Puzzling phase transitions



Chili pepper origins

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LETTERS

edited by Etta Kavanagh

A Voice over the Smoke for Academic Freedom

I CANNOT UNDERSTAND WHY THE PROPONENTS OF THE UNIVERSITY of California (UC) ban on funding from tobacco companies ("UC balks at campus-wide ban on tobacco money for research," D. Grimm, News of the Week, 26 Jan., p. 447) constantly mischaracterize tobacco company—funded research as a "collective use of sponsored research by the manufacturers and distributors of tobacco products as an industry to support a public deception about its products." That statement in the preamble of the recent action item RE-89 of the UC Board of Regents is in itself a deception.

Only a handful of UC scientists, including myself, have competed successfully for tobacco company funds to conduct, as stated in the request for proposal guidelines, "the highest quality research that contributes to the fundamental scientific knowl-

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—Jue

edge" and that "addresses the concern of public health ... regarding cigarette smoking."

I have not deceived the public, have not promoted tobacco use, and have not experienced any corporate intrusion in the collection or analysis of my research data. Yet neither I nor the other 107 awardees since 1995 have ever received the opportunity to defend ourselves against these charges.

The UC Board of Regents just has to apply the principles of academic freedom, give all awardees a voice to contest the allegations, and determine fairly if any public deception has actually occurred. They will discover that the hard evidence supports the 2006 UC Assembly of the Academic Senate resolution to assert academic freedom against a tobacco fund ban. Let's not squander the recent public health gains against smoking by attacking the foundation of freedom

of speech and inquiry, which gave rise to the gains in the first place.

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Debating Evidence for the Origin of Life on Earth

THERE ARE TWO MAIN THEORIES FOR THE origin of life on Earth: the "pioneer metabolic theory" (a hot, volcanic origin) and the "prebiotic soup theory" (a cold, oceanic origin). In their Report " α -hydroxy and α -amino acids under possible Hadean, volcanic origin-of-life conditions" (27 Oct. 2006, p. 630), C. Huber and G. Wächtershäuser describe prebiotic synthesis experiments that are claimed to "narrow the gap between biochemistry and volcanic geochemistry." However, no plausible geological environment could maintain the cited conditions of 0.1 to 0.2 M KCN at 100°C. As noted by Schwartz (1), in the "exceedingly improbable" case that all of Hadean Earth's nitrogen was converted to cyanide and dissolved in the oceans, a 0.2 M cyanide solution could be produced. Such high concentrations of cyanide in volcanic solutions would rapidly hydrolyze at 100° C ($t_{1/2} \sim 10$ hours at pH 12) to formamide, which then quickly hydrolyzes to ammonia and formate (2). Huber and Wächtershäuser suggest that Ni/Fe-cyanide precipitates would have stabilized the cyanide, but robust sources of cyanide would be needed to produce a steady-state concentration of 0.1 to 0.2 M KCN at 100° C. No such robust sources are known.

The proposed 75 bars CO in volcanic solutions is also implausible, based on outgassing models using ordinary chondritic material (3). Nor are such elevated CO pressures necessary; previous experiments have demonstrated that a rich assortment of prebiotic organic compounds can be synthesized using a variety of energy sources from a modest \sim 1 bar CO/N₂ atmosphere [see (4) and references therein].

The compounds generated by Huber and Wächtershäuser, as well as their relative abundance, are remarkably similar to those generated previously in the "prebiotic broth" experiments they disparage. They claim that the lack of tar formation (from cyanide polymerization) makes their results distinct from earlier experiments, but this difference is easily explained by the reaction of cyanide with formaldehyde, produced by metal-catalyzed reduction reactions of formate (generated in this case by cyanide hydrolysis and the direct hydration of CO). As for their experiment 14, wherein they claim that no products were detected, we suspect that if they had acid hydrolyzed the final solution, several products would have been identified (5). Finally, the results reported by Huber and Wächtershäuser are easily accommodated within the framework of an updated prebiotic soup heterotrophic theory in which pyrite and other metal sulfides are recognized as an important source of electrons for the reduction of organic compounds (6). In such a model, mineral

surfaces have the potential to select, concentrate, and organize these molecules (7).

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Response

THERE ARE TWO MUTUALLY EXCLUSIVE THEORIES on the origin of life. The "pioneer organism theory" claims a momentary, mechanistically

definite origin by autocatalytic carbon fixation within a hot, volcanic flow in contact with transition metal catalysts (1). The "prebiotic soup theory" claims a protracted, mechanistically obscure self-organization in a cold, primitive ocean, in which organic compounds accumulated over thousands or millions of years. The experiments under discussion have been designed to test the pioneer organism theory, and all experimental parameters have been chosen within this framework. The criticism presented by Bada et al. is made from the perspective of the prebiotic soup theory.

In agreement with the pioneer organism theory, we used Ni²⁺ or Fe²⁺ for catalytic purposes. These transition metals form extremely stable cyano complexes, which are similar to those found in volcanic field studies (2). This means that practically all cyanide ions become fixed as cyano ligands, with the effect that the concentration of dissolved free cyanide ions in the water phase is extremely low due to the high stability of the cyano complexes. It is a well-established fact of coordination chemistry that cyanide ions and cyano ligands have fundamentally different chemical properties. Bada *et al.*, however,

seem to ignore this difference. They appear to work from the experience of previous prebiotic soup experiments with dissolved free cyanide, which did not yield products unless the cyanide concentration in water was sufficiently high (3). Therefore, this criticism is pointless.

