

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

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We would like to thank the reviewer for the constructive comments on the manuscript. We provide a point-by-point reply to concerns prompted by the reviewer. In some cases we agree with the reviewer and in other cases we do not. In the latter case we give a full explanation as to why we regard the criticism as unfounded.

Comment #1: The authors try to interpret the scatter in the  $\delta^{13}\text{C}$  records as recrystallization with an organic carbon source during marine diagenesis. However, it is also

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possible that some of these variations may have been generated by meteoric diagenesis. Thus, more discussions on this point are required, and it's better to include some petrography or geochemical evidences. The variations may also be generated by changes of rock type, minerals and calcified fossil species. Thus more descriptions on the samples are necessary.

Response #1: We of course agree that lithology, diagenesis (including that by meteoric waters), polymorphism and polymorph-specific C isotope values can alter C isotope values. However, we point out that our conceptual model is an exercise to show that diagenetic pathways, fuelled by marine organic matter, can produce the observed patterns. This does not necessarily mean that the real variation is - in all instances - caused by this mechanism, but we merely point to its excellent potential to explain the magnitude of the variations and the temporal pattern of variability across the P-Tr boundary.

In addition, a large suite of petrological work has already been performed on most of the studied sites (referred to in the original work and the online supplementary text). These studies point to the unlikelihood of diagenetic alteration of these particular suites of rock by the interaction with meteoric fluids. We further consider it unlikely that polymorphic variations can account for some of the larger  $\delta^{13}\text{C}$  fluctuations (Section 6.1).

If we included a petrological study within the main text, it would substantially increase the length of an already long text and detract from the overall message. We will, however, stress in the revised work that the model serves as a new concept and an alternative to classical views on carbonate rock diagenesis.

Comment #2: The data compiled from the Meishan section in South China maybe can preclude the influence of seawater chemistry. However, the Iran data do not come from the same site. The scatter in  $d^{13}\text{C}$  may be generated by spatial heterogeneity in seawater chemistry rather than diagenesis.

Response #2: We agree with this possibility, as stated in lines 12 to 14 on page 22.

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However, trends in residual  $\delta^{13}\text{C}$  variability from both regions show the same temporal pattern (Figure 3), suggesting that the postulated diagenetic mechanism is of global significance. This prevents the interpretation of variations as observed among different sites of Iran in terms of heterogeneity in seawater chemistry, as it might just as well relate to the described diagenetic mechanism. Additional discussion will be added in the revised work.

Comment #3: The authors have also talked about authigenic carbonates. A definition on authigenic carbonates is required. If the carbonates were mainly formed by recrystallization, their  $\delta^{13}\text{C}$  value may have been changed due to the exchange of carbonate ions with pore-water. Can this type of carbonates be classified into authigenic carbonates? Except some shells, all ancient carbonates have suffered from recrystallization. Does this mean that all the ancient carbonates are authigenic carbonates?

Response #3: Mixing of dissolved carbonate and metabolic-derived carbon is accounted for in the current model. This is visually expressed in Figure 4b,d and mathematically expressed in equation (4) which accounts for the rate of dissolution and crystallization. Since dissolution adds new DIC to the porewaters, this constant exchange somewhat buffers the metabolic-derived carbon signal

However, the reviewer is correct in expressing concerns about the original definitions where “authigenic carbonate” included equilibrium recrystallization that occurs over a range of sediment depths and microbially-mediated carbonate cementation (mostly occurring at the sediment-water interface). The former mechanism comprises relatively buffered carbonate and is therefore probably better defined as a diagenetically altered carbonate rock. In which the carbonate has partially dissolved and been replaced by a less reactive phase. We will include an updated definition in the revised manuscript, where we divide between diagenetically altered carbonates and authigenic carbonate addition.

Comment #4: Page 2, line 13 methanogenesis belongs to degradation of organic mat-

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ter.

Response #4: Methanogenesis will be omitted.

Comment #5: Page 5, section 3.1.2. Some of the d13C data for the Meishan section are very old and are less -5‰ which may be generated by analytical error.

