

Comment on "A Hydrogen-Rich Early Earth Atmosphere"

David C. Catling^{1,2}

Tian *et al.* (Reports, 13 May 2005, p. 1014) proposed a hydrogen-rich early atmosphere with slow hydrogen escape from a cold thermosphere. However, their model neglects the ultraviolet absorption of all gases other than H₂. The model also neglects Earth's magnetic field, which affects the temperature and density of ions and promotes nonthermal escape of neutral hydrogen.

Tian *et al.* (1) argued that Earth's early atmosphere contained ~30% H₂, suggesting that the rate of hydrogen escape to space would be extremely low because the base of Earth's exosphere (or exobase) would be cold. They further reasoned that a hydrogen-rich atmosphere would synthesize organic molecules important for the origin of life, an idea that has previously been dismissed (2). Do these findings undermine research concerning meteorite or hydrothermal sources of prebiotic organics? I argue that the assumptions behind the cold exobase in the Tian *et al.* model (1) are too unrealistic for their exobase temperature to be relevant. Second, whether the exobase temperature affects the rate of hydrogen escape needs more careful consideration, bearing in mind that today's escape of hydrogen is predominantly nonthermal.

To properly calculate early Earth's exobase temperature requires balancing the energy budget in the early upper atmosphere, accounting for all important neutral and ionic species and higher extreme ultraviolet (EUV) fluxes from the early Sun (3). Tian *et al.* [supporting online material for (1)] stated that their model "contains only one component—hydrogen molecules," an assumption that automatically invokes a cold exobase because EUV absorption by other species is neglected. Other gases in a real atmosphere would not readily escape (and carry energy away), would absorb EUV, and would get hot. A related issue omitted in (1) is that the exobase temperature depends on the proportions of molecular versus atomic species. As a result of photolysis, the latter tend to increase with higher EUV fluxes and get hotter; in addition, atomic hydrogen escapes more easily than molecular hydrogen. Although

Tian *et al.* assumed pure H₂, they applied an EUV heating efficiency of 15%, which is appropriate for atomic hydrogen but too low for H₂ by a factor of ~4. Regardless, one still needs to calculate the exobase temperature for a multigas atmosphere. In the absence of a multigas calculation, Tian *et al.* assert that the early exobase would be cold, quoting a primitive (anoxic) atmosphere model (4) that used the EUV flux from the present-day Sun. With an enhanced EUV flux (3) appropriate for ~4 billion years ago (Ga), the multigas model of (4) actually produces a mean exobase temperature >1400 K, greater than today's mean value (5). At this temperature, hydrogen escapes efficiently and cannot build up as a major constituent of the atmosphere. It is unconvincing to then appeal to an early atmosphere highly enriched in CO₂ to engineer a cold Venus- or Mars-like exobase by CO₂ radiative cooling. CO₂ was limited on early Earth by a large loss flux due to seafloor weathering (6). Data from the ancient seafloor (7) indicate that the atmospheric CO₂ mixing ratio was less than ~1% (compared with >95% on Venus and Mars), which could not have greatly affected early Earth's exobase temperature (8).

The exobase temperature is also not the sole arbiter of Earth's hydrogen escape rate. Satellite measurements prove that today's hydrogen escape is predominantly nonthermal and that the proportion of nonthermal escape increases with a cooler exobase, maintaining the same diffusion-limited escape rate (9–11). Nonthermal escape is linked to Earth's magnetic field: H ions accelerated by Earth's magnetic field collide with neutral H atoms, exchange their charge, and become fast-moving neutral atoms with escape velocity; hydrogen also escapes along open polar field lines. Tian *et al.* dismiss the importance of nonthermal hydrogen escape from early Earth by comparison with the low nonthermal escape rates on Venus. However, Venus has no magnetic field and has different

escape physics (10). Terrestrial helium fluxes further demonstrate the importance of non-thermal escape. Helium continuously fluxes to Earth's atmosphere from radioactive decay in Earth's interior. Today's exobase is sufficiently cold that thermal escape of helium accounts for less than one-millionth of the total helium escape flux (11). Thus, if we only considered thermal escape, we would incorrectly conclude that Earth's present atmosphere should be relatively rich in helium. In reality, ⁴He escapes efficiently by processes that do not depend on the exobase temperature (12, 13).

Finally, data suggest that hydrogen actually did escape from early Earth at rates close to its upper limit. The isotopic mass fractionation of atmospheric xenon is consistent with the idea that hydrogen escaped so strongly that it dragged even xenon, the heaviest gas in the atmosphere, to space (13, 14).

References and Notes

1. F. Tian, O. B. Toon, A. A. Pavlov, H. De Sterck, *Science* **308**, 1014 (2005).
2. J. C. G. Walker, *Evolution of the Atmosphere* (Macmillan, New York, 1977).
3. F. M. Walter, D. C. Berry, in *The Sun in Time*, C. P. Sonnett *et al.*, Eds. (Univ. of Arizona Press, Tucson, 1991), pp. 633–657.
4. G. Visconti, *J. Atmos. Sci.* **32**, 1631 (1975).
5. The time history of the globally averaged solar EUV flux normalized to present, $S(t)/S$, has been estimated by using recent astronomical observations of representative young Sun-like stars as $S(t)/S = 6.13 \times [t \text{ (Gy)}]^{-1.19}$, where t is time after zero-age main sequence (15). Thus at ~4 Ga ($t = 0.5$), the EUV flux was ~14 times as high as at present. Using figure 3 in (4) and applying a mean EUV flux 14 times the present, which is greater than today's solar maximum output, one obtains an exobase temperature >1400 K.
6. N. H. Sleep, K. Zahnle, *J. Geophys. Res.* **106**, 1373 (2001).
7. K. Nakamura, Y. Kato, *Geochim. Cosmochim. Acta* **68**, 4595 (2004).
8. Using a global carbon flux of 3.8×10^{13} mol/year inferred from data (8) and the model of (7) gives a CO₂ level at 3.5 Ga only ~10 times that of the present. The mesopause (the cold base of the thermosphere where CO₂ cools radiatively) occurs at a pressure level inversely proportional to $f_{\text{CO}_2}^{0.5}$, where f_{CO_2} is the mixing ratio of CO₂. With f_{CO_2} some 10 times as high as today, the mesopause would be higher by only ~2 mesospheric scale heights (~10 km) compared with today. This altitude is still in the mixed region below the homopause, so diffusive separation in the overlying thermosphere would limit thermospheric CO₂ abundances and prevent radiative thermospheric cooling.
9. J. L. Bertaux, *J. Geophys. Res.* **80**, 639 (1975).
10. L. J. Maher, B. A. Tinsley, *J. Geophys. Res.* **82**, 689 (1977).
11. B. D. Shizgal, G. G. Arkos, *Rev. Geophys.* **34**, 483 (1996).
12. O. Lie-Svendsen, M. H. Rees, *J. Geophys. Res.* **101**, 2435 (1996).
13. D. M. Hunten, *Icarus* **85**, 1 (1991).
14. R. O. Pepin, *Icarus* **92**, 2 (1991).
15. H. Lammer *et al.*, *Icarus* **165**, 9 (2003).

¹Department of Earth Sciences, University of Bristol, Queen's Road, Bristol BS8 1RJ, UK. ²Department of Atmospheric Sciences and Astrobiology Program, University of Washington, Seattle WA, USA. E-mail: David.Catling@bristol.ac.uk

22 July 2005; accepted 30 November 2005
10.1126/science.1117827