**Controls on subsurface methane fluxes and shallow gas formation in Baltic Sea sediment
(Aarhus Bay, Denmark)**

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ABSTRACT

Shallow gas accumulates in coastal marine sediments when the burial rate of reactive organic matter beneath the sulfate zone is sufficiently high and the methanogenic zone is sufficiently deep. We investigated the controls on methane production, methane accumulation, and gas bubble formation along a 400 m seismo-acoustic transect across a sharp transition from gas-free into gas-bearing sediment in Aarhus Bay (Denmark). Twelve gravity cores were taken, in which the pore water was analyzed for inorganic solutes while rates of organic carbon mineralization were measured experimentally by $^{35}\text{SO}_4^{2-}$ radiotracer method. The thickness of organic-rich Holocene mud increased from 5 to 10 m along the transect concomitant with a shallowing of the depth of the sulfate-methane transition from >4 m to 2.5 m. In spite of drastic differences in the distribution of methane and sulfate in the sediment along the transect, there were only small differences in total mineralization, and methanogenesis was only equivalent to about 1 % of sulfate reduction. Shallow gas appeared where the mud thickness exceeded 8-9 m. Rates of methanogenesis increased along the transect as did the upward diffusive flux of methane. Interestingly, the increase in the sedimentation rate and Holocene mud thickness had only a modest direct effect on methanogenesis rates in deep sediments. This increase in methane flux, however, triggered a shallowing of the sulfate-methane transition which resulted in a large increase in methanogenesis at the top of the methanogenic zone. Thus, our results demonstrate a positive feedback mechanism that causes a strong enhancement of methanogenesis and explains the apparently abrupt appearance of gas when a threshold thickness of organic-rich mud is exceeded.

1. INTRODUCTION

Methane production in marine sediments is determined primarily by the flux of organic matter to the sea floor, its reactivity and its rate of burial (e.g. Borowski et al., 1999, and references therein). The sequence of pathways by which organic matter is mineralized includes aerobic respiration, denitrification, and manganese, iron and sulfate reduction (e.g. Canfield and Thamdrup, 2009). When sulfate (SO_4^{2-}) is exhausted - in coastal settings typically within one to several meters beneath the sediment surface - the continued organic matter degradation leads to the formation of methane (CH_4) which makes the largest contribution to the total gas pressure in the sediment. Due to the steep decrease in degradation rates of organic matter with depth, most methanogenesis takes place in the uppermost part of the methane zone. As a result, most of the CH_4 diffuses up to the sulfate-methane transition (SMT) where the anaerobic oxidation of methane (AOM) is coupled to the reduction of SO_4^{2-} (Sansone and Martens, 1978; Reeburgh, 1980). The depth of the SMT depends on a balance between the total production and upward flux of CH_4 and the downward diffusion and consumption of SO_4^{2-} (Borowski et al., 1996).

In many shallow-water marine sediments, the total gas pressure exceeds the ambient hydrostatic pressure which results in the formation of gas bubbles trapped in the sediment (Fleischer et al., 2001). The majority of the accumulated gas is produced in the methanogenic layer, where the potential for bubble formation primarily depends on the amount and reactivity of organic matter in this layer and on the water depth (Mogóllon et al., 2013).

Shallow free gas in organic-rich marine sediments can be detected by seismo-acoustic surveys from the strong reflection and scattering by minute gas bubbles (Anderson and Hampton, 1980; Judd and Hovland, 1992; Tóth et al., 2014b). In many areas of the Baltic Sea, free gas appears where the organic-rich Holocene mud layer (HML), deposited since the end

of the last ice age, exceeds a thickness of 5-10 m (e.g. Whiticar, 2002; Thiessen et al., 2006; Jensen and Bennike, 2009; Mogollón et al., 2013; Tóth et al., 2014b). It is currently uncertain how the combined effects of eutrophication and climate warming may shift the balance between CH₄ production, accumulation, and oxidation in Baltic Sea sediments and thereby modulate the emission of CH₄ to the overlying water column (cf. Best et al., 2006).

Sediment cores retrieved from methane-rich deposits often experience a rapid loss of gas due to super-saturation at atmospheric pressure, which leads to formation of bubbles and cracks upon retrieval. Reliable CH₄ concentration data are therefore usually only available for the uppermost part of the CH₄ gradient where the partial pressure of CH₄ is below atmospheric pressure. Hence, the in situ concentration profile and production rate of methane can be difficult to reconstruct.

To estimate the entire methane production in the zone that is partly supersaturated with methane, we used an approach developed by Jørgensen and Parkes (2010). The underlying principle is that the initial enzymatic attack on macromolecular organic matter is the process that limits the overall carbon mineralization rate in the seabed. The anaerobic degradation of the organic matter then takes place in several steps leading to key fermentation products, notably acetate and H₂ that are both useable substrates by sulfate reducers and methanogens. The sulfate reducers or methanogens take up the fermentation products as fast as they are produced and, consequently, both sulfate reduction and methanogenesis are limited by the rate of fermentation. Fermentation is controlled by the initial attack on the macromolecular organic matter and not by the consumption of the reduced fermentation products, be it via sulfate reduction or methanogenesis. In accordance with this, the concentrations of acetate and H₂ are generally very low in both the sulfate zone and the methane zone (Hoehler et al, 1998; Glombitza et al. 2014).

In the Jørgensen and Parkes (2010) approach, the organic carbon mineralization in the sulfate zone is first determined by experimental sulfate reduction rate measurements and the relation between mineralization rate and sediment depth (and age) is then determined. This relationship is further extrapolated from the sulfate reduction zone and down into the methane zone, thereby estimating the total methanogenesis and its depth distribution. The methane flux up to the SMT, determined from the upper, reliable part (CH_4 concentrations $< 2.5 \text{ mM}$) of the pore water CH_4 profiles, can be used as a reference to check the validity of the extrapolation (cf. Jørgensen and Parkes, 2010). This approach can also be applied to gassy sediments where the methane transport may be facilitated by bubble migration but where the bubbles dissolve before they reach the SMT and do not rise up into the sulfate zone (Boudreau, 2012; Dale et al., 2013; Treude et al., 2005).

