

SUPPORTING INFORMATION

Iron-Mediated Anaerobic Oxidation of Methane in Brackish Coastal Sediments

Matthias Egger^{a*}, *Olivia Rasigraf*^b, *Célia J. Sapart*^{c,d}, *Tom Jilbert*^{a,e}, *Mike S. M. Jetten*^b, *Thomas Röckmann*^c, *Carina van der Veen*^c, *Narcisa Bândă*^c, *Boran Kartal*^{b,f}, *Katharina F. Ettwig*^b, *Caroline P. Slomp*^a

^a Department of Earth Sciences - Geochemistry, Faculty of Geosciences, Utrecht University, Budapestlaan 4, 3584 CD Utrecht, The Netherlands; ^b Department of Microbiology, Institute for Water and Wetland Research, Faculty of Science, Radboud University Nijmegen, Heyendaalseweg 135, 6525 AJ Nijmegen, The Netherlands; ^c Institute for Marine and Atmospheric research Utrecht (IMAU), Utrecht University, Princetonplein 5, 3584 CC Utrecht, The Netherlands; ^d Laboratoire de Glaciologie, Université Libre de Bruxelles, 50 Avenue F. D. Roosevelt, B-1050 Bruxelles, Belgium; ^e Now at: Department of Environmental Sciences, University of Helsinki, Viikinkaari 2a, 00014 Helsinki, Finland; ^f Department of Biochemistry and Microbiology, Laboratory of Microbiology, Ghent University, K. L. Ledeganckstraat 35, 9000 Gent, Belgium

The 8 pages of supporting information consist of 2 Figures (Figure S1: correction of AVS dissolution during Fe-oxide extraction; Figure S2: determination of Fe-AOM rate) and 3 Tables (Table S1: porewater data; Table S2: solid-phase data; Table S3: model parameters).

POREWATER CALCULATIONS

The diffusive flux of dissolved Fe^{2+} into the SMTZ can be used to estimate the rate of Fe-reduction below the SMTZ. Thus, assuming that all of the Fe-reduction below the SMTZ is due to Fe-AOM and limited removal of dissolved Fe^{2+} below the SMTZ, one can estimate the contribution of CH_4 removal by Fe-AOM to the total amount of CH_4 removed in the sediment.

Porewater gradients were used to calculate diffusive fluxes of CH_4 and Fe^{2+} into the SMTZ applying Fick's first law ¹:

$$J = \phi D_s \frac{dC_i}{dx}$$

where J equals the diffusive flux in $\text{mol m}^{-2} \text{ year}^{-1}$, ϕ is the measured porosity, D_s is the sediment diffusion coefficient in $\text{m}^2 \text{ year}^{-1}$, C is the concentration of molecule i in mol m^{-3} , and x is the depth in m. Sediment diffusion coefficients were calculated as follows:

$$D_s = \frac{D_{i,sw}}{1 - \ln \phi^2}$$

where $D_{i,sw}$ (diffusive flux of i in seawater) was corrected for in-situ temperature and salinity according to ref ². Based on the porewater profiles, our estimated diffusive fluxes for CH_4 and Fe^{2+} are $J_{\text{CH}_4} = 60 \mu\text{mol cm}^{-2} \text{ year}^{-1}$ and $J_{\text{Fe}^{2+}} = 13 \mu\text{mol cm}^{-2} \text{ year}^{-1}$, respectively. Thus, taking into account that only one molecule of CH_4 is needed to reduce 8 $\text{Fe}(\text{OH})_3$, CH_4 removal by Fe-AOM is estimated to account for about 3 % of total CH_4 removal. If part of the Fe^{2+} production below the SMTZ were still due to organoclastic Fe reduction, the contribution of the Fe-AOM to the total removal of CH_4 would even be lower. Thus, the 3 % should be seen as an upper estimate.

