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Paleoatmospheric Temperature Structure

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Radiative equilibrium and radiative convective temperature profiles for the Earth's evolving atmosphere have been calculated. If the atmosphere evolved from one rich in carbon dioxide, and deficient in oxygen, to its present composition, the temperature structure showed considerable change. The models of 3 to 4 billion years ago display steadily decreasing temperatures with altitude, being 185°K at pressures associated with the present-day upper stratosphere. A lapse rate feature similar to the present-day tropopause is not indicated until about 1 billion years ago; but the stratospheric region is approximately 15°K colder than presently found at comparable pressures. Surface temperatures approximately 10°K warmer than at present existed until nearly 1 billion years ago. When the oxygen content exceeded roughly 0.1 times the present level, surface temperatures began to decrease. If biological processes are important to carbon dioxide—ozone variations, such as has been suggested during the Ice Ages, then estimates of surface temperature should include the effects of both gases.

INTRODUCTION

No previous attempt has been made to investigate the temperature structure of the evolving atmosphere for atmospheric models appropriate to particular geologic periods. Such a determination is important since the rate constants of reactions for many minor constituents are temperature dependent. Nearsurface temperatures are also important to climatic variations and the evolution of life forms.

Previous studies related to the temperatures of the paleoatmosphere estimated exospheric temperatures or deduced variations in planetary albedo, constituent concentrations, etc., based on variations from an assumed mean global temperature (Holland, 1962, 1963; Jastrow, 1964; Rasool, 1966, 1967; McGovern, 1969; Sagan and Mullen, 1972). Estimates of the changes expected to the present-day thermal structure, as might be brought about through changes in the vertical distribution of individual constituents, were made by Berkner and Marshall (1964, 1965, 1967), Abelson (1966), and Walker (1974). Finally, in some studies (Holland, 1962; Jastrow, 1964; Berkner and Marshall, 1966, 1967; Rutten, 1971; Ratner and Walker, 1972) one finds a trend toward acceptance of the present-day temperature structure, and its associated thermodynamic processes, throughout much of geologic time.

This study presents calculated radiative–convective, mean global, vertical temperature profiles of the Earth's evolving atmosphere extending back to about 4.5 billion years. We assume the atmosphere evolved from one rich in carbon dioxide and deficient in oxygen, and thus ozone. The resultant temperature profiles are obviously

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dependent upon the assumed concentrations and distributions of the radiatively active gases. However, the thermal profiles for other postulated carbon dioxide and ozone distributions can be at least qualitatively inferred from the results presented.

ATMOSPHERIC MODELS

Atmospheric oxygen concentrations form the basis for correlation between the model atmospheres and geologic eras. The correlations are primarily derived from the evolutionary descriptions as found in the several articles of Berkner and Marshall (1964–1967) but with a more liberal interpretation of the times involved. We have further based the evolutionary atmospheric models on the carbon dioxide/oxygen combinations suggested by Rutten (1966, 1971). It must be emphasized that this study does not attempt to delve into the chemical reactions or geologic processes producing or destroying any particular constituent; we only determine the thermal environment that would have existed for that postulated atmospheric composition.

Seven models describe the evolving atmosphere (refer to Table I). Model 1 represents the present-day atmosphere. Concentrations for the constituents of this model were obtained from the COESA preliminary report (Ellis *et al.*, 1973). The water vapor profile is one of fixed specific humidity.

The Ice Age model, Model 2, was included to provide some insight as to the possibility that glacial periods may have been initiated by oscillations in the carbon dioxide and oxygen concentrations. Such a dependence has been presented in the literature by Berkner and Marshall (1964, 1965) and Cloud (1968). We have used a carbon dioxide concentration of 0.65 PAL (present atmospheric level) from their study and Levine's (1975) ozone profile corresponding to their oxygen abundance of 2 PAL.

The Cambrian, Algonkian, Cryptozoic, and Archean models, Models 3 though 6, respectively, are sequential in that they reflect the proposed evolution of oxygen as based upon the works of Berkner and Marshall (1964, 1965, 1967), and carbon dioxide as proposed by Rutten (1966, 1971).

