Response to review 1

This paper addresses the effect of O2 variation on hydrogen escape from early Earth using 3D modeling with a General Circulation Model (GCM). The study explores a very interesting question with a rigorous method. It focuses on a single parameter, the surface abundance of O2, and investigates its impact on the abundance of water vapor, the main contributor to hydrogen escape in this configuration. Despite the rigorous approach, the paper was somewhat confusing in its organization of the results and discussion. Some aspects also remain unclear and need to be described more precisely in the manuscript. I would suggest a major restructuring of the manuscript.

We thank the reviewer for carefully reading our manuscript and for the constructive suggestions provided. We have addressed each of the points raised and altered the manuscript where necessary. We appreciate the reviewer's perspective on the structure and organisation, and we have therefore reconfigured the manuscript to provide better context and improve the overall flow for the reader.

General comments:

The confusion comes from the fact that, in the results section, the findings are presented alongside the beginning of a discussion that lacks proper context. This context is only addressed later in the discussion section, where the results are not thoroughly analyzed. Instead, the discussion section primarily provides background, raises questions, and offers some perspective analysis. As a result, the information is scattered throughout the paper, making it difficult to follow.

In the results section, it is repeatedly discussed that O2 indirectly impacts temperature through O3, which in turn affects the diffusion of water vapor to the upper atmosphere, ultimately driving hydrogen escape. However, this raises several controversies, some of which are addressed later (too late), while others are not addressed at all:

(1) H2O is not the only gas that bring hydrogen to escape, what are the others? The justification of why the paper focuses only on water arrive late with figure 7. In the meantime we don't understand why other species such as CH4 are not discussed at all. Especially that CH4 levels could have been higher in the past, which is mention to late in section 4.2. What would happen for higher abundance of CH4? Where is the critical point between H2O and CH4 to dominated hydrogen escape?

Thank you for this comment, we appreciate that many readers may be wondering about the effects of other atmospheric molecules and changes to Earth's system through time. Our intention is not to ignore these important parameters, but instead to focus on the mechanism by which O_2 can affect hydrogen escape. Towards the end of the introduction section, we now provide context for why the focus is on H_2O. We mention that other gases (including that methane was likely higher in the past) and parameters are important in the introduction, but that they will be examined in more detail in the discussion section. Whilst methane was probably higher during the Archean, the jury is still out on whether CH_4 was higher during the Proterozoic, however, and this is considered in further detail in the Discussion section.

(2) Since the temperature is the real driver of the H2O abundace, O2 is not the only factor that could impact the temperature, what are the others?
The context of this discussion started in the results section is given to late in sections 4.1, or this discussion is started to early.

Sections 3-3.2 present the changes to water vapour from changing oxygen, which as the reviewer mentions, comes from temperature changes. The aim of the manuscript is to make the community aware that both oxygen concentrations and 3D modelling are required to predict stratospheric water vapour and associated hydrogen escape. We mention important factors on temperature in the Introduction section, such as CH_4 and CO_2 abundances, and the fainter Sun.

With the new writing in the introduction providing more context for the focus on oxygen and water vapour, we believe discussing further context and caveats to our work is most relevant in the discussion section.

(3) O2 levels drive methane oxidation. What are the consequences for methane concentrations, given that methane acts both as a greenhouse gas and a source of hydrogen escape? Could we therefore expect an impact on hydrogen escape?

We could definitely expect an impact on hydrogen escape if the methane abundance outweighs the contribution from H_2O. However, recent work has predicted lower ozone columns and lower methane lifetimes when oxygen is reduced compared to present day. We have not seen that such results have been contradicted yet. We have now added similar comments and relevant citations to the Discussion section.

It is valuable to investigate the isolated effect of O2 by keeping all other conditions fixed. However, this limitation should not be overlooked and needs to be highlighted more clearly. It is only briefly mentioned late in Section 4.2, but it should be made clear from the beginning what the assumptions are, their limitations, and the implications for interpreting past Earth's climate. CH4 and CO2 have varied significantly throughout Earth's history and have also influenced temperature. The discussion of the results should better reflect this approximation and consistently emphasize that the findings relate specifically to variations in O2 levels, not to different climatic periods in Earth's past.

