

A hybrid origin for the Martian atmosphere

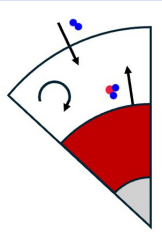
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Abstract

- Chondritic outgassing
- Nebular capture
- Fluid dynamical mixing of the components



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 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 enhances the nebular

captured gas inventory by ≈ 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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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 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 (Pepin, 1991; Conrad *et al.*, 2016). These observations prompt questions about the relationship between Martian interior and atmospheric volatiles.

The volatile dichotomy between a chondrite-like mantle and a solar-like atmosphere has recently been interpreted to mean that the Martian atmosphere cannot be the result of magma ocean outgassing and must be the result of nebular capture (Péron and Mukhopadhyay, 2022). There is, however, empirical evidence that silicate Mars experienced outgassing during the lifetime of the short-lived and volatile radionuclide

¹²⁹I ($\tau_{1/2} = 16$ Myr), resulting in the observed ¹²⁹Xe depletion in Martian interior reservoirs (Marty and Marty, 2002). Early selective removal of volatile elements from silicate Mars – for example *via* outgassing from a molten state (Elkins-Tanton, 2008) – points towards transport of chondritic volatiles into the primordial atmosphere. Although this episode of primordial outgassing is empirically supported, it has yet to be reconciled with the observed dichotomy between the Martian interior and atmospheric volatiles (Péron and Mukhopadhyay, 2022). Here, we consider hybrid accretionary atmospheres (Saito and Kuramoto, 2018) in which an outgassed high molecular weight gas is mixed into the distended low molecular weight nebular atmosphere. We show that such mixing can reconcile primordial outgassing of chondritic volatiles with nebular capture of solar-like gases into the Martian atmosphere, that mixing before dissipation of the solar nebula strongly enhances the mass of nebular captured gas, and that comparison of hybrid-source compositions with that of the present day atmosphere can yield new insights into the history of Martian atmospheric evolution. As an example, the hybrid origin model implies that most Martian argon loss occurred primordially rather than during subsequent geologic epochs as commonly assumed. We show that a hybrid initial composition is a viable initial condition for understanding Martian atmospheric history.

Model and Results

Enhancement of nebular capture via mixing. We calculate structures for dusty (Eq. S-4) captured Martian atmospheres present

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during accretion in hydrostatic equilibrium and thermal steady state 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 of the energetics of mixing *via* thermal convection). Atmospheres without a high molecular weight component are called “pure” and are presented as a reference. The atmospheres are convective at depth and radiative at altitude, and are assumed to blend into the solar nebula at the Hill radius at ≈ 320 Mars radii. Because the mass (and heat capacity) of these atmospheres is relatively small, a heat source other than secular cooling is needed to calculate quasi-static structures. An absolute lower limit on the heat flow derives from long-lived radioactive decay and is equivalent to accretion rates $\approx 10^{-4}$ Mars masses/Myr ([Erkaev et al., 2014](#)). 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 – and/or ^{26}Al 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), covering the range from energetic accretion consistent with large-scale melting ([Dauphas and 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 $\approx 0.2\text{--}3.1 \times 10^{18}$ kg and equivalent to $\approx 0.05\text{--}0.8$ bars of H_2 at the Mars surface (Fig. 1). Lower accretion rates produce cooler, denser atmospheres that are more massive, a behaviour summarised with the maxim: “to cool is to accrete” ([Lee and Chiang, 2015](#)).

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 illustrate the magnitude of this effect, we calculate the structure of hybrid-source atmospheres in which the outgassed component ($\mu_{\text{CO}_2} = 44$ amu with an inventory size characterised by M_{CO_2}) and the nebular component ($\mu_{\text{H}} = 2.4$ amu with an inventory size characterised by M_{H}) are assumed to be fully-mixed into a homogenous atmosphere (see equations S-1 to S-3 and S-7 to S-12 in the [Supplementary Information](#)). To find solutions, we take the mean molecular weight of the mixture as a free parameter, varying it across a range ($\mu = 6.6\text{--}19$ amu) that allows sampling of the solution 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 the inventory of the high molecular weight gas (M_{CO_2}) with which it is mixed (see Gas-assisted capture; Fig. 1). For planetesimal accretion rates of 0.01–1 Mars masses/Myr and heavy gas inventories ($M_{\text{CO}_2} = 3.9\text{--}390 \times 10^{19}$ kg) equivalent to 10–1000 bars of CO_2 at the planetary surface ([Elkins-Tanton, 2008](#)), the captured nebular inventory (M_{H}) is in the range of $1.2\text{--}120 \times 10^{19}$ kg, equivalent to $\approx 3\text{--}300$ bars of H_2 at the surface (Fig. 1). The strong enhancement of nebular capture *via* mixing an outgassed component is mainly due to an 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. This behaviour can be summarised with another maxim: “to mix is to accrete.”

