

Interactive comment on “The Oxic Degradation of Sedimentary Organic Matter 1.4 Ga Constrains Atmospheric Oxygen Levels” by Shuichang Zhang et al.

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Response to reviewer's comments

We thank the reviewers for their detailed comments and criticisms of our manuscript. Please find our detailed response to these comments below.

Anonymous Referee #1 Received and published: 16 November 2016 Review of Zhang et al., Biogeosciences Discussion DOI: 10.5194/bg-2016-413

General Comments:

This paper provides analysis for support of a compelling idea that oxygen was sufficient

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in the mid-Proterozoic ocean for evolution of higher-order species long before their actual evolution, suggesting that biological evolution was not limited by oxygen levels, as has been the suggested and currently accepted paradigm. This idea has been the subject of much debate in recent publications with recent work on Cr isotopes published in Science and Nature suggesting the O₂ levels in the Mesoproterozoic are even lower (<1% PAL) than is currently widely accepted (1% PAL), and, therefore, this topic certainly warrants further study and evidence to determine oxygen levels in this important Eon. The authors are leaders in their field, and have presented other lines of evidence to support the view of an oxygenated Mesoproterozoic world in related recent publications. However, in general, I feel that the overall presentation of this paper could be clearer, better structured and more fluent. Often both the sentence structure and the argument structure are confusing, weakening the overall presentation of very novel and interesting work. The discussions presented in this paper rely heavily on a diagenetic model to determine oxygen necessary for estimated carbon mineralization (inferred from measured [TOC] and HI) in the paleo-ocean. I applaud the efforts of the authors for their efforts to calibrate the model to many modern “analogues”. However, the presentation of this model and the subsequent conclusions are often convoluted, and do not present strong enough arguments to back the authors claims, especially in regards to the recent controversial evidence from other paleo-reconstruction work of oxygen levels in this Eon. Therefore, it is hard to follow the applied methodology (diagenetic model) from the way the discussion is currently presented. As much of the conclusions of this work rely on heavy data interpretation, I would recommend a clearer dialogue throughout the manuscript, which would strengthen the conclusions this work has in our understanding of Mesoproterozoic oxygen levels.

Response: We appreciate these comments and the general support for our approach. We will strive to provide better focus to our discussion as illuminated in our response to the points below.

Specific Comments: Comments for throughout the manuscript- It seems like there are

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many “missing” references for methodology used and some discussion points. This opens room for debating the usage of the approaches outlined in the paper. e.g. lines 105, 110, 135-138 for methodology lines 211, 220, 250, 293 to support specific claims made in the paper.

Response: Thanks for this comment, we will supply the “missing” references.

1 Introduction- Authors must keep in mind the broad readership of Biogeosciences as a journal and define the background and significance of this work in a bit more detail. The intro feels short and incomplete, especially in regards to framing the current state of the research and preparing the readers for the in-depth models that follow.

Response: We agree. This was also a comment of Reviewer 2. We will work to expand the introduction and to place our work more solidly in the context of what is known not only of the history of atmospheric oxygen, but also the methods we have used to reconstruct the history and the present manuscript.

2 Methods- 2.1 Study Site: While the authors have obviously been working with the Xiamaling Formation and are very familiar with its stratigraphy, the readers would benefit from a figure defining the “units” of the formation and its overall place in the paleo-record (ie. dating).

Response: Good point. We will supply a stratigraphic overview of the Xiamaling Formation in the revised manuscript.

2.2 Sample Collection and Analytical Methods: Lines 103-105: for the geochemical data, do you have a reference for the preparation of these samples?

Response: These are pretty standard techniques, but we will supply reference on revised MS.

Line 109: Are the accuracies presented adequate? For example, it is often accepted in organic geochemical analyses that over 10% variability is “too high”. Is this acceptable for trace metal work? Do you have a reference to support that your methodology is

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acceptable?

Response: Prompted by this comment, we have gone back to reevaluate our methods and methods description. We realize that we should have been more careful in our presentation of the methods and their uncertainties. By far the most of our trace metal data was obtained by ICP-MS with uncertainties in the 1% range, not the ranges reported in the manuscript. We also generated some of our results with a hand-held XRF calibrated against numerous international standards and several splits of Xiamaling sediment independently calibrated with ICP-MS. Our uncertainties with this method were all better than 5%. We will carefully redraft our methods description to reflect what we have done, and in the supplementary information we will note which method would use to generate the different trace metal analyses.

