Biogeosciences
Discussions

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

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We thank Devon Cole (hereafter DC) for her comments and welcome the opportunity to comment on them. The comments of DC will be listed in italics. (See .pdf for proper formating of this response)

This study by Zhang et al. seeks to improve our understanding of mid-Proterozoic oxygen levels by examining the 1.4 Ga Xiamaling Formation of North China. Atmospheric oxygen through this interval has been the subject of debate, and recent work on the Xiamaling Formation has also incited discussion (Planavsky et al., 2016; Zhang et al., 2016a; Zhang et al., 2016b). This study takes a somewhat different approach than that of Zhang et al. (2016a) to tracking global oxygen signals preserved in the Xiamaling,

but comes to the same conclusions. It appears, however, that there are a number of issues in this manuscript that have resulted in potentially spurious conclusions.

Please see our comments below.

The introduction of the paper also does not present a very balanced view of work on Proterozoic pO2 evolution.

We agree that the introduction was too short and could better provide a more nuanced discussion of the history of the problem and a better background for our approach. This issue will be addressed during manuscript revisions.

The introduction of this paper does not cover all of the basic background of our current understanding of mid-Proterozoic oxygen levels, failing to acknowledge much of the significant work that has previously laid the groundwork on which recent studies are based.

Agreed, see above.

Traditional estimates for mid-Proterozoic (1.8 to 1.4 Ga) oxygen levels are typically considered to be those based on detrital pyrite and paleosol records (Hol- land, 2006). While there are not detrital pyrite occurrences in the mid-Proterozoic, the only well documented paleosols through this interval are characterized by Fe and Mn loss (Mitchell and Sheldon, 2009). This suggests, using the traditional framework for quantifying atmospheric oxygen levels from paleosols, that atmospheric oxygen levels were less than 1% PAL (e.g., Crowe et al., 2013; Rye and Holland, 1998; Zbinden et al., 1988).

The paleosols referred to by DC (Mitchell and Sheldon, 2009) are around 1.1 Ga in age. They are very interesting paleosols in they are weathered fluvial deposits, where the soils themselves formed in river overbanks and in ponds when the sediments were periodically exposed. Thus, these paleosols have a complex history and hydrology. We are not aware of any attempts to model atmospheric oxygen levels from these paleosols, but we note that each paleosol must be considered individually with mod-

eling based on the chemical composition of the parent material, soil depth, pCO2, hydrology, among other things. Therefore, one cannot simply set an atmospheric oxygen (< 1% PAL as DC does) level without a detailed understanding of the paleosol chemistry (including mineral redox state) and a carefully-considered model. We note also that these paleosols are typically hematite-cemented, indicating oxidative weathering of the sediments when weathering occurred. Furthermore, the extent of iron loss (or enrichment) in these weathered sedimentary deposits depends very much on the element one chooses as immobile. Choosing aluminum as immobile (as has been typically done in paleosol oxygen reconstructions, see (Rye and Holland, 1998) for example), Fe becomes enriched in almost all of the paleosols. Both iron and aluminum are mobilized in choosing Zr, as Mitchell and Sheldon (2009) did, and the mobilization iron and aluminum is much less in choosing Ti as immobile. Indeed, in fluvial deposits, due to sorting of heavy grains and the initial weathering of rock materials before fluvial transport, it is difficult to decide which element to choose as an "immobile" baseline, but Zr and Ti, largely associated with heavy minerals, may be poor choices. We also note that the near contemporaneous Sturgeon Falls paleosol, as reported by Zbinden et al (1988) displays iron retention and extensive iron oxidation during weathering. This paleosol offers a minimum atmospheric oxygen concentration estimate, not a maximum one, as implied by DC. All of these paleosols also formed contemporaneously with independent evidence for elevated atmospheric oxygen including elevated chromium isotope compositions extracted from carbonates (Gilleaudeau et al., 2016). We suspect that DC will have some issues with this later contribution, but, all of these points underscore the importance of applying additional methodologies, as we do in our contribution, to understanding the evolution of Proterozoic atmospheric oxygen.

More recently, additional geochemical proxies such as chromium iso- topes and Zn/Fe ratios have also yielded estimates for mid-Proterozoic atmospheric oxygen as low as < 1% PAL (Cole et al., 2016; Liu et al., 2016; Planavsky et al., 2014).

