Polar vortex evolution during the 2002 Antarctic major warming as observed by the Odin satellite

P. Ricaud,[1,2] F. Lefèvre,[3] G. Berthet,[3] D. Murtagh,[4] E. J. Llewellyn,[5] G. Mégie,[3] E. Kyrölä,[6] G. W. Leppelmeier,[6,7] H. Auvinen,[6] C. Boonne,[3] S. Brohede,[4] D. A. Degenstein,[5] J. de La Noë,[1] E. Dupuy,[1] L. El Amraoui,[1] P. Eriksson,[4] W. F. J. Evans,[8] U. Frisk,[9] R. L. Gattinger,[5] F. Girod,[10] C. S. Haley,[11] S. Hassinen,[6] A. Hauchecorne,[3] C. Jimenez,[4] E. Kyrö,[6] N. Lautié,[4] E. Le Flochmoën,[1,2] N. D. Lloyd,[5] J. C. McConnell,[11] I. C. McDade,[11] L. Nordh,[9] M. Olberg,[4] A. Pazmino,[3] S. V. Petelina,[5] A. Sandqvist,[12] A. Seppälä,[6] C. E. Sioris,[13] B. H. Solheim,[11] J. Stegman,[14] K. Strong,[15] P. Taalas,[6] J. Urban,[1,4] C. von Savigny,[16] F. von Scheele,[9] and G. Witt[14]

Received 14 May 2004; revised 2 December 2004; accepted 20 December 2004; published 11 March 2005.

[1] In September 2002 the Antarctic polar vortex split in two under the influence of a sudden warming. During this event, the Odin satellite was able to measure both ozone (O_3) and chlorine monoxide (ClO), a key constituent responsible for the so-called "ozone hole", together with nitrous oxide (N_2O), a dynamical tracer, and nitric acid (HNO_3) and nitrogen dioxide (NO_2), tracers of denitrification. The submillimeter radiometer (SMR) microwave instrument and the Optical Spectrograph and Infrared Imager System (OSIRIS) UV-visible light spectrometer (VIS) and IR instrument on board Odin have sounded the polar vortex during three different periods: before (19–20 September), during (24–25 September), and after (1–2 and 4–5 October) the vortex split. Odin observations coupled with the Reactive Processes Ruling the Ozone Budget in the Stratosphere (REPROBUS) chemical transport model at and above 500 K isentropic surfaces (heights above 18 km) reveal that on 19–20 September the Antarctic vortex was dynamically stable and chemically nominal: denitrified, with a nearly complete chlorine activation, and a 70% O_3 loss at 500 K. On 25–26 September the unusual morphology of the vortex is monitored by the N_2O observations. The measured ClO decay is consistent with other observations performed in 2002 and in the past. The vortex split episode is followed by a nearly complete deactivation of the ClO radicals on 1–2 October, leading to the end of the chemical O_3 loss, while HNO_3 and NO_2 fields start increasing. This acceleration of the chlorine deactivation results from the warming of the Antarctic vortex in 2002, putting an early end to the polar stratospheric cloud season. The model simulation suggests that the vortex elongation toward regions of strong solar irradiance also favored the rapid reformation of $ClONO_2$. The observed dynamical and chemical evolution of the 2002 polar vortex is qualitatively well reproduced by REPROBUS. Quantitative differences

[1]Laboratoire d'Astrodynamique, d'Astrophysique et d'Aéronomie de Bordeaux, Observatoire Aquitain des Sciences de l'Univers, Floirac, France.
[2]Now at Laboratoire d'Aérologie, Observatoire de Midi-Pyrénées, Toulouse, France.
[3]Service d'Aéronomie, Institut Pierre-Simon Laplace, Paris, France.
[4]Department of Radio and Space Science, Chalmers University of Technology, Göteborg, Sweden.
[5]Institute of Space and Atmospheric Studies, University of Saskatchewan, Saskatoon, Saskatchewan, Canada.
[6]Department of Geophysics, Finnish Meteorological Institute, Helsinki, Finland.
[7]G & S Associates, Espoo, Finland.
[8]Physics Department, Trent University, Peterborough, Ontario, Canada.
[9]Swedish Space Corporation, Solna, Sweden.
[10]Centre National d'Etudes Spatiales, Toulouse, France.
[11]Centre for Research in Earth and Space Science, York University, Toronto, Ontario, Canada.
[12]Stockholm Observatory, Stockholm Center for Physics, Astronomy and Biotechnology, Stockholm, Sweden.
[13]Harvard-Smithsonian Center for Astrophysics, Cambridge, Massachusetts, USA.
[14]Department of Meteorology, Stockholm University, Stockholm, Sweden.
[15]Physics Department, University of Toronto, Toronto, Ontario, Canada.
[16]Institute of Environmental Physics, University of Bremen, Bremen, Germany.

0148-0227/05/2004JD005018$09.00

are mainly attributable to the too weak amounts of HNO_3 in the model, which do not produce enough NO_2 in presence of sunlight to deactivate chlorine as fast as observed by Odin.

Citation: Ricaud, P., et al. (2005), Polar vortex evolution during the 2002 Antarctic major warming as observed by the Odin satellite, *J. Geophys. Res.*, *110*, D05302, doi:10.1029/2004JD005018.

1. Introduction

[2] The Antarctic early spring is usually characterized by a cold and stable stratospheric vortex, with elevated amounts of active chlorine and ongoing ozone destruction [*World Meteorological Organization*, 1998]. In September 2002 an unusual event occurred in the stratosphere over Antarctica. At isentropic levels above about 600 K, the polar vortex split in two under the influence of a sudden stratospheric warming. This phenomenon had never been observed before in the Southern Hemisphere [see, e.g., *Simmons et al.*, 2003] and has been recently studied in several articles dealing with the dynamical evolution of the vortex [e.g., *Manney et al.*, 2005] or the evolution of the ozone field [e.g., *Hoppel et al.*, 2003].

[3] During this period, the Odin satellite was able to monitor both the evolutions of ozone (O_3) and chlorine monoxide (ClO), the key constituent for destroying ozone in polar vortices, producing the so-called "ozone hole" [*Farman et al.*, 1985]. In addition, Odin has observed other chemical species related to polar ozone depletion, such as nitric acid (HNO_3) and nitrogen dioxide (NO_2), as well as the dynamical evolution of the vortex that can be inferred from the measurements of nitrous oxide (N_2O). These measurements combined with the calculations from the three-dimensional (3-D) chemical transport model REPROBUS allow the characterization of the chemical and dynamical evolution of the Southern Hemisphere vortex in late September to early October 2002. We particularly focused on four periods: 19–20 September 2002, prior to the vortex split; 25–26 September 2002, during the vortex split; and 1–2 and 4–5 October 2002, after the vortex split.

[4] Section 2 deals with the Odin measurements in terms of sensitivity, horizontal and vertical resolutions, vertical coverage and errors. Section 3 briefly presents the calculations performed with the three-dimensional (3-D) model. The detailed description of the vortex evolution in terms of chemistry and dynamics, as observed by Odin and as calculated by REPROBUS, is presented in section 4.

2. Odin Measurements

[5] The Odin minisatellite is a Swedish-led project funded jointly by Sweden, Canada, France, and Finland [*Murtagh et al.*, 2002; *Nordh et al.*, 2003]. It was placed into a 600-km Sun-synchronous, terminator orbit by a START-1 rocket on 20 February 2001 from Svobodny, Russia. Odin includes two instruments. A UV-visible and infrared instrument, the Optical Spectrograph and Infrared Imager System (OSIRIS), that is capable of detecting O_3, NO_2, and aerosol in the scattered sunlight in the wavelength range 280–800 nm and the related oxygen airglow emission at 1.27 mm [*Llewellyn et al.*, 2004]. The second instrument is the submillimeter radiometer (SMR) [*Frisk et al.*, 2003] that can simultaneously measure O_3, ClO and N_2O in the frequency domain 501.18–502.38 GHz, together with HNO_3 at 544.20–545.00 GHz. Other molecules such as water vapor (H_2O) and its isotopes, as well as carbon monoxide (CO) [*Dupuy et al.*, 2004], can also be detected in the stratosphere and in the mesosphere. It should be noted that the microwave measurements are not degraded by the presence of Polar Stratospheric Clouds (PSCs) and aerosols in the stratosphere.

[6] In the basic stratospheric observation mode, the Earth's limb is scanned from 7 to 70 km in about 90 s. The horizontal resolution of Odin measurements along the orbit plane is ~500 km. The SMR data analysis uses the optimal estimation method [*Rodgers*, 1976] to retrieve vertical profiles of the atmospheric constituents having lines in the frequency band under consideration [*Baron et al.*, 2002]. For OSIRIS, global number density profiles of O_3 and NO_2 are retrieved from limb-scattered sunlight measurements using the maximum a posteriori estimator method [*Rodgers*, 2000], with some intermediate spectral analysis. For O_3, measurements at three wavelengths in the Chappuis region are combined [*von Savigny et al.*, 2003] and for NO_2, differential optical absorption spectroscopy (DOAS) is applied in the wavelength window 435–451 nm [*Haley et al.*, 2004]. Data processing for both instruments uses temperature and pressure fields analyzed by the European Centre for Medium-range Weather Forecast (ECMWF). The vertical resolution of the measurements depends on the species and the integration time versus altitude domain considered. For SMR [*Urban et al.*, 2004], at polar latitudes, measured ClO profiles cover the altitude range 17–50 km, with a vertical resolution of typically 2–2.5 km and a corresponding single-scan retrieval precision of about 0.15–0.20 ppbv. N_2O is retrieved above 14 km with a vertical resolution of 2 km and a precision in the order of 5% (10–20 ppbv). The SMR measurement range for O_3 is 20–50 km in the 501 GHz band, with a resolution of around 2.5 km and a single-scan precision in the order of 25% (0.5–1.5 ppmv). The HNO_3 profile can be retrieved from 20 to 35 km with a resolution of 2 km, and a single-scan precision of 1–1.5 ppbv. Upper limits for the systematic errors of the measurements in the lower stratosphere can be estimated to be about 0.2 ppbv for ClO, 25 ppbv for N_2O, and 1 ppmv for O_3. Systematic errors for HNO_3 are not clearly determined yet from our preliminary validation studies. For OSIRIS, the accuracy of the ozone retrievals is estimated to be better than 10% over an altitude range of 15 to 35 km with a resolution of about 2 km [*Petelina et al.*, 2004; *von Savigny et al.*, 2005]. The NO_2 vertical profiles can be retrieved over an

altitude range of 15 to 40 km with a resolution of 2–3 km and an accuracy of about 10% at the peak [*Haley et al.*, 2004].

