

**Original comments are given in black, our reply is given in red.**

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The paper by Roth et al. is well written, clearly structured, and a pleasure to read. It illustrates the importance of benthic processes for the long-term evolution of ocean chemistry and atmospheric pCO<sub>2</sub>. More specifically, it shows that a shift of POM degradation to larger water depths has a strong impact on seawater composition and atmospheric pCO<sub>2</sub> when sediments are included in the model set-up. The paper is very nice and innovative.

**We thank the reviewer for his valuable comments that helped to improve the manuscripts and for his time and effort to review this manuscript.**

However, I find it very difficult to evaluate the model results since the benthic model is not fully explained. Even though I read the accompanying paper by (TSCHUMI et al., 2011) which provides more detail on the benthic model, I have a number of questions that should be addressed in the preparation of the final version:

1. The model excludes the burial of neritic carbonates at continental shelves and uses a low estimate for pelagic carbonate burial (only 0.096 Gt C/yr, Tab. 1). On the other hand, the global POC burial rate is quite high and apparently includes POC burial at continental margins (0.181 Gt C/yr, Tab. 1). The authors should explain how their model distributes POC burial between the deep-sea (>1000 m water depth) and the continental margins (<1000 m water depth). Sedimentary data show that about 80 – 90 % of global POC burial occurs at continental margins while the deep-sea contributes only about 0.01 – 0.05 Gt C/yr to the total POC burial rate (BERNER, 1982; BURDIGE, 2007; BURWICZ et al., 2011; HEDGES and KEIL, 1995; MIDDELBURG et al., 1993; WALLMANN et al., 2012). Does the model reproduce and consider these important observations?

**Our coupled model is tuned to match observational estimates of a total POC burial flux of 0.19±0.07 GtC/yr (Sarmiento & Gruber, 2006, page 261, table 6.5.1). The POC burial flux is distributed in our model as 70% (<1000 m water depth) and 30% (>1000m water depth). Although these numbers do not fall within the stated range (80-90% on continental margins), we think that our model does a reasonable job, given the fact our coarse-resolution ocean model uses a strongly lowpass-filtered bathymetry by design.**

**The following lines were added in the section where the preindustrial model state is discussed (p481):**

**"The partitioning of POM burial between the deep ocean (>1000 m water depth) and the continental margin (<1000 m water depth) is 70% and 30%, respectively, while observations indicate that 80-90% of the POM burial is on continental margins. This model bias is likely linked to the coarse horizontal resolution and the simple**

continental runoff-scheme, compromising the representation of near-coast processes."

2. In the real ocean, the benthic turnover of phosphorus and organic carbon are partly decoupled and do not follow Redfield stoichiometry. The mean molar ratio between POC and total P in deep-sea sediments is not 106 but rather 20-30 since phosphate released from organic matter forms authigenic minerals in sediments and adsorbs to iron oxides and other sediment surfaces (BATURIN, 2007; WALLMANN, 2010). Moreover, a decrease in bottom water oxygen tends to enhance POC burial (BURDIGE, 2007) while less P is buried under low oxygen conditions (VAN CAPPELLEN and INGALL, 1994). I do not fully understand how these opposing trends are considered in the benthic model. Does the benthic model assume Redfield stoichiometry? How does bottom water oxygen affect the burial efficiency of POC, P, and POM?

A description of the sediment diagnosis model and the governing equation is given in Tschumi et al., 2011. The spatial model domain is restricted to the diagenetical zone of the sediments which is assumed here to be the top 10 cm of the surface sediments. Any solid material leaving this domain disappears into the subjacent diagenetically consolidated zone.

The model strictly relies on fixed Redfield ratios in organic matter (C:P = 117:1). Adsorption and desorption of P on oxides is not taken into account. For example, the oxidation rate of organic carbon,  $R_{oxy}$ , is governed by the concentration of oxygen in the pore water ( $[O_2]$ ) and the concentration of POC in the solid phase,  $c_{POC}$ :

$$R_{oxy} = r_{oxy}^* c_{POC} [O_2] \quad \text{for } [O_2] > 0$$

$r_{oxy}^*$  is a rate constant. Thus, the higher the oxygen concentration and the higher the POC concentration the larger the flux of carbon from the solid phase to the pore water. Fluxes of other elements are coupled to fluxes of carbon by fixed Redfield ratios (P:N:C:O<sub>2</sub>=1:16:117:-170).

The ratio of C:P in organic material found in various sediments has found to deviate by more than an order of magnitude (between 1:20 up to ~4500) from the classical Redfield ratio (1:106). This was interpreted as evidence for preferential burial of organic P compared to organic C under low oxygen conditions and as preferential burial of organic C under high oxygen conditions (e.g. van Cappellen and Ingall, 1994).

