

Biogeochemical controls on carbonate dynamics driven by methane and freshwater inputs in shallow sediments of a brackish continental shelf sea

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Abstract. Continental shelf seas are essential to the carbon cycle, supporting nearly one-third of global marine primary production and significantly contributing to the burial of organic and inorganic carbon. Processes such as organoclastic sulfate reduction (OSR), methane production or anaerobic oxidation of methane (AOM), occurring in coastal sediments, have a significant impact on the carbon cycling in the marine environment. That impact may be modified by an increased organic matter (OM) supply or freshwater input. In the present interdisciplinary study, we investigated carbonate dynamics in three benthic environments of a brackish continental shelf sea: (1) anoxic sediments dominated by OSR; (2) nearshore sediments with high terrigenous OM input and active methanogenesis; and (3) sediments influenced by groundwater infiltration and pore-water freshening, coupled with methanogenesis. We analyzed pore-water chemistry (DIC, total alkalinity, major ions, nutrients), sediment geochemistry (CH₄, total organic carbon, total nitrogen, total sulfur), and mineralogy, including authigenic carbonates and iron sulfides. We used stable isotopes of DIC ($\delta^{13}\text{C}$ -DIC), methane ($\delta^{13}\text{C}$ -CH₄, $\delta^2\text{H}$ -CH₄) and organic matter ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$) to trace carbon transformations. We also determined rates of OSR and AOM experimentally. Based on these data, we have proposed conceptual models of carbon cycling in the three sedimentary environments. In the methane-free sediment, organic matter degradation was primarily governed by OSR, producing 54 mmol m⁻² d⁻¹ of DIC within the top 100 cm, accompanied by limited carbonate burial and dominant pyrite accumulation. In sediments where the flux of OM exceeded sulfate supply, a substantial portion of OM remineralization shifted to methanogenesis in the uppermost decimeters, leading to rapid sulfate depletion, a shoaled sulfate–methane transition, and elevated DIC concentrations; these processes were especially pronounced in sediments affected by freshwater seepage, where pore water freshening further limited sulfate availability. In such conditions carbonate dynamics were markedly enhanced: methane-related processes - in particular AOM, which reached up to 1077 $\mu\text{mol dm}^{-3} \text{ d}^{-1}$ in freshwater-influenced sediments - produced additional DIC, contributed to carbonate supersaturation and promoted pronounced authigenic carbonate (mainly dolomite) formation. Depth-integrated DIC production from AOM (331 mmol m⁻² d⁻¹ over 0–100 cm)

33 substantially exceeded OSR-derived DIC ($58 \text{ mmol m}^{-2} \text{ d}^{-1}$) in these settings, corresponding with elevated authigenic
34 dolomite burial rates ($467\text{--}994 \text{ } \mu\text{mol m}^{-2} \text{ d}^{-1}$). To our knowledge, this study provides the first quantitative estimate of
35 authigenic carbonate burial rates for Baltic Sea sediments.

36 **1 Introduction**

37 Continental shelf seas cover $\sim 7\%$ of the global ocean surface but play a disproportionate role in the carbon (C) cycle. They
38 support 10–30% of global marine primary production due to high nutrient availability (Bauer et al., 2013). Shelf sediments
39 account for 30–50% of marine inorganic C burial and $\sim 80\%$ of organic C burial (Bauer et al., 2013; Liu et al., 2010).

40 Over recent decades, enhanced nitrogen and phosphorus inputs from watersheds have intensified coastal eutrophication
41 (Rabalais et al., 2010; Paerl et al., 2014). In shallow systems, a large fraction of organic matter (OM) from primary
42 production reaches the seabed (Berner, 1982; Hedges and Keil, 1995; Wollast, 1998; Cai, 2011; Bauer et al., 2013). The
43 oxidation of OM in surface sediments follows a redox cascade determined by available electron acceptors (Froelich et al.,
44 1979). Under oxic conditions aerobic respiration dominates. Degradation of the increased OM resulting from eutrophication
45 rapidly consumes oxygen and promotes the expansion of bottom water hypoxia and anoxia (Rabalais et al., 2010; Fennel and
46 Testa, 2019). Once bottom-water O_2 is depleted, OM oxidation shifts to anaerobic pathways via denitrification, reduction of
47 Mn(IV), Fe(III) and sulfate (SO_4^{2-}), although their relative importance depends on local electron-acceptor availability and
48 sedimentary conditions.

49 Organoclastic sulfate reduction (OSR) commonly dominates in coastal and margin sediments accounting for up to 70% of
50 OM oxidation (Thamdrup and Canfield, 1996; Jørgensen and Kasten, 2006). When OM supply exceeds SO_4^{2-} availability,
51 methanogenesis occurs (Froelich et al., 1979). Most biogenic methane (CH_4) produced in subsurface environment is oxidized
52 within sediments, predominantly by sulfate-driven anaerobic oxidation of methane (SO_4^{2-} –AOM) at the sulfate–methane
53 transition (SMT) zone, where downward-diffusing sulfate meets upward-migrating methane (Boetius et al., 2000; Beulig et
54 al., 2019; Egger et al., 2018); however CH_4 may also be oxidized anaerobically with nitrate (In’t Zandt et al., 2018), Mn(IV),
55 or Fe(III) (Beal et al., 2009; Sturm et al., 2019).

56 Degradation of OM in marine sediment contributes to the production of dissolved inorganic carbon (DIC) (Table S1: R1–
57 R6). Anaerobic reactions (Table S1: R2–R5) additionally lead to the production of total alkalinity (TA). Methanogenesis
58 itself does not change TA (Table S1: R6); anaerobic CH_4 oxidation, however, increases both DIC and TA (Table S1: R12–
59 R14). Overall, anoxic diagenesis elevates DIC and TA in pore waters relative to seawater (e.g. Chatterjee et al., 2011).
60 Sediments therefore act as internal alkalinity sources to the water column (Chen, 2002; Thomas et al., 2009). This flux may
61 buffer seawater against acidification driven by rising atmospheric $p\text{CO}_2$ (Friedlingstein et al., 2020). Elevated alkalinity also
62 promotes supersaturation with respect to carbonate minerals and favors authigenic carbonate precipitation (Baker and Burns,
63 1985; Jørgensen, 1992). In this way, sediments may constitute a long-term sink for inorganic C (Akam et al., 2020).

64 Porewater alkalinity can be also modified by reoxidation of reduced by-products of OM degradation. Reoxidation consumes
65 alkalinity (Table S1: R7–R11) and lowers pH, promoting CaCO_3 dissolution (Table S1: R17). By contrast, precipitation and
66 preservation of reduced species as authigenic minerals - for example the reaction of sulfide with Fe(III) to form pyrite (Table
67 S1: R15) - yields a net alkalinity gain and favors carbonate precipitation (Mucci et al., 2000; Budrige, 2011). This process is
68 also considered as a long-term sink for both iron and sulfur, because pyrite is thermodynamically stable (Chanton et al.,
69 1987).

70 Sedimentary processes described above have important implications for the carbon cycle and are particularly important in
71 shallow shelf seas with strong benthic-pelagic coupling (Rassmann et al., 2016; Griffiths et al., 2017). The Baltic Sea
72 represents such a system. It is a shallow, semi-enclosed water body with substantial riverine input and pronounced
73 eutrophication. High sedimentation rates and elevated OM supply enhance rates of anaerobic remineralization, producing
74 high concentrations of DIC in subsurface sediments. Relatively low sulfate availability from reduced salinity together with
75 high input of OM promote shallow methanogenesis (Egger et al., 2018) and causes the SMT to shift upward toward the
76 sediment surface (Jilbert et al., 2021). Local fresh groundwater discharge may also influence the progression of these
77 processes by further lowering sulfate availability. In shallow Baltic waters, release of DIC and TA from anoxic sediments
78 can significantly modify water-column chemistry (Gustafsson et al., 2019). Alternatively, precipitation of authigenic
79 carbonates can act as a long-term sedimentary sink for inorganic carbon, which is especially relevant in the Baltic Sea where
80 planktonic calcifiers are largely absent except in the westernmost region (Tyrrell et al., 2008).

81 This study investigates carbonate dynamics in three benthic environments of a continental shelf sea: (1) anoxic sediments
82 dominated by OSR; (2) nearshore sediments with high terrigenous OM input and active methanogenesis; and (3) sediments
83 influenced by groundwater infiltration and pore-water freshening, coupled with methanogenesis.

84 We aim to constrain the biogeochemical controls on DIC and TA production and on authigenic carbonate precipitation. We
85 analyzed pore-water chemistry (DIC, TA, major ions, nutrients), sediment geochemistry (CH_4 , total organic carbon, total
86 nitrogen, total sulfur), and mineralogy (bulk phases and authigenic carbonates and iron sulfides). Stable isotopes of DIC
87 ($\delta^{13}\text{C}$ -DIC), methane ($\delta^{13}\text{C}$ - CH_4 , $\delta^2\text{H}$ - CH_4), and organic matter ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$) were used to trace carbon transformations. Rates
88 of OSR and AOM were determined experimentally. Based on these data, we propose conceptual models of carbon cycling in
89 the three sedimentary environments.

90 **2 Materials and methods**

91 **2.1 Sampling**

92 Sediment and water samples were collected from three stations located in the Gdańsk Basin (southeastern Baltic Sea) at
93 water depths of 50–103 m: ZGG, MET2, and MET1-MP (Fig. S1). Station MET1-MP represents an active deepwater
94 pockmark influenced by both methane seepage and freshwater infiltration. Station MET2 is characterized by shallow
95 methane accumulation without distinct seabed morphology and freshwater infiltration (Jaśniewicz et al., 2019; Brodecka-

96 Goluch et al., 2022). Station ZGG, designated as the reference site, shows no evidence of methane occurrence or freshwater
 97 discharge. Sampling was conducted from RV *Oceanograf* in July 2023 and February 2024. Hydroacoustic surveys were
 98 performed prior to coring using a Reson Teledyne SeaBat 7125 multibeam echosounder, an EdgeTech SB-216S subbottom
 99 profiler, and a Simrad EK80 split-beam echosounder to determine precise sampling locations.

100 Sediment cores were collected with a Rumohr-Lot gravity corer equipped with Plexiglas liners (7.5 cm diameter, 150 cm
 101 length). At each station, seven cores (90–110 cm long) were collected during the July 2023 sampling campaign and an
 102 additional seven cores in February 2024. These cores were used for analyses of: (1) total organic carbon (TOC), total
 103 nitrogen (TN), total sulfur (TS), stable isotopes of organic matter ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$), loss on ignition (LOI), and water content (W);
 104 (2) CH_4 , CO_2 and their stable isotopes ($\delta^{13}\text{C}\text{-CH}_4$, $\delta^{13}\text{C}\text{-CO}_2$, $\delta^2\text{H}\text{-CH}_4$), and oxidation–reduction potential (ORP); (3) pH and
 105 total alkalinity (TA); (4) dissolved inorganic carbon (DIC) and $\delta^{13}\text{C}\text{-DIC}$; (5) sulfate (SO_4^{2-}), chloride (Cl^-), calcium (Ca^{2+}),
 106 magnesium (Mg^{2+}), hydrogen sulfide ($\Sigma\text{H}_2\text{S}$, the sum of H_2S , HS^- and S^{2-}), ammonia (ΣNH_4^+ , the sum of NH_4^+ and NH_3),
 107 phosphate (PO_4^{3-}), manganese (Mn^{2+}) and iron (Fe^{2+}) in pore water; (6) mineralogy and micromorphology; and (7)
 108 experimental rates of organoclastic sulfate reduction (R_{OSR}) and anaerobic oxidation of methane (R_{AOM}).

109 Pore waters were extracted from intact, sealed cores using Rhizon® samplers (0.15 μm pore size). For each core liner, 4 mm
 110 holes matching the Rhizon® sampler fitting were pre drilled at 5 cm intervals and sealed with a tape. After cores retrieval
 111 aboard, the tape was pierced and samplers inserted; to minimize contact with air, cores remained sealed throughout
 112 porewater collection. The uppermost sampler (1–4 cm above the sediment surface, depending on station) collected bottom
 113 water overlying the core. Porewater was drawn into attached 20 cm^3 plastic syringes. To minimize oxidation, all subsequent
 114 subsampling and treatment were performed immediately after porewater sampling. Immediately after extraction, TA, pH,
 115 $\Sigma\text{H}_2\text{S}$, ΣNH_4^+ , and PO_4^{3-} were measured onboard. Samples for major ions, Mn^{2+} , and Fe^{2+} were acidified with HNO_3 . DIC
 116 samples were poisoned with HgCl_2 and stored in sealed, nearly full tubes (<1% headspace) at 4°C. Sampling for carbon
 117 isotopic composition of DIC ($\delta^{13}\text{C}\text{-DIC}$) was carried out in an N_2 glove box; porewater samples were collected into 2 cm^3
 118 septum vials that were filled by injecting porewater with one needle while displacing N_2 through a second needle; vials were
 119 completely filled with porewater and stored at 4°C prior to analysis.

120 For CH_4 analysis, sediment was subsampled through 12-mm holes in the liners and transferred immediately to glass vials
 121 containing 2.5% NaOH, which were sealed with butyl rubber stoppers and aluminum crimp caps (Jørgensen et al., 2001).
 122 NaOH was added to halt microbial activity, preventing biological production or consumption of CH_4 . A headspace was
 123 equilibrated by shaking, and vials were stored caps-down at 4°C until gas chromatographic analysis. Samples for carbon
 124 isotopic composition of methane and carbon dioxide ($\delta^{13}\text{C}\text{-CH}_4$, $\delta^{13}\text{C}\text{-CO}_2$) were collected in the same manner as the CH_4
 125 samples but the procedure was carried out inside an N_2 glove box. Instead of adding NaOH, vials were pre filled with Milli
 126 Q water.

127 Cores designated for solid-phase analyses were sectioned at 5 cm intervals using a PVC ring and plastic spatula; samples
 128 were taken from the central part of each section. Each sample was placed in a separate polyethylene bag. Samples for
 129 microbial analyses were collected from five depth intervals (0–20, 20–40, 40–60, 60–80, and 80–100 cm) using sterile tools.

130 Samples for mineralogical analyses were taken from 10–15, 40–45, and 80–85 cm. All sediment samples were stored at
131 -21°C until analysis.

