Title
An Environmental Experiment with H2?

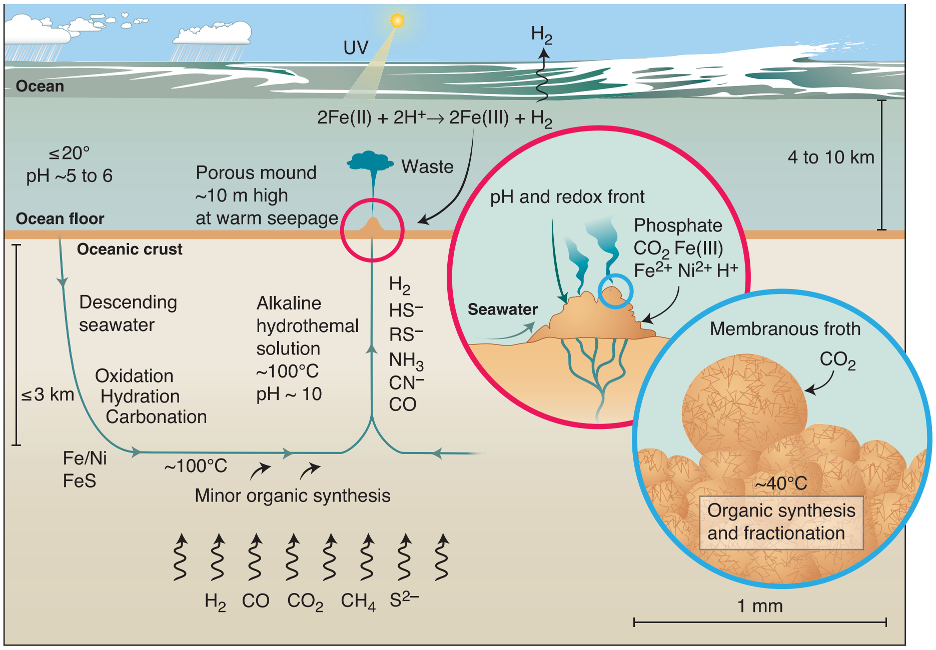
Journal
Science, 302(5645)

ISSN
0036-8075

Author
Prather, Michael J

Publication Date
2003-10-24

DOI
10.1126/science.1091060



The submarine setting for the emergence of life. The initially alkaline conditions required by both Hanczyc *et al.* (*1*) and Huber *et al.* (*7*) in their respective demonstrations of the emergence of RNA-bearing vesicles and a possible primordial peptide cycle are met on the 4.3-billion-year-old ocean floor. This vertical section through atmosphere, ocean, and oceanic crust illustrates how alkaline hydrothermal solution of constant temperature (~100°C) and pH (~10) is convectively pumped through a confining porous mound of freshly precipitated clays, hydroxides such as $Mg(OH)_2$, and iron-nickel sulfides into a cool and acidulous ocean—a kind of natural hydroponic feed to the first cells.

CREDIT: ADAPTED FROM (3, 12) BY PRESTON HUEY/SCIENCE

is no evidence that lipids would be produced in sufficient quantities, either in hydrothermal interactions or from extraterrestrial sources, to allow vesicle formation.

Instead of lipids, the easily synthesized amino acids, joined together as polypeptides, could have formed the first organic membranes. Huber and Wächtershäuser have shown that amino acids can be converted into peptides under alkaline conditions (*6*). Huber *et al.* (*7*) have established a peptide cycle using chemicals similar to those that exist at porous hydrothermal mounds (see the figure). For example, they use $Mg(OH)_2$ to stabilize pH at ~9.8. In nature, this is the mineral brucite, which is formed during the convective hydration of rocks expected to have existed on the early ocean floor (*3*), and also occurs at alkaline submarine mounds predicted as the hatchery of emergent life (*3*, *5*).

These studies suggest that submarine alkaline seepages provide a more congenial site for life to emerge than the acidic, high-temperature, and violent "CO-laden volcanic exhalations" favored in Wächtershäuser's theory of surface metabolism (*8*). Alkaline fluids have other advantages: They favor both phosphate and amine chemistry, encourage acid-base catalysis, and provide a sink for protons, which drives the protonmotive force across membranes that is required for all cells.

