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Evidence for midwinter chemical ozone destruction over Antarctica

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Abstract. Two ozone profiles on June 15 and June 19, obtained over McMurdo, Antarctica, showed a strong depletion in stratospheric ozone, and a simultaneous profile of water vapor on June 19 showed the first clear signs of dehydration. The observation of Polar Stratospheric Clouds (PSCs) beginning with the first sounding showing ozone depletion, the indication of rehydration layers, which could be a sign for recent dehydration, and trajectory calculations indicate that the observed low ozone was not the result of transport from lower latitudes. During this time the vortex was strongly distorted, transporting PSC processed air well into sunlit latitudes where photochemical ozone destruction may have occurred. The correlation of ozone depletion and dehydration indicates that water ice PSCs provided the dominant surface for chlorine activation. An analysis of the time when the observed air masses could have formed type II PSCs for the first time limits the time scale for the observed ozone destruction to about 4 days.

1. Introduction

The springtime ozone depletion over Antarctica has been extensively studied, and has been clearly linked to a complicated interplay of polar stratospheric clouds (PSCs), chlorine, and sunlight [*Solomon*, 1990]. The level of ozone destruction occurring in the months between late August and November depends strongly on the amount of chlorine in the stratosphere, the vortex temperature, and the aerosol load (e.g. volcanic aerosol after the eruption of Mount Pinatubo). The dynamics controls all of these factors and the exposure of the air to sunlight. Since 1986 ozone has been studied in a year-around ozonesonde program conducted at Amundsen-Scott station at South Pole [e.g. *Hofmann and Oltmans*, 1993 and *Hofmann et al.*, 1994] and with ozone soundings between late August and November of each year at McMurdo station [*Hofmann et al.*, 1987]. Only a few cases have been reported so far indicating the photochemical destruction of ozone in the Antarctic vortex prior to the usual springtime depletion. Spectroscopic observations in April and May of 1992 showed significantly increased amounts of OClO [*Solomon et al.*, 1993], indicating chlorine activation, which was most likely caused by high levels of volcanic sulfate aerosols after the eruption of Mt. Pinatubo in 1991. Chlorine activation is a necessary condition for heterogeneous ozone destruction. During this same time period reduced ozone was observed between 10 and 18 km at South Pole [*Hofmann and Oltmans*, 1993]. This was attributed to the heterogeneous chlorine activation in the presence of volcanic aerosol. Here we present results showing that under special conditions, but in the absence of volcanic aerosol, chemical ozone destruction can happen even during mid winter, much earlier than has been previously observed. These conditions involve only PSCs which occur regularly over Antarctica.

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2. Observations

In 1994 ozone soundings were launched at McMurdo station (77.83°S 166.69°E) for a continuous 12 month period in conjunction with an intensive program of frost-point, aerosol, and nitric acid soundings between February and October. Ozonesondes were launched once every two weeks between February and April, four times in May and at least twice a week between June and October. Frost-point hygrometers were launched once a month between February and April, twice in May and once a week in June through the first half of August. Ozone vertical profiles were measured using a digital version of the Electrochemical Concentration Cell (ECC), which has been used in Antarctica since 1986 [*Hofmann et al.*, 1987]. The frost-point soundings, which were conducted to study the development of the dehydration of the Antarctic vortex [*Vömel et al.*, 1995], usually had an ozonesonde as part of the payload.