Our goal in this study is to understand the controls on methanogenesis and shallow gas formation relative to the rates of organic matter mineralization and their depth distribution in marine sediments. To finalize this, we used the described combination of extrapolated mineralization rates and the upwards CH_4 flux in Baltic Sea sediments where organic-rich Holocene mud overlays late-glacial organic-poor sand and till. We analyzed data from twelve gravity cores along a 400-m long transect that extended from gas-free to gas-bearing sediment in Aarhus Bay (Denmark) with a gradually increasing thickness of the Holocene mud layer. The analysis was based on a) pore water SO_4^{2-} and CH_4 data, b) experimental determination of mineralization rates, and c) seismic and acoustic imaging.

2. MATERIALS AND METHODS

2.1. Study site

Aarhus Bay (Denmark) is located in the southwest Kattegat on the North Sea - Baltic Sea transition (Fig. 1). The seabed consists of late Quaternary sediments with glacial deformation and till related to the Weichselian ice advances and the ice marginal deposits from the final Baltic advance (Houmark-Nielsen, 1987). Glacio-dynamic morphologic elements show up as shallow ridges in areas of the seabed with no mud deposition (Jensen and Bennike, 2009). The first postglacial intrusion of saltwater into the area, dated to about 9,000 yr BP (years before present), established an initial brackish estuarine phase in Aarhus Bay (Jensen et al., 2004). Dating of mollusk shells from Aarhus Bay shows that fully marine conditions were established around 7,700 yr BP. Organic-rich Holocene marine mud has since accumulated up to >10 m thick layers on top of the glacial deposits.

The water depth in the central and eastern basin of Aarhus Bay is 15–20 m and the surface sediments are characterized as mud and sandy mud. Seismic studies show that gas-bearing sediments extend over a large part of the bay in areas where the mud thickness exceeds 8-9 m (Fig. 1; Jensen and Bennike, 2009).

2.2. Seismic survey

Sampling took place along an acoustic Chirp transect (METROL-502110) recorded by Jensen and Bennike (2009) during the EU project METROL in 2003 (Fig. 2). The occurrence of gas bubbles in the sediment and resulting acoustic turbidity prevented imaging of the underlying sediment structures by the high-frequency chirp acoustics. To determine the base of the Holocene mud beneath the gas-bearing sediment, multichannel seismics with lower frequency were therefore performed along the same transect in April 2012 (GeoB12-035).

Multichannel seismics was performed with a micro GI gun (0.1 L) with a main frequency of 200 Hz (~7.5 m wavelength) and a 60-m long, high resolution digital streamer with 60 channels. Seismic data processing followed a conventional processing flow with special emphasis on precise velocity modeling. In order to correct for the velocity decrease in and beneath the gas-bearing sediment, the initially determined velocity field was corrected using migration velocity analysis in the processing software VISTA. The best image velocity was picked for every reflector on pre-stacked time-migrated data (Tóth et al., 2014a). These velocity values were used to convert two-way travel time (TWT) to depth. Accuracy of the depth calculation depends on several factors: sample rate and noise level of the seismic data, accuracy in picking the TWT of the reflectors, accuracy of the velocity determination, and the variability of the geological structure. The error of the depth calculation considering these factors was estimated to be ~25 cm across the relevant depth interval. The seismic data were used to determine the depth of the base of the Holocene mud layer underneath the gas-bearing sediment.

2.3. Sediment coring

Twelve stations for sediment coring were positioned 20 to 50 m apart along the acoustic transect (Fig. 1 and 2). The total distance between the two end stations, M22 (N56° 6.745', E10° 24.880') and M30 (N56° 6.636', E10° 25.208'), was 408 m. The water depth increased slightly from 18.8 to 19.3 m along the transect while the thickness of the HML increased by a factor of two from 4.7 to 9.7 m (Fig 2, Table 1). Stations M22 to M26 were located in the gas-free area whereas M27 to M30 were located within the gas-bearing sediment. Station M26 was positioned only 12 m NW of the point where acoustic blanking was first observed on the acoustic transect (Fig. 2, Table 1). Stations M22 to M30 were sampled in October 2009, while additional cores (denoted with suffix A) were sampled in May 2010.

One gravity core of 5 to 7.5 m length was retrieved from each site. A shorter Rumohr core (Meischner and Rumohr, 1974) of 0.5 to 1 m length was also taken to obtain undisturbed surface sediment. The sediment loss (8 to 22 cm) from the top of the gravity cores was then determined by aligning the SO_4^{2-} concentration profiles of the two sets of cores (Jørgensen et al., 2004). Immediately after the gravity core was on deck, samples for CH_4 analysis were taken at every 25 cm or 33 cm (starting from the bottom) by drilling small holes through the core liner and extracting 3 mL of sediment with a cut-off plastic syringe (see details in 2.4.1.). The gravity cores were then sectioned on deck into 1 m or 2 m sections, capped, and stored at 4 °C until further processing (within 72 h). The CH_4 samples taken on board the ship were analyzed immediately upon return to the laboratory by gas chromatography (see below) to determine the position of the SMT. The gravity cores were then sub-sampled in the laboratory on land at 12.5 cm depth resolution. The Rumohr cores and the SMT interval of the gravity cores were sampled at 5 cm depth resolution.

2.4. Analytical methods

2.4.1. Methane

For CH_4 analyses, 3 mL of sediment was sampled with cut-off syringes, immediately transferred to 20 mL glass vials containing 6 mL 2.5% NaOH, and crimp capped with butyl rubber stoppers. Samples were shaken thoroughly and stored upside down at 4 °C until analysis within a few days. Prior to analysis, the samples were again shaken to equilibrate the CH_4 and 100 μL of the head space was injected with a Hamilton glass syringe into a gas chromatograph equipped with a 0.9 m packed silica gel column (3.1 mm inner diameter) and a flame ionization detector (SRI 310C, SRI Instruments).

2.4.2. Sulfate

Porewater samples were collected with Rhizon soil moisture samplers (Rhizosphere Research Products, Wageningen, The Netherlands) pushed into the whole cores through 3.8 mm wide holes drilled in the core liner. The Rhizons consist of an inert porous polymer tube with a length of 5 cm and a pore size of $< 0.2 \mu\text{m}$ through which pore water is extracted by vacuum created with disposable 10 mL syringes.

