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Early diagenesis in anoxic sediments of the Gulf of Gdańsk (southern Baltic Sea): Implications for porewater chemistry and benthic flux of carbonate alkalinity

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Being a measure of acid-neutralizing capacity, alkalinity determines carbon dioxide (CO_2) uptake from the atmosphere and the pH of seawater. However, the alkalinity budget in the Baltic Sea is still poorly understood. According to recent modeling studies, anaerobic processes in sediments are an important internal source of alkalinity in the Baltic Sea. Nevertheless, determining the role of sediments in alkalinity enhancement is difficult due to the high variability of environmental conditions and, consequently, biogeochemical processes. Here, we describe the geochemistry of different types of anoxic sediments from the Gulf of Gdańsk: methanic, methanic with freshwater seepage, and methanefree, emphasizing dissolved inorganic carbon, methane, and sulfate. We estimate the benthic flux of carbonate alkalinity (J_{CA}) and the sulfate reduction rate (SRR) due to the dissimilatory sulfate reduction (DSR) and anaerobic methane oxidation with sulfate (SO₄²⁻-AOM), the main alkalinity-producing processes. We show that the role of anaerobic sediments as a source of alkalinity can vary significantly, depending on the benthic conditions. The concentration and the release of carbonate alkalinity (CA) from sediments depend on the SRR, type of the process producing CA (DSR and SO₄²⁻-AOM), and the depth of sulfate-methane transition (SMT) in the sediment. The estimated SRR is ranging from 0.1 to 26 nmol cm⁻³ d⁻¹. The range of J_{CA} obtained in the present study varies from 1037 to 2084 μ mol m⁻² d⁻¹. Assuming the complete oxidation of sulfide released from the sediment to the bottom water, the net flux of CA (J^*_{CA}) in the study area is 943–2064 $\mu mol~m^{-2}~d^{-1},$ with the highest values for sediment dominated with SO₄²⁻-AOM with fresh groundwater seepage, shallow SMT, and high SRR in the subsurface sediment layer. Our results may be useful for further studies to determine the role of sediments as an internal source of alkalinity to help close the alkalinity budget in the Baltic Sea.

KEYWORDS

alkalinity, anoxic diagenesis, microbial activity, anaerobic methane oxidation, sulfate reduction, marine sediment

1 Introduction

Alkalinity provides a measure of acid-neutralizing capacity of seawater. This in turn determines carbon dioxide (CO₂) uptake from the atmosphere and pH of seawater (Caldeira and Berner, 1999). As atmospheric pCO_2 increases, CO₂ uptake by surface ocean waters increases, mitigating the increase in atmospheric CO₂ concentration and the greenhouse effect (Le Quéré et al., 2015; Friedlingstein et al., 2020). At the same time, this leads to changes in seawater chemistry that involve a decrease in pH and carbonate (CO₃²⁻) concentration, a process known as ocean acidification (Orr et al., 2005; Doney et al., 2009). Therefore, the knowledge of the spatial and temporal variability of alkalinity is crucial for understanding the global carbon (C) cycle and predicting environmental changes under the impact of increasing atmospheric pCO_2 due to the anthropogenic emission.

Total alkalinity (TA) of seawater is defined as the excess of bases (proton acceptors) over acids (proton donors) in solution (Dickson, 1981) and can be expressed as follows:

$$TA = HCO_{3}^{-} + 2CO_{3}^{2^{-}} + OH^{-} + B(OH)_{4}^{-} + HPO_{4}^{2^{-}} + 2PO_{4}^{3^{-}} + H_{3}SiO_{4}^{-} + NH_{3} + HS^{-} + 2S^{2^{-}} - H^{+} - HF - HSO_{4}^{-} - H_{3}PO_{4}.$$
 (1)

TA is dominated by bicarbonate and carbonate, which represent carbonate alkalinity (CA):

$$CA = HCO_3^{-} + 2CO_3^{2-}.$$
 (2)

In the surface water of the open ocean, TA changes in parallel with salinity, reflecting evaporation and precipitation patterns (Millero et al., 1998; Jiang et al., 2014), whereas in coastal areas and estuaries, TA is largely influenced by riverine input, calcification, anaerobic processes (i.e., denitrification and the reduction of manganese, iron, and sulfate), pyrite burial, and silicate weathering in anoxic marine sediments (Wolf-Gladrow et al., 2007; Wallmann et al., 2008; Hu and Cai, 2011; Gustafsson et al., 2014; Łukawska-Matuszewska and Graca, 2018; Gustafsson et al., 2019). Additionally, due to much shallower depth of the water column than that in the open ocean and easier exchange of substances between the benthic and pelagic zones, the diagenetic processes in the sediments may have a significant impact on the acid–base system in the shelf seas (Liu et al., 2012; Griffiths et al., 2017; Szymczycha et al., 2023).

Many different processes in marine sediments during early diagenesis contribute to the production or consumption of TA in pore waters. Although most anaerobic processes increase TA, aerobic processes generally have the opposite effect (Berner et al., 1970; Krumins et al., 2013; Chatterjee et al., 2011). In anoxic marine sediments, the most significant process for TA generation is probably dissimilatory sulfate (SO₄²⁻) reduction (DSR) (Equation 3; CH₂O – simplified organic matter) during organic matter (OM) mineralization (Krumins et al., 2013; Rassmann et al., 2016):

$$2CH_2O + SO_4^{2-} \rightarrow 2HCO_3^{-} + HS^{-} + H^+.$$
 (3)

Even though the production of alkalinity during DSR per 1 mol of OM is lower than that in the case of the reduction of Fe and Mn (Rassmann et al., 2016), as shown in Equations 4, 5,

$$CH_2O + 4Fe(OH)_3 + 7H^+ \rightarrow HCO_3^- + 4Fe^{2+} + 10H_2O,$$
 (4)

$$CH_2O + 2MnO_2 + 3H^+ \rightarrow HCO_3^- + 2Mn^{2+} + 2H_2O,$$
 (5)

it should be remembered that this process dominates the anaerobic mineralization of OM in coastal and continental margin sediments (Jørgensen and Kasten, 2006), accounting for up to 70% of all OM mineralization (Thamdrup and Canfield, 1996). When the concentration of OM in the sediment is higher than the availability of oxidants for its mineralization, methanogenesis takes place (Froelich et al., 1979). Methanogenesis itself does not change TA, but following the anaerobic oxidation of methane (AOM), significant amounts of HCO_3^- are produced (Ritger et al., 1987). It has been demonstrated that under anaerobic conditions, methane (CH_4) is microbially oxidized with nitrate (In't et al., 2018), Mn, and Fe (Beal et al., 2009; Sturm et al., 2019):

$$CH_4 + 4NO_3^- \to 4NO_2^- + CO_2 + 2H_2O_3$$
 (6)

$$CH_4 + 4MnO_2 + 7H^+ \rightarrow 4Mn^{2+} + HCO_3^- + 5H_2O,$$
 (7)

$$CH_4 + 8Fe(OH)_3 + 15H^+ \rightarrow 8Fe^{2+} + HCO_3^- + 21H_2O.$$
 (8)

