

Clim. Past Discuss., referee comment RC1  
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## Comment on cp-2021-150

Jim Kasting (Referee)

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Referee comment on "Dynamics of the Great Oxidation Event from a 3D photochemical-climate model" by Adam Yassin Jaziri et al., Clim. Past Discuss., <https://doi.org/10.5194/cp-2021-150-RC1>, 2021

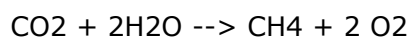
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This is an ambitious paper that attempts to follow up on the Goldblatt et al. (2006) analysis of the bistability of atmospheric O<sub>2</sub> at times surrounding the GOE. The authors are to be commended for producing a 3-D coupled dynamical-chemical model of the atmosphere that is useful in many ways for testing the predictions of simpler 1-D photochemical models.

That said, there are fundamental problems with the hypothesis put forward in this paper. The main one is that the authors have an incomplete understanding of the redox balance of the early atmosphere. They focus on the reaction between O<sub>2</sub> and CH<sub>4</sub> and on hydrogen escape, while largely ignoring such factors as organic carbon burial and the input of reductants (reduced volcanic gases and ferrous iron) to the system. To their credit, they begin the paper by writing out some of the important redox reactions. The two most important are eqs. (1) and (3)



The first of these reactions represents oxygenic photosynthesis. The second represents fermentation and acetogenic methanogenesis. What the authors do not do is to combine these together and consider the consequences. If one multiplies eq. (1) by 2 and add it to eq. (3), one gets (after cancelling out two CO<sub>2</sub>'s):



In other words, if the CH<sub>4</sub> is all coming from organic matter produced by oxygenic photosynthesis, and if none of the organic matter is buried, then CH<sub>4</sub> and O<sub>2</sub> are produced in stoichiometric quantities. CH<sub>4</sub> can thus not be a net sink for O<sub>2</sub>, and vice versa. CH<sub>4</sub> does indeed contribute to O<sub>2</sub> production when it leads to hydrogen escape. But that process cannot cause O<sub>2</sub> to accumulate, i.e., it cannot trigger the Great Oxidation Event (GOE), because as soon as O<sub>2</sub> starts to accumulate, atmospheric CH<sub>4</sub> decreases. To trigger the GOE, one needs for one of two things to occur: 1) Organic carbon burial must increase, producing more net O<sub>2</sub>, or 2) the abiotic sinks for O<sub>2</sub>, e.g., reduced volcanic gases and ferrous iron in the oceans, must decrease. These points are discussed in more detail in points 6-8 below. In the latter half of the paper, the authors do begin to consider the O<sub>2</sub> sinks, which are represented by the variable 'r' in the Goldblatt et al. (2006) paper. But this part of the paper has other problems, as discussed in point (11).

In revising their paper, the authors should read up on the concepts of atmospheric and global redox balance. One place to do this is in the 2017 book by Catling and Kasting (see point 6). That discussion is taken from Kasting, *Chem. Geol.* 362: 13-25, 2013, and that discussion, in turn, relies on a parameter, K<sub>oxy</sub>, defined by Claire et al. (2006), referenced in the present manuscript. K<sub>oxy</sub> represents the ratio of O<sub>2</sub> source to O<sub>2</sub> sinks, neglecting those that only arise after the atmosphere has become oxygenated, or that disappear at that time. The GOE is triggered when K<sub>oxy</sub> becomes > 1. The terms in K<sub>oxy</sub> have nothing to do with biogenic methane; indeed, even hydrogen escape does not enter into its definition.

In summary, there are some good points to this paper. It is interesting to see the comparisons between 1-D and 3-D photochemical results. But it is important to frame the discussion properly and to not get confused about what is causing what. The mechanism discussed here cannot be the cause of the GOE, but it could potentially influence the question of O<sub>2</sub> bistability, first pointed out by Goldblatt et al. (2006). Indeed, Fig. 15 makes it look like this phenomenon might largely disappear in 3-D. That is what I would focus on in the revision.

