Earth and Mars: Evolution of Atmospheres and Surface Temperatures

Carl Sagan; George Mullen

Science, New Series, Vol. 177, No. 4043 (Jul. 7, 1972), 52-56.

Stable URL:
http://links.jstor.org/sici?sici=0036-8075%2819720707%293%3A177%3A4043%3C52%3AEAMEOA%3E2.0.CO%3B2-6

Science is currently published by American Association for the Advancement of Science.

Your use of the JSTOR archive indicates your acceptance of JSTOR's Terms and Conditions of Use, available at http://www.jstor.org/about/terms.html. JSTOR's Terms and Conditions of Use provides, in part, that unless you have obtained prior permission, you may not download an entire issue of a journal or multiple copies of articles, and you may use content in the JSTOR archive only for your personal, non-commercial use.

Please contact the publisher regarding any further use of this work. Publisher contact information may be obtained at http://www.jstor.org/journals/aaas.html.

Each copy of any part of a JSTOR transmission must contain the same copyright notice that appears on the screen or printed page of such transmission.

JSTOR is an independent not-for-profit organization dedicated to creating and preserving a digital archive of scholarly journals. For more information regarding JSTOR, please contact support@jstor.org.

http://www.jstor.org/
Thu Dec 1 21:27:52 2005

Reports

Earth and Mars: Evolution of Atmospheres and Surface Temperatures

Abstract. *Solar evolution implies, for contemporary albedos and atmospheric composition, global mean temperatures below the freezing point of seawater less than 2.3 aeons ago, contrary to geologic and paleontological evidence. Ammonia mixing ratios of the order of a few parts per million in the middle Precambrian atmosphere resolve this and other problems. Possible temperature evolutionary tracks for Earth and Mars are described. A runaway greenhouse effect will occur on Earth about 4.5 aeons from now, when clement conditions will prevail on Mars.*

The present surface temperature of Earth represents an energy balance between the visible and near-infrared sunlight that falls on the planet and the middle-infrared thermal emission that leaves. In the absence of an atmosphere this equilibrium is written $\frac{1}{4}S \times (1 - \bar{A}) = e\sigma T_e^4$, where S is the solar constant; $\bar{A}$ is the Russell-Bond spherical albedo of Earth, a reflectivity integrated over all frequencies; e is the mean emissivity of Earth's surface in the middle infrared; σ is the Stefan-Boltzmann constant; and T_e is the effective equilibrium temperature of (atmosphereless) Earth. The factor $\frac{1}{4}$ is the ratio of the area πR^2 that intercepts sunlight to the area $4\pi R^2$ that emits thermal infrared radiation to space. When the best estimates of these parameters are used, a value for T_e of 250° to 255°K is obtained; this is far less than the observed mean surface temperature, T_s, of Earth, 286° to 288°K. The difference is due to the greenhouse effect, in which visible and near-infrared sunlight penetrates through Earth's atmosphere relatively unimpeded, but thermal emission by Earth's surface is absorbed by atmospheric constituents that have strong absorption bands in the middle infrared. Thus, time variations in S, $\bar{A}$, e, or atmospheric composition may induce important changes in T_s. The present heat flow from the interior of Earth is about 2×10^{-5} the solar constant and plays a negligible role in determining T_s.

To calculate T_s, allowing for the greenhouse effect, we divide the emergent flux into two parts, one emitted by the surface at temperature T_s directly into space through atmospheric windows, and the other emitted by the atmosphere into space in wavelength regions of strong atmospheric absorption. In the latter case we consider the emission to occur from the skin temperature of the approximately isothermal outer boundary of an atmosphere in radiative equilibrium, which is, in the Eddington approximation, at a temperature of $2^{-1/4}T_e$. Thus,

$$\frac{1}{4}S(1 - \bar{A}) = \sum_i eB_{\lambda i}(T_s)\Delta\lambda_i + \sum_j B_{\lambda j}(2^{-1/4}T_e)\Delta\lambda_j \quad (1)$$

Here B_λ is the Planck specific intensity, and the wavelength intervals $\Delta\lambda$ are chosen to pack with adequate density those wavelength regions where B_λ is changing rapidly. The equation is solved iteratively for T_s on an electronic computer. The adopted step-function approximation to the actual nongray absorption spectrum, which is due to rotation-vibration transitions in Earth's atmosphere, is compared with the measured transmission spectrum in (*1*). The resulting values of T_s are shown in Table 1. The correct value of e is, from studies of a wide variety of minerals (*2*), closer to 0.9 than to 1.0. Extensive calculations (*3*) based on measurements made from Earth yield values for $\bar{A}$ of 0.33 to 0.35, and an analysis of observations made over 5 years by meteorological satellites (*4*) yields 0.30 for $\bar{A}$. Since we are concerned with differential effects, we have adopted $\bar{A} \simeq 0.35$ to secure agreement with the observed T_s in our approximation (*5*).

