

## Crucial role of the magnetic field in the evolution of life

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**Abstract.** The formation of a steady ozone layer in the earth's atmosphere is the most significant event in the evolutionary cycle of the earth which, in turn, has been responsible for the development of life with an oxygen metabolism. In addition to protecting biological life from exposure to ultraviolet radiation the ozone layer has also been responsible for maintaining the water and oxygen balance in the atmosphere. It is argued that the magnetic field of the earth is really responsible for the formation of this steady ozone layer in the earth's atmosphere. Because of the earth's magnetic field and associated trapped charge particle belts and the magnetosphere, the earth's atmosphere does not directly interact with the interplanetary space. Without such a shielding, the free oxygen atoms could have been depleted considerably causing a severe depletion in the ozone concentration to start with. The impact of charged particles from galactic and solar cosmic rays over the entire earth's atmosphere and the consequent production of  $\text{NO}_x$  would have given rise to a major ozone sink, if earth were devoid of a magnetic field. The net result would have been the absence of a steady ozone layer and the absence of life with an oxygen metabolism, as in the case of the atmospheres of Venus and Mars, if the earth did not have a magnetic field.

**Keywords.** Ozone; geomagnetic field; nitric oxide; trapped particles; ozone sink.

### 1. Introduction

The large amount of information gathered during the last two decades through *in situ* explorations and laboratory experiments now provides us an unique opportunity to reexamine our fundamental ideas and assess their role in the evolution of biological life, as it exists today on the earth. The condensation of solar nebula and the formation of the solar system, about 5 billion years ago, the planetary formation as we know today and the virtual loss of hydrogen and helium from the inner or terrestrial planets, through molecular escape as also due to the sweeping action of solar wind, are fairly well understood. From the observed physical properties of planets such as density, atmospheric pressure, temperature, chemical composition and surface gravity, it is clear that the solar system of planets can be classified under two broad headings namely (i) high density terrestrial planets with a heavy core like Mercury, Venus, Earth and Mars and (ii) lighter gaseous outer planets such as Jupiter, Saturn and other outer planets.

An examination of the atmosphere of outer planets indicates that they have primarily a non-oxidising, primordial atmosphere with a fluidic surface unlike all the inner planets which possess an oxidising secondary atmosphere with a solid surface, evolved through the venting of trapped gases from within the planet. It is, therefore, clear that only the inner planets can, if at all, sustain life with an oxygen metabolism.

Even amongst the inner planets, Viking experiments have indicated that life even in its primitive biological form exists only on earth. Even though the non-existence of life on Mercury is readily explainable because of its nearness to the Sun and the consequent escape of the bulk of its atmosphere, the uniqueness of Earth in sustaining life and intelligence as distinct from Mars and Venus is one of the major problems in present-day investigations.

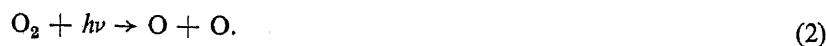
The formation of a permanent steady-state ozone layer is the most crucial incident which resulted in the evolution of earth's atmosphere capable of sustaining life with an oxygen metabolism. The primary root cause for the formation of an ozone layer on earth, in our opinion, is the dipole magnetic field of the earth. It is significant that none of the terrestrial planets have a significant magnetic field, even though they all have oxidising secondary atmospheres. Mercury has a very small and insignificant magnetic field (less than 350 gamma) which may or may not be due to a dipole magnetic field. Consequently, none of the other inner planets have trapped radiation belts and earth like magnetospheres. Whereas the origin of the dipole magnetism of a planet is beyond the purview of this paper, we propose that the fundamental magnetic character of the earth is responsible for the formation of the ozone layer in the earth's atmosphere, which in turn has been the major factor in the evolution of life with oxygen metabolism on earth.

