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# **Chemical Geology**



journal homepage: www.elsevier.com/locate/chemgeo



# Controls on organic carbon and molybdenum accumulation in Cretaceous marine sediments from the Cenomanian–Turonian interval including Oceanic Anoxic Event 2

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### ARTICLE INFO

Article history: Accepted 8 October 2011 Available online 15 October 2011

Keywords: Cretaceous Ocean Anoxic Event 2 Model Molybdenum Iron Sediment

# ABSTRACT

This study investigates the controls on organic carbon and molybdenum (Mo) accumulation in sediments deposited within the Western Interior Seaway across the Cenomanian–Turonian boundary interval (94.34–93.04 Ma) including Oceanic Anoxic Event 2 (OAE2). Carbon fluxes to the sediment–water interface (reflecting changes in primary productivity) and bottom-water oxygen concentrations (reflecting preservation effects) are reconstructed from field data and used to constrain a benthic model that simulates the geochemistry of unconsolidated sediments as they were deposited. The results show that increased availability of reactive iron prevents Mo sequestration as thiomolybdate ( $MOS_4^2$ –) during OAE2 ( $O_2$ ~105  $\mu$ M) by (i) inhibiting sulfate reduction, and (ii) buffering any free sulfide that becomes available. In the post-OAE2 period ( $O_2 ~ 50 \mu$ M), Mo accumulation is favored by a large reduction in iron flux. Importantly, this occurs in parallel with oxygenated bottom waters and high rates of aerobic carbon degradation in the surface sediments, implying that elevated Mo burial fluxes in ancient marine facies do not necessarily reflect euxinic or even anoxic conditions within the water column. Our findings suggest that both an increase in production and preservation lead to enrichment in organic carbon in the Western Interior Seaway. More generally, the results demonstrate that a careful consideration of the coupling between iron, carbon and oxygen cycles during the early stages of diagenesis is critical for interpreting geochemical proxies in modern and ancient settings.

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# 1. Introduction

The Cretaceous period (145.5–65.5 Ma) was characterized by warm climates and high eustatic sea level (Barron, 1983). The corresponding marine sedimentary record is punctuated by dark colored fully- or partially-laminated facies enriched in organic carbon (OC) and trace metals known as black shales (Arthur and Sageman, 1994). Within these sequences, which were deposited over  $10^4$ – $10^5$  yr timescales, the  $\delta^{13}$ C values for OC and marine carbonates show a positive excursion, explained as regional to global scale perturbations in the coupled ocean–atmosphere carbon cycle (Arthur et al., 1988). Multiproxy data suggest that these sediments were deposited under water column anoxia or even euxinia, conditions more generally described as ocean anoxic events (OAE) (Schlanger and Jenkyns, 1976; Stein et al., 1986; Jenkyns, 2010).

One of the most widely studied anoxic events is OAE2, which straddles the Cenomanian–Turonian (C–T) boundary interval (94.34–93.04 Ma). The extent of OC enrichment in OAE2 strata varies by region (Jenkyns,

2010). For example, OC contents of 13 wt.% are observed in the deepsea proto-North Atlantic, while 20 wt.% OC is preserved in continental shelf sediments off the coast of Suriname (Hetzel et al., 2009; Kraal et al., 2010). These contents compare to ca. 2 wt.% on the continental shelf in modern marine sediments and <1 wt.% in the deep sea (Seiter et al., 2005). Significantly higher contents of 10 wt.% or more are to be found in anoxic basins, upwelling areas and oxygen minimum zones in the contemporary ocean which are generally seen as analogs of OAEs (Algeo and Lyons, 2006). Yet these settings comprise a small surface area of the modern global ocean compared to the extensive nature of anoxia believed to characterize OAE2 (Arthur et al., 1987; Schlanger et al., 1987).

The factors leading to OC enrichment in ancient marine sediments are not well substantiated, and discussions often center on the dichotomy of export production versus preservation (Demaison and Moore, 1980; Pedersen and Calvert, 1990). On the one hand, sediments underlying anoxic bottom waters are thought to better preserve OC because the rate of carbon degradation by anaerobic bacteria appears to be slower than that for aerobic bacteria, at least for less reactive OC fractions (Middelburg et al., 1993; Canfield, 1994; Moodley et al., 2005). This has led to the concept of oxygen exposure time (OET), that is, where OC degradation is enhanced when the residence time of OC in



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<sup>0009-2541/\$ –</sup> see front matter 0 2011 Elsevier B.V. All rights reserved. doi:10.1016/j.chemgeo.2011.10.004

the oxic sediment layers increases (Hedges and Keil, 1995). However, Middelburg et al. (1993) caution that the perceived importance of oxygen could simply be a consequence of diagenetic maturity, whereby aerobic respiration consumes the most reactive OC fractions, leaving behind the less reactive material for the anaerobic microorganisms. Mechanistically, the relationship between OET and OC accumulation could also be attributed to changes in the rate of delivery of labile OC to sulfide-rich pore water, as hydrogen sulfide serves as control on organic matter vulcanization, 'hydrogenation' and preservation (e.g., Hebting et al., 2006; Arndt et al., 2009). With regard to the production argument, higher rates of primary production and deposition of organic detritus may simply enrich the sediment in OC. However, because anoxic sediments preferentially release phosphorus back to the water column, the potential exists for a positive feedback between primary production and benthic OC enrichment (Van Cappellen and Ingall, 1994; Ingall and Jahnke, 1997). Consequently, higher levels of production and preservation are both possible drivers for OC enrichment during anoxic events; a fact that is not always obvious from the debate in the geological literature (Demaison and Moore, 1980; Pedersen and Calvert, 1990).

Key to interpreting measured data with regard to the extent to which production and preservation processes may have developed at the start of anoxic events and their ultimate control on OC accumulation is a mechanistic understanding of the coupled physical and biogeochemical processes occurring within the sediments themselves. A transition towards anoxia at the start of the anoxic event would have been met by a shift from predominantly aerobic respiration of OC (c.f. the contemporary deep ocean) towards sulfate-based anaerobic respiration (c.f. the contemporary silled basins and productive shelf settings). A thinner aerobic layer will lead to enhanced transport of labile OC to the anaerobic sulfate reduction zone where preservation is more likely (Canfield, 1994; Tyson, 2001; Meyers et al., 2005; Burdige, 2007). Preservation will be further enhanced if bulk accumulation rates also increase simultaneously. Yet, too high sedimentation rates will dilute the OC concentration to the point where OC enrichment is no longer perceptible (Tyson, 2001). Paradoxically, the sediment carbon burial efficiency (CBE = burial flux / deposition flux  $\times 100\%$ ) in this case will be high because of the enhanced delivery flux to the sulfate reduction zone (Burdige, 2007). On the other hand, OC will be extensively degraded in sediments that accumulate very slowly under oxic bottom waters due to the long residence time of particles in the oxic layer, leading to a low CBE. These coupled processes imply that to accurately interpret sedimentary proxy records, due consideration must be given to the dynamic interplay between the major transport and biogeochemical processes in sediments (Arndt et al., 2009).

An additional and widely-considered indicator for ocean anoxia is the enrichment of trace metals in black shales (Sageman and Lyons, 2003). Molybdenum (Mo) is currently of high interest in this regard because of the different geochemical speciation it exhibits under different redox conditions. Dissolved molybdate  $(MoO_4^{2-})$  behaves conservatively in oxic aquatic environments, yet undergoes quantitative sulfidization to dissolved thiomolybdate  $(MoO_xS^{2-}_{4-x})$  when hydrogen sulfide ion (HS<sup>-</sup>) reaches a critical concentration threshold of ca. 50–250 µM (Helz et al., 1996; Zheng et al., 2000). Tetrathiomolybdate (MoS<sub>4</sub><sup>2-</sup>) is immobilized through adsorption onto mineral phases and organic substrates and eventually becomes buried to the sediment repository (Helz et al., 1996; Tribovillard et al., 2004). Consequently, Mo concentrations in black shales  $(10^1-10^2 \text{ ppm})$  tend to be at least an order-of-magnitude larger than average crustal values (1–2 ppm) (Wedepohl, 1991) and they also show a degree of correlation with the OC content in both contemporary (Algeo and Lyons, 2006; McManus et al., 2006) and ancient facies (Kolonic et al., 2005). This indicates that the controls on OC and Mo accumulation rates may be related. However, the reductive dissolution of reactive iron by sulfide can dramatically modulate the concentration of free hydrogen sulfide in the porewater (Jørgensen, 1977; Raiswell and Canfield, 1996) and prevent formation of  $MoS_4^{2-}$ . This sulfide sink can potentially limit the utility of Mo as a paleoproxy (Meyers, 2007).

In this study, our prime objective is to quantify the processes controlling OC and Mo enrichment in marine sediments from OAE2. We employ a numerical reaction-transport model that integrates physical processes and biogeochemical reactions into a quantitative framework. As a case study, we focus on the Cretaceous Western Interior Seaway — a shallow (300 m paleo-water depth) epicontinental water body linking the Boreal Ocean to the north and the Tethys Ocean to the south in what is now the western USA. Specifically, we address the Bridge Creek Limestone Member, which brackets the C–T boundary, including OAE2 and the post-OAE2 period (94.34–93.04 Ma) (Sageman et al., 2006). Our approach constitutes a new quantitative framework for the analysis of deep-time biogeochemical perturbations, and the results are of significance for the accurate interpretation of proxy records in both ancient and modern sediments.

#### 2. Geological and paleoceanographic setting of the WIS

During the late C–T interval, high eustatic sea level and foreland basin subsidence led to the development of the Western Interior Seaway (WIS) in western North America (Kauffman, 1977). The WIS was a meridional seaway that connected the high-latitude Boreal Ocean to the low-latitude Tethys Sea, with the Sevier Orogenic Belt lying to the west (e.g. Kauffman, 1977). Reconstructions of water mass dynamics within the seaway, based on paleobiologic, sedimentologic, geochemical evidence and circulation modeling (e.g. Slingerland et al., 1996; Kump and Slingerland, 1999; Fisher and Arthur, 2002), indicate a dynamic interplay between distinct Boreal and Tethyan water masses during the Cenomanian and Turonian. In summary, these studies suggest that the WIS hosted a cyclonic gyre, with Boreal surface water influx from the north and Tethyan surface water influx from the south. Turbulent mixing within the seaway likely prohibited the development of a stable density stratification of the water column (Kump and Slingerland, 1999).

The present study evaluates data from the USGS #1 Portland core (Sageman et al., 1997; Meyers et al., 2005), located in the central portion of the seaway, and composed of sediments deposited at approximately 300 m paleowater depth (Sageman and Arthur, 1994). At this location, the C–T boundary interval is predominantly composed of rhythmically alternating decimeter-scale limestone and marlstone beds, which constitute the Bridge Creek Limestone Member (Greenhorn Formation) (Sageman et al., 1997). Individual beds of the Bridge Creek Limestone Member can be traced for over 1000 km (Elder et al., 1994). This basin-wide rhythmic sedimentation has been quantitatively linked to an orbital driver (Sageman et al., 1997; Meyers et al., 2001; Meyers and Sageman, 2007), yielding a high-resolution chronometer that permits detailed evaluation of geochemical fluxes through the C–T boundary interval, both during and immediately following OAE2 (Meyers et al., 2001; 2005).

A selection of the Bridge Creek data from Meyers et al. (2005) which have been smoothed with a 2 m moving average filter (Fig. 1) reveals large secular changes in OC, Fe and Mo concentrations and accumulation rates across the C-T interval. These rates are not spectacular compared to other OAE2 sequences (e.g. Kolonic et al., 2005) and are more comparable to those encountered in modern deep sea settings. However, the data are unique because the OC and Mo accumulation rates are highest post-OAE2, which suggests that 'OAE2-like' conditions in the WIS lagged behind the global ocean. According to Meyers et al. (2005) and Meyers (2007), the elevated fluxes of reactive oxidized iron (i.e. iron oxidehydroxides) relative to OC during OAE2 (Fig. 1e), perhaps enhanced by an additional (hydrothermal?) iron source decoupled from the detrital flux, had a strong influence on these trends. They hypothesized that abundant reactive iron efficiently removed dissolved sulfide from sedimentary pore waters through oxidation reactions, effectively inhibiting molybdate sulfidization. This hypothesis is analyzed in detail in the present study in the context of OC and Mo accumulation.



**Fig. 1.** Measured data from the Western Interior Seaway (black lines) represented with a 2 m moving average filter redrawn from Meyers et al. (2005). Height refers to relative spatial location within the Bridge Creek Limestone Member. (a) sediment burial velocity ( $\omega_{BCM}$ ), (b) bulk sediment accumulation rate ( $F_{BS-BCM}$ ), (c) OC accumulation rate ( $F_{C-BCM}$ ), (d) calcium carbonate accumulation rate ( $F_{C-BCM}$ ), (e) iron accumulation rate ( $F_{Fe-BCM}$ ), (f) molybdenum accumulation rate ( $F_{MO-BCM}$ ), and (g) frequency of lamination (FOL). The stippled area in (e) is the 'excess' iron flux decoupled from the local terrigenous (detrial) flux calculated from Ti accumulation (Meyers et al., 2001). The dashed horizontal lines indicate the separation of the data into 15 distinct time intervals and the mean values of the data within each interval are shown by the white circles. The gray shaded area highlights the domain of OAE2. The C/T boundary is located at 4.88 m height (Meyers et al., in press).

