

This discussion paper is/has been under review for the journal *Atmospheric Chemistry and Physics (ACP)*. Please refer to the corresponding final paper in *ACP* if available.

Simultaneous measurements of OCIO, NO₂ and O₃ in the Arctic polar vortex by the GOMOS instrument

C. Tétard¹, D. Fussen¹, C. Bingen¹, N. Capouillez¹, E. Dekemper¹, N. Loodts¹,
N. Matshvili¹, F. Vanhellefont¹, E. Kyrölä², J. Tamminen², V. Sofieva²,
A. Hauchecorne³, F. Dalaudier³, J.-L. Bertaux³, O. Fanton d'Andon⁴, G. Barrot⁴,
M. Guirlet⁴, T. Fehr⁵, and L. Saavedra⁵

¹Institut d'Aéronomie Spatiale de Belgique, Brussels, Belgium

²Finnish Meteorological Institute, Helsinki, Finland

³Service d'Aéronomie du CNRS, Verrières-le-buisson, France

⁴ACRI-ST, Sophia-Antipolis, France

⁵European Space Research Institute (ESRIN), European Space Agency, Frascati, Italy

Received: 7 May 2009 – Accepted: 26 May 2009 – Published: 4 June 2009

Correspondence to: C. Tétard (cedric.tetard@aeronomie.be)

Published by Copernicus Publications on behalf of the European Geosciences Union.

12707

Abstract

We present the first nighttime measurements of OCIO from a limb-viewing satellite instrument in the Arctic polar vortex. The relationship between OCIO, NO₂ and O₃ slant column densities in the Arctic polar vortex are analyzed from the GOMOS measurements. The retrieval process is based on a differential optical absorption spectroscopy (DOAS) method applied on the weighted median GOMOS transmittances. A study about the longitudinal distributions of OCIO, NO₂ and O₃ above 65° north in January 2008 is presented. It shows a strong halogen activation in the lower stratosphere and a strong denoxification in the entire stratosphere inside the Arctic polar vortex. Time series of temperatures and OCIO, NO₂ and O₃ slant column densities for the winters 2002/2003 to 2007/2008 are also presented. They highlight the correlation between temperature, OCIO and NO₂. The GOMOS instrument appears to be a very suitable instrument for the monitoring of OCIO, NO₂ and O₃ in the stratosphere during nighttime.

1 Introduction

Since the discovery of the stratospheric ozone depletion by Farman et al. (1985), several studies have been performed to better understand this recurrent phenomenon (a historical review of this research can be found in Solomon, 1999). Inorganic chlorine species (Cl_y) play an important role in the stratospheric chemical processes that lead to ozone depletion in both Arctic and Antarctic polar regions. The inert reservoir species (like ClONO₂ or HCl) are converted into active chlorine (ClO, Cl₂O₂) by heterogeneous reactions, which occur on the surface of polar stratospheric clouds (PSC) formed during the polar night (Solomon et al., 1986) if stratospheric temperatures are below 198 K (T_{PSC}). These active species will strongly contribute to catalytic cycles that destroy ozone. A consequence of the halogen activation is the production of OCIO

12708

via one of the three reactions between ClO and BrO:



5 The study done by Sessler et al. (1995) shows that OClO is a good qualitative indicator of chlorine activation and a good quantitative indicator of BrO. This study highlights also that OClO is a poor quantitative indicator of the ClO presence. The monitoring of OClO appears to be crucial to better understand the polar stratospheric chemistry by constraining the chemical models. The only significant sink of OClO is its rapid photolysis by the solar radiation in the UV wavelength range. Consequently OClO is almost
10 constant during night.

Nitrogen species NO_x ($\text{NO} + \text{NO}_2$) also play an important role by reforming the halogen reservoir species:



The reactions R4 and R5 limit the formation of OClO. Nevertheless, in the polar vortex, NO_2 is removed via the formation of HNO_3 . This is the well-known denoxification of the polar vortex.

The first measurements of OClO in the stratosphere were performed in Antarctica by
20 Solomon et al. (1987) from a ground-based station. Since then, other measurements have been performed by using ground-based (Miller et al., 1999), balloon-borne (Canty et al., 2005; Pommereau and Piquard, 1994; Renard et al., 1997; Riviere et al., 2003) or satellite measurements (Krecl et al., 2006; Wagner et al., 2002). Some of these
25 satellite instruments used a nadir geometry to retrieve the total vertical column densities of OClO: it is the case for the instruments Global Ozone Monitoring Experiment

12709

(GOME) on ERS-2 (Burrows et al., 1999), SCanning Imaging Absorption spectrometer for Atmospheric CHartography (SCIAMACHY) onboard ENVISAT (Bovensmann et al., 1999) and Ozone Monitoring Instrument (OMI) on Aura (Levelt et al., 2006). The instrument Optical Spectrograph and InfraRed Imager System (OSIRIS) onboard the
5 Odin satellite (Llewellyn et al., 2004) uses the limb scattering technique to retrieve vertical profiles of concentrations of OClO (Krecl et al., 2006). Moreover, SCIAMACHY has a limb-viewing mode and can also retrieve such vertical profiles. However, no results have been published for the moment. Note that the Stratospheric Aerosol and Gas Experiment III (SAGE III) on the Meteor-3M satellite (McCormick et al., 1991) can
10 also perform lunar occultations and limb-scatter measurements in order to retrieve the OClO vertical distributions but, for the moment, no results concerning this has been published. The Global Ozone Monitoring by Occultation of Stars (GOMOS) instrument on ENVISAT (see e.g., Bertaux et al., 1991; Kyrölä et al., 2004) is designed to retrieve the vertical concentrations of trace gases, including nighttime OClO. Preliminary results
15 for the year 2003 have suggested the presence of a maximum of the OClO concentration in the equatorial upper stratosphere (Fussen et al., 2006). The stellar occultation technique used by GOMOS allows the measurements of OClO during nighttime. GOMOS is the only satellite instrument able to perform nighttime measurements in the stratosphere. For the moment, the OClO product obtained from the GOMOS spectra
20 has not been validated with data from other instruments. This is why we consider this work as preliminary.

