

Rates and pathways of carbon oxidation in permanently cold Arctic sediments

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ABSTRACT: We report here a comprehensive study of the rates and pathways of carbon mineralization in Arctic sediments. Four sites were studied at 115 to 329 m water depth in fjords on Svalbard and in coastal Norway. The Svalbard coastal region is characterized by permanently cold bottom water temperatures of -1.7 to 2.6°C . Carbon oxidation (avg = 20 to $400\text{ nmol cm}^{-3}\text{ d}^{-1}$) and sulfate reduction rates (avg = 10 to $350\text{ nmol cm}^{-3}\text{ d}^{-1}$) were measured at high resolution to 10 cm depth in sediment incubations. The distribution of oxidants available for microbial respiration was determined through porewater and solid phase geochemistry. By comparing the distribution of potential oxidants to the depth-integrated mineralization rates, the importance of various respiratory pathways to the oxidation of organic C could be quantified. Integrated C oxidation rates measured in sediment incubations (11 to $24\text{ mmol m}^{-2}\text{ d}^{-1}$) were comparable to within a factor of 2 to dissolved inorganic carbon (DIC) fluxes measured *in situ* using a benthic lander. Sulfate reduction was the dominant microbial respiration pathway (58 to 92% of total C oxidation) followed by Fe(III) reduction (10 to 26%), oxygen (5 to 14%), and nitrate respiration (2 to 3%). At sediment depths where sulfate reduction was dominant, C oxidation equivalents, calculated from independently measured sulfate reduction rates, matched DIC production rates in incubations. Sediment geochemistry revealed that the same vertical sequence of oxidants is reduced/respired in these Arctic sediments as in temperate continental shelf sediments of equivalent water depths. Microbial communities in permanently cold Arctic sediments exhibited mineralization rates and pathways comparable to temperate nearshore environments. This study completely partitioned C oxidation pathways, showing a predominance of sulfate respiration and a substantial contribution of Fe(III) reduction to organic matter mineralization in Arctic sediments for the first time. Microbial communities in cold sediments exposed to relatively high C deposition appear to respond to the input or availability of organic matter rather than to temperature.

KEY WORDS: Arctic · Sediment · Sulfate reduction · Fe(III) reduction · Organic matter mineralization · Carbon cycle

INTRODUCTION

Due to the large areal extent of its continental shelves, the biogeochemistry of the Arctic Ocean is largely influenced by processes occurring in its relatively shallow shelf seas (Anderson 1995). Interaction

between benthic processes on the shelf and nutrient cycling in the Arctic Ocean proper has been demonstrated but is not well understood. For example, benthic-pelagic coupling was indicated by nutrient release and O_2 consumption in high salinity bottom water in the Storfjorden, southern Svalbard (Anderson & Jones 1988, Hulth et al. 1994), and the outflow of this bottom water was traced down the continental slope of the Norwegian Sea to the Fram Strait (Quadfasel et al. 1988). These observations argue for a strong connection between benthic shelf processes and the chemistry of the Arctic Ocean.

Benthic-pelagic coupling has been indicated in Arctic sediments by correlating benthic metabolism and

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standing stocks with overlying water column production (Grebmeier & McRoy 1989, Grebmeier et al. 1995, Reigstad & Wassman 1996, Wassman et al. 1996). However, much less data is available on the quantification of benthic processes (rates, pathways) which control nutrient release in Arctic sediments relative to temperate environments. Few studies have measured rates of microbial respiration associated with organic diagenesis or characterized the dominant, operative pathways of respiration (Nedwell et al. 1993, Rysgaard et al. 1996). In addition, fewer studies still have focused on the biogeochemistry of anoxic sediments existing under permanently cold temperatures (Hulth et al. 1996).

Many ecologists have considered, based mainly on water column studies, that microbial communities at high latitudes, though similar in biomass to their temperate counterparts, exhibit low rates of metabolism due to temperature limitation (Pomeroy & Deibel 1986, Pfannkuche & Thiele 1987). Pomeroy et al. (1991) postulated, based on rate measurements in the water column and benthos in Newfoundland, that microbial metabolism at cold temperatures was limited by the ability of bacteria to assimilate organic substrates at the low concentrations usually present. However, several studies have challenged this hypothesis. Based on a review of published data, Rivkin et al. (1996) observed that temperature had little effect on bacterial growth rates. Furthermore, high rates of sedimentary C oxidation and O₂ consumption have been measured in cold, polar sediments (Blackburn 1987, Grebmeier & McRoy 1989, Nedwell et al. 1993, Rysgaard et al. 1996) and in the deep sea (Jahnke & Jackson 1992). In a study of polar sediments at constant cold temperatures (–1.8 to 0.5°C), Nedwell et al. (1993) concluded that seasonal variation in benthic activity was regulated by the input and availability of organic matter and not by water temperature.

Organic matter is oxidized in marine sediments via a complex web of fermentative and respiratory microbial pathways where the oxidation of organic C is balanced by the concomitant reduction of inorganic electron acceptors [O₂, NO₃[–], Mn(IV), Fe(III) and SO₄^{2–}]. Many previous studies have explored the relative importance of different C oxidation pathways in temperate environments (Jørgensen 1982, Henrichs & Reeburgh 1987, Reimers et al. 1992, Canfield et al. 1993a,b, Thamdrup et al. 1994, Hines et al. 1997). Complete characterization of C oxidation processes has been hampered, however, by our inability to directly measure rates of many of the oxidation pathways. No direct assays are available for quantification of heterotrophic O₂ or metal respiration in sediments, for example, and difficulties in constraining the amount of O₂ consumed through the reoxidation of respiration products further confounds our analysis of C oxidation pathways.

New techniques allow the significance of various C oxidation pathways to be determined in marine sediments (Canfield et al. 1993a,b, Thamdrup & Canfield 1996), and a similar approach has been applied in freshwater sediments (Roden & Wetzel 1996). Thus, using a comprehensive approach wherein a range of measurements together constrain the rates, suboxic/anoxic mineralization processes such as sulfate reduction and metal reduction have been shown to contribute to a larger portion of C oxidation than was previously perceived (Canfield et al. 1993a, Thamdrup & Canfield 1996). Conversely, these new studies determined that aerobic respiration accounts for a smaller percentage of organic C oxidation (<20%) compared to previous estimates in coastal marine sediments (Canfield et al. 1993b). To date, the new comprehensive technique has been applied only in temperate, coastal marine systems with bottom water temperatures of 5°C and above.

Cold temperatures are the rule rather than the exception in the world ocean with a majority of the sea bottom exposed to temperatures of 5°C or less. These temperatures are below those at which most process studies of C mineralization have been made. Therefore, the present study was carried out in fjords of Svalbard and coastal Norway, an area where sediments are exposed to relatively high organic C input under exceptionally low temperatures (7 to –1.8°C). Given the paucity of data on Arctic sediments, the primary goal was to characterize the sediment biogeochemistry in detail, especially with regard to organic remineralization. More specifically, the purpose was to use a combination of geochemical methods and direct rate measurements to determine the effect of temperature on the rates and pathways of C oxidation.