3. Model Calculations

[7] Three-dimensional simulations of the 2002 ozone hole have been performed with the REPROBUS chemical transport model [*Lefèvre et al.*, 1994, 1998] which has been widely used in previous studies of the stratospheric chemistry [e.g., *Lefèvre et al.*, 1994; *Deniel et al.*, 1998; *Hoppel et al.*, 2002]. The model is designed to perform annual simulations as well as detailed process studies. It computes the evolution of 55 species by means of about 160 gas-phase and heterogeneous reactions, with a time step of 15 min in this study. A semi-Lagrangian code transports 40 species or chemical families, typically long-lived tracers but also more unstable compounds which may have a long lifetime in darkness. Kinetics parameters used in the present study are based on the most recent data [*Sander et al.*, 2003]. The new laboratory measurements of photodissociation cross sections of HO_2NO_2 both in the UV [*Knight et al.*, 2002] and in the near IR [*Roehl et al.*, 2002] have been included in the photodissociation calculations. The heterogeneous chemistry module used in the present simulation includes reactions on binary and ternary liquid aerosols, as well as on water-ice particles. The composition and volume of the liquid droplets are computed from the temperature and pressure conditions and the available amounts of H_2SO_4, HNO_3, and H_2O [*Carslaw et al.*, 1995]. Sedimentation of polar stratospheric cloud particles is triggered in the model when the temperature reaches the ice frost point. The ice particles are assumed to include HNO_3 in the form of nitric acid trihydrate (NAT). Their mean radius is calculated as a function of the amount of condensed water and a density of 5×10^{-3} particles/cm^3.

[8] REPROBUS was integrated from 1 April 2002 to 15 October 2002. Temperatures, winds and ground pressure were specified from the 6-hourly ECMWF operational analysis. The model extends from the surface up to 0.1 hPa on 42 levels, resulting in a vertical resolution of about 1.3 km in the lower stratosphere. The horizontal resolution is 2° latitude by 2° longitude. The ozone field was initialized on 1 April 2002 from the three-dimensional ECMWF ozone analysis. Other species were initialized from an April zonal mean computed from a long-term simulation of REPROBUS. Model profiles were extracted online during the simulation to coincide to the time and location of the Odin measurements.

4. Vortex Evolution

[9] We focus here on four periods: 19–20 September 2002, 25–26 September 2002, 1–2 October 2002, and 4–5 October 2002. Each period corresponds to measurements performed over 24 hours starting from 1200 UT and includes about 14 orbits. Figures 1, 3, 5, and 7 show O_3, ClO, N_2O, HNO_3, as well as sunrise and sunset NO_2 linearly interpolated onto the 500 K potential temperature surface, corresponding to an altitude range from ~18 to ~22 km for latitudes poleward of 30°S for the corresponding four periods. Data have been triangularly interpolated into bins of 5° wide in latitude and 10° wide in longitude. The fields for ClO, N_2O, and HNO_3 are from SMR measurements. The fields for O_3 and NO_2 are from OSIRIS, except on 19–20 September when solar zenith angles (SZA) larger than 90° in the Antarctic region precluded optical measurements. The SMR ozone is displayed for that date. For each period, Figures 2, 4, 6, and 8 show a latitude versus height representation of the Odin measurements along one selected orbit (indicated by a thick black line on Figures 1, 3, 5, and 7). Odin measurements are compared to the REPROBUS results coincident in time and location. Species not measured by Odin (HCl and $ClONO_2$) and additional diagnostics (chlorine activation ratio, ozone loss, SZA) together with ECMWF temperature fields are also presented at 500 K.

4.1. Polar Vortex Prebreakup

[10] N_2O is a long-lived species in the lower stratosphere and is consequently a good tracer of dynamical motion. As a result of the subsidence, which started at the beginning of the winter, and the negative gradient of N_2O with height, the Odin measurements at 500 K show very low mixing ratios in the polar vortex on 19–20 September (Figure 1). Indicated in red on each plot is the 120 ppbv N_2O isopleth which coincides well at 500 K and during the period studied in this work to the maximum gradient of potential vorticity representative of the vortex edge. On 19–20 September, it can be seen from that criterion that the vortex is detected to be relatively symmetric and pole centered. This is consistent with meteorological analyses that indicate a compact, stable, and circular vortex [*Simmons et al.*, 2003], with temperatures well below 195 K on these two days. The REPROBUS N_2O field is in good agreement with SMR in terms of horizontal extension of the polar vortex at 500 K but tends to overestimate slightly N_2O at midlatitudes. This results from a too strong upward vertical transport above the Equator when using ECMWF analysis to drive the model, bringing too large N_2O amounts to the tropical midstratosphere. This bias then propagates to midlatitudes by the descending branch of the Brewer-Dobson circulation and the quasi-horizontal transport of N_2O from the tropics.

[11] The compactness of the vortex at this time of year is also visible from the observed vertical distribution of N_2O (Figure 2). A strong horizontal gradient is visible across the vortex edge below 30 km altitude, with low N_2O amounts over Antarctica, revealing a pronounced subsidence inside the vortex. The computed vertical distribution shows that this strong diabatic descent is well reproduced by REPROBUS in the core of a compact vortex well isolated from extra-vortex air.

[12] The O_3 field measured by Odin at 500 K shows a distinct minimum inside the vortex, with values lower than 1 ppmv. This is also shown by REPROBUS, but the model tends to overestimate the O_3 absolute amount compared to SMR. A 21% difference (1.5 versus 1.2 ± 0.1 ppmv) is found in vortex average. The cumulative O_3 chemical loss since the beginning of the REPROBUS simulation can be obtained by calculating the difference between the chemically integrated ozone and a passive tracer initialized in the same way as ozone on 1 April 2002. On 19–20 September, the model indicates a O_3 chemical loss of the order of 70% at 500 K. Along the vertical (Figure 2), SMR O_3 retrievals