The ozone profiles (Fig. 1) are from Levine (1975), who calculated ozone concentrations from the assumed oxygen evolutionary model. We have introduced variations in the water vapor distribution from that of the present-day mean annual

TABLE I

ATMOSPHERIC MODELS[a]

Compound	Model (years ago)						
	1 Present-day	2 Ice Age	3 Cambrian 300–800 MY	4 Algonkian 800 MY–2.5 BY	5 Cryptozoic 2.5–3.5 BY	6 Archean 3.5–4.0 BY	7 Pre-Archean 4.0–4.5 BY
CO_2	PAL	0.65 PAL	3.5 PAL	5 PAL	8 PAL	10 PAL	0.01 PAL
O_2	PAL	2 PAL	0.1 PAL	0.01 PAL	0.001 PAL	0.0001 PAL	0.000001 PAL
H_2O	Curve 1, Fig. 2			Curve 4 Fig. 2	Curve 5 Fig. 2	Curve 6 Fig. 2	Curve 7 Fig. 2
	PAL	PAL	PAL				
CH_4	PAL	PAL	PAL	PAL	PAL	PAL	20% by total number density
NH_3	Not included in calculation →						9 ppm

[a] The present atmospheric levels (PAL) for CO_2, O_2, and CH_4 (assumed uniformly mixed) are 320 ppm, 21% by volume, and 1.5 ppm, respectively. The H_2O distribution is shown in Fig. 2.

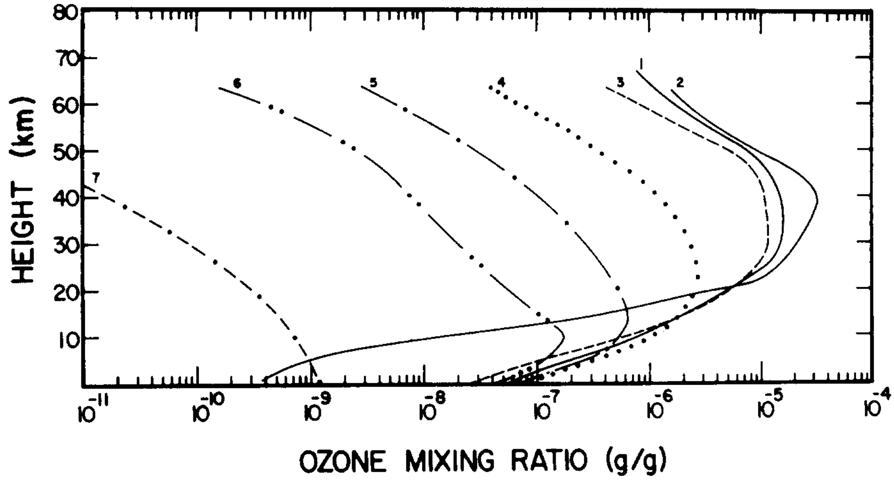

FIG. 1. Ozone mixing ratios (g/g) used in the evolving atmospheric models. Values illustrated are based on the work of Levine (1975). The column abundance for each model is: Model 1, 0.347 atm-cm; Model 2, 0.562 atm-cm; Model 3, 0.250 atm-cm; Model 4, 0.069 atm-cm; Model 5, 0.012 atm-cm; Model 6, 0.0008 atm-cm. See Table I for relation of model number to approximate geologic time.

model beginning with Model 4 of the Algonkian period as shown on Fig. 2. No tropopause, and thus cold trap, was apparent in these calculated temperature profiles and water vapor would most likely have been transported to higher elevations. Each water vapor profile represents near saturation at the stratospheric elevations.

The earliest model, Model 7, which may be representative of 4 to 4.5 billion years ago, represents a reducing atmosphere and is the most uncertain of the models

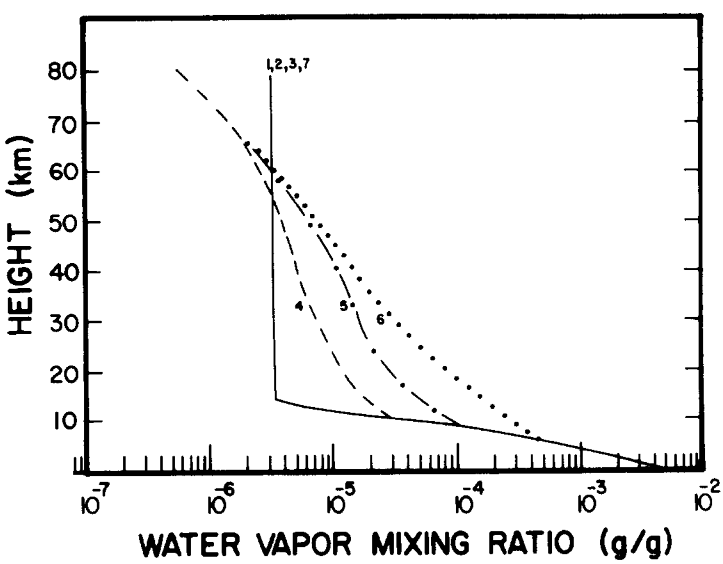

FIG. 2. Water vapor mixing ratios (g/g) used in the models of the evolving atmosphere. See Table I for relation of model number to approximate geologic time.

