Coupling of dissolved organic carbon, sulfur and iron cycling in Black Sea sediments over the Holocene and the late Pleistocene: Insights from an empirical dynamic model

Pei-Chuan Chuang a,b,⇑, Andrew W. Dale b, Verena B. Heuer a, Kai-Uwe Hinrichs a, Matthias Zabel a

a MARUM – Center for Marine Environmental Sciences, University of Bremen, Leobener Str. 8, 28359 Bremen, Germany
b GEOMAR Helmholtz Centre for Ocean Research Kiel, Wischhofstr. 1–3, 24148 Kiel, Germany

Received 4 December 2020; accepted in revised form 26 April 2021; available online xxxx

Abstract

An understanding of how the coupled cycles of carbon, iron and sulfur in sediments respond to environmental change throughout Earth history requires the reconstruction of biogeochemical processes over a range of spatial and temporal scales. In this study, sediment cores from the southwestern Black Sea were analyzed to gain insight into past changes in biogeochemical processes with particular focus on the cycling of dissolved organic carbon (DOC). The sediment consists of Late Pleistocene deposits of iron oxide-rich and organic-poor lacustrine sediments, a Holocene sapropel layer deposited after the inflow of saline Mediterranean seawater about 9300 yr BP, and overlying recent marine sediments. The porewaters displayed high concentrations of DOC, acetate, dissolved iron and an extended depth interval over which sulfate and methane were both present. The historical fluctuations of the fluxes of carbon, sulfur and iron species at the seafloor that led to these present-day geochemical profiles, and which cannot be easily interpreted from the measured data alone, were hindcasted with a reaction-transport model. The model suggests that the inflow of Mediterranean seawater impacted the rain rate and reactivity of organic matter reaching the sediments, which shifted the sedimentary redox regimes throughout the Holocene that now are reflected on different lithology units. Organic matter in the sapropel layer is apparently the main source of modern-day accumulations of DOC and acetate, both of which probably sustained subsurface microbial activity throughout the post-glacial period. The ratio between DOC and dissolved inorganic carbon (DIC) flux to the bottom water decreased from ~40% before the inflow of Mediterranean water to ~2% at the present day. We suggest that the coexistence of methanogenesis and sulfate reduction was associated with sulfate-reducing bacteria and methanogens sharing common substrates of acetate and lactate and utilizing non-competitive substrates such as methylated compounds in the sapropel layer and in the bottom of modern marine deposits. Intense sulfur and iron cycling mainly took place in the organic-poor freshwater deposits, today characterized by high concentrations of dissolved iron and methane. In contrast to previous studies in similar environments, anaerobic oxidation of methane coupled to the reduction of ferric iron was negligible. The results have broad implications for coastal environments that are currently experiencing deoxygenation and seawater intrusion and also for understanding the role of DOC in the sedimentary carbon cycle.

© 2021 Elsevier Ltd. All rights reserved.

Keywords: Dissolved organic matter; Sulfate reduction; Iron reduction; Early diagenetic modeling; Black Sea

* Corresponding author at: GEOMAR Helmholtz Centre for Ocean Research Kiel, Wischhofstr. 1–3, 24148 Kiel, Germany.

E-mail address: pchuang@geomar.de (P.-C. Chuang).

https://doi.org/10.1016/j.gca.2021.04.032
0016-7037/© 2021 Elsevier Ltd. All rights reserved.
1. INTRODUCTION

The preservation and remineralization of particulate organic carbon (POC) in marine sediments is an important component of the global carbon cycle. It is directly linked to biogeochemical processes in the sediments that control the cycles of inorganic carbon, nutrients and other elements, as well as the dissolution and precipitation of minerals and the activity of the deep biosphere (e.g., Berner, 1990; Burdige, 2007; Tranvik et al., 2009; Arndt et al., 2013; Ridgwell and Arndt, 2015; Daines et al., 2017). Remineralization of DOC to dissolved inorganic carbon (DIC) takes place via dissolved organic carbon (DOC) intermediates (Hedges 2002; Kujawinski, 2011). Because DIC and DOC concentrations in sediments are usually higher than in the water column, the sediments act as a source of both constituents to the bottom water (Burdige et al., 1999). DOC accounts for ~10% of the total dissolved carbon (DIC + DOC) flux in the modern ocean (Alperin et al., 2019; Burdige and Komada, 2015; Burdige et al., 2016), which may partly explain the build-up of old DOC in the deep ocean (Hansell, 2002). However, some studies suggest that the benthic DOC source is largely refractory (e.g., Komada et al., 2013; Burdige and Komada, 2015; Burdige et al., 2016), which may partly explain the build-up of old DOC in the deep ocean (Hansell, 2002). Large swings in oceanic DOC levels in response to changes in, for example, oxygen availability and temperature, have been proposed to impact atmospheric pCO₂ and climate in the past (e.g., Ridgwell, 2011; Sexton et al., 2011; Hansell, 2013; Ridgwell and Arndt, 2015). A more accurate framing of the role of DOC to the past and present carbon cycle requires an enhanced understanding of DOC cycling in marine sediments and the reactivity of the DOC fraction that is exported to the water column.

The chemical composition and reactivity of DOC regulate microbial activity and biogeochemical cycles in aquatic environments (Moran and Miller, 2007). Hydrolysis and fermentation of macromolecular organic compounds into simpler moieties such as H₂ and acetate provide important substrates for microbial respiration using available electron acceptors (e.g., Froelich et al., 1979; Jorgensen and Kasten, 2006; Middelburg, 2018). Usually, in the basic conceptual model of organic matter oxidation, electron acceptors are utilized in a well-defined sequence (O₂ > NO₃⁻ > Mn(IV), > Fe(III), > SO₄²⁻, > CO₂) reflecting the energy produced per mole of substrate oxidized (Froelich et al., 1979; Jorgensen and Kasten, 2006). Carbon turnover in sediments can be quantified by simulating the distribution of electron acceptors and their reduced counterparts with models that couple physical transport processes such as diffusion and burial with biogeochemical reactions (Berner, 1980; Boudreau, 1997). However, previous reaction-transport models (RTMs) of marine sediments have tended to focus exclusively on POC as the principal metabolic substrate. DOC, by contrast, is seldom considered (Alperin et al., 1999; Dale et al., 2008; Komada et al., 2013; Burdige et al., 2016). This is partly due to a lack of analytical techniques for the molecular characterization of DOC (Tissot and Welte, 1978; Schmidt et al., 2011, 2017; Oni et al., 2015; Valle et al., 2018).

Secular variations in seafloor redox conditions can alter organic matter mineralization pathways, leading to atypical sequences of terminal respiration processes over time (e.g., Egger et al., 2016a; Riedinger et al., 2017; Dijkstra et al., 2018; März et al., 2018). Sedimentary records showing distinct changes in environmental conditions offer a unique opportunity to test our understanding of benthic DOC cycling and its role in the past and present carbon cycle. The Black Sea is an ideal example where postglacial sea-level rise has led to the formation of sapropel layers and the accumulation of sulfidic sediments above iron oxide-rich deposits that were formed when the Black Sea was a freshwater basin (Degens and Ross, 1974; Soulet et al., 2011). The sediments are characterized by high POC concentrations within and at the base of the sapropel layer (e.g. Jorgensen et al., 2004; Coolen et al., 2013; Egger et al., 2016a).

