

The Evolution of the Atmosphere of the Earth

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Computer simulations of the evolution of the Earth's atmospheric composition and surface temperature have been carried out. The program took into account changes in the solar luminosity, variations in the Earth's albedo, the greenhouse effect, variation in the biomass, and a variety of geochemical processes. Results indicate that prior to two billion years ago the Earth had a partially reduced atmosphere, which included N_2 , CO_2 , reduced carbon compounds, some NH_3 , but no free H_2 . Surface temperatures were higher than now, due to a large greenhouse effect. When free O_2 appeared the temperature fell sharply. Had Earth been only slightly further from the Sun, runaway glaciation would have occurred at that time. Simulations also indicate that a runaway greenhouse would have occurred early in Earth's history had Earth been only a few percent closer to the Sun. It therefore appears that, taking into account the possibilities of either runaway glaciation or a runaway greenhouse effect, the continuously habitable zone about a solar-type star is rather narrow, extending only from roughly 0.95 to 1.01 AU.

I. INTRODUCTION

Since the papers of Brown (1952) and Rubey (1951) it has become generally accepted that the Earth lost any primordial atmosphere it may have had, and that the present atmosphere is derived from materials degassed from the interior. This paper is based on a set of attempts to follow, by a computer simulation, the evolution of the Earth's atmosphere over the last 4.5 billion years, with particular emphasis on changes in the chemical composition and mean surface temperature.

Many factors have influenced that evolution. Some of the factors considered explicitly in the computer program were: the rate of degassing from the interior, and the mean composition of the juvenile volatiles; condensation of water vapor into oceans; solution of atmospheric gases in the oceans; photodissociation of water vapor in the

upper atmosphere; escape of hydrogen from the exosphere; chemical reactions between atmospheric gases; the presence of life, and variations in the biomass; photosynthesis, and burial of organic sediments; the Urey reaction; oxidation of surface minerals; variations in solar luminosity; variations in the Earth's albedo; and the greenhouse effect.

This project is perhaps the first attempt to include such a wide range of processes in simulating the evolution of our atmosphere. It should be pointed out that each of the factors mentioned above is important, and that a change of 20% in any one of them would have resulted in a substantially different atmosphere than we now have.

The results of the computer simulations indicate that it is possible to understand the evolution of our atmosphere to its present condition through the interplay of known processes, and that no extraordinary

events (subsequent to the formation of the Earth and its core) need be postulated.

It also appears that the evolutionary process is very sensitive to the Earth-Sun distance. Had the Earth been situated slightly closer to the Sun, a runaway greenhouse effect would have occurred fairly early in Earth's history [a result obtained earlier by Rasool and de Bergh (1970)]. Had the Earth's orbit been slightly larger instead, then runaway glaciation would have occurred about two billion years ago.

II. ASSUMPTIONS AND APPROXIMATIONS USED IN COMPUTER SIMULATION

A. Degassing

Almost all of the argon in the Earth's atmosphere is derived from the radioactive decay of K_{40} . The analysis in Turekian (1964) leads to the conclusion that the rate of supply of argon to the atmosphere can be approximated by

$$R_{\text{argon}} = K_1[\exp(-K_2t) - \exp(-K_3t)]. \quad (1)$$

The computer program used the values $K_1 = 2.64 \times 10^{10} \text{ g yr}^{-1}$, $K_2 = 2.81 \times 10^{-11} \text{ yr}^{-1}$, $K_3 = 5.51 \times 10^{-10} \text{ yr}^{-1}$, which are equivalent to Turekian's figures.

The only other volatile elements kept track of in the program were carbon, oxygen, hydrogen and nitrogen. It was assumed that the degassing rate of each of those has been proportional to $e^{-t/\lambda}$. We estimated λ , the time constant for degassing, to be 800 million years,¹ a slightly shorter time than the 862 million years computed by Li (1972).

For simplicity it was assumed that the net composition of *juvenile* volatiles (argon aside) has been constant through geologic time. Since the actual composition of the juvenile volatiles is not known exactly,

¹ A few computer runs were made using much smaller values for λ . All such runs resulted in a runaway greenhouse effect occurring at an early stage of Earth's history.

many separate computer runs were made, using a variety of plausible compositions.

B. Condensation of Water Vapor

As the pressure increased, most of the degassed H_2O condensed to form oceans. In the program, the boiling point curve of water was approximated by the formula (derived from Hass and Newton, 1966-1967)

$$\text{bp} = 373.15 \times (5.78 - 0.15 \log P) / (5.78 - 1.15 \log P), \quad (2)$$

where P is the total pressure in atmospheres.

Assuming liquid water is present, the amount of H_2O remaining in vapor form in the atmosphere will be approximately

$$Q_{\text{water vapor}} = Q_1 \exp[Q_2(\langle T_{\text{surf}} \rangle - 288)], \quad (3)$$

where $\langle T_{\text{surf}} \rangle$ is the mean surface temperature of the Earth (in $^\circ\text{K}$), $Q_2 = 0.0698 \text{ K}^{-1}$, and $Q_1 = 1.258 \times 10^{19} \text{ g}$. Equation (3) approximates the results of numerical integrations in which the atmosphere (up to the tropopause) was divided into horizontal slices and the water vapor content of each slice computed in accordance with its mean temperature and pressure. It was assumed that the mean *relative* humidity of the troposphere remains constant in time, although the absolute humidity depends on T_{surf} .

C. Photodissociation and Escape of Hydrogen

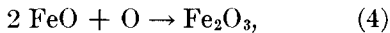
Free hydrogen escapes from the exosphere in a geologically short time (Spitzer, 1952). A slower, but still geochemically important, process is the photodissociation of water molecules in the upper atmosphere, followed by the loss of hydrogen. To estimate the rate of photolysis the calculations of Brinkmann (1969) were employed.

Of the hydrogen atoms released by photolysis, only a fraction f_e escape; the others recombine before escaping. The expected value of f_e is difficult to compute theoretically. We have used $f_e = 6.7\%$.

That value (in conjunction with the photolysis rate calculations of Brinkmann) matches the number of hydrogen atoms now escaping from the exosphere—which is about 10^8 atoms $\text{cm}^{-2} \text{sec}^{-1}$, according to Liu and Donahue (1974).

D. Oxidation of Surface Minerals

Most iron atoms in igneous rocks are in the ferrous state. In comparison, sedimentary rocks contain a far higher proportion of ferric iron. The conversion of ferrous to ferric ion, represented schematically by



removes oxygen from the atmosphere-ocean system. The quantity so removed, over the course of geologic time, is much larger than the amount of free oxygen now in the atmosphere. Perhaps even more important is the conversion of sulfides to sulfates, which has also acted as a sink for large quantities of oxygen.