Figure 1 shows the column ozone in the layer between 15 km and 17 km from May through the first half of September of 1994. In this layer very low ozone was observed during a short period in the middle of June, with values comparable to the early period of the ozone hole in late August and early September. These unusually low ozone values were observed in two consecutive soundings on June 15 and June 19, which are shown in figure 2a together with a sounding on June 13, showing an unperturbed

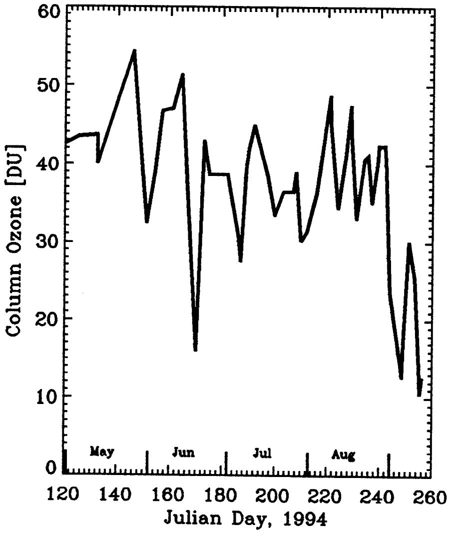

Figure 1. Column ozone between 15 and 17 km observed in balloon soundings from McMurdo, Antarctica (77.8°S).

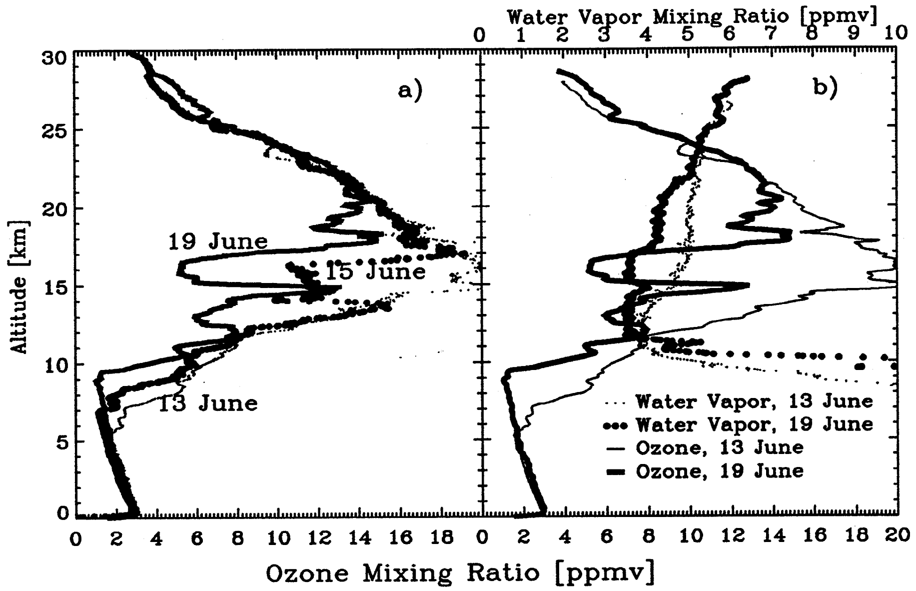

Figure 2. (a) Consecutive ozone profiles showing the development of the first observed ozone depletion in a region from 12 to 21 km between June 13 and June 19, 1994. (b) Comparison of water vapor and ozone for the sounding showing the strongest ozone depletion (June 19) and a sounding before this event (June 13). Note that the entire region showing dehydration also shows a reduction in ozone.

ozone profile. The sounding on June 15 shows a sharp 2 km thick layer at about 15 km, in which the ozone partial pressure is reduced to about 11 mPa, compared to 16 to 20 mPa normally found in this region. On June 19, the region of reduced ozone extended from about 12 to 20 km, with a minimum layer between 15 and 17 km, and a minimum value of about 5 mPa. This value is more than 4 standard deviations below the amount of ozone usually found in this region between May and mid August. The water vapor profiles on June 13 and June 19 are shown in figure 2b along with the corresponding ozone profiles. The sounding on June 19 marks the onset of dehydration, showing the first clear signs of dehydration in the range from 12 to 22 km. Over this entire region, ozone is reduced as well, with strong reduction occurring in the regions of strongest dehydration. After June 19, all water vapor soundings except one showed strong levels of dehydration, whereas none of the previous soundings showed any signs of dehydration. However, clear evidence for photochemical ozone depletion was not observed again before the beginning of the springtime ozone hole at the end of August. Synoptic maps for this period show that the vortex was strongly distorted, but McMurdo still inside the vortex edge. Trajectory calculations for June 19 obtained from two different models using ECMWF data (Figure 3) and NMC data (not shown) indicate that air parcels had reached a latitude up to 50°S.