However, due to the high concentration of SO_4^{2-} in seawater, it is probably the most important oxidant in AOM (Boetius et al., 2000; Egger et al., 2018):

$$CH_4 + SO_4^{2-} \rightarrow HS^- + HCO_3^- + H_2O.$$
(9)

The anaerobic oxidation of CH_4 with SO_4^{2-} (SO_4^{2-} AOM), mediated by anaerobic methanotrophic archaea (ANME) in syntrophic consortia with sulfur-reducing bacteria (SRB) (Boetius et al., 2000), takes place within the sulfate-methane transition (SMT) zone. In this sediment horizon, the downward flux of SO_4^{2-} encounters an upward flux of CH_4 , and their concentrations are low (Beulig et al., 2019). The process strongly affects the alkalinity of pore waters, as it produces large amounts of HCO_3^{-} , as well as HS⁻, also a component of TA (Equation 1).

The Baltic Sea is an example of a shallow shelf sea, with a large riverine inflow and limited water exchange with the ocean; therefore, the internal source associated with the production and release of TA from anaerobic sediments is likely an important part of its budget. This is indicated by the modeling studies of Gustafsson (2013) and Gustafsson et al. (2014), which demonstrated that the load from the external sources (rivers and the North Sea) does not explain the high alkalinity in the Baltic water. Most of the internal sources of TA are believed to be related to denitrification, Fe reduction, and pyrite burial, till erosion on the seabed and other unresolved sedimentary processes (Gustafsson et al., 2014; Gustafsson et al., 2019; Wallmann et al., 2022). However, the role of sediments as an internal source of alkalinity remains poorly understood, and until now, the TA budget in the Baltic Sea is not closed.

The estimation of the role of sediments as a source of alkalinity to the water column is a challenging task due to the high variability of environmental (benthic) conditions within the Baltic Sea. Here, we describe the geochemistry of anaerobic sediments from the Gulf of Gdańsk (southern Baltic Sea), with particular emphasis on dissolved inorganic carbon (DIC), CH_4 , and SO_4^{2-} . We estimate the benthic flux of CA and the sulfate reduction rate (SRR) in sediments.



To elucidate the impact of benthic conditions, in our study, we include different types of anoxic sediments: methanic, methanic with freshwater seepage, and methane-free.

2 Materials and methods

2.1 Sediment and pore water sampling

Samples were collected in July 2023 during cruise onboard RV Oceanograf (vessel of the University of Gdańsk) at three research stations located in the Gdańsk Basin (Figure 1). The water depth of the stations ranged from 52 to 103 m (Table 1). At stations MET1-MP and MET2, methane was present in the examined sediment layer. Station MET1-MP is an active deepwater pockmark (Brodecka-Goluch et al., 2022), and MET2 is an area of shallow gas regular accumulation (Jaśniewicz et al., 2019; Brodecka-Goluch et al., 2022). Station ZGG represents the seabed without gas accumulation in the sediment and without a specific structure on the seafloor (Table 1).

Sediment cores were collected using a Rumohr Lot gravity corer, with 7.5 cm diameter and 150 cm long liners. Sampling was always preceded by hydroacoustic measurements using EK80 splitbeam echosounders (Simrad) to reproduce the exact sampling position. Three sediment cores were taken from each station, with lengths ranging from 90 to 110 cm. One core was used for

pore water analysis, another for CH4 analysis, and the third core for water content (WC), organic matter (estimated as loss on ignition, LOI), and organic carbon (CORG) analyses. Pore waters were retrieved without contact with air, from intact and tightly sealed sediment cores, using Rhizon® samplers. The samplers were inserted through holes drilled in the liners at 5 cm intervals. The first sampler was placed a few centimeters above the sediment (0.5-2.0 cm, depending on the station) to sample water collected with the sediment cores. Temperature (T), practical salinity (S_{PSU}), and dissolved oxygen concentration (O₂) in water ca. 5 cm above the sediment were measured using a portable multiparameter meter (WTW MultiLine[®] 3630 IDS) with a conductivity sensor (TetraCon[®] 925) and an oxygen probe (FDO[®] 925). pH was determined spectrophotometrically using m-cresol purple as an indicator dye (Hammer et al., 2014). The precision (RSD) of pH measurements in the analyzed samples was ≤0.009%. Nearbottom water for further analysis was collected using a syringe with a hose.

2.2 Geochemical parameters

The following parameters were analyzed in water samples: TA, pH, concentration of DIC, SO_4^{2-} , chloride (Cl⁻), hydrogen sulfide (H₂S), iron (Fe²⁺), and manganese (Mn²⁺). Measurements of TA, pH, and H₂S were performed immediately after sampling in

| Station | Depth [m] | Location/bottom structure | Sediment type | T [°C] | S _{PSU} | O ₂ [µmol dm ⁻³] | |
|--|-----------|---|--------------------------|--------|------------------|---|--|
| Confirmed presence of methane in the sediment | | | | | | | |
| MET1-MP | 82 | Central Gulf of Gdańsk/active pockmark with a scattered gas outflow and freshwater infiltration | Silt ^a | 9.2 | 10.8 | 6.3 | |
| MET2 | 52 | Outer Puck Bay/area of shallow gas accumulation | Sandy silt ^a | 8.5 | 8.0 | 96.9 | |
| No methane detected in the examined sediment layer | | | | | | | |
| ZGG | 103 | Western Gdańsk Deep | Clayey silt ^a | 8.1 | 12.2 | 3.1 | |

TABLE 1 Overview of sampling stations with information about the type of station, depth, and sediment type, as well as temperature (T), salinity (S_{PSU}), and concentration of oxygen (O_2) in near-bottom water during sampling.