The solar constant is varying; the luminosity, L, of the sun has increased by about 40 percent in geologic time (*6*). This variation has profound consequences for the surface temperatures of the terrestrial planets (*7*). The main-sequence brightening of the sun is one of the most reliable conclusions drawn from the modern theory of stellar evolution, which explains in considerable detail the observed Hertzsprung-Russell diagram. The models of solar evolution used in this report give an age for the sun in excellent agreement with the age determined on independent grounds for Earth, the moon, and the meteorites. The principal uncertainties in such calculations are in the age of the sun and its initial abundance of helium. Much larger possible errors in such parameters as thermonuclear reaction rates or opacities have much smaller effects on dL/dt (*8*). Katz (*8*) concludes that $(1/L)$ (dL/dt) is in error by at most 25 percent for the best contemporary evolutionary models. A variety of calculations of main-sequence solar evolution give a variation, ΔL, of 30 to 60 percent over geologic time (*6*). The best present estimate of ΔL is 40 ± 10 percent. For most of the following calculations, we conservatively adopt $\Delta L = 30$ percent.

We then run the sun backward through time and assume initially that the terrestrial atmospheric composition, e, and $\bar{A}$ remain constant. The results from Eq. 1 are shown in Fig. 1. We see that the global temperature of Earth dropped below the freezing point of seawater less than 2.3 aeons ago (1 aeon is 10^9 years); 4.0 to 4.5 aeons ago global temperatures were about 263°K. Had we used 50 percent for ΔL, the freezing point of seawater would have been reached about 1.4 aeons ago, and temperatures 4.0 to 4.5 aeons ago would have been about 245°K. Because of albedo instabilities (discussed below) it is unlikely that extensive liquid water could have existed anywhere on Earth with such global mean temperatures.

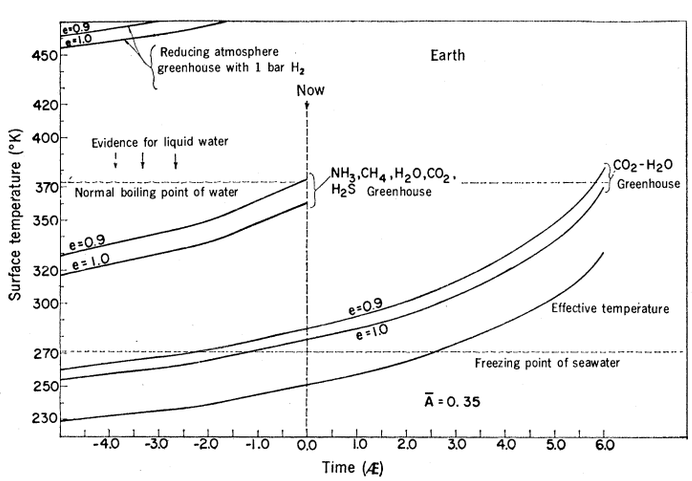
The presence of pillow lavas, mud cracks, and ripple marks in rocks from the Swaziland supergroup strongly implies abundant liquid water 3.2 aeons ago (*9*). The earliest known microfossils (*10, 11*), 3.2 ± 0.1 aeons old, include blue-green algae, which would be very difficult to imagine on a frozen Earth. Algal stromatolites, 2.0 to 2.8 aeons old, exist in various parts of the world (*12, 13*). If they are intertidal (*13*), there must have been at least meters of liquid water; if they are subtidal (*14*), much greater depths are im-

plied. The time required for surface water to accumulate sediments in geosynclinal trough suggests (*15*) the presence of extensive bodies of water on Earth 4 aeons ago or more. Finally, liquid water is almost certainly necessary for the origin of life; if we believe that life began shortly after the formation of Earth (*16*), liquid water must have been present for most of the period between 3.5 and 4.5 aeons ago. Thus, even using our most conservative value of ΔL, we find a serious discrepancy between theory and observation.

This discrepancy indicates an error in at least one of our initial assumptions. There are only three likely sources of error: S, $\bar{A}$, and the atmospheric composition. The solar constant is unlikely to be sufficiently in error to account for the discrepancy; the most probable value of S considerably widens the discrepancy. For small greenhouse corrections, the variation of δT_s *with* $\delta\bar{A}$ can be written $\delta\bar{A} = -4(1-\bar{A})\delta T_s/T_s$. Thus, for T_s 3.5 to 4 aeons ago to be increased from the values shown in Fig. 1 to the freezing point of seawater requires an albedo decrement of about 0.06 to 0.09; for $\Delta L = 50$ percent, an albedo decrement of more than 0.20 is required. Such albedos are unacceptably small. At global temperatures 10° or more below contemporary values, the cloud cover may be somewhat less, but the fraction of Earth covered by ice, snow, and glaciation will be very much larger. The albedos of thick deposits of ice or snow are 0.50 to 0.70. A decline in the global temperature of Earth is likely to increase rather than decrease the albedo, but in any case the albedo decline required to explain the discrepancy appears to be out of the question. Indeed, detailed global climatic models (*17*) suggest that a relative increase in $\bar{A}$ of only 2 percent is enough to induce extensive glaciation on Earth, which implies that the present climate is extremely sensitive to albedo.

