Geochemical Perspectives Letters A hybrid origin for the Martian atmosphere --Manuscript Draft--

Manuscript Number:	GPL-D-24-00088R1
Full Title:	A hybrid origin for the Martian atmosphere
Article Type:	Article
Keywords:	Mars; primordial outgassing; atmosphere; nebular capture; hydrodynamic escape
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Abstract:	The Martian isotopic record displays a dichotomy in volatile compositions. Interior volatiles from the mantle record a chondritic heritage (e.g., H, N, Kr, Xe) whereas the atmospheric reservoir of Kr and Xe – which do not currently experience escape – record heritage from a solar-like source. Motivated by disparate inferences on the source of Martian atmospheric volatiles (outgassed versus nebular captured), we consider hybrid-source accretionary atmospheres in which a high molecular weight (e.g., CO2-rich) outgassed component is mixed in with the low molecular weight H2-rich nebular atmosphere. We conduct calculations of nebular capture with and without a high molecular weight outgassed component mixed into the atmosphere during the lifetime of the solar nebula. Mixing an outgassed component into the nebular layer enhances the captured gas inventory by \approx 1-3 orders of magnitude – depending on the outgassed inventory – relative to "pure" nebular capture. These observations and calculations suggest that the Martian atmosphere arose as a subequal mixture of outgassed and nebular-derived components, and provide a framework for assessing the role of various mechanisms of gas loss over the entire history of the planet.
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Question	Response
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Claudine Stirling: isotope geochemistry, trace element biogeochemical cycles, palaeoceanography, palaeoclimatology, ocean & freshwater geochemistry

Andreas Kappler: Geomicrobiology, biogeochemistry, aqueous geochemistry, microbe-mineral interactions, biominerals, metals

Francis McCubbin: Experimental petrology, high-temperature geochemistry, meteoritics, cosmochemistry, magmatic volatiles

Raúl Fonseca: Experimental petrology, stable isotope geochemistry, trace element behaviour, magmatic sulfides, highly siderophile elements

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Answer Required Word count - an article should not be 3273 more than 3000 words (including abstract, text, figure/table captions) and should have a maximum of 30 references and a maximum 4 figures or tables. Kevin Zahnle Suggested Reviewers: kevin.j.zahnle@nasa.gov Expertise on hydrodynamic escape Bernard Marty bernard.marty@univ-lorraine.fr Expertise on geochemistry in general and Martian geochemistry in particular Bruce Jakosky bruce.jakosky@colorado.edu Expertise on the Martian atmosphere Kiyoshi Kuramoto

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February 19th, 2025

Dear Prof Helen Williams,

Thank you for granting us the additional time to revise our manuscript. Please consider the revised manuscript (GPL-D-24-00088) entitled "A hybrid origin for the Martian atmosphere" for publication in Geochemical Perspectives Letters. Our revisions address the specific points made by the two reviewers. Moreover, our response to the reviewers' comments and the changes we have made in response can be found below, using (new) line numbers to reference to changes.

As a last point: reviewer #2 mentioned that he was unable to access the supplementary information as submitted, and this led him to request some information that was already present in the original submission (e.g., the table of abundances). Based on the reviews it was clear that reviewer #1 *was* able to access the supplementary information. Whatever the issue, we will also upload the revised manuscript to the first author's website and place the revised manuscript on arxiv, so that whatever the accessibility issue may have been, reviewer #2 can be ensured access to the revised manuscript and the supplementary information both.

Thank you for handling our submission. I look forward to hearing from you.

Best Regards,

2hl. O.O.

Kaveh Pahlevan Principal Investigator Carl Sagan Center SETI Institute

Reviewer #1: In this paper the authors investigate a novel means of explaining a recently observed conundrum in the composition of Mars's noble gas reservoirs: that the interior is apparently chondritic in origin and the surface environment (atmosphere) is solar. The authors propose a neat solution to this: that outgassing of high mean molecular weight components (CO2, H2O) from the interior reduce the atmospheric scale height and thereby allow enhanced nebular accretion. I like the idea and the paper is a nice investigation of this, and its consequences. With moderate revision the paper could be published.

We are grateful to the reviewer for a careful reading of the manuscript and a positive appraisal.

- Could the authors point out the relationship between the heat source required to hydrostatically stabilise the atmosphere and the degassing? I.e., it seems to me that the impacts needed to provide the luminosity might themselves drive substantial melting of the surface and therefore degassing? The paper already describes the likely molten state of the surface, so it would be a small step to further say that the high mean molecular weight component was supplied by this melting.

Indeed, the envisioned planetesimal accretion would provide both a source of atmospheric heating as well as a source for high molecular weight components. Accordingly, in lines 65-67, we now state: "More likely heat flows relevant to the first few million years of Martian history derive from ongoing planetesimal accretion, which also delivers high molecular weight volatiles", making the link between the heat and volatile source explicit. We cannot unambiguously link volatile outgassing to melting because models of impacts degas impactors even at temperatures too low for silicate melting (e.g., Tyburczy et al. 1986 *EPSL*, 80, 3-4, 201-207).

- Another point about the melting of the surface: How do the authors envisage this avoiding the whole mantle-atmosphere system, or a substantial fraction of it, becoming homogenised? The fact that meteorites record chondritic noble gasses suggests the interior was somehow preserved from this equilibration with the (solar-like, for Kr) atmosphere. I think this requirement that the interior not be entirely melted favours slower accretion scenarios, and therefore proportionately greater mass addition?

Indeed, the preservation of the mantle-atmosphere dichotomy places constraints on early Martian evolution. In the supplementary section on "Energetics, Mechanisms, and Extent of Mixing", we have added the paragraph: "One constraint on the extent of mixing in the accretionary Mars system is the apparent preservation of chondritic mantle volatiles in the presence of nebular contributions to the atmosphere. The persistence of the mantle-atmosphere volatile dichotomy may indicate one of several possible histories. First, it is possible that significant portions of silicate Mars may have already solidified at the time of the nebular capture, effectively isolating chondritic mantle volatiles from mixing with the captured atmosphere. Secondly, although we have considered fully-mixed hybrid atmospheres for the calculations of nebular capture, it is possible that the compositional gradient in the accretionary atmosphere was smooth, with a CO2dominated lower atmosphere gradually transitioning to an H2-dominated upper atmosphere, effectively sealing off the silicate planet from nebular additions. Finally, it is possible that there once was complete homogenization of the silicate-atmosphere hybrid volatile system on Mars, and that the chondritic character observed in the Martian mantle is the overprint of chondritic volatiles delivered during late accretion after the solidification and effective isolation of silicate Mars. At present, we have no way to clarify these scenarios other than to state that the persistence of the mantle-atmosphere dichotomy places constraints on the sequence of volatile acquisition, mixing, and isolation in the accretionary Mars system."