METHODS

Site description. The study was part of a larger expedition which focused on the microbial ecology of cold sediments carried out from 10 to 25 September, 1995, on board the Norwegian RV 'Jan Mayen'. Sediments were sampled in several fjords near coastal Norway and the Svalbard archipelago, with emphasis on sites at Svalbard (Fig. 1, Table 1). Two stations, Sv 2 at Hornsund and Sv 3 at Van Mijen fjord, were visited on the western side of Svalbard, where the Western Spitsbergen current flows north along the coast keeping the fjords ice-free for most of the year (Andruleit et al. 1996). One site, Storfjorden (Sv 5), was sampled on the eastern side of Svalbard, which is influenced by colder polar currents originating from the Arctic Ocean (Andruleit et al. 1996). Overall, the Svalbard region, situated well above the Arctic Circle, is characterized

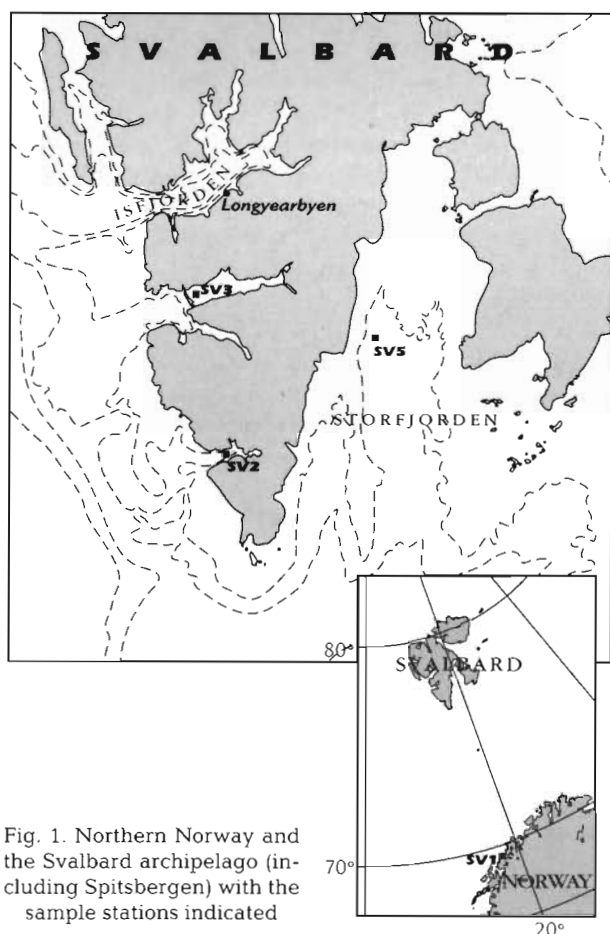


Fig. 1. Northern Norway and the Svalbard archipelago (including Spitsbergen) with the sample stations indicated

by consistently cold bottom water temperatures and an extended period of ice cover. Bottom water temperatures are provided in Table 1. All bottom waters contained O_2 concentrations near saturation, and nitrate concentrations ranged from 9 to 12 μM (Glud et al. 1998).

Table 1. Sample site information and sediment characteristics

Stn:	Sv 1	Sv 2	Sv 3	Sv 5
Position				
Latitude	69° 29.4' N	76° 58.2' N	77° 45.8' N	77° 33.0' N
Longitude	18° 07.5' W	15° 34.5' W	15° 03.9' W	19° 05.0' W
Water depth (m)	329	155	115	175
Bottom water temperature ($^{\circ}C$)	7.0	2.6	0.2	-1.7
Wet density ($g\ cm^{-3}$) ^a	1.30	1.29	1.32	1.25
Porosity ^a	0.79	0.83	0.77	0.83
Organic C (%) ^b	0.6	1.5	1.8	2.4
Sediment accumulation ($g\ m^{-2}\ d^{-1}$) ^b	2.8	12.9	5.3	3.8
O_2 penetration depth (cm) ^b	1.0	0.6	1.0	1.1

^aAt a sediment depth of 0 to 1 cm; ^btaken from Glud et al. (1998)

Primary production in the Barents Sea near Svalbard is estimated at up to $150\ g\ C\ m^{-2}\ yr^{-1}$ and undergoes a large seasonal variation similar to other seasonally ice-covered areas (Eilertsen et al. 1989). Relevant sediment characteristics are given in Table 1. In general, sediments sampled for the present study were a clayey silt with relatively few drop stones (<1% by volume) in the upper 25 cm. Sediment accumulation rates were determined from the depth distribution of unsupported ^{210}Pb and were relatively rapid (Table 1). Organic C concentrations varied between 0.6 and 2.4%, gradually decreasing with depth; this range in organic C concentrations overlapped with those observed for areas of the Svalbard shelf visited by Hulth et al. (1996). Bioirrigating macrofauna were observed to be abundant and were estimated to enhance benthic exchange rates by up to a factor of 3 in the sediments sampled for this study. Sediment mixing, presumably due to bioturbating fauna, was inferred from the ^{210}Pb profiles (Glud et al. 1998), and benthic fauna caused heterogeneous O_2 profiles as measured with microelectrodes.

Sediment sectioning and pore water extraction. Sediments were sampled by a multicoring device in polycarbonate liners (9.6 cm id) at all stations (Barnett et al. 1984). Eight to 10 cores were used and only accepted when the surface appeared to be unaffected by resuspension or disruption during coring. Cores were immediately transferred to an incubator set to bottom water temperature while sectioning at each station. A large advantage of the Svalbard sites was that the air temperature was always close to $0^{\circ}C$ at the time of sampling, minimizing the warming of sediment during sectioning and sampling, which was conducted on deck.

For geochemical analyses, an additional 1 to 2 cores were sectioned within 1 h of retrieval and the sediment was loaded into polypropylene centrifuge tubes in a N_2 -filled glove bag. The tubes were tightly capped and centrifuged for 10 to 20 min in a cold room at $0^{\circ}C$. After reintroduction into the glove bag, pore waters were sampled and filtered through 0.2 μm cellulose acetate syringe filters. Sediments for solid phase analysis were frozen under N_2 for later use.

For determination of C mineralization rates and pathways, sediment from the upper 10 cm of 8 to 10 cores (723 cm^2 total) was incubated as described by Canfield et al. (1993b) and Thamdrup & Canfield (1996) in laminated ethylvinyl alcohol plastic bags with a very low gas permeability (Kruse 1993). Briefly, the cores were

sectioned and parallel sections pooled under strict anoxia in a glove bag. After sectioning, sediment from each of 8 depth intervals was placed into the bags within a few hours of core retrieval. Incubation bags were sampled initially, sealed, and incubated dry at bottom water temperature (Table 1). Bags were placed within larger N₂-filled bags during incubation to further maintain anoxic conditions as per Canfield et al. (1993b). The bags were then sampled at regular intervals, and the pore waters were extracted by centrifugation/filtration as described above.

Sulfate reduction rates were determined twice on 10 ml splits of sediment with ³⁵SO₄²⁻ (Jørgensen 1978) in 2 h incubations at bottom water temperature. At termination, the sediment was fixed in 20% Zn acetate and frozen. The reduced ³⁵S was recovered by distillation with boiling acidic Cr²⁺ solution using the single-step method of Fossing & Jørgensen (1989). Sulfate reduction measurements were carried out in short-term incubations (2 h) where the effects of sulfide oxidation (Fossing 1995) and calcium carbonate precipitation/dissolution should be minimal.

Pore water analyses. Pore water for the determination of ΣCO₂ and ammonium analyses was filtered into 1.8 ml glass vials that were capped with Teflon-coated butyl rubber septa, leaving no gas phase and maintaining anoxia. The samples were stored at 0°C and analyzed within a few days of sampling by flow injection with conductivity detection (Hall & Aller 1992; SD 2% for both ΣCO₂ and NH₄⁺) on board ship. Hydrogen sulfide can interfere with ΣCO₂ measurements with this method (Hall & Aller 1992, Lustwerk & Burdige 1995). However, no dissolved sulfide was detected (methylene blue method, det. limit 1 μM, SD 5%; Cline 1969) in the top 10 cm of any of the pore waters sampled.

Concentrations of NO₃⁻ + NO₂⁻ were determined on frozen pore water after reduction with V(III) to NO with subsequent detection by chemiluminescence (det. limit 0.1 μM; SD 1%; Braman & Hendrix 1989). Dissolved Fe²⁺ was determined immediately after filtration by colorimetry with a ferrozine solution (det. limit 1 μM; SD 2%; Stookey 1970). Dissolved Mn²⁺ was analyzed in acidified pore water by flame atomic absorption spectroscopy (det. limit 0.5 μM; SD 2%). Sulfate concentrations were measured in acidified pore water using the turbidometric method of Tabatabai (1974). Sediment pH was determined at the end of the incubations with a glass electrode, calibrated with NBS standards, that was inserted into the bags. For all pore water chemistry, samples from duplicate cores generally varied by no greater than 10% and usually were within 5% of the concentration average between cores.