We report in this paper the distributions of OClO, NO_2 and O_3 slant column densities (SCD) retrieved from GOMOS measurements during the Arctic winters from 2003 to 2008. After a brief summary of the GOMOS instrument, the retrieval algorithm is described. Then, we present the spatial distributions of OClO, NO_2 and O_3 measured in
25 the Arctic region in January 2008. Finally, we analyze time series of these species in the Arctic regions for the winter 2002/2003 to 2007/2008.

2 The GOMOS instrument

GOMOS is one of the ten instruments onboard ESA's ENVISAT satellite launched on 1 March 2002 in a sun-synchronous orbit at an altitude of 800 km. It is a stellar occultation spectrometer dedicated to the stratospheric and mesospheric remote sounding of the Earth. Operating in the UV, visible and NIR wavelength range (from 245 to 942 nm), it allows the retrieval of vertical profiles of O₃, H₂O, NO₂, NO₃, O₂, aerosols and temperature. OCIO is not a species retrieved systematically from the GOMOS operational algorithm because its slant optical thickness is small with respect to the instrumental signal-to-noise ratio. Nevertheless, a global determination of the stratospheric OCIO distribution is possible if several GOMOS measurements are co-added (see Sect. 3 and Fussen et al., 2006). GOMOS is also equipped with two fast photometers used to correct for star scintillation and to retrieve temperature profiles.

GOMOS measures light from several stars that are setting behind the Earth horizon. The transmittance along the line of sight is obtained at each tangent altitude by dividing the stellar spectrum measured through the atmosphere by the reference stellar spectrum measured outside the atmosphere. This method is self-calibrated and offers the advantage of a large number of occultations per day (30 to 50 measurements per orbit compared to only 2 occultations for the solar occultation method). The wide variety of stars used combined with the sun-synchronous orbit allows a global coverage in about 3 days. Nevertheless, the light intensity of stars is weak, influencing the signal-to-noise ratio of GOMOS measurements that depends on the star used.

3 OCIO retrieval

Due to the difficulties of the detection of OCIO in a single GOMOS spectrum, we co-add transmittances (interpolated on a common altitude grid) in latitude bins of 10 degrees with a temporal resolution of one month. The transmittances used are already corrected for scintillation and dilution effects (Dalaudier et al., 2001). The consistency of

12711

each data set is checked by using statistical normality tests after which we calculate for each consistent bin a weighted median spectrum and the associated variances. A differential optical absorption spectroscopy (DOAS, Platt et al., 1979) technique is then applied on this weighted median spectrum in the [355–390 nm] wavelength region. In this spectral window, the main contributions of the total extinction are the molecular scattering, the aerosol extinction and the absorptions by OCIO and NO₂. Even if the ozone absorption in this wavelength range is weak, we take it into account in order to obtain a better accuracy of the retrieval. For the sake of an optimal signal-to-noise ratio, we have decided to use only measurements from the star Sirius (Temperature=11000 K, Magnitude=-1.44) in this study.

The key principle of the DOAS method is to separate the total transmittances $T(\lambda)$ into two components, one varying slowly with the wavelength ($T_s(\lambda)$) and the other rapidly varying (noted $dT(\lambda)$ and named experimental differential transmittance). The slowly varying transmittances are calculated using a second order polynomial. It corresponds to the molecular scattering, the aerosol extinction and the slowly varying components of the gaseous absorptions. In the same way, we separate the absorption cross sections (σ_i) of each species into a slowly varying component (calculated also with a second order polynomial) and a high frequency component. The differential cross sections $\delta\sigma_i$ are then calculated as the differences between the absorption cross sections and the smoothed ones. Thus, the modelled differential transmittance $M(\lambda)$ can be written as:

$$M(\lambda) = T_s \left(1 - \exp \left[- \left(N_{O_3} \delta\sigma_{O_3} + N_{NO_2} \delta\sigma_{NO_2} + N_{OCIO} \delta\sigma_{OCIO} \right) \right] \right) \quad (1)$$

where N_i are the slant column densities (SCD). The N_i are then obtained by a non-linear least-squares minimization of the difference between $M(\lambda)$ and $dT(\lambda)$ weighted

12712

by the experimental errors. In the minimization procedure, the wavelength is eventually shifted by $\Delta\lambda$. The estimated retrieval error is extracted from the jacobian. Note that the cross sections used in the retrieval are the same regardless of the temperature.

Unfortunately, for the moment, no direct validation of the OCIO SCD obtained can be achieved. In the future, a validation exercise will be done with the OSIRIS, SCIAMACHY, OMI and GOME results. Nonetheless, we can compare the NO_2 SCD obtained from our DOAS procedure and from the GOMOS operational algorithm. Figure 1 shows a typical comparison for August 2003 for the $[60\text{--}65^\circ\text{S}]$ latitudinal band. The NO_2 SCDs of each measurement in this bin, retrieved from the GOMOS operational algorithm are combined to obtain the weighted median SCD observed in the left panel (dashed line). The relative differences between these two profiles are mostly lower than 10% (in absolute values) and this result holds for the other latitudinal bands. We can therefore conclude that the results of our DOAS process are consistent with the results of the operational algorithm. Furthermore, in a previous article, Fussen et al. (2006) shows a comparison between OCIO obtained from GOMOS measurements and calculated from the Belgian Assimilation System of Chemical Observations of ENVISAT (BASCOE) model (Errera and Fonteyn, 2001) for the year 2003. A good agreement results from this comparison. Thus, we can be confident with the OCIO product obtained from the DOAS approach used in this study.

