

Fig. 4 Contour map of the nucleus of M87 at 1.35 cm wavelength. A circular gaussian restoring beam of diameter 0.15 marc s (shown in the bottom left-hand corner) has been used. Contours are shown at 10, 20, 30, 40, 50, 60, 70, 80 and 90% of the peak brightness of 0.34 Jy per beam.

value of $\sim 400 \text{ km s}^{-1}$ at 1 arc s from the nucleus, but 'seeing' and any departures from a spherically symmetric gravitational system mean that this is a lower bound on ΔV . Thus, if a star cluster has produced the potential well, then it must contain a mass of at least $10^6 M_{\odot}$ within a radius of 10^{-2} pc. The star density within such a cluster would be extremely high (assuming a reasonable mass function for the cluster), and consequently the cluster would have a relaxation time of $\sim 10^5$ yr. This cluster would then evaporate in a time which is brief when compared with the lifetime of the large-scale structure of the source ($\sim 10^8$ yr)¹⁴, suggesting that such a model is unlikely.

Accretion disks orbiting massive black holes have been proposed in order to explain many observed features of active galactic nuclei such as that of M87. In particular, the 'funnels' formed in thick accretion disks can collimate the ejected material to form jets¹¹. Such disks may be characterized naturally by Q , the ratio of the outer radius to the inner¹⁵. Thick accretion disks with large values of Q would produce well-collimated jets. If a massive black hole of mass $5 \times 10^9 M_{\odot}$ exists in M87, then, for a funnel size of $< 10^{-2}$ pc as suggested by our observations (assuming that the unresolved core encompasses the entire accretion disk), Q must be less than 30. However, much higher values of Q are required for the production of highly collimated jets, such as that of M87.

The radio power in the jet, estimated from the stored energy in the large-scale radio source¹⁴ divided by the lifetime, is $\sim 10^{36}$ W. This amount of power is equal to the Eddington luminosity of accretion onto a black hole of mass $\sim 10^6 M_{\odot}$. Our observations indicate a Q value of $\sim 10^3$ for a disk surrounding a black hole of this mass: such an arrangement would be more able to produce a collimated jet. It has been pointed out¹¹ that if a very massive black hole of mass $5 \times 10^9 M_{\odot}$ were present in the nucleus of M87 it would have to be extremely underluminous, and, in view of the uncertainties^{16,17} of the existence of such a massive object, a black hole of $10^6 M_{\odot}$ surrounded by a thick accretion disk fed from material from a much larger star cluster (> 0.1 arc s) is a more likely model. The resolution given by the Space Telescope should enable further studies of this star cluster to be made. Also, the proposed Quasat VLBI satellite may yield more information on the radio jet and perhaps set tighter limits on the massive object in M87.

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On the depletion of Antarctic ozone

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Recent observations by Farman *et al.*¹ reveal remarkable depletions in the total atmospheric ozone content in Antarctica. The observed total ozone decreased smoothly during the period from about 1975 to the present, but only in the spring season. The observed ozone content at Halley Bay was $\sim 30\%$ lower in the Antarctic spring seasons (October) of 1980-84 than in the springs of 1957-73. No such obvious perturbation is observable in other seasons, or at other than the very highest latitudes in the Southern Hemisphere, and the magnitude of the observed change there far exceeds climatological variability². We present here balloonsonde ozone data^{3,4} which show that these ozone changes are largely confined to the region from about 10 to 20 km, during the period August to October. We show that homogeneous (gas phase) chemistry as presently understood cannot explain these observed depletions. On the other hand, a unique feature of the Antarctic lower stratosphere is its high frequency of polar stratospheric clouds⁵, providing a reaction site for heterogeneous reactions. A heterogeneous reaction between HCl and ClONO₂ is explored as a possible mechanism to explain the ozone observations. This process produces changes in ozone that are consistent with the observations, and its implications for the behaviour of HNO₃ and NO₂ in the Antarctic stratosphere are consistent with observations of those species there, providing an important check on the proposed mechanism. Similar ozone changes are obtained with another possible heterogeneous reaction, H₂O + ClONO₂.