Solid phase analyses. Wet chemical extractions were used to determine the poorly crystalline Fe and Mn

oxide pools (Canfield 1989, Kostka & Luther 1994, Thamdrup et al. 1994). Iron was extracted in 0.5 M HCl for 1 h (Kostka & Luther 1994). The oxidation state of Fe in the extract was further determined by analysis in (a) ferrozine buffer (50 mM HEPES, 0.1% ferrozine, pH 7), and (b) ferrozine buffer +1% (w/v) hydroxylamine hydrochloride (pH 7) (Kostka & Luther 1994). Iron determined in the HCl extract with hydroxylamine addition is operationally defined as the total HCl-extractable fraction [(Fe(II) + Fe(III))] while Fe in the HCl extract without hydroxylamine addition is defined as the HCl-extractable Fe(II). Solid Fe(III) was determined by difference between these 2 fractions. Calibration experiments with pure Fe phases have confirmed the selectivity of this extraction towards poorly crystalline Fe phases (Canfield 1988, Kostka 1993). Manganese was extracted with dithionite-citrate-acetic acid (DCA; pH 4.8; Lord 1980, Canfield 1989) and Mn concentration was measured in extracts using the same method described above for pore waters.

Acid-volatile sulfide (AVS = FeS + H₂S) and chromium-reducible sulfur (CRS = S⁰ + FeS₂) were determined after a 2-step distillation with cold 2 M HCl and boiling 0.5 M Cr²⁺ solution (Fossing & Jørgensen 1989). Elemental sulfur was extracted by shaking the samples in 100% methanol for 24 h and then determined with HPLC as in Ferdelman et al. (1997). Sediment fixed with Zn acetate from the sulfate reduction measurements was used for sulfur determinations. Concentrations of FeS and FeS₂ were determined by difference (AVS - H₂S and CRS - S⁰, respectively). For all solid phase measurements, samples from duplicate cores generally varied by no greater than 10% and usually were within 5% of the concentration average between cores.

RESULTS

Pore water chemistry

Profiles of pore water constituents are presented to between 20 and 30 cm depth in the sediment. Oxygen penetration depths, measured *in situ* using a benthic lander, were observed at 1.0, 0.6, 1.0 and 1.1 cm at Sv 1, Sv 2, Sv 3, and Sv 5 (Table 1). Nitrate concentrations (Fig. 2a.) were depleted to a few micromolar in the top 1 cm at all stations. Sulfate concentrations remained relatively constant at all stations with little or no depletion observed to below 20 cm (Fig. 2b). As mentioned previously, no dissolved sulfide was detected (to <1 μM) in any of the pore waters at all stations.

Just below the sediment depth where oxygen and nitrate were depleted, subsurface maxima were observed for pore water Mn at 1 to 2 cm (Fig. 2c) and for

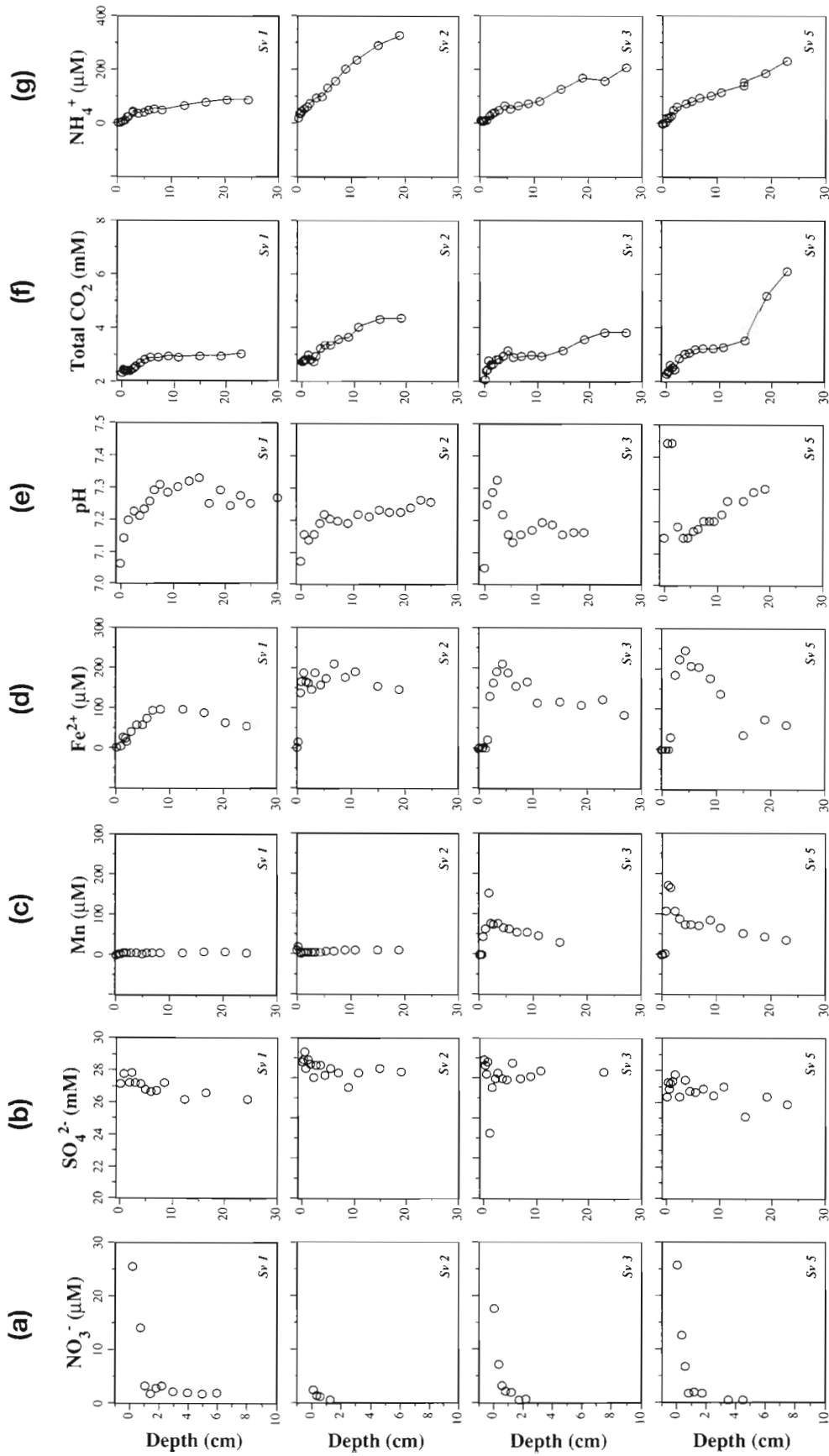


Fig. 2. Concentration of pore water constituents measured on separate long cores sampled exclusively for pore water/solid phase analysis. (a) NO_3^- , (b) SO_4^{2-} , (c) Mn^{2+} , (d) Fe^{2+} , (e) pH, (f) ΣCO_2 , (g) NH_4^+

pore water Fe^{2+} at 2 to 6 cm (Fig. 2d), indicative of Fe and Mn reduction zones, respectively. Sediment pH distribution (Fig. 2e) followed closely with the redox-sensitive pore water constituents, showing larger vertical gradients at stations where larger gradients of solid phase Fe, Mn were observed close to the sediment surface (Sv 3, Sv 5; Fig. 3).

Mineralization products, ΣCO_2 and NH_4^+ , exhibited parallel distributions and the curvature of the profiles (close to the sediment surface) was indicative of relatively rapid organic matter decomposition (Fig. 2f,g). Ammonium profiles were concave up, suggesting a significant effect of pore water irrigation to ≥ 10 cm depth, especially at Sv 3 and Sv 5.

