nature portfolio

Peer Review File

# Volatile depletion in rocky planets as a chemical fingerprint of hybrid accretion

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**This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.**

Version 0:

Reviewer comments:

Reviewer #1

(Comments for the Author)
This paper aims to explain the depletion pattern of volatile elements in terrestrial planets using a combined model of pebble accretion, protoplanet impacts, and planetesimal accretion. It assumes pristine pebbles with CI composition. When these pebbles accrete onto a planetary envelope, volatile elements sublimate. The vapor is carried outward by convection in the envelope and is removed by recycling flow to the protoplanetary disk. The model also assumes that convection is suppressed when the envelope temperature reaches about 1400 K, so elements that sublimate at higher temperatures are not removed by recycling. For planetesimal accretion, it assumes Vesta-type planetesimals that are depleted in volatiles. Under this framework, the authors vary model parameters and use reduced chi-squared and Bayesian inference to compare different formation scenarios. They conclude that Earth formed with more than 75% contribution from pebble accretion and 25% from planetesimals. For Mars, they conclude 27% from pebble accretion and 73% from planetesimals.

This study is valuable because it compares multiple formation scenarios statistically and provides quantitative constraints on the relative contributions of pebble accretion and planetesimal accretion to planet formation. It is also important because it connects astrochemical compositional data to tests of planet formation scenarios. However, I have some concerns because the validity of the models is not always clear, and the choice of models may affect the results.

1. As stated in the Discussion, Supplementary Figure 4 suggests that the assumption of CI composition pebbles affects the results. It may not be widely accepted that pebbles in the terrestrial planet formation region have CI composition (e.g., Burkhardt et al. 2021, Miyazaki and Korenaga 2021, Morbidelli et al. 2025). It would be better to discuss this more clearly in the main text, ideally with figures.

2. The model uses Vesta-type planetesimals that are depleted in volatiles. However, planetesimals may also exist that are not depleted in volatiles. How would the results change if such planetesimals were included?

3. The model assumes that an inner radiative zone forms in the silicate cloud layer at 1400 K. This creates a jump in the depletion pattern near 1400 K in Figure 3, and it seems important for explaining Earth. It may be possible for an inner radiative zone to form at high temperature (e.g., Markham et al. 2022, Misener and Schlichting 2022), but is there a clear reason for choosing 1400 K? If this threshold were 1300 K or 1500 K, would the results change?

4. The 1D model uses Piso and Youdin (2014). Could this choice affect the results? For example, infalling pebbles can increase the metallicity and opacity of the envelope gas, which may change the temperature–pressure profile (e.g., Brouwers and Ormel 2020). It may be useful to discuss whether the curve in Extended Data Figure 1 would change if a more realistic model than Piso and Youdin (2014) were used.

5. What envelope mass is assumed in the 1D model? Depending on the setup, Piso and Youdin (2014) can produce a relatively large envelope. Exoplanet observations suggest envelope mass fractions of a few percent for super-Earths (e.g., Rogers and Owen 2021), and smaller fractions for Earth-sized planets. It would be helpful to check whether the 1D model is consistent with plausible envelope masses.

6. Previous hydrodynamic studies often show recycling flow with inflow from high latitudes and outflow near the midplane (e.g., Kurokawa and Tanigawa 2018). Why is this pattern not visible in Figure 2B? What setup differences cause this? Could

this affect the results?

7. The paper considers one or two giant impacts for Earth, but N-body simulations of terrestrial planet formation often suggest that Earth experienced more giant impacts (e.g., Quintana et al. 2016). How should we understand this inconsistency?

8. The model seems to assume that impacts do not change chemical composition. The last giant impact may have occurred after the protoplanetary disk dispersed, and even if the atmospheric composition changed, it could return to the mantle over time. However, giant impacts can also occur during the disk phase or during disk dispersal (e.g., Iwasaki et al. 2002, Kominami and Ida 2002). If impacts occur while the disk is present, volatile elements that evaporate during the impact (e.g., Kurosaki et al. 2023) could escape with the atmosphere. It would be useful to discuss this effect. (The amount of evaporation depends on impact speed and angle etc, so if this effect matters, the model would need to be more complex.)

9. How much do the adopted bulk composition models for Earth and Mars affect the results? For Earth, the paper uses Wang et al. (2018). If a different model were used, how much would the values in Table 1, such as ln Z, change? The current differences are not very significant (ln Z < 1), so I would like to know how robust this is.

(Remarks on code availability)

Reviewer #2

(Comments for the Author)
'Volatile depletion in rocky planets is a chemical fingerprint of hybrid accretion' uses statistical methods combined with a model of volatile loss in a gaseous proto-planetary envelope during pebble accretion to assess whether this is a viable method to account for volatile lithophile budget of Earth and Mars. The authors propose two scenarios, both of which represent a hybrid between the classical and pebble accretion models of terrestrial planet formation. They start with planetary embryos forming via pebble accretion from CI-like material which devolatilises during the accretion. In one scenario, this planetary embryo then accretes a small number of planetesimals with a Vesta-like composition followed by at least one impact with another planetary embryo. In the other scenario, only the planetary embryo impacts. While the authors test the impact of more than one planetary embryo in both scenarios, they find that a singular impact (akin to the Moon-forming impact) best reproduces the Earth's volatile lithophile budget. For Mars, the proposed scenarios are similar but minus the impact of a planetary embryo (as Mars didn't experience a Moon-forming event). The authors find that Earth's volatile budget is best matched when pebble accretion (forming two planetary embryos which collide) is the dominant driver of Earth formation with a small amount of planetesimal accretion. Conversely, they find that, for Mars, planetesimal accretion is the dominant formation method that allows for its volatile budget to be matched.
I found this paper to be an interesting read. It adds an important addition to the debate regarding planetesimal or pebble accretion as a main driver for terrestrial planet formation and provides a basis for both sides of the debate to further investigate the provenance of Earth's volatile budget. As such, I have no qualms in recommending it for publication.
I do, however, have some questions/observations that I would like addressed with a line or two in the work.
1. In the introduction, you mention the ongoing debate concerning pebble and planetesimal accretion yet don't cite any of the papers that detail this debate until the discussion, only citing works that outline both the theories. Perhaps those later cited papers should be cited at this point too.
2. How would the accretion of mostly CI-like, with the addition of some Vesta-like, compositions effect the non-volatile element budgets of the BSE and BSM indeed bulk Earth and bulk Mars?
3. As a follow on from the last question, how would isotopic compositions look? Neither of these compositions are isotopically similar to Earth.
4. There is no extra volatile loss during the giant (Moon-forming) impact. While a citation is provided to counter this idea, it seems no work has been done to assess whether volatile loss at this stage would affect the final results. To me this seems like a major weakness in this work as a catastrophic impact is unlikely to result in no volatile loss. While I'm aware that this is something that is very difficult to model, an assessment of what the effect of different (assumed) percentages of volatile loss at this stage would have on the final results would be good.
5. I notice in figures 3 and 5 that the volatile budget of Mars is far easier to account for than Earth (reduced chisq as low as 0.6 compared to 3.3). What do the authors think the reason for this is?
6. The caption of Table 1 mentions a TriImp scenario (I' assuming where a body undergoes collisions with three other planetary embryos). This should be removed from the caption if these scenarios are not addressed in the paper.

