Biogeochemistry **65:** 295–317, 2003.

Rates and regulation of microbial iron reduction in sediments of the Baltic-North Sea transition

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Received 5 December 2001; revised 20 February 2002; accepted in revised form 15 July 2002

Key words: Anaerobic carbon oxidation, Iron reduction, Kattegat, Sediment, Sulfate reduction

Abstract. The rates and pathways of anaerobic carbon mineralization processes were investigated at seven stations, ranging from 10 to 56 m water depth, in the Kattegat and Belt Sea, Denmark. Organic carbon mineralization coupled to microbial Mn and Fe reduction was quantified using anaerobic sediment incubation at two stations that were widely separated geographically within the study area. Fe reduction accounted for 75% of the anaerobic carbon oxidation at the station in the northern Kattegat, which is the highest percentage so far reported from subtidal marine sediment. By contrast, sulfate reduction was the dominant anaerobic respiration pathway (95%) at the station in the Great Belt. Dominance of Fe reduction was related to a relatively high sediment Fe content in combination with active reworking of the sediment by infauna. The relative contribution of Fe reduction to anaerobic carbon oxidation at both stations correlated with the concentration of poorly crystalline Fe(III), confirming that the concentration of poorly crystalline Fe(III) exerts a strong control on rates of Fe reduction in marine sediments. The dependence of microbial Fe reduction on concentrations of poorly crystalline Fe(III) was used to quantify the importance of Fe reduction at sites where anaerobic incubations were not applied. This study showed that Fe reduction is an important process in anaerobic carbon oxidation in a wider area of the seafloor in the northern and eastern Kattegat (contribution 60 – 75%). By contrast, Fe reduction is of little significance (6 – 25%) in the more coarse-grained sediments of the shallower western and southern Kattegat, where a low Fe content was an important limiting factor, and in fine-grained sediments of the Belt Sea (4 – 28%), where seasonal oxygen depletion limits the intensity of bioturbation and thereby the availability of Fe(III). A large fraction of the total deposition of organic matter in the Kattegat and Belt Sea occurs in the northern Kattegat, and we estimate 33% of benthic carbon oxidation in the whole area is conveyed by Fe reduction.

Introduction

In coastal and continental margin environments, a significant fraction of the primary production sinks through the water column and reaches the sea floor (Wollast 1991; Jørgensen 1996). Most of the deposited organic material is oxidized in the surface sediments, recycling the inorganic constituents to the water column, while a smaller fraction escapes mineralization and becomes permanently buried (Canfield 1993). Both aerobic and anaerobic respiration processes are important in

benthic carbon oxidation. Microbial Mn and Fe reduction are the least explored of the anaerobic respiration processes because of a relatively late discovery of the processes (Lovley 1991; Lovley et al. 1997) and late development of suitable techniques for the quantification of rates (Thamdrup and Canfield 2000).

The availability of Mn oxides and poorly crystalline Fe oxides is an important factor influencing the significance of microbial Mn and Fe reduction in sedimentary environments (Lovley and Phillips (1987a, 1988)). Microbial Mn reduction dominates carbon oxidation over Fe and sulfate reduction in marine sediments rich in Mn oxides such as the Panama Basin and Skagerrak (Aller 1990; Canfield et al. 1993b). However, these Mn-rich sites are unusual and in most marine sediments Mn reduction plays an insignificant role in carbon oxidation (Aller 1994; Thamdrup and Canfield 1996; Thamdrup et al. 1996; Rysgaard et al. 1998; Kostka et al. 1999; Glud et al. 2000). This makes Fe and sulfate reduction the most important pathways of anaerobic carbon oxidation in many continental sediments, contributing 22% and 78% to anaerobic carbon oxidation, respectively, as an average of $\sim$20 widely scattered sites in a recent compilation (Thamdrup 2000). The relative contributions of the two processes are highly variable, however, with the contribution of Fe reduction ranging from below detection to 64%.

In sediments with abundant poorly crystalline Fe oxides, Fe-reducing bacteria outcompete sulfate-reducing bacteria for carbon substrates and thereby dominate anaerobic carbon oxidation (Lovley and Phillips 1987a; King 1990; Canfield et al. 1993b; Rysgaard et al. 1998). However, several studies have demonstrated a co-existence of Fe reduction and sulfate reduction (Sørensen 1982; Canfield 1993; Achtnich et al. 1995; Thomsen 2001). High substrate concentrations may alleviate the competition between the two processes (Lovley and Phillips 1987a). Thus, a pulse of organic substrates allowed the transient co-existence of the two microbial processes in recently wetted sediment from a rice paddy (Achtnich et al. 1995; Thomsen 2001). In marine sediments, however, hydrolysis and fermentation typically limit rates of carbon oxidation, and the concentration of substrates for Fe and sulfate-reducing bacteria is kept low (Sørensen 1982; Hoehler 1998). There, the relative contribution of Fe reduction to carbon oxidation has been found to depend on the concentration of poorly crystalline Fe oxides, and microbial Fe reduction rates appear to be generally limited by the availability of Fe oxides, thus allowing for concurrent sulfate reduction (Thamdrup 2000).

The maintenance of high concentrations of poorly crystalline Fe oxides in the sediments requires reoxidation of ferrous iron by physical reworking through bioturbation, waves, or currents. Thus, microbial Fe reduction is controlled by a hierarchy of several factors, including sediment reworking, availability of reactive organic material, and concentration and reactivity of Fe oxides in the sediment. The interactions of the factors that regulate Fe reduction are not well understood and progress in their investigation is complicated by the labor intensity of the methods available for quantifying Fe reduction.

The aim of the present study is to quantify the role of microbial Fe reduction in anaerobic carbon oxidation in a wider marine region, and to identify important factors in its geographical variation. We also explore the relationship between relative

Table 1. Stations, geographical positions, water depths and mean porosity.

Station	Lat., N	Long., E	Water depth (m)	Porosity (v/v)
BB2	55°25′	10°57′	25	0.84
BB5	56°47′	10°45′	14	0.42
BB6	56°39′	11°46′	43	0.88
BB7	56°11′	11°35′	24	0.43
BB13	57°37′	10°48′	25	0.61
GT1	57°00′	11°16′	10	0.43
K3	57°50′	11°13′	56	0.86

importance of Fe reduction and the concentration of poorly crystalline Fe oxides. The geographical variation of water depths, rates of sedimentation and sediment types in the Baltic Sea-North Sea transition, makes this area well suited for our investigation. A previous investigation of this area has focused on sulfate reduction and concluded that this process accounted for approximately half of the total benthic carbon mineralization (Jørgensen 1989). The other half of the carbon oxidation was mainly attributed to oxic respiration, but subsequent studies in other geographical areas have indicated that microbial Fe reduction may contribute significantly to this fraction (Canfield et al. 1993a).

Materials and methods

Study sites and sampling

Sediments were sampled onboard R/V Gunnar Thorson in May 2000 at seven stations in the northern Belt Sea and Kattegat (Table 1). These waters are sections of a complex estuarine system that connects the North Sea and the Baltic Sea (Jørgensen 1996). The Belt Sea consists of a series of sounds separated by the Danish isles. Sediment accumulation rates are generally moderate due to currents, yet seasonal oxygen depletion frequently occurs below the pycnocline (Kronvang et al. 1993; Madsen et al. 2001). Kattegat is an open water body characterized by relatively shallow sandy sediments to the west grading into finer textures towards the deep waters (> 40 m) along the Swedish coast. An area of sediment deposition rates as high as 6.2 mm yr^{-1} (Jørgensen et al. 1990) is found in the northernmost part. The seafloor in this area receives finegrained material from the North Sea and Skagerrak, as well as fresh organic material produced along the Kattegat-Skagerrak front (de Haas and van Weering 1997; Josefson and Conley 1997). Rates of benthic oxygen uptake and sulfate reduction and a range of other sediment characteristics have previously been determined at our study sites (Jørgensen 1989; Jørgensen and Revsbech 1989; Jørgensen et al. 1990).