4 Spatial distribution of OCIO, NO_2 and O_3 in the Arctic vortex in January 2008

According to the report of the Arctic winter stratosphere 2007/2008 (available at http://www.ozone-sec.ch.cam.ac.uk/scout_o3/), the stratosphere in the winter 2007/2008 was very cold. The temperature started to decrease in November and remained low until a major stratospheric warming in late February. Inside the polar vortex, the temperatures were below the PSC temperature threshold until the end of February. Indeed, PSCs were observed from different Arctic stations, a possible sign of a strong chlorine activation.

12713

In January 2008, the polar vortex was not centered on the geographical north pole. It gradually moved towards Europe. Figure 2 shows a potential vorticity map obtained from the MIMOSA model (Hauchecorne et al., 2002) at 675 K (about 27 km) on 10 January 2008. It highlights that the polar vortex extends from the North pole down to 60°N latitudes above the regions whose longitude lies between 70°W and 135°E . Consequently, a 5 degree latitudinal band in the northern hemisphere was not homogeneous for the highest latitude. In January 2008, only the latitudinal band near 72° was sounded by GOMOS (Sirius occultations). In Fig. 2, the white circle represents the spatial distribution of these GOMOS Sirius occultations. They are distributed along the entire longitudinal range: some of them were performed inside the polar vortex and the others outside. Hence, we cannot bin together all these measurements. Figure 3 shows that the distribution of the transmittances at 385 nm and at 30 km for the GOMOS measurements in this latitudinal band are bimodal. Note that for other altitudes and wavelengths, this bimodality of the transmittances is also observed. One expects that high transmittances correspond to measurements inside the polar vortex. Indeed, because of the denoxification of the polar vortex, the NO_2 absorption is weak.

To take into account the specificity of the position of the polar vortex in January 2008, we have divided the latitudinal band into 10° longitudinal boxes. In each box, we check the consistency of the measurements (statistical test) and we calculate the weighted median transmittance spectra. Then, we use the DOAS technique to retrieve OCIO, NO_2 and O_3 SCDs in each box. The results concerning OCIO are presented in Fig. 4. It represents the longitudinal variations of OCIO SCD for three different altitudes: 17, 24 and 29 km. It appears clearly that maxima of OCIO SCD occur in the activated polar vortex (between 70°W and 135°E) at the two lowest altitudes. At 29 km, the shape of the distribution is flatter (around $5 \times 10^{14} \text{ cm}^{-2}$). The isopleths longitude-altitude for OCIO, NO_2 , O_3 SCDs and for the temperature provided by the European Center for Medium-range Weather Forecasts (ECMWF) are presented in Fig. 5. The NO_2 and O_3 SCDs represented in this Figure are from the operational algorithm. The activated vortex region is marked by a strong OCIO SCD in the lower stratosphere and by low NO_2 SCDs.

12714

This is in a good agreement with our current knowledge of stratospheric chemistry (Brasseur and Solomon, 2005). According to Sessler et al. (1995), OCIO presence is an indicator of halogen activation. The presence of ClO in the lower stratosphere in the polar vortex is confirmed by the instrument Microwave Limb Sounder (MLS) instrument onboard EOS Aura (Earth Observing System, Schoeberl et al., 2006): in Fig. 6, a maximum of ClO volume mixing ratio in the lower stratosphere is located in the Arctic polar vortex (at high equivalent latitude, Santee et al., 2008). Figure 5 shows also the longitudinal and vertical distribution of ozone SCD. It shows a slow decreasing of ozone inside the polar vortex. This is in a good agreement with the halogen activation and with the denoxification observed. One may also notice the low temperatures (lower than 200 K) encountered in the areas where the halogen activation and the denoxification are observed, a condition for the presence of PSCs.

5 Temporal evolution of OCIO, NO₂ and O₃ in Arctic winters

In this section, we study the temporal evolution of the OCIO, NO₂ and O₃ SCDs in the Arctic regions during winter from 2002/2003 to 2007/2008. Figure 7 shows the geolocation of the Sirius occultations in the northern hemisphere (latitude greater than 65°). All these measurements occurred during polar nights. This study was performed with a temporal resolution of two days. Bins with less than 4 measurements are not considered as statistically significant and are not taken into account. This restriction eliminates only 11 bins among a total of 200 bins. The same method is then applied on each set: the weighted median is calculated and the DOAS retrieval is applied. Thus, we retrieve the OCIO SCD, the NO₂ SCD and the O₃ SCD as a function of time in the Arctic winter. Note that, for this study, we do not take into account the position of measurements relative to the polar vortex. In other terms, no longitudinal separation (like in the previous section) has been done because the number of measurements available is not sufficient to perform spatio-temporal binning with a two days resolution. One should keep in mind that this can cause the averaging of inconsistent GOMOS

12715

measurements (like for the winter 2007/2008, cf Sect. 4) introducing some uncertainty in our temporal study.

Figure 8 shows the minimum temperature reached in the stratosphere (panels A) and the O₃ (panels B), NO₂ (panels C) and OCIO (panels D) SCDs (with the error bars) at the altitude of 19 km as a function of time. This level has been chosen because at this altitude both denoxification and halogen activation are clearly observable. The winter 2006/2007 was not studied due to the lack of data. In the next paragraphs, we will describe the results obtained for each winter.

