



Greenhouse Effect Due to Chlorofluorocarbons: Climatic Implications

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as an excursion. Genuine global paleomagnetic excursions can only be confirmed by evidence of spatial, temporal, and internal consistency in replicate cores or sampled sections from each of several areas. Until such evidence is available, it is premature to advocate the use of paleomagnetic excursions as magnetostratigraphic horizons.

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18. An intermediate case of 50 percent remagnetization in a fold has been reported by N. Niitsuma, International Union of Geological Sciences International Geological Correlation Program Conference on Late Cenozoic Magnetostratigraphy, Tokyo and Otsu, Japan, 1974.
19. The importance of the "reinforcement syndrome" [N. D. Watkins, *Geol. Soc. Am. Bull.* **83**, 551 (1972)] should not be underestimated. The initial report of a paleomagnetic excursion will encourage other workers to reexamine previously unexplained or disregarded "curious" results and to reinterpret sedimentation rates so that the anomalous behavior seen by them is contemporaneous with the paleomagnetic excursion. Subsequent work will also focus on sediments of the same age. Reported excursions will then tend to cluster around a single date, whereas negative results showing no anomalous behavior will tend to remain unpublished because they are "not interesting." Thus the initial reports exert considerable leverage on the direction of future research.
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Greenhouse Effect Due to Chlorofluorocarbons: Climatic Implications

Abstract. *The infrared bands of chlorofluorocarbons and chlorocarbons enhance the atmospheric greenhouse effect. This enhancement may lead to an appreciable increase in the global surface temperature if the atmospheric concentrations of these compounds reach values of the order of 2 parts per billion.*

It has recently been suggested (1, 2) that atmospheric concentrations of chlorofluorocarbons (CF₂Cl₂ and CFCl₃) may increase by as much as 20 to 30 times the present-day value, 0.1 part per billion (ppb) by volume, if the present level of injection into the atmosphere is maintained. The primary reason for this expected buildup seems to be the lack of any significant tropospheric removal mechanisms for these compounds. In addition, Lovelock's (3) recent measurements indicate substantial concentrations (≈ 0.1 ppb) of CCl₄ within the troposphere, and Lovelock suggests the presence of other chlorocarbons (CHCl₃, CH₃Cl, and CH₂Cl₂) within the atmosphere. The consequences of a significant buildup of these compounds for the chemical balance of the atmosphere has already been investigated (1, 2, 4). In this report I examine another important aspect of the problem, the impact on the overall thermal energy balance of the earth-atmo-

sphere system due to a significant buildup in the concentrations of the chlorofluorocarbons and chlorocarbons.

The chlorofluorocarbons and chlorocarbons have strong infrared bands (5-8). The infrared bands of these compounds would absorb radiation from the surface and emit it at the atmospheric temperature. Since

Table 1. Chlorofluorocarbon band positions and intensities.

| Species | Assignment | Band | | Reference |
|---------------------------------|----------------|-------------|------------------------|-----------|
| | | Center (μm) | Intensity (cm/mole) | |
| CF ₂ Cl ₂ | ν ₁ | 9.132 | 2.98 × 10 ⁷ | (5) |
| | ν ₆ | 8.681 | 2.0 × 10 ⁷ | (5) |
| | ν ₈ | 10.93 | 3.07 × 10 ⁷ | (5) |
| CFCl ₃ | ν ₁ | 9.217 | 1.75 × 10 ⁷ | (6) |
| | ν ₄ | 11.82 | 3.75 × 10 ⁷ | (6) |

the atmosphere is at a lower temperature than the earth's surface, these bands would cause a reduction in the net infrared radiative flux (F , watts per square meter) emitted to space by the earth-atmosphere system. This trapping of the surface radiation by the infrared bands, also known as the greenhouse effect, would tend to increase the surface and atmospheric temperature. The strongest bands of these compounds are located in the spectral region 8 to 13 μm where the atmosphere is relatively transparent. Because of this relative transparency, the atmospheric and surface temperatures are most sensitive to constituents that have absorption bands in this spectral region. In order to estimate the increase in the surface temperature (T_s), the reduction in F due to the infrared bands of the chlorofluorocarbons and chlorocarbons is computed first. The procedure for the flux calculation is described only for chlorofluorocarbon bands since the same procedure can be applied to the chlorocarbon bands.