132 **2.2 Analytical procedures**

133 **2.2.1 Pore-water and bottom-water parameters**

134 Sulfate (SO_4^{2-}) and chloride (Cl^-) concentrations were determined by high-performance ion chromatography (Metrohm 850
135 Professional IC). Calcium (Ca^{2+}), magnesium (Mg^{2+}), manganese (Mn^{2+}), and iron (Fe^{2+}) were measured using inductively
136 coupled plasma–optical emission spectrometry (ICP-OES; PerkinElmer OPTIMA 8300).

137 Concentrations of $\Sigma\text{H}_2\text{S}$, ΣNH_4^+ , and PO_4^{3-} were determined spectrophotometrically (Hach-Lange DR6000). The methylene
138 blue method was applied for $\Sigma\text{H}_2\text{S}$ (Cline, 1969), the indophenol blue method for ΣNH_4^+ , and the molybdenum blue method
139 for PO_4^{3-} (Grasshoff et al., 1999). The limit of quantification (LOQ) was 0.03 mmol dm^{-3} for SO_4^{2-} and $<2.5\text{ }\mu\text{mol dm}^{-3}$ for
140 other major ions. For Mn^{2+} , Fe^{2+} , $\Sigma\text{H}_2\text{S}$, ΣNH_4^+ , and PO_4^{3-} , LOQ values ranged from 0.05 to $1.00\text{ }\mu\text{mol dm}^{-3}$. Analytical
141 precision (RSD) was $\leq 5\%$ for all parameters.

142 DIC concentrations were measured in duplicate using a VarioTOC Cube analyzer (Elementar GmbH) equipped with a
143 nondispersive infrared detector. Samples were acidified in-line with 1% H_3PO_4 , and liberated CO_2 was quantified after
144 purging. Accuracy, based on certified reference material recovery, was 98% . RSD was $\leq 1\%$.

145 Carbon isotopic composition of DIC ($\delta^{13}\text{C}$ -DIC) was determined using a Thermo Delta V plus isotope ratio mass
146 spectrometer coupled to a Thermo GasBench II under continuous helium flow. Samples were reacted with H_3PO_4 for 24 h at
147 25°C . The evolved CO_2 was analyzed for carbon isotope composition. Standards NBS-19, NBS-18 were measured with each
148 analytical series. The assigned $\delta^{13}\text{C}$ values for the standards were: NBS-19 = $+1.95\text{‰}$ and NBS-18 = -5.014‰ (VPDB).
149 Results are reported in δ -notation (‰) relative to Vienna Pee Dee Belemnite (VPDB; Coplen, 2011). Analytical precision
150 was $\pm 0.1\text{‰}$.

151 Total alkalinity (TA) was determined by potentiometric titration with 0.01 M HCl using an automatic titrator (SM-Titrino
152 702, Metrohm). Data were evaluated using the Gran method over pH 4.5–3.5 (10–12 points). pH was monitored with a
153 combined pH/ATC electrode (accuracy ± 0.002 units). The HCl titrant was standardized against certified Na_2CO_3 (Sigma-
154 Aldrich) dissolved in $0.2\text{ mol dm}^{-3}\text{ NaCl}$ to match Baltic Sea ionic strength. Accuracy of TA determination was $\leq 3\text{ }\mu\text{mol kg}^{-1}$.
155 Precision was $\leq 0.2\%$ for standards and $\leq 0.3\%$ for samples.

156 pH was measured spectrophotometrically using m-cresol purple as indicator (Hammer et al., 2014). Precision was $\leq 0.010\%$.
157 Salinity and dissolved oxygen in bottom water were measured with a WTW Multi 3630 IDS multimeter equipped with
158 TetraCon® 925 and FDO® 925 sensors.

159 Methane concentrations were determined by the headspace method using a PerkinElmer gas chromatograph equipped with a
160 flame ionization detector and an HP-5 column ($30\text{ m} \times 0.32\text{ mm} \times 0.25\text{ }\mu\text{m}$). The detection limit was $0.2\text{ }\mu\text{mol dm}^{-3}$.

161 Concentrations were corrected for sediment porosity (ϕ), calculated from water content (W) after Håkanson and Jansson
162 (1983) and Graca (2006):

$$163 \quad \phi = W[(100 - W)d^{-1} + W]^{-1} \quad (1)$$

164 where W is water content (%) and d is wet bulk density (g cm^{-3}):

$$165 \quad d = 260(100 + 1.6(W + IG))^{-1} \quad (2)$$

166 where IG is the loss on ignition (LOI) in percent of wet sediment. LOI was determined after ignition at 450°C to constant
167 mass. Water content was determined by drying at 105°C to constant mass.

168 Carbon isotopic composition of methane and carbon dioxide ($\delta^{13}\text{C-CH}_4$, $\delta^{13}\text{C-CO}_2$) was measured using a Finnigan Delta
169 Plus isotope ratio mass spectrometer coupled via a GC Combustion III interface to an HP 6890 gas chromatograph. After
170 chromatographic separation, CH_4 was oxidized at 980°C to CO_2 in a ceramic reactor containing CuO , Cr_2O_3 , and Pt catalyst.
171 Calibration employed RM8563, NBS 22, NBS 19, and two certified methane standards (Methane #2 and Methane #7,
172 Indiana University). Results are reported in δ -notation (‰) relative to VPDB (Coplen, 2011). Analytical precision was
173 $\pm 0.2\text{‰}$. The detection limit for obtaining reliable $\delta^{13}\text{C}$ data was 0.1% CH_4 . No pre-concentration unit was used.

174 Hydrogen isotopes in methane ($\delta^2\text{H-CH}_4$) were determined using a Delta V Plus mass spectrometer coupled via a Conflo IV
175 GC Isolink interface to a Trace GC Ultra chromatograph. Methane was converted to H_2 at 1420°C in a high-temperature
176 reactor. Calibration used VSMOW2, SLAP-2, GISP, and the methane standards Methane #2 and Methane #7. Results are
177 reported relative to Vienna Standard Mean Ocean Water (VSMOW). Analytical precision was $\pm 3\text{‰}$.

178 2.2.2 Sediment geochemistry and mineralogy

179 Total nitrogen (TN), total sulfur (TS), and total organic carbon (TOC) were determined at the Uranium-Series Laboratory,
180 Institute of Geological Sciences, Polish Academy of Sciences (Warsaw, Poland). Wet sediment samples were homogenized
181 and subsamples were weighted, dried overnight at 50°C, and reweighted (Hedges and Stern, 1984). Prior to analysis,
182 carbonates were removed by treating 400 mg of sediment with 20 cm^3 of 1 M HCl for 24 h at 50°C. Samples were rinsed
183 three times with deionized water, dried at 40–50°C, reweighted and ground in an agate mortar. Approximately 5 mg of
184 homogenized material was sealed in tin capsules and combusted at 1150°C using a Vario MicroCUBE elemental analyzer
185 (Elementar). Evolved CO_2 , N_2 , and SO_2 were separated chromatographically and quantified by thermal conductivity
186 detection. Results were calibrated against sulfanilic acid and reported as wt%. Analytical precision (1σ) was $\pm 0.6\%$ for TOC,
187 $\pm 0.2\%$ for TN, and $\pm 0.4\%$ for TS.

188 Stable carbon and nitrogen isotopes in organic matter ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$) were analyzed at the Stable Isotope Laboratory, Institute
189 of Geological Sciences, Polish Academy of Sciences. Measurements were performed using a Flash 1112 HT elemental
190 analyzer coupled via Conflo IV to a Delta V Advantage isotope ratio mass spectrometer (Thermo Scientific). Samples
191 wrapped in tin foil were combusted at 1020°C. Generated CO_2 and N_2 were purified, chromatographically separated, and
192 introduced into the mass spectrometer. Calibration employed USGS 41a, USGS 40, and IAEA 600 reference materials.

Results are reported in δ -notation (‰) relative to VPDB ($\delta^{13}\text{C}$) and atmospheric N_2 ($\delta^{15}\text{N}$). Analytical precision (1σ) was $\pm 0.1\text{‰}$ for $\delta^{13}\text{C}$ and $\pm 0.3\text{‰}$ for $\delta^{15}\text{N}$. Each sample was analyzed in duplicate, and mean values are reported.

Mineral composition was characterized by powder X-ray diffraction (PXRD), optical microscopy, scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS), ^{57}Fe Mössbauer spectroscopy. PXRD data were collected using a Rigaku SmartLab diffractometer with a graphite monochromator and rotating Cu anode. Samples were ground in ethanol in an agate mortar. Mineral composition was quantified by Rietveld full-pattern X-ray diffraction fitting technique using SIROQUANT analysis of randomly oriented powders. Uncertainty of mineral quantification was estimated from the standard deviations of individual scale factors for each phase and is 0.3 wt.% for pyrite, 0.5 wt.% for dolomite, and 0.4 wt.% for calcite. The $<2\text{ }\mu\text{m}$ clay fraction was analyzed using oriented mounts prepared as air-dried, ethylene glycol-saturated, and heated (550°C) specimens (Moore and Reynolds, 1997).

SEM analyses of powders and thin sections were performed in low-vacuum mode using a FEI Quanta 200 FEG microscope equipped with an EDS system. Undisturbed, air-dried samples of relevant horizons were embedded in Technovit EPOX resin to prepare thin sections. ^{57}Fe Mössbauer spectroscopy measurements were performed at room temperature applying the RENON MsAa-4 spectrometer (Błachowski et al., 2008) equipped with the LND Kr-filled proportional detector and the $^{57}\text{Co}(\text{Rh})$ source. Raman microspectroscopy measurements were performed with a Thermo Scientific DXR Raman Microscope. Spectra were recorded at room temperature using 532 nm diode laser and Olympus ($100\times$) objective lens.

Thermodynamic equilibrium and mineral–water interactions in pore waters were modeled using PHREEQC (version 3.6) with the validated thermodynamic database wateq4f.dat of Parkhurst and Appelo (2013), using the measured pore-water pH (Figure S2) and the measured concentrations of dissolved ions (Figure 2 and 3) as inputs; redox conditions were set from pe values calculated from measured ORP data (Figure S2), and those pe values were subsequently used to calculate dissolved Fe(II) and Fe(III) species.

2.2.3 Dolomite and pyrite burial rates

Dolomite and pyrite burial rates (A ; $\mu\text{mol m}^{-2} \text{d}^{-1}$) were calculated as:

$$A = 10^4 \cdot d \cdot [\text{Conc.}] \cdot \omega \cdot (100 - W)/100^{-1} \quad (3)$$

where d is wet bulk density of sediment (g cm^{-3}), $[\text{Conc.}]$ is mineral concentration ($\mu\text{mol g}^{-1}$ dry weight), ω is linear sedimentation rate (cm d^{-1}), and W is water content (%). Sedimentation rates were 2.06 mm yr^{-1} for MET1-MP, 0.90 mm yr^{-1} for MET2, and 2.01 mm yr^{-1} for ZGG (Zalewska et al., 2020). Burial rates were calculated using mean mineral concentrations for each station. Mineral contents were derived from PXRD data and SEM–EDS elemental distribution maps.

2.2.4 Determination of organoclastic sulfate reduction and anaerobic methane oxidation rates

Rates of organoclastic sulfate reduction (R_{OSR}) and anaerobic oxidation of methane (R_{AOM}) measured in the present study represent potential rates. Incubations were conducted without substrate limitation and thus reflect the maximum metabolic capacity of the microbial community.

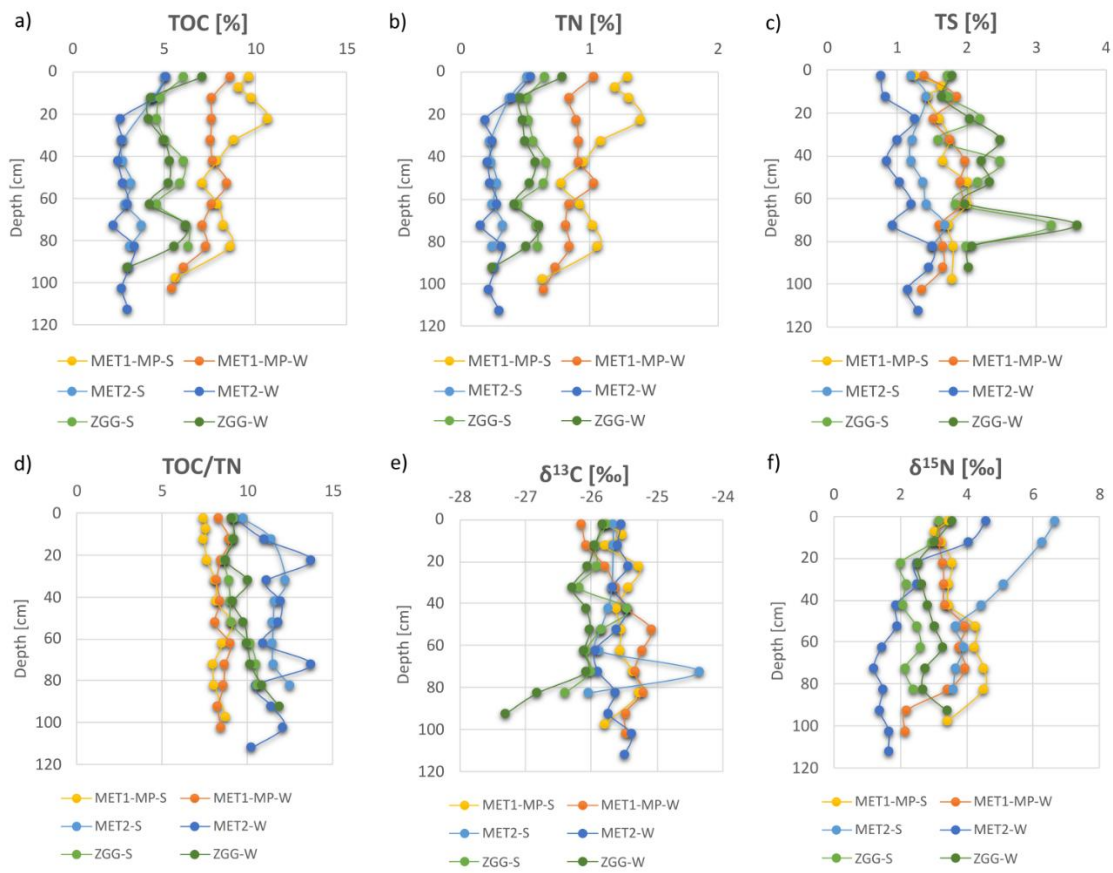
For determination of OSR, 10 cm³ of sediment was mixed with 30 cm³ of sterile seawater amended with 1% sodium lactate. Lactate was added as an electron donor during sample pre-treatment to ensure that measured H₂S production primarily reflected OSR. From this slurry, 1 cm³ aliquots (in duplicate) were transferred to incubation cuvettes. Each aliquot was amended with 0.5 cm³ Na₂SO₄ solution to obtain five substrate concentrations (0–0.1 mol dm⁻³). Incubations were conducted for 12–14 h at 20°C. For AOM, 2 cm³ of sediment was placed in sterile 20 cm³ glass flasks sealed with septum caps. Each flask was injected with 1 cm³ of ¹³C-labeled CH₄ (99 atom% ¹³C; Sigma-Aldrich). Parallel incubations without added substrate were performed to determine basal activity. Incubations lasted 70–76 h at 20°C and were terminated by adding 0.2 cm³ of tenfold-diluted HgCl₂. To analyze sulfate reduction microbial activity, sulfide concentrations were determined spectrophotometrically using N,N-Dimethyl-p-phenyl-enediamine sulfate salt (98%, SigmaAldrich), and the Michaelis–Menten relationship was plotted. For AOM, produced CO₂ was analyzed using a Delta Plus Finnigan isotope ratio mass spectrometer coupled to a Hewlett Packard 6890 gas chromatograph equipped with a Chrompack packed column (27.5 m × 0.32 mm). Helium (>99.999%) was used as the carrier gas at a constant flow rate of 2 cm³ min⁻¹. The oven temperature was programmed from 27°C to 60°C at 5°C min⁻¹. Headspace gas (0.1 cm³) was injected with a split ratio of 1:80. A 0.2% ¹³C-labeled CO₂ standard was used for calibration.