5.1 The Arctic winter 2002/2003

During this winter, stratospheric minimum temperatures retrieved using the GOMOS photometers were below the temperature of formation of PSC from mid November to mid January (panel A). Then, temperatures were higher after mid January, almost always above T_{PSC} . Consequently, the halogen activation must be more important during this cold period: we observed a slow increase of OCIO SCDs all along this period (reaching $2.0 \times 10^{15} \text{ cm}^{-2}$ at the end of December) and then, after mid January, OCIO SCDs began to decrease slightly. For NO₂, it is the reverse: we observed a decrease of the NO₂ SCDs during the cold period and then an increase. Concerning ozone, the SCDs are very noisy. This is mainly because ozone is a weak absorber in the wavelength region used in the retrieval.

5.2 The Arctic winter 2003/2004

This winter is also characterized by two periods: a cold one (from mid November to late December when, the minimum temperatures are below T_{PSC}) following by a warming. During the cold period, OCIO SCDs are increasing, NO₂ and O₃ SCDs are both decreasing. When the temperatures gets higher, NO₂ SCDs are increasing and OCIO SCDs are decreasing. However, ozone SCDs remain approximately constant. For this winter, a strong contrast (for OCIO and NO₂ SCDs) is observed between the cold and

12716

the warm period. For this winter the period of high halogen activation corresponds to the period with the highest denoxification. This is in a good agreement with our current knowledge in stratospheric chemistry.

5.3 The Arctic winter 2004/2005

5 According to the report of the Arctic winter stratosphere 2004/2005 (available at http://www.ozone-sec.ch.cam.ac.uk/scout_o3/), the temperatures in the stratosphere were the lowest since 50 years. They remained below T_{PSC} from late November to late February. Consequently, lots of PSC have been observed during the entire winter. The minimum GOMOS temperatures are in agreement with this situation. They are
10 below T_{PSC} from late November to late January. OCIO SCDs strongly increased from late November to mid December, reaching approximately $2.5 \times 10^{15} \text{ cm}^{-2}$. In the same time, NO_2 SCDs decreased strongly. From mid December, OCIO and NO_2 remained roughly constant. Ozone SCDs are weak all along this period. During this exceptionally
15 cold and stable winter, GOMOS has observed strong and long halogen activation and denoxification.

5.4 The Arctic winter 2005/2006

For this winter, GOMOS has operated measurements only during January. The minimum temperatures retrieved from the GOMOS photometers are not very low. They are below T_{PSC} only for a few days in mid January (during the GOMOS measurements period). Then the minimum temperatures in the stratosphere increased. Consequently, we observed an increase of the NO_2 SCDs (from $2.5 \times 10^{15} \text{ cm}^{-2}$ in mid January to $6 \times 10^{16} \text{ cm}^{-2}$ in early February). Nevertheless, we cannot observe a diminution of the OCIO SCDs as expected. For an unclear reason, the temporal evolution of OCIO SCDs is first decreasing and then increasing. Concerning ozone, nothing can be deduced by
25 studying the temporal evolution.

12717

5.5 The Arctic winter 2007/2008

The GOMOS measurements for this winter occurred only in January 2008. The minimum temperatures are often lower than T_{PSC} during the whole GOMOS measurement period. Nevertheless, we can distinguish neither denoxification nor halogen activation.
5 This is probably because no longitudinal discrimination is carried out for this temporal study. Indeed, the polar vortex is not centered on the geographical pole and the latitudinal band sounded by the GOMOS measurements is not homogeneous (cf. Sect. 4). This lack of homogeneity of the GOMOS measurements used generates the large error bars observed on the O_3 , NO_2 and OCIO SCDs. However, we can observe an
10 anticorrelation between NO_2 and OCIO SCDs: in mid January a sudden increase of NO_2 SCD occurred at the same time as a sudden decrease of the OCIO SCD. This is followed by a decrease of NO_2 and an increase of OCIO SCD.

6 Conclusions

This preliminary work focuses on the interactions between NO_2 , O_3 and OCIO in the
15 Arctic polar vortex. The slant column densities of these species are retrieved during nighttime from Sirius occultations as observed by the GOMOS instrument. First, the longitudinal distributions of these species in January 2008 highlight strong variations of OCIO and NO_2 (relative to the longitude) in the lower stratosphere: in the polar vortex, weak NO_2 SCD and strong OCIO SCD are observed, and the reverse situation outside
20 the polar vortex. Halogen activation (marked by high OCIO SCDs) and denoxification which occur in the polar vortex are clearly detectable. Hence, the GOMOS spectrometer appears to be a suitable instrument to perform a monitoring of such species in the polar vortex. Furthermore, the temporal study confirms that the halogen activation degree and the concomitant denoxification can be effectively monitored by GOMOS. We
25 were able to highlight the correlation between cold temperatures (below T_{PSC}), weak NO_2 SCDs and strong OCIO SCDs inside the Arctic polar vortex for several winters.

12718

This paper reports the first study of OCIO distribution using limb-viewing satellite measurements performed during night in the Arctic regions.

The next step in the use of the GOMOS measurements for the OCIO retrieval is to validate this product. For this aim, we need correlative measurements from other satellite instruments (like OSIRIS, SCIAMACHY, GOME or OMI) or balloon-borne instruments. In a forthcoming work, we will build a global OCIO climatology.

Acknowledgements. This study was funded by the PRODEX 9 contract SECPEA under the authority of the Belgian Space Science Office (BELSPO).

We thank the MLS science team for giving us the authorization to use the CIO figure.