For this analysis I consider only bands in the region 8 to 12 μm, since these bands are stronger by two orders of magnitude than bands located elsewhere in the infrared spectrum (5-8). Table 1 shows the band centers and intensities. Radiative transfer within infrared bands can be conveniently formulated in terms of the total band absorptance, A (reciprocal centimeters) (9, 10). This is the total spectrally integrated absorption by the band, and for the present analysis the bands are optically thin (11), so A can be written as

$$A = SX \quad (1)$$

where S is the band intensity and X is the amount of absorber. The formulation of F in terms of A is given by Cess and Ramanathan (9). Pertinent details of the flux calculations are given in (12).

The model atmosphere—that is, the vertical distribution of temperature, H₂O, and clouds—is adopted from Rasool and Schneider (13) and reflects the present-day globally averaged conditions. The mixing ratio, q , of CF₂Cl₂ and CFCl₃ is prescribed by

$$q = K; \quad 0 \leq z \leq 12 \text{ km} \\ = K \exp[(12 - z)/H]; \quad z > 12 \text{ km} \\ H = 3 \text{ km} \quad (2)$$

where z is the altitude with $z = 0$ denoting the surface, H is the prescribed scale height, and K is the tropospheric mixing ratio (parts per billion, by volume) which has been assumed constant. The shape of the mixing ratio profile given by Eq. 2 is consistent with the model predictions of Cicerone *et al.* (2).

When Eqs. 1 and 2 are combined with

SCIENCE, VOL. 190

the flux formulation given in (9), the following relations are obtained

$$\begin{aligned}\Delta F(\text{CF}_2\text{Cl}_2) &= -0.307 K(\text{CF}_2\text{Cl}_2) \\ \Delta F(\text{CFCl}_3) &= -0.256 K(\text{CFCl}_3)\end{aligned}\quad (3)$$

where $\Delta F(\text{CF}_2\text{Cl}_2) = F(\text{with CF}_2\text{Cl}_2) - F$ (unperturbed). As expected, the outgoing flux decreases with the addition of chlorofluorocarbons. Further, $-\Delta F$ increases linearly with the mixing ratio since the band absorption increases linearly with the mixing ratio (see Eq. 1). The optically thin condition imposed on Eq. 1 restricts the applicability of Eq. 3 to values of K less than 5 ppb.

The implications of Eq. 3 for the global climate can be examined by invoking the global energy balance condition (14), which states that on a global average the net incoming solar radiation should be in balance with F . Since the net incoming solar radiation would not change with the addition of chlorofluorocarbons, the energy balance condition implies that F has to be the same for both the perturbed and the unperturbed atmosphere. Recall that the ΔF given by Eq. 3 was calculated by fixing the atmospheric and surface temperature. Hence, it follows that the decrease in F has to be compensated by an increase in the tropospheric and surface temperature. The decrease in F can be related to an equivalent change in T_s through the relation

$$\Delta T_s = -\frac{\Delta F}{dF/dT_s}\quad (4)$$

where dF/dT_s is obtained by differentiating Budyko's (14) empirical formulation for F with respect to T_s , which yields $dF/dT_s = 1.425 \text{ watt m}^{-2} \text{ }^\circ\text{K}^{-1}$. The increase in T_s obtained by substituting Eq. 3 in Eq. 4 is shown in Fig. 1. The surface temperature calculations were also performed using the detailed radiative-convective model described by Ramanathan *et al.* (15) and the results were identical to those shown in Fig. 1; this verifies the simpler procedure defined by Eqs. 3 and 4. Chlorocarbons also have strong infrared bands, and the contributions of the chlorocarbons to the increase in T_s are listed in Table 2. If the addition of chlorofluorocarbons results in a net reduction in the atmospheric O_3 concentration, as has been predicted (1, 2), the results for ΔT_s will be slightly modified (16).