The sediments at stations BB2, BB6 and K3 were fine-grained while BB5, BB7 and GT1 were sandy sites and Station BB13 represented an intermediate (Rysgaard

et al. 2001), as reflected in the sediment porosities (Table 1). Two stations, BB2 and K3, were studied in more detail using anoxic incubations of sediment. Station K3 in the area with very high sediment deposition rates in the northern Kattegat was characterized by intensive bioturbation to a depth of several decimeters, mostly due to brittle stars and polychaetes, while the benthic fauna at Station BB2 in the Great Belt was dominated by small polychaetes (Josefson and Conley (1997); M. Holmer, unpublished data).

Sediments were sampled in polycarbonate tubes (i.d. 9.6 cm) with a multiple corer (Barnett et al. 1984), except at station GT1, where a box core was used followed by subcoring with smaller Plexiglas tubes (i.d. 5.0 and 9.0 cm). Visually undisturbed cores with a clear overlying water phase were immediately transferred to a cold room (5–6 °C). Subcores were taken in Plexiglas tubes (i.d. 2.6) equipped with small silicone-plugged holes for radiotracer injection.

Sediment incubation and porewater extraction

For the determination of total carbon oxidation rates and the contributions of Mn, Fe and sulfate reduction to carbon oxidation, sediments from Station BB2 and K3 were incubated at *in situ* temperature in gas-tight laminated NEN/PE plastic bags (Hansen et al. 2000) as previously described in Canfield et al. (1993b) and Thamdrup and Canfield (1996). Briefly, sediment from the upper 10 cm of 8 cores were sliced in 0.5- to 2.0-cm-thick intervals under N_2 atmosphere in a glove bag at *in situ* temperature, and parallel sections were pooled, homogenized and filled into separate plastic bags. The bags were sampled initially, sealed and transferred to larger N_2-filled plastic bags to ensure anoxic conditions during the incubations.

Subsamples were withdrawn from the bags under N_2 atmosphere to obtain porewater on five subsequent occasions during the four days of incubation. The sediment was centrifuged (3000 rpm for 10–15 min.) and the supernatant was filtered (0.22 μm-pore-diameter cellulose acetate filters) under N_2. Samples for determination of ΣCO_2 (total dissolved inorganic carbon) were collected in 1.8 ml glass vials, preserved with 10 μl of 125 mM $HgCl_2$, capped with Teflon-coated butyl rubber septa leaving no gas phase, and stored at 5 °C until analysis within 30 days. A 1.0 ml aliquot was immediately frozen for NH_4^+ analysis, and about 2 ml porewater was acidified with 20 μl 6 M HCl for Mn^{2+}, Fe^{2+} and SO_4^{2-} determination.

Dissolved inorganic carbon, ΣCO_2, was analyzed by flow injection with conductivity detection (Hall and Aller 1992). Ammonium was measured by the salicylate method of Bower and Holm-Hansen (1980), and dissolved Mn^{2+} was analysed by flame atomic absorption spectrometry. Dissolved Fe^{2+} was determined by colorimetry using Ferrozine without reducing agent (Stookey 1970; Thamdrup et al. 1994). Sulfate was quantified by suppressed anion chromatography. Accumulation rates of porewater constituents (ΣCO_2, NH_4^+, Mn^{2+}, Fe^{2+}) were calculated from the slope of linear regression lines of concentration versus time at different depth intervals (different bags).

Rates of sulfate reduction were determined three times during the incubation using $^{35}SO_4^{2-}$ tracer method (Jørgensen 1978). Sediments were loaded into 5 ml cut-

off plastic syringes, which were incubated in an anoxic plastic bag at *in situ* temperature for six hours in darkness. The samples were fixed in 20% Zn acetate (vol:vol = 1:1) and stored frozen until analysis. The reduced ^{35}S was recovered by distillation with boiling acidic Cr^{2+} solution and sulfate reduction rates were calculated from the fraction of reduced sulfur produced during incubation and the concentration of SO_4^{2-} as described in Fossing and Jørgensen (1989). Sulfate reduction rates were corrected by subtraction of ^{35}S regained from distillation of sediment fixed immediately with Zn acetate after injection of $^{35}SO_4^{2-}$.

Assuming an overall stoichiometry of 2 mol of organic carbon oxidized per 1 mol of sulfate reduced the difference between total carbon oxidation rates and carbon oxidation coupled to sulfate reduction provided a measure of carbon oxidation coupled to other respiration pathways than sulfate reduction. At depths below the zone of O_2 and NO_3^- penetration, the excess carbon oxidation was assigned to microbial Mn and/or Fe reduction depending on the zonation of Mn and Fe oxides, and on the patterns of accumulation of Mn^{2+} and Fe^{2+} in the porewater during incubation. Detailed discussions of the method are given by Canfield et al. (1993a, 1993b) and Thamdrup and Canfield (1996, 2000).

Sediment solid-phase analyses

Solid phase distributions of Fe and Mn were determined at all stations except Station BB2 in sediment cores sectioned into 1–2 cm depth intervals to 10 or 15 cm depth at room temperature. After centrifugation and porewater extraction, these sediment samples were stored frozen until further analysis. In addition, sub-samples of sediment from the bag-incubations performed on Station BB2 and K3 were sampled immediately after sectioning at *in situ* temperature and stored frozen under N_2 atmosphere (see above). At K3 where both types of sampling were applied, results from the two approaches were very similar, which indicated that the brief exposure of the fresh sediment to oxygen did not affect Fe(II) and Fe(III) distributions.

Concentrations of solid phase Fe(III) and Fe(II) pools were determined through cold HCl extraction (Kostka and Luther 1994) and by a combination of oxic and anoxic acidic ammonium oxalate extractions (pH 3, Thamdrup et al. (1994) and Thamdrup and Canfield (1996)). Both assays extract poorly crystalline Fe(III) oxides and particulate Fe(II) such as FeS, $FeCO_3$ (Lovley and Phillips 1987b; Canfield et al. 1993b; Thamdrup et al. 1994). Pyrite, FeS_2, is not extracted, but there might be a contribution from Fe associated with silicates (Canfield 1989; Kostka and Luther 1994). In addition, oxalate extraction is selective for magnetite ($Fe^{II}Fe_2^{III}O_4$) (Phillips and Lovley 1987). All extractions were performed with 10 ml extractant and approximately 100–150 mg wet or 50 mg dry sediment. Extraction times were 1 h for HCl and 4 h in the dark for oxalate extractions. In both extractions, the oxidation states of Fe were determined separately by using a Ferrozine solution (50 mM HEPES, 0.1% Ferrozine, pH 7) with and without 1% (w/v) hydroxylamine hydrochloride for determination of total extracted Fe and Fe(II), respectively (Canfield et al. 1993b). Particulate Mn was extracted in dithionite-cit-

rate-acetic acid for 1 h (pH 4.8, Lord (1980)) and quantified by flame atomic absorption spectrometry. Reactive Mn concentrations were estimated by subtraction of the low unreactive background concentrations measured at depth (Aller 1980). The reactive fraction of extracted Fe(III) was estimated in the same way. Concentrations determined in centrifuged sediment at all stations except BB2 were corrected for porewater loss.

Sulfate reduction rates in intact cores

Sulfate reduction rates determined in intact sediment cores during our cruise and reported by Rysgaard et al. (2001) are used in the estimation of Fe reduction rates at sites where no bag incubations were performed. These sulfate reduction rates are averages of measurements in two or three cores of 2.8 cm diameter made with the $^{35}SO_4^{2-}$ tracer method (Jørgensen 1978). Incubations were made at *in situ* temperature in the dark for 24 hours and reduced sulfide was recovered as described above.

Results

Pathways of carbon oxidation from sediment incubations

In general, the ΣCO_2 and NH_4^+ concentrations increased linearly during the incubations (K3: $r^2 > 0.92$ and BB2: $r^2 > 0.61$), indicating that the reaction rates remained constant within the incubation period (data not shown). At Station BB2, rates of ΣCO_2 accumulation in the porewater decreased sharply from the surface to lower and almost constant rates below 2 cm depth (Figure 1).