(Remarks on code availability)
The code supplied appears well formatted and well commented. All necessary files seem to have been provided. I can't find a README, however, which would be useful to separately explain the basics of the code outside of the program files. This being said, I believe it would be fairly easy (with perhaps one clarification email to the authors if needed) to produce the results presented in this article using the code provided.

Reviewer #3

(Comments for the Author)
Wang et al. present a hybrid accretion model for the formation of Earth and Mars, combining pebble accretion (with devolatilization during the process) and collisional growth from volatile-depleted planetesimals. Using Bayesian inference,

they constrain the relative contributions of these components by fitting to the bulk silicate compositions of both planets. They find that Earth requires at least ~75% contribution from pebble-accreted protoplanets (proto-Earth + impactor), with up to ~25% from Vesta-like planetesimals. Mars, by contrast, is dominated by ~73% planetesimal material with only ~27% from pebble accretion. The framework is creative, the sensitivity tests are extensive, and the idea that volatile depletion patterns encode accretion histories is compelling.

However, from a geochemical standpoint, there are several issues with the foundational assumptions that need to be addressed. Most critically, the model's treatment of early-formed planetesimals as uniformly volatile-depleted (Vesta-like) is difficult to reconcile with the volatile-rich compositions recorded by iron meteorites from the earliest inner solar system planetesimals. Additional concerns relate to the terminology around volatile elements, the treatment of alternative volatile loss mechanisms, and the implications for the volatile budgets of planetary cores. These issues do not necessarily invalidate the modeling framework, but they require careful discussion and possibly modifications to the model assumptions. With revisions addressing this point and the other comments above, the paper could make an important contribution to the field.

Detailed Comments

L38-41: The authors should clarify early on that the "volatile" elements discussed in this study are moderately volatile elements. This distinction matters because highly volatile species such as water, carbon, and nitrogen can be lost by additional processes beyond those considered here (e.g., degassing during thermal metamorphism, hydrodynamic escape). Without this clarification, readers unfamiliar with the cosmochemical usage may conflate the two categories, which would lead to misinterpretation of the paper's scope and conclusions.

L74-77: The authors cite the presence of moderately volatile siderophile elements in iron meteorites and the inferred high oxidation state of the earliest planetesimals as evidence for cool ambient conditions during their formation. This argument could be strengthened further. The presence of nitrogen and carbon in inner solar system (NC) iron meteorites requires that the precursor material accreted by the earliest NC planetesimals contained organics (see Grewal et al, 2021 Nat Ast; Grewal et al, 2022 EPSL). This places even tighter constraints on the thermal environment during accretion of these bodies, since organics would not survive the high ambient temperatures invoked in traditional disk models.

L88-93: The discussion of volatile loss mechanisms from early planetesimals should acknowledge that high-energy impacts have also been proposed as a potential cause of volatile loss (e.g., Halliday and Porcelli, 2001, EPSL).

L94-96; L154-157: This is, in my view, the most significant issue with the current manuscript. The authors adopt the position that the earliest inner solar system planetesimals were Vesta-like, i.e., with volatile-depleted mantles. However, NC iron meteorites, which most likely sample the cores of the first-formed planetesimals in the inner solar system, record volatile-rich compositions (ref. 25 in the paper). The volatile elements sampled by iron meteorites are siderophile, but their volatilities overlap substantially with the lithophile volatile elements that the authors use to constrain their models. This creates a conceptual problem. If the earliest planetesimals lost their volatiles during accretion, then siderophile volatile elements of similar volatility should have been lost as well, and the cores of these bodies should not be volatile-rich. It would be difficult to argue that elements with similar volatilities but different geochemical affinities (lithophile vs. siderophile) experienced completely different loss behaviors during accretion. Furthermore, if these earliest planetesimals did have volatile-rich cores, then those planetesimals would have contributed volatiles to the growing Earth and Mars through their core material, even if their mantles were depleted. This contribution would go into the cores of the accreting planets rather than their mantles, and it would affect the overall volatile budget in ways not captured by the current model, which focuses exclusively on lithophile (mantle) compositions. The authors should address this issue directly and discuss whether and how it affects their conclusions.

L206-208; L225-228: The same issue raised above regarding volatile-rich cores of early planetesimals applies to Mars. The model predicts that ~73% of Mars is composed of Vesta-like, volatile-depleted planetesimals. If the earliest planetesimals in the inner solar system actually had volatile-rich cores (as iron meteorite evidence suggests), then the volatile budget delivered to Mars by these bodies may have been larger than assumed. Mars has a sulfur-rich core, which is consistent with accretion of planetesimals that retained volatiles in their metallic phases. The authors should discuss whether the dominance of planetesimal material in Mars' accretion amplifies this discrepancy relative to the Earth case.