^aBrodecka et al. (2013).

the onboard laboratory. Samples for SO_4^{2-} , Fe^{2+} , and Mn^{2+} were acidified with HNO₃, and DIC samples were poisoned with $HgCl_2$ and stored in sealed, almost completely filled tubes (<1% free space) at 4°C until analysis at the laboratory on land.

Total alkalinity was determined by potentiometric titration with 0.01 M HCl using an automatic titrator (SM-Titrino 702, Metrohm). TA was determined from titration data using the Gran approach (10-12 points between pH 4.5 and 3.5 were taken for the plot). pH changes during titration were measured using a pH/ATC combination electrode. The accuracy of the pH determination was 0.002 units. The concentration of HCl used in TA titration was checked against a fresh standard sodium carbonate solution prepared from certified high-purity Na2CO3 (Sigma-Aldrich) according to Dickson et al. (2007). Na₂CO₃ was dried at 280°C for >2 h and cooled in a desiccator. The Na₂CO₃ standard solution was prepared in 0.2 mol dm⁻³ sodium chloride to adjust the total ionic strength to a value similar to Baltic water. The accuracy of TA determination obtained by titration in 2 mmol kg⁻¹ Na_2CO_3 was $\leq 3 \mu mol kg^{-1}$. The precision of TA determination in 2 mmol kg⁻¹ Na₂CO₃ expressed as RSD was $\leq 0.2\%$. The RSD of TA measurements in the analyzed samples was $\leq 0.3\%$.

Concentrations of DIC were measured in duplicates using a TOC analyzer VarioTOC Cube (Elementar GmbH) equipped with a nondispersive infrared (NDIR) detector. Samples were acidified with 1% H_3PO_4 inside the apparatus, and DIC was purged in the sparger and measured using the detector. The accuracy (percent recovery from reference material) of DIC determinations was 98%. The precision (RSD) of DIC determinations was \leq 1%.

Concentrations of SO_4^{2-} and Cl^- were determined using highperformance ion chromatography (Metrohm 850 Professional IC). Concentration of H_2S was measured spectrophotometrically using a Hach-Lange DR6000 spectrophotometer with the methylene blue method (Cline, 1969). Concentrations of Fe^{2+} and Mn^{2+} were measured using an inductively excited plasma optical emission (ICP-OES) spectrometer (PerkinElmer Optima 8300). The precisions (RSD) of analysis of SO_4^{2-} , H_2S , Fe^{2+} , and Mn^{2+} were 3%, 3%, 2%, and 2%, respectively, and the limits of quantification (LOQs) were 0.03 mmol dm⁻³, 1.5 µmol dm⁻³, 1.0 µmol dm⁻³, and 1.0 µmol dm⁻³, respectively. Samples of sediment for analysis of CH_4 were collected within 30 min after sediment core retrieval, through the holes previously made on the sides of core liners, using 3-mL syringes with the Luer-lock removed and transferred into 20-mL vials, according to the procedure described by Jørgensen et al. (2001). The CH_4 concentration was analyzed using the standard headspace technique on a gas chromatograph (Perkin Elmer) equipped with a flame ionization detector (FID) and an HP-5 column (30 m, 0.32 mm, and 0.25 μ m), with helium as the carrier gas. The detection limit (LOD) was 0.2 μ mol dm⁻³. The results of methane determinations were corrected for sediment porosity. Sediment porosity at each station was calculated based on its water content, according to the equation presented in Section 2.3.

Sediment cores for water, organic matter, and organic carbon content in the sediment were sectioned into 5-cm layers directly after retrieval, using a spatula and a PVC ring. Samples were placed into plastic zipper bags and immediately frozen at -21° C. WC was determined by drying samples to constant weight at 105°C. Organic matter content was determined as LOI at 450°C. The C_{ORG} content in the sediment was measured using a CHNS autoanalyzer (Perkin Elmer 2400), according to the method by Parsons et al. (1985). Prior to analysis, samples were acidified with 1 M HCl to remove inorganic carbon (Hedges and Stern, 1984).

2.3 Concentration and benthic flux of carbonate alkalinity

CA is equal to $[\text{HCO}_3^{-}]+2[\text{CO}_3^{2-}]$ (Equation 2), and the benthic flux of CA (J_{CA}) is equal to the sum of the fluxes of bicarbonate ($J_{\text{HCO3-}}$) and carbonate ($J_{\text{CO32-}}$), as shown in Equation 10:

$$J_{\rm CA} = J_{\rm HCO3-} + 2 \cdot J_{\rm CO32-.} \tag{10}$$

The concentrations of HCO_3^- and CO_3^{2-} were calculated from the DIC and pH in samples using mass-conservation equations and the equilibrium relationships between various species, according to Dickson et al. (2007) (all relevant equations are given in Supplementary Table S1). The dissociation



constants of carbonic acid in seawater, that is, $pK_1 = 5.9$ and $pK_2 = 9.1$, were corrected for salinity and temperature, according to Millero (2010).

The flux of $J_{\text{HCO3-}}$ and $J_{\text{CO32-}}$ at the sediment–water interface was estimated based on measured porewater profiles. The concentration gradients were calculated as the first derivative of the function describing profiles of ions, including the near-bottom water concentration. The measured values were fitted as closely as possible by a curve, as shown in Equation 11:

$$C(z) = \frac{C_{max}}{1 + \exp\left(a \cdot z + b\right)},\tag{11}$$

where C(z) stands for the molar concentration in pore water at depth z [cm] and C_{max} stands for the maximum concentration in the profile. The functions were fitted to the data, and the function parameters (a and b) were calculated using MathWorks MATLAB 2020b and 2024b. Estimations were made using the nonlinear square method. Goodness of fit (R^2) of empirically derived models was ≥ 0.96 for HCO₃⁻ and ≥ 0.84 for CO₃²⁻. Results of fitting the function to the data are presented in Figure 2. The analytically calculated first derivative from fitted functions for z = 0 was used as a concentration gradient at the sediment-water interface. This method has been commonly applied in other studies (e.g., Urban et al., 1997; Srithongouthai et al., 2003; Denis and Grenz, 2003). The application of nonlinear function allows calculating the flux in a close proximity to the diffusion boundary layer, significantly reducing errors due to coarse depth resolution in pore water concentration profiles and enabling more accurate flux estimates (Sayles et al., 1996; Zabel et al., 2000).