3. Discussion

To explain the observed profiles by transport, the air would have to have originated in the tropics. The large vertical extent of the dehydration and ozone reduction region is a first indication against transport from the tropics or subtropics, and transport from midlatitudes does not seem to be sufficient to explain the observed values of water vapor and ozone. The midlatitudes themselves are not a source of dehydrated or strongly ozone depleted air. The trajectory calculations indicate that the observed air originated in or close to the vortex and up to a latitude of 50°S (figure 3). The water vapor profile on June 19 marks the beginning of the dehydration period, and shows that the temperature of the observed air must have reached the frost-point, and that ice particles had formed and settled out or partially evaporated. A small layer at 11 km (figure 2b) could possibly be a remnant of the evaporation of these particles. Much stronger rehydration layers, which formed during the period of active dehydration, were a dominant feature of the subsequent water vapor profiles [*Vömel et al.*, 1995]. Furthermore, LIDAR observations (A. Adriani, personal communication, 1995) showed the first clear indication of PSCs on June 15. Through June 19 a weak backscatter signal was observed, which, however, showed a strong depolarization, possibly caused by nitric acid trihydrate (NAT). On June 20 and June 21 the backscatter signal increased dramatically, indicating the presence of type II PSCs over McMurdo. The presence of water ice PSCs was confirmed by an aerosol counter flight on June 21 (T. Deshler, personal communication, 1995). These type II PSCs were observed peaking at 14.7 km, with a total surface area of around 100 $\mu m^2/cm^3$. At this altitude, the water vapor profile on June 19 shows a local peak as well, which was likely formed by the evaporation of these particles. All of these observations are incompatible with transport from mid or low latitudes, thus it is highly unlikely that transport from mid or low latitudes could have led to the observed ozone profiles on June 15 and June 19.

NMC as well as ECMWF analyzed data show that the minimum temperature inside the vortex dropped sharply in late May and early June, which agrees well with the observed temperatures over McMurdo. In these data sets, the minimum temperature inside the vortex at 70 hPa reaches the frost-point temperature around June 9. The NMC data show slightly warmer temperatures, but because of the rapid drop to temperatures clearly below the frost-point, there is only a small uncertainty of a day or two in the time when the minimum temperature inside the vortex reached the frost-point. The NAT point at the 70 hPa level was reached near the end of May or the first days of June. Around June 10 the vortex begins to elongate, with a cold region forming southwest of the Palmer peninsula. This distortion persists for about 9 days, before the vortex returns to a more normal shape.

