Response to Comment on "A Hydrogen-Rich Early Earth Atmosphere"

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Catling speculates that the exobase of early Earth was hot and that the ancient nonthermal escape rate was more than 1000 times the present rate. However, low oxygen and high carbon dioxide on early Earth yields a cold exobase, and nonthermal escape rates are limited and cannot balance the volcanic outgassing of hydrogen.

Although the supply of organic compounds by hydrothermal vents and meteorites to the prebiotic Earth remains an interesting subject of study, our modeling results (*1*) suggest that research into the origin of life should be refocused on chemistry in the atmosphere, in the global oceans, and at the interface between the atmosphere and ocean.

The abundance of hydrogen in the atmosphere is currently limited by oxidation, not escape. We found that the hydrogen escape rate would have been ~1000 times as high on prebiotic Earth as it is today (~1 to 3 × 10^8 cm^{-2} s^{-1}) (*2*) and would have been the major sink for hydrogen. Therefore, our model supposes that hydrogen escape was energy-limited rather than diffusion-limited.

The current high exobase temperature on Earth is caused by absorption of sunlight by oxygen and the lack of an effective radiator. Catling (*3*) speculates that a high exobase temperature on early Earth could be caused by other gases. However, other gases are as likely to cool the atmosphere as they are to warm it. Early Earth analogs include Titan, Venus, and Mars, all of which have cold exobases (*4*). The model cited by Catling (*5*) is not appropriate for early Earth (*6*) because it contains too much O_2 and not enough CO_2. Catling argues that the CO_2 content in the early Archean atmosphere was <1% and speculates that even 30 times the current CO_2 might not cause substantial cooling in the thermosphere. These arguments are not convincing. Geological evidence supports very high CO_2 concentrations throughout the Archean (*7*). It also has been shown that a doubling of CO_2 content in the present atmosphere, to 0.072%, can cause the thermosphere to cool by ~50 K (*8*). Thus the anoxic, CO_2-rich atmosphere of early Earth should have had a cold exobase even with only 1% CO_2, and Jeans escape should have been slow. In response to some of Catling's other criticisms, our model used a constant heating efficiency of 15%, the same value as that used in a previous Venus hydrodynamic escape model (*9*). Detailed radiative transfer calculations will be needed to determine how this assumption will affect the escape rate. The escape rate of atomic hydrogen depends on its abundance, which should be much smaller than that of H_2 (*10*).

Catling's arguments on nonthermal escape are speculative and to some extent represent a misunderstanding of the escape processes. Helium in the contemporary atmosphere is in a balance between nonthermal escape and degassing (*11*), a behavior similar to that of hydrogen in early Earth's atmosphere. This does not lead to the conclusion that hydrogen escape from early Earth's atmosphere was dominated by nonthermal processes. Nonthermal escape of hydrogen is dominant under solar minimum conditions on present Earth (*12*). However, for nonthermal escape to balance the outgassing of hydrogen on early Earth, the rate must be ~1000 times as fast as it is now. Analysis of the nonthermal escape processes for a water-rich early Venus atmosphere shows that the upper limit of hydrogen nonthermal escape is ~1 × 10^{10} cm^{-2} s^{-1} (*13*), because the dominant escape mechanism, charge exchange, depends on the abundance of protons, which is limited by photoionization. Such photoionization on Earth should always be a factor of two or less than that on Venus. Regarding Catling's statement about hydrogen escape promoted by Earth's magnetic field, the permanent magnetic field can make global nonthermal escape only smaller, not higher (*14*). No one has proposed a mechanism that would result in a higher total nonthermal escape rate from a planet with a magnetic field as opposed to one without a magnetic field. Therefore, the ancient Venus nonthermal escape rate is an upper limit for the nonthermal escape on early Earth. The upper limit of nonthermal, Venus-like escape of hydrogen [~1 × 10^{10} cm^{-2} s^{-1} (*13*)] cannot balance the Archean hydrogen outgassing rate (~1 × 10^{11} cm^{-2} s^{-1}). Therefore, hydrodynamic escape has to occur.

The hydrodynamic escape required in (*15*) to explain the Xe isotope abundance started ~50 million years after the formation of Earth. The strength of solar extreme ultraviolet (EUV) flux needed is several hundred times that of today. The length of this "extreme" escape episode is only about 200 to 300 million years. The initial hydrogen escape flux is ~1 to 5 × 10^{14} cm^{-2} s^{-1}. Hence, the "close to upper limit" hydrogen escape suggested by Catling is irrelevant to the origin-of-life problem because it occurred much earlier in the history of Earth. The hydrodynamic escape values calculated in (*1*), extrapolated to an EUV flux several hundred times that of today, yield a hydrogen escape flux similar to that required to explain Xe abundance in (*15*).

The field of prebiotic atmospheric chemistry is ripe with possibilities for further research, including understanding the fractionation of heavy elements, the composition and thermal structure of the early atmosphere, and the origin of life. However, our assumption of a cold exobase is supported, and we stand by the main conclusions in (*1*). The nonthermal escape rate of hydrogen from early Earth's atmosphere should have been lower than the hydrodynamic escape rate and the rate of outgassing of hydrogen. Hence, the ancient atmosphere was hydrogen rich.

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References and Notes

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3. D. C. Catling, *Science* **311**, 38 (2006); www.sciencemag.org/cgi/content/full/311/5757/38a.
4. Titan, with an atmosphere of N_2, methane, and associated hydrocarbons, has an exobase temperature near 150 K (*15*), which is approximately twice its emission to space temperature. Venus and Mars also have very low exobase temperatures, lower even than in our H_2 escape model, because CO_2 radiates energy efficiently to space.
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6. The mixing ratios of CO_2 and O_2 in (*4*) are 300 parts per million (ppm) and 10^{-3}, respectively. The O_2 concentration in prebiotic Earth's atmosphere is determined by the H_2 concentration. For an H_2 concentration of 10^{-3}, the O_2 concentration should be ~10^{-15} (*16*). The CO_2 concentration in today's atmosphere is ~360 ppm. The Archean atmosphere should contain substantially more CO_2. It is known that nonlocal thermodynamic equilibrium (non-LTE) is important for CO_2 15 μm cooling, and only LTE is considered in (*4*).
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10. In a cold anoxic atmosphere, atomic hydrogen can be formed from H_2 photodissociation. It is found that the production rate of atomic hydrogen from photodissociation of H_2 in the atmosphere of extrasolar planet HD209458b (orbit ~0.05 astronomical units) is 9.5 × 10^{11} cm^{-2} s^{-1} (*17*). By extrapolating this production rate to early Earth

(5 times solar EUV flux today), an H production rate of $\sim 1.2 \times 10^{10}$ cm^{-2} s^{-1} is obtained. This rate is about one order of magnitude smaller than the hydrogen degassing rate for early Earth ($\sim 1 \times 10^{11}$ cm^{-2} s^{-1}), so it should be unimportant. It is possible that there were other sources of atomic hydrogen in the early Earth's atmosphere, such as CH_4 or H_2O. However, the abundance of these gases would have been much lower than that of H_2 in the upper atmosphere. We have performed photochemical simulations of the H abundance in the lower atmosphere of early Earth and find that the H abundance is negligibly small. To better understand the H escape rate requires a multifluid model with photochemistry.

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