#### 3. A model for Cretaceous sediments of the WIS

On the basis of identifiable changes in bulk sediment and carbon accumulation rates, the data in Fig. 1 were subdivided into 15 distinct time intervals. It is our intention to use a model to simulate the OC, Fe and Mo concentrations and accumulation rates for each of these time intervals in the unconsolidated (porous) sediments as they were being deposited. This presents some complications since the sediments are now fully lithified material. We thus use geochemical data measured in the strata to extract the necessary boundary conditions and parameters required to describe the changing conditions at the sea floor over the C-T interval. In other words, 15 model simulations of the unconsolidated sediments of the Cretaceous WIS are performed, each having boundary conditions and parameters which differ from one time interval to the next. Comparison of the model output with the measured data in Fig. 1 will provide a quasi-validation that the derived model forcing functions have been adequately described. The 15 time intervals are sufficiently long  $(>10^4 \text{ yr})$  so that each of the simulations was run to steady state, that is, until there is no temporal change in the concentration-depth profiles (see Section 3.1).

The strategy outlined in this section proceeds as follows. First, we introduce the model framework for simulating coupled reaction and transport in unconsolidated (porous) marine sediments. We then describe how key model boundary conditions and parameters for each time slice were extracted from the data in Fig. 1. We end this section by describing how the model can be used in conjunction with a system analysis to extract the factors controlling Mo and OC accumulation rates in Cretaceous sediments. In what follows, the subscripts 'cr', 'BCM' and 'co' indicate that the corresponding parameters or boundary conditions apply to unconsolidated Cretaceous sediments, to consolidated Bridge Creek Limestone Member strata, or to contemporary marine sediments, respectively.

# 3.1. Model set-up

#### 3.1.1. Modeling coupled reaction and transport

The model is designed to simulate the concentration profiles of aqueous,  $C_a(z)$ , and solid species,  $C_s(z)$  in the upper 150 cm of Cretaceous sediments at a water depth characteristic of the WIS (300 m, Slingerland et al., 1996; Meyers et al., 2005). Solutes considered are oxygen (O<sub>2</sub>), sulfate (SO<sub>4</sub><sup>2-</sup>), total hydrogen sulfide (TH<sub>2</sub>S), molybdate (MoO<sub>4</sub><sup>2-</sup>) and ferrous iron (Fe<sup>2+</sup>) and solids considered are pelagic particulate organic carbon deposited on the seafloor (OC, chemically defined as CH<sub>2</sub>O), reactive iron oxide–hydroxide (Fe(OH)<sub>3</sub>), iron sulfide (FeS) and thiomolybdate (MoS<sub>4</sub><sup>2-</sup>). In this paper, the term reactive iron refers to the iron oxide–hydroxide fraction. The speciation of dissolved sulfide is not explicitly calculated and unless indicated 'TH<sub>2</sub>S' refers to  $\Sigma$ H<sub>2</sub>S + HS<sup>-</sup> + S<sup>2-</sup>. The one-dimensional mass-conservation equation (Berner, 1980; Boudreau, 1997) was used to simulate concentrations along the vertical (depth) axis, z:

$$\begin{split} \phi(z) \cdot \frac{\partial C_{a}(z)}{\partial t} &= \frac{\partial}{\partial z} \cdot \left( \phi(z) \cdot (D_{cr}(z) + Db_{cr}(z)) \cdot \frac{\partial C_{a}(z)}{\partial z} \right) \\ &- \frac{\partial (\phi(z) \cdot v_{cr}(z) \cdot C_{a}(z))}{\partial z} + \alpha_{cr}(z) \cdot (C_{a}(0) - C_{a}(z)) + \Sigma r(z) \cdot \phi(z) \end{split}$$
(1a)

$$(1-\varphi(z)) \cdot \frac{\partial C_{s}(z)}{\partial t} = \frac{\partial}{\partial z} \cdot \left( (1-\varphi(z)) \cdot Db_{cr}(z) \cdot \frac{\partial C_{s}(z)}{\partial z} \right)$$
(1b)  
$$- \frac{\partial ((1-\varphi(z)) \cdot \omega_{cr}(z) \cdot C_{s}(z))}{\partial z} + \Sigma r(z) \cdot (1-\varphi(z))$$

where t is time,  $\varphi(z)$  is the sediment porosity and  $\Sigma r$  is the sum of the rates of change of concentration due to biogeochemical reactions. The model parameters are  $D_{cr}(z)$ ,  $Db_{cr}(z)$ ,  $\omega_{cr}(z)$ ,  $v_{cr}(z)$  and  $\alpha_{cr}(z)$ , which represent the molecular diffusion coefficient of solutes in sediments, mixing by bioturbation, the burial velocity of solids, the burial velocity of pore water, and solute exchange by bioirrigation, respectively. Details on how these parameters are estimated are described below. Solutes and solids are modeled as molar  $(mol L^{-1})$  and mass (weight % (wt.%)) concentrations. Model parameters and boundary conditions are listed in Table 1.

#### 3.1.2. Sediment porosity

The porosity of muddy marine sediments typically decreases fairly rapidly in the surface layers (upper dm) due to compaction and then shows a more attenuated decrease with increasing depth. The change

#### Table 1

Model parameters and boundary conditions used in the simulation of Cretaceous sediments. Values which are different for each of the 15 time intervals are indicated as 'Variable'. These are shown in Fig. 6.

Symbol (unit)	Description	Value
T (°C)	Bottom water temperature	7.5
S (-)	Bottom water salinity	35
$\rho$ (g cm <sup>-3</sup> )	Density of solid material	2.5
$\phi(0)$ (-)	Porosity at sediment-water interface	0.95
$\varphi(\infty)$ (-)	Porosity in compacted sediments	0.80
$Z_{por}(cm)$	Porosity attenuation length	5
$\omega_{\rm cr}(\infty)$ (cm ky <sup>-1</sup> )	Burial velocity in compacted sediments	Variable
$Db_{cr}(0) (cm^2 yr^{-1})$	Surface bioturbation coefficient	Variable
$\alpha_{\rm cr}(0) ({\rm yr}^{-1})$	Surface bioirrigation coefficient	Variable <sup>a</sup>
z <sub>cr</sub> (cm)	Mixing depth by animals	Variable
$D_{W}(O_{2}) (cm^{2} yr^{-1})$	Diffusion coefficient in seawater for O <sub>2</sub>	402
$D_W(SO_4^{2-}) (cm^2 yr^{-1})$	Diffusion coefficient in seawater for SO <sub>4</sub> <sup>2-</sup>	197
$D_{W}(TH_{2}S) (cm^{2} yr^{-1})$	Diffusion coefficient in seawater for TH <sub>2</sub> S	360
$D_W(Fe^{2+}) (cm^2 yr^{-1})$	Diffusion coefficient in seawater for Fe <sup>2+</sup>	132
$D_W(MoO_4^{2-}) (cm^2 yr^{-1})$	Diffusion coefficient in seawater for MoO <sub>4</sub> <sup>2-</sup>	184 <sup>b</sup>
K <sub>02</sub> (μM)	Half-saturation constant for $O_2$	4 <sup>c</sup>
$K_{\rm Fe} (\mu { m mol}{ m g}^{-1})$	Half-saturation constant for Fe(OH) <sub>3</sub>	50 <sup>c</sup>
$K_{SO4}$ (mM)	Half-saturation constant for $SO_4^{2-}$	0.5 <sup>c</sup>
$k_1 (yr^{-1})$	Rate constant for OC mineralization with O <sub>2</sub>	Variable
$k_2 (yr^{-1})$	Rate constant for OC mineralization with Fe(OH) <sub>3</sub>	Variable
$k_3 (yr^{-1})$	Rate constant for OC mineralization with $SO_4^2$	Variable
$k_4 (M^{-1} yr^{-1})$	Rate constant for ferrous iron oxidation with O <sub>2</sub>	$1.0 \cdot 10^{8}$
$k_5 (M^{-1} yr^{-1})$	Rate constant for biological sulfide oxidation	$1.0 \cdot 10^{8}$
$k_6 (M^{-1} yr^{-1})$	Rate constant for FeS precipitation	$1.0 \cdot 10^{7}$
$k_7 (M^{-1} yr^{-1})$	Rate constant for chemical sulfide oxidation	$1.0 \cdot 10^{3}$
$k_8 (M^{-1} yr^{-1})$	Rate constant for FeS oxidation with O <sub>2</sub>	$1.0 \cdot 10^{6}$
$k_9 (M^{-1} yr^{-1})$	Rate constant for $MoS_4^2$ precipitation	6.9 · 10 <sup>4d</sup>
$[TH_2S]^* (\mu M)$	Threshold TH <sub>2</sub> S concentration for $MoS_4^{2-}$ precipitation	65
τ	Dimensionless constant for onset of hypoxia	0.05
[O <sub>2</sub> ]* (µM)	Threshold concentration for hypoxia	62
$[O_2]_{cr}(0) \ (\mu M)$	Bottom water O <sub>2</sub> concentration	Variable
$[SO_4^2]_{cr}(0) (mM)$	Bottom water $SO_4^2$ concentration	10
$[Fe^{2+}]_{cr}(0) (nM)$	Bottom water Fe <sup>2+</sup> concentration	0
$[H_2S]_{cr}(0)$ (nM)	Bottom water TH <sub>2</sub> S concentration	0
$[MoO_4^{2-}]_{cr}(0) \ (\mu M)$	Bottom water $MoO_4^{2-}$ concentration	0.1
$F_{C-cr} (g cm^{-2} ky^{-1})$	OC flux to sea floor	Variable
$F_{Fe-cr}$ (g cm <sup>-2</sup> ky <sup>-1</sup> )	Fe(OH) <sub>3</sub> flux to sea floor	Variable
$F_{\text{FeS-cr}}(g \text{ cm}^{-2} \text{ ky}^{-1})$	FeS flux to sea floor	0
$F_{MoS4-cr}$ (µg cm <sup>-2</sup> ky <sup>-1</sup> )	$MoS_4^2$ flux to sea floor	0

<sup>a</sup> Irrigation of  $H_2S$  and  $Fe^{2+}$  are set to zero (see text).

<sup>b</sup> Diffusion coefficient for MoO<sub>4</sub><sup>2-</sup> is taken from Zheng et al. (2000). All other diffusion coefficients are from Schulz (2000).

<sup>c</sup> The half-saturation constants are based on values given by Jourabchi et al. (2005), Berg et al. (2003) and Van Cappellen and Wang (1996). The model is insensitive to these parameters over the range of values provided in these publications.

<sup>d</sup> From Erickson and Helz (2000), corresponding to the slowest (and final) step of  $MoO_4^2$  – sulfidization to  $MoS_4^2$ .

in porosity with depth was thus described using an exponential function:

$$\phi(z) = \phi(\infty) + (\phi(0) - \phi(\infty)) \cdot exp\left(-\frac{z}{z_{por}}\right)$$
(2)

where  $\phi(0)$  is the porosity at the sediment–water interface,  $\phi(\infty)$  is the porosity where the porosity gradient  $(\partial \varphi(z)/\partial z)$  is small relative to the surface layers, and  $z_{por}$  is the porosity depth attenuation length. Because the low rate of sediment accumulation in the WIS (Fig. 1b) resembles the contemporary deep ocean, we used the porosity profiles measured in the deep ocean by Archer et al. (1989) and Haeckel et al. (2001) to obtain  $\phi(0)$ ,  $\phi(\infty)$  and  $z_{por}$  values of 0.95, 0.80 and 0.2, respectively. The sediment thus undergoes compaction with a quadrupling of the solid volume fraction from the sediment surface to 40 cm depth. It is implicitly assumed that the sediment below the modeled depth (150 cm) continued to compact slowly until becoming the sedimentary rock present today. Although additional degrees of freedom are introduced to the model to parameterize compaction (rather than assuming depth-invariable porosity), we take this approach since a reasonable estimate for the porosity profile in surface marine sediments can be made in the absence of measured data. We anticipate that this provides more realistic modeled rates and fluxes than those obtained assuming constant porosity.

# 3.1.3. Bulk sediment burial velocities

Burial of solids ( $\omega_{cr}(z)$ , cm ky<sup>-1</sup>) and porewater ( $v_{cr}(z)$ , cm ky<sup>-1</sup>) in Cretaceous sediments are given by the following conservation equations assuming steady state compaction (Berner, 1980):

$$\omega_{cr}(z) = \frac{(1 - \phi(\infty)) \cdot \omega_{cr}(\infty)}{(1 - \phi(z))}$$
(3)

$$\mathbf{v}_{cr}(z) = \frac{\phi(\infty) \cdot \boldsymbol{\omega}_{cr}(\infty)}{\phi(z)} \tag{4}$$

where  $\omega_{cr}(\infty)$  is the unknown sediment burial velocity at the sediment depth where the porosity gradient is small relative to the sediment– water interface (around 40 cm according to Eq. (2)). Calculation of  $\omega_{cr}(z)$  and  $v_{cr}(z)$  in Cretaceous sediments thus requires a knowledge of the porosity profile (given above) and  $\omega_{cr}(\infty)$ .