This leaves changes in atmospheric composition as a possible explanation. Major variations in the CO_2 abundance will have only minor greenhouse effects because the strongest bands are nearly saturated. A change in the present CO_2 abundance by a factor of 2 will produce directly a 2° variation in surface temperature (*18*). The CO_2 abundance is highly controlled by silicate-carbonate equilibria; by buffering with seawater, which contains almost 100 times the atmospheric CO_2; and by the respiration and photosynthesis feedback loop (*19*). The negative exponential dependence of the vapor pressure of water on reciprocal temperature implies that for a lower global temperature there is no likelihood of gaining more water vapor than the contemporary global average, about 1 g cm^{-2}. The only surviving alternative appears to be that the atmosphere of Earth 1 or 2 aeons ago contained some constituent or constituents, not now present, with significant absorption in the middle infrared, in the vicinity of the Wien peak of Earth's thermal emission. A large number of candidate molecules were investigated. The ideal molecule should provide significant absorption in the present window from 8 to 13 μm, even in low abundances. Large amounts of CO, SO_2, O_3, and the various oxides of nitrogen are inadequate, as are many times the contemporary abundances of the homonuclear diatomic molecules O_2 and N_2, which have no permitted vibration-rotation transitions.

But, among the more reducing gases, NH_3 is very appropriate. A volume mixing ratio, $[NH_3]$, of about 10^{-5} at a pressure of 1 bar provides appreciable absorption at 8 to 13 μm. No other plausible reduced gas (for example, CH_4 or H_2S) provides comparable absorption. The present value of $[NH_3]$ is still in some question, but it appears to be less than 10^{-8} (*20*). At thermodynamic equilibrium in the present oxidizing atmosphere this mixing ratio would be much less than 10^{-35} (*21*). As is now the case for CH_4, a small steady-state abundance could be maintained if the



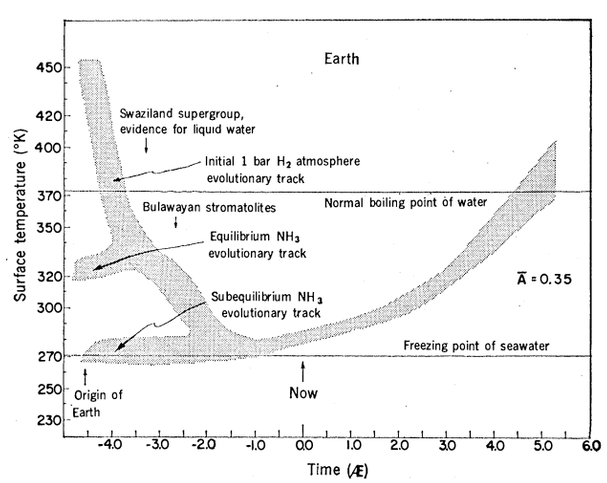


Fig. 1 (left). Calculated time-dependent model greenhouse effects for Russell-Bond albedo $\bar{A}$ about 0.35 and two surface infrared emissivities, $e = 0.9$ and $e = 1.0$, the former being more nearly valid (*2*) and giving the correct present global temperatures. The atmosphere of CO_2 and H_2O is assumed to contain the present abundances of these gases, pressure broadened by 1 bar of a foreign gas. The slightly reducing atmosphere has the same constituents with the addition of a 10^{-5} volume mixing ratio of NH_3, CH_4, and H_2S. In this case NH_3 is the dominant absorber. At the top is the greenhouse resulting from the addition of 1 bar of H_2 to the constituents already mentioned. The evidence for liquid water at 2.7 to 4.0 aeons (*Æ*) ago comes from a variety of geologic and paleontological data (*9–16*). The time evolution of the effective temperature is also displayed. All calculations are for $\Delta L = 30$ percent; for larger time-derivatives of the solar luminosity, the freezing point of seawater is reached in yet more recent times. Fig. 2 (right). Three derived evolutionary tracks for the temperature of Earth. As described in the text, the subequilibrium NH_3 track (less than 10^{-5} volume mixing ratio), while schematic, is thought to be most likely. The amplitude of global temperature oscillations in Mesozoic and Paleozoic glaciations is smaller than the width of the temperature curve shown. A runaway greenhouse effect occurs several aeons in our future.

