and insulates the core, the entire heating process would take about 1000 μsec. The mean velocity of the flue gases in pulverized coal units is the order of 15 m/sec (*8*). We believe that the short time interval for formation and freezing of the particles precludes the alternative hypothesis of plerosphere formation by mechanical interaction with surrounding gases. In addition, the spherical nature of the plerospheres suggests that pressure and surface tension are the predominant forces acting on the particles.

Microcrystals, if present on stack-emitted particles, as described for fly ash collected from ESP hoppers may have important biologic implications. The health hazard associated with inhalation of the crystalline particles, with their increased surface areas and potentially different chemical compositions, may be greater than that expected for the plerospheres. The crystals may preferentially concentrate metals, some of which may be toxic, by processes similar to that described for calcium. Thus, deposition of microcrystals in macrophages, for example, could subsequently result in high local concentrations of toxic elements. Furthermore, the existence of microcrystals may be responsible in part for the recent reports of the association of increased concentrations of heavy metals with smaller particles (*9*).

This initial study indicates that fly ash may exhibit a variety of shapes (predominantly spherical) and surfaces. Because the surface serves as the interface for biological interaction, it is essential to further define the surface characteristics of fly ash in toxicologic studies.

Note added in proof: For example, surface predominance of trace elements in fly ash has been demonstrated in a recent report (*10*).

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7. The following dimensional analysis was used to estimate the time required to heat the particle. Heat transfer may occur by either conduction, convection, or radiation. Conduction, which depends upon the thermal conductivity k, is the dominant heat transfer mechanism for the size and composition assumed for the spheres. The rate of temperature increase of the medium depends on the density ρ of the material, its specific heat c_p, and its characteristic length ℓ. These variables can be grouped to give a characteristic time τ:
$$\tau \sim \ell^2 \rho c_p k^{-1}$$
For the solid particle, k was assumed to be the thermal conductivity of clay. For the spherical shell surrounding the solid core, k was taken to be the thermal conductivity of air, as the gas would be the limiting component for heat transfer. Values used in the calculation were taken from A. J. Chapman [*Heat Transfer* (Macmillan, New York, 1967), pp. 556–567].
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20 October 1975; revised 16 December 1975

Eleven-Year Variation in Polar Ozone and Stratospheric-Ion Chemistry

Abstract. *A mechanism for producing an 11-year oscillation in ozone over the polar caps is the modulation of galactic cosmic rays by the solar wind. This mechanism has been shown to give the observed phase in ozone oscillations and the correct qualitative dependence on latitude. However, the production of nitrogen atoms from cosmic-ray collisions seems inadequate to account for the ozone amplitude. Negative ions are also produced as a result of cosmic-ray ionization, and negative-ion chemistry may be of importance in the stratosphere. Specifically,* NO_x^- *may go through a catalytic cycle in much the same fashion as* NO_x*, but with the important distinction that it does not depend on oxygen atoms to complete the cycle. Estimates of the relevant rates of reaction suggest that negative ions may be especially important over the winter polar cap.*

Strong evidence has been offered for an 11-year variation in the total O_3 at high latitudes, and especially at high altitudes (*1*). To account for this effect, Ruderman and Chamberlain (*2*) proposed a physical mechanism based on the well-documented 11-year modulation of galactic cosmic rays (GCR's) by magnetic fields in the solar wind. The cosmic rays were shown to produce free N atoms, which in turn react with O_2 or O_3 to form NO_x, a catalytic destroyer of odd oxygen (O, O_3). Recent estimates that the density of ambient NO_x is as high as 10 parts per billion at the important altitudes (*3*) make it appear less likely that this mechanism by itself will produce enough variation in NO_x to account for the reported 11-year O_3 cycle. However, the Ruderman-Chamberlain mechanism gives approximately the correct phase of the O_3 variation and its dependence on latitude.

Crutzen *et al.* (*4*) have noted that bursts of solar cosmic rays, which are responsible for the intense polar-cap absorption (PCA) of radio waves, would also be a strong source of NO_x in the upper stratosphere. The incidence of PCA events, however, tends to be in phase with sunspots, so that any NO_x generated would be expected to be nearly opposite in phase to that from GCR's, which fits the O_3 observations. In addition, most PCA ionization is deposited much higher in altitude than that from GCR's.

The striking increase of the amplitude of the 11-year O_3 variation with latitude and its phase make it likely, in our opinion, that the mechanism responsible for the effect is associated with the periodic component of the cosmic-ray ionization, which is limited to high latitudes. One must then understand how the ionization affects O_3 and why GCR ionization effects should dominate those from PCA events.