10 References

- Bertaux, J. L., Mégie, G., Widemann, T., Chassefière, E., Pellinen, R., Kyrölä, E., Korpela, S., and Simon, P.: Monitoring of ozone trend by stellar occultations: the GOMOS instrument, *Adv. Space Res.*, 11, 237–242, doi:10.1016/0273-1177(91)90426-K, 1991. 12710
- Bovensmann, H., Burrows, J. P., Buchwitz, M., Frerick, J., Noël, S., Rozanov, V. V., Chance, K. V., and Goede, A. P. H.: SCIAMACHY: Mission Objectives and Measurement Modes, *J. Atmos. Sci.*, 56, 127–150, doi:10.1175/1520-0469(1999)056, 1999. 12710
- Brasseur, G. P. and Solomon, S.: *Aeronomy of the Middle Atmosphere: Chemistry and Physics of the Stratosphere and Mesosphere*, Springer, Berlin., 2005. 12715
- Burrows, J. P., Weber, M., Buchwitz, M., Rozanov, V., Ladstätter-Weißenmayer, A., Richter, A., Debeek, R., Hoogen, R., Bramstedt, K., Eichmann, K.-U., Eisinger, M., and Perner, D.: The Global Ozone Monitoring Experiment (GOME): Mission Concept and First Scientific Results., *J. Atmos. Sci.*, 56, 151–175, doi:10.1175/1520-0469(1999)056, 1999. 12710
- Canty, T., Riviere, E. D., Salawitch, R. J., Berthet, G., Renard, J. B., Pfeilsticker, K., Dorf, M., Butz, A., Bösch, H., Stimpfle, R. M., Wilmouth, D. M., Richard, E. C., Fahey, D. W., Popp, P. J., Schoeberl, M. R., Lait, L. R., and Bui, T. P.: Nighttime OCIO in the winter Arctic vortex, *J. Geophys. Res.*, 110, D01301, doi:10.1029/2004JD005035, 2005. 12709
- Dalaudier, F., Kan, V., and Gurvich, A. S.: Chromatic Refraction with Global Ozone Monitoring by Occultation of Stars. I. Description and Scintillation Correction, *Appl. Opt.*, 40, 866–877, doi:10.1364/AO.40.000866, 2001. 12711

12719

- Errera, Q. and Fonteyn, D.: Four-dimensional variational chemical assimilation of CRISTA stratospheric measurements, *J. Geophys. Res.*, 106, 12253–12266, doi:10.1029/2001JD900010, 2001. 12713
- Farman, J. C., Gardiner, G., and Shanklin, J. D.: Large losses of total ozone in antarctica reveal seasonal ClO_x/NO_x interaction, *Nature*, 315, 207–210, 1985. 12708
- Fussen, D., Vanhellemont, F., Dodion, J., Bingen, C., Mateshvil, N., Daerden, F., Fonteyn, D., Errera, Q., Chabrilat, S., Kyrölä, E., Tamminen, J., Sofieva, V., Hauchecorne, A., Dalaudier, F., Bertaux, J.-L., Renard, J.-B., Fraisse, R., d'Andon, O. F., Barrot, G., Guirlet, M., Mangin, A., Fehr, T., Snoeij, P., and Saavedra, L.: A global OCIO stratospheric layer discovered in GOMOS stellar occultation measurements, *Geophys. Res. Lett.*, 33, L13815, doi:10.1029/2006GL026406, 2006. 12710, 12711, 12713
- Hauchecorne, A., Godin, S., Marchand, M., Hesse, B., and Souprayen, C.: Quantification of the transport of chemical constituents from the polar vortex to midlatitudes in the lower stratosphere using the high resolution advection model MIMOSA and effective diffusivity, *J. Geophys. Res.*, 107(D20), 8289, doi:10.1029/2001JD00049, 2002. 12714
- Krecl, P., Haley, C. S., Stegman, J., Brohede, S. M., and Berthet, G.: Retrieving the vertical distribution of stratospheric OCIO from Odin/OSIRIS limb-scattered sunlight measurements, *Atmos. Chem. Phys.*, 6, 1879–1894, 2006, <http://www.atmos-chem-phys.net/6/1879/2006/>. 12709, 12710
- Kyrölä, E., Tamminen, J., Leppelmeier, G. W., Sofieva, V., Hassinen, S., Bertaux, J. L., Hauchecorne, A., Dalaudier, F., Cot, C., Korabiev, O., Fanton D'Andon, O., Barrot, G., Mangin, A., Théodore, B., Guirlet, M., Etanchaud, F., Snoeij, P., Koopman, R., Saavedra, L., Fraisse, R., Fussen, D., and Vanhellemont, F.: GOMOS on Envisat: an overview, *Adv. Space Res.*, 33, 1020–1028, doi:10.1016/S0273-1177(03)00590-8, 2004. 12710
- Levelt, P. F., van den Oord, G. H. J., Dobber, M. R., Malkki, A., Visser, H., de Vries, J., Stammes, P., Lundell, J. O. V., and Saari, H.: The Ozone Monitoring Instrument, *IEEE Transactions on Geoscience and Remote Sensing*, 44, 1093–1101, doi:10.1109/TGRS.2006.872333, 2006. 12710
- Llewellyn, E., Lloyd, N. D., Degenstein, D. A., Gattinger, R. L., Petelina, S. V., Bourassa, A. E., Wiensz, J. T., Ivanov, E. V., McDade, I. C., Solheim, B. H., McConnell, J. C., Haley, C. S., von Savigny, C., Sioris, C. E., McLinden, C. A., Griffioen, E., Kaminski, J., Evans, W. F. J., Puckrin, E., Strong, K., Wehrle, V., Hum, R. H., Kendall, D. J. W., Matsushita, J., Murtagh, D. P., Brohede, S., Stegman, J., Witt, G., Barnes, G., Payne, W. F., Piche, L., Smith, K.,

