone. Concurrently, the H_2S reacts with buried iron oxides to form FeS, FeS_2, S^0 and a number of other solid or dissolved intermediate products. Once the reduced sulfur is bound in the solid phase, e.g. as pyrite, its further oxidation depends on a slow reaction with further Fe(III) species or its transport up to near-surface layers with oxidants of higher redox potential.

Pyrite transport in near-surface sediments generally takes place through the conveyer belt of bioturbation whereby burrowing macrofauna mix the sediment or directly move sediment particles as part of their deposit feeding behavior (Fig. 8.16). As the pyrite reaches up into the suboxic zone it may react with oxidants such as oxygen or manganese oxide and be converted into sulfate and iron oxides (or iron (oxyhydr)oxides). The iron oxides are in turn transported downwards through the same conveyer belt and thereby become available for further binding of sulfide and pyrite formation. The pyrite oxidation by manganese oxide has been implied from chemical profiles (Canfield et al. 1993) and demonstrated directly through experiments (Schippers and Jørgensen 2001, 2002). The process is interesting in that it involves the reaction between two mineral phases in the sediment that must be in close proximity for the oxidation to proceed. The initial reaction is purely chemical and was proposed to occur by a Fe(II)/Fe(III)-shuttle in the pore fluid between the mineral surfaces of FeS_2 and MnO_2. The immediate products of the oxidation are thiosulfate and polythionates. These can be further oxidized to sulfate by manganese reducing bacteria, thus

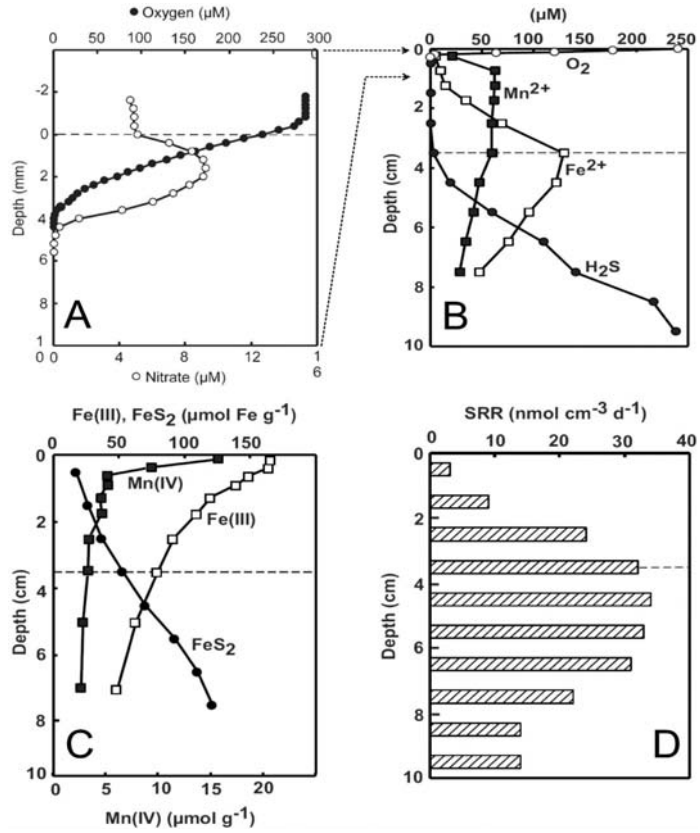

Fig. 8.17 Biogeochemical profiles of sulfur, manganese and iron species in a coastal marine sediment (Aarhus Bay, Denmark, 16 m water depth). A) Oxygen and nitrate profiles measured with O_2 and NO_3^- microsensors. B) Pore water profiles of dissolved manganese, iron and H_2S. C) Profiles of solid phase oxidized manganese and iron and of pyrite. D) Distribution of sulfate reduction rates (SRR) measured by ^{35}S-technique. The broken line at 4 cm depth indicates the transition between the suboxic zone and the sulfidic zone. Data in A) were measured at the same site but a different year than data in B)-D). (Data from Kjær 2000 and Thamdrup et al. 1994a; reproduced from Jørgensen and Nelson 2004).