In particular, RNA would have required what is known as a polymerase—that is, a polypeptide that can catalyze the joining of ribonucleotides to form RNA—for its construction. But this polymerase could only be constructed with reference to a preexisting RNA polymer. How can this "chicken or egg" conundrum be resolved?

Most promising in this regard is the suggestion that the basis for the genetic code rests on a natural affinity between an RNA codon and a particular amino acid side chain (*9*, *10*). RNA composed of polyadenine, when bound to a solid phase, does select for its coded diamino acid, lysine (*11*). And because its positively charged side chains can bind to the phosphates of RNA monomers, polylysine has many of the characteristics expected of a primitive polymerase (*9*). That RNA must be adsorbed on a solid to be able to select its appropriate amino acids is consistent with the model of Hanczyc *et al.* (*1*).

A hydrothermal mound offers a natural reactor for such interactions. Thus, the "bottom-up" geochemical approach and the "top-down" biochemical approach to the origin of life appear to be converging. With each approach informing the other, the experimental quest for the recipe for "protolife" can begin in earnest.

References

1. M. M. Hanczyc, S. M. Fujikawa, J. W. Szostak, *Science* **302**, 618 (2003).
2. J. P. Ferris, *Origins Life Evol. Biosph.* **32**, 311 (2002).
3. M. J. Russell, A. J. Hall, *Geochem. News* **113**, 6 (2002).
4. A. Geptner *et al.*, *Clays Clay Miner.* **50**, 174 (2002).
5. D. S. Kelley *et al.*, *Nature* **412**, 145 (2001).
6. C. Huber, G. Wächtershäuser, *Science* **281**, 670 (1998).
7. C. Huber, W. Eisenreich, S. Hecht, G. Wächtershäuser, *Science* **301**, 938 (2003).
8. G. Wächtershäuser, *Microbiol. Rev.* **52**, 452 (1988).
9. C. R. Woese, *The Genetic Code: The Molecular Basis for Genetic Expression* (Harper & Row, New York, 1967).
10. A. R. Mellersh, *Origins Life Evol. Biosph.* **23**, 261 (1993).
11. A. R. Mellersh, A.-S. Wilkinson, *Origins Life Evol. Biosph.* **30**, 3 (2000).
12. W. Martin, M. J. Russell, *Philos. Trans. R. Soc. London* **358B**, 27 (2003).

ATMOSPHERIC SCIENCE

An Environmental Experiment with H_2?

Michael J. Prather

Clean, hydrogen-fueled transportation—as envisioned in a recent U.S. presidential initiative (*1*)—has great appeal. When H_2 is "burned" in a fuel cell, directly producing electricity to power a vehicle, the exhaust contains none of the odd-nitrogen compounds (NO_x) associated with combustion. NO_x is the key factor in photochemical smog formation (*2*). Furthermore, if the H_2 is generated from nonfossil energy, it could eliminate the CO_2 emissions from the transport sector. H_2 thus seems to be capable of solving major environmental problems.

However, the chemicals that we dispose of in the atmosphere often return as unexpected environmental problems—witness the transport sector and local air pollution, halocarbon production and global ozone depletion, and fossil fuel use and global climate change. The seriousness of these problems was not discovered until after the technologies had been introduced, partly explaining the contentiousness of the public debate over remedying them. Given the growing interest in an H_2 economy, now is the time for assessing its environmental consequences. Three recent publications

---

The author is in the Department of Earth System Science, University of California, Irvine, CA 92697, USA. E-mail: mprather@uci.edu

(*3–5*) address how an H_2 economy might change the global atmosphere.