In this study, the factors that led to the abrupt changes in the content of DOC, POC and other solid and dissolved species in Black Sea sediments (Zabel et al., 2012; Becker et al., 2018) were investigated with a dynamic RTM that simulates the temporal evolution of diagenetic pathways. We examine the largely unexplored interplay between DOC, sulfur and iron cycling. The model was an extension of the one developed by Egger et al. (2016a) for the Black Sea, which did not consider DOC. The DOC cycle was inspired by the model put forward by Burdige et al. (2016) that includes carbon flow from POC to DOC (Fig. 2). We link DOC degradation to the reduction of electron acceptors via reactive intermediates (H₂ and acetate), and constrain the model using an extensive set of biogeochemical data from site GeoB15105 in the southwestern Black Sea (Zabel et al., 2012). This approach allows us to quantify DOC transformation pathways and their coupling to sulfur and iron turnover as well as mineral precipitation and dissolution during the Late Pleistocene and Holocene (Fig. S1). The accumulation, preservation and degradation of organic carbon and iron minerals are reconstructed and possible pathways for deep ferrous iron formation in methanic sediments are evaluated. The findings contribute to a better understanding of carbon, sulfur and iron cycling in dynamic depositional systems in response to environmental change and help to interpret sediment archives in modern and ancient systems (e.g., Egger et al., 2016a, 2017; Riedinger et al., 2017; Couture et al., 2016).

2. STUDY SITE AND METHODS

2.1. Site GeoB15105

The study site GeoB15105 (41°31.70′N; 30°53.07′E; water depth: 1268 m) is located in the southwestern Black Sea to the north of the Sakarya River mouth in Turkey (Zabel et al., 2012; Becker et al., 2018). It is located on a topographical high and unaffected by turbidites (Kwiecien et al., 2008). The stratigraphic sequence from the late glacial to Holocene can be described by three units that have been observed throughout the basin (Hay et al., 1991; Bahr et al., 2005; Lamy et al., 2006; Kwiecien et al., 2008; Verleye et al., 2009; Eckert et al., 2013). The youngest Unit
I is characterized by a modern laminated coccolith ooze of late Holocene age; Unit II consists of finely laminated marine sapropel sediments deposited during the middle Holocene; Unit III sediments are composed of lacustrine clay from the Late Pleistocene to early Holocene freshwater deposits. The first inflow of Mediterranean water to the Black Sea freshwater lake around 9300 yr BP was identified by Bahr et al. (2008) on the basis of a rapid increase in Mg/Ca, Sr/Ca, and $^{87}$Sr/$^{86}$Sr ratios in ostracods. The ages of the boundaries between Unit I/II and Unit II/III are 2760 yr BP and 7995 yr BP, respectively (Lamy et al., 2006; Kwiecien et al., 2008). Site GeoB15105 is close to sites MD04-2760, MD04-2788 and GeoB7622-2, where details on chronology and sedimentology have been reported (Lamy et al., 2006; Kwiecien et al., 2008).

2.2. Sampling and analytical methods

Solid phase sediment and porewater samples were recovered using a multiple-corer (MUC) (GeoB15105-4, core recovery of 50 cm) and a gravity corer (GeoB15105-1, core recovery of 711 cm and GeoB15105-2, core recovery of 827 cm) during R/V Meteor cruise M84/1 in February 2011 (Zabel et al., 2012). A comparison of porewater data from the gravity cores and shorter MUC cores suggests a loss of surface sediments during gravity coring of 23 cm (GeoB15105-1) and 13.5 cm (GeoB15105-2), respectively. The gravity core depths in the figures have been corrected accordingly.

Sampling and analytical methods have been described by Zabel et al. (2012) and Becker et al. (2018). In brief, wet sediments were taken immediately after core retrieval for gas analysis, after which the cores were transferred to a cold room (4°C). Porewater samples were extracted using Rhizon samplers (5 cm length, 0.15 µm porous polymer) for determining the concentration of dissolved species. Porewaters were analyzed immediately onboard for dissolved iron ($\text{Fe}^{2+}$) and ammonium ($\text{NH}_4^+$). Samples were fixed with zinc acetate for total dissolved hydrogen sulfide (Σ$\text{H}_2\text{S}$) measurements on shore. The remaining porewater was kept at 4°C for shore-based analyses. For volatile fatty acids (VFAs) such as acetate and lactate, porewater was extracted using a hydraulic press and stored in pre-combusted glass vials at -20°C. The remaining sediment samples were stored at ~80°C for elemental analysis and the determination of iron mineral phases.

Dissolved iron ($\text{Fe}^{2+}$) was analysed photometrically (Hach Lange DR 5000 photometer) at 565 nm following the method of Collins et al. (1959). 1 mL of sample was added to 50 µL of a ferrospectral reagent (Merck Chemicals) in disposable polystyrene cuvettes (Stookey, 1970). Samples with high iron concentrations were diluted with oxygen-free artificial seawater. Dissolved ammonium ($\text{NH}_4^+$) was measured by flow injection using a PTFE type gas separator technique after Hall and Aller (1992). Post-cruise, sulfate ($\text{SO}_4^{2-}$) and chloride ($\text{Cl}^-$) were determined by ion chromatography (Metrohm 861 Advanced Compact IC, Metrohm A Supp 5 column, 0.8 µm L min$^{-1}$, conductivity detection after chemical suppression). The detection limits for $\text{Fe}^{2+}$, $\text{NH}_4^+$, $\text{SO}_4^{2-}$, $\text{Cl}^-$ were 1 µM, 14 µM, 0.5 µM, 0.3 µM respectively. Total dissolved hydrogen sulfide (Σ$\text{H}_2\text{S}$) was measured in porewater samples fixed with zinc acetate using the photometric methylene blue method (Cline, 1969) with a precision of <2%. DIC was measured as liberated CO$_2$ after treatment with hydrochloric acid on a TOC analyzer (Shimadzu TOC-V) with an analytical error of 3%. DOC was determined using an Analytik Jena multiN/C 2100 s by an NDIR (non-dispersive infrared) detector. DOC was measured as NPOC (non-purgeable organic carbon) after porewater samples were diluted 2-fold with acid treatment (H$_2$PO$_4$) and stripping with CO$_2$-free air. NPOC was detected from the stripped samples by NDIR after combustion at 750°C in CO$_2$-free air with a precision of <5%. Concentrations of VFAs were analyzed at the University of Bremen by irn-LC/MS as described previously (Heuer et al., 2006, 2009). The detection limits for acetate and lactate are 5 µM and 3 µM, respectively (Heuer et al., 2009).

Dissolved methane (CH$_4$) was analyzed on board following the headspace method described by Kvenvolden and McDonald (1986) and D’Hondt et al. (2003). Wet sediment samples (2–3 mL) were taken by a cut-off syringe from the inner part of a core and transferred into 22-mL glass vials, which were closed gas-tight with a teflon septum and crimp cap, and subsequently heated for 20 min at 60°C. After heating, gas samples of 100–500 µL taken from the headspace were injected into a Thermo Finnigan Trace gas chromatograph equipped with a flame ionization detector and a Carboxen-1006 PLOT fused-silica capillary column (0.32 mm by 30 m; Supelco, Inc., USA). Dissolved CH$_4$ concentrations were derived from the partial pressure of CH$_4$ in the headspace gas (calibrated against hydrocarbon gas standards; Scotty), the headspace volume and the porewater volume of the extracted sediment sample (Becker et al., 2018). The porewater content of each headspace vial was determined from the mass difference between wet and freeze-dried sediment samples. For dissolved methane, the detection limit was 0.1 µM.

For POC analysis, approximately 3 g of homogenized and freeze-dried sediment samples were weighed and treated by adding 10% HCl to remove any calcium carbonate, followed by rinsing with distilled water, centrifugation and freeze-drying. The decalcified sediment (between 10 and 30 mg) was weighed into tin capsules and analyzed in duplicate on a Thermo Scientific Flash 2000 elemental analyzer connected to a Thermo Delta V Plus IRMS. POC content refers to initial dry weight of sediment in weight percent (wt%) of C. For TOC concentrations ranging from 0.4 to 3.7 wt%, standard deviations of duplicate analyses were around 0.01 wt%, corresponding to an analytical precision of 1%.

