

## Replies to Referee #3: K. Wallmann on “OMEN-SED 0.9: A novel, numerically efficient organic matter sediment diagenesis module for coupling to Earth system models”

### 1. Comment:

The model ignores sulfide precipitation and pyrite formation. Consequently, dissolved sulfide produced by sulfate reduction and AOM at depth diffuses upward to be either oxidized by oxygen or released into ambient bottom waters. This is a very unrealistic set-up. In most sediments dissolved sulfide is removed from the pore water by pyrite precipitation while the remaining sulfide is oxidized with ferric iron, nitrate and nitrite before it can reach the oxic surface layer or the ocean. Aerobic sulfide oxidation is only important in highly reactive surface sediments where the diagenetic sequence is not maintained but several electron acceptors are used simultaneously. The model is based on the assumption that electron acceptors are used sequentially rather than simultaneously. Hence, it cannot simulate situations where aerobic sulfide oxidation is important but creates high rates of aerobic sulfide oxidation in geological settings where this process does in fact not occur. The authors should try to fix this problem. They could for example abandon the model parameter that defines the fraction of dissolved sulfide that escapes into bottom waters. In the modern ocean, sulfide leakage from sediments occurs only in very rare situations and it does not make sense to simulate these anoxic sediments with a model that ignores iron cycling, pyrite formation and sulfide precipitation. The authors could instead introduce a parameter that defines the fraction of sulfide that is precipitated as pyrite and update the alkalinity model accordingly.

### Response:

We thank Prof. Wallmann for this very valid suggestion. We made the following changes to OMEN-SED:

When coupled to an ESM the  $\gamma_{\text{H}_2\text{S}}$  value (fraction of H<sub>2</sub>S that is oxidised) becomes dependent on the bottom water oxygenation state. That is,  $\gamma_{\text{H}_2\text{S}} = 1.0$  for oxic bottom waters and a user defined value  $\gamma_{\text{H}_2\text{S}} < 1.0$  for anoxic bottom waters. For simplicity this is still implemented as aerobic sulfide oxidation. In addition, we introduce another parameter ( $\gamma_{\text{FeS}}$ ) representing the fraction of sulfide that is precipitated as pyrite (i.e.  $0.0 \leq \gamma_{\text{FeS}} < 1 - \gamma_{\text{H}_2\text{S}}$ ) in the sulfate reduction zone.  $\gamma_{\text{FeS}}$  is an auxiliary parameter used as a fix until iron is explicitly represented (see pg. 54 lines 10-11, “... already planned future extensions of OMEN-SED include an explicit description of carbonate dissolution iron.”). We thus assume that a user-defined fraction of the produced H<sub>2</sub>S precipitates as FeS(FeS<sub>2</sub>) in the sulfate reduction zone. If a user does not want to make any assumptions about FeS precipitation – it can be set it to 0.

The text, tables and equations (for O<sub>2</sub>, SO<sub>4</sub>, H<sub>2</sub>S and alkalinity) are changed accordingly. The presented results have not been changed and we note that  $\gamma_{\text{FeS}} = 0.0$  for all simulations, as we do not want to make any assumptions.

Changes made in:

2.2.2 Oxygen: Table 3 boundary condition 4.2 + Text pg. 12 lines 14-16:

*“ It is assumed that respective fractions ( $\gamma_{\text{NH}_4}$  and  $\gamma_{\text{H}_2\text{S}}$ ) are directly reoxidised at the oxic/anoxic interface and the remaining fraction escapes reoxidation (or is precipitated as pyrite,  $\gamma_{\text{FeS}}$  ).”*

2.2.4 Sulfate and Sulfide (pg. 14 lines 9-10): + Equations 23 + Table 5 boundary condition 5)  
“In the sulfidic zone a defined fraction of sulfide,  $\gamma_{FeS}$ , can be precipitated as pyrite (in the presented simulations  $\gamma_{FeS} = 0.0$  as we do not want to make any assumptions about pyrite precipitation).”