The program used as an estimate of the net rate of oxidation of surface minerals

$$R_{\text{oxid}} = X_1 + X_2 \cdot [\text{O}_2], \quad (5)$$

where $[\text{O}_2]$ represents the mass of free oxygen in the atmosphere, and X_1 and X_2 are constants. We chose the value of X_1 to be quite small, since R_{oxid} was presumably low before free oxygen appeared in the atmosphere. X_2 was estimated at slightly over $5 \times 10^{-8} \text{ yr}^{-1}$.

If $[\text{O}_2]$ is very large then (5) overestimates R_{oxid} , as in reality R_{oxid} would then be limited by the rate at which fresh minerals can be brought to the surface and eroded. The restriction was therefore added: $R_{\text{oxid}} \leq X_3$, where X_3 is about $2.9 \times 10^{13} \text{ g yr}^{-1}$.

E. Urey Reaction

It has been suggested by Urey (1951, 1952) and others that the partial pressure of CO_2 in the atmosphere is governed by reactions between CO_2 and silicates. Such

reactions might be represented schematically by



(Of course the metal involved need not be calcium.) Such reactions will take place much more rapidly in solution, i.e., if there are oceans. The effect of such reactions is to remove CO_2 from the atmosphere-ocean system, while building up deposits of limestone, dolomite, and other sedimentary carbonates.

In the computer simulation, the *net* rate at which dissolved CO_2 is deposited has been approximated by

$$R_{\text{urey}} = U_1 \cdot ([\text{CO}_2] - [\text{CO}_2]_{\text{equil}}), \quad (7)$$

where $[\text{CO}_2]$ is the actual quantity of dissolved CO_2 at a given time, while $[\text{CO}_2]_{\text{equil}}$ is the quantity at which equilibrium would prevail (averaging over the oceans as a whole). For the constant U_1 , which was treated as a free parameter (see Section V) the value $6 \times 10^{-9} \text{ yr}^{-1}$ was adopted.

At present, limestone is being deposited in some parts of the ocean while it is being redissolved in other parts. We might therefore guess that under current conditions $[\text{CO}_2]_{\text{equil}}$ is not far from the actual quantity of CO_2 in the oceans, which is estimated to be about $1.3 \times 10^{20} \text{ g}$ (El Wardani, 1972). The value of $[\text{CO}_2]_{\text{equil}}$ at a given time depends, among other things, on the mass of the oceans.

It was assumed that if $[\text{CO}_2]$ should ever fall below $[\text{CO}_2]_{\text{equil}}$ limestone will be redissolved quickly, i.e., in such circumstances a higher proportionality constant, U_2 , would prevail. In the absence of oceans (e.g., on Venus) an equation similar to (7) might be applicable, but with a very low proportionality constant, U_3 .

F. Presence of Life

In the program it was assumed that the only geochemical requirements necessary for photosynthetic organisms to arise on

Earth were:

(i) the existence, somewhere on the surface of the planet, for at least 800 million years, of considerable quantities of liquid water at a temperature of under 42°C;²

(ii) the presence, during the same interval, of reasonable quantities of carbon and nitrogen (or their compounds) in the atmosphere-ocean system; and

(iii) the absence, during the same interval, of free oxygen from the atmosphere. [The necessity for this restriction seems generally acknowledged. See, for example, Miller and Orgel (1974), p. 119.]

It was also assumed that once life arose it would continue and evolve as long as the first two requirements were met.

Since H₂O is abundant on Earth, requirement (i) will probably be satisfied unless $\langle T_{\text{surf}} \rangle$ rises above about 365°K (making even the poles too warm), or falls below about 258°K (causing even the equatorial regions to be ice-covered).

G. Limits on the Biomass

It was suggested by Berkner and Marshall (1964, 1965) that, in the period before free oxygen and ozone appeared in the Earth's atmosphere, ultraviolet radiation from the Sun made the continents uninhabitable. Indeed, since 10 m of water were required to reduce the intensity of uv radiation to tolerable levels, an important portion of the hydrosphere was uninhabitable also. If the Berkner and Marshall hypothesis is correct, then the solar uv radiation has set a limit (varying through geologic time in accordance with the oxygen and ozone content of the atmosphere) on the possible biomass at any given time.

To apply their theory, one must first compute D_{water} , the depth below the surface

² Because of denaturation of proteins it is difficult for most simple organisms to withstand much higher temperatures. The figure of 800 million years comes from Junge *et al.* (1975).

of the hydrosphere at which the intensity of solar uv radiation will be reduced to a tolerable level. First assume that

$$I_{\text{tolerable}} = I_{\text{top}} \cdot \exp(-\tau_{\text{ozone}}) \cdot \exp(-\tau_{\text{water}}), \quad (8)$$

where I_{top} is the intensity at the top of the atmosphere and $I_{\text{tolerable}}$ is the maximum intensity tolerable. Assuming $\tau_{\text{water}} \propto D_{\text{water}}$, after some rearrangement one obtains

$$D_{\text{water}} = D_1 + D_2 \ln(L/L_{\text{now}}) - D_3([\text{O}_3]/[\text{O}_3]_{\text{now}})^{1/2}, \quad (9)$$

where D_1 , D_2 , D_3 are constants and L represents the luminosity of the Sun. In the program the values $D_1 = 10$ m, $D_2 = 1.4$ m, and $D_3 = 33.2$ m were employed. [Those values were derived from the discussion and graphs in Berkner and Marshall (1964).]

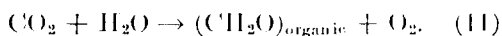
Whenever $D_{\text{water}} < 0$, the continents are inhabitable. It was assumed that in such circumstances B_{land} , the carbon content of the land biomass, will have approximately its present value, which according to Whittaker and Likens (1973) is about 8.72×10^{17} g. For $D_{\text{water}} > 0$ we set $B_{\text{land}} = 0.0$ and approximated B_{ocean} , the carbon content of the marine biomass, by

$$B_{\text{ocean}} = B_{\text{now}} \cdot [1.0 - (D_{\text{water}}/D_{\text{bot}})]. \quad (10)$$

D_{bot} , the depth above which most marine organisms live, was estimated at 20 m; B_{now} , the present value of B_{ocean} , was estimated by Whittaker and Likens to be about 1.76×10^{16} g. Since the absence of plankton from the upper layer of the ocean will also reduce the quantity of life in the lower regions, we reduced B_{ocean} by a further factor of 4.0 whenever D_{water} was greater than 30 cm.