## 2. Development of oxygen and ozone in the atmosphere

Assuming the primitive atmosphere to have been non-oxidising, the conversion of a non-oxidising atmosphere to an oxidising one and its relationship with the evolution of life forms a fascinating story. The first step in the evolution of an oxidising atmosphere is now understood to have been due to the photo-dissociation of water vapour by solar ultraviolet radiation which, in the absence of an ozone layer, would have penetrated to the lower levels of the atmosphere where water vapour was present,



Whereas the lighter  $\text{H}_2$  molecules quickly escaped into space, the free O atoms left behind combined to form  $\text{O}_2$ . Some of the highly reactive  $\text{O}_2$  combined with  $\text{NH}_3$  and  $\text{CH}_4$  to yield  $\text{N}_2$  and  $\text{CO}_2$ , thus enabling the atmosphere, as a whole, to move towards an oxidising atmosphere having  $\text{CO}_2$ ,  $\text{N}_2$  and  $\text{O}_2$ . The gradual upward drift of  $\text{O}_2$  molecules to higher levels and their transformation to ozone under the action of solar ultraviolet radiation, was the most important phenomenon in the cycle of evolution. The  $\text{O}_2$  molecules dissociated into oxygen atoms under the bombardment of ultraviolet photons with wavelengths less than 242 nm in the Hertzberg continuum to form oxygen atoms.



These oxygen atoms combined with  $\text{O}_2$  to form ozone



In spite of ozone being a minor constituent in the earth's atmosphere, it has played an extremely significant role in the evolution of life. The efficient absorption of ultraviolet by the ozone layer preventing solar UV to reach lower levels of atmosphere, not only stopped further dissociation of  $H_2O$  but also helped in the levelling off of oxygen which also can dissociate through UV irradiation. Further, by cutting off the ultraviolet food supply to complex organic molecules, the ozone layer initiated the first major revolution in the history of evolution due to which only those organisms which could use energy from visible radiation such as porphyrins and new types of organisms, which could adapt to the changed conditions, survived (Field *et al* 1978). Plants which derive energy from sunlight thrived and through photosynthesis further enhanced the oxygen content in the atmosphere, rapidly aiding the evolution of the atmosphere as we know it today. Thus without a steady ozone layer, plant life would not have come into existence and photosynthesis would not have played any role in the oxygen balance of the atmosphere. Even though there are anaerobic organisms which do not need oxygen, all the animal life, we know, require oxygen to metabolise their food. The ozone also formed an important protective layer shielding animal and human life from harmful biological effects arising from exposure to the ultraviolet radiation. The fact that no significant, quasi-permanent ozone layer has been observed in the atmosphere of other terrestrial planets provides us with the major clue to the understanding of the evolution of life on earth. Venus, in addition to its high temperature, has essentially a carbon dioxide atmosphere with some oxygen. The Martian atmosphere has practically no oxygen or liquid water even though it has an oxidising  $CO_2$  atmosphere. Neither of the above planets have a protective steady ozone layer.

### 3. Role of the magnetic field

The interaction of the radially blowing supersonic solar wind on the earth's magnetic field is well-known. Solar wind carrying a frozen-in magnetic field forms a bow shock and magnetosphere in front of the earth on the sunward side. On the night side, the earth's magnetic field is stretched in the form of a highly elongated tail. Particles are accelerated in the tail and enter the earth's atmosphere along the magnetic field lines near the poles.

The geomagnetic field exerts a major influence on the penetrating radiations from space, in particular on the charged particle radiation. The magnetic field of the earth essentially blocks the charged particles such as cosmic rays entering the earth's atmosphere, the minimal energy required for the parent particle to penetrate being around 15 GeV at the equator. At the poles, even the lowest energy particles can reach the earth, the depth of penetration being essentially controlled by absorption by the Earth's atmosphere. The trapped van Allen radiation belts around the earth containing electrons, protons and even alpha particles effectively shield the ionosphere from the interplanetary space. It is, therefore, clear that a planet which has no intrinsic magnetic field is devoid of trapped radiation belts and hence its atmosphere will be continuously exposed to the solar wind as well as cosmic ray bombardment. The impact of charged particles on a continuous basis would have produced large amounts of  $NO_x$  which is an effective sink for  $O_3$  and would have thus destroyed whatever ozone was formed. The net result would have been the absence of an ozone layer.

