Large losses of total ozone in Antarctica reveal seasonal ClO-/NOx interaction

J. C. Farman, B. G. Gardiner & J. D. Shanklin

British Antarctic Survey, Natural Environment Research Council, High Cross, Madington Road, Cambridge CB3 0ET, UK

Recent attempts1,2 to consolidate assessments of the effect of human activities on stratospheric ozone (O3) using one-dimensional models for 30°N have suggested that perturbations of total O3 will remain small for at least the next decade. Results from such models are often accepted by default as global estimates3. The inadequacy of this approach is here made evident by observations that the spring values of total O3 in Antarctica have now fallen considerably. The circulation in the lower stratosphere is apparently unchanged, and possible chemical causes must be considered. We suggest that the very low temperatures which prevail from midwinter until several weeks after the spring equinox make the Antarctic stratosphere uniquely sensitive to growth of inorganic chlorine, ClX, primarily by the effect of this growth on the NO2/NO ratio. This, with the height distribution of UV irradiation peculiar to the polar stratosphere, could account for the O3 losses observed.

Total O3 has been measured at the British Antarctic Survey stations, Argentine Islands 65°S 64°W and Halley Bay 76°S 27°W, since 1957. Figure 1a shows data from Halley Bay. The mean and extreme daily values from October 1957 to March 1973 and the supporting calibrations have been discussed elsewhere1,2,5. The mean daily value for the four latest complete observing seasons (October 1980–March 1984) and the individual daily values for the current observing season are detailed in Fig. 1. The more recent data are provisional values. Very generous bounds for possible corrections would be ±30 mm atm. There was a changeover of spectrophotometers at the station in January 1982; the replacement instrument had been calibrated against the UK Meteorological Office standard in June 1981. Thus, two spectrophotometers have shown October values of total O3 to be much lower than March values, a feature entirely lacking in the 1957–73 data set. To interpret this difference as a seasonal instrumental effect would be inconsistent with the results of routine checks using standard lamps. Instrument temperatures (recorded for each observation) show that the March and October operating conditions were practically identical. Whatever the absolute error of the recent values may be, within the bounds quoted, the annual variation of total O3 at Halley Bay has been extraordinary.

Figure 1b shows data from Argentine Islands in a similar form, except that for clarity the extreme values for 1957–73 have been omitted. The values for 1980 to the present are provisional, the extreme error bounds again being ±30 mm atm. The...
changes are similar to those seen at Halley Bay, but are much smaller in magnitude.

Upper-air temperatures and winds are available for these stations from 1956. There are no indications of recent departures from established mean values sufficient to attribute the changes in total $O_3$ to changes in the circulation. The present-day atmosphere differs most prominently from that of previous decades in the higher concentrations of halocarbons. Figure 2a shows the monthly mean total $O_3$ in October at Halley Bay, for 1957–84, and Fig. 2b that in February, 1958–84. Tropospheric concentrations of the halocarbons F-11 (CFC$_3$) and F-12 (CFC$_2$) in the Southern Hemisphere are also shown, plotted to give greatest emphasis to a possible relationship. Their growth, from which increase of stratospheric Clx is inferred, is not evidently dependent on season. The contrast between spring and autumn $O_3$ losses and the striking enhancement of spring loss at Halley Bay need to be explained. In Antarctica, the lower stratosphere is $\sim 40$ K colder in October than in February. The stratosphere over Halley Bay experiences a polar night and a polar day (many weeks of darkness, and of continuous photolysis, respectively); that over Argentine Islands does not. Figure 3 shows calculated amounts of NO$_x$ in the polar night and the partitioning between the species. Of these, only NO$_x$ and NO$_2$ are dissociated rapidly by visible light. The major reservoir, N$_2$O, which only absorbs strongly below 280 nm, should be relatively long-lived. Daytime levels of NO and NO$_2$ should be much less in early spring, following the polar night, than in autumn, following the polar day. Recent measurements support these inferences. The effect of these seasonal variations on the strongly interdependent Clx and NO$_x$ cycles is examined below.