The dependence of the nebular captured inventory (M_{H}) on the outgassed inventory (M_{CO_2}) in fully-mixed hybrid-source atmospheres (Fig. 1, and Eqs. S-11 and S-12) sets upper limits on the contribution of the nebular component to the Martian

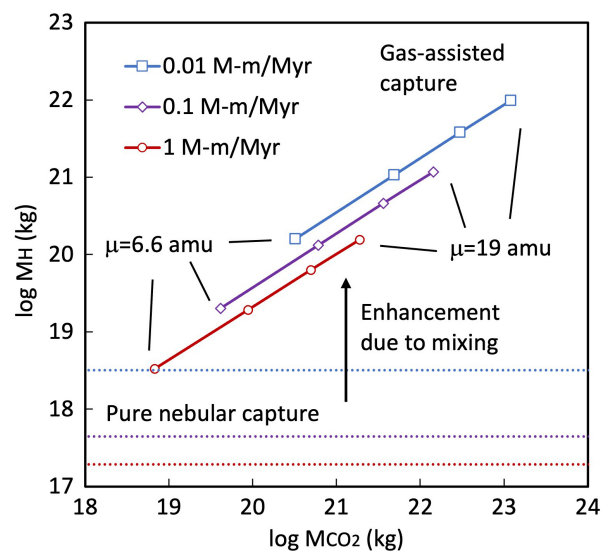


Figure 1 The captured gas inventory (M_{H}) as a function of the outgassed inventory (M_{CO_2}) for fully-mixed hybrid atmospheres. Curves correspond to different accretion rates in units of Mars masses per million years (M-m/Myr) and therefore to different planetary luminosities. “Pure nebular capture” (dotted lines) refers to nebular atmospheres with no outgassed component ($M_{\text{CO}_2} = 0$) shown for reference and 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 model atmospheres. The four data points along each curve correspond to a range of mean molecular weights characterising fully-mixed hybrid atmospheres.

atmosphere. A measure of the relative contribution of captured and outgassed inventories is the mean molecular weight of the mixture, which only varies by a factor of \sim three for the full range of conditions that we consider (Fig. 1). Although the mass of the outgassed component is dominated by carbon species (*e.g.*, CO_2), other 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 – to further constrain the nebular contribution to Martian volatiles. Whereas the physics of nebular capture into fully-mixed hybrid atmospheres yields upper limits on the nebular contribution, lower limits can be derived from the cosmochemistry of chondritic-nebular gas mixtures, as we show in the following section.

Chondritic-nebular gas mixtures. To describe cosmochemical consequences of mixing a nebular component into an outgassed atmosphere, we calculate two-component mixtures including major volatiles (H , C , N) and noble gases (Ne , Ar , Kr , Xe) with chondritic and nebular end members. We neglect He because – like He in Earth’s atmosphere – the lifetime of this noble gas with respect to escape from the Martian atmosphere is extremely short relative to geological time scales and its present day abundance simply reflects a balance between recent supply and loss ([Krasnopolsky et al., 1994](#)). For the chondritic end member, we adopt the 55 % H chondrite, 45 % EH chondrite model for Mars ([Sanloup et al., 1999](#)). For the purposes of the mixing calculations, we include all chondritic volatiles (interior and outgassed), although a substantial fraction of chondritic H (or “water”) is expected to remain sequestered in the interior ([Sim et al., 2024](#)). The assumption of complete outgassing may be more accurate for C , N , and the noble gases. With end

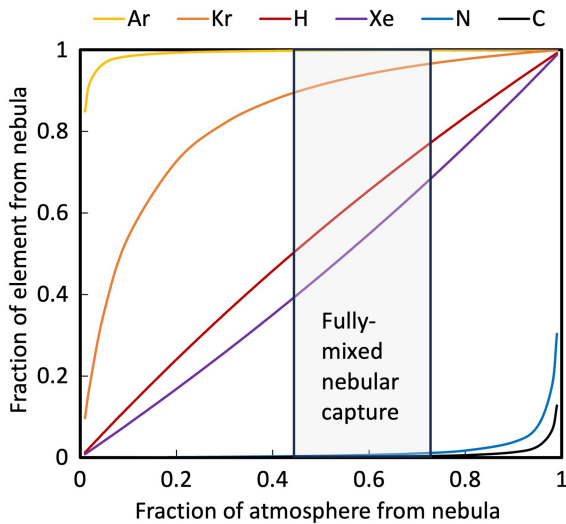


Figure 2 Mixtures of chondritic and solar composition gases make specific predictions for the provenance of elements deriving from each component. The krypton isotopic composition of the Martian atmosphere – like solar and distinct from chondrites (Pepin, 1991; Conrad et al., 2016) – suggests the nebular 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 in fully-mixed hybrid atmospheres. Data used to make this plot are given in Table S-1.

member compositions specified, the composition of the mixture can be described with one parameter, the relative contribution of the two components.

