

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 O₂ can affect hydrogen escape. Towards the end of the introduction section, we now provide context for why the focus is on H₂O. 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 CH₄ 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 abundance, 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 too 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 CH₄ and CO₂ 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 H₂O. 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 O₂ 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 H₂ 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:

I.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 H₂O 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.

I19: "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.

I.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).

I.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.

I.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 CH₄, N₂O, and CO₂, 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 CH₄ may actually have played only a minor role in hydrogen escape since the GOE, but future work is needed in this regard.

I.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 algorithms 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 ± 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 CH₄ mixing ratio, the CO₂ 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.

I.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 there 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 H₂O because it is the most abundant hydrogen carrier in the modern atmosphere.

I.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 expected 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.

I.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.

I.246: This paragraph 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.

Response to review 2

Summary

This study uses a 3-D Earth System Model (WACCM6) to investigate the effect on hydrogen escape of varying the atmospheric O₂ mixing ratio. The study finds that, to first order, atmospheric warming due to increased ozone concentrations with increased O₂ results in a weakening of the H₂O cold trap. This allows more hydrogen to be lifted into the upper atmosphere, where it can escape to space. However, changes in O₂ level alone are unlikely to have been a significant factor affecting H escape rate variations over geological time. The article ends with a comprehensive discussion of the applicability of the results to the water loss and atmospheric composition of both early Earth and other (exo)planetary bodies.

Overview

This work is a very interesting and important contribution to the field, as it thoroughly explores the effects of varying O₂ levels on other atmospheric processes. The WACCM6 Earth System Model is an excellent tool to explore the research question. The simulations are well-designed and the model results explored carefully and in sufficient detail to thoroughly assess the effect of one factor (O₂ mixing ratio) on another (H escape) and explain the relevant causes and effects.

For the most part, the figures are well-chosen and illustrate the key points well. The discussion section is comprehensive and relevant, and demonstrates the wide applicability and importance of the results to different aspects of the field. It achieves a great balance of evidence-based speculation without stretching too far. The abstract and conclusion summarize the study very helpfully.

The overall article is well structured and easy to follow. Key terms and ideas are well explained and defined (e.g., TTL, cold trap).

I have only minor comments and suggestions for improvement or consideration, as follows. A number of them could help the reader to match descriptions of the results in the text with the corresponding figures.

We would like to thank the reviewer for their reading of our manuscript and the helpful suggestions they have made. We have addressed each point and modified the manuscript accordingly, including the relevant figure captions. We have provided more context in the introduction and discussion to better outline the scope of the work.

1. Introduction

L34: “the GOE... has been proposed to have halted hydrogen escape.” I suggest a different word/phrase is used, e.g., “significantly reduced,” as hydrogen escape will have persisted, even if at a much smaller magnitude. If I’m mistaken and the word “halted” is kept, I suggest a reference is needed at the end of this sentence.

Thank you, this is a good point, and we have changed the phrase to ‘significantly reduced’ instead.

L41: Suggestion: “through several mechanisms, including Jeans escape...” (as I don’t think this is a fully exhaustive list).

Thank you, we have now used ‘including’ to make this clear.

L67: Typo: “thought”

Done.

L73: The comparison to the deepest point in the Earth's ocean is helpful for providing context to the water loss rate, but I think that the global equivalent layer of the Earth's current oceans (~3.6 km) might be an even more helpful comparison. This would also provide consistency and ease of comparison with L76.

We have included 3.6 km as an additional reference point and given a citation too.

L88-93: This is a really helpful paragraph summarizing a clear aim.

We appreciate the positive feedback, thank you.

2. Numerical methods

I think a sentence on the model's lower boundary condition for H₂O would be helpful to note, even if it is in the referenced literature; e.g., is an infinite ocean reservoir assumed?

In terms of evaporation and hydrogen feedback, an infinite water reservoir is assumed, and no water loss is explicitly simulated. We think this assumption is acceptable because we are simulating points in time rather than an evolution of the atmosphere.

We have included a new sentence stating that water vapour feedback is included through evaporation and rainout, but that water loss from the ocean is not explicitly included.

