

THE CO₂ GREENHOUSE EFFECT AND THE THERMAL HISTORY OF THE ATMOSPHERE

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ABSTRACT

The influence of the expected rise of CO₂ content in our atmosphere upon terrestrial temperature is uncertain. A significant increase in temperature could be threatening to certain aspects of terrestrial biology. On the other hand, it is a general consensus among paleobiologists that the Earth possessed a CO₂ atmosphere in the past billion years, without dramatic temperature variations endangering the continuity of life. In order to clarify this problem, and to contribute to the understanding of the CO₂ greenhouse effect on Venus we have computed the absorption spectrum of CO₂ for a wide range of atmospheric concentrations. More than 2500 spectral lines of the 15 micron band were taken into account in our line-by-line calculation. We have used an empirical exponential line-shape function at the line edges. Our results agree with the experimental data of F. W. Taylor. The estimated increase in surface temperature does not reach the boiling point of water even for CO₂ concentrations thousands of times larger than the present concentrations. Higher energy (> 666 cm⁻¹) CO₂ bands and/or an increase in atmospheric H₂O may, however, amplify the greenhouse effect.

INTRODUCTION

The surface temperature of a naked inactive planet is the result of the balance between solar heating and thermal radiation loss:

$$R^2(1 - a)S = 2\pi R^2\sigma T_0^4 \quad (1)$$

Here R is the radius of the planet, S is the solar constant at the distance of the planet, a is the planetary albedo, σ is the Stefan-Boltzmann constant and T_0 is the average surface temperature on the sunlit side in the absence of an absorbing atmosphere. For a rapidly rotating planet the whole surface radiates with an average temperature T_0 . Consequently,

$$R^2(1 - a)S = 4\pi R^2\sigma T_0^4 \quad (2)$$

At the Sun-Earth distance the present value of the solar constant is $S = 2 \text{ cal/cm}^2\text{min}$. The average surface temperature can be calculated for different albedo values:

T_0 K	for	a
279		0.
264		0.2
245		0.4
221		0.6

The albedo expresses the reflectivity of the planet. Some typical values are:

	a		a
Moon rock	0.07	Snow	0.90
Earth	0.34	Wood	0.15
Venusian cloud	0.61	Ocean	0.10 .

The observed albedo of the Earth would give $T_0 = 250$ K. The actual average temperature is $T = 288$ K. The relevant difference $\Delta T = T - T_0 = 38$ K is ascribed to the greenhouse effect: the atmosphere is transparent for the optical solar radiation ($T_{\text{sun}} = 6000$ K), but has a decreased transmissivity β for the infrared terrestrial radiation ($T = 288$ K).

$$R^2 (1 - a) S = 4\pi R^2 \beta \sigma T^4 \quad (3)$$

The main chemical species producing the greenhouse effect are atmospheric CO_2 , H_2O and O_3 . These have absorption bands in the region ν (wavenumber) = $2400 \text{ cm}^{-1} - 31400 \text{ cm}^{-1}$. This region is characteristic for the Planck spectrum of the Earth. The CO_2 molecule has a strong absorption band at the terrestrial Planck spectrum maximum $\nu = 666 \text{ cm}^{-1}$.

The role of atmospheric CO_2 in influencing the surface temperature of our planet is a subject of recent debate. The observed CO_2 content of the atmosphere is increasing at a rate of 1 ppm/year as a consequence of human activity. It is accepted that a doubling of the present 320 ppm CO_2 concentration may be expected by the middle of the next century due to the combustion of fossil fuels and to deforestation of tropical continents. The resulting variation of the terrestrial temperature has been estimated by several authors in the last decades. According to the pioneering studies of Möller [1], an increased greenhouse effect may result in an overall temperature rise of a few degrees. This has been considered by several authors to be alarming. A larger-than-average warming is expected in the arctic region. This could conceivably cause a disappearance of the polar ice cap and a catastrophic rise in sea level. The distribution of precipitation may be shifted in Europe in the coming century [2], [3].

The thermodynamics and evolution of the atmosphere and ocean is worth understanding. The past history of the atmosphere can serve as a testing ground for any predictive theory [4]. For example biologists assume the existence of a reducing atmosphere in the era during which the oceans were formed on the Earth [5]. Geophysicists, on the other hand, deduce the properties of this early atmosphere from the present concentrations of volcanic gases consisting mainly of CO_2 and H_2O . This is certainly a relevant question from the point of view of the origins of life, which appeared practically simultaneously with the formation of the oceans, about 3.8 billion years ago [6]. There is a majority consensus, however, that for a considerable part of

terrestrial history, between 3.5 and 0.75 billion years ago the main component in our atmosphere was CO₂. This was rapidly transformed into O₂ by the photosynthesis of spreading vegetation and into CaCO₃ by sea life and inorganic precipitation chemistry.

On Earth the era between 3.5 and 0.75 billion years ago resembled the present state of Mars and Venus. The calculated weight of present-day terrestrial CO₂, bound mainly as CaCO₃ and in organic compounds, is equivalent to about 100 atm [7], comparable to the present Venusian atmosphere. The planet Venus shows, however, a surface temperature of 500° C. From a simple estimation of the greenhouse effect, Rasool and De Breghe [8] concluded that atmospheric CO₂ had never exceeded a pressure of one-tenth atmosphere on Earth. According to this view the present composition of the terrestrial atmosphere might be a product of recent outgasing from the crust. This differs from the view generally accepted in the literature of the history of life.