The increase in T_s will be higher by about 15 percent if the coupling between T_s , the amount of H_2O , and solar absorption by H_2O is included. Including this effect, it is seen from Fig. 1 that the mean global surface temperature could, under the assumption of this simplified model, increase by as much as 0.9°K if the concentrations of CF_2Cl_2 and CFCl_3 were each in-

Table 2. Chlorocarbon band parameters and contribution to surface temperature (T_s). In column 5 K is the tropospheric mixing ratio for the species identified in parentheses; applicability of the equations used in the calculations is restricted to $K < 5$ ppb.

| Species | Band | | Reference | Increase in T_s ($^\circ\text{K}$) |
|--------------------------|--------------------------|---------------------|-----------|--|
| | Center (μm) | Intensity (cm/mole) | | |
| CCl_4 | 12.987 | 3.9×10^7 | (7) | $0.14 K(\text{CCl}_4)$ |
| CHCl_3 | 13.00 | 2.7×10^7 | (6) | $0.104 K(\text{CHCl}_3)$ |
| | 8.19 | 4.2×10^6 | (6) | |
| CH_2Cl_2 | 14.0 | 7.9×10^8 | (5) | $0.052 K(\text{CH}_2\text{Cl}_2)$ |
| | 13.58 | 1.19×10^7 | (5) | |
| | 7.92 | 3.282×10^7 | (5) | |
| CH_3Cl | 13.66 | 2.32×10^6 | (8) | $0.013 K(\text{CH}_3\text{Cl})$ |
| | 9.85 | 4.02×10^8 | (8) | |
| | 7.14 | 1.9×10^6 | (8) | |

creased to 2 ppb. Such a concentration of chlorofluorocarbons is expected to be reached by the year 2000 if the present level of injection is maintained (1, 2). Further, Table 2 shows that the chlorocarbons can also have appreciable effects on T_s . The increase in T_s may be amplified several times in the polar regions because of the positive feedback mechanism between ice cover, albedo, and surface temperature (17). This possibility underscores the importance of these results. However, the model presented here is a simplified one that neglects several atmospheric feedback mechanisms and all effects due to circulation. Hence, these calculations should not be considered as a definitive prediction of the response of the actual atmosphere system, but rather as indicative of the potential consequences for the climate of anthropogenic sources of chlorofluorocarbons.

The significance of these results can best be evaluated by referring to the papers by Bryson (18) and Schneider (19), which indicate that a surface temperature change of the order of 0.5°K may be sufficient to substantially alter some of the important climatic variables (rainfall and ice cover) in at least parts of the globe. The effect of chlorofluorocarbons and chlorocarbons on the chemical balance of the earth-atmo-

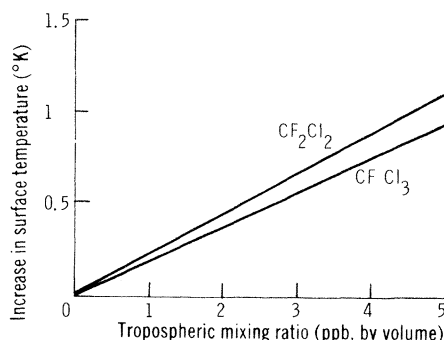


Fig. 1. Increase in global surface temperature is a function of the tropospheric concentrations of CF_2Cl_2 and CFCl_3 . Results are for globally averaged conditions with 50 percent cloud cover.

sphere system is currently a subject of concern. The major conclusion of this report is that their effect on the earth's thermal energy balance must also be given serious consideration.

