PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Recent Measurements of Total Ozone at British Antarctic Survey Stations

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Recent measurements of total ozone at British Antarctic Survey stations

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The deep minimum in total ozone, the 'ozone hole', which is now observed each year in early spring in Antarctica, appears to be confined to the cold core of the polar vortex. The breakdown of the vortex in 1986 followed an unusual course, and produced an atypical variation of total ozone at Halley Bay. Upper-air data show that the cold core in this year was subjected to large displacement and rapid deformations. Despite these dynamic perturbations, the ozone amount within the core seems to have been scarcely affected.

This is consistent with the observed behaviour of other tracers at high latitudes. The observations are most readily explained by supposing that the core of the polar vortex is maintained as a material entity or isolated air mass, even when it suffers erosion of material from its edge (as happens throughout the period leading up to the final warming). It has recently been suggested, solely on dynamical grounds, that the process of erosion is essentially one sided; the eroded material is readily mixed into middle latitudes, but the main vortex is remarkably impervious to even small-scale incursions of the surrounding air.

Formerly, the timing of the final warming was very variable from year to year. Since 1979, no early final warming has occurred. The effect on monthly mean temperatures has been described by some workers as a cooling of the lower stratosphere. What should be said is that temperature in the core of the vortex rises more slowly now than formerly. This is not unexpected, because the heating rate in the lower stratosphere is strongly dependent on ozone amount. It is suggested that this slower warming can, by its influence on the diabatic mass circulation, affect ozone amounts outside the vortex.

The limited evidence available suggests that no significant depletion of ozone occurs in darkness. However, by the time that the Sun is high enough to permit frequent measurements of ozone the loss rate is high and remains so until the equinox. It then diminishes rapidly, and the minimum value of ozone is attained by mid-October, well before the final warming of the lower stratosphere. This suggests a greater degree of solar control than is evinced by other aspects of vortex behaviour.

It is inferred that the depletion of ozone arises largely from chemical sinks, and some reactions likely to be important are discussed. Attention is drawn to the photochemically labile reservoirs HOCl and NO_3. Competitive reactions between their photoproducts determine critically the persistence, or otherwise, of an HO_x catalytic cycle in early spring.

1. Introduction

The British Antarctic Survey has made systematic measurements of total ozone at two stations, Argentine Islands (65° S, 64° W) and Halley Bay (75° S, 27° W), since 1957. The data obtained from 1957 to 1973 have been discussed in some detail (Farman & Hamilton 1975; Farman 1977). In those years, the annual variation consisted essentially of a simple maximum in November/December, the rise to it accompanying the rise in temperature associated with

the breakdown of the winter polar stratospheric vortex. Whereas the temperature fell only slightly in the next few months, ozone amount decayed almost exponentially, reaching at the March equinox values similar to those recorded in the early spring (figure 1). In the last ten years, a new feature has appeared and intensified. There is now a deep minimum in early spring (September/October), comparable in range with the subsequent maximum (Farman *et*

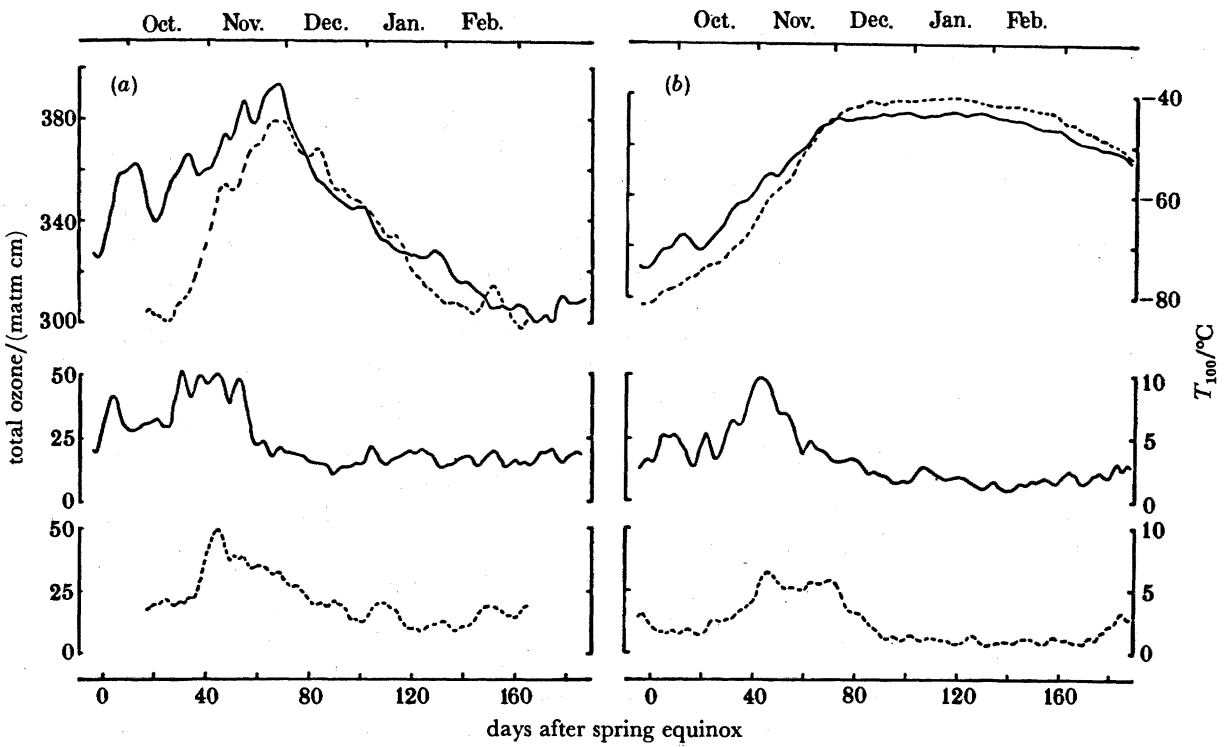

FIGURE 1. (*a*) Variations of total ozone amounts at Argentine Islands, 65° S, 64° W (solid lines) and at Halley Bay, 75° S, 27° W (broken lines); mean values for 1957–1972 (top) and their standard deviations (bottom). (*b*) Temperatures at 100 mbar, otherwise as above.

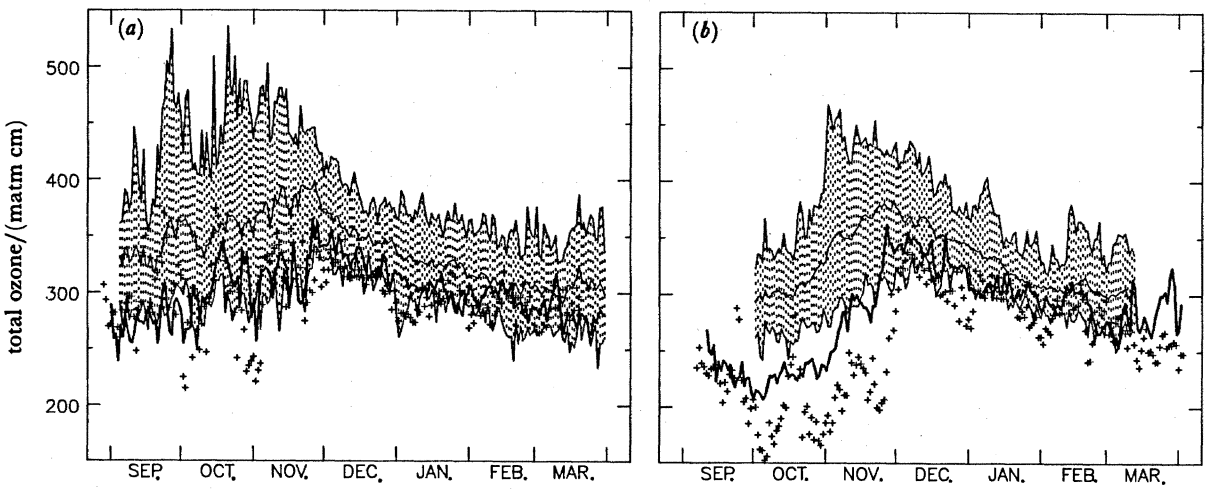

FIGURE 2. (*a*) Variations of total ozone amount at Halley Bay, 76° S; mean and extreme values for 1957–1972 (thin lines), mean values for 1980–1984 (thick line), and daily values for 1985 (crosses). (*b*) At Argentine Islands, 65° S; otherwise as above.

