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Manganese and iron reduction dominate organic carbon oxidation in surface sediments of the deep Ulleung Basin, East Sea

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Abstract. Rates and pathways of benthic organic carbon (C_{org}) oxidation were investigated in surface sediments ofthe Ulleung Basin (UB) characterized by high organic carbon contents (> 2.5 %, dry wt.) and very high contents of Mn oxides (> 200 μmol cm^{-3}) and Fe oxides (up to 100 μmol cm^{-3}). The combination of geochemical analyses and independently executed metabolic rate measurements revealed that Mn and Fe reduction were the dominant C_{org} oxidation pathways in the center of the UB, comprising 45 % and 20 % of total C_{org} oxidation, respectively. By contrast, sulfate reduction was the dominant C_{org} oxidation pathway accounting for 50 % of total C_{org} mineralization in sediments of the continental slope. The relative significance of each C_{org} oxidation pathway matched the depth distribution of the respective electron acceptors. The relative importance of Mn reduction for C_{org} oxidation displays saturation kinetics with respect to Mn oxide content with a low half-saturation value of 8.6 μmol cm^{-3}, which further implies that Mn reduction can be a dominant C_{org} oxidation process even in sediments with lower MnO_2 content as known from several other locations. This is the first report of a high contribution of manganese reduction to C_{org} oxidation in offshore sediments on the Asian margin. The high manganese oxide content in the surface sediment in the central UB was maintained by an extreme degree of recycling, with each Mn atom on average being reoxidized ~3800 times before permanent burial. This is the highest degree of recycling so far reported for Mn-rich sediments, and it appears linked to the high benthic mineralizationrates resulting from the high organic carbon content that indicate the UB as a biogeochemical hotspot for turnover of organic matter and nutrient regeneration. Thus, it is important to monitor any changes in the rates and partitioning of C_{org} oxidation to better understand the biogeochemical cycling of carbon, nutrients and metals associated with long-term climatic changes in the UB, where the gradual deoxygenation and warming of the bottom water have resulted in an ～10% decrease in dissolved oxygen and ～0.04 °C increase in potential temperature for the past three decades.

Keywords. Benthic mineralization, Manganese reduction, Iron reduction, Sulfate reduction, Ulleung Basin, East Sea

1 Introduction

Although they cover only 15 % (47 x 10^6 km^2) of the ocean surface area, sediments of continental margins (200 – 2000 m depth) are characterized by enhanced organic matter flux generated either by vertical transport from the highly productive overlying water column or by lateral transport from adjacent shelves, and thus play an important role in deposition and mineralization of organic matter (Romankevich, 1984, Jahnke et al.,1990; Walsh, 1991; Jahnke and Jahnke, 2000). Organic particles that reach the seafloor are quickly mineralized by hydrolysis, fermentation, and a variety of respiratory processes using different electron acceptors such as oxygen, nitrate, Mn oxides, Fe oxides, and sulfate (Froelich et al., 1979; Jørgensen, 2006). The partitioning of organic carbon (C_{org}) oxidation among the different electron accepting pathways has profound influence on the distribution and the release and/or retention of Mn, Fe, S and nutrients (nitrogen and phosphate) (Canfield et al., 2005; Hansen et al., 2006; Jørgensen, 2006; Slomp et al., 2013). Therefore, it is particularly important to elucidate the contribution of each C_{org} oxidation pathway in order to better understand the role of sediments in biogeochemical element cycles.

The relative significance of each carbon oxidation pathway is largely controlled by the combination of organic matter supply and availability of electron acceptors. In general, aerobic metabolism dominates the organic matter mineralization in deep-sea sediments that are characterized by low organic matter content (Jahnke et al., 1982; Glud, 2008), especially in organic carbon-starved deep-sea sediments with low sedimentation rates (Mewes et al., 2014, 2016; D'Hondt et al. 2015; Mogollón et al., 2016). In contrast, owing to high sulfate concentrations in marine sediment, sulfate reduction might account for up to 50% of total carbon oxidation in continental margins with high organic matter flux (Jørgensen, 1982; Jørgensen and Kasten, 2006; Bowles et al., 2014). However, in sediments where manganese and iron oxides are abundant or rapidly recycled, microbial reduction of manganese and iron can be the dominant electron accepting processes over sulfate reduction (Sørensen and Jørgensen, 1987; Aller, 1990; Canfield et al.,1993b). The significance of dissimilatory iron reduction for C_{org} oxidation is well established in the sediments of various continental margins and coastal wetlands (Thamdrup, 2000; Thamdrup and Canfield, 1996; Jensen et al. 2003, Kostka et al., 2002a, 2002b; Vandieken et al., 2006; Hyun et al., 2007, 2009b). However, only a few locations such as the Panama Basin (Aller, 1990), the coastal Norwegian trough in Skagerrak and an adjacent fjord (Canfield et al., 1993a, 1993b;

Vandieken et al., 2014), the Black Sea shelf (Thamdrup et al., 2000) and the continental shelf of the northern Barents Sea (Vandieken et al., 2006; Nickel et al., 2008) are known where microbial manganese reduction significantly contributes to carbon mineralization.

The East Sea (often referred to as Japan Sea), located in the far eastern part of the Eurasian continental margin, consists of three major basins deeper than 2000 m, the Japan Basin, the Yamato Basin and the Ulleung Basin (Fig. 1). Compared to the other two basins, the surface waters of the Ulleung Basin (UB) are characterized by higher phytoplankton biomass and primary production (Yamada et al., 2005; Yoo and Park, 2009), which is associated with coastal upwelling (Hyun et al., 2009a). The enhanced biological production in the euphotic zone of the UB is responsible for the high organic carbon content (> 2.5 % wt) in the sediment, and the highest rates of C_{org} oxidation compared to other deep-sea sediments with similar depth range (Lee et al.,2008; Hyun et al., 2010). An intriguing geochemical property of the UB surface sediment is the high content of Mn oxides (>200 μmol cm^{-3}) and Fe oxides (up to 100 μmol cm^{-3}) (Cha et al., 2007; Hyun et al., 2010). In accordance with these geochemical findings, the suppression of sulfate reduction (Hyun et al., 2010) and accumulation of Mn^{2+} in anoxic incubation of surface sediment (Vandieken et al., 2012) strongly implied that the C_{org} oxidation in the surface sediment of the UB is dominated by microbial manganese and iron reduction, but actual rates and partitioning of each electron accepting pathway in C_{org} oxidation remain to be determined in this deep marginal sediment underlying highly productive surface waters.

The primary objective of this paper was to characterize the sediment biogeochemistry with regard to the rate of C_{org} oxidation and partitioning of major terminal electron accepting pathways at two contrasting sites at the continental slope and rise in the UB. Here, for the first time in sediments of the Asian marginal seas, we document that Mn and Fe reduction are the dominant C_{org} oxidation pathways accounting for respectively 45% and 20% of total C_{org} oxidation in the center of the UB, and suggest that Mn and Fe reduction may be of greater importance in deep-sea sediments than previously recognized.

2 Materials and methods

2.1 Study site

The East Sea is a marginal sea surrounded by the east Asian continent and Japanease Islands

(Fig.1, Kang et al., 2010; Liu et al., 2010). The UB located in the southwestern part of the East Sea is a bowl-shaped deep basin (2000 – 3000 m depth) (Fig. 1) delimited by continental slopes of Korean Peninsula and the southwestern Japanese Archipelago on the west and south, respectively, and by the Korea Plateau and the Oki Bank on the north and east, respectively (Chough et al., 2000).

Shipboard experiments were conducted in June, 2009 at two sites onthe continental slope (Station M1, hereafter M1) and in the center (Station D3, hereafter D3) of the the UB (Fig. 1, Table 1). Surface sediments consist of fine-grained clay with a mean grain size less than 0.004 mm in diameter (Cha et al., 2007). Two stations were characterized by two contrasting sediment colors. The Mn oxide-enriched surface sediment at the basin site (D3) was reddish-brown, whereas at the slope site (M1) it exhibited the typical gray-brown color of muddy continental margin sediments (Fig. 1). Further environmental properties are listed in Table 1.

2.2 Sampling and handling

Sediment samples were collected with a box corer. Onboard, duplicate or mostly triplicate sub-samples for geochemical analyses were collected using acrylic cores (6–9 cm in diameter and 30–40 cm in length). The sub-cores for geochemical analyses were immediately sealed with butyl rubber stoppers and transferred to a N_2-filled glove bag for sectioning and loading into polypropylene centrifuge tubes that were then tightly capped and centrifuged for 15 min at 5000 × *g*. After reintroduction into the N_2-filled glove bag, pore-waters were sampled and filtered through 0.2-µm cellulose ester syringe filters (ADVANTEC, Toyo Rashi Kaisha, Ltd). One to two mL of pore water to determine NH_4^+ was fixed with saturated $HgCl_2$, and frozen. For determination of Fe^{2+}, Mn, SO_4^{2-} and Ca^{2+}, 2 mL of the pore water were acidified with 12M HCl and stored at 4 °C. Pore-water for sulfide analysis was preserved with Zn acetate (20%). Sediments for solid-phase analysis were frozen at −25℃ for future analyses.

2.3 Anoxic bag incubations

Anaerobic carbon mineralization rates and dissimilatory Mn and Fe reduction rates were determined in batch incubations based on the procedures of Canfield et al. (1993b) and Thamdrup and Canfield (1996). Sediment cores were transferred to a N_2-filled glove bag and sliced in 2-cm intervals to a depth of 10 cm. Sediment from parallel sections was pooled, mixed and loaded into gas-tight plastic bags (Hansen et al., 2000). The bags were sealed without gas space, and incubated in the dark at near in situ temperature (ca. 1 –2℃) in larger N_2 filled bags to ensure anoxic conditions. Over a period of 18 days of incubation, sub-samples to determine the accumulation of total dissolved inorganic carbon (DIC) and Mn in pore water were withdrawn on days 0, 1, 3, 5, 9 and 18. Two 50-mL centrifuge tubes per bag were filled completely with sediment in a N_2-filled glove bag, and pore-water was extracted as described above. For DIC analysis, we collected 1.8 mL aliquots into glass vials without head space, fixed with 18 µL of $HgCl_2$ (125 mM), and stored at 4 ℃ until analysis within 4 weeks. Samples for Mn analysis were acidified with 12 M HCl and stored at 4℃. Sediment remaining after the collection of pore water was frozen at −25℃ for later analysis of oxalate extractable solid Fe(II).

2.4 Pore-water analyses

Total dissolved inorganic carbon (DIC) and NH_4^+ were measured by flow injection analysis with conductivity detection (Hall and Aller, 1992). Nitrate was measured spectrophotometrically (Parsons et al., 1984). Dissolved Fe^{2+} was determined by colorimetric method with Ferrozine (Stookey, 1970). Dissolved Mn^{2+} and Ca^{2+} were analyzed in acidified pore water by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Optima 3300DV, Perkin-Elmer Co.) and flame atomic absorption spectrometer (SpectrAA 220/FS, Varian), respectively (Thamdrup and Canfield, 1996). Dissolved sulfide was determined by the methylene blue method (Cline, 1969). Sulfate concentrations were measured using ion chromatography (Metrohm 761). The detection limit of H_2S, Ca^{2+}, Mn^{2+} and Fe^{2+} was 3 µM, 1.8 µM, 3 µM and 1 µM, respectively. Reproducibility of DIC and NH_4^+ was better than 10%. Precision of NO_3^- was 1 – 2%.