The compositional characteristics of a nebular-chondritic mixture can be calculated for comparison with the observed atmospheric abundances. For “Gas-assisted capture” (Fig. 1), representing fully-mixed hybrid-sourced atmospheres in hydrostatic equilibrium with the solar nebula, the nebular contribution to the total volatile budget of Mars, counting atoms, is $\approx 46\text{--}77\%$, depending on the accretion rate and outgassed volatile inventory. The total volatile budget is dominated by H and He from the nebular component and H and C from the chondritic component. For these relative proportions of the nebular component to the hybrid mixture, the neon (>99 %), argon (>99 %) and krypton (>90 %) inventories are dominated by the nebular component, whereas carbon (<1 %) and nitrogen (<2 %) inventories experience negligible nebular additions and continue to be dominated by the outgassed component (Fig. 2). Hydrogen and xenon are intermediate cases in which the inventories in the mixture are derived from comparable contributions from the two sources. In summary, nebular capture *via* complete mixing into a hybrid-source atmosphere produces Martian Ne, Ar and Kr with solar heritage, C and N with chondritic heritage, and H and Xe with mixed heritage.

A hybrid primordial mixture is consistent with the observed isotopic composition of the Martian atmosphere. Mass-selective loss has fractionated stable Ar isotopes (^{36}Ar from ^{38}Ar) but a solar-like source is a viable starting composition for atmospheric argon (Atreya et al., 2013). Krypton in the atmosphere is distinct from chondrites but nearly indistinguishable from solar (Pepin, 1991; Conrad et al., 2016). Atmospheric xenon can be modelled either as mass-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 (<46–77 %), partial mixing could yield a lower nebular contribution. The requirement that Martian Kr be nearly indistinguishable from solar but distinct from chondrites constrains the nebular contribution to the total Martian volatile budget to >10 %, counting atoms (Fig. 2). Next, we consider the consequences of primordial hybrid mixtures for inferring Martian atmospheric history.

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 normalised to krypton and relative to solar 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 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.

We consider elemental ($^{36}\text{Ar}/^{84}\text{Kr}$) and isotopic ($^{36}\text{Ar}/^{38}\text{Ar}$) fractionation accompanying argon loss. Argon is suitable for examining ancient processes because the inventory of atmospheric ^{36}Ar is primordial meaning it cannot be accounted for by volcanic outgassing over time (Jakosky 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 lower than plausible sources by $\approx 25\%$ (Atreya et al., 2013). A loss process that strongly separates Ar from Kr but weakly discriminates ^{36}Ar from ^{38}Ar is indicated. We consider an episode of extreme ultraviolet (EUV) powered hydrodynamic escape in which an outflow of H_2 and CO_2 entrains trace gases *via* frequent collisions (Zahnle et al.,

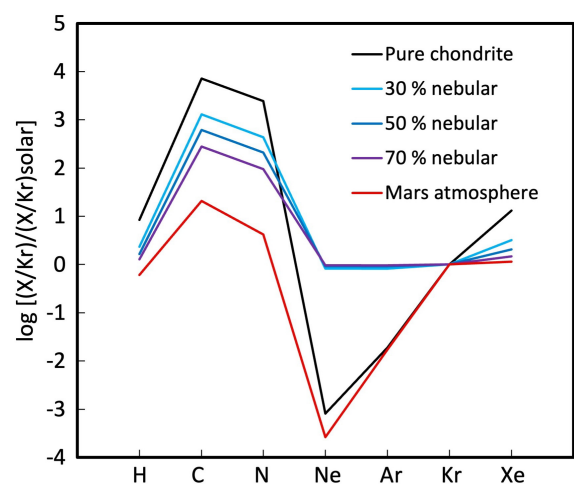


Figure 3 Relative abundances of volatile elements in mixtures of chondritic and solar composition gases normalised to krypton and to solar composition. Percentages refer to the fraction of total atoms in the mixture contributed by the solar component. Mixtures with varying proportions of the nebular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

