

## 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. Some of these responses reiterate what we have written in our initial response to the reviews comments. However, we elaborate on these and highlight where we have made additions and corrections to the MS. All in all, we have made moderate revisions to the MS. Please note that none of these revisions has altered our approach or conclusions. The most important of our major additions are:

- We have substantially expanded the Introduction as requested by all of the reviews (including Devon Cole, who added a comment to the MS). Thus, we have added to the Introduction a review of existing information on the state of atmospheric oxygen concentrations during the Mesoproterozoic Era. This helps us highlight on the novelty of the current contribution as noted by reviewer 2 and the editor.
- We have added a section on the nature of the Mesoproterozoic Era carbon cycle. We do this to emphasize the similarities and difference between the Mesoproterozoic and modern carbon cycles. This is important because we use the modern carbon cycle to evaluate and quantify the ancient carbon cycle yielding our oxygen estimates. This is aimed at the comments of reviewer 1. We remain firm in our belief that this is an appropriate approach.
- We have expanded our discussion on the use of HI to assess the maturity and state of decomposition of sedimentary organic matter.
- We have sharpened our methods section and added a table (Table S1) summarizing the results of repeat analyses of many international standards for most of the geochemical parameters reported here. This is in response to both of the reviewers and to the editor's comments.
- We have both sharpened and expanded our discussion as to how we use our geochemical parameters to assess bottom water chemistry. This has included both the addition of new text and rearrangement of the original text.
- We have both clarified and re-arranged the discussion in many places.

## Specific responses to reviewers' comments

Anonymous Referee #1

Received and published: 16 November 2016

Review of Zhang et al., Bioegosciences 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 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 have taken these comments to heart in our revisions as outlined both above and below.

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.*

Response: Thanks. We have carefully evaluated our Methods section and added 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. As noted above, the Introduction has been considerably expanded.

*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 it’s overall place in the paleo-record (ie. dating).*

Response: Good point. We have added a stratigraphic overview of the Xiamaling Formation including a general stratigraphy of the upper 4 units of the Formation, including an indication of where dating has been done, and a more detailed stratigraphy of the upper 45 meters of unit 1.

## *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: Yes, added.

*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?*

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 have redrafted this discussion, and we summarized our repeat analysis of standards and samples in Table S!

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

Response: Done.

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

Response: Done.

*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. This has been clarified.

*Line 125: How did you dry your samples?*

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

*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?*

Response: Good point, we have 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. As noted in the MS, the procedures we use lead to carbon loss of less than 5% (Durand and Nicaise, 1980), and we doubt whether this small amount of loss 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 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. All of our methods have been carefully evaluated against standard materials. We have added a discussion of this in the revised MS.

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

Response: Done.

### *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: Done. Added Table 1.

*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?*

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. Most of this discussion has been re-written.

*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 Fe<sub>HR</sub>/Fe<sub>T</sub>. This has been discussed in the literature, and we reference these discussions (also referenced in the text; e.g. (Lyons and Severmann, 2006)), but have also expanded this discussion in the MS. We note, however, that Fe/Al has not been as carefully calibrated as the Fe<sub>HR</sub>/Fe<sub>T</sub>, 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 they are weathered, which would compromise the results.

*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, by far most of the green-gray samples had a TOC content of  $<0.5$  wt% while the black shales had a TOC content of  $>2$  wt%. As a guide helping to relate the field samples to the core samples, we have indicated with boxes these TOC ranges in Figure (now) 3a.

#### *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". Also, there was intention to suggest that such a "relationship" is linear. But, it is clear, however, 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-aged sediments when the source of the organic matter is not heavily influenced by terrestrial plant material. This text has been significantly reworked and expanded in the revised MS.

*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 have added a whole new section in the discussion describing the Mesoproterozoic Era carbon cycle.

*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?*

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. We have expanded our discussion to bring even more example of the relationship between HI, organic matter preservation, and oxygen. 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. As mentioned above, we have added a new section describing the nature of the Mesoproterozoic Era carbon cycle. Remember also 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 do not 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. As mentioned above, in the revised MS we have expanded our discussion of both the Mesoproterozoic Era carbon cycle and of the relationship between HI, oxygen and carbon preservation.

*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 very least, you need to discuss that the depositional regimes were likely similar for the sediments even though Eons apart.*

Response: It's not clear to us what 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 of 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 deposition conditions, seems a bit of a leap from the arguments presented in the section above.*

Response: We disagree and have rearranged and expanded our discussion to more clearly develop the relationship between our geochemical indicators and our assessment of bottom water oxygenation. We believe that our data provides about the most compelling evidence for fluctuating bottom water conditions that exists in the literature.

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

Response: Sure, we have referenced the original iron speciation papers and more 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.*

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. We have further validated this value in the revised MS.

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

Response: It is defined in line 434. We have reorganized the text to make the reference to the various equations more clear.

*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 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 4C.

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

Response: Mentioned in site description and obvious from new Figure 1.

*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: Corrected. Also, we have dealt with all of the corrections and suggestions presented below.

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  $S2*100/TOC$ ” (i.e.  $HI = S2*100/TOC$ ) 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 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.

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).*

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 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.

We have expanded in our introduction evidence related to the history of atmospheric oxygen. This makes a robust case for the need of the present contribution.

*(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. As noted above in response to reviewer, our discussion of the evidence related to the presence or absence of bottom water oxygen during the deposition of unit 1 has been reorganized and expanded. 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.*

Response: Good point. The Introduction has been considerably expanded:

*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: This part of the Introduction has been rewritten and expanded.

*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: No, TOC was determined on whole rock samples after decarbonization. We have made this statement explicitly in the revised MS.

*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: The oxygen index is compromised in outcrop samples, so is of little values here. These samples contained negligible carbonate.

*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. This discussion has been included in the revised text.

*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 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. We have, however, revised our text make these arguments clearer.

*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 reorganized our discussion to better describe how our results are used to distinguish the chemistry of depositional environments.

*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.

*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: This discussion has been completely reworked.

*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. In the revised MS we have tried 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: This discussion has been rewritten.

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

Response: This whole discussion has been rewritten and sharpened.

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

*<sup>13</sup>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 <sup>13</sup>C. Have you any evidence that such a bias does not  
affect the <sup>13</sup>C values ?*

Response: This is discussed above.

*Anyway, I don't really understand the relevance of the <sup>13</sup>C.*

Response: As mentioned in the text, we use the <sup>13</sup>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 under-  
stand the approach. Otherwise, I've no concern about the calculations.*

Response: Agreed and we have rewritten to simplify the structure and to clarify the arguments.

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# **The oxic degradation of sedimentary organic matter 1.4 Ga constrains atmospheric oxygen levels**

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## Abstract

We studied sediments from the ca. 1400 million-year-old Xiamaling Formation from the northern China Block. The upper unit of this formation (unit 1) deposited mostly below storm wave base and contains alternating black and green-gray shales with very ~~distinct~~different geochemical characteristics. The black shales are enriched in redox sensitive trace metals, have high concentrations of total organic carbon (TOC), high hydrogen index (HI) and iron speciation indicating deposition under anoxic ~~c, mostly euxinic,~~ conditions. In contrast, the green-~~grey~~gray shales show no trace metal enrichments, low TOC, low HI and iron speciation consistent with an oxygenated depositional setting. Altogether, unit 1 displays alternations between oxic and anoxic depositional environments, ~~driving~~and differences in carbon preservation consistent with observations from the modern ocean. We combined our TOC and HI index results to calculate the differences in carbon ~~mineralization~~mineralization and preservation between the oxygenated and anoxic depositional environments. Through comparisons of these results with modern sedimentary environments, and by use of a simple diagenetic model, we conclude that the enhanced carbon mineralization under oxygenated conditions ~~in unit 1 of the~~at Xiamaling Formation required a minimum of 4% to 8% of present-day oxygen levels (PAL). These oxygen levels are higher than estimates based on chromium isotopes ~~and, furthermore, were likely sufficient for early animal respiration. Therefore, our results~~and reinforce the idea that the environment contained enough oxygen for animals long before their evolution.

**Keywords:** atmospheric oxygen, Mesoproterozoic, hydrogen index, carbon preservation, oxic respiration, anoxic, animal evolution, marine sediment

## 1 Introduction

The Mesoproterozoic Era (1600 to 1000 million years ago, Ma) was a time of profound biological transition. It witnessed the emergence of nascent eukaryote ecosystems, and more generally, it linked the dominantly prokaryote world of the Paleoproterozoic Era (2500 to 1600 Ma), and before, to the Neoproterozoic Era (1000 to 541 Ma), where eukaryotes greatly diverged and where animals first evolved (Butterfield, 2015; Knoll, 2014). In a widely held view, limited oxygen availability may have restricted the evolution and diversification of eukaryote clades, including animals, until a permissive environment emerged with a rise in oxygen levels in the late Neoproterozoic Era ~~era~~ (Berkner and Marshall, 1965; Knoll, 2011, 2014; Nursall, 1959).

Unfortunately, there are few constraints on oxygen levels during the Mesoproterozoic Era. The original idea that Mesoproterozoic oceans were largely anoxic below the surface mixed zone generated a model providing maximum oxygen concentrations in the range of 40% of present atmospheric levels (PAL) (Canfield, 1998). Subsequently, relatively low concentrations of redox-sensitive trace metals like uranium (U) and molybdenum (Mo) in black shales have reinforced the idea of wide-spread Mesoproterozoic ocean anoxia and ~~lower~~ levels of atmospheric oxygen lower than today (Partin et al., 2013; Scott et al., 2008). Recently, the lack of observable fractionation in chromium (Cr)-associated with ironFe-enriched marine sediments through the Mesoproterozoic Era has suggested a lack of oxidative weathering of chromium minerals on land, and subsequently, atmospheric oxygen levels of  $\leq 0.1\%$  PAL (Planavsky et al., 2014), an idea reinforced by low Cr isotope fractionations preserved in Mesoproterozoic shales (Cole et al., 2016). In contrast, Cr associated with a number of 900 to 1100 Ma marine carbonates reveal highly fractionated isotopes consistent with oxidative weathering of Cr from land under elevated atmospheric oxygen concentrations (Gilleaudeau et al., 2016). Thus, taken

at face value, Cr isotopes offer an equivocal view of the Mesoproterozoic history of atmospheric oxygen levels.

The chemistry of ancient soils, paleosols, offers possible constraints on Mesoproterozoic Era atmospheric oxygen levels. Thus, Zbinden et al., (1988) modelled the retention and oxidation of iron during the weathering of the 1100 Ma Sturgeon Hills paleosol, developed on hydrothermally altered Keweenaw basalt, obtaining a minimum atmospheric oxygen concentration of 0.1% PAL. Other studies of the same paleosol profile, however, have not reproduced the same chemistry (Mitchell and Sheldon, 2010), indicating that further work on this paleosol is likely required.

Similarly aged paleosols have also developed on fluvium derived from weathered Keweenaw basalt (Mitchell and Sheldon, 2009). These paleosols formed in over-bank river sediments and adjacent pond environments that were alternatively flooded and air-exposed (Mitchell and Sheldon, 2009). The chemistry of these paleosols is thus complicated by an admixture of oxidative (during exposure) and reductive (during flooding) processes. When ratioed against the Ti content of unweathered Keweenaw basalt, Fe was apparently lost during the formation of these paleosols, although Fe oxides are also prominent in the paleosols (Mitchell and Sheldon, 2009). In contrast, if paleosol chemistry is ratioed against Keweenaw basalt Al content, Fe was either fully retained or even enriched in the paleosols (Mitchell and Sheldon, 2009). Thus, interpretations of element loss or gain during weathering of these paleosols are highly dependent on the choice of the “immobile” element. We caution that Ti is typically associated with dense mineral phases such as rutile ( $\text{TiO}_2$ ) and ilmenite ( $\text{FeTiO}_2$ ), and these minerals may undergo sorting during fluvial transport (Chen et al., 2013). Therefore, the magnitude of element mobility during the weathering of this fluvium is uncertain. Even with this

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uncertainty, there has been no attempt yet to model atmospheric oxygen levels from the chemistry of these paleosols.