To calculate  $\omega_{cr}(\infty)$  for each time interval we used the measured bulk sedimentation velocities,  $\omega_{BCM}$  (cm ky<sup>-1</sup>) (Fig. 1a). Assuming that the unconsolidated sediments below 150 cm gradually

compacted to become rock,  $\omega_{cr}(\infty)$  was approximated from  $\omega_{BCM}$  using a similar conservation equation applied to Eq. (3):

$$\omega_{cr}(\infty) = \frac{\omega_{BCM} \cdot (1 - \phi_{BCM})}{(1 - \phi(\infty))}$$
(5)

where the porosity of the sedimentary rock ( $\phi_{BCM}$ ) is zero and  $\phi(\infty)$  is given in Eq. (2).

# 3.1.4. Solute diffusion coefficients

Depth-dependent molecular diffusion coefficients for Cretaceous sediments  $(D_{cr}(z), cm^2 yr^{-1})$  were calculated from the molecular diffusion coefficients in seawater  $(D_{w}, cm^2 yr^{-1})$ :

$$D_{cr}(z) = \frac{D_W}{1 - \ln(\phi(z)^2)} \tag{6}$$

Values for  $D_W$  are listed in Table 1 and correspond to a bottom water temperature of 7.5 °C and a salinity of 35 (Schulz, 2000). The bottom water temperature was based on sea surface temperatures of the WIS predicted by Slingerland et al. (1996) and the decrease in temperature with depth in the modern ocean. Temperature and salinity in the model were assumed constant in time and with sediment depth.

# 3.1.5. Bioturbation and bioirrigation rates

Bioturbation (Db<sub>cr</sub>(z), cm<sup>2</sup> yr<sup>-1</sup>) and bioirrigation ( $\alpha_{cr}(z)$ , yr<sup>-1</sup>) coefficients were estimated by first considering their magnitude in modern ocean sediments. Bioturbation was calculated from the burial velocity using the empirical logarithmic expression derived by Tromp et al. (1995):

$$Db_{co}(0) = 43 \cdot \omega_{co}^{0.85} \tag{7}$$

where the subscript 'co' indicates contemporary ocean sediments and  $\omega_{co}$  has units of cm yr<sup>-1</sup>. Although it is not explicitly stated by Tromp et al. (1995), we assumed that  $\omega_{co}$  is analogous to  $\omega_{co}(\infty)$ , that is, the burial velocity in compacted sediments. A similar constitutive relationship for the surface bioirrigation rate,  $\alpha_{co}(0)$  (yr<sup>-1</sup>), is unavailable. We thus assumed a value of 10 yr<sup>-1</sup> based on modern pelagic sediments (Thullner et al., 2009):

$$\alpha_{\rm co}(0) = 10 \tag{8}$$

The foregoing equations are applicable to normal oxic bottom waters. However, discontinuous sequences of homogenous and laminated WIS rock strata, indicated by the frequency of sediment lamination (FOL, %) (Fig. 1g), imply that the sediments throughout the OAE2 and post OAE2 period were intermittently inhabited by bioturbating

#### Table 2

Model reaction network and rate formulations.



**Fig. 2.** Conceptual diagram of the coupled carbon, sulfur, iron and molybdenum cycles used in the model. Reactions  $r_1$ – $r_9$  are detailed in Table 2.

organisms due to fluctuating oxygen concentrations at the benthic boundary layer. Consequently, a correction must be made to Eqs. (7) and (8) for their application to Cretaceous sediments. We employed the FOL (%) as an indicator of the intensity of faunal activity through the following relationships:

$$\mathrm{Db}_{\mathrm{cr}}(0) = \left(1 - \frac{\mathrm{FOL}}{100}\right) \cdot \mathrm{Db}_{\mathrm{co}}(0) \tag{9}$$

$$\alpha_{cr}(0) = \left(1 - \frac{FOL}{100}\right) \cdot \alpha_{co}(0) \tag{10}$$

where  $Db_{co}(0)$  in Eq. (9) is calculated using Eq. (7) and the derived  $\omega_{cr}(\infty)$  values are used in place of  $\omega_{co}$ . The rate of bioirrigation for H<sub>2</sub>S and Fe<sup>2+</sup> in Cretaceous sediments was set to zero to reflect their rapid oxidation on the walls of animal burrows in surface sediments (Berg et al., 2003).

The depth dependency of bioturbation and bioirrigation was is imposed using Gaussian-type functions (Boudreau, 1996):

$$Db_{cr}(z) = Db_{cr}(0) \cdot exp\left(-\frac{z^2}{2 \cdot z_{cr}^2}\right)$$
(11)

$$\alpha_{cr}(z) = \alpha_{cr}(0) \cdot exp\left(-\frac{z^2}{2 \cdot z_{cr}^2}\right)$$
(12)

	Stoichiometry <sup>a</sup>	Rate expression <sup>b</sup>	Rate units
r <sub>1</sub> :	$CH_2O + O_2 \rightarrow CO_2 + H_2O$	$k_1 \cdot [CH_2O] \cdot F_{K-O2}/f_{OC}$	mol $CH_2O L^{-1} yr^{-1}$
r <sub>2</sub> :	$CH_2O + 4 \cdot Fe(OH)_3 + 7 \cdot H^+ \rightarrow 4 \cdot Fe^{2+} + HCO_3^- + 10 \cdot H_2O$	$k_2 \cdot [CH_2O] \cdot F_{K-Fe} \cdot (1 - F_{K-O2})/f_{OC}$	mol $CH_2O L^{-1} yr^{-1}$
r <sub>3</sub> :	$CH_2O + 0.5 \cdot SO_4^2 \xrightarrow{-} 0.5 \cdot H_2S + HCO_3^-$	$k_3 \cdot [CH_2O] \cdot F_{K-SO4} \cdot (1 - F_{K-O2}) \cdot (1 - F_{K-Fe})/f_{OC}$	mol $CH_2O L^{-1} yr^{-1}$
r4:	$Fe^{2+} + 0.25 \cdot O_2 + 2.5 \cdot H_2O \rightarrow Fe(OH)_3 + 2 \cdot H^+$	$k_4 \cdot [O_2] \cdot [Fe^{2+}]$	mol $Fe^{2+}L^{-1}yr^{-1}$
r <sub>5</sub> :	$H_2S + 2 \cdot O_2 \rightarrow SO_4^2 - + 2 \cdot H^+$	$k_5 \cdot [O_2] \cdot [TH_2S]$	mol TH <sub>2</sub> S $L^{-1}$ yr <sup>-1</sup>
r <sub>6</sub> :	$Fe^{2+} + H_2S \rightarrow FeS + 2 \cdot H^+$	$k_6 \cdot [Fe^{2+}] \cdot [TH_2S]$	mol TH <sub>2</sub> S $L^{-1}$ yr <sup>-1</sup>
r <sub>7</sub> :	$8/9 \cdot \text{Fe}(\text{OH})_3 + \text{H}_2\text{S} \rightarrow 8/9 \cdot \text{FeS} + 1/9 \cdot \text{SO}_4^2 - + 2/9 \cdot \text{H}^+ + 20/9 \cdot \text{H}_2\text{O}$	$k_7 \cdot [Fe(OH)_3] \cdot [TH_2S]/f_{Fe}$	mol TH <sub>2</sub> S $L^{-1}$ yr <sup>-1</sup>
r <sub>8</sub> :	$FeS + 2 \cdot O_2 \rightarrow Fe^{2+} + SO_4^{2-}$	$k_8 \cdot [O_2] \cdot [FeS]/f_{Fe}$	mol $Fe^{2+}L^{-1}yr^{-1}$
r9:	$MoO_4^{2-}(aq) + 4 \cdot H_2S(aq) \rightarrow MoS_4^{2-}(s) + 4H_2O_{(1)}$	$k_9 \cdot [MoO_4^2] \cdot ([TH_2S] - [TH_2S]^*) \cdot \beta$	mol $MoO_4^{2-}L^{-1}yr^{-1}$

Conversion factor between particulate (wt.%) and dissolved inorganic carbon (mol L<sup>-1</sup>):  $f_{OC} = \frac{100\% 12 \frac{gC}{mol} \cdot \phi(z)}{12 \frac{gC}{mol} \cdot \phi(z)}$ 

Conversion factor between particulate (wt.%) and dissolved iron (mol L<sup>-1</sup>): 
$$f_{Fe} = \frac{100\%56\frac{\mu^2}{L^2}\phi_{21}}{\frac{100\%56}{100\pi}\phi_{21}(1-\phi(2))}$$
.

 $\beta = 1$  if  $[TH_2S] > [TH_2S]^*$ , otherwise  $\beta = 0$ .

<sup>a</sup> Reactions are written assuming that  $TH_2S = H_2S$  for equation balancing.

<sup>b</sup> Kinetic limitation term:  $F_{K-j} = \frac{[j]}{[j]+K_j}$  (for  $j = O_2$ , Fe (=Fe(OH)<sub>3</sub>), SO<sub>4</sub><sup>2</sup>).

where  $z_{cr}$  (cm) controls the depth of irrigation and particle mixing. Since hypoxia leads to a shallowing of habitation depth of animals (Middelburg and Levin, 2009),  $z_{cr}$  was calculated from the mixing depth by animals in modern sediments ( $z_{co}$ ):

$$z_{cr} = \left(1 - \frac{FOL}{100}\right) \cdot z_{co} \tag{13}$$

 $z_{co}$  was assigned a value of 5 cm based on a global database complied by Teal et al. (2008).

# 3.2. Biogeochemical reaction network

The reaction network was designed to elucidate the major controls on OC preservation and Mo accumulation rate during the OAE and post-OAE period. For expediency, only the most important reactions were implemented and those suspected of having minor importance were excluded. A conceptual diagram of the reaction network is shown in Fig. 2 and the kinetic rate expressions are listed in Table 2.

The primary redox reactions describe the rate of degradation of OC through aerobic respiration  $(r_1)$ , dissimilatory iron reduction  $(r_2)$  and sulfate reduction  $(r_3)$ . The rates are first-order in OC to reflect the general observation that OC availability is the rate-limiting step of the reaction (Berner, 1980). The rate of each pathway is determined by the concentrations of the oxidants (i.e.  $O_2$ , Fe(OH)<sub>3</sub>, SO<sub>4</sub><sup>2-</sup>) through kinetic limitation terms. These were formulated so that the reactions proceed sequentially as each electron acceptor becomes depleted with depth in the sediment. Denitrification was ignored since nitrogen cycling is not the focus of the study and only becomes a major pathway of carbon diagenesis in sediments underlying severely hypoxic bottom waters ( $O_2 < 20 \,\mu\text{M}$ ) (Canfield, 1993; Bohlen et al., 2011). Carbon mineralization coupled to manganese oxide reduction was also ignored because Mn concentrations in the WIS formation are 10 times lower than iron (Sageman and Lyons, 2003) and it is generally a minor pathway of carbon mineralization (Thullner et al., 2009). Finally, methanogenesis was not considered because it is inhibited by sulfate concentrations of >1 mM; conditions which do not occur in our simulations. These omissions do not seriously affect the model result since >90% of benthic OC is oxidized by  $O_2$  and  $SO_4^2$  (Jørgensen and Kasten, 2006).

The secondary redox reactions are centered on Fe, S and Mo geochemistry ( $r_4$ - $r_9$ , Table 2). The rate laws used to describe these processes employ encounter-limited, or bimolecular, kinetics. This approach minimizes the number of parameters to be defined and is consistent with the idea that the rate law should depend linearly on the concentrations of the reactants in reactant limited-environments (Van Cappellen and Wang, 1996). Ferrous iron (Fe<sup>2+</sup>) liberated by dissimilatory iron reduction can be oxidized aerobically back to particulate iron oxide  $(r_4)$  or precipitated as FeS using dissolved sulfide  $(r_6)$ . FeS can be oxidized aerobically  $(r_8)$  or permanently buried. Dissolved sulfide can be oxidized biologically to sulfate using oxygen  $(r_5)$ . In addition to oxidizing OC, Fe(OH)<sub>3</sub> can also be used as the oxidant for chemical sulfide oxidation (r<sub>7</sub>). Normally, this reaction is assumed to produce ferrous iron and elemental sulfur (S<sup>0</sup>) (Van Cappellen and Wang, 1996). Yet, for clarity, the net reaction is written assuming that  $Fe^{2-1}$ production is coupled to FeS precipitation and that S<sup>0</sup> disproportionates to sulfide and sulfate  $(S^0 + H_2O \rightarrow 3/4 H_2S + 1/4 SO_4^{2-})$ . For additional insight into the complexities of benthic Fe and S cycles, the interested reader is referred to Jørgensen and Kasten (2006).

The final geochemical sink for  $H_2S$  is through reaction with  $MoO_4^2$ <sup>-</sup>. In sulfidic solution, the latter undergoes sulfidization leading to the production of tetrathiomolybdate ( $MoS_4^2^-$ ):

$$MoO_{x}S_{4-x}^{2-}(aq) + H_{2}S(aq) \rightleftharpoons MoO_{x-1}S_{5-x}^{2-}(aq) + H_{2}O(l)$$
(14)

where  $1 \le x \le 4$ .