H. Photosynthesis and the Burial of Organic Sediments

Photosynthesis might be represented schematically by



(The reverse reaction, of course, occurs in respiration, forest fires, etc.) Most organic material is fairly promptly recycled; however a small portion is buried. Coal formation might be represented schematically by



(Actually, most sedimentary carbon is in black shales, rather than coal deposits, but the effect is the same for purposes of the present computation.)

The net effect of (11) and (12) is the breakup of CO_2 , with the oxygen remaining in the ocean-atmosphere system while carbon is removed. The crucial figure then is not the gross rate of photosynthesis, but rather the net rate of transfer of organic carbon to the sediments, here designated by R_{sed} .

One might guess that R_{sed} is proportional to the total biomass; however, since dead organic matter is far better protected from prompt recycling if it is underwater, that would be a poor approximation. Instead, we approximated R_{sed} by

$$R_{\text{sed}} = (B_{\text{land}} \cdot S_{\text{land}}) + (B_{\text{ocean}} \cdot S_{\text{ocean}}), \quad (13)$$

where S_{land} and S_{ocean} are constants. The rate so obtained was decreased by a factor of 4.0 whenever free oxygen was present in the atmosphere, as such a condition obviously favors prompt recycling. The constants S_{land} and S_{ocean} were treated as adjustable parameters (see Section V). In the main computer runs the values $S_{\text{land}} = 2.8 \times 10^{-5} \text{ yr}^{-1}$, $S_{\text{ocean}} = 0.128 \text{ yr}^{-1}$ were used.

I. Chemical Reactions and Solubility of Gases

To simplify the calculation of chemical reactions between atmospheric gases, only the following nine gases were considered: N_2 , O_2 , H_2 , H_2O , CO_2 , CO , CH_4 , NH_3 , and Ar. The solubility of CO_2 and NH_3 in seawater was explicitly considered; the solubility of the other seven gases was set equal to zero.

For speed of computation it was assumed that the reactions



go to completion, as well as the reactions of free oxygen with H_2 , NH_3 , CH_4 , or CO . (The errors introduced by these assumptions seem negligible.) It was also assumed that chemical equilibrium between the compounds considered is approached rapidly, i.e., by the end of each time step. (The time step used in the main runs was $2.5 \times 10^6 \text{ yr}$.)

J. Changes in Solar Luminosity

Theoretical analyses of stellar interiors indicate that most main sequence stars gradually increase in luminosity with time. (This is a consequence of the increasing mean molecular weight in the interior, which results from the transformation of hydrogen to helium.) In the program it was assumed that the Sun was 25% less luminous 4.5 billion years ago than it is now. This figure is similar to those obtained from the evolutionary solar models of Sears (1964) and Boury *et al.*, (1975). See also Ulrich (1975) and Newman and Rood (1977). It was assumed that the increase in luminosity of the Sun occurred at a uniform rate, and at a nearly uniform effective temperature.

K. Albedo

Variations in the Earth's albedo play an important part in determining its effective temperature. The program estimated the Bond albedo of the Earth by the formula

$$\begin{aligned} \text{Albedo} = & (f_{\text{cloud}} \cdot A_{\text{cloud}}) + (f_{\text{ice}} \cdot A_{\text{ice}}) \\ & + (f_{\text{sea}} \cdot A_{\text{sea}}) + (f_{\text{veg}} \cdot A_{\text{veg}}) \\ & + (f_{\text{rock}} \cdot A_{\text{rock}}). \quad (15) \end{aligned}$$

In (15), f_{cloud} represents the fraction of the Earth's surface covered by clouds at a given epoch and f_{ice} represents the fraction

TABLE I
A BREAKDOWN OF THE PRESENT ALBEDO OF THE
EARTH BY TYPE OF COVER

Type of cover	A_i	f_i (present)	$f_i \times A_i$ (present)
Clouds	0.52	0.472	0.245
Rocks	0.15	0.021	0.003
Water	0.04	0.353	0.014
Ice	0.70	0.032	0.022
Vegetation	0.13	0.122	0.016
		1.000	0.300

covered by ice (without supervening clouds), etc. The constants A_{cloud} , A_{ice} , etc., represent the mean albedo of clouds, ice, etc. Table I lists the values used for the A_i , and estimates of the current values of the f_i . From the last column it is apparent that the main contribution to the present albedo comes from the cloud cover.

The estimate given for f_{cloud} today is consistent with satellite photographs. To estimate f_{cloud} at earlier epochs it was assumed that f_{cloud} would be proportional to the total mass of water vapor in the atmosphere. The area covered by ice caps was deemed proportional to $[(328.0 - \langle T_{\text{surf}} \rangle) / 70.0]^2$; however, f_{ice} must be reduced slightly because of supervening clouds.

Equation (15) and the auxiliary formulas used in computing the f_i are, of course, at best first-order approximations. But they do match the observed present albedo of the Earth [0.30 according to Vonder Haar *et al.* (1973)] quite well, and seem to give reasonable figures for most circumstances of interest.

L. Greenhouse Effect

From the solar luminosity and the Earth's albedo one can readily compute T_{eff} , the effective temperature of the Earth. However, because of the greenhouse effect, the mean surface temperature of the Earth is given by

$$\langle T_{\text{surf}} \rangle = T_{\text{eff}} + (\Delta T)_{\text{green}}, \quad (16)$$

an equation which will only be correct if $(\Delta T)_{\text{green}}$ is adjusted to include the effects of convective heat transport.

In computing the greenhouse effect a grey atmosphere approximation was used. Since the actual atmosphere is far from grey, one should not expect such an approximation to be very close. However, it does provide a reasonable first-order estimate, and in view of the various approximations elsewhere in the program, a more detailed greenhouse calculation would add little to the overall accuracy of the results.