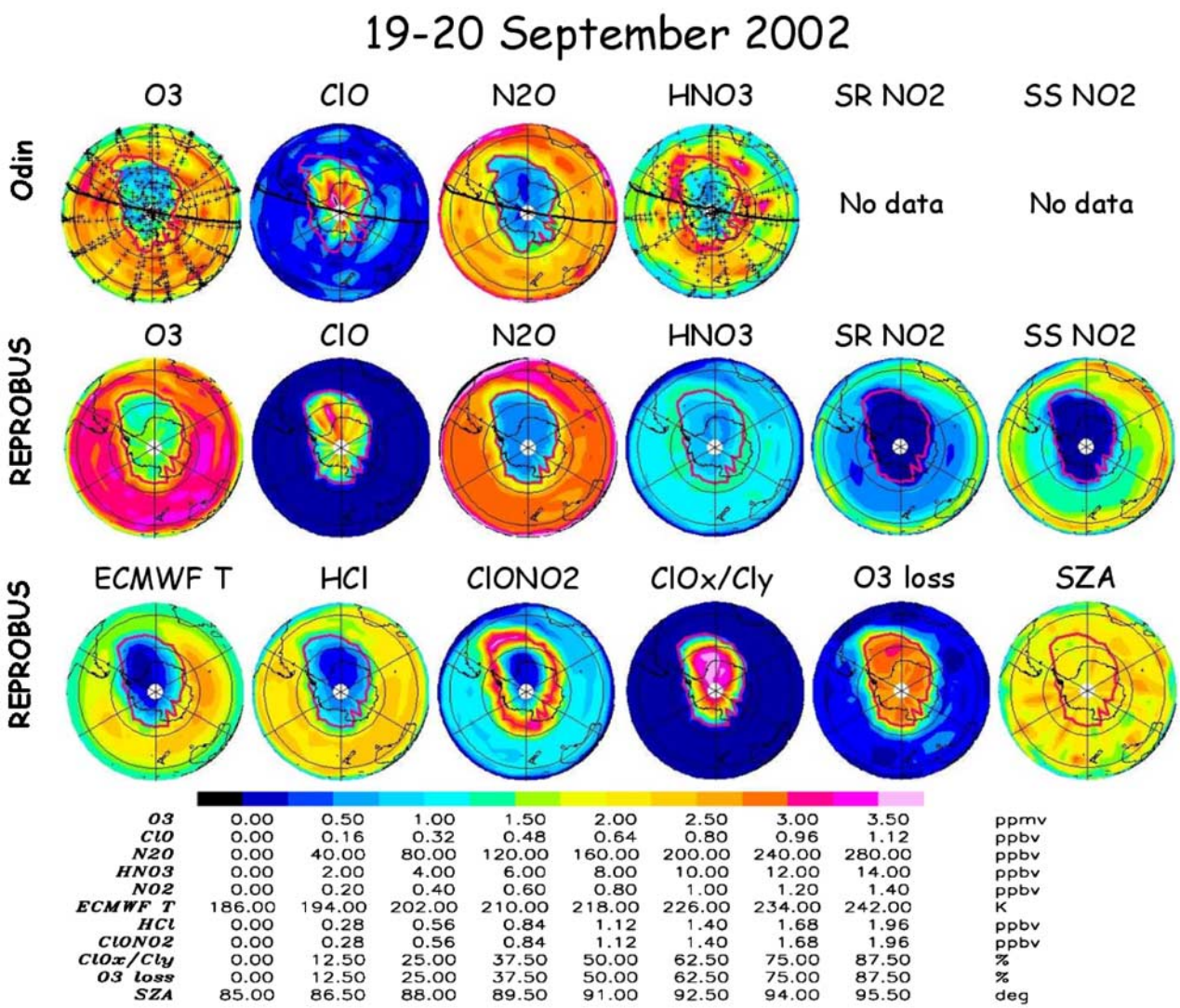

Figure 1. (top) From left to right, O_3, ClO, N_2O, and HNO_3 fields measured by Odin/SMR on 19–20 September 2002, interpolated onto the 500-K potential temperature surface. The maps are polar orthographic projections with black circles at 30°S and 60°S. Crosses represent the Odin orbit tracks over the 24-hour period starting from 1200 UT. Locations of ClO and N_2O measurements are the same as O_3 and are not represented. The red line corresponds to the 120-ppbv N_2O contour, which can be considered as the approximate edge of the polar vortex. The black line indicates the orbit track selected on Figure 2. Blank spaces represent data gaps or bad data points. Note that Odin measurements were performed at twilight ($90° < SZA < 92.5°$) on 19–20 September 2002 and during daytime (SZA ~85°) for the other days. (middle) From left to right, O_3, ClO, N_2O, HNO_3, and sunrise (SR) and sunset (SS) NO_2 fields calculated by the REPROBUS chemical transport model on 19–20 September 2002, interpolated onto the 500-K potential temperature surface. Calculations are coincident in time and space with the Odin measurements. (bottom) From left to right, ECMWF temperature, HCl, $ClONO_2$, ClO_x/Cl_y ratio, O_3 chemical loss calculated by REPROBUS (see text), and the solar zenith angle (SZA) at the time of the Odin measurements.

show that the depletion extends up to about 25 km. The large increase in ClO that is usually observed in the polar vortices in winter and spring is clearly detected by SMR. Even in the twilight conditions of the measurements (SZA range of 90–92.5°) on 19–20 September 2002, high values of ClO (0.5–1 ppbv) fill almost the entire vortex at 500 K. A good general agreement is observed between SMR and REPROBUS, with a vortex-averaged difference of 9% (0.70 versus 0.64 ppbv) at 500 K. This result reveals that chlorine activation processes are well reproduced by the model. A near complete removal of HCl and $ClONO_2$ is computed in the vortex core. At the edge of the vortex, the $ClONO_2$ field exhibits the typical collar structure that has often been observed at this time of year [e.g., *Roche et al.*, 1993]. From the assumption of photochemical equilibrium between ClO and its dimer Cl_2O_2, we calculate that the maximum

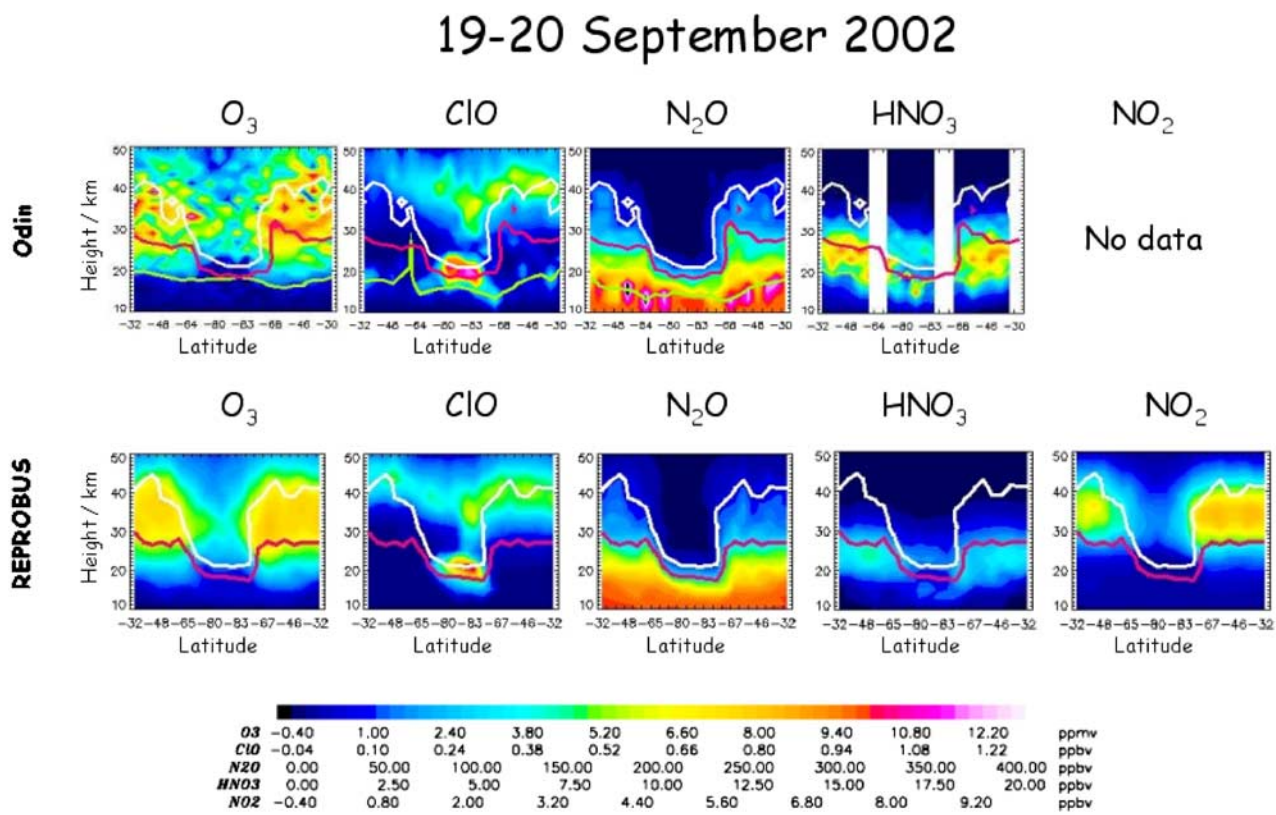

Figure 2. (top) From left to right, latitude-height distribution of Odin/SMR O_3, ClO, N_2O, and HNO_3 on 19–20 September 2002 along the orbit selected in Figure 1. Measurements are shown for latitudes southward of 30°S and were linearly interpolated onto a vertical grid of 2 km resolution. Each vertical tick on the *x* axis corresponds to one measured profile. The southernmost latitude is 85°S and is located at the center of the plot. The red line corresponds to the 120-ppbv N_2O contour also shown in Figure 1, and the white line corresponds to the 40-ppbv N_2O contour chosen to highlight the diabatic descent inside the vortex. The green line represents the lowermost altitude of significant measurements. Note that the plots gather sunrise measurements on the left-hand side and sunset measurements on the right-hand side. This is particularly important for NO_2, and to a lesser extent for midstratospheric ClO, which have an asymmetrical diurnal variation. (bottom) From left to right, coincident latitude-height distribution of O_3, ClO, N_2O, HNO_3, and NO_2 fields calculated by the REPROBUS chemical transport model.

twilight ClO mixing ratios measured by SMR on 19–20 September correspond to a daytime ClO amount close to 2 ppbv. This is in good agreement with the largest values measured at 475 K inside the polar vortex by the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) satellite instrument during the same period [*Glatthor et al.*, 2004]. We define the chlorine activation ratio as ClO_x/Cl_y with $ClO_x = Cl + ClO + 2Cl_2O_2$ and Cl_y as the total inorganic chlorine. On 19–20 September this ratio is calculated by REPROBUS to be about 85% at 500 K. Chlorine activation is observed between 19 and 25 km inside the vortex and correlates with the altitude range where O_3 is depleted. In the midstratosphere, the ClO observed by Odin is maximum at about 40 km at midlatitudes and goes down to about 35 km inside the vortex as a result of subsidence. This is consistent with earlier observations from the ground in Antarctica [*Emmons et al.*, 1995; *De Zafra et al.*, 1995; *Solomon et al.*, 2002].