Some of the effects of the earth's magnetic field on biological species are established, even though they are not fully understood. The magnetization of the molecular structure of some of the very primitive species found at high latitudes and near poles have been known for sometime, even though the role of the magnetic field itself in the evolution of the species is not understood. Likewise, experiments have conclusively shown that many migrating birds use the magnetic field for navigation. Historical evidence gathered from a study of rocks indicates that the earth's magnetic field has apparently reversed a few times during the last few million years. During such reversals, the geomagnetic field must have passed through the null value during which the earth would have been exposed to all the radiation from outside and the van Allen belts would have emptied into space. Evidence exists that during such periods, several plant and animal lives on earth were very seriously affected, with some specific species such as radiolaria becoming extinct (Field *et al* 1978). Whereas the effect during such short periods of transition (short compared to the evolutionary time-scale) would be drastic, the effect of the non-existence of magnetic field on a permanent basis could be totally disastrous from the point of evolution of life.

#### 4. Effect of geomagnetic field on the formation of ozone

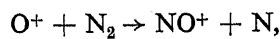
A striking feature of the atmosphere of inner planets is that their atmospheres can be roughly divided into two main parts, the lower portion below the turbopause where convective vertical mixing and eddy diffusion dominate and the upper portion above the turbopause, where molecular diffusion dominates (Goody 1979). Molecular diffusion above the turbopause is dependent on the molecular weight of the species itself, the scale height increasing with decrease in molecular weight. The vertical distribution of each species such as nitrogen, helium, atomic oxygen, etc., in the thermosphere and above ( $> 100$  km.) is consequently dependent on the exospheric temperature profile.

The interaction between the ionic species in the *F* region ionosphere and the protonosphere is essentially characterised by molecular diffusion. The interaction between protons from the protonosphere and  $O^+$  ions in the ionosphere involves continuous charge exchange and, hence, the dynamics of the ionic species above the exobase is significantly affected by the electric fields in the ionosphere and the magnetosphere (Lemaire and Scherer 1974; Torr and Torr 1979). The upward drift of oxygen atoms and ions are thus shielded by the protonosphere and the magnetosphere, in the case of earth.

If earth did not have the magnetic field, the solar wind would have directly interacted with the earth's ionosphere as in the case of Mars or Venus. The magnetosphere, in that case would be very close to the earth, where the piled up magnetic field above the ionospheric current system balances the stagnation pressure of the solar wind (Dessler 1968; Johnson and Midgley 1969). The solar wind carrying a frozen-in magnetic field, as it deflects and flows round the ionosphere, will sweep the  $O^+$  ions along with it thus depleting  $O^+$ , even though quantitative estimates of its effect are quite difficult. In other words, the sweeping by solar wind is an additional important effect which must be considered along with Jean's (1925) escape for estimating the escape of gases. Further, the solar wind energy which is about  $0.5 \text{ erg/cm}^{-2}\text{S}^{-1}$  (only a factor of 6 lower than solar EUV radiation), through application

of direct pressure  $\sim B^2/2\mu_0$ , where  $B$  is the interplanetary magnetic field, will cause a downward motion of the ionosphere in addition to heating the upper atmosphere. Because of the strong thermal coupling of the ionospheric plasma and neutral gas (Henry and McElroy 1969), the above effect would cause an increase in the thermospheric temperatures (Zahn and Fricke 1977). Such an increase in temperature would cause a depletion of atomic oxygen at lower altitudes.

The downward penetration of solar wind ions in the absence of the magnetic field alone would produce ions at a rate of  $\sim 10^{10}$  amu/cm<sup>2</sup>sec. (Cloutier, *et al* 1969; Michel 1971). The impact of charged particle ionization has to be considered in addition, the net result being that free oxygen atoms even at very low altitudes would be ionized if the earth were devoid of a magnetic field. The reaction rates for ion-neutral reactions (McEwan and Phillips 1975) particularly for



being very high,  $\text{O}^+$  readily combines with these neutral species. Similar is the case with the reaction with  $\text{CO}_2^+$ , which through



directly depletes the available odd oxygen atoms.