making the complete pyrite oxidation to sulfate dependent on microbial catalysis (Schippers and Jørgensen 2001):

$$FeS_2 + 7.5\ MnO_2 + 11\ H^+ \rightarrow Fe(OH)_3 + 2\ SO_4^{2-} + 7.5\ Mn^{2+} + 4\ H_2O \quad (8.16)$$

Pyrite oxidation by nitrate could not be demonstrated through short-term sediment experiments but FeS is readily oxidized, both by nitrate and MnO_2 (Aller and Rude 1988; Schippers 2004). The immediate product by FeS oxidation is not thiosulfate but polysulfide which subsequently degrades into elemental sulfur:

$$FeS + 1.5\ MnO_2 + 3\ H^+ \rightarrow Fe(OH)_3 + S^0 + 1.5\ Mn^{2+} \quad (8.17)$$

The processes of sulfide oxidation described here are reflected in the chemical zonations of pore water chemistry, solid phase chemistry and bacterial activity. As an example, Fig. 8.17 shows data from organic-rich coastal sediment at the Baltic Sea - North Sea transition. Oxygen penetrated less than 0.4 cm into the sediment and showed no contact with the zone of detectable H_2S which started only from ca. 4 cm depth. Nitrate penetrated only slightly deeper than oxygen, with a peak at 0.2 cm depth due to aerobic oxidation of ammonium (nitrification) diffusing up from the sediment below. The upper 0.4-4 cm of the sediment comprised the suboxic zone where maxima in dissolved reduced manganese and iron showed the zones where the reduction of these metals was most intensive (peaks at 1- 2 cm depth for manganese and 3-4 cm depth for iron). The concentration of solid phase manganese oxide dropped steeply with depth from the sediment surface to 1 cm depth where its reduction was most intensive. Oxidized iron decreased more gradually as it was most intensively reduced in the lower part of the suboxic zone. Measurements of sulfate reduction showed that H_2S was produced throughout the sediment with maximum rates at the top of the sulfidic zone. Sulfate reduction also took place in the suboxic zone but the produced H_2S was here rapidly reoxidized and did not reach detectable concentrations. Only by the short-term experimental measurements using $^{35}SO_4^{2-}$ could the SRR activity therefore be demonstrated. Due to this sulfate reduction, a part of the manganese and iron reduction was driven by sulfide oxidation while another part was due to the direct oxidation of organic matter by heterotrophic, metal-reducing bacteria (Thamdrup et al. 1994a).

The intermediate sulfur species in sulfide oxidation, such as thiosulfate and elemental sulfur, are not stable in the sediment but are further transformed by microorganisms. Thiosulfate is turned over within hours or days and generally occurs only in sub-micromolar concentration in the sediment pore water (Thamdrup et al. 1994b). Elemental sulfur accumulates to much higher concentration in the solid phase but may also turn over on a seasonal or longer time scale in near-surface sediments (Troelsen and Jørgensen 1982). The preferred pathway of bacterial thiosulfate or sulfur transformation depends strongly on the chemical environment in the sediment. In the near-surface sediment with suitable oxidants such as oxygen, nitrate or metal oxides, these sulfur species may be used as energy sources by chemoautotrophic bacteria and be oxidized completely to sulfate (Fig. 8.17, see also Chapter 5). When formed below the suboxic zone, they may be used as oxidants (electron acceptors) in bacterial respiration to oxidize organic material. Through such a bacterial thiosulfate or sulfur respiration these intermediates are reduced back to sulfide. When the availability of oxidants and organic material are both limited, the two sulfur species may be disproportionated.