Additional Comment
The authors commendably test alternative planetesimal models by varying $T_0$ and $\sigma_0$ of the logistic function, and they also test an exponential model and direct use of Vesta's measured composition. These tests demonstrate robustness of the framework to the functional form of the depletion curve. However, none of these tests address the more fundamental question of whether the planetesimal component should be modeled as having volatile-depleted mantles at all, given the iron meteorite evidence discussed above. A test that allows the planetesimal component to retain some fraction of its moderately volatile elements (intermediate between Vesta and CI) would be informative.

Daman Grewal
New Haven

(Remarks on code availability)

Version 1:

Reviewer comments:

Reviewer #1

(Comments for the Author)
The authors have revised the manuscript in response to my comments, and I am generally satisfied with their individual responses. One of the major issues, as pointed out by all referees, was whether the assumed compositions of the building blocks affect the conclusions. In response, the authors performed additional analyses by varying the compositions of planetesimals and pebbles. These analyses have improved my understanding, but they have also raised further questions. My specific comments are as follows.

1. For Earth, Supplementary Fig. 6 shows an important result for the case where T0 and σ0 of the planetesimal logistic model are varied. In this case, the contribution from planetesimals becomes significantly larger, and this seems to affect the authors' main conclusion. I think this result should be clearly discussed in the main text, not only in the Supplementary Information.

2. For Mars, the pebble composition appears to be fixed. What would happen if pre-depleted pebbles were used, as in the case of Earth? I think this should be tested, or at least discussed.

3. In light of the above points, the conclusion in the Abstract that Earth is mainly composed of protoplanets formed via pebble accretion, with a contribution of ≳75%, and that Vesta-like planetesimals contribute at most ~25%, seems too strong. In the logistic planetesimal model shown in Supplementary Fig. 6, the planetesimal contribution is about 39^{+17}_{-14}%, which is not consistent with the number given in the Abstract. Since the uncertainty is also large, the qualitative statement that pebble accretion is clearly dominant should also be stated more cautiously. In the Supplementary Information, the authors seem to justify excluding some elements, such as Si, Mg, and Cr, from the fit by invoking effects that are not included in the current model. This could appear somewhat arbitrary. I think the conclusion should be revised accordingly.
For Mars, the conclusion that planetesimals dominate appears relatively robust at this stage. However, I would like the authors to check whether this conclusion, including the inferred PM contribution, changes when pre-depleted pebbles are tested as mentioned above.

(Remarks on code availability)

Reviewer #2

(Comments for the Author)
This work uses statistical methods combined with a model of volatile loss in a gaseous proto-planetary envelope during pebble accretion to assess whether this is a viable method to account for moderately volatile lithophile budget of Earth and Mars. The authors propose various scenarios which represent a hybrid between the classical and pebble accretion models of terrestrial planet formation. The authors find that Earth's volatile budget is best matched when pebble accretion (forming two planetary embryos which collide) is the dominant driver of Earth formation with a small amount of planetesimal accretion. Conversely, they find that, for Mars, planetesimal accretion is the dominant formation method that allows for its volatile budget to be matched.
I found this paper to be an interesting read.
I, once again, really enjoyed reading this paper. I appreciated the comments from the authors who have taken their time address all issues and questions raised by all the reviewers to what I believe is a high standard. I feel the comments I have raised can now be understood from the manuscript.
This is still a valuable contribution to the field and I, personally, would recommend it for publication.

(Remarks on code availability)

Reviewer #3

(Comments for the Author)

(Remarks on code availability)
I am pleased with the authors' response. Happy to recommend the paper for publication.

Version 2:

Reviewer comments:

Reviewer #1

(Comments for the Author)
The authors have addressed my remaining concerns satisfactorily. In particular, the description of the numerical contributions in the main text and Abstract has been revised and is now more accurate and appropriately cautious. For Mars, the authors have added a new test with pre-depleted pebbles in the Supplementary Information. As expected, this changes the inferred pebble-accreted contribution, but the overall conclusion remains unchanged: Mars still requires a hybrid formation pathway, with planetesimal accretion playing the dominant role. I agree with this interpretation.

I am therefore satisfied with the authors' response and the corresponding revisions, and I would like to recommend publication of the manuscript.

(Remarks on code availability)

**We thank all the three reviewers for their insightful and constructive comments, which have helped us improve the quality of the manuscript.**

**Below, we offer our point-to-point response to each review. There, we refer either to the relevant updates made to the manuscript or provide an explanation in the cases where we have not changed the manuscript.**

***(For clarity, our response is marked in bold, and any changes in the manuscript are marked in bold with blue colors)***

Reviewer #1 (Comments for the Author):

This paper aims to explain the depletion pattern of volatile elements in terrestrial planets using a combined model of pebble accretion, protoplanet impacts, and planetesimal accretion. It assumes pristine pebbles with CI composition. When these pebbles accrete onto a planetary envelope, volatile elements sublimate. The vapor is carried outward by convection in the envelope and is removed by recycling flow to the protoplanetary disk. The model also assumes that convection is suppressed when the envelope temperature reaches about 1400 K, so elements that sublimate at higher temperatures are not removed by recycling. For planetesimal accretion, it assumes Vesta-type planetesimals that are depleted in volatiles. Under this framework, the authors vary model parameters and use reduced chi-squared and Bayesian inference to compare different formation scenarios. They conclude that Earth formed with more than 75% contribution from pebble accretion and 25% from planetesimals. For Mars, they conclude 27% from pebble accretion and 73% from planetesimals.

This study is valuable because it compares multiple formation scenarios statistically and provides quantitative constraints on the relative contributions of pebble accretion and planetesimal accretion to planet formation. It is also important because it connects astrochemical compositional data to tests of planet formation scenarios.

However, I have some concerns because the validity of the models is not always clear, and the choice of models may affect the results.

1. As stated in the Discussion, Supplementary Figure 4 suggests that the assumption of CI composition pebbles affects the results. It may not be widely accepted that pebbles in the terrestrial planet formation region have CI composition (e.g., Burkhardt et al. 2021, Miyazaki and Korenaga 2021, Morbidelli et al. 2025). It would be better to discuss this more clearly in the main text, ideally with figures.