The rates at Station K3 were higher compared to BB2 and high rates persisted to 6 cm depth, below which rates decreased sharply. The depth profiles of NH_4^+ accumulation rates showed the same general pattern as the ΣCO_2 accumulation rates (Figure 2), confirming the higher rates of mineralization of organic matter at Station K3 compared to BB2. The depth-integrated carbon oxidation rate and the NH_4^+ accumulation rate at Station K3 were 3.5 and 4.0 times higher, respectively, than those measured at BB2 (Table 2). The determination of total mineralization rates from ΣCO_2 accumulation rates can be complicated by carbonate ($CaCO_3$, $MnCO_3$, $FeCO_3$) precipitation or, possibly, dissolution (e.g. Thamdrup et al. (2000)). The parallel depth distributions of ΣCO_2 and NH_4^+ accumulation rates indicate that no or little dissolution or precipitation of carbonates occurred (Canfield et al. 1993b). This is further supported by the good agreement between sulfate-based and measured ΣCO_2 production rates at depth in the sediments (Figure 1). Consequently, we use the ΣCO_2 accumulation rates as a measure of total carbon oxidation in the indirect quantification of Fe reduction (see below).

At Station BB2, the rates of carbon oxidation coupled to sulfate reduction were high at the surface and rates only increased slightly to an almost constant level below 2 cm depth. Only a small excess carbon oxidation was indicated at 0 to 3 cm

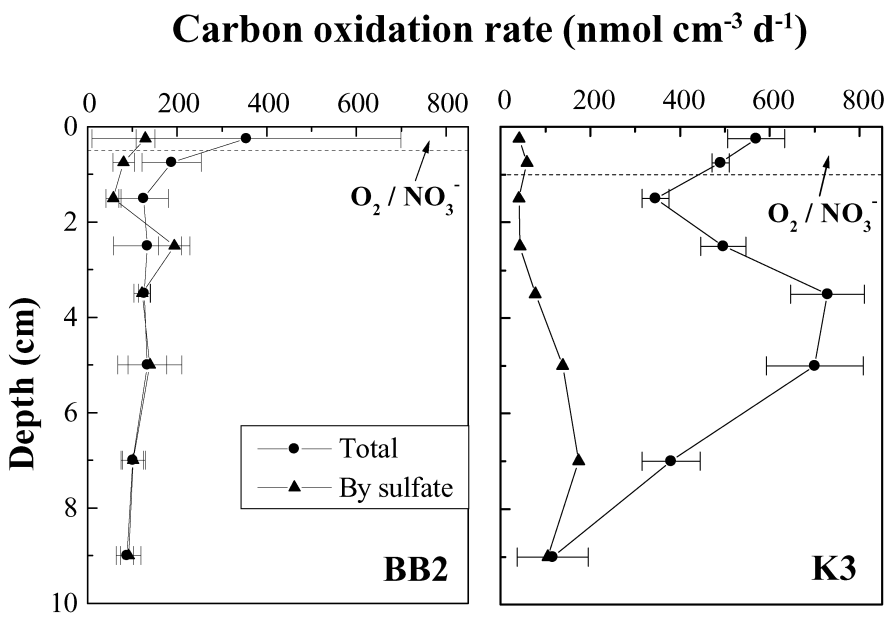

Figure 1. Depth distributions of total carbon oxidation rates (from ΣCO2 accumulation in porewater) and carbon oxidation due to sulfate reduction from anoxic bag incubations at Station BB2 in the Great Belt and Station K3 in the Kattegat. Error bars represent the standard errors of the slope of regression lines of ΣCO_2 concentration vs. time and standard deviations of triplicate sulfate reduction rates. The horizontal dashed lines represent depths of O_2 and NO_3^- penetration (Rysgaard et al. 2001).

Table 2. Depth-integrated rates (mmol m^{-2} d^{-1}, S.D. in parentheses) of ΣCO_2 and NH_4^+ accumulation in the 0 to 10 cm depth interval and in the anoxic, nitrate-free part of the sediment (1–10 cm), and depth-integrated rates of dissimilatory bacterial Fe(III) and sulfate reduction (anoxic, mmol C m^{-2} d^{-1}) and their relative contribution to anaerobic carbon mineralization (% of C ox).

Station	ΣCO_2 accumulation		NH_4^+ accumulation		Fe(III) reduction		Sulfate reduction	
	0 – 10 cm	anoxic	0 – 10 cm	anoxic	anoxic	% of C ox	anoxic	% of C ox
BB2	13.0 (2.2)	11.4	1.9 (0.1)	1.6	0.65	5	10.8 (0.84)	95
K3	44.9 (3.2)	39.6	7.8 (1.0)	7.5	29.7	75	10.0	25

depth at BB2, below which rates of carbon oxidation and sulfate reduction converted to carbon units were identical, implying that all carbon mineralization could be attributed to sulfate reduction. In contrast, the carbon oxidation coupled to sulfate reduction was suppressed in the surface layer at Station K3 and reached a maximum of ~ 150 nmol cm^{-3} d^{-1} at a depth of 6 to 8 cm. Consequently, there was a large divergence of total carbon oxidation and sulfate-based carbon oxidation from the surface to 8 to 10 cm depth at K3, implying that other respiration pathways were important. Oxygen penetrated to about 4 mm at both stations, and nitrate was detected in the upper centimeter (Rysgaard et al. 2001). Thus, these electron acceptors may be important in carbon oxidation at 0–1 cm depth. Below 1

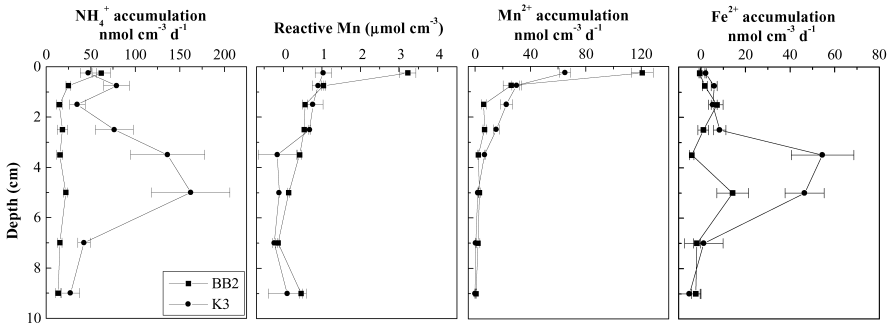

Figure 2. From left to right: Depth distributions of a) NH_4^+ accumulation rates (±SE) in porewater during anoxic bag incubations, b) reactive solid phase Mn, and c) accumulation rates (±SE) of dissolved Mn^{2+} and Fe^{2+} in porewater during anoxic bag incubations. The concentrations of Mn are means of duplicate determinations on sediment collected at the beginning of the incubations. Error bars represent the range of duplicates.

cm depth, sulfate reduction accounted for 95% and 25% of the carbon oxidation at BB2 and K3, respectively (Table 2).

Measurements of Mn and Fe confirmed that Fe reduction was the main contributor to the remaining anaerobic carbon oxidation, while Mn reduction was restricted to the uppermost sediment layers and appeared to be of little importance (Figure 2). Thus, the vertical distribution of Mn oxides showed only small enrichments of ~ 3 μmol cm^{-3} at 0–0.5 cm depth at BB2 and ~ 1 μmol cm^{-3} at 0–3 cm at K3. Mn reduction was indicated in these depth intervals by the accumulation of soluble Mn^{2+} during the incubations, and the rates of Mn^{2+} accumulation scaled with the distribution of reactive Mn (Figure 2). The depth-integrated reactive Mn pool was twice as high at Station BB2 (62 mmol m^{-2}) compared to K3 (30 mmol m^{-2}).