It is possible that important direct catalytic destruction of O_3 can result from the chemical reactions of positive or negative ions, in spite of their low densities (less than 10^4 cm^{-3} at the altitudes of interest). Thus in the conventional O_3-destroying reactions involving oxygen species only (*3*) or NO_x, the rates for destruction of O_3 by O or NO are of the order of only 10^{-14} cm^3/sec; reaction rates with ions are typically 10^3 to 10^4 times faster. [In addition, the production of NO from N_2O depends on the presence of the extremely rare, short-lived $O(^1D)$ state.] But most important at polar

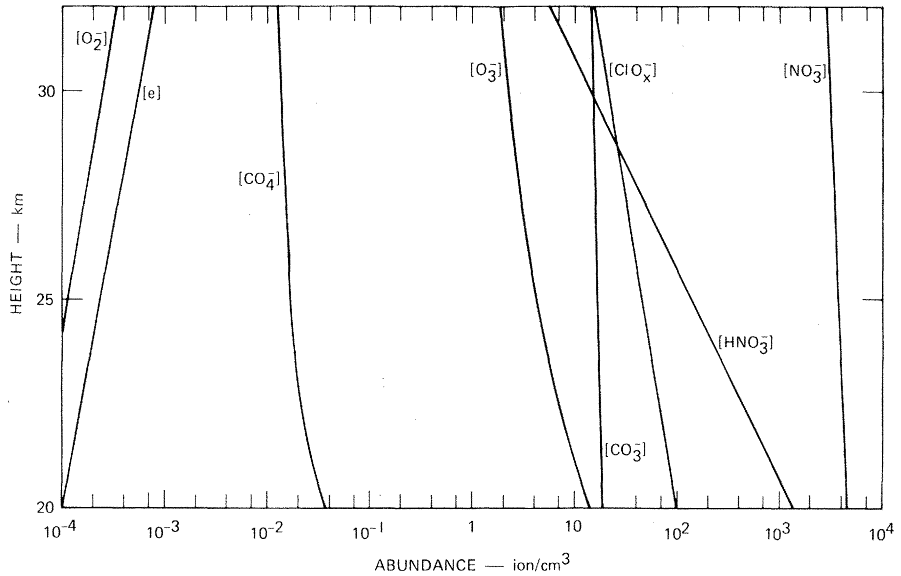

Fig. 1. Computed distribution of some negative ions with height. The sink has been taken to be mutual neutralization with positive ions. If terminal negative ions, such as NO_x^-, were to become photodetached, thereby recycling the electrons, the abundances of the other ions would be increased slightly. The longer-lived (and hence more abundant) of these ions are likely to be several times hydrated. Rate coefficients for reactions leading to these distributions were assumed not to be affected by the hydration.

latitudes is the fact that both the O + O_3 and catalytic O_3 destruction by NO_x depend on a continual supply of relatively rare free O atoms, which in turn requires ultraviolet radiation at the site of the O_3 destruction. These conventional reactions are thus expected to be totally ineffective in destroying O_3 in the polar regions at the altitudes ($\approx$ 20 km) of O_3 concentration. Even at higher altitudes the abundance of GCR-induced ions is not always negligible compared with that of O atoms, especially if the abundances are weighted by possible differences in the rate coefficients.

If ions themselves catalyze O_3 destruction during their lifetime before recombination we could also understand why GCR ionization can be more effective than PCA ionization. First, the former penetrates to lower altitudes ($\lesssim$ 20 km) where there is more O_3. Second, and perhaps even more important, the sudden large increases of PCA ionization also quickly disappear, since ion lifetime is inversely proportional to ion density. Thus the relevant product of ion density and lifetime is less effective in PCA events than it is for the same amount of incident ionization distributed over much longer intervals as in GCR modulation.

Ferguson (*5*) has reviewed the complex sequence of ion reactions in the lower ionosphere, and a similar sequence must occur in the stratosphere. Negative ions, beginning with O_2^-, pass rapidly down a chain of increasing electron-attachment energies to NO_2^- and finally NO_3^-. The electron may possibly end on the strongest significant electron attacher in the stratosphere, such as ClO_x^-. The last ion, in the conventional picture, is either photodetached (requiring a photon with energy $h\nu > 3.6$ ev) or neutralized by a positive ion in about 300 seconds. The density of NO_3^- and ClO_x^- and their hydrates is typically about 6×10^3 cm^{-3} at 20 km in the polar region. None of the intermediate species has a lifetime greater than 1 second, and their densities are correspondingly very low. Our estimates of stratospheric ion densities are shown in Fig. 1.

Our survey has been restricted to the negative ions. (Because of multiple hydration and dissociation the ultimate form of the positive ions is more obscure, and we have not studied their O_3 destruction possibilities.) We have not been able to identify a significant new source of NO_x from these reactions (*6*).