A 10-step sequential extraction scheme was used for the characterization of total iron (oxyhydr)oxides ($\text{Fe(OH)}_3$), iron carbonates ($\text{FeCO}_3$) and iron sulfides ($\text{FeS}_2$) following Rutten and De Lange (2003). Approximately 250 mg freeze-dried sediment sample was successively washed with 25 ml of (1) 1 M MgCl$_2$ (pH 8; 16 h), (2) 2 M NH$_4$Cl (pH 9; 2 times 16 h), (3) 2 M NH$_4$Cl (pH 8; 2 times 16 h), (4) 2 M NH$_4$Cl (pH 7.5; 2 times 16 h), (5) 2 M NH$_4$Cl (pH 7; 3 times 16 h), (6) ascorbic acid/sodium bicarbonate/sodium...
citrate solution (pH 8; 16 h), (7) 1 M sodium acetate buffer (pH 6; 16 h), (8) 1 M sodium acetate buffer (pH 5; 16 h), (9) sodium dithionite/sodium citrate/sodium acetate solution (pH 4.8; 16 h), and (10) concentrated HNO₃ (16 h). The extracted iron components include adsorbed iron (step 1), carbonate-associated iron (steps 2–5), amorphous iron (oxyhydr)oxides (step 6), crystalline iron (oxyhydr)oxides (step 9) and iron associated with pyrite (step 10). All solutions were analysed by elemental analysis as iron by inductively coupled plasma optical emission spectrometry (ICP-OES) with a precision of <5% and a detection limit of 0.04 μM. Total iron (oxyhydr)oxides (Fe(OH)₃; the sum of steps 6 and 9), iron carbonates (FeCO₃; the sum of steps 2–5 and steps 7–8) and iron sulfides (FeS₂; step 10) are reported in dry weight percent (wt%) of Fe. From here on, iron (oxyhydr)oxides minerals are referred to as iron oxides.

2.3. Set-up of the reaction-transport model

To quantify the turnover of carbon and other elements in the sediment, a non-steady state RTM was used to simulate the data from site GeoB15105. A schematic of the model is illustrated in Fig. 1. The model broadly combines the POC and DOC model of Burdige et al. (2016) (Table S1; R1-R5) and the iron and sulfur model of Egger et al. (2016a). Eleven solid species were simulated, including four pools of POC with different “bulk” degradation rates reflecting different hydrogeological time intervals (POC₁, POC₂, POC₃, POC₄), three pools of iron oxides (i.e., Feoxα for highly reactive, Feoxβ for less reactive and Feoxγ for nonreactive phases), FeS, FeS₂, FeCO₃ and S⁰. Fourteen dissolved species were considered (Cl⁻, SO₄²⁻, ΣH₂S, CH₄, NH₃, DIC, DOC₁, DOC₂, DOC₃, DOC₄, DOCr, CH₃COO⁻ (acetate), Fe²⁺ and H₂) including four fractions of DOC derived from their respective parent POC fraction, and refractory DOC (DOCr). DOC is fermented to H₂ and acetate (see below). A detailed description of the model including boundary conditions and parameters can be found in the Supplementary Information.

The primary redox reactions are listed in Table S1 (R8-R13). These include iron and sulfate reduction and methanogenesis coupled to DOC degradation through the consumption of H₂ and acetate (Table S1). Note that the model simulates H₂ implicitly for these reactions. H₂ is only simulated explicitly as a product of pyrite precipitation (Table S1; R19) and removed through carbonate reduction (Table S1; R28). The secondary redox reactions (those not directly coupled to DOC degradation) of the S, Fe and C cycles follow Egger et al. (2016a) (Table S1; R15-R27). They include sulfidic dissolution of iron oxides, FeS and FeS₂ precipitation, canonical anaerobic oxidation of methane by SO₄²⁻ (AOM, R15) and AOM by iron oxides (R22, R23). The kinetic rate constants were either constrained with the model or taken from the literature (Table S3).

The total rate of POC degradation (ROPΟCdeg) is the sum of the degradation rates of the four POC fractions with different reactivities, i.e. a so-called multi-G model (Jørgensen, 1978; Westrich and Berner, 1984; Burdige, 1991). Each POC pool (POCi, i = 1–4) was associated with a unique first-order remineralization rate constant (kPOCi, i = 1–4) and is linked to a single daughter DOC fraction (DOCi, i = 1–4) and DOCr rather than a multitude of DOC fractions (Burdige et al., 2016). The alternative approach would entail too many unconstrainable and redundant parameters and a lack of transparency in the results. The linkage between the reactivity of POC and its hydrolyzed DOC product is unknown to our knowledge and presents a general

Fig. 1. Schematic diagram of the breakdown of POC deposited at the sediment-water interface and subsequently degraded to DOC (c.f. Burdige et al., 2016) by hydrolysis and then to DIC/H₂ and acetate (Ac) by fermentation. The arrows on the right denote the coupling of H₂ and Ac oxidation to the primary redox reactions considered in the model (see Table S1, R1-R13).
gap in our understanding of carbon turnover in sediments. The rate constants of the DOC fractions in our model are simply fitting parameters and not imposed a priori.

Four POC fractions were sufficient to capture the evolving trends in solid phases and solution chemistry at the study site. The concept of the multi-G model applied here differs slightly from previous studies in that we simulate the bulk POC degradation rates through time that give the best fit to the contemporary data set. Thus, the most recently-deposited fraction, POC1, is also the most reactive one. It was deposited after 2760 yr BP, which is the age of the boundary between Unit I and Unit II. POC2 was deposited between 2760 yr BP and 9300 yr BP, and POC3 was deposited between 1637 yr BP and 2760 yr BP. The least reactive fraction, POC4, was deposited before 9300 yr BP when Mediterranean seawater infiltrated the Black Sea. These POC fractions correspond to the various origins of organic matter deposited during different time periods proposed by Coolen et al. (2013) on the basis of operational taxonomic unit (OTU) abundances within ancient DNA. Whilst some highly reactive POC must have been deposited over the entire simulation period, its impact on the modern-day geochemical profiles is no longer detectable. However, model results are quite sensitive to the historical flux and reactivity of POC, which leads us to believe that there has been an overall increase in POC reactivity over time at the study site (Coolen et al., 2013).

The total degradation rate of POC to DOC is:

$$R_{\text{POCdeg}} = \sum_{i=1}^{4} k_{\text{POC}} \cdot \text{POC}_i$$  \hspace{1cm} (1)

Each DOC pool similarly undergoes degradation with a first-order rate constant ($k_{\text{DOC}}$, $i = 1-4$ and $k_{\text{DOCr}}$ for DOCr). The total rate of reactive DOC production from POC and degradation is then:

$$R_{\text{DOC}} = \sum_{i=1}^{4} (1 - a_i) \cdot f_i \cdot k_{\text{POC}} \cdot \text{POC}_i - \sum_{i=1}^{4} k_{\text{DOC}} \cdot \text{DOC}_i$$  \hspace{1cm} (2)

A fraction ($a_i$) of each POC pool was degraded to DOCr (Burdige et al., 2016). The rate of refractory DOC production from POC, and its degradation is then:

$$R_{\text{DOCr}} = \sum_{i=1}^{4} a_i \cdot f_i \cdot k_{\text{POC}} \cdot \text{POC}_i - k_{\text{DOC}} \cdot \text{DOC}_i$$  \hspace{1cm} (3)

In the above expressions, $f_i$ converts between solid and dissolved unit concentrations (see Table S1).

DOC produced from hydrolysis and/or oxidative cleavage of particulate carbon is subsequently degraded by fermentation to either DIC/H2 ($R_{\text{DOCdeg}}$) or acetate ($R_{\text{acDOCdeg}}$) (e.g., Wellsbury and Parkes, 2000; Parkes et al., 2007; Burdige and Komada, 2015). We define the fraction $f_{\text{term}}$ that determines the relative pathways:

$$\text{CH}_3\text{O}_2(\text{aq}) + 2 f_{\text{term}} \cdot \text{H}_2\text{O} \rightarrow f_{\text{term}} \cdot \text{HCO}_3^- + 2 f_{\text{term}} \cdot \text{H}^+ + \frac{(1-f_{\text{term}})}{2} \cdot \text{CH}_3\text{COO}^- + \frac{(1-f_{\text{term}})}{2} \cdot \text{H}^+$$  \hspace{1cm} (4)

where CH3O2(aq) denotes the assumed chemical composition of dissolved organic matter with a carbon oxidation state of zero. Note that because the model does not simulate dissolved organic nitrogen, production of NH4+ is coupled to the initial POC degradation step (Eq. R14 in Supplement) since deamination is not strongly linked to DOC remineralization (Burdige et al., 2016).