- The opacity of the envelope is important for setting the thermal structure of the atmosphere and therefore the mass of nebula that can be accreted. The authors use the classic nebular dust opacity model of Bell and Lin. This is then scaled down for the high-mean molecular weight atmosphere that results from mixing of outgassed components. I wonder whether the authors could provide more justification for this in the high pressure environment of the planetary envelope, would there not be significant opacity coming from H2 collisionally induced absorption, molecular lines etc? How important is the opacity function to the results? If the opacity wasn't also varying with atmosphere composition, how much less efficient would the addition of high mean molecular weight components be?

We thank the reviewer for highlighting the need for more justification for the rationale of using dust opacity. To address this concern, between supplementary equations 4 and 5, we now state: "For conditions typical of the radiative-convective boundary ($\rho_{\rm rcb}\sim10-8$ g cm-3,T_rcb~200 K, P_rcb~0.2 millibars), the opacity is dominated by the dust, with molecular lines and collision-induced absorption of H2 contributing several orders of magnitude lower opacity, as evident in e.g., Figure 1 of (LEE et al., 2014). Although opacity in deeper layers can be dominated by pressure-broadened gas absorption, the entropy of the adiabat is determined by conditions in the upper atmosphere where dust opacity dominates."

We are grateful for the incisive question about the relative roles of opacity and mean molecular weight in enhancing the captured nebular inventory. To address this question, we carried out numerical calculations in which the opacity of the two atmospheric components were artificially set equal to one another. We found that the influence of the opacity function is present but small, and secondary to the influence of the mean molecular weight. We incorporate this insight by rephrasing the statement starting on Line 93: "The strong enhancement of nebular gravitational capture via mixing an outgassed component is mainly due to an the increase in mean molecular weight, which increases the gravitational coupling between the atmosphere and planet and decreases the atmospheric scale height, which – like cooling – causes contraction and an increase in the hydrogen density of the lower atmosphere where most of the atmospheric mass resides."

- The paper describes martian Kr as not being isotopically fractionated. I don't believe this is quite true, it is marginally mass fractionated from solar (e.g., Zahnle+2019 Fig 1; Shorttle+2024 Figure 1), although, substantially less so than Xe, for example.

We are grateful to the reviewer for alerting us to this subtle feature of the Martian Kr composition, which even the published report from the Mars Science Laboratory team (Conrad et al. 2016) fails to point out. To incorporate the notion that the Martian atmosphere could be nearly but not identically solar in its krypton isotopic character, we have added qualifying adverbs to lines 145, 150, 156, and 181 (e.g., changed "indistinguishable" to "nearly indistinguishable"). Given that data from Martian meteorites have not independently confirmed a slightly non-solar character to Martian atmospheric krypton, we do not elaborate on this distinction further.

Reviewer #2: This study uses the observed isotopic dichotomy between atmospheric and lithospheric martian noble gases as a spur to developing a more complete description of how planets accrete nebular gases. The idea is that degassing of a secondary atmosphere from the planet must occur at the same time as gravitational capture of nebular gases. The heavy secondary atmosphere then greatly increases the planet's ability to gravitationally capture nebular gases - provided that there is mixing --- such that a small planet like Mars can feed more efficiently. This leads to the authors proposing... well, let us quote from the abstract: "These observations and

calculations suggest that the Martian atmosphere arose as a hybrid mixture of outgassed and nebular-derived components and that - irrespective of the precise composition of the outgassed component - was mainly composed of molecular hydrogen." (IMHO, this is more a restatement of the hypothesis than an actual conclusion, but it is a good description of what they have in mind.)

We are grateful to the reviewer for lending his deep expertise on this topic. In specific response to the statement that the abstract only restates the hypothesis rather than a conclusion, we now state: "These observations and calculations suggest that the Martian atmosphere arose as a subequal mixture of outgassed and nebular-derived components." As we will discuss below, that the nebular and chondritic contributions to the hybrid atmosphere are approximately equal is a conclusion that arises out of our models and was not anticipated when the hybrid atmosphere hypothesis was first formulated.

The hypothesis is interesting and I think it must be at least partly true. I think the paper will be publishable once it is made more quantitative. I recommend tables that present quantities (of C, H2O, He, Ne, Ar, Kr, Xe) in grams/gram, following Pepin 1991. This way one can directly compare the quantities in the source materials to the quantities on Mars today, and one can compare the different models in context.

We have made several revisions to make the presentation more quantitative.

First, we point out that we did have a table in the supplementary information with all the data necessary to reproduce the abundance calculations. We now reference this table (Table S-1) in the caption to Figure 2. Moreover, following the referee's suggestion, we have added the neon abundances in chondrites, solar composition gas, and the present-day Martian atmosphere to Table S-1, added mention of the behavior of Ne in chondrite-solar mixtures in the caption to Figure 2, and now plot the Kr-normalized Ne abundances in Figure 3.

Second, we note that our model constrains the *relative* proportion of chondritic-to-solar gases (>10% and <46-77%, see Figure 2) much more stringently than the absolute abundances of either component (equivalent to 10-1000 bars CO_2 and 3-300 bars of H_2 as discussed in lines 91-93). Accordingly, we think that the *relative* elemental abundances of hybrid mixtures are a much more robust feature of our model than any absolute abundance we could tabulate (note the similarity between the cyan, blue, and magenta curves in Figure 3, which we now point out in the caption). Accordingly, we have chosen to express *relative* elemental abundances in Table S-1.

Finally, because Kr is nearly isotopically unfractionated, we can use its absolute abundance (in kg) in comparison with the abundance in the modern Martian atmosphere (in kg) to make a statement about the magnitude of non-fractionating loss (presumably due to impact erosion) affecting the Martian atmosphere throughout its history. This calculation implies ~2-4 orders-of-magnitude of non-fractionating loss, as now presented in a section at the end of the Supplementary Information.

