Response to reviewer 1

Summary

Accepted as is

We thank the reviewer for taking time to review our revised manuscript.

Response to reviewer 2

Summary

Accepted subject to technical corrections

Thank you for the opportunity to review the revised manuscript. The manuscript has been greatly improved in response to the comments from both reviewers. I just have a small handful of very minor suggestions remaining, as follows.

We thank the reviewer for taking time to review our revised manuscript and for providing their suggestions for improving the manuscript below.

L186: "In every simulation… respectively." I suggest this sentence is moved to somewhere in the paragraph in Section 2.1 beginning "The first simulation we perform…" where the other inputs are described.

We understand the point the reviewer is making and have modified the sentence as a result. Only H_2 and CH_4 are specified as fixed mixing ratios at the surface, whereas H and H_2O are left to freely evolve. We give the mixing ratio of all four important molecules to set the scene at the surface for the reader, and we mention in the methods that these gases are fixed at the surface.

L251: Thanks for making the edit I suggested. It's great that a Fourier analysis has been conducted on the two simulations to support the tape recorder point. If possible, I suggest a further sentence to add a little more detail about what this analysis showed, rather than only mentioning that it was done.

We are happy to clarify this point and have now specifically mentioned that there is a peak in the Fourier spectrum for the PI case but not the 0.1% PAL case, consistent with expectations for the presence and absence of a tape-recorder signal, respectively.

References. Just a small note that there are a few references for which updated reference details are available as they have recently been published in peer-reviewed journals. These include Chaffin and Cangi et al (2024), Graham et al (2024), Malinieme et al (2021), and Sergeev et al (2024). I suggest that the peer-reviewed versions are cited instead, if they provide the same information as the originally-cited conference abstracts or arXiv versions.

Thank you for pointing this out. We have updated the references with the journal versions.

Response to reviewer 3

Summary

Accepted subject to minor revisions

Cooke *et al*. employ a 3-D atmospheric chemistry–climate model (WACCM6) to investigate how changes in atmospheric O_2 following the Great Oxidation Event influence the diffusion-limited hydrogen escape rate. Their strategy of isolating the effect of pO_2 is well justified, and the mechanistic framework linking O_2 to hydrogen escape through O_3 production and its impact on tropopause height and temperature is clearly articulated. This study will be a valuable contribution to both the Precambrian-Earth and Exoplanet communities.

One general comment I would like to raise here is that at lower pO_2, Rayleigh scattering in the Schumann–Runge bands (175–192 nm) becomes increasingly important because solar UV radiation penetrates deeper into the lower atmosphere. For the same reason, absorption by H_2O and CO_2 in the Schumann–Runge bands also becomes critical under lower pO_2 conditions. I recall seeing paper showing that neglecting these effects could lead to overestimation of OH production by orders of magnitude at low pO_2 (Ji et al., 2023 JGR). I note an earlier paper by the lead author (Cooke et al., 2024 Planetary Science Journal) mentions that absorption in the Schumann–Runge bands has been newly implemented in the WACCM6, which is great. However, it would be helpful to clarify whether Rayleigh scattering in this wavelength range is included in this study.

We thank the reviewer for taking time to review our revised manuscript and providing useful feedback. We have specified that these simulations are the original Cooke *et al*. (2022) simulations which were performed with the largest range of O_2 mixing ratios simulated with WACCM6. We have mentioned this in both the methods and discussion section, and from our more limited range of simulations in Ji *et al*. (2023), we do not think that our conclusions are affected. Minor deviations in the exact numerical results may be expected, and we have encouraged further work with updated calculations.

Most of my remaining comments are either minor or technical and are discussed in detail below. Lines 134–135: I am a little concerned about holding other gases, particularly CH_4 and H_2, fixed at a given surface mixing ratios may not fully isolate the effect of changing O_2 alone. Altering pO_2 inevitably changes the abundances of OH and $O(^1D)$, which in turn affects the lifetimes of CH_4 and H_2. Moreover, the model would automatically adjust the upward flux (or number density) of CH_4 and H_2 at the surface, in order to maintain those surface mixing ratios fixed at 0.8 ppmv and 0.5 ppmv. For the sake of argument, let's assume a biological methane source of ~300 Tg yr^{-1} yields a surface mixing ratio of 0.8 ppmv under 1 PAL of O2, but at lower pO_2 the flux required to maintain the same surface CH_4 abundance could be substantially different. So my question is, to what extent might the results in Table 1 reflect combined changes in O_2 and methane source strength, rather than O_2 alone.