The $O_3$ loss rate resulting from NO$_x$ and Clx may be written:

$$L = N + C = 2 k_d[O][NO_2] + k_d[O][CI]$$

(1)

$L$ accounts for over 85% of $O_3$ destruction in the altitude range 20–40 km. At 40 km, $N$ and $C$ are roughly equal. Lower down, $C$ decreases rapidly to 10% of $L$ at 30 km, 3% at 20 km (refs 6, 8). Equation (1) is based on two steady-state approximations, (see Table 1a for the reactions involved)

$$\psi = \frac{[NO_2]}{[NO]} \approx \frac{k_d[O]+k_d[CI]}{k_d[O]+j_3}$$

(2)

and

$$x = \frac{[CI]}{[CI]} \approx \frac{k_d[O]+k_d[NO]}{k_d[O_3]}$$

(3)

valid in daytime, with [O] in steady state with [O$_3$]. Reaction (4) has a negative temperature coefficient, whereas reaction (1)
has large positive activation energy9, with the result that ψ is strongly dependent on [ClO] at low temperature, as shown in Fig. 4. [ClO] is not simply proportional to total ClX, because ClONO2 formation (reaction (10)) intervenes. Throughout the stratosphere, χ < 1, so that [ClO] = [Cl + ClO]. From a steady-state analysis of the reactions given in Table 1b,

\[ [\text{Cl} + \text{ClO}] = \frac{k_1 \text{[HCl]} [\text{OH}] + k_2 \text{[ClONO2]} + k_3 \text{[HOCI]}}{k_4 \text{[NO2]} + k_5 \text{[H2O]} + \chi (k_6 \text{[CH4]} + k_7 \text{[H2O]})} \]  

Values of ψ, χ and [Cl + ClO] obtained from equations (2), (3) and (4) are in good accord with full one-dimensional model results for late summer in Antarctica9. Neglecting seasonal effects other than those resulting from temperature and from variation of [NO + NO2], it is possible to solve simultaneously for [NO2] and [ClO], and to derive L. Results are shown in Table 2 as relaxation times9, [O3]/L, for various conditions. The spring values (lines 2, 3 and 4) are highly dependent on ClX amount (compare columns a and b), the autumn values (line 1) much less so. At Antarctic Islands, the sensitivity to ClX growth should resemble that seen in line 2, attributable solely to low temperature. Lines 3 and 4 show the enhanced sensitivity possible at stations within the Antarctic Circle, such as Halley Bay, arising from slow release of [NO + NO2] following the polar night. It remains to be shown how stable O3 budgets were achieved with the relaxation times for the lower chlorine level (Table 2, a).

Much O3 destruction is driven by visible light, but production requires radiation below 242 nm. On the dates shown (Table 2), destruction persists for some 11 h, while, because of the long UV paths, production is weak (except around noon) at 29 km, and is virtually absent below that altitude. Line 1 of Table 2 then demands O3 transport in autumn from the upper to the lower stratosphere, which is consistent with inferred thermally-driven lagrangian-mean circulations10. A mean vertical velocity of 43 m per day is in good accord with calculations of net diabatic cooling11 and gives a realistic total O3 decay rate in an otherwise conventional one-dimensional model9. The short relaxation times in the lower stratosphere in autumn are tolerable, with adequate transport compensating for lack of O3 production.

In early spring, on the other hand, wave activity scarcely penetrates the cold dense core of the Antarctic polar vortex and with very low temperatures the net diabatic cooling is very weak11. Lagrangian transport in the vortex should then be almost negligible. (The virtual exclusion of Agung dust from the vortex supports this view12.) The final warming signals the end of this period of inactivity and is accompanied by large dynamically induced changes in O3 distribution. However, before the warming, with low chlorine, total O3 was in a state of near-neutral equilibrium, sustained primarily by the long relaxation times.