Life has existed on Earth without interruption for the past 3.8 billion years [6], [9]. This fact contains a very valuable message about this planet: the temperature of the world's oceans did not exceed the boiling point of H₂O (100° C) or the melting point of DNA (80° C) in the last 3.8 billion years. This argument about the thermal stability of the surface of Earth is valid even in the case of an atmospheric origin of life, as suggested by C.R. Woese recently [10]. However during the last 0.75 billion years the mean chemical composition of the atmosphere changed drastically from CO₂ to O₂ and N₂: the sky became transparent to the infrared radiation from the Earth's surface within a time interval less than one billion years. In order to understand the thermal stability on the surface of the Earth in spite of these drastic recent changes, one must determine the atmospheric absorption of thick CO₂ layers. This will be done in the next section. Then one has to combine the calculated greenhouse effect with other long-term phenomena influencing the temperature. This will be done in the closing sections. The theoretical conclusions can be compared with the thermal history of Earth, as deciphered by geochemical methods.

ATMOSPHERIC ABSORPTION IN THE INFRARED: DEPENDENCE ON WAVE NUMBER, PRESSURE, TEMPERATURE AND CO₂ CONCENTRATION

An atmospheric layer of geometrical thickness dz modifies the infrared radiation intensity $I_\nu(z)$ by absorption and by emission [11]:

$$dI_\nu(z) = -k_\nu(z) \xi(z) I_\nu(z) dz + J_\nu(z) \xi(z) dz \quad (4)$$

Here $k_\nu(z)$ is the absorption coefficient at wave number ν , $\xi(z)$ is the gas density at altitude z . $J_\nu(z)$ is the source function, this can be described by the Planck function in the case of local thermodynamical equilibrium. The total differential can be integrated to give the radiation intensity coming from the Earth's surface and the atmosphere at a certain wave number in the infrared region of the emission spectrum:

$$I_\nu = \epsilon_\nu B_\nu(T_s) \tau_{\nu,s} + \int_{\tau_{\nu,s}}^1 B_\nu(T(p)) d\tau_\nu(T,p,u) \quad (5)$$

Where $B_\nu(T)$ is the Planck function ϵ_ν is the emissivity of the surface, p is the pressure, u is the optical mass of the absorbing gas, τ_ν is the transmissivity, ν is the wave number, and the subscript "s" refers to surface values. On the right side of this equation the first term gives the

radiation of the surface, the second term gives that of the atmosphere at a pressure level p . The transmissivity function takes the form

$$\tau_{\nu, s} = \exp\left(-\frac{1}{g} \int_0^{p_0} k_{\nu}(p, T) q(p) dp\right), \quad (6)$$

where p_0 is the pressure at the surface, and $q(p)$ is the mixing ratio of the absorbing gas. The absorption coefficient k_{ν} is determined by the sum of all elementary absorption lines in a given band. The integrated absorption over the whole band is given as

$$A = \int_{\nu_{\min}}^{\nu_{\max}} (1 - \tau_{\nu, s}) d\nu. \quad (7)$$

Here ν_{\min} and ν_{\max} are limit wave numbers depending on the intensity of the absorption band.

If we are interested in the percentage absorption of the outgoing radiation we can define the absorption \tilde{A} :

$$\tilde{A} = 1 - \frac{\int \tau_{\nu, s} B_{\nu}(T_s) d\nu}{\int B_{\nu}(T_s) d\nu} \quad (8)$$

Here we have to integrate over the whole infrared spectrum. It is easy to calculate the value of \tilde{A} from the integrated values of $\tau_{\nu, s}$ over a suitably short wave number interval because the Planck function is a slowly varying function of ν compared with $\tau_{\nu, s}$.

The value of A and \tilde{A} will depend upon the physical conditions of the atmosphere, described by the functions $q(p)$ and upon its chemical composition. Here we do not intend to go into the details of the computation. As usual, one can use a model atmosphere dividing it into several plane-parallel isothermal layers. The number of layers required is determined by the condition that a further increase of the number of divisions does not increase the accuracy of the transmissivity $\tau_{\nu, s}$. By performing the calculation with different CO_2 concentrations, one obtains information about the greenhouse effect as a function of increasing concentrations of atmospheric CO_2 . The predictive value of the calculation, dealing with climatic changes² and the evolution of the atmosphere, depends critically upon an accurate knowledge of the absorption processes [12].

Because of the complicated structure of absorption bands, different investigators have made use of different band models. These models introduce simplifying assumptions which help in the integration of the transmissivities over a given wave number interval. The regular model assumes that the line-intensity and line-spacing are uniform in a narrow spectral region [13]. The statistical model uses a certain probability distribution for the line intensities and line distributions [14]. The simplest calculations work with rectangular band profiles [3]. Under atmospheric conditions, where pressure broadening of the spectral lines plays a dominant role, the Lorentz shape is

in general use. Experimental observations, which were recently confirmed theoretically [15], have shown, however, that at the edges of the line the absorption decreases much faster than in the case of a Lorentz-shaped band profile. Benedict and Shilverman [16] introduced, empirically, an exponential factor into the line shape function:

$$f(\nu - \nu_1) = f_L(\nu - \nu_1) \exp(-0.135|\nu - \nu_1|^{0.7}) \quad (9)$$

where $f_L(\nu - \nu_1)$ is the Lorentz line shape. Equation (9) certainly leads to calculated transmittances that fit the empirical data [17] of Taylor (at JPL) better than those calculated from the Lorentz function (Fig. 1).