There is, however, a possibility of direct catalytic O_3 destruction by a pair of exothermic reactions, such as

$$NO_2^- + O_3 \rightarrow NO_3^- + O_2 + 2.2\,\text{ev}$$
$$k_1 = 1.8 \times 10^{-11}\ \text{cm}^3/\text{sec} \qquad (1)$$

and

$$NO_3^- + O_3 \rightarrow NO_2^- + 2O_2 + 0.8\,\text{ev}$$
$$k_2 = ? \qquad (2)$$

which would give a net O_3 destruction rate of $2k_2[NO_3^-]$ sec^{-1} (brackets denote concentration). A similar cycle may proceed through ClO_x^- and ClO_{x-1}^-. For a hypothetical (but typical) value, $k_2 = 10^{-11}$ cm^3/sec, the sequence of reactions 1 and 2 would give a decay time for O_3 of order 10^7 seconds for the ambient NO_3^- density expected at 20 km. Even with a rate coefficient an order of magnitude smaller, this process would be important at polar latitudes, where it has little competition. Reaction 2 seems not to have been observed as yet.

The mean density of polar O_3 (with seasonal variations averaged) will then be governed by an equation of the form

$$\frac{d}{dt}[O_3] = S - (\alpha + \beta\cos\omega t)[O_3] \qquad (3)$$

Here S is an approximately constant source term (including the divergence of O_3 flow from other regions); α is the rate of O_3 outflow from the polar region plus its destruction rate, $2k_2[NO_3^-]_0$, where $[NO_3^-]_0$ is the mean ion density; and $\beta = 2k_2\Delta[NO_3^-]$, with $\Delta[NO_3^-]$ being half the 11-year variation from GCR's. At 20 km in polar regions we have approximately (*7*)

$$[NO_3^-]_0 = 6.0 \times 10^3\ \text{cm}^{-3}$$
$$\Delta[NO_3^-] = 0.7 \times 10^3\ \text{cm}^{-3}$$

The solution to Eq. 3, to a first-harmonic approximation, is

$$[O_3] = \frac{S}{\alpha}\left[1 - \frac{\beta\cos(\omega t - \phi)}{(\omega^2 + \alpha^2)^{\frac{1}{2}}}\right]$$
$$\tan\phi = \omega/\alpha \qquad (4)$$

For $\omega/\alpha \ll 1$ the fractional variation in O_3 is β/α.

A fit to the reported polar-cap O_3 variation, about 6 percent between maximum and minimum, is obtained for $k_2 \sim 3 \times 10^{-12}$ cm^3/sec and an outflow time for polar O_3, $\tau \sim 3$ months. For other assumed values the same fit is obtained as long as the product $k_2\tau$ is unchanged. Thus the polar O_3 variation associated with sunspots (as well as related variations at lower latitudes) is consistent with what seem to be reasonable estimates for the unmeasured reaction rate k_2.

Because it is the "soft" component of the GCR's that is modulated by the solar wind, the relative oscillation in ionization decreases at lower altitudes. The fractional variation in O_3 is correspondingly an increasing function of altitude. The predicted phase lag of the (negative) O_3 amplitude in Eq. 4 is referred to the ionization minimum, which in turn lags the sunspot maximum by nearly 1 year. The additional phase lag from Eq. 4 will vary from 0.26 to 1.6 years with reaction rates $k_2 = 10^{-11}$ to 10^{-12} cm^3/sec. In all such models the O_3 deficiency created over the polar caps will diffuse to lower latitudes with the phase and amplitude variations previously discussed (*2*) for GCR-produced NO_x.

Other possible long-lived terminal negative ions such as ClO_x^- (whether natural or artificially introduced) might play a role similar to that postulated above for NO_x^-. However, it is conceivable that such ions with high electron affinities could simply reduce the NO_x^- population and thereby reduce, rather than enhance, the catalytic destruction of O_3 by negative ions.

Terminal negative ions may have an alternative sink (other than their eventual mutual neutralization with positive ions) in attachment to natural aerosols, generally thought (*8*) to be sulfuric acid droplets. It is known that negative ions in the stratosphere have pronounced vertical stratifications that are associated with sharp temperature inversions (*9*). It seems likely that the aerosol content can suppress negative ions and indirectly modify the O_3 density (*10*).

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$$O_3^- + N_2O \rightarrow NO + NO_3^-$$

as a source of catalytic NO_x. We are very grateful to E. E. Ferguson for communicating to us the result of a recent experiment (F. C. Fehsenfeld and E. E. Ferguson, *J. Chem. Phys.*, in press), in which the rate for this reaction was determined to be less than 10^{-14} cm³/sec. Our proposal for O_3 destruction by this mechanism must accordingly be rejected.