al. 1985*a*, *b*; WMO 1986; Stolarski *et al.* 1986). Figure 2 shows the mean and the range of the 1957–1973 data, mean values for 1980–1984 inclusive, and daily values for 1985, at Halley Bay and Argentine Islands. In this last year, at both stations, the minima were overlain by large fluctuations. Plots of the daily values of total ozone for the separate years 1980 to 1985 have been presented by Gardiner & Shanklin (1986).

2. Variations of total ozone and stratospheric temperatures in 1986

Figures 3 and 4 show preliminary results from Argentine Islands and Halley Bay for September to November 1986. The temperatures at 100 mbar† shown with the Argentine Islands ozone data were taken at the Russian station, Bellingshausen (62° S, 58° W). Large

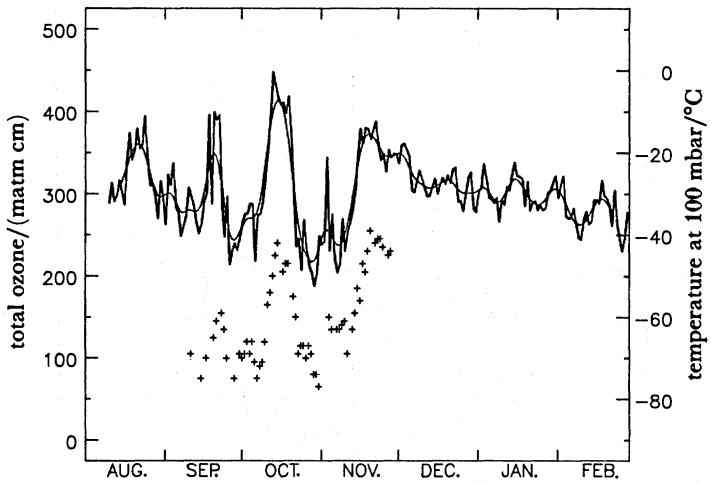

Figure 3. Variations of total ozone amount at Argentine Islands, 65° S, 64° W (top), and of temperature at 100 mbar at Bellingshausen, 62° S, 58° W (bottom), August–November 1986. Smoothed versions of the ozone data are also shown (thin lines).

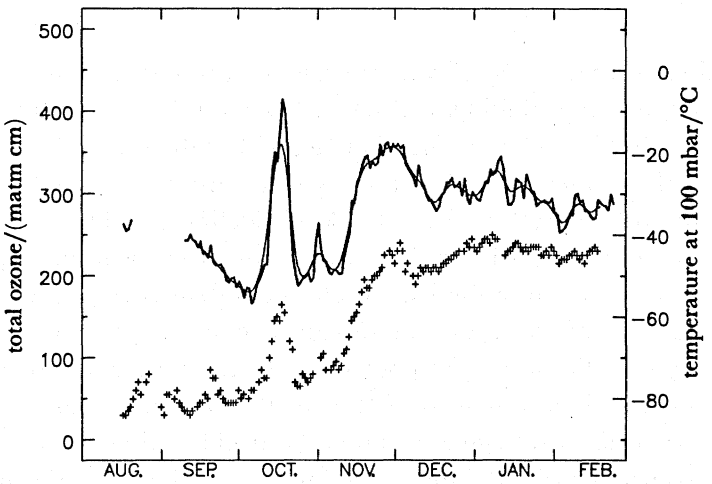

Figure 4. Variations of total ozone amount (top) and temperature at 100 mbar (bottom) at Halley Bay, August–November 1986. Smoothed versions of the ozone data are also shown (thin lines).

† 1 mbar = 10^2 Pa.

fluctuations in ozone amount are apparent at Argentine Islands from the start of the record. They lead by a few days the weak temperature fluctuations at Halley Bay, but are clearly coherent with these and with the Bellingshausen temperatures in October. The ozone record at Halley Bay in September is surprisingly quiet, and shows little dependence on the temperature. The depletion is dominant, amounting to some 2.4 m atm cm d^{-1} in late September (then almost 1% d^{-1} (by volume)). At both stations, the October record is dominated by a very large pulse in both temperature and ozone amount, with ranges of some 40 °C and 250 m atm cm at Argentine Islands, 20 °C and 230 m atm cm at Halley Bay. The background trends are different, being upwards at Halley Bay, downwards at Argentine Islands. The increases in ozone amounts and temperatures in November show the final warming in progress.

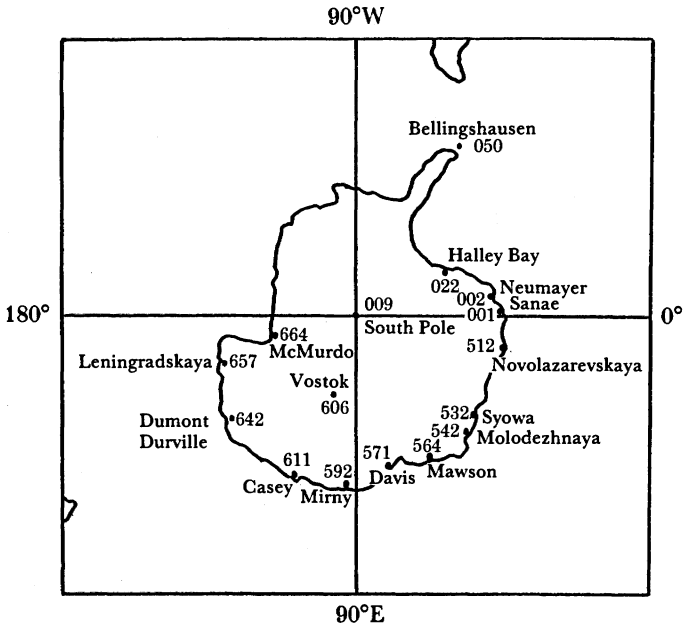

FIGURE 5. Radiosonde stations in Antarctica, 1986.