For SO_4^{2-} analysis, the extracted pore water was acidified with HCl and stripped for hydrogen sulfide (H_2S) by shaking on a Vortex mixer. SO_4^{2-} was analyzed on an ion chromatograph (Dionex IC 2000) equipped with GP50 Gradient Pump (flow 1 mL min^{-1}), EG50 Eluent Generator, E AS18 Column (column temperature 30°C), ASRS–UltraII 4 mm suppressor, D50 Electrochemical Detector, AS50 Thermal compartment, and AS50 Auto sampler. Depending on the expected concentration, the pore water samples were diluted 10 to 100-fold before analysis.

2.4.3. Sulfate reduction rates

Sulfate reduction rates (SRRs) were determined in sediment sampled during October 2009. Sub-cores of 3 mL sediment were taken in sterile cut-off syringes at 5, 10, 20 and 60 cm depth in the Rumohr cores and at 120 and 240 cm depth (measured from the core top) in the gravity cores. Samples for SRR determination were kept anoxic in gas-tight plastic bags containing an Oxoid AnaeroGen™ pad (Oxoid A/S, c/o Thermo Fisher Scientific, Roskilde, Denmark) at 4°C for up to 24 h until incubation. Rates were measured by injecting 100 kBq carrier-free $^{35}\text{SO}_4^{2-}$ tracer into the sub-cores followed by 3.5 days of anoxic incubation at 4°C (Røy et al., 2014). The O_2 was stripped from the plastic bags after sealing by an Oxoid AnaeroGen™ pad (Oxoid A/S, c/o Thermo Fisher Scientific, Roskilde, Denmark) that does not develop H_2 . The incubation was terminated by freezing the sediment samples at -20°C without opening the

bags. The samples were stored at $-20\text{ }^{\circ}\text{C}$ for up to 4 weeks before analysis. The frozen samples were then extruded into 3 mL 20% (w/v) Zn-Acetate and thawed. After thawing, the total reduced inorganic sulfur (TRIS = H_2S , S^0 , FeS , and FeS_2) was separated from the $^{35}\text{SO}_4^{2-}$ by a single step cold chromium distillation (Kallmeyer et al., 2004). The radioactivity of $^{35}\text{SO}_4^{2-}$ and ^{35}S -TRIS was counted in 20 mL scintillation cocktail (Ecoscint A, National Diagnostics) on a TriCarb 2900TR liquid scintillation analyzer (Packard Instrument Company). The SRRs (SRR_{ex}) were then calculated as:

$$\text{SRR}_{\text{ex}} = \frac{F \cdot [\text{SO}_4^{2-}] \cdot 1.06}{t} \cdot \varphi \quad \text{Eq. (1)}$$

where F is the fraction of $^{35}\text{SO}_4^{2-}$ reduced ($F = \frac{A_{\text{TRIS}}}{A_{\text{SO}_4^{2-}} + A_{\text{TRIS}}}$) with A denoting the radioactivity in ^{35}S -TRIS and $^{35}\text{SO}_4^{2-}$, respectively, $[\text{SO}_4^{2-}]$ is the pore water concentration of sulfate, t is incubation time in days, and φ is porosity. The constant of 1.06 corrects for the estimated isotope effect during sulfate reduction between the radioisotope, ^{35}S , and the predominant stable isotope, ^{32}S (Jørgensen, 1978a).

The temperature in the bottom water of Aarhus Bay varies seasonally between $5\text{ }^{\circ}\text{C}$ and $11\text{ }^{\circ}\text{C}$ and the variation propagates down into the upper meters of sediment towards an annual mean temperature of $9\text{ }^{\circ}\text{C}$ (Dale et al., 2008). Because SRRs were determined at $4\text{ }^{\circ}\text{C}$, the measured rates were recalculated to a mean annual SRR at each depth in the sediment. To achieve this, the vertical temperature profile in the upper 10 m of the sediment column was first simulated for each day of the year using Comsol Multiphysics software. The model was driven by input of the daily bottom-water in the top, and the dynamic temperature variations down-core were calculated from the thermal conductivity and the heat capacity of the

sediment (Dale et al., 2008). The mean annual SRR at each depth in the sediment adjusted to *in situ* temperature was then calculated:

$$SRR = \frac{1}{365} \times \sum_{day=1}^{365} \frac{SRR_{ex}}{Q_{10}^{\frac{T_{ex}-T_{in}}{10}}} \quad \text{Eq. (2)}$$

where SRR_{ex} is the measured SRR at 4 °C, Q_{10} is the factor of increase by a temperature increase of 10 °C, estimated to 2 (Dale et al., 2008), T_{ex} is the *ex situ* temperature of the incubation (4 °C), and T_{in} is the simulated *in situ* seasonal depth-dependent temperature. Using this approach the rates were revised upwards by a factor of 1.3 to 1.4 depending on depth. Volumetric rates are reported in $\text{nmol cm}^{-3} \text{ d}^{-1}$ of wet sediment.

2.5. Diffusive Fluxes of SO_4^{2-} and CH_4

2.5.1. Methane and sulfate fluxes

Diffusive fluxes of SO_4^{2-} and CH_4 were estimated from their concentration gradients using Fick's First Law:

$$J_i = -\varphi \cdot \frac{1}{1 - \ln(\varphi^2)} \cdot D_i \cdot \frac{\partial C_i}{\partial z} \quad \text{Eq. (3)}$$

where J_i is the diffusive flux of species i , C_i is the concentration, z is depth (cm), and φ is porosity. D_i is the diffusion coefficient in free solution (Boudreau, 1997) for a salinity of 30 and the mean annual temperature of 9 °C (Dale et al., 2008): $D_{\text{CH}_4} = 0.918 \text{ cm}^2 \text{ d}^{-1}$; $D_{\text{SO}_4^{2-}} =$

0.570 cm² d⁻¹. The factor $1-\ln(\phi^2)$ corrects for the lower diffusion coefficient in sediment due to tortuosity (Boudreau, 1997).