Maximum oncentrations of HCl and oxalate extractable Fe(III) at Station BB2 and K3 were considerably higher than those of reactive Mn oxide (Figures 2 and 3). At Station BB2, the concentration of solid phase Fe(III) determined by oxalate extraction decreased with depth from the surface to 4 cm, below which it reached a constant value of ~ 10 μmol cm^{-3} (Figure 3). Such stable background levels of Fe(III) have been interpreted as non-reducible Fe(III) (Canfield 1989; Thamdrup 2000) and the reactive Fe(III) fraction (hereafter referred to as poorly crystalline Fe(III)) was estimated by subtracting the average background concentration determined at 4–10 cm depth (Figure 3). At Station K3, poorly crystalline Fe(III) was 2 times more abundant in the surface layer than at BB2, and a decrease in concentration was first observed below 3 cm depth. The concentration of Fe(III) did not reach a constant value within the 0 to 10 cm depth range sampled for bag incubation from K3. Instead, a background value of ~ 15 μmol cm^{-3} obtained from the solid phase distribution at 10 to 15 cm depth in whole sediment cores (see below) was used. The integrated poorly crystalline Fe(III) pool at Station BB2 was 0.42 mol m^{-2}, 7-fold greater than that of reactive Mn, whereas it was 2.6 mol m^{-2}, i.e. nearly 100-fold greater than that of reactive Mn at K3. Based on the good agreement between the depth distributions of non-sulfate-based carbon oxidation and

poorly crystalline Fe(III), we attribute the excess carbon oxidation in the anoxic sediment to microbial Fe reduction. Thus, Fe reduction was the most important pathway of anaerobic carbon oxidation at K3 accounting for 75% of the mineralization, while it was of little significance at BB2 (Table 2).

The role of Fe reduction was further supported by the distribution of Fe(II). Oxalate extractable Fe(II) made up a major fraction of the extracted Fe at both stations, particularly on Station BB2 (Figure 3). The depth distributions of Fe clearly demonstrate concomitant Fe(III) consumption and solid Fe(II) accumulation at 0.5 – 4 cm and below $\sim$2 cm depth at Station BB2 and K3, respectively. Soluble Fe^{2+} accumulated steadily in the porewater in the 2 to 7 cm depth interval at K3 (Figure 2), corresponding well with the sediments depth where the Fe(III) reduction zone was defined by a gradient in poorly crystalline Fe(III) (Figure 3). In contrast to this rapid accumulation of soluble Fe^{2+}, there was only a small peak of Fe^{2+} accumulation at 1 to 2 cm depth at Station BB2 (Figure 2). In accordance with the dominance of solid Fe(II) over soluble Fe^{2+}, the accumulation rates of Fe^{2+} were small in comparison to carbon oxidation rates at both stations (Figure 1), indicating rapid adsorption or precipitation of Fe^{2+} ions. In agreement with oxalate extractable Fe, the profiles of HCl-extractable Fe showed considerably higher concentrations of poorly crystalline Fe(III) at Station K3 compared to BB2 (Figure 3). Depth distributions of oxalate and HCl extractable Fe were parallel. However, oxalate extraction yielded more Fe(III) than did HCl extraction, whereas the concentrations of Fe(II) determined by HCl extraction was higher than oxalate extractable Fe(II) by $\sim$20 μmol cm^{-3} at both stations.

Depth distributions of solid phase Mn and Fe, and sulfate reduction rates

The depth distributions of sulfate reduction rates determined in intact cores showed a large variation between the six different stations, with a 10-fold difference between the lowest integrated rates observed at Station BB7 to the highest at BB2 (Table 3). In general, sulfate reduction rates were suppressed near the sediment surface at all stations, but increased to a maximum at different depths ranging from 3–4 cm to 6–8 cm. Particularly deep maxima were found at Station BB5 and K3 where the rates peaked at approximately 6 to 8 cm's depth. The maximum at Station BB2 was found closest to the sediment surface than at the other stations. The depth distribution of sulfate reduction in the intact cores and bag-incubations were quite similar at both Station BB2 and K3 (Figure 1, Table 3).

An enrichment of extractable reactive Mn (7.0 μmol cm^{-3}) was only present at the sediment surface (0–1 cm) at Station BB6 (Figure 4), whereas concentrations of reactive Mn were low (< 1.5 μmol cm^{-3}) and decreasing with depth at all other stations (data not shown). In contrast to the low Mn content at the majority of the stations, the depth distribution of poorly crystalline Fe(III) and particulate Fe(II) phases showed a large heterogeneity between the different stations (Figure 5). Large pools of poorly crystalline Fe(III) were found at Station BB6, BB13 and K3 (< 45.0 μmol cm^{-3}) whereas the concentrations of Fe(III) were quite low at the sandy sites BB5 and GT1 (< 9.0 μmol cm^{-3}). At Station BB6, BB13 and K3, the poorly

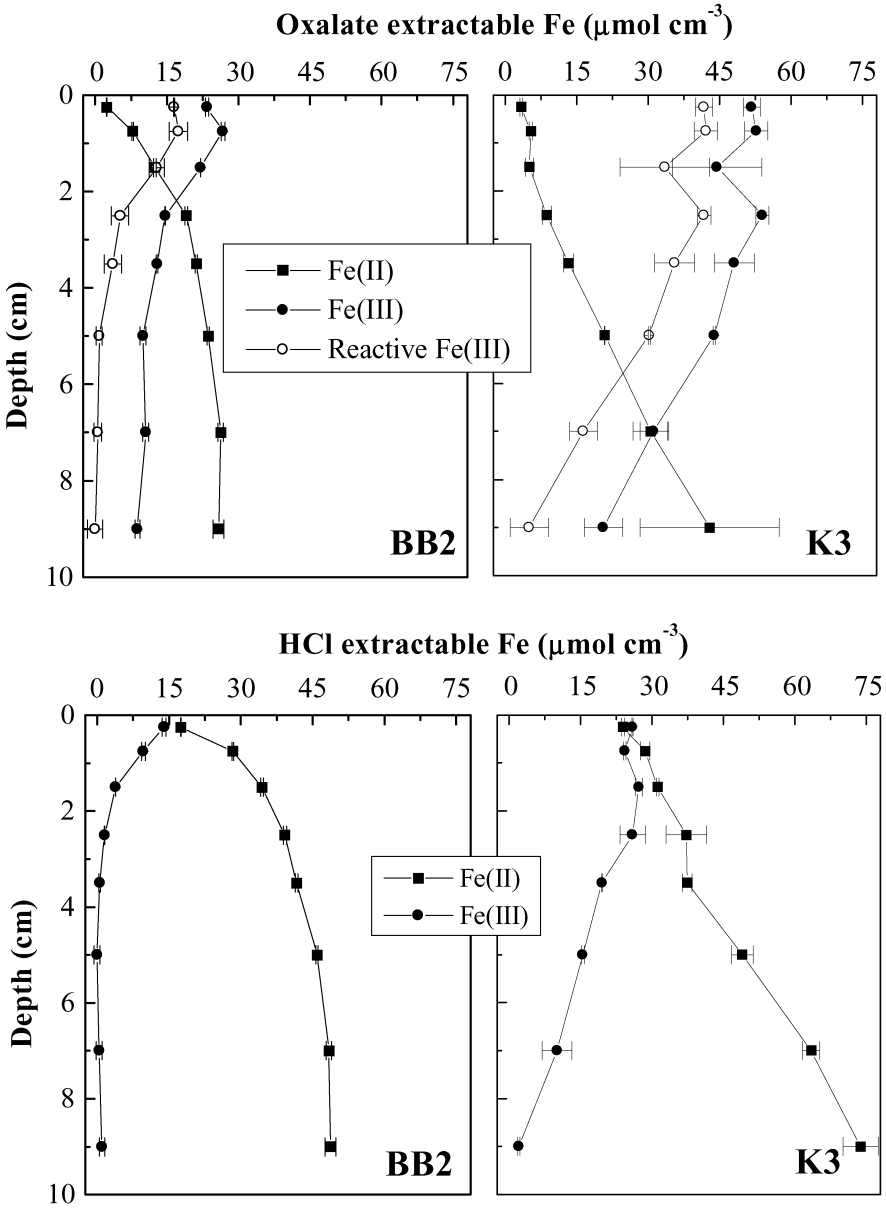

Figure 3. Top: Depth distributions of oxalate extractable Fe(II) and Fe(III). Reactive Fe(III) indicates the poorly crystalline Fe oxides available for microbial reduction (see text for details). *Bottom*: Depth distributions of HCl extractable Fe(III) and Fe(II). Both oxalate and HCl extractable Fe(III)-Fe(II) represent concentrations at in the beginning of the bag incubation experiments and are means of duplicate determinations. Error bars represent the range of duplicates. In order to compare the distributions of solid phase Fe to rate measurements, the Fe pools are presented on a volume basis, although this partly conceals changes occurring within the solids due to compaction.

