SUPPLEMENTARY INFORMATION

Anaerobic oxidation of methane alters sediment records of sulfur, iron and phosphorus in the Black Sea

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1 Multicomponent model formulation

Molecular diffusion coefficients D_m ($cm^2\ yr^{-1}$) were corrected for tortuosity in the porous medium according to Boudreau (1996).

$$D' = \frac{D_m}{1 - 2\ln(\phi)}$$

To account for sediment compaction, a depth-dependent porosity (ϕ) was described by

$$\phi(x) = \phi_\infty + (\phi_0 - \phi_\infty)e^{-\frac{x}{\gamma}}$$

where x is the distance from the sediment-water interface (cm), ϕ_∞ the porosity at depth in the sediment, ϕ_0 the porosity at the sediment surface, and γ the porosity attenuation factor (see Fig. S1 and Table S1).

The advective velocity of solids at depth v_∞ was described by

$$v_\infty = \frac{F_{sed}}{\rho(1 - \phi_\infty)}$$

where F_{sed} denotes the sediment accumulation rate ($g\ cm^{-2}\ yr^{-1}$) and ρ the sediment density ($1008\ kg\ m^{-3}$) (Meysman et al., 2005).

2 Supplementary tables

Table S1. Environmental parameters used by the diagenetic model.

Parameter	**Symbol**	**Value**	**Units**
Porosity at surface	ϕ_0	0.97	-
Porosity at depth	ϕ_∞	0.61	-
Porosity e-folding distance	γ	95	cm
Sediment density	ρ	2.31	g cm^{-3}
Temperature	T	1	^oC
C:N ratio of organic matter	C/N	6.625	-
C:P ratio of organic matter	C/P	106	-
C:P ratio of organic matter under anoxia	C/P_{anoxic}	424	
P:Fe ratio for $Fe(OH)_3^{\alpha}$	χ^{α}	0.1	-
P:Fe ratio for $Fe(OH)_3^{\beta,}$	χ^{β}	0.055	-
P:Fe ratio for $Fe(OH)_3^{\gamma}$	χ^{γ}	0.03	-

Table S2. Time-dependent boundary conditions at the sediment surface.

Parameter	$> 9000\ yrs\ B.P.$	$< 9000\ yrs\ B.P.$
J_{FeCO_3}	3.81	1.14
J_{S_0}	0	0
J_{CaP}	0.18	0.18
J_{DetrP}	0.32	0.095
$[O_2]$	0.18	0
$[Fe^{2+}]$	0	0
$[\sum H_2S]$	0	0.08
$[CH_4]$	0	0
$[\sum NH_4^+]$	0	0
$[NO_3^-]$	0	0
$[H_2PO_4^-]$	0	0
$[DIC]$	3	3

Fluxes have units of mmol m^{-2} yr^{-1} and concentrations are in mmol L^{-1}. yrs B.P. = years before present.

3 Supplementary figures

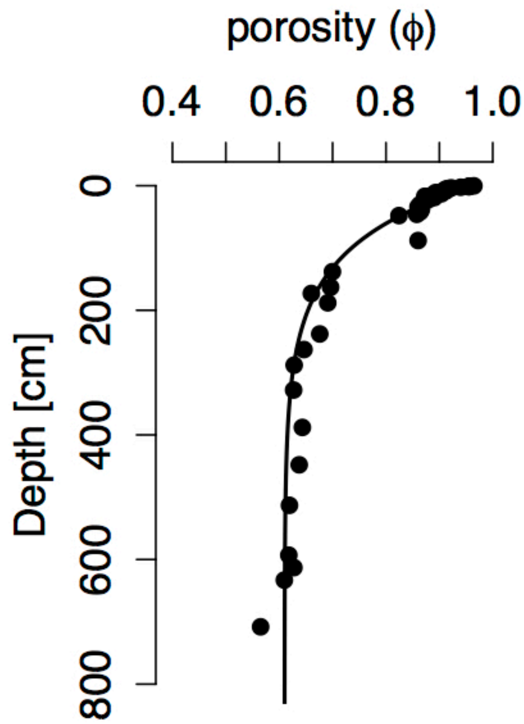

Figure S1. Porosity measurements (black circles) and modeled porosity profile (black line) at site 4.