12720

- Warshaw, G., Deslauniers, D. L., Marchand, P., Richardson, E. H., King, R. A., Wevers, I., McCreath, W., Kyrola, E., Oikarinen, L., Leppelmeier, G. W., Auvinen, H., Megie, G., Hauchecorne, A., Lefevre, F., de La Noe, J., Ricaud, P., Frisk, U., Sjoberg, F., von Scheele, F., and Nordh, L.: The OSIRIS instrument on the Odin spacecraft, *Can. J. Phys.*, 82, 411–422, doi:10.1139/p04-005, 2004. 12710
- 5 McCormick, M. P., Chu, W. P., Zawodny, J. M., Mauldin, L. E., and McMaster, L. R.: Stratospheric aerosol and gas experiment III (SAGE III) aerosol and trace gas measurements for Earth Observing System (EOS), in: *Society of Photo-Optical Instrumentation Engineers (SPIE) Conference Series*, 125–141, 1991. 12710
- 10 Miller, H. L. J., Sanders, R. W., and Solomon, S.: Observations and interpretation of column OCIO seasonal cycles at two polar sites, *J. Geophys. Res.*, 104, 18769–18783, 1999. 12709
- Platt, U., Perner, D., and Pätz, H. W.: Simultaneous measurement of atmospheric CH₂O, O₃, and NO₂ by differential optical absorption, *J. Geophys. Res.*, 84, 6329–6335, doi:10.1029/JC084iC10p06329, 1979. 12712
- 15 Pommereau, J.-P. and Piquard, J.: Observations of the vertical distribution of stratospheric OCIO, *Geophys. Res. Lett.*, 21, 1231–1234, doi:10.1029/94GL00390, 1994. 12709
- Renard, J. B., Lefevre, F., Pirre, M., Robert, C., and Huguenin, D.: Vertical profile of night-time stratospheric OCIO, *J. Atmos. Chem.*, 26, 65–76, 1997. 12709
- Riviere, E. D., Pirre, M., Berthet, G., Renard, J. B., Taupin, F. G., Huret, N., and Chartier, M.: 20 On the interaction between nitrogen and halogen species in the Arctic polar vortex during THESEO and THESEO 2000, *J. Geophys. Res.*, 108, 8311, doi:10.1029/2002JD002087, 2003. 12709
- Santee, M. L., Lambert, A., Read, W. G., Livesey, N. J., Manney, G. L., Cofield, R. E., Cuddy, D. T., Daffer, W. H., Drouin, D. J. and Froidevaux, L., Fuller, R. A., Jarnot, R. A., Knosp, B. W., Perun, V. S., Snyder, W. V., Stek, P. C., Thurstans, R. P., Wagner, P. A., Waters, J. W., Connor, B., Urban, J., Murtagh, D., Ricaud, P., Barrett, B., Kleinboehl, A., Kuttippurath, J., Kullmann, H., von Hobe, M., Toon, G. C., and Stachnik, R. A.: Validation of the Aura Microwave Limb Sounder ClO Measurements, *J. Geophys. Res.*, 113, D15S22, doi:10.1029/2007JD008762, 2008. 12715
- 30 Schoeberl, M. R., Douglass, A. R., Hilsenrath, E., Bhartia, P. K., Beer, R., Waters, J. W., Gunson, M. R., Froidevaux, L., Gille, J. C., Barnett, J. J., Levelt, P. F., and de Cola, P.: Overview of the EOS Aura Mission, *IEEE Transactions on Geoscience and Remote Sensing*, 44, 1066–1074, doi:10.1109/TGRS.2005.861950, 2006. 12715

12721

- Sessler, J., Chipperfield, M. P., Pyle, J. A., and Toumi, R.: Stratospheric OCIO measurements as a poor quantitative indicator of chlorine activation, *Geophys. Res. Lett.*, 22, 687–690, 1995. 12709, 12715
- Solomon, S.: Stratospheric ozone depletion: A review of concepts and history, *Rev. Geophys.*, 37, 275–316, 1999. 12708
- 5 Solomon, S., Garcia, R. R., Rowland, F. S., and Wuebbles, D. J.: On the depletion of antarctic ozone, *Nature*, 321, 755–758, 1986. 12708
- Solomon, S., Mount, G. H., and Sanders, R.W. Schmeltekopf, A. L.: Visible spectroscopy at McMurdo station, Antarctica 2. Observations of OCIO, *J. Geophys. Res.*, 92, 8329–8338, 10 1987. 12709
- Wagner, T., Wittrock, F., Richter, A., Wenig, M., and Burrows, J.P. Platt, U.: Continuous monitoring of the high and persistent chlorine activation during the Arctic winter 1999/2000 by the GOME instrument on ERS-2, *J. Geophys. Res.*, 107, 8267, doi:10.1029/2001JD000466, 2002. 12709