developed. It has generally been held that the earth had a reducing atmosphere in its early history, and geologic evidence points to its existence as recently as 2 billion years ago (Rankama, 1955; Rutten, 1966, 1971; Cloud, 1968). Additional evidence is found in the analysis of volcanic gases (Holland, 1962, 1963). Indirect support may also be found from the laboratory experiments that attempt to create basic proteins and amino acids (Fox and McCauley, 1968; Lasaga *et al.*, 1971).

The degree to which the atmosphere was reducing is currently undecided, and its composition is also a subject open to debate with the arguments centering on a methane versus carbon dioxide dominated atmosphere. For this very early atmosphere, we assumed a methane concentration of 20% by volume and ammonia of 9 ppm.

METHODOLOGY

Radiative equilibrium temperature profiles were calculated by a forward difference iterative method. Heating rates ($\delta T/\delta t$) were determined from the equation

$$\delta T/\delta t = (g/C_p)\delta F/\delta p,$$

where g is the acceleration due to gravity, C_p is the specific heat at constant pressure and $\delta F/\delta p$ is the flux divergence (F is the net flux and p is pressure).

Heating rates were determined at 57 levels in each model atmosphere. A pressure incrementing model between 0.1 mb and the surface was devised to give high spatial resolution in the lower regions of the atmosphere. All models except the Pre-Archean (Model 7) were run with a time increment of 24 hr. The Pre-Archean model used a 12-hr time increment, such change being required to maintain stability.

The net flux for infrared or terrestrial radiation is given by

$$F(U_0) = \sum_i \pi \left[\tau_f^i(U_0) \int_{\delta_i} B_\omega^i(0) d\omega + \int_{\delta_i} B_\omega^i(U) d\omega \int_0^{U_0} d\tau_f^i(U_0 - U) - \int_{\delta_i} B_\omega^i(U) d\omega \int_{U_\infty}^{U_0} d\tau_f^i(U - U_0) \right],$$

where τ_f^i is the mean flux transmissivity over spectral interval of width δ_i, and $B_\omega^i(0)$ and $B_\omega^i(U)$ are the Planck functions for the surface and the level corresponding to mass path U, respectively.

Solar heating rates for ozone were obtained from the divergence of the energy deposition rate Q, as given by Lindzen and Will (1973),

$$\delta T/\delta t = (gU/C_p)\delta Q/\delta p,$$

where U is the absorber mass path and $\delta Q/\delta p$ is the energy deposition divergence. For the other constituents, the solar heating is given as a function of the integrated absorption A,

$$\delta T/\delta t = (gS/C_p)\delta A/\delta p,$$

where S is the incident solar flux. Absorption data used in this study are summarized in Table II.

For all the models considered, the radiative equilibrium lapse rate in the lower troposphere became superadiabatic. Thus we have included a "convective adjustment" as explained in Manabe and Strickler (1964). The convective lapse rate provides an estimate of the extent of latent heat exchange and convective processes (cloud formation) within the dynamic atmosphere which the dry adiabatic lapse rate does not.

We assume that convection and latent heat exchange were comparable in previous atmospheres to that of the present-day so that the ratio of the dry adiabatic to the critical convective lapse rate should be the same for all models. Each atmospheric