To compute τ , the optical thickness of the atmosphere, it was first assumed that for each component gas

$$\tau_i \propto (q_i^*)^{1/2}, \quad (17)$$

where q_i^* , the adjusted quantity of a component, is related to q_i , the mass of that component in the atmosphere, by

$$q_i^* = q_i (P/P_0) (T_0/T)^{1/2} \quad (18)$$

(see Elsasser, 1960). We then summed the τ_i to get τ , and used as a provisional estimate of the ground temperature

$$\langle T_{\text{surf}} \rangle_{\text{prov}} = (1 + \frac{3}{4}\tau)^{1/4} T_{\text{eff}}. \quad (19)$$

The provisional value of $(\Delta T)_{\text{green}}$ which was obtained from (19) was then reduced (in order to compensate for the effects of convection) by multiplying it by a "convection factor," F_{conv} . This gives

$$(\Delta T)_{\text{green}} = [(1 + \frac{3}{4}\tau)^{1/4} - 1] T_{\text{eff}} F_{\text{conv}}. \quad (20)$$

The value $F_{\text{conv}} = 0.43$ was selected solely in order to match the current value of $(\Delta T)_{\text{green}}$ for the Earth (which is about 33°K), using $(\tau_{\text{H}_2\text{O}})_{\text{current}} = 2.34$ and $(\tau_{\text{CO}_2})_{\text{current}} = 0.15$. It is interesting, however, that the same values give a fair approximation to the surface temperature of Venus.

M. Procedure

As a starting point for the computer simulation it was assumed that the Earth

had no atmosphere 4.5 billion years ago, and had an albedo of 0.15 at that time. The simulation was carried forward, step by step, using intervals of 2.5×10^6 yr. (As a test, some runs were carried out using time steps of 2.5×10^5 yr, but the resulting changes in the output were negligible.)

The program calculated the mass of each element added to the atmosphere-ocean system (or lost from it) during each time interval, in accordance with the processes described above (see Fig. 1). At the end of each time step the program calculated the mass of the oceans, the mass and composition of the atmosphere, the quantities of dissolved gases, the albedo, T_{eff} , $\langle T_{\text{surf}} \rangle$, and various related quantities. Since there are important feedbacks between several of these quantities (e.g., absolute humidity, greenhouse effect, and surface temperature) the program was designed to iterate at the end of each time step until the numbers converged to a consistent result.

III. RESULTS OF COMPUTER RUNS

A. Changes in Atmospheric Composition

The computer simulation was run many times, using several different assumed compositions of juvenile volatiles. In the computer run which resulted in the best fit with currently observed data, the assumed composition of the juvenile volatiles was: oxygen, 85.36%; hydrogen 9.71%; carbon, 4.70%; nitrogen, 0.23% (by mass fraction, and excluding argon). A mixture consisting of 84.42% H_2O , 14.29% CO_2 , 1.06% CH_4 , and 0.23% N_2 would contain the same ratio of elements.

Some of the results from that "best-fitting" computer run are presented in Table II. (Figures 2-9 are also based on the output from that run.) In that simulation, as in all others which came at all close to the present composition of the atmosphere, most of the water vapor condensed quite promptly to form oceans. The early atmosphere was therefore dominated by CO_2 ,

PRINCIPAL SOURCES AND SINKS OF ATMOSPHERIC CONSTITUENTS

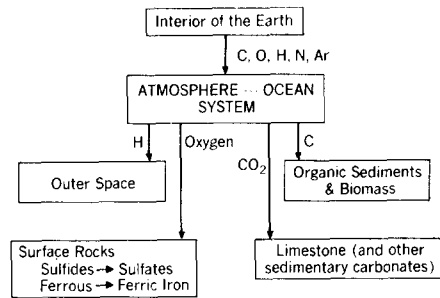


FIG. 1. Principal sources and sinks of atmospheric constituents.

which was the next most abundant component of the volcanic gases.

As CO_2 was removed from the atmosphere-ocean system by the Urey reaction, an atmosphere developed whose main constituents were methane (or perhaps higher hydrocarbons, or other reduced carbon compounds) and nitrogen. (The extent to which methane—which is chemically the most stable hydrocarbon—would polymerize under the influence of solar uv radiation is unclear. The suggestion that the process would continue until a considerable fraction of the hydrocarbons was bound up in an oil slick 1-10 m thick on the surface of the oceans (Lasaga *et al.*, 1971), though quite possibly correct, has not yet been generally accepted.) Most of the NH_3 (or other reduced nitrogen compounds) was dissolved in the oceans; NH_3 never constituted as much as 100 ppm of the atmosphere. [This is in accord with the calculations of Miller and Orgel (1974) which are based on equilibrium relations between NH_3 , NH_4^+ , clay minerals, and aspartic acid.] However, the small quantities present did have a noticeable effect on $(\Delta T)_{\text{green}}$, as suggested by Sagan and Mullen (1972). Only trace amounts of free H_2 were present.

Oxygen was released from photolysis of water vapor, and (after the first 800 million years) by photosynthesis. The oxygen so released gradually destroyed the CH_4 and NH_3 . By roughly 2.0 billion years ago all

TABLE II
EVOLUTION OF EARTH'S ATMOSPHERE ACCORDING TO BEST-FITTING COMPUTER RUN

Time (billions of years before present)	Surface pressure (atm)	Mass of atmospheric components							T_{eff} (°K)	$\langle T_{\text{surf}} \rangle$ (°K)
		N ₂ (10 ²¹ g)	O ₂ (10 ²¹ g)	CO ₂ (10 ²⁰ g)	CH ₄ (10 ²¹ g)	NH ₃ (10 ¹⁷ g)	Ar (10 ¹⁹ g)	H ₂ O (10 ¹⁹ g)		
4.25	1.25	0.75	0	23.2	3.37	0.74	0.04	4.18	217	305
4.00	1.37	0.56	0	13.4	5.13	1.79	0.16	7.68	218	314
3.75	1.39	0.32	0	8.28	6.00	2.23	0.34	9.67	219	317
3.50	1.32	0.31	0	5.27	5.93	2.29	0.57	8.27	219	315
3.25	1.22	0.52	0	3.54	5.39	2.15	0.86	5.75	220	310
3.00	1.10	0.87	0	2.48	4.56	1.90	1.18	3.77	221	304
2.75	0.97	1.31	0	1.81	3.52	1.62	1.54	2.61	224	299
2.50	0.73	1.57	0	1.37	2.22	1.46	1.93	2.30	230	297
2.25	0.62	2.14	0	1.03	0.93	1.09	2.35	1.86	238	294
2.00	0.75	3.76	0.06	0.646	0	0	2.79	0.77	250	281
1.75	0.76	3.81	0.06	0.365	0	0	3.25	0.69	251	279
1.50	0.77	3.84	0.08	0.215	0	0	3.72	0.69	252	279
1.25	0.77	3.87	0.08	0.117	0	0	4.21	0.71	253	280
1.00	0.78	3.89	0.09	0.049	0	0	4.70	0.72	254	280
0.75	0.78	3.90	0.10	0.024	0	0	5.21	0.79	255	281
0.50	0.79	3.91	0.10	0.024	0	0	5.72	0.90	256	283
0.40	0.85	3.91	0.43	0.024	0	0	5.93	1.02	256	285
0.30	0.90	3.92	0.69	0.024	0	0	6.14	1.10	256	286
0.20	0.94	3.92	0.86	0.024	0	0	6.35	1.16	255	287
0.10	0.97	3.92	1.03	0.024	0	0	6.55	1.21	255	288
0	1.00	3.92	1.21	0.024	0	0	6.76	1.27	255	288

but trace amounts of reduced gases had been removed from the atmosphere, and at that point the atmosphere consisted primarily (about 96%) of N₂. Since that time there has been a slow buildup of free O₂ in the atmosphere.