The rate of DOC degradation to DIC/H2 that is coupled to hydrogenotrophic redox reactions is:

$$R_{\text{hyDOCdeg}} = \sum_{i=1}^{4} k_{\text{DOC}} \cdot \text{DOC}_i \cdot f_{\text{term}} + \frac{k_{\text{DOC}} \cdot \text{DOC}_i \cdot f_{\text{term}}}{2}$$  \hspace{1cm} (5)

and the rate of DOC degradation to acetate which is utilized for acetoclastic redox reactions is:

$$R_{\text{acDOCdeg}} = \sum_{i=1}^{4} k_{\text{DOC}} \cdot \text{DOC}_i \cdot \frac{(1 - f_{\text{term}})}{2} + \frac{k_{\text{DOC}} \cdot \text{DOC}_i \cdot (1 - f_{\text{term}})}{2}$$  \hspace{1cm} (6)

Reactions describing the coupling of iron reduction, sulfate reduction and methanogenesis with hydrogenotrophic redox reactions ($R_{\text{hyFeR}}$; $R_{\text{hySR}}$; $R_{\text{hyME}}$) and acetoclastic redox reactions ($R_{\text{acFeR}}$; $R_{\text{acSR}}$; $R_{\text{acME}}$) are listed in Table S1 (R8-R13). As mentioned, DOC-derived H2 is implicit in the model and its production ($R_{\text{hyDOCdeg}}$) is directly coupled to its oxidation (R8-R10). Thus, whilst we have assumed that H2 and acetate are the main products of DOC degradation, it remains a possibility that substrates in addition to H2 may be produced along with acetate.

POC degradation rates were mainly constrained from the measured NH4+, DOC and POC data. DOC degradation rates were constrained from the measured DOC, acetate and DIC data. The secondary redox reactions were constrained from other measured geochemical data.

The known age of the boundary of marine and limnic strata determined in core MD02-2788/2790 (Kwiecien et al., 2008) was used to constrain the sediment accumulation rate ($w_f$, Eq. S6). The age model was further derived using the following equation:

$$\text{age}(x) = \frac{x}{w_f} + \left(\frac{x}{w_f} \cdot \frac{(\phi_f - \phi_0) \cdot (e^{\frac{x}{w_f}} - 1)}{p \cdot w_f \cdot (\phi_f - 1)}\right)$$  \hspace{1cm} (7)

where $x$ is depth in the sediment, and the other terms account for the decrease in porosity over depth (listed in Table S3). The decrease in porosity (compaction) is assumed to be constant over time. The age model allows for the temporal reconstruction of key upper boundary conditions, including POC, iron oxides, and iron sulfides (Fig. 2d-f). Since these species are reactive and evolve over time, the time-dependent boundary conditions were not simply adjusted to the surface burial rate determined from the age model. Instead, the boundary fluxes were constrained from measured solid and dissolved biogeochemical data through the sediment core. Further details are given in the Supplement.

Inflow of Mediterranean seawater into the Black Sea basin was reconstructed assuming an initial salinity of 1
for the freshwater basin and a linear increase to 22 between 9300 and 2000 yr BP (Bahr et al., 2008; Soulet et al., 2010; Fig. 2a). The transient evolution of salinity was used to calculate Cl\textsuperscript{−} and SO\textsubscript{4}\textsuperscript{2−} at the upper boundary (Egger et al., 2016a; Fig. 2a, b). Seawater DIC increased from <1 mM to 5.3 mM based on modern bottom seawater values (Fig. 2b). Best results were obtained by applying measured bottom water \( \sum \text{H}_2\text{S} \) concentrations (Fig. 2c) of 0.9 mM to 5.3 mM to the upper boundary after 1500 yr BP, coincident with the establishment of modern salinity levels (Soulet et al., 2010). Simulation results with high bottom water sulfide levels prior to this were unsatisfactory, and previous work suggests that bottom water \( \sum \text{H}_2\text{S} \) may have been <0.1 mM at this time (Egger et al., 2016a). The simulation of porewater Cl\textsuperscript{−} data was achieved by including upward fluid advection with a velocity of 130 cm kyr\textsuperscript{−1}. This is six-fold larger than the sediment burial velocity based on the \(^{14}\text{C} \) age model (23.3 cm kyr\textsuperscript{−1}, Eq. S6) and resulted in a small net upward-directed flux of all solutes at the lower boundary and a better overall fit of the complete dataset. Whilst upward fluid advection is not well constrained at this site, fluid seepage at nearby locations has been observed throughout the Black Sea (Bahr et al. 2005; Lamy et al., 2006; Kwiecien et al., 2008). Unit I (\textasciitilde0–210 cm) consists of finely laminated coccolith ooze (~1 to 2 wt\% POC), Unit II consists of laminated organic-rich sapropelic sediments (up to \textasciitilde4 wt\% POC), and Unit III (\textasciitilde417 cm) is an organic-lean freshwater deposit (Zabel et al., 2012). Sediment porosity was highest in Unit I and decreased gradually to Unit III (Fig. 3j). Within Unit I, RF1 marks the sulfate-methane transition zone where sulfate becomes depleted and CH\textsubscript{4} concentrations rise with increasing depth at \textasciitilde130 cm. RF2 corresponds to the boundary between marine (Unit II) and limnic (Unit III) deposits at \textasciitilde417 cm, and RF3 coincides with a sedimentary color change from gray to black at \textasciitilde505 cm (Zabel et al., 2012).

Porewater concentrations of DIC and NH\textsubscript{4}+ (Fig. 3d, e) increased from the surface to RF1. From RF1 to RF2, NH\textsubscript{4}+ increased slightly whereas DIC decreased. Below RF2, DIC and NH\textsubscript{4}+ decreased toward the deepest sampling depth. Trends in DOC and acetate were closely associated with the POC content with maximum values close to RF2 where the maximum POC content of 3.7% was measured (7.1 mM for DOC, 245 \(\mu\)M for acetate; Fig. 3g, h, k).

3. RESULTS

3.1. Porewater and sediment geochemistry

Geochemical data for site GeoB15105 are shown in Fig. 3. Based on the observed trends and visual core inspection (Zabel et al., 2012), we identified three geochemical reaction fronts (RF) (Fig. 3a-n) superimposed on three sedimentary units (Unit I-III) (Fig. 3o). The latter closely agree with previous observations throughout the Black Sea (Bahr et al. 2005; Lamy et al., 2006; Kwiecien et al., 2008). Unit I (0–210 cm) consists of finely laminated coccolith ooze (~1 to 2 wt% POC), Unit II consists of laminated organic-rich sapropelic sediments (up to ~4 wt% POC), and Unit III (~417 cm) is an organic-lean freshwater deposit (Zabel et al., 2012). Sediment porosity was highest in Unit I and decreased gradually to Unit III (Fig. 3j). Within Unit I, RF1 marks the sulfate-methane transition zone where sulfate becomes depleted and CH\textsubscript{4} concentrations rise with increasing depth at ~130 cm. RF2 corresponds to the boundary between marine (Unit II) and limnic (Unit III) deposits at ~417 cm, and RF3 coincides with a sedimentary color change from gray to black at ~505 cm (Zabel et al., 2012).
SO$_2^-$ concentrations (Fig. 3a) decreased steadily from modern bottom water values (16 mM) to RF1 where an abrupt change in its concentration gradient was observed. At this point, SO$_2^-$ decreased more gradually to concentrations below the analytical detection limit at RF3. CH$_4$ concentrations increased below RF1 to almost 17 mM at 736 cm (Fig. 3b). SO$_2^-$ and CH$_4$ thus coexisted over a thick sediment interval (~250 cm) between RF1 and RF2. Dissolved sulfide reached maximum levels (~5 mM at RF1), and decreased with increasing depth down to RF2 at the base of the sapropel.

