**Geoscientific
Model Development
Discussions**

Interactive comment on "LOSCAR: Long-term Ocean-atmosphere-Sediment CArbon cycle Reservoir Model" *by* R. E. Zeebe

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1 General comments

In this paper R. Zeebe describes the Long-term Ocean-atmosphere-Sediment CArbon cycle Reservoir model (LOSCAR). Detailed model equations are provided together with comprehensive sets of parameter values and in- and output examples for two applications.

The paper falls within the scope of *Geoscientific Model Development*. As stated and discussed at (in my opinion, unnecessary) length, applications of the model have been published before. I do not see any inconvenience with respect to that kind of prior

publication. However, I would then expect some significant extra added value from the model description in this paper that would compensate for the reduced "novelty" aspect expected from any newly published scientific paper. The current version of the manuscript falls somewhat short of providing this extra added value. Actually, not only applications, but even the details of the most important parts of the model have been published before. The salient feature of the sediment model, the variable porosity as a function of the detrital/carbonate composition, has been described in full detail in Zeebe and Zachos (2007); large parts of the description provided here are actually identical to that in Zeebe and Zachos (2007). Unfortunately, shortcomings in that description have not been addressed here: e. g., it is still not known how chemical erosion is implemented, i. e., how the below-surface sediment characteristics are stored and used in case of chemical erosion. The more fundamental ocean tracer equations are far from complete, important information is missing.

While the scope of applicability is described and illustrated in an adequate manner, the expected discussion of the limitations of the approaches adopted (see *Manuscript Types* http://www.geoscientific-model-development.net/submission/manuscript_types.html) is insufficient. The two most important aspects of the model – according to the presentation in the paper – would actually need some in-depth discussion: the representation of carbonate dissolution and the weathering feedback. It is not clear to what extent the adopted sedimentary carbonate dissolution model is realistic; the adopted pCO_2-weathering feedback representation is certainly *not* realistic on all of the time scales focused on here (see *Specific Comments* below for details).

The rooting of the work in the existing literature also needs to be improved: some of the references provided are not well focused, some of them are not entirely comprehensible, others even misleading (see examples in the *Specific Comments* below). In this regard, I find that already the motivation for the development and the inferred importance of LOSCAR is overstated. There are a number of models similar to LOSCAR that have been around for 10–20 years and that differ only in details from it or that

could be in no time at all amended to become equivalent to LOSCAR. The "gap" that LOSCAR is supposed to fill is actually already well populated. This does not reduce the relevance of an additional model such as LOSCAR. I find it always recommendable to have different models of similar complexity to address a given problem and therefore surely welcome this new model.

Because of the nature and amount of shortcomings and weaknesses made out, I recommend a major revision of this discussion paper before it will be suitable for publication. The paper should provide a significant complement to the information already published, present a fair description of how this model compares to other, previously published ones and also provide a consistent discussion of the fundamental hypotheses and the limitations of the adopted procedures.

2 Specific comments

2.1 General model features

There are clearly too many box models of the ocean-atmosphere carbon cycle to list only one tenth of them. However, there are not only "a few studies that have considered sediments" (p. 1436, l. 25), but actually quite an impressive number of them (by order of first publication of a variant):

- Keir and Berger (1983, 1985) and Berger and Keir (1984) use the same sedimentary carbonate dissolution flux formulation in their box-model studies as the one used here;

- Keir (1988) uses a sedimentary representation based up Keir (1982), the same as the one used here;

- Opdyke and Walker (1992) and Walker and Opdyke (1995) include carbonate dissolution flux in the surface sediment in their model (albeit with linear dissolution rate) and also consider chemical erosion;

- the model of Munhoven and François (1996) mentioned in the general list, as well as the earlier version described in Munhoven and François (1994) include sedimentary carbonate dissolution based upon the same formulation as the one used here, and also consider chemical erosion;

- Sigman et al. (1998) use the CYCLOPS model of Keir (1988), but replace the original formulation by a parametric representation of the carbonate dissolution processes based upon results from the more comprehensive one-dimensional early diagenesis model of Martin and Sayles (1996);

- Ridgwell et al. (2003) use the well-known PANDORA box model of the ocean carbon cycle coupled to a sediment model derived from Ridgwell et al. (2002);

- Toggweiler (2008) uses a parametrization of the carbonate compensation, which can be seen as a simplistic representation of sedimentary processes;

- and there are certainly still others.

Obviously, every model that has sediments where there is burial of material must include riverine fluxes, i. e., weathering fluxes. Some of the studies cited above even distinguish between carbonate and silicate fluxes. Munhoven and François (1994, 1996) do so; Toggweiler (2008) uses a linearized version of the same weathering flux expressions as those used here.

The remarkable feature with LOSCAR, in comparison with previously existing models, is the consideration of variable porosity. This is actually also the only noteworthy difference with the model of Munhoven and François (1996) (see Munhoven (1997) for full details).