You may reveal my name to the authors.

Jim Kasting

Detailed comments:

1. (l. 20) 'During this event, the amount of oxygen increased from less than 10<sup>-5</sup> present atmospheric level (PAL) to a maximum of 10<sup>-1</sup> PAL around 2.2 Gyr ago before stabilising approximately at 10<sup>-2</sup> PAL (Lyons et al., 2014).'

--This misstates the conclusions of Lyons et al. The upper limit on Mid-Proterozoic pO<sub>2</sub> is more like 0.4 PAL, as that is when the deep oceans are predicted to become oxic. The pO<sub>2</sub> range favored by Lyons et al. is actually well below 0.01 PAL. They consider values as low as 10<sup>-4</sup> PAL.

2. (l. 23) 'In the Archean anoxic atmosphere, the sulfur photochemistry was responsible for mass-independent fractionation of sulphur isotopes in sedimentary rocks (Kasting et al., 1989).'

--A better reference for this statement is Pavlov and Kasting, *Astrobiology* 2: 27-41, 2002. This is the paper that explicitly studied mass-independent fractionation of S isotopes using a 1-D photochemical model.

3. (l. 26) '~0.01 PAL of oxygen is sufficient to generate enough UV shielding by ozone to block the sulfur photolysis (Zahnle et al., 2006).'

--Read Pavlov and Kasting (2002). 10<sup>-5</sup> PAL of O<sub>2</sub> is sufficient to eliminate S-MIF production in the atmosphere. Shielding of SO<sub>2</sub> from photolysis has little to do with this. Rather, it's a question of how many atmospheric exit channels exist for sulfur.

4. (l. 30) 'Consequently, the GOE likely induced a mass extinction for anoxygenic form of life, including heterotrophic methanogens (i.e. organisms producing methane).'

--Many microbiologists would argue that microbes never go extinct. They simply retreat to different habitats where they can continue their existence. Methanogens are poisoned by O<sub>2</sub>, yet they are ubiquitous in anaerobic soils (or in anaerobic chambers within animals) on the modern Earth.

5. (l. 34) 'The decrease of the biological methane productivity and the methane photochemical lifetime could have reduced its abundance and thus its warming contribution, potentially triggering the Huronian glaciations that took place between 2.4 and 2.1 Gyr.'

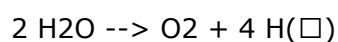
--You might consider adding a reference to Kasting et al., *Precambrian Res.* 20: 121-148, 1983. This is not a new idea. Also in this paragraph, a good reference to greenhouse warming by methane is Haqq-Misra et al., *Astrobiology* 8: 1127-1137, 2008. Earlier calculations by Pavlov et al., *JGR* 105: 11,981-11990, 2000, turned out to be in error.

6. (l. 38) 'Before the appearance of oxygenic photosynthesis, the redox state of the atmosphere was ruled by the balance between reductant fluxes from volcanism and metamorphism and the hydrogen atmospheric escape (Catling et al., 2001).'

--Well, these processes are important but other factors enter in, as well. One needs to consider both the atmospheric redox budget and the global (combined atmosphere-ocean) redox budget. See Catling and Kasting, *Atmospheric Evolution*, Cambridge Univ. Press, 2017, Ch. 8.

7. (l. 59) ' $\text{CO}_2 + 2\text{H}_2\text{O} \rightarrow \text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + \text{O}_2 + 4\text{H}(\square)$ '

--This reaction is somewhat misleading. If you leave out the intermediate products and cancel out the remaining  $\text{CO}_2$ 's you are left with



This is something that was going on well before the GOE. Water vapor photolyzes quite rapidly in the absence of UV shielding by  $\text{O}_2$  and  $\text{O}_3$ . But in the Archean, something (volcanic gases plus other reductants like dissolved  $\text{Fe}^{+2}$ ) was taking up the resultant  $\text{O}_2$ . You have to make organic carbon and bury it before atmospheric  $\text{O}_2$  can rise.