Recent satellite observations^{6,7} have revealed Antarctic ozone depletions over a very extended region in general agreement with the local ground-based data of Farman *et al.*¹. It was suggested¹ that the dramatic decreases may arise from a change

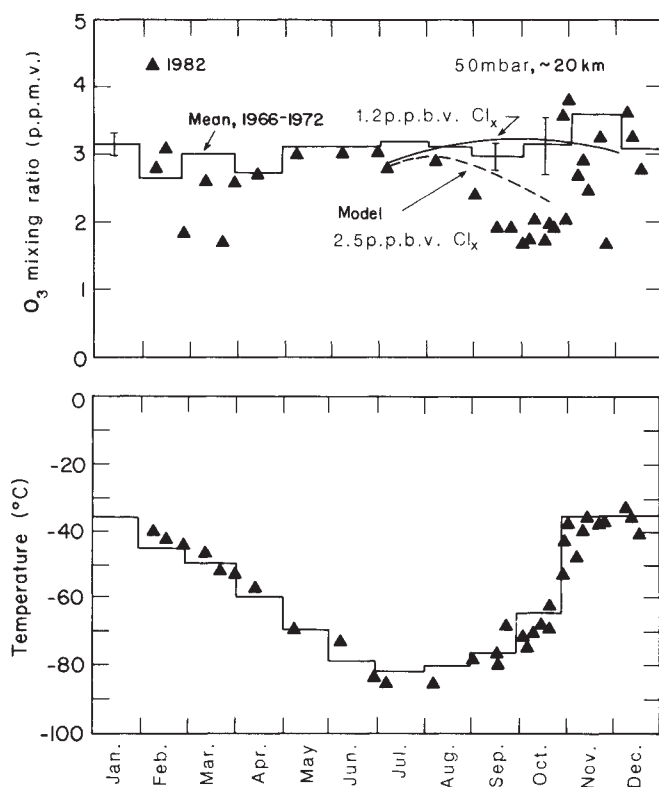
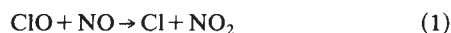


Fig. 1 Temporal behaviour of ozone mixing ratio at the 50-mbar level over Syowa, 69° S, compared with model calculations, for the late 1960s and early 1970s (histogram) and in 1982 (\blacktriangle)^{3,4}. Error bars represent standard deviations of the observations. Temperature observations for the same periods are also shown³.

in the NO_2/NO ratio due to the reaction



(and its relationship to ozone chemistry) which is of particular importance at the very low temperatures characteristic of Antarctic spring (-80°C). Clearly, this process should be expected to be of increasing importance with time as the chlorofluorocarbon content of the atmosphere increases due to anthropogenic releases. As Farman *et al.*¹ showed, reaction (1) can be effective in perturbing the ratio between NO and NO_2 near 30 km, and hence can influence ozone at those altitudes. However, the bulk of the ozone layer is located well below these levels in Antarctic spring, and so perturbations to ozone near 30 km can have only a modest influence on the total column (see Fig. 2 for a typical ozone profile). Most of the total ozone column at these latitudes and seasons resides near 15–20 km, where the ozone photochemical timescale is of the order of several years⁸ using presently accepted homogeneous photochemistry; it is at these low levels that a change must occur for the total column to be perturbed by such a substantial amount. Using a climatology of Antarctic winter temperatures presented by Labitzke⁹, we tested the role of reaction (1) in our dynamical-chemical two-dimensional model of the middle atmosphere^{10,11}. During the period from 1965 to about 1980 the total chlorine content of the atmosphere is estimated to have increased from about 1.2 to 2.5 p.p.b.v. (parts per 10^9 by volume)¹². This increase produced a 3–5% change in calculated ozone in Antarctic spring near 30 km, while the calculated changes at 20 km and below were less than 1%. The corresponding change in column-integrated ozone was, therefore, much smaller than that observed.