2.2 Tracer equations

The list of tracers considered in LOSCAR includes O_2 and $\delta^{13}C$. Although there are some results related to these two tracers in Figure 4, the paper does not provide any information whatsoever regarding their evolution equations. The omission of details regarding $\delta^{13}C$ is especially surprising, as this tracer is explicitly discussed in the tuning section (pp. 1457-1458). It would be useful to have at least a general description of the features of the relevant equations (no need to multiply the equations). Details to be provided should, at least, include fractionation factors, specify how $\delta^{13}C$ is traced in sedimentary carbonates, what $\delta^{13}C$ signatures of the weathering fluxes are used, hos air-sea-exchange is represented, etc. I guess O_2 is mainly used as a diagnostic tracer, with no limiting function.

It is also not entirely clear how the dissolution of $CaCO_3$ in the water column is implemented. Does this process lead to a water depth dependency of the carbonate rain at the sea-floor?

2.3 Sediment model

2.3.1 Rationale behind carbonate dissolution?

The carbonate dissolution flux is essentially proportional to the square root of the abundance of carbonate in the sedimentary mixed layer and to a given power n_{sd} of the deviation of the carbonate ion concentration from saturation (equations (24)-(25), p. 1449). The work of Sigman et al. (1998) is cited as a reference for this expression, although Keir (1982), cited elsewhere, already derived it more than fifteen years before.

The actual rationale behind the expression adopted in LOSCAR is, regrettably, not presented, not even summarized. We only read (p. 1446, ll. 13–14) that the model

"[. . .] has been constructed similar to other models of this class (e. g. Keir, 1982; Sundquist, 1986; Sigman et al., 1998)." Although the final expressions relating the flux of CO_3^{2-} in the two models by Keir (1982) and Sigman et al. (1998) are identical, they were derived along sensibly different lines:

- Keir (1982) considers a homogeneous sedimentary mixed layer and solves the diffusion-reaction equation for porewater CO_3^{2-} concentration to establish expression (24) in the manuscript;

- Sigman et al. (1998) fit an expression of the same form to results from the more complete 1D diagenesis model of Martin and Sayles (1996) that also considers the effect of organic matter respiration on carbonate dissolution in the surface sediment, not considered here.

Sundquist (1986) does not give sufficiently detailed information about how exactly his model was built; however, that information can be found in Sundquist (1990), which would thus be more appropriate as a reference; it furthermore turns out that Sundquist uses a slightly different expression.

In the kind of technically oriented model description paper that we are commenting on here, the basic hypotheses behind the approach actually used should be clearly and explicitly stated.

2.3.2 Limitations of the adopted approach?

The very same model is also described and solved by Boudreau (1997, pp. 235–238) who emphasizes that he is "[. . .] not trying to defend this approach as a good model for carbonate diagenesis". Unfortunately, Boudreau (1997) does not provide any further hints about why this model fails to be a good one. An important question to address and discuss here is thus:

What are the shortcomings and limitations of the approach?

This is also required by the *Geoscientific Model Development* instructions.

There are a few potential shortcomings that come immediately to my mind.

- The effect of organic matter respiration in promoting carbonate dissolution (Emerson and Bender, 1981) is neglected. Sigman et al. (1998) report that the dissolution at the saturation horizon represents 32% of the calcite rain when respiration-driven carbonate dissolution is included in their parametrization.

- The author himself (Zeebe, 2007) has shown that it is critical to consider the effect of a diffusive boundary layer at the top sediment interface. However, such a boundary layer was not considered in the model.

2.3.3 How is chemical erosion implemented?

Chemical erosion is emphasized as being a prominent feature of the model. Other models comparable to LOSCAR have taken this process into account before (e. g., Walker and Opdyke (1995) Munhoven and François (1996), Munhoven (1997), Ridgwell et al. (2002), Ridgwell et al. (2003)). The description about the way sub-surface sedimentary information is stored and used in case of chemical erosion in LOSCAR has not been provided before and needs therefore to be provided here.

2.3.4 Miscellaneous

The difference between "effective" rate law parameters (would it not be more appropriate to call them "apparent"?) and the reaction rate parameters is emphasized, but the

link between the two is not given: $n_{sd} = \frac{n+1}{2}$, where n is the reaction rate order (see Keir (1982), Munhoven (1997) or Zeebe (2007) for a details about this relationship). This link only holds if an approach similar to Keir (1982) is used. With the empirical approach of Sigman et al. (1998), it is only approximate.

2.4 Weathering flux and weathering feedback formulations

2.4.1 How realistic is the adopted weathering feedback?

Although appealing and also adopted in other models, the proposed weathering rate laws are not necessarily realistic on all of the time scales that the model is advocated for. First of all, the link between atmospheric pCO_2 and weathering rates is most probably not as direct as suggested by the rate laws from equations (11) and (12) – see, e. g., Gwiazda and Broecker (1994) and Roelandt et al. (2010).

Munhoven (2002), e. g., has shown that there was only little change in the global weathering fluxes to the ocean between glacial and interglacial times, essentially due to the changing continental outlines as a result of the changing sea-level. Expressions such as those used here cannot capture this effect.