TABLE II

ABSORPTION DATA AND REFERENCES

Constituent	Band	Reference
Terrestrial		
Ozone	9.6 μm	Walshaw (1957)
Carbon dioxide	15 μm	Rodgers and Walshaw (1966)
Water vapor		
Rotation band	0–1000 cm^{-1}	Rodgers and Walshaw (1966)
6.3 μm Band	1200–2200 cm^{-1}	
Ammonia	6.1 μm 10.5 μm	Statistical model semiempirically curve fit to data of France and Williams (1966)
Methane	3.3 μm 7.6 μm	Cess and Khetan (1973) except Pre-Archean, Burch *et al.* (1962) for Pre-Archean model
Solar		
Ozone		
Hartley band	2500 Å	
Huggins band	3200 Å	Lindzen and Will (1973)
Chappuis band	6000 Å	
Carbon dioxide	1.4, 1.6, 2.0, 2.7, 4.3, 4.8, and 5.8 μm	Howard *et al.*, (1973)
Water vapor	0.8, 0.9, 1.1, 1.38, 1.9, 2.7, 3.3, and 6.3 μm	Rodgers (1967)
Methane	3.3 μm 7.6 μm	Same as for terrestrial wavelengths

model has a different specific heat and thus a unique dry adiabatic lapse rate. The critical convective lapse rate Γ_{PR} is then determined from $\Gamma_{PR} = \Gamma_{PD} \cdot \Gamma_R / \Gamma_D$, where Γ_R and Γ_D are the present-day values for the convective and dry adiabatic lapse rates and Γ_{PD} is the dry adiabatic lapse rate for the particular model. Values for Γ_{PR} and Γ_{PD} are given in Table III.

The surface temperature was determined by adjusting the radiative convective temperature profile until the out-going flux to space and absorbed solar energy agreed within 0.5%. A planetary albedo of 30% was used which includes not only the albedo of the surface but clouds as well. Thus implicit in this assumption is that global cloud cover in the past was not much different from what we observe today. A more detailed model is not justified since no information is available on possible water vapor variations over geologic time.

We have also not considered a variable solar constant. Margulis and Lovelock (1974) indicate that a change in the solar constant of ±10% would have caused catastrophic events which have no basis in geologic records. On the other hand there are investigators who believe the solar output may have increased nearly 40%.

RESULTS

A comparison of the thermal structure for the present-day model and the U. S.

TABLE III

VALUES OF $\bar{C}_p$ AND LAPSE RATES FOR EACH MODEL[a]

Atmospheric model	$\bar{C}_p$ (erg gm^{-1} $°K^{-1}$)	Dry adiabatic lapse rate (°K km^{-1})	Radiative convective lapse rate (°K km^{-1})
1. Present era	1.00×10^7	9.77	6.5
2. Ice Age	1.25×10^7	7.82	5.2
3. Cambrian	0.97×10^7	10.14	6.78
4. Algonkian	1.02×10^7	9.58	6.37
5. Cryptozoic	1.44×10^7	8.57	5.7
6. Archean	1.22×10^7	8.00	5.32
7. Pre-Archean	1.07×10^7	9.14	6.03

[a] See Table I for composition corresponding to model number.

Standard Atmosphere is shown in Fig. 3. The agreement is quite good, particularly in the stratospheric regions. Our temperatures in the stratosphere especially near the tropopause are somewhat larger than those of Manabe and Strickler (1964) but this is due to differences in water vapor and ozone concentration (see, e.g., Manabe and Wetherald, 1967) and in the treatment of the boundary flux.

We have also compared changes in surface temperature, for various amounts of absorbing gases, with those from previous studies. We find that doubling the carbon dioxide amount would increase the surface temperature by 2.9°K, while a reduction to one-half decreases the temperature by 2.3°K. Manabe and Wetherald (1967) calculated these changes to be 2.4 and 2.3°K, respectively. Reck (1976) investigated the change in the thermal structure due to ozone variations and found for a 50% ozone reduction, the temperatures at 10 and 100 mbar decreased by about 8.7 and 7.5°K, respectively. We calculated temperature reductions of 6 and 7°K, respectively. Thus, our model gives results comparable to those of previous studies.

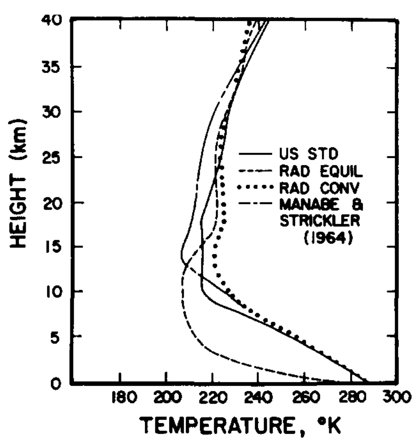

FIG. 3. Temperatures for the present-day model compared with the U. S. Standard Atmosphere, Mid-Latitude Spring/Fall profile. Also shown is radiative convective profile from Manabe and Strickler (1964) with average cloudiness.