**>> We thank the reviewer for the comment. First, we would like to emphasize that by 'CI composition' we refer only to the pristine elemental abundances, not to the isotopic signature. In fact, there are meteorites from the inner Solar System, specifically EH chondrites, that have pristine elemental abundances but are not CI-like in their isotopes. We show the composition of the EH chondrites now in the updated version of Figure 1. We have also rephrased from 'CI-like' to 'protosolar-like' in several places in the manuscript to avoid conflating elemental abundances with isotopic abundances. We have furthermore lifted our test of volatile-poor (pre-depleted) pebbles into the Results section of the main paper for the case of Earth, with expanded figures presented in Extended Data Fig. 5 and additional details on the pre-depletion model written into the Methods section.**

**Our test results show that inclusion of pre-depleted pebbles does not significantly reduce the Bayesian evidence, since the retrieved component fractions remain approximately the same (as constrained by other moderately volatile elements and refractory ones). However, pre-depletion does give a poorer fit to the overall volatile depletion with the increase of the pre-depletion factor. In other words, pre-depletion of pebbles is allowed (though not preferred) in the model. As pointed out (L216-218), such volatile-depleted pebbles could nevertheless have contributed to the later stages of proto-Earth's growth, where all moderately volatile elements would anyway be sublimated and lost during the accretion.**

2. The model uses Vesta-type planetesimals that are depleted in volatiles. However, planetesimals may also exist that are not depleted in volatiles. How would the results change if such planetesimals were included?

**>> Indeed, we have now tested various scenarios including CI-like planetesimals as a volatile-rich endmember of the building blocks for both Earth and Mars. Our test results (Extended Data Fig. 3c-e and Fig. 6) suggest that inclusion of a volatile-rich CI-like component is not favored given the significantly reduced Bayesian evidence, with the case where no pebble-grown component is considered (the CI+Plm model) rejected 'decisively' (based on Jeffreys' criteria). In the cases where a CI-like planetesimal component is an addition to the pebble component (instead of a replacement), the maximum contribution from such volatile-rich planetesimals is capped below ~10% by mass, for both Earth and Mars. We discuss these results on L173-186 for Earth and in L227-241 for Mars, with the statistics summarized in Table 1.**

3. The model assumes that an inner radiative zone forms in the silicate cloud layer at 1400 K. This creates a jump in the depletion pattern near 1400 K in Figure 3, and it seems important for explaining Earth. It may be possible for an inner radiative zone to form at high temperature (e.g., Markham et al. 2022, Misener and Schlichting 2022), but is there a clear reason for choosing 1400 K? If this threshold were 1300 K or 1500 K, would the results change?

**>> We have now clarified that this characteristic temperature of ~1400 K is adopted to correspond to the onset of an inner radiative layer (due to the rapid saturation of SiO-dominated vapor; Steinmeyer & Johansen 2024) and to approximate the boundary in sublimation temperature between MVLEs (moderately volatile lithophile elements) and refractory elements. We explain in detail in the Methods section (L429-444) about this adoption. We note that the two papers suggested by the referee use an SiO equilibrium pressure**

**expression that is only applicable to the interiors of high-mass planets (sub-Neptunes/super-Earths). This expression does not extrapolate well into the lower-pressure regime of our envelopes.**

**To be clearer, we have also highlighted in Fig.2a this inner radiative layer regime, with a shadow, for its protective role of refractory vapors.**

4. The 1D model uses Piso and Youdin (2014). Could this choice affect the results? For example, infalling pebbles can increase the metallicity and opacity of the envelope gas, which may change the temperature–pressure profile (e.g., Brouwers and Ormel 2020). It may be useful to discuss whether the curve in Extended Data Figure 1 would change if a more realistic model than Piso and Youdin (2014) were used.

**>> This is a very good point. We discuss in the revised version (Methods, L417-426) that an increase in the metallicity/opacity by a factor of 3 (and even higher) will not lead to significant changes to the sublimation temperatures of the elements, since their sublimation temperatures depend only weakly on their partial pressures (Extended Data Fig.1).**

5. What envelope mass is assumed in the 1D model? Depending on the setup, Piso and Youdin (2014) can produce a relatively large envelope. Exoplanet observations suggest envelope mass fractions of a few percent for super-Earths (e.g., Rogers and Owen 2021), and smaller fractions for Earth-sized planets. It would be helpful to check whether the 1D model is consistent with plausible envelope masses.

**>> Our envelope masses are actually very low. We calculate $10^{19}$ kg for a 0.6-Earth-mass protoplanet and $10^{17}$ kg for a Mars-mass protoplanet. These low mass fractions are a consequence of the relatively low masses of terrestrial protoplanets, compared to sub-Neptunes, as well as the high opacity set by the influx of pebbles and dust into the envelope.**

6. Previous hydrodynamic studies often show recycling flow with inflow from high latitudes and outflow near the midplane (e.g., Kurokawa and Tanigawa 2018). Why is this pattern not visible in Figure 2B? What setup differences cause this? Could this affect the results?

**>> We thank the reviewer for pointing this out. We clarify that our convection model as shown in Figure 2b is agnostic of the preferable direction of the disk flow as demonstrated in Kurokawa & Tanigawa (2018). However, in the recent simulation of envelope-disk flow interactions by Kuwahara & Lambrechts (2026), they show that for a fully convective envelope, a realistic disk flow will still deplete most of the tracer particles in the envelope within a timescale of a couple of years ($3\Omega^{-1}$, where $\Omega$ is the orbital frequency) (see their Figs. 3, 10 and 11). This timescale is comparable to what we show in Figure 2b.**

**We have added this comparison, along with these two important references, to clarify this point (L120-L123).**

7. The paper considers one or two giant impacts for Earth, but N-body simulations of terrestrial planet formation often suggest that Earth experienced more giant impacts (e.g., Quintana et al. 2016). How should we understand this inconsistency?