The fluxes (*J*) at the sediment–water interface were calculated using MathWorks MATLAB 2020b and 2024b according to equations implemented in RADIv1 (Sulpis et al., 2022) and consisted of a diffusive and an advective component. The component associated with bioirrigation was omitted in calculations as no macrofauna was present at any of the sampling stations. The fluxes were estimated using Equation 12:

$$J = -\varphi \cdot D_S \cdot \frac{\partial C}{\partial z} + \varphi \cdot u \cdot C, \qquad (12)$$

where *J* is the flux [mol m⁻² a⁻¹]; φ is the sediment porosity; $\delta C/\delta z$ is the concentration gradient at the sediment–water interface; D_S is the molecular diffusion coefficient in sediment [m² a⁻¹] expressed as $D_S = D_{SW}/\Theta^2$, where Θ is the tortuosity and D_{SW} is the molecular diffusion coefficient in seawater [m² a⁻¹]; *u* is the burial velocity [m a⁻¹]; and *C* is the concentration of HCO₃⁻ or CO₃²⁻ [mol m⁻³]. Diffusion coefficients in seawater (D_{SW}) adopted in the calculations were as follows: 11.8·10⁻⁶ cm² s⁻¹ for HCO₃⁻ and 9.55·10⁻⁶ cm² s⁻¹ for CO₃²⁻ (Li and Gregory, 1974) and were corrected for temperature and salinity in accordance with the Stokes–Einstein equations (Li and Gregory, 1974).

Porosity was calculated from Equation 13 (Engvall, 1978):

$$\varphi = WC \cdot \left[(100 - WC) \cdot d^{-1} + WC \right]^{-1}, \tag{13}$$

where *WC* denotes the water content of sediment [%] and *d* is the bulk density of sediment (2.5 g cm^{-3}) . Changes in porosity with depth were parametrized as represented in Equation 14 (Boudreau, 1996):

$$\varphi_z = \varphi_{\infty} + (\varphi_0 - \varphi_{\infty}) \cdot e^{-\beta \cdot z}, \qquad (14)$$

where φ_0 is the porosity in the surface sediment layer, φ_{∞} is the porosity in the deepest sediment layer, and β is the attenuation coefficient [m⁻¹].

| Parameter | Equation number | Description | | Station | | |
|--------------------|-----------------|---|-----------------------------------|----------------------|----------------------|-----------------------|
| | | | | MET1-MP | MET2 | ZGG |
| | | Parameter of function fitted to the | for HCO ₃ ⁻ | -0.3393 | -0.1019 | -0.1544 |
| a | 11 | concentration profile | for CO ₃ ^{2–} | -0.3479 | -0.0645 | -0.0293 |
| | | Parameter of function fitted to the | for HCO ₃ ⁻ | 3.2722 | 1.4982 | 1.2531 |
| в | 11 | concentration profile | for CO ₃ ²⁻ | 4.0419 | 2.6393 | 1.4297 |
| R^2 | | | for HCO ₃ ⁻ | 0.99 | 0.93 | 0.93 |
| | | Goodness of fit of the model | for CO ₃ ²⁻ | 0.98 | 0.85 | 0.84 |
| 2012 | | Concentration gradient at the | of HCO ₃ ⁻ | 0.0362 | 0.0339 | 0.0227 |
| 0C/02 | 12 | sediment-water interface [mol m ⁻¹] | of CO ₃ ²⁻ | $8.11 \cdot 10^{-4}$ | $2.48 \cdot 10^{-4}$ | 8.86.10 ⁻⁵ |
| 2 | 10 | Molecular diffusion coefficient in sediment | of HCO ₃ ⁻ | 0.0200 | 0.0163 | 0.0183 |
| D_{S} | 12 | $[m^2 a^{-1}]$ | of CO ₃ ^{2–} | 0.0156 | 0.0127 | 0.0143 |
| $arphi_0$ | 14 | Porosity in the surface sediment layer | | 0.99 | 0.88 | 0.94 |
| φ_{∞} | 14 | Porosity in the deepest sediment layer | | 0.81 | 0.78 | 0.86 |
| β | 14 | Porosity attenuation coefficient [m ⁻¹] | | 0.058 | 0.028 | 0.025 |
| θ | 15 | Tortuosity in the surface sediment layer | | 1.01 | 1.12 | 1.06 |
| и | 16 | Porewater burial velocity $[m a^{-1}]$ | | $3.82 \cdot 10^{-4}$ | $3.57 \cdot 10^{-4}$ | $5.80 \cdot 10^{-4}$ |

TABLE 2 Parameters and variables used in the calculation of the benthic flux of carbonate alkalinity.

Tortuosity (Θ) was defined using Equation 15 (Boudreau, 1997):

$$\theta_z = \sqrt{1 - 2\ln\left(\varphi_z\right)}.\tag{15}$$

The pore water burial velocity $[m a^{-1}]$ at depth $z (u_z)$ was calculated according to Equation 16:

$$u_z = v_{\infty} \cdot \varphi_{\infty} / \varphi_z \tag{16}$$

where v_{∞} is the pore water burial velocity [m a⁻¹] in the deepest sediment layer (Sulpis et al., 2022).

The coefficients, constants, and data used in calculating bicarbonate and carbonate benthic fluxes are summarized in Table 2.

2.4 Sulfate reduction rate calculation

The SRR was calculated from the concentration profile of SO_4^{2-} in pore water based on Berner's diagenetic equation (1980). No macrofauna that could affect SO_4^{2-} concentrations in pore water through bioturbation and bioirrigation were present at any of the stations, so this term of Berner's (1980) equation was omitted. Assuming a steady state and transport within sediment only by molecular diffusion, the equation was simplified to Equation 17:

$$SRR = -\frac{1}{\varphi} \frac{\partial \cdot \left(\varphi \cdot D_S \cdot \frac{\partial C}{\partial z}\right)}{\partial z},$$
 (17)

where SRR is the net rate of sulfate reduction [nmol cm⁻³ d⁻¹]. The seawater diffusion coefficient (10.7 \cdot 10⁻⁶ cm² s⁻¹) with correction for temperature (Li and Gregory, 1974) and tortuosity was used to calculate the SO₄^{2–} flux between sediment layers.