What is happening in other sectors of Antarctica in these months? Figure 5 shows the positions of stations at which upper-air soundings are made. The temperatures at 100 mbar from stations in the longitude range 58° W–90° E are shown in figure 6*a*; these are all coastal stations. Figure 6*b* shows data from three other coastal stations with longitudes between 90° and 180° E, and from the interior stations, Vostok and South Pole. Cooling is evident at Mirny, Casey and Mawson in early October, suggesting recovery from an earlier warming episode. This would not be unusual; the sector south of the Indian Ocean and/or Australia was recognized as the preferred site for the onset of the stratospheric anticyclone in Antarctica in spring in an early study by Godson (1963). Warming is in progress at Leningradskaya, further east, but is only temporary. There are no observations from 180° to 48° W, but it seems that this disturbance intensified and moved westward to give the intense warming episode at Bellingshausen in mid-October. The westward progress of this warming is then evident, through all the coastal stations, back to Leningradskaya. At this station the ensuing warming is 'final'. As the wave makes a second circuit, westward, there is apparently a rapid drift of the cold core towards and

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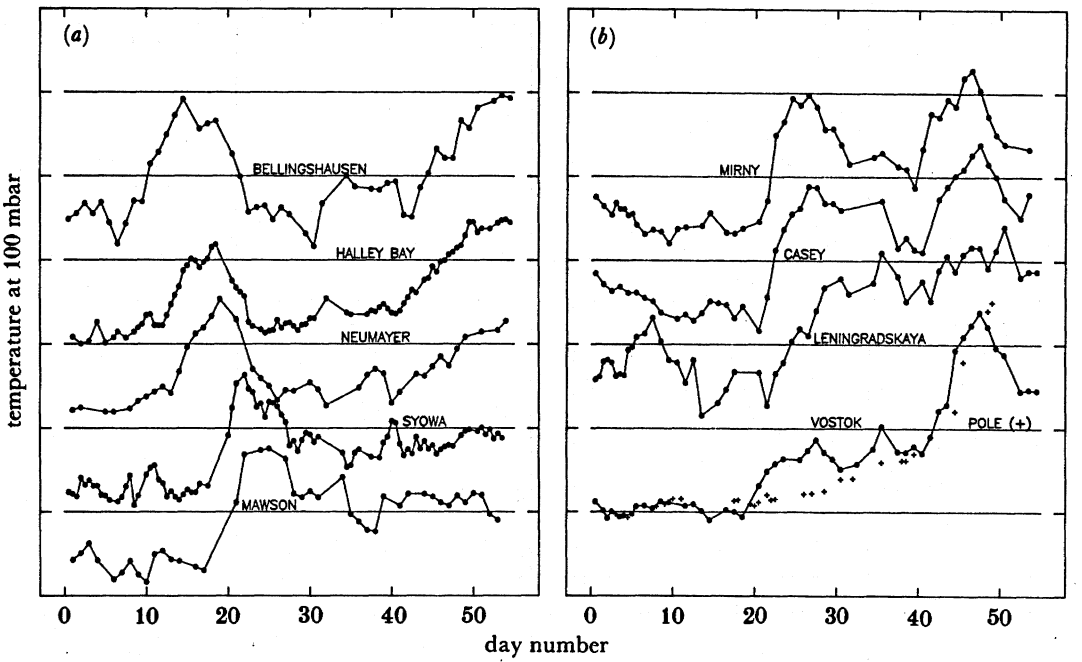

FIGURE 6. (*a*) Variations of temperature at 100 mbar, October–November 1986, at coastal stations from 58° W to 90° E. (*b*) As above but from 90 to 180° E, and at two continental stations.

finally across Syowa. Stations in the 0°–90° E quadrant will presumably see a very late and weak final warming episode in early December.

It would be misleading to claim that this sequence is quite abnormal. Rather, attention should be drawn to the variability from year to year of the detailed course of the breakdown of the polar vortex. The unusual features of 1986 seem to be most notably the amplitude of the mid-October event at high latitudes in the sector south of the Atlantic Ocean (not however quite without precedent; figure 7 shows large fluctuations in ozone amount at Halley Bay in October/November 1975, a spring in which unfortunately no upper-air soundings were possible because of equipment failure) and the return of cold air in late November to a station so far east as Mirny. In fact, very few map sequences are available for comparison. Palmer &

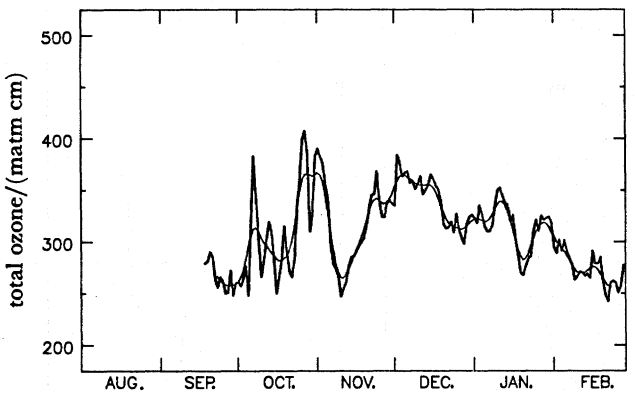

FIGURE 7. As figure 4, but for August 1975 to March 1976.