The ability of certain anaerobic bacteria to disproportionate intermediate sulfur species such as thiosulfate was discovered only in the late 1980'ies (Bak and Pfennig 1987; Krämer and Cypionka 1989; Finster et al. 1998) but has since been shown to play an important role in the sulfur cycle of aquatic sediments (Jørgensen 1990; Jørgensen and Bak 1991; Thamdrup et al. 1993). It is characteristic for the disproportionation that the sulfur species are concurrently reduced to sulfide and oxidized to sulfate. This is an energy yielding reaction under appropriate sediment conditions and is independent of external reductants or oxidants. The process can be considered a type of inorganic fermentation and it provides sufficient energy for bacteria to live on. By thiosulfate disproportionation, the inner (sulfonate) sulfur atom changes oxidation step from +5 in $S_2O_3^{2-}$ to +6 in SO_4^{2-}, while the outer (sulfane) atom changes from -1 in $S_2O_3^{2-}$ to -2 in H_2S (Vairavamurthy at al. 1993; Eq. 8.18). By elemental sulfur with an oxidation state of 0, some of the atoms are reduced to H_2S and some oxidized

to SO_4^{2-} in a proportion of 3:1 that maintains electron balance (Eq. 8.19):

$$S_2O_3^{2-} + H_2O \rightarrow H_2S + SO_4^{2-} \quad (8.18)$$

$$4\ S^0 + 4\ H_2O \rightarrow 3\ H_2S + SO_4^{2-} + 2\ H^+ \quad (8.19)$$

Disproportionation reactions do not cause a net oxidation of the sulfur species, yet they have a key function in sulfide oxidation. Disproportionation provides a shunt in the sulfur cycle whereby the H_2S formed by this reaction may be oxidized again to the same sulfur intermediate by metal oxides. Manganese oxide, for example, rapidly oxidizes H_2S to S^0 without participation of bacteria, but does not oxidize the S^0 further to sulfate (Burdige 1993). The elemental sulfur may, however, be disproportionated (Eq. 8.19) whereby a fourth of it is oxidized completely to sulfate while the remaining three fourths return to the sulfide pool. Through repeated partial oxidation of sulfide to elemental sulfur with manganese oxide and subsequent disproportionation of the elemental sulfur to sulfate and sulfide a complete oxidation of sulfide to sulfate by manganese oxide may be achieved (Fig. 8.16; Thamdrup et al. 1993; Böttcher and Thamdrup 2001):

$$4\ H_2S + 4\ MnO_2 \rightarrow 4\ S^0 + 4\ Mn^{2+} + 8\ OH^- \quad (8.20)$$

Sum of Eq. 8.20 and 8.19:

$$H_2S + 4\ MnO_2 + 2\ H_2O \rightarrow SO_4^{2-} + 4\ Mn^{2+} + 6\ OH^- \quad (8.21)$$

An interesting biological mechanism of sulfide oxidation in coastal upwelling regions and other high-productivity coastal ecosystems was discovered in the mid 1990'ies (Fossing et al. 1995). The sediment underlying some of the most intensive upwelling systems, e.g. off the Pacific coast of South and Central America or the Atlantic coast of southwest Africa, is densely populated with sulfur bacteria (species of *Thioploca*, *Thiomargarita*, and *Beggiatoa*) that have a peculiar mode of life and an unusually large cell size (Schulz et al. 1999). Within a liquid vacuole inside each cell they accumulate nitrate from the ambient sea water and later use this nitrate down in the sediment as an electron acceptor for sulfide oxidation from which they gain energy. The sulfide is oxidized first to elemental sulfur, which is stored transiently in the cells, and then to sulfate. This adaptation is unique in that it enables the motile types of the bacteria to commute up and down between the nitrate source in the sea water and the sulfide source in the sediment without having access to both at the same time (Jørgensen and Gallardo 1999; Schulz and Jørgensen 2001; see Chapter 6).

8.6 Determination of Process Rates

The rates of biogeochemical processes such as sulfate reduction in marine sediments can be determined by different approaches that all have strengths and weaknesses and may demonstrate fundamentally different aspects of the process. It is important for each application to consider carefully the properties of the sediment to be analyzed and the limitations of the method applied. The study of shallow and highly dynamic surface sediments requires a different approach than the study of deep sediments that have undergone stable diagenesis over a long time period. By the shallow sediment an experimental measurement of the process rate may be optimal whereas deep in the sediments generally a modeling approach is preferred. Dependent on the method, however, either the gross or the net rate of sulfate reduction is measured. The extent to which these differ has been determined only in a few cases.