[13] The nominal character of the 2002 ozone hole until 19–20 September is reinforced by the SMR observations of HNO_3, which show a distribution similar to that measured in previous Antarctic winters by the Microwave Limb Sounder (MLS) satellite-borne instrument [*Santee et al.*, 1999]. Low HNO_3 mixing ratios (less than 5 ppbv) are observed by SMR in the polar vortex (Figure 1), while just outside of the vortex HNO_3 values at 500 K are greater than 10 ppbv. Aerosol measurements by the Polar Ozone and Aerosol Measurement (POAM) satellite-borne instrument indicate that PSCs had nearly disappeared at the latitude of the observations (poleward of 85°S) on 20 September [*Nedohula et al.*, 2003]. This is also supported by REPROBUS, which calculates that the maximum amount of condensed HNO_3 at 500 K (not shown) is only of the order of 0.5 ppbv, and is confined to a limited area above the Weddel Sea where the ECMWF temperature is lowest. Thus it is likely that the low HNO_3 mixing ratios observed by Odin on 19–20 September inside the vortex are due to irreversible loss by sedimentation of HNO_3-containing PSC particles, rather than to temporary removal from the gas phase by

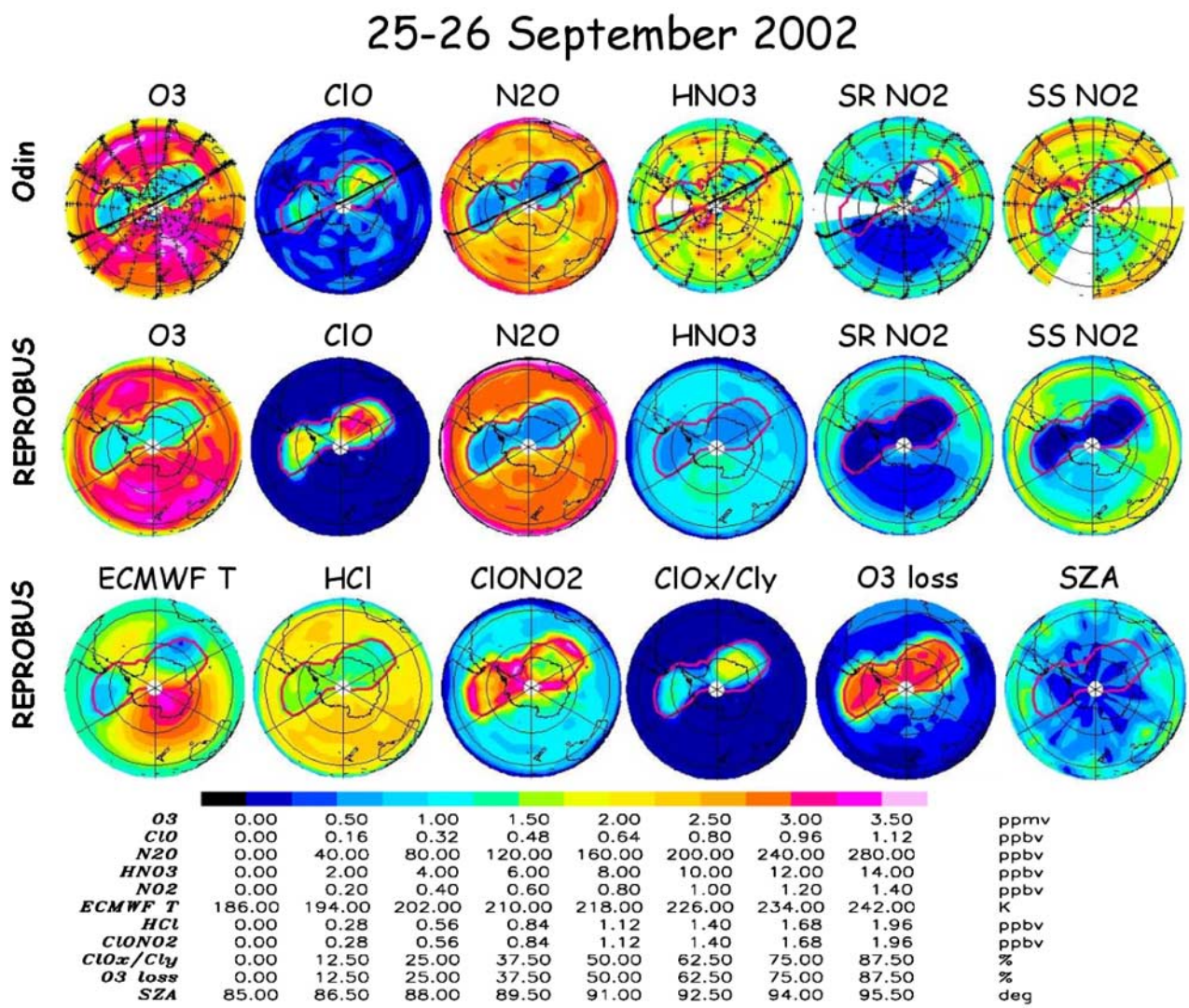

Figure 3. Same as Figure 1 but for the 25–26 September 2002 period. In Figure 3 (top), O_3, sunrise (SR) and sunset (SS) NO_2 fields are measured by OSIRIS.

sequestration in cloud particles. Outside the polar vortex, the model underestimates the HNO_3 amount by almost a factor of two, a result also supported by the comparison of REPROBUS to preliminary HNO_3 observations by the MIPAS instrument (not shown). This bias is again related to the too fast vertical transport of N_2O in the tropical midstratosphere, resulting in too weak production of NO_y in the model.

4.2. Polar Vortex Breakup

[14] During the last week of September 2002, meteorological analyses reveal the development of a Southern Hemisphere major stratospheric warming that results in a strong dynamical disturbance of the polar vortex [*Manney et al.*, 2005]. On 25–26 September the elongated shape of the polar vortex at 500 K is evident in the N_2O distribution measured by the SMR (Figure 3). REPROBUS also reproduces the horizontal extension of the vortex toward midlatitudes. From a consideration of the measurements in the orbit plane (Figure 4), it is evident that extra-vortex air, characterized by larger values of N_2O, is present above the pole between 20 and 25 km altitude. Further, the SMR observations show that the vortex structure is not as vertically uniform as on 19–20 September 2002: there is an N_2O-rich layer above the low N_2O values measured in the vortex lobe extending toward the Indian Ocean that clearly indicates the presence of midlatitude air above 30 km. The model outputs reveal intrusion of extra-vortex air above polar latitudes in good agreement with SMR. Thus dynamics seems to be well reproduced by the model during such perturbed conditions, even though the model still overestimates N_2O at high altitudes. The split of the vortex is also visible from the OSIRIS ozone measurements that also show ozone-rich air being transported toward the pole above the vortex, in agreement with *Hoppel et al.* [2003]. At 500 K the ozone distribution mimics the shape of the N_2O field with two ozone-poor elongated lobes. It should be noted that the O_3 mixing ratios in the polar vortex on 25–26 September do not show a significant reduction compared to those measured

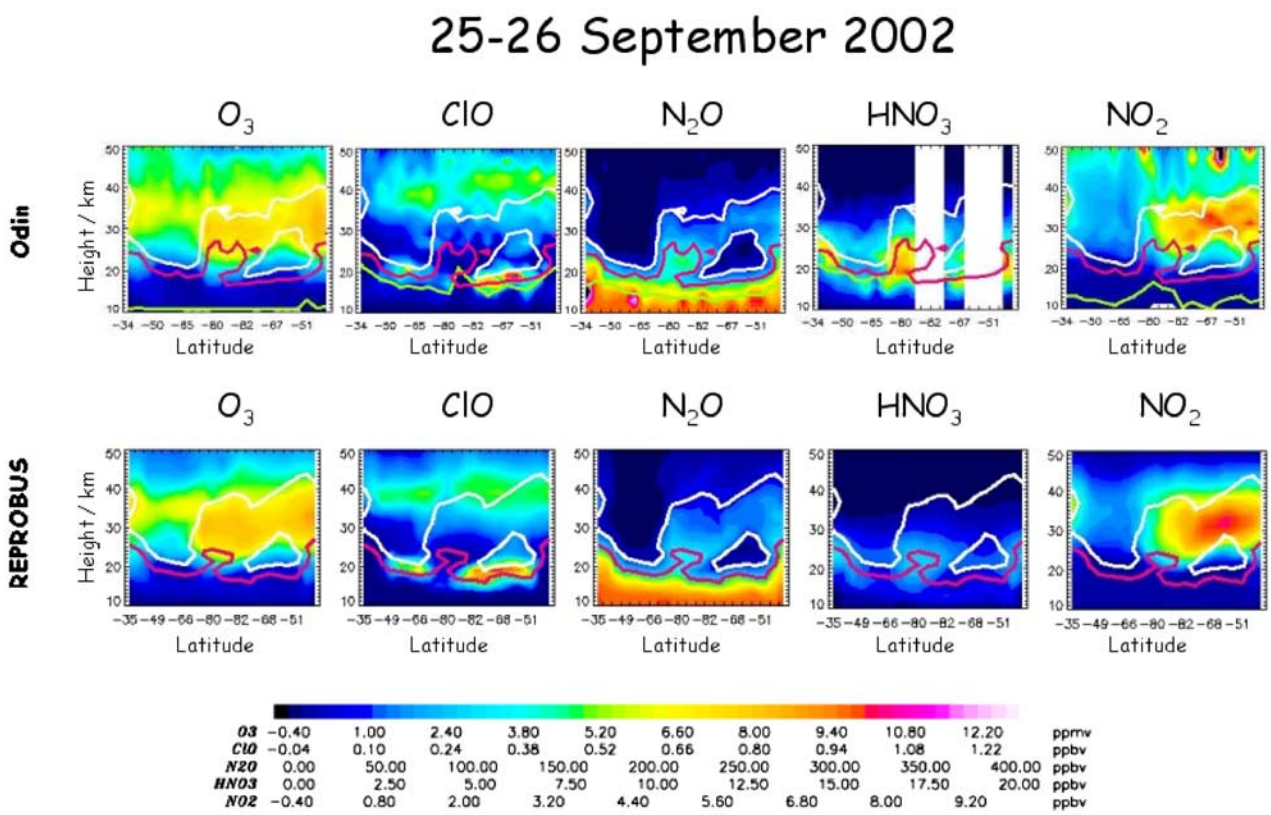

Figure 4. Same as Figure 2 but for the 25–26 September 2002 period. In Figure 4 (top), O_3 and NO_2 fields are measured by OSIRIS.