2.5 Solid-phase analyses

Total oxalate-extractable Fe [Fe(II) + Fe(III)] was extracted from air-dried sediment in a 0.2 M oxic oxalate solution (pH 3) for 4 h (Thamdrup and Canfield,1996), and Fe(II) was extracted from frozen sediment in anoxic oxalate (Phillips and Lovley, 1987). The total oxalate-extractable Fe and Fe(II), hereafter total $Fe_{(oxal)}$ and $Fe(II)_{(oxal)}$, were determined as described for the pore-water analysis of Fe^{2+}. Oxalate-extractable Fe(III), hereafter

$Fe(III)_{(oxal)}$, was defined as the difference between total $Fe_{(oxal)}$ and $Fe(II)_{(oxal)}$. This fraction represents poorly crystalline Fe(III) oxides. Particulate Mn, hereafter $Mn_{(DCA)}$ was extracted with dithionite-citrate-acetic acid (DCA; pH 4.8) for 4 h from air-dried sediment and was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Optima 3300DV, Perkin-Elmer Co). The DCA extraction aims at dissolving free Mn oxides and authigenic Mn(II) phases. The reproducibility of the measurements was better than 10% and the detection limits was 3μM for Mn and 1 μM for Fe. For the determination of total reduced sulfur (TRS) that includes acid volatile sulfide (AVS = FeS + H_2S and small amounts of other metal sulfides, see Rickard and Morse, 2005; Luther, 2005) and chromium-reducible sulfur (CRS = S^0 + FeS_2), sediment samples were fixed with Zn acetate, and sulfide was determined according to the method of Cline (1969) after a two-step distillation with cold 12 M HCl and boiling 0.5 M Cr^{2+} solution (Fossing and Jørgensen, 1989). The contents of particulate organic carbon (POC) and nitrogen (PON) in the surface sediment were analyzed using a CHN analyzer (CE Instrument, EA 1110) after removing $CaCO_3$ using 12 M HCl.

2.6 Oxygen micro-profiles

Oxygen profiles were measured at 50 µm resolution using Clark-type microelectrodes (Unisense, OX-50) while stirring the overlying water. Microelectrodes were calibrated between 100% air-saturated *in situ* bottom water and N_2 purged anoxic bottom water. Three profiles were measured at each site. The diffusive boundary layer (DBL) and sediment-water interface (SWI) were determined according to Jørgensen and Revsbech (1985). To estimate the volume-specific oxygen consumption rate, we used the PROFILE software (Berg et al., 1998).

2.7 Rate measurements

The diffusive oxygen uptake (DOU) was calculated from the calibrated oxygen microprofiles.

$$DOU = -D_o \Delta C / \Delta z, \qquad (1)$$

where D_o (1.07×10^{-9} m^2 s^{-1} at M1 and 1.03×10^{-9} m^2 s^{-1} at D3) is the temperature-corrected molecular diffusion coefficient estimated from Schulz (2006), and C is the oxygen concentration at depth z within the diffusive boundary layer (DBL) (Jørgensen and Revsbech, 1985).

The volume-specific O_2 consumption rates exhibited a bimodal depth distribution (see results section 3.2) with activity peaks near the sediment-water interface and the oxic/anoxic interface, respectively. Thus, O_2 consumption rates by aerobic organotrophic respiration was defined as the O_2 consumption rate near the sediment-water interface, whereas the oxygen consumption at the oxic-anoxic interface was assigned to re-oxidation of reduced inorganic compounds (Rasmussen and Jørgensen,1992; Canfield et al., 2005).

Total anaerobic C_{org} mineralization rates were determined by linear regression of the accumulation of total DIC with time during the anoxic bag incubations (Fig. 3) after correcting for $CaCO_3$ precipitation (Thamdrup et al., 2000). Briefly, $CaCO_3$ precipitation was calculated from decreasing dissolved Ca^{2+}concentration during the anoxic bag incubation:

$$\Delta CaCO_3 = \Delta[Ca^{2+}]_{sol} \times (1+K_{Ca}), \qquad (2)$$

where, K_{Ca} is the adsorption constant for Ca^{2+} ($K_{Ca} = 1.6$) (Li and Gregory, 1974). Then rate of DIC production rate corrected for $CaCO_3$ precipitation was calculated as:

$$\text{DIC production} = \text{DIC accumulation} + CaCO_3 \text{ precipitation} \qquad (3)$$

Fe(III) reduction rates were determined by linear regression of the increase in solid-phase $Fe(II)_{(oxal)}$ content with time during anoxic bag incubations.The dissimilatory microbial Fe(III) reduction rate was derived by subtracting abiotic Fe reduction coupled to the oxidation of sulfide produced by sulfate reduction (Gribsholt et al. 2003):

$$\text{Dissimilatory microbial Fe(III) Red} = \text{Total Fe(III) Red} - \text{Abiotic Fe(III) Red} \qquad (4)$$

assuming that abiotic Fe reduction coupled to H_2S oxidation occurred at a stoichiometry of 2 Fe(III) per 3 H_2S (Pyzik and Sommer, 1981; Melton et al., 2014):

$$2FeOOH + 3H_2S_{(\text{produced by SR})} = 2FeS + S^o + 4H_2O \qquad (5)$$

Finally, to estimate the C_{org} oxidation by microbial Fe reduction, the 4:1 stoichiometry of iron reduction coupled to C_{org} oxidation was used from the stoichiometric equation (Canfield et al., 1993a):

$$CH_2O + 4FeOOH + 8H^+ = CO_2 + 4Fe^{2+} + 7H_2O \qquad (6)$$

Mn reduction rates were determined from linear regression of the production of dissolved Mn^{2+} with time during the anoxic bag incubations. Similar to previous studies (e.g., Canfield et al.,1993a, 1993b; Thamdrup and Dalsgaard, 2000), we assumed that accumulating dissolved Mn was Mn^{2+}. This ignores a potential contribution from Mn^{3+}, which in some cases can constitute a substantial fraction of the dissolved Mn pool at the upper boundary of the zone with soluble Mn accumulation in marine sediments (Madison et al., 2013). Further studies of the dynamics of soluble Mn^{3+} are required to evaluate its potential importance in anoxic incubations. Such studies pending, we find justification for our assumption in the good agreement observed in the previous studies between Mn reduction rates calculated based on the assumption that soluble Mn is Mn^{2+} (Eq. 7) and independent estimates of rates of carbon mineralization through dissimilatory Mn reduction based on DIC or NH_4^+ accumulation. Due to strong adsorption of Mn^{2+} to Mn oxide surfaces (Canfield et al., 1993b), the Mn reduction rates were estimated after compensating for the adsorption effect of Mn^{2+} to Mn-oxides according to Thamdrup and Dalsgaard (2000):

$$\text{Mn reduction rate} = Mn^{2+}\ \text{accumulation rate} \times (1 + K^*_{Mn}{}^{2+} \times (1 - \Phi) \times \Phi^{-1} \times \delta_s) \qquad (7)$$

where, Φ = porosity

δ_s=density of sediment

$K^*_{Mn}{}^{2+} = 4.8 + 0.14 \times [Mn(IV)]$ (ml g^{-1})

[Mn(IV)] = the content of Mn(IV) (μmol g^{-1})

We here assume that extracted $Mn_{(DCA)}$ represents Mn(IV) as observed in surface sediments of another Mn-rich site (Canfield et al.,1993b, Thamdrup and Dalsgaard, 2000). Small levels of $Mn_{(DCA)}$ remaining at depth further suggest that little Mn(II) accumulates in the solid phase (*see* Results). C_{org} oxidation by dissimilatory Mn(IV) reduction was calculated from the stoichiometric equation (Canfield et al., 1993a):

$$CH_2O + 2MnO_2 + 4H^+ = CO_2 + 2Mn^{2+} + 3H_2O \quad (8)$$

Sulfate reduction rates were determined using the radiotracer method of Jørgensen (1978). Sediment cores (35 cm long with 2.9 cm i.d.) were collected in triplicate, injected horizontally at 1-cm vertical interval with 5 μL radiolabeled sulfate ($^{35}S\text{-}SO_4^{2-}$,15 kBq μl^{-1}, Amersham) diluted in sterilized NaCl solution (3.0 %), and incubated for 12 h at *in situ* temperature. At the end of the incubation, the sediment was sliced into sections, fixed in Zn acetate (20 %), and frozen at −25°C until processed in the laboratory. The reduced ^{35}S was recovered using distillation with a boiling acidic Cr^{2+} solution according to Fossing and Jørgensen (1989). Background radioactivity of ^{35}S was 32.4±3.7 cpm cm^{-3} (*n*=10) at site D3 and 87.5±38.7 cpm cm^{-3} (*n*=10) at site M1. Detection limits of the SRR, estimated from the double standard deviation of the blank value (i.e., 7.4 and 77.4 cpm) according to Fossing et al. (2000), ranged from 0.79 to 2.62 nmol cm^{-3} d^{-1}. To elucidate the contribution of sulfate reduction in anaerobic carbon oxidation, the SRRs (Fig. 5B, 5G) were converted to carbon oxidation using a stoichiometric equation (Thamdrup and Canfield, 1996):

$$2CH_2O + SO_4^{2-} + 2H^+ = 2CO_2 + H_2S + 2H_2O \quad (9)$$

3 Results

3.1 Pore-water and solid-phase constituents

The depth distributions of NH_4^+, NO_3^-, Mn^{2+} and Fe^{2+} in the pore-water as well as solid phase Mn, Fe and S for the two stations are shown in Fig. 2. NH_4^+ concentrations at M1 increased steadily with depth (Fig. 2A) whereas at D3 it decreased down to 3 cm depth before it increased below (Fig. 2F). Highest concentrations of nitrate were measured at0 to 1 cm sediment depth at the two stations and concentrations decreased below a background level (< 2 μM) below 1cm at both M1 and D3 (Fig. 2A, 2F). Dissolved Mn^{2+} concentrations differed widely between the sites showing a maximum of 56 μM between 0 and 3 cm depth and not exceeding 10 μM below at M1 (Fig. 2B), whereas at D3 concentrations increased to a maximum of 286 μM at 10 – 12 cm depth (Fig. 2G). Conversely, dissolved Fe^{2+}

concentrations at M1 increased from 11 µM at 0 – 0.5 cm to 32 µM at 6 – 7 cm depth, and stayed constant below (Fig. 2C), whereas at D3, concentrations were uniformly low showing a slight increase to 12 µM at 15 cm (Fig. 2F).