Fluxes of SO₄²⁻ to the SMT were estimated from the quasi-linear part of the concentration gradients in the depth interval right above the SMT whereas CH₄ fluxes were estimated from the steepest slope below the SMT. The depth of the SMT was defined as the depth of equimolar SO₄²⁻ and CH₄ concentrations. SO₄²⁻ fluxes were always directed downwards (into the sediment), whereas CH₄ fluxes were always directed upwards (out of the sediment). All fluxes are reported numerically as absolute numbers.

2.5.2. Methanogenesis rates estimated from SRR

Rates of methanogenesis beneath the SMT were estimated by the approach described by Jørgensen and Parkes (2010, see above), who extrapolated the log-log-linear depth trend in mineralization rates measured experimentally in the sulfate reduction zone down into the methanogenesis zone. Since the general sedimentation regime for the deeper parts of Aarhus Bay has been constant for most of the Holocene period (Langerhuus et al., 2012) there is an approximately linear relation between depth and age. The constant porosity below 10 cm sediment depth (0.66 ± 0.003 SE, Fig. S5) suggests that compaction of sediment below 10 cm and in the zone of interest is negligible. Furthermore, we can assume that the compaction above 10 cm is constant because the water depth (and thus the static pressure) only changed by < 2 m over the relatively short distance of the transect (400 m). This should thus results in a ‘similar’ distortion of the age-depth relationship by compaction at each station between 0-10 cm sediment depth. For each coring site it is thereby possible to establish the relation between mineralization rate and depth or the, mathematically equivalent, relation between mineralization rate and sediment age. The functional driver for the trend, however, is that degradability of the organic matter decreases according to a power function of the age of the

organic material (Middelburg, 1989). Thus, the relation to age provides a general control on the mineralization rates, while the relation to depth depends on the local sedimentation rate. As compaction of sediment is negligible in the zone of interest (below 10 cm sediment depth) and to simplify the modeling we have not included compaction when determining the age and sedimentation rates. The relation between carbon mineralization rates and sediment age was therefore determined by fitting a straight line to log-log transformed data of measured SRR vs. sediment age at the specific depths from where the samples originated (see section 3.1. for determination of sediment age) resulting in the empirical function of age (yr) for SRR (nmol cm⁻³ day⁻¹) (Eq. 4).

Such a linear regression after log-log transformation, however, causes a mathematical artifact because high rates lose significance relative to low rates in the fit. If the log-log linear relation is transferred to a power function in linear space (Eq. 4), then this function will fall systematically below the fitted data. The underestimation is proportional to the variance in the log-transformed experimental data. If the variance in log(SRR) is constant at all depths, then the underestimation is independent of depth. To correct the underestimation, the average of all measured SRRs can be compared to the average of all SRRs predicted from the power function. The constant, a, in the power function represented by Eq. 4 can then be corrected to make the average of all predicted rates agree with the average of all measured rates.

$$\text{SRR}(\text{age}) = a \times \text{age}^{-b} \quad \text{Eq. (4)}$$

where a and b are the fitted parameters of the power function. The relation can be recalculated for each station to relate sulfate reduction at the individual stations (SRR_{st}) to sediment depth based on the local sedimentation rate according to the function

$$SRR_{st}(\text{depth}) = a \times (\text{depth} / \omega_{st})^{-b} \quad \text{Eq. (5)}$$

where depth is given in cm and ω_{st} is the sedimentation rate at a given station in cm yr^{-1} (see below). Note that a and b do not change by this conversion.

3. RESULTS

3.1. Lithology

The late-Glacial to Holocene development of sediments in Aarhus Bay and along the transect is described in Supplementary Data. The sediment consists of organic-rich Holocene mud deposited on top of organic-poor glacial sand and till (recovered in the core catcher from Station M22). The acoustic transect (METROL-502110; Jensen and Bennike, 2009) is shown in Fig. 2 together with the position and approximate penetration depth of twelve gravity cores numbered from M22 to M30. A prominent feature of the acoustic image was acoustic blanking caused by free gas in the sediment from M27 past M30. To resolve the lower boundary of the HML below the gas charged area (broken curve in Fig. 2), a multichannel seismic profile (GeoB12-035, Supplementary Data Fig. S1) was recorded along the acoustic line.

The thickness of the HML increased from NW towards SE (from left to right in Fig. 2), ranging from 4.7 to 9.7 m. Several weaker acoustic reflectors in the HML caused by slight variations in sediment density or grain size were continuous across the transect and marked past sediment surfaces. The weaker reflectors lapped onto the glacial sand and till between M22 and M24 (Fig. 2), showing discontinuous sedimentation in this interval in the early part of the Holocene. The analysis of methanogenesis by extrapolation of sulfate reduction rates was therefore not performed on this segment of the transect. The internal reflection pattern

and the increasing depths of the HML from M24 to M30 showed that the Holocene deposit was complete and had gradually increasing sedimentation rates from M24 towards M30. Thus this section could be used for calculation of methanogenesis by extrapolation of sulfate reduction rates.

We used the increasing depth of two continuous reflectors (marked on and Fig. 6a) across the M24 to M30 section to calculate the sedimentation rate at each station relative to Station M26. M26 was chosen as a reference because of its position at the transition between gas-free and gas-charged sediment at the middle of the transect, and because the absolute sedimentation rate at this station could be determined from the strong reflector at the Holocene base at 8.7 mbsf (meter below seafloor, see below). The depth of the reflectors, and thereby the sedimentation rates, changed gradually across the transect from 89% (M24) to 119% (M30) relative to M26. The same depth of the Holocene basis as at M26 (27 m below sea surface) was found in a previous core only 3000 m away at Station M1 (Fig. 1). Here the age structure was determined from ^{14}C dating of multiple bivalve shells and the base of the HML was dated to 9,000 yr BP (Langerhuus et al., 2012, see also Supplementary Data, Section S.1.). Their similar depth below sea surface implies that the post glacial landscape at M1 and M26 was inundated by seawater simultaneously during the marine transgression and that the age of the Holocene basis at station M26 must also be 9,000 years. Dividing the 8.7-m thick marine mud layer at M26 by 9,000 years yields an average sedimentation rate of 0.097 cm yr^{-1} at Station M26 (ω_{26}). From this absolute sedimentation rate at M26, combined with the relative sedimentation rates calculated from the weaker reflectors above, we calculated the absolute sedimentation rate for each station from M24 to M30 ($\omega_{24..30}$; Table 1). The weak correlation ($R^2=0.35$) of the HML depth presented in Table 1 with the calculated sedimentation rates likely results from the uncertainty of the depth calculation in the gas-bearing area ($\pm 25 \text{ cm}$). A different explanation could be slightly depressed sedimentation

rates in the earliest part of the Holocene from M28 to M30. Note that this would have little influence on the extrapolated rates of methanogenesis because the “missing” sediment is old and has little contribution to mineralization.

