season in the evergreen forests of tropical South America, Africa, and Indonesia are needed to conclude which source type is responsible for the observed discrepancy and to what extent this discrepancy is caused by an underestimated or hitherto unknown methane source. In addition, investigations of satellite data for longer time periods are necessary to estimate the annual methane excess and to constrain the source attribution.

An additional methane source of 30 Tg in 4 months is large but can be accommodated by the uncertainty in the global budget, which is estimated to be 50 to 100 Tg year^{-1} (1). Further, surface observations (24) are not in disagreement with a large additional tropical source. Methane emitted in the tropics is generally rapidly uplifted by convection, so that the surface stations, which are located in remote ocean sites, are sensitive to these emissions only to a limited extent. Inverse modeling studies based on ground-based measurements (25, 26) have also indicated higher tropical emissions than those estimated from bottom-up inventories. However, this evidence has been rather indirect and uncertain. The present satellite measurements over the tropical land masses are sensitive to the entire atmospheric column, thus directly reflecting enhancement patterns.

Global measurement from space has proven feasible for detection of CH_4 emissions. The satellite's ability to sense sources globally is unique and opens a new window for the analysis of the biogeochemical cycle of methane and anthropogenic impacts. With SCIAMACHY hopefully in operation for several years to come, we should be able to examine the temporal and spatial variations of CH_4 over longer time periods. The integration of these measurements with atmospheric models and precise ground-based observations should greatly reduce uncertainties in the methane source strength, helping to draw a consistent picture of the global methane budget. This will be a high priority for climate research.

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A Hydrogen-Rich Early Earth Atmosphere

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We show that the escape of hydrogen from early Earth's atmosphere likely occurred at rates slower by two orders of magnitude than previously thought. The balance between slow hydrogen escape and volcanic outgassing could have maintained a hydrogen mixing ratio of 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 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 early Earth was a necessary step toward the origin of life. Biologically important molecules can be formed efficiently in a highly reducing atmosphere (CH_4- and/or NH_3-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 ratio of hydrogen to carbon (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 CH_4 and NH_3 are thought to have been low (9), and the hydrogen mixing ratio is believed to be of the order of 10^{-3} or smaller (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 was 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 could be produced efficiently.

The assumption that the escape of hydrogen is limited by diffusion into the hetero-

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sphere 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 1000 K as a result of the efficient absorption of solar ultraviolet (UV) radiation by atomic oxygen. The prebiotic Earth's atmosphere was anoxic and probably contained substantial amounts of CO_2 (12), similar to modern Venus or Mars. CO_2 absorbs UV, but unlike oxygen, it can effectively radiate energy back to space and keep the exobase temperatures low. The CO_2-rich venusian and martian exobases have temperatures of 275 K and 350 K, respectively (13). In the anoxic early Earth's atmosphere with low exobase temperature (14), Jeans escape of hydrogen would have been inhibited. For present-day Earth and Mars atmospheres, which have low hydrogen concentrations, the relatively low hydrogen escape rates caused by nonthermal processes are comparable to the Jeans escape rate (15, 16). It is important to consider how the nonthermal escape rate might increase in an atmosphere with large hydrogen abundance. For an H_2O-rich early venusian atmosphere, the maximum limit of the nonthermal hydrogen escape rate (caused by the saturation of ionization of hydrogen atoms, which occurs when the homopause hydrogen mixing ratio reaches 2×10^{-3}) is $\sim 10^{10}$ cm^{-2} s^{-1} (17). The maximum nonthermal escape rate on early Earth should be similar to that on Venus (18). Given the low Jeans and nonthermal escape rates, the total hydrogen escape rate would not have been in balance with the volcanic H_2 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.

H_2 can absorb extreme ultraviolet (EUV), as can O_2 and CO_2, but cannot effectively radiate energy back to space. However, H_2 can escape because of 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 report, we describe the application of a hydrodynamic escape model, which was recently developed to study transonic hydrogen hydrodynamic escape (14), 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 were used in the simulations for sensitivity studies.