Extractable Mn ($Mn_{(DCA)}$) contents were low (< 3 µmol cm^{-3}) in the upper 20 cm at the slope site (M1) (Fig. 2B), but up to 200 µmol cm^{-3} in the upper 4 cm depth of the sediment at the center of the basin (D3), with a sharp decrease to near depletion (~1 µmol cm^{-3}) below 10 cm (Fig. 2G). At the slope site (M1), contents of $Fe(III)_{(oxal)}$ decreased slightly with increasing depth from 28 µmol cm^{-3} near the surface to 13 µmol cm^{-3} at 20 cm depth, mirroring an increase in $Fe(II)_{(oxal)}$ (Fig. 2D). At the center of the basin (D3), $Fe(III)_{(oxal)}$ increased slightly from 67 µmol cm^{-3} at 0 – 0.5 cm to 90 µmol cm^{-3} at 4 – 6 cm depth, and decreased steeply below to 4.8 µmol cm^{-3} at 12 – 14cm depth (Fig. 2I). Of total $Fe_{(oxal)}$, $Fe(III)_{(oxal)}$ comprised > 98 % at 0 – 2 cm and > 97 % at 0 – 8 cm depth at M1 and D3, respectively. The fraction of $Fe(III)_{(oxal)}$ in $Fe_{(oxal)}$ then decreased to 40 % at 10 – 12 cm depth at both sites. Acid volatile sulfur (AVS) exhibited a slight increase with depth at M1 from 0.8 µmol cm^{-3} at the surface to 7.2 µmol cm^{-3} at 20 cm depth (Fig. 2E), but was not detected at D3 (Fig. 2J). Chromium reducible sulfur (CRS) contents at M1 increased rapidly with depth from 1.9 µmol cm^{-3} at 0 – 0.5 cm to 21.8 µmol cm^{-3} at 20 cm depth (Fig. 2D), whereas the CRS contents remained < 0.1 µmol cm^{-3} at D3 (Fig. 2J).

3.2 O_2 microprofiles and diffusive oxygen uptake rate

Oxygen penetrated less than 4 mm into the sediments (Fig. 3), and rates of diffusive oxygen uptake (DOU) were 7.1 and 6.0 mmol O_2 m^{-2} d^{-1} at M1 and D3, respectively (Table 2). Oxygen consumption by aerobic respiration estimated from the O_2 micro-profiles (area I and II in Fig. 3) was higher at the slope site M1 (4.0 mmol O_2 m^{-2} d^{-1}) than at the D3 in the center of the basin (2.5 mmol O_2 m^{-2} d^{-1}). O_2 consumption by re-oxidation of reduced inorganic compounds indicated by increased activity at the oxic/anoxic interface (area III in Fig. 3) accounted for 43 % and 57 % of the DOU at M1 and D3, respectively. From the profiles of geochemical constituents (Fig. 2), O_2 consumption was mainly attributed to the re-oxidation of sulfide and Fe^{2+} at M1 and of Mn^{2+} at D3.

3.3 Anoxic bag incubations

Changes in concentrations of DIC, Ca^{2+} and dissolved Mn^{2+} and solid $Fe(II)_{(oxal)}$ contents over time during anoxic bag incubations from sediment of 0 – 2, 2 – 4, 4 – 6 and 6 –8 cm depth intervals are presented in Fig. 4. The DIC concentrations increased linearly over time during incubations of sediment in all bags from M1 and D3, except the bag from 6 – 8 cm at D3. The DIC accumulation rates were generally higher at the slope site (M1) than at the basin site (D3) (Table 4). The concentrations of Ca^{2+} decreased with time at all depth intervals of M1, whereas a decrease of Ca^{2+} was observed only forthe 2 – 4 cm depth interval at D3. The decrease of Ca^{2+} indicates $CaCO_3$ precipitation, which consequently underestimates DIC accumulation, especially at M1.

Coinciding with high solid $Mn_{(DCA)}$ contents (Fig. 2G), prominent Mn^{2+} accumulation appeared at 0 – 6 cm depth of D3, whereas no increase of Mn^{2+} was observed at M1 except a slight accumulation at 0 – 2 cm interval (Fig. 4). Solid $Fe(II)_{(oxal)}$ contents increased linearly with time at 0 – 4 cm depth of M1, whereas highest $Fe(II)_{(oxal)}$ accumulation was observed at 4 – 6 cm depth at D3. An increase of $Fe(II)_{(oxal)}$ was not discernible in the Mn-oxide-rich surface sediment (0 – 2 cm) of D3.

3.4 Sulfate reduction rates (SRR)

At the slope site (M1), SRR increased from 18 nmol cm^{-3} d^{-1} at the surface to 97 – 103 nmol cm^{-3} d^{-1} at 1.5 – 2 cm depth, and decreased below to 12.5 nmol cm^{-3} d^{-1} at 20 cm depth (Fig. 5B). In contrast, SRR at the manganese oxide-rich basin site (D3) ranged from 1.7 to 8.7 nmol cm^{-3} d^{-1}, and did not vary with depth. Depth integrated SRR down to 10 cm depth was 10 times higher at M1 (4.3 mmol m^{-2} d^{-1}) than at D3 (0.4 mmol m^{-2} d^{-1}) (Table 3).

3.5 DIC production rates

Vertical profiles of the DIC production rate that were derived from the linear regression of the DIC production measured in anoxic bag incubation (Fig. 4) after correcting for $CaCO_3$ precipitation, are presented in Fig. 5C and 5H for M1 and D3, respectively. At M1, the DIC production rates decreased with depth from 280 nmol cm^{-3} d^{-1} (0 – 2 cm depth) to 69 nmol cm^{-3} d^{-1} (8 – 10 cm depth) (Fig. 5C), whereas the DIC production rates at D3 were relatively similar across the upper 6 cm ranging from 86 to 136 nmol cm^{-3} d^{-1}, and decreased to 8 – 15 nmol cm^{-3} d^{-1}at 6– 10 cm (Fig. 5H). The integrated DIC production rate within 10 cm depth of the sediment was twice as high at M1 (14.0 mmol m^{-2} d^{-1}) as at the D3 (7.2 mmol m^{-2} d^{-1}) (Table 4).

3.6 Rates of Mn and Fe reduction

The accumulationof Mn^{2+} presented evidence that manganese reduction was occurring in the surface sediment (0 – 6 cm) of D3 (Fig. 4).The manganese reduction rate (MnRR) derived from Mn^{2+} accumulation with correction for adsorption ranged from 7.5 nmol cm^{-3} d^{-1} (0 – 2 cm depth) to 198 nmol cm^{-3} d^{-1} (2 – 4 cm depth) at D3 (Fig. 5I). In contrast, MnRR at M1 was indiscernible except for low activity (2.2 nmol cm^{-3} d^{-1}) at 0 – 2 cm depth (Fig. 5D). Depth integrated MnRR at D3 (8.21 mmol m^{-2} d^{-1}) was 200 times higher than the MnRR at M1 (0.04 mmol m^{-2} d^{-1}) (Table 3). The iron reduction rate (FeRR), derived from $Fe(II)_{(oxal)}$ accumulation, at M1 was highest in the 0 – 2 cm interval (237 nmol cm^{-3} d^{-1}), and then decreased with depth to 38 nmol cm^{-3} d^{-1} at 8 – 10 cm depth (Fig. 5E). In contrast, Fe reduction was not detected in the surface sediment at D3, but increased to its maximum rate of 240 nmol cm^{-3} d^{-1} at 4 – 6 cm depth. The FeRR then decreased with depth to 12 nmol cm^{-3} d^{-1} at 8 – 10 cm (Fig. 5J) where a few data points were adopted to derive the line of best-fit regression. Depth integrated total FeRR was slightly higher at M1 (11.4 mmol m^{-2} d^{-1}) than at D3 (7.53 mmol m^{-2} d^{-1}) (Table 3). The ratio of microbial Fe reduction, Fe $Red_{(microbial)}$, to abiotic Fe reduction coupled to sulfide oxidation, Fe $Red_{(abiotic)}$, ranged from 1.14 (8 – 10 cm at M1) to 52.3 (2 – 4 cm at D3), which indicated that the Fe reduction at Mn- and Fe oxides rich basin site was mostly a microbiologically mediated process (Table 3).

4 Discussion

4.1 Partitioning of C_{org} oxidation in accordance with the distribution of terminal electron acceptors

One of the most prominent features revealed from the vertical distributions of geochemical constituents at the basin site (D3) was that electron acceptors such as O_2, nitrate, Mn- and Fe oxides were systematically distributed with discrete zonation according to the order of decreasing energy yield for C_{org} oxidation (Fig. 5F). Such biogeochemical zones are not sharply separated in most aquatic sediments due to, e.g., sediment heterogeneity and mixing resulting from bioirrigation, bioturbation, and bottom turbidity currents. The profiles of dissolved and solid phase geochemical constituents in the sediment provide indications as to specific diagenetic reactions prevailing (Froelich et al., 1979). However, reoxidation of reduced inorganic compounds often mask the primary reactions involved in carbon oxidation (Sørensen and Jørgensen, 1987; Hines et al., 1991). Together with the discrete geochemical zonation of the electron acceptors, the independently executed metabolic rate measurements (Fig. 5) allowed us to evaluate the relative contribution of each terminal electron-accepting pathway with sediment depth.

Previous experimental studies that have quantified pathways of anaerobic carbon oxidation in subtidal marine sediments have generally determined the contributions of Mn and Fe reduction indirectly from the difference between rates of DIC production and sulfate reduction converted to carbon equivalents (e.g., Canfield et al., 1993b; Thamdrup and Canfield, 1996; Vandieken et al., 2006). The inferred rates of Mn and Fe reduction were further supported by the depth distribution of metal oxides and patterns of Mn^{2+} and Fe^{2+} accumulation in the pore water, but could not be verified because the accumulation of particulate Mn(II) and Fe(II) – which represents the overwhelming fraction of the reduced pools – was not quantified. Here, we combined the indirect approach with independent determination of Mn and Fe reduction rates. Thus, we obtained two separate estimates of anaerobic carbon oxidation rates; based on DIC production and on the sum of sulfate, Fe, and Mn reduction converted to carbon equivalents, respectively (Table 4). At M1, within the 0 – 10 cm depth interval, the average ratio between total anaerobic C_{org} oxidation rate (10.7 mmol C m^{-2} d^{-1}) and the C_{org} oxidation from DIC production (14.0 mmol C m^{-2} d^{-1}) was 0.77 (Table 4). Similarly, at D3, the average ratio between total anaerobic C_{org} oxidation (6.79 mmol m^{-2} d^{-1}) and anaerobic DIC production (7.22 mmol m^{-2} d^{-1}) was 0.94. There was a good agreement between the two estimates with a ratio of total anaerobic C_{org} oxidation by Mn + Fe + sulfate : DIC production for individual depth intervals of 0.8 – 1.2 (Table 4) with the exception at the 0 – 2 cm depth of slope site (M1) where the ratio was slightly lower, 0.66, possibly due to a contribution from the C_{org} oxidation by nitrate reduction. The similarity of the two estimates across all incubations spanning a range of redox conditions provides confidence in our approach for calculating dissimilatory Mn and Fe reduction rates. Specifically, the good agreement indicates that the underlying assumptions concerning Mn adsorption and reactions of Fe(III) and sulfide are valid as first-order approximations. The general agreement further supportsthe validity of previous determinations of dissimilatory

Mn and Fe reduction rates based on the difference between DIC production and SO_4^{2-} reduction (Canfield et al., 1993a, 1993b; Thamdrup et al., 2000; Vandieken et al., 2006; Vandieken et al., 2014).