Line 110: Define what major elements you looked at with X-ray fluorescence and a reference to the method used.

Response: Good point. Will do.

Line 113: Redefine HI, as you only have defined it in the abstract.

Response: Good point. Will do.

Line 115: How was TOC and S2 measured? Pyrolysis? This description is a little Confusing.

Response: TOC was measured with an elemental analyzer, while S2 was measured with standard Rock-Eval pyrolysis. We will clarify this description.

Line 125: How did you dry your samples?

Response: Samples were dried in a muffle furnace with the temperature <40°C

Line 125-130: Is this TOC measured on the C-S analyzer and the EA used for the HI presented in the paragraph above? If so, you should present this first so the readers aren't wondering where the data came from. Is the uncertainty presented for the same

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standards an inter-lab comparison, or is it for the uncertainty between replicates in the same lab?

Response: Good point, we will reorganize our methods description as suggested. The uncertainties in TOC were presented for replicates run in the same lab.

Lines 131- 139: Are these methods previously published? References?

Response: Yes, (Durand and Nicaise, 1980).

Line 138: Has there been any work done on losses or transformations of kerogen OM in regards to the removal methods of the carbonates, silicates, and fluorides? For example, in modern terrestrial and aquatic samples, significant losses and alterations to OM content, composition and isotopic fractionation have been observed with use of concentrated acids and rinse steps (See e.g.: Gélinas et al., *Organic Geochemistry*, 2001 DOI: 10.1016/S0146-6380(01)00018-3 and discussion in Brodie et al., *Chemical Geology*, 2011 DOI: 10.106/j.chemgeo.2011.01.007).

Response: We have followed standard protocols in all of our analytical techniques. It is true that these techniques could have removed or transformed some organic matter during their application. However, previous studies have shown that organic matter hydrolysis during the recovery of kerogen by our methods can lead to carbon loss on the order of less than 5% (Durand and Nicaise, 1980). We doubt, however, whether this removal will have seriously impacted our isotopic interpretations, particularly as the methods were applied in the same way throughout the stratigraphic column and we are most interested in relative differences in isotopic compositions between the different sediment types rather than the absolute compositions. Also, simple acid treatment, typically, has a negligible influence on sediment organic isotopic composition (Könitzer et al., 2012). Finally, when we compare between the isotopic composition of bulk sediment TOC and kerogen TOC for unit 1 organic matter, the isotopic values are almost always within 1 per mil of one another, and typically within 0.5 per mil (see figure 1). We can view these differences as the maximum influence of analyses conducted in

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different laboratories (bulk sediment in Odense and kerogen in Beijing) as well as all of the accumulated extraction steps.

Lines 161-172: What is the rationale behind the 3 methods of iron determination? Why did you not do a split comparison on the unit 1?

Response: The rationale is that we did not have access to ICP-MS for all of our samples as this is a very expensive method. The utilization of concentrated HCl after sample heating is a common method for "total" Fe, and we find that it routinely extracts >95% of the total iron in standard reference materials. We prefer this to routine methods utilizing concentrated HF acid. Recognizing, however, that the HCl method leaves a small Fe residual, we have also begun to calibrate and use our hand-held x-ray fluorescence unit for total iron analyses. This device is excellent for iron with great reproducibility, stability, and accuracy when properly calibrated. This data set has evolved over the span of two years as we have added more data to best understand its geochemistry. Thus, the evolution of our methodology is in part due to the evolution of the data set and our understanding of unit 1. We have done many comparisons of our data utilizing these three different methods both on international standards and samples from unit 1 and other units within the Xiamaling Formation. We will add some of these comparisons to our supplemental information.

Lines 173-182: This should not be in the Methods section, please move to results and/or discussion.

Response: OK

3 Results Line 184: Please describe a bit of the results rather than just referring me to a supplemental table. For example, averages and standard deviations could be given for black and green-gray shales within the text.

Response: OK.

Figure 1: How does the stratigraphic height on the Y axis relate within your or to your

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unit number and the lithology? Descriptions of variations in the constituents with stratigraphic heights are largely lacking. For example in lines 188-189 the U/Al ratios are not always near the crustal values (e.g. around 30 m). Why?