Table 3. Sulfate reduction rates, in carbon units (nmol C cm^{-3} d^{-1}) quantified by the whole-core incubation technique from Rysgaard et al. (2001). Rates are mean of three cores at K3 and two cores at the other stations.

Depth (cm)	BB2	BB5	BB6	BB7	BB13	K3	GT1
0–1	138	6.7	38.1	1.5	3.3	13.5	3.4
1–2	92.1	41.2	13.5	7.8	3.1	11.2	26.1
2–3	142	12.2	16.6	8.9	7.8	17.7	32.4
3–4	130	16.6	67.5	11.3	14.7	15.3	33.7
4–6	127	30.4	36.1	9.6	11.2	25.2	16.6
6–8	100	94.2	47.8	8.0	8.0	66.1	34.2
8–10	62.3	104	40.2	7.6	10.8	56.5	33.4
Σ, mmol C m^{-2} d^{-1}	10.8	5.3	3.8	0.8	0.9	3.5	2.6

crystalline Fe(III) fraction decreased with depth with a concomitant increase in solid phase Fe(II), indicating that Fe reduction could contribute significantly to carbon oxidation in these sediments. In addition to the low concentrations of poorly crystalline Fe(III) at Station BB5 and GT1, the Fe(II) concentrations were very low and almost constant with depth, suggesting that Fe reduction did not play a significant role in carbon oxidation in these sediments. Station BB7 was intermediate between these two extremes.

Discussion

Previous experimental studies have demonstrated a variable but often significant contribution from microbial Fe reduction to carbon oxidation in continental shelf sediments from the Arctic to the tropics (Thamdrup (2000) and references therein; Kristensen et al. (2000)). So far, however, only few sites have been studied within each geographical region. An important limiting factor for the number of quantifications has been the labor-intensiveness of the incubation technique. In the present study we performed detailed incubation-based determinations of microbial Fe reduction rates at two sites that were widely separated within our study area and represented two extremes with respect to the importance of the process. From these results we can derive a general relationship between Fe(III) concentrations and Fe reduction, and we use this relationship to estimate the importance of Fe reduction at the remaining sites.

The widely different importances of microbial Fe reduction determined at Station BB2 and K3 (Table 2) were consistent with all the different analyses that were performed in conjunction with the incubations. Thus, the large contribution from the process at K3 was supported by high concentrations of poorly crystalline Fe(III), high rates of accumulation of soluble Fe^{2+}, and a strong suppression of sulfate reduction in the upper part of the profile, while the patterns were reversed at BB2 (Figures 1, 2 and 3). The variation in the different parameters agreed closely with

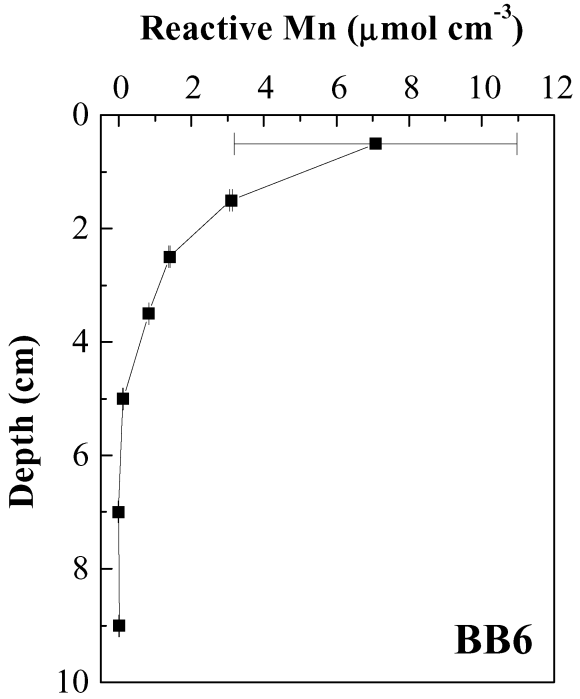

Figure 4. Depth distribution of reactive solid phase Mn at Station BB6. Concentrations are means of duplicate determinations. Error bars represent the range of duplicates.

the patterns previously observed at sites with low or high contributions of Fe reduction (e.g. Thamdrup (2000)). The shallow penetration of reactive Mn oxides and the small pool of reactive Mn ruled out Mn reduction as a significant pathway of carbon oxidation (Figure 2). Mn reduction was most likely coupled mainly to reoxidation of reduced iron and sulfur compounds as found in other temperate coastal sediments (e.g. Canfield et al. (1993b) and Aller (1994), Thamdrup et al. (1994)). The 75% contribution of Fe reduction to anaerobic carbon oxidation at K3 is the highest percentage so far reported from subtidal marine sediment. The significance and deep extension of Fe reduction in the sediment of Station K3 agrees with previous studies made in this area (Fossing et al. 1992; Canfield 1993). Based on rates of sulfate reduction and soluble Fe^{2+} and Mn^{2+} accumulation, Canfield (1993) provided evidence of an important role of Fe reduction in carbon cycling at a site slightly east of K3. Likewise, Fossing et al. (1992) observed that sulfate reduction was suppressed in a > 10 cm thick surface layer of the sediment, indicating a broad zone of Fe reduction, both at K3 and at most other sites on a transect through the sediment accumulation area of northern Kattegat. The highest rates of carbon oxidation coupled to Fe reduction at K3, $\sim$600 nmol C cm^{-3} d^{-1} (Figure 1), were also higher than maximum rates determined by similar techniques in other marine sediments (range 30–300 nmol C cm^{-3} d^{-1}, Thamdrup (2000)). In combination with

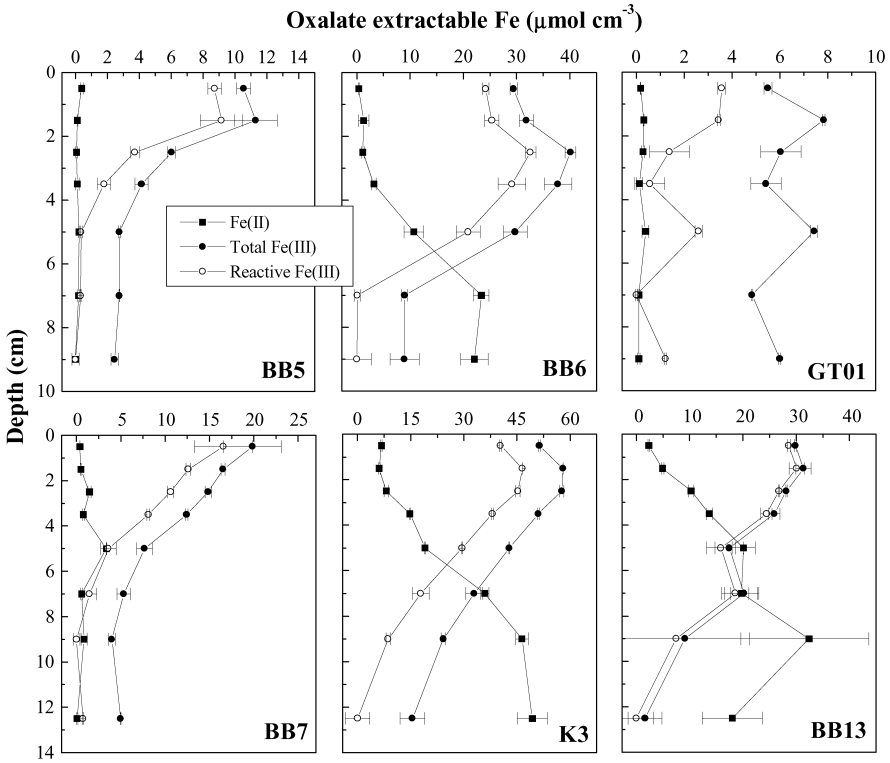

Figure 5. Depth distributions of oxalate extractable Fe(III) and Fe(II) at stations BB5-7, BB13, K3 and GT1. At Station BB2, solid phase Fe was only measured on sediments from the bag incubations. Reactive Fe(III) indicates the poorly crystalline Fe oxides available for microbial reduction and was calculated by subtraction of the average background concentration remaining at depth. Concentrations are means of duplicate determinations. Error bars represent the range of duplicates. Note different scales.