molecule were generated at a high rate, as by biological activity (*21*), but this calculation does indicate the great thermodynamic instability of NH_3 in the present O_2 atmosphere. On the other hand, Bada and Miller (*22*) calculated NH_3 mixing ratios on the preoxygenic Earth by using clay mineral equilibria in the oceans and, independently, by assuming that the deamination of aspartic acid is reversed, since this amino acid is required for the origin and early evolution of life. They found the following approximate values for $[NH_3]$: 10^{-7} at 0°C, 3×10^{-5} at 25°C, and 3×10^{-4} at 50°C, in good accord with our requirements. Lower values of the NH_3 mixing ratio are possible because of ultraviolet photolysis (*23*), but the steady-state NH_3 abundance would have been maintained by an equilibrium between photolysis and production. An NH_3 mixing ratio even as small as 10^{-6} will produce a high-temperature equilibrium mesopause layer, somewhat analogous to the terrestrial ozone layer, and will also serve to protect other gases closer to the surface, notably water vapor, from photodissociation (*24*).

Accordingly, we calculated (*1*) greenhouse temperatures for atmospheres in which NH_3 is a minor constituent. We assumed that water vapor is present in approximately its present abundance, determined largely by T_s and by meteorology; that CO_2 is present in approximately its present abundance, maintained by mineral equilibria and oceanic buffering reactions; and that CH_4 and H_2S are present in amounts comparable to that of NH_3. Because CH_4 and H_2S are not as effective absorbers, their presence does not significantly affect the results. The surface temperature in this (slightly) reducing atmosphere is shown as a function of time in Fig. 1. We see that such an atmosphere is entirely adequate to resolve the discrepancy and keep the global temperature of Earth well above the freezing point of water, which confirms a conjecture (*25*) made by one of us some years ago (*26*).

If even small quantities of hydrogen were present in the early atmosphere, the primitive exosphere would, by diffusive equilibrium, be dominated by H. Because of the high thermal conductivity of hydrogen, such an exosphere would cool very efficiently by conduction downward; in addition, the presence of polyatomic reduced molecules with strong emission features in the middle and far infrared would thermostat such an exosphere efficiently. A primitive reducing atmosphere would have been stable against gravitational escape for periods approaching 1 aeon. Accordingly, there may have been a significant epoch in the early history of Earth in which H_2 was an important constituent of the atmosphere. It is estimated (*24*) that the maximum H_2 mixing ratio in the lower atmosphere was 0.10 to 0.15 after a possible initial period in which exospheric blowoff occurred because the gas kinetic energy of H_2 exceeded its gravitational potential energy. We have no way of knowing the $[H_2]$ history in early times; for heuristic purposes we calculate the additional greenhouse effect due to 1 bar of H_2. At such a pressure, permitted quadrupole and pressure-induced dipole transitions produce major absorptions at longer wavelengths than 7.5 μm. One bar of H_2 fills in the long-wavelength windows in the atmospheric greenhouse, producing nearly complete absorption at all wavelengths longer than 4.9 μm and increasing T_s well above the normal boiling point of water.

Table 1. Calculated contemporary surface temperatures, T_s, for Earth; e is the mean emissivity of Earth's surface in the middle infrared; $\bar{A}$ is its Russell-Bond spherical albedo.

e	T_s (°K)	
	$\bar{A} = 0.35$	$\bar{A} = 0.30$
0.9	286	292
1.0	278	284

Accordingly, we are left with three evolutionary tracks for the temperature history of primitive Earth (Fig. 2):

1) With an initial extensive H_2 atmosphere, Earth originates at temperatures above the normal boiling point of water, even in the absence of endogenous heat sources. The temperature rapidly declines in the first aeon because of the escape of hydrogen into space, and then, about 3.5 aeons ago, enters a milder climate dominated by the NH_3 and water greenhouses. The photodissociation, reaction, and oxidation of the reduced gases of such an atmosphere produce a gradual decline in temperatures, and the planet approaches the evolutionary track for the present greenhouse constituents, perhaps 1 to 2 aeons ago. We do not know whether as much as 1 bar of H_2 could have been retained by Earth during its formation, but we are skeptical about this evolutionary track, because it prohibits temperatures suitable for the origin of life even close to epochs when the prokaryotes—organisms requiring a major time interval for their evolutionary antecedents—were present in abundance.

2) An insignificant amount of H_2 is present initially and the atmospheric greenhouse is dominated by H_2O and by NH_3 in its calculated equilibrium abundance, which then declines as before toward the CO_2/H_2O track.