Response: The lithology changes on a centimeter-decimeter scale which is way too detailed to indicate in a lithological reconstruction. Because of the tight correlation between lithology and TOC content, the TOC content of a sample is an excellent indicator of its lithology, be it black shale or green-gray shale. There could be many reasons as to why U/Al is not always at the crustal average. One could be small differences in the U/Al ratio of the depositing clastic material. Another could be that U can also be enriched in sediments also depositing in oxygenated environments (Barnes and Cochran, 1990). The main point, however, is the difference between uranium enrichment in the gray versus black shales. We agree that it would be important to discuss how U is also enriched in many modern sediments depositing under oxygenated environments, and will do so in the revised manuscript.

Lines 189-191: What is the significance of the higher Fe/Al values? No context for what a “higher value” even is- for example, is the difference observed between the ratios with shale type significant? Then what’s the explanation of the differences with depth, which is often greater than differences between shale types?

Response: Higher values of Fe/Al are taken to indicate iron enrichments in a similar fashion to the ratio of FeHR/FeT. This has been discussed in the literature, and we reference these discussions (also referenced in the text; e.g. (Lyons and Severmann, 2006)). However, Fe/Al has not been as carefully calibrated as the FeHR/FeT, and is not generally the method of choice for determining iron enrichments and for elucidating bottom water chemical conditions. However, in the present case, there is a clear trend of higher Fe/Al ratios in the outcrop samples experiencing also large trace metal enrichments. Therefore, the Fe/Al is consistent with our trace metal determinations in differentiating oxic and anoxic depositional conditions. We did not perform our standard iron extraction procedure on the outcrop samples, as these were somewhat weathered,

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which could compromise the results. We do not believe that the Fe/Al ratio is critical to our interpretation, but it is a way that we can bind the outcrop and core results together.

Figure 2: This figure could benefit greatly from color separation of the green-gray and the black shales in ALL panels (such as in Figure 1). The figure description and much of the subsequent text is not clearly supported by the actual figure (e.g. the conclusion in line 309 is impossible to tell from the Figure 2 as is). Color-coding would help alleviate some of this confusion (for example discussions on lines 299-305, lines 307-309). Don’t refer to another figure in a figure caption! The figure caption should be self-sufficient to the figure. Also, please explain in the text the significance of the line denoting the TOC wt % of 1%.

Response: These are all good points. One of the difficulties in the core samples is that the black and green-gray shales were not always easy to distinguish. This color differentiation becomes much more vivid and easy to see in the field samples where weathering has influenced the coloration of the rocks. However, for the field samples, 1 wt% TOC differentiates the black shales from the green-gray shales, and it is for this reason that we have highlighted this value of TOC in the Figure 2A. We will re-plot the data in Figure 2 to differentiate between the high TOC and low TOC samples, clarifying these points in the revised text.

4 Discussion Line 210: The figures referenced in this sentence don’t support the claim. The best figure to support this statement is probably Figure 2, but based on this figure, HI and TOC don’t look that correlated among like-shale types, as the different shale types separate out completely. The “linear” relationship across the two shale types don’t support your conclusions here.

Response: Perhaps “relationship” is a better word than “correlation”. But, it is clear that there is a strong “relationship” between HI and TOC among different shale types and this is the main point; that high TOC shales are associated with high HI and Low TOC shales are associated with low HI. Such a “relationship” is common in Phanerozoic-

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aged sediments when the source of the organic matter is not heavily influenced by terrestrial plant material. We will change this in the revised manuscript and we agree that figure 2 best supports this discussion.

Line 215-217: What are the potential sources of OM for these age sediments?

Response: Good point. The potential sources are prokaryotic biomass, including cyanobacteria and other microbes involved in producing and degrading organic matter, as well as eukaryotic algae. There is no biomarker evidence for eukaryotes in this formation, but we cannot rule out the possibility that they were a part of the ecosystem as they likely have evolved by 1.4 Ga. We will clarify in the manuscript the potential sources of OM.

Lines 223-232: I don't understand the purpose of this whole discussion. How can you compare your sediments to these when the terrestrial/aquatic assemblages are totally different and the depositional regimes were likely vastly different? For example, you stated in line 215 that your sediments were deposited before land-plant evolution, so how can you compare the HI index (even with relation to O₂ availability) you see in your samples to these other, newer sediments?