5 days earlier. This suggests a reduced O_3 chemical loss between these two dates. Continuing O_3 destruction might be compensated by increased mixing with O_3-rich midlatitude air during the warming event. However, the mixing would be accompanied by an increase in N_2O values between 19–20 and 25–26 September, which is not unambiguously observed by Odin.

[15] On 25–26 September the ClO measurements by the SMR were made in daytime at all latitudes (SZA range of 85–88°). The maximum ClO mixing ratios are about 0.7 ppbv at 500 K. This corresponds to a ~70% reduction relative to the estimated daytime ClO on 19–20 September, in agreement with the decrease in ClO measured by MIPAS after 20 September [*Glatthor et al.*, 2004]. The vortex averaged ClO mixing ratio measured by SMR on 25–26 September (0.35 ± 0.03 ppbv) is also in good agreement with the daily averages derived from MIPAS at 520 K on the same days (0.25 and 0.40 ppbv on 25 and 26 September, respectively). The decline in ClO is a typical feature of the mid to late September period in Antarctica, as shown by the 6-year climatology derived from the MLS satellite measurements [*Santee et al.*, 2003], although MLS could never observe the complete chlorine recovery period. Ground-based observations performed in Antarctica in 1992 [*Emmons et al.*, 1995], in 1993 [*De Zafra et al.*, 1995], and over the 1996–2000 period [*Solomon et al.*, 2002] also gave evidence of the chlorine deactivation that occurs during the third week of September. Daytime ClO mixing ratios at 20 km were found to be in general smaller than 1 ppbv around 25–26 September, which is consistent with the SMR observations in 2002.

[16] It must be noted that the model ClO values on 25–26 September are larger than those measured by SMR: the vortex averaged ClO is overestimated by 60%. Thus the actual rate of chlorine deactivation was faster than calculated by the model. This can be related to the underestimation of NO_2 in the vortex by REPROBUS (see Figure 3), which does not allow a conversion of ClO to $ClONO_2$ as fast as detected by SMR. This result is very sensitive to the absolute amount of NO_y available in the polar vortex. In a simulation for which the initial HNO_3 mixing ratio at 500 K is increased by 1.5 ppbv relative to the reference experiment presented here, the substantially faster deactivation rate that is calculated by the model reduces by a factor of three the overestimation of ClO on 25–26 September. In addition to this effect, the slight model overestimation of O_3 may not have favored the HCl recovery, which is known to be inversely proportional to the absolute amount of O_3 [see, e.g., *Douglass et al.*, 1995].

[17] A rapid rise of the lower stratospheric temperatures occurred during the 2002 vortex split episode: On 25–26 September, minimum ECMWF temperatures are above 195 K at most altitudes (Figure 3), i.e., above the threshold for PSC formation. The absence of PSCs is supported by the POAM [*Nedohula et al.*, 2003] and OSIRIS (D. Gattinger, personal communication) aerosol measurements, which do not exhibit high extinction coefficients for these two days. This is in contrast to years prior to 2002, when PSCs were

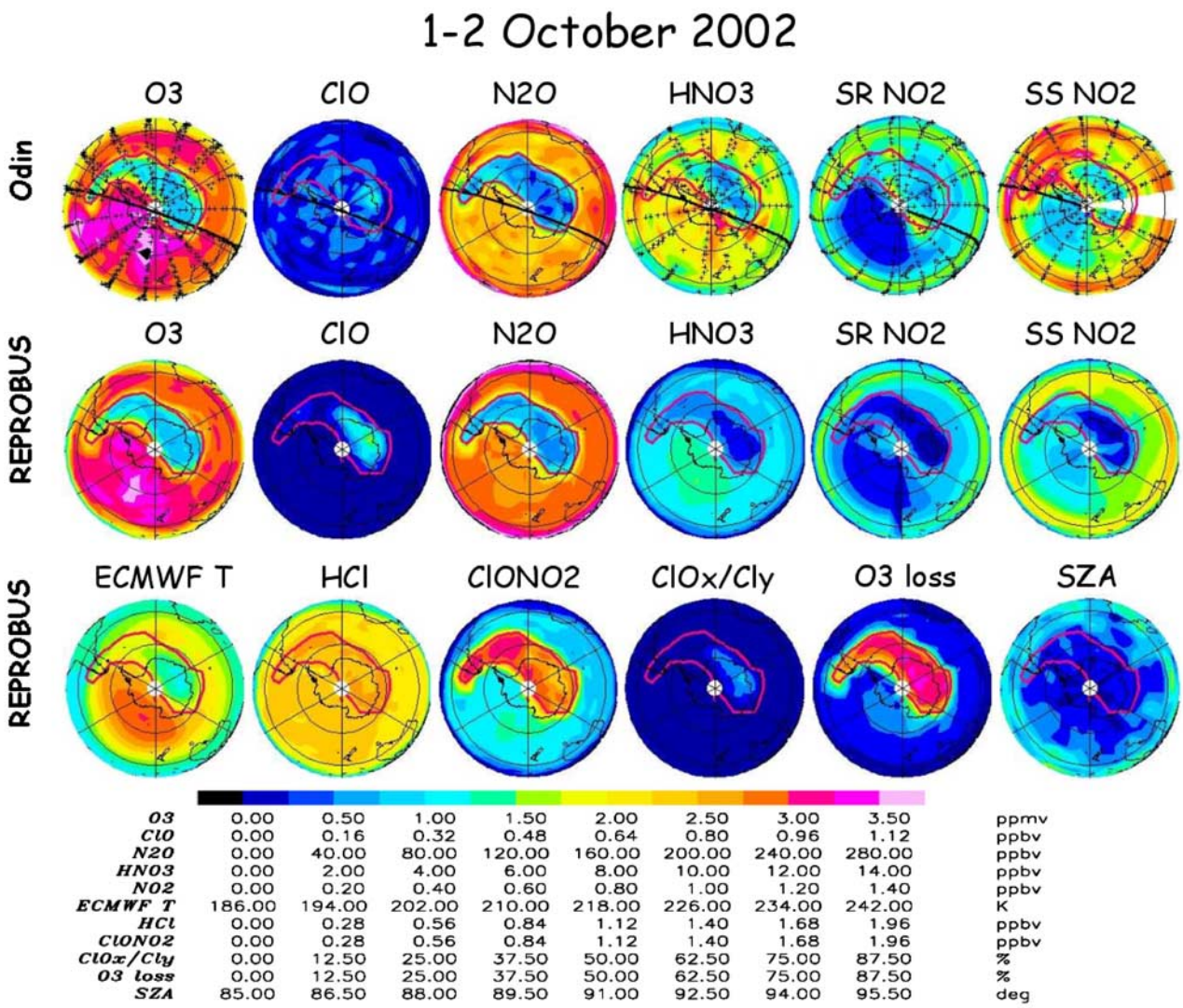

Figure 5. Same as Figure 3 but for the 1–2 October 2002 period.

usually observed until the middle of October [*Poole and Pitts*, 1994; *Fromm et al.*, 1997]. Despite the absence of PSCs, it is important to note that the HNO_3 distribution measured by SMR on 25–26 September still shows a marked contrast between the vortex (VMR < 5 ppbv) and midlatitude air (VMR > 8 ppbv) although few HNO_3 measurements are available at 500 K for that period. This confirms that the low HNO_3 mixing ratios detected in the vortex are the result of irreversible loss (or denitrification) of nitric acid via the earlier sedimentation of PSC particles. The in-vortex HNO_3 values measured by SMR at 500 K (2–4 ppbv) are in good agreement with ground-based measurements [e.g., *De Zafra and Smyshlyaev*, 2001] for this time of year. They are also consistent with the HNO_3 climatology established from 6 years of data by the MLS satellite instrument [*Santee et al.*, 1999].

[18] On 25–26 September, NO_2 was measured by OSIRIS at sunrise (SR) and sunset (SS). Outside the vortex, OSIRIS observations show the expected increase in NO_2 during the day. Over the Pacific Ocean, the large-scale NO_2 minimum correlates well with elevated O_3 and high temperatures. This is consistent with the standard gas-phase photochemical theory represented at midlatitudes by REPROBUS. Inside the polar vortex, OSIRIS shows low values of NO_2 and a limited increase during the day, in agreement with the model. The removal of the nitrogen oxides in the polar vortex results from their conversion to reservoir forms of nitrogen during the polar night and from denitrification. However, the calculated NO_2 underestimate the measured values in the two vortex lobes, a rather typical bias of photochemical models in wintertime polar latitudes [*Payan et al.*, 1999]. In the orbit plane (Figure 4), the diurnal variation of NO_2 is clearly visible above 25 km in the OSIRIS measurements. The main features of the NO_2 vertical distribution and the diurnal variation measured by OSIRIS are well reproduced by REPROBUS.