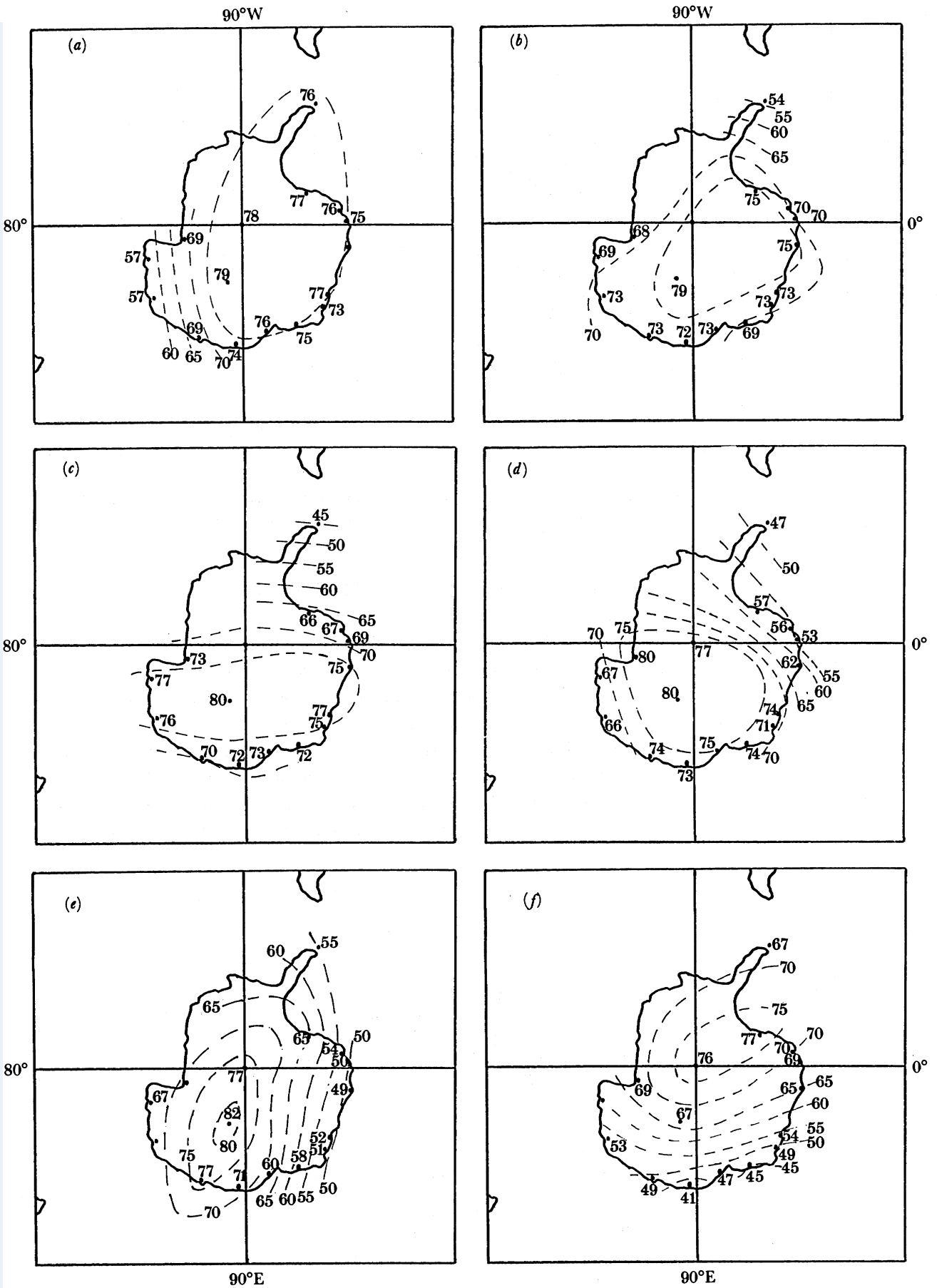

FIGURE 8 (a)–(f), For description see opposite.

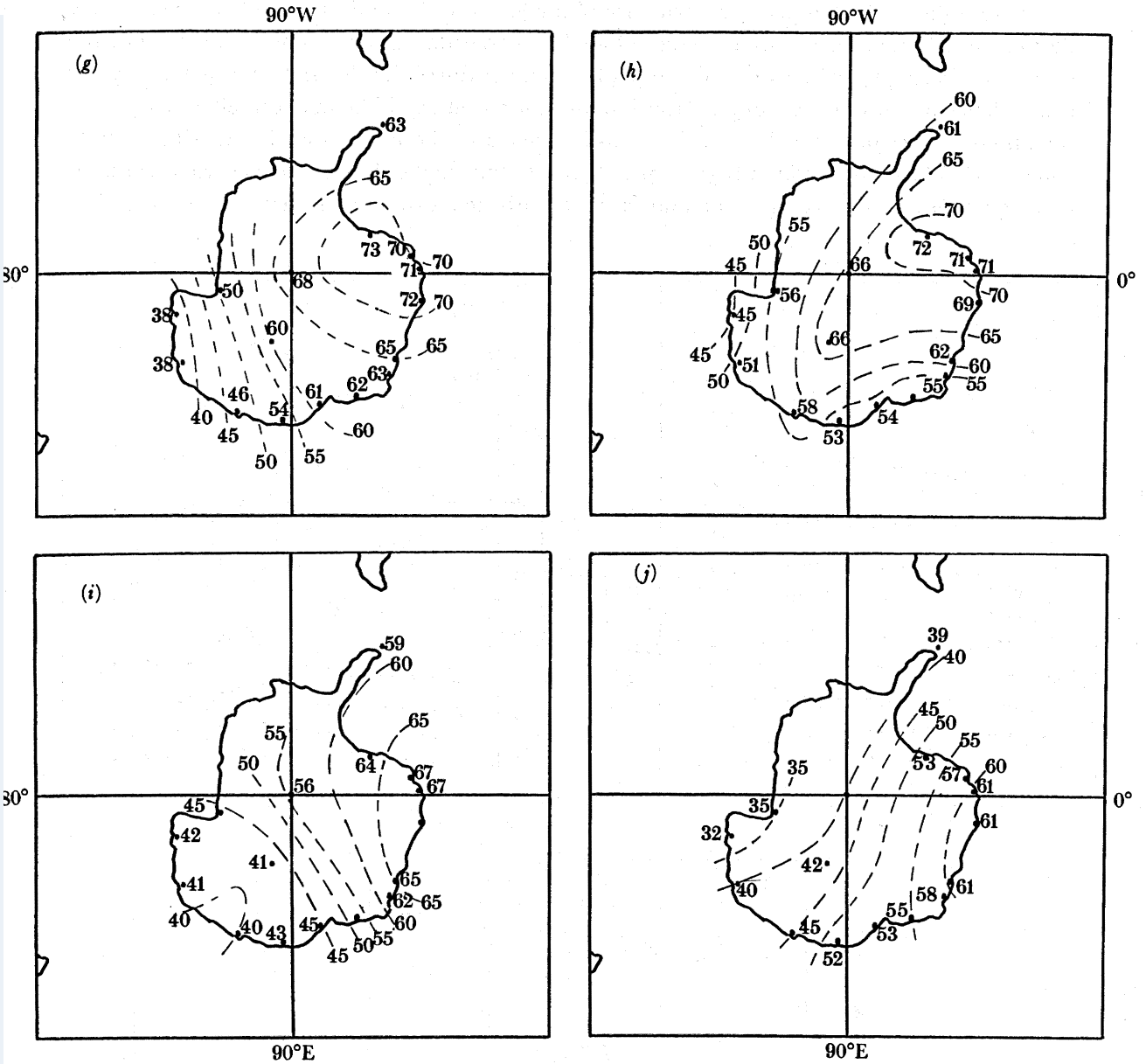

FIGURE 8. Isotherms at 100 mbar over Antarctica in 1986. (*a*)–(*f*) 7, 12, 14, 18, 21 and 25 October; (*g*)–(*j*) 5, 10, 14 and 20 November.

Taylor (1960; see Taylor 1960, which incorporates Palmer & Taylor) show that in 1957 the vortex moved out along the Antarctic Peninsula (about 60° W) in the course of filling. The pattern consisted essentially of a growing asymmetric wave ($n = 1$) only. Godson (1963) identifies the sector south of the Atlantic Ocean as that showing the latest warmings.

The contrast between the apparently simple course of the breakdown in 1957 and that in 1986 is so extreme that it seemed worthwhile to translate figure 6 (with additional, but sparser, data from other stations) into a map sequence. Figure 8 shows sketches of the isotherms at 100 mbar on ten days. A detailed description is not needed. It is clear that waves of numbers up to at least three are involved. A detailed analysis requires supporting evidence from global analyses and from satellite maps of ozone.