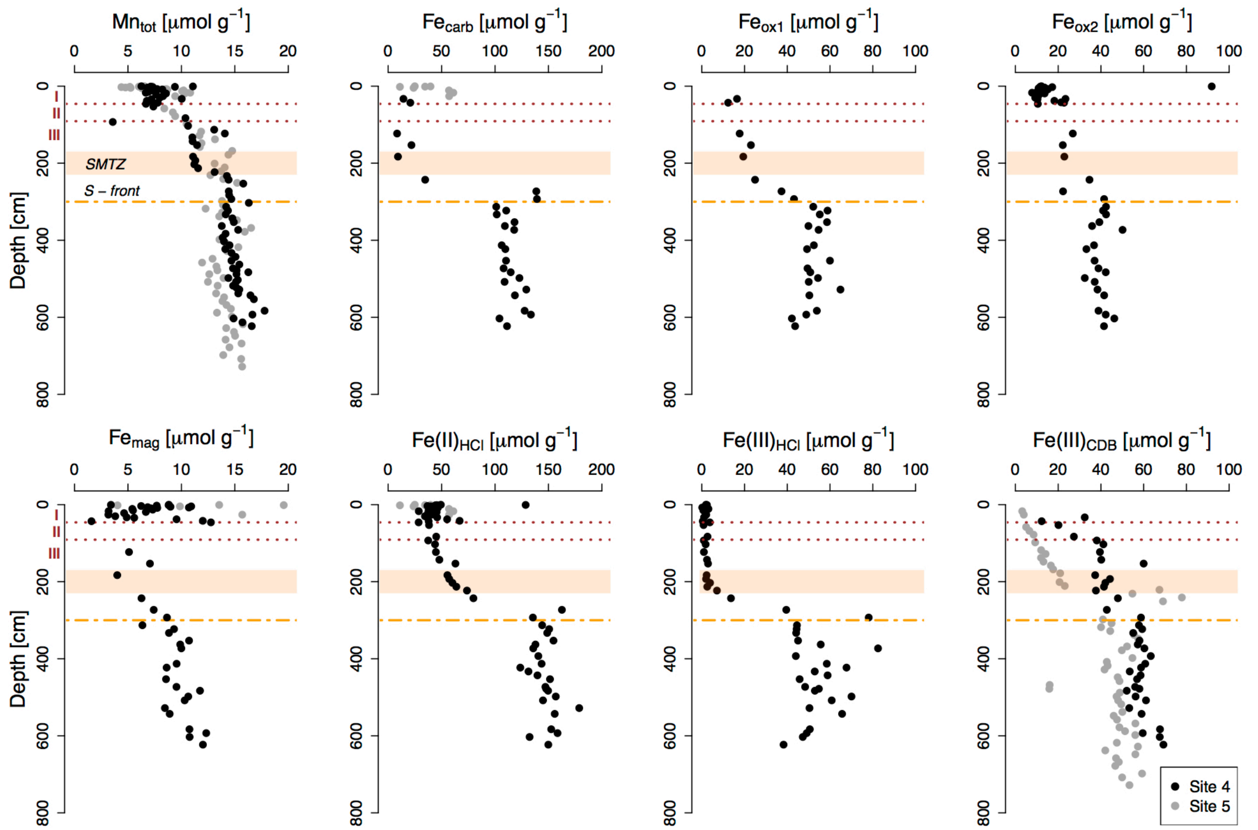

Figure S2. Solid phase profile of total sedimentary Mn and Fe extraction results for site 4 (black dots) and 5 (grey dots). See Table 1 for a description of the different Fe phases. Note that Fe_{carb} is not corrected for dissolution of AVS during the Na acetate extraction step. $Fe(III)_{CDB}$ for site 5 represents the amount of Fe extracted during the CDB-step of the SEDEX P extraction. Red dotted lines and roman numbers indicate the transitions between the lithological Unit I (modern coccolith ooze), Unit II (marine sapropel) and Unit III (limnic deposits). The orange bar represents the sulfate-methane transition zone (SMTZ) and the orange dashed line shows the current position of the downward migrating sulfidization front (S-front).