The velocity distributions in the high-energy input cases ($\times 2.5$ and $\times 5$) (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 ($\times 2.5$ and $\times 5$) are near 10 Earth radii (14). Near the upper boundary of the model, the flow velocity is com-parable 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 still occurred. Figure 1B shows the temperature profiles in the correspond-
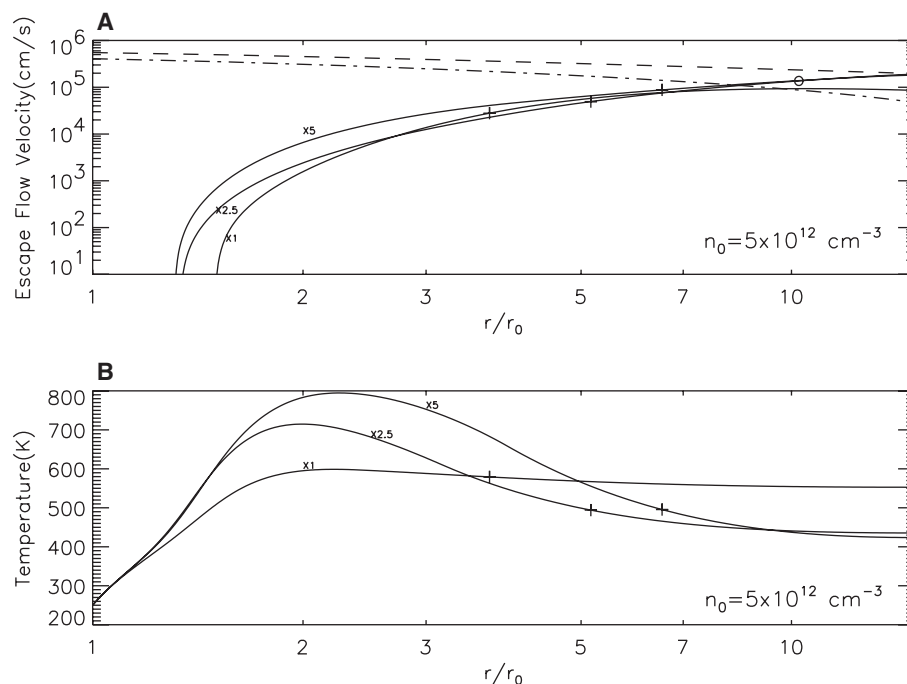

Fig. 1. (A) Flow velocity profiles in hydrodynamic escape of hydrogen under solar EUV levels $\times 1$, $\times 2.5$, and $\times 5$ that of today. r_0 is the distance between the lower boundary and the center of Earth. The homopause hydrogen density is 5×10^{12} cm^{-3}, corresponding to a mixing ratio of 50%. The dashed curve represents the escape velocity from Earth. The transonic point is marked approximately by a circle. The dash-dotted curve shows the difference between the escape velocity and the thermal velocity. The exobases are marked by crosses. (B) Temperature profiles in the corresponding cases. Although the peak temperatures are in the range of 700 to 800 K, the temperature at the exobases (marked by crosses) is low (500 to 600 K).