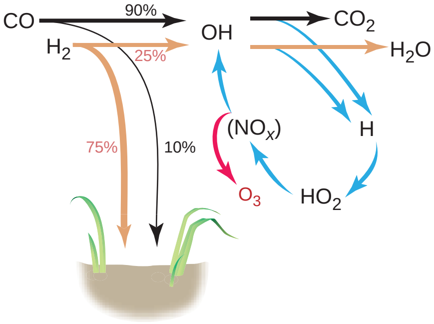
For an H_2 economy, Tromp *et al*. (*3*) postulate large increases in atmospheric H_2 that affect stratospheric water vapor, temperature, and ozone. Rahn *et al*. (*4*) use new observations of DH, an isotopically heavy analog of H_2, to determine the removal rate of H_2 from the atmosphere. Knowledge of this atmospheric lifetime allows the atmospheric buildup of H_2 due to additional emissions to be estimated. And on page 624 of this issue, Schultz *et al*. (*5*) calculate atmospheric H_2 increases from projected H_2 leakage. They consider the impact of these H_2 emissions together with the concurrent reductions in NO_x and carbon monoxide (CO) emissions achieved by conversion to fuel cells.

H_2 is a naturally occurring trace gas with an abundance of ~0.5 ppm (parts per million molecules of air). The atmosphere thus contains a total of ~175 Tg of H_2. About half of this total is produced in the atmosphere by photochemical oxidation of methane and other hydrocarbons. The other half originates from biogenic processes and combustion, including biomass burning, at Earth's surface (*6–9*). Of the estimated total emissions of 70 to 90 Tg/year, one-quarter is associated with human activities. H_2 is destroyed photochemically in the atmosphere through reaction with the hydroxyl radical (OH) and biologically at the surface through consumption by soil microorganisms (*6–8*) (see the figure).

The photochemical loss of H_2 is well constrained, but the soil loss is quite uncertain. The analysis of Rahn *et al*. (*4*) confirms the current view (*7–9*) that today, the soil sink is three to four times the size of the photochemical sink. The dominance of the soil sink is the reason why H_2—unusually for a trace gas influenced by human activities—is less abundant in the Northern Hemisphere than in the Southern Hemisphere (*9*).

Rahn *et al*. derive a total atmospheric lifetime of H_2 of ~2 years. Given this lifetime, H_2 leakage of 18 Tg/year would increase its atmospheric abundance by 36 Tg (0.1 ppm or 20%). Thus, the H_2 increase from 0.5 to 2.3 ppm postulated by Tromp *et al*. (*3*) would require leakage rates of 320 Tg/year. This amount exceeds their highest leakage estimates.

Schultz *et al*. (*5*) consider leakage rates of 3 to 10% for a hypothetical future in which 50% of today's fossil fuel combustion has been replaced by hydrogen technology. They do not report annual usage of H_2. Using their case L3N, for which the OH sink is unchanged, we can estimate leakage of 20 to 26 Tg/year, and hence a total usage of 700 to 900 Tg/year. For the cases considered, the authors project average increases in atmospheric H_2 ranging between 0.15 and 0.6 ppm.



The fate and impact of atmospheric H_2 and CO. Both gases have parallel reaction sequences that impact the HO_x cycle (blue: OH, H, HO_2), thereby increasing the greenhouse gas CH_4 and both augment the production of tropospheric O_3 (red), another greenhouse gas.

H_2 is often portrayed as an environmentally friendly gas whose atmospheric degradation yields only water vapor. However, chemically reactive gases such as H_2 have been recognized as indirect greenhouse gases in international climate assessments since 1990 (*10, 11*). Atmospheric H_2 affects global atmospheric chemistry in the same way as CO: Its photochemical loss reaction with the OH radical takes up one OH and releases one HO_2 radical (plus water vapor; see the figure). The net effect of adding H_2 to the atmosphere is to reduce OH (the primary methane sink) and thereby increase methane abundance. Thus, H_2, like CO, is an indirect greenhouse gas.

Current three-dimensional chemistry models predict that reaction of each CO molecule with OH is equivalent to emitting 0.09 additional molecules of methane (*11*). (This indirect effect of CO does not include additional greenhouse warming due to the short-lived increase in tropospheric ozone caused by CO emissions.) We can scale the greenhouse effect of H_2 by the relative rates of reaction with OH. An extra 0.60 ppm of H_2 would react with tropospheric OH at a rate of 0.062 ppm/year and would lead indirectly to an increase in methane emission by 0.006 ppm/year.