The reviewer raises a good point about fixed methane mixing ratios, rather than fixed fluxes. As part of Ji *et al.* (2023), we ran a limited number of simulations where the Schumann-Runge band absorption of H_2O and CO_2 was included, and the lower boundary conditions were fixed fluxes rather than mixing ratios. Whilst the numbers of the mixing ratios for specific gases are affected, this is minor compared to the effect of changing O_2 concentrations, which we have now included a commentary on in the discussion. We do think that a comprehensive suite of simulations with different fluxes and mixing ratios would be a more thorough exploration, and we hope that is done in future work.

Lines 168–169: I did not see a citation for the binary diffusion coefficients used here, which have different temperature dependence. Please clarify the source of these coefficients, or how they were derived.

This has now been specified for each gas.

Lines 202–205: This is an interesting result. I recall the classic O_2–O_3 calculations by Ratner and Walker (1972, Journal of the Atmospheric Sciences), who also found that ozone mixing ratios peak near ~10% PAL O_2. In that study, however, the vertical temperature structure was held fixed. It would be helpful to further discuss why the ozone mixing ratio at the tropopause reaches a maximum near ~10% PAL, given that this behavior may be driven by processes different from what currently being discussed here (the temperature/greenhouse effects because of peak ozone).

This is a good point raised by the reviewer and we are happy to address it in more detail in the text. The O_3 mixing ratio maximises for the 10% PAL simulation due to a combination of O_2 number density and incoming radiation. Instead of photolysis oxygen in the middle stratosphere around 25 hPa as in the 100% PAL atmosphere, as O2 is reduced, the UV radiation penetrates deeper and instead photolyses O_2 closer to the tropopause. This is similar for the lower oxygen cases of 1% PAL – 0.1% PAL, but these are limited by the O_2 number density and do not produce as much ozone through the TTL region.

Line 351: Could the authors clarify whether the stated "20× modern iodine concentration" refers to oceanic iodine, atmospheric iodine, or both?

The iodine is marine iodine that is then emitted to the atmosphere. We have now clarified this in the manuscript.

Response to reviewer 4

Summary

Accepted subject to minor revisions

The review In this manuscript, Cooke et al. investigate how variations in atmospheric oxygen (O_2) mixing ratio since the Great Oxidation Event influence the total hydrogen (H) mixing ratio at the homopause, and consequently the diffusion-limited H escape rate over the past 2.4 Gyr. To address this question, the authors employ WACCM6, a three-dimensional chemistry–climate configuration of the Community Earth System Model (CESM). They perform eight simulations spanning a wide range of atmospheric O_2 levels, from 0.1 % to 150 % of the present atmospheric level (PAL). The main result is that although the diffusion-limited escape rate of H varies with O_2 abundance, it remains within a factor of about 5 of the present-day value across all scenarios. These escape rates are sufficiently small to be negligible on geological timescales, supporting the conclusion that substantial H loss did not occur after the onset of the Proterozoic. The authors further show that the stratospheric H mixing ratio responds nonlinearly to O_2 mixing ratio, with maximum H escape predicted for O_2 mixing ratio between 5 to 10 % PAL. This behaviour is attributed to changes in ozone (O_3) mixing ratio in the tropical tropopause layer, which modulate UV heating, local temperatures, and the efficiency of the cold trap. Overall, the study highlights the role of atmospheric oxygen as a nonlinear "valve" regulating H escape and motivates the necessity of three-dimensional chemistry–climate models to accurately capture the processes controlling Earth's H loss through time. I believe this manuscript is suitable for publication after minor revisions. I particularly appreciated the well-structured and thoughtful introduction, which clearly outlines the key concepts and mechanisms that are subsequently developed throughout the paper. The main results are clearly presented, well illustrated, and adequately justified. However, more can be done (see comments below) to further improve the manuscript.