There is much to discuss here. First, the Planavsky et al (2014) paper promotes a max-

imum mid-Proterozoic atmospheric oxygen level < 0.1% PAL ("These data suggest that atmospheric O2 levels were at most 0.1% of present atmospheric levels."). As Cole et al. (2016) did not perform any additional modeling or offer additional quantitative constraints, we assume that DC still supports < 0.1% PAL as a maximum mid-Proterozoic oxygen level. If not, we don't understand how and why their maximum estimate has changed and whether it is based on any type of solid modeling or just a hunch? But, let's consider each of these three contributions in turn.

Starting with Planavsky et al. (2014), we have already expressed our concerns that the chromium from mid-Proterozoic samples measured in the Planavsky et al. (2014) had a large, if not dominant, detrital component, and are therefore inappropriate for understanding the isotopic composition of chrome in contemporaneous seawater (Zhang et al., 2016).

We also have serious misgivings about the Liu et al (2016) paper. These misgivings are fully explored in a contribution in review by one of us (Canfield, in review). However, the short of the story is that the Liu et al (2016) paper requires that calcium carbonates capture dissolved iron in seawater at concentrations in equilibrium with atmospheric oxygen. In the (Canfield, in review) contribution it is shown that the equilibrium iron concentrations are many orders of magnitude lower than those predicted from the measured iron contents of the carbonates used in the Liu et al (2016) study. Indeed, in our view, this contribution is fundamentally flawed and we will not cite it.

As for Cole et al (2016), we also have concerns about a dominant detrital chromium isotope contribution in their chromium isotope record. In this paper, the authors used a "selective" extraction technique to dissolve authigenic chrome from the shale samples they analyzed. As in the original contribution by Planavsky et al. (2014), the chromium isotopes showed little variation from crustal values, leading the authors to argue that there was little oxidative weathering of the chromium supplied to the oceans and therefore low concentrations of atmospheric oxygen. In the figure below, taken from (Wang et al., in review), we have re-plotted the data from the Cole et al (2016)

contribution together with data from Gueguen et al (2016), which includes a summary of chromium isotope contributions from modern sediments. In the upper panel, we see that both the isotopic compositions and concentrations of chrome in Mesoproterozoic shale samples fall exactly in line with those from modern oxic sediments where no authigenic chrome enrichment is believed to occur. These results do not give confidence that Cole et al (2016) have captured a non-fractionated authigenic component in their Mesoproterozoic shale samples; rather, a non-fractionated detrital contribution seems likely. Furthermore, chrome is also leached during the "selective" extraction procedure from modern oxic sediments Gueguen et al (2016) (therefore, the extraction is not as selective as one would hope), and the isotopic composition of this chrome is similar to the whole rock. This would be expected if a small amount of the detrital component was leached during the extraction. The same is true for the Mesoproterozoic samples, with the leach and the whole rock samples showing almost the same isotopic composition. This interpretation does not prove that Cole et al (2016) did not leach a small amount of authigenic chrome from the shale samples they analyzed (although, by analogy with the modern oxic sediments, it's hard to imagine that no detrital chrome was included in this leach). However, we do not believe that Cole et al (2016) have sufficiently demonstrated that they have extracted an authigenic chrome component, and we believe that their data is completely consistent with a detrital chrome source in the Mesoproterozoic shales.

The 40% PAL upper estimate for pO2 levels of Canfield (1998) rests on a number of Assumptions such as roughly constant productivity through Earth history, despite changing oxygen levelsthat have been questioned by multiple researchers. Fore- most, both Laakso and Schrag (2014) and Derry (2015) have articulated that the only means to achieve a low-oxygen ocean–atmosphere system is to greatly reduce pro- ductivity. More importantly, regardless if the 40% PAL estimate is considered valid, it is a "maximum estimate," which, by definition, does not exclude any lower estimates. This estimate is, therefore, perhaps not the most useful framework to introduce and consider low oxygen levels in the mid-Proterozoic.

We're not quite sure of the problems that DC has with our referencing the Canfield (1998) paper. This was the first quantitative constraint on Mesoproterozoic atmospheric oxygen concentrations as well as a new insight into Mesoproterozoic ocean chemistry. It is also been the inspiration for many, if not most, subsequent studies of the evolution of Proterozoic atmospheric and oxygen chemistry. We in no way mean to consider 40% as a "valid" estimate for Proterozoic atmospheric oxygen levels; we have always promoted this as a maximum model-based estimate. Again, we don't quite see where DC is coming from here.

