Supporting Online Material

1) Materials and Methods

Several models have been developed before to study the hydrodynamic escape from hydrogen-rich planetary atmospheres by solving the time-independent hydrodynamic equations directly (*S1-S3*). However, because of the existence of a singularity point in the time-independent hydrodynamic equations, transonic steady-state solutions are difficult to find. Our hydrodynamic model solves the 1D time-dependent non-viscous Euler equations with thermal conduction in spherical geometry:

$$
\begin{cases}
\dfrac{\partial(\rho r^2)}{\partial t} + \dfrac{\partial(\rho u r^2)}{\partial r} = 0, \\[2mm]
\dfrac{\partial(\rho u r^2)}{\partial t} + \dfrac{\partial(\rho u^2 r^2 + p r^2)}{\partial r} = -\rho GM + 2pr, \\[2mm]
\dfrac{\partial(E r^2)}{\partial t} + \dfrac{\partial[(E+p)u r^2]}{\partial r} = -\rho u GM + q r^2 + \dfrac{\partial}{\partial r}(\kappa r^2 \dfrac{\partial T}{\partial r}),
\end{cases}
$$

with $E = \rho(u^2/2 + e)$, $e = \dfrac{p}{\rho(\gamma-1)}$, $p = \rho RT$

Here ρ =gas density, r=distance from the planet center, u=gas flow velocity, p=pressure, G=universal gravitational constant, M=mass of the planet, E=total energy density (which is the sum of the kinetic energy density and the internal energy density of the gas flow), κ=thermal conductivity, T=temperature, γ=adiabatic constant, R=molar gas constant, q=volume heating rate. $\rho u r^2$ is a measure of the globally integrated escape rate and is a constant in space in the steady state.

The first order Lax-Friedrichs scheme is used to solve the hydrodynamic equations. The solution technique has been validated in an isothermal atmosphere and applied to the

atmospheres of extrasolar planets (*S4*). For the early Earth application, we assume that the dominant gas in the upper atmosphere is hydrogen and the only energy source to drive the hydrodynamic escape is the solar EUV radiation below 105 nm. The solar EUV spectrum is taken from (*S5*). The heating efficiency is fixed at 15%, the same value used by Watson et al. (*S1*).

The hydrodynamic escape model used in this paper is a simple model, meant to take a first step in exploring hydrogen rich atmospheres. The temperature is fixed to a constant 250 K at the lower boundary. A variation of solar EUV input will probably have an influence on the lower boundary temperature, and thus will have a more complicated impact on the hydrogen escape rate than we have considered. Intuitively a higher temperature will result in a stronger escape flux. Because the temperature, as well as the density at the lower boundary, is influenced by lower atmosphere dynamics and radiative transfer processes, other models working in the lower part of the atmosphere are required to accurately determine these parameters for the early Earth's atmosphere. It will be an important future study to include a detailed photochemical model solving the energy absorption, radiation, and net deposition. The hydrodynamic escape model contains only one component – hydrogen molecules. The expected escape rate can be further decreased by including other heavier gases into the model because of the downward drag force exerted on hydrogen by other gases. One might also include minor species, some of which may be radiatively active, although photochemical simulations to date do not suggest radiatively active species will be present. We expect that the conclusions presented here will not be changed dramatically by including the contributions of the

heavier gases or the radiatively active minor species. It is also important to consider the transition from the primordial atmosphere, whose composition is unknown, to the hydrogen dominated atmosphere discussed here.

2) Supporting online text

Hydrogen mixing ratio calculation

Because hydrogen is not the dominant gas at the homopause, the position of the lower boundary is located where the hydrogen number density becomes 10 times that of the rest of the air. Given a certain hydrogen density at the lower boundary, our escape model calculates the steady state hydrogen escape flux. The homopause is defined as the atmospheric level where the molecular diffusion coefficient starts to exceed the eddy diffusion coefficient. The eddy diffusion coefficient depends on the atmospheric density n ($\sim \sqrt{n}$). Therefore even though the altitude of the homopause would certainly change in the hydrogen rich or CO2 rich atmospheres due to changes in the average atmospheric molecular weight, the density level of the homopause would most likely stay close to its present value $\sim 10^{13}$ cm^{-3}. Assuming the homopause air density is the same as that of today $\sim 10^{13}$ cm^{-3}, the hydrogen density at the lower boundary can be related to the hydrogen mixing ratio at the homopause level by the following relationship:

$$n_0 = n_z \cdot \exp(z/H)$$

$$\chi = n_0 / 10^{13}$$

where χ is the hydrogen mixing ratio at the homopause level, n_0 is the hydrogen number density at the homopause level in units of cm^{-3}, H is the scale height of hydrogen

molecules, n_z is the hydrogen number density at the lower boundary, and z is the distance between the homopause and the lower boundary. We note that the position of the homopause in early Earth's atmosphere may be different from that of today, which is about 100 km. However, even a 50-km change of the homopause altitude results in less than 1% change of the distance between the lower boundary and the planet center. Such small changes do not change our simulation results substantially.