**>> We have now expanded our tests by including more than two giant impactors, as presented in L193-206 and in Extended Data Fig. 4. Given the constraint by moderately volatile depletion, we find that a triple-impactor scenario would be statistically disfavored and the retrieved mass of the third impactor is negligible ($0.01^{+0.02}_{-0.01} M_{\oplus}$). Notably, our inclusion of CI-composition impactors (mentioned earlier) also suggests that our Earth model could buffer several large impacts with volatile-rich Moon-mass bodies grown by pebble accretion. We believe that Earth experiencing a low number of giant impacts, which we infer from its volatile depletion, is a consequence of the important role of pebble accretion for Earth**

**formation. The addition of pebble accretion to terrestrial planet formation naturally implies that fewer planetesimal seeds are required to form terrestrial-mass planets, resulting in fewer protoplanets and hence fewer giant impacts.**

8. The model seems to assume that impacts do not change chemical composition. The last giant impact may have occurred after the protoplanetary disk dispersed, and even if the atmospheric composition changed, it could return to the mantle over time. However, giant impacts can also occur during the disk phase or during disk dispersal (e.g., Iwasaki et al. 2002, Kominami and Ida 2002). If impacts occur while the disk is present, volatile elements that evaporate during the impact (e.g., Kurosaki et al. 2023) could escape with the atmosphere. It would be useful to discuss this effect. (The amount of evaporation depends on impact speed and angle etc, so if this effect matters, the model would need to be more complex.)

**>> We have extended our discussion of devolatilization in giant impacts (L273-285). We discuss there particularly the recent paper by Calogero et al. (2025), where they show that impact-driven devolatilization is limited to bodies up to about Moon mass. Larger-mass planets indeed, as pointed out by the referee, experience return of the volatiles to the mantle. Calogero et al. (2025) applied their model of K loss to Grand Tack terrestrial planet formation simulations and found that only 1/6 of the formed planets experienced any measurable K loss. Therefore, it is unlikely, given current knowledge of giant impacts, that the giant impact that we need to fulfill Earth's volatile budget led to any loss of moderately volatile elements.**

**We appreciate the comment by the referee that giant impact devolatilization in the disc phase could be more efficient. We mention now this possibility towards the end of this new paragraph as an area for further studies.**

9. How much do the adopted bulk composition models for Earth and Mars affect the results? For Earth, the paper

uses Wang et al. (2018). If a different model were used, how much would the values in Table 1, such as ln Z, change? The current differences are not very significant (ln Z < 1), so I would like to know how robust this is.

**>> We would like to point out that the Wang et al 2018 model is a concordance model calibrated from various models based on geochemical, cosmochemical, and geophysical constraints. This is exactly the strength of this model as it is designed to capture the discrepancies across canonical Earth compositional models, thus providing a robust (if not the most precise) constraint on this present work. We have now also compared this model with the latest update of bulk silicate Earth composition by McDonough (2025) and confirm that our adopted values remain consistent with theirs within uncertainties for all elements considered in our mode fitting. We have pointed this out in L349-351 in the Methods section.**

**For Mars, we have compared and included the two most recent estimates of bulk silicate Mars composition (Yoshizaki & McDonough 2020 and Khan et al. 2022), and we are not aware of any more recent updates that would be significantly different from those adopted.**

**We would also like to highlight that since our model inference is based on lithophile elements (i.e. those concentrated in the mantle), any remaining large uncertainty in the core does not directly influence our inferences. For a different test on the implication for bulk sulfur content, we have adopted both the traditional estimates as in Wang et al. (2018) and the latest in Fischer & McDonough (2025).**

Reviewer #2 (Comments for the Author):

‘Volatile depletion in rocky planets is a chemical fingerprint of hybrid accretion’ uses statistical methods combined with a model of volatile loss in a gaseous proto-planetary envelope during pebble accretion to assess whether this is a viable method to account for volatile lithophile budget of Earth and Mars. The authors propose two scenarios, both of which represent a hybrid between the classical and pebble accretion models of terrestrial planet formation. They start with planetary embryos forming via pebble accretion from CI-like material which devolatilises during the accretion. In one scenario, this planetary embryo then accretes a small number of planetesimals with a Vesta-like composition followed by at least one impact with another planetary embryo. In the other scenario, only the planetary embryo impacts. While the authors test the impact of more than one planetary embryo in both scenarios, they find that a singular impact (akin to the Moon-forming impact) best reproduces the Earth’s volatile lithophile budget. For Mars, the proposed scenarios are similar but minus the impact of a planetary embryo (as Mars didn’t experience a Moon-forming event). The authors find that Earth’s volatile budget is best matched when pebble accretion (forming two planetary embryos which collide) is the dominant driver of Earth formation with a small amount of planetesimal accretion. Conversely, they find that, for Mars, planetesimal accretion is the dominant formation method that allows for its volatile budget to be matched.
I found this paper to be an interesting read. It adds an important addition to the debate regarding planetesimal or pebble accretion as a main driver for terrestrial planet formation and provides a basis for both sides of the debate to further investigate the provenance of Earth’s volatile budget. As such, I have no qualms in recommending it for publication.
I do, however, have some questions/observations that I would like addressed with a line or two in the work.

1. In the introduction, you mention the ongoing debate concerning pebble and planetesimal accretion yet don’t

cite any of the papers that detail this debate until the discussion, only citing works that outline both the theories. Perhaps those later cited papers should be cited at this point too.

**>> Thanks for the suggestion. We have now cited two specific references on this debate in L53.**

2. How would the accretion of mostly CI-like, with the addition of some Vesta-like, compositions effect the non-volatile element budgets of the BSE and BSM indeed bulk Earth and bulk Mars?