2.2.7 Alkalinity: Table 8 boundary condition 5)

Text (pg. 20 lines 5-7):

“ In addition, the effect of secondary redox reactions, such as nitrification, sulfide and methane oxidation, **as well as pyrite precipitation**, are implicitly accounted for in the boundary conditions. ”

Text (pg. 20 lines 21-23):

“The decrease of alkalinity due to oxidation of reduced species produced in the anoxic zones **and due to the precipitation of pyrite** (with stoichiometry  $ALK^{NIT}$ ,  $ALK^{H2S}$  and  $ALK^{FeS}$ ) is implicitly taken into account through the flux boundary condition at zox (Table 8 Eq. 5). ”

2.4.2 Stoichiometries and reaction parameters: (pg. 27 lines 19-23):

“However, when coupled to an ESM  $\gamma_{H2S}$  becomes dependent on the bottom water oxygenation state. That is,  $\gamma_{H2S} = 1.0$  for oxic bottom waters and a user defined value  $\gamma_{H2S} < 1.0$  for anoxic bottom waters. The parameter  $\gamma_{FeS}$  represents the fraction of sulfide that is precipitated as pyrite in the sulfidic zone. The majority of  $H_2S$  produced by sulfate reduction is reoxidised, but it is estimated that  $\sim 10 - 25\%$  is eventually buried as pyrite (Bottrell and Newton, 2006). However, this fraction can vary significantly over geological timescales (Berner, 1984). If a user does not want to make any assumptions about pyrite precipitation – it can be set to 0 (as in the results presented here).”

We also added pyrite precipitation to Table 1 and A1 in the Appendix.

## 2. Comment:

The authors use an empirical equation by Middleburg et al. (1997) to define burial velocity ( $w$ ) as function of water depth (Eq. 46). Unfortunately,  $w$  is seriously overestimated by this equation. As an example,  $w$  at 1000 m water depth results as 160 cm kyr<sup>-1</sup> applying Eq. 46 whereas the available data indicate global mean rates in the order of 10 – 20 cm kyr<sup>-1</sup> for this water depth (Burwicz et al., 2011). The extremely high burial velocities derived from Eq. 46 compromise the TOC concentration and other model results especially when the model is applied at global scale.

## Response:

The Middleburg et al. (1997) equation is just used in the stand-alone OMEN-SED version. When coupled to cGENIE we use the burial velocity of the ESM. In addition, the Burwicz et al. (2011) parameterisation is already added as an option in OMEN-SED (see pg. 24). We made it the default version for the stand-alone model. The sentence as been changed accordingly (compare pg. 24 line 28 – pg. 25 line 3).

## 3. Comment:

**Comment 3.1:** OMEN-SED is able to reproduce the strong down-core decrease in organic matter reactivity observed in marine sediments by using two or more organic matter fractions with widely different reactivity. This strength is nicely demonstrated in section 3.3 where the authors are able to show that typical pore water profiles are reproduced by

the model applying kinetic constants ( $k_1$ ,  $k_2$ ) that span several orders of magnitude (Tab. 13). Subsequently, the authors try to reproduce the TOC distribution at the deep-sea floor by coupling OMEN-SED to an earth system model. I think that TOC in surface sediments is not a good parameter to validate the model because almost the entire organic matter raining to the deep-sea floor is degraded in the surface sediment rather than preserved as sedimentary TOC. TOC concentrations in surface sediments at the deep-sea floor are governed by TOC rain rates, mass accumulation rates (burial velocity), adsorption of organic matter on mineral surfaces, and the kinetic properties of the very small refractory fraction that survives degradation (about 1 % of the total rain rate). The strength of OMEN-SED to degrade the reactive fractions in a meaningful way does not play out in this application.

**Response:**

We agree with the statement that TOC is not necessarily a good way to validate the coupled model and we would also favor fluxes or rates. However, we are not convinced that they give much better results if the database is limited. TOC in surface sediments was the data available on a global scale and also other ESM studies compare their results to it (e.g. HAMOCC, Palastanga et al. (2011)). As mentioned earlier, we will put in some more effort in a follow-up study where we compare calculated SWI-fluxes with observations.