3) Ammonia is initially present in subequilibrium abundances, because of photodissociation and reaction with other atmospheric constituents. The NH_3 absorption, pressure-broadened with a foreign gas at 1 bar, declines appreciably between $[NH_3] \sim 10^{-5}$ and $[NH_3] \lesssim 10^{-6}$. The flatness of this third track represents a rough balance between the slow decline of $[NH_3]$ and the slow increase of L. Calculations (*27*) of the thermodynamic stability of a number of amino acids in aqueous phase show a variation of several orders of magnitude in half-life for a decline of 10° or 20°. The subequilibrium NH_3 in the third track therefore (i) keeps T_s above the freezing point of water; (ii) is responsive to comments (*23*) on the photodissociation of NH_3; and (iii) provides increases of many orders of magnitude in the concentrations of organic constituents in the primitive seas, thus enhancing the likelihood of the origin of life on primitive Earth. The subsequent decline in NH_3 abundance is most likely due to oxidation by O_2 produced in green plant photosynthesis. The evolution of green plants could have significantly cooled off Earth.

Our conclusions would not be significantly different if we had used larger values of ΔL. With such values, however, the argument requires small quantities of NH_3 in Earth's atmosphere almost up to the Precambrian-Cambrian boundary. Because of the thermodynamic instability of NH_3 in an excess of O_2 (*21*), such results suggest the absence of contemporary values of $[O_2]$ for a major fraction of the history of Earth. This is consistent with a variety of other evidence—including data on banded iron formations (*13, 19, 28*), on the oxidation of uraninite (*19, 28, 29*), and on the relatively small ^{34}S enrichment of Swaziland barites (*30*)—and makes quite implausible the suggestion (*31*) of an early oxidizing atmosphere on Earth. A long epoch in which small quantities of such reduced gases as NH_3

might coexist with small quantities of photosynthetically or photolytically produced O_2 is not excluded. Our conclusion that significant quantities of O_2 did not arise until 1 to 2 aeons ago is in excellent accord with the conclusions of Cloud (*13*), based on the chronology of banded iron formations and the oldest fossil eukaryotes. By this period an extensive evolutionary development of catalase, peroxidases, and peroxisomes to defend the cells against oxidation products must have occurred (*16, 32*), and selection pressures for defenses against or avoidance (at oceanic depths) of solar ultraviolet light gradually eased (*16, 33*).

The presence of NH_3 in Earth's atmosphere for most of the Precambrian has a range of biological implications. It is, of course, a very useful precursor compound for prebiological organic chemistry. There is strong evidence (*34*) that NH_3 is the key intermediary in the fixation of atmospheric N_2. By the Horowitz (*35*) hypothesis on the backward evolution of enzymatic reaction chains, this must imply an earlier evolutionary stage in which NH_3 was available, which is consistent with the present argument. While most microorganisms can utilize NH_3 directly as a source of N_2, it is largely the prokaryotes that are N_2 fixers (*36*). The hydrogenase-ferredoxin system for N_2 fixation is not specific for N_2, and can reduce C_2H_2, NO_2, azides, and cyanides (*34*); its original function, in times of excess NH_3, may not have been N_2 fixing.

Analogous calculations have been performed for Mars. The present greenhouse effect on Mars is due almost entirely to CO_2; the water-vapor abundance of a few tens of precipitable micrometers makes no significant contribution. The total greenhouse effect is only a few degrees Kelvin; T_s on Mars is roughly 210° to 220°K, depending on the choice of $\bar{A}$. The meridional and diurnal temperature gradients on Mars are both extreme because of the paucity of liquid water and the thin atmosphere. Thus, temperatures much warmer than the global mean exist on Mars, but could not have existed extensively on primitive Earth. Earlier conditions on Mars may have been much more clement. After very rapid blowoff of a possible initial H_2 atmosphere, the equilibrium NH_3 evolutionary tracks give T_s near the freezing point of seawater. There appears to be an epoch in the first aeon after the origin of Mars in which global temperatures were not far from the freezing point of seawater and in which the origin of life may have occurred, as it did on primitive Earth in the same period. Because of the smaller martian gravitational acceleration, photodissociation and escape should have changed the intermediate oxidation state atmosphere much more rapidly on Mars than on Earth. Any martian organisms would have had to face low temperatures and increasingly inaccessible liquid water. Over geologic time, Mars could have lost meters to tens of meters of liquid water by photodissociation, escape of hydrogen, and oxidation of surface material (*37*); these are not oceans, but they are respectable depths. It is a debatable but hardly quixotic contention that martian organisms may have been able to adapt to the increasingly rigorous martian environment and may still be present (*38*). Fairly abundant liquid water early in the history of Mars would also be helpful in explaining the puzzling large-scale erosion of the oldest martian craters—a phenomenon distinctly different from lunar crater erosion (*39*).