To elucidate the contribution of sulfate reduction in anaerobic carbon oxidation, the SRRs (Fig. 5B, 5G) were converted to carbon oxidation (Thamdrup and Canfield, 1996), and then compared to the DIC production rates from anoxic bag incubation (Fig. 5C, 5H). At the slope site (M1), the fraction of anaerobic C_{org} oxidation coupled to sulfate reductionincreased with depth from 48 % at 0 – 2 cm, to 80 % at 8 – 10 cm (Table 4). Thus, the excess C_{org} oxidation in the upper layers should be coupled to other electron accepting processes. Indeed, the C_{org} oxidation by Fe reduction (0.96 mmol m^{-2} d^{-1}) accounted for most of the remaining anaerobic C_{org} oxidation (12 – 18 % of DIC production) at 0 – 8 cm depth, consistent with the distribution of Fe(III) decreasing from > 25 µmol cm^{-3} near the surface (Fig. 6, Table 4). Mn reduction was of minor importance at M1 because of the low content of Mn oxide (< 3 umol cm^{-3}). Carbon oxidation coupled to aerobic respiration was estimated to 3.1 mmol m^{-2} d^{-1} corresponding to 18% of the total aerobic + anaerobic oxidation, while the contributions of Fe and sulfate reduction to this total were 12 % and 50 %, respectively (Table 4). As mentioned above, nitrate reduction/denitrification may contribute part of the unexplained 19 % of carbon oxidation, but most of this imbalance likely reflects the combined uncertainties in the estimates of the individual pathways. Additionally, our partitioning of carbon oxidation pathways could be biased towards the anaerobic electron acceptors due to the use of the diffusive oxygen uptake (DOU) rather than total oxygen uptake (TOU), which will exceed DOU if bioirrigation is active (Glud 2008). Bioirrigation was not determined at our sites, but the pore water profiles show no indication of strong irrigation (Fig. 2). An average DOU/TOU ratio of ~0.6 has been reported for sediments at 1.5 – 2.5 km depth (Glud 2008). Using this ratio, and assuming that TOU is partitioned similarly as DOU between aerobic carbon oxidation and reoxidation, aerobic carbon oxidation would account for 25 %, while Fe and sulfate reduction would account for 11 % and 46 % of of carbon oxidation, respectively. This, the potential bias from using DOU is not expected to affect the ranking of electron acceptors by quantitative importance (SO_4^{2-}> O_2> Fe(III)), and, as discussed further below, the partitioning of C_{org} oxidation at M1 falls within the range previously reported for continental margin sediments.

In contrast to M1, C_{org} oxidation by sulfate reduction at the basin site (D3) accounted for only a small fraction (< 11 %) of anaerobic C_{org} oxidation at 0 – 6 cm interval and it only dominated carbon oxidation at 8 – 10 cm (Fig. 5H, Table 4). Oxygen and NO_3^- were depleted within 3.6 mm and 1 cm depth of the sediment surface, respectively (Fig. 5F), while Mn and Fe(III) oxides were abundant at 0 – 4 cm and 0– 6 cm, respectively. Consistent with the abundance of electron acceptors, high rates of Mn and Fe reduction (Fig. 5I and 5J) implied Mn and Fe reduction as the most significant C_{org} oxidation pathways to 6 cm depth. At 0 – 2 cm depth, C_{org} oxidation by aerobic respiration and Mn reduction accounted for 53 % and 43 % of total C_{org} oxidation, respectively (Fig. 6). At 2 – 4 cm, Mn reduction accounted for 73 % of total C_{org} oxidation and 92 % of anaerobic C_{org} oxidation (Table 4, Fig. 6). Its importance decreased to 22 % at 4 – 6 cm due to lower Mn contents, while microbial Fe(III) reduction here contributed 51 %, and the partitioning of sulfate reduction increased to 11 % (Fig. 6). Consequently, the relative distributionof each C_{org} oxidation pathway with depth at D3 (Fig. 6) matched well with the depth distribution of the respective electron acceptors (Fig. 5F). Overall, within the 10 cm depth sediment interval, Mn and Fe reduction were the dominant C_{org} oxidation pathways comprising 45 % and 20 % of total carbon oxidation, respectively, at the Mn and Fe oxide-rich site in the center of the UB (Table 4). Correction for a potential underestimation of TOU, as discussed for M1, would reduce the contributions of Mn and Fe reduction slightly to 41 % and 18 %, respectively.

Despite the high Fe oxide content at 0 – 4 cm at D3 (Fig. 5F), no solid $Fe(II)_{(oxal)}$ accumulation was observed at this depth range (Fig. 6). This indicates that Fe(III) reduction may not occur under these Mn-oxide rich conditions. Indeed, using acombination of 16S rRNA-stable isotope probing and geochemical analysis in three manganese oxides-rich sediments including the UB, Vandieken et al. (2012) identified bacteria related to *Colwellia*, *Oceanospillaceae* and *Arcobacter* as acetate-oxidizing bacteria that potentially reduce manganese, whereas no known iron reducers were detected in the Mn-rich sediment. Similarly, Thamdrup et al. (2000), in Mn oxide- rich Black Sea sediment, found that the abundance of viable Fe-reducing bacteria in most probable number counts was low in comparison to Mn reducers and the addition of ferrihydrite did not stimulate Fe reduction, which implied that Fe reduction should be outcompeted by the Mn reduction process.

Nonetheless, Mn reduction estimated from the increase of Mn^{2+} at 0 – 4 cm interval at D3 (Fig. 6) could be due to oxidation of Fe^{2+} or sulfide. Fe^{2+} may readily react with Mn oxides (Myers and Nealson, 1988; Lovley and Phillips, 1988) by the reaction $2Fe^{2+} + MnO_2 + 4H_2O = Mn^{2+} + 2Fe(OH)_3 + 2H^+$. However, in the Mn oxide-rich sediment of the Skagerrak, Canfield et al. (1993b) revealed that the addition of Ferrozine, a strong complexation agent for Fe^{2+}, had no inhibitory effect on the Mn^{2+} liberation, indicating that the chemical reaction of MnO_2 with Fe^{2+} generated by Fe reduction was not responsible for the accumulation of Mn^{2+}. As manganese reduction is thermodynamically more favorable than iron and sulfate reduction, the Mn^{2+} liberation (Fig. 3) likely resulted from dissimilatory Mn reduction.

Despite the anoxic conditions and nitrate depletion during the bag incubation, Mn reduction rates at 0 – 2 cm depth (Fig. 5I) based on Mn^{2+} accumulation were substantially lower than the rates inferred from DIC accumulation (Fig. 5H). A similar discrepancy was previously observed for the uppermost part of the Mn reduction zone (Thamdrup et al., 2000), and is likely explained by particularly strong sorption of Mn^{2+} to fresh Mn oxide surfaces, which is not included in the adsorption coefficient used here. Low Mn^{2+} together with the rapid decrease of nitrate at 0-2 cm depth at D3 (Fig. 2F, 2G) also suggested that dissolved reduced manganese might act as a reducing agent for nitrate as it was suggested by Aller et al. (1998) in the Panama Basin and Mogollón et al. (2016) in the deep-sea sediment of the Clarion-Clierton fracture zone in the northeast equatirial Pacific.

Previous estimation of denitrification in 0 – 2 cm depth of the UB ranged from 0.01 to 0.17 mmol N m^{-2} d^{-1} (Lee, 2009), which is equivalent to a C_{org} oxidation of 0.013– 0.213 mmol C m^{-2} d^{-1} using the stoichiometric equation of $4H^+ + 5CH_2O + 4NO_3^- = 5CO_2 + 2N_2 + 7H_2O$. Based on the average, the contribution of carbon oxidation by denitrification (0.11 mmol C m^{-2} d^{-1}) should be minor at the basin site (≤ 3 % of total C_{org} oxidation at 0 – 2 cm; ~1 % of integrated C_{org} oxidation). This is consistent with the general consensus that C_{org} oxidation by denitrification is of little importance in most marine sediments (Sørensen et al., 1979; Canfield et al., 1993a; Trimmer and Engström, 2011). Denitrification may be even further suppressed in Mn-rich sediments due to competitive inhibition from Mn reduction (Trimmer et al., 2013).

4.2 C_{org}oxidation dominated by manganese reductionin the UB

Microbial Fe reduction has been quantified directly in sediments of various coastal oceans (Gribsholt et al., 2003; Kostka et al., 2002a, 2002b; Hyun et al., 2007, 2009b) and indirectly in deeper continental margins (Thamdrup and Canfield, 1996; Jensen et al., 2003; Kostka et al., 1999). Earlier estimation from 16 different continental margin sediments indicated that Fe(III) reduction contributed 22 % on average to anaerobic carbon oxidation (Thamdrup, 2000). Thus, the contributions from Fe(III) reduction of 12 % and 20 % of anaerobic C_{org}

oxidation onthe slope (M1) and in the basin (D3) of the UB (Table 4) fall in the range of the previous indirect estimates.

Unlike Fe reduction, direct estimation of manganese reductionrates is not easy, mainly because of the restriction of the process to a thin surface layer (Sundby and Silverberg, 1985), the rapid reduction of manganese oxides with H_2S and Fe^{2+} (Postma, 1985; Burdige and Nealson, 1986; Kostka et al., 1995; Lovley and Phillips, 1988), and the adsorption of Mn^{2+} to Mn oxide surface (Canfield et al., 1993b). For that reason, only two studies, from the Skagerrak and Black Sea, are available for direct comparison on the partitioning of Mn reduction. The process has also been indicated to be of importance in the Panama Basin based on diagenetic modeling (Aller, 1990) and at some Artic shelf sites where it was however not quantified separately from Fe reduction (Vandieken et al., 2006, Nickel et al., 2008). Mn reduction was responsible for over 90 % of total C_{org} oxidationat 600 m depth in the Skagerrak (Canfield et al., 1993b), and accounted for 13 – 45 % of anaerobic C_{org} oxidation in the Black Sea shelf sitesat 60 – 130 m of water depth (Thamdrup et al., 2000). To our knowledge, this report of C_{org} oxidation dominated by Mn reduction comprising 45 % of total C_{org} oxidation and 57 % of anaerobic C_{org} respiration in the center of the UB (Table 4) represents the first from deep-offshore basin of the eastern Asian marginal seas.