Response #5: The precision of carbonate carbon isotope measurements has not changed over the last decades, and therefore does not introduce an increasing measurement bias with progressively older studies.

Comment #6: Page 7, equation (1), why is not a concentration conversion factor  $(1-\varphi)/\varphi$  in the reaction term? equation (2), I guess  $D_b(z)$  is biodiffusion here, should describe it and also write down the function.

Response #6: This is because we express our reaction terms as [moles /volume sediment /time], and our concentrations as [moles/volume pore water] or [moles/volume solid phase]. In order to come to the right units in the total partial derivatives, one needs to correct only the concentrations (see e.g. Meysman et al., 2015).

$D_b(z)$  is indeed the biodiffusion coefficient, which is assumed to be constant in a layer with thickness  $z_b$  (2 cm, after Dale et al. 2016 for the Palaeozoic) and had a value of 1 for the exponential coefficient  $\lambda_{D_b}$  and 5 cm<sup>2</sup> yr<sup>-1</sup> for  $D_{b0}$  (after Dale et al. 2016 for the Palaeozoic) ;

$$D_b(z) = D_{b0} \text{ for } z \leq z_b$$

$$D_b(z) = D_{b0} \exp(-(z-z_b)/\lambda_{D_b}) \text{ for } z > z_b$$

This form has been described before by Soetaert et al., 1996.

We will add a short description and an explicit mention of the function of the biodiffusion coefficient.

Dale A.W. et al. (2016) Geochim. Cosmochim. Acta. 189:251-268

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Meysman F.J.R. et al. (2015) *Geochim. Cosmochim. Acta.* 152:122-141

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

Comment #7: Table 2. I don't know why  $SO_4/(SO_4+KSO_4)$  is in in the reaction rate law of anaerobic oxidation of methane

Response #7: This is a typo and has to be corrected; the limitation of sulfate concentration is already included in the direct dependence of the AOM rate on the sulfate concentration. Thanks for noticing this.

Comment #8: Page 9, line 15. The sedimentary rate may have been changed across the P-T boundary.

Response #8: Yes, and we account for this as well in the timeseries simulation. However, as can be seen in Figure 5 and 6, the sedimentation rate has little effect on the sediment chemical zonation, and consequentially on the  $\delta^{13}C$  variance.

Comment #9: Page 14, line 15. "The inverse relationship suggest that  $d^{13}C_{carb}$  variability is not controlled by the increased potential sample size." This doesn't make sense to me. If there is more sampling effort on short interval, it is possible to capture larger  $d^{13}C$  variability. Could you show the relationship between the  $d^{13}C$  variabilities and the numbers of data of different intervals?

Response #9: This has admittedly been written in an awkward manner and needs more clarification in an updated manuscript. Essentially the whole of section 3.1.3 (i.e. the subsampling routine) is already designed to mitigate this effect. Indeed sampling intensity increases over the P-Tr boundary beds and so we needed confirmation that this sampling artefact did not skew our results. This exercise is an integral part of the original work. The results of the subsampling routine are depicted in Figure 3. (Watercolour Regression curves), which show that sampling intensity does not create the pattern of increased  $\delta^{13}C$  variability.

What has been written at line 15, merely points to the uneven distribution in time cap-



tured by some of the biozones. Units of longer duration could theoretically corroborate with more temporal variation of marine DIC-  $\delta^{13}\text{C}$ . However, this does not seem to be the case, so we concluded that besides the changing sampling resolution, expanded biozones did not generate the  $\delta^{13}\text{C}$  variability.

Comment #10: Figure 5 is good. Could you also show the influence of biodiffusion? The intensity of biodiffusion could be a function of oxygen level. It is better if bioirrigation is also included.