The radiative convective temperature profiles for each model atmosphere are shown on Fig. 4. Model 3, the Cambrian model (0.1 PAL O_2 and 3.5 PAL CO_2) indicates a troposphere slightly warmer than we find today; this is due to the larger amount of CO_2 and thus an increased "greenhouse effect." A weak tropopause is apparent and the stratosphere is about 10 to 15°K colder than at similar elevations in the present atmosphere. Because of the smaller amount of ozone (see Fig. 1), the ultraviolet radiation penetrates to lower levels in the atmosphere creating a smaller heating in the stratosphere (and thus lower temperature) and a somewhat higher temperature further down near the tropopause. In addition, the larger amount of carbon dioxide contributes to the lowering of temperature in the stratosphere, in this case 5 to 10°K (see, e.g., Manabe and Wetherald, 1967). Since carbon dioxide causes an increase in tropospheric temperature, a lowering of temperature in the stratosphere is necessary in order that the Earth atmosphere system remain in radiation balance, i.e., the outgoing planetary radiation balance the absorbed solar radiation.

With larger amounts of carbon dioxide and lesser amounts of oxygen, and thus ozone, the temperature in the lower atmosphere (<12 km) would increase while at higher elevations the opposite effect is observed. If, e.g., the carbon dioxide amount were 5 PAL and oxygen, 0.01 PAL, which is Model 4 and may be representative of about 1 billion years ago, the troposphere would have been 10°K warmer than today and there would have been essentially no tropopause. The mid- and upper stratosphere is nearly isothermal with temperature near 210°K. Absorption of the ultraviolet radiation is now occurring low in the atmosphere and along with carbon dioxide contributes to the increased tropospheric temperature. The stratospheric temperature is determined primarily by carbon dioxide.

Models 5 and 6 which represent early periods in the Earth's history contain so little ozone that its influence on the thermal structure is negligible. Carbon dioxide primarily determines the temperature structure in the stratosphere with a small contribution (about 5°K) from water vapor. Both models exhibit very cold stratospheres, the Archean reaching a temperature of 185°K. In the troposphere, the temperature is determined by water vapor (which was not varied in the models below about 10 km) and carbon dioxide. The tropospheres of both are warmer than the present-day model by as much as 20°K.

Model 7, the "Pre-Archean" model,

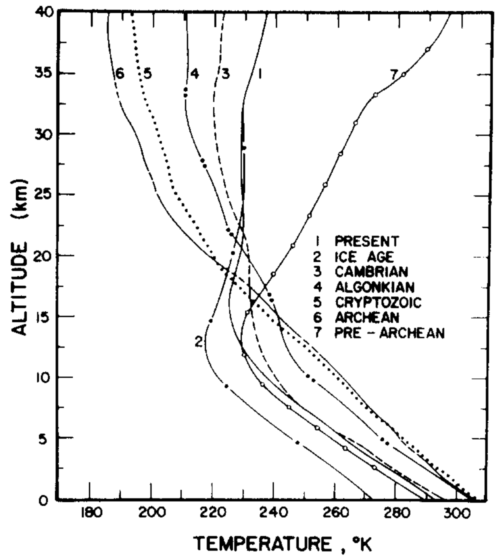

FIG. 4. Radiative-convective temperature profiles. See Table I for composition corresponding to each model.

represents an atmosphere rich in methane (20% volume) and an ammonia concentration of 9 ppm. The surface temperature was not allowed to vary since cloud cover, water vapor amount, albedo, and solar output in these early stages of the Earth's existence were probably much different from what we find today. In any case, if an appreciable concentration of methane were present, then absorption of solar radiation by methane would permit a well-developed tropopause and a very stable high-temperature stratosphere, which could have been 100°K or more higher than in later stages of the atmosphere's evolution. Ozone and carbon dioxide have a negligible effect on the temperature and methane and water vapor are the constituents determining the tropospheric temperature.

The surface temperature appears to have been warmer than today with little variation over most of geologic time, if the atmosphere did indeed evolve from one rich in carbon dioxide and deficient in oxygen (Table IV); carbon dioxide is the constituent primarily responsible for this higher surface temperature. Ozone is

TABLE IV

SURFACE TEMPERATURE CHANGE FOR PROPOSED ATMOSPHERIC MODELS RELATIVE TO PRESENT-DAY MODEL (292.8°K)[a]

Model	Temperature change (°K)
Cambrian	2.5
Algonkian	11.5
Cryptozoic	13.0
Archean	12.5

[a] See Table I for atmospheric composition.

present in such small concentrations that it has little effect on the surface temperature.