The difference in partitioning of Mn reduction in C_{org} oxidation between the UB, Black Sea and Skagerrak reflects the close relationship between Mn oxide content in the sediment and Mn reduction (Thamdrup et al., 2000). From the vertical distribution of electron acceptors (Fig. 5J) and contribution of each C_{org} oxidation pathway with depth (Fig. 6), it is apparent that the availability of Mn(IV) largely controls the relative contribution to C oxidation. In the Skagerrak, the Mn oxides are abundant in high content down to 10 cm depth (Canfield et al., 1993b), whereas Mn oxides in the Black Sea and the Ulleung Basin were enriched only down to 2 cm and 4 cm, respectively (Thamdrup et al., 2000, Fig. 2). Using the available data set for the three marine sediments, we further plotted the relative contribution of manganese reduction to anaerobic carbon oxidation as a function of Mn-oxides content to expand data from Thamdrup et al., 2000 (Fig. 7). The plot indicates saturation kinetics with a close correlation between Mn oxide content and the importance of Mn reduction at low contents. Curve-fitting yields a content of MnO_2 at 50 % of contribution of manganese reduction to total C_{org} oxidation (K_s) of 8.6 µmol cm^{-3} similar to the approx. 10 µmol cm^{-3} suggested before (Thamdrup et al., 2000). This indicates that Mn reduction can be a dominant C_{org} oxidation process even at low contents of Mn oxides compared to those found at UB.

Manganese enrichments of this magnitude have been reported for several locations on the continental margins and in deep basins (Murray et al., 1984; Gingele and Kasten, 1994; Gobeil et al., 1997; Haese et al., 2000; Mouret et al., 2009; Magen et al., 2011; Macdonald and Gobeil, 2012; Mewes et al., 2014) in addition to the relatively few places where dissimilatory Mn reduction was already indicated to be of importance, as discussed above. Thus, the process may be of more widespread significance, particularly in deep basin settings such as UB that allow geochemical focusing of manganese.

4.3 Source of high Mn oxide content

The strong enrichment of Mn in the UB surface sediment is primarily of diagenetic origin as indicated by similar Mn contents at depthin the sediment at D3 (0.95 – 3.02 µmol cm^{-3}) compared to M1 (0.36 – 3.74 µmol cm^{-3}) (Fig. 2) combined with higher sediment accumulation rates at the slope (0.15 – 0.3 cm y^{-1}) than in the basin (0.07 cm y^{-1}; Cha et al., 2005). Thus, the burial flux of Mn, and thereby the net input assuming steady state deposition, is higher at M1 than at D3. Furthermore, Mn is likely subject to geochemical focusing in the basin as Mn depositing at shallower depths is reductively mobilized and incompletely oxidized in the thin oxic surface layer, resulting in release to the water column and net down-slope transport, as inferred in other ventilated basins (Sundby and Silverberg, 1985; Canfield at al., 1993b; Schaller and Wehrli, 1997). A diagenetic source of Mn enrichment was also concluded in previous studies (Yin et al., 1989; Cha et al., 2007; Choi et al., 2009). The Mn remaining and being buried at M1 likely represents unreactive detrital forms to a larger extent than at D3 (Cha et al., 2007). Adopting the sediment accumulation rate of 0.07 cm y^{-1} in the UB determined at a station 50 km from D3 (Cha et al., 2005), the average $Mn_{(DCA)}$ content of 1.1 µmol cm^{-3} at 10 – 20 cm depth (Fig. 2G) corresponds to a flux for permanent burial of 0.002 mmol m^{-2} d^{-1} or just 0.03 % of the Mn reduction rate (Table 3), i.e., an Mn atom is recycled 3800 times before it finally gets buried – first by stripping from the particles that settle to the seafloor and subsequently, over and over, by reductive dissolution of the Mn oxides that from by reoxidation in the oxic surface layer (or, potentially, in the nitrate zone; Aller et al., 1998; Mogollón et al., 2016). This is a much more extensive recycling than found in the Mn sediment of Skagerrak (130 – 260 times; Canfield et al., 1993b). The difference results mainly from a much higher burial flux of Mn (as authigenic Mn[II]) in the Skagerrak (~40 µmol cm^{-3}; Canfield et al., 1993b). The reason that little, if any, authigenic Mn(II) is buried in the UB is not clear.

As noted in previous studies (Aller, 1990; Canfield et al., 1993b), high contributions of Mn and Fe reduction to carbon oxidation in off-shore sediments requires physical mixing, which typically occurs through bioturbation. This is also the case for the UB, where the burial flux from the oxic surface layer into the Mn reduction zone corresponded to 0.4 mmol m^{-2} d^{-1} or 5 % of the Mn reduction rate (213 µmol cm^{-3} x 0.07 cm y^{-1}). Bioturbation has previously been inferred, but not quantified, from ^{210}Pb profiles in the UB (Cha, 2002), and thin polychaete worms were observed during our sampling. Assuming bioturbation to be a diffusive process, we estimate, in a similar manner as in the previous studies and based on the average gradient in $Mn_{(DCA)}$ from 0.5 – 1 to 7 – 8 cm, that the Mn reduction rate would be supported at a biodiffusion coefficient of 9.5 cm^2 y^{-1}. This value is 3.6 times lower than the coefficient estimated for the Skagerrak (Canfield et al.,1993b) and consistent with estimates for other sediments with similar deposition rates (Boudreau, 1994). Thus, it is realistic that bioturbation drives Mn cycling in the UB.

4.4 The UB as a biogeochemical hotspot

The SRRs measured in this study (0.43 – 4.29 mmol m^{-2} d^{-1}) are higher than those measured in productive systems such as the Benguela upwelling system in the Southeast Atlantic (Ferdelman et al., 1999; Fossing et al., 2000), and even comparable to those reported at the continental slope of the Chilean upwelling system (2.7 – 4.8 mmol m^{-2} d^{-1}) (Thamdrup and Canfield, 1996) at a similar depth range of 1000 – 2500 m. The total anaerobic DIC production rates at the slope (14.0 mmol m^{-2} d^{-1}) and basin site (7.2 mmol m^{-2} d^{-1}) were also comparable to those measured at the same depth range of a Chilean upwelling site (9.2 – 11.6 mmol m^{-2} d^{-1}) (Thamdrup and Canfield, 1996). Since rates of benthic carbon oxidation are largely controlled by the supply of organic carbon (Canfield et al., 2005), a high organic carbon flux reflected in the high organic carbon content (> 2.5%, dry wt.) in the sediment of the UB (Table 1) is likely to explain the high metabolic activities. A similar high organic carbon content as in the UB is rarely found in deep-sea sediment underlying oxic bottom water at depths exceeding 2000 m, except for a Chilean upwelling site (Lee et al., 2008). This high organic carbon content in the UB is mainly associated with the combination of enhanced biological production resulting from the formation of coastal upwelling (Hyun et al., 2009a), occurrence of an intrathermocline eddy resulting in the extraordinary subsurface chlorophyll-a maximum (Kim et al., 2012), high organic C accumulationrates exceeding 2 g C m^{-2} yr^{-1} (Lee et al., 2008), and high export production (Kim et al., 2009). In addition to the large vertical sinking flux, the lateral transport of the organic matter along the highly productive southeastern slope of the UB also contributes to the high organic carbon content (Lee et al., 2015). Consequently, high benthic mineralization resulting from the high organic content in the sediment implied that the UB is a biogeochemical hotspot where significant turnover of organic matter and nutrient regeneration occur.

The East Seais often called as “a miniature ocean” because of the independent thermohaline convection system that is driven by the high density surface water sinking (Kim et al., 2001) in a manner similar to that of the Great Ocean Conveyor Belt (Broecker, 1991). The turnover time (ca. 100 – 300 years) of the thermohaline circulation is shorter than that of the global conveyor belt of 1000 – 2000 years (Broecker and Peng, 1982). Because of the shorter time-scale, together with the relatively small volume, the East Sea is expected to be much more sensitive to global environmental changes (such as global warming) compared with the open oceans. In this regard, the East Sea has been considered as a natural laboratory that provides a useful field for large-scale oceanographic experiments to predict the response of oceans associated with long-term climatic/oceanographic changes (Kim et al., 2001). Over the last two decades (1982 – 2006), a rapid increase of sea surface temperature (SST) of 1.09 ℃ has been recorded in the East Sea, which is the fourth highest among the 18 large marine ecosystems in the world ocean (Belkin, 2009). Increased SST reduces the soubility of O_2 in the surface mixed layer and enhances stratification, which ultimately affects biological production in the water column and suppresses transport of O_2-rich surface water into the deep bottom. Indeed, recent oeanographic observations revealed that the gradual deoxygenation and warming of the bottom water of the East Sea over the last 30 years have resulted in an ～10 % decrease in dissolved oxygen and ～0.04 ℃ increase in potential temperature, which suggested a weakening of the deep convection system (Kim et al., 2001; Gamo et al., 2011). Benthic metabolism and respiratory C_{org} oxidation coupled to various TEAP in the sediments are largely controlled by the combination of O_2 content, temperature and biological production overlying water column (Canfield et al., 2005). It is thus important to monitor any changes in the rates and partitioning of C_{org} oxidation to better understand and predict the variations of biogeochemical cycles of carbon, nutrients and metals potentially associated with long-term climatic changes in the UB, the biogeochemical hotspot of the East Sea.

5. Conclusions

Surface sediments of the Ulleung Basin (UB) in the far east Eurasian continent are characterized by a high organic carbon content (> 2.5 %, dry wt.), high contents Fe oxides (up to 100 μmol cm^{-3}), and very high contents of Mn oxides (> 200 μmol cm^{-3}). We show that microbial Mn and Fe reduction are the dominant C_{org} oxidation pathways, comprising 45 % and 20 % of total C_{org} oxidation, respectively. The high Mn content results from highly efficient recycling through reoxidation with very low permant burial of authigenic Mn(II) phases. The basin topography may ensure that any Mn^{2+} escaping to the overlying water returns to the sediment after reprecipitation. The relative importance of Mn reduction to C_{org} oxidation displays saturation kinetics with respect to Mn oxide content with a low half-saturation value (8.6 μmol cm^{-3}), which further implies that Mn reduction can be a dominant C_{org} oxidation process in sediments with lower MnO_2 content, and thereby that the process might be more important in continental margin and deep basin sediments than previously thought. Vertical distributions of the major terminal electron acceptors such as O_2, nitrate, Mn- and Fe oxides were systematically zonated with discrete sequential depletion according to the order of decreasing energy yield for C_{org} oxidation, which are not sharply separated in most aquatic sediments due to, e.g., sediment heterogeneity and mixing resulting from bioirrigation, bioturbation, and bottom turbidity currents. High benthic mineralization resulting from the high organic carbon content in the sediment implied that the UB is a biogeochemical hotspot where significant turnover of organic matter and nutrient regeneration occur. Over the last 30 years, the gradual deoxygenation and warming of the bottom water of the East Sea have resulted in an ～10 % decrease in dissolved oxygen and ～0.04 °C increase in potential temperature. If this continues, the UB sediment provides with an ideal natural laboratory to monitor changes in the rates and partitioning of C_{org} oxidation in order to better understand the biogeochemical cycling of carbon, nutrients and metals associated with long-term climatic changes.