3.2. Sediment characteristics

Sediment density and porosity data show that the physical properties of the sediment did not change systematically along the transect (Supplementary Data, Fig. S5). The depth distributions of total carbon (TC) and total nitrogen (TN) were also very similar at all stations along the transect (Supplementary Data, Fig. S6). The TC content showed a slight increase with depth, with concentrations ranging from 2 to 3%, while TN gradually decreased from 0.3 to 0.15%. Accordingly, the TC:TN ratio increased with depth from 10:1 to 20:1. At M22, where the HML thickness was only 4.7 m, the gravity core penetrated the organic-poor glacial material below and the TC dropped to 1.6% while the TC:TN ratio increased rapidly to 33.

3.3. Sulfate and methane

SO_4^{2-} concentrations decreased with depth with a slightly concave down-curvature in all cores (Fig. 3). Beneath the sulfate-methane transition (SMT), SO_4^{2-} concentrations were <0.2 mM. Methane concentrations increased steeply below the sulfate zone (cores M22 and M22A did not quite reach the methanogenic zone). Due to fast sampling, CH_4 loss appeared to be minimal up to approximately 2.5 mM CH_4 and the measured CH_4 profiles were smooth and continuous (black symbols in Fig. 3). Measured concentrations exceeding 2.5 mM were scattered and presumably underestimated due to degassing of dissolved CH_4 from the supersaturated sediment upon core retrieval (gray symbols in Fig. 3). Although CH_4

concentrations above 2.5 mM are presented in Fig. 3 they were not considered in the calculation of diffusive fluxes.

The depth of the SMT, defined here as the depth of equimolar concentrations of SO_4^{2-} and CH_4 , shifted upwards along the transect from about 5 m at Station M22 to 2.57 m at Station M30 (Fig. 3, Table 1). Thus, from NW towards SE (increasing station numbers) the SMT depth became shallower, the SO_4^{2-} and CH_4 gradients became steeper, and the SO_4^{2-} and CH_4 diffusive fluxes increased (Fig 4a, b). The ratio of SO_4^{2-} flux to CH_4 flux in the SMT ranged from 1 to 2.5, averaging 1.5 for the entire transect with no clear trend (Fig. 4c). The sulfate flux into the SMT was thus relatively higher than the CH_4 flux into the SMT. This deviation from a 1:1 AOM stoichiometry may be partly explained by organoclastic sulfate reduction that took place within the SMT. The correlation of SO_4^{2-} flux with CH_4 flux (Table 1) results in a slope of 1.15 and an intercept of 1.7 suggesting that in average about 1.7 $\text{nmol cm}^{-2} \text{ d}^{-1}$ of the SO_4 flux is due to organoclastic sulfate reduction. Depending on the place in the transect the organoclastic sulfate flux corresponds to about 31% ($\pm 7\%$ SD) in the gas-free area and 16% ($\pm 4\%$ SD) in the gas-bearing area of the total sulfate flux.

3.4. Sulfate reduction rates

Sulfate reduction rates (SRR) are plotted for each station in Fig. S4 and for all stations together in Fig. 5a. The highest SRR of up to 200 $\text{nmol cm}^{-3} \text{ d}^{-1}$ were measured at 10 cm sediment depth (Fig. 5a). Towards the sediment surface the measured rates corresponded well to the annual mean SRR measured at nearby Station M1 by Thamdrup et al. (1994), marked in Fig 5a by triangles. Integrated over the top 10 cm the SRR from Thamdrup et al. result in 470 $\text{nmol cm}^{-2} \text{ d}^{-1}$. From 10 cm and deeper in the sediment our measured rates decreased to $\sim 0.02 \text{ nmol cm}^{-3} \text{ d}^{-1}$ at 200-300 cm depth. The SRR versus depth in the sediment showed a linear relation in the log-log plot (Fig. 5a; Fig. S4 in Supplementary Data). This implies that the

rates can be approximated by a power law function of depth (Jørgensen, 1978b; Jørgensen and Parkes, 2010; Holmkvist et al., 2011). The sedimentation rate in the deeper areas of Aarhus Bay has been near constant throughout the Holocene. Thus, the SRR can be expressed equally well by a power law function of sediment age (Eq. 4). Note that the loss of reactivity of organic matter is linked mechanistically to age rather than depth (Middelburg, 1989), and that the relation between SRR and age, therefore, is slightly different from the relation between SRR and depth when comparing the different stations. We calculated the best fit of Eq. 5 to the combined dataset from all stations. Data from the top 0-10 cm were excluded to avoid the surface zone where sulfate is not the primary terminal electron acceptor. The best power law function describing SRR as a function of age and corrected for skewing (factor of 1.79, see section 2.5.2.) was:

$$\text{SRR}(\text{age}) = 3.8 \times 10^6 \times \text{age}^{-2.36} \quad \text{Eq. (6)}$$

or

$$\text{SRR}_{\text{st}}(\text{depth}) = 3.8 \times 10^6 \times (\text{depth} / \omega_{\text{st}})^{-2.36} \quad \text{Eq. (7)}$$

where SRR_{st} is the sulfate reduction rate at a specific station ($\text{nmol cm}^{-3} \text{d}^{-1}$), age is in years and depth is in cm. ω_{st} is the sedimentation rate at each station (cm yr^{-1} , Table 1). The 95% confidence interval of the estimate of the exponent, b, was -2.17 to -2.58. The 95% confidence interval of the estimate of the constant, a, was 0.79×10^6 to 120×10^6 .