4.3. Polar Vortex Postbreakup

[19] On 1–2 October 2002 the N_2O-poor air representative of the vortex reveals that the vortex is displaced from the pole with a large elongation over South America well reproduced by the model (Figure 5). In the orbit plane chosen in Figure 6, the main vortex is clearly detected from the N_2O field around 87S with its elongation, centered on

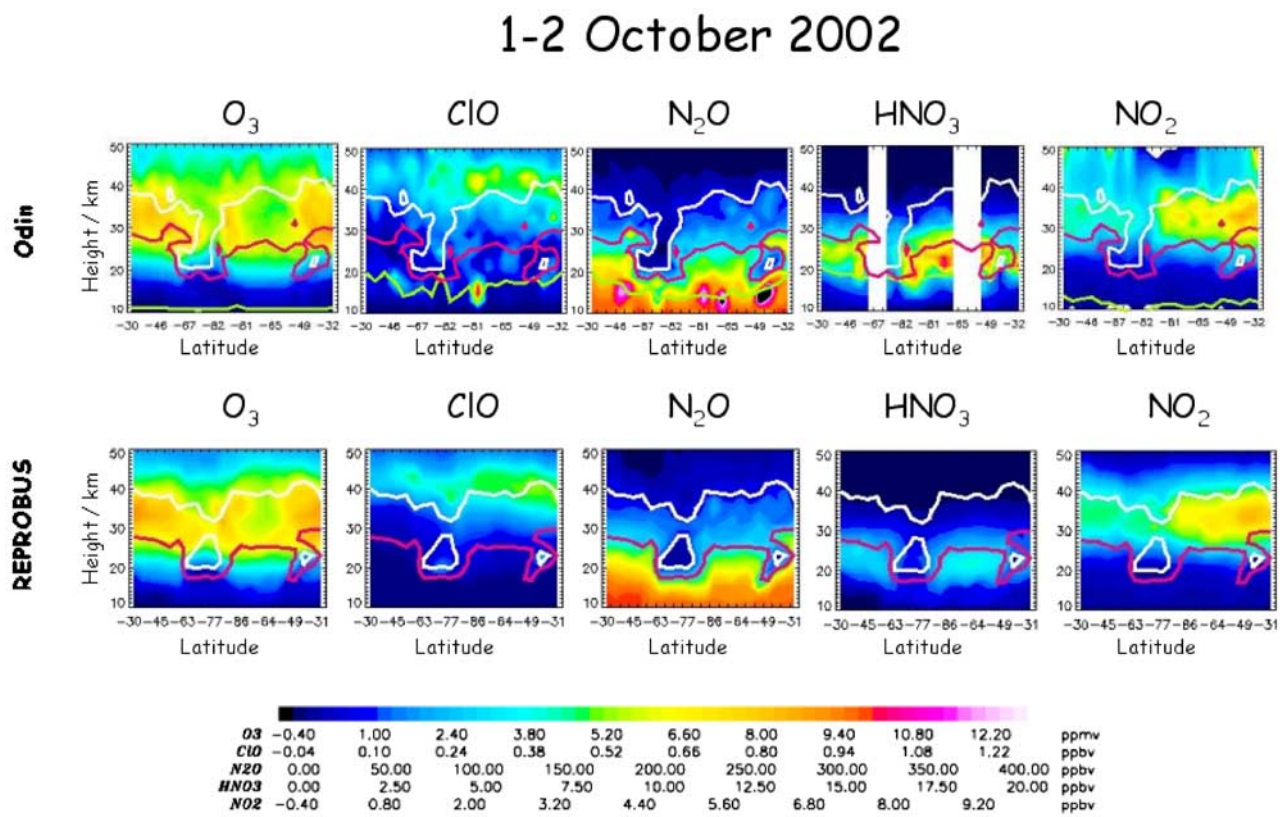

Figure 6. Same as Figure 4 but for the 1–2 October 2002 period.

49S, only visible in the lowermost stratosphere. The O_3-depleted area correlates very well with the region of low N_2O. The vortex averaged ozone mixing ratio (0.99 ± 0.02 ppmv) is nearly identical to that measured on 25–26 September (1.01 ± 0.02 ppmv), this indicates that little further loss occurred at 500 K after that date. In the model, the too large ClO amounts that were still present on 25–26 September have yielded to an additional O_3 loss peaking at 80% on 1–2 October. The signature of the ozone hole is also detected far from the Antarctic region, with O_3 mixing ratios lower than 1.5 ppmv above southern Chile and Argentina. A striking feature of the Odin daytime observations on 1–2 October is that ClO is close to the SMR detection limit (0.2 ppbv) inside the vortex. REPROBUS also calculates a rapid ClO decrease, although the maximum ClO amounts (0.3 ppbv) are still slightly larger than measured by SMR. The chlorine activation ratio passed from ~50% to less than ~15% in 5 days. In the orbit plane, Figure 6 shows that the vortex is free of enhanced ClO at all vertical levels below 30 km. Atmospheric chlorine has therefore evolved from a situation of nearly complete activation to a situation of complete recovery in less than 10 days. This change appears to be faster than the only continuous observations of ClO available over the late September to early October period, performed from the Scott Base (Antarctica, 78°S) by *Solomon et al.* [2002] in 1996 and 2000.

[20] On 1–2 October, in the elongated part of the vortex at latitudes northward of 60°S, OSIRIS measurements show a substantial increase of SS NO_2, with values larger than 1 ppbv. SMR gives an indication of elevated abundances of HNO_3 in this region, which must be considered with caution as only three profiles are available in the vortex tongue that extends over the tip of South America. Nevertheless, it is likely that the displacement from the pole and the elongated shape toward midlatitudes favored the exposure to unusually strong solar irradiance at this time of the year so leading to the early photolysis (and oxidation by OH) of HNO_3 and the subsequent enhanced production of NO_2. Even with HNO_3 amounts lower than those measured by SMR, the model indicates that the HNO_3 photolysis and oxidation are fast enough to titrate entirely ClO in the vortex tongue, so leading to a substantial $ClONO_2$ buildup in the same area (Figure 5). Thus Odin and REPROBUS both indicate that the unusual morphology of the Antarctic vortex may have been an important cause for the acceleration of the chlorine deactivation in late September to early October 2002.

[21] On 4–5 October 2002 the N_2O field at 500 K (Figure 7) indicates that the core of the polar vortex is returning to a more typical behavior, centered over the Antarctic continent. A filament extends over South America where REPROBUS calculates a cumulative ozone loss of about 40%. From the measured and simulated N_2O vertical structure (Figure 8), it is evident that the polar vortex is far from vertically uniform. About half of the vortex is observed in the form of a ~3-km-thick slice in the lower stratosphere, overlaid by midlatitude air extending up to the stratopause. The "boot shape" of the polar air visible in Figure 8 is also clearly visible in the vertical distributions of ozone and nitric acid.

[22] It is also noteworthy that the O_3 and N_2O values measured at 500 K have not increased in the main polar

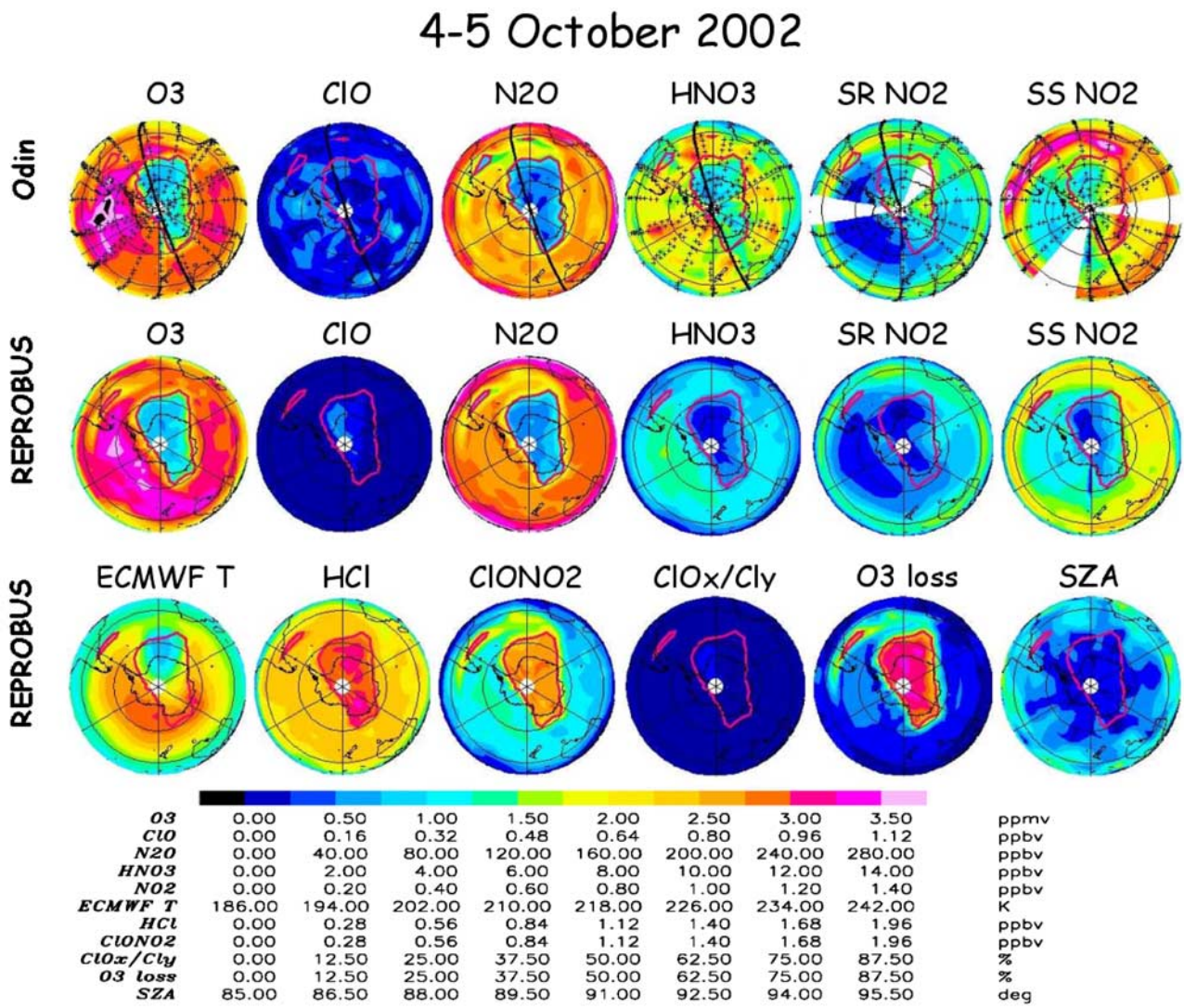

Figure 7. Same as Figure 3 but for the 4–5 October 2002 period.

vortex since 19–20 September. This supports the idea of a relatively isolated vortex during the whole period, and that mixing with midlatitude air did not play a major role in the observed deactivation of chlorine. In contrast, in situ production of NO_x is suggested by the measured NO_2 distribution showing a gradual increase in the region of the vortex where HNO_3 is less affected by denitrification. Daytime ClO is maintained at a level below the SMR detection limit. REPROBUS results show very low values of ClO, in good agreement with the observations, and the chlorine activation ratio calculated by the model is close to zero.