Fig. 2. Calculated hydrogen escape rate from early Earth's atmosphere as a function of the 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 overestimated 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 Earth today ($\sim 1.8 \times 10^{10}$ hydrogen molecules cm^{-2} s^{-1}) (29). The upper horizontal line is the estimated outgassing rate of hydrogen from the interior of early Earth (~ 5 times the outgassing rate today) (30).
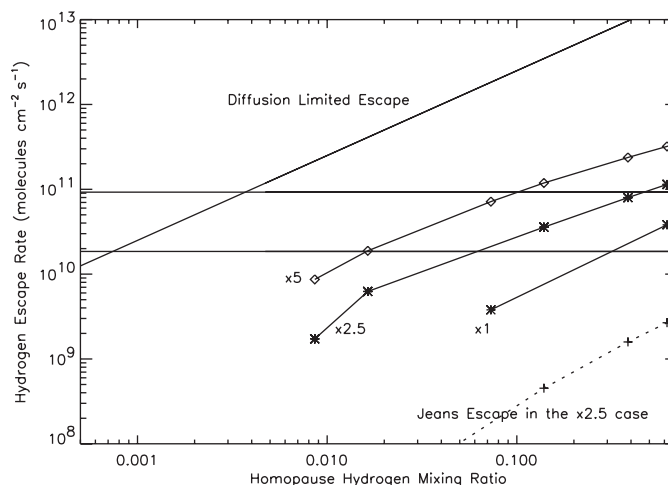
ing cases. Although the peak temperatures are 700 to 800 K in the high-energy input cases, the temperatures at the exobases (marked by crosses) are in the range of 500 to 600 K because of adiabatic cooling associated with the hydrodynamic escape.

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 because of 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 cm^{-2} 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. A hydrogen-rich early Earth's atmosphere could be maintained even for the modest hydrogen outgassing rates appropriate if the oxidation state of 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. Endogenous sources of prebiotic organics, such as production by lightning or photochemistry, are dominant in a reducing early Earth's atmosphere, whereas 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, 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 shown that the hydrogen mixing ratio could have been greater than 30%. Most photochemistry of interest occurs well below the homopause. Because the CO_2 concentration is likely to be less than 30%, H_2/C ratios in early Earth's atmosphere could have been greater than 1 throughout the chemically interesting part of the atmosphere. The formation of certain prebiotic organic compounds in an atmosphere of CO_2 or CO by electric discharge is almost as productive as that in an atmosphere of CH_4, when $H_2/C \geq 1$ (7, 8). The conservative estimate of amino acid production rate by electric discharge is 10^7 kg/year when $H_2/C \geq 1$ (23). Although 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 because of 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 a steady-state amino acid concentration $\sim 10^{-6}$ mol/liter (24), which is 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 because neither the production rate nor the destruction rate is well known. In addition, organic films may have formed at the ocean surface, leading to higher concentrations of organic compounds 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 Lyman-α (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 hydrogen cyanide (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 (14). Figure 4 shows that the production rate of hydrocarbons is enhanced by about three orders of magnitude (from $<10^7$ kg/year to 10^{10} kg/year) when the hydrogen concentration in early Earth's atmosphere changes from 10^{-3} to 30%. Hence, the atmospheric production rate of organics through UV photolysis would have been orders of magnitude greater than the rate of either the synthesis of organic compounds in hydrothermal systems or the exogenous delivery of organic compounds to early Earth (28).

On the basis of 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 invok-

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.
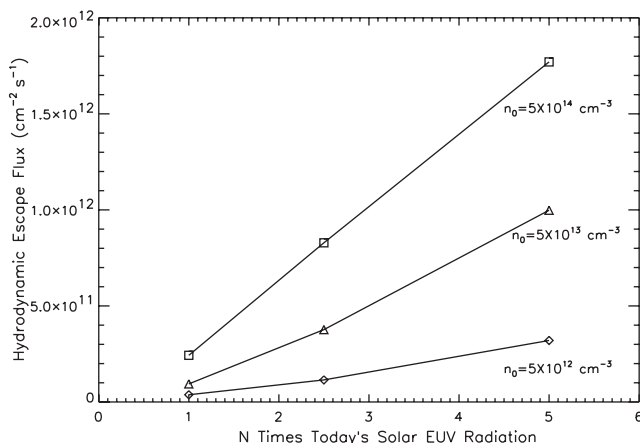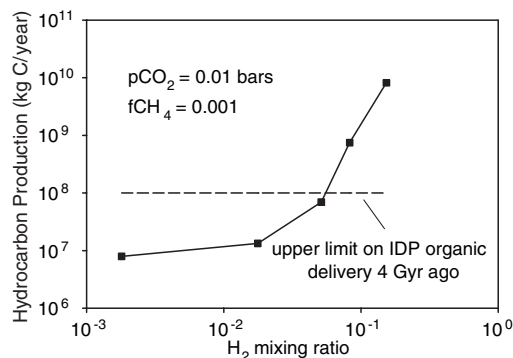
Fig. 4. Hydrocarbon production rate increases rapidly as the hydrogen concentration increases, and exceeds the delivery of organics by interplanetary dust particles (IDPs) for H_2 mixing ratios above 10%. pCO_2 is the partial pressure of CO_2 and fCH_4 is the mixing ratio of CH_4.