Table 2  Relaxation times in days, [O3]/L, for maximum chlorine levels 1.5 p.p.b.v. (a) and 2.7 p.p.b.v. (b) (1980)

<table>
<thead>
<tr>
<th>Date</th>
<th>Relative NO + NO2</th>
<th>22</th>
<th>25.5</th>
<th>29</th>
<th>32.5</th>
<th>36</th>
<th>39.5</th>
<th>43</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 March</td>
<td>1</td>
<td>105</td>
<td>103</td>
<td>38</td>
<td>37</td>
<td>16</td>
<td>15</td>
<td>6.9</td>
</tr>
<tr>
<td>17 September</td>
<td>1</td>
<td>224</td>
<td>210</td>
<td>86</td>
<td>77</td>
<td>32</td>
<td>27</td>
<td>12.2</td>
</tr>
<tr>
<td>17 September</td>
<td>0.75</td>
<td>288</td>
<td>265</td>
<td>107</td>
<td>93</td>
<td>39</td>
<td>31</td>
<td>14.2</td>
</tr>
<tr>
<td>17 September</td>
<td>0.5</td>
<td>398</td>
<td>353</td>
<td>141</td>
<td>118</td>
<td>47</td>
<td>36</td>
<td>17.0</td>
</tr>
</tbody>
</table>

Noon values at 75.5°S, solar elevation 12.5°. Lower stratosphere at 230 K on 25 March; 190 K on 17 September. The altitudes shown apply to the summer temperature profile used in the model9.
at sunrise, not treated in equation (4). The polar-night boundary is, therefore, the natural testing ground for the theory of nonlinear response to chlorine\(^{-1}\). It might be asked whether a nonlinear response is already evident (Fig. 2a). An intensive programme of trace-species measurements on the polar-night boundary could add greatly to our understanding of stratospheric chemistry, and thereby improve considerably the prediction of effects on the ozone layer of future halocarbon releases.

We thank B. A. Thrush and R. J. Murgatroyd for helpful suggestions.

Received 24 December 1984; accepted 28 March 1985.


---

**An Ordovician ophiolite in County Tyrone, Ireland**

D. H. W. Hutton*, M. Aftalion† & A. N. Halliday†

*Department of Geological Sciences, University of Durham, Durham DH1 3LE, UK
†Scottish Universities Research and Reactor Centre, East Kilbride, Glasgow G75 0QU, UK

Ophiolites are regarded widely by geologists as remnants of old oceanic crust that has been obducted onto the continental margins during ocean or marginal basin closure and orogeny. Therefore, they provide evidence for the existence of old oceans and oceanic basins and are a key to the extension of plate tectonic modelling into pre-Mesozoic rock assemblages. In the Caledonian–Appalachian orogen, ophiolites are known although very few of these are dated well enough to provide accurate constraints on plate-tectonic kinematics. We report here the discovery of an ophiolitic sequence within the rocks of the Tyrone Igneous Complex in Northern Ireland. U/Pb dating combined with field evidence indicates that the Tyrone ophiolite was formed and then obducted onto the northern margins of the Iapetus Ocean close to 470 Myr BP (Arenig).

The Tyrone Igneous Complex (Fig. 1) occurs in an approximate along-strike continuation of the Midland Valley of Scotland; it is partly overlain by Upper Palaeozoic sediments within a shallow graben structure bounded by Dalradian rocks to the north and the Lower Palaeozoic of the Southern Uplands–Longford–Down zone to the south. The complex consists of three units (Fig. 1): a middle Ordovician (Llandeilo–Cathaysian) volcanic sequence; a high metamorphic grade gneiss unit ‘the central inlier’; and a unit of gabbros and dolerites previously called ‘the basic plutonic complex’. Opinions on the age relationships and significance of the units have varied. Originally the basic plutonic complex and volcanics were grouped together as Llandeilo–Cathaysian and regarded as being altogether younger and in tectonic contact with the central gneisses. Alternatively, the basic complex has been correlated with layered basic intrusions of Connemara and Aberdeenshire. This led to the view that both basic rocks and gneisses were older than and in unconformable contact beneath the Ordovician volcanic sequence.©1985 Nature Publishing Group