It is clear that further information regarding the vertical profile of the ozone perturbation is essential to any theory regarding

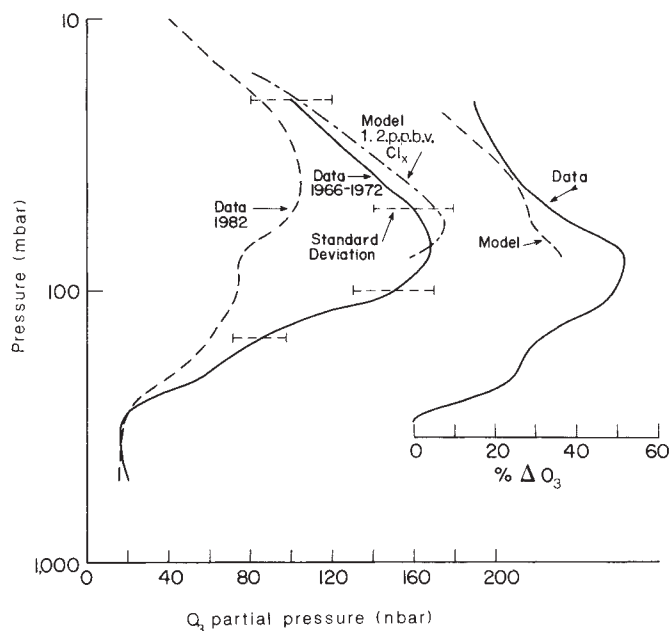
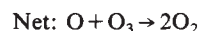


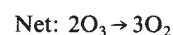
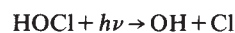
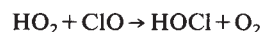
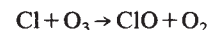
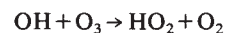
Fig. 2 Vertical profile of the ozone partial pressure observed over Syowa in the late 1960s and early 1970s, and the standard deviation, compared with observations in 1982, for the month of October^{3,4}. The model vertical profile in the late 1960s is shown for comparison. Percentage changes of the model and the data for the same time period are also indicated.

the ozone column change. We present below Antarctic balloonsonde data which show that the observed perturbation is indeed greatest at about 15–20 km, where it develops over a timescale of the order of 2 months. No significant changes in dynamical processes are indicated by the observed temperature structure there¹ (see also Fig. 2), suggesting that the cause of the ozone depletion is chemical rather than dynamical. If the observed depletions are the result of a chemical process, then that process must obey the following constraints: (1) it must be essentially confined to the Southern Hemisphere², (2) it must be a strong function of latitude and season; (3) it must produce an acceleration of the ozone chemical loss rate from a timescale of the order of several years to about a month near 15–20 km; and (4) it must increase with time over at least the past 10 yr. Constraint (4) suggests that we examine the photochemistry of atmospheric chlorine.

Chlorine can destroy ozone catalytically in the Earth's atmosphere through the following reactions:



At lower altitudes, the following catalytic cycle should also be considered:



With present chemical schemes, the depletion due to increasing levels of atmospheric chlorine maximizes near 40 km, where much of the available chlorine resides as ClO and Cl . At lower levels, these catalytic free radicals are effectively converted to the 'reservoir' species, HCl and ClONO_2 , which are inert towards ozone. Both of these reservoirs are expected to be ~ 100 times

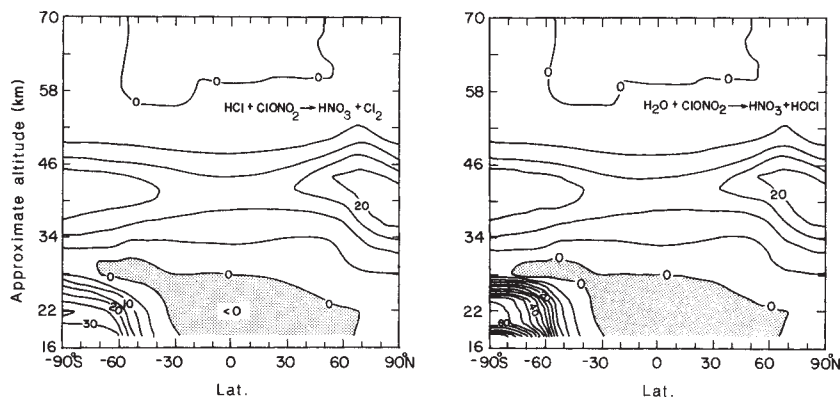
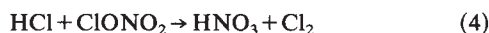