Author contribution

J-H Hyun as first author and leader of the Korean research group designed the original experiments and conducted most writing; S-H Kim, JS Mok, and H-Y Cho participated in onboard research activities and analytical processes; V Vandieken participated in onboard research and was actively involved in the discussion of the manuscript; D Lee, as project manager of the EAST-1 program, paid the ship-time and has participated in discussion of the results; B Thamdrup, as leader of the Danish research group, collaborated with J-H Hyun in designing the experiments and writing and discussing the manuscript.

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Table 1. Environmental settings and sediment characteristics

Environmental parameter	M1 (Continental slope)	D3 (Center of the basin)
Latitude	36° 10’ N	37° 00’ N
Longitude	130° 10’ E	131° 00’ E
Water depth (m)	1,453	2,154
Sediment temperature (^{o}C)	1.3	0.6
Pore-water salinity (psu)	34.2	34.8
Water content (%)	85 (± 3.1)	77 (± 1.8)
Porosity	0.95 (± 0.03)	0.86 (± 0.01)
Density (g cm^{-3})	1.10 (± 0.02)	1.12 (± 0.02)
Total organic carbon (%, dry wt.)	3.96 (± 0.27)	2.66 (± 0.09)
Total organic nitrogen (%, dry wt.)	0.38 (± 0.01)	0.35 (± 0.01)

Numbers in parenthesis indicate ± 1SD of triplicate samples.

Table 2. Oxygen penetration depth (OPD), diffusive oxygen utilization (DOU) rate and O_2 consumption rate by aerobic respiration and re-oxidation of reduced inorganic compounds (RIC) in the pore water.

Station	OPD (mm)	DOU (mmol O_2 m^{-2} d^{-1})	O_2 consumption (mmol O_2 m^{-2} d^{-1}) by	
			Aerobic respiration	Re-oxidation of RIC
M1	3.2 (± 0.20)	7.12 (± 1.36)	4.04 (± 2.03)	3.07 (± 0.68)
D3	3.6 (± 0.03)	5.95 (± 0.16)	2.53 (± 0.72)	3.42 (± 0.58)

Values represent averages ± 1SD ($n = 3$)

Table 3. Depth integrated rates (mmol m^{-2} d^{-1}) of Mn reduction, Fe reduction, and sulfate reduction and the partitioning of abiotic and microbial Fe(III) reduction in total Fe(III) reduction with depth.

St.	Depth Interval (cm)	SO_4^{2-} Red	Mn Red	(a)Total Fe(III) Red	Fe reduction by		Fe $Red_{(Microbial)}$ / Fe $Red_{(Abiotic)}$
					(a)Abiotic Fe Red	(a)Microbial Fe Red	
M1	0 – 2	1.35	0.04	4.75	0.90	3.86	4.28
	2 – 4	1.04	-	3.02	0.70	2.33	3.33
	4 – 6	0.84	-	1.58	0.56	1.21	2.16
	6 – 8	0.54	-	1.25	0.36	0.89	2.47
	8 – 10	0.53	-	0.77	0.36	0.41	1.14
	Sum (0-10)	4.30	0.04	11.4	2.88	8.70	
D3	0 – 2	0.06	(b)3.19	-	-	-	n.a.
	2 – 4	0.11	3.96	1.63	0.07	1.56	22.3
	4 – 6	0.13	1.05	4.80	0.09	4.71	52.3
	6 – 8	0.06	0.01	0.86	0.04	0.83	20.8
	8 – 10	0.07	0.00	0.24	0.05	0.19	3.80
	Sum (0-10)	0.43	8.21	7.53	0.25	7.29	

(a) Stoichiometric equations were used to evaluate the relative significance of abiotic and microbial Fe reduction:
Abiotic reduction of Fe(III) by sulfide oxidation, $3H_2S + 2FeOOH = 2FeS + S^o + 4H_2O$; Microbial Fe(III) reduction = Total Fe(III) reduction – abiotic Fe(III) reduction.

(b) back-calculated from the C oxidation by Mn reduction in the 0 – 2 cm interval in Table 5 using the stoichiometric equation, $2MnO_2 + CH_2O + H_2O = 2Mn^{2+} + HCO_3^- + 3OH^-$.

‘ – ’ indicates that the process does not occur or is regarded as negligible at the depth interval based on the OPD for aerobic respiration and geochemical profiles or anoxic bag incubations for Mn(IV) and Fe(III) reduction

‘n.a.’ indicates that data are not available.

Table 4. Organic carbon (C_{org}) oxidation (mmol C m^{-2} d^{-1}) by each C_{org} oxidation pathway, and its partitioning in total C_{org} oxidation (% Total C_{ox}) and anaerobic C_{org} oxidation (% Anaerobic C_{org} ox) at each depth interval within 10 cm of the sediment. Mn Red, Mn reduction; Fe Red, Fe reduction; and SO_4^{2-} Red, sulfate reduction

St.	Depth Interval (cm)	C_{org} oxidation measured by		(c)Total C_{org} oxidation (DOU + DIC)	Anaerobic C_{org} oxidation by dissimilatory			Total anaerobic C_{org} oxidation (Mn Red + Fe Red + SO_4^{2-} Red)	Total Anaerobic C_{org} oxidation / Anoxic DIC production
		(a)DOU (Aerobic respiration)	(b)DIC prod. (Anaerobic respiration)		(d)Mn Red	(d,e)Fe Red	(d)SO_4^{2-} Red		
M1	0 – 2	3.11	5.59	8.70	0.02	0.96	2.69	3.67	0.66
	2 – 4	-	3.31	3.31	-	0.58	2.09	2.67	0.81
	4 – 6	-	2.26	2.26	-	0.26	1.67	1.93	0.85
	6 – 8	-	1.50	1.50	-	0.22	1.08	1.30	0.87
	8 – 10	-	1.37	1.37	-	0.10	1.06	1.17	0.85
	Sum (0 – 10)	3.11	14.0	17.1	0.02	2.13	8.59	10.7	0.77
	(% Total C_{org} ox)	(18.1)	(81.9)	(100)	(0.13)	(12.4)	(50.1)	(62.7)	
	(% Anaerobic C_{org} ox)				(0.16)	(15.2)	(61.2)		
D3	0 – 2	1.94	1.72	3.66	(f)1.59	-	0.13	1.72	1.00
	2 – 4	-	2.72	2.72	1.98	0.39	0.22	2.58	0.95
	4 – 6	-	2.32	2.32	0.52	1.18	0.26	1.96	0.84
	6 – 8	-	*0.30*	0.30	0.01	0.21	0.12	0.33	1.10
	8 – 10	-	*0.16*	0.16	-	0.05	0.15	0.19	1.21
	Sum (0 – 10)	1.94	*7.22*	9.2	4.10	1.82	0.86	6.79	0.94
	(% Total C_{org} ox)	(20.6)	(78.8)	(100)	(44.8)	(19.9)	(9.41)	(77.8)	
	(% Anaerobic C_{org} ox)				(56.8)	(25.2)	(11.9)		

(a Aerobic C_{org} oxidation rate (= O_2 consumption by aerobic respiration x (106C/138O_2) calculated using the Redfield ratio; O_2 consumption by aerobic respiration rate (= DOU - re-oxidation rates) is calculated from Table 2 that is derived from the O_2 micro-profiles in Fig. 2.

(b) independently measured from the DIC accumulation rate in anoxic bag incubation experiment in Fig. 6 and 7.

(c) Total C_{org} oxidation = aerobic C_{org} oxidation + anaerobic C_{org}.oxidation

(d)C_{org} oxidation by dissimilatory Mn(IV) reduction, Fe(III) reduction, and sulfate reduction was calculated from the stoichiometric equations: $2MnO_2 + CH_2O + H_2O = 2Mn^{2+} + HCO_3^- + 3OH^-$; $4Fe(OH)_3 + CH_2O = 4Fe^{2+} + HCO_3^- + 7OH^-$; $SO_4^{2-} + 2CH_2O = H_2S + 2HCO_3^-$, $H_2S = HS^- + H^+$

(e) Dissimilatory Fe(III) reduction = (Total Fe(III) reduction in Fig.7) – (Abiotic Fe(III) reduction coupled to H_2S oxidation; $3H_2S + 2FeOOH = 2FeS + S^o + 4H_2O$)

(fback-calculated from: DIC production rate - (C oxidation by SO_4^{2-} Red and Fe Red). See text for further discussion

‘ – ’ indicates that the process does not occur or is regarded as negligible based on the OPD for aerobic respiration and geochemical profiles or anoxic bag incubations for Mn and Fe Red.

Figure legends

Fig. 1. Sampling stations in the East Sea and pictures showing contrasting colors between surface sediments of the continental slope (M1) and center of the basin (D3)

Fig. 2. Concentrations of dissolved NH_4^+, NO_3^-, Mn^{2+} and Fe^{2+} in pore water and contents of solid phase $Mn_{(DCA)}$, $Fe(II)_{(oxal)}$, $Fe(III)_{(oxal)}$, acid volatile sulfur (AVS) and chromium reducible sulfur (CRS) in the sediment at M1 and D3.

Fig. 3. Vertical profiles of O_2. The slashed area indicates the diffusive boundary layer in the sediment-water interface. The shaded area indicates that O_2 consumption by aerobic respiration (I and II) and re-oxidation of reduced inorganic compounds (III), respectively.

Fig. 4. Changes of concentrations of DIC, Ca^{2+} and Mn^{2+} in pore water and contents of solid phase $Fe(II)_{(oxal)}$ during anoxic bag incubations of sediments from 0-2, 2-4, 4-6, and 6-8 cm depth at M1 and D3. Data obtained at 8-10 cm depth interval is not shown.

Fig. 5. Vertical distribution of terminal electron acceptors (O_2, NO_3^-, Mn and Fe) and rates of sulfate reduction measured from whole core analyses, and rates of anaerobic carbon oxidation (DIC production rates), Mn reduction and Fe reduction measured from anoxic bag incubations in Fig. 4. C_{org} by sulfate reduction in panel C and H was calculated from the stoichiometry of 2:1 of C_{org} oxidized to sulfate reduced.

Fig. 6. Depth variations of partitioning of each carbon oxidation pathway in total carbon oxidation at M1 and D3

Fig. 7. The relative contribution of Mn reduction to anaerobic carbon oxidation as a function of the content of Mn(DCA) at 3 different sites. BS, Black Sea (Thamdrup et al. 2000); UB, Ulleung Basin (This study); Sk, Skagerrak (Canfield et al. 1993b).