Likewise, the rapid charge exchange reaction of solar wind protons interacting with upper ionosphere will follow



The net result of these reactions is a copious ionization of O atoms, compression of the ionosphere, depletion of free oxygen atoms at lower levels and consequent reduction in the formation of ozone as given in equation (3). Thus, if the earth did not have the magnetic field, the extension of ionosphere into the interplanetary space would have resulted in a substantial reduction in the ozone flux.

##### 5. Role of magnetic field in providing an ozone sink

The ozone balance in the stratosphere is maintained by several competing chemical reactions and atmospheric transport processes. There is a considerable amount of uncertainty in our understanding of both transport process and reaction constants. The destruction of ozone is primarily through two major processes. Ozone is dissociated by ultraviolet photons with wavelengths longer than 242 nm in the Hartley continuum as follows:



It is also destroyed by  $\text{NO}_x$  produced primarily by cosmic ray-induced activity and partly by anthropogenic phenomena such as the usage of fertilizers, increased indus-

trial activity and avionic induction of  $\text{NO}_x$  in the lower stratosphere. Thus, any mechanism which increases the production of odd oxygen atoms (equation (2)) will increase ozone whereas increase of photon flux above 242 nm or other operative sinks will reduce ozone. A final balance in ozone is then achieved by quasi-balance between its production and loss (Campbell 1977; Chamberlain 1978).

The destruction of ozone by absorption of UV and through interaction with oxides of nitrogen are the two major sinks of ozone. Extensive studies have been carried out to understand the long and short term behaviour of ozone in the earth's atmosphere at different altitudes and latitudes and as a function of the solar cycle of activity. In spite of this, the complex coupled nature of atmospheric phenomena and uncertainty in rate coefficients (Callis 1978; Smith 1978) have made the theoretical understanding of the phenomena difficult. The observations indicate about a 30% change in the mid and high latitude-integrated ozone content with the maximum occurring around the spring months and minimum in the local autumn months in each hemisphere. Even though the total ozone content over the equator is roughly half that at high latitudes, the ozone content above 10 mb level shows a positive gradient going equatorward. Whereas the latitudinal profile of total ozone is dictated more by the circulation pattern rather than the production mechanism of ozone (ozone production being higher at the equator), ozone at higher latitudes is strongly influenced by solar activity.

Extensive investigations of long term changes of ozone with the solar cycle of activity indicate that the effect due to a change in UV radiation itself, even though could be locally as high as 15% at altitudes of about 40 km is less than 4% on an integrated level (Penner and Chang 1978; Dütsch, 1979). The major effect on ozone is from oxides of nitrogen, induced by cosmic radiation (Johnston 1971; Crutzen 1975), the main operative reaction responsible for the creation of NO being

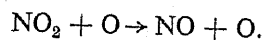
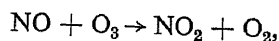


Ionization due to cosmic rays (Delgarno 1967) is produced mainly by secondary electrons ejected by heavy particles. The dissociation ionization cross-section increases to a maximum at around 100 eV, beyond which it decreases with increasing energy. Taking reasonable values for the dissociation ionization cross-section for  $\text{N}_2$  and  $\text{O}_2$  molecules, Nicolet (1975) has shown that the production of nitrogen atoms through dissociative ionization and dissociation is about one nitrogen atom for each ion pair produced by cosmic radiation.

At altitudes of about 25 km, the NO so produced removes the odd oxygen atom and thus reduces the production of ozone itself through the reaction



The major effect, however, is the catalytic destruction of ozone itself through the reactions



The net result being



Ruderman and Chamberlain (1975) have established a functional relationship between the increase in NO and the resultant depletion of ozone through its absorption which indicates that the relative decrease in ozone would be roughly half the relative increase in NO concentration

$$\Delta[\text{O}_3]/[\text{O}_3] = \frac{1}{2} \Delta[\text{NO}]/[\text{NO}] \quad (11)$$

The enhancement of cosmic ray intensity during the sunspot minimum and consequent enhancement in the NO production by almost a factor of two at high latitudes to about 40 molecules  $\text{cm}^{-3} \text{sec}^{-1}$  (Nicolet 1975) or about  $2 \times 10^{23}$  molecules of NO, according to Ruderman and Chamberlain (1975) causes a 30% decrease in ozone production at middle and high latitudes. Taking into account the time lag effects due to the reasonably well-accepted residence time of NO in the stratosphere of about 2 years, the above authors conclude that the observed solar cycle variation of ozone including the time lag is consistent with it being cosmic-ray-modulated. Even though subsequent calculations by Crutzen *et al* (1975) using more recent values for the reaction coefficients seem to indicate a reduced magnitude of this effect, the galactic cosmic ray-induced NO as an effective sink for  $\text{O}_3$  particularly at altitudes above 20 km is well established.