Figure 9 shows the temperature structure of the lower and middle stratosphere over Halley Bay in three Octobers, 1986, 1985 and 1980. The variation of total ozone is also shown; the curve has been placed between the potential temperatures for 30 and 50 mbar solely for convenience of plotting. A more appropriate pressure level would be between 50 and 70 mbar (or about 18 km altitude). However, it will be seen that the four lowest levels behave quite coherently. Warming is evidently more pronounced at the higher levels, occurs earlier, contains a stronger progressive component and is apparently less coherent from level to level. The

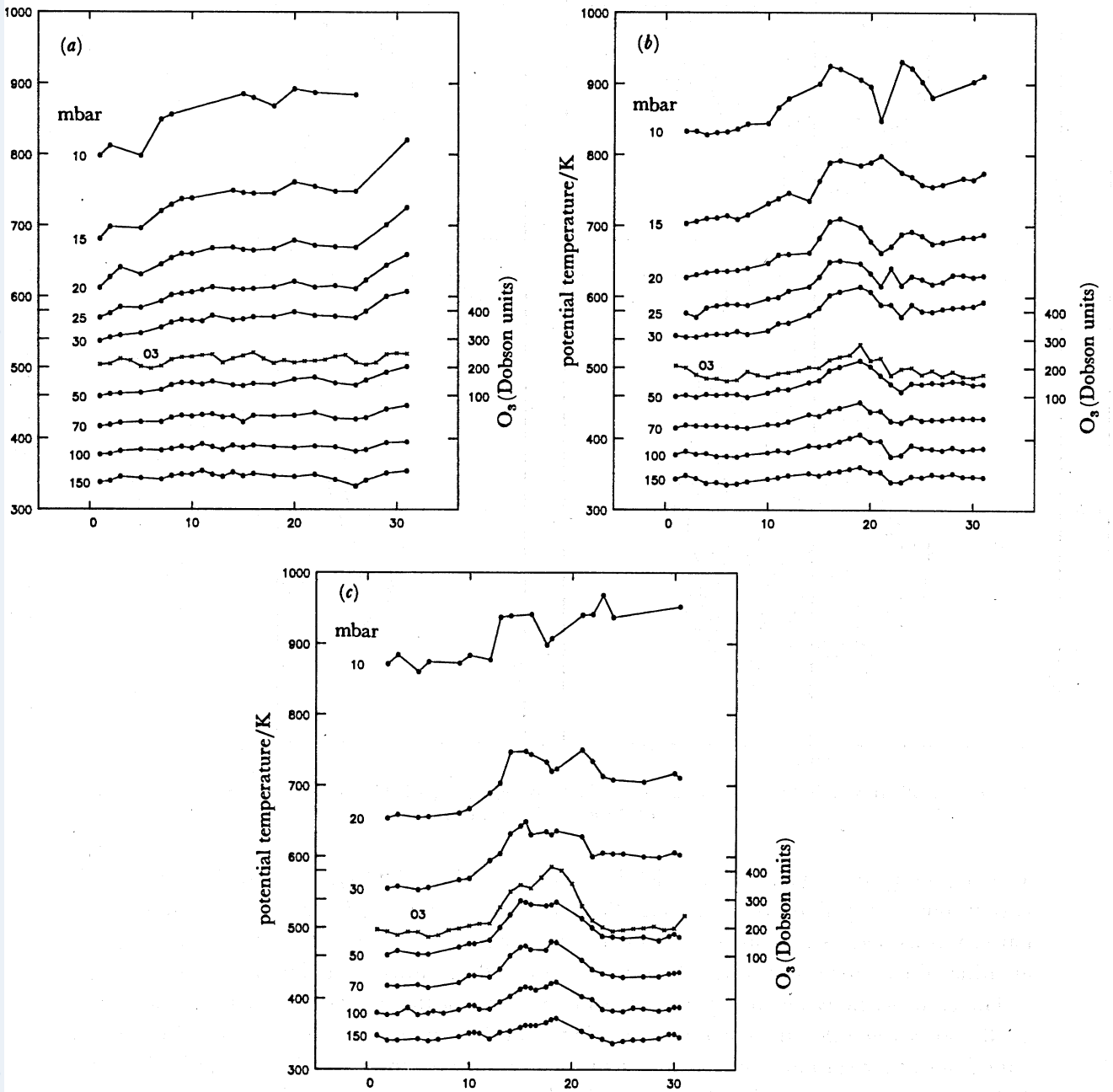

FIGURE 9. Variations of potential temperature at standard pressure levels in the lower stratosphere, and of total ozone amount, over Halley in three Octobers, (*a*) 1980, (*b*) 1985 and (*c*) 1986.

disturbed years, 1985 and 1986, are noticeably warmer at the higher levels at the beginning of the month than the quiet year 1980, consistent with the view that planetary waves exert a controlling influence. There is little variation from year to year in the initial temperatures at the lower levels. The final temperatures at these levels are slightly lower in the later years, a possible consequence of the ozone depletion, as discussed in §3. The relation between ozone amount and potential temperature in 1986 was clearly very different to that in 1985; this is consistent with the view that active subsidence is needed to produce the strongest gradients of temperature and ozone amount.

3. Ozone depletion and vortex dynamics

The detailed maps of the distribution of total ozone in the Southern Hemisphere, derived from data obtained by the total ozone mapping spectrometer (TOMS) on the *Nimbus* 7 satellite, have not only revealed the temporal and spatial extents of the depletions but have also vividly portrayed some of the processes inferred by Godson (1963) in his discussion of Arctic and Antarctic final warmings and the associated ozone variations. In particular, the evolution of ozone-rich active areas or cells in the warm belt surrounding the vortex can be readily followed. Summarizing the temperature variations, he said:

> The picture which emerges is one with quasi-zonal symmetry in winter, with minor mobile waves superimposed that are trivial poleward of 65° S. In August and September this zonal flow shrinks in size and warm cells in the sub-Antarctic (principally in the Australian sector) now produce perceptible asymmetries and a much deeper continental penetration by waves or surges, which characteristically produce the final warming by a stepwise process.

Discussing the ozone data from Antarctic stations, he concluded:

> The ozone evidence is for in-situ subsidence at high latitudes, rather than for a marked meridional exchange of air with southerly temperate latitudes...

A similar view was expressed by Dobson (1963) in discussing the observations made at Halley Bay in the *International Geophysical Year*:

> It seems as if in winter the south polar stratosphere is cut off from the general worldwide circulation of air by the very intense vortex of strong westerly winds which blow round the Antarctic continent, enclosing very cold air rather weak in ozone; neither the ozone nor the temperature rises much until this vortex suddenly breaks down in November.

If the core of the vortex is indeed an isolated air mass, as inferred by these authors, then explanations of the ozone depletions are severaly constrained. A notable advance in the visualization of large-scale dynamical processes has come from the use of synoptic maps of Ertel's potential vorticity (Q) on isentropic surfaces (McIntyre & Palmer 1983, 1984). Q is approximately a material tracer, and permits an objective analysis of the winter stratosphere into a polar vortex of high Q air, characterized by steep gradients of Q at its edge, surrounded by a broad 'surf zone', within which systematic large-scale gradients of Q are weak. The surf zone is a region of breaking waves – planetary-scale Rossby waves originating in the troposphere. Under the action of the breaking waves, the area of the vortex decreases, material being eroded from its edge. This is the dynamical view of the 'shrinking zonal flow' noted by Godson, and his warm belt may be identified with the surf zone. The persistence of high Q values inside the vortex indicates that transport into the vortex is weak. However, the Q maps are relatively coarse grained. Juckes & McIntyre (1987), reporting a high-resolution numerical simulation

of a barotropic vortex, find that the process of erosion is esentially one-sided. The eroded material is rapidly redistributed within the surf zone, but the main vortex is remarkably impervious to even small-scale incursions of the surrounding air. They conclude that

> It seems reasonable to suppose, purely on dynamical grounds, that the real stratospheric polar vortex should exhibit a similar tendency to maintain its integrity as a material entity even when it suffers erosion of material from its edge.