Gross sulfate reduction rates (gross SRR) can be measured by experimental incubation of recovered sediment samples on board ship or in the laboratory. Today, this is mostly done by the use of radioactively labeled sulfate, $^{35}SO_4^{2-}$, as a tracer in order to obtain sufficiently high sensitivity of the method (see Chapter 5). Originally developed by Sorokin (1962), Ivanov (1968), Jørgensen (1978), this method has been modified and refined over the years (e.g., Howarth 1979; Canfield et al. 1986; Fossing and Jørgensen 1989; Kallmeyer et al. 2004). By adaptation of the radiotracer method it has been possible to directly measure sulfate reduction rates that vary over more than 7 orders of magnitude, for example on the Peruvian shelf, from >1000 nmol SO_4^{2-} cm^{-3} day^{-1} at the sediment surface to <0.001 nmol SO_4^{2-} cm^{-3} day^{-1} at 100 m subsurface (Parkes et al. 2005; J. Kallmeyer et al. in prep.).

The *gross SRR* as measured by $^{35}SO_4^{2-}$ technique comes closest to the overall sulfate reduction that takes place in the sediment. The

radiotracer experiment generally lasts for only a few hours to a day and little reoxidation of produced ^{35}S-sulfide takes place during this time interval, unless the sediment is rich in reactive oxidized iron which may be the case in the suboxic zone near the sediment surface. The measurement should be kept short in order to minimize changes in the chemistry or microbial activity of the sediment under the laboratory conditions used. This is an important criterion for the use of radiotracer instead of just following the gradual disappearence of pore water sulfate over time as has been used earlier and is still applied when safety considerations prohibit the use of radiotracer. Tracking the sulfate concentration over time is, however, a rather insensitive method that mostly requires incubations over many days or weeks during which significant changes in measured rates occur.

Another approach is based on the experiment that nature has already done, namely by generating decreasing sulfate concentrations down through the sediment column due to sulfate reduction acting over many years. The resulting pore water profile of sulfate reflects the rate of *net SRR,* which represents the gross SRR minus the (long-term) rate of reoxidation of reduced sulfur species back to sulfate. Such profiles, combined with solid-phase data on the sulfur chemistry and organic carbon content, have been used to calculate the distribution of sulfate reduction over longer periods by 1-dimensional reaction-transport modeling (e.g., Berner 1980; Canfield 1991; Schulz et al. 1994). Modeling of the net SRR generally assumes steady state conditions of reduction rate, transport and sedimentation and requires qualified information on the transport coefficients of pore water species down through the sediment column. Since disturbing factors such as burrow irrigation by the benthic macrofauna or current-induced advective pore water flow may strongly enhance transport in addition to molecular diffusion, it is mostly difficult to provide accurate transport coefficients in the near-surface sediment. At depth in the sediment, however, molecular diffusion and steady state are more likely to prevail. Here the modeling approach has its obvious strength relative to the radiotracer measurements that are increasingly prone to disturbance artifacts the deeper in the sediment the samples are taken.

In the following, we will use data of Jørgensen et al. (2004) from the Black Sea as an example to illustrate the differences between the two approaches. Fig. 8.18 shows results from the deep sulfidic part of the Black Sea where macrofauna are unable to live and where bioirrigation is therefore absent (although current-induced advective pore water transport may take place near the sediment surface). Sulfate reduction rates were measured experimentally by the radiotracer method down to 20 cm depth in the sediment (Fig. 8.18 A).

