

Interactive comment on “Latest Permian carbonate-carbon isotope variability traces heterogeneous organic carbon accumulation and authigenic carbonate formation” by Martin Schobben et al.

Martin Schobben et al.

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Received and published: 31 July 2017

On behalf of my co-authors, I would like to thank the reviewer for the detailed and constructive assessment of our manuscript. We have thoroughly considered the issues raised in the reviews of the original manuscript, and we provide a point-by-point response below.

Comment #1: I have two primary concerns for this paper, both related to the treatment of carbonate chemistry. First, how does the diagenetic (reactive-transport) model ac-

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count for changes in the carbonate system? It seems that the model considers CO₂ aqueous, bicarbonate, and DIC, but this is incomplete. Bicarbonate/CO₂ additions and subtractions to the DIC pool do not simply add/subtract to those supplies. Additions of those species will cause re-equilibrium among all species. These re-equilibrations will result in non-linear changes to calcite saturation.

Response #1: The carbonate chemistry is not accounted for in the current model, instead we chose to represent calcification by equation (4), the same approach used in other studies such as those of Fantle and DePaolo. We did so, for one important reason: although carbonate saturation is an important parameter that can be modulated by microbial activity, the extracellular polymeric substance produced by the same microbes has been invoked as well to control calcite nucleation. Considering this uncertainty we preferred a rate expression (equation 4) that does not put one particular mode of carbonate production over the other. So, in extension, there is also no re-equilibration among DIC species envisioned in the current model. In addition, it is quite challenging to incorporate parameters, such as pH, in these types of diagenetic models.

In our opinion, a more in depth understanding of microbial-steered calcification would be needed before carbonate chemistry could be included in models, similar to introduced here.

Fantle M.S. & DePaolo D.J. (2006) *Geochim. Cosmochim. Acta.* 70 : 3883-3904

Fantle M.S. & DePaolo D.J. (2007) *Geochim. Cosmochim. Acta.* 71 : 2524-2546

Comment #2: On a related note, I don't understand the kinetic rate expressions that are provided, and the explanations are insufficient. The authors cite Boudreau 1997 checked the reference and could not find an explanation, though it could be because the reference is a ~400pg book. Why are all of the rate expression factors of O₂ and SO₄²⁻? How does a monod constant compare to a solubility product or rate constant? Obviously I am not as well versed in these things as the authors of this paper, but I

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asked to other scientists in related fields and they were similarly confused. The authors must make these concepts more accessible to their target audience. Citing a 400 pg book is not sufficient.

Response #2: These rate expressions are the classical equations, as they have been used for the past 20 years (e.g. Meysman et al., 2003; Soetaert et al., 1996; Berg et al., 2003; Van Cappellen and Wang, 1996). Monod constants are factors that represent the inhabitation/limitation of a certain electron acceptor (in this case O₂ or SO₄²⁻). At high concentrations of oxygen, oxygen reduction will be efficient and other mineralisation pathways will be inhibited. At lower concentrations, oxygen reduction will be less efficient, and other pathways will gain importance. High sulfate concentrations will then in its turn inhibit methanogenesis. This leads to the chemical zonation as described by Froelich et al. (1979).

Although we appreciate that not everybody is experienced with the literature on theoretical modelling of sediment diagenesis, we do not think a detailed description of these formulations is required, as these have been standard for decades. We will change the text in order to make the meaning of a monod constant versus a rate constant and solubility constant more clear and we do understand that the reference might be not appropriate for people who want to find detailed descriptions, and therefore we will update these with the once mentioned above.

Meysman F.J.R. et al. (2003) *Comp. Geosci.* 29:301-318

Soetaert K. et al. (1996) *Geochim. Cosmochim. Acta.* 60 :1019-1040

Van Cappellen and Wang (1996) *Am. J. Sci.* 296:197-243

Berg et al. (2003) *Am. J. Sci.* 303:905-955

Froelich P.N. et al. (1979) *Geochim. Cosmochim. Acta.* 43:1075-1090

Comment #3: Second the authors assume constant boundary conditions for their model, but also recognize changes in the carbon isotope composition of seawater DIC

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as a result of “changes in the sources and sinks of the long term (>100 ky) carbon cycle.” The changes in the carbon cycle are also affecting changes in the carbonate chemistry, which should affect the ability of authigenic carbonate to precipitate and how much dissolution/equilibration takes place. See Payne et al., 2010 PNAS to start.