**>> For non-volatile (refractory) elements, the accretion of 'compositionally' CI-like (solar-composition) building blocks in our pebble-accretion model or otherwise treated as non-depleted planetesimals, along with Vesta-like planetesimals (with non-depleted refractories), will not make their budgets in the BSE and BSM (and by extension, their bulk compositions) significantly different from their solar values. However, we note that for the group of moderately 'refractory' elements (Si, Mg, and Cr), they are indeed depleted by a non-trivial 10-15% (relative to the most refractory Al and Ca) in bulk Earth (Wang et al. 2019) and potentially in rocky exoplanetary materials inferred from polluted white dwarfs (Aguilera-Gómez et al. 2025). This is, however, not the within the level of accuracy that our current pebble-devolatilization model has reached; also Earth may have accreted a small fraction of planetesimals that are more volatile-depleted than Vesta, as previously discussed in Supplementary Information and now more clearly laid out in the Methods section.**

**Nevertheless, inspired by this comment (along with a comment by Reviewer #1), we have introduced a population of CI-like planetesimals as a volatile-rich endmember during the accretion (Table 1 and Extended Data Figs.3c-e and 6). Our tests suggest that the inclusion of such a volatile-rich CI-like component is not favored given the significantly reduced Bayesian evidence. Even if at the best compatible scenarios, their mass contributions for both Earth and Mars cannot exceed more than 10% of the individual planets' total masses.**

3. As a follow on from the last question, how would isotopic compositions look? Neither of these compositions are isotopically similar to Earth.

**>> We first clarify that our assumed composition of pristine pebbles is solar-like – we have now avoided using 'CI-like' to refer to that due to the unintended isotopic implications. In the second last paragraph of Discussion, we have expanded the discussion on the implications of our model for a few of key isotopic signatures, along with the recognition of existing tension between the interpretations by different groups. We particularly highlight that agreement with the isotopic composition of Earth in elements such as Mo and Zr can be achieved through thermal processing of pebbles and loss of an isotopically distinct component from sublimation of FeS/CaS/MgS grains (Onyett et al., 2023, Nature) and water ice (Johansen et al., 2021; Bizzarro et al., 2025), which contain embedded heavy elements within them. Our composition-based results, complementary to isotopic analyses that remain debated, help refine the range of viable formation pathways for Earth and Mars.**

4. There is no extra volatile loss during the giant (Moon-forming) impact. While a citation is provided to counter this idea, it seems no work has been done to assess whether volatile loss at this stage would affect the final results. To me this seems like a major weakness in this work as a catastrophic impact is unlikely to result in no volatile loss. While I'm aware that this is something that is very difficult to model, an assessment of what the effect of different (assumed) percentages of volatile loss at this stage would have on the final results would be good.

**>> We share the reviewer's concern regarding any potential volatile loss triggered by giant impacts like a catastrophic Moon-forming impact, as proposed (but not actually simulated) in previous work (e.g., Hin et al. 2017; Norris & Wood 2017). We first clarify that impact-driven melting and vaporization has been demonstrated to occur on various sizes of planetary bodies (e.g., Nakajima & Stevenson 2015; de Vries et al.**

**2016; Saurety et al. 2025). The uncertainty lies on whether vapor loss did happen given available impact energy and planetary gravitational potential. This has been calculated on recent Grand Tack terrestrial planet formation simulations in Calogero et al. (2025, including coauthors Nimmo and Hin). Based on their calculations in the case of K (a typical moderately volatile element), volatile loss would only be significant for planetary bodies up to about Moon mass (see their Fig. 3 to the right; they have also set a lower-mass threshold, but we don't discuss that here). For higher masses, volatile loss is effectively absent due to insufficient energy to overcome the strong gravity of such high-mass planets. This has also been evaluated and concluded similarly in an earlier work (Sossi et al. 2022).**

**Given the simulated work mentioned above, we feel that it is not necessary for us to include in our model an assessment based on assumed values in further. We nevertheless recognize that this is an important topic and therefore we have discussed it in more detail in the 1st paragraph of Discussion.**

[redacted]

5. I notice in figures 3 and 5 that the volatile budget of Mars is far easier to account for than Earth (reduced chisq as low as 0.6 compared to 3.3). What do the authors think the reason for this is?

**>> We appreciate the reviewer's carefulness. The discrepancy in the accountability (i.e. goodness-of-fit) of the best models for Earth and Mars is primarily due to the larger deviation of the normalized Si composition in BSE from the solar unity line compared to that in BSM. This may be partially due to the unaccounted, higher degree of partitioning of Si into Earth's core compared to that on Mars, or otherwise to any unquantified/unknown thermal processing of Si (along with Mg and Cr) during the accretion process (as mentioned earlier and added in text in L445-455). We have performed a sensitivity test of the effect of**

**including or not Si, Mg and Cr (due to any unaccounted reasons) on the goodness-of-fit presented in Supplementary Figs. 6 and 7. This demonstrates that once these elements are removed from the fit, the goodness-of-fit for Earth (in the case of the reference model) is brought down to 0.4, comparable to the lowest value in the reduced-$\chi^2$ map for Mars.**

6. The caption of Table 1 mentions a TriImp scenario (I'm assuming where a body undergoes collisions with three other planetary embryos). This should be removed from the caption if these scenarios are not addressed in the paper.

**>> Due to another reviewer's concern on the number of impactors considered, we have now brought back the TriImp scenario (that was previously not included to save space). Now by adding it (as shown in Table 1 and Extended Data Fig.4b), our argument on the required number of giant impacts is even stronger.**

Reviewer #2 (Remarks on code availability):

The code supplied appears well formatted and well commented. All necessary files seem to have been provided. I can't find a README, however, which would be useful to separately explain the basics of the code outside of the program files. This being said, I believe it would be fairly easy (with perhaps one clarification email to the authors if needed) to produce the results presented in this article using the code provided.

**>> We thank the reviewer for also checking the code and the comment. We have now added a README file.**

Reviewer #3 (Comments for the Author):

Wang et al. present a hybrid accretion model for the formation of Earth and Mars, combining pebble accretion (with devolatilization during the process) and collisional growth from volatile-depleted planetesimals. Using Bayesian inference, they constrain the relative contributions of these components by fitting to the bulk silicate compositions of both planets. They find that Earth requires at least ~75% contribution from pebble-accreted protoplanets (proto-Earth + impactor), with up to ~25% from Vesta-like planetesimals. Mars, by contrast, is dominated by ~73% planetesimal material with only ~27% from pebble accretion. The framework is creative, the sensitivity tests are extensive, and the idea that volatile depletion patterns encode accretion histories is compelling.