Another problem of exposition is that the main text does a poor job of describing what is in the Supplements. This is a problem because the arguments developed in the main text depend on arguments that are hidden in the Supplements. The main text needs to summarize the specific arguments developed in the Supplements and the main text should include explicit pointers to specific equations or figures in the Supplements. (I don't have access to the Supplements as submitted, but I reviewed them in a pre-submission draft.)

We thank the referee for this critique. We regret that there was no access to the submitted supplements, as they were significantly beefed up compared to the pre-submission draft that the reviewer looked at. In particular, the table of abundance data used to carry out the mixing calculations and to determine the initial composition of the Rayleigh distillation via escape sequence is in the supplements and is now (as of this revision) explicitly referenced from the main text. In order to closely link the main text with the supplementary material, we have added text in lines 55, 58-59, 68, 79, 84-85, 101, and 177 with specific references to the supplementary material.

Most of my detailed review addresses noble gases, but first we should start with the general concept, as I think this will be more generally questioned. By assumption, the hybrid atmosphere fully mixes nebular hydrogen into the CO2 yet is stable enough against mixing that it doesn't dissipate back into the nebula. Should one picture an atmosphere that grades continuously from a CO2-rich composition at the surface to a nebula composition at the Hill sphere, or is the paper proposing a compositional discontinuity at the Hill sphere? What is lifting the CO2? It is not entirely clear that the general concept is self-consistent. I think a good way to address these general questions is to draw a cartoon that illustrates the overall scenario as it is imagined here. If the authors can't draw such a cartoon, I'd worry that the authors aren't telling a self-consistent story. It may be a good idea for the authors to explicitly state that their work describes an end-member hypothesis.

We thank the referee for pointing out the need for greater clarity. As to the compositional discontinuity, we now state this explicitly in the supplementary material explaining the capture via mixing model: "A fully-mixed hybrid atmosphere is distinct from the pure nebular atmosphere because it hosts a compositional boundary at the Hill radius between the hybrid mixture and the nebular-composition gas." As to the question of "What is lifting the CO2?" we now have a section in the Supplementary Information titled "Energetics, Mechanisms, and Extent of Mixing", in which we show that thermal convection associated with getting rid of the heat of accretion is more than sufficient to eliminate the initial chemical stratification. We do not agree with the referee's suggestion that a cartoon is needed here for two reasons. First, we are at the figure limit (4) and consider each of the current figures essential to the story we want to convey, of which the capture is only one part. Second, it is absolutely true that there are ambiguities regarding the capture scenario, for example, whether there is full mixing of the two components or only partial mixing. However, drawing a cartoon would not resolve this ambiguity. We agree with the referee that it would be beneficial to state that we are considering an end-member hypothesis, and therefore now state in the supplementary information that: "A fully-mixed state describes the maximum enhancement of the nebular captured gaseous inventory and is therefore a useful and easily calculable end-member [emphasis added here] state."

I note that the abstract fails to mention that this paper explains martian Ar fractionation as ancient (effectively primordial) and NOT a tracer of Martian atmospheric evolution during the geologic past. I think it is important to state very clearly (certainly in the Introduction and probably in the abstract) that this paper is presenting an alternative to the accepted story of Mars.

We agree that it is important to be explicit about how our scenario differs from other published scenarios about Martian atmospheric evolution. To this end, and given that we are at the word limit for the abstract, we end the abstract by stating: "These observations and calculations ... provide a framework for assessing the role of various mechanisms of gas loss over the entire history of the planet." Later, at the end of the introduction (Lines 48-52), we state: "As an example, the hybrid origin model implies that most Martian argon loss occurred primordially rather than during

later geologic epochs as commonly assumed. We show that a hybrid initial composition followed by an early episode of hydrodynamic escape is consistent with the observed heavy noble gas abundances (Ar/Kr) and is a viable initial condition for understanding Martian atmospheric history."

Detailed Review:

Lines 18-48. Good review of the paradox and a statement of the paper's hypothesis.

Line 50 "Results" is a misleading word to put here. The model has yet to be explained, and the observational constraints have yet to be quantified.

We agree that "Results" appearing after "Introduction" seems a bit abrupt. However, given the short format of the journal (3,000 words including abstract and captions), this is not an uncommon practice. Looking over the latest articles published in the journal confirms this. To alleviate the impression that the results are being presented prematurely, and given that we describe the model and results together, we rename this section "Model and Results". We cannot separate these into two sections given the length limitations of the format without sacrificing other essential portions of the presentation.

Lines 51-70. What are the opacity sources in the radiative-convective model? Nebular dust? Water vapor? Even if these are quantitively documented in the supplementary information, the basic ideas should be presented here with a pointer to the relevant equation in the supplement. How do these assumptions compare to, say, Hayashi et al 1979?

The opacity source adopted in the radiative-convective model is dust opacity, with a reference to the relevant supplementary equation now appearing in line 55 of the main text and a justification for dust-based opacity now appearing between supplementary equations S-4 and S-5. Hayashi et al. 1979 assumed a severely dust-depleted opacity without considering, e.g., ablation from planetesimals which later researchers incorporated (Mizuno and Wetherill, 1984). To make this feature of our model explicit, we now use the adjective "dusty" in line 55 to describe it.

Lines 51-70. Note that a radiative-convective model explicitly imposes mixing below the tropopause, but there is no surety of mixing above the tropopause. The detailed discussion of mixing can be left to the Supplement (include a pointer in the text to the relevant equations), but a concise summary of the argument needs to be included in the main text here.

We thank the referee for pointing out the necessity of making explicit references to specific discussion points in the supplementary materials regarding mixing. To address this deficiency, we now add the qualifying phrase on lines 78-79: "Mixing of the nebular atmosphere with an outgassed high molecular weight gas – for which there is sufficient energy (Eq. S-13) – sharply enhances the mass of the captured gas inventory." Due to severe length limitations we do not expound on the mixing discussion further here.

Lines 51-70. How do the baseline results (dotted lines in Fig 1) compare to previous calculations? Pepin 1991 extensively documents his calculations (for H, C, and noble gases), which makes Pepin's work the obvious published work to compare to.

Although we acknowledge the importance of Pepin (1991), there are also more recently published works that discuss nebular capture into the Martian atmosphere. For example, Erkaev et al. 2014 include nebular capture without mixing (what we call "pure" nebular capture) in their calculations, and they compare favorably with the dotted lines in Figure 1. This is now explicitly stated in the capture to this figure.