3 Results

3.1 Distribution of TOC, TN, and TS and stable isotopic composition of carbon (δ¹³C) and nitrogen (δ¹⁵N) in sedimentary organic matter

OM content is highest in surface sediments (0–20 cm) at all stations (Fig. 1). TOC correlates positively with TN (Fig. 1a, b), indicating that nitrogen is predominantly associated with organic matter. TOC ranges from 2.8 to 10.7 wt%, TN from 0.2 to 1.4 wt%, and TS from 0.8 to 3.6 wt% (Fig. 1a–c). The molar TOC:TN ratio varies between 7.4 and 13.7 (Fig. 1d). The highest OM contents occur at station MET1-MP. TOC ranges from 5.5 to 10.7 wt%, and TN from 0.6 to 1.4 wt%. This station also shows the strongest downcore variability. The lowest OM contents are observed at MET2, with similar values in both seasons. TOC ranges from 2.5 to 5.0 wt% and TN from 0.2 to 0.5 wt%. Station ZGG exhibits intermediate values. TOC ranges from 3.0 to 6.3 wt% and TN from 0.3 to 0.8 wt%. TS contents exceed 1 wt% at most depths (Fig. 1c). The highest average TS (2.2 wt%) occurs at ZGG. Maximum values (≥3.2 wt%) are recorded at 70–75 cm in both seasons. The lowest average TS (1.2 wt%) occurs at MET2. At MET1-MP, mean TS is 1.7 wt%. The TOC:TN ratio at MET1-MP ranges from 7.4 to 9.1. At ZGG, values range from 8.7 to 11.9. The highest ratios occur at MET2 (9.3–13.7). Sediment oxidation–reduction potential (ORP) ranges from –502 to –5 mV. The highest values occur in surface layers (Fig. S2). Loss on ignition (LOI) ranges from 5.5 to 20.2 wt% (Fig. S2). Values are highest at MET1-MP (13.5–20.2 wt%), intermediate at ZGG (6.5–14.4 wt%), and lowest at MET2 (5.5–10.5 wt%). Water content (W) follows a similar pattern (Fig.

257 S2). The highest values occur at MET1-MP (67.4–97.7%). At ZGG, W ranges from 66.0 to 90.6%. At MET2, W ranges
 258 from 50.4 to 79.5%.
 259 The isotopic composition of organic carbon ($\delta^{13}\text{C}$) ranges from -27.3 to -24.4‰ , and that of nitrogen ($\delta^{15}\text{N}$) from 1.2 to
 260 6.7‰ (Fig. 1e, f). The lowest $\delta^{13}\text{C}$ values occur at station ZGG in both seasons. The highest values are observed at MET2 in
 261 summer. The largest $\delta^{13}\text{C}$ variability ($\sim 1.5\text{‰}$) is recorded at ZGG (-27.3 to -25.5‰) and MET2 (-26.0 to -24.4‰). At
 262 MET1-MP, $\delta^{13}\text{C}$ varies within a narrower range ($<1\text{‰}$), from -26.2 to -25.2‰ . The greatest $\delta^{15}\text{N}$ variability occurs at
 263 MET2 (1.2 – 6.7‰). At this station, deeper sediments are depleted in ^{15}N relative to surface layers. The depletion reaches
 264 $\sim 3\text{‰}$ in the deepest intervals. At MET1-MP and ZGG, $\delta^{15}\text{N}$ varies over a narrower range (2.0 – 4.5‰).
 265



266
 267
 268 **Figure 1: Depth distribution of total organic carbon (TOC), total nitrogen (TN), and total sulfur (TS), molar TOC:TN ratio, and**
 269 **stable isotopic composition of carbon ($\delta^{13}\text{C}$) and nitrogen ($\delta^{15}\text{N}$) in sedimentary organic matter at the reference station (ZGG), the**
 270 **methane-influenced station (MET2), and the station affected by both methane and freshwater discharge (MET1-MP). Data are**
 271 **shown for summer 2023 (S) and winter 2024 (W).**

272 3.2 Composition of pore water and bottom water

273 Results from summer and winter show that spatial differences among stations exceed seasonal variability (Figs. 2, 3). Depth
274 profiles of major ions (Cl^- , SO_4^{2-} , Ca^{2+} , Mg^{2+}) are shown in Fig. 2. The concentration of Cl^- ranges from 70.30 mmol dm^{-3} to
275 180.40 mmol dm^{-3} , SO_4^{2-} from 0.03 mmol dm^{-3} to 9.23 mmol dm^{-3} , Ca^{2+} from 2.52 mmol dm^{-3} to 4.84 mmol dm^{-3} , while
276 Mg^{2+} from 8.34 mmol dm^{-3} to 18.37 mmol dm^{-3} .

277 Major-ion concentrations in bottom water and surface-most sediments reflect salinity. Salinity is highest at ZGG (12.2 in
278 summer; 12.1 in winter) and lowest at MET2 (8.0 in summer; 7.5 in winter). At MET2, Cl^- , Ca^{2+} , and Mg^{2+} remain nearly
279 constant with depth. In contrast, these ions decrease markedly with depth at MET1-MP. At ZGG, Ca^{2+} increases significantly
280 downcore. Sulfate remains relatively high ($\geq 3.5 \text{ mmol dm}^{-3}$) throughout the ZGG profile. At MET1-MP and MET2, sulfate
281 is restricted to the upper 30–40 cm.

282 $\Sigma\text{H}_2\text{S}$ reaches maximum concentrations at ZGG (up to 2026 $\mu\text{mol dm}^{-3}$). At MET1-MP and MET2, $\Sigma\text{H}_2\text{S}$ ranges from
283 <LOQ to 1783 $\mu\text{mol dm}^{-3}$ and is confined to discrete sediment intervals (Fig. 2e), corresponding to zones of sulfate-
284 dependent methane oxidation. Bottom waters at MET2 are oxic (3.1 $\text{mg dm}^{-3} \text{ O}_2$ in summer; 5.9 mg dm^{-3} in winter). At ZGG
285 and MET1-MP, O_2 concentrations are <0.2 mg dm^{-3} in summer and <1.7 mg dm^{-3} in winter.

286 Pore-water Fe^{2+} concentrations are generally <30 $\mu\text{mol dm}^{-3}$ (Fig. 2h). Elevated values occur only at MET1-MP, reaching
287 139.3 $\mu\text{mol dm}^{-3}$ below 60 cm in summer. Mn^{2+} concentrations range from <LOQ to 51.6 $\mu\text{mol dm}^{-3}$, with highest values at
288 ZGG (Fig. 2g).

289 ΣNH_4^+ ranges from 22.2 to 3794.9 $\mu\text{mol dm}^{-3}$. PO_4^{3-} ranges from 1.4 to 950.2 $\mu\text{mol dm}^{-3}$. Both species attain maximum
290 concentrations at MET1-MP (Fig. 3d, e). At ZGG and MET2, concentrations are lower, ranging from 22.2 to 2027.0 μmol
291 dm^{-3} for ΣNH_4^+ and from 1.4 to 361.1 $\mu\text{mol dm}^{-3}$ for PO_4^{3-} .

292 The pH at all sampling sites was from 7.00 to 8.31, with an average of 7.57 ± 0.21 at station MET1-MP, 7.66 ± 0.26 at station
293 MET2, and 7.57 ± 0.20 at station ZGG (Fig. S2).

294 The TA in the pore water varied in the range of 1911.3–32747.2 $\mu\text{mol kg}^{-1}$. Overall, the highest TA in pore waters was found
295 in the sediment of pockmark MET1-MP, while the lowest values were observed at ZGG, similarly to DIC, which is the main
296 component of TA in seawater (Fig. 3a).

297 DIC concentrations range from 1851 to 33,323 $\mu\text{mol kg}^{-1}$ (Fig. 3b). The highest values occur at MET1-MP. The lowest
298 concentrations and the smallest downcore variability are observed at the non-methane station ZGG.

299 The $\delta^{13}\text{C}$ -DIC values range from -16.2‰ to 17.3‰ (Fig. 3c). At ZGG, $\delta^{13}\text{C}$ -DIC remains negative throughout the profile. At
300 MET2, negative values are restricted to the upper ~25 cm, whereas deeper layers show positive values. At MET1-MP, $\delta^{13}\text{C}$ -
301 DIC exhibits limited variability. Negative values occur only in the surface layer (0–5 cm) during summer.

302

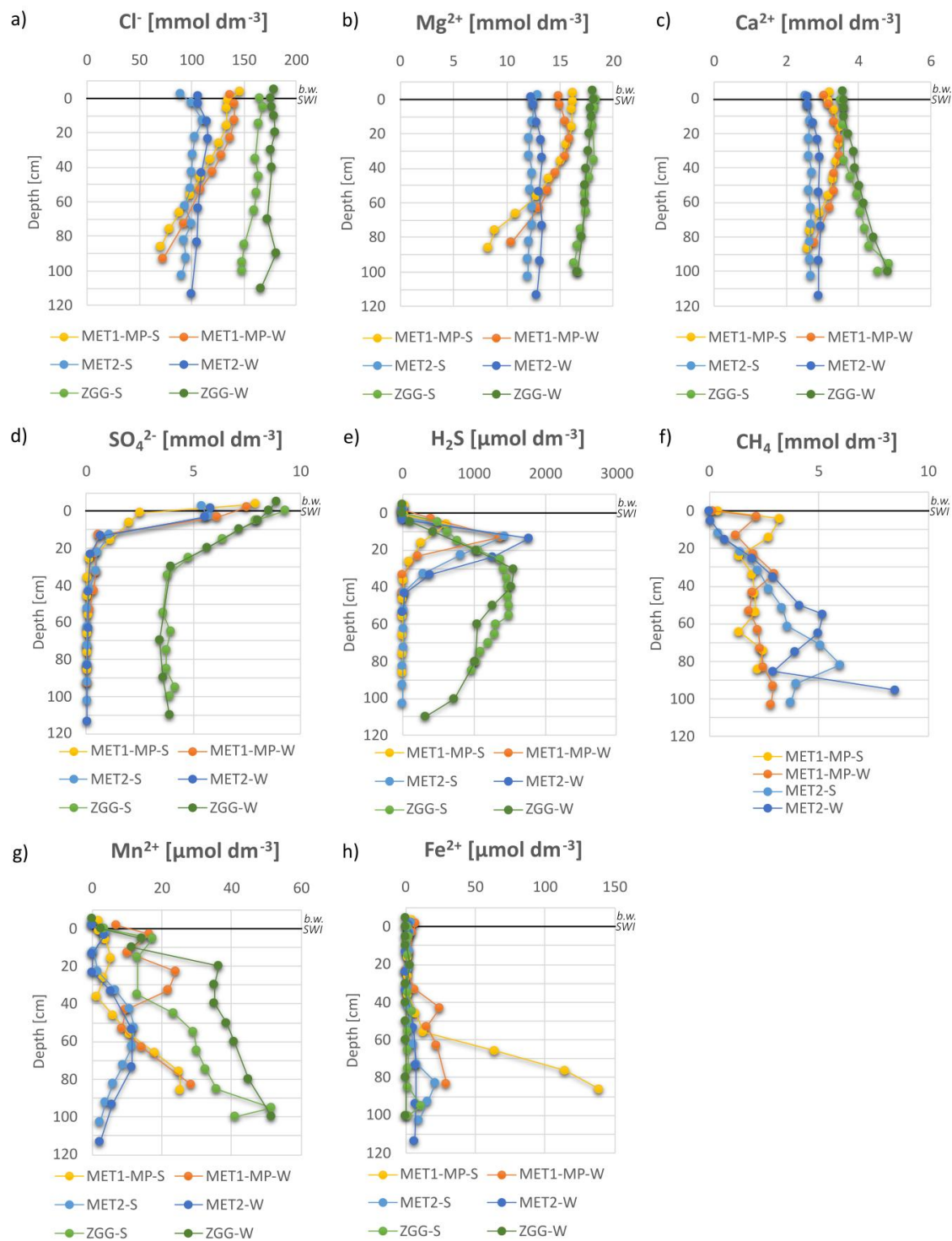


Figure 2: Concentrations of (a) chloride, (b) magnesium, (c) calcium, (d) sulfate, (e) hydrogen sulfide, (f) methane, (g) manganese, and (h) iron in bottom water (b.w.) and pore water at the reference station (ZGG), the methane-influenced station (MET2), and

the station affected by both methane and freshwater discharge (MET1-MP) during summer 2023 (S) and winter 2024 (W). SWI denotes the sediment–water interface.