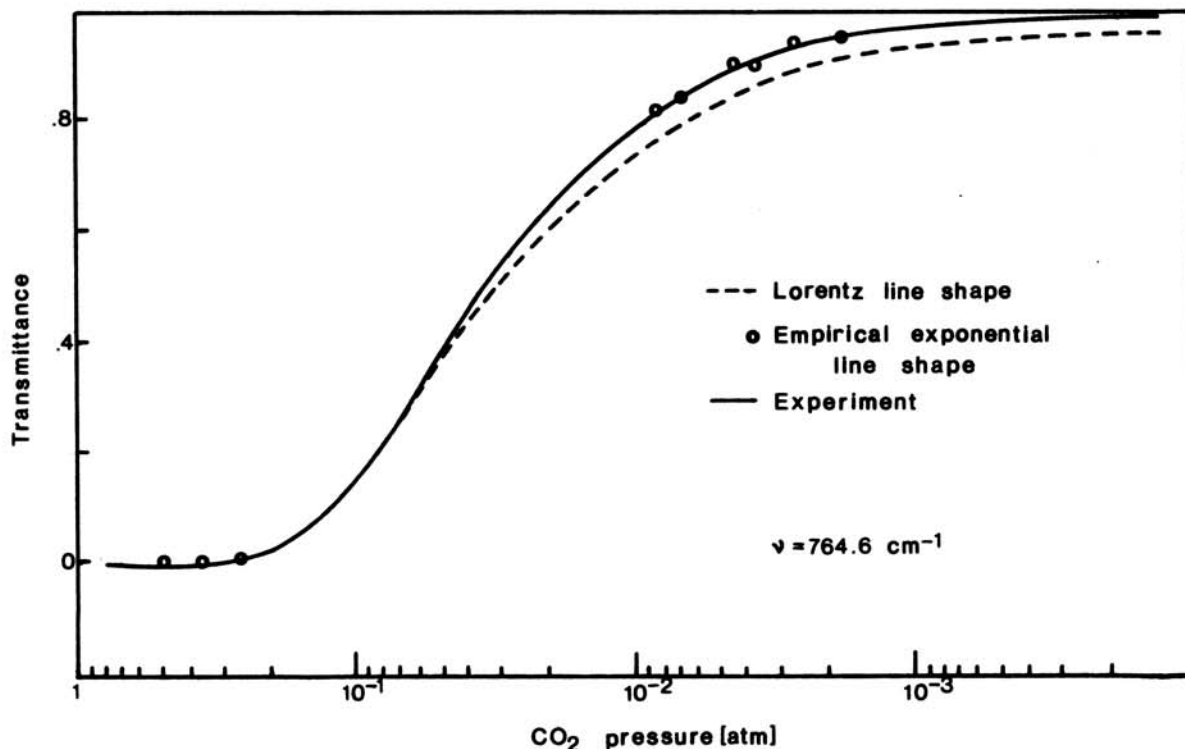


Fig. 1 Comparison of the empirical and theoretical transmittances for different line profiles [17].

To make a comparison between the simplified model calculations and the detailed realistic ones possible, we computed the absorption of the $\nu = 666 \text{ cm}^{-1}$ CO₂ band for a wide range of CO₂ concentration. The relevance of the 666 cm⁻¹ band is given by the fact that it lies at the maximum of the Planck curve valid for the Earth's measured mean surface temperature $T_s = 288 \text{ K}$ (Fig. 2).

The calculation of the average value of $\bar{\tau}_{\nu,s}$ was made by numerical integration for 0.1 cm⁻¹ wide intervals between 450 cm⁻¹ and 870 cm⁻¹ and for the 1962 US Standard Atmosphere [18]. The parameters of the 2500 strong absorption lines of CO₂ were taken from the line compilation of McClatchey [19].

Let us compare the absorption values obtained by us with the values quoted in the literature.

Drayson, who published the most accurate spectroscopic calculations calculated transmittance averages over 5 cm⁻¹ wide intervals in the region $500 \text{ cm}^{-1} < \nu < 860 \text{ cm}^{-1}$. He gave his results in tabulated form [20].

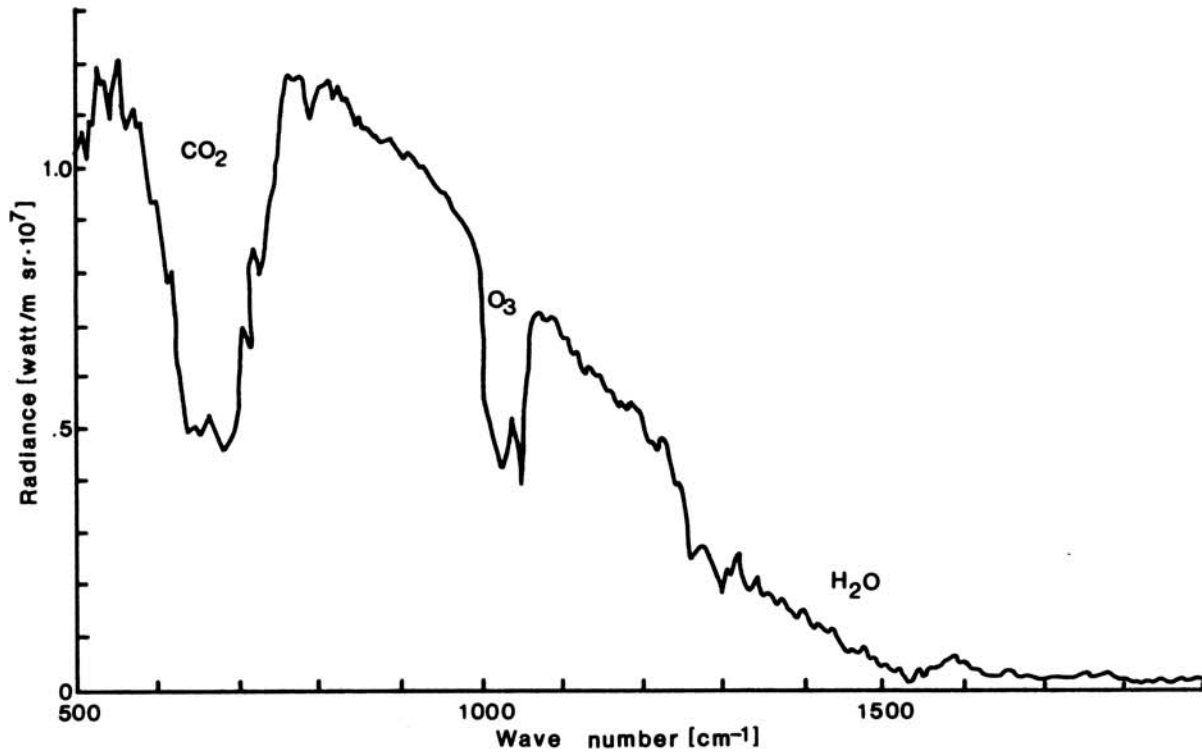


Fig. 2. The emission spectrum of the Earth at $T_s = 288$ K.