the deep extension of Fe reduction, these rates resulted in an integrated contribution of Fe reduction to anaerobic carbon oxidation of 30 mmol C cm^{-2} d^{-1} (Table 2), which is much higher than previous values for steadily accreting subtidal marine sediments ($\leqslant$ 5 mmol C cm^{-2} d^{-1}, Thamdrup (2000)), but similar to rates estimated for the mobile mud belts off the Amazon River (Aller et al. (1986, 1991)). In correspondence to the high rates, the turnover time of poorly crystalline Fe(III) at K3 (Fe[III] inventory/Fe reduction rate) was only $\sim$20 days, whereas typical values for other sediments are in the order of several months (Canfield et al. 1993a; Thamdrup and Canfield 1996; Rysgaard et al. 1998).

Previous studies have showed a tendency for higher rates of carbon oxidation and sulfate reduction in bag or jar incubations compared with rates and fluxes measured by wholecore incubations, possibly as an effect of sediment homogenization (Hansen et al. 2000). A potential stimulation of carbon mineralization during bag incubations at Station K3 was indicated by a 3.0-fold higher integrated sulfate reduction rate compared to whole-core results, and by a 1.5-fold higher integrated

ΣCO_2 accumulation rate compared to the benthic ΣCO_2 flux at that time (Rysgaard et al. 2001). This potential methodological bias should not affect the conclusions concerning the high rates of Fe reduction at K3 relative to other sites, because our comparisons are all based on similar incubation techniques. Furthermore, the main focus of this study is on the relative importance of Fe and sulfate reduction, and it is generally assumed that this ratio is not affected by a stimulation of mineralization (e.g., Canfield et al. (1993a) and Rysgaard et al. (1998)).

A deep penetration and rapid turnover of poorly crystalline Fe(III), and thus a dominance of Fe reduction relative to sulfate reduction can only be maintained through intense reworking of the sediment (e.g., Canfield et al. (1993b) and Hines et al. (1997)). Indeed, the sediments underneath the Skagerrak-Kattegat front are characterized by a high faunal biomass (Josefson and Conley 1997), and at the time of our sampling, the biomass at K3 (dominated by burrowing echinoderms and polychaetes) was more than twice as large as at any other of the stations we studied (130 g afdw m^{-2}, M. Holmer, unpublished results). Extreme bioturbation in this area is further indicated by high and stable levels of unsupported ^{210}Pb to 15 cm depth (van Weering et al. 1987; Jørgensen et al. 1990) and by the presence of burrows to depths of several decimeters. The high rates of carbon mineralization observed to 6 cm depth (Figure 1) also indicate that reactive organic matter is rapidly mixed into the sediment. In addition to supplying both reactive organic matter and Fe(III) to dissimilatory Fe reduction, the reworking and irrigation caused by the infauna may enhance remineralization in general through the removal of metabolites (Aller and Aller 1998). Furthermore, it has been speculated that a rapid cycling between reduced and oxidized Fe exerts a positive feedback on microbial Fe reduction by maintaining the oxides in a poorly crystalline state, as Fe(III) oxides crystallize with age after precipitation (Thamdrup 2000). Thus, the optimal conditions for Fe reduction at K3 are critically dependent on the fauna, which relies on large and steady supplies of organic matter and oxygen (Josefson and Conley 1997).

Kinetics of Fe reduction

The depth distributions of microbial Fe reduction rates at Station BB2 and K3 correlated nicely with the concentration of poorly crystalline Fe(III) (Figures 1 and 3), suggesting that the Fe(III) concentration is an important controlling factor for Fe reduction rates, as also observed by Hines et al. (1997) and Roden and Wetzel (2002). In sediments, however, this correlation may in part be caused by changes in the availability of organic matter since both concentrations of Fe(III) and the availability of organic matter (reflected in total carbon oxidation rates) tend to decrease with depth. The dependence of Fe reduction on Fe(III) can be isolated by considering the relative contribution of Fe reduction to anaerobic carbon oxidation, and this parameter has demonstrated a remarkably reproducible dependence on poorly crystalline Fe(III) concentrations in several marine sediments including sites in the Kattegat-Skagerrak region (Thamdrup 2000). The results from our incubations agreed closely with the previously published results, confirming that the concentration of poorly crystalline Fe(III) exerts a strong control on rates of Fe reduc-

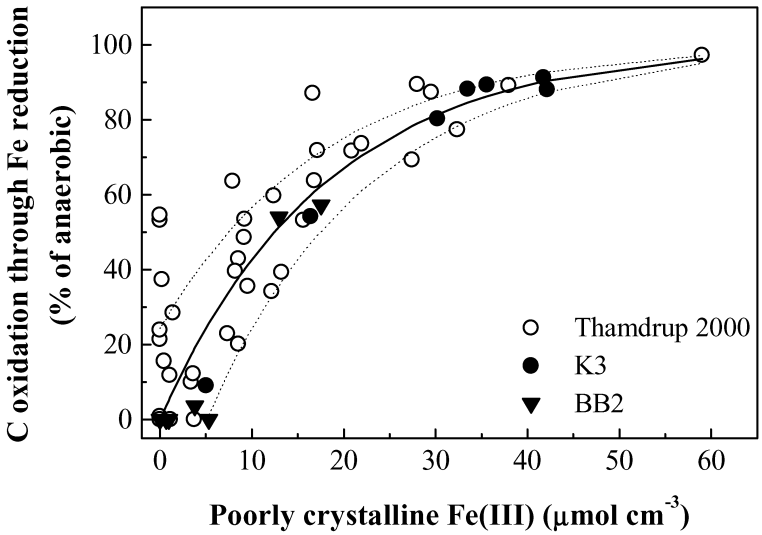

Figure 6. The relative contribution of dissimilatory Fe reduction to carbon oxidation as a function of the poorly crystalline Fe(III) in sediment from individual depth intervals. Data represented by open circles is from Thamdrup (2000). The solid curve represent the function (Fe reduction = 100% × (1 – exp(-[Fe(III)] × 0.056)), the dashed curves represent the functions used in sensitivity analysis (see text for details).

tion in marine sediments. All poorly crystalline Fe(III) concentrations in Figure 6 were determined by oxalate extraction, and the high reproducibility of the relationship in Figure 6 indicates that this extraction scheme provides a good measure of the Fe(III), which is available for organotrophic Fe reduction in a wide range of marine sediments. The HCl-extractable Fe(III) pool correlated well with Fe(III) from the oxalate extraction, but yielded $\sim$40% less Fe(III). Thus, HCl extraction does not capture all the Fe(III) that is available for microbial reduction. This underestimation may to some extent be due to a reduction of Fe(III) during the extraction (Moeslund et al. 1994; Thamdrup et al. 1994).