5. Conclusions

[23] The SMR and OSIRIS instruments onboard the Odin satellite have measured stratospheric constituents such as O_3, ClO, N_2O, HNO_3 and NO_2 during the 2002 Antarctic major warming. These observations enabled the study of the dynamical and chemical evolutions of the polar vortex at and above the 500 K isentropic surface. On 19–20 September the Antarctic vortex was dynamically stable and chemically nominal with a nearly complete activation of chlorine and ozone amounts consistent with a 70% chemical loss on the 500 K isentropic surface. Our 3-D model simulation suggests that the low HNO_3 mixing ratios measured by Odin inside the polar vortex result from earlier denitrification. On 25–26 September, Odin N_2O observations reveal the unusual morphology of the Southern Hemisphere vortex associated to a stratospheric warming, signature of the vortex split episode. Observations show a decrease in ClO that is quantitatively consistent with measurements performed during the same period in 2002 and in the previous years. On 1–2 October a nearly complete deactivation of the ClO radicals is observed, translating into the end for the ozone-destroying chemical cycles. This acceleration of the chlorine deactivation results both from the warming of the Antarctic vortex in 2002, putting an early end to the polar stratospheric cloud season, and from the vortex elongation toward regions of strong solar irradiance, which is shown by our model simulation to have favored the rapid reformation of $ClONO_2$. Once the vortex split episode is over, the O_3 field is measured to be stable within the vortex while NO_2 gradually increases. The

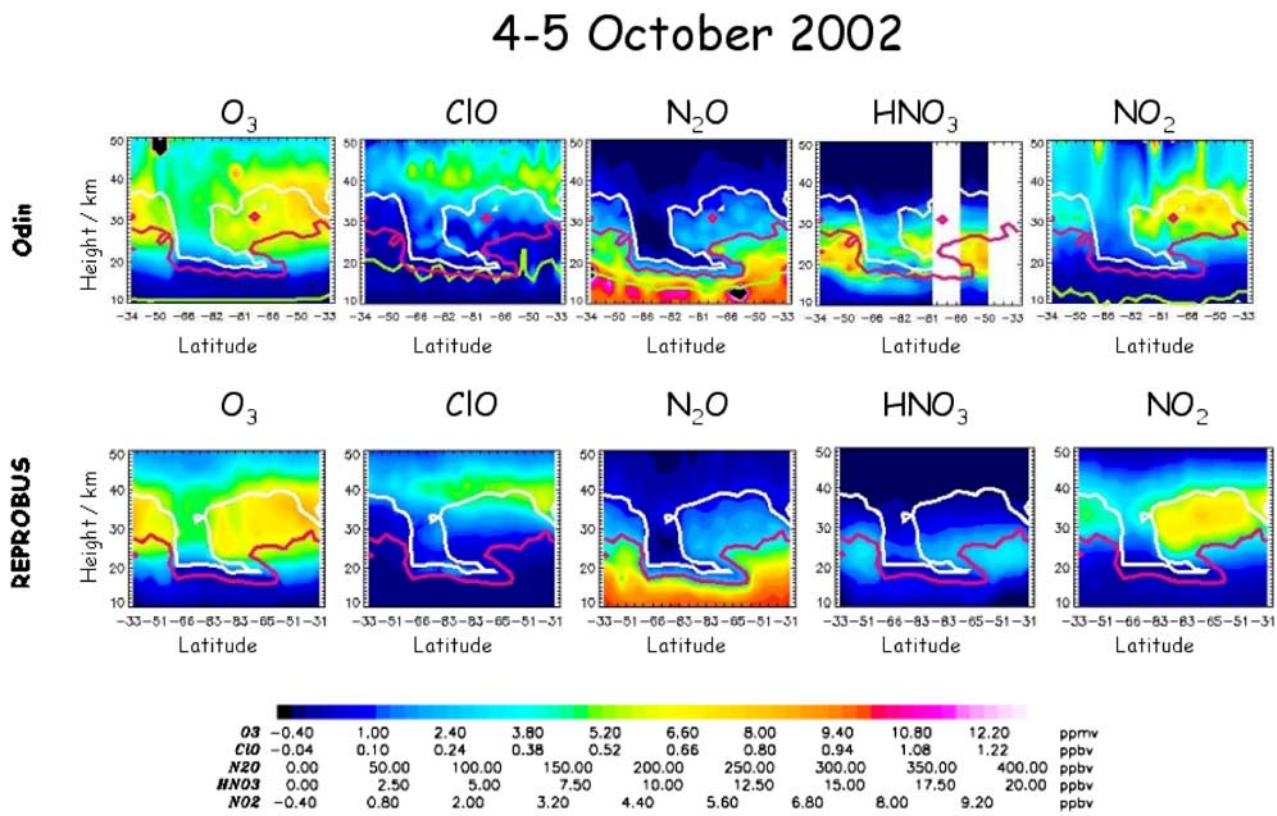

Figure 8. Same as Figure 4 but for the 4–5 October 2002 period.

dynamical and chemical evolution of the vortex is qualitatively well reproduced by the model. Quantitative differences are shown to be mainly attributable to the too weak amounts of HNO_3 in the model, which do not produce enough NO_2 in presence of sunlight to deactivate ClO as fast as observed by Odin in 2002.

[24] **Acknowledgments.** Odin is a Swedish-led satellite project funded jointly by the Swedish National Space Board (SNSB), the Canadian Space Agency (CSA), the National Technology Agency of Finland (Tekes) and the Centre National d'Etudes Spatiales (CNES). The Swedish Space Corporation has been the industrial prime contractor. The scientific investigations in Canada were funded by CSA and the Natural Sciences and Engineering Research Council (NSERC) and in France by the Centre National de la Recherche Scientifique (CNRS), Ministère de l'Education Nationale, de la Recherche et de la Technologie (MENRT) and CNES. Odin data are available in the French database for atmospheric chemistry, Ether, at http://ether.ipsl.jussieu.fr. OSIRIS data can be found at http://osirus.usask.ca. We thank J.-P. Pommereau for providing useful comments on the manuscript and anonymous reviewers for their helpful comments. We dedicate this article to the memory of G. Mégie, Principal Investigator in the Odin aeronomy Science Team.

References

Baron, P., et al. (2002), Studies for the Odin sub-millimeter radiometer: II. Retrieval methodology, *Can. J. Phys.*, *80*, 341–356.

Carslaw, K., B. Luo, and T. Peter (1995), An analytic expression for the composition of aqueous HNO_3-H_2SO_4 stratospheric aerosols including gas phase removal of HNO_3, *Geophys. Res. Lett.*, *14*, 1877–1880.

Deniel, C., J. P. Pommereau, R. M. Bevilacqua, and F. Lefèvre (1998), Arctic chemical depletion during the 1994–95 winter deduced from POAM II satellite observations and the Reprobus-3D model, *J. Geophys. Res*, *103*, 19,231–19,244.

De Zafra, R. L., and S. P. Smyshlyaev (2001), On the formation of HNO_3 in the Antarctic mid to upper stratosphere in winter, *J. Geophys. Res.*, *106*, 23,115–23,125.

De Zafra, R. L., J. M. Reeves, and D. T. Shindell (1995), Chlorine monoxide in the Antarctic spring vortex over McMurdo station, 1993: 1. Evolution of midday vertical profiles, *J. Geophys. Res.*, *100*, 13,999–14,008.

Douglass, A. R., M. R. Schoeberl, R. S. Stolarski, J. W. Waters, J. M. Russel III, A. E. Roche, and S. T. Massie (1995), Interhemispheric differences in springtime production of HCl and $ClONO_2$ in the polar vortices, *J. Geophys. Res*, *100*, 13,967–13,978.

Dupuy, E., et al. (2004), Strato-Mesospheric measurements of carbon monoxide with the Odin sub-millimetre radiometre: Retrieval and first results, *Geophys. Res. Lett.*, *31*, L20101, doi:10.1029/2004GL020558.

Emmons, L. K., D. T. Shindell, J. M. Reeves, and R. L. de Zafra (1995), Stratospheric ClO profiles from McMurdo Station, Antarctica, spring 1992, *J. Geophys. Res.*, *100*, 3049–3055.

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

Frisk, U., et al. (2003), The Odin satellite I: Radiometer design and test, *Astron. Astrophys.*, *402*(3), L27–L34, doi:10.1051/0004-6361:20030335.