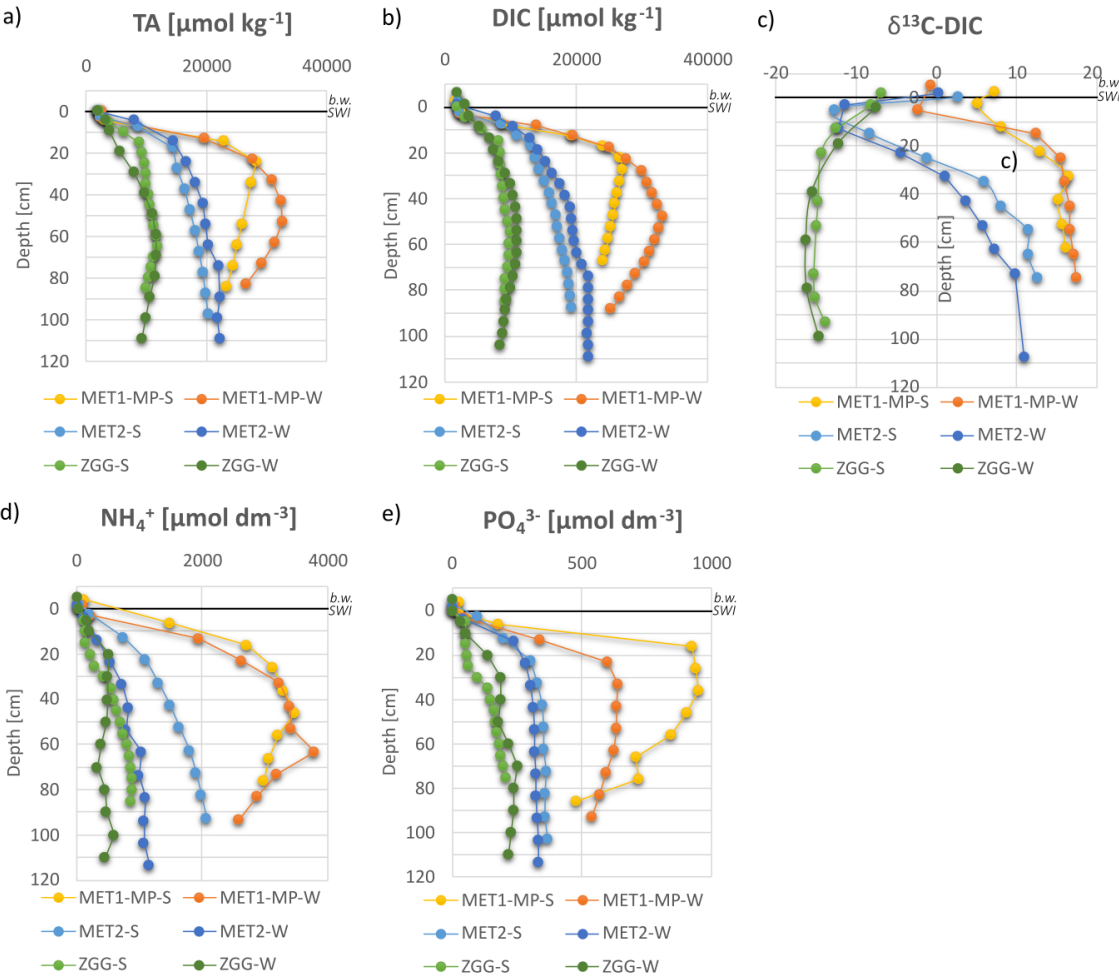


Figure 3: Total alkalinity (TA) (a), dissolved inorganic carbon (DIC) (b), stable carbon isotopic composition of DIC ($\delta^{13}\text{C-DIC}$) (c), ammonium (d), and phosphate (e) concentrations in bottom water (b.w.) and pore waters. Labels as in Fig. 2.

3.3 Methane concentration and stable C and H isotopes in gases

Methane concentrations at MET1-MP range from 0.17 to 3.24 mmol dm⁻³, and at MET2 from <LOQ to 8.49 mmol dm⁻³ (Fig. 2f). At MET1-MP, maximum CH₄ concentrations occur near the sediment surface (~5 cm bsf). Concentrations decrease with depth and stabilize at ~2 mmol dm⁻³. At MET2, CH₄ increases progressively with depth and reaches a maximum at ≤80 cm bsf. Methane is not detected at ZGG.

Depth profiles of $\delta^{13}\text{C-CH}_4$, $\delta^2\text{H-CH}_4$, and $\delta^{13}\text{C-CO}_2$ at MET1-MP and MET2 are shown in Fig. S3. At MET1-MP, $\delta^{13}\text{C-CH}_4$ ranges from -62.6 to -55.8‰. At MET2, values are lower, from -76.6 to -69.6‰. The $\delta^2\text{H-CH}_4$ values range from -271 to

319 -257‰ at MET1-MP and from -250 to -239‰ at MET2. At MET2, $\delta^{13}\text{C-CO}_2$ remains negative throughout the profile
320 (-8.1 to -2.6‰). At MET1-MP, $\delta^{13}\text{C-CO}_2$ ranges from -1.0 to 5.7‰ and is predominantly positive, except in the surface
321 layer and at ~90 cm bsf.

322 **3.4 Rate of organoclastic sulfate reduction and anaerobic methane oxidation**

323 The measured rates of organoclastic sulfate reduction (R_{OSR}) and anaerobic oxidation of methane (R_{AOM}) presented in
324 Table 1 represent the maximum metabolic capacity of the microbial community (potential rates); incubations were
325 conducted without substrate limitation and therefore reflect relative microbial activity between samples rather than absolute
326 in situ rates.

327 R_{OSR} ranges from 15 to 164 $\mu\text{mol dm}^{-3} \text{ d}^{-1}$ (Table 1). At ZGG, values range from 24 to 46 $\mu\text{mol dm}^{-3} \text{ d}^{-1}$. At MET2, rates
328 vary between 21 and 48 $\mu\text{mol dm}^{-3} \text{ d}^{-1}$. The highest variability occurs at MET1-MP (16–163 $\mu\text{mol dm}^{-3} \text{ d}^{-1}$). At MET1-MP
329 and MET2, maximum rates are observed in the 0–20 cm interval. At ZGG, the highest R_{OSR} occurs at 20–40 cm depth.

330 R_{AOM} ranges from 6 to 1077 $\mu\text{mol dm}^{-3} \text{ d}^{-1}$. At MET1-MP, rates are elevated throughout the profile (59–1077 $\mu\text{mol dm}^{-3} \text{ d}^{-1}$).
331 Maximum values occur at 40–60 cm and 80–100 cm depth (Table 1). At MET2, R_{AOM} is lower (6–33 $\mu\text{mol dm}^{-3} \text{ d}^{-1}$) and is
332 concentrated in surface sediments. At ZGG, rates are relatively uniform with depth (8–10 $\mu\text{mol dm}^{-3} \text{ d}^{-1}$). Additional raw
333 data concerning the determination of OSR and AOM are provided in the Supplementary Materials (Tables S2 and S3).

334

335 **Table 1: Organoclastic sulfate reduction (R_{OSR}) and anaerobic methane oxidation (R_{AOM}) rates (mean of two replicates), and the**
336 **corresponding DIC production calculated from the stoichiometry of OSR (R_1) and AOM (R_3), at the reference station (ZGG), the**
337 **methane-influenced station (MET2), and the station affected by both methane and freshwater discharge (MET1-MP).**
338

Station	Sediment layer	R_{OSR}	R_{AOM}	Depth integrated rates			
				R_{OSR}	$R_{\text{DIC-OSR}}$	R_{AOM}	$R_{\text{DIC-AOM}}$
	[cm]	[$\mu\text{mol dm}^{-3} \text{ d}^{-1}$]		[$\text{mmol m}^{-2} \text{ d}^{-1}$]			
MET1-MP	0-20	164	95				
	20-40	23	106				
	40-60	15	1077	29	58	331	331
	60-80	16	59				
	80-100	18	731				
MET2	0-20	21	33				
	20-40	48	6				
	40-60	36	7	29	59	9	9
	60-80	31	9				
	80-100	42	8				
ZGG	0-20	24	10				
	20-40	46	9				
	40-60	25	10	27	54	7	7
	60-80	34	9				
	80-100	33	8				

339

340 Depth-integrated R_{OSR} and R_{AOM} (0–100 cm) and the corresponding DIC production are summarized in Table 1. DIC
341 production from OSR is comparable among stations. In contrast, MET1-MP exhibits exceptionally high R_{AOM} and associated
342 DIC production, exceeding values at the other stations by two orders of magnitude. The lowest process rates and DIC
343 production occur at ZGG.

344 **3.5 Mineralogy**

345 The studied sediments are fine-grained (Brodecka et al., 2013) and classified as silt (MET1-MP), sandy silt (MET2), and
346 clayey silt (ZGG). They are dominated by a matrix composed of clay minerals, biogenic silica, and organic matter (Fig. S5).
347 This matrix constitutes ~20–50 vol% of the sediment and generally increases with depth. At MET1-MP it ranges from 30 to
348 54%, at MET2 from 20 to 39%, and at ZGG from 36 to 53%.

349 Detrital aluminosilicates (mainly quartz, feldspars, and micas) occur as dispersed grains within this matrix. Their proportion
350 remains relatively constant at MET2 (~30–35%) but decreases with depth at MET1-MP (13 to 8%) and ZGG (24 to 13%).

351 PXRD analyses of bulk samples (Fig. S6) and clay fractions (Fig. S7) indicate that phyllosilicates are dominated by
352 mica/illite, chlorite, and kaolinite. A ~17 Å reflection in glycolated samples that disappears upon heating indicates mixed-
353 layer illite–smectite. The position of the (060) reflection is consistent with dioctahedral phyllosilicates (Moore and Reynolds,
354 1997). Microscopy also reveals glauconite, an Fe-rich mica-group mineral. It occurs sporadically at MET1-MP and MET2
355 and is more common at ZGG.

356 Authigenic carbonates and sulfides are minor components (< several wt%; Table 2). Pyrite (FeS_2) is the dominant sulfide. It
357 occurs as isolated euhedral crystals (cubic or octahedral, $\leq 1 \mu m$) or as framboids with diameters of a few to ~20 μm (Fig. 4).
358 Irregular framboidal aggregates also occur. Pyrite framboids are commonly associated with diatom frustules or organic-rich
359 domains. Microscopy and PXRD indicate higher average pyrite contents at ZGG than at MET1-MP and MET2 (Table 2).

360

361 **Table 2: Dolomite and pyrite contents in sediments (range and mean values determined by PXRD and SEM–EDS elemental**
362 **mapping) and corresponding burial rates. Burial rates are reported as mean values (based on PXRD and SEM–EDS) and as**
363 **ranges derived from both methods within a 10–85 cm sediment column.**

364

Station	Dolomite (PXRD)	Dolomite (SEM)	Pyrite (PXRD)	Pyrite (SEM)	Dolomite burial rate		Pyrite burial rate	
					wt%		$\mu mol m^{-2} d^{-1}$	
MET1-MP	2.9–4.9 (3.9)	3.9–12.2 (7.2)	3.7–7.2 (5.9)	1.8–11.6 (6.8)	XRD: 484±13 SEM: 888±87 (467–994)		XRD: 556±18 SEM: 640±153 (453–828)	
MET2	0.0–2.9 (2.0)	0.1–8.1 (4.0)	2.3–5.6 (3.5)	2.5–18.9 (8.0)	XRD: 254±58 SEM: 517±7 (184–525)		XRD: 341±5 SEM: 785±4 (334–789)	
ZGG	0.0–1.4 (0.4)	0.0–4.6 (0.8)	5.4–9.4 (7.4)	2.3–21.7 (10.5)	XRD: 60±35 SEM: 136±110 (1–271)		XRD: 959±16 SEM: 1341±87 (940–1447)	

365

366 Dolomite [$\text{CaMg}(\text{CO}_3)_2$] is the predominant carbonate phase. Its presence is indicated by the 2.88 Å reflection in PXRD
367 patterns (Fig. S6). Due to low concentrations, unambiguous interpretation is not possible because diffraction peaks (101),
368 (015) and (021) indicative of space group of dolomite (Gregg et al., 2015; Lukoczki et al., 2026) are not apparent. However,
369 SEM–EDS analyses (Fig. S8) show near-equimolar Ca and Mg, consistent with dolomite rather than high-Mg calcite. Also
370 Raman microspectroscopy of carbonate crystals revealed typical dolomite (and not Mg-calcite) features (Fig. S9): strong
371 sharp bands at 1100 cm^{-1} (symmetric stretching), 305 cm^{-1} (librational mode), and 180 cm^{-1} (translational mode), as well as
372 weak bands at 730 cm^{-1} and 1445 cm^{-1} , related to in-plane bending and asymmetric stretching, respectively (Sun et al., 2014,
373 Zheng et al., 2021, Alves et al., 2023). Comparison of the Raman spectra with that of proper dolomite (Rędziny quarry,
374 Southern Poland, Kowalski et al., 1976) indicates that the band broadening (Sun et al., 2014, Zheng et al., 2021) that should
375 be associated with structural disorder (expected in protodolomite and high-Mg calcite) does not occur, as the band half-
376 widths are of the same order as for crystalline dolomite (Fig. S9b). Moreover, euhedral to subhedral rhombohedral habits are
377 typical for authigenic dolomite (Fig. 4), and not nanocrystalline aggregates characteristic of protodolomite (Liu et al., 2020,
378 Zheng et al., 2021). Therefore, despite the lack of unambiguous PXRD evidence, both the chemical composition,
379 morphology, and Raman features suggest that the dominant carbonate in the sediments is dolomite.

380 Dolomite is most abundant at MET1-MP, slightly less abundant at MET2, and nearly absent at ZGG (Table 2). At MET1-
381 MP, dolomite forms euhedral crystals several to $\sim 20\text{ }\mu\text{m}$ in size (Fig. 4). At MET2, both fine ($<20\text{ }\mu\text{m}$) euhedral or subhedral
382 crystals and larger subhedral to anhedral grains occur. The euhedral/subhedral morphology of many of the crystals indicates
383 that they are authigenic. At ZGG, small ($5\text{--}10\text{ }\mu\text{m}$) subhedral to anhedral grains are restricted to the subsurface layer ($10\text{--}15$
384 cm).