In a different approach, studies of unit 3 of the 1400 Ma Xiamaling Formation from the North China Block

sediments from unit 3 of the Xiamaling Formation demonstrated trace metal and biomarker signatures consistent with deposition in oxygenated waters below an ancient oxygen-minimum zone (OMZ) (Zhang et al., 2016). A simple ocean water column -carbon--cycle model demonstrated was constructed to determine the amount of atmospheric oxygen that would have been required to oxygenate these deep waters, with results revealing a minimum value that of  $\geq 4$  PAL oxygen % PAL was needed to have oxygenated these deep marine waters (Zhang et al., 2016).

Taken together, these studies show that Thus, available constraints on Mesoproterozoic levels of atmospheric oxygen are contradictory. One could argue that what appears to be uncertainty in Mesoproterozoic Era atmospheric oxygen levels,- actually reflects temporal variability. This is a valid point, but still, focusing on studies of the 1400 Ma Xiamaling Formation, and as mentioned above, shale Cr isotope results support low levels of atmospheric oxygen (Cole et al., 2016) of  $< 0.1\%$  PAL, while modelling OMZ conditions in unit 3 revealed oxygen levels of  $\geq 4$  PAL (Zhang et al., 2016)and,-e Clearly, other lines of evidence are required to constrain the evolution of Mesoproterozoic Era atmospheric oxygen and its role in biological evolution.

Here, we ~~report~~ focus on evidence from unit 1 of the 1400 Ma Xiamaling Formation. This unit shows transitions between sediment deposition under oxygenated and anoxic water-column conditions as revealed through trace metal systematics, iron speciation and organic geochemical results, in particular, total organic carbon contents (TOC) and the hydrogen index (HI). The results from the Xiamaling Formation are reviewed in the context of modern sediments, allowing the construction of a simple diagenetic model that ~~for sediment oxygenation and oxic organic matter mineralization. These observations combine with a simple diagenetic model to~~ allows us to constrain atmospheric oxygen to a minimum of 4 to 8 % PAL. These new results, thus, support elevated atmospheric oxygen levels at 1400 Ma.

## 2 Study site and methods

### 2.1 Study site.

We explored rocks from unit 1 the Xiamaling Formation of the North China Block. The Xiamaling Formation is part of Paleoproterozoic to Mid-Mesoproterozoic sedimentary sequence, depositing onto Paleoproterozoic crystalline rocks that were likely formed during the breakup of supercontinent Columbia (Meng et al., 2011). The sedimentary sequence begins as an opening rift basin that developed into a passive margin and eventually a back-arc setting (Meng et al., 2011; Qu et al., 2014). The Xiamaling Formation itself contains relatively few volcanoclastic layers, and was first intruded by diabase sills at  $1323 \pm 21$  Ma (Li et al., 2009). These intrusive ~~sills~~ are taken to indicate back-arc development, but they occurred, but some 60 to 70 million years after sediment deposition in units 2 and 3. This is evident from ~~dated with~~ high-precision thermal ionization mass spectrometry (TIMS) dating yielding an age of  $1384.4 \pm 1.4$  Ma for a tuff layer located at 210 m depth in ~~the stratigraphy~~ unit 2, and an age of  $1392.2 \pm 1.0$  Ma for a bentonite layer in unit 3, 52 m below the unit 2 tuff ~~levelayer~~. (Figure 1; Zhang et al., 2015).

Thus, the Xiamaling Formation likely deposited in a passive-margin setting like the sediments depositing just before before back-arc development (Meng et al., 2011; Qu et al., 2014).

Overall, the Xiamaling Formation has a total thickness of about 450-500 m, and is composed of highly-laminated sediments deposited, mostly, in deeper quiet waters below storm wave base (>100 m) through most of its history (Zhang et al., 2015). Paleogeographically, the Xiamaling Formation deposited in a tropical to sub-tropical setting between 10°N and 30°N latitude (Zhang et al., 2012), and the patterns of sediment lamination and chemistry are consistent with the influence of climate forcing on sedimentation dynamics (Zhang et al., 2015).

The sediments are also of exceptionally low thermal maturity, likely never heated to greater than 90°C (Zhang et al., 2015).

~~The Xiamaling Formation deposited in a tropical to sub-tropical setting between 10°N and 30°N latitude (Zhang, 2012 #12412), and the patterns of sediment lamination and chemistry are consistent with the influence of climate forcing on sedimentation dynamics (Zhang, 2015 #12825).~~ We focus here on the sediments deposited in unit 1. This unit is differentiated from underlying unit 2 by the first occurrence of TOC-poor green-gray shale layers, in a background of TOC-rich black shales upper 45 meters of the Xiamaling Formation, as contained within unit 1 (Figure 1) (Zhang et al., 2015). The green-gray shales become more prominent in moving up-section, and by 40 to 45 m depth in the stratigraphy, green-gray and black shales alternate regularly with layer thicknesses of 1 to several cm's. Sedimentation is continuous between the black and green-gray layers, and both represent fine-grained muddy silts. This part of unit 1 is composed of centimeter scale alternations between high TOC black shales and low TOC green-

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~~gray shales (Zhang, 2015 #12825). Previous work placed this unit in the downwelling limb of an ancient Hadley Cell where fluctuations in sediment chemistry resulted from periodic changes in Hadley Cell placement and the location of the Intertropical Convergence Zone (ITCZ) as these influenced patterns of trade wind intensity and ocean circulation (Zhang, 2015 #12825).~~

A deep-water setting is indicated through most of the unit 1, but at about 15 m depth, there appear occasional strata with hummocky-cross bedding indicating the influence of storm waves on deposition. From here and upwards, the sediments deposited at or above storm wave base, which can range in depth from about 50 to 200 meters (Immenhauser, 2009). Thus, overall, unit 1 likely deposited in waters in the depth range of  $100 \pm 50$  meters, with deeper waters towards the bottom of the unit and shallower waters towards the top. There is no precise dating of unit 1 sediments.

Previous work placed this unit 1 in the downwelling limb of an ancient Hadley Cell. Here, where fluctuations in sediment chemistry resulted from periodic changes in Hadley Cell placement and the location of the Intertropical Convergence Zone (ITCZ) as these influenced patterns of trade wind intensity and ocean circulation (Zhang et al., 2015).

## 2.2 Sample collection and analytical methods

Both outcrop and core samples from the Xiamaling Formation were used in this study. Outcrop samples were collected at ~0.5m intervals along road cuts within 2 to 4 y after they were made.

The different rock types were easy to discriminate in outcrop, and all samples were collected after removal of the weathered outer layer (see further; Zhang et al., 2015). Core samples were

collected using a diamond drill lubricated with fresh water to minimize contamination from drilling fluids (see further; Zhang et al., 2016). Core depths were correlated to outcrop height based on reconstructions from drilling depth, ~~and~~ angle and cross calibration of geochemical parameters such as trace element geochemistry (e.g. Zhang et al., 2015, Zhang et al., 2016). For geochemical analyses, ~~all~~ samples were rinsed with purified water, dried, and then crushed to fine powder (less than 74  $\mu\text{m}$ ) using a stainless steel puck mill, which was cleaned between samples by grinding with baked quartz sand multiple times. All of the geochemical data were obtained from the homogeneous powder.

~~T~~Trace metal concentrations we report were ~~were~~ measured by ICP-MS following the methods outlined in Zhang et al. (2015). Accuracy and precision were tested with multiple runs of international standards (GBW07309, GBW07310, GBW07312, GBW07104, GBW07106) that were included with our sample runs (Table S1). With multiple analyses of each of these standards, the accepted values for vanadium (V), molybdenum (Mo) and uranium (U) were all reproduced to within < 1%, and the standard deviation of individual analyses was in the range of 2.1% to 3.8% (Table S1). For the outcrop samples, Al and Fe were determined by X-ray fluorescence following the methods outlined in Zhang et al. (2015). Some of the total Fe data from the core samples were also obtained by this method, was tested with the shale standard (GBW 03014) that was measured along with the samples and determined to be within 3.0% for V, 11% for Mo and 17% for U. The major elements were measured with X-ray fluorescence. Accuracy was tested with the whole rock standard materials (GBW 07109-07112), and the relative standard deviation of major element concentrations was < 1%, but total Fe was also obtained with a hand-held XRF (HHXRF), calibrated against a range of certified standard (see methods outlined in Zhang et al., 2016)). Overall, HHXRF Fe had a precision of about 1.5%, and

an accuracy of > 95% when compared with total Fe for an international standard (PACS-3) and a Xiamaling whose Fe content was determined with traditional XRF (Table S1). In some instances, total Fe was also determined using the hot hydrochloric acid (HCl) boiling method of Aller et al. (1986). Repeated analyses (n=22) of the certified sediment standard PACS-2 (NRC) showed a recovery of >95% of the total Fe using this method. The different methods used for total Fe determinations reflect the evolution of total Fe methodology in the lab during the course of our Fe speciation data collection. Total Fe results are coupled to their respective analytical method in Table S3.

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The hydrogen index (HI) expresses the amount of bound hydrocarbon-like compounds released during sample pyrolysis, ratioed against the total amount of organic carbon (TOC) in the sample (Espitalie et al., 1977). HI is defined as  $S_2(\text{mg/g}_{\text{rock}}) * 100 / \text{wt\% TOC}$  (Espitalié, 1986 #12419; Tissot, 1984 #12421) (Espitalié, 1986 #1109; Tissot, 1984 #1469), where  $S_2$  represents a specific peak generated during pyrolysis that is generally assumed to comprise of the longer-chained, non-volatile hydrocarbons cracked and liberated from kerogen during heating pyrolysis (Espitalié, 1986; Tissot and Welte, 1984). Pyrolysis was accomplished by programmed heating of samples in with a Rock-Eval 6 instrument (Vinci Technologies, France), where the hydrocarbons were liberated and measured by flame ionization detection. The initial and final pyrolysis temperatures were 300 °C and 650 °C, respectively, and the programmed heating rate was 25 °C/min. Pyrolysis was conducted under a  $N_2$  atmosphere and, operating with data were obtained and interpreted with the software ROCKINT for data interpretation, with a nitrogen ( $N_2$ ) atmosphere. The initial and final pyrolysis temperatures were 300 °C and 650 °C, respectively, and the programmed heating rate was 25 °C/min. The instrument was calibrated

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using standard material [GBW (E) 070064~070066]. The TOC for HI calculations were determined as described below. These HI analyses were previously reported in Zhang et al. (2015).

~~The measurement of total organic carbon (TOC) on outcrop samples was performed at the Key Laboratory of Petroleum Geochemistry in China. All samples were powdered and decarbonated (1M HCl for 2 h), and subsequently dried. TOC concentrations were measured with a LECO CS 230HC carbon-sulfur analyzer. TOC on core samples was determined after decarbonation (same as for outcrop samples) at the Nordic Center for Earth Evolution (NordCEE), University of Southern Denmark, on a Thermo Analytical element analyzer Flash EA 2000. Analytical uncertainties for all TOC analyses were less than 5% based on the concentrations of known standard materials (n=5 for analyses in China and n=11 for analyses in Denmark).~~

Isolation of kerogen involves successive removal of soluble organic matter (bitumen), mineral matter, and water from the shale, such that predominantly kerogen remains. The sediment powders were extracted for 72 h using a Soxhlet apparatus (9:1 v/v DCM/MeOH) to remove soluble bitumen. Minerals in the sediments were then removed with the following procedure (Durand and Nicaise, 1980): 1) carbonates were dissolved by reacting with  $6 \text{ mol} \cdot \text{l}^{-1}$  HCl at 60 to 70 °C for 1 to 2 h, 2) silicates were dissolved by reacting with a mixture of 40% HF and 6 M HCl (3:2 v/v) at 60 ~ 70 °C for 2 h, 3) newly formed fluorides were removed with 3% HNO<sub>3</sub>. After each step, the samples were flushed with deionized water to remove soluble material. The kerogen was finally obtained as a coarse malleable mass after drying overnight at 90 °C. According to (Durand and Nicaise, 1980), the loss of kerogen from shales during this procedure is typically around 5.8% (n=45), where most of this loss is most likely from sample handling and not a result of chemical digestion (Durand and Nicaise, 1980).