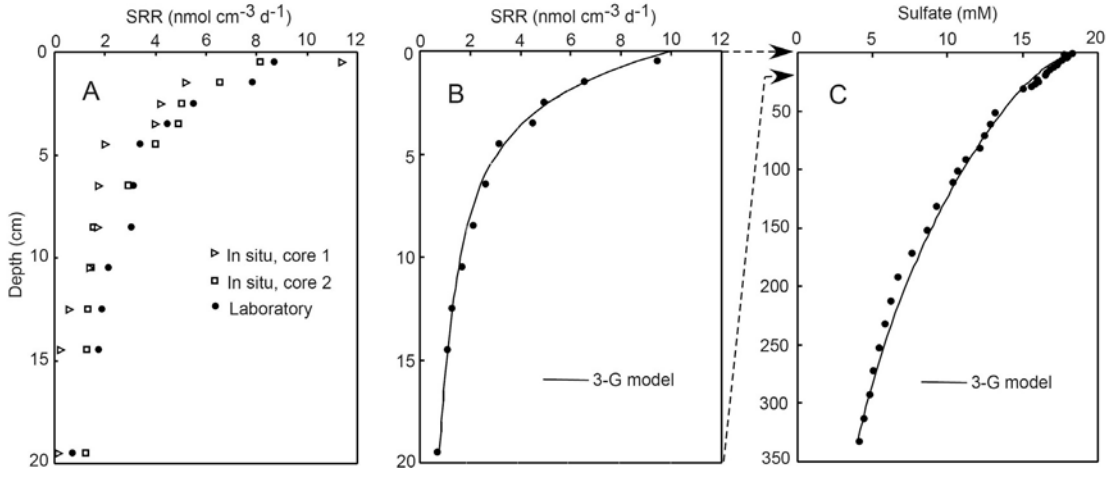

Fig. 8.18 Determination of sulfate reduction rates in sediment cored by multicorer (A and B) and by gravity corer (C) from 1176 m water depth in the sulfidic part of the western Black Sea. A) Sulfate reduction rates (SRR) measured experimentally using $^{35}SO_4^{2-}$, either directly *in situ* on the sea floor using a benthic lander or shipboard in the laboratory. B) Mean experimental sulfate reduction rates (data points) and a model curve fitted to these rates. C) Sulfate concentrations measured in the pore water (data points) and modeled sulfate profile (smooth curve) that matches the fitted SRR in the uppermost 20 cm. After Jørgensen et al. (2001).

A multi-G model of Westrich and Berner (1984) was applied to fit a smooth curve to these rate data. The model assumes that the sediment organic matter that feeds sulfate reduction consists of three pools, each of which is degraded exponentially over depth and time, but each having its own pool size and exponential decay constant. Fig. 8.18 B and C show that this model fits well with both the measured sulfate reduction rates in the upper sediment layer and the sulfate curve in the deeper sediment down to 330 cm depth.

A point to observe in Fig. 8.18 C is that the measured and modeled profiles of pore water sulfate in the uppermost 0-20 cm hardly show any curvature and, thus, indicate zero sulfate reduction in this layer. The radiotracer measurements in Fig. 8.18 B, however, show that 66% of the sulfate reduction in the entire sulfate zone takes place in the top 15 cm where, in the deep sulfidic part of the Black Sea, sulfate reduction is the predominant pathway of organic carbon mineralization (Jørgensen et al. 2001). One possible reason for this discrepancy is that modeling has low sensitivity over narrow depth intervals because diffusion is fast over short distances and thereby reduces changes in concentration in spite of high reaction rates. In contrast, over the entire sulfate zone even a deep zone of relatively low sulfate reduction rates may affect the entire sulfate profile. This is why enhanced reduction rates in the sulfate-methane transition tend to shape the entire sulfate distribution in the sediment as seen in Fig. 8.18 C. Thus, experimental measurements are required to determine the sulfate reduction in the near-surface sediment. Such a discrepancy between measured and modeled rates is characteristic also of other sediments and is important to consider in relation to the global SRR estimates made in Fig. 8.3 and 8.4. Data from ocean margin sediments were there mostly determined by the radiotracer method (gross SRR) whereas those from the deep sea were modeled (net SRR).