Solid phase distributions

Solid phase concentrations are presented to 10 cm depth on a per volume basis in order that the distributions may be more easily compared to rate measure-

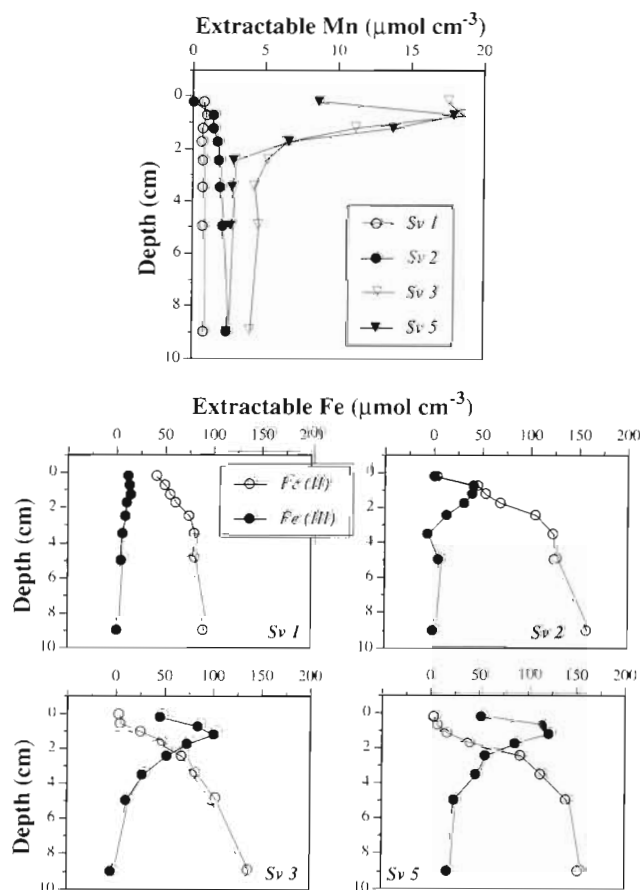


Fig. 3. Solid phase extractable Fe(III) and Mn(IV) indicative of the poorly crystalline metal oxides available for biological and chemical reduction. Solid Fe is further speciated into reduced and oxidized pools (see 'Methods')

ments. Wet chemical extractions were used to determine the poorly crystalline Fe and Mn oxide pools, as these compounds are thought to be available for bacterial respiration (Lovley & Phillips 1986, Lovley 1991). The total amount of poorly crystalline Fe oxide [hereafter referred to as solid Fe(III)] extracted was on the high end of the range observed in temperate marine sediments in the subtidal zone (Canfield 1989, Thamdrup et al. 1994, Thamdrup & Canfield 1996) indicating a large amount of reactive Fe(III) was available for respiration. Similar solid Fe(III) concentrations were measured at all stations sampled on Svalbard (Sv 2 through Sv 5), and about half the amount of Fe(III) was extracted at Sv 1 (Fig. 3). A large gradient in solid Fe(III), consistent with the corresponding vertical pore water Fe gradient (Fig. 2d), was observed at Sv 3 and Sv 5 from 1 to 4 cm depth, while a smaller solid Fe(III) gradient was observed at Sv 2 and the whole profile was shifted closer to the sediment surface (Fig. 3). At Sv 1, the majority of extracted Fe was reduced at all sediment depths and Fe(III) concentrations were lower than at all other stations.

The range of poorly crystalline Mn oxide (hereafter referred to as solid Mn) concentrations was approximately 10 times lower than solid Fe(III) (Fig. 3), while the vertical distributions of solid Mn and Fe were similar. Substantial depth gradients of solid Mn were only observed at stations Sv 3 and Sv 5 close to the sediment surface with vertical distributions mirroring those of pore water Mn (Fig. 2c).

At all stations, solid S fractions (pyrite, AVS, S^0 ; see Fig. 4) increased with sediment depth. The highest solid S concentrations were observed at Sv 2 with much lower concentrations at the other 3 stations. Pyrite was the dominant solid S pool at all stations. Solid S concentrations were an order of magnitude lower than solid Fe concentrations at all stations and were in the middle of the range observed in shallow, temperate continental margin sediments (Jørgensen 1977, Fossing & Jørgensen 1989, Canfield et al. 1993b). The calculated burial of reduced S ($= \text{H}_2\text{S} + \text{S}^0 + \text{FeS} + \text{FeS}_2 = \text{AVS} + \text{CRS}$) below 10 cm was 0.033 to $0.8201 \text{ mmol m}^{-2} \text{ d}^{-1}$, accounting for only <1 to 7% of the daily integrated sulfate reduction rate, consistent with the rapid recycling or reoxidation of sulfides at the top of the sulfate reduction zone. Burial was calculated using the total concentration of reduced S at the deepest depth sampled (Fig. 4) multiplied by the sediment accumulation rate.

Rate measurements in sediment incubations

In order to constrain the amount of C oxidation coupled to various respiration pathways, we have mea-

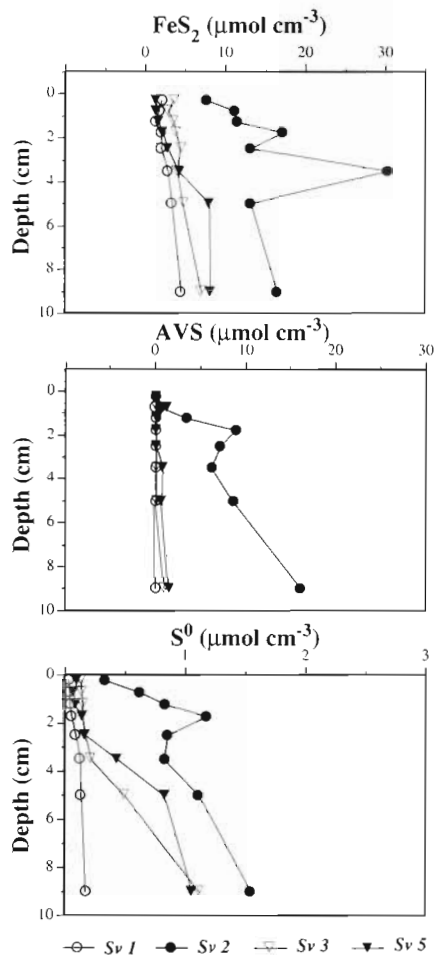


Fig. 4. Solid phase reduced S pools which are the products of bacterial sulfate reduction

sured the total accumulation of mineralization products (ΣCO_2 and NH_4^+), sulfate reduction rates, and denitrification rates in sediment samples at high resolution to 10 cm depth. The accumulation of mineralization products was measured in 60 h incubations and the rate of accumulation was calculated by regression of the increase in concentration vs time. In general, production rates were highly linear showing no systematic deviation with time as shown for Sv 2 in Fig. 5. In duplicate core incubations, mineralization rates agreed to within 10% of the average rate between incubations, and agreement was usually better than 7%.

Rates of ΣCO_2 and ammonium accumulation first decreased with depth and then showed a mid-depth maximum near that of surface rates centered around 2 to 3 cm depth at all stations (Figs. 6 & 7). The mid-depth maximum could be the result of sediment mixing or a focusing of organic material caused by the high macrofaunal activity in the area. The depth-integrated C oxidation rate at Hornsund (Sv 2) was nearly twice that measured at other stations, whereas the

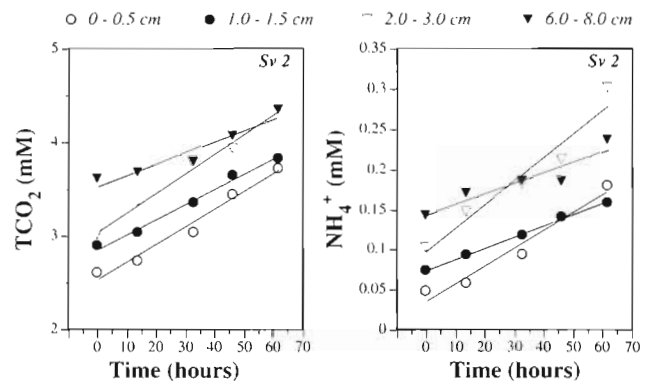


Fig. 5. Examples of the accumulation of ΣCO_2 and NH_4^+ over time in pooled sediment incubations at Hornsund fjord (Sv 2)

ammonium accumulation rate was similar in magnitude at Sv 1, Sv 2, and Sv 3 (Table 2). The unusually high integrated ammonium accumulation rate observed at Sv 5 (Table 2) largely originates from the high rate measured in the 4 to 6 cm depth interval (Fig. 7), which also produced a very low C/N ratio of mineralization products (Table 2).