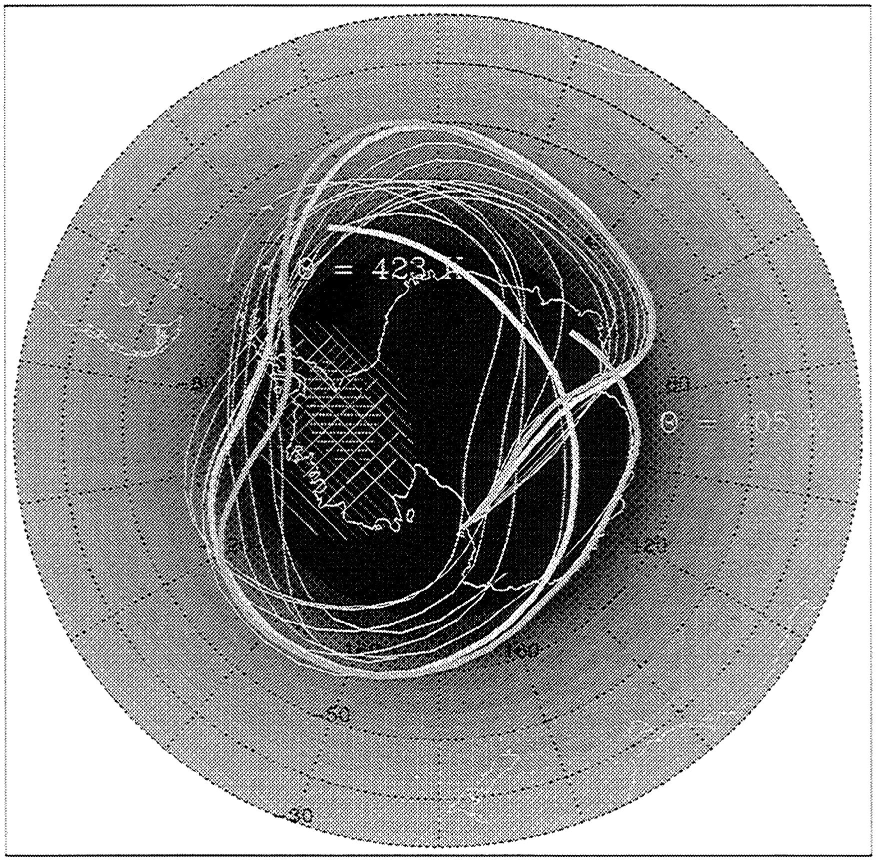

Figure 3. Isentropic backtrajectory calculations from McMurdo for levels between 390 K and 600 K on June 19. The trajectories at 405 K (15.6 km) and 423 K (17 km), which is the altitude range of the strongest ozone depletion, are emphasized. The grey shading indicates the amount of sunlight at each latitude. The hatched area indicates the cold region where the ambient temperature at the 70 hPa level was likely to have dropped below the frost-point temperature. This area is based on the temperature analysis for June 13, i.e. roughly the time when the trajectories passed this cold region.

This distortion is also evident in the trajectories (figure 3). These trajectories are calculated backward for 10 days and show that during this time, the air passed the cold region southwest of Palmer peninsula only once. Passage through this cold region is apparent in the temperature history of the trajectories (figure 4), where a temperature minimum is reached between 4 to 5 days prior to arrival at McMurdo. This time scale also agrees well with the first observation of PSCs on June 15, six days after the temperature minimum in the cold region of the vortex reached the frost-point, although at this point the composition of the observed early PSCs is not yet known.

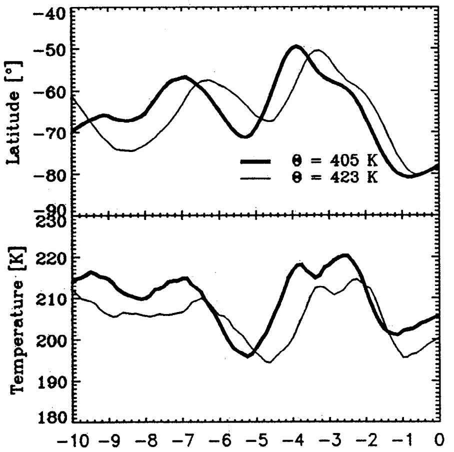

Figure 4. Temperature and latitude history for two isentropic backtrajectories from McMurdo at 405K and 423K on June 19.