However, from a geochemical standpoint, there are several issues with the foundational assumptions that need to be addressed. Most critically, the model's treatment of early-formed planetesimals as uniformly volatile-depleted (Vesta-like) is difficult to reconcile with the volatile-rich compositions recorded by iron meteorites from the earliest inner solar system planetesimals. Additional concerns relate to the terminology around volatile elements, the treatment of alternative volatile loss mechanisms, and the implications for the volatile budgets of planetary cores. These issues do not necessarily invalidate the modeling framework, but they require careful discussion and possibly modifications to the model assumptions. With revisions addressing this point and the other comments above, the paper could make an important contribution to the field.

Detailed Comments

L38-41: The authors should clarify early on that the "volatile" elements discussed in this study are moderately volatile elements. This distinction matters because highly volatile species such as water, carbon, and nitrogen can be lost by additional processes beyond those considered here (e.g., degassing during thermal metamorphism, hydrodynamic escape). Without this clarification, readers unfamiliar with the cosmochemical usage may conflate the two categories, which would lead to misinterpretation of the paper's scope and conclusions.

**>> Good point. We have now clarified at the beginning of the text and wherever else necessary that the model anchors on 'moderately volatile lithophile elements (MVLEs)'.**

L74-77: The authors cite the presence of moderately volatile siderophile elements in iron meteorites and the inferred high oxidation state of the earliest planetesimals as evidence for cool ambient conditions during their formation. This argument could be strengthened further. The presence of nitrogen and carbon in inner solar system (NC) iron meteorites requires that the precursor material accreted by the earliest NC planetesimals contained organics (see Grewal et al, 2021 Nat Ast; Grewal et al, 2022 EPSL). This places even tighter constraints on the thermal environment during accretion of these bodies, since organics would not survive the high ambient temperatures invoked in traditional disk models.

**>> We appreciate this suggestion. We have now added these two specific references on carbon and nitrogen in iron meteorites, together with our reference to moderately volatile siderophile elements (MVSEs), to strengthen the argument on this aspect, in L69-72.**

L88-93: The discussion of volatile loss mechanisms from early planetesimals should acknowledge that high-energy impacts have also been proposed as a potential cause of volatile loss (e.g., Halliday and Porcelli, 2001, EPSL).

**>> We have now added this overlooked but important reference to L46 and L79 where we mention the mechanism of volatile loss driven by energetic planetesimal collisions.**

L94-96; L154-157: This is, in my view, the most significant issue with the current manuscript. The authors adopt the position that the earliest inner solar system planetesimals were Vesta-like, i.e., with volatile-depleted mantles. However, NC iron meteorites, which most likely sample the cores of the first-formed planetesimals in the inner solar system, record volatile-rich compositions (ref. 25 in the paper). The volatile elements sampled by iron meteorites are siderophile, but their volatilities overlap substantially with the lithophile volatile elements that the authors use to constrain their models. This creates a conceptual problem. If the earliest planetesimals lost their volatiles during accretion, then siderophile volatile elements of similar volatility should have been lost as well, and the cores of these bodies should not be volatile-rich. It would be difficult to argue that elements with similar volatilities but different geochemical affinities (lithophile vs. siderophile) experienced completely different loss behaviors during accretion. Furthermore, if these earliest planetesimals did have volatile-rich cores, then those planetesimals would have contributed volatiles to the growing Earth and Mars through their core material, even if their mantles were depleted. This contribution would go into the cores of the accreting planets rather than their mantles, and it would affect the overall volatile budget in ways not captured by the current model, which focuses exclusively on lithophile (mantle) compositions. The authors should address this issue directly and discuss whether and how it affects their conclusions.

**>> We thank the reviewer for this important comment. Although our hybrid-accretion models (including the Vesta-like planetesimal component) are anchored on MVLEs, they do carry important implications for the abundances of MVSEs, as pointed out by the reviewer. We also agree that the volatile-rich compositions recorded by NC iron meteorites cannot be reconciled with a simple picture in which early planetesimals were uniformly volatile-depleted. However, core formation and silicate volatile loss may have been**

**temporally decoupled. Siderophile volatile elements could have been sequestered into metallic cores during early differentiation, whereas later silicate melting and magma-ocean degassing depleted the mantles in lithophile moderately volatile elements. In that case, a differentiated planetesimal may retain a volatile-rich core while contributing a volatile-depleted silicate component.**

**In our framework, the Vesta-like planetesimal component is intended to approximate this silicate contribution. We have first clarified this in L86-88, while acknowledging the implications of this adoption. Specifically, the potential accretion of volatile-rich metallic cores from such bulk planetesimals would contribute additionally to the overall volatile budget of Earth and Mars, which is not captured explicitly by the present model anchored on MVLEs. To quantitively assess this potential effect, we now include a first-order sulfur consistency check in the Discussion (2nd para) and Extended Data Fig. 8, using the sulfur contents inferred for iron meteorite parent bodies (Grewal et al., 2025) as a proxy for volatile-rich metallic cores. This exercise shows that our preferred accretion models are compatible with the higher inferred S contents of the cores of Earth (McDonough, 2025) and Mars (Stähler et al., 2021), rather than only with the lower estimates derived from extrapolated mantle volatility trends and core–mantle mass balance arguments (e.g., McDonough, 2014; Wang et al., 2018; Yoshizaki & McDonough, 2020; Khan et al., 2022). We therefore conclude that this issue does not invalidate the MVLE-based accretion inferences developed here, but it does highlight an important area to further improve the present framework: a fully self-consistent treatment including siderophile volatile delivery and partitioning to the core will be required to predict the bulk volatile siderophile budgets of Earth and Mars in the future.**

L206-208; L225-228: The same issue raised above regarding volatile-rich cores of early planetesimals applies to Mars. The model predicts that ~73% of Mars is composed of Vesta-like, volatile-depleted planetesimals. If the earliest planetesimals in the inner solar system actually had volatile-rich cores (as iron meteorite evidence suggests), then the volatile budget delivered to Mars by these bodies may have been larger than assumed. Mars has a sulfur-rich core, which is consistent with accretion of planetesimals that retained volatiles in their metallic phases. The authors should discuss whether the dominance of planetesimal material in Mars' accretion amplifies this discrepancy relative to the Earth case.