Previous studies on competition between Fe and sulfate reduction have shown that with abundant microbially reducible Fe oxides, Fe-reducing bacteria can outcompete sulfate-reducing bacteria by maintaining fermentation products at levels too low for sulfate-reducing bacteria to metabolize (Lovley and Phillips 1987a; King 1990). In all sediments plotted in Figure 6, sulfate reduction accounts for the fraction of carbon oxidation, which is not coupled to Fe reduction. Thus, the relationship in Figure 6 shows that the concentration of poorly crystalline Fe(III) is a strong parameter controlling the competitive relationship between Fe and sulfate reduction, with a gradual shift from sulfate to Fe reduction as the dominating oxidative process associated with increasing Fe(III) concentrations. Above $\sim$30 μmol Fe(III) cm^{-3}, as in the upper layers of the sediment at K3 (Figure 3), the Fe-reducing bacteria are not limited by the availability of readily reducible Fe(III) and thus almost completely outcompete sulfate-reducing bacteria for electron donors,

thereby dominating carbon mineralization. Although poorly crystalline Fe(III) was present throughout the profile at Station K3 (Figure 3), Fe reduction became limited by poorly crystalline Fe(III) as the Fe(III) concentration decreased below 30 μmol cm^{-3} deeper in the sediment, resulting in a gradual shift from Fe reduction to sulfate reduction. The presence of both Fe and sulfate reduction in the same sediment intervals (Figure 1; e.g., Canfield (1993)) indicates that through most of the Fe reduction zone in marine sediments, Fe-reducing bacteria can not completely outcompete sulfate-reducing bacteria. The coexistence of competing Fe- and sulfate-reducing bacteria and the gradual shift from one to the other has been suggested to result from the restriction of Fe reducers to the surfaces of Fe oxides (Thamdrup 2000).

Calculation of Fe reduction rates from depth profiles of poorly crystalline Fe(III)

In addition to K3, high concentrations of Fe(III) were also found at stations BB6 and BB13 in the northern and eastern Kattegat, and active Fe reduction at these sites was further indicated by the accumulation of Fe(II) that accompanied consumption of Fe(III) with depth (Figure 5). Low concentrations and rapid disappearance with depth of Fe(III) suggested that Fe reduction was of less importance at stations GT1, BB5, and BB7 in the shallower western Kattegat. There was a large variation in the sulfate reduction rates between the stations. Moreover, there was a tendency towards suppression of sulfate reduction in the surface layers at the stations BB6, BB13, and K3 compared to GT1 and BB7 where sulfate reduction varied less with depth. Thus, the sediment strata where sulfate reduction was suppressed coincided with high and decreasing concentrations of poorly crystalline Fe(III) and increasing concentrations of solid Fe(II) with depth, indicating that Fe reduction could contribute significantly to carbon oxidation in these sediment strata. Suppression of sulfate reduction rates in the surface layers of marine sediments, in combination with high concentrations of dissolved Fe^{2+}, has been interpreted as an indication of Fe reduction (Sørensen and Jørgensen 1987; Hines et al. 1991). Both studies suggested that Fe reduction may contribute significantly to carbon oxidation in such coastal sediments, but they were not able to quantify the role of Fe reduction.

According to the discussion above and Figure 6, we find that the concentration of poorly crystalline Fe(III) is a good predictor of the relative contribution of Fe reduction to anaerobic carbon mineralization and we can therefore calculate Fe reduction rates at the sites where we did not perform bag incubations using the concentration of poorly crystalline Fe(III) and sulfate reduction rates. The details of the relationships that govern the dependence of Fe reduction on Fe(III) concentrations remain yet to be determined. We therefore chose to describe the relationship in Figure 6 by an empirical function, which captures the essential features of the relationship with only one fitting parameter:

$$\%FeR = 100\% \times (1 - e^{-[Fe(III)] \times A}) \quad (1)$$

Table 4. Microbial Fe reduction rates (nmol C cm^{-3} d^{-1}) determined from concentrations of poorly crystalline Fe(III) and rates of sulfate reduction (see discussion for calculations)[1]. Oxygen and nitrate were present in the upper cm at all sites and this depth interval is not included in the calculations.

Depth (cm)	BB5	BB6	BB7	BB13	K3	GT1
1–2	27.4	41.8	8.0	13.5	138.3	5.5
2–3	2.8	85.6	7.1	26.9	202.5	2.6
3–4	1.7	274.6	6.5	42.6	111.7	1.1
4–6	0.6	79.6	2.1	15.9	105.1	2.6
6–8	1.7	0.2	0.7	14.5	112.3	0
8–10	0	0	0	5.6	35.1	2.4
Σ, mmol C cm^{-2} d^{-1}	0.4	5.6	0.3	1.5	9.6	0.2
% of anaer. C oxid.	6.4	59.4	25.4	63.6	73.0	6.7

[1] At BB2, solid phase Mn and Fe distributions were only determined in sediment used for incubations, and an independent calculation of Fe reduction rates was therefore not possible.

where %FeR is the carbon oxidation through iron reduction in % of total carbon oxidation, Fe(III) is the concentration of poorly crystalline Fe oxides and A is the fitting parameter. A nonlinear least-squares curve fit using the Leventhal-Marquardt algorithm (Marquardt 1963) yielded A = 0.056 ± 0.005 (estimated standard error). Thus, based on the assumption that only Fe and sulfate reduction contributes to anaerobic carbon mineralization, Fe reduction rates can be calculated as:

$$FeRR = \frac{\%FeR}{100} \times (FeRR + SRR) \tag{2}$$

where FeRR represents the Fe reduction rate (nmol C cm^{-3} d^{-1}), and SRR the sulfate reduction rate (nmol C cm^{-3} d^{-1}).

Solving for FeRR, we obtain

$$FeRR = \frac{SRR}{1 - \frac{\%FeR}{100}} \times \frac{\%FeR}{100} \tag{3}$$

Using Equations (1) and (2), the contribution of Fe reduction to anaerobic carbon oxidation at the stations BB5-BB7, BB13, GT1 and K3 was calculated by using the vertical profiles of poorly crystalline Fe(III) (Figure 5) and sulfate reduction rates (Table 3). At each station, the relative contribution of carbon oxidation channeled through Fe reduction in each depth interval below the zone of O_2 and NO_3^- penetration (1 cm; S. Rysgaard, unpublished results) was determined from Equation (1) and the concentration of poorly crystalline Fe(III) (Figure 5). From the measurements of sulfate reduction rates in carbon equivalents (Table 3) and Equation (2), these percentages were then converted to rates in carbon equivalents (Table 4).

As mentioned above, this way of calculating Fe reduction rates is based on the assumption that microbial Mn reduction does not play a significant role in anaerobic carbon oxidation. For the present study, this assumption is justified by very low Mn concentrations at all stations ($\leqslant$ 7 μmol cm^{-3} at BB6, < 1.5 μmol cm^{-3} at all other sites, Figure 4 and data not shown). Previous studies have indicated that microbial Mn reduction is of little importance in sediments having maximum concentrations of reactive Mn of < 10 μmol cm^{-3} (Thamdrup et al. 2000), and that Mn reduction in such Mn-poor sediments is mainly coupled to the reoxidation of reduced Fe and sulfur species (Canfield et al. 1993b; Aller 1994; Thamdrup et al. 1994).

To estimate the accuracy of our approach, we repeated the calculations substituting the relationship in Equation (1) with two other functions that bracket our recent results and also most of the previous data (Figure 6). These functions correspond to a displacement of the original function (Equation 1) along the x-axis by 5 and – 5 μmol cm^{-3}, respectively. At the Fe(III)-rich sites these extreme scenarios corresponded to a variation in the relative importance of Fe reduction of ±10%, while at BB5 and GT1 the upper function resulted in $\sim$20% higher contribution from Fe reduction (data not shown). Thus, although this analysis demonstrates a sizeable uncertainty, it also shows that our general conclusions concerning the dominance of either Fe or sulfate reduction (see below) are robust.