Since the profile of June 19 shows clear evidence of dehydration, the air temperature must have reached the frost-point and ice particles must have formed and settled out. These initial particles must have fallen out fairly rapidly, because only a weak PSC signal was observed with the LIDAR on June 19 and because significant dehydration was observed. Thus they must have been relatively large and provided a sufficient surface area for chlorine activation. On June 21, a surface area of about 100 $\mu m^2/cm^3$ was observed just below the strongest ozone depletion region. Under these conditions, the time scale for heterogeneous chlorine activation is only a few hours, and nearly complete chlorine activation could occur well within a day (A. Ravishankara, personal communication 1995). Furthermore, the presence of large ice particles would allow for rapid denitrification through the uptake of HNO_3 onto ice crystals and subsequent sedimentation. This step inhibits the recombination of the activated chlorine with reactive nitrogen into chlorine reservoir species. After passing through the cold region the air was transported well into sunlit latitudes (up to 50°S), before reaching McMurdo. Our observation limits the time scale for chemical ozone depletion of the extent observed on June 19 to about 4 days. This time scale is significantly shorter than previously reported [see *Solomon,* 1990], however, not necessarily in contradiction with these numbers, since the conditions for our observation were substantially different than those of earlier measurements. The total available chlorine in the Antarctic vortex has been estimated to be about 3.5 ppbv [*Albritton et al.,* 1995] and a large fraction of this may have been activated on the early PSCs. The air was then transported into well sunlit latitudes, which could have accelerated the ClO-dimer photolysis substantially. Assuming that the ClO-dimer formation is the rate-limiting step in the catalytic cycle destroying ozone, then, under these conditions, the time scale for ozone destruction could be on the order of a few days.

Since the temperature minimum in the vortex reached the NAT point roughly 10 to 14 days prior to the frost-point, the possibility remains that the chlorine could have been substantially activated prior to the formation of ice particles, which could almost triple our estimate for the time scale of ozone destruction in this early period. However, the strong correlation of dehydration and ozone depletion suggests that chlorine activation was strongest in altitudes experiencing the strongest dehydration, in other words, at altitudes, in which water ice particles had formed. Furthermore the vortex distortion changed the flow pattern such that the air observed at McMurdo was likely to have passed through the cold region 4 to 5 days earlier; but with the more symmetric vortex prior to this distortion, it is less likely that the air passed through this cold region earlier, which was located nearer the center of the vortex.

The sounding on June 21 showed a largely unperturbed ozone profile, which was due to the recovery of the vortex symmetry between June 19 and June 21. The trajectories for the sounding on June 21 indicate that the air had seen very little sunlight. The sharp recovery within less than 3 days indicates that only a relatively small band close to the vortex edge, which was sufficiently exposed to sunlight, was affected by this perturbation.

4. Summary and Conclusion

In a simultaneous sounding of ozone and water vapor on June 19, we observed severe ozone depletion and the initial stages of dehydration in a region between 12 and 20 km. Trajectory calculations for the layer of strongest ozone depletion clearly show that the observed air had passed through a cold region, where the vortex temperature reached the frost-point for the first time during the winter of 1994. The observed dehydration and the time when the vortex minimum temperature reached the frost-point for the first time imply that, during the passage through this cold region, ice particles must have formed and settled out. The available surface area provided by these particles was sufficient to activate large fractions of the available chlorine. In a distortion of the vortex the air was then transported well into sunlit latitudes, up to 50°S, where ozone could have been photochemically destroyed. The time scale for the ozone destruction under these conditions is estimated to be about 4 days.

Since this observation was clearly linked to the edge of the vortex, it may be speculated that at the vortex edge ozone can be destroyed as soon as PSCs are formed in the middle of winter. This would imply that even in the middle of winter the ozone content of the vortex may already be chemically distorted, however, not on a scale comparable to the spring time depletion, which typically sets in with sunrise in late August. If on the other hand there is a significant amount of air skimmed off the vortex edge during the winter, midlatitudes in the southern hemisphere could experience ozone depleted air as early as late June [*Lehman et al.*, 1992]. However, the lack of other similar observations from the ongoing ozonesonde programs at South Pole and McMurdo indicate that observations of the kind presented here are rare. Furthermore, since the bulk of the vortex is well isolated from midlatitudes, this effect will not have a very strong impact on the southern hemisphere ozone distribution.

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