Before deriving quantitative estimates of the effect of NO on ozone, the interactions between  $\text{NO}_x$  and  $\text{HO}_x$  radicals have also to be considered, which causes a depletion in  $\text{NO}_x$  itself. The photochemistry of ozone is an extremely complicated subject involving a large number of interactions, the reaction rates of many of which are poorly known. Nevertheless, reactions involving  $\text{HO}_x$  radicals such as

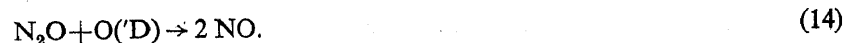


do destroy NO. However, photolysis of  $\text{NO}_2$  at wavelengths 300–400 nm and the reaction (10) restores part of NO. Since the recent measurements for reaction (12) indicate increased reaction rates from  $2 \times 10^{-13} \text{ cm}^3/\text{sec}$  to  $8 \times 10^{-12} \text{ cm}^3/\text{sec}$ , it is clear that  $\text{NO}_x$  and  $\text{HO}_x$  catalysed ozone destruction cycles interfere with each other (Dewar *et al* 1978). The destruction of  $\text{HO}_2$  itself in the reaction



being lower (Luther 1976, interactions between  $\text{NO}_x$  and  $\text{HO}_x$  radicals have the net effect of reducing the efficiency of NO as a sink for ozone.

Compensating the above reaction is the production of NO in the stratosphere through



A detailed calculation taking all these effects is in progress. We wish here to explore the possible consequences by considering some of the major reactions in a

simplistic form bearing in mind that the conclusions reached are subject to further confirmation by more detailed analysis. In spite of these uncertainties, since the reaction (14) above is now estimated to yield about  $10^{33}$  molecules of NO, the destruction of NO by  $\text{HO}_x$  radicals and production of  $\text{NO}_x$  by nitrogen oxides seem to almost balance each other, we conclude that cosmic ray-produced NO is still the major sink of ozone, particularly in the upper stratosphere.

Due to the well-known variations of cosmic ray intensity with geomagnetic latitude, the cosmic ray-induced  $\text{NO}_x$  production at equatorial latitudes ( $<5 \times 10^6$  molecules  $\text{cm}^{-2} \text{sec}^{-1}$ ) is less than a factor of five as compared to that at mid and high latitudes. It is, therefore, only natural that the ozone intensity variation at high latitudes should show a greater dependence on solar activity since the cosmic ray-induced effect is predominant there. Further, due to the penetration of cosmic rays of even low energies well into the atmosphere at high latitudes, the altitude of the peak ozone level will be lower than at equatorial latitudes.

If the earth did not have a magnetic field, and the galactic cosmic radiation were to impinge on the earth's atmosphere uniformly, the cosmic ray production of  $\text{NO}_x$  even at equatorial latitudes would be a factor of five to six higher causing a very significant depletion of ozone. Extensive calculations performed using the known values of galactic cosmic ray intensity indicate that the number of ion pairs produced at an altitude of  $15 \text{g. cm}^{-2}$ , the peak altitude of ion production, is  $600 \text{ cm}^{-3} \text{ S}^{-1} \text{ atm}^{-1}$  of air at latitudes above  $60^\circ$  that is above the cosmic ray knee (Neher 1971). Simple calculations indicate that in the case of the earth having no magnetic field, the total ion pairs produced by galactic cosmic ray impact over the top of the atmosphere and the consequent  $\text{NO}_x$  intensity would have been a factor of about five above than what is today, which in itself, can reduce the total ozone by almost 60%.