Lines 71-88. The atmosphere is treated as a uniform mix of CO2 and H2 from the surface to where it meets the nebula. The outer boundary is therefore a surface of discontinuity. This assumption needs to fully spelled out. One does not have to prove that it is true, nor even show that it is a good assumption. What is important is that the assumption be stated clearly. I recommend a cartoon that fully illustrates the ideas. It should not be hard for the authors to sketch out what the authors are thinking (certainly much easier than it would be for the reader to try to sketch out what the authors are thinking).

We thank the referee for pointing out the necessity of pointing out our assumptions. Although this point is a bit buried (between Equations S-8 and S-9), it does appear in the supplementary materials: "A fully-mixed hybrid atmosphere is distinct from the pure nebular atmosphere because it hosts a compositional boundary at the Hill radius between the hybrid mixture and the nebular-composition gas." As discussed elsewhere in our response, we have opted not to produce a cartoon and instead opt for clarifications via additional text where possible.

Line 77 One is referred here to Supplementary materials for an explanation of how these calculations are actually done. At minimum, the pointer to the Supplement should specify which equations in the Supplement are being solved.

We now list the equations in the Supplementary Information that are being solved. However, due to severe word limit pressure, do not expound further on the justifications for these equations in the main text.

Lines 91-102 - the model is described here as setting an upper bound on accreted H2, which I think seems correct.

Line 107 ff. The argument given here for neglecting He and Ne is very weak. It would be better to compute the model's predictions for He and Ne before discussing why one might (or should) choose to ignore them. At least this way one would have a quantitative appreciation of what is being ignored. Line 110. IMHO, the Kurokawa model is not credible because, among other things, it requires unrealistically exuberant volcanic activity today.

The authors acknowledge that some researchers, including the referee, doubt the widely discussed scenario that Martian argon and neon primarily record the process of sputtering acting over geologic time. Accordingly, following the referee's suggestion, we have included the captured Ne inventory in the hybrid mixture model (e.g., Figure 3). However, we continue to neglect helium because, to our knowledge, no researcher claims that the helium abundance on Mars is anything other than a balance between recent supply and recent loss. Given the change in focus in this part of the text – from neglecting He and Ne to neglecting only He – we now replace the Kurokawa reference to that of Krasnopolsky et al. 1994.

Line 111. I presume that EH and H chondrites are average compositions. Are these average values used for C and H2O, or just the noble gases? In any case the quantitative data as used in this paper

needs to be presented explicitly in this paper (i.e., do what Pepin 1991 did). I am going to request a table (see comment Line 124) with actual numbers in it and this base composition (the 45:55 recipe) would be a column in that table.

All the quantitative abundance data used in this work is now presented explicitly in Table S-1.

Line 121, line138, Figure 1. (i) The "<46-77%" quoted from the text must come from Figure 1, but how? Please explain. (ii) What are the 4 circles, diamonds, squares? Please explain in the caption. (iii) Presumably the circles, diamonds, squares refer to different mean molecular weights. Why is mean molecular weight a free parameter? Why are these 4 values chosen? Please explain in the text. (iv) Split text into separate paragraphs for H2 and CO2 (which map back to Fig 1) and for noble gases (which map to Fig 2). The reason I ask for this is to encourage the authors to provide fully developed explanations of what they have done in these figures.

We thank the referee for the detailed feedback. (i) Indeed, the 46-77% number comes from Figure 1. To clarify how it does so, in the caption to this figure, we now state: "The closeness of the solid line slopes to unity indicates the near constant proportion of nebular to chondritic gases in the calculated atmospheres." (A unity slope on this plot would indicate an exact proportion), (ii) Later in the caption to Figure 1, we state that "The four data points along each curve correspond to a range of mean molecular weights characterizing fully-mixed hybrid atmospheres." To explain why these values are chosen, we have added text (on lines 85-87): "To find solutions, we take the mean molecular weight of the mixture as a free parameter, varying it across a range (μ =6.6-19 amu) that allows sampling of the solution space." In the physical world, the free parameter is the mass of the outgassed inventory (M_{CO2}) but it is numerically easier to take the mean molecular weight as the free parameter and solve for the outgassed inventory rather than vice-versa. (iv) This is one of the few places in the review where we disagree with the referee. Figure 2 does not merely involve the noble gases. It matters that H in the primordial atmosphere has mixed heritage. It matters that small chondritic additions (via volcanism or impacts) can reset Martian C and N without altering, e.g., Ar. For this reason, we do not see Figure 1 as referring only to H_2/CO_2 and Figure 2 referring only to noble gases. To facilitate providing "fully developed explanations" of what we have done in these figures, we add to the caption in Figure 2: "Data used to make this plot is given in Table S-1."

Line 124 - Computed model inventories (results). Figure 2 for the noble gases is rather schematic. A Table here of quantitative inventories of noble gases that included Mars today would be highly desirable to put the different inventories into context. How much stuff is going to have to go away or be hidden? Units could be teramoles, or grams per gram (of planet - this is the unit Pepin used, I think). This paper could use more specifics. Let us make this table a demand.

Although Figure 2 may look schematic, it is actually based on real abundance data from a supplementary table, which is now explicitly references in the caption to the figure. The table being requested also contains abundance data that clarifies the magnitude of the required elemental fractionations. As discussed in the second response paragraph to reviewer #2, we do not use absolute abundances both because of the ~2 order-of-magnitude uncertainty in the initial mass of the primordial atmosphere (but not its composition!) and also because of the apparently large role that non-fractionating impact erosion has had on the Martian atmosphere, as most clearly illustrated by the Kr abundances discussed in the same response paragraph above.

b/t/w, the deduction that Xe is 50:50 seems likely to lead to an actual testable prediction. (A GOOD THING). In practice it takes very precise data to distinguish between mass fractionation

processes and plutonium fission products. That said, if you have too much chondritic Xe, you will be left with no room for any plutonium fission Xe.

We agree that having testable predictions is a good thing, and that the xenon interpretation is complicated by the (later than our scenario) mass fractionation episode as well as plutonium fission additions, to the extent that Mars outgassed interior gases after the magma ocean episode. In this same vein, we mention that our scenario predicts that Martian krypton is *mostly* but not *entirely* solar in character (Fig. 2). Reviewer #1 points out that Martian Kr is apparently slightly isotopically heavy relative to solar (a point that appears in e.g., Shorttle et al. 2024), which, if true, would be consistent with a small chondritic contribution to the primarily solar-like Kr, as predicted in Figure 2.