However, surf-zone erosion is not the only means of redistributing potential vorticity. Indeed, in the Southern Hemisphere, planetary-wave activity is apparently not sufficient to force the transition to anticyclonic flow (summer conditions) until well after the spring equinox. It is usually inferred that the warming has a relatively strong radiative component (Godson 1963). The diabatic effects are, however, slow acting, and the timing of the final warming remains variable from year to year, dependent on the planetary-wave activity. The most variable quantity determining the net radiative drive is ozone amount. The main loss of ozone in recent years occurs in September, and low values persist until mid-November. The effects, taking the most simple view, should be slower temperature rises than formerly, and delayed final warmings, most evident, probably, in the lowest levels of the stratosphere. There can be little doubt that these effects have occurred. At Halley Bay, all the final warmings since 1979 have been later than the mean warming for 1957–1972. In 1984 and 1985 the delay amounted to some 15 days, comparable, however, to that for the latest warming observed previously, in 1959 (a year with marked planetary-wave activity in September and October, but little later). The unusual behaviour of the vortex in 1986 has been discussed above; the final warming was nevertheless some five days later than the 1957–1972 mean. The slower temperature rises in October 1985 and 1986 (relative to 1980) at all levels from 50 to 150 mbar have been noted in discussing figure 9. At 100 mbar, on 31 October, the temperature ranged from −58 to −71 °C, with a mean value of −65 °C, in 1957–1972. The values in 1984, 1985 and 1986 fell in the range −74 to −76 °C. By contrast, the temperatures at 100 mbar in these last three years in September only once (for a few days in 1986) crossed the envelope of the 1957–1972 temperatures; within the limitations of radiosonde measurements, the temperatures in September have not changed.

The simplest interpretation is that the cold core of the vortex is indeed an isolated air mass, and that the temperatures within it are largely under radiative control in late winter and spring. Very roughly, if one half of the ozone below 30 mbar has been lost (some 30% loss of monthly mean total ozone), the rises in temperature at 100 mbar at Halley Bay during the mean Octobers 1957–1972 and 1984–1985 are consistent with ozone heating rates of about 0.6 K d^{-1} and 9.3 K d^{-1} respectively, opposed by a (carbon dioxide) cooling rate of about 0.2 K d^{-1}. Possible dynamical effects of the delayed warming should be considered. Previously (before the ozone depletions) the gradients of temperature and of potential vorticity between the surf zone (warm belt) and the vortex core weakened considerably as the core warmed. An apparent consequence of this was the weakening during the spring of successive ozone maxima in successive poleward surges of the warm belt. Now that the gradients remain large until much later (to mid-November, roughly) it seems reasonable to suppose that the ozone maxima will weaken less markedly; a dynamical basis for the implied relation between planetary-wave 'breaking' events in the surf zone and the transport of ozone by the general diabatic mass circulation is explicitly noted by Haynes & McIntyre (1987). Because the wave activity varies greatly from year to year, identification of this effect will not be easy. There is, moreover, an

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opposing effect, as the ozone-poor air eroded from the vortex is mixed into the warm belt. This latter effect should be small, on purely geometrical grounds, since the area of the vortex is only some 5% of that of the warm belt, and only a small fraction of the vortex is eroded.

In the discussion above, the cold core of the vortex has been tacitly identified with the region, from 200 to 40 mbar, in which the largest seasonal variation of ozone amount occurs. The evolution of potential vorticity on the relevant isentropic surfaces (from 350 to 400 K, roughly) cannot yet be studied synoptically, as a result largely of practical difficulties in deriving potential vorticity from satellite data. However, it may reasonably be inferred from consideration of diabatic heating rates that seasonal changes on these surfaces are slower and later than changes at greater heights (see figure 9).

4. Chemical processes

The total chlorine content of the stratosphere in 1985 was about 2.7 p.p.b.v.† (WMO 1986). It is generally accepted that about one half of this is man made, derived from the emissions since 1965 of the chlorofluorocarbons (CFCs). The evidence for this is indirect. Hydrogen fluoride (HF) has no known source except for reactions following the photodecomposition of CFCs in the stratosphere. The column abundance of HF was observed to increase by about 90% from 1977 to 1985, in good agreement with predictions based on the measured concentrations of the CFCs in the troposphere (WMO 1986).

Much effort has been devoted to assessing the effects of this increase in total chlorine, and of slower increases in other constituents, on the ozone layer. A comprehensive account of current models, and of the results obtained with them, has recently been published (WMO 1986). Most of the early assessments used one-dimensional models. Prather *et al.* (1984) found that when the amount of total chlorine exceeded a certain threshold, very rapid destruction of ozone occurred. This has been referred to as the 'chlorine catastrophe'. The process can be seen as a switch from nitrogen dominance to chlorine dominance of stratospheric chemistry. The threshold value of total chlorine is very much greater in two-dimensional models. In these models, transport is the dominant process in the lower stratosphere, and can suppress nonlinear chemical processes. However, the two-dimensional models did not predict the Antarctic ozone depletions. If, as argued in §3, there is virtually no transport in spring into the core of the polar vortex, then it may be that these models are, incorrectly, suppressing an Antarctic 'chlorine catastrophe'.

Explanations of the Antarctic ozone depletions should be consistent with the historical ozone record. They have to show why depletions did not occur before 1977. They should preserve also the apparently correct simulation by current models that only very small changes of total ozone occurred in the Northern Hemisphere from 1965 to 1982. The hypothesis that an appropriate threshold of total chlorine was crossed in 1977 is satisfactory in both respects. Measurements of NO_2 in Antarctica (Noxon 1978; McKenzie & Johnston 1984) have yielded very low column abundances in winter and early spring, showing that the 'catastrophe threshold' is indeed low. Only rather general inferences can be drawn from the other observations at present available. These suggest that no significant losses of ozone occur in darkness. The depletion seems to run more or less smoothly (see figure 4), being most rapid in mid- to late September. Ozone amount attains its minimum value by mid-October. The losses are now so large (some 50%

† Parts per billion by volume; in this paper 1 billion represents 10^9.

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of total ozone is removed in about 30 days) that processes which can destroy ozone rapidly at altitudes around the peak of the ozone layer must be important. It has been suggested that the major changes occur below 20 km (S. Solomon, personal communication 1985; National Ozone Expedition, press release 1986).

(*a*) HOCl: *the critical reservoir?*

Most of the important catalytic cycles, including that of chlorine itself, are rate limited by the $O:O_3$ ratio, which is strongly dependent on altitude. The main exception is

$$O_3 + HO \rightarrow O_2 + HO_2, \tag{1}$$

$$O_3 + HO_2 \rightarrow 2O_2 + HO. \tag{2}$$

The constituent that links this cycle to chlorine chemistry is hypochlorous acid (HOCl), and

$$HOCl + h\nu \rightarrow HO + Cl, \tag{3}$$

$$O_3 + Cl \rightarrow ClO + O_2, \tag{4}$$

$$ClO + HO_2 \rightarrow HOCl + O_2, \tag{5}$$

in combination with reactions (1) and (2), provide rapid ozone destruction even at large solar zenith angles. The rate coefficient for reaction (5) has a large negative temperature dependence, giving a fast rate in the cold core of the vortex. The rate coefficients for reactions (1) and (2) are not well determined at low temperatures.