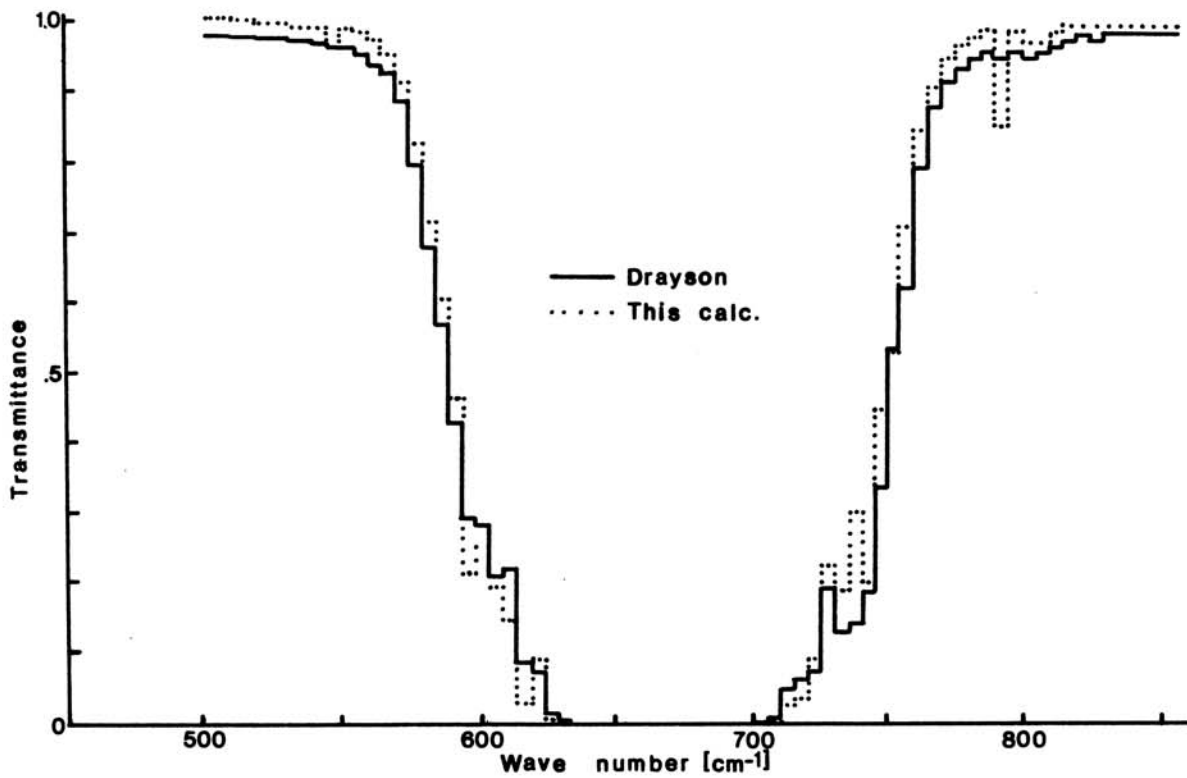


Fig. 3. Comparison of the atmospheric CO₂ transmittance, calculated by two independent groups.

Figure 3 offers a comparison of his calculated transmittances with those obtained by us in the present study. Though there are significant differences at specific wave numbers, the integrated absorptions \underline{A} are in good agreement (Table 1).

TABLE 1 Integrated Absorption Values \underline{A} as a Function of Atmospheric Pressure

Atmospheric Pressure	Drayson	Present authors
1 mb	1.45 cm ⁻¹	1.93 cm ⁻¹
10 mb	9.10 cm ⁻¹	9.90 cm ⁻¹
100 mb	52.48 cm ⁻¹	57.66 cm ⁻¹
1000 mb	161.75 cm ⁻¹	157.20 cm ⁻¹

The slight differences may have several possible reasons: 1) The present calculation used 320 ppm by volume compared with 310 ppm used by Drayson; the influence of this difference on the calculation is small. 2) The line parameters used were not completely identical. 3) Drayson divided the atmosphere into 34 homogeneous layers, the present calculation used 16 layers. 4) At the line edges the shape function used by Drayson was rather different from the one used by us.

In spite of these differences one may regard the general agreement of the two calculations as an indication of the correctness of this method for the determination of the integrated absorptions \underline{A} and \tilde{A} . Therefore we continued the calculation to compute the dependence of \underline{A} and \tilde{A} on CO₂ concentration. We also examined the influence of variations in temperature and pressure on the absorption.

In order to determine the concentration dependence, the present atmospheric CO₂ concentration of 320 ppm was increased 5-, 10-, 50-, 100- and 1000-fold.

The variation of the transmittance is shown in Fig. 4. The variation of the absorptions \underline{A} and \tilde{A} is in Fig. 5. In the case of \underline{A} the integration limits were $\nu = 10 \text{ cm}^{-1}$ and $\nu = 2500 \text{ cm}^{-1}$. It can be seen from the solid curve of Fig. 5 that the integrated absorption \underline{A} depends on the concentration as a power function. We fitted a power function to the points of \underline{A} by the least square method:

$$A = 156.13 \left(\frac{c}{c_0} \right)^{0.1016} \text{ cm}^{-1}, \quad (10)$$

where c is the CO₂ concentration and $c_0 = 320 \text{ ppm}$ is the present CO₂ level. The correlation coefficient was larger than 0.99.