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- The optically thin condition requires that $SX/\Delta\omega \ll 1$, where $\Delta\omega$ is the bandwidth (9, 10). Person *et al.* (6) suggest that $\Delta\omega \approx 100 \text{ cm}^{-1}$. The maximum value of X that will be considered in this work is about 0.001 cm atm , so even for the strongest band $SX/\Delta\omega \ll 1$. Similar conclusions can also be reached from Person *et al.*'s discussion.
- In the flux calculations the band absorbance is defined as $A = 2SX$, where the factor 2 accounts for the angular integration over isotropic radiation. The bands of chlorofluorocarbons and chlorocarbons are overlapped by the continuum band of H_2O , and this overlap has been accounted for by multiplying the band absorbance by the transmissivity of the continuum band. The absorption coefficients for the continuum band of H_2O were obtained from K. J. Bignell, *Q. J. R. Meteorol. Soc.* **96**, 390 (1970).
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- It has been indicated (1, 2) that increasing CF_2Cl_2 and CFCl_3 concentrations to 2 ppb would decrease O_3 by 10 percent. A 10 percent decrease in O_3 , if distributed uniformly between 12 to 40 km, would decrease T_s by about 0.07°K (15). Ramanathan *et al.* (15) consider a uniform reduction in O_3 within the stratosphere while, as pointed out by R. E. Dickinson (private communication), the fluorocarbons reduce O_3 mainly above 30 km. Preliminary calculations indicate that reducing O_3 above 30 km might lead to a slight increase in T_s .
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Precambrian Eukaryotic Organisms: A Reassessment of the Evidence

Abstract. *Comparison of partially degraded unialgal cultures of *Chroococcus turgidus* with coccooid microfossils from the Late Precambrian Bitter Springs formation, Australia, suggests that the Precambrian fossil record has been seriously misinterpreted. Use of degradational features as taxonomic characters has resulted in unrealistically high estimates of Precambrian algal diversity. There is at present no compelling evidence for the presence of eukaryotic microfossils in rocks from the Bitter Springs formation or any older sedimentary sequences.*

A decade ago one of us (1) suggested that certain coccooid microfossils occurring in profusion in the then recently discovered cherts of the Late Precambrian Bitter Springs formation, central Australia, represented the earliest evidence of eukaryotic organisms in the evolutionary record of life. These fossil algae, which were found either as isolated cells or as loose aggregates of few to many individuals, were sometimes devoid of cellular contents, but often possessed an internal discrete structure excentrically or peripherally located with respect to the delimiting "wall." Cytoplasmic remnants (interpreted as inner cell walls) surrounded the internal body in certain cells. The well-defined internal structures were interpreted as nuclear or organellar bodies (2-4), and a series of supposedly discrete taxa of both prokaryotic and eukaryotic algae was erected on the assumption that the presence or absence of these blebs and coagulated protoplasmic remnants constituted valid taxonomic characters (2, 3). This interpretation was seriously questioned by Awramik *et al.* (5), who emphasized that this taxonomy failed to take into account the variability of internal structure caused by partial degradation of blue-green algae.

Because of the importance of proper interpretation of Precambrian fossils, we undertook a new series of degradation experiments and found that the entire range of morphologic variation exhibited by a dozen taxa of coccooid algae (supposedly both prokaryotic and eukaryotic) from the Ellery Creek locality of the Bitter Springs formation could be duplicated in detail by partially degrading a unialgal culture of the chroococcalean species *Chroococcus turgidus* (Kütz.) Nägeli. Our results suggest that the Precambrian fossil record has been seriously misread. The three-dimensional morphology of microfossils is generally not preserved by the cell wall as has been previously assumed, but rather by one

or more mucoidal sheaths (6). The putative organellar remnants are in reality degraded protoplasm representing the entire contents of the cell. This fact, coupled with an appreciation of the morphologic variability within living chroococcalean species, indicates that there is no compelling evidence for the presence of eukaryotes in the Bitter Springs formation or any older rocks. It also demonstrates that published estimates of the taxonomic diversity of the Bitter Springs and other Precambrian floras are excessive.

The experimental procedure is simple. Unialgal cultures of cyanophytes were grown at room temperature in reduced natural light on mineral agar slants prepared with Bold's basal medium (7). As the cultures became stale, smears were prepared and stained with a dilute aqueous solution of safranin to enhance observation and photomicrography. A *Chroococcus turgidus* culture was selected for detailed examination because of its almost uncanny resemblance to described Bitter Springs fossils; however, other chroococcalean cultures exhibited a similar pattern of variation and degradation. This pattern has also been observed in algal mats growing in Massachusetts, Australia, and the Persian Gulf by Golubic and his colleagues (5, 6).