3 Results

3.1 Sediment parameters

Profiles of WC, porosity, LOI, and C_{ORG} in sediments from three research stations are presented in Supplementary Figure S1. At all the stations studied, WC ranged from 57.3% to 97.6%, porosity was 0.78–0.98, LOI was 5.4%–20.2%, and the C_{ORG} content was 3.7%–8.4%. For all parameters, there was a decrease with increasing sediment depth. The lowest WC, porosity, LOI, and C_{ORG} were characteristic of sediments at station MET2, which is the shallowest and where sandy silt occurs. The highest values of WC, LOI, and C_{ORG}, as well as porosity in the surface layer, were recorded in the silt sediment in the MET1-MP pockmark.

3.2 Geochemistry of pore water

As shown in Figures 3, 4, the chemical composition of pore water differed markedly between sampling stations. DIC



concentration was the highest at station MET1-MP (deepwater pockmark), where it ranged from 1.85 to 27.52 mmol kg⁻¹. At station MET2, located within the area of shallow gas accumulation, DIC concentration ranged from 2.08 to 19.40 mmol kg⁻¹. The lowest values ($2.01-10.01 \text{ mmol kg}^{-1}$) and the smallest variation in DIC concentration were recorded at the non-methanic sediment at station ZGG in the western part of the Gdańsk Deep. At all stations, DIC concentrations increased with sediment depth. The pH in pore water of all sampling sites ranged from 7.20 to 7.89.

The concentration of CH₄ in the examined sediments varied over a wide range (0.41–5.99 mmol dm⁻³), with an average concentration at station MET1-MP being lower (2.00 \pm 0.79 mmol dm⁻³) than that at station MET2 (3.25 \pm 1.65 mmol dm⁻³). For MET1-MP, the concentration of CH₄ increased abruptly in the surface sediment layer to a maximum value at a depth of 5 cm (Figure 3). Deeper in the sediment, the concentration decreased slightly and then stabilized at approximately 2 mmol dm⁻³. At station MET2, there was a gradual increase in CH₄ concentration, reaching a maximum value at 80 cm below the sea floor (bsf).

Concentration of SO_4^{2-} varied from values <LOQ to 9.3 mmol dm⁻³ (Figure 3). In the case of station MET1-MP, SO_4^{2-} was present only to a depth of 20 cm bsf. In this layer, its concentration decreased rapidly and remained <LOQ at deeper layers. At the MET2 station, SO_4^{2-} was present down to a depth of 40 cm bsf, and the decrease in concentration with depth occurred

less abruptly than it did in MET1-MP pore waters. The highest SO_4^{2-} concentrations were recorded at station ZGG. In the upper 40 cm of the sediment, SO_4^{2-} concentration decreased from 9.3 to 3.8 mmol dm⁻³. Deeper in the sediment, the concentration was approximately constant and did not decrease below 3.7 mmol dm⁻³.

Chloride concentrations in the pore waters of all the sampling stations varied from 165 mmol dm⁻³ to 70 mmol dm⁻³. In the deep-water pockmark MET1-MP, there was a marked decrease in concentration with depth (from 135 mmol dm⁻³ to 70 mmol dm⁻³), whereas at MET2 and ZGG, concentrations throughout the sediment profile were relatively constant (95–105 mmol dm⁻³ at MET2 and 149–165 mmol dm⁻³ at ZGG; Supplementary Figure S2).

In the case of H_2S , the highest concentrations in pore waters were found at station ZGG, where it was present throughout the sediment profile, and its concentration reached 1433 µmol dm⁻³ (Figure 4). At stations MET1-MP and MET2, H_2S was present only in a particular layer of sediment (up to approximately 30–40 cm bsf), where sulfate reduction took place (Figure 3). In deeper layers, concentration of H_2S was <LOQ.

Concentration of Fe²⁺ in most cases was below 10 μ mol dm⁻³. Higher values were measured ca. 80 cm bsf in MET2 and ca. 55 cm bsf in MET1-MP (in this case, Fe²⁺ concentration reached 140 μ mol dm⁻³, the highest measured value). The highest concentration of Mn²⁺ (4–51 μ mol dm⁻³) was found on ZGG. For the other stations, the concentration increased in the deep sediment layers but did not exceed 26 μ mol dm⁻³.



3.3 Carbonate alkalinity and its benthic flux

CA in pore waters of all stations varied in the range of $1.76-27.25 \text{ mmol kg}^{-1}$. CA was always smaller than TA (Figure 5), which varied from 1.89 to 28.39 mmol kg⁻¹. Depending on the station and depth bsf, the difference between TA and CA was $0.09-2.09 \text{ mmol kg}^{-1}$. The largest differences between TA and CA occurred at station ZGG, and the smallest at MET2. At all stations, there was an increase in CA (and TA) in pore water with increasing depth, and the shape of the profiles was very similar to that of DIC in pore water (Figure 3).

The average benthic flux of CA obtained in the present study was 1540 ± 419 µmol m⁻² d⁻¹. Values of J_{CA} are presented in Table 3. The highest J_{CA} of 2037 ± 47 µmol m⁻² d⁻¹ was obtained for pockmark MET1-MP. J_{CA} estimated for station MET2 was 1507 ± 80 µmol m⁻² d⁻¹. The lowest J_{CA} of 1078 ± 40 µmol m⁻² d⁻¹ was obtained for the non-methanic station ZGG. The dominant component of J_{CA} at all stations was J_{HCO3-} , accounting for 96.6%–99.4% of J_{CA} .

3.4 Sulfate reduction rate

The highest SRR values were recorded in the surface layer of the MET1-MP pockmark — the maximum was narrow, and the highest rate (26.1 nmol cm⁻³ d⁻¹) was observed at a depth of 2–4 cm bsf (Figure 6). Deeper in the sediment, the SRR decreased rapidly and below 25 cm was <0.5 nmol cm⁻³ d⁻¹. Station MET2

showed two SRR maxima — one at a depth of 17 cm, with a maximum value of 17.3 nmol cm⁻³ d⁻¹, and a smaller maximum at approximately 3 cm bsf, with a maximum value of 3 nmol cm⁻³ d⁻¹. At the ZGG station, the SRR value decreased exponentially with sediment depth, from 4.6 nmol cm⁻³ d⁻¹ near the surface to 0.2 nmol cm⁻³ d⁻¹ deep in the sediment.