DIFFUSION MODEL PARAMETERS

Implemented rate constants for SO_4 -AOM (32.2 year^{-1}) and Fe-AOM (0.64 year^{-1}) are based on porewater profiles of CH_4 and Fe^{2+} . CH_4 production rates were chosen in each scenario such that the model best represents measured values of dissolved CH_4 . Diffusive mixing reduces porewater gradients and therefore will also result in a reduction of isotope differences along a gradient, lowering the isotopic fractionation implemented in the model ('effective AOM fractionation') to the one derived from Figure 4 ('apparent AOM fractionation', with ϵ_H

= 98 ‰ and $\epsilon_C = 9$ ‰). Effective fractionation factors for SO₄-AOM ($\epsilon_H = 138$ ‰ and $\epsilon_C = 13$ ‰) were therefore estimated by fitting the model with the observations in the top 8.5 cm, i.e. the zone with SO₄-AOM as the main mechanism effecting porewater CH₄. As an approximation, isotope fractionation for Fe-AOM was assumed to be the same as for SO₄-AOM. In a last step, $\delta^{13}\text{D}$ and $\delta^{13}\text{C}$ source signatures for methanogenesis were defined.

SUPPLEMENTARY REFERENCES

- (1) Berner, R. A. *Early diagenesis: A theoretical approach*; Princeton University Press, **1980**.
- (2) Boudreau, B. P. *Diagenetic models and their implementation: Modelling transport and reactions in aquatic sediments*; Springer Verlag, **1997**.
- (3) Poulton, S.; Canfield, D. Development of a sequential extraction procedure for iron: implications for iron partitioning in continentally derived particulates. *Chem. Geol.* **2005**, *214*, 209–221.

SUPPLEMENTARY FIGURES

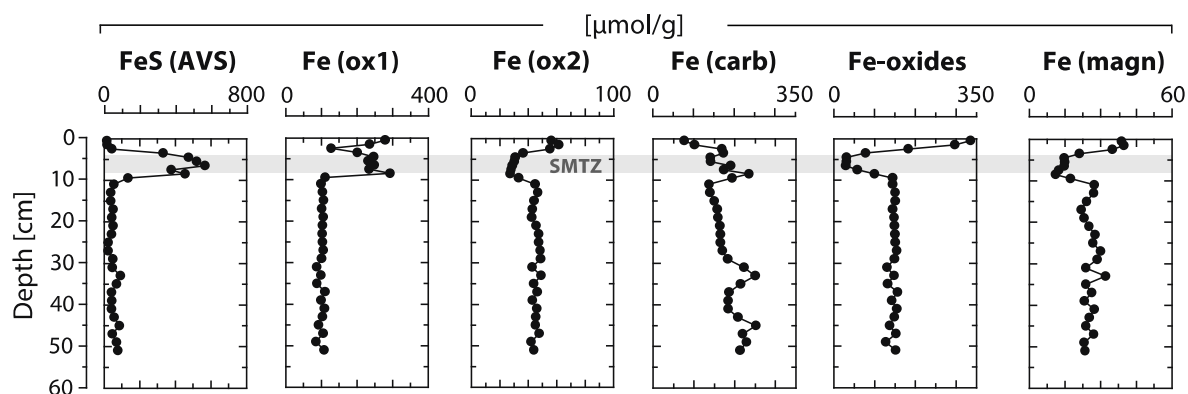


Figure S1. Results for the Fe(ox_1) and Fe(carb) fractions suggest that most of the AVS (Acid Volatile Sulfide) present in the SMTZ was extracted during those two initial extraction steps. Thus, AVS was subtracted from the sum of the Fe(ox_1) + Fe(carb) within the SMTZ (Fe-oxides). The Fe(ox_1) fraction includes ferrihydrite and lepidocrocite. Fe(ox_2) is assumed to represent Fe associated with goethite, hematite and akagenéite. Fe(carb) is an estimate for Fe associated with siderite and ankerite. Fe(magn) represents Fe in recalcitrant oxides (mostly magnetite)³.