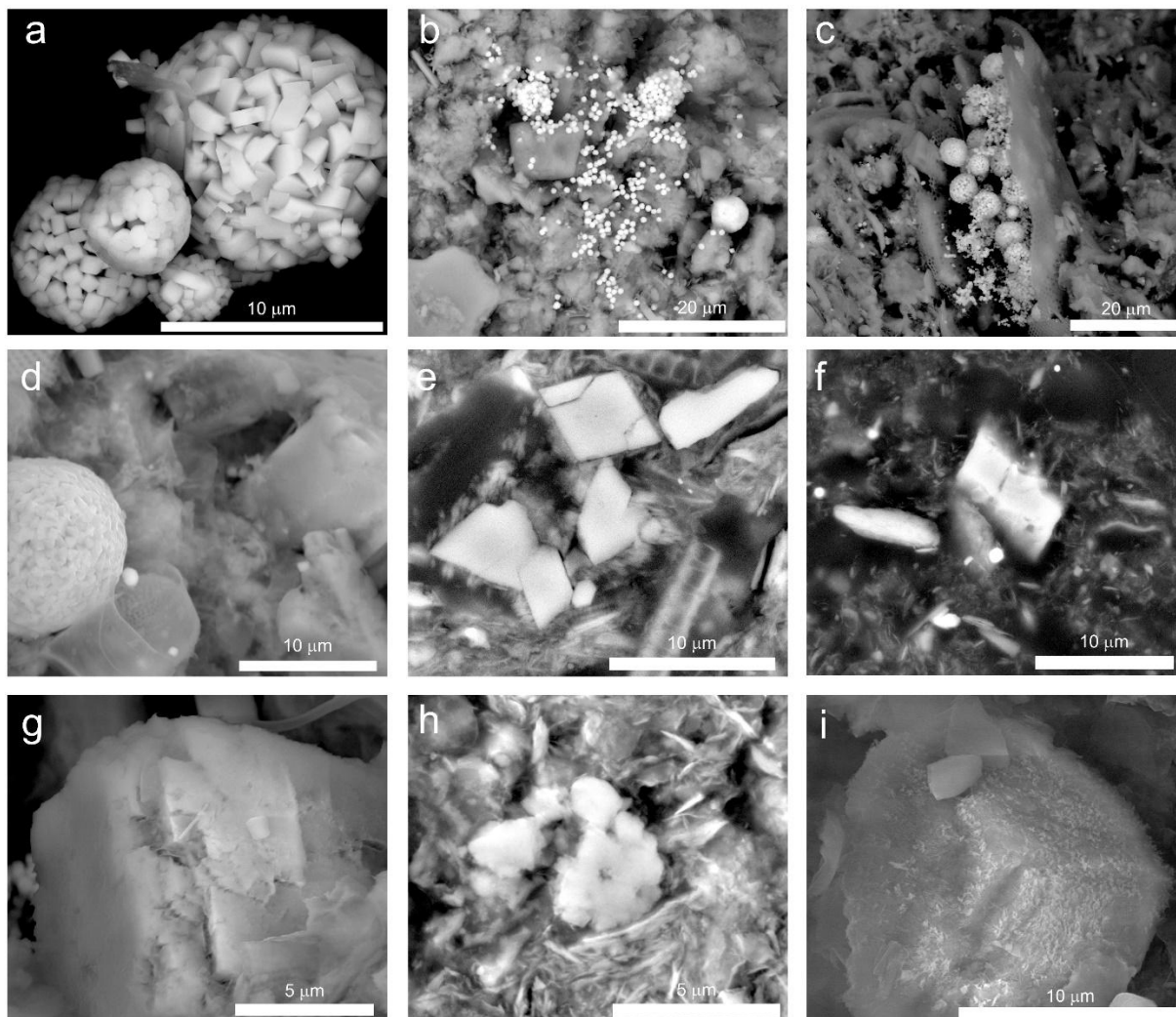


Figure 4: Examples of SEM-BSE images of authigenic sulfides and carbonates: (a) pyrite framboids, MET2 (40–45 cm); (b) pyrite framboid and disseminated pyrite crystals, ZGG (10–15 cm); (c) pyrite framboids within a diatom shell, ZGG (40–45 cm); (d) pyrite framboid, diatom, dolomite, MET1-MP (40–45 cm); (e) euhedral and subhedral dolomite crystals, MET1-MP (10–15 cm; thin section); (f) euhedral dolomite, MET1-MP (10–15 cm; thin section); (g) dolomite, MET1-MP (40–45 cm); (h) calcite surrounded by clay minerals, ZGG (40–45 cm; thin section); (i) siderite, MET2 (40–45 cm)

All sediments contain trace amounts of calcite (CaCO_3), occurring as fine ($<10\ \mu\text{m}$) subhedral grains (Fig. 4h). Isolated euhedral siderite (FeCO_3) crystals were identified only at MET2 (Fig. 4i).

All Mössbauer spectra (Fig. S10; Table S4) are similar and dominated by Fe(II) components. The principal doublet, comprising ~50–60% of the spectral area, exhibits an isomer shift (IS) of $\sim 0.3\ \text{mm s}^{-1}$ and quadrupole splitting (QS) of $\sim 0.6\ \text{mm s}^{-1}$. These parameters are characteristic of Fe(II) in pyrite (Byrne and Kappler, 2019). Two additional doublets contribute ~25–30% of the spectral area. They display high IS and QS values typical of Fe(II) in silicates (Dyar et al. 2006), although

398 those of the minority doublet are also similar to Fe(II) in siderite (Rothwell et al., 2025). A further doublet, accounting for
399 ~10–28% of the spectral area, shows relatively low IS (~0.4–0.6 mm s⁻¹) and moderate QS (~0.7–0.9 mm s⁻¹). These
400 parameters indicate high-spin Fe(III) in octahedral coordination. The precise mineral host of this component cannot be
401 resolved. The hyperfine parameters are consistent with paramagnetic Fe(III) oxyhydroxides at room temperature (Byrne and
402 Kappler, 2019). However, Fe(III) incorporated in phyllosilicates such as micas/illite, chlorites, or glauconite is also plausible
403 (De Grave et al., 1987).

404 **3.6 Burial rate of dolomite and pyrite**

405 Carbonate burial rates were calculated using dolomite contents, as dolomite is the dominant carbonate phase. Pyrite burial
406 rates were also determined due to pronounced inter-station variability. The highest dolomite burial occurs at MET1-MP
407 (Table 2). Rates are $484 \pm 13 \mu\text{mol m}^{-2} \text{d}^{-1}$ based on PXRD and $888 \pm 87 \mu\text{mol m}^{-2} \text{d}^{-1}$ based on SEM-EDS. Intermediate
408 values are observed at MET2 (254 ± 58 and $517 \pm 7 \mu\text{mol m}^{-2} \text{d}^{-1}$, respectively). The lowest rates occur at ZGG (60 ± 35
409 $\mu\text{mol m}^{-2} \text{d}^{-1}$ from PXRD and $136 \pm 110 \mu\text{mol m}^{-2} \text{d}^{-1}$ from SEM-EDS). In contrast, pyrite burial is highest at ZGG. Rates
410 reach $959 \pm 16 \mu\text{mol m}^{-2} \text{d}^{-1}$ (PXRD) and $1341 \pm 87 \mu\text{mol m}^{-2} \text{d}^{-1}$ (SEM-EDS). At MET1-MP, values are 556 ± 18 and $640 \pm$
411 $153 \mu\text{mol m}^{-2} \text{d}^{-1}$, respectively. At MET2, pyrite burial rates are $341 \pm 5 \mu\text{mol m}^{-2} \text{d}^{-1}$ (PXRD) and $785 \pm 4 \mu\text{mol m}^{-2} \text{d}^{-1}$
412 (SEM-EDS).

413 **4 Discussion**

414 **4.1 Typical anoxic sediment dominated by organoclastic sulfate reduction as the primary pathway of organic matter** 415 **decomposition (station ZGG)**

416 Nutrient enrichment associated with intensified fertilizer application has promoted widespread coastal eutrophication.
417 Elevated nitrogen and phosphorus inputs stimulate primary production and increase the flux of OM to the seafloor. Enhanced
418 organic carbon delivery raises sedimentary oxygen demand and promotes hypoxia and anoxia in bottom waters (Rabalais et
419 al., 2010). These effects are amplified under strong density stratification, which limits vertical mixing and oxygen
420 replenishment from surface layers (Carstensen et al., 2014). Under anoxic conditions, sulfate reduction becomes the
421 dominant mineralization pathway, leading to hydrogen sulfide accumulation in bottom water.

422 Station ZGG, located in the western Gdańsk Deep in the southern Baltic Sea (Fig. S1), represents such an environment. The
423 seafloor is covered by fine-grained sediments with mean water and OM contents of 76% and 11%, respectively,
424 characteristic of an accumulation bottom type (Jönsson et al., 2005). TOC and TN values fall within the range typical for
425 deep Baltic sediments (Uścinowicz, 2011). Maximum concentrations occur in the uppermost centimeters (Fig. 1a, b),
426 reflecting enhanced eutrophication.

427 The molar TOC:TN ratio ranges from 8.5 to 11.8, exceeding typical marine values of 4–8 and indicating a contribution of
428 terrestrial OM, for which TOC:TN commonly exceeds 12 (Meyers, 1997; Carneiro et al., 2021; Yadav et al., 2025). Carbon

isotopic compositions further support this interpretation. $\delta^{13}\text{C}$ values at ZGG range from -27.3‰ to -25.5‰ (Fig. 1e). These values are more negative than those of marine phytoplankton (-18‰ to -24‰ ; Yadav et al., 2025) and typical mid-latitude marine OM (-22‰ to -20‰ ; Meyers, 1994), and fall within the range characteristic of terrestrial C_3 plants (-35‰ to -25‰ ; average $\sim -27\text{‰}$). The combined TOC:TN and $\delta^{13}\text{C}$ data indicate a significant input of vascular plant-derived organic carbon, which is carbon-rich and isotopically depleted relative to marine primary production (Meyers, 1994, 1997), in all the studied sediments. Riverine discharge is a major source of terrestrial carbon, contributing up to 10–30% of the total carbon pool in Baltic sediments (Miltner and Emeis, 2001). Nitrogen isotopic compositions ($\delta^{15}\text{N} = 2.0\text{--}3.6\text{‰}$; Fig. 1f) are at or slightly below the typical range for marine OM (3–12‰; Maksymowska et al., 2000; Wada and Hattori, 1991). In contrast, terrestrial C_3 plants exhibit a broader range (-10‰ to $+10\text{‰}$). The relatively low $\delta^{15}\text{N}$ values at ZGG therefore further support a substantial allochthonous contribution. Increased biomass development may also lead to a modification of the isotopic composition of both nitrogen and carbon in sediments, the effect of which may also be visible in the case described. For example, a decrease in the $\delta^{15}\text{N}$ value of OM can be caused by the addition of isotopically light nitrogen to the N pool, bound by diazotrophic cyanobacteria, as in the case described by Struck et al. (2000) for the Gotland Basin. In turn, increased primary production can lead to an increase in ^{13}C content in sediment organic matter. For example, in the Oder Haff an increase of $\delta^{13}\text{C}$ in OM of 1.7 ‰ was found, while in the Gotland Basin it was 2.6 ‰ (Struck et al. 2000). Sediments at ZGG are also characterized by elevated TS contents (1.59–3.58 wt%; Fig. 1c). The TOC:TS ratio provides insight into depositional redox and salinity conditions (Berner et al., 1979; Berner and Raiswell, 1984). A ratio of 2.8 ± 0.4 is typical of normal marine sediments underlying oxygenated waters (Berner, 1982). Lower values indicate enhanced sulfide formation under anoxic conditions, whereas $\text{TOC:TS} > 2.8$ is characteristic of freshwater environments. The mean TOC:TS ratio at ZGG (2.5 ± 0.6) is slightly lower below the marine oxic benchmark. This suggests suboxic to anoxic depositional conditions, controlled by substantial water depth, persistent stratification, and bottom-water oxygen depletion. In the uppermost centimeters, pore-water composition closely resembles that of bottom water (Fig. 2). With increasing depth, diagenetic processes progressively modify the chemical composition. Sulfate concentrations decrease rapidly within the upper ~30 cm and stabilize at $\sim 3.5 \text{ mmol dm}^{-3}$ in deeper layers (Fig. 2d). In parallel, H_2S concentrations increase (Fig. 2e), reflecting active microbial sulfate reduction. Concentrations of NH_4^+ , PO_4^{3-} , DIC, and TA also increase with depth (Fig. 3), indicating that a common mineralization process supplies these components to pore waters. Sulfate can be consumed during both OSR (Table S1: R5) and AOM (Table S1: R14). Although methanogenesis and AOM may occur deeper in the sediment at ZGG, sulfate remains relatively abundant throughout the studied profile, and CH_4 concentrations are below LOQ (Fig. 2f). These observations indicate that sampling captured the sulfate reduction zone above the sulfate–methane transition (SMT). This interpretation is consistent with the inhibitory effect of sulfate on methanogenesis, as sulfate-reducing microorganisms outcompete methanogens for H_2 and acetate (Reeburgh, 2007). The $\delta^{13}\text{C}$ -DIC profile further supports this conclusion. $\delta^{13}\text{C}$ -DIC values decrease with depth (Fig. 3c), whereas methanogenesis typically increases $\delta^{13}\text{C}$ -DIC due to preferential removal of ^{12}C into CH_4 (Whiticar, 1999). Moreover, DIC and $\delta^{13}\text{C}$ -DIC exhibit a strong linear correlation ($R^2 = 0.98$), and no $\delta^{13}\text{C}$ -DIC minimum characteristic of the SMT is observed (Malinverno and Pohlman, 2011). The slope of the

regression corresponds to $\delta^{13}\text{C}$ values typical of marine OM (-22‰ to -20‰ ; Meyers, 1994), indicating that DIC is derived predominantly from organic carbon oxidation (Chen et al., 2024).