Response: We believe that this discussion is highly relevant. Please note that in both of the cases from Phanerozoic sediments that we highlight, terrestrial plant material is a minor component of the TOC pool. Thus, relationships between TOC and HI in these cases are a result of the influence of oxygen on marine organic matter degradation. The same principles would have influenced organic matter preservation in the Mesoproterozoic. Indeed, there is nothing particularly weird to be expected about this marine microbial biomass. It would have contained lipids, proteins and carbohydrates like Phanerozoic eukaryotic algae, and all expectations would be that it decomposes like any other lignin and cellulose-free algal biomass. There will of course be some differences in the exact nature of and relative proportions of these biomass components. But still, these are basic biomass components. We have performed some elemental

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analysis of kerogens from unit 1, and they contain elemental ratios of H/C and O/C completely consistent with Type 1 biomass when plotted on a van Krevelen diagram (Figure 2). This would also be expected from microbial biomass. Thus, we have every reason to believe that unit 1 biomass fits well into what we know from the characteristics of Phanerozoic algal biomass (excluding land plants). Will include figure 2 into a revised version of the manuscript together with a more complete and nuanced discussion of the likely nature of unit 1 biomass. Remember also, it is critical that the trends in HI in the Xiamaling Fm correlate with other independent geochemical indicators of bottom water oxygenation, precisely as would be expected based on modern analogues.

Couldn't the HI index be similar/different for completely different reasons at this point? If this is not the case, please make a less confusing and sounder argument for why high TOC and HI samples are deposited under anoxic conditions and how this can be utilized for older sediments.

Response: We have absolutely no alternative explanation as to our observed trends in HI is related to bottom water oxygenation. As noted above, the trends in HI are completely compatible with independent geochemical evidence for the presence and absence of bottom water oxygenation and with the expectations based on modern analogues. Honestly, we don't feel that it gets much better or more compelling than this. One can argue that because the sediments deposited a long time ago, when the dominant sources of organic matter were different than today, that we cannot apply modern analogues to this ancient record. However, this would be an assertion without any justification, and it would not square with our independent geochemical observations of bottom water oxygenation as discussed above and in the manuscript. In the revised manuscript we can try to make these points more forcefully and to explain more clearly why the Phanerozoic sediments are applicable to sediments 1 billion years older. Perhaps a broader discussion of the types of organic matter available in the Mesoproterozoic would help.

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This become especially important when you are discussing processes that can influence HI in more modern sediments (Lines 274-278), as these depositional processes could have been very different for the sediments you are comparing and using to build your argument. As the vary least, you need to discuss that the depositional regimes were likely sim- ilar for the sediments even though Eons apart.

Response: It's not clear to us that the reviewer is after here? What kind of changes in depositional conditions where organic carbon characteristics are comparable, other than oxygen, can influence similar relationships between HI and TOC in sediments, even though they are separated in time 1 billion years? We cannot come with any plausible alternatives without starting to make stuff up. In this case we feel it is best to apply Occam's razor and appeal to the most obvious explanation, which is oxygen, and a link between the Phanerozoic examples we discuss and the Mesoproterozoic samples that we report. Please recall that the Phanerozoic examples we discussed are not influenced by terrestrial organic matter. This point was made clearly in both of the publications that we quote.

I feel that much of this discussion in Section 4.1 could be condensed, strengthened and over all clarified. I feel like your conclusion in Lines 289-291, that there are fluctuations between anoxic and oxic de- position conditions, seems a bit of a leap from the arguments presented in the section above.

Response: We disagree, but hopefully a revised discussion will clarify this point.

Lines 292-293- Do you have a figure or reference to support this claim?

Response: Sure, we can reference the original iron speciation papers and some of the numerous trace metal papers that link trace metal enrichments to the presence or absence of oxygen in the bottom waters depositing sediments.

Lines 295-300- How do you know this is Fe enrichment and not Al depletion? A depletion in Al would give you the same ratio as an enrichment as Fe, potentially.

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Response: We cannot be hundred percent certain. Indeed, as discussed above, the dynamics of Fe/Al are consistent with our interpretations of the dynamics of bottom water oxygenation, but are not, in themselves, proof of it.