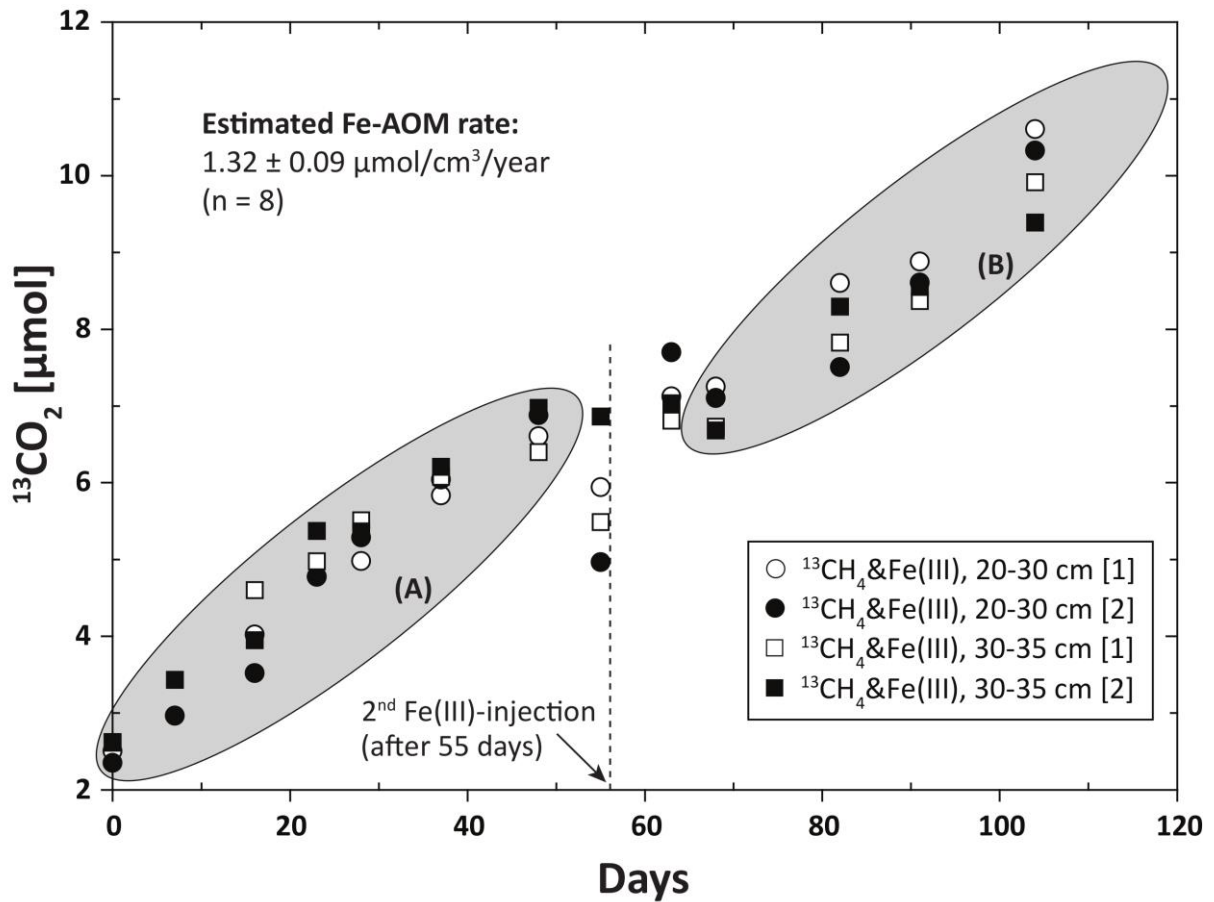


Figure S2. Determination of Fe-AOM rate based on linear intervals (marked gray) of $^{13}\text{CO}_2$ production after the initial (0 days; (A)) and second (55 days; (B)) Fe(III) addition. In total, 8 different slopes were calculated from slurry incubations of sediments from 20-30 cm and 30-35 cm depth. Headspace $^{13}\text{CO}_2$ concentrations are corrected for dissolved $^{13}\text{CO}_2$ and changes in the slurry volume during the experiment.

SUPPLEMENTARY TABLES

Table S1. Measured porewater concentrations at site US5B in 2012. $\delta\text{D-CH}_4$ and $\delta^{13}\text{C-CH}_4$ are in ‰ vs. SMOW (Standard Mean Ocean Water) and vs. VPDB (Vienna Pee Dee Belemnite), respectively. $\Sigma\text{H}_2\text{S}$ equals the sum of the different sulfide species ($\text{H}_2\text{S} + \text{HS}^- + \text{S}^{2-}$) and “n.d.” = no data available. $[\text{SO}_4^{2-}]$ = values below detection limit of 75 μM .