We used 1 bar CO (Table 1, run 1), and we discussed at length that such CO pressure is in agreement with the volcanic setting of the pioneer organism theory. In other runs, we used 10 or 75 bar CO to shorten the reaction time. It is a well-established practice to expedite reactions by increasing a parameter such as pressure. Therefore, the criticism of our use of 75 bar CO is pointless. We note that our use of 1 bar CO was not criticized.

Therefore, the above two points of geochemical criticism do not cast a reasonable doubt on the ability of our reactions to have taken place within a volcanic, hydrothermal flow system of early Earth.

We note that our critics differ from us as to the fate of reaction products we have found.

From the point of view of the pioneer organism theory, we see our reaction products, e.g., α -hydroxy acids or α -amino acids [or

peptides arising therefrom (4, 5)], as exhibiting positive autocatalytic feedback in situ by providing transition metal ligands for ligand-accelerated catalysis (6) of carbon fixation pathways, which constitutes evolvable reproduction (1). Reaction products that spill out into vast expanses of the ocean lose all chemical potential by dilution and are irreversibly lost for the origin of the pioneer organism (7).

From the point of view of the prebiotic soup theory, our critics see our reaction products as entering the primitive ocean to become additional ingredients of the prebiotic soup, wherein after some thousand or million years, and under all manner of diverse influences, the magic of self-organization is believed to have somehow generated an unspecified first form of life.

The two theories are categorically different from the perspective of experimental science. The prebiotic soup theory is restricted to the testing of individual aspects of a long, protracted overall process (3). The pioneer organism, by contrast, is expected to be experimentally realizable in toto (1).

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A Clarification on Global Access to Drugs

MARTIN ENSERINK'S ARTICLE "WHO PANEL weighs radical ideas" (News of the Week, 1 Dec. 2006, p. 1373) misrepresents the position of the European Commission in the important debate on global access to medicines.

In the final paragraph, there is a reference to the World Health Assembly (WHA) resolution establishing a World Health Organization (WHO) Intergovernmental Working Group (IGWG) on Public Health, Innovation, and Intellectual Property, followed by the sentence "(The drug companies and the European Commission opposed the plan.)".

In fact, the European Commission was a strong proponent of WHA Resolution 59.24 at last May's World Health Assembly. The Commission worked with the European Union (EU) to support the resolution, including the establishment of the WHO IGWG. The Commission was represented at the WHO IGWG in December by officials from five different Directorate Generals who worked closely with EU Member States at the meeting and actively intervened to support the process.

The three stated priorities of the European Union at the IGWG were (i) to promote research and development focused on products for diseases that disproportionately affect developing countries; (ii) to ensure that these products are affordable and accessible within national health systems; and (iii) to ensure that all countries can use the flexibilities provided in international legal agreements on intellectual property rights.

The European Commission funds research into neglected diseases affecting developing countries, acts as a partner in clinical trials, and uses development funding and policy to improve global access to medicines. A Commission legislative proposal for compulsory licensing was adopted by the European Parliament and Council earlier this year (Regulation 816/2006). The EU also fully respects the right of trading partners to use compulsory licensing in all bilateral free trade agreements.

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Who Is et al.?

ET AL. 'S WORK IS REFERENCED IN DIVERSE journal articles demonstrating technical and research abilities that cross many scientific fields. Et al. does work in AIDS research, cancer discoveries, diabetes, geology, anthropology, astrophysics, and even in research on a worm called C. elegans. How does et al. do it? I could benefit from having et al. as my next mentor. But who is et al.? If et al. is a professor at a university, what does et al. teach? With all

the work et al. has published, maybe I can find et al.'s contact information by researching the patent and trademark office. To my surprise, I find no et al. listed on any patents or trademarks. I guess et al. wants all the work to remain in the public domain. Now I know I must have et al. as my next mentor, even if at a distance. Maybe I can find et al.'s contact information on an NIH-sponsored research project. Amazingly, NIH has not funded projects under et al.'s name. Et al. has more than 10,000 publications on a myriad of topics, so why is that not impressive (or sufficiently interdisciplinary) enough to receive funding? Does et al. lack focus in the eyes of peer reviewers? Are et al.'s

Letters to the Editor

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projects too ambitious for peer reviewers to fund? I did notice that *et al.*'s author lines are generally fourth or sixth. Is the lack of first authorship the reason *et al.* does not receive government-sponsored funding? It is not that *et al.* is an author in all those papers only because of supplying key reagents or involvement in patient care. The days of automatic authorship as the reward for providing key components to a project are over; such individuals are now consigned to the acknowledgment section. I e-mailed my former professors to see if they know *et al.*, but so far, I have not received a reply. Does anyone know where to find *et al.*?

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CORRECTIONS AND CLARIFICATIONS

Reports: "Ultrafast bond softening in bismuth: Mapping a solid's interatomic potential with x-rays" by D. M. Fritz *et al.* (2 Feb., p. 633). In the acknowledgments note (27), one of the funding groups was misidentified. FLASH stands for "Understanding Fast Light-Actuated Structural Changes."

Reports: "Global-scale similarities in nitrogen release patterns during long-term decomposition" by W. Parton *et al.* (19 Jan., p. 361). William Parton and Whendee L. Silver should have been listed as co—lead authors.