3.5. Estimation of methanogenesis rates

The power law functions (Eq. 6 and 7) that describe the rate of organic matter mineralization with depth and age were extrapolated down into the methanic zone to the bottom of the HML as described in section 2.5.2 (Fig 5a). Our analysis of pore water fluxes of

sulfate and TCO_2 indicated that the mean oxidation state of organic matter being mineralized in the sulfate zone was statistically not different from zero, corresponding to an organic matter composition of simple carbohydrate, e.g. CH_2O (Supplementary Data, Section S.6). Thus, one mol of SO_4^{2-} reduced is equivalent to two mol of C_{org} mineralized. The rate of organic carbon mineralization was then calculated from the extrapolated sulfate reduction rates by multiplying by a factor of two. This information was used to calculate the vertical distribution of carbon mineralization in the entire sediment column. The results show that the vast majority of anaerobic mineralization occurs near the sediment surface (Fig. 5b).

Methane production from C_{org} with an average oxidation state of zero leads to equal amounts of CO_2 and CH_4 . Thus, the depth-integrated rate of methane production in any depth interval in the sediment can be calculated by integrating the rate of carbon mineralization for that specific interval and dividing by 2. The result is shown for stations A24 to M30 in Fig. 4d.

The depth-integrated rate of methanogenesis calculated by this extrapolation was, as a first estimate, assumed to result in a corresponding upwards CH_4 flux while the accumulation of CH_4 or the downwards flux of CH_4 into the glacial till was assumed to be less significant (Mogollón et al., 2012). The CH_4 production ($J_{\text{CH}_4,\text{ex}}$), predicted from this SRR-extrapolated calculation followed the trend in diffusive flux of CH_4 (J_{CH_4}) up from the methanogenic zone but was on average only 51% of the calculated diffusive flux (Fig 4b, d). The 1:1 ratio between the upwards diffusive flux and the extrapolated methane production, however, was often contained within the 95% confidence interval of the extrapolation (Fig. 4d).

The entire depth-integrated rate of carbon mineralization at station M26 was ca. 1,800 $\text{nmol C cm}^{-2} \text{ d}^{-1}$ (Fig 5b). The carbon mineralization in the methanogenic zone was 0.8-6 $\text{nmol C cm}^{-2} \text{ d}^{-1}$. Methanogenesis ($J_{\text{CH}_4,\text{ex}}$) thus accounted for only 0.05-0.3 % of the total amount of carbon mineralized. Concordantly, the methane flux estimated from the pore water gradients

(J_{CH_4}) to the SMT accounts for ~ 1% compared to the amount of carbon mineralized by sulfate reduction.

4. DISCUSSION

The Holocene deposit was strikingly homogeneous along the transect (Fig 2; Table 1). Density and porosity showed some scatter whereas the total C and N content was more uniform. Neither differed systematically between the stations (Supplementary Data, Fig. S5 and Fig. S6). The concentrations and gradients of total inorganic carbon and ammonium in the pore water increased only gradually from M22 to M30 (Fig. S2) but there was no trend along the transect in the calculated C:N ratio of *mineralized* organic matter ($r_{C:N}$ in Table 1; Supplementary Data Fig. S8). This could also be expected as the transect covers only a small area in the middle of Aarhus Bay with a rather uniform bathymetry and with the same source of sedimenting material.

The age trend that controlled mineralization was expressed both along the depth of the cores due to burial, and across the transect due to systematic variation in burial rate. The horizontal age trend was, however, much weaker than the age trend along the core depth. Accordingly, the trend in SRR across the transect was much less pronounced than along depth and the correlation between age and SRR was primarily driven by the depth trend. The difference in sediment age at any fixed depth between station M24 and M30 was a factor of 1.4 (youngest age at M30). The expected difference in sulfate reduction rate caused by this age difference, according to Eq. 6, was a factor of 2.5 (highest SRR at M30). The stochastic variation in sulfate reduction rate between samples at any fixed depth, however, was one order of magnitude. This sample-to-sample variation in sulfate reduction is typical, even for replicates in the same core (e.g. Jørgensen and Parkes 2010; Holmkvist et al. 2011). Thus, the

expected change in measured sulfate reduction rate across the transect by a factor of 2.5 remained hidden in the natural variation.

There were no indications that the sudden appearance of free gas near M26 was triggered by a shift in the concentration or the quality of organic matter in the Holocene mud. The only apparent cause of the increased methanogenesis rates along the transect was the gradual increase in sedimentation rate and the corresponding gradual thickening of the Holocene deposit. It is, however, not intuitive how an increase in the thickness of the Holocene mud layer of only 34% from M24 to M30 (Table 1) can lead to a 2.5-fold increase in the estimated methane flux (Fig. 4b) and a 7-fold increase in the estimated methane production (Fig 4d).

The explanation appears to lie in the steep power law decrease in mineralization rates with depth and age (Fig 5a). This can be illustrated by dividing the methanogenic zone from Stations M24 to M30 into three sub-zones (I, II and III in Fig 6b). Zone II corresponds to the methanogenic zone at M24 and provides the basis for our analysis. Zone III is the methanogenic zone that appears below Zone II as the depth of the Holocene mud layer increases towards Station M30. Zone I is the methanogenic zone that is added on top of Zone II from Station M24 because the SMT shifts towards the sediment surface.

Figure 6c shows the methane production in the 3 sub-zones calculated by extrapolation and depth-integration of Eq. 7. It is immediately apparent that the depth-integrated methanogenesis is not proportional to the thickness of the zones. The deepening of Zone III has little direct impact on the total methanogenesis because the deep sediment is old and has low reactivity. The methane production in Zone II increases moderately along the transect although its thickness and depth is constant. This is because the sediment becomes younger within this depth interval due to increased burial rate and, as described by Eq. 6, because a small change towards younger age leads to a relatively large increase in the rate of mineralization. In combination, the added volume of methanogenic sediment in zone III and

the increased methanogenesis rate in zone II cause a higher depth-integrated methanogenesis and thereby a higher upwards methane flux. The increased methane flux stimulates sulfate consumption via AOM and thus pushes the SMT upwards, exposing relatively young sediment at the top of Zone I to methanogenesis rather than organoclastic sulfate reduction. The organic carbon mineralization rates in zone I are much higher than below so that even a small shift upwards has a large impact on overall methanogenesis.

