

A Hydrogen-Rich Early Earth Atmosphere

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We show that the escape of hydrogen from the early Earth's atmosphere should occur at rates two orders of magnitude slower than previously thought. The balance between slow hydrogen escape and volcanic outgassing could have maintained a hydrogen mixing ratio more than 30%. The production of prebiotic organic compounds in such an atmosphere would have been more efficient than either exogenous delivery or synthesis in hydrothermal systems. The organic soup in the oceans and ponds on the early Earth would have been a more favorable place for the origin of life than previously thought.

It is generally believed that the existence of prebiotic organic compounds on the early Earth is a necessary step toward the origin of life. Biologically important molecules can be formed efficiently in a highly reducing atmosphere (CH₄ and/or NH₃ rich) (1, 2). They can also be produced efficiently in a weakly reducing atmosphere (3–5), where one important factor influencing the efficiency of production is the hydrogen to carbon ratio (6–8). However, our current understanding of the composition of early Earth's atmosphere suggests it was neither strongly reducing nor hydrogen rich. The concentrations of CH₄ and NH₃ are thought to have been low (9) and the hydrogen mixing ratio is believed to be of the order of 10⁻³ or less (10). Because it is difficult to produce organics in the atmosphere, two directions of research into the origin of life on Earth have become dominant: synthesis of organic compounds in hydrothermal systems and exogenous delivery of organic compounds to early Earth (11). Here we reexamine the theory of diffusion limited escape of hydrogen and show that hydrogen escape from early Earth's atmosphere is not as rapid as previously assumed. Hydrodynamic escape should be the dominant mechanism of escape, implying a hydrogen-rich early Earth atmosphere, in which organic molecules can be produced efficiently.

The assumption that the escape of hydrogen is limited by diffusion into the heterosphere from below is applicable only when the escape is efficient. For Jeans escape to be efficient, the exobase temperature must be high. This condition is satisfied in the current Earth's atmosphere, where exobase

temperatures exceed 1000K due to the efficient absorption of solar UV radiation by atomic oxygen. The prebiotic Earth's atmosphere was anoxic and probably contained substantial amounts of CO₂ (12), as on modern Venus or Mars. CO₂ absorbs UV, but unlike oxygen, it can effectively radiate energy back to space and keep the exobase temperatures low. The CO₂-rich Venusian and Martian exobases have temperatures of 275K and 350K respectively (13). In the anoxic early Earth's atmosphere with low exobase temperature (supporting online text), Jeans' escape of hydrogen would have been inhibited. For present day Earth and Mars, which have low hydrogen concentrations, the relatively low hydrogen escape rates due to nonthermal processes are comparable to the Jeans escape rate (14, 15). It is important to consider how the non-thermal escape rate might increase in an atmosphere with large hydrogen abundance. For a H₂O rich early Venusian atmosphere, the maximum limit of the nonthermal hydrogen escape rate (due to the saturation of ionization of hydrogen atoms, which occurs when the homopause hydrogen mixing ratio reaches 2×10^{-3}) is $\sim 10^{10} \text{ cm}^{-2} \text{ s}^{-1}$ (16). The maximum nonthermal escape rate on the early Earth should be similar to that on Venus (17). Given the low Jeans' and non-thermal escape rates, the total hydrogen escape rate would not have been in balance with the volcanic H₂ outgassing rate on early Earth (10) at the previously suggested hydrogen mixing ratio of 10⁻³. Instead, hydrogen would have been one of the major constituents in the ancient atmosphere.

H₂ can absorb EUV (like O₂ and CO₂) but cannot effectively radiate energy back to space. However, H₂ can escape due to its low molecular weight and thereby carry energy away to space in a hydrodynamic hydrogen escape flow. When hydrogen is the major gas in the heterosphere and the major absorber of EUV, the escape of hydrogen would not be diffusion-limited but would be controlled by the solar EUV flux available to drive the escape flow (energy-limited), which would produce an escape rate smaller than the diffusion-limited escape rate.

In this paper we apply a hydrodynamic escape model, recently developed to study transonic hydrogen hydrodynamic escape (18), to a hydrogen-rich early Earth's atmosphere. Because the solar EUV radiation level could have been much stronger during the Archean era than today (19), EUV radiation levels $\times 1$, $\times 2.5$, and $\times 5$ that of today are used in the simulations for sensitivity studies.