In general, the C/N ratio of mineralization products varied greatly and for some stations was low relative to Redfield stoichiometry (Redfield 1958) and to other studies (Thamdrup & Canfield 1996). Low C/N ratios

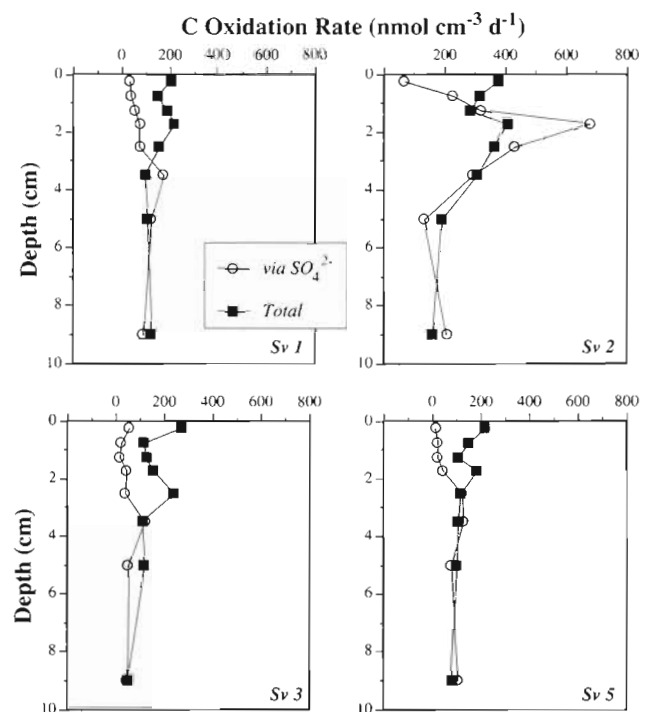


Fig. 6. Total carbon oxidation rates (from ΣCO_2 accumulation) and the carbon oxidation equivalents derived from independently measured sulfate reduction rates from sediment incubations

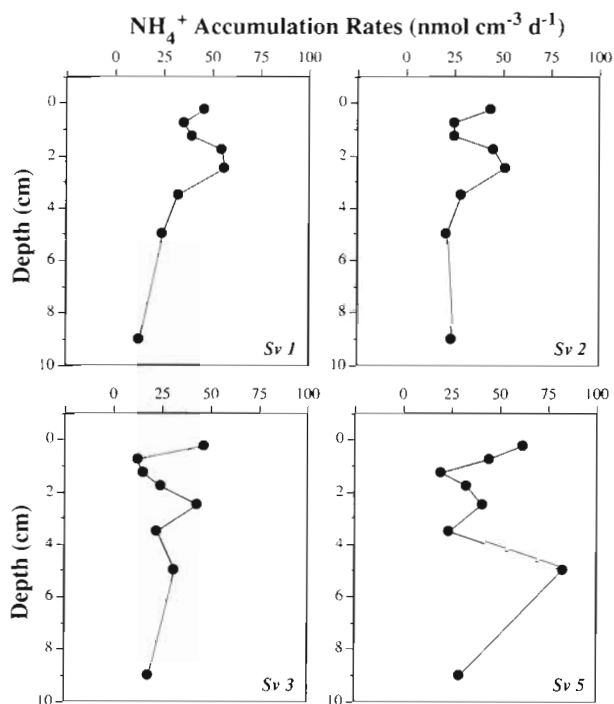


Fig. 7. Accumulation rates of NH_4^+ in the pore waters of sediment incubations

(<6) could result from the oxidation of short chain fatty acids which do not contain N or the assimilation of N from dissolved NH_4^+ . The highest C/N ratio of 10 was observed at the station with the highest mineralization rates, Sv 2 (Table 2).

Rates of sulfate reduction (Fig. 8) were depressed in all surface sediments sampled, generally in the 0 to 4 cm depth zone, indicating that other respiratory processes dominated C oxidation in this zone. At Sv 2, average sulfate reduction rates were 3 to 5 times higher than at the other stations, and the rate maximum was observed closer to the sediment surface at 1.5 to 2.0 cm depth. Higher sulfate reduction activity at Sv 2 was also evidenced by high integrated rates

Table 2. Depth-integrated rates of respiration and the accumulation of mineralization products ($\text{mmol m}^{-2} \text{d}^{-1}$) in the 0 to 10 cm depth range

Stn	ΣCO_2 accumulation	NH_4^+ accumulation	SO_4^{2-} reduction	Denitrification	C/N ratio ^a
Sv-1	13.3	2.9	5.0	0.2	4.7
Sv-2	24.2	2.8	12.0	0.6	9.4
Sv-3	11.9	2.6	2.6	0.3	5.9
Sv-5	11.0	4.8	4.4	0.2	3.7

^aMean ratio of accumulated mineralization products ($\Sigma\text{CO}_2/\text{NH}_4^+$ on a mol:mol basis)

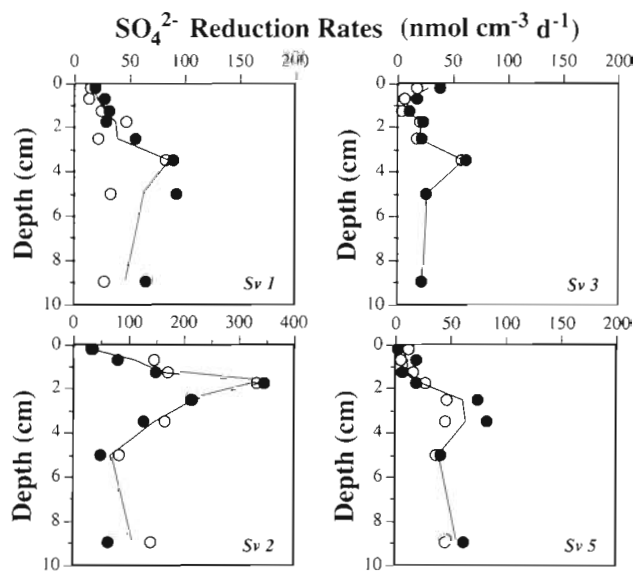


Fig. 8. Sulfate reduction rates measured in sediment incubations. Bold lines represent the averages of duplicate rate measurements

(Table 2). The remaining stations showed a maximum sulfate reduction rate of 60 to 100 $\text{nmol cm}^{-3} \text{d}^{-1}$ at 3.0 to 4.0 cm depth. Denitrification rates, measured using the isotope-pairing technique (Nielsen 1992), were 2 to 3 times higher at Sv 2 compared to the other stations (Table 2).

Direct rate measurements together with the distribution of potential oxidants were used to completely partition microbial respiration pathways. A concise description of the deduction scheme used in this study can be found in Thamdrup & Canfield (1996), and the stoichiometries of respiration reactions used during data interpretation can be found in Canfield et al. (1993a). In Fig. 6, sulfate reduction rates have been converted to the amount of C oxidized using a 2:1 stoichiometry of C oxidized to sulfate reduced (Thamdrup & Canfield 1996). C oxidation via sulfate reduction is then compared with the total C oxidation rates derived from ΣCO_2 accumulation in sediment incubations. The rates converge at depth at all stations, indicating that sulfate reduction is the dominant respiratory process, whereas the rates diverge in surface sediments, indicating that other respiration pathways are operative. Our incubations were not long enough to accurately measure the stoichiometry of SO_4^{2-} depletion to ΣCO_2 accumulation. However, the match of radiotracer-derived sulfate reduction rates to total C oxidation rates at depth is a good indication that the $\Sigma\text{CO}_2 : \text{SO}_4^{2-}$ relationship holds for this study.