The isotopic composition ( $\delta^{13}\text{C}_{\text{org}}$ ) of dry kerogen was measured with a Delta V Advantage mass spectrometer (Thermo Scientific Co. Ltd.) after the carbon was first combusted to carbon dioxide using a Flash EA 1112 HT. The mass spectrometer was standardized with NBS-18 ( $\delta^{13}\text{C} = -5.014\text{‰}$ ) and Chinese standards GBW04405 ( $\delta^{13}\text{C} = 0.57\text{‰}$ ) and GBW04407 ( $\delta^{13}\text{C} = -22.40\text{‰}$ ) ~~standards~~ with a relative standard deviation of 0.2‰ based on replicate analyses of the standards (n=5). Isotopic compositions are reported relative to the Pee Dee Belemnite (PDB).

The measurement of total organic carbon (TOC) on outcrop samples was performed at the Key Laboratory of Petroleum Geochemistry in China. All samples were powdered and de-carbonated (1M HCl for 2 h), and subsequently dried in an oven at < 40 °C. TOC concentrations were measured with a LECO CS-230HC carbon-sulfur analyzer after standardization with certified standard materials. Replicate analyses of standards gave a standard deviation of < 5%. TOC concentrations on core samples were determined after de-carbonation (same procedure as for outcrop samples) at the Nordic Center for Earth Evolution (NordCEE), University of Southern Denmark, on a Thermo Analytical element analyzer Flash 2000 after calibration against standard materials with and standard deviation of < 5%.

Iron speciation was performed on powders of samples collected from fresh core material. The analytical method followed that of Poulton and Canfield (2005). In the Fe speciation technique, four different pools of highly reactive iron (FeHR) are extracted from the sediment~~evaluated~~. These are: carbonate associated iron (FeCARB; siderite ~~and~~ ankerite), ferric oxide and ferric oxyhydroxide minerals (FeOX; ferrihydrite, lepidocrocite, goethite,

hematite), magnetite- (FeMAG) and sulfidized iron, mainly pyrite (FePYY). The concentrations of the non-sulfidized iron pools were quantified by atomic adsorption spectroscopy (AAS), and the analytical error for each iron extraction was less than 5% (as monitored through comparisons with the internally calibrated extractions of NRC PACS-2 and PACS-3 sediment standards, n=5 per set of ~~outerop and core~~ samples). Pyrite sulfur was extracted by chromium digestion, where the sulfide was trapped as Ag<sub>2</sub>S, and its concentration determined gravimetrically (Canfield et al., 1986; Zhabina and Volkov, 1978). Replicate chromium digestions ~~extractions~~ of the sediment standard NRC PACS-2 indicate an analytical error for evaluating pyrite iron contents of less than 9% (n=6 per set core sample set). ~~The sum of the four pools of reactive iron gives the total concentration of the highly reactive iron (FeHR).~~ The Fe(HR) is typically normalized to the total concentration of Fe in the sample (FeT; the determination of which is described above.), yielding the ratio FeHR/FeT.

~~Total iron concentrations were obtained through X ray fluorescence (XRF) analysis at the PetroChina laboratory (China), handheld XRF (HHXRF) analysis at the University of Southern Denmark (see methods outlined in {Zhang, 2016 #13213}), as well as through wet extractions (boiling HCl) at SDU in Denmark. In determining the total Fe through XRF, the relative standard deviation (SD) was less than 1.0% and the accuracy was 0.2 % (n=5) against shale standard material (GBW 03014). Iron determinations through both HHXRF and the wet extractions were calibrated against the PACS 2 standard and the error determined to be less than 5% (n=33) in the case of HHXRF and less than 8% in the case of wet extractions (n=22). Total Fe extracted through the different methods XRF, HHXRF and HCl were compared in split samples (n=24) from the Xiamaling unit 3. The correlations of FeT in these samples of data obtained with XRF~~

and HHXRF (slope=0.9) and of data obtained with XRF and HCl (slope=1.0) both have an  $r^2$  value  $> 0.99$  respectively.

The ratio of highly reactive iron over total iron (FeHR/FeT) rarely exceeds 0.38 during oxic deposition, as observed in modern sediments (Raiswell, 1998 #3383). FeHR/FeT values above 0.38, in contrast, are often found in sediments below anoxic water columns, both in modern and ancient depositional settings (Raiswell, 1998 #3383; Poulton, 2002 #6423). Still, the pool of reactive iron can be influenced by rapid sedimentation (Raiswell, 1998 #3383; Poulton, 2004 #8209) and diagenesis (Poulton, 2011 #11984) and references therein), yielding lower FeHR/FeT values. Therefore, while FeHR/FeT values above 0.38 can be taken to indicate anoxic water column conditions, values below 0.38 do not necessarily represent oxic deposition and other geochemical indicators are best applied to evaluate oxic deposition conditions as explored in more detail below.

### 3 Results

The results for TOC concentration,  $\delta^{13}\text{C}$ , HI and our trace metal analyses are shown in Table S1, while Fe speciation results are shown in Table S2. Many geochemical patterns correlate with rock type and TOC content as seen in Figure 2 and Table 1. Thus, compared to the green-gray shales, the black shales show elevated TOC, and HI, and also elevated concentrations ratios of Mo/Al, V/Al and U/Al, compared to the green-gray shales, where as expressed through ratios with Al. Indeed, the green-grey shales the ratios show of Mo/Al, and V/Al ratios are very just at near the crustal average values (using crustal averages from Rudnick, 2004), and the U/Al ratio is very close to the crustal average value. In the black shales, the ratio of Fe/Al tends towards higher values (Figure 2, Table 1), particularly below 15 m in the stratigraphy (Figure 42). Iron

speciation shows that elevated ratios of FeHR/FeT are generally associated with samples containing high-TOC, ~~and trace metal enrichment, as shown through the V/Al ratio~~ (Figure 3a2). ~~The results for TOC concentration,  $\delta^{13}\text{C}$ , HI and our trace metal analyses for the outcrop material are shown in Table S2, while Fe speciation results are shown in Table S3.~~

## 4 Discussion

### 4.1 Mesoproterozoic Era sedimentary organic matter

~~Much of the discussion to follow is based on patterns of organic carbon preservation as revealed in our geochemical data, so we begin with a short discussion of the nature of the Mesoproterozoic Era carbon cycle. Generally, the Mesoproterozoic Era saw the emergence of eukaryotic organisms (Javaux, 2011; Knoll, 2014), and by 1400 Ma there is compelling evidence for eukaryotic algae in marine ecosystems (Javaux, 2011; Knoll, 2014; Zhu et al., 2016). Still, fossil eukaryotes are rare, and there is little well-verified biomarker evidence for marine eukaryotes at or prior to 1400 Ma. Therefore, while eukaryotes, including algae, likely populated marine ecosystems by 1400 Ma, there is little evidence that they were a major part of the carbon cycle (Brocks and Banfield 2009). Rather, the carbon cycle was likely dominated by prokaryotic organisms, with cyanobacteria as the most important primary producers. Indeed, by 1400 Ma the fossil record reveals a variety of cyanobacterial forms ranging from single coccoidal cells and coccoid colonies, to multicellular filaments (e.g. Golubic and Seong-Joo (1999). In addition to cyanobacteria, anoxic water column settings also supported anoxygenic phototrophic bacteria living off the oxidation of chemically-reduced species such as  $\text{Fe}^{2+}$  and  $\text{H}_2\text{S}$  (Brocks et al., 2005; Zhang et al., 2016). The carbon cycle would have also included the myriads of heterotrophic and autotrophic prokaryotes involved in elemental cycling.~~

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From a biochemical perspective, prokaryotes, including cyanobacteria, are composed primarily of carbohydrates, lipids, and proteins, just as eukaryotic algae, although in different proportions (e.g. Hedges et al., 2002; Mouginot et al., 2015). Indeed, the biggest difference in chemical composition among photosynthetic organisms is between cyanobacteria and algae, on one hand, and land plants, on the other, where land plants contain significant proportions of lignin and cellulose. These compound classes have very different elemental stoichiometries than aquatic phototrophs (Sterner and Elser, 2002), and are much more resistant to diagenetic decomposition (e.g. Cowie et al., 1992). However, terrestrial land plants emerged around a billion years after the deposition of the Xiamaling Formation, and would, therefore, not have influenced the Mesoproterozoic Era carbon cycle.

The carbon cycle of the Mesoproterozoic Era produced sedimentary organic carbon concentrations ranging from very low, nearly undetectable, to 20 wt% or more (e.g. Cox et al., 2016; Strauss et al., 1992; Zhang et al., 2015; Zhang et al., 2016) very similar to the range observed in modern sediments (e.g. Jahnke, 1996). However, in comparing organic carbon concentrations in modern and Mesoproterozoic Era sediments, one must consider the possibility that low concentrations of atmospheric oxygen could have inhibited the weathering of sedimentary organic carbon on land (e.g. Bolton et al., 2006; Daines et al., 2017), thus providing elevated concentrations of recycled ancient organic matter to marine sediments. There is no evidence for a significant contribution of recycled organic matter to Xiamaling unit 1 sediments. Rock-Eval analysis of both low and high-TOC samples from unit 1 of the Xiamaling Formation produced similar Tmax values in the range of 430 to 440 °C (Zhang et al., 2015). This range of Tmax values is characteristic of immature to early mature organic matter just entering the oil production window (Espitalié, 1986). In contrast, one would expect much higher maturity, and

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Tmax values, for recycled organic matter having experienced many cycles of deposition, burial and weathering. Therefore, there is no evidence for the recycling of ancient continental organic matter into unit 1 Xiamaling Formation sediments. Overall, organic matter cycling during the Mesoproterozoic Era appears to reflect processes and dynamics that we can relate to modern marine environments.

#### 4.2 Water column chemistry

Our geochemical data reveals fluctuating water column conditions during the deposition of unit 1. This interpretation of fluctuating bottom water chemical conditions is consistent with trace metal dynamics and iron speciation results. Thus, compared to the green-gray shales, the black shales are enriched in TOC (Figure 2; Table 1). They are enriched in the all of the redox-sensitive trace metals V, Mo and U are enriched in the black shales (Figure 2; Table 1) compared to both the green-gray shales and compared to crustal average values. Enrichments in these trace metals, and TOC, are typical for deposition under anoxic water-column conditions (Algeo and Rowe, 2012), and such enrichments are typical for deposition under anoxic water-column conditions (Brumsack, 2006 #11751). Furthermore, There is also some indication black shales are of enriched in Fe enrichment in the black shales, as expressed through the Fe/Al ratio (Figure 2, Table 1), compared to the green-gray shales. Such enrichments would be indicative of the water-column mobilization of Fe and its enhanced deposition of Fe under anoxic bottom water conditions (Lyons and Severmann, 2006). Therefore, trace metal results, and patterns in Fe/Al ratios, are fully consistent with black shale deposition under an anoxic water column. In contrast, the lack of enrichment in trace metals during in the green-gray sediments are consistent with deposition under oxygenated bottom waters (e.g. Piper and

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Calvert, 2009; Tribovillard et al., 2006). Trace metal concentrations, however, also typically correlate with TOC concentration (e.g. Algeo and Lyons, 2006; Tribovillard et al., 2006). Therefore, the low TOC content of the green-gray shales could partially explain the low trace metal abundance in these shales, and alternative geochemical indicators of bottom-water chemistry would strengthen our geochemical interpretations.

We also see sequential Fe extraction results enrichments from our sequential Fe extraction offer another assessment of water column chemistry of the core samples. Indeed, sequential Fe extractions have become a standard tool for evaluating bottom water chemistry during sediment deposition (Poulton and Canfield, 2005; Raiswell and Canfield, 2012, 1998). Thus, from a compilation of data from modern environments, the ratio of highly reactive iron over total iron (FeHR/FeT) rarely exceeds 0.38 during deposition in oxygenated marine waters (Raiswell and Canfield, 1998). In contrast, when FeHR/FeT values exceed 0.38, this indicates sediment deposition below anoxic water columns, both in modern and ancient depositional settings (Poulton and Raiswell, 2002; Raiswell and Canfield, 1998).

Our Fe extractions were performed on fresh core material where it was not always easy to distinguish between black shales and green-gray shales, as was straightforward in the outcrop samples. Therefore, we have organized our extraction results as a function TOC concentration (Figure 3), recalling that in outcrop, TOC concentrations of > 2 wt% easily distinguished black shales, whereas the green-gray shales were easily distinguished at TOC values of mostly < 0.5 wt% (Figure 2, Table S2). We collected very few samples from the outcrop with TOC concentrations of between 0.5 and 2 wt%, so the shale color (type) in this TOC range is uncertain.