Hyun et al. – Figure 1

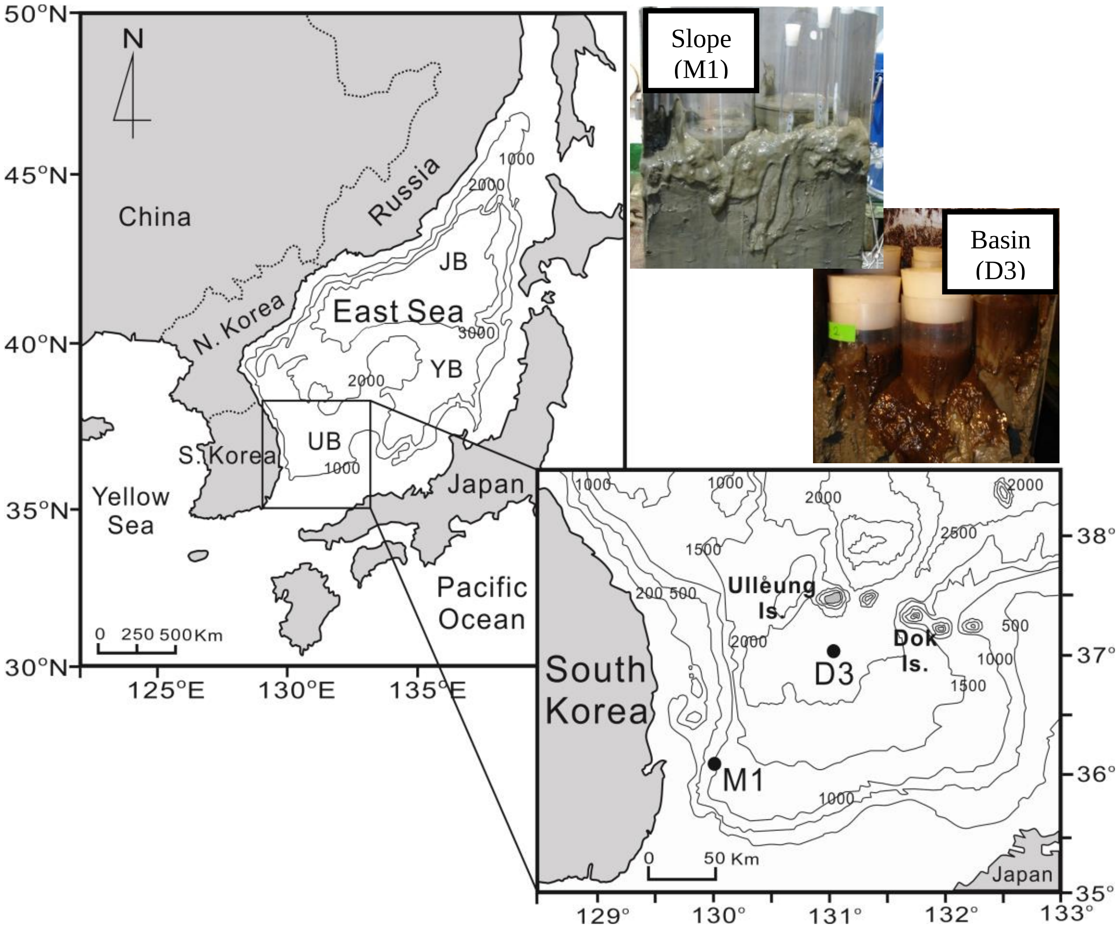

Fig. 1. Sampling stations in the East Sea and pictures showing contrasting colors between surface sediments of the continental slope (M1) and center of the basin (D3)

Hyun et al – Figure 2

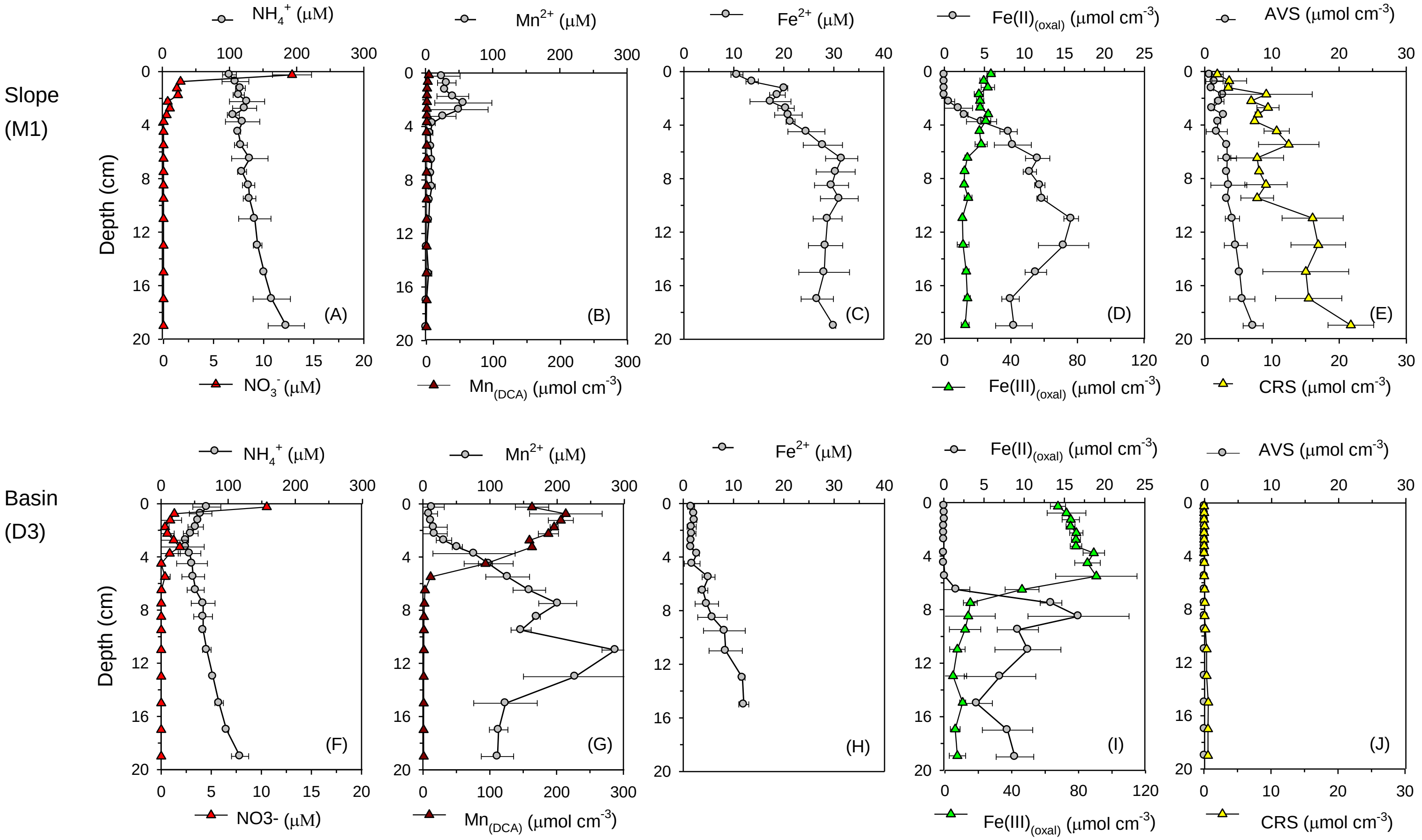

Fig. 2. Concentrations of dissolved NH_4^+, NO_3^-, Mn^{2+} and Fe^{2+} in pore water and contents of solid phase $Mn_{(DCA)}$, $Fe(II)_{(oxal)}$, $Fe(III)_{(oxal)}$, acid volatile sulfur (AVS) and chromium reducible sulfur (CRS) in the sediment at M1 and D3.

Hyun et al – Figure 3

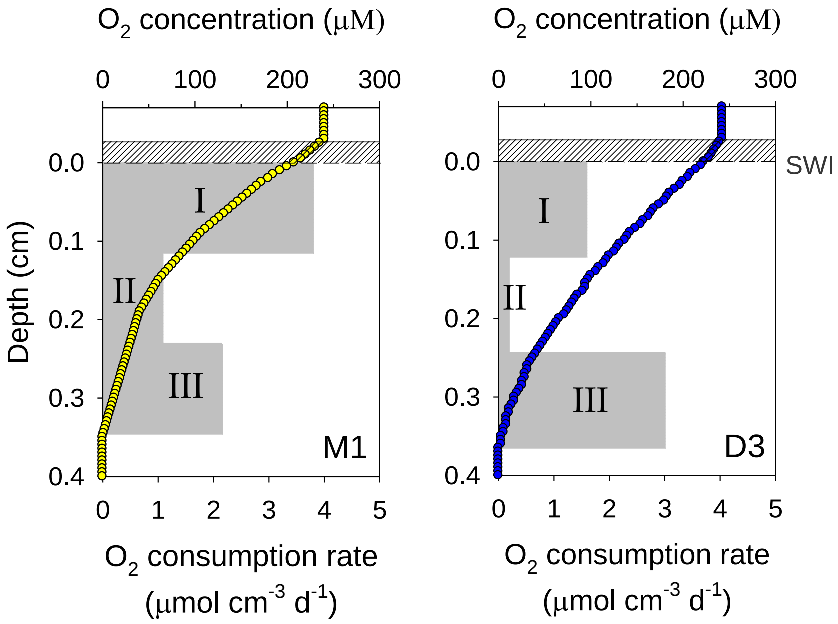

Fig. 3. Vertical profiles of O_2The slashed area indicates diffusive boundary layer in the sediment-water interface. The shaded area indicates that O_2 consumption by aerobic respiration (I and II) and re-oxidation of reduced inorganic compounds (III), respectively.