These data demonstrate that OSR is the principal process consuming SO_4^{2-} and controlling pore-water DIC and TA at ZGG. According to stoichiometry, OSR produces two moles of DIC per mole of sulfate reduced (Table S1: R5), whereas sulfate-driven AOM yields a 1:1 ratio (Table S1: R14). The relationship between the increase in DIC (ΔDIC) and the decrease in sulfate (ΔSO_4^{2-}) therefore provides a diagnostic criterion for distinguishing these processes (Masuzawa et al., 1992; Rassmann et al., 2016). At ZGG, the $\Delta\text{DIC}:\Delta\text{SO}_4^{2-}$ ratio is 1.85:1 (Fig. S4), close to the theoretical 2:1 value expected for OSR. Minor deviations from the theoretical ratio may reflect partial DIC removal by authigenic carbonate precipitation (Akam et al., 2020). Chemoautotrophic CO_2 fixation may also contribute to DIC consumption (Treude et al., 2007). In addition, a fraction of sediment-produced DIC diffuses into the overlying water. Assuming oxidation of H_2S at the sediment–water interface, the estimated net diffusive benthic flux of carbonate alkalinity ($[\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]$) and DIC at ZGG is 983 ± 40 and $942 \mu\text{mol m}^{-2} \text{d}^{-1}$, respectively (Łukawska-Matuszewska and Kielczewska, 2016; Łukawska-Matuszewska and Dwornik, 2025).

The R_{OSR} values in ZGG sediments ($24\text{--}46 \mu\text{mol dm}^{-3} \text{d}^{-1}$) are consistent with rates reported from other Baltic regions using radioisotope methods. These include $0.2\text{--}42.3 \mu\text{mol dm}^{-3} \text{d}^{-1}$ in the Curonian and Vistula Lagoons (Pimenov et al., 2013), $0\text{--}43 \mu\text{mol dm}^{-3} \text{d}^{-1}$ in the Gdańsk Basin (Pimenov et al., 2010), and $<1.0\text{--}21.4 \mu\text{mol dm}^{-3} \text{d}^{-1}$ in Kattegat (Iversen and Jørgensen, 1985). The measured values also fall within the lower range of rates reported from Eckernförde Bay ($10\text{--}465 \mu\text{mol dm}^{-3} \text{d}^{-1}$; Treude et al., 2005), Himmerfjärden ($0.2\text{--}338 \mu\text{mol dm}^{-3} \text{d}^{-1}$; Sawicka and Brüchert, 2017), and the Gotland Deep ($<250 \mu\text{mol dm}^{-3} \text{d}^{-1}$; Piker et al., 1998). Incubation-derived potential R_{OSR} values are several times higher than rates previously calculated for the same area from sulfate pore-water gradients ($0.2\text{--}4.6 \mu\text{mol dm}^{-3} \text{d}^{-1}$; Łukawska-Matuszewska and Dwornik, 2025). This discrepancy is expected, as incubation experiments determine gross sulfate reduction, whereas pore-water profiles reflect net sulfate consumption (Iversen and Jørgensen, 1985). Experiments with labeled substrates in the present study indicate the potential for AOM at ZGG (Table 1), with rates up to $\sim 10 \mu\text{mol dm}^{-3} \text{d}^{-1}$. This suggests that methane could be oxidized if supplied from deeper layers. However, geochemical evidence indicates that the sampled interval corresponds to the sulfate reduction zone above the SMT. Consequently, AOM does not significantly contribute to DIC and TA production in the studied sediments. It should be also mentioned that experimentally-derived AOM rates represent the potential activity of the microbial community under substrate-replete conditions rather than the actual in situ process rates. Therefore, the similar experimentally-derived rates at MET-2 and ZGG indicate a comparable microbial potential for AOM at both sites. In contrast, the porewater profiles reflect in situ conditions, where methane availability differs substantially between the sites. At MET-2, methane is present and supports active AOM, which is reflected in the porewater profiles. At ZGG, methane concentrations are negligible, so AOM appears less significant in situ despite the presence of a microbial community capable of performing this process if methane became available.

Based on stoichiometry (Table S1: R5) and measured R_{OSR} , OSR contributes $49\text{--}92 \mu\text{mol dm}^{-3} \text{d}^{-1}$ of DIC to ZGG pore waters. The depth-integrated DIC production from OSR within the $0\text{--}100 \text{ cm}$ interval equals $54 \text{ mmol m}^{-2} \text{d}^{-1}$ (Table 1).

497 Reduction of Mn(IV) during OM degradation may represent an additional DIC source, as indicated by the presence of Mn^{2+}
 498 in pore waters (Fig. 2g). However, Mn^{2+} concentrations are low relative to H_2S , the byproduct of sulfate reduction.
 499 Therefore, Mn(IV) reduction likely contributes only marginally to DIC production and is not included in the quantitative
 500 assessment. Besides Mn(IV) reduction, organic matter oxidation in marine sediments can proceed via denitrification.
 501 However, in the reducing sediments examined here nitrate was consistently below detection limit and nitrite occurred only at
 502 trace levels (data not shown), so denitrification was not quantified. While denitrification can produce DIC, we have no
 503 evidence for substantial availability of oxidized nitrogen species in these samples and therefore expect its contribution to be
 504 negligible.

505 The progressive increase in DIC with depth leads to pore-water supersaturation with respect to carbonate minerals, primarily
 506 calcite and dolomite, throughout most of the sediment column, except for the upper 5–10 cm (Fig. S11). Despite
 507 thermodynamic supersaturation, carbonate contents remain low (Table 2). Calcite occurs only in trace amounts, and dolomite
 508 was identified exclusively in the subsurface layer during summer. Moreover, anhedral morphology of many grains raises
 509 uncertainty as to whether all these carbonates are entirely authigenic. The dolomite burial rate is substantially lower than in
 510 methane-bearing sediments (Table 2) and does not exceed $271 \mu\text{mol m}^{-2} \text{d}^{-1}$. For comparison, burial rates reach $525 \mu\text{mol m}^{-2}$
 511 d^{-1} at MET2 and $994 \mu\text{mol m}^{-2} \text{d}^{-1}$ at MET1-MP. Comparable rates to those recorded at the ZGG - $60 \pm 35 \mu\text{mol m}^{-2} \text{d}^{-1}$ from
 512 PXRD and $136 \pm 110 \mu\text{mol m}^{-2} \text{d}^{-1}$ from SEM-EDS - were reported by Zha et al. (2022) for sediments on the northern slope
 513 of the South China Sea. Using reactive transport modeling, they estimated the burial rate of Ca-Mg carbonates to be 65
 514 $\mu\text{mol}^{-2} \text{d}^{-1}$ in the upper 30 cm of sediment at one site and $79 \mu\text{mol}^{-2} \text{d}^{-1}$ in the upper 10 cm at another.

515 The DIC:TA ratio is a simple diagnostic of the relative contribution of non-carbonate bases to total alkalinity. In seawater,
 516 DIC defined as the sum of $[\text{CO}_2^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$ with $[\text{CO}_2^*]$ denoting the sum of dissolved $[\text{CO}_2]$ and $[\text{H}_2\text{CO}_3]$
 517 (Dickson et al., 2007), typically represents over 95% of TA (Emerson and Hedges, 2008). In this concept, lower DIC:TA
 518 values signal a larger non-carbonate alkalinity fraction (e.g., HS^- , NH_3), whereas values near unity indicate TA is dominated
 519 by carbonate species. The mean DIC:TA ratio in ZGG pore waters is 0.75. This value indicates that approximately 25% of
 520 total alkalinity derives from non-carbonate bases, primarily H_2S . Hydrogen sulfide constitutes an independent acid–base
 521 system capable of proton exchange (Hu et al., 2010) and is therefore included in TA calculations. Upward diffusion of H_2S
 522 toward the sediment–water interface followed by oxidation leads to partial consumption of alkalinity (Table S1: R10)
 523 generated during anaerobic mineralization (Krumins et al., 2013). In contrast, precipitation of sulfides within the sediment
 524 (Table S1: R15) prevents complete reoxidation and results in a net increase in pore-water TA.

525 Geochemical modeling indicates that pore waters at ZGG are supersaturated with respect to iron sulfides, including greigite,
 526 mackinawite, and pyrite, throughout the sediment column (Fig. S11). Increasing TS content with depth and relatively low
 527 TOC:TS ratios further support enhanced sulfide accumulation compared to the methane-affected stations. Mineralogical data
 528 confirm that pyrite is more abundant at ZGG than at MET1-MP and MET2. Its burial rate ranges from 940 to $1447 \mu\text{mol m}^{-2}$
 529 d^{-1} , several times higher than at the other sites, where OSR rates and pore-water H_2S concentrations are lower. These values

530 are high and comparable to the upper range reported by Jørgensen et al. (1990) for sediments from the Baltic–North Sea
531 transition zone (50–1240 $\mu\text{mol m}^{-2} \text{d}^{-1}$).
532 The rate of sulfate reduction in the studied sediments likely exceeds the rate of reaction between H_2S and reactive iron
533 phases. This imbalance promotes the accumulation of dissolved H_2S in pore waters (Boesen and Postma, 1988; Canfield et
534 al., 1992). Accordingly, H_2S concentrations remain high throughout the sediment profile, whereas Fe^{2+} is largely depleted
535 from pore waters (Fig. 2). Mössbauer spectroscopy indicates that iron is predominantly divalent (Fig. S10). Thus, the
536 availability of reactive Fe(III) phases likely limits pyrite formation. Such limitation is typical of anoxic to euxinic marine
537 environments (Raiswell and Berner, 1985; Boesen and Postma, 1988) and has previously been documented for sediments of
538 the Gdańsk Deep (Łukawska-Matuszewska et al., 2019). Incomplete removal of H_2S as solid sulfides and its reoxidation
539 (Table S1: R10) may contribute to pore-water acidification. The observed increase in Ca^{2+} concentration with depth (Fig. 2)
540 may therefore reflect carbonate dissolution driven by lowered pH.

541 **4.2 Nearshore methane-bearing sediment with high terrigenous organic matter input (station MET2)**

542 High OM loading from local primary production and terrigenous sources increases oxygen demand in coastal sediments and
543 frequently exceeds oxygen supply (Hedges et al., 1997; Schlünz and Schneider, 2000). Oxygen penetration is therefore
544 shallow. It is typically <1 mm in muddy and silty sediments and only a few centimeters in sands (Glud, 2008), owing to
545 limited transport and rapid consumption. As a consequence, anaerobic mineralization dominates in most coastal settings
546 (Soetaert et al., 1996), with sulfate serving as the principal electron acceptor, as observed at station ZGG. When organic
547 carbon input exceeds sulfate availability, mineralization proceeds via methanogenesis (Froelich et al., 1979). Diagenetic
548 zonation in coastal sediments differs markedly from that in open-ocean environments. Redox zones are thinner and shifted
549 closer to the sediment surface (D'Hondt et al., 2004; Egger et al., 2018). In low-salinity settings, sulfate reduction, the SMT,
550 and methanogenesis commonly occur at shallow depths (Albert et al., 1998; Thang et al., 2013; Egger et al., 2015). Station
551 MET2 is located in a nearshore zone (Fig. S1) with bottom-water salinity of ~7–8. The molar TOC:TN ratio (9.3–13.7; Fig.
552 1d) indicates a substantial contribution of terrestrial OM, which is relatively nitrogen-poor compared to protein-rich marine
553 phytoplankton. Carbon isotopic compositions support this interpretation. $\delta^{13}\text{C}$ values range from –26.0‰ to –24.4‰, i.e.,
554 below –24‰, consistent with terrestrial input (Yadav et al., 2025). Nitrogen isotopic values ($\delta^{15}\text{N} = 1.21\text{–}6.66\text{‰}$) show the
555 greatest ^{15}N enrichment in the upper 0–20 cm, coinciding with elevated TOC and TN contents. Terrestrial OM is generally
556 less degradable than marine OM due to the abundance of cellulose and lignin in vascular plant tissues (Dickens et al., 2006).
557 The observed isotopic and compositional variations therefore reflect preferential degradation of labile phytoplankton-derived
558 compounds and the relative accumulation of more refractory terrestrial material in the sediment.
559 Because MET2 is located in a shallower, transport-dominated setting, the sediment consists of sandy silt and contains lower
560 TOC and TN than the silty and clayey sediments at the other stations (Fig. 1a, b). Owing to the relatively low salinity, major
561 ion concentrations in bottom and pore waters are the lowest among all sites. These concentrations remain nearly constant
562 with depth, except for SO_4^{2-} (Fig. 2a–d). Sulfate decreases rapidly within the upper 0–40 cm due to microbial reduction and

falls below LOQ at greater depths. In the upper ~20 cm bsf, the $\Delta\text{DIC}:\Delta\text{SO}_4^{2-}$ ratio ranges from 1.0 to 2.1, consistent with contributions from both sulfate-driven AOM and OSR. The mean ratio of 1.51:1 indicates a mixed origin of DIC. Below this interval, DIC production becomes disproportionately high relative to sulfate consumption, and the $\Delta\text{DIC}:\Delta\text{SO}_4^{2-}$ ratio increases to ~4.0 (Fig. S4). Such excess DIC may reflect processes that produce DIC but do not consume sulfate, including methanogenesis, or alternative AOM pathways coupled to Mn(IV) or Fe(III) reduction (Meister et al., 2019). Elevated Mn^{2+} concentrations between 30 and 80 cm and Fe^{2+} below 80 cm (Fig. 2g, h) may suggest involvement of these pathways. However, the absolute concentrations of Mn^{2+} and Fe^{2+} are low, indicating that metal-driven AOM likely contributes only marginally to DIC and TA production and is not considered further.

Methane concentrations at MET2 reach 6.5 mmol dm⁻³ in summer and 8.45 mmol dm⁻³ in winter (Fig. 2f). Stable isotope data for $\delta^{13}\text{C}\text{-CH}_4$, $\delta^2\text{H}\text{-CH}_4$, and $\delta^{13}\text{C}\text{-CO}_2$ (Fig. 5) indicate a microbiological origin, predominantly via hydrogenotrophic methanogenesis (Whiticar, 1999). Methane concentrations decrease upward from maxima in deeper layers to values below LOQ in the uppermost centimeters. Methane is absent from the overlying water column, demonstrating that the sediment acts as an efficient methane filter despite the shallow SMT at ~5–13 cm bsf. In Baltic Sea sediments, SMT depths vary widely, ranging from 80–160 cm in the Danish Straits (Iversen and Jørgensen, 1985), ~150 cm in Aarhus Bay (Thomsen et al., 2001), and 30–40 cm in the Gotland Deep (Piker et al., 1998). SMT depths comparable to those observed here have been reported from Storfjärden and Pojo Bay (Myllykangas et al., 2020; Jilbert et al., 2021), the western Gotland Basin (Ketzer et al., 2024), and Eckernförde Bay in the southwestern Baltic Sea (Treude et al., 2005; Maltby et al., 2018).