Line 144ff. Agreed.

Line 156ff. It appears from the topic sentence that modeling is going to be restricted to 36Ar/38Ar and Ar/Kr. These models (fractionation starting from solar Ar/Kr) should be compared to previous work by Sekiya et al 1980, 1981; Sasaki and Nakazawa 1989; Pepin 1991 (and probably Lammer 2xxx as well).

In the current manuscript, we are already at or slightly beyond the reference limit (<30), the figure limit (<4), and the word limit (<3,000). If there is one specific aspect of these works that requires comparison (e.g., mass loss rate), we are happy to provide that comparison in a short sentence. But length limitations of the format prevent a blanket comparison to all aspects of previous works.

I think it would be wise politically to allow for some Ar fractionation by sputtering (after all, the community seems to regard the sputtering model as a proven fact) and thus the Ar isotopic constraint becomes an upper bound on fractionation by hydrodynamic escape.

Indeed, we have recognized two observations that lead to a constructive conflict: 1) that most of the community seems to regard the sputtering model as a proven fact and the dominant sculptor of Martian neon and argon, and 2) that the hybrid mixture model we have proposed requires only *slightly* fractionating argon loss, which sputtering alone cannot provide. We remain open to the possibility that sputtering has played some role in the Martian atmosphere (lines 182-183) but the implication is clear: our model implies sputtering on Mars is not as important as currently believed.

Line 183. There are Japanese papers that have suggested this route to water (cf, Ikoma). It is more interesting to keep this option on the table for Mars than say for Earth.

We are aware of the Ikoma papers but given that: 1) those works consider water production via nebular capture for terrestrial planets generically rather than specifically for Mars, and 2) we are already at the 30 reference limit for the journal format, we do not add citations to those papers here.

Line 192 ff. I agree that P67/C-G-like comets can be ruled out for Mars. However, we strongly suspect that there was (and may still be) a large mass of much colder comets that contributed a nearly uniform Ar/Kr/Xe/C/N/S pollution of Jupiter's atmosphere (Owen et al 1999). These provide a plausible alternative to the nebula as a source of isotopically solar noble gases. Indeed, they are better than the nebula, because one does not have to explain away why one isn't seeing the predicted amounts of Ne.

We agree with the reviewer that the uniform enrichment of Ar/Kr/Xe on Jupiter points towards the delivery of solar-composition icy planetesimals. We agree that Jupiter would have no trouble absorbing these high velocity projectiles and incorporating them into its bottomless atmosphere. Invoking these planetesimals for Mars raises the question of why such high velocity planetesimals would contribute to the Martian atmosphere but comets like P67/C-G apparently did not contribute. It appears to the authors that any explanation seeking to sort comets into retentive and lossy is, at present, speculative. By contrast, we now know that Mars accreted fast enough to coexist with the solar nebula, and the scenario we have described – of capturing noble gases in solar proportions (via another process that Jupiter experienced!) and then losing the bulk of the light noble gas inventory in an episode of moderately vigorous hydrodynamic escape – is a testable scenario. We believe this contribution is a first step towards testing it.

A hybrid origin for the Martian atmosphere

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3273 words (abstract, acknowledgements & captions included)

30 references

4 Figures

Revised for publication in Geochemical Perspectives Letters

Keywords: Mars, primordial outgassing, atmosphere, nebular capture, hydrodynamic escape

1 Abstract

2 The Martian isotopic record displays a dichotomy in volatile compositions. Interior volatiles from the mantle record a chondritic heritage (e.g., H, N, Kr, Xe) whereas the atmospheric reservoir of 3 Kr and Xe – which do not currently experience escape – record heritage from a solar-like source. 4 Motivated by disparate inferences on the source of Martian atmospheric volatiles (outgassed 5 versus nebular captured), we consider hybrid-source accretionary atmospheres in which a high 6 molecular weight (e.g., CO₂-rich) outgassed component is mixed in with the low molecular weight 7 8 H₂-rich nebular atmosphere. We conduct calculations of nebular capture with and without a high 9 molecular weight outgassed component mixed into the atmosphere during the lifetime of the solar 10 nebula. Mixing an outgassed component into the nebular layer enhances the captured gas inventory 11 by $\approx 1-3$ orders of magnitude – depending on the outgassed inventory – relative to "pure" nebular capture. These observations and calculations suggest that the Martian atmosphere arose as a 12 13 subequal mixture of outgassed and nebular-derived components, and provide a framework for 14 assessing the role of various mechanisms of gas loss over the entire history of the planet.

15

16 1. Introduction

Mars has recently emerged as a natural laboratory for studying the acquisition and processing of volatile elements on the terrestrial planets. Because undifferentiated building blocks of terrestrial planets were likely volatile-bearing (SCHAEFER AND FEGLEY, 2017) and Martian accretion likely occurred in the presence of the volatile-rich solar nebula (DAUPHAS AND POURMAND, 2011), questions about different volatile sources and formation processes for the primordial Martian atmosphere can now be addressed (SAITO AND KURAMOTO, 2018; PÉRON AND MUKHOPADHYAY, 2022). High-precision isotopic measurements display a dichotomy in the sources of Martian volatiles. Volatiles dissolved in melts derived from the Martian mantle are observed to have an
isotopic composition akin to chondrites for hydrogen, nitrogen, krypton and xenon (USUI, 2019;
PÉRON AND MUKHOPADHYAY, 2022; DELIGNY *et al.*, 2023) whereas the isotopic composition of
krypton and xenon in the Martian atmosphere – which do not currently experience escape – record
a solar-like source composition (PEPIN, 1991; CONRAD *et al.*, 2016). These observations prompt
questions about the relationship between Martian interior and atmospheric volatiles.