The velocity distributions in the high energy input cases ($\times 2.5$, $\times 5$) (Fig. 1A) level off and converge near the upper boundary of the model where the sound speed is exceeded (supersonic flow). Transonic points in the higher energy input cases ($\times 2.5$, $\times 5$) are near 10 Earth radii (supporting online text). Near the upper boundary of the model the flow velocity is comparable to the escape velocity from the planet. Escape velocity is exceeded by the combination of the flow velocity and the thermal velocity at an altitude below the transonic points. In the $\times 1$ EUV level case, the energy absorbed is not adequate to drive supersonic flow, but escape would still occur. Fig. 1B shows the temperature profiles in the corresponding cases. Note that although the peak temperatures are 700 to ~ 800 K in the high energy input cases, the temperatures at the exobases (marked by the crosses) are in the range of 500 to ~ 600 K due to the adiabatic cooling associated with the hydrodynamic escape.

Figure 2 illustrates our calculated escape rates for varying hydrogen homopause mixing ratios. The Jeans' escape rates computed for the exobases are more than one order of magnitude smaller than the corresponding hydrodynamic escape rates due to the low exobase temperatures. If the solar EUV radiation level was 2.5 times that of today and the volcanic hydrogen outgassing rate was 5 times that of today ($\sim 9.25 \times 10^{10}$ hydrogen molecules $\text{cm}^{-2} \text{s}^{-1}$), a hydrogen mixing ratio of more than 30% could have been maintained everywhere below the homopause by balancing the volcanic hydrogen outgassing with the hydrodynamic escape of hydrogen (Fig. 2). By increasing the solar EUV radiation level to 5 times that of today, the hydrogen mixing ratio could still have been maintained at $\sim 10\%$. These mixing ratios are two orders of magnitude greater than the 10^{-3} hydrogen concentration considering the diffusion-limited hydrogen escape rate. So a hydrogen-rich early Earth's atmosphere could be maintained even for the modest hydrogen outgassing rates appropriate if the oxidation state of the Earth's mantle 3.9 billion years ago were the same as it is today.

The hydrodynamic escape rate increases nearly linearly as the solar EUV radiation level increases (Fig. 3), which reflects the energy limited nature of the hydrodynamic escape. The slope depends on the hydrogen density at the homopause (20).

An early Earth's atmosphere with high hydrogen concentration has important consequences for the origin and evolution of life. Generally speaking, endogenous sources of

prebiotic organics, such as production by lightning or photochemistry, are dominant in a reducing early Earth's atmosphere while exogenous sources, such as delivery from space or production in hydrothermal systems, become major contributors in an atmosphere of an intermediate oxidation state (1). To provide more specific examples of the influence of high hydrogen concentration, we consider two organic molecule formation mechanisms in the following, realizing that these are not the only prebiotic organic molecule formation mechanisms that are affected by the high hydrogen concentration.

Both H_2 and CO_2 are uniformly mixed below the homopause (21, 22), where we have just shown that the hydrogen mixing ratio could have been greater than 30%. Most photochemistry of interest will occur well below the homopause. Since the CO_2 concentration is likely to be less than 30%, H_2/C in early Earth's atmosphere could have been greater than 1 throughout the chemically interesting part of the atmosphere. Formation of certain prebiotic organic compounds in an atmosphere of CO_2 or CO with electric discharge is almost as productive as that in an atmosphere of CH_4 when $\text{H}_2/\text{C} \geq 1$ (7, 8). The conservative estimate of amino acid production rate by electric discharge is 10^7 kg/yr when $\text{H}_2/\text{C} \geq 1$ (23). Although the early Earth's atmosphere might have been dominated by CO_2 immediately after the heavy bombardment period, as continents formed on early Earth, the atmospheric CO_2 concentration would decline due to weathering and the H_2/C ratio would become suitable for efficient formation of prebiotic organic compounds through electric discharge. Formation of prebiotic organic compounds by electric discharge at this conservative rate in a hydrogen-rich early Earth's atmosphere would have created an ocean with steady state amino acid concentration $\sim 10^{-6}$ moles/L (24), orders of magnitude greater than the amino acid concentration estimated for a hydrogen-poor early Earth's atmosphere (25). This amino acid concentration is highly uncertain since neither the production rate nor the destruction rate is well known. In addition, organic films may have formed at the ocean surface, concentrating organic compounds further than in the bulk sea water (26).