Dissolved Fe$^{2+}$ concentrations were below detection limit in and above the sapropel and then strongly increased with depth below RF3 to almost 1 mM in the limnic Unit III (Fig. 3f). Iron oxides (Fe(OH)$_3$) and siderite (FeCO$_3$) displayed low values in Units I and II and higher levels in Unit III. Below RF3, both Fe phases decreased with depth and then increased again slightly (Fig. 3i, m). Pyrite (FeS$_2$) displayed high and near-constant values (~1.1%) from the surface down to RF2 where dissolved Fe$^{2+}$ was low, and then decreased with depth from 1.13% to 0.33% between RF2 and RF3, with near-constant values below RF3 (~0.45%) (Fig. 3n).

3.2. Key model findings

The model was tuned to match the field observations mainly via the rate and timing of organic carbon degradation as well as particulate fluxes to the seafloor (Fig. 2d-f). Best-fit results were obtained by assuming four pools of reactive particulate organic matter (POC$_i$, $i=1-4$) undergoing remineralization at different rates. These were coupled to four reactive and one refractory DOC fractions (DOC$_i$, $i=1-4$ and DOC$_r$). Model simulation results closely tracked the field data (Fig. 3) with one exception; CH$_4$ below RF2, presumably due to degassing during core recovery.

The reactive POC fractions corresponded well with lithology; POC$_1$ and POC$_3$ to Unit I, POC$_2$ to Unit II...
(sapropel) and POC4 to Unit III (Fig. 4a). The degradability of the POC pools (kPOC) decreased from POC1 to POC3 with values of 4 × 10^{-4} yr^{-1} for kPOC1 and 5.04 × 10^{-8} yr^{-1} for kPOC3 (Table S3). The maximum flux of POC at the sediment surface (1.15 mg C cm^{-2} yr^{-1}) was associated with the sapropel at ~8 kyr BP (Fig. 2d). POC degradation rates showed peaks at RF1 (RPOCdeg), RF2 (RPOCdeg), at the Unit I/II boundary (RPOCdeg) and immediately below RF2 (RPOCdeg) (Fig. 4b). RPOCdeg and RPOCdeg were three to four orders of magnitude lower than RPOCdeg.

Over the Holocene and the Late Pleistocene, only 1% to 2% of DOC produced from POC was refractory DOC (a, Table S3). Yet, DOC3 now comprises the bulk of DOC in Unit I (Fig. 4c). kPOC of the reactive fractions ranged from 35.9 yr^{-1} to 1.36 × 10^{-3} yr^{-1} and are thus substantially higher than the parent kPOC values (Table S3). In the sapropel (Unit II), DOC2 now dominates whereas DOC3 is the major fraction in Unit III (Fig. 4c). DOC3 is hardly present since its production from POC3 occurred for only a brief period around 2.76 kyr ago (Fig. 2). The best-fit values of \( \lambda \) ranged from 0 to 1 depending on the DOC fraction. DOC1 degradation was entirely channeled into DIC/H2 (hyDOCdeg), implying that this fermentation pathway or some other non-competitive substrate has been dominant in Unit I above RF1. Between 80% and 100% of the other DOC fractions were degraded to acetate (RacDOCdeg), possibly due to varying carbon sources to the Black Sea (see Discussion). Below the Unit I/II boundary, rates of DOC degradation along the acetate pathway exceeded those of the DIC/H2 pathway and both now showed a peak where maximum DOC concentrations were measured at RF2 (Fig. 4d). The elevated DOC accumulation between RF1 and RF3 was attributed to production from POC2 (Fig. 2; red versus blue curves). In addition, DOC2, rather than DOC1, is currently the main source of acetate (Fig. S3, blue curves).

In the contemporary situation, the cycling of DIC/H2 and acetate is directly coupled to the turnover of Fe and S (Fig. 1; Fig. 4). Dissimilatory iron reduction is negligible (<0.002 nmol Fe cm^{-2} yr^{-1}; Fig. 4g) compared to sulfate reduction and methanogenesis (Fig. 4e and f). Dissimilatory sulfate reduction is currently the dominant terminal respiration process above RF2. Sulfate reduction displays three peaks depending on the substrate being oxidized; H2 at RF1 (\( R_{SO4H2S} \): 103 nmol cm^{-2} yr^{-1} of SO4^2-), CH4 above RF1 (\( R_{SO4CH4} \): 103 nmol cm^{-2} yr^{-1} of SO4^2-) and acetate above RF2 (\( R_{SO4Ac} \): 9.04 nmol cm^{-2} yr^{-1} of SO4^2-).

Methanogenesis and methane oxidation by SO4^2- (i.e. canonical anaerobic oxidation of methane, AOM) both occur in Unit I and Unit II. Above RF1, AOM (R15, Table S1) is higher than methanogenesis and contributes to the initial sharp decrease in SO4^2-. Below RF1, AOM rates showed a decrease whereas acetoclastic

methanogenesis increased at low levels, leading to SO$_2^-$ tailing down into the methane sediment. $R_{\text{ACME}}$ is apparently the major CH$_4$ production pathway at RF2 and both $R_{\text{ACME}}$ and $R_{\text{SYME}}$ exceeded AOM (Fig. 4f, red and blue curves versus green curve).

Elevated rates of sulfidic dissolution of iron oxides ($R_{\text{contH}_2S}$) were simulated at the sediment surface ($1.4 \times 10^9$ nmol cm$^{-2}$ yr$^{-1}$ of Fe). The dissolved Fe$^{2+}$ produced from this pathway was incorporated into iron sulfide minerals (Fig. 3n; Fig. 4i). Iron oxide reduction was also predicted to increase below RF3 where iron oxide content was high (Fig. 4g). The model further suggests that AOM by iron oxides is currently insignificant, being five orders of magnitude lower than canonical AOM with SO$_2^-$ (Fig. 4f, green curve versus black curve).

4. DISCUSSION

4.1. POC origin and reactivity

Large-scale alteration of the Black Sea geochemistry during the transition from the Late Pleistocene into the Holocene greatly altered the flux of POC from the surface waters to the seafloor as well as the availability of electron acceptors for microbial respiratory pathways. This, in turn, led to a pronounced restructuring of biogeochemical process rates in the sediment column (Egger et al., 2016a). At the same time, the origin of buried POC has evolved from lacustrine and terrestrial to marine, and thus POC has presumably become more reactive over time (Cowie and Hedges, 1984; Sun and Wakeham, 1994; Wakeham et al., 1997).

The results suggest that the POC deposited on the seafloor since the Late Pleistocene can be broadly characterized by four pools of differing reactivity. These correspond to the sources of organic matter suggested by Coolen et al. (2013) who based their findings on operational taxonomic unit (OTU) abundances within the pool of ancient DNA. POC$_1$ (lying above RF1) reflects the more taxonomic unit (OTU) abundances within the pool of ancient DNA. POC$_1$ (lying above RF1) reflects the more recent marine deposits of calcareous coccoliths of the haptophyte *Emiliania huxleyi* since 2760 yr BP where the Unit I/II boundary is located (Lamy et al., 2006; Kwicien et al., 2008). The highest flux of POC$_1$ during this period (0.68 mg C cm$^{-2}$ yr$^{-1}$, Fig. 2d) is of the same order of magnitude with a previous estimate of 0.21 mg C cm$^{-2}$ yr$^{-1}$ for Unit I sediments (Calvert et al., 1991). The model suggests that the POC$_1$ flux at the seafloor is elevated compared to POC$_1$ and coincident with the main sapropel formation period (2.5 kyr BP to ~9.4 kyr BP) defined by Coolen et al. (2013). POC$_2$ flux displayed two peaks that align with high OTUs for marine fungi and terrestrial vegetation (4.620 yr BP) and for marine plankton (8.020 yr BP). The POC maximum (4%) at the base of the sapropel layer has been observed elsewhere in the Black Sea (e.g. Jorgensen et al., 2004; Coolen et al., 2013; Egger et al., 2016a).