We thank the reviewer for taking the time to review our manuscript and appreciate the constructive comments below which we feel have helped us to improve the manuscript and further clarify some important points.

1.1 Major comments

1) My main comment relates to the interpretation of the results presented in Table 2. While a modest increase in the hydrogen escape rate is observed at 5 and 10 % PAL, the overall trend suggests a substantial decrease in escape rate with decreasing O_2 mixing ratio. Based on these results alone, one might reasonably expect this trend to continue

toward even lower O2 levels, which are more representative of pre-GOE conditions. This appears somewhat at odds with the broader conclusion that hydrogen escape rates should have been significantly higher prior to the GOE. It would therefore be very helpful to clarify this apparent discrepancy. In particular, an additional simulation at much lower O2 levels (e.g., 10−3–10−4 % PAL), representative of pre- GOE conditions, could help resolve what I refer to here as a low-O2–low-H-escape paradox. Would it be feasible to add such a simulation to the experimental set?

While it would be feasible to do an extra experiment, this would take some more time to simulate the lower O_2 level and for it to come into equilibrium. We estimate about 100 years of model time based on the prior simulations. However, because of the imposed CH_4 mixing ratio at the surface, there comes a point where the CH_4 mixing ratio actually outweighs the water vapour contribution, and this is near 0.1% PAL as shown in this paper.

The broader conclusion that hydrogen escape rates were higher pre-GOE is due to much higher amounts of CH_4 and/or H_2 gas. CH_4 concentrations will have lowered once oxygen concentrations increased. Additionally, to offset the fainter Sun, higher amounts of CO_2 would be required. The radiative transfer for WACCM6 would break down at such high concnetrations of CO_2, so simulating the Archean (pre-GOE) atmosphere with WACCM6 would require an overhaul of the radiative transfer which is beyond the scope of this work. Our work does not aim to solve the entirety of hydrogen escape throughout the Proterozoic, but point out a relevant mechanism for hydrogen escape on early-Earth and Earth-like worlds.

2) A second major comment concerns the description of the model setup and the assumptions underlying the simulations. In particular, it is not entirely clear which orbital configuration is used in this study (presumably modern). Similarly, while the use of contemporary ocean and land settings is mentioned (line 101), it would be useful to clarify whether adopting a modern continental configuration is common practice in deep-time atmospheric studies, and how this choice compares with previous work. I strongly encourage the authors to clearly and explicitly specify these aspects in the model description section, and possibly to reiterate them in the conclusions, especially given that the importance of such parameters is acknowledged later in the discussion (lines 271–273). Additional information on the ocean configuration (slab versus fully coupled, resolution), prescribed pCO2, and solar constant would also improve transparency and reproducibility. While I agree with the statement in line 290 that a full reconstruction of Proterozoic conditions is not required, it should nevertheless be made explicit which aspects of the climate system represent Proterozoic conditions and which do not. If all parameters except O2 are kept at or close to 1850 conditions, it becomes less clear how directly these simulations can be used to infer hydrogen escape over the past 2.4 Gyr. In that case, a more developed justification, beyond what is currently provided in lines 290–291, would strengthen the interpretation of the results.

We appreciate that work should be reproducible and following this comment, we have added further description to the methods section. We have described the model configuration in more detail and included more information in the discussion section regarding caveats.

3) My final major comment relates to the Discussion section. Overall, I found it to be rather long and primarily focused on outlining potential future research directions. While this is useful, the discussion would benefit from a stronger emphasis on interpreting the results presented in this study. In particular, a more explicit comparison with previous modelling or theoretical studies, as well as a clearer link to available geological constraints, would help to place the results in a broader context. A dedicated subsection (or paragraph) on model limitations would also be valuable. Moreover, some key results, such as the role of clouds or the behaviour of the tropical tape recorder, are not revisited in the discussion. The Discussion could also be used to further explore the physical mechanisms underlying the nonlinear dependence of hydrogen escape on O2 mixing ratio. For example, why does the O3 abundance itself respond nonlinearly to changes in O2? The discussion could also be used to resolve the low-O2–low-H-escape paradox mentioned above.

We have included a model limitations section and expanded on why hydrogen escape responds non-linearly to O_2 by including a more detailed description on TTL temperatures in the results section.