These calculations have also been extended into the future of Earth and Mars. As the sun continues to evolve, the surface temperature of Earth will increase; more water vapor will be put into the atmosphere, enhancing the atmospheric absorption; and eventually a runaway greenhouse effect will occur, as previously discussed for Venus (*40, 41*). According to calculations by Pollack (*41*) a value of the solar constant 1.5 times the present terrestrial value is adequate to cause such a runaway for a planet with 50 percent cloud cover. For $\Delta L = 30$ percent, this event occurs about 4.5 aeons in our future; for $\Delta L = 50$ percent, 3 aeons in our future. Earth will then resemble contemporary Venus, but with an atmospheric pressure of 300 bars of steam. It is difficult to imagine what could be done to prevent this runaway, even with a very advanced technology (perhaps a progressive increase in atmospheric aerosol content), but at the same epoch the global temperature of Mars will become very similar to that of present-day Earth. If there are any organisms left on our planet in that remote epoch, they may wish to take advantage of this coincidence.

CARL SAGAN
GEORGE MULLEN*
Laboratory for Planetary Studies, Cornell University, Ithaca, New York

References and Notes

1. C. Sagan and G. Mullen, Report 460, Center for Radiophysics and Space Research, Cornell University (1971).
2. R. J. P. Lyon, NASA Contractor Report CR-100, Stanford Research Institute (1964).
3. J. London, Final Report, contract AF 19(122)-165, Department of Meteorology and Oceanography, New York University (1957); ——— and T. Sasamori, in *Space Research*, K. Kondratyev, R. Rycroft, C. Sagan, Eds. (Akademie Verlag, Berlin, 1971), vol. 11. In standard textbooks, R. M. Goody [*Atmospheric Radiation* (Clarendon Press, Oxford, 1964)] adopts a value for $\bar{A}$ of about 0.4, and K. Ya. Kondratyev [*Radiation in the Atmosphere* (Academic Press, New York, 1969)] chooses $\bar{A}$ about 0.35.
4. T. H. von der Haar and V. Suomi, *J. Atmos. Sci.* **28**, 305 (1971).
5. While we believe this step-function approximation to be adequate for the present discussion, we are pursuing a more detailed set of calculations, which allows for much finer wavelength and altitude grids.
6. Estimated values of the increase in solar luminosity, ΔL, over geologic time are: 60 percent [M. Schwarzschild, R. Howard, R. Härm, *Astrophys. J.* **125**, 233 (1957); (*7*)]; 30 percent [F. Hoyle, in *Stellar Populations*, D. J. K. O'Connell, Ed. (Specola Vaticana, Vatican City, 1958), p. 223; C. B. Haselgrove and F. Hoyle, *Mon. Not. Roy. Astron. Soc.* **119**, 112 (1959); D. Ezer and A. G. W. Cameron, *Can. J. Phys.* **43**, 1497 (1965)]; 50 percent [I. Iben, in *Stellar Evolution*, R. F. Stein and A. G. W. Cameron, Eds. (Plenum, New York, 1966), p. 237]; 35 percent [J. H. Bahcall and G. Shaviv, *Astropys. J.* **153**, 113 (1968)]; 40 percent [I. Iben, *Ann. Phys. New York* **54**, 164 (1969)]. A weighted mean of these values is 40 percent ± 10 percent.
7. One of the earliest recognitions of this possibility occurs in M. Schwarzschild's *Structure and Evolution of the Stars* [(Princeton Univ. Press, Princeton, N.J., 1958), p. 207] "We may thus conclude that the solar luminosity must have increased by about a factor 1.6 during the past five billion years. Can this change in the brightness of the sun have had some geophysical or geological consequences that might be detectable?"
8. The discrepancy between theory and experiment in the ^8B solar neutrino flux depends insensitively on the parameters which strongly affect dL/dt. A wide range of postulated convective cores, extending to 0.4 solar radii, if essentially constant in time, do not significantly affect dL/dt. J. Katz has examined many other conceivable sources of error in the theory of solar evolution, including the possibility that the sun may be burning other elements in addition to hydrogen; influences of rotational and magnetic energy and of quarks; errors in the weak-interaction theory; variations with time of the Newtonian gravitational constant, the fine-structure constant, the strong and weak coupling constants, the ratio of electron to proton masses, and other physical constants; and the time dependence of the size of a solar convective core.
9. J. G. Ramsay, *Trans. Geol. Soc. S. Afr.* **66**, 353 (1963).
10. J. W. Schopf and E. S. Barghoorn, *Science* **156**, 508 (1967).
11. J. W. Schopf, *Biol. Rev. Cambridge Phil. Soc.*, in press.
12. P. F. Hoffman, *Geol. Surv. Can. Pap. 68-42* (1969); J. W. Schopf (*11*).
13. P. Cloud, *Science* **160**, 729 (1968).
14. M. R. Walter, *Science* **170**, 1331 (1970).
15. W. L. Donn, B. D. Donn, W. G. Valentine, *Bull. Geol. Soc. Amer.* **76**, 287 (1965).
16. C. Sagan, *Radiat. Res.* **15**, 174 (1961).
17. W. D. Sellers, *J. Appl. Meteorol.* **8**, 392 (1969); M. I. Budyko, *Tellus* **21**, 611 (1969); M. I. Budyko, *J. Appl. Meteorol.* **9**, 310 (1970).
18. S. Manabe, in *Global Effects of Environmental Pollution*, S. F. Singer, Ed. (Springer-Verlag, New York, 1970), p. 25.
19. H. C. Urey, *The Planets* (Yale Univ. Press, New Haven, 1952); H. D. Holland, in preparation; F. S. Johnson, in *Global Effects of Environmental Pollution*, S. F. Singer, Ed. (Springer-Verlag, New York, 1970), p. 4.
20. G. E. Hutchinson, in *The Earth as a Planet*,