The maximum degradation rate of POC within the sapropel was one order of magnitude lower than in the modern unit, possibly because the latter is associated with higher abundances of fresh, reactive marine-derived carbon (Coolen et al., 2013). This is reflected in the degradation constants $k_{\text{POC1}}$ (4.0 $\times$ 10$^{-2}$ yr$^{-1}$) and $k_{\text{POC2}}$ (1.7 $\times$ 10$^{-2}$ yr$^{-1}$).

The genesis of the sapropel was therefore probably linked to higher primary production during the evolution of the basin from Pleistocene lacustrine to modern marine in addition to enhanced organic matter preservation (i.e. $k_{\text{POC2}} < k_{\text{POC1}}$) caused by reduced deep-water ventilation and basin anoxia (Arthur and Dean, 1998; Eckert et al., 2013). A sensitivity analysis shows that mineralization of POC$_1$ and POC$_2$ are the main drivers for the redox reactions taking place at RF1 and RF2, respectively (Fig. S2).

The reactivity of POC$_3$ was substantially lower than POC$_1$ and POC$_2$ and was deposited during a brief episode between the marine and sapropel periods. It might represent the faint laminated layers observed at site GeoB15105 near the Unit I/II boundary (Zabel et al., 2012). Similar light laminae seen elsewhere in the Black Sea were deposited during the first invasion of *E. huxleyi* into the Black Sea and mark the base of Unit I at 2760 yr BP (Lamy et al., 2006). Although the rate constant for POC$_3$ mineralization is 100-fold lower than $k_{\text{POC2}}$ (3.3 $\times$ 10$^{-2}$ yr$^{-1}$), elimination of this pool from the model leads to large discrepancies between measured and modeled POC (Fig. S4, blue curves). NH$_4^+$ and DOC concentrations are also sensitive to the rate constant for POC$_3$ degradation (Fig. S4, red curves). The least labile POC$_4$ pool (5.0 $\times$ 10$^{-8}$ yr$^{-1}$) was required to simulate carbon accumulation in deeper time between ~11.4 kyr BP and 9.4 kyr BP before the inflow of Mediterranean seawater (Fig. S4, green curves). The origin of this fraction is mainly freshwater plankton (Coolen et al., 2013). Overall, the model results support observations of an evolving source and reactivity of organic matter over the Late Pleistocene and Holocene.

4.2. DOC turnover and benthic fluxes

The degradation of POC is carried out by microorganisms via a multi-step process (e.g., Megonigal et al., 2003; Arnosti, 2008; Burdige and Komada, 2015). Large and complex organic polymers are firstly broken down into high-molecular-weight DOC compounds via extracellular hydrolysis and oxidative cleavage. These products are subsequently transformed into low-molecular-weight labile and refractory DOC compounds (DOC in the model) that can be broken down further into even smaller moieties such as VFAs and H$_2$ (Burdige and Martens, 1990). This last step was parameterized in the model assuming first-order mineralization ($k_{\text{DOCi}}$).

The maximum DOC concentration in the core (7.1 mM) was similar to values reported in other marine sediments underlying anoxic bottom waters (Burdige et al., 2016; Komada et al., 2016; Logina et al., 2020) and freshwater or brackish sediments (Weston et al., 2006; Lee et al., 2008; Segarra et al., 2013). The decreasing reactivity of DOC (e.g., $k_{\text{DOC1}} > k_{\text{DOC2}} > k_{\text{DOC3}} > k_{\text{DOC4}}$) mirrors the reactivity of the parent POC fractions (Burdige et al., 2016). Yet, $k_{\text{DOCi}}$ were several orders of magnitude higher than $k_{\text{POCi}}$, which is consistent with the detailed DOC study in the Santa Barbara Basin by Burdige et al. (2016). These differences might reflect a rate limiting step in carbon flow at the point of initial hydrolysis or oxidative cleavage of POC.

compared to relatively rapid turnover of DOC intermediates (Burdige et al., 2016). Our results also confirm the idea that the accurate simulation of the bulk DOC concentrations is achievable with concurrent production of labile DOC and refractory DOC (Burdige et al., 2016). Although the fraction of DOC$_r$ produced relative to labile DOC is small ($\alpha_l \sim 1–2\%$), the negligible reactivity of DOC$_r$ allows it to accumulate in the porewater over thousands of years to the extent that DOC$_r$ is now the major DOC pool in the modern section (Unit I), similar to observations in the anoxic Santa Barbara Basin (Burdige et al., 2016). The general resemblance of DOC dynamics in the Black Sea and Santa Barbara Basin suggests a common set of controls on DOC cycling in these two different environments, and further implies that most porewater DOC consists of refractory DOC (Burdige and Gardner, 1998). In the deeper lacustrine sediments, the least reactive of the labile fractions (DOC$_L$) is predominant (see also Fig. 4c; Fig. S4).

The partitioning of bulk organic matter into discrete POC and DOC fractions is a necessary step to simplify the modeling work. The reactivity distribution of bulk DOC might instead be better represented by a continuous function of age as described for POC (Middelburg, 1989; Boudreau and Ruddick, 1991). It is not obvious how this can be done for DOC in a system where DOC molecules of different ages openly diffuse through the sediment porewater. It should also be noted that the DOC conceptual model is relatively simple, and does not account for DOC adsorption onto particles, DOC preservation by iron mineral phases and/or complex geopolymerization reactions that might otherwise explain the accumulation of a low-reactivity DOC pool (Lalonde et al., 2012; Barber et al., 2017). Our understanding of how these processes operate in nature is very fragmentary. The discrete DOC rate constants reported here should therefore be viewed as parameters that integrate these poorly understood processes into apparent first-order reactivities.

DOC is mainly fermented to DIC/H$_2$ above Unit I and to acetate below it (see Fig. S3 for model sensitivities). Acetate is well-recognized as a major intermediate of organic matter mineralization (Heuer et al., 2009; Komada et al., 2016; Zhuang et al., 2019). Porewater acetate concentrations at the study site are mainly determined by production through fermentation reactions (R$_{acDOCdeg}$) and consumption by sulfate reduction (R$_{acSSR}$) and methanogenesis (R$_{acME}$) (Fig. 4). The maximum acetate concentrations measured in this study (200 µM) are at the high end for shallow marine sediments, and 10-fold higher than the previous values reported for the Black Sea (Knab et al., 2009). Lower concentrations have been measured in the Skagerrak (Denmark) (<100 µM, Dale et al., 2008), Santa Barbara Basin (~30 µM, Komada et al., 2016), Lake Towuti, Indonesia (~35 µM, Friese et al., 2021) and the western Mediterranean Sea (~10 µM, Zhuang et al., 2018). The concentrations in the southwestern Black Sea are on the same order as those measured in wetlands (e.g., ~440 µM, Dalcin Martins et al., 2017). Given that acetate is the main substrate for methanogenic microorganisms in freshwater sediments (Whiticar 1999; Conrad 2005), the elevated acetate turnover rates in Unit II and below (Fig. 4) suggest that the brackish period when the sapropel was being formed is comparable to modern brackish sediments displaying high DOC and acetate concentrations (e.g., Weston et al., 2006; Lee et al., 2008; Segarra et al., 2013; Dalcin Martins et al., 2017). Acetate production from mineralization of the sapropel would have been important for sustaining subseafloor microbial activity throughout the post-glacial period. This is evident from observed chemoorganotrophs, Acetohalobium, in Black Sea sediments as well as pyruvate ferredoxin oxidoreductase (PFOR), carbon monoxide dehydrogenase and acetyl-CoA synthase encoding genes (More et al., 2019). Note that the role of VFAs to carbon mineralization is not strictly limited to acetate, however, as lactate concentrations of 30–40 µM have been measured at the same site (Fig. S5a).