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31 The volatile dichotomy between a chondrite-like mantle and a solar-like atmosphere has recently 32 been interpreted to mean that the Martian atmosphere cannot be the result of magma ocean outgassing and must be the result of gravitational nebular capture (PÉRON AND MUKHOPADHYAY, 33 34 2022). There is, however, empirical isotopic evidence that silicate Mars experienced outgassing during the lifetime of the short-lived and volatile radionuclide ¹²⁹I ($\tau_{1/2}$ =16 Myrs), resulting in the 35 36 observed ¹²⁹Xe-depletion in Martian interior reservoirs (MARTY AND MARTI, 2002). Early selective removal of volatile elements from silicate Mars - for example via outgassing from a molten state 37 38 (ELKINS-TANTON, 2008) – points towards the transport of chondritic volatiles into the primordial 39 atmosphere. Although this episode of primordial outgassing is empirically supported, it has vet to 40 be reconciled with the observed dichotomy between the Martian interior and atmospheric volatiles 41 (PÉRON AND MUKHOPADHYAY, 2022). Here, we consider hybrid accretionary atmospheres (SAITO 42 AND KURAMOTO, 2018) in which an outgassed high-molecular weight gas is mixed into the 43 distended low-molecular weight nebular atmosphere. We show that such mixing can reconcile 44 primordial outgassing of chondritic volatiles with nebular capture of solar-like gases into the 45 Martian atmosphere, that mixing before dissipation of the solar nebula strongly enhances the mass 46 of nebular captured gas, and that comparison of hybrid-source compositions with that of the 47 present-day atmosphere can yield new insights into the history of Martian atmospheric evolution.
48 As an example, the hybrid origin model implies that most Martian argon loss occurred primordially
49 rather than during later geologic epochs as commonly assumed. We show that a hybrid initial
50 composition followed by an early episode of hydrodynamic escape is consistent with the observed
51 heavy noble gas abundances (Ar/Kr) and is a viable initial condition for understanding Martian
52 atmospheric history.

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54 2. Model and Results

55 Enhancement of nebular capture via mixing. We calculate structures for dusty (Eq. S-4) captured Martian atmospheres present during accretion in hydrostatic equilibrium and thermal steady state 56 57 with the solar nebula. We consider atmospheres both with and without mixing of an outgassed high mean molecular weight layer (see Supplementary Information for discussion on the energetics 58 59 of mixing via thermal convection). Atmospheres without a high molecular weight component are 60 called "pure" and are presented as a reference. The atmospheres are convective at depth and 61 radiative at altitude, and are assumed to blend into the solar nebula at the Hill radius at \approx 320 Mars 62 radii. Because the mass (and heat capacity) of these atmospheres is relatively small, a heat source 63 other than secular cooling is needed to calculate quasi-static structures. An absolute lower limit on 64 the heat flow derives from long-lived radioactive decay and is equivalent to accretion rates $\approx 10^{-4}$ 65 Mars masses/Myr (ERKAEV et al., 2014). More likely heat flows relevant to the first few million 66 years of Martian history derive from ongoing planetesimal accretion, which also delivers high 67 molecular weight volatiles, and/or ²⁶Al decay. We consider heat flows at the base of the atmosphere equivalent to planetesimal accretion rates of 0.01-1 Mars masses/Myr (Eq S-1), 68 covering the range from energetic accretion consistent with large-scale melting (DAUPHAS AND 69

POURMAND, 2011) down to reduced heat flows unable to maintain a magma ocean (SAITO AND KURAMOTO, 2018) and more consistent with sweep-up of planetesimals during the waning stages of accretion. For heat flows equivalent to accretion rates of 0.01-1 Mars masses/Myr, the mass (M_H) of a "pure" nebular captured atmosphere is ≈ 0.2 -3.1x10¹⁸ kg and equivalent to ≈ 0.05 -0.8 bars of H₂ at the Mars surface (Fig. 1). Lower accretion rates produce cooler, denser atmospheres that are also more massive, a behaviour summarized with the maxim: "to cool is to accrete" (LEE AND CHIANG, 2015).

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78 Mixing of the nebular atmosphere with an outgassed high molecular weight gas – for which there is sufficient energy (Eq. S-13) – sharply enhances the mass of the captured gas inventory. To 79 80 illustrate the magnitude of this effect, we calculate the structure of hybrid-source atmospheres in 81 which the outgassed component consists of pure CO_2 (μ =44 amu with an inventory size characterized by M_{CO2}) with the nebular component (μ =2.4 amu with an inventory size 82 83 characterized by M_H) assumed to be fully-mixed into the outgassed layer, producing a homogeneous hybrid-source atmosphere (see equations S-1 to S-3 and S-7 to S-12 in the 84 Supplementary Information). To find solutions, we take the mean molecular weight of the mixture 85 as a free parameter, varying it across a range (μ =6.6-19 amu) that allows sampling of the solution 86 87 space. When a well-mixed hybrid atmosphere hydrostatically equilibrates with the solar nebula and achieves thermal steady state, the mass of the captured inventory (M_H) strongly depends on 88 89 the inventory of the high molecular weight gas (M_{CO2}) with which it is mixed (see Gas-assisted 90 capture, Fig. 1). For planetesimal accretion rates of 0.01-1 Mars masses/Myr and heavy gas inventories (M_{CO2}=3.9-390x10¹⁹ kg) equivalent to 10-1000 bars of CO₂ at the planetary surface 91 (ELKINS-TANTON, 2008), the captured nebular inventory (M_H) is in the range of 1.2-120x10¹⁹ kg, 92

93 equivalent to \approx 3-300 bars of H₂ at the surface (Fig. 1). The strong enhancement of nebular 94 gravitational capture via mixing an outgassed component is mainly due to an increase in mean 95 molecular weight, which increases the gravitational coupling between the atmosphere and planet 96 and decreases the atmospheric scale height, which – like cooling – causes contraction and an 97 increase in the hydrogen density of the lower atmosphere where most of the atmospheric mass 98 resides. This behaviour can be summarized with another maxim: "to mix is to accrete."

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100 The dependence of the nebular captured inventory (M_H) on the outgassed inventory (M_{CO2}) in 101 fully-mixed hybrid-source atmospheres (Fig. 1, and Eq S-11 and S-12) sets upper limits on the contribution of the nebular component to the Martian atmosphere. A measure of the relative 102 103 contribution of captured and outgassed inventories is the mean molecular weight of the mixture, 104 which only varies by a factor of ~three for the full range of conditions that we consider (Fig. 1). 105 Although the mass of the outgassed component is dominated by carbon species (e.g., CO₂), other 106 outgassed volatiles (H, N, and noble gases) were also present and the elemental abundances and isotopic composition of the hybrid mixture can be used – in comparison with observed abundances 107 108 - to further constrain the nebular contribution to Martian volatiles. Whereas the physics of nebular 109 capture into fully-mixed hybrid atmospheres yields upper limits on the nebular contribution, lower 110 limits can be derived from the cosmochemistry of chondritic-nebular gas mixtures, as we show in 111 the following section.