Roughly 420 million years ago the amounts of O₂ and O₃ in the atmosphere become great enough to reduce the intensity of uv radiation at the surface to a level tolerable by living organisms. Soon thereafter plant life spread to the continents and there was a great increase in the biomass. The resulting increase in photosynthetic activity (and in the rate of burial of carbon) caused a rapid increase in the amount of free oxygen in the atmosphere, an increase which was still going on when man appeared on the scene.

These changes in composition are shown

in Fig. 2. (The extrapolation past the present era, which is shown on that and succeeding figures, indicates only what might have occurred in the absence of human activity). Figure 3 shows how the total pressure (at sea level) has varied through geologic time, according to our optimum computer run.

B. Changes in Albedo and Temperature

Perhaps the most significant results of the computer simulation are shown in Fig. 4, in which the long-term variations of the Earth's effective temperature and mean surface temperature are plotted. The difference between the two curves, of course, represents $(\Delta T)_{\text{green}}$. That was very large during the first 2.5 billion years, due to the combined effect of reducing gases (such as

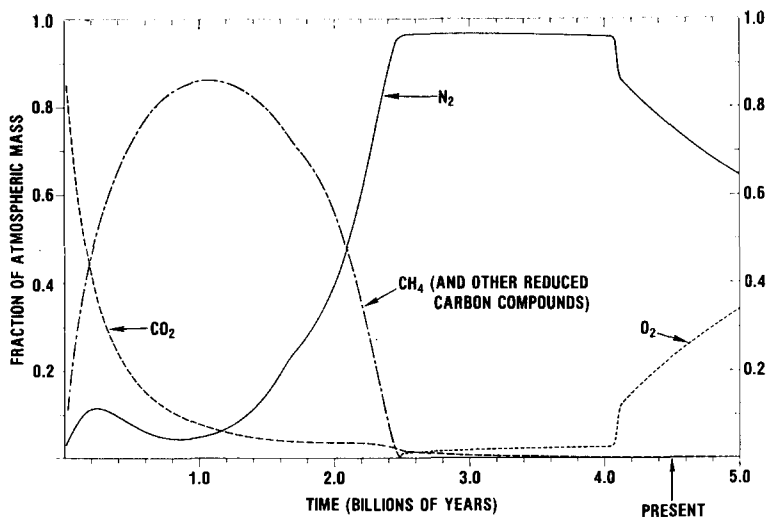


FIG. 2. Variations, over the course of geologic time, of the composition of the Earth's atmosphere. The line for each constituent shows what fraction of the total atmospheric mass that constituent represented.

NH_3 and CH_4) and of large quantities of H_2O and CO_2 . The high surface temperature caused a large amount of water to evaporate (see Fig. 5) which resulted in a cloud-covered Earth (see Fig. 6). That in turn caused a high albedo (Fig. 7). The effective temperature was therefore low throughout the first half of Earth's history.

After CH_4 , NH_3 , and all other reduced

gases were oxidized away the situation changed drastically. $(\Delta T)_{green}$ went down sharply, and the mean surface temperature decreased. By the time free oxygen appeared in the atmosphere (about 2 billion years ago), $\langle T_{surf} \rangle$ had fallen to 280°K, and ice caps of considerable size had formed.

That the drop in temperature was not even larger is primarily due to the thermo-

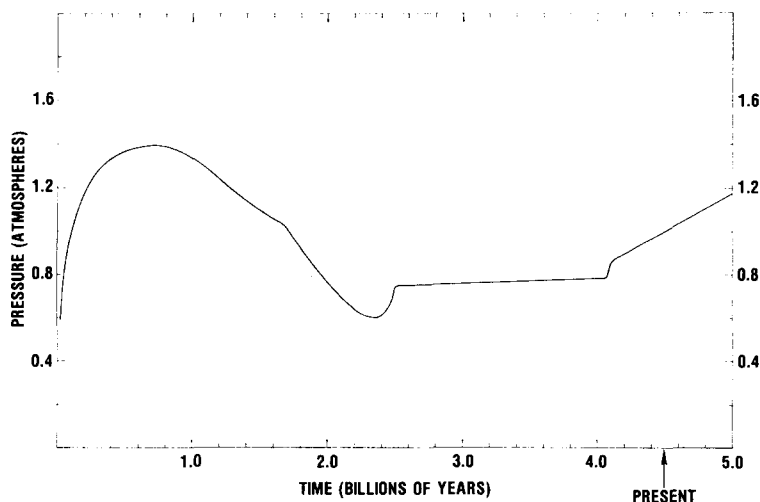


FIG. 3. This shows the variation, over the course of geologic time, in the mean (sea-level) atmospheric pressure.

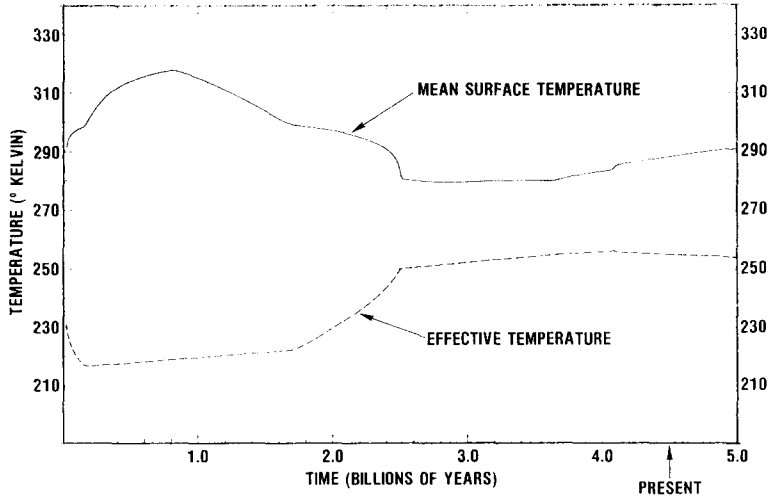


FIG. 4. Variations in the mean surface temperature and effective temperature of the Earth over geologic time.

static effect of the variations in cloud cover. As $\langle T_{\text{surf}} \rangle$ falls, the quantity of H_2O in the atmosphere drops, the cloud cover and albedo decrease, and T_{eff} goes up. However, it seems plain that if $\langle T_{\text{surf}} \rangle$ ever became much lower than 0°C this thermostatic mechanism would break down. For, with large ice caps and little cloud cover, any further drop in temperature will *raise* the albedo (because of the growth in ice caps)

rather than lowering it, thereby causing T_{eff} and $\langle T_{\text{surf}} \rangle$ to drop still further.