This increased flux, amplified by methane feedback effects through the OH radical, would increase methane global mean abundances by 0.072 ppm or 4%, corresponding to a greenhouse gas forcing of ~0.026 W m^{-2}. This climate forcing is a fraction of that due to methane and CO_2 emissions since the pre-industrial era (+0.5 and +1.5 W m^{-2}, respectively) and is a little larger than the climate forcing due to CO_2 emissions from present-day aviation (*12*).

Schultz *et al*. (*5*) note that the largest impact of an H_2 economy may be the reduction in NO_x emissions from the switch to fuel cells. NO_x reductions would reduce tropospheric ozone across the Northern Hemisphere and improve regional air quality. The premise of Schultz *et al*. that increased NO_x emissions reduce methane was identified in the Intergovernmental Panel on Climate Change (IPCC) aviation assessment (*12*). The near-cancellation of the greenhouse warming between a methane decrease and a tropospheric ozone increase was demonstrated for a wide range of location of NO_x emissions (*13*).

Leakage of fuel gases is inevitable. Idealized, well-maintained fuel systems can keep leakage to a minimum, but experience with natural gas, particularly with petroleum gas in Mexico City (*14*), indicates that some leakage will most certainly occur. H_2 is more leak-prone than methane, and leakage from a mature and aging hydrogen economy might approach a few percent before economic costs would force corrective action. Thus, the leakage rates assumed by Schultz *et al*. (*5*) represent an appropriate upper range.

Evaluation of the climate impacts of a shift in the transport sector from fossil fuel combustion to H_2 fuel cells has just begun. Technologically based bounds on the leakage rates are needed, the total atmospheric impact from the ground to the top of the atmosphere needs to be evaluated, and—as shown by Schultz *et al*. (*5*)—the concurrent changes in other transport-related emissions must be considered. Only with this information will we be able to say with confidence what the advantages and disadvantages of an H_2 economy will be.

References

1. U.S. Department of Energy, *The President's FreedomCAR and Fuel Initiative: A Clean and Secure Energy Future*, 5 February 2003 (www.eere.energy.gov).
2. J. H. Seinfeld *et al.*, *Rethinking the Ozone Problem in Urban and Regional Air Pollution* (National Academy Press, Washington, DC, 1991).
3. T. K. Tromp *et al.*, *Science* **300**, 1740 (2003).
4. T. Rahn *et al.*, *Nature* **424**, 918 (2003).
5. M. G. Schultz, T. Diehl, G. P. Brasseur, W. Zittel, *Science* **302**, 624 (2003).
6. R. Conrad, *Microbiol. Rev.* **60**, 609 (1996).
7. P. C. Novelli *et al.*, *J. Geophys. Res.* **D104**, 30427 (1999).
8. D. A. Hauglustaine, D. H. Ehhalt, *J. Geophys. Res.* **D107**, 4330 (2002).
9. R. L. Langenfelds *et al.*, *Global Biogeochem. Cycles* **16**, 1048 (2002).
10. K. P. Shine, R. G. Derwent, D. J. Wuebbles, J. J. Morcrette, in *Climate Change: The IPCC Assessment*, J. T. Houghton, G. J. Jenkins, J. J. Ephraums, Eds. (Cambridge Univ. Press, Cambridge, 1990), pp. 41–68.
11. M. Prather, D. Ehhalt, in *Climate Change 2001: The Scientific Basis*, J. T. Houghton *et al.*, Eds. (Cambridge Univ. Press, Cambridge, 2001), pp. 239–287.
12. I. Isaksen, C. Jackman, in *Aviation and the Global Atmosphere, A Special Report of the Intergovernmental Panel on Climate Change*, J. E. Penner *et al.*, Eds. (Cambridge Univ. Press, Cambridge, 1999), pp. 121–163.
13. O. Wild, M. J. Prather, H. Akimoto, *Geophys. Res. Lett.* **28**, 1719 (2001).
14. D. R. Blake, F. S. Rowland, *Science* **269**, 953 (1995).