Because the magnitude of energy deposition from electric discharge in the ancient atmosphere is poorly understood, it is difficult to predict the exact production rate of organic materials from these sources. Alternatively, organics can be formed through photolysis of methane by Ly- α photons with subsequent polymerization. The rate of photochemical haze production is critically dependent on the CH_4/CO_2 ratio (27). A similar dependence on the CH_4/CO_2 ratio has been found for HCN formation in an atmosphere with N_2 , CO_2 , and CH_4 (5). We used a one-dimensional photochemical model to study the organic production rate in a hydrogen-rich early Earth's atmosphere (supporting online text). Fig. 4 shows that

the production rate of hydrocarbons is enhanced by approximately 10^3 times (from $< 10^7$ kg/yr to 10^{10} kg/yr) when the hydrogen concentration in the early Earth's atmosphere changes from 0.1% to 30%, which makes the atmospheric production rate of organics through UV photolysis orders of magnitude greater than either the synthesis of organic compounds in hydrothermal systems or the exogenous delivery of organic compounds to early Earth (28).

Based on our new model of hydrodynamic hydrogen escape, we conclude that diffusion-limited escape theory does not apply to a hydrogen-rich early Earth atmosphere. Rather, the escape of hydrogen was energy limited. Hydrogen mixing ratios greater than 30% could have been maintained in the atmosphere of prebiotic Earth without either invoking huge volcanic hydrogen outgassing rates or assuming a reduced mantle. The efficient production of organics in a hydrogen-rich early Earth's atmosphere would have led to an organic soup in the oceans and ponds on the early Earth. The world ocean could have been the birthplace of life (supporting online text).

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9. Both CH_4 and NH_3 in the atmosphere of the early Earth would have been subject to rapid loss driven by solar UV radiation. It is unlikely that the volcanic outgassing rate of CH_4 or NH_3 could have been adequate to maintain high concentrations of these gases.
10. The hydrogen concentration is determined by the balance between the volcanic outgassing rate of hydrogen and the escape of hydrogen to space. The modern volcanic hydrogen outgassing rate is $\sim 1.8 \times 10^{10}$ hydrogen molecules $\text{cm}^{-2} \text{s}^{-1}$ (29). Due to higher heat flow in the past, the overall outgassing rate of gases, and hydrogen in particular, might be ~ 5 times greater on the ancient Earth (30). In the present Earth's atmosphere, oxygen is dominant at the exobase level (defined as the boundary beyond which rapidly moving molecules may escape without collision). The current exospheric temperature is high (1000 to $\sim 2500\text{K}$) because of the efficient absorption of solar UV radiation by oxygen. If the exospheric temperature on the early Earth were as high as it is today, Jeans' escape of hydrogen from the atmosphere would have been efficient and the diffusion of hydrogen through the background gases to the homopause level would have been the limiting process. The rate of diffusion limited escape can be expressed as $F(\text{H}_2) = 2.5 \times 10^{13} f_{\text{total}}$ molecules $\text{cm}^{-2} \text{s}^{-1}$, with f_{total} the total mixing ratio of hydrogen (in all chemical forms) at the homopause (31). By balancing the diffusion limited escape rate of hydrogen with the hydrogen outgassing rate, the hydrogen mixing ratio up to the homopause in the early Earth atmosphere should be of the order of 10^{-3} or below (21, 31), unless the oxidation state of the Earth's mantle was more reduced than its current oxidation state. But the Earth's mantle has been suggested to be in a similar oxidation state as that of today for the past 3.96 Ga (32). The common consensus among planetary scientists for the past 30 years has been that early Earth's atmosphere had low hydrogen concentration.
11. However, experiments to date generate only methane or formate in realistic hydrothermal-like systems (33). The exogenous flux of organic materials at about 4 Ga, primarily interplanetary dust particles, may be less than 150 times present (34), although the interpretations of the Akilia rocks are debatable (35).
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17. Nonthermal escape from a hydrogen-rich early Earth has not been studied in detail. Although a similar upper limit of nonthermal hydrogen escape rate should apply to early Earth, it is important to note that nonthermal hydrogen escape processes may also be rather different for Earth than for Venus because of the presence of a strong magnetic field on Earth. It would be an important future work to include these processes in escape models to make more accurate estimates.
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20. Assuming that the linear relation between escape flux and EUV still holds for even higher solar EUV input, the hydrogen escape flux would be about $7.5 \times 10^{12} \text{cm}^{-2} \cdot \text{s}^{-1}$ for a solar EUV level 100 times

that of today if the homopause hydrogen density is kept at $\sim 5 \times 10^{12} \text{ cm}^{-3}$. This escape rate is still slower than the diffusion limited escape rate ($> 1 \times 10^{13} \text{ cm}^{-2} \cdot \text{s}^{-1}$) for the same homopause hydrogen density. Hence the diffusive flux does not become limiting except for extreme EUV input.