**>> As detailed in the preceding response, we have also done the test for Mars (Extended Data Fig. 8b). As the reviewer reasonably predicted, a higher amount of Vesta-like planetesimals accreted to form Mars – than to form Earth – indeed makes the S content in bulk Mars higher (while within the error bar of the geophysical constraint of Stähler et al., 2021), and deviate more significantly from the value that would otherwise be inferred from a volatility curve constrained by mantle compositions (BSM vs. BSE).**

Additional Comment

The authors commendably test alternative planetesimal models by varying T0 and σ0 of the logistic function, and they also test an exponential model and direct use of Vesta's measured composition. These tests demonstrate robustness of the framework to the functional form of the depletion curve. However, none of these tests address the more fundamental question of whether the planetesimal component should be modeled as having volatile-depleted mantles at all, given the iron meteorite evidence discussed above. A test that allows the planetesimal component to retain some fraction of its moderately volatile elements (intermediate between Vesta and CI) would be informative.

**>> We have addressed this point in further (along with similar comments from the other two reviewers), by introducing a population of CI-like planetesimals as a volatile-rich endmember for our hybrid accretion models. Given our test results and the measured strength of Bayesian evidence (Table 1 and Extended Data Figs. 3c-e and 6), we conclude that a mixture of Vesta-like and CI-like planetesimals – together with pebble-**

**grown components – is plausible (but with significantly reduced Bayesian evidence), and the maximum mass contribution from CI-like planetesimals should not be more than 10% of the total mass of the planet. This conclusion is found to be true for both Earth and Mars (Table 1).**

Daman Grewal
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**Haiyang Wang and Anders Johansen**

**On behalf of all coauthors**

**We thank all the three reviewers for their very positive views of the revised version of the manuscript. We here provide our response to the remaining points of Reviewer #1.**

Reviewer #1 (Comments for the Author):

The authors have revised the manuscript in response to my comments, and I am generally satisfied with their individual responses. One of the major issues, as pointed out by all referees, was whether the assumed compositions of the building blocks affect the conclusions. In response, the authors performed additional analyses by varying the compositions of planetesimals and pebbles. These analyses have improved my understanding, but they have also raised further questions. My specific comments are as follows.

1. For Earth, Supplementary Fig. 6 shows an important result for the case where T0 and σ0 of the planetesimal logistic model are varied. In this case, the contribution from planetesimals becomes significantly larger, and this seems to affect the authors' main conclusion. I think this result should be clearly discussed in the main text, not only in the Supplementary Information.

**>> We have now summarized the sensitivity-test result by artificially varying T0 and σ0 of a hypothetical population of planetesimals in the main text at L260-263. However, we note that this sensitivity-test result comes with a caveat. Any potential devolatilization of Mg, Si, and Cr during pebble accretion (unprescribed in our model but pointed out for this possibility in Methods – '1D envelope model', at L431-440) could also bring down the apparent higher planetesimal contribution to values consistent with the result of our reference model as tested and shown in Supplementary Information (Supplementary Fig. 8).**

2. For Mars, the pebble composition appears to be fixed. What would happen if pre-depleted pebbles were used, as in the case of Earth? I think this should be tested, or at least discussed.

**>> We have now included this test for Mars and shown the results in Supplementary Fig. 2. The test results show that assuming pre-depleted**

**pebbles to be accreted to Mars, the contribution of the PM component would actually increase slightly – by about 10% (as due to the compensation of pre-depleted volatiles in pebbles by a higher number of such pebbles to be accreted). However, this increase does not change our conclusion – in terms of Mars being grown dominantly through planetesimal accretion (instead of via pebble accretion). We have pointed out this test result in L232-234.**

3. In light of the above points, the conclusion in the Abstract that Earth is mainly composed of protoplanets formed via pebble accretion, with a contribution of ≳75%, and that Vesta-like planetesimals contribute at most ~25%, seems too strong. In the logistic planetesimal model shown in Supplementary Fig. 6, the planetesimal contribution is about $39^{+17}_{-14}$%, which is not consistent with the number given in the Abstract. Since the uncertainty is also large, the qualitative statement that pebble accretion is clearly dominant should also be stated more cautiously. In the Supplementary Information, the authors seem to justify excluding some elements, such as Si, Mg, and Cr, from the fit by invoking effects that are not included in the current model. This could appear somewhat arbitrary. I think the conclusion should be revised accordingly.

**>> Following the clarification in point 1 and the suggestion, we have now added this potentially higher contribution of a hypothetical population of planetesimals (with its calculated value range) into the abstract.**

For Mars, the conclusion that planetesimals dominate appears relatively robust at this stage. However, I would like the authors to check whether this conclusion, including the inferred PM contribution, changes when pre-depleted pebbles are tested as mentioned above.

**>> As explained in point 2, our conclusion for Mars does not change when pre-depleted pebbles are accreted.**

Reviewer #2 (Comments for the Author):

This work uses statistical methods combined with a model of volatile loss in a gaseous proto-planetary envelope during pebble accretion to assess whether this is a viable method to account for moderately volatile lithophile budget of Earth and Mars. The authors propose various scenarios which represent a hybrid between the classical and pebble accretion models of terrestrial planet formation. The authors find that Earth's volatile budget is best matched when pebble accretion (forming two planetary embryos which collide) is the dominant driver of Earth formation with a small amount of planetesimal accretion. Conversely, they find that, for Mars, planetesimal accretion is the dominant formation method that allows for its volatile budget to be matched.

I found this paper to be an interesting read.

I, once again, really enjoyed reading this paper. I appreciated the comments from the authors who have taken their time address all issues and questions raised by all the reviewers to what I believe is a high standard. I feel the comments I have raised can now be understood from the manuscript.

This is still a valuable contribution to the field and I, personally, would recommend it for publication.

**>> We thank the reviewer for their high opinion of the quality of the revision and the value of this work, as well as their recommendation for publication of this work.**

Reviewer #3 (Remarks on code availability):

I am pleased with the authors' response. Happy to recommend the paper for publication.

**>> We thank the reviewer for their recommendation of our work for publication.**