The Ice Age model, Model 2, demonstrates the necessity for including with the carbon dioxide reduction, the corresponding increase in ozone which should have occurred if such variation in carbon dioxide was due to biological processes. If the carbon dioxide is lowered to 0.65 PAL, then the surface temperature would drop about 2.3°K, but when the corresponding change in ozone is included (see Fig. 1), the temperature reduction is near 17°K. One should note that although the ozone column abundance has increased to about 0.56 atm-cm, the distribution with height is significantly altered. The large amount of ozone above about 20 km produces a larger contribution to the outward flux from the stratosphere which requires a lower tropospheric temperature in order to maintain radiative balance. The smaller troposphere and lower stratosphere ozone concentrations accentuate the surface temperature reduction. Our major conclusion is not the magnitude of the temperature change, but to indicate the importance of the coupled carbon dioxide–ozone variations induced by biological processes. Indeed, one would expect other variations during an ice age, such as albedo, cloud cover, and water vapor amount, to influence the surface temperature as well.

Perhaps the most significant result of this study is the colder stratospheric temperatures and the effect they would have upon stratospheric processes. In particular, the eddy diffusion coefficient was probably quite different than that used in present-day studies, especially when the carbon dioxide concentration was much larger than we find today. These results indicate that the stratospheric regions were considerably less stable in prior eras, which could have significantly influenced the dynamics as well as the distributions of photochemically produced minor constituents. In addition, the effect of such lower stratospheric temperature on chemical reaction rates may be significant. For example, the rate constant for ozone formation $O + O_2 + M \rightarrow O_3 + M$ is

$$K_{12} = 1.8 \times 10^{-35} \exp(1000/RT) \quad \text{cm}^6 \text{ molec}^{-2} \text{ sec}^{-1},$$

while the destruction of ozone can occur as $O_3 + O \rightarrow 2O_2$, with rate

$$K_{13} = 1.9 \times 10^{-11} \exp(-4600/RT) \quad \text{cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}.$$

If the carbon dioxide column abundance were greater than about 5 PAL, which may have corresponded to times earlier than 0.8 billion years ago, then the rate constant for formation would be about twice as large as the value used today, while the rate constant for destruction would only be one-twentieth as large. Thus, it is not sufficient for these early studies to simply incorporate the present-day temperature structure. Fortunately, Levine (1975) used a nearly isothermal stratosphere in calculating his ozone concentrations which corresponds closely to our Model 4 and appears to represent an average stratospheric temperature over geologic time.

Evolution of water vapor in the Earth's atmosphere is a subject which has not been adequately addressed and represents perhaps the most uncertain aspect of the model atmospheric composition. To assess the impact of this constituent on the temperature profile and surface temperature, a "dry" model, representing a one-hundredfold decrease from the present-day mean water vapor model, was incorporated into the Archean model atmosphere. The temperature profile in the stratosphere changed only slightly, being some 2 to 4°K cooler. However, the surface temperature decreased 24°K. The reduced water vapor content results in a smaller "greenhouse effect," thus a larger amount of energy from the surface and lower troposphere escapes to space, which requires lower surface and tropospheric temperatures if radiative balance is to be maintained.

SUMMARY

Radiative convective temperature profiles for the paleoatmosphere, extending back in time to 4.5 billion years, have been calculated for an atmosphere initially rich in carbon dioxide, deficient in oxygen, and evolving to the present composition. Only within the last 1 billion years, or for carbon dioxide abundances less than 5 PAL, and within a methane dominated atmosphere, if indeed one did occur, was there a tropopause similar to that of the present day.

The majority of the models, which may represent most of geologic time, exhibit steadily decreasing temperatures with height at pressures where the current atmosphere displays an inversion. Thus the use of present-day stratospheric temperatures in studies of atmospheric chemical evolution is justified for only about the most recent 300 million years, if the carbon dioxide–ozone atmosphere as studied by Rutten, Berkner, and Marshall, and Levine represents conditions in the Earth's past.

Surface temperatures during much of geologic history would appear to have been some 10°K warmer than currently found. As oxygen content, and by association an accompanying increase in ozone and reduction in carbon dioxide occurred, the surface temperature decreased to its present-day value.

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