Whether or not depletions occur is determined by the competition for ClO between HO_2 by reaction (5) and NO_2 by

$$M + ClO + NO_2 \rightarrow ClONO_2 + M. \tag{6}$$

For when (6) inhibits the reformation of HOCl, there is no other source of HO_x in early spring, because at large solar zenith angles neither

$$H_2O + O(^1D) \rightarrow 2HO \tag{7}$$

nor

$$HNO_3 + h\nu \rightarrow HO + NO_2 \tag{8}$$

can proceed rapidly. The main source of NO_2 at polar sunrise is the vary labile reservoir NO_3. During the polar night the oxides of nitrogen are partitioned by the reactions

$$O_3 + NO_2 \rightarrow NO_3 + O_2, \tag{9}$$

$$M + NO_2 + NO_3 \rightarrow M + N_2O_5. \tag{10}$$

The rate of reaction (9) falls rapidly with temperature. The build up of NO_3 required to give rapid formation of N_2O_5 has to be achieved early in the winter. The back reaction in (10) practically ceases when the temperature falls below 210 K. This sets an upper limit to the amount of NO_3 left free; NO_2 is virtually removed completely. The robustness of the partitioning against inter-annual variability of temperature and trajectories needs careful assessment. Photolysis of NO_3 by moonlight cannot be ignored. N_2O_5 (and other reservoirs requiring short ultraviolet wavelengths for photolysis) has little influence during the period of rapid depletion. Indeed it will be its dissociation (by photolysis mainly, but thermal decomposition may be significant on some trajectories) that, by releasing odd NO_x, brings the depletion to an end.

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HOCl will be formed at polar sunset by reaction (5). It is not clear that this provides a sufficient source, because the stratosphere is then relatively warm, and nitrogen dominated. However, HOCl may also be formed during the polar night by

$$ClONO_2 + H_2O \rightarrow HOCl + HNO_3 \qquad (11)$$

as discussed by Rowland *et al.* (1986). The rate of the homogeneous reaction is not well determined; it may be noted that a rate constant as low as 5×10^{-21} cm^3 per molecule s^{-1} represents a major source of HOCl over 90 days (about 10^8 molecules cm^{-3} at 18 km). Laboratory studies of this process, both as a gas-phase reaction and as a heterogeneous reaction, are being undertaken by several groups, and a definitive assessment should be available soon.

It should be noted that, in the scheme outlined above, rapid destruction of ozone is achieved by eliminating the null sequences involving the reaction of NO with ClO and HO_2, rather than by requiring large amounts of HO_x and ClO_x. Moreover, the destruction is fully effective, because there is little vertical transport of ozone (§3), and practically no photochemical production. Note that the methane oxidation cycle should be quite ineffective in the Antarctic spring, because the reactions of methane with HO and with Cl proceed very slowly at the low temperatures that prevail in the core of the vortex.

(*b*) *Other features of chlorine and bromine chemistry*

Some catalytic cycles, previously thought (WMO 1986, pp. 38–40) to be of importance only when the ClO_x level exceeds about twice the present value, are now being discussed as possible causes of the ozone depletions. McElroy *et al.* (1986) have stressed the importance of the BrO + ClO reaction, and a comprehensive survey has been attempted by Crutzen & Arnold (1986; acknowledgements are given to personal communications from R. A. Cox, and from L. T. and M. Molina on the self-reaction ClO + ClO). But, if HOCl is the critical polar-night reservoir, the ClO + BrO and ClO + ClO reactions have to compete with reaction (5), and are unlikely, on the kinetics data currently available, to do so effectively at an early stage of a depletion. However, at a later stage, if HO_x losses prevent the re-formation of HOCl, they could prolong the duration of active depletion considerably. It should be noted that if bromine compounds are already making significant contributions to Antarctic ozone depletions, then, on present understanding, it is difficult to avoid the conclusion that effects should by now be evident at other latitudes.

Another reaction that can lead to redistribution of ClO_x during the polar night is

$$ClONO_2 + HCl \rightarrow Cl_2 + HNO_3, \qquad (12)$$

also discussed by Rowland *et al.* (1986). They note that to be competitive with reaction (11), very high particle-collision efficiencies would be required. Cl_2 is readily photolysed by visible radiation, and if this is the main source of ClO_x, then the cycles initiated by the ClO + ClO and ClO + BrO reactions would be the main processes leading to loss of ozone.

(*c*) *Clouds in the Antarctic stratosphere*

Solomon *et al.* (1986) studied the possible effects of reactions (11) and (12) occurring, heterogeneously, on polar stratospheric cloud (PSC). This 'cloud' is perhaps better described

as an optically thin haze, which seems to occur whenever the temperature drops below −80 °C. It is detected by solar-occultation measurements at 1 μm wavelength from satellites (McCormick *et al.* 1982). The measurements yield vertical profiles of extinction, but give no information on the composition, phase or size distribution of the particles. Cloud veils, described as stratospheric cirrostratus, have been reported by many polar expeditions. Liljequist (1956) noted that these cloud veils did not produce halos, and inferred that they did not contain ice crystals. Nacreous clouds have also been reported. They occur mainly as wave-cap patches in the lee of mountains, and are often optically thick. The colouring of these clouds gives some information on particle sizes. Hallet & Lewis (1967) infer the presence of sulphuric acid. The critical temperature for the formation of nacreous cloud is about −90 °C.

The patchiness of nacreous cloud suggests that their influence on wide-spread ozone depletion is small. There seems to be little doubt that the PSC detected by satellites and the stratospheric cirrostratus observed from the ground are essentially identical. It follows that although PSC may be a necessary part of an explanation of ozone depletion, it is not a sufficient explanation. The thinness of PSC shows that the concentration of particles is small, so that associated heterogeneous reactions should be slow. This is consistent with the view that their main chemical effect is to repartition reservoirs.

It has been suggested recently (Crutzen & Arnold 1986) that PSC is composed mainly of hydrates of nitric acid. A large reduction in the concentration of nitric-acid vapour will tend to prolong the duration of chlorine dominance by inhibiting the reaction

$$HO + HNO_3 \rightarrow H_2O + NO_3, \qquad (12)$$

which is both a sink for HO_x and a source of NO_x. If the haze particles grow sufficiently large, then sedimentation may lead to appreciable vertical transport of nitric acid within the stratosphere, and perhaps even to a flux into the troposphere. Analyses of snow cores might reveal this seasonal effect. Laboratory studies of the formation, growth and evaporation of the hydrates of nitric acid, and of associated heterogeneous reactions, are needed if this theory of PSC is to be incorporated into models.

(*d*) *Crucial measurements*

The importance of reactions (1)–(5) could, in principle, be determined definitively by measuring the diurnal variations of HOCl, HO, HO_2, Cl and ClO in early September at a station with as low a latitude as possible (to obtain a large variation of solar zenith angle), consistent with being under the core of the vortex. However, HOCl has not yet been detected in the atmosphere, and measurements of HO, HO_2 and Cl in the lower stratosphere remain, despite considerable developments, among the most difficult to achieve. What inferences might be drawn from measurements of ClO alone? The diurnal variation of column ClO should suffice to rule out some of the more extreme speculations. If good height and time resolution of ClO profiles can be achieved, then it should be possible to discriminate between some possible nighttime reservoirs from the timescales of sunset and sunrise changes.

$ClONO_2$ measurements may be difficult to interpret at first, in the absence of previous data. The quantity most needed is the April–August difference, again with good height resolution if reaction (11) is largely confined to a limited altitude range. HNO_3 measurements will be very interesting, in view of the recent suggestions about the composition of PSC, and of possible

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sedimentation of the condensed material. Measurements of N_2O_5 could reveal the significance, or otherwise, of the heterogeneous reaction

$$N_2O_5 + H_2O \rightarrow 2HNO_3, \quad (13)$$

which may be important in promoting further growth of PSC particles.

