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Discussions

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

Anonymous Referee #2

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Review of CP-2017-66 Latest Permian carbonate-carbon isotope variability traces heterogeneour organic carbon accumulation and authigenic carbonate formation

Schobben et al. analyze a large suite of new and existing carbon isotope data from the P/T boundary of Meishan, China, and Abadeh, Iran. Using a subsampling routine over a timeline normalized by biozones, the authors determine median first order trends at each location and the variance around the median. The authors then utilize a diagenetic reactive-transport model to probe the potential for authigenic carbonate precipitation and recrystallization to push bulk d13C values of carbonate sediments

away from primary values, creating secondary trends in d13C that do not or indirectly reflect ancient seawater conditions. The authors suggest that higher and more spatially variable fluxes of organic carbon, as well as lower sulfate concentrations, during the P/T event lead to greater variance of bulk d13C values due to greater production of authigenic carbonate.

Overall, this is a great study that will impact the P/T paleobiology community, as well as the broader isotope geochemistry community. I am excited to see the authors take a rigorous, statistical approach to their isotope data, and embrace the "nuanced view on the nature of bulk-rock carbon isotope composition...where pure primary and strictly diagenetic end member states are considered as a continuum." Generally, the paper is well-written, though at times the language is a bit dense and hard to follow. I have tried to outline some examples below.

I have two primary concerns for this paper, both related to the treatment of carbonate chemistry. First, how does the diagenetic (reactive transport) model account 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 DIC species. These re-equilibrations will results in non-linear changes to calcite saturation.

On a related note, I don't understand the kinetic rate expressions that are provided, and the explanations are insufficient. The authors cite Boudreau 1997âĂŤI checked the reference and could not find an explanation, though it could be because the reference is a ~400 pg book. Why are all of the rate expression factors of O2 or 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 asked two 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.

Second, the authors assume constant boundary conditions for their model, but also recognize changes in the carbon isotope composition of seawater DIC 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 carbonate chemistry, which should affect the ability of authigenic carbonate to precipitate and how much dissolution/equilibration takes place. See Payne et al. 2010 in PNAS to start.

Below are some minor comments I have on the text and figures: âĂŤThe 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 specificâĂŤperhaps "carbonate sedimentation rate" or "calcite sedimentation rate".

âĂŤPg. 3, line 22: What do the authors mean by "High carbonate ion concentrations"? Are we talking about DIC or CO32-? If these high values are predicted, why did the authors use modern DIC values in their model?

âĂŤPg. 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.

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

âĂŤPg. 4, lines 16: should be "studied". "To carry out this investigation" implies action in the past.

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

âĂŤSection 3.2.1: Have the authors considered the role of other metabolisms, such as Fe and Mn reduction? These metabolism can yield much more alkalinity than sulfate

reduction (see Bergmann et al. 2013 in Palaios). I suspect that Fe reduction is not quantitatively important for most of the Phanerozoic when sulfate and O2 are high, but if sulfate and O2 is low at the P/T it could be significant.

âĂŤPg. 10, lines 10–12: "The previous...solid carbonate." This sentence is hard to follow. Please consider clarifying.

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

âĂŤPg. 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."

âĂŤFigure 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?

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

âĂŤPg. 19, line 5: Can the authors elaborate on how D13C_primary-bulk was derived in Schobben et al. 2016? It would be useful to do here, so the reader can understand this paper without first reading the other.