4 Discussion

4.1 Geochemical variations between research stations

Based on the analysis of parameters in sediments and pore waters, the research stations can be characterized as three systems with significantly different geochemical conditions. Accordingly, station ZGG located within the Gdańsk Deep represents sediment that is fine grained and OM rich (Supplementary Figure S1), yet methane free. The bottom water in the area is usually hypoxic or anoxic, which was also the case during sampling (Table 1). Owing to the very high concentrations of H₂S in the pore water and the lack of CH₄ (Figure 3), it can be assumed that the predominant pathway of mineralization of OM in the sediment and source of CA in pore water of this station is DSR (Equation 3). Based on the Mn²⁺ profile (Figure 4), it can be concluded that the source of CA in the pore water of the ZGG station is also microbial Mn(IV) reduction related to OM mineralization (Equation 5); however, concentrations of Mn²⁺ are two orders of magnitude lower than those of H₂S,



indicating the dominant role of DSR. It is also noteworthy that at the ZGG station, the share of CA in TA was the smallest among all sampling stations (Figure 5). The difference between TA and CA was as high as 2 mmol kg⁻¹, indicating a significant contribution of non-carbonate inorganic bases (NCIBs) to TA. The presence of high concentrations of other components (mainly H₂S, ammonia, and phosphate) that form separate acid–base systems capable of accepting and donating protons is typical of anaerobic sediments and makes the TA in pore waters usually higher than it would be expected from the concentration of DIC (Berner et al., 1970; Hu et al., 2010; Lukawska-Matuszewska et al., 2018).

The other two stations, MET1-MP and MET2, represent anoxic sediment containing CH4. Therefore, it can be assumed that at both stations, the variability of CA in pore water will be influenced by microbial processes associated with the oxidation of this gas (Equations 6–9). Nevertheless, if we analyze the variability of geochemical parameters, it is possible to identify differences between the stations, potentially relevant to the concentration and benthic flux of CA. Starting from the deep-water pockmark MET1-MP, it should be pointed out that SO₄²⁻ concentrations are low compared to those in the other stations (Figure 3). Pockmark MET1-MP is an area of upward infiltration of fresh groundwater (Brodecka et al., 2013; Brodecka-Goluch et al., 2022; Kurowski et al., 2024) and its possible outflow from the seafloor (Szymczycha et al., 2018; Ehlert von Ahn et al., 2024). Freshwater seepage also occurred during the sampling for the present work, as illustrated by the decrease in Cl⁻ concentration with depth (Supplementary Figure S2). The seeping freshwater dilutes pore water and lowers concentration of SO42-, reducing their availability for decomposition of OM accumulating in the pockmark in significant amounts (Supplementary Figure S1). The depletion of SO4²⁻, together with the high rate of OM accumulation, promotes shallow methanogenesis in sediments, as confirmed by isotopic studies conducted by Ehler von Ahn et al. (2024) at the nearby station, M1. As a consequence, relatively high concentrations of CH_4 are observed in the pockmark MET1-MP in the upper sediment layer, and SMT is close (ca. 3 cm bsf) to the sediment surface (Figure 3).

In most marine settings, CH4 diffusing from the methane production zone is efficiently oxidized (Equation 9) by microorganisms that catalyze the SO42-AOM (e.g., Reeburgh, 1976; Borowski et al., 1999). This makes the SMT an effective barrier against CH4 release from the bottom (e.g., Treude et al., 2003). However, very high sedimentation rates (Egger et al., 2016), insufficient availability of SO42-, and physical processes involving ebullition and gas bubble migration (Martens and Klump, 1980; Kipphut and Martens, 1982; Treude et al., 2005) can cause CH₄ leakage through SMT. Alternatively, microbial oxidation of CH₄ in the sediment can occur with the involvement of other oxidants, such as nitrate (Equation 6), Fe(III) (Equation 8), and Mn(IV) (Equation 7) (Raghoebarsing et al., 2006; Beal et al., 2009). In our work, we did not study the concentration of inorganic forms of nitrogen, so we cannot conclude about the former process. However, given the profiles of Fe^{2+} and Mn^{2+} (Figure 4), it is plausible that CH₄ is oxidized with Fe(III) and Mn(IV) compounds. This is mainly supported by a sharp increase in Fe²⁺ concentration below 50 cm in the sediment, indicative of AOM with Fe(III) (Fe-AOM). Fe²⁺ accumulates in the pore water because there is no H₂S (Figure 3) with which it could precipitate in the form of sulfides. This makes sediments of pockmark with an active fresh groundwater seepage different from the typical marine sediments, where Fe sulfide (mainly pyrite) formation results in the complete removal of Fe²⁺ from pore water. In typical marine settings, the limiting factor for pyrite formation is the availability

| Location | J _{CA} (or J _{DIC}) [µmol m ⁻² d ⁻¹] | J* _{CA} [µmol m ⁻² d ⁻¹] | Reference |
|--------------------------|---|--|---|
| MET1-MP (Gulf of Gdańsk) | 2037 ± 47 | 2017 ± 47 | Present study |
| MET2 (Gulf of Gdańsk) | 1507 ± 80 | 1498 ± 80 | Present study |
| ZGG (Gulf of Gdańsk) | 1078 ± 40 | 983 ± 40 | Present study |
| Gulf of Gdańsk | 200-4000 | | Lengier et al. (2021) |
| Gulf of Gdańsk | 2260-8710 | | Brodecka-Goluch and Łukawska-Matuszewska (2018) |
| Gulf of Bothnia | 822 ± 23 | | Winogradow and Pempkowiak (2014) |
| Bothnian Sea | 250 | | Lengier et al. (2021) |
| Gotland Deep | 2055 ± 137 | | Winogradow and Pempkowiak (2014) |
| Bornholm Basin | 330-490 | | Lengier et al. (2021) |
| Bornholm Deep | 2123 ± 68 | | Winogradow and Pempkowiak (2014) |
| Location | SRR [nmol cm ⁻³ d ⁻¹] | | Reference |
| MET1-MP (Gulf of Gdańsk) | <0.1-26.1 | | Present study |
| MET2 (Gulf of Gdańsk) | <0.1-17.3 | | Present study |
| ZGG (Gulf of Gdańsk) | 0.2-4.6 | | Present study |
| Gdańsk Basin | 0-43 | | Pimenov et al. (2010) |
| Gotland Deep | <250 | | Piker et al. (1998) |
| Himmerfjärden | 0.2–338 | | Sawicka and Brüchert (2017) |
| Vistula Lagoon | 0.2-42.3 | | Pimenov et al. (2013) |
| Curonian Lagoon | 0.2–24.1 | | Pimenov et al. (2013) |
| Eckernförde Bay | 10-465 | | Treude et al. (2005) |
| Kattegat | <1-21.4 | | Iversen and Jørgensen (1985) |
| Skagerrak | ≤52.1 | | Iversen and Jørgensen (1985) |