Manganese accumulation rates calculated by linear regression of sediment incubation results are provided in Fig. 9. These rates scaled with the solid phase Mn

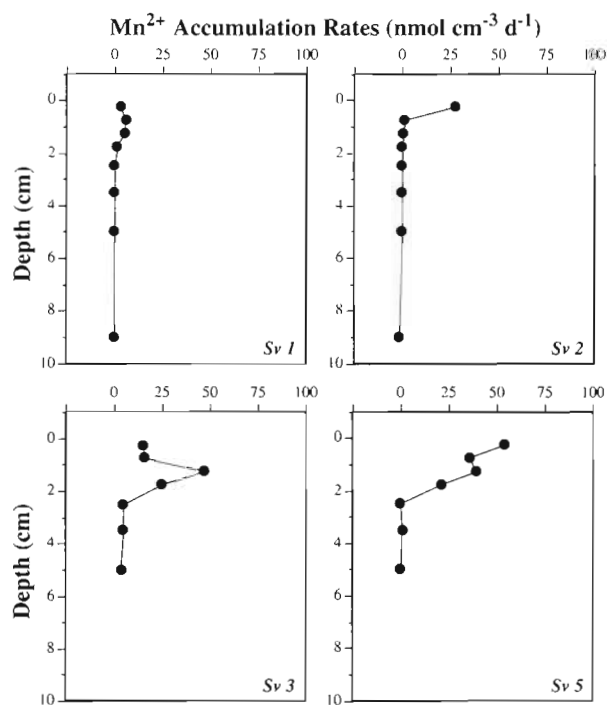


Fig. 9. Accumulation rates of Mn^{2+} in the pore waters of sediment incubations

concentrations (Fig. 3) with the highest rates observed at Sv3 and Sv5, followed by Sv2 and Sv1, respectively. Iron accumulation rates measured in sediment incubations were not as easily evaluated as those for Mn. Accumulation appeared to be largely affected by adsorption and precipitation reactions (data not shown). However, Fe(II) accumulation was generally observed only at sediment depths where the Fe(III) reduction zone was delineated by a gradient in solid phase Fe(III).

The lack of significant gradients of solid Mn in the 0 to 1 cm depth interval at Sv1 and Sv2 (avg solid Mn $< 1 \mu\text{mol cm}^{-3}$; Fig. 3) suggest that insignificant Mn(IV) is available for reduction at these stations. In contrast, substantial gradients in solid Mn were observed at Sv3 and Sv5. Dissimilatory Mn(IV) reduction by metal-reducing bacteria has been shown to outcompete abiotic reduction reactions coupled to AVS, S^0 (Aller & Rude 1988, Canfield et al. 1993b), and Fe^{2+} oxidation (Postma 1985, Burdige & Nealson 1986). Assuming that sediment solids are mixed in a diffusional manner, we can compare gradients of solid Mn with those of potential reductants (AVS, S^0 , Fe^{2+}) to evaluate abiotic and biotic reduction pathways (see also Canfield et al. 1993b).

Given that bioturbation mixes both oxidant and reductant at a rate proportional to their concentration gradients, chemical gradients of all reductant species

Table 3. Solid phase and pore water gradients in the Mn(IV) reduction zone (0.5 to 2.0 cm depth). AVS = acid-volatile sulfide

Stn	Mn oxide	Gradient ($\mu\text{mol cm}^{-4}$)			Fe(II) ^a
		AVS	S^0	Fe^{2+}	
Sv 3	12.1	0.006	0.009	0.016	43.4
Sv 5	11.4	(-)	0.080	0.016	38.7

^aExtractable Fe(II), presumed to be adsorbed and therefore reactive toward Mn(IV)

$$2\text{Fe}^{2+} + \text{MnO}_2 + 2\text{H}_2\text{O} \longrightarrow 2\text{FeOOH} + \text{Mn}^{2+} + 2\text{H}^+$$

except solid phase, extractable Fe(II) are at least 3 orders of magnitude too low to support reduction of the solid Mn present (Table 3). However, adsorbed Fe(II), which would only be observed in the solid phase extractions, is available to react with poorly crystalline Mn oxides (see balanced reaction in Table 3). The demand of solid Mn for reduction is more than balanced by the solid Fe(II) available for oxidation (Table 3). We conclude the consumption of solid Mn is due to the abiotic reduction by adsorbed Fe(II) or soluble Fe(II) desorbed from the solid phase, and not due to dissimilatory reduction by bacteria (at Sv3 and Sv5). Therefore, after subtracting out C mineralized via SO_4^{2-} reduction, all of the remaining C oxidation in the suboxic zone is coupled to dissimilatory Fe(III) reduction. This interpretation also follows for the profiles of solid Mn and Fe observed at Sv1. Extractable Fe(II) is high to the sediment surface while little or no maximum in solid Mn was observed (Fig. 3).

DISCUSSION

Pore water and solid phase geochemistry

Geochemical gradients resulting from the consumption of oxidant and the accumulation of reduction products in shallow polar sediments are consistent with a diagenetically active system containing the same vertical sequence of microbial respiration reactions found in temperate marine sediments exposed to relatively high sedimentation rates. There was substantial overlap between redox zones, especially in suboxic areas of the sediments. As observed for temperate shelf sediments exposed to relatively high C deposition (Canfield et al. 1993b), oxygen and nitrate were depleted in the top 1 cm depth of the sediment at all stations, indicative of active aerobic respiration and denitrification in this zone. Immediately below, at 1 to 2 cm depth, chemical gradients of Mn revealed a distinct Mn(IV) reduction zone which was interpreted to

be supported by abiotic reduction reactions. Overlapping by 1 cm below the Mn(IV) reduction zone, a broader Fe(III) reduction zone (1.5 to 5 cm) was observed from gradients in solid phase Fe. Products of sulfate reduction (solid phase reduced S compounds) showed that this zone overlapped extensively with that of metal reduction.

Mineralization rates under permanently cold conditions

Few studies have directly measured rates of organic mineralization in permanently cold sediments with most researchers having used oxygen fluxes to infer rates of C oxidation (Pfanckuche & Thiel 1987, Grebmeier & McRoy 1989, Henriksen et al. 1993, Nedwell et al. 1993, Rysgaard et al. 1996). O_2 uptake rates of up to $25 \text{ mmol m}^{-2} \text{ d}^{-1}$ were observed in shelf sediment of the Bering/Chukchi Seas (Henriksen et al. 1993), and a range of 11 to $17.8 \text{ mmol m}^{-2} \text{ d}^{-1}$ was found in the eastern Arctic (Hulth et al. 1994, Rysgaard et al. 1996), while up to $90 \text{ mmol m}^{-2} \text{ d}^{-1}$ of oxygen uptake was measured in the South Orkney Islands, Antarctica (Nedwell et al. 1993). As long as denitrification rates are low, the amount of O_2 uptake should be roughly equal to the total C oxidation rate in marine sediment (Canfield et al. 1993a), and the range of our directly measured integrated C oxidation rates (10 to $25 \text{ mmol m}^{-2} \text{ d}^{-1}$; Table 2, Fig. 6) is nearly identical to that of previously measured O_2 uptake rates in Arctic sediments (11 to $25 \text{ mmol m}^{-2} \text{ d}^{-1}$; above references). Furthermore, C mineralization rates from this study largely overlap with the range of rates reported for temperate shelf sediments (2 to $28 \text{ mmol m}^{-2} \text{ d}^{-1}$; Archer & Devol 1992, Canfield et al. 1993b, Devol & Christiansen 1993), strongly suggesting that microbial communities in polar sediments are capable of processing organic matter at rates no different from rates measured in temperate shelf environments.