Finally, the two subsections devoted to future work might be merged and condensed to reduce the introduction of new material at this stage of the manuscript, thereby allowing more space for a deeper discussion of the study's key results and their implications.

We feel that the implications of this work may be broad, and we wanted to point out why it is important to two separate but related fields. We have also included implications regarding the tape recorder in the discussion section.

1.2 Minor comments

1) Caption Table 1. In the sentence: "The mixing ratios or fluxes of other gases specified at the surface we kept constant as O2 was altered.", "we" should be replaced by "were". Please check and correct.

Thank you, this has been changed.

2) Line 102. Consider rephrasing to "70 atmospheric layers along the vertical" rather than "70 vertical atmospheric layers".

Thank you, this has been modified.

3) Line 112. To avoid potential confusion, I suggest rephrasing as: "were computed using implicit numerical schemes" and "were computed using explicit numerical schemes".

This has now been change.

4) Line 144. Consider replacing "at pressures greater (altitudes below) 10 hPa" with "at pressures greater than (altitudes below) 10 hPa".

This has now been reworded.

5) Line 173. Please specify whether the longitude range is expressed in ◦E or ◦W.

This has now been implemented as East.

6) Figure 4. The yellow–orange–pink contour levels should be consistent between the two panels. As currently presented, the differing scales are misleading and hinder comparison. Adding additional contour levels and extending the colour gradient would greatly improve the interpretability of the figure. The same comment applies to Figure 5.

This has now been implemented.

7) Figure 5. Please check the small white gap at the extreme right of each panel, which gives the impression that the final month may not be correctly displayed. Same for Figure 3.

Thank you for pointing this out, this has now been altered in the manuscript.

8) Figure 6. In the first panel, consider replacing "Warmest" with "Highest" in the label of the vertical axis and in the caption. Please also check the text, as this was also at lines 201, 203, and 211. In addition, in the final sentence of the caption, should the range be ±24◦ rather than ±20◦? If this is intentional, a brief explanation of why the tropical range differs here would be helpful.

With regards to ±20° and ±24°, we believe that the reviewer is referencing the original preprint rather than the updated document where we changed this caption to ±24° so this has already been done. Warmest means highest temperature, whereas highest is associated with altitudes too, and because we reference altitudes, we prefer to retain the word warmest instead.

9) Tropical tape recorder Results section. Is the Tropical tape recorder essential to the core message of the paper? Alternatively, the focus could be placed on the persistence of seasonal cycles and their phase lag of about 6 to 12 months relative to surface conditions, rather than on the "tape recorder" metaphor. I also wonder about the robustness of these seasonal signals, given that many parameters are held constant. For example, changes in continental configuration and astronomical forcing through time are expected to significantly affect seasonality. Some justification of why these seasonal-cycle results remain relevant over the last 2.4 Gyr would strengthen this part of the analysis.

We think that the tape recorder is a result that many readers will be interested in so we have decided to keep it in the manuscript. The fact that the signal disappears may be independent of the other seasonal influences because shortwave heating does not significantly affect local TTL temperatures when ozone concentrations are low. However, in light of the reviewer's comment, we have included additional remarks on the tape recorder in the discussion, including how it may be relevant to exoplanet atmospheres and observations.

10) Code availability and data availability. References to the model version, the ExoCESM GitHub repository, and the Dryad data repository should be accompanied by a DOI and/or a direct URL.

We have now made the links available with their URLs.

Again, I would like to congratulate the authors on their manuscript. I found the manuscript enjoyable to read and, in the end, had the clear impression of learning something useful.

Thank you very much, we appreciate the supportive feedback and comments.

Response to editor

Dear Dr. Cooke and co-authors,

In general the reviewers were positive about this revision and their comments should be included in the final version of the manuscript.

It would be helpful to clarify the wavelength range for the Rayleigh scattering as commented by one reviewer.

Please send the minor revision to CP no later February 20, 2026.

Kind regards,

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.

We have responded to all the comments from the reviewers, including specifying the wavelength range for Rayleigh scattering.

We have marked modifications in red and made minor changes to the figures as requested by reviewer 4.