From our Fe extraction ~~Thus, from these results, the ratio FeHR/FeT exceeds~~ 0.38 for sediments with TOC exceeding 1 to 2 wt% (Figure 2a) (Figure 3a). As ; these TOC levels are comparable to those for black shales from outcrop material (Figure 1). As mentioned above, when FeHR/FeT values of greater than exceeds 0.38 this is generally taken to indicate sediment deposition under bottom-water anoxia (Raiswell and Canfield, 2012, 1998). These results, therefore, reinforce our conclusions from trace metal dynamics that the black shales of unit 1 deposited in anoxic waters. In addition, euxinic (sulfidic) water column conditions are indicated when FePY/FeHR > 0.7-0.8 for sediments deposited in anoxic waters, and when FePY/FeHR < 0.7-0.8 ferruginous conditions are indicated (Raiswell and Canfield, 2012). The chemical nature of anoxic deposition is not a focus here, but from the data in Table S3, it is clear that the anoxic waters of unit 1 contained a mixture of euxinic and ferruginous chemistry.

Unlike the high-TOC sediments, those with low-TOC ~~Furthermore, samples deposited with elevated FeHR/FeT are also generally associated with elevated V/Al as would be expected for anoxic depositional environments (Figure 2b) (Raiswell, 2012 #12208; Lyons, 2006 #8330).~~

In contrast, ~~particularly with TOC concentrations of < 0.5wt%, have FeHR/FeT values of less than 0.38. These FeHR/FeT values are compatible with sediment deposition under oxygenated bottom waters, providing further evidence, in addition to the trace metals, that the green-gray shales deposited under oxygenated bottom water conditions. As we will see below, our assessments of bottom water chemistry during unit 1 deposition is compatible with additional organic geochemical constraints.~~ the low-TOC green-gray shales from outcrop show either low or no enrichments in U, Mo and V (Figure 1). They also have low values of Fe/Al and, from the Fe extraction results of core material, low TOC also have low ratios of FeHR/FeT below the anoxic

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threshold (Figure 2). Taken together, these geochemical indicators are consistent with an oxic depositional environment for the green gray shales, and overall support depositional environment interpretations from TOC and HI systematics.

#### **4.34 HI and $\Theta$ organic carbon preservation and water column chemistry**

We begin by Hydrogen index (HI) is often used to assess organic matter maturity and state of organic matter preservation. Thus, high HI values are associated with better preserved organic matter with lower maturity, while low values of HI are associated with poorly preserved and organic mature with organic matter of high maturity (Espitalie et al., 1977; Tissot and Welte, 1984). From the outcrop materials, the HI is considerably higher in the black shales compared to the green-gray shales (Table 1, Figure 2, 3c), and overall, HI correlates with TOC concentration (Figure 3c). Despite these differences, the green-gray and black shales share similar organic matter  $\delta^{13}\text{C}$  values (Figure 1) consistent with a similar source of organic carbon to each sediment type. As mentioned above, high degrees of thermal maturity can reduce the HI (Espitalie et al., 1977; Tissot and Welte, 1984), but unit 1 sediments have all experienced the same thermal history, so this cannot account for differences in the HI between the different sediment types.

considering the strong correlation between HI and TOC in unit 1 sediments of the Xiamaling Formation (Figure 1, 3). Such a correlation is also seen in sediments deposited during the Phanerozoic Eon, whereThe magnitude of the HI has often been linked with the degree organic carbon preservation. In general, a higher HI is associated with more H-rich aliphatic organic matter and better organic matter preservation, while low HI is associated with poorer organic matter preservation (Espitalie et al., 1977; Tissot and Welte, 1984). Terrestrially derived

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~~lignin and cellulose rich organic matter (with a low HI) from vascular land plants can also contribute to low HI values in the sediment (Espitalie, 1977 #13110; Tissot, 1984 #12421). This, however, is not a consideration for Mesoproterozoic aged sediments that deposited well before land plant evolution.~~

~~In From~~ Phanerozoic-aged examples, alternations in bottom water oxygenation have been argued to explain stratigraphically controlled differences in TOC and HI; similar differences to those observed inorganic carbon preservation, as it drove correlations between TOC HI to those for unit 1 of the Xiamaling Formation, have been ascribed to the presence or absence of oxygen during sediment diagenesis. Thus, in one example, TOC-rich, laminated to micro-burrowed shales from the Cretaceous Greenland Formation ~~from the western interior of North America~~ deposited with high HI, whereas moderately-to-highly bioturbated low-TOC shales deposited with low HI (Pratt, 1984). Palynological and organic geochemical analyses revealed a limited contribution of terrestrial organic matter to all sediments types, and differences in HI were attributed to the influence of oxygen on organic carbon preservation. In particular, oxygen was much more available to the bioturbated sediments compared to the laminated and micro-burrowed sediments, and more oxygen availability resulted in more extensive organic matter decomposition (Pratt, 1984), yielding both lower TOC and lower HI values. In another example, careful palynological and organic-geochemical analyses from the Upper Jurassic Kashpir shales of the Volga Basin, Russia, revealed that TOC-poor low-HI sediments were most likely associated with intensive oxic organic matter decomposition, whereas TOC-rich high-HI sediments were likely deposited in a continuously anoxic environment (Riboulleau et al., 2003).

In addition, alternating black and green claystone sequences from Cretaceous-aged sediments of the proto-North Atlantic (Kuypers et al., 2004) displayed dynamics in TOC and HI

that are highly reminiscent of those from unit 1 of the Xiamaling Formation. Thus, the black claystones contained organic matter predominantly of marine origin, and biomarker evidence demonstrated the presence of sulfide-oxidizing phototrophs in the water column (Kuypers et al., 2002). This evidence, coupled with trace metal enrichments in the black claystones, demonstrated water-column anoxia during black claystone deposition. The green claystone, some of which were heavily bioturbated, and thus clearly deposited in oxygenated waters, had low concentrations of TOC and low HI values. In addition, biomarker evidence showed an enhanced contribution of relatively refractory biomarkers such as n-alkanes in the green claystones, compared to the black claystones, where more labile hopanoids and steroids were much more abundant (Kuypers et al., 2002). These biomarker patterns were argued to reflect greater oxygen exposure times and more extensive organic matter decomposition in the green claystones compared to the black claystones (Kuypers et al., 2002). Thus, at least in part, differences in HI and TOC between the green and black claystones reflected differences in carbon preservation as controlled by oxygen availability. Some of the low HI in the green claystones may also be attributed to a relatively higher contribution of terrestrial organic matter to the sediments (Kuypers et al., 2002). But, the terrestrial organic matter contribution in the green claystones was likely only evident due to extensive decomposition of the marine organic carbon pool by oxygen.

There are also examples where relationships between HI and oxygen availability are not so straightforward. For example, in surface sediments of the eastern Arabian Sea, an intense oxygen minimum zone (OMZ) impinges on the sediment surface at water depths between about 100 and 700 m, with oxygenated water above and below (Naqvi et al., 2005). In these sediments, HI does not correlate with TOC, and HI values are equally high in sediments in the OMZ and those in oxygenated waters above and below the OMZ (Calvert et al., 1995). In this case, organic

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carbon is heavily affected by the sorting associated with active water currents and hydrodynamic processes (Cowie, 2005; Cowie et al., 2014). But even here, patterns of biomarker preservation and other indices of organic matter preservation suggests that organic matter is more heavily degraded under well-oxygenated conditions compared to low-oxygen to anoxic conditions in the heart of the OMZ (Cowie et al., 2014; Damste et al., 2002).

Returning to the Xiamaling Formation, and in reference to the studies as mentioned above, it deposited well before the evolution of terrestrial land plants, and the green-gray and black shales share similar organic matter  $\delta^{13}\text{C}$  values (Figure 1) consistent with a similar source of organic carbon to each sediment type. High degrees of thermal maturity can reduce the HI (Espitalie, 1977 #13110; Tissot, 1984 #12421), but unit 1 sediments have all experienced the same thermal history, so this cannot account for differences in the HI between the different sediment types. We conclude, therefore, that the patterns of HI in unit 1 Xiamaling sediments indicate enhanced organic matter preservation in the high-TOC black shales compared to the low-TOC green-gray shales. Also, and by analogy with modern and ancient sedimentary environments, Thus, patterns of TOC and HI in Xiamaling unit 1 are best understood in terms of differences in carbon preservation as driven by the presence or absence of oxygen during sediment organic matter mineralization. In this way, view, fluctuations between TOC-rich black shales and TOC-poor shale resulted from fluctuations between anoxic and oxic depositional conditions. This conclusion is completely compatible with, and indeed supports, the patterns of bottom-water oxygenation as revealed from trace metal and Fe speciation results as discussed above.

#### 4.4 Modern studies of organic carbon preservation

These ~~relationships~~ ~~Phanerozoic relationships~~ between oxygen availability and organic carbon preservation as explored above are completely consistent with ~~both~~ experimental observations of decomposing organic matter ~~and observations from observations from modern marine sediments.~~ Thus, from experiments on ~~aged~~ algae that was pre-decomposed for 40 days (to about one half of its initial biomass and thus representing the type of “aged” organic matter that deposits onto shelf sediments), organic matter in the presence of oxygen decomposed at rates 5 to 10 times greater ~~than compared to~~ organic matter decomposed anaerobically (Kristensen and Holmer, 2001). These experiments were not ~~run continued~~ until all of the labile organic matter was exhausted (this would have taken many years), but the results strongly indicate enhanced ~~preservation of~~ organic matter preservation under anoxic conditions compared to its preservation in the presence of oxygen.

These experimental results further support observations of organic carbon preservation reinforce in observations from mmodern marine sediments (Canfield, 1994; Hartnett et al., 1998). Thus, in one approach, organic carbon preservation was compiled for marine sediments across a wide range of sedimentary environments, from continental shelf to the deep sea, and for oxygenated, low-oxygen, and fully anoxic bottom-water conditions (Canfield, 1994). ~~where at the same rate of sedimentation (and for sedimentation rates  $< 0.1 \text{ g cm}^{-2} \text{ y}^{-1}$ ), sediments depositing in anoxic and low oxygen environments preserve considerably more organic carbon compared to sediments depositing in oxygenated environments (Figure 3a) (Canfield, 1994 #2559).~~ Here, carbon preservation (%) is defined as:

$$\%C_{\text{pres}} = 100 * C_{\text{bur}} / C_{\text{dep}} = 100 * C_{\text{bur}} / (C_{\text{bur}} + C_{\text{resp}}) \quad (1)$$

Where %C<sub>pres</sub> is the percent of organic matter falling onto the sediment surface that is buried and preserved, C<sub>bur</sub> is the burial flux of organic carbon, and C<sub>dep</sub> is the flux of organic carbon depositing onto the sediment surface. For practical reasons, C<sub>dep</sub> is usually determined as sum of the organic carbon burial flux (C<sub>bur</sub>) and the rate of organic carbon respiration (C<sub>resp</sub>) (Canfield, 1994, 1989). This compilation is shown in Figure 4a, and where we see that at the same rate of sedimentation (and for sedimentation rates <0.1 g cm<sup>-2</sup> y<sup>-1</sup>), sediments depositing in anoxic and low-oxygen environments preserve considerably more organic carbon compared to sediments depositing in oxygenated environments (Figure 3a) (Canfield, 1994 #2559).

In another approach, the degree of organic carbon preservation (as derived in equation 1) were related to amount of time the surface sediments have been exposed to oxygen, the so-called oxygen exposure time (Hartnett et al., 1998). The oxygen exposure time (O<sub>2</sub>-exp) is calculated from the depth of oxygen penetration into the sediment (O<sub>2</sub>-pen) and the linear sedimentation rate (Linear rate)

$$O_2\text{-exp (y)} = O_2\text{-pen (cm)} / \text{Linear rate (cm y}^{-1}\text{)} \quad (2)$$

In the original publication by Hartnett et al. (1998), calculations of oxygen exposure times were mostly based on calculated oxygen penetration depths. In this calculation, oxygen penetration was derived from a simple model where measures rates of sediment oxygen uptake were balanced by a linear decrease in oxygen concentration in the sediment. Normally, however, oxygen will penetrate much deeper than a linear gradient derived from the sediment surface would indicate (e.g. Glud, 2008). For this reason, we have compiled our own database (Table S4), that relies on actual measurements of oxygen penetration depth and for which carbon preservation (burial efficiency) is also calculated. Our compilation includes data from many parts

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of the global ocean and is summarized in graph form in Figure 4b. Consistent with Hartnett et al. (1998), however, lower carbon preservation accompanies greater oxygen exposure times. This idea is consistent with the experimental observations of enhanced organic matter mineralization in the presence of oxygen (Kristensen and Holmer, 2001) and the observations of carbon preservation from Figure 4a as discussed above.