According to our model, the total DOC efflux from Black Sea sediments over the period under investigation ranged between 0.32 and 1.24 µmol C cm$^{-2}$ yr$^{-1}$ (Fig. 5a, black curve). After 9300 yr BP, an increase in remineralization led to a gradual rise in DIC flux. The ratio between total DOC efflux and DIC efflux appears to have been nearly constant before the inflow of Mediterranean water (~40%) and then decreased to 2.3% at the present day (Fig. 5b, black curve). The high ratios estimated for the Late Pleistocene sediments have also been observed in modern sediments with low remineralization rates such as the Weddell Sea (3–150%; Hulth et al., 1997), the NW European continental margin (2–32%; Otto and Balzer, 1998) and Santa Monica Basin (39%; Komada et al., 2013). The present-day ratio is comparable to the Santa Barbara Basin (4%, Burdige et al., 2016) and indicates rapid cycling of DOC to DIC (Burdige and Komada, 2015).

Refractory DOC accounted for ~5% of the total DOC efflux from Black Sea sediments in the Late Pleistocene (Fig. 5b, red curve). This ratio is within the range of modeled values (the lowest lability DOC fluxes to total DOC fluxes) from Santa Monica Basin (Komada et al., 2013). The DOC$_r$ flux to total DOC flux ratio increased to 41% at present, again close to the 53% derived for Santa Barbara Bain (Burdige et al., 2016). Interestingly, the modern Black Sea appears to display similar DOC$_r$/DOC and DOC/DIC ratios as the Santa Barbara Basin whereas the Late Pleistocene environment is more similar to the Santa Monica Basin.

Historical depth-integrated rates of biogeochemical processes driven by DOC degradation show a correspondence to organic matter composition, the available terminal electron acceptors, and the bottom water geochemistry at time of deposition (Fig. 5). Despite the low salinity, the organic-poor sediment prior to 9300 yr BP was dominated by sulfidic-dissolution of iron oxides (Fig. 5b), with the sulfate being supplied by AOM (Fig. 5d, green curve). These processes intensified between 9300 yr BP and 7995 yr BP under the ensuing brackish bottom waters. After 7995 yr BP, DOC degradation was mainly coupled to sulfate reduction and methanogenesis rather than iron reduction (Fig. 5c, d, g). Although direct DOC coupling to dissimilatory iron reduction was negligible over the study period, the indirect coupling between DOC-driven
sulfate reduction (producing sulfide) and iron reduction by sulfide was not negligible (Figs. S2, S3 and S4). This has led to the prediction of iron sulfide minerals, mainly in methanic sediments where Fe\(^{2+}\) concentrations are elevated. In modern marine sediments, by contrast, iron sulfides tend to be formed at the top of the sulfate reduction zone where Fe\(^{2+}\) availability is highest (Jørgensen and Kasten, 2006; Jørgensen et al., 2019a). Hence, as a result of the seawater inflow, the major zones of sulfate reduction and iron oxide reduction by sulfide are now inverted over depth (Egger et al., 2016a).

4.3. Coupled sulfur, iron and methane cycling

In marine sediments, SO\(_4^{2-}\) and CH\(_4\) tend to be consumed by microbial communities that perform AOM (R15, Table S1) (Barnes and Goldberg, 1976; Boetius et al., 2000; Hinrichs and Boetius, 2002). The AOM layer is typically indicated by the sulfate-methane transition zone (SMT), which separates the overlying sulfate reducing sediments from underlying methanogenic layers. AOM therefore largely prevents the escape of CH\(_4\) to the bottom waters. During the Late Pleistocene when SO\(_4^{2-}\) levels were low, a flux of CH\(_4\) from the sediment was predicted (Fig. 5). In reality, much of this CH\(_4\) might have been oxidized aerobically at the sediment-water interface; a process not included in our model. The present SMT is very broad with SO\(_4^{2-}\) and CH\(_4\) coexisting for over 200 cm in Unit II and Unit I below RF1. A wide SMT characterized by either a long tailing of the SO\(_4^{2-}\) into the methanic layer or CH\(_4\) into SO\(_4^{2-}\) -containing sediments has been observed at other Black Sea sites (e.g., Jørgensen et al., 2001, 2004; Holmkvist et al., 2011) and beyond (Dale et al., 2008; Treude et al., 2014; Maltby et al., 2016; Jørgensen et al., 2019b). These studies have explained the tailing as a lack of thermodynamic drive for AOM, the usage of non-competitive substrates by methanogens in the SMT, and cryptic CH\(_4\) and sulfur cycling in the SMT.
At site GeoB15105, the long SO$_4^{2-}$ tail begins at RF1 with a change in the SO$_4^{2-}$ concentration gradient, indicating a decrease in the downward flux (Fig. 3a). Degradation of DOC$_1$ to DIC/H$_2$ in addition to AOM was mainly responsible for the SO$_4^{2-}$ depletion at RF1 (Fig. 4e). Below RF1, sulfate reduction coupled to acetate oxidation became more prominent. The total rate of sulfate reduction is at the lower end of those reported from other Black Sea sites (e.g., Jorgensen et al., 2001; Knab et al., 2009; Holmkvist et al., 2011; Egger et al., 2016a). Methanogenesis via the DIC/H$_2$ pathway ($R_{\text{DIC/H}_2}$) in Unit I is concomitant with sulfate reduction ($R_{\text{SR}}$, $R_{\text{SO4CH}_4}$). Methanogenesis rates are lower than AOM rates but nonetheless significant. Indeed, experimental and modeling studies have shown that maximum rates of methanogenesis can be found in the SMT (Beulig et al., 2018, Dale et al., 2019). Acetoclastic methanogenesis currently co-occurs with sulfate reduction in Unit II and at higher rates than total sulfate reduction at RF2. These findings suggest that a cryptic CH$_4$ cycle (e.g. Beulig et al., 2018) in the broad SMT might therefore explain the large SO$_4^{2-}$ and CH$_4$ overlap observed in the core.

Co-existence of SO$_4^{2-}$ and CH$_4$ is favored by an abundance of common substrates for sulfate reducing bacteria and methanogens. For instance, an increase in sulfate reduction and methanogenesis following the addition of acetate and lactate in laboratory incubations demonstrates that both groups of microorganisms readily consume these substrates (Sela-Adler et al., 2017). Here, we simulated the SO$_4^{2-}$ and CH$_4$ data in the sapropel stage (Unit II) by assuming common usage of acetate by both processes. The increase in POC degradation and acetate production in the sapropel allowed sulfate reduction and methanogenesis rates to increase simultaneously.

The relative importance of competitive versus non-competitive substrates is poorly understood, but is known to be significant in organic-rich sediments underling oxygen-depleted bottom waters (Ferdeman et al., 1997; Treude et al., 2005; Maltby et al., 2016). There are indications that co-existence of SO$_4^{2-}$ and CH$_4$ in coastal marine sediments is driven by non-competitive substrates (Chuang et al., 2016; Egger et al., 2016b; Zhuang et al., 2018). An abundance of non-competitive substrates will allow methanogenesis to take place in the presence of SO$_4^{2-}$ (Oremland and Polcin, 1982). Archaeal respiratory quinone classes diagnostic of methanogens (methanophenazine, MP) have been detected in Unit I and Unit II at the study site (Becker et al., 2018) and are indicative of the utilization of non-competitive methylotrophic substrates (Becker et al., 2018). The low $\delta^{13}$C of butanetiol dialkyl glycerol tetraethers (BDGTs) lipids detected in Unit I and Unit II further implies that hydrogenotrophic and methylotrophic methanogenesis pathways are co-occurring (Coffinet et al., 2020). The non-competitive substrate argument also is supported by the increase in $R_{\text{ME}}$ in sulfate-enriched sediments above RF1 (Fig. 4f). As mentioned in Section 2.3, the presumed reaction stoichiometry of $R_{\text{ME}}$ may not necessarily imply H$_2$-based catabolism. An increase in $R_{\text{DOCdeg}}$, $R_{\text{SSR}}$ and $R_{\text{ME}}$ above RF1 (Fig. 4d-f) and after 2760 yr BP (Fig. 5c-e) may suggest that H$_2$ and non-competitive substrates were both being produced at this time. If H$_2$ were the sole substrate in this layer, the presence of SO$_4^{2-}$ ought to thermodynamically inhibit hydrogenotrophic methanogenesis since sulfate-reducing bacteria have a higher affinity for H$_2$ (Hoehler et al., 1998). Taking these results at face value, some of the DOC degradation products must be being consumed either partly or exclusively by methanogens.