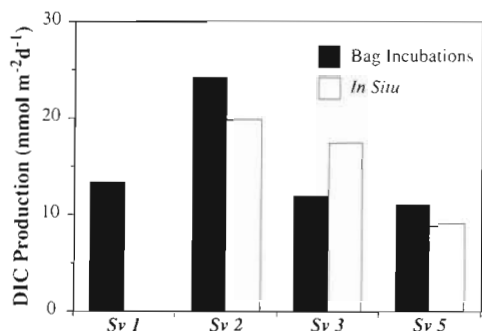


Fig. 10. Comparison of the depth-integrated (to 10 cm depth) C oxidation rates measured in sediment incubations to those measured *in situ* using a free-vehicle benthic lander

To check for possible stimulation of microbial carbon mineralized in our bag incubation procedure, we have compared the depth-integrated C oxidation rates (measured by DIC accumulation) from incubations to DIC fluxes measured *in situ* using a free-vehicle benthic lander (Fig. 10). It was impossible to compare these approaches at Malangen Fjord (Sv 1) because the benthic lander did not function properly. However, at the remaining stations, integrated rates of C oxidation measured using our bag incubation technique covaried and approached closely to the fluxes measured *in situ* to within a factor of 1.5 (Fig. 10).

Though pore water profiles indicate a significant portion of organic matter remineralization could occur below 10 cm depth, the bag incubations were only carried out to 10 cm. Previous bag incubation studies compared C mineralization rates extending farther down in the sediment column to rates measured in intact cores as well as to *in situ* benthic fluxes (Thamdrup & Glud unpubl.). The conclusion from these methodological studies was that the bag incubation technique was consistent with other rate measurements, but in some cases, remineralization rates were enhanced in the bags by up to a factor of 2. If we estimate approximately 50% of C mineralization is occurring below 10 cm depth in the sediments of this study (B. B. Jørgensen unpubl. results), it would follow that the C oxidation rates from bags (Fig. 10) could be stimulated by a factor of 2, making them equal to DIC fluxes measured *in situ*.

The bag incubation technique also may cause the artificial elimination of a certain amount of O_2 from the sediment. We assume aerobic respiration and denitrification are not significantly coupled to C oxidation below the depths to which O_2 and nitrate penetrate. However, because abundant macrofauna (which potentially bioirrigate) were observed at all sites sampled, O_2 removal could affect most of the depths sampled. As discussed above, C mineralization rates from bag incubations were similar to those measured by an *in situ* benthic lander. Because *in situ* O_2 fluxes and sulfate reduction rates from bag incubations also scaled closely with measured C oxidation rates, the O_2 flux roughly balances the demand for the reoxidation of reduction products (Canfield et al. 1993a), and we maintain that any O_2 artifacts caused by the bag incubations should be minimal. Despite the additive variability inherent to all of the measurements that bag incubations incorporate, we contend rate measurements using this technique are internally consistent, and the partitioning of microbial respiration pathways is not significantly altered. Our interpretation is supported by the match of measured sulfate reduction and ΣCO_2 production rates at sediment depths where SO_4^{2-} is the only oxidant available for respiration. The

match of sulfate reduction and ΣCO_2 production rates also indicated that little or no precipitaton/dissolution of CaCO_3 was occurring which might influence our measurement of total C oxidation.

Partitioning of microbial respiration pathways

Mineralization pathways, especially under suboxic/anoxic conditions in polar environments, have been studied to a smaller extent (Nedwell 1989, Nedwell et al. 1993, Rysgaard et al. 1996). Previous studies used O_2 fluxes and sulfate reduction rates to partition oxic/anoxic mineralization processes, finding that 12 to 32% of organic matter mineralization was anoxic. Using this simple comparison, our study found that a much higher percentage (60 to 90%; Table 4) of C oxidation was mediated by anoxic processes. Previous estimates of anoxic mineralization in Arctic sediments may be lower than those described here due to longer incubation times used in previous sulfate reduction rate measurements (20 to 24 h). Longer incubation times can be affected by sulfide oxidation to cause spuriously low rates of sulfate respiration (Fossing 1995). Another explanation could be that previous investigators did not include Fe(III) and Mn(IV) as potential oxidants for organic matter mineralization.

As has been found in previous studies of temperate continental margin sediments (Jørgensen 1977, 1982, Canfield et al. 1993b, Thamdrup & Canfield 1996), sulfate reduction was the dominant microbial respiration pathway in permanently cold, Arctic sediments (Table 4), comprising 58 to 92% of the C oxidized. On the average, Fe(III) reduction was the second most important pathway, responsible for up to 26% of the C oxidized in Arctic sediments. In agreement with previous studies (Canfield et al. 1993b, Thamdrup & Canfield 1996), the importance of aerobic respiration overlapped with Fe(III) reduction at 5 to 14% of the C oxidized (Table 4). Denitrification made up only 2 to 3% of the C oxidized, in agreement with previous studies of marine sediment overlain by an oxic water column.

For the first time, we show that Fe(III) reduction is a significant contributor to the terminal decomposition of organic matter in permanently cold marine sediments. These data support the small, but growing database which indicates that Fe(III) and Mn(IV) respiration support a substantial amount of C oxidation in a wide range of marine sediments, from the Amazon delta (Aller et al. 1986, 1996) to the Danish shelf (Canfield et al. 1993a,b), the Chilean margin (Thamdrup & Canfield 1996), and shallow coastal embayments such as Long Island Sound (Aller 1994).

The importance of sulfate reduction to C oxidation (and rapid sulfate reduction rates) at all sites would

Table 4. Summary of the partitioning of C mineralization pathways at each station. Presented as the amount of C oxidation integrated to 10 cm depth from sediment incubations at each site in $\text{mmol m}^{-2} \text{d}^{-1}$ with the percentage of the total integrated C oxidation rate in parentheses

Stn	O_2	NO_3^-	Fe(III)	Mn(IV)	SO_4^{2-}
Sv 1	1.51 (11.3)	0.25 (1.9)	2.15 (16.2)	0	9.41 (70.6)
Sv 2	1.13 (4.7)	0.75 (3.1)	0	0	22.34 (92.2)
Sv 3	1.58 (13.3)	0.37 (3.2)	3.05 (25.7)	0	6.89 (57.8)
Sv 5	1.58 (14.4)	0.25 (2.3)	1.09 (9.9)	0	8.08 (73.4)

appear to be at odds with the lack of sulfate depletion measured with depth in the pore waters. We suggest that pore water irrigation is occurring at rates similar to temperate marine sediments and is vital to the recycling of oxidant in these Arctic sediments.

We can further support our interpretation of Fe reduction processes by calculating the biodiffusion coefficients necessary to support the solid Fe(III) demand of dissimilatory and abiotic reduction combined. At Sv 2, no contribution of dissimilatory Fe(III) reduction was observed from rate measurements; therefore Table 5 provides biodiffusion coefficients for only Sv 1, Sv 3, and Sv 5. The demand of Fe(III) necessary to support C oxidation was first calculated from the inferred C oxidation rate (see above discussion) using a 4:1 stoichiometry of Fe reduced to C oxidized (Canfield et al. 1993a). The abiotic portion of Fe(III) reduction was obtained using the measured sulfate reduction rates adjusted for the stoichiometry of sulfide oxidation (Thamdrup et al. 1994; Table 5). The total demand for Fe(III) (dissimilatory + abiotic; $J_{\text{bi,Fe}}$) together with the measured solid Fe(III) gradient ($dC_{\text{Fe(III)}}/dx$) at each station was then utilized to derive a biodiffusion coefficient (D_b) (Table 5). The resulting biodiffusion coefficients ($D_b = 0.010$ to 0.15), are well within the range of D_b 's reported previously ($D_b \approx 0.014$ to 0.30 ; Van Cappellen et al. 1993, Boudreau 1994) for shallow, temperate marine sediments with relatively rapid sediment accumulation rates (0.1 to 1.0 cm yr^{-1}).