Thus, the presence or absence of oxygen significantly influences the preservation of organic matter in sediments. Unfortunately, the relationship between organic matter preservation and HI has not been explored in modern sediments. However, for the oxygen minimum zone (OMZ) of the Peruvian margin, sediment HI generally correlates with TOC, and when TOC > 10 wt% in the anoxic portion of the OMZ, HI is high and in the range of 400 mgHC/gTOC. In contrast, for sediments depositing in deeper, oxygenated, waters, HI is much lower, in the range of 50 mgHC/gTOC when TOC is around 1 wt% (Arthur, 1998 #5374). Trends between HI and oxygenation, though, are somewhat blurred by sediment re-suspension and cross-shelf transport as well as particle sorting (Arthur, 1998 #5374). Such physical processes have also influenced the distribution of HI in sediments of the eastern Arabian Sea (Calvert, 1995 #13340; Cowie, 2005 #7840).

~~Returning to the Xiamaling Formation, as mentioned above, it deposited well before the evolution of terrestrial land plants, and the green-gray and black shales share similar organic matter  $\delta^{13}\text{C}$  values (Figure 1) consistent with a similar source of organic carbon to each sediment type. High degrees of thermal maturity can reduce the HI (Espitalie, 1977 #13110; Tissot, 1984 #12421), but unit 1 sediments have all experienced the same thermal history, so this cannot account for differences in the HI between the different sediment types. We conclude, therefore, that the patterns of HI in unit 1 Xiamaling sediments indicate enhanced organic matter~~

preservation in the high TOC black shales compared to the low TOC green gray shales. Also, and by analogy with modern and ancient sedimentary environments, patterns of TOC and HI in Xiamaling unit 1 are best understood in terms of differences in carbon preservation as driven by the presence or absence of oxygen during sediment organic matter mineralization. In this view, fluctuations between TOC rich black shales and TOC poor shale resulted from fluctuations between anoxic and oxic depositional conditions.

This interpretation of fluctuating bottom water chemical conditions is consistent with trace metal dynamics and iron speciation results. Thus, the redox sensitive trace metals V, Mo and U are enriched in the black shales (Figure 1), and such enrichments are typical for deposition under anoxic water column conditions (Brumsack, 2006 #11751). Furthermore, black shales are enriched in Fe, as expressed through the Fe/Al ratio (Figure 1), and such enrichment would indicate the enhanced deposition of Fe under anoxic bottom water conditions (Lyons, 2006 #8330). We also see Fe enrichments from our sequential Fe extraction of the core samples. Thus, from these results, the ratio FeHR/FeT exceeds 0.38 for sediments with TOC exceeding 1 to 2 wt% (Figure 2a); these TOC levels are comparable to those for black shales from outcrop material (Figure 1). As mentioned above, when FeHR/FeT exceeds 0.38 this is generally taken to indicate sediment deposition under bottom water anoxia (Raiswell, 1998 #3383; Raiswell, 2012 #12208). Furthermore, samples deposited with elevated FeHR/FeT are also generally associated with elevated V/Al as would be expected for anoxic depositional environments (Figure 2b) (Raiswell, 2012 #12208; Lyons, 2006 #8330).

In contrast, the low TOC green gray shales from outcrop show either low or no enrichments in U, Mo and V (Figure 1). They also have low values of Fe/Al and, from the Fe extraction results of core material, low TOC also have low ratios of FeHR/FeT below the anoxic

threshold (Figure 2). Taken together, these geochemical indicators are consistent with an oxic depositional environment for the green-gray shales, and overall support depositional environment interpretations from TOC and HI systematics.

#### **4.52 Organic carbon decomposition in the sediment and water column Constraining oxygen levels**

As discussed above, our geochemical results indicate enhanced considerable amounts of oxic organic matter decomposition during the deposition of the green-~~grey~~gray shales compared to black shales units of in unit 1. As outlined above, High amounts of oxic degradation are obvious from differences in the HI is much reduced between the in the green-gray shales compared to the and the black shales. Furthermore, the, and also in TOC concentration averages 0.29 wt% in the green-gray shales, where the average TOC for the black shales is compared to 3.12 wt% for the black shales, and 0.33 wt% for the green gray shales, just over 10 nearly 10 times reduced/reduced (Table 1, Figure 2c). In the modelling that follows what follows, we use observations from modern environment to convert these trends in carbon preservation to sediment organic matter mineralization rates, and from here, to the minimum levels of atmospheric oxygen needed to drive these rates of mineralization. Therefore, to provide the best sediment model for carbon mineralization, we must evaluate the comparative histories of organic matter decomposition under oxic and anoxic conditions from the water column to the sediment.

Beginning in the water column, To begin, we recognize that organic carbon mineralization occurs both in sediments and in the water column, and therefore, we must consider how both environments contribute to organic carbon preservation. As our model is based on differences in organic carbon preservation between sediments deposited in oxic and

~~anoxic settings, we consider first the potential role of water column mineralization in generating these differences.~~ Keil et al. (2015) ~~provides one of the few studies to compare organic carbon transport through oxic and anoxic waters. In this study~~~~In one of the few studies to address this issue directly,~~ Keil et al. (2015) explored with sediment traps the composition of particles settling through waters of the Arabian Sea. In two stations, the water column was nitrite-containing and completely anoxic between 130-150 meters to > 500 meters water depth. ~~In contrast, a, while at a third site, the water also became anoxic at about 150 meters depth, but oxygen began~~ ~~oxygen began~~ to accumulate at about 200 meters water depth, below a narrow anoxic zone ~~of some 50 meters depth. In sediment traps at~~ ~~By~~ 500 meters depth, TOC averaged about 11 wt% for particles settling through oxygenated waters and 15 wt% for particles settling through anoxic OMZ waters (Keil et al., 2015). Thus, in the Arabian Sea, there is a relatively small difference (27%) in the carbon content of particles settling through oxic and anoxic waters to 500 meters depth.

~~This difference could relate to differences in the relative efficiencies of oxic vs anoxic mineralization, or~~~~We would expect this~~ ~~to differences in the initial composition of the particles originating at the different sites. If oxic vs anoxic decomposition is the main factor driving these TOC differences, then the differences would likely~~~~difference to~~ be even smaller for particles settling to ~~the shallower water~~ depths of 50 to 200 meters ~~as we surmise for unit 1 of the~~ ~~representing the likely water depth range for the parts of the~~ Xiamaling Formation ~~unit 1 we are exploring.~~ The Arabian Sea results also reinforce a general observation that ~~throughout the global ocean,~~ particles settling through the upper ~~100s of meters~~ ~~layer of the~~ oxygenated marine water ~~columns (100s of meters)~~ are quite TOC-enriched, with values much ~~closer~~ ~~higher~~ (typically 3 to 15 wt% ~~; Armstrong et al., 2002; Honjo et al., 1982~~) ~~to (Honjo, 1982~~

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~~#1245;Armstrong, 2002 #12828} than those observed in the black shales than those observed in the green-gray shales of unit 1 (Table 1). Overall~~~~Thus, we argue that~~ the differences in the TOC content between the green-gray and black shales in unit 1 were ~~likely most likely~~~~mostly~~ driven by differences in sediment organic carbon preservation, as determined by the presence or absence of bottom-water oxygen, ~~and not by differences in water column processes. This assessment is based on: 1) the relatively small differences in the TOC content of particles settling through oxic and anoxic waters of the Arabian Sea, and 2) the observation that the green-gray shales of unit 1 have TOC contents much reduced compared to particles settling through the upper 100s of meters of the marine water column.~~

#### ~~4.6 Constraining oxygen levels~~

~~Our goal now is to determine the levels of bottom-water~~

~~We will now draw from modern observations and develop a simple sediment diagenetic model to constrain the oxygen levels required to account for the patterns of carbon preservation in Xiamaling unit 1. First, however, we note that even though the TOC content of particles settling through the oxic and anoxic water columns of Xiamaling unit 1 was likely similar, some 20% to 60 % of the settling organic matter likely mineralized as particles settled from the base of the upper mixed layer to the sediment surface at some 50 to 200 meters water depth (e.g. (Martin, 1987 #1776; Marsay, 2015 #13088; Lamborg, 2008 #13091; Keil, 2015 #13217)). This organic matter mineralization amounts to an oxygen sink and a reduction in water column oxygen levels, that is not included in our model. To include this oxygen sink would raise our minimum oxygen estimates by the magnitude of the sink. Thus, ignoring this oxygen sink is one way in which our model provides a conservative minimum estimate for atmospheric oxygen levels.~~

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~~Returning to the sediment model, we now estimate the amount of~~ oxygen required to account for ~~yield~~ the differences in carbon preservation between the green-gray and black shales of unit 1, which we assume, from the discussion above ~~(Seet.4.2)~~, to be a factor of 10. Our model is constrained from modern observations through a multi-step process. Our first step is to revisit the observation that organic carbon ~~TOC~~ preservation in modern marine sediments ~~scales is~~ controlled by ~~with~~ both sedimentation rate and ~~with~~ sedimentary environment as shown in (Figure 43a). ~~To utilize these trends, To proceed, therefore,~~ we must first estimate the rate of sediment ~~depositionation rate~~ for Xiamaling unit 1. From precise zircon dating, we previously determined an average linear (after compaction and lithification) sedimentation rate of  $6.7 \times 10^{-4}$   $\text{cm y}^{-1}$  for a 52 meter section encompassing upper unit 3 into lower unit 2 of the Xiamaling Formation (Zhang et al., 2015). This linear sedimentation rate translates into a mass accumulation rate of  $1.7 \times 10^{-3} \text{ g cm}^{-2} \text{ y}^{-1}$ , assuming an average rock density of  $2.5 \text{ g cm}^{-3}$  (a density similar to quartz at  $2.65 \text{ g cm}^{-3}$ ; and typical for marine sediments). We call this the XML rate. We cannot be certain that this rate applies to unit 1, which is undated, but to accommodate this uncertainty, we will also consider sedimentation rates of one half of the XML rate and 10 times greater than this rate.

To demonstrate our approach, we begin with a sedimentation rate consistent with the XML rate ( $1.7 \times 10^{-3} \text{ g cm}^{-2} \text{ y}^{-1}$ ). In modern anoxic environments, sediments at this sedimentation rate experience carbon preservation of between about 20% and 30% as seen by extrapolating between existing data points in Figure 43a. This degree of carbon preservation would, ~~therefore~~, be relevant for the black shales of unit 1 of the Xiamaling Formation. With a factor of 10 times lower organic carbon preservation (reflecting a 10 times lower TOC content) for the green-gray shales, the carbon preservation ranges from between 2% and 3% (see also

Figure 43a). Similar calculations for 10 times ~~and one half of~~ the XML sedimentation rate, ~~and ½~~ ~~this rate~~, are shown in Table 24. Our ~~calculated-derived~~ organic carbon preservation percentages for the green-gray shales compare reasonably well with observations from modern oxic marine environments-sediments (Figure 43a).