8.7 The Sulfur Cycle

The sea bed functions as a giant anaerobic reactor where element cycles are coupled in a way that differs fundamentally from the cycles in the oxic ocean. The microbiological and geochemical processes of sulfur transformation thereby play key functions that control the mineralization of deposited organic matter and thereby the chemistry of the ocean. In the following we briefly summarize some main aspects of the sulfur cycle in marine sediments and discuss its role for the dynamics of sulfate in the ocean.

Rather than being a simple cycle, composed of anaerobic bacterial reduction of sulfate to hydrogen sulfide and aerobic reoxidation of H_2S to SO_4^{2-}, the transformations of sulfur in aquatic sediments include a combination of intermediate cycles or shunts and interactions with other element cycles (e.g., Jørgensen 1990; Luther and Church 1991; Thamdrup et al. 1993; van Cappellen and Wang 1996) schematically illustrated in Figure 8.16. Within this complex cycle, sulfur compounds occur in oxidation states ranging from -2 (H_2S) to +6 (SO_4^{2-})

By bacterial sulfate reduction H_2S is produced as the extracellular end-product (Widdel and Hansen 1991). During the oxidation of H_2S, oxic or anoxic, chemical or biological, compounds such as zero-valent sulfur (in elemental sulfur, polysulfides, or polythionates), thiosulfate ($S_2O_3^{2-}$), and sulfite (SO_3^{2-}) are produced (Cline and Richards 1969; Pyzik and Sommer 1981; Kelly 1988; Dos Santos Afonso and Stumm 1992). These intermediates may then be further transformed by one or several of the following processes:

- Respiratory bacterial reduction to H_2S,
- bacterial or chemical oxidation,
- chemical precipitation (e.g. FeS formation), or
- bacterial disproportionation to H_2S and SO_4^{2-}.

By bacterial disproportionation H_2S and SO_4^{2-} are produced concurrently without participation of an external electron acceptor or donor (Bak and Pfennig 1987; Thamdrup et al. 1993). The biogeochemical transformations of sulfur in marine sediments are closely coupled to the cycles of iron and manganese. Sulfate, iron oxides, and manganese oxides all serve as electron acceptors in the respiratory degradation of organic matter. As there are also non-enzymatic reactions between iron, manganese and H_2S within the sediment, the quantification of dissimilatory, heterotrophic Fe and Mn reduction is particularly difficult.

The precipitation of (authigenic) iron sulfides resulting from the reaction between H_2S and Fe phases exerts an important control on the distribution of H_2S in marine pore waters (Goldhaber and Kaplan 1974; Canfield 1989; Canfield et al.

1992). Depending on the abundance and reactivity of the Fe(III) minerals present as well as on the rate of sulfate reduction, H_2S may be undetectable despite its production at high rates. As the H_2S accumulates in the pore water, it diffuses up towards the sediment surface where most of it is ultimately oxidized back to sulfate. Only a small fraction, 5-20%, of the produced H_2S is trapped as solid phase iron-sulfur minerals or organic sulfur within the sediment. Over longer periods of thousands to millions of years, most of this trapped sulfur becomes exposed to oxidants and again returns to the great sulfate reservoir of the ocean.

Over geological time, ocean sulfate is thus continuously recycled through sulfate reduction in the sea bed. During this recycling, the sulfur atom in sulfate undergoes a major redox transformation of 8 oxidation steps between sulfate (+6) and sulfide (-2) and is thereby an effective oxidant for the mineralization of marine organic matter. Importantly, the sulfur atom in sulfate is separated from the oxygen atoms during the reduction process ($SO_4^{2-} \rightarrow H_2S$), and is subsequently combined with new oxygen atoms from sediment pore water upon reoxidation of the sulfide. How fast is this recombination of the elements and how long is the residence time of sulfate in sea water? We have calculated above that the magnitude of sulfate reduction in the global sea bed is $7.5 \cdot 10^{13}$ mol SO_4^{2-} yr^{-1}. The mean sulfate concentration of sea water is 29 mM and the total volume of ocean water is 1.37 billion km^3 (Garrison 1997). Thus, the ocean contains $1.37 \cdot 10^{21}$ liter of sea water with a total pool of $4.0 \cdot 10^{19}$ mol SO_4^{2-}. The turnover time of this global ocean sulfate pool through bacterial sulfate reduction is $(4.0 \cdot 10^{19})/(7.5 \cdot 10^{13})$ = ca. 0.5 million years.