The reaction proceeds in four steps that conserve Mo(VI), and the reaction rate decreases by an order-of-magnitude over each successive step (Erickson and Helz, 2000). Consequently, mixtures of thiomolybdates can accumulate in seasonally or intermittently sulfidic porewaters. Yet, due to the long time scales of the 15 intervals modeled in this study (>10<sup>4</sup> yr), we assume that the equilibria can be simplified as a single step reaction between molybdate and sulfide to produce  $MoS_4^{2-}$  (r<sub>9</sub>, Table 2). The bimolecular rate law prescribed for this pathway is consistent with laboratory experiments which show that the sulfidization steps are first-order in the reactants (Erickson and Helz, 2000).  $MoS_4^{2-}$  is particle-reactive and can be rapidly scavenged from the pore water by metal oxyhydroxides, iron sulfide or organic material (e.g. Vorlicek et al., 2004). Therefore,  $MoS_4^{2-}$  is modeled as a solid species on the assumption that it is immediately sequestered by particulate phases and undergoes no further reaction.

Experiments and theory have shown that the rate of MoS<sub>4</sub><sup>2-</sup> scavenging is rapid when HS<sup>-</sup> concentration reaches a critical pH-dependent threshold (Helz et al., 1996; Erickson and Helz, 2000). For a pH of 7.5 and 8.3, this threshold is equal to ca. 50 and 250 µM HS<sup>-</sup>, respectively, at 298 K (Helz et al., 1996). The pH of anoxic marine sediments is typically of the order 7.5. For this pH and the in situ temperature (280 K) and pressure (30 bar) of the WIS, HS<sup>-</sup> accounts for around 80% of TH<sub>2</sub>S. This implies that the geochemical switch for the above reaction should occur at in situ TH<sub>2</sub>S concentrations upwards of ca. 65 µM. There is some field evidence to suggest that lower sulfide thresholds (0.1  $\mu$ M) are required for MoS<sub>4</sub><sup>2-</sup> scavenging onto iron minerals compared to organic material (100 µM) (Zheng et al., 2000). Since these values have yet to be confirmed by laboratory studies, we use the higher pH-dependent threshold sulfide concentration,  $[TH_2S]^*$ , of 65  $\mu$ M whilst noting that it is likely to be somewhat site specific. The reaction formulation only allows MoS<sub>4</sub><sup>2-</sup> formation if  $[TH_2S]$  is greater or equal to  $[TH_2S]^*$  (r<sub>9</sub>, Table 2).

# 3.3. Boundary conditions

Boundary conditions at the top and bottom of the sediment column are required to solve Eqs. (1a) and (1b). At the top, the  $SO_4^2$  – concentration in seawater was fixed at 10 mM to represent the Cretaceous ocean (Horita et al., 2002) and TH<sub>2</sub>S was set to zero since the WIS was not sulfidic (Table 1). Proposed fluctuations in  $SO_4^2$  – concentration throughout



**Fig. 3.** Relationship between bottom water oxygen concentration and frequency of lamination calculated with Eq. (15) using different values for the parameter  $\tau$  (see text for explanation). The gray shaded area indicates the range of frequency of lamination measured in the Bridge Creek Limestone data shown in Fig. 1g.

the Cretaceous of between 2 and 12 mM (Wortmann and Chernyavsky, 2007; Adams et al., 2010) are not likely to have an important impact on the model results since methanogenesis will only become important if  $SO_4^{2-}$  falls to <1 mM. Boundary conditions for the other species are described separately below. At the bottom of the simulated sediment column (150 cm depth), all species are prescribed with zero-gradient (Neumann) boundary conditions.

#### 3.3.1. Bottom water oxygen concentration

Oxygen concentrations at the benthic boundary layer in the WIS,  $[O_2]_{cr}(0)$ , were estimated using a method borrowed from a study on the hypoxic St. Lawrence River estuary by Katsev et al. (2007). These workers scanned intact sediment cores from sites with different bottom water oxygen concentrations using computerized axial tomography in order to observe the effect of decreasing oxygen on bioturbation and sediment structure. They derived a non-linear empirical relationship between bioturbation and oxygen concentrations which we use as the basis for our model. Using this relationship and the equality between Db<sub>cr</sub>(0) and FOL in Eq. (9),  $[O_2]_{cr}(0)$  can be calculated as follows:

$$[O_2]_{cr}(0) = [O_2]^* - \frac{1}{\tau} \cdot ln \left[\frac{FOL}{100 - FOL}\right]$$
(15)

where  $[O_2]^*$  is the threshold oxygen concentration due to hypoxia which leads to large changes in faunal community structure. Mechanistically,  $[O_2]^*$  defines the oxygen concentration at which  $Db_{cr}(0)$  falls to half the value of  $Db_{co}(0)$  due to severe hypoxia (Katsev et al., 2007). It is assigned a value of 62  $\mu$ M based on work by Diaz and Rosenberg (1995). The time-invariant coefficient,  $\tau$ , controls the steepness in decline of [O2]cr(0) with increasing FOL. This parameter was assigned a value of 0.3 by Katsev et al. (2007).

The relationship between  $[O_2]_{cr}(0)$  and FOL for two values of  $\tau$  is shown in Fig. 3, where the shaded band indicates the region corresponding to the FOL from the WIS. The parameter  $\tau$  controls the steepness of the curve whereas  $[O_2]^*$  determines its vertical displacement. The range in  $[O_2]_{cr}(0)$  is small (61–70 µmol L<sup>-1</sup>) for the value



**Fig. 4.** Carbon burial efficiency (CBE) as function of bulk sediment accumulation rate in contemporary ocean sediments ( $F_{BS-co}$ ). Squares and circles represent data taken from Burdige (2007) and Betts and Holland (1991), respectively. Solid symbols and the solid regression curve indicate stations with oxygen-bearing bottom waters ( $> 30 \ \mu$ M) while oxygen-depleted stations ( $< 30 \ \mu$ M) are represented by the open symbols and the dashed regression curve. The gray shaded band indicates the sediment accumulation rates applicable to Cretaceous sediments derived with Eq. (3). (CBE = burial flux / deposition flux × 100%.).

of  $\tau = 0.3$  and implies that fully laminated sediments occur at oxygen concentrations of ~50 µM which are well-above tolerance levels for many macrofauna and meiofauna (Levin, 2003). Furthermore, zero lamination corresponds to a bottom water oxygen concentration of 86 µM. One would expect higher baseline oxygen concentrations in a shallow oligotrophic setting system such as the WIS (Bralower and Thierstein, 1984; Pratt, 1985). We thus adjusted the value of  $\tau$  to 0.05 so that the bottom water oxygen concentration for non-laminated sediments reflects contemporary oxygenated bottom water values, assumed to be 200 µM, and that only anoxic conditions lead to laminated sediments. The range in  $[O_2]_{cr}(0,t)$  using  $\tau = 0.05$  then increases to 54–106 µmol L<sup>-1</sup> for the observed range of FOL.

# 3.3.2. Carbon deposition flux

Meyers et al. (2005) report values of organic carbon accumulation in the Bridge Creek Limestone Member ( $F_{C-BCM}$ , Fig. 1c). These are used in conjunction with the carbon burial efficiency (CBE, %) to calculate the rate of organic carbon flux deposited at the sediment surface during the Cretaceous. In practical terms, the CBE is almost impossible to calculate accurately because of the long time, potentially millions of years, between deposition at the sea floor and preservation as kerogen. However, evidence suggests that the bulk of the reactive carbon is mineralized at an early stage of diagenesis, leading to asymptotic carbon concentrations close to the sea floor (Berner, 1982). Burdige (2007) collated data of CBE and the bulk sediment accumulation rate in contemporary marine sediments ( $F_{BS-co}$ , g cm<sup>-2</sup> ky<sup>-1</sup>), redrawn in Fig. 4 with additional data from Betts and Holland (1991). Environments with normal (>30 µM) and low (<30 µM) bottom water oxygen concentrations which include euxinic environments, are distinguished.

The following logistic equation was identified as an appropriate regression to the data in Fig. 4:

$$CBE = \frac{A_1 - A_2}{1 + \frac{F_{BS-co}}{A_3}} + A_2$$
(16)

where  $A_1$  and  $A_2$  are the burial efficiencies at zero and infinite sedimentation accumulation rates, respectively, and  $A_3$  is the center of the regression. For normal marine conditions,  $A_1 = 0.5\%$ ,  $A_2 = 75\%$  and  $A_3 = 0.07$  g cm<sup>-2</sup> yr<sup>-1</sup>. Sediments underlying low-oxygen environments are better represented using  $A_1 = 5.0\%$ ,  $A_2 = 75\%$ , and  $A_3 = 0.01$  g cm<sup>-2</sup> yr<sup>-1</sup>. The CBE was calculated for Cretaceous sediments for high and low oxygen conditions by substituting the bulk accumulation rates ( $F_{BS-BCM}$ , Fig. 1b) for  $F_{BS-co}$  in Eq. (16). If the curve for low oxygen concentration in Fig. 4 corresponds to  $[O_2](0) = 30 \,\mu$ M, and assuming that the curve for normal oxygenated bottom waters can be assigned a value of  $[O_2](0) = 200 \,\mu$ M as defined above, then the end-member OC fluxes to the sea floor during the Cretaceous are:

$$F_{C-30} = 100 \cdot \frac{F_{C-BCM}}{CBE(O_2 = 30 \ \mu M)}$$
(17)

$$F_{C-200} = 100 \cdot \frac{F_{C-BCM}}{CBE(O_2 = 200 \ \mu M)}$$
(18)

The carbon deposition flux during the Cretaceous ( $F_{C-cr}$ ) can then be estimated from Eqs. (17) and (18) by scaling to the previously derived  $[O_2]_{cr}(0)$  values:

$$F_{C-cr} = (F_{C-200} - F_{C-30}) \cdot \frac{[O_2]_{cr}(0) - 30}{200 - 30} + F_{C-30}$$
(19)

#### 3.3.3. Iron boundary conditions

The accumulation rate of iron in Fig. 1e ( $F_{Fe-BCM}$ ) distinguishes between a terrigenous or detrital iron source and an 'excess' iron pool during OAE2 (Meyers, 2007). A cornerstone of the hypothesis by Meyers (2007) is that the excess iron was highly reactive, possibly hydrothermal in origin (e.g., Snow et al., 2005), and promoted sulfide buffering and low Mo accumulation rates during OAE2 in the WIS. To address this hypothesis effectively, the fluxes and reactivity of detrital and excess iron must be considered individually.

Based on Fe-C-S relationships, Dean and Arthur (1989) argued that the iron is mainly present as particulate iron sulfides. Sedimentary iron can be visualized as a continuum of mineral assemblages, each with a discrete reactivity, yet whose chemical properties are generally poorly characterized. Operationally-defined chemical extractions on natural and synthetic iron minerals have been employed to determine the reactivity of sedimentary particulate iron (Raiswell and Canfield, 1996; Poulton and Raiswell, 2002). These workers defined the following reactive fractions; (i) highly reactive (Fe<sub>HR</sub>) iron as the fraction which reacts on short timescales and which includes amorphous and crystalline iron oxides, (ii) poorly reactive iron (Fe $_{\mbox{\scriptsize PR}})$  as the fraction which reacts slowly on 10<sup>5</sup>–10<sup>6</sup> yr time scales and includes reactive silicate iron, and (iii) a fraction bound within sheet silicates which is reactive on much longer times scales and termed unreactive (Fe<sub>II</sub>). A compilation of data by Poulton and Raiswell (2002) further indicates that the relative proportions of  $Fe_{HR}$  (25%),  $Fe_{PR}$  (25%), and  $Fe_U$  (50%) are broadly uniform in non-euxinic sediments and have changed little throughout the Phanerozoic. This is in contrast with the present data where most of the particulate iron appears to be present as sulfides and was thus available for reductive dissolution (Dean and Arthur, 1989). However, it is not possible to infer from the Bridge Creek data whether Fe<sub>11</sub> was absent in the deposited iron oxide or whether Fe<sub>U</sub> was slowly converted to sulfide during lithification. Therefore, in line with Poulton and Raiswell (2002), we defined the flux of sulfidizable reactive iron  $(\equiv Fe_{HR} + Fe_{PR})$  to the Cretaceous sediments ( $F_{Fe-cr}$ , g cm<sup>-2</sup> ky<sup>-1</sup>) as half the measured detrital iron flux in Fig. 1e plus the excess iron flux. This should be viewed as a conservative estimate given the findings of Dean and Arthur (1989). Fe<sub>U</sub> comprises the remaining 50% of the detrital iron and is not considered in the model. For simplicity, the same reactivity toward dissolved sulfide was prescribed for the reactive detrital iron and excess iron with a rate constant whose value allows the iron to be reduced on the time scale of sediment burial over the modeled 150 cm column ( $10^4$ – $10^5$  yr). The importance of the rate of iron dissolution by sulfide on Mo accumulation is addressed through the system analysis (see below). The concentration of Fe<sup>2+</sup> at the sedimentwater interface and the deposition flux of FeS were set to zero due to the presence of oxic bottom waters in the WIS (Kump and Slingerland, 1999).

#### 3.3.4. Molybdenum boundary conditions

The flux of thiomolybdate  $(MoS_4^{2-})$  to the sea floor was set to zero since the WIS was not euxinic. An additional flux of detrital Mo was implicitly included by multiplying the mass accumulation rate ( $F_{BS-BCM}$ ) by the Mo concentration in world average shale (1.5 ppm; Wedepohl, 1991). Detrital Mo is considered to be unreactive and is included for the sake of completion.