112

113 Chondritic-nebular gas mixtures. To describe cosmochemical consequences of mixing a nebular 114 component into an outgassed atmosphere, we calculate two-component mixtures including major 115 volatiles (H, C, N) and noble gases (Ne, Ar, Kr, Xe) with chondritic and nebular endmembers. We

neglect He because – like He in Earth's atmosphere – the lifetime of this noble gas with respect to 116 117 escape from the Martian atmosphere is thought to be extremely short relative to geological 118 timescales and its present-day abundancemay simply reflect a balance between recent supply and loss (KRASNOPOLSKY et al., 1994). For the chondritic endmember, we adopt the 55% H chondrite 119 45% EH chondrite model for Mars (SANLOUP et al., 1999). For the purposes of the mixing 120 calculations, we include all chondritic volatiles (interior and outgassed), although a substantial 121 fraction of chondritic H (or "water") is expected to remain sequestered in the interior (SIM et al., 122 123 2024). The assumption of complete outgassing may be more accurate in the case of C, N, and the 124 noble gases. With endmember compositions specified, the composition of the resulting mixture 125 can be described with one parameter, the relative contribution of the two components.

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127 The compositional characteristics of a nebular-chondritic mixture can be calculated for comparison 128 with the observed atmospheric abundances. For "Gas assisted capture" (Fig. 1), representing fully-129 mixed hybrid-sourced atmospheres in hydrostatic equilibrium with the solar nebula, the nebular contribution to the total volatile budget of Mars, counting atoms, is $\approx 46-77\%$, depending on the 130 131 accretion rate and outgassed volatile inventory. The total volatile budget is dominated by H and 132 He from the nebular component and H and C from the chondritic component. For these relative 133 proportions of the nebular component to the hybrid mixture, the neon (>99%), argon (>99%) and 134 krypton (>90%) inventories are dominated by the nebular component, whereas carbon (<1%) and 135 nitrogen (<2%) inventories experience negligible nebular additions and continue to be dominated 136 by the outgassed component (Fig. 2). Hydrogen and xenon are intermediate cases in which the 137 inventories in the resulting mixture are derived from comparable contributions from the two sources. In summary, nebular capture via complete mixing into a hybrid-source atmosphere 138

produces Martian Ne, Ar and Kr with solar heritage, C and N with chondritic heritage, and H andXe with mixed heritage.

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A hybrid primordial mixture is consistent with the observed isotopic composition of the Martian 142 atmosphere. Mass-selective loss has fractionated stable Ar isotopes (³⁶Ar from ³⁸Ar) but a solar-143 like source is a viable starting composition for atmospheric argon (ATREYA et al., 2013). Krypton 144 in the atmosphere is isotopically distinct from chondrites but nearly indistinguishable from 145 146 solar(PEPIN, 1991; CONRAD et al., 2016). Atmospheric xenon can be modelled either as mass-147 fractionated solar or mass-fractionated chondritic gas (SWINDLE, 2002). Although the physics of nebular capture into fully-mixed hybrid atmospheres sets upper limits on the nebular contribution 148 149 (<46-77%), partial mixing could yield a lower nebular contribution. The requirement that Martian 150 Kr be nearly indistinguishable from solar but clearly distinct from chondrites conservatively 151 constrains the nebular contribution to the total Martian volatile budget to >10%, counting atoms 152 (Fig. 2). Next, we consider the consequences of primordial hybrid mixtures for inferring Martian atmospheric history. 153

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Elemental abundances elucidate escape processes. Of all the major volatiles (H, C, N) and noble gases (Ne, Ar, Kr, Xe) we consider, krypton is most nearly isotopically unfractionated in Mars's atmosphere relative to its apparent source, the solar nebula. Accordingly, to gain insight into the nature of evolutionary processes, we consider elemental abundances normalized to krypton and relative to solar elemental abundances. Hybrid-source elemental abundances have some affinity to modern Mars (Fig. 3), with important differences. Relative to hybrid-source mixtures, the modern Martian atmosphere is elementally depleted in H, C, N, Ne, Ar, and Xe, each of which is also enriched in the heavy isotopes in the Martian atmosphere (BOGARD *et al.*, 2001). Such coupled
elemental and isotopic fractionation suggests the viability of a hybrid-source mixture as a precursor
to the modern Martian atmosphere, the two being linked via compositional evolutionary processes,
among which mass-selective losses to space looms large.

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We consider elemental (³⁶Ar/⁸⁴Kr) and stable isotopic (³⁶Ar/³⁸Ar) fractionation accompanying 167 argon loss. Argon is suitable for examining ancient processes because the inventory of atmospheric 168 ³⁶Ar is primordial meaning it cannot be accounted for by volcanic outgassing over time (JAKOSKY 169 170 AND TREIMAN, 2023). The non-radiogenic Ar/Kr ratio in the modern Martian atmosphere is lower than that of a hybrid mixture by a factor of ≈ 50 (Fig. 3) whereas the ${}^{36}\text{Ar}/{}^{38}\text{Ar}$ is only lower than 171 172 plausible sources by $\approx 25\%$ (ATREYA *et al.*, 2013). A loss process that strongly separates Ar from Kr but only weakly discriminates ³⁶Ar from ³⁸Ar is indicated. We consider an episode of extreme 173 174 ultraviolet (EUV) powered hydrodynamic escape in which an outflow of H₂ and CO₂ entrains trace 175 gases via frequent collisions (ZAHNLE et al., 1990). This loss process is thought to be the main way by which H₂-dominated atmospheres dissipate.. Entrainment involves all trace gases up to a 176 177 maximum molecular mass whose value depends on the strength of the escape flow (See Eq S-16 178 in the Supplementary Information for details). Model results reveal the existence of a 179 hydrodynamic outflow sufficiently strong to reproduce the chemical (Ar/Kr) and isotopic 180 (³⁶Ar/³⁸Ar) fractionation observed in the Martian atmosphere starting from a hybrid mixture while 181 remaining sufficiently weak to allow Kr to be retained and its essentially solar isotopic heritage to 182 be preserved (Fig. 4). Of course, mass-selective argon loss from Mars via other mechanisms (e.g., 183 solar wind sputtering) occurs and is ongoing (JAKOSKY et al., 2017). The hybrid mixture model provides a framework for assessing the relative importance of various mechanisms of atmospheric
loss over the entire history of the planet.

