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Interactive comment

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

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.

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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). (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

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.

"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. 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 ?

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

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ceous compounds are also determined during the combustion step (oxidation oven). It must be clarified. 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. 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. L131-139: Isolation procedure does not correspond to the classical procedure, why ? 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.

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

Discussion 4.1 Organic carbon preservation and water column chemistry This discussion section is too long and not really pertinent. 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. 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 ? Moreover, interpretation of element traces is by far more complicated. In this case, there is again a lack of contextualization.

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. L248-261: the good preservation of organic matter in anoxic environment is not new and does not deserve such a large paragraph. L269-270: This sentence is in contradiction

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with your previous statement (see comment on L210) L274; If HI values are "blurred" by sediment re-suspension or transport, why is it not the case for the TOC values? Indeed, HI and TOC characterize the same organic matter. L279-280: It is redundant with a previous sentence. L280: δ 13C 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 HCI can degrade then aliphatic content leading in turn to a bias in the determination of the δ 13C. Have you any evidence that such a bias does not affect the δ 13C values ? Anyway, I don't really understand the relevance of the δ 13C.

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

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