To further check the reliability of our interpretation, we used Eq. (3) from Boudreau (1994) to calculate biodiffusion coefficients based on measured sediment accumulation rates (Table 1). The D_b 's obtained from this alternative method were almost identical to those obtained from the Fe mass balance for the Svalbard stations Sv 3 and Sv 5 (Table 5). We contend that these coefficients of sediment mixing intensity, obtained from the balance of inferred rate measurements and measured Fe(III) gradients, support our interpretation of the importance of dissimilatory Fe(III) reduction to organic matter oxidation at the Svalbard sites.

In contrast, at Sv 1, the D_b from the Fe mass balance was 10 times higher than that obtained from the sedi-

Table 5. Comparison of biodiffusion coefficients required to produce the observed Fe demand at stations where dissimilatory Fe(III) reduction is significant using rate measurements/solid Fe(III) gradients and biodiffusion coefficients calculated from the measured sediment accumulation rates

	Inferred rate ^a (mmol m ⁻² d ⁻¹)	Dissimilatory demand ^b (mmol m ⁻² d ⁻¹)	Abiotic demand ^c (mmol m ⁻² d ⁻¹)	Solid Fe(III) gradient ^d (μmol cm ⁻⁴)	Required D _b (cm ² d ⁻¹)
Sv 1	2.17	8.68	3.33	-7.99	0.15 ^e 0.011 ^f
Sv 3	3.05	12.2	1.73	-53.8	0.026 ^e 0.022 ^f
Sv 5	1.09	4.36	2.93	-69.9	0.010 ^e 0.015 ^f

$3\text{H}_2\text{S} + 2\text{FeOOH} \longrightarrow \text{S}^\circ + 2\text{FeS} + 4\text{H}_2\text{O}$
 $\text{S}^\circ + \text{FeS} \longrightarrow \text{FeS}_2$

^aInferred rate of C oxidation attributed to dissimilatory Fe(III) reduction (inferred from rate measurements in bag incubations and distribution of potential oxidants; see 'Results' and 'Discussion')
^bDemand of solid Fe(III) necessary to support dissimilatory reduction calculated as 4× the inferred C oxidation rate [stoichiometry of dissimilatory Fe(III) reduction taken from Canfield et al. 1993]
^cDemand of solid Fe(III) necessary to reoxidize sulfide produced from sulfate reduction calculated as 2/3× the integrated sulfate reduction rate from stoichiometry of reactions shown above (as in Thamdrup et al. 1994)
^dCalculated from the interfacial gradient of solid Fe(III) according to Van Cappellen (pers. comm.) (data shown in Fig. 3)
^eBiodiffusion coefficient calculated from the total Fe demand (^b + ^c above) and the solid Fe(III) gradient with the following equation as described by Goldberg & Koide (1962) and Guinasso & Schink (1975):

$$J_{\text{bio}} = -D_b \times dC_{\text{vol}}/d_x$$

^fBiodiffusion coefficient calculated from the sediment accumulation rate as in Boudreau (1994) according to the following equation:

$$D_b = 15.7w^{0.69}$$

ment accumulation rate (Table 5). In addition, lower sediment mixing intensities and a shallower mixed zone were observed using radionuclide profiles at Sv 1 as compared to the Svalbard stations Sv 2, Sv 3, and Sv 5 (Table 1). This would appear to be at odds with our interpretation that substantial dissimilatory Fe(III) reduction is occurring at Sv 1. We suggest that the Fe cycle in sediments at Sv 1 is being supported by irrigation from a different benthic fauna relative to the Svalbard stations, resulting in a higher apparent biodiffusion coefficient from the Fe mass balance. That would explain how rapid metal reduction is supported at a lower mixing intensity relative to the Svalbard stations. It follows that a substantially different benthic fauna exists at Malangen Fjord which is much farther south and exhibits higher bottom water temperatures compared to the other stations. An alternative explanation would be that the kinetics of Fe sorption/reoxidation differ between Svalbard and the Norwegian coast.

We observed substantial variability in the partitioning of microbial respiration pathways between sta-

tions. Amongst potential variables controlling C oxidation pathways, organic matter input and macrofaunal activity are prominent. At higher C deposition rates, O₂ is rapidly consumed in surface sediments and anoxic C oxidation pathways become important. Also the importance of sub-oxic electron acceptors [NO₃⁻, Fe(III), Mn(IV)] depends upon recycling/rejuvenation via reoxidation reactions. It is thought that Fe(III) and Mn(IV), as solid electron acceptors, depend upon physical (Aller et al. 1986, 1996) or biological mixing (Aller 1994) to be significant contributors to C oxidation. Oxidant and reactive C are mixed down into the sediment while soluble products of respiration diffuse out to be reoxidized in the oxic zone.

Hornsund Fjord (Sv 2), which displayed the highest C mineralization rates and sulfate reduction activity, also showed the highest sedimentation rate and a relatively shallow mixing zone (Table 1). Here it is suggested that a combination of high organic C deposition and lower rates of macrofaunal mixing contributed to the predominance of sulfate respiration. At Van Mijen (Sv 3) and Storfjorden (Sv 5), intermediate sediment accumulation rates were observed while a deeper mixing zone was detected. The

importance of Fe(III) reduction at these sites, quantified from rate measurements and solid Fe gradients, is suggested to be stimulated by higher macrofaunal mixing rates together with slightly lower rates of organic matter accumulation.

An alternative explanation would be that the differences in partitioning of respiratory pathways are not site-specific but due to sample variability. Another confounding factor in these studies is the lateral advection of organic matter. Especially in the fjords surrounding Svalbard, most of the organic matter oxidized in the sediment is likely to originate from primary production occurring kilometers away as bottom currents mix allochthonous POC into the fjord over the sill (Reigstad & Wassman 1996). This makes it difficult to construct a C budget for these sediments without more extensive, site-specific data. Future studies of Arctic sediments should focus on an interdisciplinary approach emphasizing direct rate measurements over seasonal cycles to answer the questions posed above.

Temperature limitation of organic mineralization

The standing stock of microbial biomass (bacteria, protozoa, ciliates) in these cold Svalbard sediments was found to be similar to that of temperate marine sediments (Sahm & Berninger 1998). Based on our observations of the rates/pathways of C oxidation in Svalbard sediments, we conclude, that in polar sediments exposed to relatively high rates of organic matter deposition, microbial metabolism is able to rapidly mineralize a majority of the labile C deposited. Therefore, in polar shelf environments, microbial metabolism does not appear to be inherently limited by temperature. Bacterial metabolism may still be limited by an interaction of temperature and C substrate in permanently cold environments as described by Pomeroy et al. (1991). However, high C deposition appears to offset any low substrate affinity of cold-adapted microbial populations. Therefore, microbial communities in cold polar sediments exposed to relatively high C deposition appear to respond to the input/availability of organic matter over temperature.

SUMMARY

This study comprehensively characterizes the biogeochemistry and directly measures the rates/pathways of C oxidation in permanently cold Arctic sediments. For the first time, microbial respiration pathways coupled to organic matter mineralization are completely partitioned for polar sediments. Conclusions are as follows:

- (1) Sediment biogeochemistry revealed reactants and products of microbial respiration indicating that the same hierarchy of oxidants is utilized by microbes in polar sediments as in temperate environments.
- (2) Depth-integrated rates of total C oxidation and sulfate reduction observed in cold sediments were no different from rates measured in temperate shelf environments.
- (3) Anoxic/suboxic mineralization processes, sulfate respiration and Fe(III) reduction, play a dominant role in oxidizing the C reaching the sediment surface in at least some cold shelf environments.
- (4) Comparison of depth-integrated C oxidation rates from sediment incubations to those measured *in situ* with a free vehicle benthic lander indicated that the sediment incubation method is not only internally consistent, but it is also fairly accurate.

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