Hyun et al – Figure 4

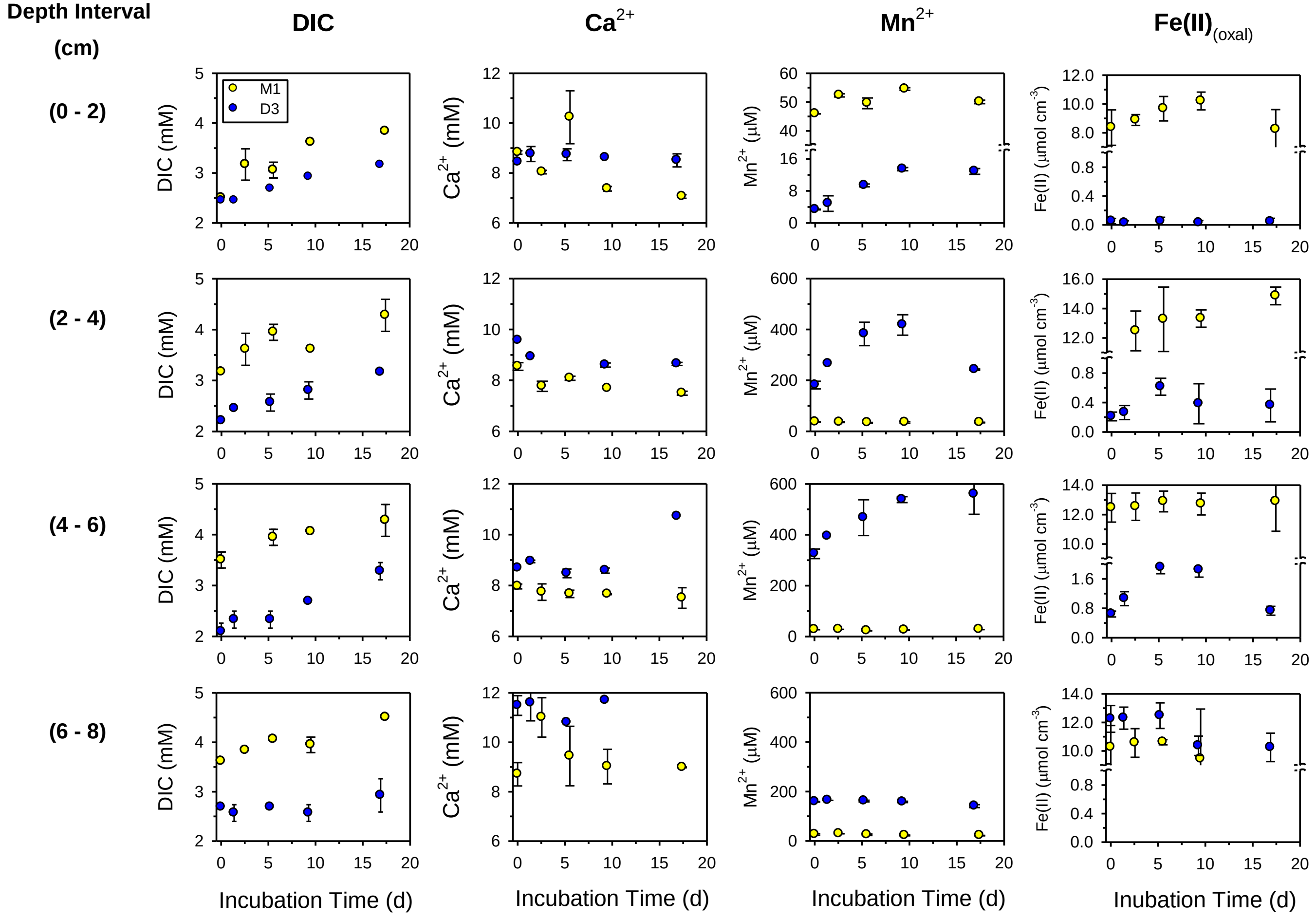

Fig. 4. Changes of concentrations of DIC, Ca^{2+} and Mn^{2+} in pore water and contents of solid phase $Fe(II)_{(oxal)}$ during anoxic bag incubations of sediments from 0-2, 2-4, 4-6, and 6-8 cm depth at M1 and D3. Data obtained at 8-10 cm depth interval is not shown.

Hyun et al. – Figure 5

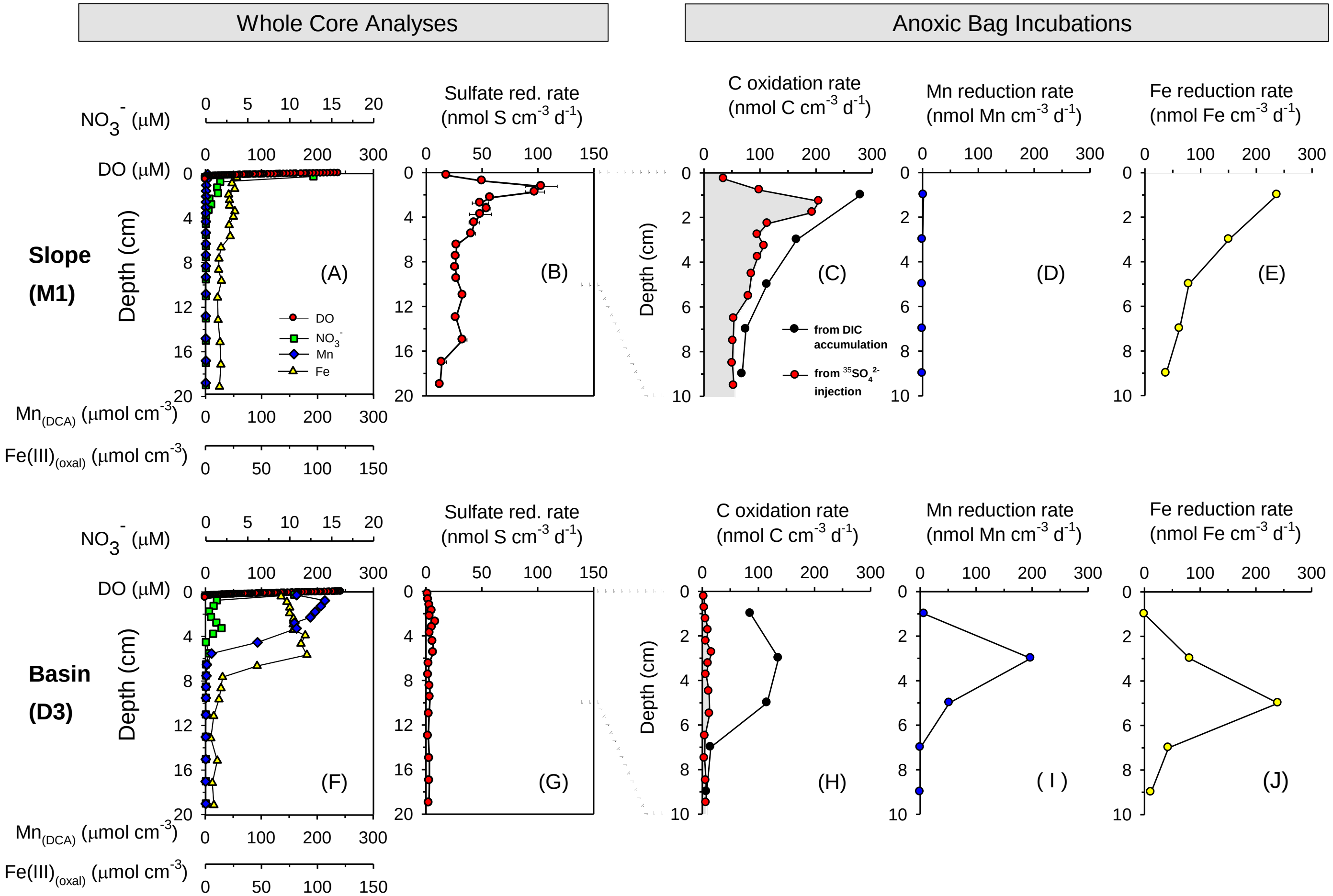

Fig. 5. Vertical distribution of terminal electron acceptors (O_2, NO_3^-, Mn and Fe) and rates of sulfate reduction measured from whole core analyses, and rates of anaerobic carbon oxidation (DIC production rates), Mn reduction and Fe reduction measured from anoxic bag incubations in Fig. 4. C_{org} by sulfate reduction in panel C and H was calculated from the stoichiometry of 2:1 of C_{org} oxidized to sulfate reduced.

Hyun et al. – Figure 6

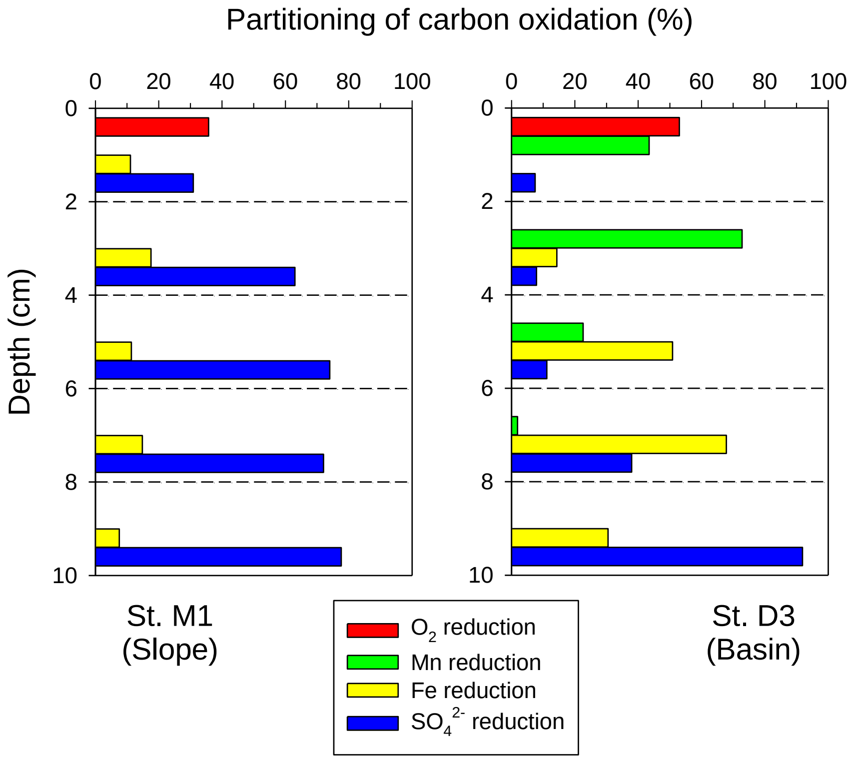

Fig. 6. Depth variations of partitioning of each carbon oxidation pathway in total carbon oxidation at M1 and D3

Hyun et al - Figure 7

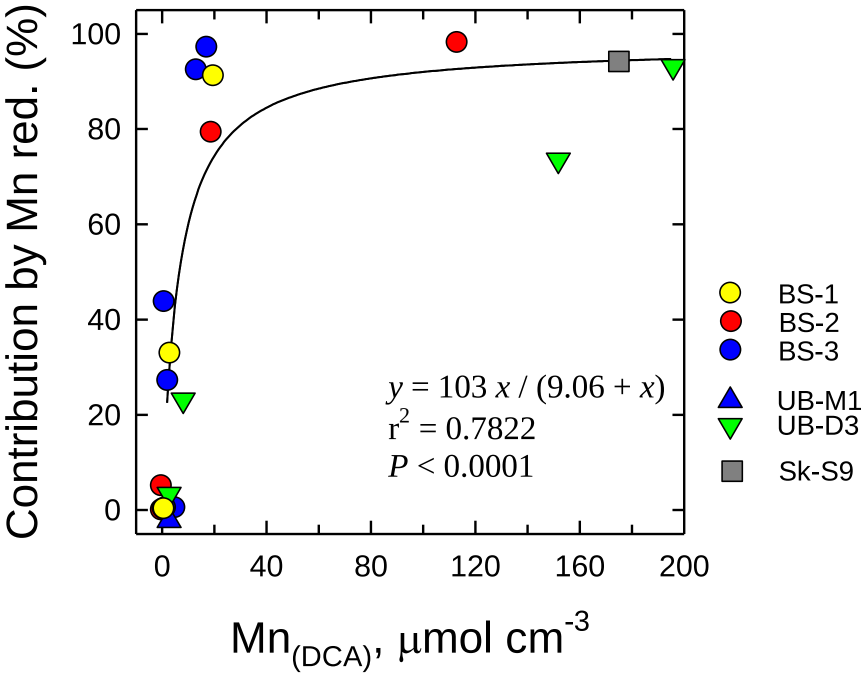

Fig. 7. The relative contribution of Mn reduction to anaerobic carbon oxidation as a function of the content of Mn(DCA) at 3 different sites. BS, Black Sea (Thamdrup et al. 2000); UB, Ulleung Basin (This study); Sk, Skagerrak (Canfield et al. 1993b).