Sulfate is reduced in the sea bed not only through bacterial catalysis but also through thermochemical catalysis at high temperature. At mid-oceanic ridges sea water is slowly convected through the hot magmatic crust where a part of it is heated to >350°C (see Chapter 13). At such high temperatures sulfate reacts as an oxidant for ferrous iron and other reduced minerals and the sulfate is reduced to H_2S without the participation of microorganisms which are excluded by temperatures above ca. 100°C (Weber and Jørgensen 2002). The global sea water flux that undergoes heating to >350°C has been estimated to be $3\text{-}6 \cdot 10^{13}$ liter yr^{-1} (Elderfield and Schultz 1996). By a complete reduction of the 29 mM of sea water sulfate, this corresponds to the reduction of $0.08\text{-}0.16 \cdot 10^{13}$ mol SO_4^{2-} yr^{-1} or 1-2% of the global microbiological sulfate reduction. The turnover time of the entire volume of ocean water at >350°C, and thus of the oceanic sulfate pool through thermochemical reduction, in hot mid-oceanic crust is thus 20-40 million years (cf. Elderfield and Schultz 1996).

The hydrothermal systems associated with the mid-oceanic ridges harbor some of the richest biological communities on the ocean floor and include giant clams, mussels, tube worms and shrimps. These animals are nourished by symbiotic bacteria that oxidize sulfide and methane from the vent water and use the energy for chemoautotrophic biomass production that in turn feeds the hosts. It is an interesting perspective that their energy source is independent of light and photosynthesis but is instead of geothermal origin and based on chemical reactions at high temperature. (It should be remembered, however, that the oxygen used for the oxidation of sulfide and methane is derived from photosynthesis in the surface ocean, so the chemosynthetic processes would still not run without sunlight.) Although the hydrothermal vent communities are rich oases of life on the sea floor, their total contribution to the oceanic carbon cycle is marginal. Bach and Edwards (2003) estimated that the global chemosynthetic biomass production from oxidation of new ocean crust may be up to 10^{12} g C yr^{-1}. The total potential for chemosynthetic primary production at the deep sea hydrothermal vents is globally estimated to be about 10^{13} g biomass per year (McCollom and Shock 1997). This represents only about 0.02% of the global primary production by photosynthesis in the oceans. As the chemosynthetic production takes place in the otherwise nutrient-poor deep sea, however, it makes a much more important contribution to the local carbon supply to the deep sea floor. Based on the oxygen uptake data presented in Fig. 8.4, the global organic carbon mineralization by oxygen in the deep sea bed at >3000 m water depth is only $5 \cdot 10^{13}$ mol yr^{-1}, relative to which the chemoautotrophic production at mid-oceanic ridges corresponds to 20%.

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8.8 Problems

Problem 1

Organic matter is oxidized in the suboxic zone through iron or manganese reduction. This may be a direct oxidation by metal reducing bacteria or an indirect oxidation via sulfate reduction and sulfide oxidation. Does it matter for the end products which pathway dominates?

Problem 2

H_2S can be oxidized completely to sulfate by manganese oxide in marine sediments although the chemical reaction oxidizes H_2S only to elemental sulfur, S^0. How is the oxidation to sulfate then possible?

Problem 3

Which factors determine how large a fraction of the deposited organic material in the sea bed is mineralized through sulfate reduction relative to other mineralization pathways?

Problem 4

Only about 5% of the total mineralized organic carbon in marine sediments is ultimately degraded to methane. Why, then, does the anaerobic oxidation of methane with sulfate often generate quasi-linear sulfate profiles that indicate methane to be the dominant energy source for sulfate reduction?

Problem 5

Which factors may cause a lock-in of a diagenetic front in the sea bed and thereby lead to the diagenetic overprinting of paleoceanographic signals in a specific sediment horizon?

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