The occurrence of sulfate-dependent AOM within the 5–13 cm bsf interval is indicated by the most negative $\delta^{13}\text{C}\text{-DIC}$ values (Fig. 3c) (Malinverno and Pohlman, 2011). In the overlying sediment, OM is oxidized primarily via OSR. However, separation of OSR and AOM zones based solely on isotopic data is difficult, as both processes produce ¹³C-depleted DIC. OSR shifts $\delta^{13}\text{C}\text{-DIC}$ from values near 0‰, typical of seawater, toward approximately -21‰, characteristic of marine OM. Subsequent sulfate-driven AOM may further deplete DIC in ¹³C through oxidation of isotopically light CH_4 (Meister and Reyes, 2019). At MET2, $\delta^{13}\text{C}\text{-DIC}$ values range from -12.7‰ to -1.2‰. These values are markedly less negative than expected for only AOM or OSR end-members. If DIC generated by sulfate-AOM inherited the isotopic signature of methane entering the SMT, $\delta^{13}\text{C}\text{-DIC}$ values would approach ~-76‰. Conversely, DIC derived from OSR should approximate the $\delta^{13}\text{C}$ of sedimentary OM (-25.6‰ at MET2). The relatively enriched $\delta^{13}\text{C}\text{-DIC}$ values observed in both AOM and OSR intervals suggest mixing with ¹³C-enriched DIC diffusing upward from the methanogenic zone (Malinverno and Pohlman, 2011; Meister and Reyes, 2019). Overall, pore-water DIC at MET2 reflects a mixture of inorganic carbon produced by overlapping diagenetic processes. A comparable situation has been reported from Storfjärden, where OSR, sulfate-driven AOM, and methanogenesis co-occur within compressed redox zones (Jilbert et al., 2021).

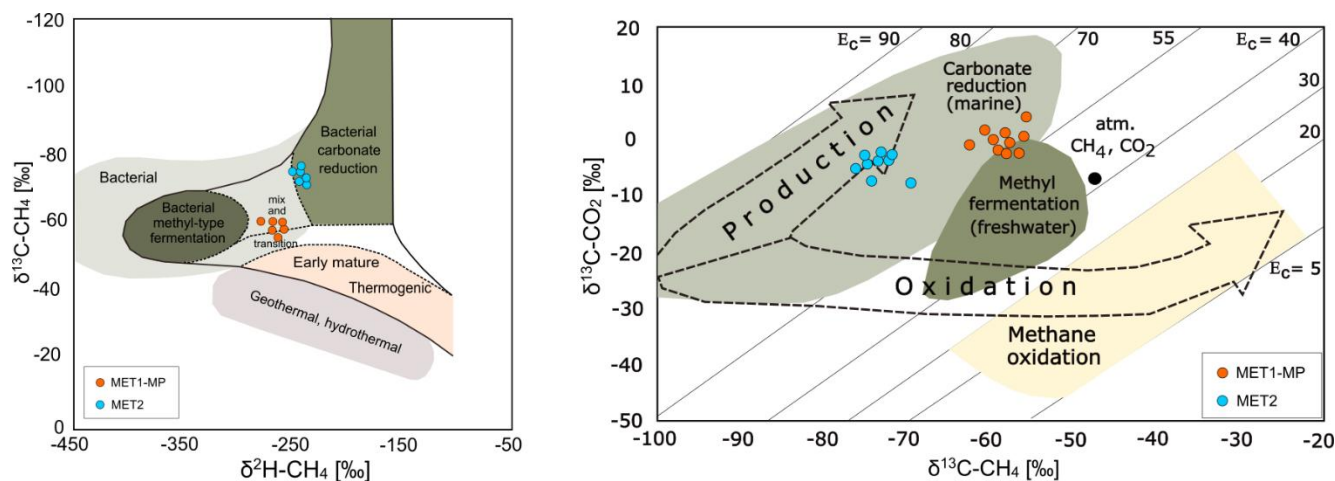


Figure 5: Origin of methane inferred from the combined $\delta^{13}\text{C}$ and $\delta^2\text{H}$ composition of methane (a) and from $\delta^{13}\text{C}$ values of methane and carbon dioxide (b) in sediments at stations MET1-MP and MET2 in the Gdańsk Basin (modified after Whiticar, 1999).

The R_{OSR} values at MET2 range from 21 to 48 $\mu\text{mol dm}^{-3} \text{d}^{-1}$. These rates are comparable to those measured at the other stations (Table 2) and fall within ranges reported in the literature (Sect. 4.1). The R_{AOM} values (6–33 $\mu\text{mol dm}^{-3} \text{d}^{-1}$) are also consistent with data from other Baltic regions, including 0–50 $\mu\text{mol dm}^{-3} \text{d}^{-1}$ in the Gdańsk Basin (Pimenov et al., 2010), 0.03–14 $\mu\text{mol dm}^{-3} \text{d}^{-1}$ in Eckernförde Bay (Treude et al., 2005), and 0.002–6.2 $\mu\text{mol dm}^{-3} \text{d}^{-1}$ in Kattegat and Skagerrak (Iversen and Jørgensen, 1985). The highest R_{AOM} occurs within the 0–20 cm layer. Rates in this interval are up to six times higher than those in the 20–40 cm layer. This distribution corresponds to geochemical indicators, including the steepest SO_4^{2-} gradient, maximum H_2S concentrations, $\Delta\text{DIC}:\Delta\text{SO}_4^{2-}$ ratios lower than expected exclusively for OSR, and negative $\delta^{13}\text{C-DIC}$ values in the upper sediment. At MET2, R_{OSR} contributes 41–96 $\mu\text{mol DIC dm}^{-3} \text{d}^{-1}$ to pore waters. The depth-integrated DIC production from OSR within the 0–100 cm interval equals 59 $\text{mmol m}^{-2} \text{d}^{-1}$, similar to values obtained for ZGG (Table 1). In addition, AOM contributes 6–33 $\mu\text{mol dm}^{-3} \text{d}^{-1}$ of DIC, corresponding to an integrated production rate of 9 $\text{mmol m}^{-2} \text{d}^{-1}$. The pronounced chemical gradients at the sediment–water interface correspond to a diffusive benthic flux of carbonate alkalinity ($[\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]$) estimated at $1498 \pm 80 \mu\text{mol m}^{-2} \text{d}^{-1}$ (Łukawska-Matuszewska and Dwornik, 2025). The mean DIC:TA ratio in MET2 pore waters is 0.97. This value indicates a relatively minor contribution of non-carbonate bases to total alkalinity compared to ZGG. The dominance of carbonate alkalinity suggests that alkalinity production at MET2 is less reversible. In contrast, at ZGG, substantial H_2S production and its subsequent oxidation release H^+ and partially consume alkalinity (Table S1: R10).

Pore waters at MET2 exhibit higher saturation indices with respect to calcite and dolomite than those at methane-free ZGG (Fig. S11). Intense diagenesis leads to a strong increase in DIC, which raises porewater saturation with respect to carbonates and thereby promotes precipitation of authigenic phases. This is consistent with the greater abundance of dolomite throughout the sediment column, as documented by PXRD and microscopic observations (Table 2). The dolomite burial rate at MET2 (184–525 $\mu\text{mol m}^{-2} \text{d}^{-1}$) substantially exceeds that at ZGG (1–271 $\mu\text{mol m}^{-2} \text{d}^{-1}$). Taken together, the porewater

619 chemistry and burial rates suggest that methane-bearing sediments in our study area sequester more inorganic carbon than
620 methane-free, OSR-dominated sediments (ZGG) - likely because methane-related processes generate additional DIC.
621 In deeper layers at MET2, pore waters are also supersaturated with respect to siderite. In contrast, siderite is undersaturated
622 throughout the ZGG profile (Fig. S11). This difference likely reflects Fe^{2+} availability. At ZGG, Fe^{2+} is efficiently removed
623 from pore waters through reaction with abundant H_2S and subsequent sulfide precipitation. At MET2, H_2S is restricted to a
624 narrow interval, with maximum concentrations at ~13 cm bsf (Fig. 2e). Below this depth, H_2S concentrations fall below
625 LOQ. Under these conditions, a fraction of dissolved Fe^{2+} may precipitate as siderite rather than as iron sulfides.
626 In MET2 sediments, the mean TOC:TS ratio is 2.8. This value corresponds to typical marine sediments deposited beneath
627 oxygenated bottom waters (Bernier, 1982). Under such conditions, H_2S required for pyrite formation is produced within the
628 anaerobic sediment during OM degradation. The rate of FeS_2 formation is controlled primarily by sedimentation rate and
629 organic matter supply (Bernier, 1982).
630 In contrast, at ZGG, H_2S frequently occurs in the overlying water column. This allows pyrite to form not only within the
631 sediment but also in the water column (Raiswell and Bernier, 1985) and, as a result, pyrite is more abundant at ZGG than at
632 MET2 (Table 2). At MET2, the pyrite burial rate ranges from 334 to 789 $\mu\text{mol m}^{-2} \text{d}^{-1}$, the lowest among the studied sites.
633 This reflects oxygenated bottom waters and comparatively low H_2S concentrations in pore waters. These conditions likely
634 explain the Mössbauer results, which show a slightly lower proportion of Fe(II) associated with pyrite in the upper sediment
635 layers at MET2 compared to deeper layers and to the other stations (Table S4).

636 **4.3 Sediment affected by freshwater infiltration and methanogenesis (pockmark MET1-MP)**

637 Sedimentation rate and organic carbon burial strongly regulate sulfate consumption and the depth of the SMT in marine
638 sediments (Canfield, 1991; Egger et al., 2018). In coastal settings, submarine groundwater discharge (SGD) constitutes an
639 additional controlling factor. SGD involves the exchange of terrestrial groundwater mixed with recirculated seawater that has
640 infiltrated coastal aquifers. Its chemical composition often deviates from conservative mixing due to biogeochemical
641 reactions within the aquifer (Moore, 2010). In the Gdańsk Basin, SGD occurs in both coastal and deeper offshore areas. It is
642 expressed by anomalous salinity distributions, with lower salinity in bottom and pore waters relative to the overlying water
643 column (Piekarek-Jankowska et al., 1994; Falkowska and Piekarek-Jankowska, 1999; Ehlert von Ahn et al., 2024; Matciak
644 et al., 2024). In nearshore zones, SGD significantly affects water quality by supplying carbon, nutrients, and contaminants
645 (Szymczycha et al., 2012, 2013, 2023). However, station MET1-MP, located in central Gulf of Gdańsk ~80 m water depth,
646 represents a deepwater pockmark where freshwater originates from the Upper Cretaceous aquifer beneath the seafloor
647 (Kozerski et al., 1987). Fresh groundwater infiltration into the pockmark has been documented previously (Brodecka-Goluch
648 et al., 2022) and is confirmed here by the Cl^- profile in pore waters (Fig. 2a). The inflow of freshwater dilutes pore waters
649 and reduces SO_4^{2-} availability for OM and methane oxidation. This alteration of sulfate supply modifies early diagenetic
650 processes and promotes shallow methanogenesis (Pimenov et al., 2010; Ehlert von Ahn et al., 2024).

651 As a seabed depression formed by gas expulsion, this pockmark acts as a natural sediment trap. It accumulates both
652 autochthonous and allochthonous OM. Consequently, silty sediments at MET1-MP exhibit the highest TOC and TN
653 concentrations among the studied sites (Fig. 1a, b). The TOC:TN ratio (7.8–8.7) approaches that typical of marine OM.
654 However, the isotopic composition of carbon and nitrogen in the organic fraction (Fig. 1e, f) indicates an additional
655 contribution of terrestrial material.

656 The pockmark's physical and sedimentary characteristics concentrate OM, raising demand for electron acceptors and fueling
657 intense diagenesis; as a result, porewater sulfate is rapidly consumed in the uppermost decimeters and the sulfate–methane
658 transition shifts toward the sediment surface. Methanogenesis and AOM supply additional DIC alongside OSR, causing
659 elevated porewater DIC through intense diagenesis. Pore waters at MET1-MP are also characterized by very high
660 concentrations of NH_4^+ and PO_4^{3-} (Fig. 3d, e). These elevated nutrient levels further indicate intense degradation of the
661 substantial OM inventory accumulated within the pockmark sediments.

662 The substantial water depth and persistent stratification at MET1-MP further constrain oxygen supply to the sediment,
663 similar to conditions at ZGG. Under these conditions, SO_4^{2-} is rapidly depleted from pore waters. The SMT is extremely
664 shallow. The $\delta^{13}\text{C}$ -DIC profile (Fig. 3c) indicates that the SMT center is located immediately below the sediment surface,
665 likely within 3–5 cm bsf. Within the upper ~8 cm, $\Delta\text{DIC}:\Delta\text{SO}_4^{2-}$ ratios reflect contributions from OSR, AOM, or both
666 processes. The mean ratio of 1.24:1 suggests that sulfate-driven AOM plays a dominant role in SO_4^{2-} consumption in this
667 interval (Miller et al., 2017). At greater depths, ΔDIC values exceed those expected from OSR and AOM, indicating an
668 additional DIC source unrelated to SO_4^{2-} consumption. With increasing depth, $\delta^{13}\text{C}$ -DIC shifts toward positive values,
669 reaching up to +16.4‰ (Fig. 3c). Similar values (up to +14‰) and comparable pore-water profiles were reported by Ehlert
670 von Ahn et al. (2024) from a station located in similar area. This enrichment likely reflects the upward diffusion of ^{13}C -
671 enriched DIC generated during methanogenesis, as observed at MET2. However, groundwater infiltration may also
672 contribute.

673 Groundwaters from the Upper Cretaceous aquifer in the Gdańsk region are predominantly of the $\text{HCO}_3\text{--Na}$ and $\text{HCO}_3\text{--Ca}$
674 types (Sadurski, 1985). They are alkaline (pH 7.5–8.3) and exhibit variable dissolved solute concentrations, with DIC values
675 reaching ~11 mmol dm^{-3} (Kozerski et al., 1987). These waters circulate through glauconitic sands forming the principal
676 aquifer and migrate upward through carbonate and siliceous strata, including carbonates, gaizes, and marls (Sadurski, 1985).
677 Infiltrating groundwater can dilute pore waters and reduce DIC concentrations in deeper sediment layers (Fig. 3b).
678 Moreover, groundwater DIC is commonly enriched in ^{13}C due to carbonate dissolution and isotopic exchange with CaCO_3 ,
679 for which $\delta^{13}\text{C}$ values typically exceed 0‰ (Walter et al., 2007; Han et al., 2014; Campeau et al., 2017). Consequently, both
680 methanogenesis and SGD influence the $\delta^{13}\text{C}$ -DIC signature in pore waters of the MET1-MP pockmark.