Our calculations showed that Fe reduction is the dominating pathway of anaerobic carbon oxidation in the northern and eastern Kattegat with similar relative contributions at the stations BB6, BB13, and K3 (Figure 7). The calculations resulted in a similar importance of Fe reduction at K3 as determined in the bag incubations (73% vs. 75%), thus confirming the consistency of the two approaches. With the support of previous results discussed above (Fossing et al. 1992; Canfield 1993) this provides what we believe to be the first evidence of the importance of Fe reduction in a wider area of the seafloor. By contrast, Fe reduction was of little importance in the coarse-grained sediments of southern and western Kattegat (6–25% at stations GT1, BB5 and BB7). The results from BB2 can be supplemented with other determinations at similar, fine-grained sites in the Belt Sea (Thamdrup (2000); B. Thamdrup unpublished; Figure 7), and together these show a variable but minor importance (4–28%) of Fe reduction in this region. The mean contributions of Fe and sulfate reduction to anaerobic carbon oxidation at all stations in the Kattegat and Belt Sea were 30% and 70%, respectively. The importance of Fe reduction in northern Kattegat is of particular interest, however, because this region has been estimated to receive 44% of the total sedimentation of organic matter in the inner Danish waters Madsen and Larsen (1986) and Jørgensen et al. (1990)). Thus, a rough estimate of the contribution of Fe reduction to the oxidation of organic carbon depositing in the Kattegat and Belt Sea can be obtained from the averages of the northeastern Kattegat and the southern Kattegat and Belt Sea, 68% and 15%, respectively, weighted by the relative significance of these regions in sedimentation. This calculation shows that 38% (0.68 × 0.44 + 0.15 × 0.56), i.e., approximately one third of the anaerobic benthic carbon oxidation in the whole region is through Fe reduction.

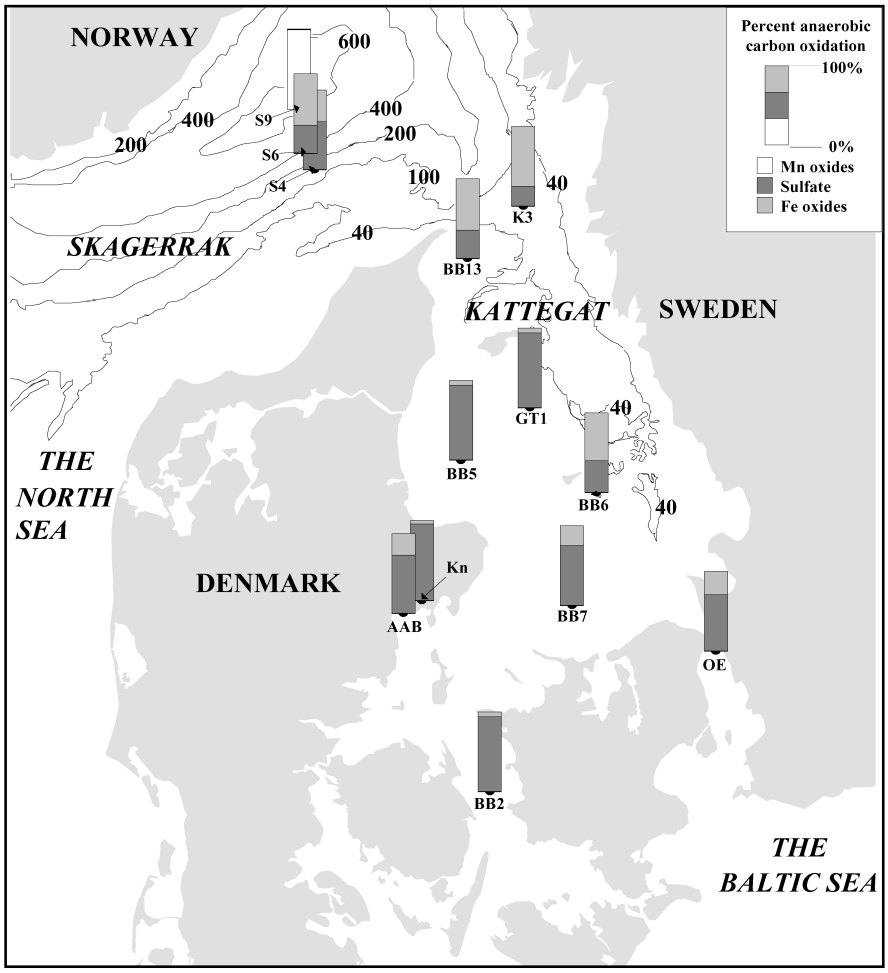

Figure 7. Relative importance of anaerobic carbon oxidation pathways in the Great Belt, Kattegat and Skagerrak. Data from stations S4, S6 and S9 have been presented by Canfield et al. (1993a) and values at Station AAB, Kn (Thamdrup 2000) and OE (B. Thamdrup, unpublished) were determined according to Thamdrup and Canfield (1996).

The small contribution of Fe reduction in the sandy eastern Kattegat sediments was governed by low concentrations of redox active Fe (oxalate extractable Fe(II) + Fe(III)) (Figure 5). Thus, although little Fe(II) accumulated in these sediments, poorly crystalline Fe(III) concentrations were much below the saturating level of ~ 30 μmol cm^{-3} (Figure 6). The small contribution is in agreement with a comprehensive study in the North Sea and Skagerrak, where Slomp et al. (1997) found low concentrations of Fe(III) in the sandy North Sea sediments and predicted that Fe(III) did not play an important role as electron acceptors in decomposition of organic material there. By contrast, Canfield et al. (1993a) found large contribu-

tions of Fe reduction at 200 and 380 m depth in the finer grained Skagerrak sediments, while Mn reduction dominated carbon oxidation at the deepest site at 700 m depth, due to an extreme Mn oxide content (Figure 7). Thus, it is likely that the region with significant contribution from Fe (and, locally, Mn) reduction extends from the Kattegat into much of the Skagerrak, which is also an important area of sedimentation for particulates from the North Sea (de Haas and van Weering 1997).

Fe reduction was of minor importance in the fine-grained sediments of the Belt Sea although the content of total Fe was relatively high (Figure 3 and data not shown). However, the concentrations of Fe(III) were low, probably due to periods of oxygen depletion in the bottom water of this area (e.g., Madsen et al. (2001)) which limits the intensity of bioturbation and thereby the reoxidation of Fe(II).

In contrast to the laborious incubation technique, the procedure based on Equations (1) and (2) is rapid and simple. Further investigations are needed to determine how widely this approach can be applied. Thus, the sediments included in Figure 6 are marine sediments ranging from sandy to clayey silts, with similar concentrations of Fe (Thamdrup 2000). We have assumed that the relationship also applies for more coarse-grained sediments with low concentrations of Fe(III) as found at Station GT1, but incubation experiments with such sediments are needed to confirm this, although the results are supported by previous studies (Slomp et al. 1997). It should be noted that Fe concentrations in sandy sediments are not always low. Thus, high concentrations and intense redox cycling of Fe was observed in coarse sand from a shallow bay in Italy (Huettel et al. 1998).

Other uncertainties are related to the input variables. Thus, in sediments with low sulfate reduction rates that have large relative errors, these errors will propagate to the Fe reduction rates, though they will not affect the relative importance of Fe reduction. At all stations, concentrations of poorly crystalline Fe(III) were obtained by subtraction of an un-reactive background level of Fe(III), although Fe(III) at some stations did not quite reach a stable background concentration within the sampled depth interval (Figure 5). In general, however, the background concentrations were relatively small, and calculations without this background correction did not substantially change the results (data not shown).

With the above uncertainties in mind, the quantification of microbial Fe reduction based on Fe(III) concentrations and sulfate reduction rates can be used to survey larger areas than it is manageable with the incubation approach, while incubations at selected sites can be included for verification and calibration. Furthermore, the tight functional relationship between Fe(III) concentrations and the relative importance of Fe reduction in anaerobic carbon mineralization (Figure 6) can be used to include microbial Fe reduction in diagenetic models.

Acknowledgements

Special thanks to Lilian Salling and Tanja Quottrup for technical assistance during analyses. We gratefully acknowledge Captain Rasmussen and his crew aboard R/V Gunnar Thorson for their skillful assistance during the cruise. This study was partly funded by the Danish National Research Foundation. The Danish National Research Councils contract no. 9901901 sponsored the research vessel.

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