G. P. Kuiper, Ed. (Univ. of Chicago Press, Chicago, 1954), p. 371.
21. E. R. Lippincott, R. V. Eck, M. O. Dayhoff, C. Sagan, *Astrophys. J.* **147**, 753 (1967).
22. J. L. Bada and S. L. Miller, *Science* **159**, 423 (1968).
23. P. H. Abelson, *Proc. Nat. Acad. Sci. U.S.A.* **55**, 1365 (1966).
24. W. E. McGovern, *J. Atmos. Sci.* **26**, 623 (1969).
25. C. Sagan, in I. S. Shklovskii and C. Sagan, *Intelligent Life in the Universe* (Holden-Day, San Francisco, 1966), pp. 222–223.
26. Donn *et al.* (*15*) unaccountably concluded that the amount of gas-phase NH_3 in equilibrium with seawater would yield an insignificant greenhouse effect.
27. J. Bada, in *Proceedings of the 5th Conference on the Origins of Life, Belmont, Md., April 1971*, L. Margulis, Ed. (Gordon & Breach, New York, in press).
28. M. G. Rutten, *The Geological Aspects of the Origin of Life on Earth* (Elsevier, Amsterdam, 1962). But R. T. Cannon [*Nature* **205**, 586 (1965)] has described occasional oxidized red beds more than 2 aeons old, which suggests at least local oxidizing conditions in this epoch.
29. P. Ramdohr, *Abh. Deut. Akad. Wiss. Berlin Kl. Chem. Geol. Biol.* **3**, 35 (1958); D. R. Derry, *Bull. Geol. Soc. Amer.* **70**, 1587 (1959).
30. E. C. Perry, J. Monster, T. Reimer, *Science* **171**, 1015 (1971).
31. L. van Valen, *Science* **171**, 439 (1971).
32. See also J. M. Olson, *ibid.* **168**, 438 (1970).
33. See also L. V. Berkner and L. C. Marshall, *J. Atmos. Sci.* **22**, 225 (1965).
34. See, for example, A. L. Lehninger, *Biochemistry* (Worth, New York, 1970), pp. 560–561.
35. N. H. Horowitz, *Proc. Nat. Acad. Sci. U.S.A.* **31**, 153 (1945).
36. R. Y. Stanier, M. Doudoroff, E. A. Adelberg, *The Microbial World* (Prentice-Hall, New York, ed. 2, 1963).
37. C. Sagan, in *International Dictionary of Geophysics*, S. K. Runcorn, Ed. (Pergamon, London, 1967), p. 97; C. Barth, A. Stewart, C. Hord, A. Lane, *Icarus*, in press.
38. See, for example, W. Vishniac, K. C. Atwood, R. M. Bock, H. Gaffron, T. H. Jukes, A. D. McLaren, C. Sagan, H. Spinrad, in *Biology and the Exploration of Mars*, C. S. Pittendrigh, W. Vishniac, J. P. T. Pearman, Eds. (Publication No. 1296, National Academy of Sciences–National Research Council, Washington, D.C., 1966); J. Lederberg and C. Sagan, *Proc. Nat. Acad. Sci. U.S.A.* **48**, 1473 (1962); C. Sagan, "Life," in *Encyclopaedia Britannica* (Benton, Chicago, 1970); *Icarus* **15**, 511 (1971).
39. B. C. Murray, L. A. Soderblom, R. P. Sharp, J. A. Cutts, *J. Geophys. Res.* **76**, 313 (1971); C. R. Chapman, J. B. Pollack, C. Sagan, *Astron. J.* **74**, 1039 (1969); A. Dollfus, R. Fryer, C. Titulaer, *C. R. H. Acad. Sci. Ser. B* **270**, 424 (1970); C. Sagan and J. Veverka, *Icarus* **14**, 222 (1971); W. K. Hartmann, *ibid.* **15**, 410 (1971).
40. C. Sagan, Technical Report TR 32-34, Jet Propulsion Laboratory, Pasadena (1960); A. P. Ingersoll, *J. Atmos. Sci.* **26**, 1191 (1969); S. I. Rasool and C. deBerg, *Nature* **226**, 1037 (1970).
41. J. B. Pollack, *Icarus* **14**, 295 (1971).
42. We are grateful to E. E. Salpeter, J. W. Schopf, M. Schwarzschild, and J. Bahcall for stimulating conversations; to B. N. Khare for the laboratory infrared spectra; to L. D. G. Young for the calculated H_2 spectra; and to J. Katz for a comprehensive discussion of the reliability of current models of main-sequence solar evolution. This research was supported by the Atmospheric Science Section, National Science Foundation, under grant GA 23945.
* Present address: Department of Physics, Mansfield State College, Mansfield, Pennsylvania 16993.