ing 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 (14).

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9. Both CH_4 and NH_3 in the atmosphere of 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 cm^{-2} s^{-1} (29). Because of higher heat flow in the past, the overall outgassing rate of gases, and hydrogen in particular, might have been ~ 5 times greater on 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 2500 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 $F(H_2) = 2.5 \times 10^{13} f_{total}$ molecules cm^{-2} s^{-1}, with f_{total} defined as 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 early Earth's atmosphere should be of the order of 10^{-3} or below (21, 31), unless the oxidation state of Earth's mantle was more reduced than its current oxidation state. But Earth's mantle has been suggested to be in a similar oxidation state to that of today for the past 3.96 billion years (32). The common consensus among planetary scientists for the past 30 years has been that early Earth's atmosphere had a 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 billion years ago (Ga), primarily interplanetary dust particles (IDPs), may be less than 150 times the present value (34), although the interpretations of the Akilia rocks are debatable (35).
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22. H_2 is not a chemically reactive gas. So in the steady state, hydrogen has a 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 ~ 0.4 nmol cm^{-2} year^{-1} (8) in electric discharge experiments when $H_2/CO_2 = 4$, equivalent to 2×10^8 kg/year assuming a mean molecular weight of 100. This estimate is based on an annual electric discharge rate $\sim 2 \times 10^{19}$ J/year, which is ~ 20 times the contemporary electric discharge rate, $\sim 1 \times 10^{18}$ J/year (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 1×10^7 kg/year when $H_2/CO_2 = 4$. Extrapolating the contemporary data back to early Earth faces large uncertainty. So here the conservative estimate (1×10^7 kg/year) of the amino acid production rate by electric discharge is taken.
24. Assuming the ocean volume is 1.4×10^{21} liters and that there is no loss of organics within the ocean, the amino acid concentration in the ocean can reach 7×10^{-8} kg/liter (equivalent to 7×10^{-7} mole/liter, assuming a mean molecular weight of 100) in 10 million years, which is the time scale for the entire ocean to circulate through submarine vents at 300°C, potentially destroying the organics (25).
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Lichen-Like Symbiosis 600 Million Years Ago

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The fossil record of fungi and lichens is scarce. Here we report the discovery of lichen-like fossils, involving filamentous hyphae closely associated with coccoidal cyanobacteria or algae, preserved in marine phosphorite of the Doushantuo Formation (between 551 and 635 million years old) at Weng'an, South China. These fossils indicate that fungi developed symbiotic partnerships with photoautotrophs before the evolution of vascular plants.

Fungi are a major eukaryote kingdom and perform critical ecological roles in nutrient recycling. Many living fungi maintain facultative or obligate interactions with marine and terrestrial photoautotrophs (1, 2). However, the fossil record of fungi is poor and includes Ordovician [460 million years ago (Ma)] glomaleans (3) and microfossils interpreted as probable fungi dating to >720 Ma (4). Fossil evidence for fungal interactions (such as cyanolichenization, mycoparasitism, and vesicular arbuscular mycorrhizal symbiosis) with other organisms comes from the ~400-million-year-old Rhynie chert in Scotland, which also preserves a diverse

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