The value of T_{crit} , the temperature at which runaway glaciation will commence, depends on many factors and is hard to compute. However, the computer simulations carried out in this research program suggest that whenever reducing gases are absent from the atmosphere, and the solar constant is within about 20% of its present

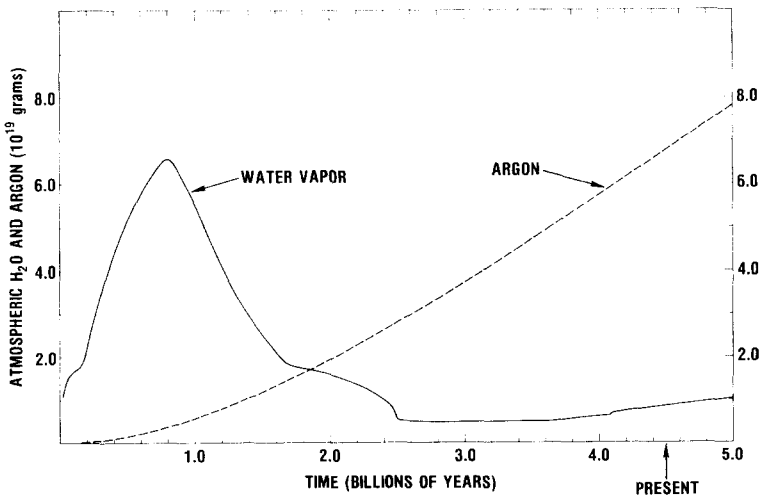


FIG. 5. This shows the variation, over the course of geologic time, in the masses of water vapor and argon in the Earth's atmosphere.

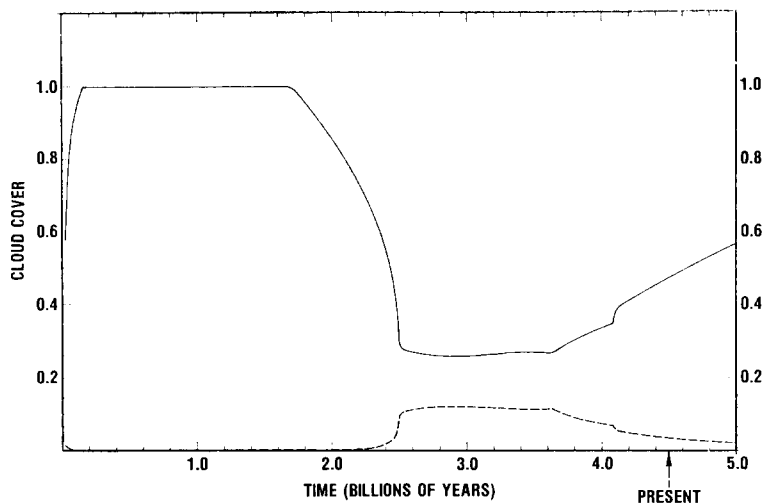


FIG. 6. The upper curve shows the fraction of the Earth's surface covered by clouds at different periods of geologic time. The dashed line shows the fraction of Earth's surface covered by ice, without supervening clouds.

value, T_{crit} will be in the neighborhood of 278°K . This is consistent with the climatological analysis of Budyko (1969), who found that a drop in the solar constant sufficient to cause $\langle T_{\text{surf}} \rangle$ to decrease to 279°K would not cause runaway glaciation, whereas a slightly larger decrease would have that result.

Runaway glaciation occurred in many of my computer runs. In every such case the

computation was continued—often for an additional 2 billion years, or even longer—with CO_2 (from volcanoes) accumulating in the atmosphere, and with the greenhouse effect computed. In not a single such case was runaway glaciation reversed.

C. Comparison with Observations

Our optimum computer run resulted in an atmosphere which contained, after 4.5

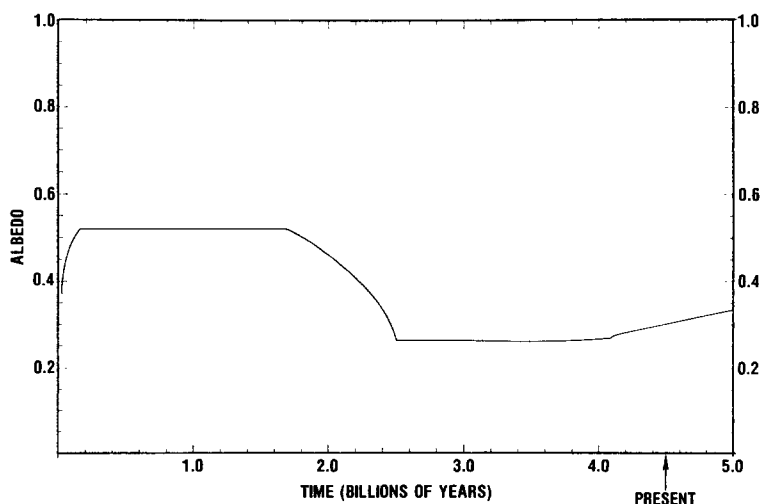


FIG. 7. Variations in the Bond albedo of the Earth over geologic time.