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22. H_2 is not a chemically reactive gas. So in the steady-state hydrogen has virtually constant mixing ratio all the way from the surface to the homopause as does CO_2 (21). Therefore the homopause mixing ratio of hydrogen is representative of the whole homosphere.
23. The amino acid production rate is found to be $\sim 0.4 \text{ nmol} / \text{cm}^2 / \text{yr}$ (8) in electric discharge experiments when $\text{H}_2/\text{CO}_2 = 4$, equivalent to $2 \times 10^8 \text{ kg} / \text{yr}$ assuming a mean molecular weight of 100. This estimate is based on an annual electric discharge rate $\sim 2 \times 10^{19} \text{ J} / \text{yr}$, which is ~ 20 times greater than the contemporary electric discharge rate, $\sim 1 \times 10^{18} \text{ J} / \text{yr}$ (36). If the electric discharge rate on early Earth is the same as that of today, the rate of amino acid production by electric discharge would be $1 \times 10^7 \text{ kg} / \text{yr}$ when $\text{H}_2/\text{CO}_2 = 4$. Extrapolating the contemporary data back to early Earth faces large uncertainty. So here the conservative estimate ($1 \times 10^7 \text{ kg} / \text{yr}$) of the amino acid production rate by electric discharge is taken.
24. Assuming the ocean volume is $1.4 \times 10^{21} \text{ l}$ and that there is no loss of organics within the ocean, the amino acid concentration in the ocean can reach $7 \times 10^{-8} \text{ kg} / \text{l}$ (equivalent to $7 \times 10^{-7} \text{ mole} / \text{l}$ assuming a mean molecular weight of 100) in 10 million years, which is the timescale for the entire ocean to circulate through submarine vents at 300°C potentially destroying the organics (25).
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40. We thank two anonymous reviewers and J. F. Kasting for valuable comments. This study was supported by the NASA Institute of Astrobiology.

Supporting Online Material

www.sciencemag.org/cgi/content/full/1106983/DC1

Materials and Methods

SOM Text

References

1 November 2004; accepted 24 March 2005

Published online 7 April 2005; 10.1126/science.1106983

Include this information when citing this paper.

Fig. 1. (A) Flow velocity profiles in hydrodynamic escape of hydrogen under solar EUV levels $\times 1$, $\times 2.5$ and $\times 5$ that of today. r_0 is the distance between the lower boundary and the center of the Earth. The homopause hydrogen density is $5 \times 10^{12} \text{ cm}^{-3}$, corresponding to a mixing ratio of 50%. The dashed curve represents the escape velocity from the Earth. The transonic point is marked approximately by a circle. The dash-dotted curves show the difference between the escape velocity and the thermal velocity. The exobases are marked by the crosses. **(B)** Temperature profiles in the corresponding cases. Although the peak temperatures is in the

range of 700 to ~800K, the temperature at the exobases (marked by the crosses) is low (500 to ~600K).

Fig. 2. Calculated hydrogen escape rate from early Earth's atmosphere as a function of homopause hydrogen mixing ratio. The homopause air composition is assumed to be the same as that of today except for the higher hydrogen concentration and lack of oxygen. The diffusion limited escape rates, previously assumed to apply, are one or two orders of magnitude greater than the hydrodynamic escape rates because of over-estimated exobase temperature. The dotted curve shows the Jeans' escape rate as a function of homopause hydrogen mixing ratio under the $\times 2.5$ energy input level for the exobase temperatures that are likely to have been present for early Earth. The lower horizontal line represents the volcanic outgassing rate of hydrogen from the interior of the Earth today ($\sim 1.8 \times 10^{10}$ hydrogen molecules $\text{cm}^{-2} \text{s}^{-1}$) (29). The upper horizontal line is the estimated outgassing rate of hydrogen from the interior of early Earth (~ 5 times greater than the outgassing rate today) (30).

Fig. 3. The hydrogen escape rate increases nearly linearly as the solar EUV level increases. The slope is regulated by the homopause hydrogen density n_0 .

Fig. 4. Hydrocarbon production rate increases rapidly as the hydrogen concentration increases, and exceeds the delivery of organics by interplanetary dust particles (IDP) for H_2 mixing ratios above 10%.