In addition to the galactic cosmic radiation, the effect of solar proton events has also to be considered. Even though the solar proton events are sporadic, and the average energy of solar protons is lower than that of galactic cosmic rays, these events do produce substantial amount of  $\text{NO}_x$  through dissociation ionization at altitudes of 30–40 km. Since the half life of  $\text{NO}_x$  is about one year at these altitudes, in spite of the sporadicity of these events, the solar flare effect is quite significant and long lasting. A detailed analysis of a number of solar proton events indicate that the global production of NO can range from  $2 \times 10^{33}$  molecules for an event of the type which occurred in November 1960 to  $6 \times 10^{33}$  molecules for the August 1972 event, which is a few times that produced by galactic cosmic rays. The actual observations during the August 1972 event indicate an abrupt decrease of ozone by about 16% at high latitudes above 4 mb level and the effect seems to have persisted for an entire month following the flare event (Fabian *et al* 1979). In fact the direct measurements of ozone reduction during flare events clearly indicate that cosmic ray produced NO is an efficient sink for the destruction of ozone at stratospheric levels and the cosmic ray produced NO estimation, as pointed by Fabian *et al* (1979) is much higher than the model calculation of Crutzen *et al* (1975). Whereas, these effects are essentially confined to higher latitudes, if the earth were devoid of the magnetic field, the solar protons would be impinging on the top of the atmosphere at all latitudes and would produce global reduction of ozone. Quantitative estimates of the effect of solar events on ozone requires the consideration of the superposition of the various solar proton events, because of the long lasting effect. Considering the frequency and size distribution of various solar proton events as given by McCracken and Rao



(1970), the net effect of all such events could be to additionally to reduce ozone on a global scale by as much as 15%, if the earth did not possess a magnetic field.

#### **6. Effect of ozone on the temperature of the earth**

Reduction of ozone causes a decrease in the temperature of the stratosphere. However, the increased transmissivity of stratosphere to UV radiation due to a reduction in ozone, tends to warm the troposphere. The stratospheric temperature reduction being much more predominant, the net result of ozone depletion is the lowering of temperature of the lower atmosphere and the surface of the earth. From extensive numerical modelling and calculations Ramanathan *et al* (1976) have shown that a reduction of 14% in ozone would reduce the surface temperature by as much as 0.13°K, assuming ozone reduction to be uniformly distributed between 12 and 40 km. Extrapolation of this argument indicates that the lack of a steady ozone layer alone, which is what we predict in the absence of the magnetic field of the earth, would result in a reduction of surface temperature by about 1.0–1.5°K, which would have had disastrous effect on the terrestrial climate.

Looking back at the historical records it is clear that when the earth went through the Maunder minimum during 1615 to 1715, the earth experienced the little ice age. In fact, detailed correlation studies indicate that every decrease in solar activity such as the Maunder sunspot minimum was coincident with the glacier advance and every increase in solar activity with glacier retreat (Herman and Goldberg 1978). During the little ice age, for example, it is estimated that the mean surface temperature was lower by about 0.5–0.6°C (Lamb 1966). Instability of Antarctic ice, changes in the orbital parameters of the earth and various other reasons have been proposed to explain the above phenomena. We propose that the decreased solar activity during these periods and the consequent increase in cosmic ray flux could have significantly contributed to the lowering of the surface temperature through increased NO<sub>x</sub> production and depletion of ozone. If the earth did not have the magnetic field, and consequently no steady ozone layer, the global surface temperature would have been at least 1°K lower and probably the earth would have experienced only the ice age with most of its water in permafrost form.

#### **7. Conclusions**

From the foregoing discussion we propose that the earth's magnetic field has played a very crucial role in the evolution of life on earth. The most significant event in the evolutionary history of the earth is the formation of a 'steady' ozone layer, which in addition to protecting biological life from harmful radiations, was responsible for the water and oxygen balance in the atmosphere. Without the formation of such an ozone layer, life with an oxygen metabolism could not have come into existence. Unless the other processes not considered in this paper combine to nullify or reverse the trend, we are forced to conclude that the root cause for the formation and sustenance of such an ozone layer is the magnetic field of the earth. Earth devoid of a magnetic field and hence devoid of trapped radiation belts and the classical terrestrial magnetosphere would have had a different thermal structure and atmospheric dyna-

