Geochemistry of seabed sediments in area of pockmarks in Gulf of Gdansk, Baltic Sea

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INTRODUCTION

Pockmarks are depressions in the seabed, which are formed by freshwater and/or gas outflow. Gas (mostly methane) is derived from methanogenesis of accumulated organic matter (OM) and leads to bottom collapse. Methane is a significant greenhouse gas and has also huge impact on geochemical conditions in sediment and water by increasing metal remobilisation and nutrients release. Microbiological processes in the pockmarks are mediated by organisms such as methane-producing archaea (methanogens), anaerobic methanotrophic archaea (ANME) and sulphur-reducing bacteria (SRB). Iron is strongly linked to these processes due to its abundance in sediments and its ease in oxidation state changing. In sediments, following forms of iron are distinguished: carbonates (Fe_{CARB}); oxyhydr(oxides) (Fe_{OX1}, Fe_{OX2}); magnetite (Fe_{MAG}); sulphides (Fe_S) and sheet silicate Fe (Fe_{PRS}). Iron speciation in the sediment depends mainly on redox conditions and has huge impact on marine ecosystems. Dissolved Fe(II) deficiency is a limiting factor for phytoplankton growth, responsible for atmospheric CO_2 bonding. Fe(II) deficiency affects about 20-30% of the world's water surface

OBJECTIVES

- Comparison of pockmark and non-pockmark station in term of iron speciation;
- Comparison of pockmark and non-pockmark station in term of redox conditions and pore-water concentrations of hydrogen sulphide, sulphate and chloride
- Analysis of dissolved carbon concentrations and its correlation with methane, iron and suphate, and how methanogenesis affects the Fe cycle;

RESEARCH AREA:

Gulf of Gdansk is an area in Southern Baltic Sea divided between Poland and Russian Federation characterised by temporal anoxia, max. depth – 118 m and low salanity (7 – 8 PSU). The area is strongly affected by human activity due to large riverine input, dense population in the coast and industrial activity.
Pockmarks are located in Central part of Gulf of Gdansk.

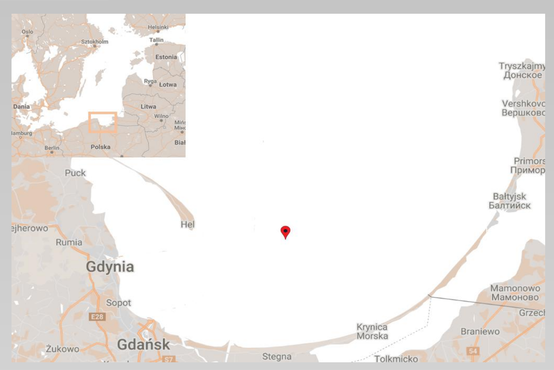


Fig.1 Map of the area

MATERIALS & METHODS

During two RV Oceanograf cruises sediment cores and pore- and bottom-water were collected in Nov 2020 - Feb 2021. Two reference stations were selected, where neither methane nor freshwater is emitted. In bottom water temperature, [O_2], pH, Eh and salanity were measured. Hydrogen sulphide (ΣH_2S) , silicates (SiO_4-), phosphates (ΣPO_4^{3-}) and ammonia (ΣNH_4^+) were analyzed on UV/Vis spectrometer. Sulphates (SO_4^{2-}) chlorides (Cl^-) and dissolved iron (Fe_d) were analyzed with ion chromatograph. Dissolved organic carbon (DOC) and inorganic carbon (DIC) were analysed with using temperature catalytic oxidation and NDIR (nondispersive infrared sensor) detection.

In the sediment, water content, loss on ignition (LOI) and iron speciation were determined. Total Fe (Fe_{TOT}) was dereminded by mineralization with conc. acids and microwaves. Fe speciation was determinded with sequential extraction. Both, total Fe and Fe speciation were measured with FAAS (flame atomic absorbance spectrometer).

Fig. 2-10 Left to right, top to bottom**. 2** – MBES image of the pockmark area; 3 – slicing the sediment core; 4 – pore water collecting; 5- collometric analysis of nutrients on board, 6 - bottom water, 7- microwave mineralizator, 8 - sample shaker, 9 – flame atomic absorbance spectrometer

RESULTS & DISCUSSION

All results for two pockmark stations are presented in comparision with coresponding refrence station (REF).