Depth	SO_4^{2-}	$\Sigma\text{H}_2\text{S}$	Fe^{2+}	Depth	CH_4	$\delta\text{D-CH}_4$	$\delta^{13}\text{C-CH}_4$
[cm]	[$\mu\text{mol/l}$]	[$\mu\text{mol/l}$]	[$\mu\text{mol/l}$]	[cm]	[mmol/l]	[‰]	[‰]
0.0	n.d.	0.0	0.0	0.0	0.0	n.d.	n.d.
0.5	4870	0.0	0.0	1.0	0.0	-23.9	n.d.
1.5	4269	0.0	5.4	3.5	0.1	-29.1	-52.5
2.5	3781	0.0	19.7	6.0	0.3	-100.1	-60.5
3.5	2801	0.3	9.0	8.5	0.8	-184.9	-67.6
4.5	2118	16.8	1.8	11.0	1.7	-223.5	-68.7
5.5	1389	111.1	1.8	13.5	1.9	-230.2	-68.7
6.5	751	186.7	1.8	16.0	2.5	-235.8	-68.3
7.5	115	95.4	1.8	18.5	3.0	-238.5	-68.5
8.5	304	123.7	1.8	21.0	3.3	-239.1	-68.3
9.5	*19	1.3	275.8	23.5	3.8	-245.8	-68.0
11.0	*25	1.8	275.8	26.0	3.7	-243.6	-68.4
13.0	*52	0.7	551.5	28.5	4.3	-240.5	-68.0
15.0	*15	0.9	827.3	31.0	4.5	-243.2	-67.7
17.0	*15	0.8	1002.8	33.5	5.0	-248.6	-67.9
19.0	*41	0.0	1178.3	36.0	5.2	-244.8	-67.5
21.0	*19	0.2	1281.0	38.5	5.2	-245.0	-67.6
23.0	*6	2.2	1371.3	41.0	5.4	-246.9	-67.8
25.0	*8	0.2	1451.5	43.5	5.2	-239.8	-67.5
27.0	*17	0.3	1594.4	46.0	4.9	-237.3	-67.5
29.0	*7	0.2	1586.9	48.5	5.2	-243.5	-67.6
31.0	*8	0.0	1684.7	51.0	5.5	-248.8	-67.6
33.0	*8	0.2	1764.9	53.5	4.8	-238.3	-67.4
35.0	*6	0.4	1757.4				
37.0	*8	0.0	1664.6				
39.0	*5	0.0	1810.0				
41.0	*7	0.0	1717.3				
43.0	*4	0.6	1617.0				
45.0	*6	0.0	1830.1				
47.0	*6	0.0	1827.6				
49.0	*10	0.0	1722.3				
51.0	*6	1.5	1762.4				

Table S2. Measured solid phase sediment concentrations of different elements at site US5B in 2012. Fe_{carb} = carbonate associated Fe, including siderite and ankerite. Fe_{ox1} = easily reducible (amorphous) oxides, such as ferrihydrite and lepidocrocite. Fe_{ox2} = reducible (crystalline) oxides, including goethite, hematite and akagenéite. Fe_{magn} = Fe in recalcitrant oxides (mostly magnetite). AVS = Acid Volatile Sulfide (Fe-monosulfide, FeS) and CRS = Chromium Reducible Sulfide (pyrite, FeS₂). All values are per g dry weight sediment. “n.d.” = no data available.