What is happening at the 15 and 35 m mark in your core? The ratios also seem to overlap within the same range between the two types of shales. How do you know the variation you see is significant and indicative of the changes in depositional environment?

Response: Good point. As mentioned above, the Fe/Al ratio is supportive, not definitive evidence for bottom water chemical conditions. We actually debated whether or not to report the Fe/Al at all in the manuscript. However, as also mentioned above, the Fe/Al ratio results are completely consistent with our other geochemical indicators of bottom water oxygenation and they help to tie the outcrop and core material results together..

Line 408: Is the use of this density value in this context something that is already published in the literature? Cite if yes, but if not, this needs to be further validated!

Response: This is a typical density for dried mud. It is also the density most commonly used in sediment calculations. The actual value we use makes very little difference given the broad range of sedimentation rates that we explore. But, on revision, we will further validate this value.

Line 426-430 (Equation 3): A is not defined in the equation description

Response: It is defined in line 434. We can move this up into the previous paragraph.

Lines 519-527: I don't follow the logic of this argument. How can you compare your oxygen estimates with modern observations? Isn't it likely the mid-Proterozoic ocean was different (in terms of oxygen penetration depth especially) than your modern analogues, as we now live in a more oxygen rich world? So how does this comparison support your conclusions?

Response: There are lots of modern observations such as the Borderline Basins of

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California and the low-oxygen regions where oxygen minimum zones impinge on sediments where bottom water oxygen levels are much lower than typical in the marine environment. Oxygen penetration depths and oxygen uptake rates have been determined in many of these environments, as shown in Figure 3C.

Line 550: I feel like it should be mentioned that there is no precise dating of unit 1 MUCH earlier in the text!

Response: OK. No problem.

Technical Corrections: This paper would benefit from a careful proofreading and calibration of citation software used. For example, there are many citation-related errors that probably have resulted from the citation software used: e.g. Lines 99, 147, etc. where parenthetical citations are inappropriate, lines 115-116 where the exact citations are presented twice in a row, lines 594-599 where the same exact reference is presented as two distinct references (Cole et al., 2016a and 2016b), line 542 where two references in a row are presented separately "(Planavsky et al., 2014) (Cole et al., 2016a)" as opposed to "(Planavsky et al., 2014; Cole et al., 2016)".

Response: Oops. Thanks

Lines 41-43: Sentence starting with "The original idea ... " is not a complete thought. Line 43, 44, 46, etc: Please define the element names before using their symbols at first use. There is a shift back and forth between the element name and symbol (e.g. in line 46 "chromium-associated" and "Fe-enriched"). Please at least be consistent with the usages. Line 50, 56: Please provide more background on your "unit" numbers. The lack of context what unit 3 is vs unit 1 is confusing for the readers to follow. A figure might help with this! Lines 68-72: Sentence starting with "These intrusive sills ... " is wordy and confusing! Line 73: "... like the sediments depositing just before" I would consider rewording this phrase as it sounds a bit weird. Line 79-80: Add space between the degree symbol and N Lines 84-88: Sentence starting with "Previous work ... ". This sentence is 5 lines long! Break into shorter sentences. Line 103: This

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should read "... drilling depth, angle, and cross calibration ... " Line 115: "HI is defined as $S2 \cdot 100 / TOC$ " (i.e. $HI = S2 \cdot 100 / TOC$) This is an equation, shouldn't this have an equation number? Line 148: "... highly iron ..." do you mean highly reactive iron? Line 159: You already defined FeHR on line 148 Lines 218-220: This not a complete thought. Line 220-223: This sentence is confusing ! C7 Line 266: After organic carbon burial flux maybe place the abbreviation used in the equation? Cbur? Line 354: This transition "Returning to the sediment model ..." is awkward. I would consider rewording it. Line 543: "... chrome, and its isotopes ..." Do you mean chromium? "Its isotopes" should read "its isotopes", as it's used as a possessive pronoun here. Line 546: "... chrome component" do you mean chromium? Line 548: the usage of "square" is awkward. I would consider rewording this sentence. Interactive comment on Biogeosciences Discuss., doi:10.5194/bg-2016-413, 201