L105: "that have been estimated to have existed on the Earth over..." I suggest a very minor rewording to something like "within estimates for the Earth over..."

Thank you for the suggestion, this has been altered.

L118: suggest, for clarity and conciseness: "The diffusion-limited hydrogen escape rate (Hunten, 1973; Kasting and Catling, 2003), Φ_{esc} , is proportional to the total mixing ratio of hydrogen components at the homopause: $\Phi_{esc} \propto fT(H)$, $fT(H)$ can be written..."

We have modified this to make it more concise based on the reviewer's suggestion.

3. Results

L162: "measured" is perhaps slightly misleading, as the text is referring to model results. Suggest "< 3K in terms of global averaged surface temperature" or something similar, instead.

This has been changed as per the reviewer's suggestion.

L164: "PI, 1%, and 0.1% PAL

This has been added in, thank you.

L168: There is no explanation of how low and medium clouds are defined.

Medium and low cloud definitions have now been added, thank you.

L170: Suggest that “ $\pm 0-60^\circ$ ” might be clearer than “ $\pm 60^\circ$.”

This has been modified.

L171: Suggest “ice content (blue shading) and a lower amount of H₂O (colored contours),” for ease of understanding Fig. 4 quickly.

Thank you, we have modified this caption to improve this.

L194: It is not clear what is meant by “visual discernment,” as this depends on the scale used on the figure. Suggest “a visual discernment on the scale of Fig. 4” or equivalent.

This has been modified in the text. Additionally, to confirm the visual discernment, we have performed a phase lag and Fourier analysis of the data which shows there is no tape recorder affect for the 0.1% PAL case, but there is a clear tape recorder effect for the pre-industrial simulation. We have now mentioned this in the manuscript.

L201: A brief explanation of the focus on 88 hPa (and also 100 hPa on L207) in particular might be helpful. In general, if there is a way to contextualize these pressure levels with altitudes or atmospheric levels (e.g., tropopause, homopause, etc.) a little more often, that might be helpful to the reader.

This pressure level is the pressure level that roughly corresponds to the top of the tropopause, so most water vapour has passed through the tropical tropopause layer by this stage. Linear regression fits show that it is also the pressure level which has the coefficient of determination (R^2) value closest to 1. In other words, the total hydrogen mixing ratio at other pressure levels is less strongly correlated with the warmest atmospheric temperature reached at that pressure level in the tropics. We have added this explanation in and also given the approximate height that it corresponds to.

L204: “A positive correlation is not present when comparing $fT(H)$ with global mean temperature alone.” Is this referring to global mean temperature in the tropics (at all pressures) or at 88 hPa (in the tropics) or at all latitudes and pressures?

We agree this was not as well-defined as it should be in the manuscript. So, in this case, it is all latitudes and longitudes for the 88 hPa pressure level. We have now made this clearer in the manuscript.

L218-219: “Above the cold trap in the TTL... due to CH₄ reacting with OH.” It is unclear where the 5 ppmv value comes from and how it corresponds to Fig. 7. I suggest that some further description is given of where in Fig. 7 we see this, as I am looking at the solid black line (for H₂O) in the lower left subpanel, where the maximum above 1 hPa is ~10 ppmv rather than 5 ppmv. In addition, I suggest moving this sentence to the below paragraph, after the lower panels of Fig. 7 have been introduced.

The mixing ratio of H₂O is 5 ppmv which corresponds to 10 ppmv of hydrogen atoms. Fig. 7 shows the contribution that each molecule has to the total hydrogen mixing ratio, so H₂O and H₂ are multiplied by 2 here and CH₄ by 4. But we did not make this clear, so we have now explicitly stated this in the caption of Fig. 7. The sentence has also been moved to the next paragraph.

L222: Suggest specifying in parentheses which species are being referred to, e.g., “...the lighter atmospheric constituents (H) increase...” It seems from the figure that this is only the case for H, rather than multiple species. I also suggest that this sentence is moved to the paragraph below, as it is more connected to the discussion of the different species’ mixing ratios.