Fig. 3 Contour plot of the calculated change in ozone from the late 1960s to the early 1980s.

more abundant than ClO near 20 km, strongly inhibiting the Cl and ClO densities. Thus, if the densities of the catalytic species in the lower stratosphere are to be appreciably enhanced, both HCl and ClONO₂ must be severely reduced. One means of achieving this is the process



The Cl₂ will photolyse rapidly in the sunlit atmosphere, producing Cl. Laboratory studies suggest that reaction (4) does not occur rapidly in the gaseous phase, but is much faster on laboratory surfaces¹³⁻¹⁵. To alter the balances between the catalytic species and their reservoirs, which occur on a timescale of a few days, this reaction must proceed in Antarctic spring on a comparable timescale, requiring an equivalent two-body reaction rate of $\sim 2 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$. Farman *et al.*¹ suggested that this reaction could be an alternative explanation for their observations, but they did not consider the need for a very rapid rate of this process in order to perturb the equilibrium between ClO and its reservoirs following the return of sunlight. Since reaction (4) is heterogeneous, it presumably takes place only in the presence of stratospheric aerosol, and indeed, the stratospheric aerosol surface area increases substantially in the vicinity of polar stratospheric clouds. These clouds are very common in the cold environment of Antarctic winter and early spring near 10–20 km, where their occurrence frequency is far greater than in the warmer Northern Hemisphere. They are observed predominantly between about July and September, and their presence is closely coupled to the temperature structure. The mean 1- μm aerosol optical depth in Antarctica is about an order of magnitude greater in winter and early spring than it is either during other seasons in Antarctica, or during any season in the Arctic⁵, suggesting that reaction (4) should be enhanced specifically during Antarctic winter and spring.

Figure 1 shows balloonsonde temperature and ozone observations from Syowa station, Antarctica (69° S, 39° E), at the 50 mbar (20 km) level³ (for the complete dataset, see the tape available from Ozone Data for the World). There are several years of historical data covering the period from about 1966 to 1972; the monthly mean of these data is shown as the histogram. In recent years, the station has been operated much less frequently, and virtually the only data available are those of an intense measurement programme carried out in 1982. Chubachi⁴ has shown that large changes in ozone were observed there during this period, similar to those obtained by Farman *et al.*¹. The temperatures obtained at this particular station in 1982 were in general agreement with the historical data, while the ozone exhibited a dramatic departure in September and October.

Figure 1 also shows the results of our model calculations for 1.2 p.p.b.v. and for 2.5 p.p.b.v. including the hypothetical reaction (4) at an equivalent two-body rate as indicated above, imposed uniformly over the region from the model lower boundary at 100 mbar (about 16 km) to 26 km, for latitudes from

61° S to the Pole. The calculated seasonal trend in the unperturbed case, and the timescale of the calculated perturbation, are in reasonable agreement with those observed at the 50 mbar level. Calculated daytime-averaged ClO mixing ratios are about 1.8 and 0.4 p.p.b.v. at this level in September for 2.5 and 1.2 p.p.b.v. total chlorine (respectively), compared with ~ 0.02 and 0.01 p.p.b.v. when reaction (4) is not considered. Note that although the clouds are expected to be present in July, no ozone perturbation is observed or predicted then. This is consistent with the notion that the perturbation is photochemical, because the sunlight required to drive the photochemistry is present only after about August, when polar night ends at this latitude. Because this chemical perturbation occurs more rapidly (timescale of about a month) than do transport processes in this region (timescale of more than a season), this model can be used to study the problem even at levels near to the lower boundary at 100 mbar without significant bias due to the boundary conditions imposed^{10,11}. As mean temperatures rise above -80°C in October, the polar stratospheric clouds disappear⁵; the ozone remains low throughout October, but returns rapidly to levels much closer to the historical pattern in early November. This recovery is probably dominated by the acceleration of wave-driven transport accompanying the final spring warming of the Antarctic stratosphere, which brings in ozone-rich air from higher altitudes and lower latitudes. Because the behaviour of planetary waves cannot be calculated explicitly with our model, we are unable to simulate this rapid ozone increase.