To provide an example of this effect, the calculated ages of the sediment at the upper and lower boundary of Zone II at M24 are 5,000 and 8,500 years, respectively. According to Eq. 7, the volumetric rate of methanogenesis is thus 3.5-fold higher at the upper boundary than at the lower boundary. Thus, a moderate increase in CH₄ flux from Zone III and II causes the pathway of mineralization at the base of Zone I to shift from sulfate reduction to methanogenesis. At this shallower depth methanogenesis rates are much higher than the rates of methanogenesis anywhere else in the sediment. This increases the total methane flux and pushes the SMT up even higher.

Such a positive feedback mechanism leads to a strong amplification of total methanogenesis. While the enhancement due to the higher sedimentation rate and deepening of the Holocene mud layer contribute only very little to it, it is the actual trigger of the feedback loop. A steady state is reached at each coring site when the total depth-integrated methanogenesis leading to upward CH₄ flux is balanced by the downward flux of SO₄²⁻. The enhancement of methanogenesis along the transect eventually causes the CH₄ partial pressure to build up in excess of the *in situ* hydrostatic pressure and triggers the formation of free gas in the sediment beyond Station M26.

Anaerobic oxidation of CH₄ in the SMT zone dominated the trends in the SO₄²⁻ and CH₄ profiles (Fig. 3). Methane oxidation was indeed tightly coupled to SO₄²⁻ reduction, as can be seen from the ratio between the flux of CH₄ and the flux of SO₄²⁻ into the SMT (Fig. 4c). The

small difference relative to the 1:1 ratio expected from the stoichiometry is possibly due to heterotrophic (non-methane based) SO_4^{2-} reduction within the SMT. We make here no assumptions regarding methane transport by migration of gas bubbles upwards through the gassy sediment beneath the SMT (Mogollón et al., 2012) and enhanced diffusivities due to the presence of free gas (Flury et al., 2015). Our calculations or conclusions, however, are not dependent on whether there is enhanced gas transport or not, as the CH_4 fluxes were calculated from the top of the CH_4 profile where the partial pressure of CH_4 was well below *in situ* hydrostatic pressure and no bubbles were present.

In spite of the strong control that CH_4 oxidation exerted on the SO_4^{2-} profile the CH_4 -dependent SO_4^{2-} consumption was only 1% of the overall sulfate reduction above the SMT (Fig. 5b). It is therefore counter-intuitive that a small change in methanogenesis can cause a strong effect on the division of the sediment into SO_4^{2-} reducing and methanogenic zones. This, however, is again a result of the power-law decrease in mineralization rates with depth and age which means that by far most of the SO_4^{2-} reduction takes place near the sediment surface where it causes only a very modest drop in SO_4^{2-} concentration (compare Fig. 3 and Fig. 5b). In contrast, rates of organic carbon mineralization are very low at the bottom of the SO_4^{2-} zone so that the additional substrate provided by CH_4 from below has a significant local effect at the SMT and appears to steer the entire shape and depth of the SO_4^{2-} curve. Because total methanogenesis is very small compared to total SO_4^{2-} reduction, a shift in mineralization pathway at the SMT from SO_4^{2-} reduction to methanogenesis can have a profound effect on the methane budget and at the same time be insignificant for the overall sulfate reduction or the total mineralization of organic carbon in the sediment column.

5. SUMMARY

After the marine transgression about 9,000 yr BP, the till layers left by the receding glaciers became covered with an organic-rich Holocene mud layer (HML) that has since accumulated in Aarhus Bay to different thicknesses. The 400-m long transect studied here shows that a HML thickness of at least 5 m (at station M22, Fig. 3) was required for a complete depletion of SO_4^{2-} and establishment of a methanogenic zone. The HML thickness increased along the transect and a new threshold of HML thickness of 8-9 m (between M26 and M27, Fig. 3) was reached beyond which the CH_4 partial pressure exceeded the *in situ* hydrostatic pressure of ca. 3.5 bar, corresponding to an *in situ* CH_4 concentration of ca. 6 mM. Exceeding the second threshold thickness caused gas bubbles to appear.

We determined the anaerobic mineralization of buried organic matter as a function of depth and age in the sediment through experimental measurements of sulfate reduction rates. Extrapolation of the log-log linear trend in these mineralization rates with age down through the Holocene methanogenic sediment provided an estimate of the overall CH_4 production rate. This extrapolated rate compared systematically along the transect with the upward diffusion flux of CH_4 . From the combined data we deduce that there is a strong positive feedback whereby a small increase in sedimentation rate and thickness of the HML lead to an upwards expansion of the methanogenic zone and thereby to a relatively large increase in the total methanogenesis. This positive feedback is responsible for the sharp appearance of gas bubbles despite only a gradual increase of the Holocene mud layer thickness.

The transect studied here was chosen to represent a sedimentation basin of uniform bathymetry and apparently uniform sedimentology but with abrupt appearance of shallow gas. The applied combination of shallow seismics, sediment coring and biogeochemical analyses revealed that an irregular glacial landscape buried beneath the mud exerted a strong control on the overall methane production, a control that was enhanced through a simple feedback

mechanism. We believe that this example of feedback mechanism and parameters that constrain methane accumulation in the sediment is of general relevance to marine sediments.

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SUPPLEMENTARY DATA

Supplementary data contains 8 additional figures that support the data presented in the main text. It contains a section describing the lithology in more details, a section with general background parameters such as dissolved ions (TCO₂, NH₄, Mg²⁺ and Ca²⁺) in the porewater, porosity, density, total C, total N and C:N ratios. Additionally we present the SRR at the individual stations and describe the stoichiometry of the mineralization of organic matter.

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700

FIGURE CAPTIONS

Fig. 1. Location of Aarhus Bay (box) on the transition between the North Sea and the Baltic Sea and close-up where the stippled areas denote free gas (modified from Jensen and Bennike, 2009). The positions of the transect and of Station M1 are shown.