Anonymous Referee #2 Received and published: 22 December 2016 "General comments" This paper aims to determine oxygen levels prevailing in oceans 1.4 Gyr ago. This topic is of interest and debated as evidenced by the numerous publications in high-rank journals. As stressed by the authors, the use of the chromium isotopes as a redox indicator can be discussed implying the need for complementary or new approaches as the one published by the same authors in PNAS (Zhang et al., 2016). However, this manuscript shares the same conclusion than Zhang et al., 2016. There are too many similarities between the two manuscripts to fully consider this one as a new manuscript. In my opinion, the manuscript must refocus on the approach rather than the already published conclusion. The two studies are only distinguished by (i) the studied geological units and (ii) the determination of oxygen exposure time and penetration depth: (i) Their previous study dealt with units 2,3 and 4 while this one focus on the unit 4. Unfortunately and as stressed by the authors (L550), there is no precise dating of unit 1 in the Xiamaling Formation. Hence, the main original conclusion of the manuscript (persistent atmospheric oxygen over million years) is not convincing especially in the light of the alternating gray (oxidizing conditions) and black shales (anoxic conditions; see Zhang et al., 2016).

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Response: With all due respect to the reviewer's concerns, we are puzzled by the idea that "there are too many similarities between the two manuscripts [this manuscript and an earlier one by our group published in PNAS] to fully consider this one is a new manuscript" because "...this manuscript shares the same conclusion than Zhang et al. 2016." We stress: 1) that there is no consensus on levels of oxygen during the Mesoproterozoic Era. Basically, there is a pair of chromium isotope studies suggesting very low levels of atmospheric oxygen, and our PNAS contribution suggesting much higher levels, 2) that the relationship, therefore, between the history of atmospheric oxygen and animal evolution is currently unresolved, 3) the current manuscript uses a completely different methodology to also establish oxygen concentrations – that turns out to be similar - as the PNAS paper, which focused on a completely different section of the Xiamaling Formation, 4) the methodology explored in the current manuscript is completely novel and is the first to evaluate the consequences of oxygen exposure on carbon preservation during the Precambrian. In short, the method is novel and holds promise to future application, which is a gain for the community no doubt, and additionally these independently achieved results contribute to resolve oxygen concentrations in the Mesoproterozoic. We also point to the impassioned comment to this manuscript by Devon Cole, the author of one of the chromium isotope papers referenced above. This comment is further demonstration that additional evidence on the levels of Mesoproterozoic oxygenation is critically needed.

Therefore, we view our manuscript as a novel contribution to an important scientific debate. The fact that our two contributions, utilizing completely different methods, offer similar conclusions as to levels of Mesoproterozoic atmospheric oxygen strengthens the idea that atmospheric oxygen levels were higher than predicted from chromium isotope studies and reinforce the idea that sufficient oxygen for animal respiration was available in the environment long before the evolution of animals themselves.

The reviewer also states that "The two studies are only distinguished by (i) the studied geological units and (ii) the determination of oxygen exposure time and penetration

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depth" Yes, the studies do look at different parts of the Xiamaling Formation, but the methodology used to constrain atmospheric oxygen is completely and fundamentally different. In the PNAS paper we utilized a water column model to determine the minimum levels of atmospheric oxygen required to allow bottom water oxygenation. In the present manuscript we utilize a sediment diagenetic approach to explore the minimum levels of bottom water oxygen required to generate the amounts of carbon oxidation needed to reproduce the HI values we observe in the sediments

(ii) Although very interesting, providing a fair review on the determination oxygen exposure time and penetration depth is too difficult in the current state of the manuscript. The overall presentation is too confusing as for the distinction between anoxic and oxic depositional environments.

Response: The first reviewer also raised concerns about our discussion of the distinction between anoxic and anoxic depositional environments. We accept that a clearer discussion is in order, but we fully stand by our conclusions.

Finally, the quality of figures and tables does not stand for the publication standard. In my opinion, this manuscript is not fully original (because of its redundant conclusion with the PNAS paper) but presents an innovating approach. I suggest the authors to modify this manuscript focusing on the new unique feature of this version (TOC-derived calculations) with a significant improvement of the overall presentation.

Response: We have already addressed most of this comment above. However, we agree that the manuscript needs more focus on the nature and sources of organic matter to unit 1 of the Xiamaling Formation.

"Specific comments": Introduction The introduction is very short. There is an overall lack of contextualization. Moreover, authors finalize their introduction by evidencing that they will present equivalent results than their former publication. It is quite destabilizing.