Another important question is how the integrated absorption depends on pressure and temperature at high CO₂ concentrations. Higher CO₂ concentration will result in an increase of the average molecular weight of the atmosphere, and consequently in an increase of the surface pressure. This effect was investigated only at the thousandfold CO₂ concentration. In this case the pressure on the Earth's surface was 1261.0 mb, and the atmosphere consisted of about 30 % CO₂ and 70 % N₂. The dependence of the differential integrated absorption $\Delta \underline{A}$ on the variation of the total surface pressure ΔP is shown in

Fig. 6. The relation is linear in the region examined. At 320 000 ppm CO₂ concentration an increase of the surface pressure by 200 mb produces an increase of \underline{A} by 2.5 per cent. The effect of the pressure may be more important in a thicker atmosphere with extremely high CO₂ concentrations.

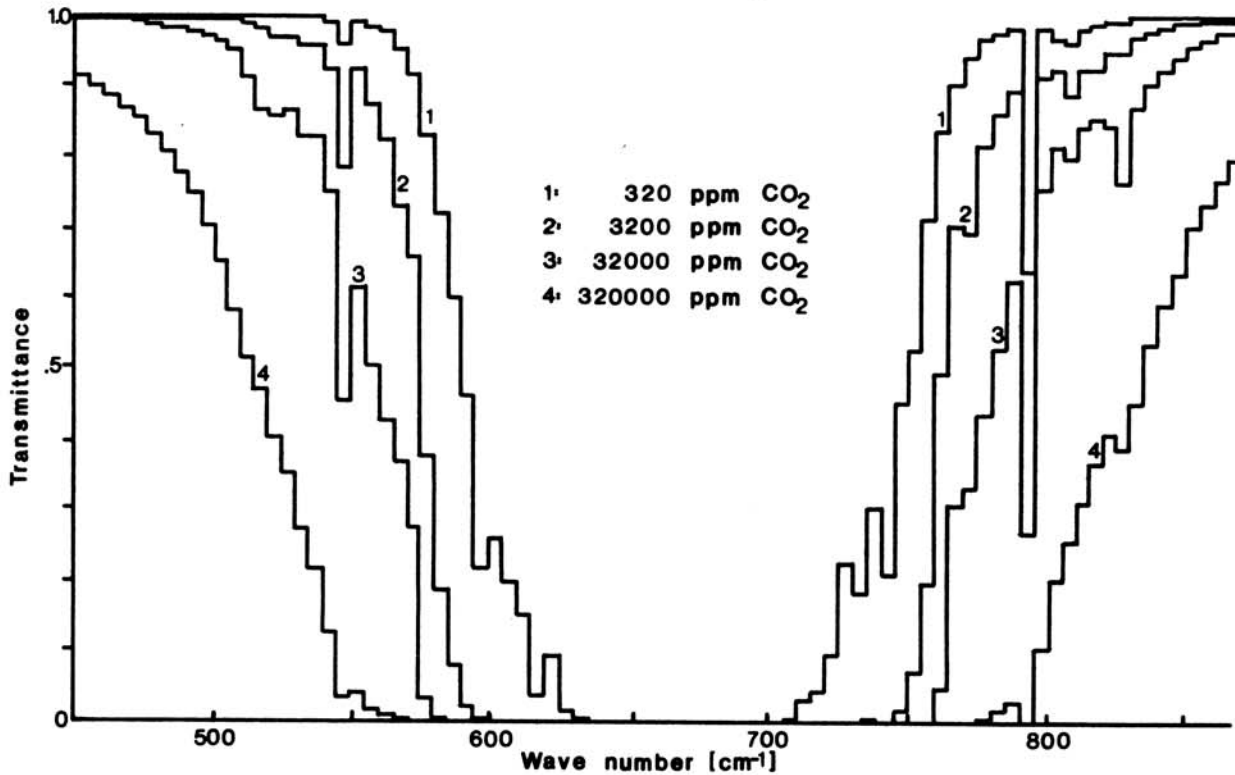


Fig. 4 The dependence of the transmittance on the CO₂ concentrations

The dependence of the absorption \underline{A} on the average temperature of the atmosphere was also examined. Figure 7 shows the results. Increasing average temperature produces decreasing absorption. The explanation of this effect is that the intensity of the strong lines is in inverse ratio to the temperature and in the case of high CO₂ concentrations the absorption caused by the edges of the strong lines dominates. Increasing the temperature by + 45 degrees at each atmospheric level induces a decrease in the integrated absorption \underline{A} of about 2.7 per cent. In the case of Earth this slight temperature dependence can be neglected as a consequence of the known temperature stability of the planet.

CALCULATION OF THE GREENHOUSE EFFECT

Having computed the dependence of the absorption \tilde{A} on the CO₂ concentration c , one may try to estimate the increase of the surface temperature due to an increase in the atmospheric CO₂. The real situation is complicated by continental variations, cloud cover, climate differences, atmospheric circulations, and locally different albedo values. For a first orientation Equation (3), above, will be used, by using the Eddington approximation [8], [21]:

$$\beta = \left[1 - \frac{3}{4} \ln(1 - A) \right]^{-1} \quad (11)$$

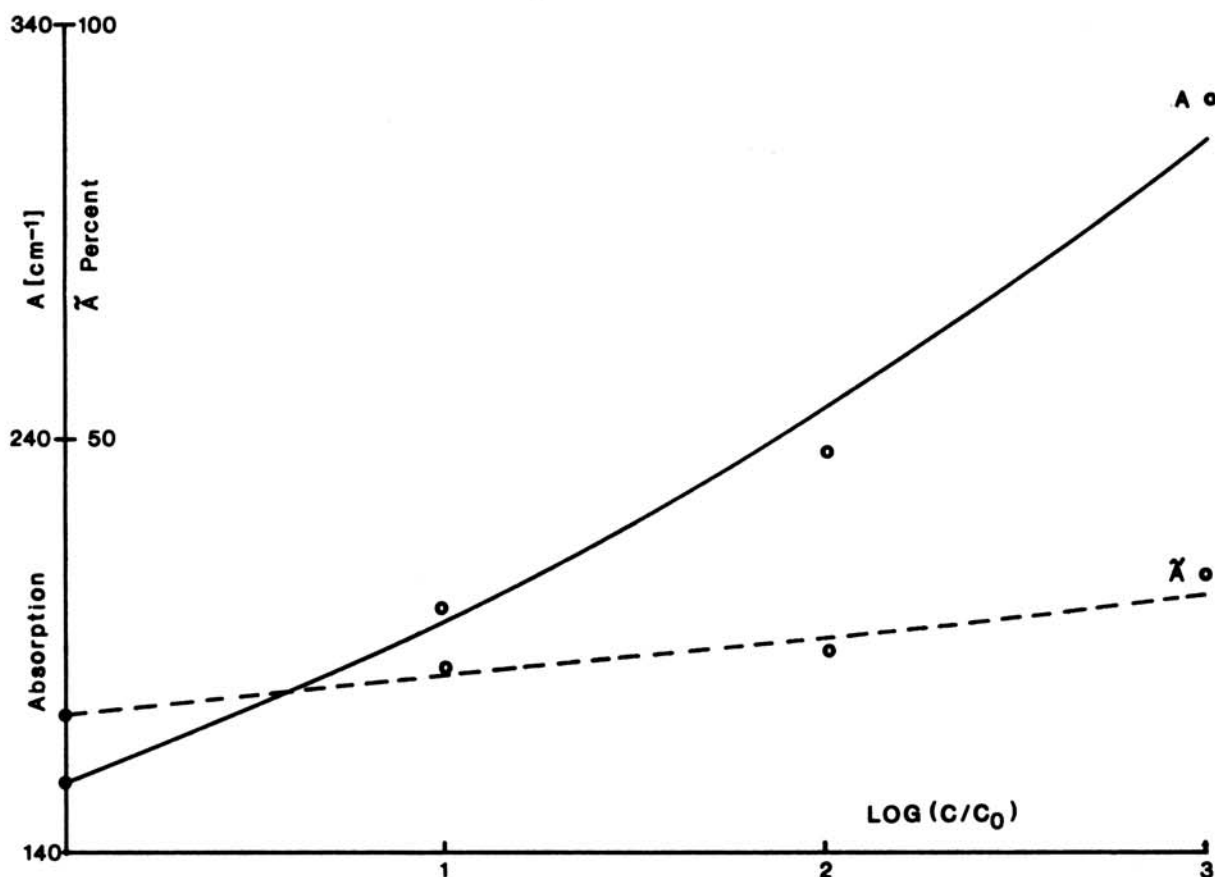


Fig. 5. The dependence of the absorption A and \tilde{A} on the CO₂ concentration. c = concentration, $c_0 = 320$ ppm

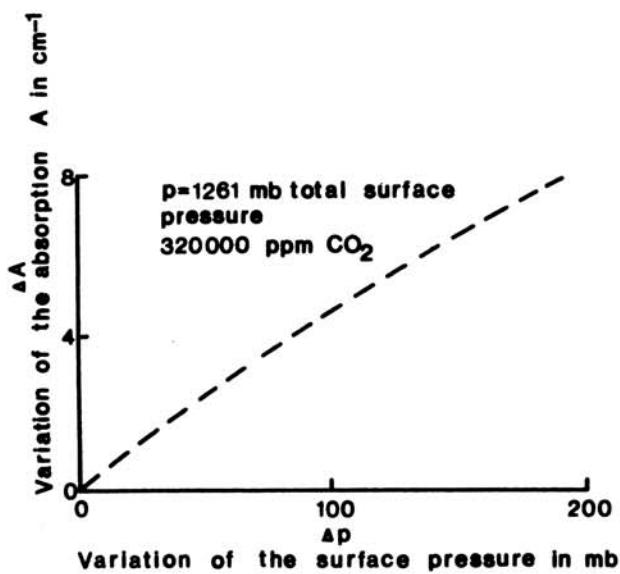


Fig. 6. The dependence of the differential integrated absorption ΔA on pressure variations.

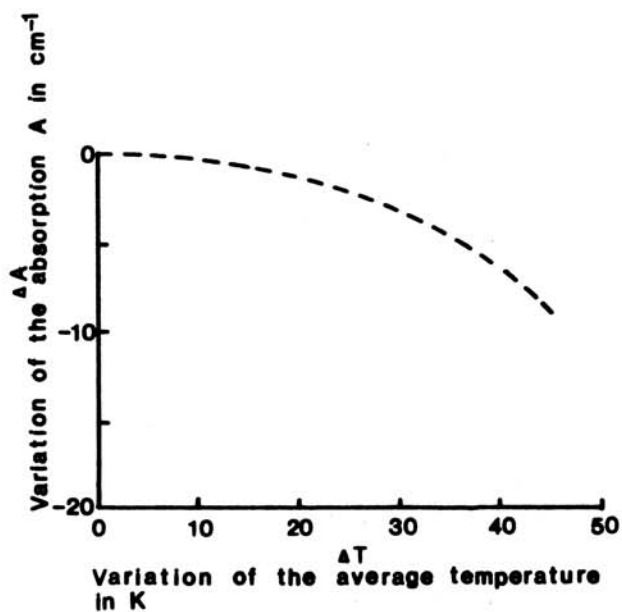


Fig. 7. The dependence of the differential integrated absorption ΔA on temperature variations.