TABLE 3 Benthic flux of carbonate alkalinity (J_{CA}) and net benthic flux of carbonate alkalinity (J^*_{CA}), as well as sulfate reduction rates (SRRs) at three sampling stations examined in the present study (MET1-MP, MET2, and ZGG) and in other areas of the Baltic Sea (in the case of data from the literature, the flux of dissolved inorganic carbon (J_{DIC}) is presented instead of J_{CA}).

of OM and/or Fe(III) (Raiswell and Berner, 1985; Sternbeck and Sohlenius, 1997). Concentration of $SO_4^{2^-}$ is usually high, and the rate of $SO_4^{2^-}$ reduction is high enough to provide sufficient H₂S for the process (Berner, 1970). However, in pockmarks, pyrite formation may be limited by the availability of $SO_4^{2^-}$ for the reduction (Boesen and Postma, 1988), especially when groundwater infiltration reduces its concentration. In such a situation, iron sulfide formation is restricted with the low availability of H₂S, and Fe²⁺ accumulates in pore waters. Similarly, Fe²⁺ enrichment of pore water has been observed in other marine sediments with active Fe-AOM (D'Hondt et al., 2004; Riedinger et al., 2014), as well as in previous studies of deepwater pockmarks in the Gulf of Gdańsk (Kurowski et al., 2024). On the other hand, in the upper layer, to approximately 30 cm bsf, $SO_4^{2^-}$ -AOM occurs, resulting in an increase in H_2S concentration in this particular sediment layer.

Station MET2 is located in an area of shallow gas accumulation, with no specific structure on the bottom (Table 1) and no evident signals of groundwater infiltration (Supplementary Figure S2). At station MET2, CH₄ concentration decreases linearly toward the sediment surface to <LOD values at approximately 10 cm bsf. CH₄ oxidation occurs mainly through the SO₄²⁻-AOM pathway (Equation 9), as evidenced by a decrease in CH₄ concentration with a concomitant decrease in SO₄²⁻ and a sharp increase in H₂S concentration, which reaches 1400 µmol dm⁻³ at a depth of 16 cm bsf. AOM involving Fe(III) and Mn(IV) is probably far less important, as supported by the minor increase in Fe²⁺ and Mn²⁺ concentrations in the deep sediment layers (Figure 3). Compared



to the MET1-MP pockmark, the availability of SO_4^{2-} for various microbial processes in the sediment at MET2 station is higher — SO_4^{2-} is present here down to a depth of approximately 40 cm and in much higher concentrations than at MET1-MP. Consequently, the SMT is deeper below the sediment surface (approximately 16 cm bsf) than at MET1-MP (Figure 3).

4.2 Comparison of the benthic flux of CA with existing data

The range of J_{CA} obtained in the present study (1037–2084 µmol m⁻² d⁻¹) agrees well with the results of previous studies from the Baltic Sea (Table 3). For example, Winogradow and Pempkowiak (2014) studied DIC (approximately equivalent to CA) fluxes in different areas of the Baltic Sea, obtaining values of $822 \pm 23 \text{ µmol m}^{-2} \text{ d}^{-1}$ in the Gulf of Bothnia, $2123 \pm 68 \text{ µmol m}^{-2} \text{ d}^{-1}$ in the Bornholm Deep, and $2055 \pm 137 \text{ µmol m}^{-2} \text{ d}^{-1}$ in the Gotland Deep. Lengier et al. (2021) reported a benthic DIC flux of 2160 µmol m⁻² d⁻¹ in the Gdańsk Basin. Fluxes obtained for the Bornholm Basin and Bothnian Sea were lower: $330-490 \text{ µmol m}^{-2} \text{ d}^{-1}$ and 250 µmol m⁻² d⁻¹, respectively. In turn, the values reported by Brodecka-Goluch and Łukawska-Matuszewska (2018) are higher than the J_{CA} calculated in the present work, ranging from 2260 to 8710 µmol m⁻² d⁻¹.

4.3 Factors affecting the benthic flux of CA

Based on the analysis of geochemical variations between research stations, two processes were identified that potentially affect J_{CA} : DSR and SO₄²⁻-AOM. At this point, it is worth mentioning that alkalinity production associated with the sulfate reduction during DSR and AOM is partially reversible. J_{CA} can partially be diminished by the oxidation of H₂S, the main by-product of bacterial sulfate reduction, at or near the water-sediment interface (Krumins et al., 2013). Oxidation of H₂S releases H⁺ and leads to the consumption of alkalinity. To assess the potential effect of H_2S oxidation on J_{CA} , we calculated the flux of HS^- (J_{HS-}), the main ionic form of H₂S, across the sediment-water interface. $J_{\rm HS-}$ represents the amount of H₂S that can be oxidized when released into the overlying water and corresponds to the fraction of CA that will be consumed. The J_{HS} value was calculated analogously to $J_{\text{HCO3-}}$ and $J_{\text{CO32-}}$ (Section 2.3). The parameters and variables used in the calculation of $J_{\rm HS\-}$ are presented in Supplementary Table S1. The resulting $J_{\rm HS-}$ is at least an order of magnitude smaller than J_{CA} : 20 µmol m⁻² d⁻¹ at station MET1-MP, $9\,\mu mol\;m^{-2}\;\;d^{-1}$ at station MET2, and $95\,\mu mol\;m^{-2}$ d^{-1} at station ZGG. This suggests that J_{CA} can be diminished by approximately 1% in the case of stations MET1-MP and MET2 and approximately 9% in the case of station ZGG as a result of H₂S oxidation. Assuming the complete oxidation of H₂S released from the sediment to the bottom water, the net benthic flux of CA (J_{CA}^*) from the sediment in the study area is 943–2064 $\mu mol \; m^{-2} \; d^{-1}$ (Table 3).