This view is challenged by (Anderson et al., 2001) who suggest that early analyses suffered from limited analytical abilities and that detrital P must be distinguished from other phases of P for a correct interpretation of P:C ratios in sediments. These authors define reactive P as the sum of organic P, oxide-associated P and authigenic P and call for the conversion of organic P to oxide-associated P and authigenic P. Anderson et al. state: "*Because most P is delivered to the sediment as P<sub>organic</sub> and is transformed to P<sub>authigenic</sub>, sometimes with P<sub>oxide-associated</sub> as an intermediate phase, organic C/P<sub>reactive</sub> ratios give a better indication of the original C /P ratios of the organic matter buried in the sediments.*" The mean over all their data yields a C<sub>organic</sub>/P<sub>reactive</sub> ratio of 124 +/- 63, indistinguishable from the Redfield ratio used in our model. Thus, they explain high C:P ratios in organic matter within consolidated sediments by the transfer of organic P to authigenic P.

These authors explain the lower than Redfield C:P ratio of organic matter in sediments with low organic carbon (< 2% weight-fraction) with the degradation of POC with age within buried sediments.

Here, we follow the view of Anderson et al. and apply fixed Redfield ratios. Thus the burial flux of POP and POC scale with a factor of 117 and no preferential burial of C or P occurs. We complicity state this fact in the paragraph discussing caveats (p495,114).

The description of the sediment module at the bottom of p480 is modified to read:

A 10-layer sediment diagenesis model (Heinze et al., 1999; Gehlen et al., 2006) is coupled at the ocean floor. It features the same horizontal resolution as the ocean model. It dynamically calculates the transport, remineralisation/redissolution and bioturbation of solid material within the top 10 cm of the seafloor as well as pore-water chemistry and diffusion as described in detail in Tschumi et al. (2011). Modeled tracers are the four solid components ( $\text{CaCO}_3$ , opal, POM and clay) and the eight pore water substances (DIC, DIC-13, DIC-14, total alkalinity, phosphate, nitrate, oxygen and silicic acid). The pore water  $\text{CO}_3^{2-}$  concentration determines whether, and at which rate,  $\text{CaCO}_3$  dissolves. The inclusion of the dissolution and burial process of  $\text{CaCO}_3$  is crucial for simulating the so-called carbonate compensation. The oxidation rate of POM within the diagenetic zone depends linearly on the pore water concentration of  $\text{O}_2$  and the weight fraction of POM within the solid phase. Denitrification is not taken into account in this version of the model. The corresponding reaction rate parameters are global constants and a decrease in the reactivity of organic material by aging within the diagenetic zone is not considered (Middleburg et al., 1993). Fluxes of carbon and related elements due to POC degradation are coupled by fixed Redfield ratios ( $\text{P:N:C:O}_2 = 1:16:117:-170$  for oxidation). The model assumes conservation of volume, i.e. the entire column of the sediments is pushed downwards if deposition exceeds redissolution into pore waters. In this manuscript, the term “burial” refers to the net tracer-flux at the ocean–sediment interface, i.e. deposition–redissolution of the particulate material. The burial-efficiency, i.e. the ratio burial/deposition of a solid species, is controlled by i) the rate of redissolution within the sediments and ii) by the rain-rate of solid species, which controls how fast the sediment-column is pushed downwards. Any solid material that is pushed out of the diagenetic zone (top 10 cm) disappears into the subjacent diagenetically consolidated zone. The fate of the material pushed below 10 cm depth is of no further interest for this study (it is known that preferential degradation of POC versus that of POP and the conversion of POP to oxide-associated P and authigenic P within the consolidated zone cause C:P ratios of organic material to deviates substantially from the classical Redfield ratio (Anderson et al., 2001)). Input of terrestrial organic matter into the ocean and burial of terrestrial organic matter is not explicitly considered (see e.g. Regnier et. al, 2013). Similarly, the cycling of P associated with iron and other oxides is neglected as estimates suggest that 97% of the P delivered to the sediment-water interface is in the form of organic matter (Delaney, 1998). The specific chemical composition of the organic matter, particle grain size of the sedimentary material and available area for absorption for organic matter (Hedges and Keil, 1995) as well as spatio-temporal variations in mineral deposition rates or sediment porosity, which likely influence organic matter preservation and burial (Burdige, 2007), are neglected.

3. Towards the end of the transient model runs, the global POM burial rate relaxes to the steady state value determined by the constant riverine phosphorus flux (s. Fig. 3f) while the depositional rate of POM (= POM rain rate to the seafloor) is maintained at an elevated level by the deepening of the remineralisation depth (s. Fig. 3d). The burial efficiency of POM =burial rate/rain rate is thus reduced at this stage (50 – 100kyr) compared to the control run. The authors should explain how their benthic model facilitates this change in burial efficiency. Is this change related to the changing oxygen contents of ambient bottom waters? Where does this change happen: in the deepsea or at continental margins? What is affected: POC, P or both (POM)? The POM deepening experiments result in a dissolved oxygen depletion at the deep-sea floor and an oxygen increase in shallow waters (<1000 m water depth, s. Fig. 5d). Are these changes responsible for the overall decrease in POM burial efficiency and -if so, what model assumptions are made?