Response #3: We thank the reviewer for this important suggestion. Although carbonate chemistry is not explicitly incorporated in the model, the observations, as made in the Payne et al., (2010), could be envisioned to have consequences for the adopted DIC concentration and carbonate recrystallization/ dissolution rate (equation 4). We performed a new sensitivity test, and judged that increased DIC concentration (2–7 μm cm⁻³ DIC, Ridgwell 2005) can dampen δ¹³C variability, but only to a very small degree, see Figure 1d (of the response) below.

Ridgwell A. (2005) *Mar. Geol.* 217: 339-357

According to Payne et al, transient ocean acidification at the end-Permian mass extinction would have stimulated carbonate dissolution. If the DIC pool increased over the studied time interval, this change would have suppressed the temporal trend in the amplitude of the δ¹³C variance, as observed for both Iran and China. In addition, dissolved carbonate, but also alkalinity input via weathering, could have increased the post-extinction carbonate ion inventory. Carbonate saturation could, in such scenario, elevate the production of authigenic carbonates. When accepting both observations, this would in addition require a modulation of our simulated carbonate reactivity (i.e., expressed in equation 4) over the Permian–Triassic interval. As reactivity of carbonate equates to more δ¹³C variability, this would largely cancel out concomitant suppression of δ¹³C variability by an enlargement of the DIC pool (see above Figure 1d). As such these two parameters would largely oppose each other. Since, we do not know how to scale the carbonate reactivity (justifiable to the natural situation); we think that it is better to dismiss temporal variation in this parameter, at least, in the current model simulation. A model that incorporates all the nuances associated with biologically-controlled (or microbial-induced) calcite precipitation, dissolution and overall carbonate

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chemistry would presumably be an answer to the lack of this control. But, as already outlined, we think that far too many variables would be loosely (or un)constrained in such model, with our current knowledge of these processes. Hence, validation of our simple model remains more trustworthy and straightforward to interpret.

However, we will change the boundary conditions for DIC, from 2.2 $\mu\text{m cm}^{-3}$ (modern) to 4.5 $\mu\text{m cm}^{-3}$ (Payne et al. 2010), to better represent the Permian situation. These adjustments will slightly suppress the generated $\delta^{13}\text{C}$ variability (see above Figure 1d). Hence, we will replace Figure 8 of the original work, and include the results of the updated sensitivity test (Figures 5 and 6).

Comment #4: Below are some minor comments I have on the text and figures: The authors often use the term “sedimentation rate”, which I take to mean F_{carb} ? They do not seem to include F_{OC} under this definition? Regardless, the use of “sedimentation rate” is confusing and should be made more specific. Perhaps “carbonate sedimentation rate” or “calcite sedimentation rate”.

Response #4: This will be implemented where applicable.

Comment #5: Pg. 3, line 22 : What do the authors mean by “High carbonate ion concentrations”? Are we talking about DIC or CO_3^{2-} ? If these high values are predicted, why did the authors use modern DIC values in their model?

Response #5: This statement was not very precise and we will refer to the larger DIC pool, as discussed in Payne et al. (2010) and Ridgwell (2005), for the Permian–Triassic ocean. In addition, the boundary conditions of the model will be changed (as discussed above).

Comment #6: Pg. 3, line 26: “High carbonate ion concentrations are invoked..” True, and this implies a change in seawater carbonate chemistry that should be considered in the time series diagenetic model.

Response #6: This change will be implemented.

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Comment #7: Pg. 4, lines 7–15: The phrases in italics are confusing. I am having a hard time parsing their meaning and tying them to clauses before them. Are they even used later? I would just get rid of them.

Response #7: These phrases return in the section dealing with time series simulation (Section 5). But we will omit these phrases in the revised version.

Comment #8: Pg.4, lines 16: “should be studied”. To carry out this investigation” implies action in the past.

Response #8: Ok

Comment #9: Pg. 6, lines 3–13: Can the authors reference a figure here? It would be easier to follow the explanation with a visual aid.