While assumptions must be made in any model-based attempt at reconstructing paleoenvironmental parameters, the simplification of natural fluxes and phenomena must be carefully chosen, justified, and explored. Unfortunately, I fear the authors here have made assumptions that oversimplify the processes that shaped the paleoenvironment of the Xiamaling Formation and have failed to explore the results of these choices. Namely, the authors assume both constant organic matter input and a constant sedimentation rate throughout the deposition of the unit (on the order of millions of years).

This is patently incorrect. We have explored sedimentation rates ranging over a factor of 20, with organic matter input rates constrained by the concentrations of organic matter in the sediments and our constraints on carbon oxidation from our analysis of Xiamaling sediments and modern analogs. Organic matter input rates also vary by a factor of 20.

Instead, dramatic variations in both of these fluxes would, over a range of time scales, be expected in a continental margin setting, and it is likely that these variations would be the primary drivers of changes in preserved organic matter (e.g., Liu et al., 2000, and references therein). It is reasonable to consider that alternating organic-rich and organic-poor layers in shallow marine settings can be driven by increased or pulsed sedimentation, pulsed productivity, variations in the extent of degradation, or any combination thereof. Instead, the authors here assume all variations are tied to changes in the extent of degradation. Further, the assumption of a constant organic flux is em-

bedded into the remineralization estimates that are used to derive the pO2 estimates.

We agree that fluxes in organic matter input can vary over time, which is one of the reasons that we explored sedimentation rates spanning a factor of 20. However, we disagree that changes in organic matter deposition should have consequences for the state of preservation of the organic matter at the time of deposition. We note also that in hundreds of sediment trap experiments throughout the global ocean, the organic matter concentration in the sediment in particles is never less than 2 wt% for sediments settling through the upper couple hundred meters of the water column, and much more commonly in the 4 to >10 weight % range (data from http://usjgofs.whoi.edu/mzweb/data/Honjo/sed_traps.html). These concentrations represent the concentrations of organic matter settling to the sediment surface. Therefore, organic matter concentrations in the low range we observe in the Xiamaling Formation unit 1 (0.1 to 0.3 wt%) are very unlikely without substantial sediment TOC decomposition. The fact that these low organic matter concentrations are associated with: 1) low HI index, 2) low trace metal content, 3) and a lack of Fe enrichment gives us good confidence that these low concentrations of organic matter are associated with oxygenated bottom waters and aerobic oxidation of organic matter in the sediment; completely consistent with modern observation on the controls of organic carbon preservation. Conversely, the high concentrations of TOC that we observe are associated with, 1) high HI, 2) high trace metal content, and iron speciation consistent with anoxic depositional conditions. We cannot imagine a sedimentalogically controlled scenario that would accommodate these observations, unless we just started to make things up.

More plainly, the authors make the likely dubious assumption of static conditions and this assumption directly affects their conclusions.

As stated above, we have modeled a large range of possible carbon preservation amounts and carbon depositional fluxes based on the complete range viewed in modern sediments. Our model, therefore, has explored an enormous range of possibilities, and our final oxygen estimates are based on the lowest, most conservative estimates

that we obtained.

These expected variations are also likely important in the interpretation of the hydrogen index (HI), which has not been fully explored in this manuscript. Importantly, the HI reflects organic matter degradation, alteration, and composition broadly, not just the effects of aerobic marine alteration.

We agree that many factors can control hydrogen index. These sediments deposited before the evolution of land plants, so the influence of lignin and cellulose can be ignored. We expect that all algal (although there is no evidence for eukaryotic algae in these deposits) and prokaryotic sources will have characteristics, as expressed through HI, of type 1 to 2 organic matter as expressed in van Krevelen diagrams. There is no difference in the isotopic composition of organic matter between the high and low TOC sediments, suggesting (but we admit not proving) a similar organic carbon source. Furthermore, during Rock-Eval analysis, there is no systematic differences in the Tmax values between the green-gray shales and the black shales (Zhang et al., 2015), demonstrating similar thermal maturity for organic matter in both of the sediment types. The Tmax values are also low, in the range of 430-440 oC demonstrating the low thermal maturity for all unit 1 organic matter.