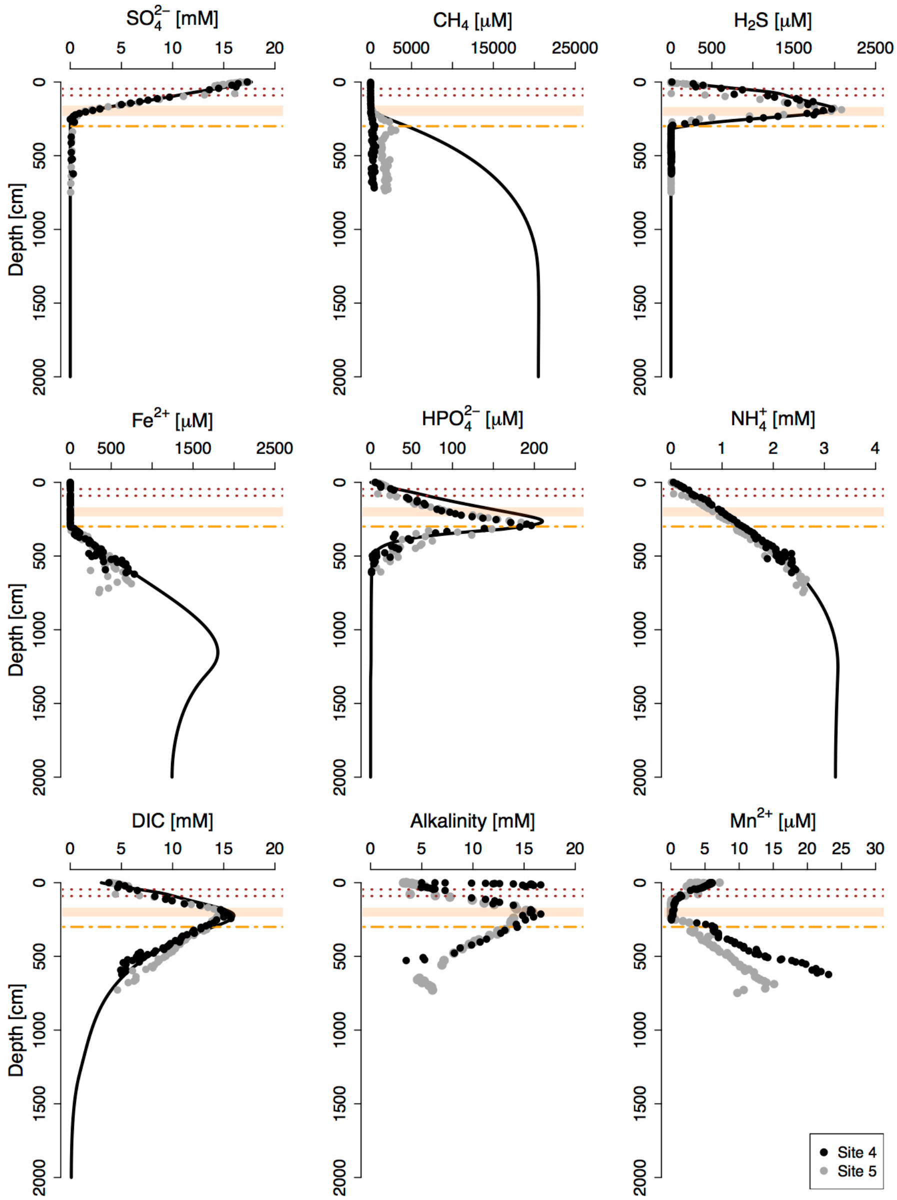

Figure S3. Pore water profiles (whole model domain, i.e. 2000 cm) for site 4 (black dots) and 5 (grey dots). Black lines represent profiles derived from the diagenetic model. Red dotted lines and roman numbers indicate the transitions between the lithological Unit I (modern coccolith ooze), Unit II (marine sapropel) and Unit III (limnic deposits). The orange bar represents the sulfate-methane transition zone (SMTZ) and the orange dashed line shows the current position of the downward migrating sulfidization front.