Response #9: Ok

Comment #10: Section 3.2.1: Have the authors considered the role of other metabolisms, such as Fe and Mn reduction? These metabolisms can yield much more alkalinity than sulphate reduction (see Bergmann et al., 2013 in Palaios). I suspect that Fe reduction is not quantitatively important for most of the Phanerozoic when sulphate and O_2 are high, but if sulphate and O_2 is low at the P/T it could be significant.

Response 10: Alkalinity and carbonate chemistry do not play a role in the current model construction (see above). The selection was primarily based on whether carbonate precipitates formed by these specific metabolic pathways have been described in the literature. In addition, the quantitative importance of sedimentary OC consumption by aerobic heterotrophs, sulfate reducing microbes and methanogens was used as a selection criterion.

Comment #11: Pg. 10, lines 10–12: “The previous...solid carbonate.” This sentence is hard to follow. Please consider clarifying.

Response #11: Ok

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Comment #12: Figure 1: The median line is completely obscured for the Iran plot. Can the authors move the line to in front of the data points?

Response #12: Ok

Comment #13: Pg. 14, line 27: “depleted and “heavier” are incorrect terms. Should be “lower” and “higher”. From Sharp 2007 (Principle of Stable Isotope Geochemistry pg. 16): “As numbers, delta values can be high or low, positive or negative, but not heavy or light,(nor can they be) . . . depleted or enriched.”

Response #13: This will be corrected accordingly.

Comment #14: Figure 3: What is the range of values represented by the green colors in the biozone thickness/duration graphs? Does more saturated mean shorter or longer?

Response #14: This will be clarified.

Comment #15: Figure 7: I don't understand the point of this figure. I understand that the authors are changing the distributions from which the F_OC is generated in the model, but the rest of figure is lost on me.

Response #15: This will be better explained in the revised version.

Comment #16: Pg. 19, line 5: Can the authors elaborate in how D13C_primar-bulk was derived in Schobben et al, 2016? It would be usefull to do here, so the reader can understand the paper without first reading the other.

Response #16: A full explanation will be given in the revised version.

Interactive comment on Clim. Past Discuss., <https://doi.org/10.5194/cp-2017-66>, 2017.

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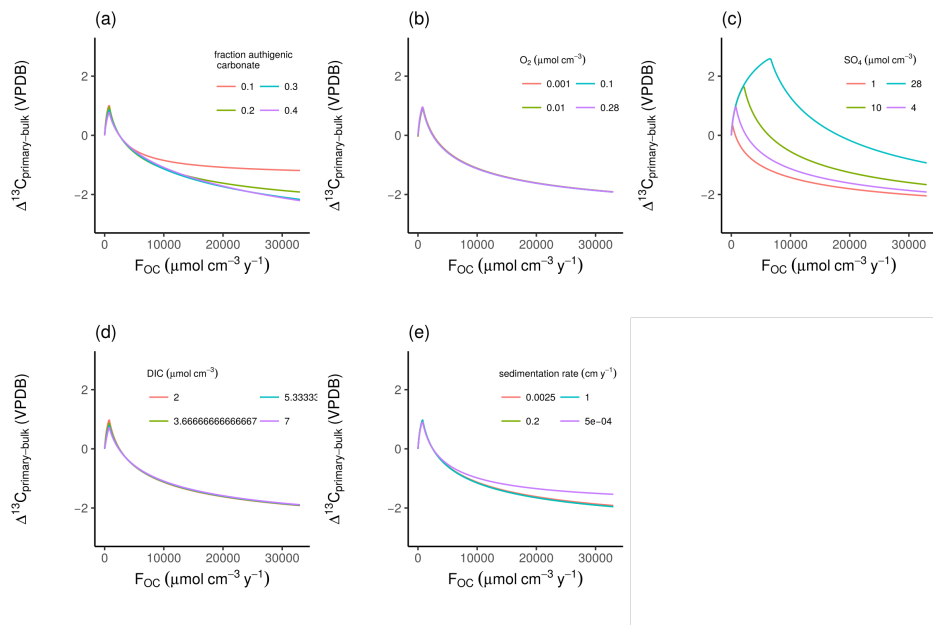


Fig. 1. Sensitivity experiments for a range of parameters of the sedimentary and marine environment on diagenetic altered carbonate (Palaeozoic bio-irrigation and bio-diffusion included, see AC1)

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