From here, we determine the amount of oxygen exposure that sediments require to achieve the degrees of carbon preservation we have determined. These oxygen exposure times ( $O_2$ -exp) are obtained from the compilation in Figure 4b, where we utilize the full range of oxygen exposure times as determined in modern environments. These oxygen exposure times are summarized in Table 2. ~~The concept of oxygen exposure time, and its influence on carbon preservation, was initially introduced by (Hartnett, 1998 #13102). The idea is that more extensive organic carbon oxidation accompanies longer exposure to oxygen. As mentioned above, this idea is consistent with the experimental observations of enhanced organic matter mineralization in the presence of oxygen (Kristensen, 2001 #5524) and the observation that carbon preservation in oxygenated environments is lower at slower rates of sediment deposition, giving more time for oxic decomposition to occur (Figure 3a). Oxygen exposure time is calculated by dividing the sediment oxygen penetration depth (cm) by the linear sedimentation rate ( $\text{cm y}^{-1}$ ). In the original publication by (Hartnett, 1998 #13102), calculations of oxygen exposure time were mainly based on a simple model for oxygen penetration depth assuming a linear decrease in oxygen concentration in the sediment. This is typically not the case, and oxygen will generally penetrate much deeper than a linear gradient derived from the sediment surface (e.g. (Glud, 2008 #8821)). For this reason, we have compiled our own database (Table S2), which relies on actual measurements of oxygen penetration depth and for which carbon preservation (burial efficiency) can be calculated. Our compilation includes data from many~~

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parts of the global ocean and is summarized in graph form in Figure 3b. From this graph, we determine the range in oxygen exposure times associated with the different degrees of green gray shale carbon preservation as summarized in Table 1. The oxygen exposure time results are also shown in Table 1.

With the oxygen exposure times we have determined, we can now calculate the depth of oxygen penetration necessary to generate these exposure times. To do this, we must also know the linear sedimentation rate (Linear rate  $\text{cm y}^{-1}$ ) which is related to the mass sedimentation rate (mass rate) through the following expression:

$$\text{Linear rate (cm y}^{-1}\text{)} = \text{mass rate (g cm}^{-2}\text{ y}^{-1}\text{)} * [1 / (1 - \phi) * \rho \text{ (g/cm}^3\text{)}] \quad (32)$$

where,  $\phi$  is sediment porosity and  $\rho$  is dry sediment density. Sediment porosity and dry density ~~These parameters~~ are often measured, but rarely reported and not compiled, to our knowledge, for surface muds (top few  $\text{cm}^2$ 's). ~~In our experience,~~ As mentioned above, and from our experience, a value of  $2.5 \text{ g cm}^{-3}$  is a good approximation for the dry density of sediment particles ~~(we also used this value above to determine mass accumulation rates for the Xiamaling), and this value is typically used.~~ Surface sediment porosities can vary, and in our experience ~~with surface muds,~~ a range of 0.7 to 0.9 for the upper couple of centimeters encompasses ~~all of~~ our dozens of observations ~~from a of a great~~ variety of different marine muds. Exceptions include, except for organic-rich euxinic sediments that can have porosities of  $> 0.95$ , and sands which have porosities in the range of 0.4 to 0.5. The Xiamaling Formation sediments of unit 1, however, are relatively fine-grained silty muds, so comparisons with sands are inappropriate. In our calculations, we explore a range of porosities from 0.7 to 0.9. The oxygen penetration depth ( $\text{O}_2$ -pen) is determined by rearranging Equation 2 and is given as:

$$O_2\text{-pen (cm)} = \text{Linear rate (cm y}^{-1}\text{)} * O_2\text{-exp (y}^{-1}\text{)} \quad (4)$$

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Calculations of oxygen penetration depths at different porosities and at different oxygen exposure times for the XML sedimentation rate are provided in Table 32. From here, we determine how much bottom water oxygen ( $[O_2]_{BW}$ ) is required to generate the oxygen penetration depths ( $O_2\text{-pen}$ ) we have calculated. Generally, oxygen penetration will depend on the concentration of bottom water oxygen, the rate of sediment oxygen uptake, and the kinetics of organic carbon mineralization including any oxygen dependency on mineralization and the depth-distribution of organic matter quality. Numerous models have been proposed relating these parameters (e.g. Hartnett et al., 1998; Hulth et al., 1994; Rasmussen and Jørgensen, 1992), and we will build on the simple model proposed by Rasmussen and Jørgensen (1992), and shown in Eq. 53, rearranged to yield  $[O_2]_{BW}$ .

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$$[O_2]_{BW} = O_2\text{-pen} * O_2\text{-flux} / A * \phi D_{sed} \quad (53)$$

where, in addition to the terms already named,  $O_2\text{-flux (mmole cm}^{-2} \text{y}^{-1}\text{)}$  is the flux of oxygen into the sediment,  $D_{sed} \text{ (cm}^2 \text{y}^{-1}\text{)}$  is the sediment diffusion coefficient for oxygen approximated as  $D * \phi^2$  (Ullman and Aller, 1982), where  $D$  is the free diffusion coefficient, which we take as  $536 \text{ cm}^2 \text{y}^{-1}$ , the value for seawater at  $15^\circ\text{C}$  (Broecker and Peng, 1982) and  $A$  is a variable that we will explore below.

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When in this equation,  $A$  is a variable, and a value of  $A=1$ , Equation 5 is consistent with a linear oxygen profile in the sediment as assumed, for example, by (e.g. Hartnett et al. (1998)). This formulation would represent is consistent with a sediment containing a source of oxygen from the overlying water and a fixed sink at the depth of oxygen penetration, but no oxygen removal in between. A value of  $A=2$  generates an equation consistent with a constant rate of

oxygen removal with depth in the sediment, but no dependency of oxygen removal rate on oxygen concentration (thus zero-order reaction kinetics on oxygen concentration) as developed in Rasmussen and Jørgensen (1992). Other values for A may also be chosen as explored below.

To evaluate these equations, and to determine most appropriate value for A, we have compiled a database on the relationship between oxygen uptake rate and oxygen penetration depth for a broad range of marine sediments depositing in a range of different bottom water oxygen concentrations (Figure 43c; data in Table S45; note that some of this data is also presented in Table S4). We see that a value of A=2 clearly underestimates the oxygen penetration depth at a given rate of oxygen uptake (and A=1 is even worse; not shown). ~~T, but~~ the data, however, are consistent with a value of A=4, which generates a relationship between oxygen penetration depth and oxygen uptake rate very similar to the best-fit power function of the data ( $O_2 \text{ uptake} = 0.203O_2\text{-pen}^{-0.868}$ ;  $R^2=0.7526$ ). With the value of A=4, Equation 53 also seems to work through the range of oxygen concentrations explored in (Figure 43c). Therefore, in subsequent modelling as described below, we will use Equation 53 with a value of A=4 and consider it reliable for the range of oxygen concentrations explored. We note, however, that with a value of A=4, Equation 5-3 is simply an empirical fit of the data in Figure 43c and ~~isn~~ not based on first-principle diagenetic relationships as is true when A=1 and when A=2.

Our next step is to determine rates of sediment oxygen uptake ( $O_2$ -flux, mmol cm<sup>-2</sup> y<sup>-1</sup>) for the Xiamaling Formation green-gray shales for each of our model scenarios (~~Table 1~~); which, in In modern sediments, the oxygen uptake rate is approximately equivalent to the total carbon mineralization rate (C<sub>resp</sub>; see Equation 1) as described, for example, in Canfield et al. (1993). The equivalency arises because oxygen is also used to oxidize the reduced products of anaerobic mineralization. ~~We calculate total rates of carbon mineralization by combining the~~

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burial fluxes of TOC (the product of average green gray shale TOC concentration and the mass accumulation rate,  $C_{bur}$ ) and from our estimates of carbon preservation ( $\%C_{pres}$ ) as revealed in Table 4. Therefore, from rearranging Equation 1, we can isolate  $C_{resp}$ : Thus:

$$O_2\text{-flux} = C_{resp} = (100 * C_{bur} / \%C_{pres}) - C_{bur} \quad (64)$$

The values for  $C_{resp}$  (and thus  $O_2$ -flux) obtained this way are internally consistent mass-balance values and do not require any additional assumptions.  $O_2$ -flux These results are shown in Table 43 for the different modeling scenarios.

With our calculations of  $O_2$ -pen and  $O_2$ -flux, we then use the Equation 53 with a value of  $A=4$ , as derived above, to calculate bottom water oxygen levels at different sediment porosities. The results are shown in Table 34. Our estimates for bottom water oxygen concentration vary widely, and are highest for scenarios with the longest sediment oxygen exposure times. Long oxygen exposure times accompany deep oxygen penetration (see Table 34), and higher concentrations of bottom water oxygen are required to balance the oxygen flux into the sediment against a smallshallow oxygen gradient as required by the deeper oxygen penetration. In many cases, our calculations with high oxygen exposure times yield bottom water oxygen concentrations that exceed modern values by a factor of 10 or more. One could view these as upper estimates for bottom water oxygen concentrations using our modeling approach, but this is not particularly useful, as such high oxygen concentrations during the Mesoproterozoic Eratimes are very unlikely.

Just as our high estimates for bottom water oxygen concentrations are unrealistically high, our minimum estimates are probably also too low. However, as our goal here is to constrain minimum oxygen levels during Xiamaling Formation unit 1 deposition, we view these

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values as highly informative. Thus, for both the case of XML sedimentation rates and sedimentation rates one half of these (XML\*0.5), a minimum estimate of 18 to 19  $\mu\text{M}$  bottom water oxygen is obtained. ~~These oxygen concentrations, which~~ translates into an atmospheric oxygen concentration of 7% to 8% PAL assuming that the bottom water is in equilibrium with ~~modern~~ atmospheric oxygen at a temperature of 15°C (~~yielding with~~ an equilibrium concentration of 250  $\mu\text{M}$ ). ~~TAs explored above,~~ this calculation of atmospheric oxygen concentration does not account for any reduction in bottom water oxygen concentration that might have occurred due to ~~water column~~ respiration ~~as particles settled through the oxic water column. Accommodating this oxygen loss would increase our atmospheric oxygen concentration estimates.~~ ~~Not accounting for this oxygen loss is another way in which our calculated atmospheric levels are minimum values.~~

One potential criticism of our approach is that the factor of 10 difference in carbon preservation indicated between the black shales and the green-gray shales of unit 1 is an overestimate. ~~TWhile the HI results, together with the TOC concentrations, strongly indicate a difference in carbon preservation between the black and green gray shales, there is no established relationship as to how these two parameters correlate as a result of carbon mineralization.~~ Thus, if the organic matter deposited onto the green-gray shales with a lower concentration than the black shales, then the difference in carbon preservation could be less than indicated by the difference in TOC concentration between the sediment types. ~~As discussed above, we do not believe than differences would have been significant. We have already noted that such differences are not apparent for organic matter settling through the upper several hundred meters of oxygenated and anoxic waters of the Arabian Sea water column,~~ but we still must entertain this possibility ~~for the Xiamaling Formation.~~

Thus, we have also calculated carbon preservation, oxygen exposure times, oxygen-penetration depths and, finally, estimates for bottom water oxygen for XML sedimentation rate and a factor of 5 difference in preservation between the black and green-gray shales (Figure 43a, Tables 32-4). These results yield a lower minimum bottom water oxygen concentration of 4.4  $\mu\text{M}$  and about 2 % PAL atmospheric levels. This value, however, is likely too low for at least two reasons. First, these low bottom water oxygen estimates are accompanied by steep oxygen gradients and shallow oxygen penetration in the sediment (Table 3). In this case, at both low oxygen concentrations and steep concentration gradients one must also consider that oxygen is supplied to the sediment surface, and subsequently into the sediment, through a viscous boundary layer, which varies in thickness from 0.04 to 0.08 cm in continental margin sediments, where transport is by molecular diffusion (Glud, 2008). Transport through this boundary layer is by molecular diffusion. Thus, strictly speaking, our oxygen estimate of 4.4  $\mu\text{M}$  (Table 34) is the oxygen concentration at the sediment surface, below the viscous boundary layer. We calculate that a minimum  $[\text{O}_2]_{\text{BW}}$  of between 10.1  $\mu\text{M}$  (with a 0.04 cm boundary layer) and 15.7  $\mu\text{M}$  (with a 0.08 cm boundary layer) is required to supply the 4.4  $\mu\text{M}$  of oxygen to the sediment surface, needed to satisfy this minimum oxygen calculation. These  $[\text{O}_2]_{\text{BW}}$  are calculated from Eq. 53 using the benthic boundary layer thickness for  $\text{O}_2$ -pen,  $A=1$  (as would be true through a viscous boundary layer above the sediment), the free diffusion coefficient for oxygen and after adding the 4.4  $\mu\text{M}$  oxygen concentration at the sediment surface. The bottom water oxygen concentrations of 10.1% to 15.7% PAL- $\mu\text{M}$  transfer to atmospheric oxygen levels of between 4% to 6% PAL. TL, and these should be considered the proper calculation values. A consideration of benthic boundary layer diffusion is not important for any of our other calculations.