The flux of molybdate  $(MoO_4^{2-})$  adsorbed to iron oxide particles was not considered in the model since its significance is essentially unknown. A tenuous interpretation of laboratory results presented by Goldberg et al. (2009) suggests that the adsorbed Mo concentration in oxic seawater is smaller than the detrital Mo concentration. Furthermore, several studies across a broad range of oxic and anoxic settings have reported that processes occurring at or below the sediment water interface are mainly responsible for Mo accumulation (e.g. Crusius et al., 1996; Erickson and Helz, 2000; Zheng et al., 2000). Transport of dissolved molybdate across the sediment–water interface was thus assumed to be the only source of reactive Mo, although the processes responsible for Mo accumulation are still poorly understood.

It should be mentioned that Mo enrichment in some black shales from the proto-North Atlantic is lower in the OAE2 sections compared to those marking the onset and termination of the anoxic event (Hetzel et al., 2009). This has been suggested as a drawdown of the global Mo inventory due to sulfidization and burial. Algeo and Lyons (2006) discuss how a similar reservoir effect could operate in modern-day silled basins such as the Black Sea. However, Meyers (2007) argued that this was a second-order effect in the WIS because the major shifts in Mo accumulation are extremely rapid relative to the Mo residence time and are associated with independent evidence for pronounced environmental changes. The concentration of dissolved  $MOQ_4^2^-$  in the sea water was thus set to contemporary values (100 nM) and assumed to be time-invariable across the C–T interval.

# 3.4. Parameterization of the biogeochemical reactions

Distinct rate constants were imposed for the degradation of OC through aerobic respiration  $(k_1)$  and anaerobic respiration by sulfate reduction  $(k_3)$ . Specifically,  $k_1$  was prescribed a higher value than  $k_3$ . We used the study by Tromp et al. (1995), based on earlier work by Toth and Lerman (1977), as an empirical basis to constrain the rate constant for aerobic respiration and dissimilatory sulfate reduction from the sediment accumulation velocity (in cm yr<sup>-1</sup>):

$$k_1 = 2.97 \cdot \omega_{\rm cr}^{0.62} \tag{20}$$

$$k_3 = 0.285 \cdot \omega_{\rm cr}^{1.94} \tag{21}$$

No information is available on the rate constant for dissimilatory iron reduction  $(k_2)$ . We assumed that this parameter value was equivalent to  $k_3$  and tested this further with the system analysis (see below). Note that we increased the value of the empirical constant in Eq. (21) by a factor of 5 from the original value of 0.057 to 0.285 since lower values failed to generate sulfide. This may be because the anaerobic rate constants were extracted from deep anoxic layers where the material is more refractory or because the reported accumulation velocities





Data sources: Berg et al. (2003); Boudreau (1991); Brigolin et al. (2009); Canavan et al. (2006); Dhakar and Burdige (1996); Eldridge and Morse (2000); Fossing et al. (2004); Furukawa et al. (2004); Jourabchi et al. (2005, 2008); Katsev et al. (2006, 2007); König et al. (1999); Linke et al. (2005); Meysman et al. (2003); Thullner et al. (2009); Van Cappellen and Wang, (1995, 1996); Wang and Van Cappellen (1996); and Wijsman et al. (2002).

correspond to surface sediments where sediment burial velocities are higher. Nonetheless, the resulting  $k_3$  values using Eq. (21) are within the scatter of the data presented by Tromp et al. (1995).

No similar constitutive relationships exist for the rate constants of the secondary redox reactions ( $r_4$ - $r_8$ , Table 2). We attempted to overcome this problem by analyzing previous modeling studies from a range of oxic and anoxic basins from the continental shelf to the deep sea where bimolecular rate constants have been reported (Fig. 5). The range of values over many orders-of-magnitude is quite striking. For example, the rate constant values for aerobic sulfide oxidation  $(k_5)$  extend over 10 orders-of-magnitude. The lower end estimates of  $1.6 \cdot 10^5 \,\mathrm{M^{-1} \, yr^{-1}}$  (Van Cappellen and Wang, 1995; Wang and Van Cappellen, 1996) were based on experiments by Millero et al. (1987a). At the upper end of the scale, Boudreau (1991) constrained  $k_5$  to  $1.0 \cdot 10^{15} \text{ M}^{-1} \text{ yr}^{-1}$  using field data from Aarhus Bay sediments. This anomaly is easily explained by the role of sulfide-oxidizing microorganisms. The laboratory experiments were performed under abiological conditions whereas sulfide-oxidizing bacteria are present in abundance at the site investigated by Boudreau (1991) and efficiently catalyze the reaction between sulfide and oxygen.

Rate constants for secondary redox reactions are generally regarded as fitting parameters in models and thus integrate the effect of many environmental variables. These include (i) the role of ionic strength and pH, (ii) thermodynamic constraints on reactions imposed though the pore water chemistry, (iii) geochemical catalysts or inhibitors, and (iv) microbial community structure. The spread of reported values in Fig. 5 likely reflects a change in the relative importance of these variables among the contrasting environments. Nonetheless, more than half of the studies listed report that the rate constants were 'constrained' or 'fitted' using site-specific data, yet contain little or no relevant model-data comparison to evaluate the goodness-of-fit. It should be remembered that sediment reaction-transport models are coupled through the chemical species and that 'fitted' may refer to a specific aspect or output of the model. This means that a parameter value could be sourced from elsewhere in the literature, yet still be reported as 'fitted' if the overall model output is satisfactory. Rate constants  $k_4$ - $k_8$  for the WIS were estimated only from those studies that provide some indication of the validity of the parameterizations, i.e. concentration or rate data, and were further assumed to be time-invariant.

The considerable uncertainty in the unknown rate constants and the parameters used to hindcast the boundary conditions, is not a major cause for concern. The highly coupled nature of the reaction network places constraints on the number of possible permutations of the entire set of model parameters when tested against field data (Van Cappellen and Wang, 1996). That is, large errors in a single parameters or forcing functions will become obvious in one or more of the modeled variables. Simultaneous reconstruction of OC, Mo and Fe concentrations and accumulation rates is a firm indication that the parameterization is satisfactory. The uncertainty if further quantified using the system analysis described below.

#### 3.5. Numerical solution

The set of coupled partial differential equations for solutes and solids was transformed using the method of lines (Boudreau, 1996). The resulting set of ordinary differential equations was solved using the NDSolve algorithm in MATHEMATICA over a grid spacing increasing from sub-mm at the top of the core to sub-cm at the bottom with a total of 100 depth intervals. The model typically requires ca. 120 s to complete a single simulation.

# 3.6. System analysis

The reaction network is limited to 9 reactions and is thus relatively small compared to other diagenetic models (e.g. Van Cappellen and Wang, 1996). Yet, it is nonetheless a highly interconnected biogeochemical system. One is thus confronted with a large number of potential couplings between parameter values and boundary conditions that control the Mo and OC accumulation rate. A piecewise analysis of the model, that is, changing single parameter values one-by-one and observing the change in model output, is not an optimal means of accurately determining the major controls on specific processes since it cannot identify important couplings between parameters.

To disentangle the interconnectivity in the model, we carried out a system analysis based on a two-level factorial design. Factorial analysis is a statistical methodology (Box et al., 1978) that determines the response of a pre-defined system output (e.g. a reaction rate or concentration) to a change in n model 'factors' (e.g. parameters or boundary conditions). Each factor is assigned a high and low level, such that for n factors there are a total of  $2^n$  system responses. The 'effect' of all possible factor permutations is calculated from the responses using a simple algorithm. The effects can then be illustrated on a normal probability plot to visualize the factor or interactions thereof that have the largest impact on the system response (Box et al., 1978). An example of an application of factorial analysis to marine sediment dynamics is given by Dale et al. (2006, 2011).

In this study, three model responses have been identified: Mo and OC accumulation rate (or the burial rate at the lower model boundary of 150 cm) and the corresponding CBE. Two factorial analyses were performed using the factors suspected to have the largest effect on these responses. The first set of factors tested were those associated with transport and boundary conditions, that is, the environmental parameters ( $F_{C-cr}$ ,  $F_{Fe-cr}$ ,  $\omega_{cr}(\infty)$ ,  $Db_{cr}(0)$ ,  $\alpha_{cr}(0)$ ,  $z_{cr}$ ,  $[O_2]_{cr}(0)$ ). The 7 environmental factors require ( $2^7$ =) 128 model simulations to fully test the complete array of factor combinations. The second set focuses on the reaction-specific parameters which are the biogeochemical rate constants ( $k_1$  to  $k_8$ ), requiring a further ( $2^8$ =) 256 simulations. The factors which directly control Mo accumulation ( $F_{MoS4-cr}$ ,  $[MOQ_4^2^-]_{cr}(0)$ ,  $k_9$  and  $[TH_2S]^*$ ) were not included since the interest is on the peripheral mechanisms which are conducive to authigenic Mo accumulation in Cretaceous sediments.

To elucidate the major controlling factors on Mo and OC burial and CBE across the C–T interval, the high and low factor levels were determined from their mean values derived for the OAE2 and post-OAE2 period. The values for the rate constants  $k_4$  to  $k_8$  were fixed in the model and not derived from the data. Their prescribed values in the factorial analysis were determined by varying the baseline values in Table 1 by  $\pm$  50%. Although this is much lower than the reported parameter values (Fig. 5), it is the same relative change calculated for the other derived parameters (see Table 3, Results). It is important to remember that the system analysis results may not be universally applicable and are only valid for the specific ranges over which the factors were varied.

#### 4. Results

# 4.1. Critical examination of model forcings and comparison with modern pelagic sediments

The parameters and boundary conditions derived in Section 3 applicable to the unconsolidated Cretaceous sediments are shown in Fig. 6. Averaged values for the OAE2 and post-OAE2 periods are summarized in Table 3 and compared to those from contemporary marine settings where possible.

The derived mean sediment burial velocity,  $\omega_{cr}(\infty)$ , varies over time, ranging from 3.2 to 4.4 cm ky<sup>-1</sup> (Fig. 6a, Table 3). These are similar to those encountered in the modern deep ocean but around 3 times lower than the OAE2 sequences of Tarfaya Basin in the proto-North Atlantic (Kolonic et al., 2005). Consequently, the bioturbation coefficients (Db<sub>cr</sub>(0), Fig. 6b) are also similar to deep sea values since Db<sub>cr</sub>(0) is derived from  $\omega_{cr}(\infty)$ . Bioirrigation coefficients,  $\alpha_{cr}(0)$ , of 4 to 9 yr<sup>-1</sup>

#### Table 3

Mean values of parameters and boundary conditions derived for the OAE2 and post-OAE2 periods shown graphically in Fig. 6 and the relative change between the two periods ( $\Delta$ ). Also listed are the rate constants  $k_4$ - $k_8$ . Representative values for the contemporary deep sea, shelf and oxygen minimum zones (OMZ) are also shown where data is available. The final column defines the range of values used in the system analyses.

Parameter	Description	Deep sea <sup>a</sup>	Shelf <sup>b</sup>	OMZs <sup>c</sup>	OAE2	Post-OAE2	Δ (%)	Range
Environmental parameter	rs							
$F_{C-cr}$ (g cm <sup>-2</sup> ky <sup>-1</sup> )	OC flux to sea floor	0.04-0.4	~101	2-14	0.37	0.45	+23	0.37-0.45
$F_{Fe-cr}$ (g cm <sup>-2</sup> ky <sup>-1</sup> )	Fe(OH)3 flux to sea floor	0.003	2.7 <sup>d</sup>	0.2-3.4	0.018	0.007	-59	0.007-0.018
$\omega_{cr}$ (cm ky <sup>-1</sup> )	Sediment burial velocity	0.1-10	$\sim 10^2 - 10^3$	50-300	4.4	3.2	-27	3.2-4.4
$Db_{cr}(0) (cm^2 yr^{-1})$	Surface bioturbation coefficient	0.2-2	10 <sup>1</sup>	~0	0.33	0.16	-52	0.16-0.33
$\alpha_{cr}(0) (yr^{-1})$	Surface bioirrigation coefficient <sup>e</sup>	2-20	>101	~0	7.7	4.8	-37	4.8-7.7
z <sub>cr</sub> (cm)	Mixing depth by animals	5	10	~0	3.8	2.4	-37	2.4-3.8
$[O_2]_{cr}(0) \ (\mu M)$	Bottom water $O_2$ concentration	>150	>120	0-40	87	61	-30	61-87
Reaction-specific parame	ters							
$k_1 (yr^{-1})$	OC mineralization with O <sub>2</sub>	0.01-0.17 <sup>f</sup>	0.7-2.9 <sup>f</sup>	2	0.103	0.085	-18	0.085-0.103
$k_2 (yr^{-1})$	OC mineralization with Fe(OH) <sub>3</sub>	?	?	0.056 (?)	$7.8 \cdot 10^{-6}$	$4.3 \cdot 10^{-6}$	-45	$(4.3 - 7.8) \cdot 10^{-6}$
$k_3 (yr^{-1})$	OC mineralization with SO <sub>4</sub> <sup>2-</sup>	$10^{-9} - 10^{-6f}$	$10^{-4} - 10^{-2f}$	$10^{-4}$	$7.8 \cdot 10^{-6}$	$4.3 \cdot 10^{-6}$	-45	$(4.3 - 7.8) \cdot 10^{-6}$
$k_4 (M^{-1} yr^{-1})$	Ferrous iron oxidation with O <sub>2</sub>	?	$10^8 - 10^{10}$	$1.0 \cdot 10^{9}$	$1.0 \cdot 10^{8}$	$1.0 \cdot 10^{8}$	-	$(0.7-1.5) \cdot 10^8$
$k_5 (M^{-1} yr^{-1})$	Biological sulfide oxidation	?	$10^{5} - 10^{15}$	$6.0 \cdot 10^{8}$	$1.0 \cdot 10^{8}$	$1.0 \cdot 10^{8}$	-	$(0.7-1.5) \cdot 10^8$
$k_6 (M^{-1} yr^{-1})$	FeS precipitation	?	10 <sup>7</sup>	10 <sup>5</sup>	$1.0 \cdot 10^{7}$	$1.0 \cdot 10^{7}$	-	$(0.7-1.5) \cdot 10^7$
$k_7 (M^{-1} yr^{-1})$	Chemical sulfide oxidation	?	$10^{1} - 10^{5}$	$10^{4} - 10^{5}$	$1.0 \cdot 10^{3}$	1.0 · 10 <sup>3</sup>	-	$(0.7-1.5) \cdot 10^3$
$k_8 (M^{-1} yr^{-1})$	FeS oxidation with O <sub>2</sub>	?	10 <sup>3</sup> -10 <sup>7</sup>	?	$1.0 \cdot 10^{6}$	$1.0 \cdot 10^{6}$	-	$(0.7-1.5) \cdot 10^{6}$

<sup>a</sup> Data sources: Betts and Holland (1991), Burdige (2007), Dhakar and Burdige (1996), Glud et al. (1994), Haeckel et al. (2001), Martin and Sayles (2006), Middelburg et al. (1997), Reimers et al. (1986), Seiter et al. (2005), Teal et al. (2008), Thullner et al. (2009), and Tromp et al. (1995).

