**Supplementary Information**

**A1. Stability of primordial atmospheres against thermally-driven hydrodynamic expansion**

The stability of a planetary atmosphere against thermally-driven hydrodynamic expansion (“blow-off”) is assessed by calculating the escape parameter:

l=GMm/rkBT (A1)

with G the gravitational constant, M the planetary mass, m the mean molecular weight of the atmospheric gas, kB Boltzmann’s constant, T the ambient atmospheric temperature, and r the planetocentric distance. Sufficiently high values of the escape parameter imply hydrodynamic stability against thermal expansion (and very slow atom-by-atom Jeans escape described by the kinetic theory of gases) whereas sufficiently low values imply wholesale hydrodynamic expansion and blow-off of the planetary atmosphere to space, requiring a fluid dynamical description. The critical value of the escape parameter marking hydrodynamic blow-off onset is 2-3 and 2.4-3.6 for monoatomic and diatomic gases, respectively (Volkov et al., 2011).

We seek to determine the conditions under which an impact-degassed H2-CO-rich atmosphere is stable with respect to such thermally-driven hydrodynamic blow-off. For this reason, we evaluate the escape parameter at the planetary surface for several H2-CO gas mixtures as a function of surface temperature. A pure H2 atmosphere (m=2) near the Martian surface (r=Rp) at magma ocean temperatures (Ts=1,500-3,000 K) would have an escape parameter (l=1-2) below the threshold for stability (l≈2-3) and would be subject to rapid dissipation via thermally-driven hydrodynamic flow. However, even modest additions of CO (e.g., CO:H2 of 1:3-1:2) significantly increase the mean molecular weight of the gas mixture (m=8.5-10.7), resulting in hydrodynamic *stability* of the atmosphere with respect to thermally-driven expansion (l=4.25-10.7). Carbon in the form of CH4 serves a similar role to CO (Saito and Kuramoto, 2018). In this context, it is noteworthy that the abundances of hydrogen and carbon in carbonaceous chondrites – the presumed source of Martian volatiles – are comparable by number (Kuramoto, 1997; Lodders and Fegley, 1997) and the magma solubility of carbon is substantially lower than that of water (Gaillard et al., 2022), promoting the partitioning of carbon into gas and facilitating its role as a stabilizer of the primordial Martian atmosphere. Such hydrodynamic stability with respect to thermally-powered expansion implies that these atmospheres can persist for geologically significant time periods (>Myr).

**A2. Primordial Martian hydrogen inventory**

In addition to the oxygen fugacity of the magma ocean, which determines the H2/H2O of the outgassed atmosphere, primordial atmosphere models require specification of the total hydrogen inventory. For this purpose, we use two approaches. First, both hydrogen (Hallis et al., 2012; Peslier et al., 2019; Usui et al., 2012) and nitrogen (Marti and Mathew, 2000; Mathew et al., 1998) isotopic abundances inferred for the Martian mantle are broadly chondritic. Indeed, proposed chondritic Martian building blocks include carbonaceous (Lodders and Fegley, 1997) or enstatite (Sanloup et al., 1999) chondrites, which are volatile-rich. Moreover, shock-degassing and impact release of volatiles into the primordial atmosphere is expected during accretion when proto-Mars exceeds one lunar mass (Lange and Ahrens, 1982; Tyburczy et al., 1986). Accordingly, we calculate primordial atmospheric inventories by assuming that volatile abundances of chondritic building blocks are quantitatively released into the Martian atmosphere.

Proposed chondrite mixtures for Mars range from 0.85-0.11-0.04 H-CI-CV (Lodders and Fegley, 1997) to 0.3-0.7 H-EH or 0.55-0.45 H-EH (Sanloup et al., 1999). These chondritic mixtures are consistent with the stable isotopic data (Warren, 2011). The initial inventory of the primordial atmosphere can therefore be constrained by volatile element abundances of chondritic building blocks (Schaefer and Fegley, 2017; Wasson and Kallemeyn, 1988). Restricting the discussion to hydrogen and assuming atmospheric retention during low-velocity collisions characterizing accretion (Melosh and Vickery, 1989), chondritic Martian models are endowed with >100 bars H2 (Table A1). Due to volatile loss from precursor planetesimals (Lichtenberg et al., 2019), partial retention during magma ocean solidification (Elkins-Tanton, 2008), and volatile dissolution into core-bound metals (Hirschmann, 2012), these abundances are considered upper limits to the hydrogen budget of the primordial atmosphere.