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187 **3. Discussion**

The origin of the Martian hydrosphere. A significant feature of the Martian volatile record is that 188 the surface hydrosphere inferred by geomorphology – like the atmospheric 36 Ar reservoir – cannot 189 be generated via volcanic outgassing over time (JAKOSKY AND TREIMAN, 2023). The hydrosphere 190 191 was apparently placed on the Martian surface early in planetary history. Independent evidence for the existence of a Martian surface hydrosphere in the first 100 Myrs comes from an excess of ¹²⁹Xe 192 in the atmosphere from the decay of water-soluble and short-lived ¹²⁹I (MUSSELWHITE et al., 1991). 193 194 The hybrid origin model for the Martian atmosphere suggests a new mechanism for the formation 195 of a hydrosphere. Although we have considered the nebular and chondritic gases to be chemically 196 inert, in reality, the H₂-dominated nebular gas can react with outgassed oxides (e.g., CO₂) to 197 produce new planetary water ($H_2+CO_2 \rightarrow H_2O+CO$). If the CO thus produced escapes as CO, there is a net gain of water at the Martian surface. Both the strong D/H enrichment of the early Martian 198 199 hydrosphere (GREENWOOD et al., 2008) and the anomalous oxygen recorded in ~4.43 billion year 200 old zircons (NEMCHIN et al., 2014) may result from isotopic exchange between a hydrosphere and 201 an escaping H₂-dominated atmosphere (PAHLEVAN et al., 2022; ZAHNLE AND KASTING, 2023).

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Cometary contribution to the inner Solar System. The low C/³⁶Ar and N/³⁶Ar of the Martian
 atmosphere relative to chondrites (Fig. 3) has previously been attributed to a possible contribution
 from comets, which are expected to be Ar-rich (MARTY *et al.*, 2016). However, a cometary origin
 introduces some problems even as it solves others. Results from the Rosetta mission allowed the

207 identification of cometary xenon as a likely source for terrestrial atmospheric xenon, in particular 208 the long-hypothesized component called U-Xe that is apparent in the atmosphere of Earth but not 209 Mars (MARTY et al., 2017). Assuming comet 67P/Churyumov-Gerasimenko - which Rosetta sampled - is representative of the cometary reservoir, the question arises as to why Martian 210 atmospheric xenon does not record any signature of a cometary component. The resolution to this 211 212 dilemma may be the relative retention of volatiles during impacts onto Earth and Mars. Cometary impacts onto terrestrial planets are high-velocity events sufficiently energetic to vaporize both icy 213 214 and silicate components, producing impact vapor plumes. The fate of impact plumes (retained or 215 lost) depends on the ratio of impact to escape velocity, such that cometary vapor plumes on Earth tend to be gravitationally retained whereas those on Mars tend to disperse from the weaker gravity 216 217 field present (ZAHNLE, 1993). More work is needed to better understand the role of various escape 218 processes in sculpting the volatile inventory of the terrestrial planets.

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220 Acknowledgements

K.P. acknowledges support from NASA's Solar System Workings Program (80NSSC21K1833).
The authors acknowledge discussions with Sujoy Mukhopadhyay and comments on an early draft
from Kevin Zahnle, Alessandro Morbidelli, and James Lyons, which helped to improve the
manuscript.



Figure 1. The captured gas inventory (M_H) as a function of the outgassed inventory (M_{CO2}) for fully-mixed hybrid atmospheres. Curves correspond to different accretion rates (in units of Mars masses per million years) and therefore to different planetary luminosities. "Pure nebular capture" (dotted lines) refer to nebular atmospheres with no outgassed component mixed in ($M_{CO2}=0$) for reference and is comparable to earlier calculations (ERKAEV *et al.*, 2014). Mixing with a high molecular weight component enhances nebular capture with the magnitude of the enhancement dependent on the mixed in heavy gas inventory. The closeness of the solid line slopes to unity indicates the near constant proportion of nebular to chondritic gases in the calculated atmospheres. The four data points along each curve correspond to a range of mean molecular weights characterizing fully-mixed hybrid atmospheres.



Figure 2. Mixtures of chondritic and solar-composition gases make specific predictions for the provenance of elements deriving from each component. The krypton isotopic composition of the Martian atmosphere – like solar and distinct from chondrites (PEPIN, 1991; CONRAD *et al.*, 2016) – suggests the nebular contribution to the primordial Martian atmosphere was >10% counting atoms. Upper limits on the contribution of the nebular component to Martian volatiles derive from the physics of nebular capture into fully mixed hybrid atmospheres and are <46-77% (see Fig. 1). Neon is not plotted for clarity but like Ar is derived almost entirely from the nebular component. Data used to make this plot is given in Table S-1.



Figure 3. Relative abundances of volatile elements in mixtures of chondritic and solar composition gases normalized to krypton and to solar composition. Percentages refer to the fraction of total atoms in the mixture contributed by the solar component. Mixtures with varying proportions of the nebular component can be compared to the composition of the present-day Martian atmosphere and differences between the two compositions can be used to infer the imprint of loss processes. The similarity of the cyan, blue, and magenta curves attests to a well-constrained chemical composition for the initial hybrid atmosphere.



Figure 4. Mass-dependent fractionation accompanying argon loss from the hybrid Mars atmosphere. The solid lines show the argon isotopic composition of an atmosphere after Rayleigh distillation driven by hydrodynamic escape producing 50x Ar-depletion, for various nebular to chondritic proportions (H₂/CO₂), starting with solar Ar (36 Ar/ 38 Ar=5.5). The efficiency factor is a proxy for the mass-loss rate. Preservation of solar-like isotopic Kr requires Kr non-participation in the mass-fractionating outflow and sets upper limits on the efficiency factor. The existence of solutions sufficiently vigorous to allow large (50x) reductions in Ar/Kr (see Fig. 3) without excessive Ar (and no Kr) isotopic fractionation indicates the viability of a hybrid mixture as the initial composition of the Martian atmosphere.

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