Depth	S _{tot}	Fe _{tot}	Fe _{carb}	Fe _{ox1}	Fe _{ox2}	Fe _{magn}	AVS	CRS	Fe/Al	Porosity
[cm]	[$\mu\text{mol/g}$]	[$\mu\text{mol/g}$]	[$\mu\text{mol/g}$]	[$\mu\text{mol/g}$]	[$\mu\text{mol/g}$]	[$\mu\text{mol/g}$]	[$\mu\text{mol/g}$]	[$\mu\text{mol/g}$]	[mol/mol]	
0.5	52.1	1073.4	76.1	278.9	56.2	45.9	7.8	9.1	0.40	0.94
1.5	49.4	1239.3	101.0	235.4	61.2	46.5	8.5	4.8	0.40	0.92
2.5	82.4	1194.0	168.3	127.4	55.2	43.3	21.9	11.2	0.38	0.91
3.5	324.6	1240.6	172.2	201.0	36.2	34.1	166.2	21.2	0.39	0.91
4.5	479.0	1295.0	140.0	246.9	30.8	29.8	237.2	22.3	0.40	0.91
5.5	442.4	1132.6	140.3	231.0	30.2	29.9	260.0	25.2	0.39	0.91
6.5	604.5	1344.6	189.8	248.3	28.6	29.7	283.4	21.6	0.43	0.90
7.5	468.3	1198.8	172.7	233.9	27.8	28.2	188.7	15.2	0.40	0.89
8.5	694.2	1433.0	234.8	292.6	27.1	27.4	227.6	15.4	0.45	0.89
9.5	339.4	1203.5	193.1	110.7	33.0	31.5	67.1	27.7	0.39	0.90
11.0	86.4	1189.6	136.6	99.0	44.7	38.2	27.7	13.7	0.35	0.90
13.0	43.9	1212.2	139.2	103.7	46.6	38.1	18.6	163.5	0.35	0.90
15.0	40.1	1099.4	149.9	106.4	44.0	36.0	18.4	1.6	0.35	0.90
17.0	30.1	967.4	156.8	100.9	42.9	34.5	25.0	1.4	0.34	0.89
19.0	37.2	1129.0	158.7	105.2	42.4	35.4	21.8	31.9	0.35	0.89
21.0	45.4	1165.7	163.3	103.3	45.4	36.7	25.1	25.7	0.36	0.89
23.0	45.9	1284.3	164.7	102.4	47.3	38.4	21.4	n.d.	0.37	0.89
25.0	54.7	1171.0	164.5	103.4	47.2	37.8	11.8	19.5	0.37	0.89
27.0	63.2	1143.4	169.5	105.5	48.3	40.0	11.5	6.8	0.37	0.89
29.0	92.4	1267.3	182.7	100.0	48.5	39.0	24.4	13.8	0.38	0.89
31.0	132.1	1203.8	222.2	87.1	42.7	35.8	23.4	22.8	0.39	0.90
33.0	157.6	1182.3	249.8	98.8	48.9	41.3	46.3	24.9	0.40	0.90
35.0	117.8	1135.0	214.1	87.6	43.7	35.8	35.4	10.5	0.38	0.90
37.0	98.0	1160.1	185.9	110.1	46.3	37.5	20.8	13.9	0.39	0.90
39.0	92.4	1292.9	183.3	99.0	42.9	35.4	21.9	20.0	0.37	0.90
41.0	92.0	1120.3	183.4	108.4	46.0	38.2	21.4	3.3	0.37	0.89
43.0	100.7	1134.8	207.5	102.9	45.3	36.8	28.2	14.6	0.38	0.89
45.0	140.5	1296.0	251.8	92.1	45.0	35.9	43.1	22.9	0.40	0.90
47.0	146.9	1228.0	219.4	105.0	47.5	38.0	23.6	22.8	0.39	0.90
49.0	99.0	1157.3	228.6	84.8	41.9	35.3	35.3	10.1	0.38	0.89
51.0	121.5	1232.8	212.5	107.4	43.9	35.6	38.8	18.3	0.39	0.89

Table S3. Model parameters used for the column diffusion model simulation of the total concentration and isotopic composition of porewater CH₄ at station US5B. Sim 1 = Simulation 1 with SO₄-AOM at top (0-8.5 cm), Fe-AOM and methanogenesis below (8.5-36 cm). Sim 2 = Simulation 2, with SO₄-AOM at top (0-8.5 cm), but only methanogenesis below (8.5-36 cm). Sim 3 = Simulation 3, with SO₄-AOM at top (0-8.5 cm), but no Fe-AOM nor methanogenesis below (8.5-36 cm).

Parameter	Unit	Sim 1: With Fe-AOM	Sim 2: No Fe-AOM	Sim 3: Diffusion only
SO ₄ -AOM rate constant	1/year	32.2	32.2	32.2
Fe-AOM rate constant	1/year	0.64	-	-
CH ₄ production rate constant	1/year	3.6	1.6	-
ε(H) AOM	‰	-138	-138	-138
ε(C) AOM	‰	-13	-13	-13
ε(Diffusion)	‰	3	3	3
δD source	‰	-305	-255	-
δ ¹³ C source	‰	-78.7	-75.7	-