In the methane-rich sediments below RF3, high dissolved Fe$^{2+}$ concentrations were measured (Fig. 3f). The source of the Fe$^{2+}$ below the sulfate reduction zone in the Black Sea sediments is still not clear. Previous studies emphasize the production of Fe$^{2+}$ by iron oxide reduction through cryptic sulfur cycling (Holmkvist et al., 2011) or AOM coupled with iron oxide reduction (Fe-AOM) (Egger et al., 2016a). This modeling work points towards the former explanation for site GeoB15105, as the rate of sulfidic dissolution of iron oxides in Unit III is three-orders-of-magnitude higher than Fe-AOM (Fig. 4g, green curve versus black curve). The same trend holds over the different sediment depositional periods where Fe-AOM rates are orders-of-magnitude lower than iron oxide reduction by sulfide (Fig. 5g, red curve versus Fig. 5h, black curve). This can be expected since iron reduction by sulfide is kinetically favoured relative to methane oxidation (Bar-Or et al., 2017). In fact, sensitivity analysis showed that Fe$^{2+}$ concentrations are only weakly dependent on Fe-mediated AOM compared to sulfidic dissolution of iron oxides (Fig. S6). Although the Fe$^{2+}$ data can be fit reasonably well with higher rates of Fe-AOM if sulfidic iron oxides dissolution is turned off, the resulting greater penetration depth of hydrogen sulfide into the sediment and the simulated solid phase iron species contents do not match the measured data (Fig. S6, red curves).

Studies of the cryptic sulfur cycle in and below the SMT have shown that sulfide oxidation coupled to iron oxide reduction produces Fe$^{2+}$ and elemental sulfur (S$_0$) at very low rates (Holmkvist et al., 2011). S$_0$ can then undergo disproportionation and stimulate canonical AOM below the SO$_4^{2-}$ depletion depth and stimulate precipitate as pyrite (FeS$_2$). Measurable FeS$_2$ contents and high dissolved Fe$^{2+}$ are evidence of sulfide oxidation coupled to iron oxide reduction below RF3 (Fig. 3f and 3n). Flow-through column experiments in natural freshwater sediments conducted by Hansel et al. (2015) have shown that S$_0$ generated from initial oxidation of dissolved sulfide coupled to iron oxide reduction is recycled back to sulfide via disproportionation, thereby providing additional dissolved sulfide for iron oxide reduction. Although reactive intermediates involved in the cryptic sulfur cycle are difficult to detect, model derived rates of S$_0$ disproportionation and iron reduction by sulfide (Fig. 4g and 4h) showed peaks at about 600 cm where Fe$^{2+}$ concentrations were high and amorphous iron oxides were more abundant than crystalline iron oxides (Fig. 3f; Fig. S5b). Elemental sulfur sustaining these processes at the present day is sourced from a deep reservoir that had accumulated over time (Fig. 5h). Further, following the results of Hansel et al. (2015), iron oxide reduction ought to be higher where amorphous iron oxides are abundant, i.e. in Unit III. Depth-integrated rates
were nearly constant (10.7 μmol Fe cm⁻² yr⁻¹ for \( R_{FeoxH2S} \) and 1.3 μmol S⁰ cm⁻² yr⁻¹ for \( R_{oH} \)) before the inflow of seawater and increased from 9300 yr BP until 7995 yr BP (Fig. 5h) as the result of sulfide produced by canonical AOM. Sensitivity tests show that turning off disproportionation has a large impact on Fe²⁺ concentrations below RF3 (Fig. S6n, brown curve).

Our findings have broader implications for coastal environments that are subject to long-term sea level rise or seawater intrusion (e.g., Herbert et al., 2015; Weston et al., 2011). The predicted potential changes in biogeochemical cycles due to seawater intrusion of freshwater wetlands include increased generation of hydrogen sulfide, sulfate reduction rates and CO₂ emissions, decreased CH₄ emissions and reduced carbon sequestration (Herbert et al., 2015). This transient reorganization of biogeochemical processes and fluxes can be quantified with the general model approach presented here. Furthermore, it has been suggested that refractory DOC may control variations in paleoclimate (Hansell, 2013). For instance, oxidation of large reservoirs of refractory oceanic DOC during the Palaeocene–Eocene Thermal Maximum (PETM, ~66 Myr ago) may have contributed to climate hyperthermals (Sexton et al., 2011). Our work raises the possibility that the contribution of labile and refractory DOC to the total dissolved carbon flux from sediment is not constant and may have been very different in the geological past. This should be considered in Earth system models applied to carbon cycling in ancient ocean settings.

5. CONCLUSIONS

Sediments in the southwestern Black Sea provide a detailed geochemical record for the evolution of biogeochemical element cycling over time. A diagenetic model was developed to simulate DOC concentrations, its degradation to DIC/H₂ and acetate and coupling with iron and sulfur turnover. The transient evolution of reactive POC fluxes to the seafloor agrees well with the known biogeochemistry of observed sedimentary units. Reactive marine organic matter provides an ongoing carbon source for microorganisms, with the sapropel at the boundary between marine and limnic deposits providing the main supply of DOC and acetate. Extensive co-existence of SO₄²⁻ and CH₄ are interpreted as non-competitive and common substrates utilization by sulfate reducing bacteria and methanogens. A cryptic sulfur cycle is proposed to lead to the occurrence of high Fe²⁺ levels in the deep methanogenic zone. In addition, iron reduction coupled to AOM is argued to have a minor impact on the Fe²⁺ concentrations in deep sediments, suggesting that this pathway is negligible. The model reveals shifts of redox regimes from iron cycling to sulfur cycling and of DOC degradation pathways over the Holocene and the Late Pleistocene. These results enhance our understanding of the interactions between carbon, sulfur and iron cycles in both modern and ancient settings and how these interactions might evolve in response to paleoenvironmental changes.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

ACKNOWLEDGEMENTS

We thank the captain, crew and the scientific shipboard party of R/V Meteor, cruise MS841 (DARCSEAS 1). We also thank the Zabel and Hinrichs research group members for sample collection and analysis (Becker, K., Braun, S., Broda, N., Dibke, C., Elvert, M., Goldhammer, T., Lin, Y.-S., Lipp, J., Meador, T., Pape, S., Peters, C., Schmal, J., Schmidt, F., Schröder, J., Taubner, H., Wendt, J., Wörmer, L., Yoshinaga, M., Zhu, C.). We acknowledge the help of Jutta Eckert at Department of Hydrology, University of Bayreuth, for DIC analyses. Silvana Pape is specially acknowledged for invaluable technical and analytical support for the sequential extraction and DOC analysis. Matthias Haeckel and Matthias Eggert are thanked for the fruitful discussions and helpful suggestions at the initial stage of this modeling study. Many thanks to Mark Zindorf and Sebastiaan van de Velde for their constructive comments which helped to improve the manuscript substantially and to the Associate Editor Filip J. R. Meyssman for handling the manuscript. This study was funded through DFG-Research Center/Cluster of Excellence “The Ocean in the Earth System” (Sediment Geochemistry) to M. Z. and P.-C.C. Porewater and TOC analyses were co-funded by the European Research Council under the European Union’s Seventh Framework Programme–‘Id eas’ Specific Programme, ERC grant agreement No. 247153 (Advanced Grant DARCLIFE; PI: Kai-Uwe Hinrichs). A.W.D. and P.-C.C. received funding from the project EVAR (03F0814) of the German Federal Ministry of Education and Research (BMGF), in which the model was partly developed (https://www.ebus-climate-change.de/home).

APPENDIX A. SUPPLEMENTARY MATERIAL

Supplementary data to this article can be found online at https://doi.org/10.1016/j.gca.2021.04.032.

REFERENCES


Associate editor: Filip Meysman