<sup>b</sup> Data sources: Middelburg et al. (1997), Thullner et al. (2009), and Tromp et al. (1995).

<sup>c</sup> Data sources: Berelson et al. (1987), Bohlen et al. (2011), Böning et al. (2004), Hartnett and Devol (2003), Keeling et al. (2010), Levin (2003), Meysman et al. (2003), Middelburg and Levin (2009), Middelburg et al. (1997), and Niggemann et al. (2007). k<sub>1</sub>, k<sub>2</sub> and k<sub>3</sub> were estimated from the data and profiles in Meysman et al. (2003) for the Santa Barbara basin ([O<sub>2</sub>](0) = 10 \mu M).

<sup>d</sup> Based on the shelf sediment fluxes given in Wallmann (2010) and an iron content of 5%.

<sup>e</sup> Irrigation by animals, not by nitrate-storing bacteria. Irrigation of H<sub>2</sub>S and Fe<sup>2+</sup> is set to zero (see text).

<sup>f</sup> Estimated using the constitutive equations of Tromp et al. (1995)

(Fig. 6c) are in the expected range for slowly accreting sediments where molecular diffusion dominates solute transport across the sediment–water interface (Glud et al., 1994; Haeckel et al., 2001). The imposed irrigation rates imply that the porewater pool at the surface is exchanged by this process every 1–2 months, which compares to a turnover time of days in continental margin sediments (Burdige, 2006).

The modern ocean basins are generally well-ventilated and measured bottom water oxygen concentrations are typically above >150  $\mu$ M (Table 3). In contrast, the derived bottom water oxygen concentration for the WIS,  $[O_2]_{cr}(0)$ , decreases from a maximum of ca. 100  $\mu$ M at the start of the OAE2 period and stabilizes at ca. 60  $\mu$ M throughout the post-OAE2 period (Fig. 6e). The bottom water at this time can thus be tentatively classified as hypoxic (<62.5  $\mu$ M of O<sub>2</sub>) to normal oxic (>62.5  $\mu$ M of O<sub>2</sub>), but not anoxic. The difference in oxygen levels in the WIS between the OAE2 and post-OAE2 periods is derived from the FOL (10–64%) and the choice of the parameter  $\tau$  in Eq. (15). The dependence of the FOL data on ambient  $[O_2]_{cr}(0)$  is poorly known and open to much interpretation due to the broad spectrum of metazoan tolerances to oxygen levels (Levin, 2003). It should also be remembered that the raw Bridge Creek data were processed with a 2 m moving average filter and short intervals of lamination, indicating anoxia, are present in the raw data set (not shown). However, the same filtering procedure also ameliorates the contribution of intermittent unlaminated sections, such that the derived  $[O_2]_{cr}(0)$  reflect the average oxygen concentration. The absence of anoxia has also been argued by Meyers et al. (2005) on the basis of preservation indices and is supported by model simulations indicating that wind-induced mixing would have regularly ventilated the



**Fig. 6.** Derived parameters and boundary conditions for Cretaceous sediments corresponding to the 15 time intervals defined in Fig. 1. Height refers to relative spatial location within the Bridge Creek Limestone Member; (a) sediment burial velocity ( $\omega_{cr}(\infty)$ ), (b) bioturbation coefficient ( $DD_{cr}(0)$ ), (c) bioirrigation coefficient ( $\alpha_{cr}(0)$ ), (d) depth of faunal activity ( $z_{cr}$ ), (e) bottom water oxygen concentration ( $[O_2]_{cr}(0)$ ), (f) OC flux to the sediment surface ( $F_{C-cr}$ ), (g) total iron flux to the sediment surface and the reactive fraction used in the model ( $F_{Fe-cr}$ ), (h) rate constant for aerobic degradation of OC ( $k_1$ ), and (i) rate constant for anaerobic degradation of OC by sulfate ( $k_3$ ). The gray shaded band indicates the OAE2 interval.

shallow bottom waters of the WIS (Kump and Slingerland, 1999). On balance, the presence of a deep hypoxic water layer across the C–T interval seems more reasonable than anoxic or sulfidic bottom waters.

The flux of OC to the sediment–water interface ( $F_{C-Cr}$ , Fig. 6f), ranges from 0.37 to 0.45 g cm<sup>-2</sup> ky<sup>-1</sup>. This is comparable to those on the lower continental slope and abyss in the modern ocean, but at least a factor of 10 lower than sediments on the shelf and from oxygen minimum zones (Table 3). This is a further indication that the WIS must have been significantly oligotrophic compared to the modern ocean of comparable water depths (300 m) where one would expect to find OC fluxes of ca. 1–5 g cm<sup>-2</sup> ky<sup>-1</sup> (Burdige, 2007; Thullner et al., 2009). Our approach further predicts that the post-OAE2 sediments received a 20% higher flux of OC relative to those in the OAE2 period. Yet, the data show that carbonate accumulation rates were lower post-OAE2 (Fig. 1d), which led Meyers et al. (2005) to argue that paleoproduction, and thus  $F_{C-Cr}$ , were also lower during this interval. We return to this discrepancy in more detail in the Discussion.

The imposed reactive iron fluxes are compared with the total iron flux in Fig. 6g which includes the unreactive iron fraction. There is very little data in the literature for comparison of these fluxes. Model-constrained reactive iron fluxes for the deep MANOP sites (Dhakar and Burdige, 1996) and mass balances for Pacific pelagic clays (Glasby, 1991) are in the region of 0.003 g cm<sup>-2</sup> ky<sup>-1</sup>. These are up to a factor of 10 lower than those measured in the Bridge Creek data. On this basis, we infer that the WIS sediments received a disproportionately large flux of reactive iron compared to carbon with respect to other modern deep sea (Table 3) or ancient (e.g. Hetzel et al., 2009) ocean analogs. For comparison, iron fluxes in contemporary shelf sediments are 2–3 orders-of-magnitude higher (Table 3) since most terrigenous particulate material is trapped and buried there (Wallmann, 2010).

The rate constant for aerobic OC mineralization,  $k_1$ , ranges from 74 to 113 ky<sup>-1</sup>, which is ca. 4–5 orders-of-magnitude larger than the rate constant for anaerobic mineralization by sulfate reduction ( $k_3$ ) which ranges from  $5.5 \cdot 10^{-4}$  to  $2.1 \cdot 10^{-3}$  yr<sup>-1</sup> (Fig. 6h,i). There is no scientific consensus on a theory that clearly explains these differences and the major theories proposed have been detailed in the Introduction. Nonetheless, the constitutive equations used by Tromp et al. (1995) to derive the rate constants are empirically based and have been shown to provide a good estimate of carbon burial efficiencies in contemporary marine sediments (Meile and Van Cappellen, 2005). Even so, the assignment of a single rate constant value at any given time conflicts with the observation that OC degrades at different rates over a wide spectrum of temporal and spatial scales (Westrich and Berner, 1984; Middelburg, 1989). For example, the inclusion of 2 or 3 different OC pools are often

required to adequately simulate anaerobic OC mineralization by sulfate reduction (Dale et al., 2009). Yet, we argue that the need for additional OC pools in model simulations is less important for oligotrophic environments with low sediment burial velocities compared to eutrophic settings with high sediment burial velocities. This is because much more of the reactive carbon will be mineralized by aerobic processes in the water column and the uppermost surface layers in oligotrophic systems, leading to decreased burial rates of reactive fractions (Middelburg, 1989). In other words, the suitability of the Tromp et al. (1995) equations in describing a single bulk OC pool undergoing either aerobic or anaerobic decomposition may increase with decreasing sediment burial velocity. Given that the sediments of the WIS accumulated at rates similar to those in the contemporary deep sea, the use of a single rate constant in the model seems to be defensible.

#### 4.2. Geochemical characteristics of Cretaceous sediments

The results of the 15 steady state model simulations are shown in Fig. 7 (thick lines), which compares modeled and measured accumulation rates and concentrations of OC, Fe and Mo. Model-predicted CBEs are also presented. OAE2 is characterized by relatively low OC and Mo accumulation rates and high Fe accumulation, whereas OC and Mo accumulation rates are relatively high and Fe accumulation rates are low following this global event. To put these data in perspective, the Mo accumulation rates of ca.  $7-14 \,\mu g \, cm^{-2} \, kyr^{-1}$  (Fig. 7c) are much lower than the range of 50–1500  $\mu g$  cm<sup>-2</sup> kyr<sup>-1</sup> reported for modern sediments (Zheng et al., 2000; McManus et al., 2006; Morford et al., 2009; Scholz et al., 2011). Overall, the model shows good agreement with the observations and is able to reproduce the major trends in the data. This provides some confidence that the reaction network and parameterizations are satisfactory. A series of causal mechanisms explaining these trends has been proposed (Meyers et al., 2005; Meyers, 2007) which we discuss later in conjunction with the results from the system analysis. Beforehand, we explore how the sediment porewater and solid phase concentration profiles may have evolved in the unconsolidated sediments.

The geochemical profiles of solids and solutes in the unconsolidated Cretaceous sediments shown in Fig. 8 are generated by running the model using the mean parameter values for the OAE2 and post-OAE2 period (Table 3). The model predicts a ca. 20 mm penetration depth of  $O_2$  into the sediment during OAE2. Thus, despite contemporaneous global anoxia, the WIS sediments retain a relatively thick upper oxic layer similar to the modern deep sea (Reimers et al., 1986). Moreover, aerobic respiration accounts for 99% of total OC mineralization over the upper



**Fig. 7.** Comparison between measured (circles, from Fig. 1) and modeled (thin lines) data from Bridge Creek Limestone Member. Accumulation rate of (a) OC ( $F_{C-BCM}$ ), (b) total iron ( $Fe(OH)_3 + FeS$ ) ( $F_{Fe-BCM}$ ), (c) Mo ( $F_{Mo-BCM}$ ), and concentrations of (d) OC, (e) total iron ( $Fe(OH)_3 + FeS$ ), (f) Mo, and (g) carbon burial efficiency (CBE). The modeled concentrations and accumulation rates are calculated at the bottom of the simulated core. (b) and (e) only show the simulation of the reactive iron pool with that calculated from the raw data in Fig. 1e (see Section 3.3.3). The dashed lines in (c) and (f) indicate detrital Mo and the gray shaded band shows the OAE2 interval. The thick lines denote the uncertainty – an indication of the error in the model. These are calculated from the system analysis (Fig. 9), and correspond to the largest observed effect (boxed numbers in each panel, see text).



Fig. 8. Modeled steady state concentration-depth profiles representative of the unconsolidated Cretaceous sediments of OAE2 (solid circles) and post-OAE2 (open circles). Note the different depth scale in the oxygen profile.

150 cm (Table 4). Iron and sulfate reduction account for <1% and sulfate concentration barely decreases over the model sediment column. The same tendencies have been quantified in contemporary deep sea sediments (Jahnke et al., 1982; Dhakar and Burdige, 1996; Haeckel et al., 2001), which reiterates the oligotrophic nature of the WIS over the C-T interval. Particulate (reactive) iron decreases from ca. 3 wt.% at the surface to ca. 1 wt.% at the base of the simulated sediment core due to reductive dissolution (Fig. 8g). This implies that sulfate reduction and release of sulfide to the porewater would only become significant at a greater depth than modeled here. These concentrations agree with observations in the Peru Basin (König et al., 1997) but are lower than Pacific red clays that have iron contents in excess of 5 wt.% (Glasby, 1991). The presence of reactive iron severely inhibits the rate of sulfide production by dissimilatory sulfate reduction and particulate Mo concentrations remain at the detrital background level of 1.5 ppm (Fig. 8h).