12722

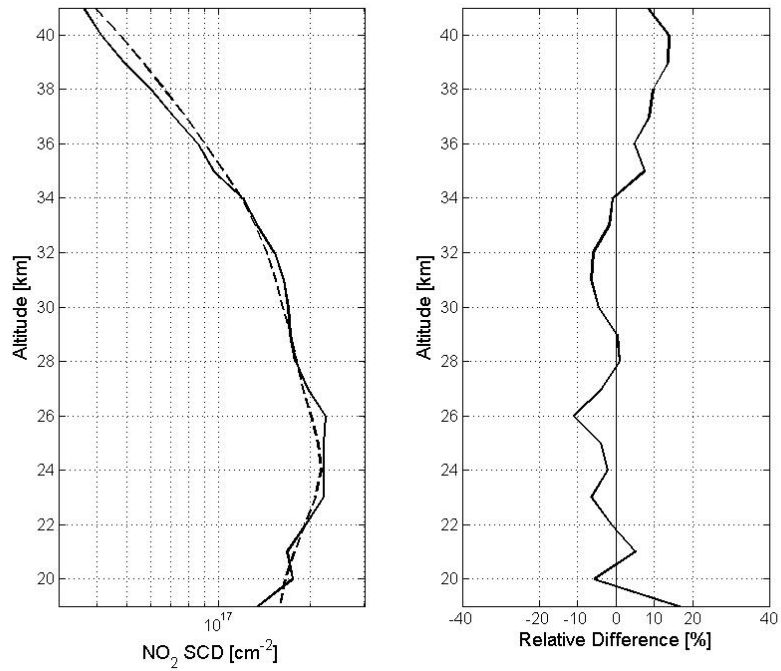


Fig. 1. On the left: vertical profiles of NO₂ slant column densities for August 2003 in the [60°–65° S] latitudinal band. The dashed line corresponds to the profile retrieved from the GOMOS operational algorithm and the solid line to the profile retrieved in this study. On the right: vertical profile of the relative differences.

12723

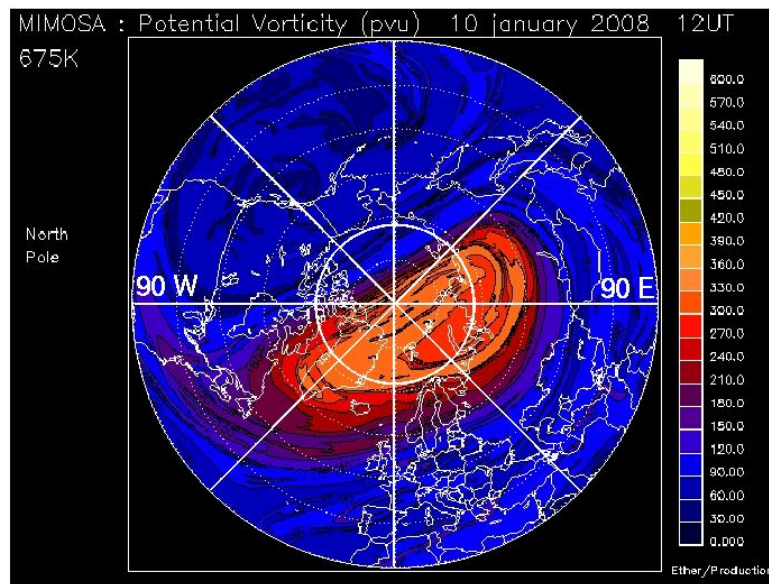


Fig. 2. Potential vorticity map calculated by the MIMOSA high-resolution advection model at 12:00 UT on 10 January 2008 at 675 K (about 27 km). The white circle at 72° N represents the geolocation of the tangent points of the GOMOS Sirius occultations in January 2008.

12724

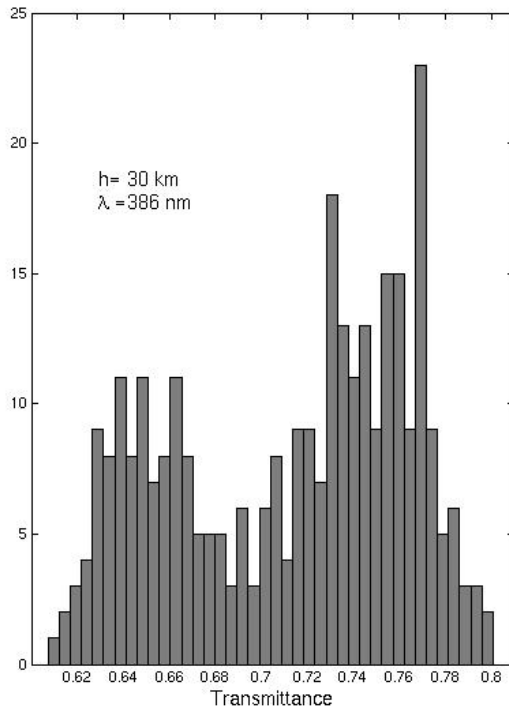


Fig. 3. Histogram of transmittances at 30 km and at 386 nm from the GOMOS Sirius occultations in January 2008 in the 70–75° N latitudinal range.

12725

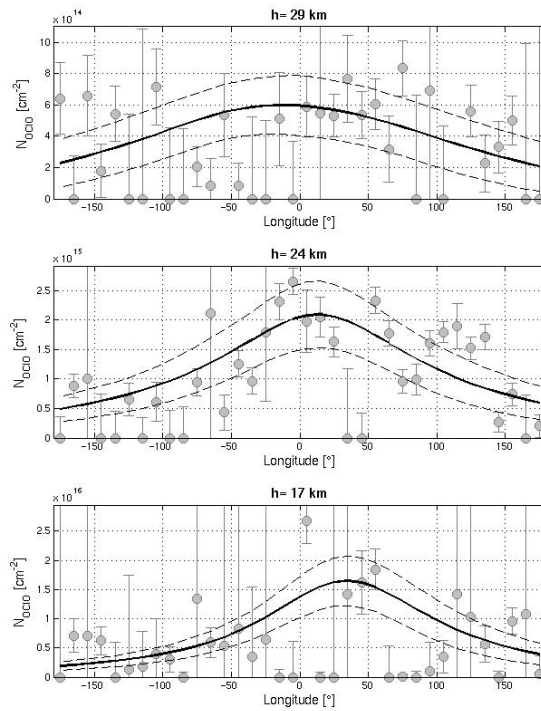


Fig. 4. OCIO slant column densities as a function of longitude with the spectral inversion error bars for January 2008 in the Arctic polar region. The solid line is the result of an error-weighted fit by a simple Lorentzian function. The dashed lines represent the associated confidence interval at 1- σ .