Some source gases, such as N_2O and the CFCs, are practically inert in the troposphere and lower stratosphere. They are therefore good tracers, and their profiles should yield valuable information on transport through the tropopause region.

5. Discussion

The stratosphere of the Southern Hemisphere has been much less intensively studied than its northern counterpart. Inhibiting factors have been the sparseness of radiosonde data (data which is still required to tie the global temperature fields derived from satellite measurements to a geopotential base level), and the early recognition that the antarctic stratosphere is dynamically less active than the Arctic, mid-winter warmings and wind reversals being confined largely to the upper stratosphere. Measurements of trace constituents have also been relatively neglected, the logistical difficulties being an added deterrent. Thus, the conditions that prevailed before the ozone depletions became so prominent were poorly observed, and remain not well understood. This is reflected in the extent to which unconstrained speculation has been a feature of subsequent discussions. The detailed work undertaken by the National Ozone Expedition (of the United States) at McMurdo from August to November 1986 should mark the beginning of a new phase of discussion, with hypotheses now subject to more rigorous constraints. The reports of the expedition are awaited with interest.

If the ozone depletions in Antarctica are linked with the increase in stratospheric chorine, then no return to an ozone climatology similar to that of the 1960s can occur until many years after CFC emissions have been stopped. In contrast, it may be expected that any component of the depletions arising from dynamical processes will show significant interannual variation. There are, indeed, several such components. The total chlorine is not in a steady state. Transpsort from the troposphere to the stratosphere (mainly in the tropics), and subsequent transport to high southern latitudes, are spasmodic rather than uniform processes. The minimum value of ozone in any one spring depends on the amounts of ozone and of total chlorine present when the vortex is forming at the end of the previous summer. The dependence of the ozone amount on the transport in late summer has been discussed by Farman *et al.* (1985). Outside the tropics, a large part of the variance of ozone amount is associated with essentially conservative redistributions in the lower stratosphere, forced by weather systems in the troposphere. Such fluctuations will be superimposed on the larger-scale structure of the vortex, and will contribute to interannual variations of the ozone minimum. Non-conservative changes of ozone may also be induced by the associated changes in temperature, if the chemistry, as suggested in §4, is strongly temperature dependent.

It is clear that many more measurements, in Antarctica and in the laboratory, are required to establish the cause of the ozone depletions. At present, it seems that the progressive deepening of the minimum should be attributed to chemical mechanisms, and that departures from a

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smooth progression can be associated with dynamical processes. The evidence implicating total chlorine, and hence the CFCs, remains circumstantial. It should, nevertheless, be heeded until more direct evidence can be obtained.

References

Crutzen, P. J. & Arnold, F. 1986 Nitric acid cloud formation in the cold Antarctic stratosphere: a major cause for the springtime 'ozone hole'. *Nature, Lond.* **324**, 651–655.

Dobson, G. M. B. 1963 *Exploring the atmosphere.* (209 pages.) Oxford University Press.

Farman, J. C. 1977 Ozone measurements at British Antarctic Survey stations. *Phil Trans. R. Soc. Lond.* B **279**, 261–271.

Farman, J. C. & Hamilton, R. A. 1975 Measurements of atmospheric ozone at the Argentine Islands and Halley Bay, 1957–72. *Brit. Antarct. Surv. Sci. Rep.* no. 90. (40 pages.)

Farman, J. C., Gardiner, B. G. & Shanklin, J. D. 1985*a* Large losses of total ozone in Antarctica reveal seasonal ClO_x/NO_x interaction. *Nature, Lond.* **315**, 207–210.

Farman, J. C., Murgatroyd, R. J., Silnickas, A. M. & Thrush, B. A. 1985*b* Ozone photochemistry in the antarctic stratosphere in summer. *Q. Jl. R. met. Soc.* **111**, 1013–1028.

Gardiner, B. G. & Shanklin, J. D. 1986 Recent measurements of ozone depletion. *Geophys. Res. Lett.* **13**, 1199–1201.

Godson, W. L. 1963 A comparison of middle-stratosphere behaviour in the Arctic and Antarctic, with special reference to final warming. *Met. Abhandl.* **36**, 161–206.

Hallett, J. & Lewis, R. E. J. 1967 Mother-of-pearl clouds. *Weather* **22**, 56–65.

Haynes, P. H. & McIntyre, M. E. 1987 On the evolution of vorticity and potential vorticity in the presence of diabatic heating and frictional or other forces. *J. atmos. Sci.* **44**, (In the press.)

Juckes, M. N. & McIntyre, M. E. 1987 A high-resolution barotropic model of the stratospheric 'surf zone': some preliminary results. *Nature, Lond.* **328**, 590–596.

Liljequist, G. H. 1956 *Halo-phenomena and ice crystals.* Norweigan–British–Swedish Antarctic Expedition, 1949–52, scientific results, vol. 2, part 2A. (85 pages.) Oslo: Norsk Polarinstitutt.

McCormick, M. P., Steele, H. M., Hamill, P., Chu, W. P. & Swissler, T. J. 1982 Polar stratospheric cloud sightings by SAM II. *J. atmos. Sci.* **39**, 1387–1397.

McElroy, M. B., Salawitch, R. J., Wofsy, S. C. & Logan, J. A. 1986 Reductions of Antarctic ozone due to synergistic interactions of chlorine and bromine. *Nature, Lond.* **321**, 759–762.

McIntyre, M. E. & Palmer, T. N. 1983 Breaking planetary waves in the stratosphere. *Nature, Lond.* **305**, 593–600.

McIntyre, M. E. & Palmer, T. N. 1984 The 'surf zone' in the stratosphere. *J. atmos. terr. Phys.* **46**, 825–850.

McKenzie, R. L. & Johnston, P. V. 1984 Springtime stratospheric NO_2 in Antarctica. *Geophys. Res. Lett.*, **11**, 73–75.

Noxon, J. G. 1978 Stratospheric NO_2 in the Antarctic winter. *Geophys. Res. Lett.* **5**, 1021–1022.

Prather, M. J., McElroy, M. B. & Wofsy, S. C. 1984 Reductions in ozone at high concentrations of stratospheric halogens. *Nature, Lond.* **312**, 227–231.

Rowland, F. S., Sato, H., Khwaja, H. & Elliott, S. M. 1986 The hydrolysis of chlorine nitrate and its possible atmospheric significance. *J. phys. Chem.* **90**, 1985–1988.

Soloman, S. R., Garcia, R. R., Rowland, F. S. & Wuebbles, D. 1986 On the depletion of Antarctic ozone. *Nature, Lond.* **321**, 755–758.

Stolarski, R. S., Krueger, A. J., Schoeberl, M. R., McPeters, R. D., Newman, P. A. & Alpert, J. C. 1986 Nimbus 7 SBUV/TOMS measurements of the springtime Antarctic ozone hole. *Nature, Lond.* **322**, 808–811.

Taylor, R. C. 1960 The topography of the 400° K isentropic surface over Antarctica, spring 1957. *IGY General Report* no. 11. (This incorporates Palmer, C. E. & Taylor, R. C. 1960 The vernal breakdown of the stratospheric cyclone over the South Pole. *J. geophys. Res.* **65**, 3319–3329.)

WMO 1986 *Atmospheric ozone 1985.* Global Ozone Research and Monitoring Project, report no. 16. (1095 pages.)

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