Secondly, we note that low values of  $[O_2]_{BW}$  in the range of even  $10 \mu M$  are at odds with modern observations. Thus, when compared to anoxic settings, modern sediments depositing between the XML sedimentation rate and the XML\*10 rate do not show enhanced degradation of organic matter for sediments depositing in oxygenated bottom water with  $< 25 \mu M O_2$  (Figure 43a). Indeed, this observation alone might suggest that our higher bottom water oxygen estimates of  $18$  to  $19 \mu M$  are also too low. Thus, while  $10 \mu M$  to  $19 \mu M$  (4% to 8% PAL) is the range of minimum bottom water oxygen concentrations produced by our model, modern observations suggest that this range may be too low and that bottom water oxygen levels of  $>25 \mu M$ , translating to atmospheric levels of 10% PAL, are a more realistic minimum estimate.

## 5. Conclusions and Perspectives

We combined observations of trace metal dynamics, iron speciation, and TOC and HI dynamics to determine that unit 1 of the Xiamaling Formation experienced alternating periods of deposition in oxygenated and anoxic waters. The relationship between TOC and HI indicates substantial oxic mineralization of organic matter when sediments deposited in oxygenated water. We utilized observations from modern sediment organic matter dynamics to constrain the levels of atmospheric oxygenation required to generate the differences in organic matter preservation we observed between ~~anoxic~~ and anoxic deposition in the Xiamaling Formation. Our modeling indicates minimum atmospheric oxygen levels at the time of Xiamaling unit 1 deposition of 4% to 8% PAL. Based on further observations from modern sediments, we believe that our estimate of 8% PAL is likely even too low.

Generally, our estimates of Mesoproterozoic atmospheric oxygen levels are consistent with the higher values of atmospheric oxygen ( $\geq 4\%$  PAL) as constrained from ocean modeling (Zhang et al., 2016) while inconsistent with the lower levels of atmospheric oxygen ( $\leq 0.1\%$  PAL) as constrained from chromium isotope systematics (Planavsky et al., 2014; Cole et al., 2016). We note, however, that the marine geochemistry of chromium, and its isotopes, are poorly known, and we have also previously documented concerns (Zhang et al., 2016) that the samples reported in the study of ~~ies, particularly~~ Planavsky et al. (2014), have a substantial, if not dominant, detrital chromium component. ~~This~~ A strong detrital component would potentially compromise the interpretation of the chromium isotopes signal.

In any event, observations of low atmospheric oxygen concentration during this time ( $<0.1\%$  PAL) do not square with the necessity of much higher oxygen levels to drive the sedimentary carbon dynamics that we observe in the Xiamaling Formation (Zhang et al., 2016).

As noted above, we have previously reported evidence for minimum atmospheric oxygen levels of 4% PAL from unit 3 of the Xiamaling Formation (Zhang et al., 2016). While we do not have precise dating of unit 1 in the Xiamaling Formation, with a deposition rate from unit 2-3, the separation in time between unit 1 and 3 would be in the range of -20 to 25 million years.

Therefore, relatively elevated levels of atmospheric oxygen appear to have been a persistent feature of the Mesoproterozoic geochemical environment for seemingly tens of millions of years. As noted previously (Zhang et al., 2016), these higher levels of atmospheric oxygen would have been sufficient to fuel animal respiration, at least at this time window in Earth history, and some 700 to 800 million years before animals first evolved.

**Data Availability:** All data used in this paper is provided in ~~t~~Table form in the supplement.

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**Author contribution:** SZ, XW, HW and DEC conceived of the project, XW, HW, EUH, JS, YW, DEC did the research and SZ, XW, EUH and DEC wrote the paper.

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Table 1. Averages for geochemical parameters in outcrop samples

<u>Shale type</u>	<u>Org-C</u> <u>wt%</u>	<u>Fe/Al</u>	<u>V/Al</u>	<u>Mo/Al</u>	<u>U/Al</u>	<u>HI</u> <u>mg/gTOC</u>
<u>black</u>	<u>3.07±0.67</u>	<u>0.49±0.13</u>	<u>26.5±6.2</u>	<u>0.75±0.29</u>	<u>0.65±0.12</u>	<u>323±67</u>
<u>green-gray</u>	<u>0.29±0.17</u>	<u>0.28±0.11</u>	<u>12.1±2.0</u>	<u>0.16±0.09</u>	<u>0.43±0.06</u>	<u>113±56</u>
<u>crystal ave.<sup>a</sup></u>		<u>0.43</u>	<u>11.9</u>	<u>0.13</u>		

<sup>a</sup>from Rudnick (2004)

Table 24. Carbon preservation at various rates of sediment deposition

scenario	Sed rate	%C pres	%C pres	O <sub>2</sub> exposure time
	g cm <sup>-2</sup> y <sup>-1</sup>	black shale	gray shale	y
XML*0.5	0.8x10 <sup>-3</sup>	12	1.2	700-6000
XML	1.7x10 <sup>-3</sup>	20-30	2-3	400-5000
XML*10	1.7x10 <sup>-2</sup>	40-80	4-8	150-2000
XML (factor 5)	1.7x10 <sup>-3</sup>	20-30	4-6	200-2000

Table 32. Linear sedimentation rates and oxygen penetration depths (O<sub>2</sub> pen) for the different mass fluxes explored in our modelling.

<b>XML*0.5</b>			
O <sub>2</sub> exposure time (y)		700	6000
Porosity (φ)	Sed rate	O <sub>2</sub> pen	O <sub>2</sub> pen
	cm y <sup>-1</sup>	cm	cm
0.7	1.1x10 <sup>-3</sup>	0.77	7.7
0.8	1.7x10 <sup>-3</sup>	1.19	11.9
0.9	3.4x10 <sup>-3</sup>	2.38	23.8
<b>XML sed rate</b>			
O <sub>2</sub> exposure time (y)		400	5000
Porosity (φ)	Sed rate	O <sub>2</sub> pen	O <sub>2</sub> pen
	cm y <sup>-1</sup>	cm	cm
0.7	2.2x10 <sup>-3</sup>	0.88	11.0
0.8	3.4x10 <sup>-3</sup>	1.36	17.0
0.9	6.8x10 <sup>-3</sup>	2.72	34.0
<b>XML *10</b>			
O <sub>2</sub> exposure time (y)		150	2000
Porosity (φ)	Sed rate	O <sub>2</sub> pen	O <sub>2</sub> pen
	cm y <sup>-1</sup>	cm	cm
0.7	2.2x10 <sup>-2</sup>	3.3	44
0.8	3.4x10 <sup>-2</sup>	5.1	68
0.9	6.8x10 <sup>-2</sup>	10.2	136
<b>XML (factor 5)</b>			
O <sub>2</sub> exposure time (y)		200	2000
Porosity (φ)	Sed rate	O <sub>2</sub> pen	O <sub>2</sub> pen
	cm y <sup>-1</sup>	cm	cm
0.7	2.2x10 <sup>-3</sup>	0.44	4.42
0.8	3.4x10 <sup>-3</sup>	0.68	6.8
0.9	6.8x10 <sup>-3</sup>	1.36	13.6

Table 43. Calculations of  $[O_2]_{BW}$  ( $\mu M$ ) for our different assumptions of sedimentation rate (lowest value for each sedimentation rate in **red**).

<b>XML*0.5</b>				
Oxygen exposure (y)	700	6000		
Carbon preservation (%)	1.2	1.2		
O <sub>2</sub> -flux (mmol cm <sup>-2</sup> y <sup>-1</sup> )	0.019	0.019		
Porosity ( $\phi$ )	$[O_2]_{BW}$	$[O_2]_{BW}$		
	$\mu M$	$\mu M$		
0.7	<b>19</b>	160		
0.8	19	170		
0.9	27	230		
<b>XML</b>				
Oxygen exposure (y)	400	5000	400	5000
Carbon preservation (%)	2	2	3	3
O <sub>2</sub> -flux (mmol cm <sup>-2</sup> y <sup>-1</sup> )	0.029	0.029	0.015	0.015
Porosity ( $\phi$ )	$[O_2]_{BW}$	$[O_2]_{BW}$	$[O_2]_{BW}$	$[O_2]_{BW}$
	$\mu M$	$\mu M$	$\mu M$	$\mu M$
0.7	35	440	<b>18</b>	230
0.8	36	450	19	230
0.9	51	630	26	330
<b>XML*10</b>				
Oxygen exposure (y)	150	2000	150	2000
Carbon preservation (%)	4	8	4	8
O <sub>2</sub> -flux (mmol cm <sup>-2</sup> y <sup>-1</sup> )	0.11	0.11	0.053	0.053
Porosity ( $\phi$ )	$[O_2]_{BW}$	$[O_2]_{BW}$	$[O_2]_{BW}$	$[O_2]_{BW}$
	$\mu M$	$\mu M$	$\mu M$	$\mu M$
0.7	500	6600	<b>240</b>	3200
0.8	510	6800	250	3300
0.9	720	9600	350	4600
<b>XML (factor 5)</b>				
Oxygen exposure (y)	200	2000	200	2000
Carbon preservation (%)	4	4	6	6
O <sub>2</sub> -flux (mmol cm <sup>-2</sup> y <sup>-1</sup> )	0.011	0.011	0.073	0.073
Porosity ( $\phi$ )	$[O_2]_{BW}$	$[O_2]_{BW}$	$[O_2]_{BW}$	$[O_2]_{BW}$
	$\mu M$	$\mu M$	$\mu M$	$\mu M$
0.7			<b>4.4</b>	
	6.6	66	<b>(10.1-15.7)<sup>a</sup></b>	44
0.8	6.8	68	4.5	45
0.9	9.6	96	6.4	64

<sup>a</sup>values in parenthesis after considering diffusion through the benthic boundary layer

## Figure Captions:

Figure 1. General stratigraphy for the upper 4 units of the Xiamaling Formation (abstracted from Zhang et al., 2015) with a more detailed stratigraphy for the upper 45 meters of unit 1.

Figure 24. Total organic carbon (TOC), HI,  $\delta^{13}\text{C}$  (relative to PDB) and metal data (Mo/Al, V/Al and U/Al, Fe/Al for unit 1 of the Xiamaling Formation. T; ~~where~~ the dashed line represents upper crust values from Rudnick (2004).

~~, for unit 1 of the Xiamaling Formation.~~

Figure 32. a) TOC vs the ratio of highly reactive to total iron (FeHR/FeT) from fresh core material in uUnit 1 of the Xiamaling Formation. The horizontal dashed line represents a FeHR/FeT of 0.38. The range of TOC values for green-gray shales from outcrop samples is shown in the green rectangular field, while the range in values for the black shales from outcrop is shown in the gray field, while the vertical dashed line indicates a TOC of 1 wt%. The green-gray shales are predominantly represented at TOC < 1 wt% and the black shales with TOC > 1 wt% (see Figure 1). b) V/Al vs FeHR/FeT, with the horizontal line as in a) and the vertical line the V/Al crustal average (Rudnick, 2004 #8862). be) TOC vs HI for outcrop material, with black and green-gray shales separately indicated. The red dots mark the averages for the black and green-gray shale groups.

Figure 43. a) Preservation of organic carbon in modern marine sediments calculated as % of carbon buried in a sediment compared to the % deposited to the sediment surface. Redrafted from Canfield (1994). The vertical lines represent the different modelled sedimentation rates. The upper red rectangles highlight the carbon preservation for the anoxic environments in the compilation, while the lower blue rectangles are 10 times less than this, representing the

estimated range of carbon preservation in Xiamaling oxic sediments. For the XML sedimentation rate a blue rectangle at 5 times less carbon preservation is also shown, b) Oxygen exposure time versus organic carbon preservation in marine sediments. The horizontal blue boxes reflect the range of oxic sediment carbon preservation at the different sedimentation rates from [used in the modelling \(see Figure 4a-a\)](#), while the dark blue fields outline the range of associated oxygen exposure times. [Oxygen exposure time data summarized in Table S4.](#) -c) oxygen penetration depth versus oxygen uptake rate from modern marine sediments with variable bottom-water oxygen concentrations. Data is from Table S54. Black line indicates the best power-function fit to the data. Red lines indicate fits from [Equation- 5](#) to the data at different bottom water oxygen concentrations and A=4. Green line represents model fit from [Equation- 5](#) with A=2 and 250  $\mu\text{M}$   $\text{O}_2$ .