8. (l. 62) 'But whatever precipitated the GOE, the rise of oxygen seems to be linked to an atmospheric instability caused by the formation of the ozone layer and its impact on the photochemical methane oxidation. Slowly increasing  $\text{O}_2$ , by oxygenic photosynthesis, would have accumulate enough starting the ozone layer formation. The ozone layer provides a photochemical shield which limits the oxygen photochemical destruction leading to the methane oxidation. Therefore, the oxygen could have accumulated more easily, producing more ozone, shielding more efficiently the oxygen destruction and then rising an instability of growing oxygen until other processes would have limited the oxygen abundance, such as rock oxidation.'

--No references are given in this paragraph, although Goldblatt et al. (2006), referenced in the following paragraph, is responsible for this idea. You should reference them here. Also, keep in mind that the atmospheric instability identified by Goldblatt et al. cannot be the sole cause of the GOE. If it were, then the GOE might have occurred earlier than it did, given the evidence that cyanobacteria were around well before it. You still need either an increases in  $\text{O}_2$  sources (e.g., organic carbon burial) or a decrease in  $\text{O}_2$  sinks (e.g., reduced volcanic gases) to trigger the GOE. The methane feedback then amplifies that change and may make the system bistable, as Goldblatt et al. suggested.

9. (l. 91) 'Halogen, heterogeneous and nitrogen chemistry is not taken into account due to the weak constraints available and considering its negligible effect on the oxygen chemistry studied.'

--I agree with you that halogen and heterogeneous chemistry can be safely neglected. I'm not sure I agree about nitrogen chemistry. Nitrogen photochemistry has been shown to play an important role in eliminating 'false positives' for life (i.e., high abiotic O<sub>2</sub> levels) by catalyzing the recombination of CO and O to form CO<sub>2</sub> (Harman et al., ApJ 866:56, 2018). This paper was concerned with NO<sub>x</sub> species produced by lightning within the troposphere. The same chemistry could conceivably be important in the development of the GOE on early Earth.

10. (l. 139) 'We ran the 1D model until steady state for a range of O<sub>2</sub> vmr from 10<sup>-7</sup> to 10<sup>-3</sup> and CH<sub>4</sub> vmr from 10<sup>-6</sup> to 10<sup>-3</sup>.'

--What do the vertical profiles of O<sub>2</sub> look like in these models? In my own 1-D photochemical models, O<sub>2</sub> is never well mixed once its surface mixing ratio goes below about 10<sup>-4</sup> PAL, or roughly 10<sup>-5</sup> by volume. See, e.g., Kasting and Donahue, JGR 85: 3255-3263, 1980, Fig. 3. ..Ah, I got down further in the paper. You show O<sub>2</sub> profiles in Fig. 6. It is well mixed at fO<sub>2</sub> = 10<sup>-3</sup> but not at fO<sub>2</sub> = 10<sup>-7</sup>. We are in agreement!

11. (l. 213) 'Figure 11 shows FCH<sub>4</sub> (equivalent to ½ FO<sub>2</sub>) as a function of surface temperature.'

--This figure shows only the photochemical effect of changing the surface temperature. But at surface temperatures below 273 K, the oceans would be frozen and most of the methanogens would be dead, so there wouldn't be any biogenic methane.

--The entire second half of the paper suffers from the same problem. The authors are trying to determine the effects of surface temperature on atmospheric oxidation. But they only consider the effect of temperature on the O<sub>2</sub>-CH<sub>4</sub> reaction rate. That neglects the much bigger effect of surface temperature on the methane production rate. This would be a fatal flaw of their hypothesis even if the CH<sub>4</sub> sink for O<sub>2</sub> was the only one that needed to be considered. But the real problem is more complicated, as discussed elsewhere in this review.