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11. This work was supported by the National Science Foundation by grants through the Physics Section (M.A.R.) and the Atmospheric Sciences Section (J.W.C.) and by the Energy Research and Development Administration (H.M.F.).

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Stratospheric Ozone Effects on Temperature

Abstract. *Calculated surface temperature changes,* ΔT_s, *due to stratospheric ozone depletion (at 35°N latitude in April) are less than previously estimated and range between −0.6 and +0.9°K. The sign of* ΔT_s *is determined by the surface albedo and the presence or absence of a low-lying particulate layer (heating with particles, cooling without particles). The calculations indicate that a 90 percent stratospheric ozone depletion does not cause the temperature inversion at the tropopause to vanish, although it is weakened substantially.*

Since O_3 is known to be one of the major trace constituents responsible for thermal heating of the stratosphere (*1*) [it absorbs solar ultraviolet (190 to 350 nm), solar visible (450 to 650 nm), and infrared (9 to 10 μm) radiation], it has been suggested by Dickinson (*2*) and others (*3*) that depletion of stratospheric O_3 could have catastrophic effects on climate. This suggestion is based on coupling of the positive feedback mechanisms of ice cover (factor of 3 or greater) and conservation of relative humidity (factor of 2) with the cooling noted by Manabe and Strickler (*4*). While I have not explicitly included the former feedback mechanism in the study reported here, I have included the latter one. The original theoretical research relating O_3 and climatic effects was conducted by Manabe and Strickler (*4*). For a cloudless sky at 35°N latitude in April (considering the effects of CO_2, H_2O, and O_3 and assuming fixed absolute humidity), they calculated that complete removal of O_3 from the atmosphere would cause a decrease of less than 1°K in the earth's steady-state surface temperature, but would cause the temperature reversal that defines the tropopause to vanish. The latter effect is important since it could lead to much-enhanced vertical mixing and a dramatic shift in the mean wind field (*5*). Later Manabe and Wetherald (*6*) calculated radiative-convective thermal profiles (assuming average cloudiness and constant relative humidity) for O_3 distributions corresponding to 0°N, 40°N, and 80°N in April and found that the tropospheric temperature would decrease as the abundance of O_3 decreased and the height of the maximum O_3 concentration increased.

In the work reported here I took the Manabe-Wetherald (*6*) thermal equilibrium model, with three layers of water clouds (corresponding to average cloudiness at 35°N latitude in April), and introduced a low-lying layer of Mie-scattering particles in order to calculate the radiative-convective steady-state temperature profile under various conditions. The calculations were performed for a mean global surface albedo of 0.1, for the present distribution of stratospheric O_3 as well as for 90, 60, 50. 30, 10, and 0 percent levels. Additional calculations were made to test the sensitivity of these results to changes in other model parameters, including the presence or absence of particulate layers and changes in surface albedo, ω_s.

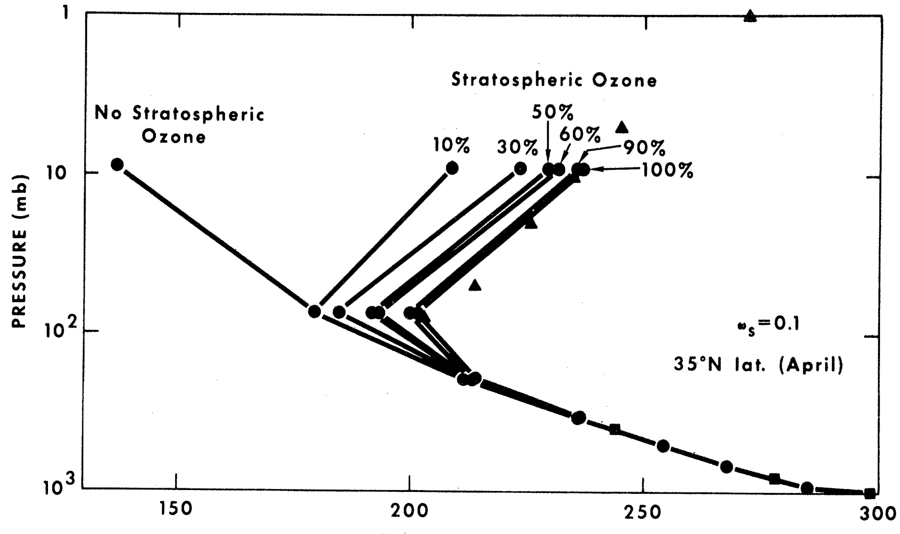

Fig. 1. Calculated steady-state temperature profiles as a function of pressure (millibars) for the present abundance of stratospheric O_3 and for 90, 60, 50, 30, 10, and ~ 0 percent of those values. Values from the subtropical (30°N) July model atmosphere (triangles) and experimental data interpolated for 35°N in April (squares) are included for comparison (*10*).