Tab. 1 Bottom water results (avarage)

Parametr	MET1-BH	MET1-BH-REF	MET1-POK	MET1-POK-REF
Temperatura, T [°C]	7,9	7,8	7,6	8,2
DO_2 [mg/dm³]	0,38	1,45	1,96	3,67
pH	6,71	7,36	7,15	7,38
Eh	-217	-79,6	-143	94,7
Zasolenie (PSU)	10,4	10,6	10,1	9,3
ΣNH_4^+ [µmol/dm³]	236,2	78,63	8,00	7,73
ΣPO_4^{3-} [µmol/dm³]	22,62	17,11	12,77	1,16
SiO_4- [µmol/dm³]	41,3	45,33	65,80	49,70
ΣH_2S [µmol/dm³]	2,92	0,10	0,00	0,00
Cl^- [mmol/dm³]	192,5	213,8	173,9	160,6
SO_4^{2-} [mmol/dm³]	10,7	10,8	8,49	7,87
Fe_d [µmol/dm³]	0,91	0,71	0,29	0,02
DIC [mmol/dm³]	1,90	2,66	-	2,7
DOC [mmol/dm³]	1,05	0,80	0,77	0,65
TDC [mmol/dm³]	2,95	3,45	-	3,37

MET1-BH

Bottom water:

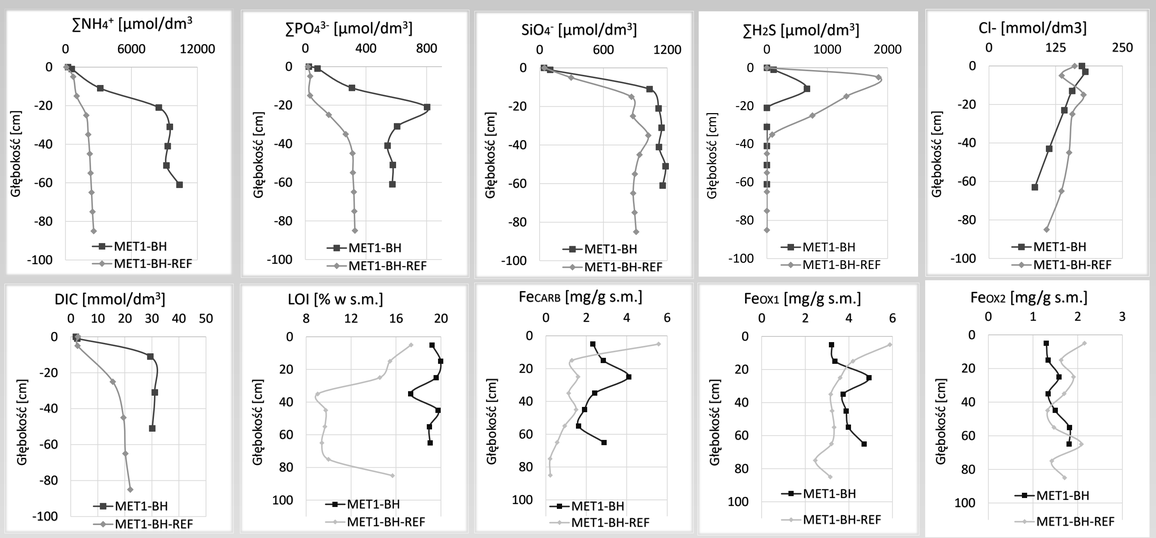
- very low oxygen content, pH and Eh - reductive conditions.

Pore water:

- high conc. of ΣNH_4^+ and ΣPO_4^{3-} what can be the result of OM degradation. Concentrations increasing with depth;
- high conc. of DIC what can be the result of AOM (anaorbic oxidation of methane);
- DOC enrichement in pore water in the deepest (50 cm bsf) layer, what can be directly the sign of methane occurance;
- faster Cl^- decrease in pore water than in REF what is the result of freshwater seeps.

Sediment:

- higher water and organic matter content (LOI);
- higher Fe_{CARB} conc. due to carbonate precipitation in conditions of DIC supersaturation;
- Fe_{OX1} and Fe_{OX2} decrease in layer 25-35 cm bsf what can show the layer of Fe(III)-AOM (iron (III)-driven anoxic methane oxidation); The conclussion is confirmed by dissolved iron enrichement in that layer;
- lower than in REF ΣH_2S contcentration in layer 0-20 cm bsf;
- depletion of Fe_{MAG} .