The sediments below the oxic layer are highly ferruginous with  $Fe^{2+}$  concentrations reaching 1 mM at 150 cm. These high levels contrast with reports of low or undetectable levels of dissolved iron in modern abyssal sediments (Froelich et al., 1979; Emerson et al., 1980; Haeckel et al., 2001), possibly because our model does not account for siderite formation or  $Fe^{2+}$  incorporation into clay lattices

(König et al., 1997). Furthermore, the apparent equilibrium constant between adsorbed and dissolved iron is on the order of  $10^3$  for marine sediments (Van Cappellen and Wang, 1996), and the model did not account for this large sink of Fe<sup>2+</sup>. Thus, the true Fe<sup>2+</sup> concentrations were likely much lower than those simulated here.

There are striking geochemical differences between OAE2 and post-OAE2 sediments. The latter are OC-enriched with concentrations (2–3 wt.%) that are without parallel in the modern deep ocean (<1 wt.%, Seiter et al., 2005). The sediments have a 10 mm thick oxic layer and aerobic respiration accounts for 98% of total OC mineralization and sulfate reduction for around 2% (Table 4). Despite this huge imbalance, the sediments below the oxic layer become sulfidic, with TH<sub>2</sub>S reaching 100  $\mu$ M at 150 cm depth (Fig. 8c). Particulate iron and dissolved iron are completely consumed and FeS burial becomes a sink for sulfide (Fig. 8i). The presence of free dissolved sulfide allows Mo to accumulate once the threshold sulfide concentration of 65  $\mu$ M is reached at ca. 60 cm.

These trends support the idea that the rate of Mo accumulation is tightly coupled to the availability of dissolved iron in the porewater (Zheng et al., 2000; Meyers, 2007). Importantly, our results also show that enhanced Mo accumulation can occur in parallel with

Table 4

Modeled depth-integrated reaction rates ( $r_1$  to  $r_9$ ) for the OAE2 and post-OAE2 periods corresponding to the species indicated in parenthesis (see Table 2 for the reaction stoichiometry).  $\Delta$ TA is the change in total alkalinity (TA) per formula reaction, and the last two columns show the net depth-integrated rate TA balance calculated by multiplying  $\Delta$ TA by the corresponding reaction rate (positive values indicate net alkalinity production).

Reaction	OAE2 <sup>a</sup>	Post-OAE2 <sup>a</sup>	ΔΤΑ	ΔTA: OAE2	ΔTA: post-OAE2
	$(mol m^{-2} yr^{-1})$	$(mol m^{-2} yr^{-1})$		$(eq m^{-2} yr^{-1})$	$(eq m^{-2} yr^{-1})$
r <sub>1</sub> (CH <sub>2</sub> O)	296 (99%)	342 (98%)	0	0	0
$r_2$ (CH <sub>2</sub> O)	2.9 (0.9%)	0.25 (<1%)	+8	+23.1	+2.0
$r_3$ (CH <sub>2</sub> O)	0.007 (<1%)	5.9 (1.7%)	+1	+0.01	+ 5.9
$r_4 (Fe^{2+})$	11.5	1.0	-2	-23.0	-2.1
$r_5$ (TH <sub>2</sub> S)	$5.8 \cdot 10^{-6}$	0.45	-2	$-1.2 \cdot 10^{-5}$	-0.90
$r_6$ (TH <sub>2</sub> S)	$3.4 \cdot 10^{-3}$	0.89	-2	$-6.7 \cdot 10^{-3}$	- 1.8
$r_7$ (TH <sub>2</sub> S)	$1.6 \cdot 10^{-4}$	1.5	-2/9	$-3.5 \cdot 10^{-5}$	-0.33
$r_8 (Fe^{2+})$	$8.6 \cdot 10^{-4}$	0.93	0	0	0
$r_9 (MoO_4^2)$	0	$1.3 \cdot 10^{-3}$	0	0	0
				$\Sigma + 0.14$	$\Sigma + 2.8$

<sup>a</sup> Values in parentheses are the fraction of OC mineralization channeled through each primary redox pathway.



**Fig. 9.** Normal probability plots of effects derived from the factorial analysis using (a–c) the environmental factors, and (d–f) the reaction-specific factors. The effects on OC accumulation are shown in panels (a) and (d), carbon burial efficiency in (b) and (e) and Mo accumulation in (c) and (f). The straight lines indicate the normal distribution.

oxygenated bottom waters and high rates of aerobic OC mineralization provided that enough labile carbon is buried to the depth of the sulfate reduction zone (Morford and Emerson, 1999; Zheng et al., 2000; McManus et al., 2006). Consequently, elevated Mo burial fluxes observed in ancient marine systems do not necessarily reflect euxinic or anoxic conditions within the water column (Calvert and Pedersen, 1993). As we show in the following section, it is the dynamic interplay between iron, organic carbon and bottom water oxygen levels that determines the extent to which Mo can accumulate.

# 4.3. System analysis of Mo and OC accumulation and CBE

The results of the factorial analysis of the 7 environmental factors  $(F_{C-cr}, F_{Fe-cr}, \omega_{cr}(\infty), Db_{cr}(0), \alpha_{cr}(0), z_{cr}, [O_2]_{cr}(0))$  generated with the model are illustrated on normal probability plots in Fig. 9a-c. The panels show the effects of single factors or their interactions on OC accumulation (Fig. 9a), CBE (Fig. 9b) and Mo accumulation (Fig. 9c) or, stated differently, the change in these responses when the factor(s) increase from their low to high level. Data points ('effects') which fall on or close to the solid line are normally distributed about zero whereas those which lie away from the line cannot be explained as chance occurrences and, consequently, are regarded to have a large impact on the model response. For example, there are 3 main environmental factors which control OC accumulation (Fig. 9a):  $[O_2]_{cr}(0)$ ,  $\omega_{cr}(\infty)$  and  $F_{C-cr}$ . Of these,  $[O_2]_{cr}(0)$  and  $F_{C-cr}$  lie farthest away from the normal line which means that they exert the largest effect on OC accumulation. In addition,  $[O_2]_{cr}(0)$  appears to the left of the normal line, such that an increase in  $[O_2]_{cr}(0)$  will decrease OC accumulation through higher rates of aerobic mineralization, as expected. F<sub>C-cr</sub> lies to the right, which is simply because higher depositional fluxes increase the rate of OC accumulation. The overall 'effect' of increasing oxygen from the low (61  $\mu$ M) to high (87 µM) concentration (Table 3) is to decrease OC accumulation by  $0.014 \text{ g cm}^{-2} \text{ ky}^{-1}$ . The effect of the most sensitive parameter, in this case  $[O_2]_{cr}(0)$ , provides an estimate of the uncertainty in the modelpredicted concentrations and rates (thick lines in Fig. 7).

A similar pattern for  $[O_2]_{cr}(0)$  emerges with the CBE, whereby the latter is reduced by ca. 4.5% if oxygen increases from the low to high level (Fig. 9b). The critical control of OC dynamics by oxygen over this conservative concentration range is quite remarkable, and alludes to oxygen limitation as the most important control on OC burial. As a first approximation, the OET can be quantified as the thickness of the oxic layer (*L*) divided by  $\omega_{cr}(\infty)$ . Using  $\omega_{cr}(\infty)$  values from the OAE2 and post-OAE2 periods in Table 3 and the depth of oxygen penetration in Fig. 8a, the OET is 50% greater during OAE2 compared to post-OAE2.

Bioturbation and bioirrigation do not exert a dominant control on OC accumulation rate and CBE (Fig. 9a,b). There is, however, a weak interaction between  $[O_2]_{cr}(0)$  and the depth of sediment mixing by animals,  $z_{cr}$ , on CBE which is identified in Fig. 9b as the  $[O_2]_{cr}(0)-z_{cr}$  term. The model includes a simplified formulation for faunal activity and does not account for the complexities of sediment transport and carbon cycling by animals caused by mechanical breakdown of aggregates, digestion and egestion of OC and production of microniches (Meysman et al., 2006). It is clear, however, that bioturbation is an ineffective mechanism of sediment oxygen uptake compared to molecular diffusion, which can be seen by comparing the in situ molecular diffusion coefficient for oxygen (ca. 400 cm<sup>2</sup> yr<sup>-1</sup>, Table 1) with the biodiffusion coefficient (ca. 0.5 cm<sup>2</sup> yr<sup>-1</sup>). Accordingly, increased  $[O_2]_{cr}(0)$  and thus rates of oxygen diffusion into the sediment (Fig. 8a) mainly explain the lower CBEs during OAE2.

The CBE data further show that  $\omega_{cr}(\infty)$  and  $F_{C-cr}$  lie to the right hand side of the normal line, such that these factors will increase the rate of OC delivery to the sulfate reduction zone where preservation is more likely (Fig. 9b). This cause–effect relationship between carbon concentration and burial velocity has been corroborated by extrapolation of experiential data into statistical generalizations (Tyson, 2001). Yet, their individual effect is to increase CBE by roughly 1.5% only, and so are of minor importance compared to  $[O_2]_{\rm cr}(0)$ . This apparently contradicts the empirical relationship in Fig. 4, which shows that accumulation rate is the most important factor influencing preservation (Betts and Holland, 1991; Canfield, 1994). This is because the accumulation rate varies by only  $\pm$  30% across the C–T interval, compared to 5 orders-of-magnitude when the whole spectrum of marine sediments is considered (Fig. 4). In contrast, the perceived role of oxygen on CBE in Fig. 4 at low sediment accumulation rates is much more pronounced, as shown by the divergence of the two regression curves for high and low oxygen environments.

Of the reaction-specific factors, the rate constant for aerobic degradation  $(k_1)$  mostly influences OC accumulation and CBE (Fig. 9d, e). The datum lies to the left of the normal line since higher  $k_1$  values will lead to more extensive carbon degradation. There are also weak interaction terms between  $k_1$  and the rate constant for sulfate reduction  $(k_3)$ . Overall, however, the effect of the rate constants on these responses is much lower than for the environmental factors.

The system analysis for Mo accumulation shows that an increase in reactive iron flux ( $F_{Fe-cr}$ ) and  $[O_2]_{cr}(0)$  will both decrease Mo burial by about 6 µg cm<sup>-2</sup> ky<sup>-1</sup>, respectively, whereas an increase in carbon flux ( $F_{C-cr}$ ) will promote Mo burial by 2–3 µg cm<sup>-2</sup> ky<sup>-1</sup> (Fig. 9c). This confirms the expectation of a prominent role for reactive iron on Mo accumulation based on previous work (Meyers et al., 2005; Meyers, 2007). The rate constants k<sub>1</sub> and k<sub>3</sub> invoke similar magnitudes of Mo accumulation (Fig. 9f). The effect of k<sub>1</sub> is to decrease the Mo accumulation rate by reducing the amount of carbon buried to the sulfate reduction zone, whereas higher k<sub>3</sub> will lead to more sulfide production and higher rates of Mo accumulation. However, because of the significant interaction terms between k<sub>1</sub> and k<sub>3</sub>,  $F_{Fe-cr}$  and  $[O_2]_{cr}(0)$  and, to a lesser extent,  $F_{Fe-cr}$  and  $F_{C-cr}$ , on Mo accumulation, additional analysis is required to fully interpret the main effects of these factors. As an example, the



**Fig. 10.** Bubble plots of Mo accumulation rate. The interaction terms shown are those between (a)  $F_{Fe-cr}$  and  $[O_2]_{cr}(0)$  and (b)  $F_{Fe-cr}$  and  $F_{C-cr}$ . The axes indicate the high and low levels of the factors tested (Table 3) and the values adjacent to the bubbles (in  $\mu g \ cm^{-2} \ ky^{-1}$ ) are the effects of the different interactions on Mo accumulation rate.

bubble plots in Fig. 10 deconvolve the interaction terms for the environmental parameters. With regards to the  $F_{Fe-cr}-[O_2]_{cr}(0)$  interaction (Fig. 10a), it is clear that iron is much more dominant in controlling Mo accumulation than oxygen. A high reactive iron flux  $(0.018 \text{ g cm}^{-2} \text{ ky}^{-1})$  decreases Mo burial to  $2-3 \,\mu\text{g cm}^{-2} \text{ ky}^{-1}$ , which is essentially equal to the detrital Mo flux (Fig. 7c). Importantly, this occurs regardless of whether oxygen is present at the high or low level. High  $[O_2]_{cr}(0)$  causes a reduction in Mo accumulation to  $4 \,\mu\text{g cm}^{-2} \text{ ky}^{-1}$  but only when the iron flux is low. The role of oxygen here is related to the lower OC accumulation rate and CBE when  $[O_2]_{cr}(0)$  is high (Fig. 9a,b), which ultimately leads to lower free dissolved sulfide in the porewater. Similarly, the  $F_{Fe-cr}$ - $F_{C-cr}$  interaction (Fig. 10b) reveals that higher OC fluxes can promote a doubling of the Mo burial rate, but only when the iron flux is low.