Figure 2 presents the vertical profile of the October monthly mean of the observed ozone at Syowa for the historical years, as well as that obtained in 1982, along with the associated percentage changes. The observed changes are largest near 15–20 km, where they approach 40%. Figure 2 also shows the vertical profile of ozone obtained in our model for 1.2 p.p.b.v. chlorine and the percentage changes obtained for 2.5 p.p.b.v. when reaction (4) is considered. The vertical profile of the calculated ozone depletions, which agrees well with that observed, is determined by the chemical lifetimes of HNO₃ and ClONO₂. The equilibrium between ClO and ClONO₂ is established very rapidly if much NO₂ is present, and the ratio between the reservoir and the catalytic agent, ClO, is then so large that it will effectively inhibit the densities of Cl and ClO. Reaction (4) sequesters virtually all of the NO₂ in HNO₃, and the slow photolysis rate of HNO₃ at low levels implies that NO₂ cannot be released quickly enough to appreciably reduce ClO. At higher levels, where the HNO₃ photolysis rate is faster, NO₂ is released more rapidly and ClONO₂ formation effectively inhibits the ClO density. Note that large abundances of ClO can occur only if NO₂ levels are extremely low; thus the production of the HNO₃ product in reaction (4) is as important to the overall mechanism as the reactants.

Reaction (4) is not the only possible heterogeneous process capable of perturbing ozone. Indeed, another reaction that is

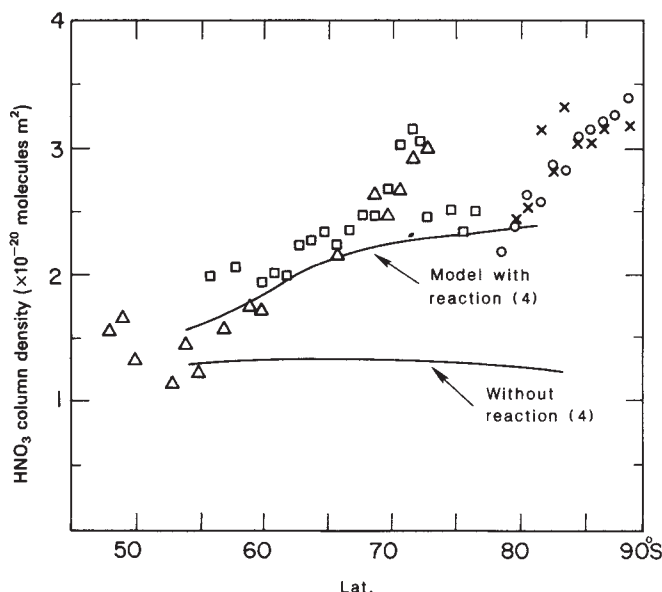
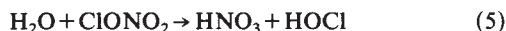


Fig. 4 Latitudinal gradient of total HNO_3 column abundance observed in Antarctic spring¹⁷, along with model calculations with and without consideration of reaction (4). \square , 17 November 1978; \circ , 20 November 1978; \times , 21 November 1978; \triangle , 27 November 1978.

similar to reaction (4) in its effects on the balance between ClO and its reservoirs, as well as in its effects on HNO_3 (if it proceeds at an equivalent two-body rate of $\sim 1 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$) is