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Response: Good point. Reviewer 1 also raised the concern that the introduction is too short. We will provide a longer introduction with a better development of the methods that we finally use in our paper to determine oxygen levels.

L19-20: Where? It is not so clear in the manuscript. L43: Uranium (U) L44: Molybdenum (Mo) L49 "in contrast, sediments from unit 3": It is probably too specific for the global purpose of an introduction. Do you have other references than yours ?

Response: These points and will be addressed on revision.

Study site and methods L113-122: What were the samples analyzed by Rock-Eval pyrolysis ? kerogens or crushed rocks ?

Response: Yes, they were crushed rocks.

According to the logic of the manuscript, it may be crushed rocks. L113 HI: Hydrogen Index L114: Using the HI index required the determination of the TOC by Rock-Eval Pyrolysis. To determine the TOC, carbonaceous compounds are also determined during the combustion step (oxidation oven). It must be clarified.

Response: TOC was determined on whole rock samples after decarbonization. This will be clarified in the revised manuscript.

Moreover, why don't you use the Oxygen Index ? It cannot be as a consequence of the presence of carbonates since Rock-Eval device provide the possibility to distinguish oxygen from both carbonates and organic matter sources (Baudin et al., 2015; organic geochemistry). OI is often used as a proxy of oxidation of the organic matter during early diagenesis. Same as before comments

Response: No problem with including the oxygen Index as well. Relationships between HI and OI show the organic matter to be a mixture of Type 1 and Type 2, as would be expected. In any event, in the revised manuscript we will include in the supplement a graph comparing H/C to O/C in order to help place this organic matter within the context of known Phanerozoic examples.

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L116-117: This assertion is not true. Following cited references, S2 corresponds to the amount of hydrocarbon released upon pyrolysis without any distinction about the molecular weight of the hydrocarbons.

Response: It is generally accepted that S2 comprises of the longer-chained, non-volatile hydrocarbons, S1 consists of the free hydrocarbons. This distinction would be consistent with textbook descriptions of Rock-Eval analyses, and with the discussion provided by the developers of the method.

L131-139: Isolation procedure does not correspond to the classical procedure, why ?

Response: Our extraction procedures are the same as the "classical" procedures introduced by (Durand and Nicaise, 1980). This reference will be included in the revised manuscript.

L131-139: have you investigated the effect of the isolation procedure on the preservation of organic matter ? HCl procedure can lead to artefactual degradation of aliphatic moieties implying in turn, a shift in the carbon isotope composition.

Response: We have discussed our extraction procedures and their possible influence on the isotopic composition of carbon in our samples above, in response to the first reviewer's comments. In short, we do not believe that our extractions have significantly influenced the isotopic composition of our samples, and especially, our ability to comment on the differences in the isotopic composition between the low TOC and high TOC samples.

Results Figures: The quality of Figure 1 and 2 is not acceptable.

Response: How so? It's not clear what we should do to improve the figures?

Discussion 4.1 Organic carbon preservation and water column chemistry This discussion section is too long and not really pertinent.

Response: We believe that the discussion in this section is central to the development

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of our arguments into distinguishing between oxic and anoxic depositional conditions in unit 1 of the Xiamaling Formation. Without more specific instructions as to what is pertinent and not pertinent in this discussion, it is difficult for us to try to presuppose the reviewer's concerns.

The TOC and HI high values are attributed to the preservation of organic matter under anoxic conditions. In turn, I have the feeling that the TOC and HI low values are allocated to oxic environments by default.

Response: No, low TOC and low HI are not allocated to oxic environments by default. We have allocated these to oxygen conditions based on comparisons with Phanerozoic environments, and in particular those without a terrestrial plant influence, where the relationship between oxygen, TOC, and HI is clearly distinguishable and well discussed. Note also that the allocations that we have provided are completely consistent with a line of independent geochemical determinations. We really don't believe that one can do a much better job than this.

Factually, the FeHR/FeT is the best criterion to distinguish between oxic and anoxic depositional environments. As the distinction between the oxic and anoxic environments is crucial to sustain the determination of O₂ level, it is essential to provide a more thorough argumentation. For instance, why their results about element traces are not compared with data from literature ?