Thank you for this comment. We have now made this clearer in the current revision through changes made to the abstract, introduction, and discussion. The conclusions also state that this work is relevant for considering O_2 changes only and that future work needs to be undertaken to fully understand the role of all parameters.

One major contradictory aspect of this paper, surprisingly never discussed, is that its main conclusion is that hydrogen escape is less significant at low O2 levels. However, geological evidence indicates that the majority of Earth's hydrogen escape occurred before the GOE, when O2 levels were indeed very low. This point is mentioned in the introduction, but it is never addressed again, and the paper ultimately focuses only on post-GOE conditions. Can the findings of this study be extrapolated to lower O2 levels? If so, what then drove hydrogen escape before the GOE?

Thank you for this raising this important point. The post-GOE atmosphere is oxidised, but the Archean atmosphere is weakly reducing. Hydrogen escape was probably occurring due to higher levels of methane, but maybe H_2 also. Therefore, we now state that the findings should only be considered for the GOE – present day (2.4 Gyr ago - present), and that the Archean atmosphere was very different.

Specific comments:

l.11-12: "These numerical predictions support geological evidence that the majority of Earth's hydrogen escape occurred prior to the GOE."

This appears to contradict the statement in lines 8–9, which claims that lower O2 levels lead to reduced O3, resulting in lower temperatures and, consequently, reduced diffusion of H2O. This would imply that before the GOE, when O2 levels were lower, hydrogen escape was less efficient, since it depends on the diffusion of H2O to the homopause.

The reviewer is correct that our initial abstract was potentially misleading. We have altered the abstract in a few places. Now, we state that H_2O is the dominant hydrogen carrier in our considered scenario. We state that the escape rates are lower post GOE, and because our estimates do not vary by orders of magnitude, and all are effectively negligible compared to the pre-GOE period, the statement quoted by the reviewer is now placed in better context and we hope it is clearer to the readers what we mean.

l19: "As all life requires liquid H2O"
We don't truly know whether life can or cannot emerge without liquid water, this reflects an Earth-centric perspective. For example, on Titan, where there are lakes and rivers of liquid methane and ethane, it is conceivable that life could emerge based on hydrocarbons instead.

We have added all 'known' life to qualify this statement.

l.23: "It's possible that Venus was never habitable (Constantinou et al., 2024)"
Constantinou et al. (2024) focus on atmospheric chemistry, but several studies more relevant to the question of whether Venus was ever habitable are cited in their

introduction. For example, Turbet et al. (2021) demonstrates that an ocean would not have condensed on early Venus.

Thanks, this is a good point, and we have added in some additional references, including Turbet *et al*. (2021).

l.43-45: "For these mechanisms, with the exception of impacts, the hydrogen escapes from the top of the atmosphere, from the exosphere."
There seems to be a missing verb, should it be "the hydrogen escapes [come] from"?

It could be written as the 'hydrogen escapes from the exosphere' or 'hydrogen escape comes from the exosphere'. We think the original wording makes sense and we have retained it.

l.110-111: "Imposed mixing ratios and fluxes follow the PI settings, apart from O2 which is varied."
How is this approximation valid up to 2.4 Gyr, which is the range of O2 levels that are supposed to be modeled?

The reviewer makes an important point. It is likely that many gases have changed in abundance through to 2.4 Gyr ago. We have commented on the validity of such an assumption. We have tried to isolate the effect that changing molecular oxygen has on the atmosphere. It would be good to do tests varying CH_4, N_2O, and CO_2, as well as other gases. A model like WACCM6 is very computationally expensive to run, so such simulations are left for future work. Much of the caveats to our simulations and the interpretation of our results were placed in the discussion. We have now restructured the paper to include motivation for the experiments earlier in the manuscript. We think CH_4 may actually have played only a minor role in hydrogen escape since the GOE, but future work is needed in this regard.

l.114-115: "once the middle atmospheric trend in total hydrogen atoms has halted"
Why middle? Does it mean that the atmospheric trend in total hydrogen atoms is not converge everywhere in the atmosphere?