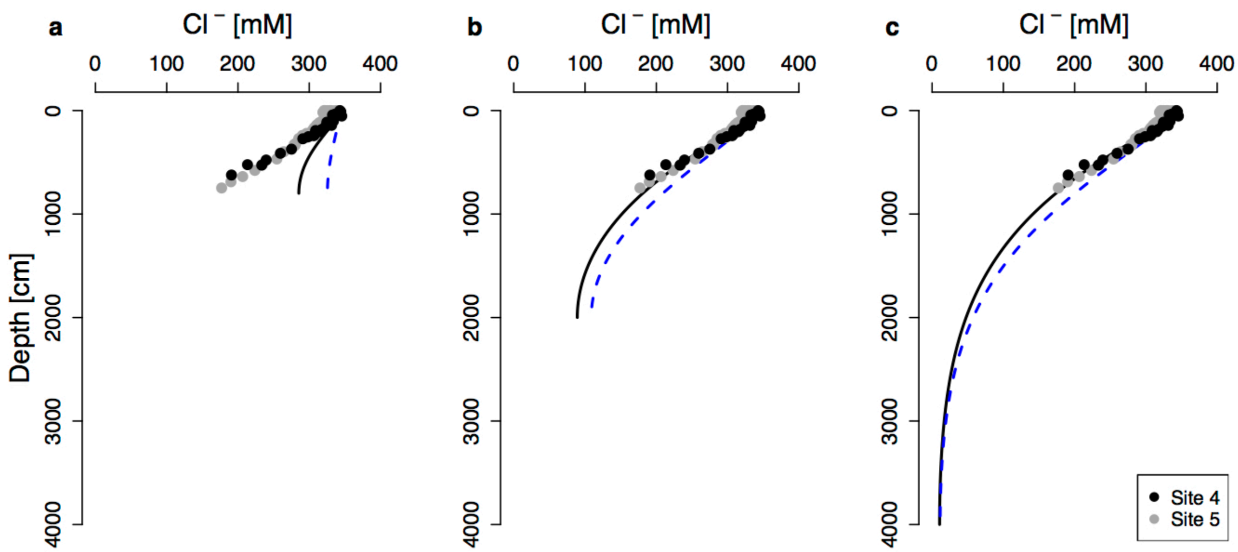

Figure S4. The influence of a zero gradient boundary condition at the base of the model domain on the pore water profile of chloride (Cl^-) is dependent on the modeled sediment depth. (a) Due to the transient diagenesis, a zero gradient is not reached within the depth range of the available data, i.e. the upper 800 cm. (b) A model length of 2000 cm results in a good fit of the modeled Cl^- profile with the measured pore water concentrations. Expanding the model domain to 4000 cm (c) largely increases the modeling time, with only minor improvement of the model fit. Thus, a depth range of 2000 cm was chosen in this study. The solid lines represent model simulations assuming an initial salinity of 1 for the freshwater phase and a linear increase to a salinity of 22 between 8500 and 100 years ago. Blue dashed lines, on the other hand, denote an increase in salinity from 1 to 22 between 8500 and 2000 years B.P., after which salinity stays constant, as proposed by Soulet et al. (2010).

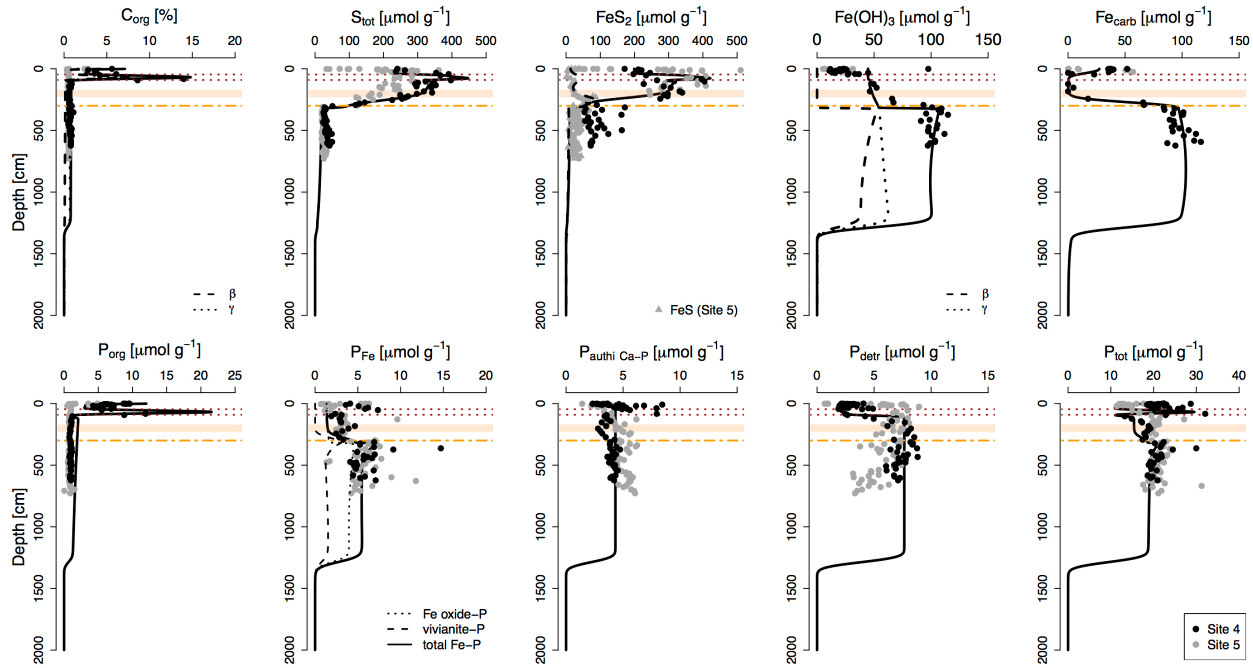

Figure S5. Solid phase profiles (whole model domain, i.e. 2000 cm) for site 4 (black dots) and 5 (grey dots). Fe_{carb} was corrected for apparent AVS dissolution during the Na acetate extraction step (the uncorrected Fe_{carb} data is given in Fig. S2). Black lines represent profiles derived from the diagenetic model. Red dotted lines and roman numbers indicate the transitions between the lithological Unit I (modern coccolith ooze), Unit II (marine sapropel) and Unit III (limnic deposits). The orange bar represents the sulfate-methane transition zone (SMTZ) and the orange dashed line shows the current position of the downward migrating sulfidization front.

Supplementary references

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Meysman, F. J. R., Boudreau, B. P. and Middelburg, J. J.: Modeling reactive transport in sediments subject to bioturbation and compaction, Geochim. Cosmochim. Acta, 69(14), 3601–3617, 2005.

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