Laboratory studies show that this process also occurs heterogeneously¹⁵. Figure 3 shows a contour plot of the percentage ozone changes calculated between about 1965 and the early 1980s for both reactions (4) and (5). The high-altitude changes and their structure are due to standard chemistry⁸, but should be considered upper limits because of the neglect of the important effects of coupled temperature and CO_2 perturbations¹⁶. The calculated latitudinal structure in the additional depletions in the Antarctic lower stratosphere is due to the assumption that the clouds occur only poleward of about 60°S , confining the perturbation to high latitudes and low altitudes. A substantial gradient in mean cloud intensity (and hence in ozone depletion) probably occurs over the latitude range $60\text{--}90^\circ \text{S}$ because of the strong gradient in temperature over this region, but this has not been included in the present calculations. In the case of reaction (5), the possible production of HOCl leads to hydrogen radical formation, and thus produces even greater ozone depletions than those due to chlorine free radicals alone. The efficiency of reaction (5) in ozone destruction is thus critically dependent on HOCl as a reaction product.

Because HNO_3 is a product of both reactions (4) and (5), observations of odd nitrogen species provide an independent check on the feasibility of these processes. Figure 4 presents HNO_3 column abundance measurements from Antarctica in November¹⁷, along with model-calculated column abundances with and without consideration of reaction (4); reaction (5) produces similar results. Reaction (4) significantly improves the agreement between the model and the observations. Examination of the chemistry and transport of HNO_3 at high latitudes in Northern Hemisphere winter by Austin *et al.*¹⁸ reveals other evidence for an additional source of HNO_3 beyond presently accepted photochemistry, and points out that it is likely to be heterogeneous. This enhancement in HNO_3 should be accompanied by a decrease in other forms of active nitrogen (such as NO_2 and N_2O_5) in the lower stratosphere below about 25 km where the HNO_3 photolysis rate is slow, as discussed above with regard to the vertical extent of the ozone depletion. This implies that the total NO_2 column, and its diurnal variation in the spring, should be smaller in the Antarctic than in the Arctic due to the far greater frequency of polar stratospheric clouds in the Antarctic. McKenzie and Johnston's¹⁹ observations in September at 78°S display a sunset total NO_2 column of $\sim 1.5\text{--}2 \times 10^{15} \text{ cm}^{-2}$, with a diurnal variation of $< 0.5 \times 10^{15}$, while those of Noxon *et al.*²⁰ in March at 71°N suggest a sunset total abundance of $3\text{--}3.5 \times 10^{15}$, and a much larger diurnal variation of about $\sim 2 \times 10^{15}$, consistent with this suggestion.

Reaction (4) is certainly very speculative, and has been modelled only crudely here. However, it is consistent with all of the available features of the observed depletion of ozone, namely its vertical, latitudinal and temporal structure, as well as with observations of HNO_3 and NO_2 . The process responsible for Antarctic ozone depletion is probably heterogeneous, and related to odd nitrogen chemistry. In view of these considerations, as well as the lack of direct laboratory data regarding the kinetics and mechanism of reaction (4), we emphasize that other possible heterogeneous reactions, such as $\text{H}_2\text{O} + \text{ClONO}_2$ and $\text{H}_2\text{O} + \text{N}_2\text{O}_5$, should also be the subject of laboratory and atmospheric studies. Further observations of polar stratospheric clouds, and in particular, their occurrence frequency, are also badly needed. If the mean temperatures in Antarctic spring decrease (or have perhaps already decreased) by even 1 or 2°C , it is likely that the cloud frequency will increase, with associated changes in the aerosol surface area and rates of heterogeneous processes. Observations of ClO, or the more easily observable species, NO_2 , near Antarctic polar stratospheric clouds would be of considerable value in evaluating the mechanism responsible for the ozone depletion there. If heterogeneous reactions are indeed the cause of the Antarctic ozone phenomenon, these large depletions will be confined essentially to this region in the near future unless there is a very large increase in stratospheric aerosol.

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