2.4.2 Parameters of the weathering feedback

The paper provides the standard values used in the model for the adopted weathering flux formulations ($n_{Si} = 0.2$ and $n_C = 0.4$, from Table 3). For a detailed discussion of the uncertainties of the parameters in the weathering rate laws, readers are asked (p. 1444, l. 24 – p. 1445, l. 1) to refer to Uchikawa and Zeebe (2008). Uchikawa and Zeebe (2008), also given as a reference in Table 3, however, actually present only a few sensitivity experiments with different values for the feedback orders, without much discussion. That paper in turn refers to Zeebe et al. (2008) and Zachos et al. (2008)

for the default values of the laws (the same as those used here). In Zeebe et al. (2008) and Zachos et al. (2008) my search for more extensive information ended fruitlessly.

Finally, I looked up Walker and Kasting (1992) where the flux expressions could also come from. Walker and Kasting (1992), however, use completely different values of $n_{Si} = 0.3$ and $n_C = 1.0$. What was the motivation for modifying the values of these parameters LOSCAR been modified from the original ones?

The used weathering rate laws need to be explained and discussed in detail here – they are presented as a key characteristic of LOSCAR – and readers must not be chased through an endless chain of papers in quest of critical information, that they possibly miss in the end.

2.4.3 Miscellaneous

The chemical reaction described by equation (10) (p. 1444, l. 3) is commonly known as the *Urey reaction* (Urey, 1952) although is has been shown (Berner and Maasch, 1996) that it had been discovered more than one hundred years before by Ebelmen (1845). It would be fair to refer to that equation as the *Urey-Ebelmen reaction* and to specify this here.

I am not convinced that the kind of reasoning followed on p. 1444, ll. 8–15 to derive a restoring time for silicate weathering makes much sense, even if it yields figures that are about right.

First of all: what should we focus on? global ocean TCO_2, as advocated here, or alkalinity (Rickaby et al., 2010)? I strongly doubt that one may apply the residence time approach on a non-conservative species such as CO_3^{2-} to derive an adjustment time. Broecker and Peng (1982, p. 281) calculate the time scale of carbonate compensation along similar lines. Their approach was convincingly criticized by Boyle (1983) who

proposed a more rigorous way for calculating that time scale. Finally, the numbers that enter this kind of calculation appear to be "adjustable." Broecker and Peng (1982) use a TCO_2/CO_3^{2-} ratio of 30 (here: 20) to derive a carbonate compensation time scale of 6000 yr (here: 10 kyr, no reference given). Note also that the calculation of Broecker and Peng (1982) is possibly biased by a residence time of inorganic carbon in the ocean that might be too long by a factor of two (Munhoven, 1997). Accordingly, their carbonate compensation time scale would have to be revised down by a factor of two as well. The validity of the approach is, in my opinion, highly debatable.

This whole paragraph is only secondary to the model description and can be safely deleted. If a time scale is really desirable here, why not resort to the original 400 kyr given by Walker et al. (1981), who base themselves on the turnover time of carbon in the atmosphere and ocean with respect to the CO_2 release from volcanism and metamorphism?

2.5 Ocean chemistry and other miscellanea

The "Miscellaneous" section, and especially subsection 7.2, is the most informative one as we get details that cold not be found in previous studies (e. g., Tyrrell and Zeebe, 2004).

I am somewhat puzzled by the potential problems reported with the *p*H calculation routine (p. 1452, l. 16). In my experience, albeit with a non simplified algorithm, trouble is more probable with low than with high TA/TCO$_2$ ratios. But this might be different with the simplified approach adopted here.

The reference to Zeebe (2011) on p. 1455 at l. 24 is rather mysterious. That commentary paper does not provide any useful information relevant in this context (meaning and choice of values of the climate sensitivity parameter s). Please explain or discard

this reference.

3 Technical corrections

Title: *Geoscientific Model Development* requires both the model name and the version number (missing) to be given in the title.

Throughout: for clarity, summation indexes should be given with summation symbols, the more since all sums do not run over the same indexes in some equations

p. 1437, l. 10: "[...] and more." Please delete, or precise *what* more. It would furthermore be helpful to have an exact definition of the CCD adopted in this work and to explain how its characteristics are determined.

p. 1438, ll. 2–3: It would be interesting to read about what bugs and numerical/scientific issues had to be addressed and about the impact of the corrections, or else, it would be better not even to mention this.

p. 1439, l. 14: avoid double negation "not unlike"; suggestion: replace by "similar to"

p. 1440, eq. (3): please specify the summation index with the summation symbols to increase readability. The exchange coefficient m_{lk} in the second sum must be inside the sum and the equation should read

$$V_k \left(\frac{dy_k}{dt} \right)_{\text{thm}} = T \sum_j (y_j - y_k) + \sum_l m_{lk}(y_l - y_k)$$

C580

Changing the summation index from j to l in the two sums is not helpful in my opinion.

p. 1469, Table notes: reference 'd' (Uchikawa and Zeebe, 2008) does not provide sufficiently relevant information about the weathering rate exponents. Please provide a significant primary reference.

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C584