Both DSR and SO42-AOM involve SO42- reduction accompanied by the release of DIC (Equations 3, 9); however, which process dominates the sediment and at what depth it occurs strongly depend on the local environmental conditions. The high input of OM to the seafloor in the study area (sedimentation rate is 1.4-1.7 mm year⁻¹; Szmytkiewicz and Zalewska, 2014; Szymczak-Żyła et al., 2017) indicates that O2, NO3, Mn(IV), and Fe(III) used by microorganisms for decomposition of OM (Froelich et al., 1979) are quickly consumed, and the sulfate reduction zone begins just below the sediment surface (e.g., Kurowski et al., 2024 and the present study). Due to the lower salinity than that in oceanic waters, the availability of SO_4^{2-} in the Baltic water is limited, resulting in a shallower methane production zone in the sediment (e.g., Brodecka et al., 2013; Kurowski et al., 2024). In the case of pockmarks, SO_4^{2-} availability can be further reduced by infiltration of fresh groundwater (Idczak et al., 2020; Brodecka-Goluch et al., 2022; Ehlert von Ahn et al., 2024, and the present study). In addition, pockmarks that take the form of depressions in the bottom serve as sedimentation traps for sinking OM; thus, the methane production zone moves even closer to the sediment surface. In the case of the MET1-MP pockmark, where J^*_{CA} is estimated to be the largest, SO_4^{2-} are mainly consumed in the SO $_4^{2-}$ -AOM, and the SMT is located just below the sediment surface.

As the production and benthic flux of CA are affected not only by the type of process in which it is generated but also by its rate, we attempted to estimate the SRR in the sediment of the investigated stations. Given that SO_4^{2-} in the sediment is consumed by both DSR and SO_4^{2-} -AOM, the SRRs estimated from the SO_4^{2-} concentration profile represent the net rate being the sum of the rates of these two processes (SRR = $R_{DSR} + R_{SO42-AOM}$). A comparison of calculated rates with literature data shows that they are similar to rates previously determined at various locations within the Baltic Sea; however, they fall in the range of lower values (Table 3). The profile-based SRRs represent net SO₄²⁻ consumption in sediments and tend to be lower than gross rates estimated from radiotracer incubations presented in other studies (Iversen and Jørgensen, 1985; Jørgensen and Kasten, 2006).

Both SRR and SRR depth trends vary significantly between stations (Figure 6). The ZGG station has a markedly lower SRR, which decreases exponentially with sediment depth, reflecting the oxidation of available OM by SRB (Berner, 1964; Jørgensen, 1978). In the case of this methane-free sediment, SO_4^{2-} is exclusively consumed on DSR; thus, SRR = R_{DSR} . At this particular station, J^*_{CA} is the smallest (twice as small as that at the MET1-MP station), likely due to the lower SRR and the reoxidation of H₂S, which further reduces the flux.

The maximum SRR (Figure 6) as well as J^*_{CA} (Table 3) obtained for methanic sediments from stations MET1-MP and MET2 are significantly higher than those at ZGG. Moreover, the SRRs at MET1-MP and MET2 vary irregularly with depth, and distinct maxima are present in the profiles. The occurrence of maximum SRRs in specific sediment layers of these stations can be attributed to different processes fed by the SO4²⁻ flux. In the case of the MET2 station, the geochemical stratification of the sediment column is apparent. Both DSR and SO4²⁻-AOM occur in the sediment; therefore, SRR reflects the sum of $R_{\rm DSR}$ and $R_{\rm SO42-AOM}.$ In the upper sediment layer, SO42- is consumed mainly during the oxidation of OM. The first maximum of SRR is connected to the use of SO_4^{2-} in this process. Deeper in the sediment, SO_4^{2-} is consumed for the oxidation of CH4, and SRRs are much higher with a maximum ca. 16-17 cm bsf. Therefore, it can be assumed that AOM is more important for the production of CA in the pore water at this station. Nevertheless, J_{CA}^{*} is significantly lower than that at MET1-MP.

Examining the geochemical parameters in the pockmark MET1-MP (Figures 3, 4) allows us to conclude that in the upper 26 cm of sediment at this station, SO_4^{2-} is consumed on AOM, and therefore, the SRR reflects $R_{SO42-AOM}$. Linear changes in SO_4^{2-} concentration with depth indicate that sulfate is consumed almost entirely by CH₄ and that sulfate reduction dominates only close to the SMT (Niewöhner et al., 1998; Jørgensen and Kasten, 2006; Sivan et al., 2007). The situation is similar in the MET1-MP pockmark, where the distinct and narrow maximum of SRR occurs in the SMT area. The shallow SMT, combined with the high SRR, makes J^*_{CA} at least 25% larger than that in the case of the other two stations.

In summary, analysis of the geochemical parameters in anaerobic sediments with different characteristics (methanic, methanic with fresh groundwater seepage, and without methane) showed that the concentration and release of CA from sediments depend on the type (DSR and AOM) and the rate of the process producing it. Another factor affecting J^*_{CA} is the depth of SMT in the sediment. The highest J^*_{CA} was obtained for AOM-dominated sediment with fresh groundwater seepage and shallow SMT. The lowest J^*_{CA} occurred for non-methanic sediment, where CA was produced mainly in DSR. Our results may be useful for further modeling studies aimed at determining the role of sediments as

an internal source of alkalinity to help close the alkalinity budget in the Baltic Sea and predicting the direction of environmental changes under stressors related to eutrophication and climate change.

An important future direction is to explore how, with the increasing eutrophication and elevated temperatures negatively affecting the oxygenation of seawater, the role of sediments as an internal source of alkalinity will change. In addition, with the expected increase in precipitation and river runoff (especially in the northern part) associated with the climate change in the Baltic Sea region (HELCOM/Baltic Earth, 2021), will there be a freshening and reduction in sulfate concentration in water, resulting in increased CH_4 production and shallower SMT in the sediment, and how this will affect the release of CA from the seabed?

Data availability statement

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

Author contributions

KL-M: funding acquisition, formal analysis, writing – review and editing, visualization, writing – original draft, data curation, conceptualization, investigation, and project administration. MD: validation, methodology, writing – review and editing, software, formal analysis, and writing – original draft.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Supplementary material

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