Fig. 2. Single channel acoustic transect (Chirp, METROL-502110), with the lower boundary of the Holocene mud layer beneath the gassy sediment digitized from a multichannel seismic profile (GeoB12-035, Supplementary Data Fig. S1). The positions and approximate penetration depths of twelve gravity cores are shown. The free gas caused a strong blanking of the acoustic signal from Station M27 to Station M30 and beyond. The depth on the right vertical axis is calculated from two-way travel time assuming the speed of sound to be 1500m/s. Note that this causes a slight underestimation of the depths in the gassy sediment due to lower speed of sound there for which the depth scale in the graph is not corrected. For true depths see Table 1.

Fig. 3. SO_4^{2-} and CH_4 pore water profiles along the transect. Stations M22 to M26 are positioned in gas-free sediment while M27 to M30 are positioned in sediment with free gas bubbles. Grey symbols represent CH_4 pore water data (≥ 2.5 mM) that are most likely affected by outgassing. The dashed lines indicate the depth of the sulfate methane transition (SMT) where $[\text{CH}_4] = [\text{SO}_4^{2-}]$ while the solid lines represent the bottom of the HML according to Fig. 2.

Fig. 4. Diffusive fluxes of (a) sulfate (J_{SO_4}) and (b) methane (J_{CH_4}) into the sulfate-methane transition (SMT) along the transect. Panel (c) shows the ratio between the diffusive fluxes of

methane up into the sulfate-methane transition and of sulfate down into the transition ($J_{\text{SO}_4}/J_{\text{CH}_4}$). Panel (d) shows the total CH_4 production, calculated by extrapolation and depth integration of measured SRR, from the SMT down to the bottom of the HML (see section 2.5.2.). The thin lines in (d) represent the 95% confidence intervals of the power function fit to the measured SRR. The vertical gray line in each frame denotes the transition between gas-free and gas-bearing sediment.

Fig. 5. (a) Sulfate reduction rates measured at Station M24-M30 plotted against age of the sediment (filled circles), both on logarithmic scales. The corresponding depth scale is calculated from the mean sedimentation rate at Station M26 and is accurate only for that station. The two lines show the upper and lower 95% confidence interval for the best fitted power law function to the data (Eq. 6). Data from the top 10 cm (open circles) were excluded from the extrapolation analysis because sulfate reduction here does not reflect the total carbon mineralization due to competition with more energetically favorable electron acceptors. The annual mean sulfate reduction at M1 in the upper 10 cm (data from Thamdrup et al., 1994) is shown with triangles. (b) Cumulative carbon mineralization rates with age and depth in the sediment. The data use the annual mean sulfate reduction rates from Station M1 of Thamdrup et al. (1994) down to 10 cmbsf ($470 \text{ nmol cm}^{-2} \text{ d}^{-1}$) and continue down through the HML according to the depth-integration of Eq. 6. Mineralization rates of organic carbon were calculated from sulfate reduction rates by assuming a SO_4^{2-} to C_{org} stoichiometry of 1:2.

Fig. 6. (a) Segment of the acoustic transect from Fig. 2 showing the Holocene layer from Station M24 to M30 and the appearance of shallow gas. Uncorrected depths below sea surface are calculated from the acoustic two-way travel time by assuming a constant sound velocity as in Fig 2. The yellow dashed lines indicate the two reflectors used for the estimation of

sedimentation rates. (b) The same cross section as in (a), but now showing depths below sea floor based on estimates of the local sound velocity at each station down to the Holocene basis. Based on pore water profiles, the Holocene layer is divided into the sulfate reduction zone above the sulfate-methane transition and the methanogenic zone below. The methanogenic zone is, in our analysis, divided further into three sub-zones. II is the sub-zone (i.e. the depth interval) that corresponds to the entire methanogenic zone at M24. III is the additional methanogenic sub-zone that is due to the Holocene layer deepening along the transect. I is the additional methanogenic sub-zone that is due to the sulfate-methane transition shallowing along the transect. (c) The predicted depth-integrated rate of methane production in the three methanogenic sub-zones. Note that the relative increase in overall rate of methane production along the transect is much larger than the relative increase in thickness of the methanogenic sub-zones, in particular due to sub-zone I.

Table 1. Solute fluxes and stoichiometry of mineralization across the transect. Station positions are given as the distance from the gas free to gas bearing sediment. The depth of the Holocene mud layer (HML) and the sulfate methane transition (SMT) as well as the sedimentation rate, ω_{st} , are indicated. All fluxes (J) are in $\text{nmol cm}^{-2} \text{d}^{-1}$ and are calculated at the depth of the SMT. The $r_{C:S}$ is the ratio between mol of total CO_2 produced per mole of SO_4^{2-} reduced during sulfate reduction while the $r_{C:N}$ is the C:N ratio (based on TOC and NH_4^+ pore water profiles) of the organic material being mineralised (Supplementary Data, Section S.6 and S.7).

Station	Distance from transition (m)	Depth of HML (cm)	SMT (cm)	ω_{st} (cm yr^{-1})	J_{SO_4}	J_{CH_4}	J_{TCO_2}	J_{NH_4}	$r_{C:S}$	$r_{C:N}$
M22	-247	466			6		10.6	0.4	1.9	14.9
M22A	-178	488			5.2		8.7	0.4	1.3	7.8
M23	-105	613	405		9.65	3.83	18.3	0.9	1.8	12.8
M24	-65	724	428	0.086	5.96	4.21	5.2	1.4	2.1	8.1
M25	-38	883	391	0.090	5.87	5.71	18.6	1.9	2.5	10.8
M26	-7	868	373	0.097	7.63	4.99	11.9	1.9	2.4	8.5
M27	37	843	328	0.096	10.11	6.36	29	2.2	2.6	10.9
M27A	50	972	284	0.102	14.54	8.55	25.5	2.5	2.9	8.9
M28	78	820	265	0.102	10.64	8.62	34.6	2.6	2.8	12.0
M29	111	864	238	0.109	13.31	9.34	33.1	2.9	2.2	11.3
M29A	158	900	268	0.111	15.37	7.8	30.5	2.5	(3.2)	10.0
M30	195	807	257	0.115	10.41	10.16	33.2	2.8	2.5	8.8