In addition, as stated in the manuscript (page 45, lines 23-26):

*“ Our objective is not to perform and discuss a detailed calibration of the coupled models as this is beyond the scope of this sediment model development paper. Rather we want to showcase the feasibility of the model coupling, illustrate the range of results and thus information that can be generated with OMEN-SED and verify that model results capture the main observed global benthic biogeochemical features.”*

**Comment 3.2:** Moreover, the model results are unrealistic. The best fit to the TOC data is apparently obtained assuming that the organic matter flux to the seabed is composed of two TOC fractions with very low reactivity in the order of 0.001 – 0.01 yr<sup>-1</sup> (Fig. 12). This result is not consistent with the case study presented in section 3.3 that yields much higher  $k$  values (Tab. 13).

**Response:**

The low reactivities obtained for the global application (e.g. Fig. 12 – old manuscript) agree with published results (see Arndt et al., (2013)), as well as with the results obtained with HAMOCC using a 1G-model (they found  $k_{ox}=0.005$  yr<sup>-1</sup> &  $k_{nox}=0.002$  yr<sup>-1</sup> for deep sea sediments, Palastanga et al. (2011)). In addition, our simulated oxygen penetration depths compare well with observations (see Fig. 16). Especially deep sea sites in the gyres are characterised by very low POC input and degradation rates which causes O<sub>2</sub> to diffuse down to the basement of the sediments (Fischer et al., 2009; D'Hondt et al., 2015).

The sites used for the stand-alone case study in section 3.3 were not really deep sea sites (complete data sets from deep sea sites within gyres are difficult to obtain).

However, we decided to shorten the cGENIE coupling section (compare also response to your comment 3.3). The sensitivity analysis for the spatially uniform degradation rate constants (Figure 12) and its discussion has been removed (compare pages 47-50).

**Comment 3.2:** Moreover, we have shown previously that this very low reactivity is not consistent with the benthic fluxes of oxygen and nitrate that have been measured at the seabed (Stolpovsky et al., 2015). The error may be caused by the too high burial velocities applied in OMEN-SED (Eq. 46) and/or may be related to the rain rate and reactivity of organic matter calculated in GENIE.

**Response:**

The Stolpovsky et al. (2015) database is a very valuable source of information and we will compare our calculated fluxes using the coupled model with it in the follow-up study. The ranges of simulated SWI-fluxes from the stand-alone OMEN-SED model are already compared to the database in Figure 6. However, we would also argue that the Stolpovsky et al. (2015) database does not contain a representative amount of very deep ocean sites (e.g. within ocean gyres) characterised by very low SWI-fluxes (see e.g. Fischer et al., 2009; D'Hondt et al., 2015). D'Hondt et al. (2009) for instance found that the net rate of diagenetic degradation in the South Pacific Gyre is 1 to 3 orders of magnitude lower than at previously explored sites and they suggest that almost 50% of the world's ocean may be characterised by these rates. In a more recent study D'Hondt et al. (2015) suggest: "...that oxygen and aerobic communities may occur throughout the entire sediment sequence in 15–44% of the Pacific and 9–37% of the global sea floor."

**Comment 3.3:** I would encourage the authors to delete the entire section 4 of the paper because it does not add useful information but presents rather misleading results. They should aim to present other more useful applications of their highly innovative analytical model in follow-up publications.

**Response:**

Here, we repeat parts of the response to comment 20 of reviewer #1:

We think that demonstrating how OMEN-SED can be coupled to an ESM and illustrating the type of output/information generated by OMEN-SED within such a coupling is a central aspect of the model description paper.

However, we agree trimming down this section (as in the re-submitted version). We will discuss an improved model-data analysis (also using observations of SWI-fluxes).

Specifically, the sensitivity analysis for the spatially uniform degradation rate constants (Figure 12) and its discussion has been removed (compare pages 47-50).