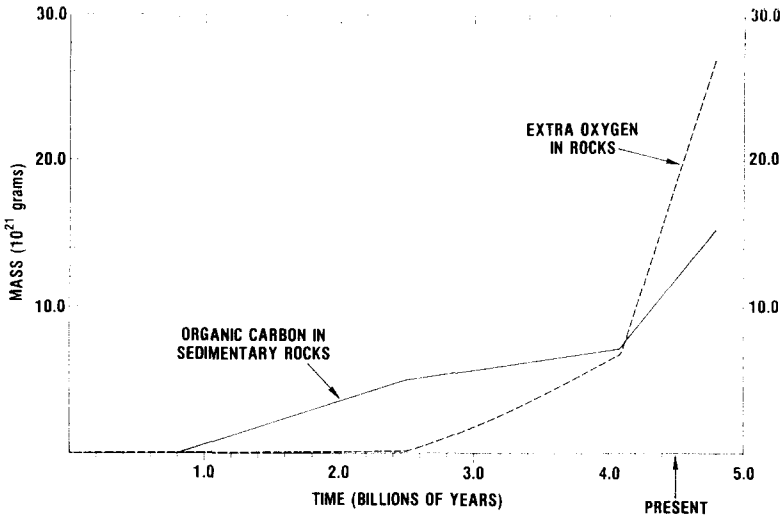


FIG. 8. The solid line shows how the mass of organic carbon in the sedimentary rocks has varied over geologic time. The dashed line indicates the net amount of oxygen which has been added to the rocks by oxidation of ferrous iron to ferric iron and by oxidation of sulfides to sulfates.

billion years: 3.92×10^{21} g of N_2 , 1.21×10^{21} g of O_2 , 6.76×10^{19} g of Ar, 1.27×10^{19} g of H_2O , 2.38×10^{18} g of CO_2 , and 3.29×10^{15} g of O_3 . This is a very close fit to our present atmosphere. The same run yielded 1.42×10^{24} g as the mass of the present hydrosphere, and 1.31×10^{20} g as the mass of CO_2 in the oceans, both in good agreement with current observations.

The program also computed the total amount of organic carbon which has accumulated in the sedimentary rocks, the accumulated quantity of atmospheric oxygen used up in oxidizing the surface rocks, and the net amount of CO_2 which has been bound up in limestone and other carbonate minerals via the Urey reaction. Figures 8 and 9 show how (according to our best run)

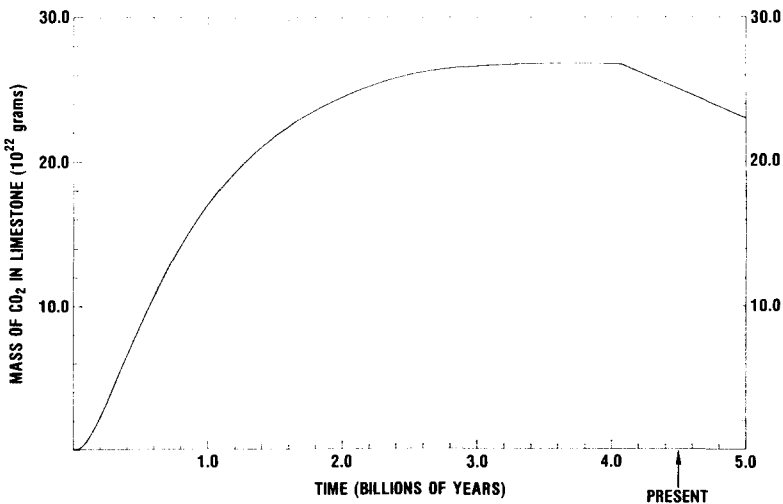


FIG. 9. This shows the variation, over the course of geologic time, in the total mass of CO_2 tied up in limestone, dolomite, or other sedimentary carbonates.

these quantities have varied in the course of time. Table III compares the results of that computer simulation with the estimates of several geochemists.

The figures of Poldervaart (1955), and Ronov and Yaroshevsky (1972), were based almost entirely on direct estimates of the thickness and areal extent of various rock types, and on analyses of their chemical composition. The other authors made extensive use of the method of geochemical balances. The results of the computer simulation seem to be well within the uncertainties in the geologists' estimates.

The simulation indicates (Fig. 9) that there was almost as much limestone present 2 or 3 billion years ago as there is today. Since most existing carbonate deposits are post-Precambrian (Garrels and McKenzie, 1971) the clear implication is that ancient limestone deposits have been extensively recycled. Figure 9 also indicates that the total mass of carbonate minerals has been decreasing for the past 420 million years. This is a consequence of the increased rate of photosynthesis (and organic sedimentation) since life spread to the continents. The large amounts of organic carbon buried during that interval could not have come from the atmosphere-ocean system alone, and must therefore have been supplied by limestone redissolving in the oceans.

The presence of uranite (UO_2) and galena (PbS) in detrital sediments formed from 2.0 to 2.5 billion years ago is generally taken as strong evidence of the absence of more than very small amounts of oxygen from the atmosphere during that period, since they are readily oxidized to UO_3 and PbSO_4 , respectively, by even small concentrations of free oxygen (Holland, 1962; Miller and Orgel, 1974). On the other hand, the presence of thick, extensive red beds (whose coloring is due to Fe_2O_3) which are at least 1.8 (perhaps 2.0) billion years old argues strongly that free oxygen must have been present by that time (Cloud, 1968). Both these observations are compatible

TABLE III
ACCUMULATED MASS OF SOME SUBSTANCES IN
SEDIMENTARY ROCKS

Author	CO_2^a (10^{22} g)	Organic carbon (10^{22} g)	Excess oxygen ^b (10^{21} g)
Poldervaart (1955)	2.28	—	12-21.7
Ronov and Yaroshevsky (1972)	2.61	1.1	—
Li (1972)	1.63	1.11	~24.0
Garrels and Perry (1974)	2.24	1.25	17.7
This study (optimum run)	2.51	1.20	18.5

^a The atmosphere of Venus contains about 5×10^{22} g of CO_2 .

^b This refers to atmospheric oxygen used up in oxidizing ferrous iron to ferric, and sulfides to sulfates.

with our best computer run, which indicates that substantial quantities of free oxygen first appeared in the atmosphere about 2.0 billion years ago.

Now of course values of several of the parameters described in Section II were deliberately chosen so that the results would match presently observed quantities (see Section V). A principal conclusion of this study is that it is possible, by assigning plausible values to those parameters, to simulate the evolution of the Earth's atmosphere in a manner consistent with the basic ideas of Rubey (1951), with those of Berkner and Marshall (1964, 1965), and with prevailing theories of stellar evolution. The resulting model yields reasonably moderate and stable temperatures throughout geologic time and is consistent with the appearance of life on Earth in the very distant past. It is also consistent with estimates of the mass of the oceans, the quantities of excess volatiles in the sedimentary rocks, and the composition of the present atmosphere. The model does not involve any extraordinary events or unknown effects, but is based entirely on processes already discussed in the literature.