Figure 1.

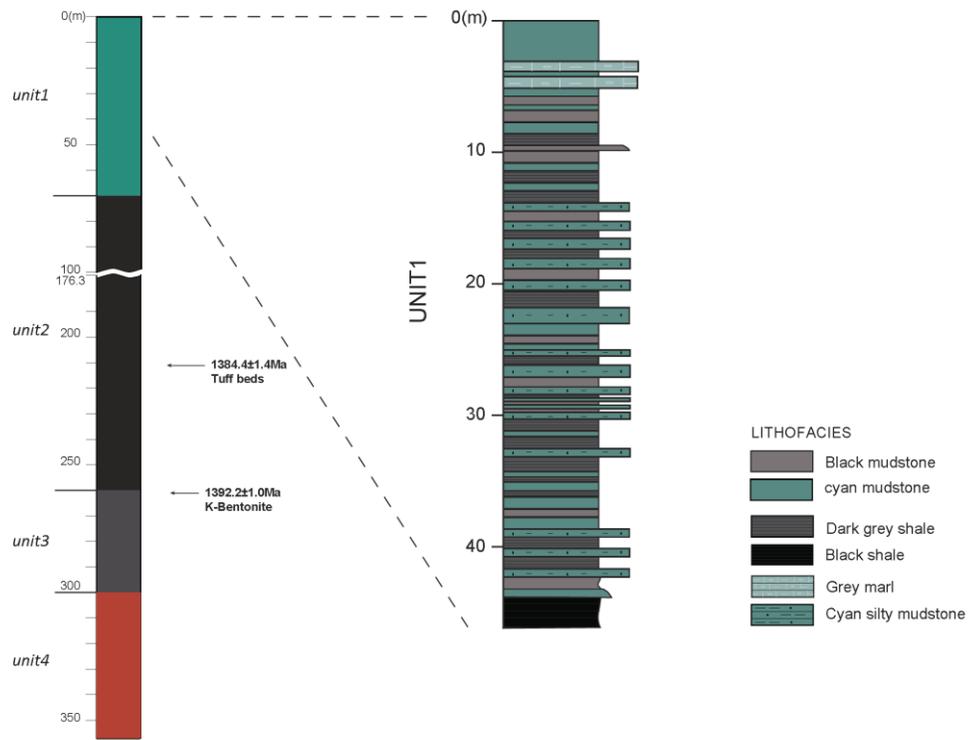


Figure 24.

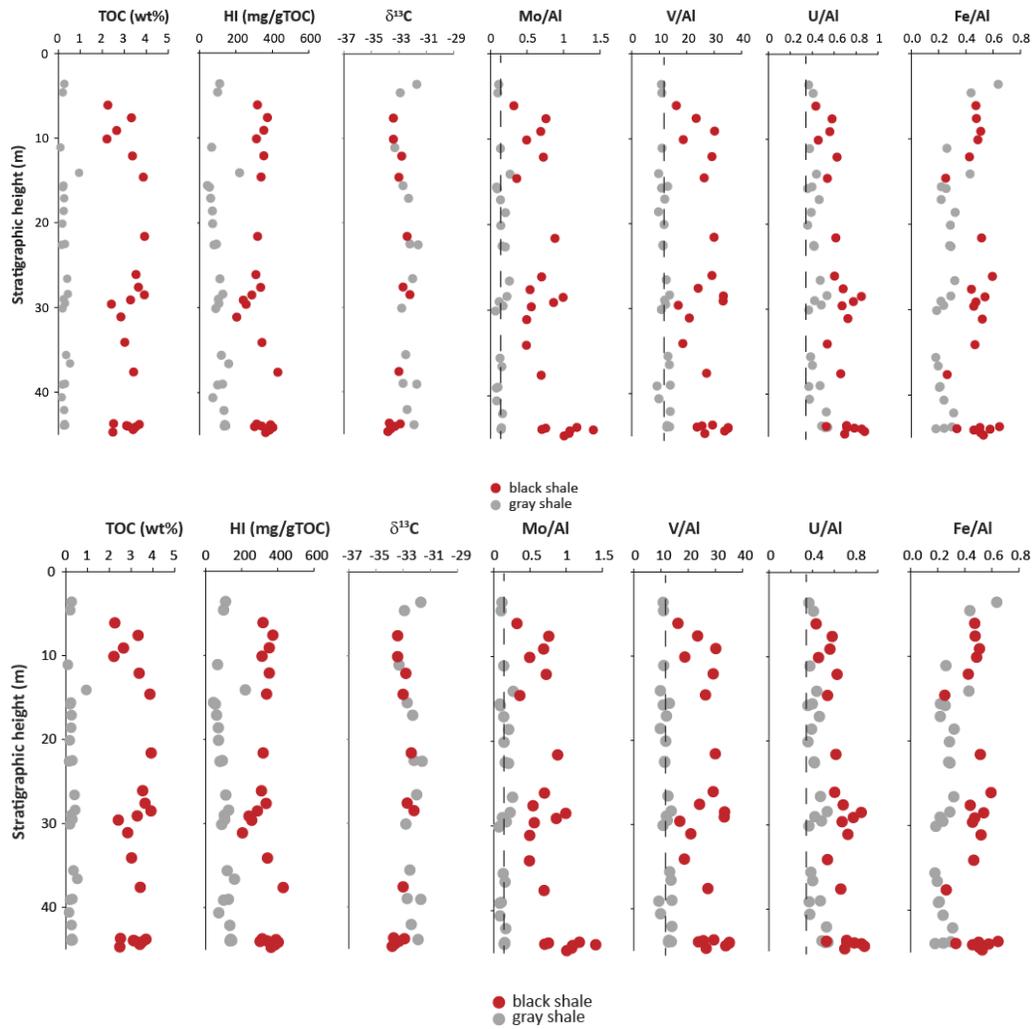
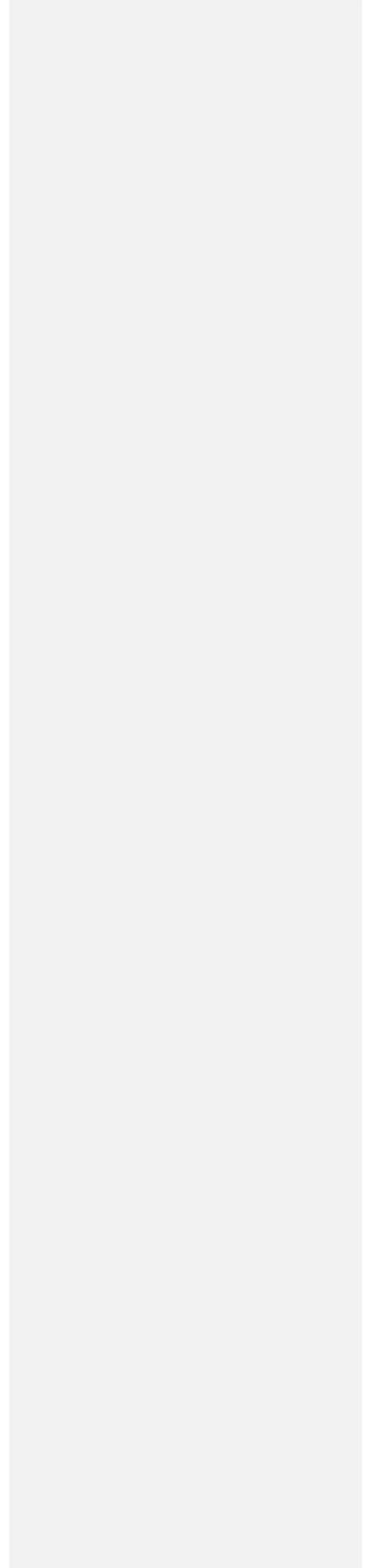
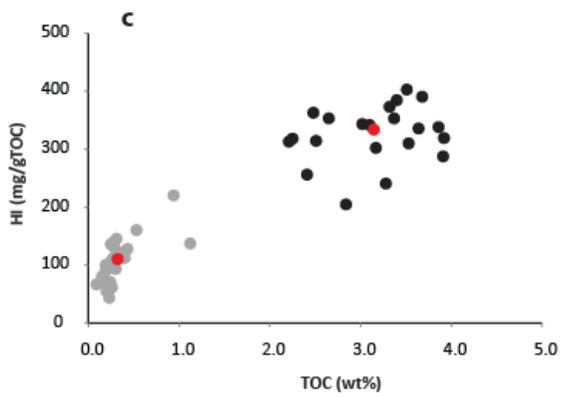
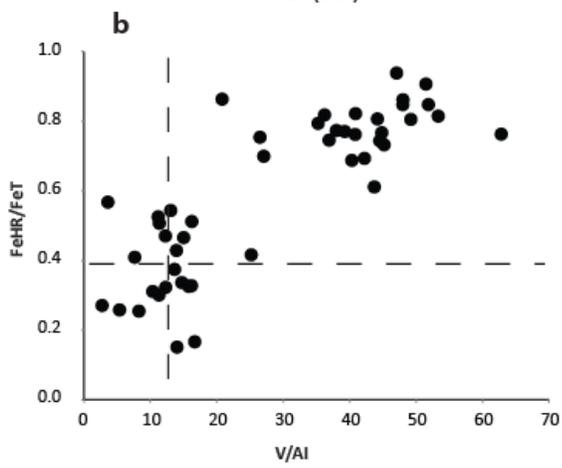
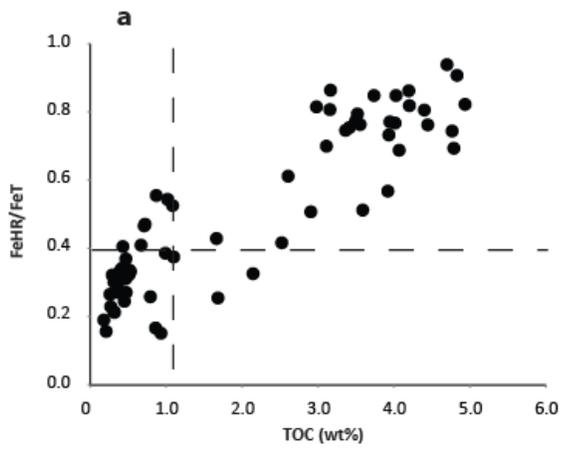


Figure 3.2





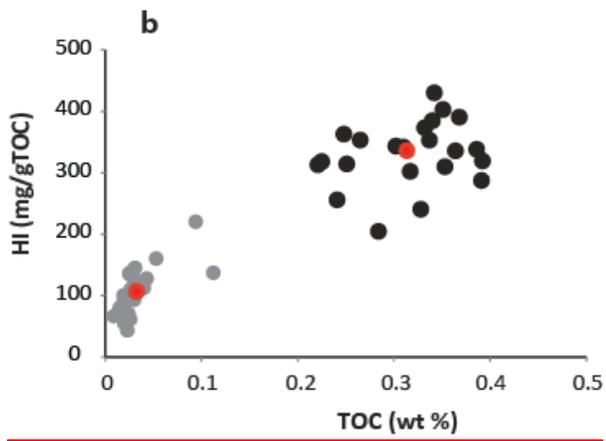
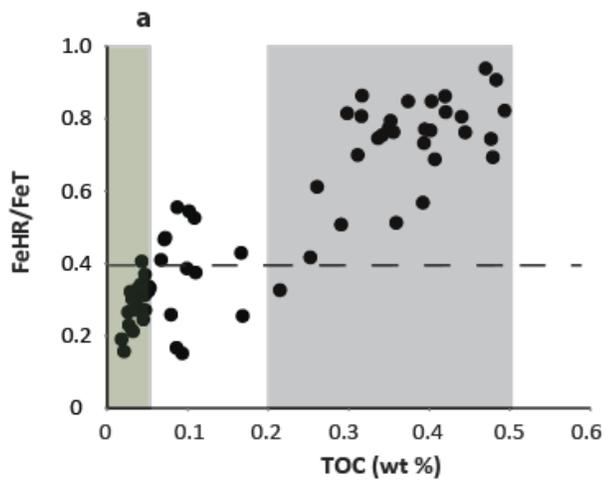


Figure 43.