Figure 1, A to P, illustrates the range of morphologies which result from the partial degradation of a naturally morphologically varied population of blue-green algal cells. Diameters of individual cells of *Chroococcus turgidus* range from 6 to 20 μm or more; the average diameter is approximately 10 to 12 μm . The number of cells per packet varies from one to four, although unicells and dyads are by far the most common. The shape of the cells forming dyads is variable, ranging from spherical, gibbous, or hemispherical to lunate (Fig. 1, A to H). The number of sheaths per cell also varies, as does the degree of protoplast degradation (6). Par-

ticularly important is the observation first made by Awramik *et al.* (5) that decomposition leaves the sheath intact, but condenses the protoplast into a globular remnant identical in every respect to the "nuclei" and "organelles" observed in Precambrian fossils (Fig. 1O). The final product of this process is an empty sheath (Fig. 1P). In spite of the wide range of variation of the organisms pictured here, all represent a single species from a pure culture.

Comparison of the *C. turgidus* culture with coccooid fossils from the Ellery Creek locality of the Bitter Springs formation (Fig. 1, Q, DD, and GG) demonstrates a remarkable similarity between the two populations, which are separated in time by almost a billion years. It is no exaggeration to state that the Bitter Springs assemblage could easily represent the remains of a single species of *Chroococcus*, a species having the same range of variability as *C. turgidus*. The Bitter Springs organisms in question have been assigned to the following taxa: *Globophycus rugosum*, *Bigeminococcus lamellosus*, *B. mucidus*, *Eozygion grande*, *E. minutum*, *Myxococcoides reticulata*, *Glenobotrydion aenigmatis*, *G. majorinum*, *Gloeodinopsis lamellosa*, *Caryosphaeroides pristina*, *C. tetras*, and *Eotetrahedron princeps*. The last six taxa have been described as eukaryotes. All of the Bitter Springs taxa listed above can be found in three petrographic thin sections

Fig. 1. All photomicrographs $\times 1100$; the bar in EE equals 20 μm . (A-P, EE) *Chroococcus turgidus* (Kütz.) Nägeli, demonstrating the variation in morphology and degree of degradation observable in a single unialgal culture. Arrows in (F) and (O) refer to pseudonuclear protoplasmic remnants within undegraded sheaths. The three groups of blue-green algae in (EE) duplicate in detail the putative mitotic sequence suggested for coccooid microfossils from the Bitter Springs formation. (M and N) Two views of a single tetrad. (Q-DD, GG) Microfossils found in slides TBS-22-1A, 1B, and 1C from the Ellery Creek locality of the Bitter Springs formation, the taxonomy according to Schopf and Blacic (3); (Q) *Gloeodinopsis lamellosa* Schopf; (R) *Globophycus rugosum* Schopf; (S and T) unnamed morphologic entities; (U) *Bigeminococcus mucidus* Schopf and Blacic (?); (V) *Eotetrahedron princeps* Schopf and Blacic. Arrow points to fold in degraded protoplasm which in this plane simulates a trilete scar; (W and Y) *Eozygion minutum* Schopf and Blacic; (X, Z, and CC) *E. grande* Schopf and Blacic. (X) and (CC) show two views of the same organism; (AA) unnamed triad; (BB) *Eotetrahedron princeps* Schopf and Blacic; (DD) *Myxococcoides reticulata* Schopf; (GG) *Glenobotrydion aenigmatis* Schopf; note pseudonucleus. (FF) Coccooid alga from the Gunflint formation, Ontario, exhibiting a pseudonucleus. (HH) *G. aenigmatis* Schopf from the Ross River locality of the Bitter Springs formation, showing prominent pseudonuclei. (II) Pseudonuclei within a blue-green algal sheath in chert from the Ross River locality of the Bitter Springs formation.