**Table A1 – Initial endowments for chondrite mixtures.** Abundances for carbonaceous (Wasson and Kallemeyn, 1988) and ordinary and enstatite (Schaefer and Fegley, 2017) chondrites adopted from literature values. Adopted values in weight percent hydrogen for CV, CI, H, and EH are 0.28, 2.0, 0.046 and 0.13, respectively. Chondritic endowments are calculated as simple mixtures.

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| --- | --- | --- | --- |
| Mixture | H (wt%) | pH2 (bars) | Reference |
| 0.85-0.11-0.04 H-CV-CI | 0.150 | 247 | (Lodders and Fegley, 1997) |
| 0.3-0.7 H-EH | 0.105 | 173 | (Sanloup et al., 1999) |
| 0.55-0.45 H-EH | 0.084 | 138 | (Sanloup et al., 1999) |

A second approach for constraining Martian initial H2 abundances is empirical. Models predict that most water dissolved in a magma ocean will outgas upon solidification (Elkins-Tanton, 2008). Indeed, recent inferences suggest that shorelines from a putative ocean in Borealis Basin predate Tharsis (Citron et al., 2018), consistent with a mainly *primordial* outgassing scenario producing a large early endowment that gradually depletes over time (Scheller et al., 2021). Hence, scaling the H2/H2O values from magma ocean outgassing (Fig. 2) by the size of the early Martian hydrosphere (≥500 m GEL) (Clifford and Parker, 2001) can constrain initial H2 abundances. In this way, initial H2 abundances can be expressed as a function of the oxygen fugacity of primordial outgassing and is equivalent to 8.8 and 28 bars of pure H2 for outgassing at log*f*O2=IW-1 and IW-2, respectively. To encompass a plausible range of hydrogen inventories using both approaches, we consider initial hydrogen abundances equivalent to 10-100 bars of pure H2. Constraining the initial H inventory is important because it determines the initial temperatures and duration of existence of the H2-based greenhouse (Figure A1).



**Fig. A1. Permitted climate scenarios.** The initial climate and the lifetime of the primordial greenhouse depend on the H2 inventory. Extreme ultraviolet (EUV) radiation from the young Sun can power escape on million year timescales. Calculating escape with the energy-limited approximation (Watson et al., 1981) results in a loss rate of ≈2.5 bars/Myrs. In such scenarios, earliest Mars experiences habitable conditions (<100°C) for several million years. The final deuterium-enrichment (fD/H) of the hydrosphere (≈2.17-2.51) only weakly depends on the H2 inventory for the full range of endowments here considered (pH2=10-100 bars) and overlaps with the enrichment observed in the Martian isotopic record (≈2-3x, cf. Fig. 1). Such a robust model outcome is evidence for the past presence of an H2 greenhouse on post-magma-ocean Mars.

Although Mars may accrete in the presence of the solar nebula (Dauphas and Pourmand, 2011) and attract nebular hydrogen (Ikoma and Genda, 2006), volatile-rich impactors would produce a high mean molecular weight degassed atmosphere underlying the low molecular weight nebular gas with stable stratification, such that escape of nebular and degassed components would be sequential (Saito and Kuramoto, 2018). Because there is no evidence of a nebular component in the Martian mantle hydrogen reservoir (Usui, 2019), and because we are interested in explaining the D/H *enrichment* due to hydrogen escape, we assume that any nebular hydrogen was lost before exposure of the magma ocean degassed atmosphere to the solar EUV photons and the associated losses. Atmospheres we consider in this work are therefore of purely degassed origin.

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