Here, the middle atmosphere refers to 12-100 km in altitude (we will now state this in the manuscript) and was used as a diagnostic because it is the middle atmospheric hydrogen content that sets diffusion limited escape. Apart from regular climate model variability, there are no significant trends in the simulations with regards to total hydrogen content.

Figure 5 caption: "pressures of 100 – 30 hPa", in the figure the legend shows 120 to 30 hPa.

Thank you for spotting this, we have updated the caption.

l.201-202: It could be better explained why these specific pressures, 88 hPa and 50 hPa, were chosen. In general, the paper does not clearly justify how the pressure ranges are precisely selected, and the criteria often appear approximate. What are the precise pressures (altitudes) of the cold trap for the simulations?

In both Earth's climate system and the WACCM6 model, the location of the tropical tropopause layer (TTL) is 3D and varies with season. It also varies with atmospheric oxygen content. There are algorithm's within WACCM6 that allow for a calculation of the tropopause pressure and temperature, but this output gives a specific location, rather than a tropical tropopause layer. We have given the altitudes of the Earth's modern TTL in the introduction, and now we give the pressures. Definitions of the TTL pressures and temperatures in the literature vary but are roughly between ~150 hPa to 70 hPa. We have added a footnote to why we have picked 88 hPa – this is the closest pressure level in our model to the winter climatic tropopause.

Figure 6 caption: "The tropical average is for latitudes +-20 degree from the equator."
Should it be +-24 degree for tropical latitudes?

Yes, it should be, thank you for this comment, we have updated all mentions to be $\pm$24 degrees.

l.211-214: "Fig. 6 suggests that the warmest TTL temperatures are the controlling factor in each atmospheric scenario, instead of the atmospheric composition. Yet because composition (i.e. the O2 mixing ratio) is the variable that is altered in each scenario, the atmospheric composition is the controlling factor for the TTL temperatures. Hence, the oxygenation state of the atmosphere is indirectly controlling the upward flow of hydrogen atoms and affecting the diffusion-limited hydrogen escape rate"
O2 is the only variable tested here, so naturally all the resulting effects stem from variations in O2, even though the actual parameter controlling hydrogen escape is temperature. However, many other factors can influence temperature, and thus hydrogen escape, such as variation of greenhouse gases (CO2, CH4), stellar flux evolution (faint young sun), or glaciation events. These influences should not be overlooked and variation of temperature solely attributed to the "oxygenation state of the atmosphere".
I noticed that this is addressed later in the discussion (l.272), but the way the paper is written is confusing. It begins an explanation in the results section, but leaves the reader with many questions that are only addressed later in the discussion.

We have now restructured the manuscript and moved the explanation earlier. Indeed, we would have liked to account for the effects of the CH_4 mixing ratio, the CO_2 mixing ratio, and the younger sun, etc. But this would be very computationally expensive to do a full grid of models, and we think it would make an interesting avenue for follow up work.

l.223-224: "the four species that carry the majority of hydrogen atoms (H, H2, H2O, and CH4)"
This could be specified earlier in the method and used to justify why their is a focus on H2O to explain hydrogen escape and not other species.

We have specified this earlier in the manuscript now and said we focus on H_2O because it is the most abundant hydrogen carrier in the modern atmosphere.

l.228-229: "CH4 is never the dominant carrier in the scenarios we present. As we will discuss later, this may not have been the case for much of the Proterozoic."
I would have expect this explanation earlier following previous comment where we can question why the focus on H2O and not other species such as CH4.

As mentioned in response to other comments, we now include reasons in the introduction for why the focus is on CH4.

l.329: Other temperature dependencies are finally cited.

We have mentioned the faint young sun problem, including continents, cloud feedback, and greenhouse gases, in the introduction. The problem of TTL temperature is multifaceted and will require follow up work which is included in the discussion section.

l.246: This paragraphe could be more conclusion/perspectives, right?

Yes, this was a little out of place. We moved this paragraph to the start of the discussion to summarise the results before continuing with caveats, context, and future work.