The burial efficiency is mainly driven by the availability of oxygen in sediment pore waters and by the total particle rain. The burial efficiency does only slightly change in our standard POM deepening experiment, namely by ~5% from 0.29 to 0.276. The reason for this small change is that the burial-efficiency increase in the deep sea roughly cancels the burial-efficiency decrease at shallow depths. This change is indeed driven by the change in ambient oxygen concentrations (Fig. 5d). The following sentence has been added in the sediment-model description:

"The burial-efficiency, i.e. the ratio burial/deposition of a solid species, is therefore controlled by i) the rate of redissolution within the sediments and ii) by the rain-rate of solid species, which controls how fast the sediment-column is pushed downwards"

The model's response is now discussed on page 486, l2ff. This text now reads:

"Increased POM deposition (rain) tends to increase POM burial and to alter POM oxidation. The change in the amount of POM oxidised in the sediments varies in space and time: in the deep ocean, reduced oxygen availability in the porewater decreases local remineralisation. On the other hand, increased oxygen levels at coastal margins promote the remineralisation in the sediments in these regions. At the equilibrium POM burial rate has to balance input of phosphorus by weathering. The result is an initial spike in POM burial by almost 80%, about four times larger than the relative initial increase in deposition, in response to an initial oxygen reduction in the pore water. Afterwards, POM deposition and POM burial decreases quickly within a few centuries and then more slowly to approach steady state over the next few millennia. As POM deposition stabilizes on a higher level while POM burial relaxes to the initial value, the so-called burial-efficiency=burial/deposition slightly decreases in the long run by ~5%.

4. As far as I understand, the burial efficiency is a key model parameter since it exerts a strong bottom up control on the final steady state results attained in the model runs (including atmospheric pCO<sub>2</sub>). The authors should thus carefully explain how their model controls the POM burial efficiency and how the burial efficiencies generated by their benthic model compare to benthic observations.

For a given POM deposition field, the burial efficiency in the model is governed by the availability of oxygen in the pore water affecting POM oxidation and by the deposition of solid material affecting how fast the sediment is pushed towards the consolidated zone. In the long run, POM burial has to match the input flux by weathering in the model. If burial exceeds weathering input, ocean phosphate inventory decline and in

turn export production and POM deposition decline to achieve a balance between burial and weathering flux.

In the global average, our benthic model simulates a steady-state burial-efficiency of ~0.29 which is too high compared with benthic observations of ~0.1 (Sarmiento & Gruber, 2006, page 261, table 6.5.1). This discrepancy is again caused by the poorly resolved bathymetry at continental margins, leading to too low deposition and remineralization and thus the model overestimates the burial-efficiency there with efficiencies close to 1 in certain gridboxes. In the area-weighted global average — which is dominated by the deep ocean — the modelled steady-state burial-efficiency is 0.085 and thus agrees well with observations.

5. The authors should try to discuss to what degree a mismatch between the predictions of the benthic model and benthic observations would affect the major conclusions of their study.

We argue that changes in the imbalance between globally integrated weathering and burial fluxes are the dominant drivers on millennial time scales for changes in seawater chemistry and atmospheric CO<sub>2</sub> in response to changes in the remineralisation depth. The absolute value of the burial-efficiency seems not to be a crucial factor. We therefore believe that our findings are robust, at least qualitatively. A situation where an increased POM rain (due to a slowed watercolumn remineralization) would result in a *decreased rate* of POM burial seems rather unlikely.

Still, we agree that it is important to discuss these points. We added the following lines in the discussion (caveats) section on p495:

"There are also limitations regarding the sediment model. For example, the spatio-temporal variability in the deposition of mineral particles or the influence of particle grain size on organic matter preservation are neglected. The coarse resolution hampers the representation of coastal and continental boundaries, where most POM deposition, remineralization and burial occurs (e.g. Wallmann et al., 2012). The model does not resolve river deltas and estuaries and their carbon cycle (see e.g. Regnier et al, 2013). Another caveat is that denitrification within the sediment is not represented by our model, eventually leading to a bias in the long-term response of POM degradation and thus burial-efficiencies. Therefore, our findings are to be confirmed and refined by a higher-resolved ocean models with a more complete representation of sediment processes."

The paper should definitely be published but it needs a more detailed presentation and critical discussion of the benthic model module.

Done, benthic model description extended (see above).

Further minor comments are given below:

Page 486, bottom: “The adjustment to a new equilibrium takes longer for the phosphorus inventory, co-governing POM burial than for the alkalinity inventory, co-governing calcite burial.” should be replaced by: “The adjustment to a new equilibrium takes longer for the alkalinity inventory, co-governing calcite burial than for the phosphorus inventory, co-governing POM burial.”

done

Page 488 line 20: “The results” should be replaced by “These results”

Text changed to "The result is ..."

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