

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

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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. The introduction of the paper also does not present a very balanced view of work on Pro-

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terozoic pO₂ evolution.

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. 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 (Holland, 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). More recently, additional geochemical proxies such as chromium isotopes 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). 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 levels—that have been questioned by multiple researchers. Foremost, 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 productivity. 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.

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.

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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). 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 embedded into the remineralization estimates that are used to derive the pO₂ estimates. More plainly, the authors make the likely dubious assumption of static conditions and this assumption directly affects their conclusions.

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. 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. 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. As pyrite abundances are anomalously not reported (see below), Fe speciation cannot be used to determine if the setting was euxinic. The higher Mo enrichments in the more organic-rich sediments can, however, be roughly tied to sulfide availability. Greater sulfide availability 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.

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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 detrital 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. Due to its potential influence, detrital organic matter 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, introducing a potential circularity to the model.

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 mixing, 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.

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

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

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

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