Varying amounts of initial organic matter coupled with the same extent of degradation (from aerobic remineralization, iron reduction, etc.) will result in varying bulk sediment HI.

The point, based on comparisons of modern observations, is that there are large differences in the organic matter preservation depending on whether organic matter is decomposed in the presence or absence of bottom water oxygen. We refer DC to (Canfield, 1994), (Hartnett et al., 1998) and (Blair and Aller, 2012) for discussions.

Further, the organic-rich samples are likely to have been deposited under a sulfidic water column (as evidenced by Mo enrichments presented by the authors), in contrast to the less organic-rich sediments, which could have been deposited under oxic or

anoxic but non-sulfidic conditions.

The iron speciation, trace metal abundances, and HI are consistent with deposition under oxic conditions for the bulk of the low-TOC shales.

As pyrite abun- dances are anomalously not reported (see below), Fe speciation cannot be used to de- termine if the setting was euxinic.

All of our iron speciation data is reported in the supplement, and cross plots of FeHR/FeT vs FePy/FeHR show a combination of euxinic and ferruginous conditions when FeHR/FeT > 0.38. We did not feel that it was important to discuss water column chemistry in any detail in the present manuscript as the important point is the presence or absence of oxygen, and in particular, the role of oxygen in enhancing organic matter decomposition. In extensive work throughout the Xiamaling Formation we see similar enrichments in trace metals under both euxinic and ferruginous conditions (Wang et al., in review).

The higher Mo enrichments in the more organic-rich sediments can, however, be roughly tied to sulfide availability. Greater sulfide avail- ability can then subsequently change the redox state of organic matter oxidation and in turn, the HI. In sum, the HI data by no means require essentially constant organic matter fluxes with variable extents of early diagenetic remineralization.

Sorry, but we really don't follow the argument here. Please see our above responses for more discussion on the role of oxygen in organic matter preservation.

The authors also assume no continentally derived detrital organic carbon input, despite a proximal setting. Non-negligible fluxes of detrital organic matter to marine systems are found under even modern atmospheric oxygen levels, and such fluxes will be higher under lower atmospheric oxygen levels (e.g., Derry, 2014). Continentally derived de- trital organic material would be expected to have a lower HI than fresh marine organic matter. With lower TOC samples the effects from detrital organic matter will be more

pronounced. Therefore, the observed correlation between HI and TOC enrichment could also be tied in part to mixing.

It is true, we do not assume any continentally organic matter contributing to the Xiama- ling Formation in unit 1. This is a good point and will be elaborated on further in our revised manuscript. It is, however, highly unlikely that the continents supplied organic matter to this unit of the Xiamaling Formation. As noted above, both high and low TOC units of unit 1 have preserved relatively immature TOC, with similar Tmax values. One would expect continentally derived recycled organic matter to display a higher de- gree of maturity than observed in these relatively immature rocks, and if one argued for a disproportionate amount of this organic matter in the low-TOC sediments, then this should be easily seen in the Tmax values, and probably also the carbon isotopic compositions. But, as noted above, there are no systematic differences. The degree of continentally-derived organic matter recycling will depend very much on the amount of oxygen one assumes there was an atmosphere. If the values were < 0.1%, then the organic matter recycling would likely be extremely important. This becomes less important as atmospheric oxygen concentrations increase.

Due to its potential influence, detrital organic mat- ter should not be excluded from the model, especially since an oxidizing atmosphere should not be assumed in the starting conditions if that is the central conclusion, intro- ducing a potential circularity to the model.

See above. There is no support for recycled continentally-derived organic matter in unit 1 of the Xiamaling. Assuming otherwise would just be making things up, and counter to the available evidence.

More broadly, numerous authors have suggested that HI does not correlate well with bottom-water oxygen availability in many cases, suggesting variations can be driven by a number of other factors including sedimentation rate, sediment dilution and mix- ing, changes in organic matter delivery, grain size, and hydrodynamic effects (e.g.,

Calvert et al., 1995; Cowie, 2005; Rao and Veerayya, 2000) and these factors are not discussed.

We do not feel it is our job to discuss all of the situations and hydrological circumstances where HI does not correlate well with bottom water oxygen. We do, however, in the MS offer a discussion of this issue, and note that in sediments off the Peruvian margin the relationship between HI and oxygen is complicated by sediment transport. In contrast, there are many situations, particularly in the geologic record, where the relationship between HI and oxygen availability is excellent. As noted above, HI correlates with other geochemical indicators of the presence or absence of bottom water oxygen, and thus we feel that the evidence is overwhelming that HI was most strongly influenced by the presence or absence of oxygen.

