Title
Atmospheric science. An environmental experiment with H2?

Permalink
https://escholarship.org/uc/item/2550z16r

Journal
Science, 302(5645)

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Publication Date
2003-10-24

DOI
10.1126/science.1091060

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Peer reviewed
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.

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 protonotive 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.

**ATMOSPHERIC SCIENCE**

**PERSPECTIVES**

An Environmental Experiment with H₂?

Michael J. Prather

Clean, hydrogen-fueled transportation— as envisioned in a recent U.S. presidential initiative (1)— has great appeal. When H₂ is "burned" in a fuel cell, directly producing electricity to power a vehicle, the exhaust contains none of the odd-nitrogen compounds (NOₓ) associated with combustion. NOₓ is the key factor in photochemical smog formation (2). Furthermore, if the H₂ is generated from nonfossil energy, it could eliminate the CO₂ emissions from the transport sector.

H₂ 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 H₂ economy, now is the time for assessing its environmental consequences. Three recent publications...
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(3–5) address how an H₂ economy might change the global atmosphere.

For an H₂ economy, Tromp et al. (3) postulate large increases in atmospheric H₂ that affect stratospheric water vapor, temperature, and ozone. Rahn et al. (4) use new observations of DH, an isotopically heavy analog of H₂, to determine the removal rate of H₂ from the atmosphere. Knowledge of this atmospheric lifetime allows the atmospheric buildup of H₂ due to additional emissions to be estimated. And on page 624 of this issue, Schultz et al. (5) calculate atmospheric H₂ increases from projected H₂ leakage. They consider the impact of these H₂ emissions together with the concurrent reductions in NO and methane and other hydrocarbons. The other half originates from biogenic processes and leakage of 20 to 26 Tg/year, and hence a total of ~175 Tg of H₂. Using their case L3N, for which the technology has been replaced by hydrogen technology. They do not report annual usage of H₂. 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 case considered, the authors project average increases in atmospheric H₂ ranging between 0.15 and 0.6 ppm.

H₂ is often portrayed as an environmentally friendly gas whose atmospheric degradation yields only water vapor. However, chemically reactive gases such as H₂ have been recognized as indirect greenhouse gases in international climate assessments since 1990 (10, 11). Atmospheric H₂ 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 H₂O radical (plus water vapor; see the figure). The net effect of adding H₂ to the atmosphere is to reduce OH (the primary methane sink) and thereby increase methane abundance. Thus, H₂, 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 H₂ by the relative rates of reaction with OH. An extra 0.60 ppm of H₂ 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 CO₂ 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 CO₂ emissions from present-day aviation (12).

Schultz et al. (5) note that the largest impact of an H₂ economy may be the reduction in NOₓ emissions from the switch to fuel cells. NOₓ reductions would reduce tropospheric ozone across the Northern Hemisphere and improve regional air quality. The premise of Schultz et al. that increased NOₓ emissions reduce methane was identified in the Intergovernmental Panel on Climate Change (IPCC) 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 NOₓ 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. H₂ 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 H₂ 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 H₂ economy will be.

References