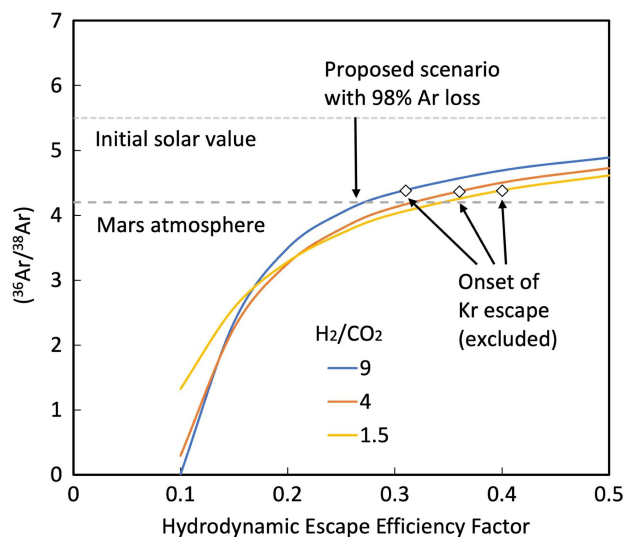


Figure 4 Mass-dependent fractionation accompanying argon loss from the hybrid Mars atmosphere. The solid lines show the isotopic composition of an atmosphere after Rayleigh distillation leading to 98 % Ar loss driven by hydrodynamic escape, for various nebular to chondritic proportions (H_2/CO_2), starting with solar Ar ($^{36}Ar/^{38}Ar = 5.5$). The efficiency factor is a proxy for mass loss rate. Preservation of solar-like isotopic Kr requires krypton non-participation in the mass fractionating outflow and sets upper limits on the efficiency factor. The existence of solutions sufficiently vigorous to produce 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.

1990). Entrainment involves all trace gases up to a maximum molecular mass whose value depends on the strength of the flow (See Eq. S-16 for details). Results reveal the existence of a hydrodynamic outflow sufficiently strong to reproduce the chemical (Ar/Kr) and isotopic ($^{36}Ar/^{38}Ar$) fractionation observed in the Martian atmosphere starting from a hybrid mixture while remaining sufficiently weak to allow Kr to be retained and its solar isotopic heritage to be preserved (Fig. 4). Of course, mass-selective argon loss from Mars *via* other mechanisms (e.g., 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.

Discussion

The origin of the Martian hydrosphere. A significant feature of the Martian volatile record is that the surface hydrosphere inferred by geomorphology – like the atmospheric ^{36}Ar reservoir – cannot be generated *via* volcanic outgassing over time (Jakosky and Treiman, 2023). The hydrosphere 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 Myr comes from an excess of ^{129}Xe in the atmosphere from the decay of water soluble and short-lived ^{129}I (Musselwhite *et al.*, 1991). The hybrid origin model suggests a new mechanism for the formation of a Martian hydrosphere, similar to the generic scenario recently explored in Kimura and Ikoma (2020). Although we have considered the nebular and chondritic gases to be chemically inert, the nebular gas can react with outgassed oxides to produce new 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 hydrosphere

(Greenwood *et al.*, 2008) and the anomalous oxygen recorded in ~4.43 billion year old zircons (Nemchin *et al.*, 2014) may result from isotopic exchange between a hydrosphere and an escaping H_2 -dominated atmosphere (Pahlevan *et al.*, 2022; Zahnle and Kasting, 2023).

Cometary contribution to the inner Solar System. The low $C/^{36}Ar$ and $N/^{36}Ar$ of the Martian atmosphere relative to chondrites (Fig. 3) has previously been attributed to a possible contribution from Ar-rich comets (Marty *et al.*, 2016). However, a cometary origin introduces some problems even as it solves others. Results from the Rosetta mission allowed the identification of cometary xenon as a likely source for terrestrial xenon, in particular the long hypothesised component called U-Xe that is apparent in the atmosphere of Earth but not 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 atmospheric xenon does not record the cometary signature. The resolution to this dilemma may be the retention of volatiles during impacts onto Earth and Mars. Cometary impacts onto terrestrial planets are high velocity events sufficiently energetic to vapourise both icy and silicate components, producing vapour plumes. The fate of vapour plumes (retained or lost) depends on the ratio of impact to escape velocity, such that cometary vapour plumes on Earth tend to be gravitationally retained whereas those on Mars tend to disperse (Zahnle, 1993). More work is needed to better understand the role of various escape processes in sculpting the volatile inventory of the terrestrial planets.

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Additional Information

Supplementary Information accompanies this letter at <https://www.geochemicalperspectivesletters.org/article2510>.



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