The inclusion of a detailed stratigraphic column would be a great (and likely necessary) addition to the paper.

Agreed

Further, there is no mention of any lithology besides shale in this unit, but it is not possible to form HCS without grains coarser in size than mud or clay (Cheel and Leckie, 1993; Dott and Bourgeois, 1982; Dumas et al., 2005). Deposition of silt or sand (as required by the presence of HCS) in a continental margin setting will, even assuming relatively constant (e.g., myr-scale) fluxes, be dynamic (i.e., pulsed) on the scale of individual beds, presenting a significant conflict with the assumptions of constancy made in this study.

Indeed, the sediments from unit 1 are mostly muds and silts, and we will provide a more detailed description of the sedimentology in the revised manuscript. There are some sand intervals as well, but these are mostly concentrated near the top of the unit. We don't get the point, however about constancy in the model. Our model is based on modern observations which experience the same stochastic dynamics in sedimentation that likely occurred in the Xiamaling. We note again, that in generating

our model results, we incorporate the whole range of observed carbon preservation rates in the modern environment at a given sedimentation rate and the whole range of oxygen exposure times at our different degrees of carbon preservation. This range of considerations generates an enormous breadth of model results and we always picked the most conservative lowest oxygen level as our reference. We believe that DC has misunderstood our modeling and its intentions.

Finally, on a more technical front, the authors have failed to report Fepy, which is not only a standard component of iron speciation, but could also contribute important information about sulfide availability in the section (which, as stated above, can have important ramifications in the interpretation of the HI signal). Pyrite to oxide ratios are also a means of gauging whether there was recent groundwater alteration.

These values were all reported in the supplemental information. Indeed, our core material was fresh, and the oxide contents are small indicating a lack of weathering or groundwater alteration.

. Also, trou- blingly, samples were crushed in a steel mill, which is not standard practice for an iron speciation or trace metal study as steel can easily contaminate many trace metals of interest (Hickson and Juras, 1986; Takamasa and Nakai, 2009). At a minimum, some information on how blanks were monitored must be provided.

Good point. We have also been sloppy in how we have described our trace metal methodology. All of the samples from the outcrop were crushed with a steel mill, (figure 1) while the vanadium samples from core material presented in Figure 2 were crushed in agate ball mill. Our blanks for the steel mill are very low and will be reported in the revised manuscript together with a more accurate description of our methodology.

Lastly, the error on the U concentration analyses of 17% makes the small variations and slight enrichments observed in this study nearly meaningless.

Our bad. Through rather careless cutting and pasting of methods, we have botched

our methods descriptions. All of the samples from outcrop (Figure 1) were measured with ICP-MS with precisions of better than 1.5%. Some of our V samples from the core (Figure 2) were also measured this way with the same uncertainties, but some are also measured with a hand-held XRF standardized against three different international standard materials with a precision of < 5%. An accurate accounting of methods and standard deviations will be reported in the revised MS, as well as an accounting in the SI of with method was used for the V outcrop samples (we did not report U as indicated in our description).

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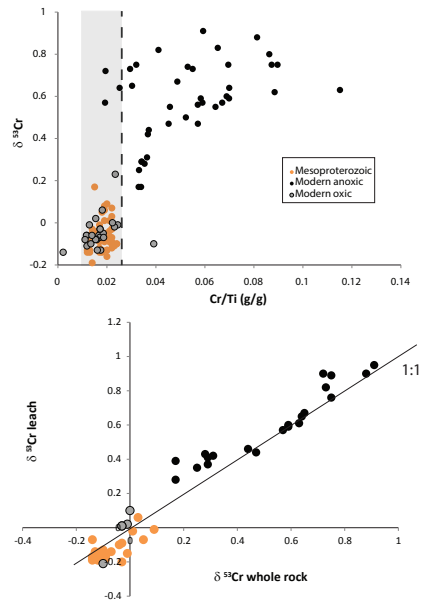
Please also note the supplement to this comment:
http://www.biogeosciences-discuss.net/bg-2016-413/bg-2016-413-SC4-supplement.pdf

C15

Fig. 1. Cr isotopes and concentrations from anciemt shales and modern sediments

C17