Photochemical model

The one-dimensional photochemical model includes 72 chemical species involved in 337 reactions and is fully described elsewhere (*S6*). The reaction list has been borrowed from models of methane photochemistry in the atmospheres of Titan (*S7, S8*) and Neptune (*S9*). The altitude grid extends from 0 to 100 km in 1-km increments. At each height the continuity equation was solved for each of the long-lived species, including transport by both eddy and molecular diffusion. The combined equations were cast in centered finite-difference form, and the resulting set of coupled ordinary differential equations was integrated to steady state using the reverse Euler method. At the top of the model we assumed that hydrogen is being lost at the escape rates from Fig 2.

It is important to note that the wavelength of solar UV flux driving the hydrogen hydrodynamic escape is below 105 nm and the UV driving photochemistry is at Ly-α and longer wavelengths. The UV that drives prebiotic photochemistry penetrates below the homopause because hydrogen (above and below the homopause) does not absorb it.

If CO_2 exceeds methane, atomic oxygen from CO_2 photolysis would shortcut polymerization. However, large hydrogen concentrations can effectively deplete atomic oxygen and allow haze formation even if $CH_4/CO_2 \ll 1$. This is the reason why the rate of the photochemical haze production is critically dependent on the H_2/CO_2 ratio.

Positions of bow shock and magnetopause

Interactions of the hydrogen hydrodynamic flow with the solar wind are not included in the model. The average position of the bow shock (the place where the solar wind is slowed and deflected) of the Earth today is at ~15 Earth radii near the subsolar region (*S10*), approximately the upper boundary in our model. The magnetopause (the location where the solar wind dynamic pressure is balanced by the magnetic pressure of the magnetosphere) is at 10.7 Earth radii near the subsolar region (*S11*). In the high solar EUV cases (x2.5, x5), the escape flows pass the transonic points near 10 Earth radii. For transonic flow, the upper boundary condition is not important because the flow can't "feel" what happens at the top. Even if the bow shock becomes substantially closer to the Earth due to strong solar activity, our model is still applicable on the night-side.

Exobase temperatures in previous studies

Several groups have previously tried to estimate the exobase temperature for the early Earth. Extremely high exobase temperatures ($>10^4$ K) have been obtained for hydrogen dominated atmospheres of terrestrial planets by considering the thermal balance of a stationary atmosphere model *(S12)*. Blow-off of the entire thermosphere is proposed to occur under this high temperature. However, the adiabatic cooling accompanying the

blow-off was not included in the thermal balance calculations. Lack of this cooling source may have caused the extremely high exobase temperature estimates. For hydrogen poor atmospheres the possible range of exobase temperature is found to be ~500 K for a low oxygen concentration case and ~1200 K for a high oxygen concentration case *(S13)*. Assuming Jeans escape as the dominant escape mechanism and hydrogen mixing ratio similar to that of today, the hydrogen escape rate is found to be about two orders smaller under the low exobase temperature ~500 K than that under high exobase temperature ~1000 K *(S14)*. Hunten *(S15)* discussed hydrogen escape rates under exobase temperatures in the range from 750 K to 2000 K. The escape rate is found to be small in the low exobase temperature case but the low exobase temperature was thought to be unlikely for a hydrogen-rich atmosphere based on previous calculations *(S12, S16)*, which had not accounted for the energy loss through hydrodynamic escape. It is important to note that the diffusion limited escape rate works if the goal is to calculate an upper limit on abiotic O_2 concentrations because it provides a lower limit on the atmospheric hydrogen concentration, which limits the concentration of oxygen. But to obtain a good estimate of hydrogen concentration in a hydrogen-rich early Earth's atmosphere, a self consistent model including the adiabatic cooling accompanying the hydrodynamic escape is needed.

Ocean as the place where life originated

The existence of a prebiotic organic soup in the Earth's ocean was proposed first in the 1920s *(S17)*. Recently it has been discovered that ionic solute concentrations that are much lower even than those of contemporary oceans may adversely affect two processes

relevant to the formation of membranes, which are required by many origin of life theories (*S18*). Other yet-to-be-discovered compartmentalization mechanisms in which proto-organisms can be sequestered from the environment may exist (*S19*). The exact environmental conditions that harbored the emergence of life on the early Earth are still unknown. Nevertheless, this finding has led to suggestion that, from the perspective of membrane biophysics, the most plausible planetary environment for the origin of life would have low ionic content concentrations (*S20*). However, to address fully the composition of early Earth's ocean or to speculate on its impact on the origin of life is beyond the scope of our manuscript.

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