681 Stable isotope data indicate that CH_4 at MET1-MP is of microbiological origin (Fig. 5). Methane is generated not only by
682 CO_2 reduction but also by acetate fermentation, a pathway commonly associated with freshwater environments (Whiticar,
683 1999; Batther et al., 2025). This dual signature further demonstrates the influence of freshwater infiltration on sedimentary
684 microbial processes. In contrast to MET2, where CH_4 concentrations increase progressively with depth, the MET1-MP

685 profile exhibits a subsurface or intermediate maximum (Fig. 2f). The extremely shallow SMT and the occurrence of methane
 686 close to the sediment surface may enhance the potential for gas escape into the water column. Lapham et al. (2024) showed
 687 that methane leakage across the SMT is widespread in organic-rich Baltic Sea sediments, with a highly variable amount of
 688 subseafloor gas escaping oxidation (0–100%). Previous investigations documented gas emissions from multiple locations
 689 within the MET1-MP pockmark (Brodecka et al., 2013; Majewski and Klusek, 2014; Łukawska-Matuszewska et al., 2025).
 690 The pockmark is a large structure (~1200 m long and ~500 m wide), and gas discharge is spatially heterogeneous. Fluid
 691 migration pathways and rates vary considerably. During the present study, CH₄ concentrations in bottom water were below
 692 LOQ, whereas surface sediments contained ~0.3 mmol dm⁻³ CH₄. Thus, diffusion into bottom water followed by aerobic
 693 oxidation cannot be excluded.

694 The R_{OSR} attains a maximum of 164 μmol dm⁻³ d⁻¹ in the 0–20 cm layer. This peak corresponds to steep SO₄²⁻ depletion and
 695 elevated H₂S concentrations, reflecting active sulfate reduction. Below 20 cm, R_{OSR} decreases markedly and remains
 696 relatively uniform across deeper layers (Table 2). Excluding the surface interval, R_{OSR} is lower than at the other stations. In
 697 contrast, R_{AOM} is substantially higher, ranging from 59 to 1077 μmol dm⁻³ d⁻¹. These R_{AOM} values exceed most rates reported
 698 for the Baltic Sea. Rates measured in the 0–20 cm, 20–40 cm, and 60–80 cm layers are comparable to those reported by
 699 Pimenov et al. (2008), who observed a maximum of 80.6 μmol dm⁻³ d⁻¹ in another gas-saturated pockmark in the Gdańsk
 700 Basin, among the highest previously documented in the region. By comparison, AOM rates in Eckernförde Bay range from
 701 0.03 to 14 μmol dm⁻³ d⁻¹ (Treude et al., 2005), in the Curonian and Vistula Lagoons from 0.07 to 2.89 μmol dm⁻³ d⁻¹
 702 (Pimenov et al., 2013), and in Kattegat and Skagerrak from 0.002 to 6.2 μmol dm⁻³ d⁻¹ (Iversen and Jørgensen, 1985). The
 703 highest R_{AOM} values at MET1-MP approach those reported for gassy sediments at a cold seep in Monterey Bay (280 ± 40
 704 μmol dm⁻³ d⁻¹) and fall within the lower range measured at a cold seep in the Gulf of Mexico, where rates reached 4800 ±
 705 400 μmol dm⁻³ d⁻¹ (Bowles et al., 2019).

706 Direct comparison of microbial rates among studies remains challenging: even when identical radiotracer protocols are used,
 707 variability in microbial community structure, sediment properties and incubation conditions can produce substantially
 708 different rate estimates. At MET1-MP, R_{AOM} varies by up to two orders of magnitude between sediment layers. Comparable
 709 intra-profile variability has been documented elsewhere in the Baltic Sea (e.g., Iversen and Jørgensen, 1985; Pimenov et al.,
 710 2008; Pimenov et al., 2013), where rates differed by as much as 300% among layers. Nevertheless, the MET1-MP pockmark
 711 exhibits a markedly greater AOM capacity than the other sites investigated in this study and than most previously studied
 712 Baltic sediments. Depth-integrated calculations demonstrate that AOM is the dominant DIC source at MET1-MP. OSR
 713 contributes 58 mmol m⁻² d⁻¹ of DIC, whereas AOM supplies 331 mmol m⁻² d⁻¹, more than five times greater. Consistently,
 714 MET1-MP represents the strongest benthic DIC source among the studied sites. The estimated net diffusive flux of carbonate
 715 alkalinity equals 2017 ± 47 μmol m⁻² d⁻¹ (Łukawska-Matuszewska and Dwornik, 2025), exceeding fluxes from the other
 716 sediments by 50–100%.

717 Intense DIC production within the MET1-MP pockmark results in markedly elevated DIC and TA concentrations relative to
 718 the other stations (Fig. 3a, b). In contrast to MET2 and ZGG, however, DIC does not increase progressively with depth.

719 Below ~30 cm, DIC concentrations decline. This pattern may partly reflect dilution by infiltrating freshwater. Because the
 720 exact chemical composition of the discharging waters is not fully constrained, their quantitative influence on DIC variability
 721 cannot be assessed. Notably, the decrease in DIC coincides with pronounced declines in Mg^{2+} and Ca^{2+} concentrations (Fig.
 722 2b, c). This relationship suggests that authigenic carbonate precipitation represents an additional controlling process.
 723 Comparable pore-water trends have been reported from methane-affected settings, including shallow sediments of the
 724 western slope of the Mid-Okinawa Trough (Xu et al., 2018), pockmark sediments of the Northern Congo Fan (Nöthen and
 725 Kasten, 2011), and pockmarks on the inner shelf of the East China Sea (Wang et al., 2024).
 726 Among the studied sites, MET1-MP affected by methanogenesis and freshwater infiltration exhibits the highest average
 727 dolomite content. Euhedral crystals are common, supporting an authigenic origin. In addition to dolomite and minor calcite,
 728 traces of siderite were identified. Authigenic carbonate formation at MET1-MP therefore constitutes an efficient inorganic
 729 carbon sink. This observation is consistent with Rzepa et al. (in press), who found that freshwater input in another deepwater
 730 pockmark in the Gdańsk Basin lowers porewater sulfate and promotes methanogenesis and Fe-mediated AOM, increasing
 731 dissolved inorganic carbon and thereby favoring authigenic carbonate formation. The dolomite burial rate ranges from 467 to
 732 $994 \mu\text{mol m}^{-2} \text{d}^{-1}$, substantially exceeding values at ZGG ($1\text{--}271 \mu\text{mol m}^{-2} \text{d}^{-1}$) and MET2 ($184\text{--}525 \mu\text{mol m}^{-2} \text{d}^{-1}$). Similarly,
 733 Chen et al. (2024) found that at the Makran continental margin, sediments with a high methane flux exhibited authigenic
 734 carbonate precipitation rates that were at least double those of the background area.
 735 In the MET1-MP pockmark influenced by freshwater infiltration, the effect of CH_4 on redox-sensitive elements (Fe and Mn)
 736 is more pronounced than at MET2. Freshening and reduced sulfate availability enhance the relative importance of alternative
 737 methane oxidation pathways (Egger et al., 2015). The observed increase in Fe^{2+} and Mn^{2+} concentrations below the sulfate
 738 reduction zone likely reflects reductive dissolution of Fe(III) and Mn(IV) phases coupled to AOM. The measured R_{AOM}
 739 values probably include contributions from both sulfate-dependent AOM and metal-dependent AOM, provided that
 740 microorganisms capable of these pathways were present. This distinction does not affect DIC production estimates, as
 741 oxidation of 1 mol of CH_4 yields 1 mol of HCO_3^- irrespective of the terminal electron acceptor (Table S1:R12-R14). MET1-
 742 MP exhibits the highest Fe^{2+} concentrations among the studied stations. This contrasts with ZGG, where Fe^{2+} is almost
 743 entirely removed from pore waters through reaction with abundant H_2S . The total sulfur content in MET1-MP sediments is
 744 lower than at ZGG, and the TOC:TS ratio is several times higher (Fig. 1). These relations indicate that H_2S availability limits
 745 pyrite formation in sediments influenced by freshwater infiltration. Despite this limitation, pyrite remains a common
 746 authigenic phase at MET1-MP. However, its mean concentration is significantly lower than at ZGG. The pyrite burial rate
 747 ranges from 453 to $828 \mu\text{mol m}^{-2} \text{d}^{-1}$, comparable to values at MET2. These rates are approximately half those observed at
 748 ZGG, where intense sulfate reduction promotes high H_2S production and enhanced iron sulfide precipitation.

749 **5 Conclusions**

750 This comparative study of shelf sediments highlights the complexity of diagenetic processes controlled by local
751 environmental conditions and their implications for the carbon cycle. It demonstrates that the function of sediments as
752 sources or sinks of inorganic carbon varies in response to redox regime, methane dynamics, sulfate availability, and
753 freshwater input. Our synthesis shows that carbonate dynamics are governed by interactions among OSR, methanogenesis,
754 AOM, sulfate supply, and freshwater input (Fig. 6). Recognition of these coupled processes is essential for predicting
755 sedimentary carbon cycling under changing environmental conditions and for refining current models of carbonate dynamics
756 in shelf environments.

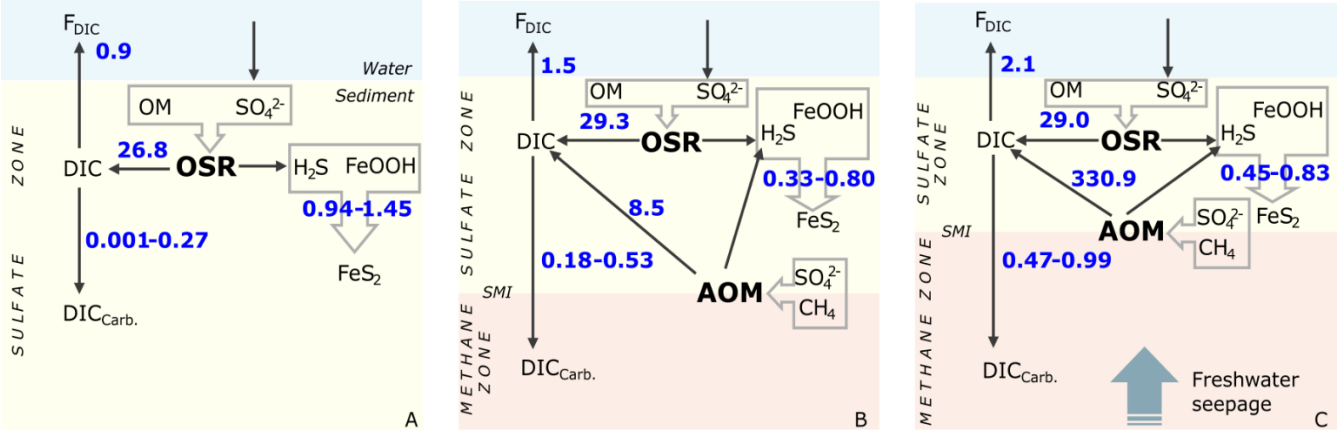
757 Methane-bearing sediments differ markedly from anoxic sediments dominated solely by OSR. In the latter, DIC production
758 is approximately 40% lower, based on the sites studied. Where OM supply exceeds sulfate availability, methanogenesis and
759 the coupled AOM become important additional sources of DIC in pore waters, contributing to the elevated DIC levels
760 observed in methane-bearing sediments. Sediments in which both OSR and AOM operate release substantially more
761 inorganic carbon to the overlying water. Benthic fluxes are 50–100% higher than in sediments lacking active
762 methanogenesis. The role of methane-related processes becomes increasingly important in sediments influenced by
763 freshwater input, where the SMT is shallower and AOM can be a principal DIC source relative to OSR. AOM - particularly
764 where freshwater inflow reduces sulfate availability - supplies additional DIC that contributes to carbonate supersaturation;
765 this favors authigenic carbonate formation, which can act as an important inorganic-carbon sink.

766 To our knowledge, this study provides the first quantitative estimate of authigenic carbonate burial rates in Baltic Sea
767 sediments. Overall, the results demonstrate that anaerobic methane oxidation can play a significant role in regulating
768 authigenic carbonate burial and, consequently, seawater chemistry.

769

770

771 **Figure 6: Simplified conceptual model of inorganic carbon cycling in shelf sediments under contrasting environmental settings:**
772 **(A) anoxic sediments dominated by organoclastic sulfate reduction as the principal pathway of organic matter oxidation;**
773 **(B) nearshore sediments characterized by substantial terrigenous organic matter input and active methanogenesis;**
774 **(C) sediments influenced by freshwater infiltration and methanogenesis.** Abbreviations: OSR – organoclastic sulfate reduction; AOM –



775 anaerobic oxidation of methane; OM – organic matter; DIC – dissolved inorganic carbon in pore water; F_{DIC} – diffusive benthic
776 DIC flux (after Łukawska-Matuszewska and Dwornik, 2025); $DIC_{carb.}$ – burial of authigenic carbonate (dolomite). Numerical
777 values represent fluxes and depth-integrated rates of DIC production and consumption associated with individual processes,
778 expressed in $mmol\ m^{-2}\ d^{-1}$.

779 **Data availability**

780 The original data presented in the study are included in the article/Supplementary Material; further inquiries can be directed
781 to the corresponding author.

782 **Supplement link**

783 Supplement of “Biogeochemical controls on carbonate dynamics driven by methane and freshwater inputs in shallow
784 sediments of a brackish continental shelf sea”

785 **Author contributions**

786 KŁM: Writing (original draft preparation); Writing (review and editing); Conceptualization; Investigation; Validation;
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791 editing); Investigation. AB: Writing (original draft preparation); Writing (review and editing); Investigation; Formal
792 Analysis. MM: Writing (original draft preparation); Writing (review and editing); Formal Analysis. JK: Formal analysis;
793 Visualization. MD: Methodology; Formal analysis; Data Curation. MR: Investigation..

794 **Competing interests**

795 The authors declare that they have no conflict of interest.

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