Response: We agree that the iron speciation data is perhaps the best tool to distinguish between anoxic and an anoxic depositional conditions. This is why we have conducted this work and reported this data, which is completely consistent with our interpretations based on HI, TOC and trace metal enrichments. We do not quite understand the reviewer's comment in relationship to comparisons with the literature. Our interpretation of the trace metals are derived from their behavior in modern environments as reported in the literature and as discussed in the text. We appreciate, however, that our argumentation may have been unclear, and we will work hard to clarify our discussion and

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the relationship between our results and those from the literature.

Moreover, interpretation of element traces is by far more complicated. In this case, there is again a lack of contextualization.

Response: Again, we could discuss the trace metals in much more depth, but we don't believe that we would come further in our utilization of the trace metals in distinguishing between oxygenated and anoxic depositional conditions. It is the patterns of trace metal enrichments that are most critical here. We will, however, make more reference to literature studies on trace metal enrichments.

L210 "HI has often been linked": References are needed L211: higher=>high L211: more => better preservation of L212 poorer => a low L218-232: This paragraph can be shortened. In its present form, it is confusing and not really interesting.

Response: We don't see quite how it is confusing, but we will work hard to try and streamline this paragraph.

L248-261: the good preservation of organic matter in anoxic environment is not new and does not deserve such a large paragraph.

Response: We agree that this discussion is straightforward. We will try to balance the wishes of this reviewer to shorten this discussion and those of reviewer 1 to enhance it.

L269-270: This sentence is in contradiction with your previous statement (see comment on L210)

Response: We agree that this sentence is unclear and we will change it.

L274; If HI values are "blurred" by sediment re-suspension or transport, why is it not the case for the TOC values?

Response: It is true for TOC values! We will clarify.

C20

Indeed, HI and TOC characterize the same organic matter. L279-280: It is redundant with a previous sentence. L280:

^{13}C was determined on the insoluble organic matter not on the whole bulk rock in contrast to Rock-Eval parameters. During the isolation of the kerogen, the use of HCl can degrade then aliphatic content leading in turn to a bias in the determination of the ^{13}C . Have you any evidence that such a bias does not affect the ^{13}C values ?

Response: This is discussed above

Anyway, I don't really understand the relevance of the ^{13}C .

Response: As mentioned in the text, we use the ^{13}C to argue for a similar source of organic matter to the black and gray shales. Such comparisons are often presented in the literature.

For the 4.2 discussion section, an extensive rewriting effort is required to simplify the whole structure. Indeed, several readings of the draft text are required to fully understand the approach. Otherwise, I've no concern about the calculations.

Response: We agree that this is a complicated discussion and will do our best to try to streamline and make it more accessible.

References Barnes, C. E. and Cochran, J. K.: Uranium removal in oceanic sediments in the oceanic U balance Earth Planet. Sci. Lett., 97, 94-101, 1990. Durand, B. and Nicaise, G.: Procedures for kerogen isolation. In: Kerogen-Insoluble Organic Matter from Sedimentary Rocks, Durand, B. (Ed.), Editions Technip, Paris, 1980. Könitzer, S. F., Leng, M. J., Davies, S. J., and Stepherson, M. H.: An assessment of geochemical preparation methods prior to organic carbon concentration in carbon isotope ratio analysis of fine-grain sedimentary rocks, *Geochem. Geophys. Geosyst.*, 13, 2012. Lyons, T. W. and Severmann, S.: A critical look at iron paleoredox proxies: New insights from modern euxinic marine basins, *Geochim Cosmochim Acta*, 70, 5698-5722, 2006.

C21

Interactive comment on Biogeosciences Discuss., doi:10.5194/bg-2016-413, 2016.

C22

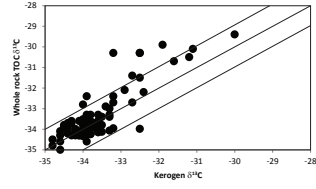


Fig. 1.

C23

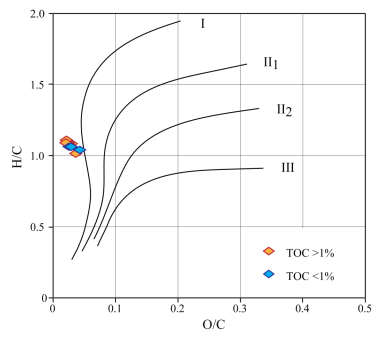


Fig. 2.

C24