Response #10: We will include the effects of bio-diffusion and bio-irrigation on  $\delta^{13}\text{C}$  variability in the updated manuscript. Hence, we will replace Figure 8 of the original work, and include the results of updated sensitivity tests (Figures 5 and 6 of the original work). To account for bio-irrigation as a non-local exchange process, in which pore water is exchanged with bottom water, we will introduce the following formulation:

$$I_{\text{irr}}(z) = \alpha(z) (C_{\text{ow}} - C(z))$$

The quantity  $\alpha(z)$  represents the depth-dependent irrigation intensity, and the solute concentrations of the bottom water and at depth are given by;  $C_{\text{ow}}$  and  $C(z)$ , respectively. The attenuation of bio-irrigation intensity will be formulated as follows:

$$\alpha(z) = \alpha_0 \exp(-z/X_{\text{irr}})$$

where,  $\alpha_0$  is the irrigation coefficient at the sediment water interface, and  $X_{\text{irr}}$  is the attenuation coefficient. For the baseline conditions we take Palaeozoic conditions for bio-diffusion and bio-irrigation that are based on Dale et al. 2016 ( $D_{\text{b0}} = 5 \text{ cm}^2 \text{ yr}^{-1}$ ,  $z_{\text{b}} = 2 \text{ cm}$ ,  $\alpha_0 = 50 \text{ yr}^{-1}$ ,  $X_{\text{irr}} = 1 \text{ cm}$ ).

By conducting sensitivity experiments, we deduced the importance of changing these parameters under average OC sedimentation ( $730.5 \mu\text{mol cm}^{-2} \text{ yr}^{-1}$ , after van de Velde & Meysman 2016). Bio-irrigation attenuation with depth and the irrigation coefficient modulate the amplitude of the carbon isotope variations to some extent (Figure 1a of the response). However, there is effectively no difference in the effect on carbon iso-

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tope alteration trajectories between the post-extinction (burrowing organisms absent) and pre-extinction (burrowing organisms present). These parameters would only become important under present conditions with elevated sediment mixing (Figure 1 of the response).

In addition, we performed an updated sensitivity experiment for the remaining parameters of the sedimentary and marine environment (fraction of authigenic carbonate, sedimentation rate and marine oxygen, sulfate and DIC) under a changing OC flux (Figure 5 and 6 of the original work), and including the new parameters for bio-diffusion and bio-irrigation for the baseline model ( $D_{b0} = 5 \text{ cm}^2 \text{ yr}^{-1}$ ,  $z_b = 2 \text{ cm}$ ,  $\alpha_0 = 50 \text{ yr}^{-1}$ ,  $X_{irr} = 1 \text{ cm}$ ). These tests do, however, not substantially deviate from the original work (Figure 2 of the response). So, we conclude that organic matter fluxes remain the dominant force behind bulk-rock carbon isotope alteration.

Van de Velde S. & Meysman, F. *Aq. Geochem.* 22: 469-504

Dale A.W. et al. (2016) *Geochim. Cosmochim. Acta.* 189:251-268

Comment #11: Page 22: The discussions about the influence of seawater chemistry and meteoric diagenesis are great. It may be better to talk about the other explanations for the scatter  $\delta^{13}\text{C}$  such as heterogeneity in seawater chemistry, meteoric diagenesis and the variation of mineralogy in one section. Also, all the other discussions can be putted in another section. These may make the structure of the discussion part more clear.

Response #11: Agreed. The discussion will be restructured.