Fromm, M. D., et al. (1997), Observations of Antarctic polar stratospheric clouds by POAM II: 1994–1996, *J. Geophys. Res.*, *102*, 23,659–23,672.

Glatthor, T., et al. (2004), Spaceborne ClO observations by the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) before and during the Antarctic major warming in September/October 2002, *J. Geophys. Res.*, *109*, D11307, doi:10.1029/2003JD004440.

Haley, C. S., S. M. Brohede, C. E. Sioris, E. Griffioen, D. P. Murtagh, I. C. McDade, P. Eriksson, E. J. Llewellyn, A. Bazureau, and F. Goutail (2004), Retrieval of stratospheric O_3 and NO_2 profiles from Odin/OSIRIS limb-scattered sunlight measurements, *J. Geophys. Res.*, *109*, D16303, doi:10.1029/2004JD004588.

Hoppel, K., R. Bevilacqua, G. Nedoluha, C. Deniel, F. Lefèvre, J. Lumpe, M. Fromm, C. Randall, J. Rosenfield, and M. Rex (2002), POAM III observations of arctic ozone loss for the 1999/2000 winter, *J. Geophys. Res.*, *107*(D20), 8262, doi:10.1029/2001JD000476.

Hoppel, K., R. Bevilacqua, D. Allen, G. Nedoluha, and C. Randall (2003), POAM III observations of the anomalous 2002 Antarctic ozone hole, *Geophys. Res. Lett.*, *30*(7), 1394, doi:10.1029/2003GL016899.

Knight, G., A. R. Ravishankara, and J. B. Burkholder (2002), UV absorption cross sections of HO_2NO_2 between 343 and 273 K, *Phys. Chem. Phys.*, *4*, 1432–1737.

Lefèvre, F., G. P. Brasseur, I. Folkins, A. K. Smith, and P. Simon (1994), Chemistry of the 1991–1992 stratospheric winter: Three-dimensional model simulations, *J. Geophys. Res.*, *99*, 8183–9196.

Lefèvre, F., K. Figarol, S. Carslaw, and T. Peter (1998), The 1997 Arctic ozone depletion quantified from three-dimensional model simulations, *Geophys. Res. Lett.*, *25*, 2425–2428.

Llewellyn, E. J., et al. (2004), The OSIRIS instrument on the Odin spacecraft, *Can. J. Phys.*, *82*(6), 411–422, doi:10.1139/P04-005.

Manney, G., et al. (2005), Simulations of dynamics and transport during the September 2002 Antarctic major warming, *J. Atmos. Sci.*, in press.

Murtagh, D., et al. (2002), An overview of the Odin atmospheric mission, *Can. J. Phys.*, *80*, 309–319.

Nedohula, G. E., R. M. Bevilacqua, M. D. Fromm, K. W. Hoppel, and D. R. Allen (2003), POAM measurements of PSCs and water vapor in the 2002 Antarctic vortex, *Geophys. Res. Lett.*, *30*(15), 1796, doi:10.1029/2003GL017577.

Nordh, H. L., et al. (2003), The Odin orbital observatory, *Astron. Astrophys.*, *402*(3), L21–L25, doi:10.1051/0004-6361:20030334.

Payan, S., C. Camy-Peyret, P. Jeseck, T. Hawat, M. Pirre, J.-B. Renard, C. Robert, F. Lefèvre, H. Kanzawa, and Y. Sasano (1999), Diurnal and nocturnal distribution of stratospheric NO_2 from solar and stellar occultation measurements in the Arctic vortex: comparison with models and ILAS satellite measurements, *J. Geophys. Res.*, *104*, 21,585–21,593.

Petelina, S. V., et al. (2004), Comparison of the Odin/OSIRIS stratospheric ozone profiles with coincident POAM III and ozonesonde measurements, *Geophys. Res. Lett.*, *31*, L07104, doi:10.1029/2003GL019299.

Poole, L. R., and M. C. Pitts (1994), Polar stratospheric cloud climatology based on Stratospheric Aerosol Measurements II observations from 1987 to 1989, *J. Geophys. Res.*, *99*, 13,083–13,089.

Roche, A. E., et al. (1993), CLAES observations of $ClONO_2$ and HNO_3 in the Antarctic stratosphere, between June 15 and September 17, 1992, *Geophys. Res. Lett.*, *20*, 1223–1226.

Rodgers, C. D. (1976), Retrieval of atmospheric temperature and composition from remote measurements of thermal radiation, *Rev. Geophys.*, *14*, 609–624.

Rodgers, C. D. (2000), *Inverse Methods for Atmospheric Sounding: Theory and Practice*, 1st ed., World Sci., River Edge, N. J.

Roehl, C. M., et al. (2002), Photodissociation of peroxynitric acid in the near-IR, *J. Phys. Chem.*, *106*, 3766–3772.

Sander, S. P., et al. (2003), Chemical kinetics and photochemical data for use in atmospheric studies, in *Evaluation Number 14*, *JPL Publ. 02-25*.

Santee, M. L., G. L. Manney, L. Froidevaux, W. G. Read, and J. W. Waters (1999), Six years of UARS Microwave Limb Sounder HNO_3 observations: Seasonal, interhemispheric, and interannual variations in the lower stratosphere, *J. Geophys. Res.*, *104*, 8225–8246.

Santee, M. L., G. L. Manney, J. W. Waters, and N. J. Livesey (2003), Variations and climatology of ClO in the polar lower stratosphere from UARS Microwave Limb Sounder measurements, *J. Geophys. Res.*, *108*(D15), 4454, doi:10.1029/2002JD003335.

Simmons, A., et al. (2003), Breakdown of the stratospheric winter polar vortex, *ECMWF Newsl.*, *96*, 2–10.

Solomon, P., B. Connor, J. Barrett, T. Mooney, A. Lee, and A. Parrish (2002), Measurements of stratospheric ClO over Antarctica in 1996–2000 and implications for ClO dimer chemistry, *Geophys. Res. Lett.*, *29*(15), 1708, doi:10.1029/2002GL015232.

von Savigny, C., et al. (2003), Stratospheric ozone profiles retrieved from limb scattered sunlight radiance spectra measured by the OSIRIS instrument on the Odin satellite, *Geophys. Res. Lett.*, *30*(14), 1755, doi:10.1029/2002GL016401.

von Savigny, C., I. C. McDade, E. Griffioen, C. S. Haley, C. E. Sioris, E. J. Llewellyn, and R. Bevilaqua (2005), Sensitivity studies and first validation of stratospheric ozone profile retrievals from Odin/OSIRIS observations of limb scattered solar radiation, *Can. J. Phys.*, in press.

Urban, J., et al. (2004), The Northern Hemisphere stratospheric vortex during the 2002–03 winter: Subsidence, chlorine activation and ozone loss observed by the Odin sub-millimetre radiometer, *Geophys. Res. Lett.*, *31*, L07103, doi:10.1029/2003GL019089.

World Meteorological Organization (1998), Scientific assessment of ozone depletion: 1998, *Rep. 44*, Geneva, Switzerland.

H. Auvinen, S. Hassinen, E. Kyrö, E. Kyrölä, G. W. Leppelmeier, A. Seppälä, and P. Taalas, Department of Geophysics, Finnish Meteorological Institute, P.O. Box 503, FIN-00101 Helsinki, Finland.

G. Berthet, C. Boonne, A. Hauchecorne, F. Lefèvre, G. Mégie, and A. Pazmino, Service d'Aéronomie, Institut Pierre-Simon Laplace, F-75252 Paris, France.

S. Brohede, P. Eriksson, C. Jimenez, N. Lautié, D. Murtagh, M. Olberg, and J. Urban, Department of Radio and Space Science, Chalmers University of Technology, SE-41296 Göteborg, Sweden.

D. A. Degenstein, R. L. Gattinger, E. J. Llewellyn, N. D. Lloyd, and S. V. Petelina, Institute of Space and Atmospheric Studies, University of Saskatchewan, Saskatoon, SK, Canada S7N 5E2.

W. F. J. Evans, Physics Department, Trent University, Peterborough, ON, Canada K9J 7B8.

J. de La Noë, E. Dupuy, and L. El Amraoui, Laboratoire d'Astrodynamique, d'Astrophysique et d'Aéronomie de Bordeaux (L3AB), Observatoire Aquitain des Sciences de l'Univers (OASU), F-33270, Floirac, France.

U. Frisk, L. Nordh, and F. von Scheele, Swedish Space Corporation, PO Box 4207, SE-17104 Solna, Sweden.

F. Girod, Centre National d'Etudes Spatiales, 18 avenue E. Belin, F-31401, Toulouse, France.

C. S. Haley, J. C. McConnell, I. C. McDade, and B. H. Solheim, Centre for Research in Earth and Space Science, York University, 4700 Keele Street, Toronto, ON, Canada M3J 1P3.

E. Le Flochmoën and P. Ricaud, Laboratoire d'Aérologie, Observatoire de Midi-Pyrénées, F-31400, Toulouse, France. (philippe.ricaud@aero.obs-mip.fr)

A. Sandqvist, Stockholm Observatory, SCFAB, Roslagstullsbacken 21, SE-10691 Stockholm, Sweden.

C. E. Sioris, Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, MA 02138, USA.

J. Stegman and G. Witt, Department of Meteorology, Stockholm University, SE-10691 Stockholm, Sweden.

K. Strong, Physics Department, University of Toronto, 60 St. George Street, Toronto, ON, Canada M5S 1A7.

C. von Savigny, Institute of Environmental Physics, University of Bremen, Otto-Hahn-Allee 1, D-28359 Bremen, Germany.