

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

## **Anonymous Referee #1**

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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 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 O<sub>2</sub> 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

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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.

#### Specific Comments:

Comments for throughout the manuscript-

It seems like there are 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.

#### 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

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and preparing the readers for the in-depth models that follow.

## 2 Methods-

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

### 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?

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 acceptable?

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

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

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

Line 125: How did you dry your samples?

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

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

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.: G elinas 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)

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?

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

### 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.

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

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?

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

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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%.

#### 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.

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

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 O<sub>2</sub> availability) you see in your samples to these other, newer sediments? 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. 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 similar for the sediments even though Eons apart. I feel that much of this discussion in

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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 deposition conditions, seems a bit of a leap from the arguments presented in the section above.

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

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. 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?

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!

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

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?

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

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

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(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)”.

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 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 !

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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 re-wording it.

Line 543: “. . .chrome, and it’s isotopes. . .” Do you mean chromium? “It’s 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.

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