IV. EXTENT OF CONTINUOUSLY HABITABLE ZONE ABOUT SUN

As is well known, Venus has a much thicker atmosphere than the Earth, and a much higher surface temperature. The usual

explanation is that on Venus a runaway greenhouse effect occurred (Sagan, 1960; Gold, 1964; Ingersoll, 1969) and that in the absence of liquid water the Urey reaction proceeded very slowly, enabling large quantities of CO_2 to accumulate in the atmosphere. That explanation, which does not require any initial difference between the two planets other than the higher solar constant on Venus, suggests that the same thing could have occurred here if the Earth had been closer to the Sun.

It is a simple matter to run the present computer simulation using different values of the Earth-Sun distance, but with all other parameters the same as in our optimum run. The results are straightforward: A runaway greenhouse would have occurred at an early stage in Earth's history if the Earth-Sun distance were ≤ 0.95 AU. This result is very close to that of Rasool and de Bergh (1970), who calculated that the critical distance was 6–10 million kilometers (4–7%) less than the actual Earth-Sun distance.

It is evident that if the Earth were too far from the Sun the oceans would ice over. In fact, as explained in Section III, runaway glaciation would commence even before $\langle T \rangle_{\text{surf}}$ reaches 0°C . Since $\langle T_{\text{surf}} \rangle$ is only 15°C today, it might be wondered why runaway glaciation did not occur 3 or 4 billion years ago, when the solar luminosity was much lower than it is now. It has been suggested that the presence of NH_3 in the atmosphere, by substantially augmenting the greenhouse effect, kept the oceans from freezing over (Sagan and Mullen, 1972). However, after free O_2 appeared in the atmosphere (about 2 billion years ago) the partial pressure of NH_3 must have been very low, and at that time $\langle T_{\text{surf}} \rangle$ must have been close to T_{crit} , where runaway glaciation would occur.

This computer simulation was run using an Earth-Sun distance of 1.01 AU, but keeping the other input parameters unchanged. The early evolution was similar,

but about 2 billion years ago runaway glaciation occurred.

It might be noted that a detailed climatological study by Schneider and Gal-Chen (1973) indicated that a decrease of 1.6% in the solar constant (which, of course, would result if the Earth were only 0.8% further from the Sun) would cause runaway glaciation. Budyko (1969) had obtained the same figure. On the other hand, Wetherald and Manabe (1975) found that, using their general circulation model of the atmosphere, even a decrease of 4% in the solar constant would not cause a runaway today. Since it is plain that runaway glaciation did not occur on Earth, their results are probably closer to the truth than the earlier studies.

All these studies seem compatible with the conclusion indicated by our computer simulations, i.e., that an only slightly larger value of the Earth-Sun distance (of the order of 1%, or even less) would have resulted in runaway glaciation a couple of billion years ago, when all but trace amounts of reduced gases were eliminated from the atmosphere.

Huang (1959, 1960) used the term "habitable zone" to denote the region (about a given star) within which planetary temperatures are neither too high nor too low for life to develop. [Dole (1964) refers to this region as the "ecosphere" and other terms have been used also.] The concept is useful; however, many writers, by not taking into account the possibility of thermal runaways, have overestimated the width of habitable zones. For example, if neither the size of the Earth's ice caps nor the absolute humidity of its atmosphere depended on $\langle T_{\text{surf}} \rangle$, then the present habitable zone about the Sun would extend outward to at least 1.15 AU and inward to at least 0.80 AU. In fact, though, because of the possibilities of either runaway glaciation or a runaway greenhouse effect, the habitable zone about the Sun is much narrower.

Furthermore, most writers have discussed the habitable zone as if its boundaries were constant in time. However, because main sequence stars slowly increase in luminosity, their habitable zones gradually move outward. For life to continue to exist on a planet, the shifting habitable zone about its Sun must continuously include the planet's orbit. The "continuously habitable zone" which meets that requirement is, at least for F and G stars, far narrower than the habitable zone at any one time.

A discussion of the width of the continuously habitable zone about different types of stars might be interesting, but will have to be deferred to a later paper, as will applications of this program to other planets which are somewhat like the Earth.

V. DEPENDENCE OF THE RESULTS OBTAINED ON THE VALUES SELECTED FOR THE PARAMETERS

Many of the constants used in this program (for example U_1 , X_2 , S_{land} , S_{ocean} , and constants representing the average composition of the juvenile volatiles) could not be computed directly. These constants were therefore treated as adjustable parameters, and the precise values which were adopted were selected in order to obtain a satisfactory solution to the overall problem. A "satisfactory solution" consists of an evolutionary model (i.e., a set of functions $[O_2](t)$, $[CO_2](t)$, $\langle T_{surf} \rangle(t)$, etc.) which satisfies the following set of constraints:

(a) It matches the observed composition of the present atmosphere, and it matches the present temperature of the Earth.

(b) It matches the present composition of the sedimentary rocks (see Table III).

(c) It provides for a reducing atmosphere during the early stages of Earth's history; the appearance of free O_2 about 2.0 billion years ago; and a partial pressure of O_2 (as of about 420 million years ago) equal to only a few percent of the present value.

(d) It avoids both runaway glaciation and a runaway greenhouse effect.

(e) It matches some miscellaneous boundary conditions and constraints, such as: the Earth had no atmosphere 4.5 billion years ago, and life appeared very early in geologic time.

The combination of parameter values which was adopted led to a solution which satisfied requirements (a)–(e). One might, of course, be able to find other combinations of parameter values which satisfy requirements (a) and (b) (i.e., the present composition of the atmosphere and rocks) and which also satisfy requirement (e). But the necessity of also satisfying the (historical) constraints of requirements (c) and (d) almost ensures that any two acceptable solutions—though they may be based on different combinations of parameters—will look much alike in several key respects. In particular, because of requirement (c), the general form of the $[O_2](t)$ curves should be similar, while (because of (c), (d) and the increasing solar luminosity) the general form of the $\langle T_{surf} \rangle(t)$ curves should be similar.

Nevertheless, it should be stressed that this paper presents only *one* example of the possible evolutionary models of the Earth's atmosphere. No attempt was made by the author to test all possible combinations of parameters. There may therefore be other solutions—based on other combinations of the adjustable parameters—which yield a larger value of the width of the continuously habitable zone than does the model presented in Table II.

Since, in the final analysis, the results depend to a large extent on requirements (a)–(e), it is reasonable to ask if we are sure those requirements are correct. There seems to be no reasonable doubt concerning requirements (a) and (d). However, the numbers involved in requirements (b) and (c) are not precisely known; to the extent that those figures are doubtful, the conclusions of this computer simulation must be treated with caution.

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