The resulting T surface temperature values are collected for different initial T₀ values in Table 2:

TABLE 2 Average Terrestrial Surface Temperature T as a Function of Atmospheric Carbon Dioxide Concentration and Average Surface Temperature T₀ of a Naked Earth

c	ppm	T K	T K	T K	T K
	0	280 T ₀	260 T ₀	240 T ₀	220 T ₀
	320	289	268	248	227
	3200	291	270	250	229
	32000	294	273	252	230
	320000	300	279	258	236

For the present CO₂ concentration $c = 320$ ppm this crude estimation predicts $\Delta T = 8$ K which is much smaller than the real value $\Delta T = 38$ K, quoted in the introduction. This discrepancy may have several explanations:

a. We took only the $\nu = 666$ cm⁻¹ band of the CO₂ into account. This band certainly has the largest influence: it produces complete absorption at the maximum of the Planck curve (Figs. 3 and 4). When the CO₂ content of the atmosphere increases, the rise in temperature may be caused mainly by the CO₂ bands of higher wave numbers the so called "hot" bands [12]. More detailed calculations, taking into account other CO₂ bands as well are in progress.

b. It seems that in the present terrestrial atmosphere, H₂O produces the major part of the greenhouse effect; CO₂ does not contribute more than 10 % [23]. The H₂O concentration depends strongly on the temperature, it influences the cloud cover and the albedo, and is also dependent on the considerable heat of evaporation for liquid water. This makes the whole situation rather complicated.

c. The continents, clouds, seasons, and winds ask for a dynamical atmospheric model. Consideration of such a comprehensive model, even if one existed, would probably make the task of computation rather hopeless [24]. To be able to estimate the course of climatic changes, for example, one must at present restrict oneself to very crude energy balance arguments.

Möller [1] predicted a temperature rise of about 2 K for a doubling of the present CO₂ concentration, expected within the first half of the coming century. This value is more or less generally accepted in the literature [25]. Our calculations, using a more sophisticated spectroscopy, but also considering CO₂ as the only relevant molecular species, concluded a smaller change of 0.5 K. By taking into account the hot CO₂ bands and the H₂O absorption, this number may be modified and these computations are in progress. Newell and Dopplik [23] also emphasize that the influence of CO₂ can not result in much more than a 0.25 K temperature rise. But the effect of the CO₂ may be amplified by the evaporation of H₂O.

The increase in the concentration of the atmospheric CO₂ is an empirical fact of the past decades, but this has not been associated with an observed global rise of temperature [26]. The explanation is not clear. One possibility is that smog increases the albedo of the Earth, which works in the direction of a temperature fall, and the two independent phenomena may compensate each other. A network of chemical and biochemical reactions may produce even a negative greenhouse effect [27]. The present trends of climatic variation are a subject of debate that careful measurements and good theory could do much to temper.

GEOCHEMICAL CONSIDERATIONS

Theoretical conclusions may be tested against paleoclimatological evidence. The sudden drop of the atmospheric CO₂ content about 1 - 0.75 billion years ago had to produce a relatively quick fall of temperature. If the CO₂ concentration dropped from 32 % to its present value, the transmittance would have increased from 75 % to 88 %, corresponding to a temperature fall of 10 - 12 K. This is the largest change compatible with the geochemical evidence [28]. By measuring the isotopic ratio of oxygen in oceanic sediments, one can obtain the water temperature for different ages, as indicated on Fig. 8. There is an indication of cooling in the last billion years.

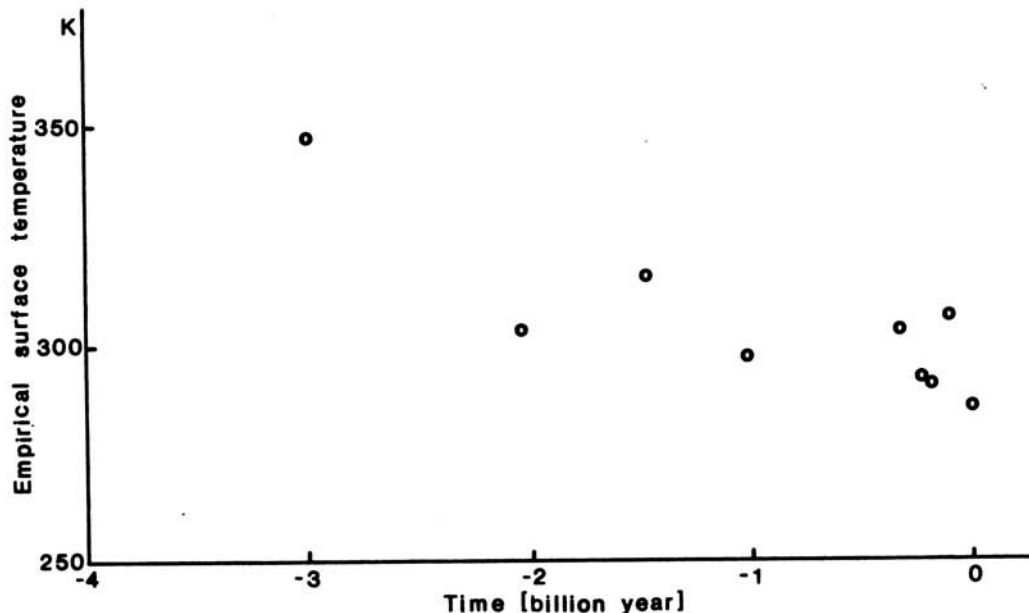


Fig. 8 Temperatures deduced from the isotopic composition of cherts.

A more drastic temperature change, such as suggested by the example of Venus, seems to be excluded empirically in the case of our planet [29].