mics due to the direct interaction of earth's ionosphere with solar wind and charged particles in interplanetary space. The net result would have been a significant depletion of oxygen atoms and thus ozone. Further, the constant unhindered impingement of galactic cosmic rays and solar protons producing large amount of  $\text{NO}_x$  in the absence of the magnetic field, would have destroyed most of the ozone produced thus preventing the formation of a 'steady' ozone layer. Since the quantitative estimates are well supported by the experimental observations of NO production and ozone destruction during solar flare events, we believe that the conclusions drawn in this paper are essentially correct.

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#### References

- Callis L B 1978 *Proc. WMO Symp. on geo-physical aspects and consequences of changes in the composition of stratosphere*, Toronto, WMO-No. 511, p. 193
- Campbell I M 1977 *Energy and the atmosphere* (New York: John Wiley)
- Chamberlain J W 1978 *Theory of planetary atmosphere* (New York: Academic Press)
- Cloutier P A, McElroy M B and Michel F C 1969 *J. Geophys. Res.* 74 6215
- Crutzen P J 1970 *Q. Meteor. Soc.* 96 320
- Crutzen P J 1975 *Proc. Fourth Conf. on climate impact assessment programme* (eds) T M Hard and A J Broderick (Washington: US Dept. of Transportation) p. 264
- Crutzen P J, Isaksen S A and Reid G E 1975 *Science* 189
- Delgarno A 1967 *Sp. Res.* 7 849
- Desslerer A J 1968 *Atmospheres of Venus and Mars* (eds) J C Brandt and M B McElroy (New York: Gordon Breach) pp. 241
- Duewar W H, Wuebbles D J and Chary J S 1978 *Proc. WMO Symp. on geo-physical aspects and consequences of changes in the composition of stratosphere*, Toronto, p. 206
- Dutsch H U 1979 *J. Atmos. Terr. Phys.* 41 771
- Fabian P, Pyle J A and Wells R T 1979 *Nature (London)* 227 458
- Field G B, Verschuer G L and Ponnampuruma C 1978 *Cosmic evolution* (Boston Houghton Mifflin Co)
- Goody R 1979 *Vistas Astron.* 19 197
- Henry R J W and McElroy M B 1969 *J. Atmos. Sci.* 26 912
- Herman J R and Goldberg R A 1978 Sun, weather and climate, NASA Rep., p. 426
- Johnson F S and Midgley J E 1969 *Sp. Res.* 9 760
- Jeans J H 1925 *The dynamical theory of gases* (Cambridge: Cambridge Univ. Press)
- Johnston H 1971 *Science* 173 517
- Lamb H H 1966 *The changing climate* (London: Methuen) p.
- Lemaire J and Scherer M 1974 *Sp. Sci. Rev.* 15 591
- Luther F M 1976 LLL Rep. to the High altitude programme FAA-EQ-77-6, Pub., U.S. Department of Transportation
- McCracken K G and Rao U R 1970 *Sp. Sci. Rev.* 11 155
- McEwan M J and Phillips L F 1975 *Chemistry of the atmosphere* (London: Edward Arnold)
- Michel F C 1971 *Rev. Geophys. Sp. Phys.* 9 427
- Neher H V 1971 *J. Geophys. Res.* 76 1637
- Nicolet M 1975 *Planet Sp. Sci.* 23 637

- Penner J E and Chang J S 1978 *Proc. WMO Symp. on geophysical aspects and consequences of changes in the composition of stratosphere*, Toronto, p. 137
- Ramanathan V, Callis L B and Boughner R E 1976 *J. Atmos. Sci.* **33** 1092
- Ruderman M A and Chamberlain J W 1975 *Planet Sp. Sci.* **23** p. 247
- Smith Jr W S 1978 *Proc. WMO Symp. on geophysical aspects and consequence of changes in the composition of stratosphere*, Toronto, p. 37
- Torr O G and Torr M R 1979 *J. Atmos. Terr. Phys.* **41** 797
- Zahn U V and Fricke K 1977 *J. Geophys. Res.* **82** 727