Overall, the system analysis reveals that there is a complex relationship between OC,  $O_2$ , Fe and Mo accumulation. Changes in OC flux and bottom water oxygen concentration can potentially radically alter the Mo burial rate when iron fluxes are low. Low iron burial fluxes characterize the post-OAE2 period in the WIS and, in general, OAEs from other geographical regions (e.g. Hetzel et al., 2009).

# 5. Discussion

### 5.1. The role of iron cycling on Mo enrichment

Black shales from sites around the world are typically enriched in carbon and trace metal sulfides (Arthur et al., 1988; Arthur and Sageman, 1994; Kuypers et al., 2002; Kolonic et al., 2005; Brumsack, 2006; Hetzel et al., 2009). The supporting paradigm for this observation relies on the idea of enhanced carbon burial through increased primary productivity and/or preservation induced by the absence of oxygen in ocean bottom waters. This leads to elevated rates of sulfate reduction and sulfide accumulation in the water column and/or porewater, conditions under which particulate trace metal sulfides become stable (Calvert and Pedersen, 1993).

On the contrary, Mo accumulation rates in the WIS were lower during OAE2 and only increased following the global anoxic event (Fig. 7c). Several studies have argued that this was due to a high rate of detrital iron flux from the adjacent Sevier Orogenic Belt supplemented by a source of non-detrital, possibly hydrothermal, iron (Sageman and Lyons, 2003; Meyers et al., 2005; Meyers, 2007). Our results support the hypothesis of an effective benthic redox control Mo accumulation by iron and further suggest that reactive iron may have accumulated to several wt.% during OAE2 (Fig. 8g). At this time, rates of iron reduction  $(r_2)$  and ferrous iron oxidation  $(r_4)$  are elevated compared to post-OAE2 (Table 4) due to efficient re-oxidation of reduced iron within the upper bioturbated layers (Canfield et al., 1993). The abundance of iron curtails Mo accumulation by (i) allowing dissimilatory iron reducing bacteria to inhibit sulfate reducers for labile substrate, and (ii) oxidizing the little free sulfide which becomes available. This type of setting closely resembles contemporary abyssal sediments that are iron-rich and sulfide-free (Glasby, 1991; König et al., 1997). The system reaches a tipping point at the C–T transition where sulfide production surpasses the buffering capacity of iron oxide, allowing concentrations to reach the threshold for Mo sequestration. Beyond this point the rate of FeS cycling becomes much higher (r<sub>6</sub>, r<sub>7</sub>, r<sub>8</sub>), indicating fundamentally different pathways of iron recycling across the C-T interval. One can expect the balance between hydrogen sulfide production and depletion to be most delicate during this transitional period towards anoxia.

The importance of iron is somewhat unique to the WIS and should not be considered representative of OAEs. However, the role of oxygen and organic carbon revealed by the system analysis are a reminder that iron alone does not definitively control Mo accumulation, and this is probably true of sediments in general. For example, Mo enrichment has been shown to be sensitive to carbon flux and oxygen levels in modern surface sediments along the oxygen minimum zones of the Americas (McManus et al., 2006; Scholz et al., 2011). Due consideration of coupled iron, carbon and oxygen cycling is critical to interpreting paleoredox indicators such as Mo.

Adsorption of  $MoO_4^2$  onto iron (and manganese) oxyhydroxides in oxic waters (Helz et al., 1996) and deposition on the seafloor provides an additional mechanism for Mo transfer to the sediment in addition to diffusion from sea water (Crusius et al., 1996). Subsequent reductive dissolution of the iron oxides releases Mo to anoxic sediment porewaters, which can then be sequestered and precipitated as thiomolybdate or diffuse back to the water column. In general, this transfer pathway is small compared to the diffusive Mo flux across the sediment water interface (Crusius et al., 1996; Erickson and Helz, 2000; Zheng et al., 2000). However, iron-associated Mo may lead to strong benthic enrichment of authigenic Mo in silled basins with weakly or seasonally anoxic bottom waters where the chemocline migrates through the sediment-water interface (Algeo and Lyons, 2006). These settings are particularly susceptible to Mo trapping because repeated ventilation of the deep water catalyzes the re-oxidation of dissolved iron and manganese to particulate oxyhydroxides, thus recreating the necessary conditions for a new flux of adsorbed Mo. This hypothetical 'Mo pump' was conceived to explain sedimentary Mo concentrations in excess of 100 ppm in modern basins such as Saanich Inlet and Cariaco Basin (Algeo and Lyons, 2006). Given the abundance of iron in the WIS, one would expect to see the Bridge Creek data punctuated with extreme Mo enrichments if the Mo pump was periodically active. However, such enrichments are absent from both the 2 meter smoothed Mo concentrations (<10 ppm, Fig. 7f) and the raw data (max. 20 ppm, data not shown). For this reason, we exclude this mechanism as a vector for Mo enrichment in the WIS.

#### 5.2. Production versus preservation of OC across the C-T interval

Increased global burial of OC during OAE2 is usually inferred from the marked positive excursion in  $\delta^{13}C_{OC}$  and  $\delta^{13}C_{CaCO3}$  followed by a return to more negative values in the post-OAE2 period as paleoproduction and OC burial decreased (Arthur et al., 1988). The Bridge Creek  $\delta^{13}C_{OC}$ data essentially track the trend of the global ocean (Sageman et al., 2006). Yet, the striking increase in OC concentration and accumulation rates occurring after OAE2 (Fig. 7) suggests that the extent and timing of 'OAE2-like' conditions in the shallow epicontinental WIS were offset from the rest of the ocean (Meyers et al., 2001; Sageman and Lyons, 2003). To help identify the contribution of productivity and preservation on OC accumulation in the WIS, Meyers et al. (2001; 2005) employed carbonate accumulation as a qualitative proxy for paleoproduction (Fig. 1d). The lower carbonate accumulation rates post-OAE2 were inferred to represent lower paleoproductivity, and the OC enrichment relative to OAE2 was thus explained as carbon preservation. In accordance with this idea, they adopted a simple preservation scaling approach, that is, dividing the carbon accumulation rate by the FOL, which predicted lower rates of paleoproduction post-OAE2 compared to OAE2. These researchers went on to argue that OC preservation was driven by (i) a decline in reactive iron flux which led to increased dissolved sulfide concentrations in the porewater, reduced bioturbation due to faunal toxicity to sulfide and a shallower sulfate reduction zone (thinner oxic layer), and (ii) a reduction in bulk sediment dilution. Equally, less OC preservation occurred during OAE2 because the decrease in sulfide levels by iron buffering led to more efficient ventilation of the sediments by burrowing animals; a hypothesis later termed the 'sulfide buffer/phosphorus trap' (Meyers, 2007). However, despite the obvious role of iron on Mo accumulation (see above), our analysis does not indicate any substantial role for iron on OC accumulation (Fig. 9a). Instead, our results which are based on a more rigorous estimate of reconstructed carbon flux allude to the combined effects of paleoproduction and preservation, whereby a modest increase in paleoproduction (i.e. higher  $F_{C-Cr}$ ) in conjunction with preservation (i.e.



Fig. 11. Reconstructed bottom water oxygen concentrations versus reconstructed organic carbon fluxes across the C–T interval.

lower  $[O_2]_{cr}(0)$ , conspired to allow OC (and Mo) to accumulate at higher rates post-OAE2 and with a higher CBE. A plot of  $[O_2]_{cr}(0)$  versus  $F_{C-Cr}$  (Fig. 11) shows the inverse relationship between the two factors across the C–T interval. We reiterate that this result is by no means certain due to the inherent uncertainties in reconstructing the boundary conditions of the WIS sediments. It does, however, illustrate how simultaneous production and preservation can give rise to geochemical trends that are characteristic of OAE-like conditions.

The use of carbonate as a paleoproductivity proxy assumes that the phytoplankton composition remained relatively uniform in the central WIS over the C-T interval and that carbonate dissolution and precipitation were constant over time (Meyers et al., 2005). The model results presented here provide circumstantial evidence that the latter condition may not have been fulfilled. To explain, the diagenetic regimes between OAE2 and post-OAE2 are radically different (Fig. 8), being highly ferruginous during OAE2 and sulfidic thereafter. There is a transition from dissimilatory iron reduction and net sulfide buffering toward sulfate reduction and sulfide accumulation between the two periods. Critically, the number of protons, or alkalinity equivalents, produced and consumed by these reactions is different ( $\Delta TA$ , Table 4). Stoichiometrically, much more alkalinity is produced by dissimilatory iron reduction (+8 equivalents per mole of carbon oxidized) compared to sulfate reduction (+1). Despite the small net production of alkalinity during OAE2  $(+0.14 \text{ eq m}^{-2} \text{ yr}^{-1})$ , it is very likely that carbonate minerals were in a state of disequilibrium in the surface sediments. For instance, dissimilatory iron reduction (r<sub>3</sub>) produces  $+23.1 \text{ eq m}^{-2} \text{ yr}^{-1}$  of alkalinity, which will favor carbonate preservation and possibly authigenic carbonate precipitation in these layers. However, ferrous iron oxidation consumes 23 eq m<sup>-2</sup> ky<sup>-1</sup> of alkalinity, which will lead to highly undersaturated pore waters within the thin upper oxic layer (Jourabchi et al., 2005). Since the rate of carbonate dissolution depends on the mineral saturation state (e.g. Keir, 1980), which in turn depends on the porewater alkalinity and pH, this reaction creates a strong thermodynamic drive for carbonate dissolution in the surface layers.

The post-OAE2 sediments are associated with a larger net alkalinity production (2.8 eq m<sup>-2</sup> yr<sup>-1</sup> of alkalinity), which is due to burial of FeS. Again, one may expect sulfide oxidation reactions in the surface layers to cause an undersaturation with respect to carbonate minerals. Furthermore, the depth-integrated rate of aerobic OC mineralization post-OAE2 and, therefore, CO<sub>2</sub> production is 46 mol m<sup>-2</sup> yr<sup>-1</sup> higher than during OAE2. Although this reaction does not affect total alkalinity directly,  $CO_2$  will rapidly neutralize carbonate ion alkalinity ( $CO_2 + CO_3^{2-} + H_2O \rightarrow 2HCO_3^{2-}$ ) and lower the carbonate saturation state. This 'metabolic dissolution', to distinguish from thermodynamically-driven dissolution, is a common characteristic of surface marine sediments (Emerson and Bender, 1981; Archer et al., 1989) and could conceivably account for the lower rates of calcite accumulation post-OAE2. This cautions against the use of carbonate content as a proxy for primary production. A more sophisticated model than the one presented here would be required to test this idea more rigorously (Jourabchi et al., 2008).

In summary, the above calculations highlight the difficulties in disentangling the role of production and preservation through a qualitative interpretation of carbonate accumulation rates where there are large shifts in benthic redox potential. Erba (2004) raised similar concerns for the interpretation of calcareous nannofossils in black shales. The interpretation of proxies through the application of models using highly resolved data from OAE2 sequences elsewhere (e.g. Kolonic et al., 2005; Hetzel et al., 2009) shows great promise in delivering a more global picture of the significance of benthic processes during the onset of ocean anoxia.

#### 6. Conclusions

Proxy signals recorded in marine sediments can be amplified or diminished by changes in the intensity of physical processes (e.g. burial rates, bioturbation) as well as biogeochemical reactions. Benthic cycles are highly coupled through the chemical species and can interact synergistically or antagonistically on the accumulation of key geochemical indicators. It thus becomes challenging, if not impossible, to adduce the major forcings by a qualitative analysis of the data. Reaction-transport models integrate transport processes and biogeochemistry into a quantitative framework and can be used to extricate the overarching controls on single- or multi-proxy inventories.

We applied a model to reconstruct the geochemical paleorecord preserved in strata of the Bridge Creek Limestone Member of the Western Interior Seaway and evaluate the controls on organic carbon (OC) and molybdenum (Mo) accumulation rate. Our attention focused on the Cenomanian–Turonian (C–T) boundary interval (94.34–93.04 Ma) which includes OAE2. To our knowledge, this is the first model application to reconstruct multi-proxy data recorded in fully consolidated sedimentary rock. This approach thus represents a new dimension for studying deep-time biogeochemical processes in a dynamic manner.

Important implications follow from this work. Our results clearly corroborate Meyers' (2007) argument that the accumulation rate of particulate Mo in black shales is a poor proxy for ocean euxinia or even anoxia in ancient marine systems. We show that high rates of Mo accumulation can occur with high rates of aerobic OC degradation in the surface sediments. Furthermore, Mo sequestration can be severely restricted by the availability of reactive iron oxides which buffer porewater sulfide to levels below those required for Mo sequestration. Evidence suggests that the bottom waters became progressively more hypoxic, but not anoxic, over the C-T interval in the WIS in parallel with increasing OC flux to the seafloor. This alludes to a positive feedback between the sea floor and the photic zone, probably via phosphate, on the advance of anoxia. Future modeling work will address this hypothesis by incorporating phosphorous data into the model. The results presented simultaneously support both long-standing notions that OC enrichment in ancient sediments is driven by increased preservation and increased export production. There is no reason why these should be regarded as uncoupled, independent processes.

# Acknowledgments

We are grateful for the useful comments of two reviewers and the guest Editor Jennifer Morford which improved the paper. The Deutsche Forschungsgemeinschaft provided support as part of the Sonderforschungsbereich 754 (http://www.sfb754.de). S.A. acknowledges financial support from NERC (Grant No. NE/I021322/1).

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