Other species do increase in relative abundance, such as He, N, and O, but these are not relevant to figure 7. We have kept the sentence in this paragraph because it is relevant to why H dominates at the top of the model in the PI simulation. However, we have also added a sentence in the next paragraph to say this is the case in all simulations.

Discussion

Another point that could have been discussed in Section 4 is whether there is any feedback whereby a change in H escape affects the O₂ mixing ratio (as H escape can be considered a source of oxygen).

We thank the reviewer for their suggestion and have included this towards the end of the Discussion section.

Figures and Tables:

Table 1: I think this table is unnecessary, as the mixing ratios (right hand column) are clear from the names of the simulations alone (left hand column). I suggest that the mixing ratio column is included in Table 2 between the ‘Simulation’ and ‘fT(H)’ columns instead. The text in the caption can then be folded into the main text, e.g., around line 104, such that the number of simulations, the full definition of PAL, the model surface pressure, and the information about the other boundary conditions is not lost.

Thanks for the suggestion to help reduce repetitiveness in the manuscript. We have removed table 1 and modified the methods text.

Figure 2 caption: Suggest “against the atmospheric mixing ratio of O₂ at the surface in terms...”

Thank you, the caption has been modified accordingly.

Thank you for the opportunity to review this paper, and I look forward to seeing it published in due course.

Thank you for your positive and constructive feedback and taking the time to review our manuscript.

Response to editor

Dear Dr. Cooke and co-authors,

Thank you for submitting your article “The Oxygen Valve on Hydrogen Escape Since the Great Oxidation Event” to EGUSphere. I have now received an assessment of the two reviewers, as well as your response to the reviewers concerns.

In summary I consent with one reviewer that suggest a major revision based on following issues:

1. A more detailed discussion on other species that may have contribute to escape of hydrogen such as from CH₄ outweighs that from escape of hydrogen from H₂O.
2. A more detailed discussion water vapour from changing oxygen
3. A discussion on the role of O₂ levels that drive methane oxidation.

I consent with that reviewer that CH₄ and CO₂ have varied significantly throughout Earth's history and have also influenced temperature, and this shall be discussed in the revision as well as the limitation of this study.

The feedback provided in the reviewer assessments of your manuscript is important and should be considered as you complete your revision. Please include a marked-up manuscript version showing the changes made in your revision. I encourage you to submit a suitably revised version of your manuscript by December, 15, 2025.

Sincerely,
Arne Winguth
Editor

We thank the editor for taking time to read the manuscript, the reviewer comments, and our response to the reviewers. We have revised the manuscript in line with the reviewer's comments and the editor's comments.

1. There is much more text discussing the contribution of CH₄ to hydrogen escape. Estimations for CH₄ throughout the last 2.4 billion years vary significantly (by orders of magnitude). Some are much greater than present day levels, and others are lower. Our own work in recent years indicates that higher fluxes may have been required to produce a significant amount of CH₄ which could outweigh the contribution of H₂O to hydrogen escape. We have now added more discussion on this in the manuscript, including relevant citations.

2. Our revised manuscript describes in further detail how H₂O has been affected by changing oxygen concentrations. E.g., We confirmed the tape recorder disappearance through a Fourier analysis, and we described tropospheric H₂O in more detail.
3. More citations have been given to recent work that has investigated how changing oxygen concentrations affect CH₄. We have described the CH₄ oxidation in the troposphere and how that affects the hydrogen escape prediction. There is more context now given in the introduction regarding CH₄ throughout history and our motivation for focussing on H₂O.

Due to the younger Sun, a larger greenhouse effect may have offset the younger Sun, rather than provide much warmer temperatures. There were also glacial periods where the Earth was colder than present day. Such changes in temperature due to the greenhouse effect have been discussed and referenced. We have described how we expect our predictions to change with hotter and warmer periods. Future work and simulations should investigate these phenomena, alongside the effect of O₂ which we present as the primary focus in our manuscript.

We would like to thank the reviewers and editor once again for their constructive comments which have helped to improve our manuscript. All changes are marked in red text in the new manuscript.