17 December 1971; revised 21 April 1972

A Binding Protein for Fatty Acids in Cytosol of Intestinal Mucosa, Liver, Myocardium, and Other Tissues

Abstract. *A protein of molecular weight ~ 12,000 which binds long-chain fatty acids and certain other lipids has been identified in cytosol of intestinal mucosa, liver, myocardium, adipose tissue, and kidney. Binding is noncovalent and is greater for unsaturated than for saturated and medium-chain fatty acids. This protein appears to be identical with the smaller of two previously described cytoplasmic anion-binding proteins. Binding of long-chain fatty acids by this protein is greater than that of other anions tested, including sulfobromophthalein, and does not depend on negative charge alone. The presence of this binding protein may explain previously observed differences in intestinal absorption among fatty acids, and the protein may participate in the utilization of long-chain fatty acids by many mammalian tissues.*

Translocation of fatty acids from cell surface to endoplasmic reticulum and mitochondria is fundamental to the intestinal absorption of lipids and to the utilization of free fatty acids in plasma by liver, muscle, and other tissues. However, although long-chain fatty acids are at best poorly soluble in aqueous media, a mechanism to account for the apparent facility with which they traverse the cytosol (aqueous cytoplasm) has not been identified.

In studies of the intestinal absorption of long-chain fatty acids (*1, 2*), we observed that although saturated and unsaturated fatty acids were taken up by everted jejunal sacs at equal rates, unsaturated fatty acids were esterified more rapidly. However, our studies and those of others (*3*) indicated that these results could not be explained by corresponding differences in the activation of fatty acids by microsomal fatty acid–coenzyme A (CoA) ligase (*4*). Accordingly, we postulated (*2*) that apparent differences in rates of esterification might be due to different rates of translocation of fatty acids from the microvillus membrane to the site of their activation in the endoplasmic reticulum. As a result, we discovered a binding protein for long-chain fatty acids in the cytosol of jejunal mucosa and of other mammalian tissues (*5*).

Male Sprague-Dawley rats—fasting if intestine was to be studied, otherwise nonfasting—were killed by decapitation. The proximal half of the small intestine, distal to the ligament of Treitz, was removed and flushed with 40 ml of 0.01*M* phosphate buffer in 0.154*M* KCl (*p*H 7.4, 4°C). Mucosa was extruded, weighed, homogenized in three volumes of buffer, and centrifuged at 105,000*g* for 2 hours. The supernatant, exclusive of floating fat, was used for gel filtration. The liver was perfused in situ through the portal vein with cold buffer before homogenization and ultracentrifugation as just described. Appropriate ligands (Figs. 1 and 2) were added in vitro to 105,000*g* supernatants, and the mixture was subjected immediately to gel filtration on Sephadex G-75. Protein concentration in the column effluent was measured as absorbance at 280 nm; radioactivity was determined by liquid scintillation spectrometry; sulfobromophthalein (BSP) was measured as absorbance at 580 nm after alkalinization.

Sephadex G-75 chromatography of rat jejunal supernatant with [^{14}C]oleate showed association of radioactivity with a protein of low molecular weight, which we have designated "fatty acid binding protein" (FABP) (Fig. 1). Variable radioactivity was also associated with macromolecules (including lipoproteins) in the excluded (void) volume, and with residual albumin in the tissue homogenate. By lipid extraction (*6*) and thin-layer chromatography of the FABP peak, more than 95 percent of ^{14}C was recovered as free fatty acid, a result indicating that binding was noncovalent and not the result of prior conversion to fatty acyl–CoA or other derivatives. A FABP with virtually identical elution characteristics was demonstrated in liver supernatant.

An estimation of the molecular weight of FABP was obtained by comparing its relative elution volume (V_e/V_o) with that of proteins of known molecular weight on Sephadex G-75. Both jejunal and hepatic FABP were consistently eluted in a volume ($V_e/V_o = 2.10 \pm .02$) slightly greater than that of cytochrome c (horse heart, Sigma, molecular weight 12,400, $V_e/V_o = 2.08 \pm .02$); this indicates a molecular weight of about 12,000. This value must be regarded as an approximation, however, because elution characteristics of proteins on gel filtration show a