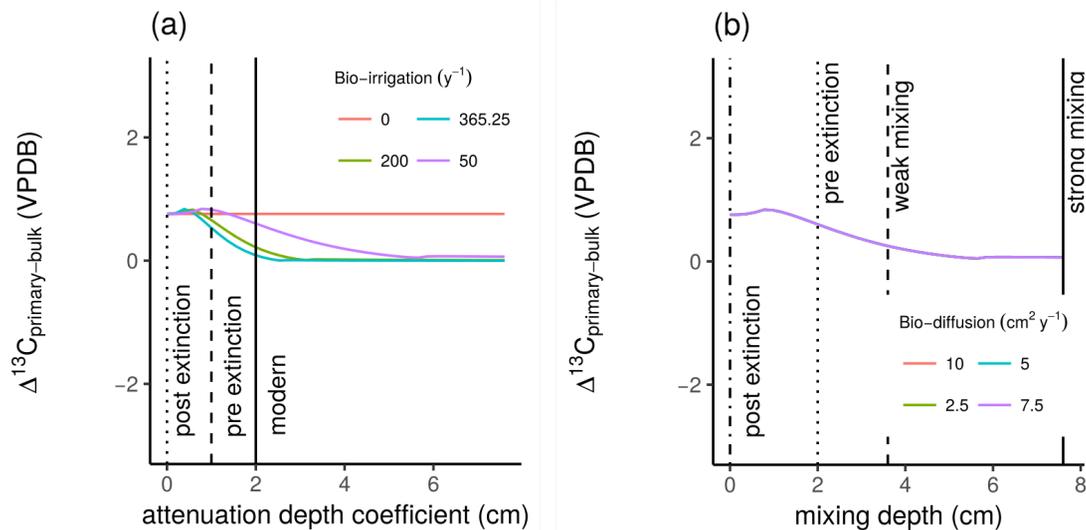
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Interactive comment on *Clim. Past Discuss.*, <https://doi.org/10.5194/cp-2017-66>, 2017.

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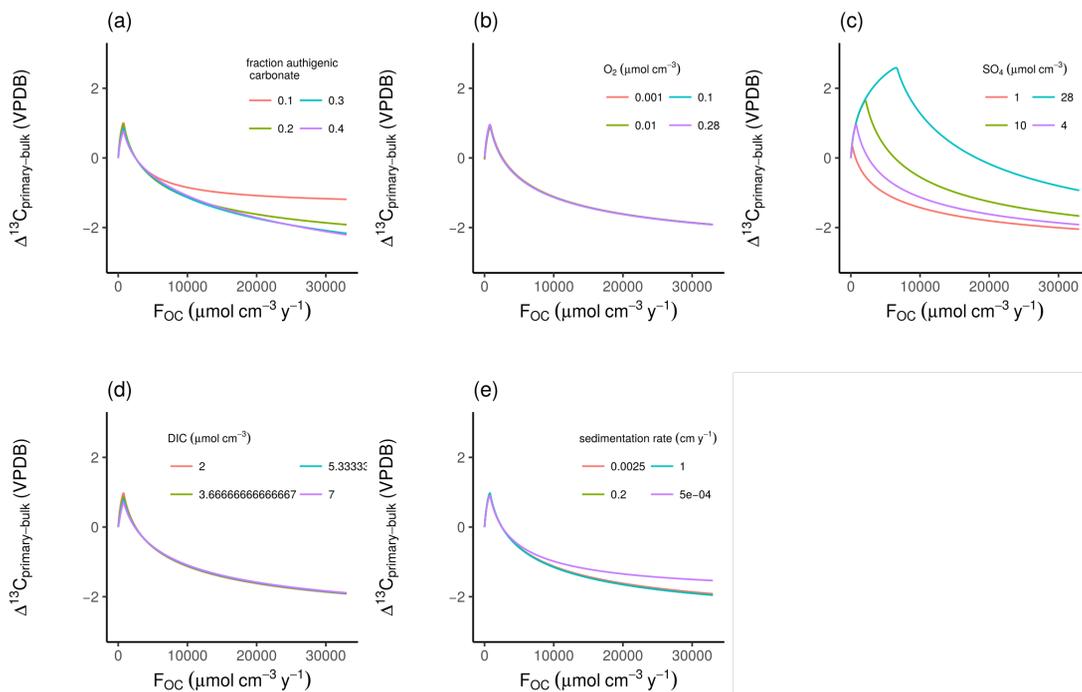


**Fig. 1.** Sensitivity experiments for bio-irrigation and bio-diffusion on the  $\Delta^{13}\text{C}_{\text{primary-bulk}}$  of diagenetic altered carbonate under a normal OC flux ( $730.5 \mu\text{mol cm}^{-2}$ ).

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**Fig. 2.** Sensitivity experiments for a range of parameters of the sedimentary and marine environment on diagenetic altered carbonate (Palaeozoic bio-irrigation and bio-diffusion included).

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