MET1-POK

Bottom water:

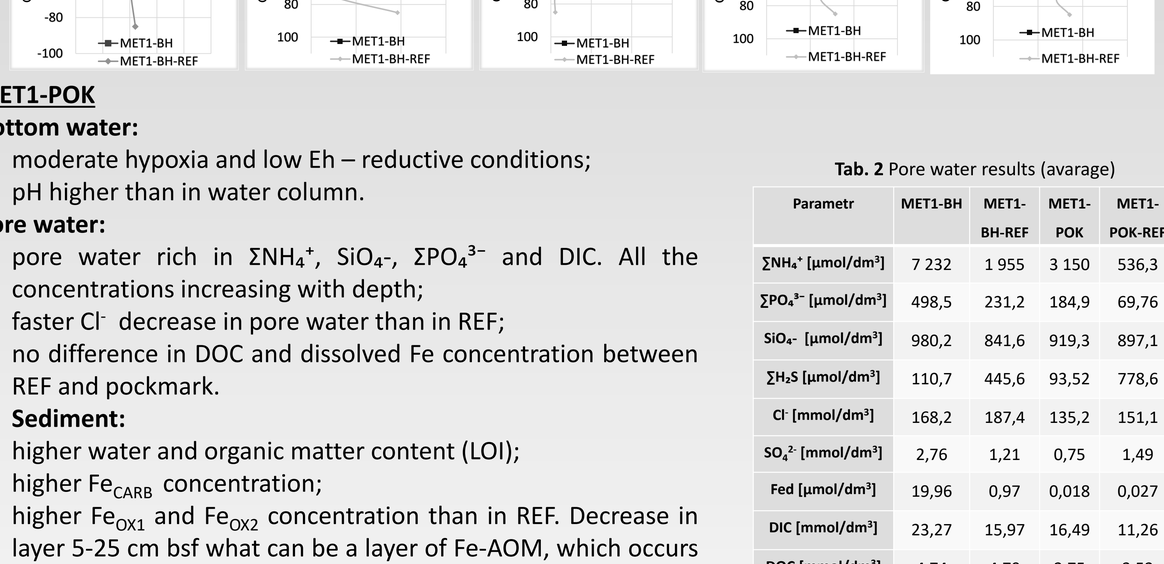
- moderate hypoxia and low Eh – reductive conditions;
- pH higher than in water column.

Pore water:

- pore water rich in ΣNH_4^+, SiO_4-, ΣPO_4^{3-} and DIC. All the concentrations increasing with depth;
- faster Cl^- decrease in pore water than in REF;
- no difference in DOC and dissolved Fe concentration between REF and pockmark.
- **Sediment:**
- higher water and organic matter content (LOI);
- higher Fe_{CARB} concentration;
- higher Fe_{OX1} and Fe_{OX2} concentration than in REF. Decrease in layer 5-25 cm bsf what can be a layer of Fe-AOM, which occurs slighlty higher than in MET-BH;
- High concentration of oxidised iron below 25 bsf as well as DOC and LOI decrease in that layer can be sign of low methane impact in that layer;
- depletion of Fe_{MAG}.

Tab. 2 Pore water results (avarage)

Parametr	MET1-BH	MET1-BH-REF	MET1-POK	MET1-POK-REF
ΣNH_4^+ [µmol/dm³]	7 232	1 955	3 150	536,3
ΣPO_4^{3-} [µmol/dm³]	498,5	231,2	184,9	69,76
SiO_4- [µmol/dm³]	980,2	841,6	919,3	897,1
ΣH_2S [µmol/dm³]	110,7	445,6	93,52	778,6
Cl^- [mmol/dm³]	168,2	187,4	135,2	151,1
SO_4^{2-} [mmol/dm³]	2,76	1,21	0,75	1,49
Fed [µmol/dm³]	19,96	0,97	0,018	0,027
DIC [mmol/dm³]	23,27	15,97	16,49	11,26
DOC [mmol/dm³]	4,74	4,79	2,75	3,52
TDC [mmol/dm³]	28,01	20,76	19,25	14,77



CONCLUSSIONS:

- Pore-water in pockmarks are characterized by higher DIC, ΣNH_4^+, ΣPO_4^{3-} and SiO_4- concentrations what is the result of organic matter oxygenation;
- In the upper layer (0-15 cm bsf) occurs sulphate-driven AOM and OM mineralization;
- In layer 15-25 cm bsf occurs iron(III)-driven AOM. Intensities are much higher for MET1-BH;
- Both pockmarks are source of freshwater to marine enviroment;
- Sediments in pockmars are enriched in Fe_{CARB} and deplated in Fe_{MAG}.

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