CONCLUDING REMARKS ON THE THERMAL HISTORY OF THE EARTH

Most geophysical calculations assume an invariable solar constant. But the standard solar model, and even nonconventional models indicate a 5 ± 1 % increase in the solar luminosity per billion years [30]. This is because decreased H concentration must be balanced by higher temperature in the Sun.

This means, that going back in time, the temperature of the Earth's surface must be decreased by 4 K each billion years taking into account the smaller solar luminosity. This helps to moderate the greenhouse effect. The time dependence of the two effects are, however, completely different: the solar reactor warms up smoothly; the sudden disappearance of the CO₂ shield, on the other hand, results in a rapid cooling in the last one billion years.

Another phenomenon, which in principle might have played an important role in the past, was the heat produced by terrestrial radioactivity. For a source producing an average power $W(t)$ per unit volume of the planetary interior, Equation (3) must be modified to

$$\frac{4\pi}{3} R^3 W(t) + \pi R^2 (1 - a) S = 4\pi R^2 \sigma \beta T^4 \quad (12)$$

The value of $W(t)$ is not known exactly, but it can be estimated. For simplicity, let us restrict ourselves to ⁴⁰K decay. The present concentration is about one gram ⁴⁰K per ton of crustal material. If the ⁴⁰K were distributed uniformly within the Earth, the energy produced by its radioactivity would correspond to 0.2 per cent of the solar constant. But this is certainly an overestimation: the light elements are concentrated in the surface layers of the planet. The life time of ⁴⁰K is 1.28 billion years, so that at the time of the Earth's formation the heat production from ⁴⁰K and from U and Th did not exceed half a per cent of the solar heating. The contribution of the radioelements thus did not have a large influence on the thermal history of the Earth in the last 3.1 billion years, and only radioelements with lifetimes considerably shorter than one billion years heated up the planet in the first billion years of its existence; but these nuclei quickly disappeared. In summary, though $W(t)$ might be significant at the beginning, because it had a half lifetime smaller than one billion years, it became negligible after the formation of the planet.

Another early energy source for the Earth was tidal friction. The Moon was much nearer in the early era of the Solar System and the Earth rotated faster. It is rather hard to estimate this effect [31], but at best it could have had a significant contribution only in the first billion years; later it became negligible.

In Fig. 9. the time dependence of these various factors is summarized. The power reaching the surface of the Earth did not decrease in the last three billion years. The observed slight temperature decrease can be explained only by a decreasing CO₂ content.

The thermal stability of Earth -- an ocean temperature between 270 K and 350 K in the past 3.8 billion years -- still needs a more convincing explanation. The different large-scale effects have completely different time dependencies, so the cancellation is still surprising. Lovelock and Margulis [32] assumed that the biological ecosystem called Earth is a selfregulating organism, which takes care of itself, even by stabilizing the climate. This idea is far from being an elaborate quantitative theory, but let us remark that the only way by which the terrestrial life can influence atmosphere is by changing its CO₂ concentration.

If the mankind is interested in its past and in its future, one has to understand the working of this greenhouse in every detail.

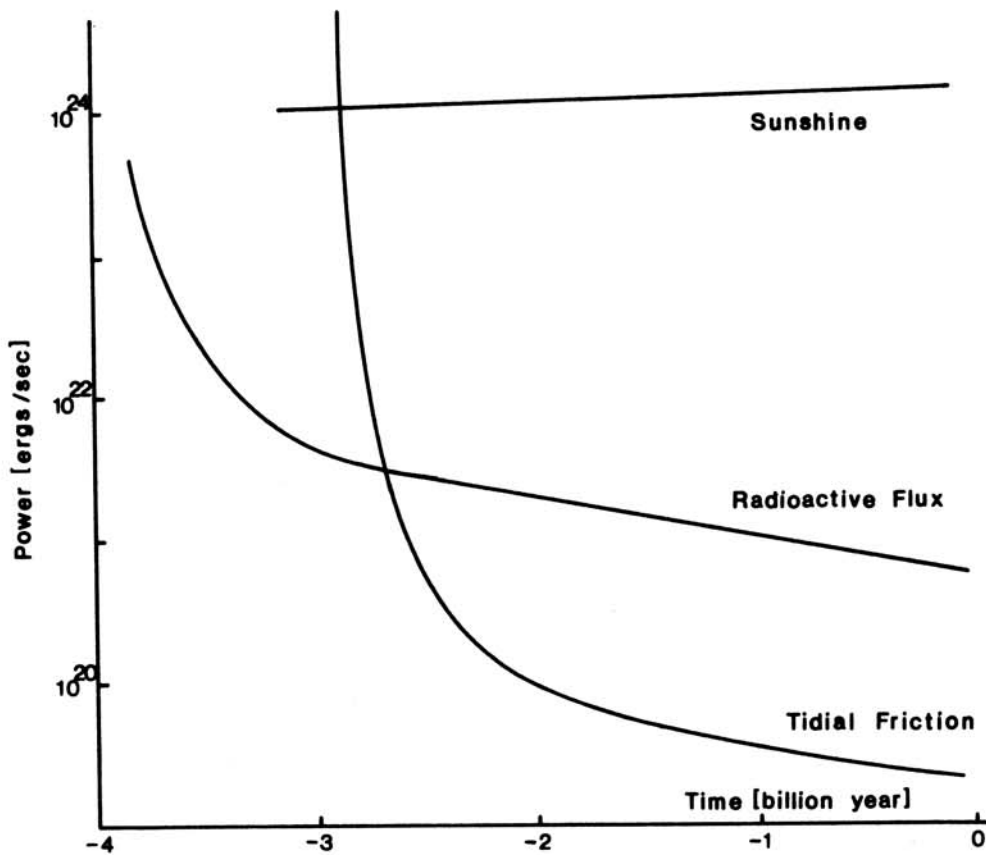


Fig. 9 Energies reaching the surface of the Earth.

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