12726

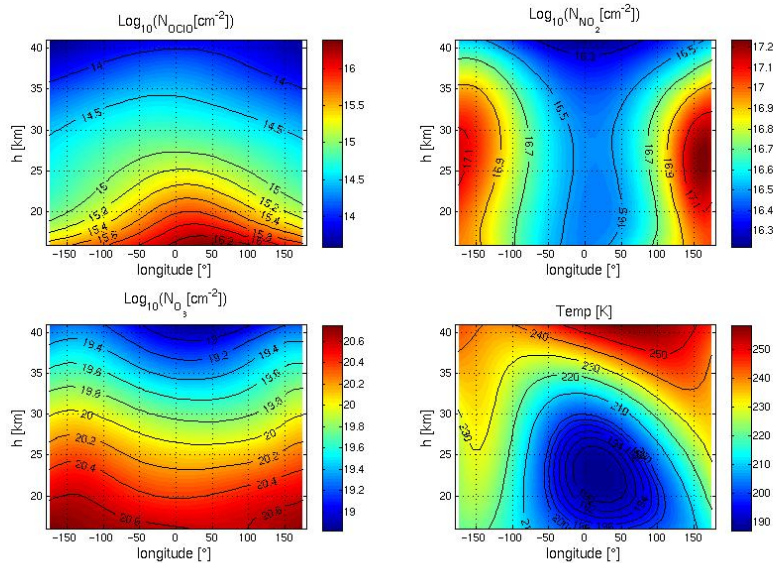


Fig. 5. Isopleths (longitude-altitude) of the OCI O SCD retrieved from the DOAS procedure, NO_2 and O_3 SCDs retrieved from the operational algorithm, and the temperature provided by the ECMWF in January 2008 in the 70–75° N latitudinal range.

12727

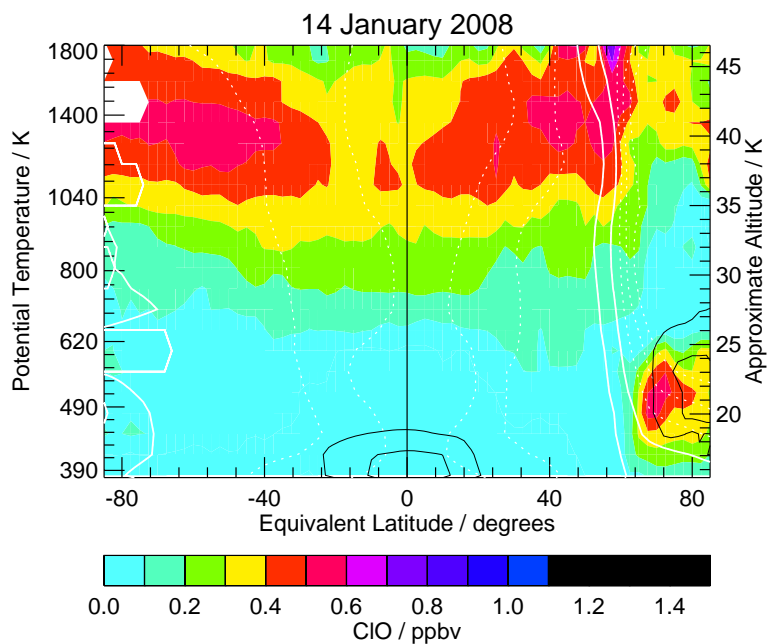


Fig. 6. Isopleth (equivalent latitude-altitude) of the CIO volume mixing ratios on January 2008 from MLS measurements (courtesy of G. Manney). The white lines represent iso-PV and the black lines represent iso-temperature from 180 to 200 K with a 5 K increment (from GEOS-5).

12728

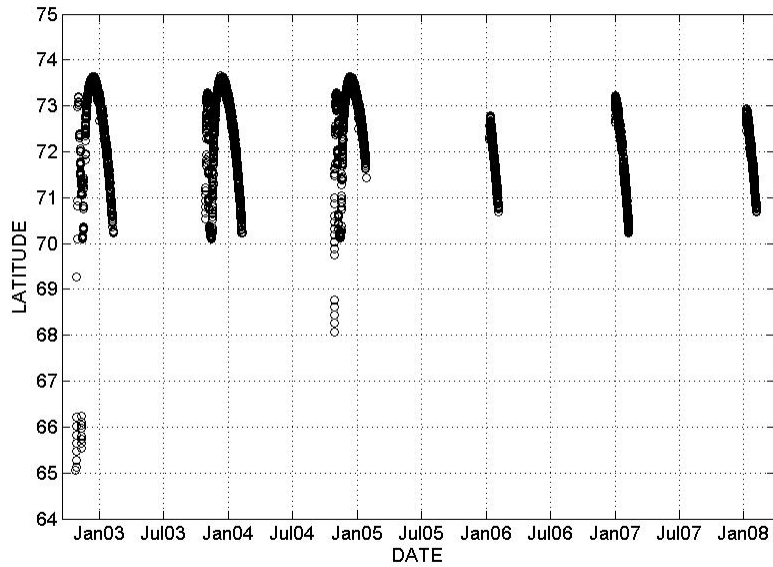


Fig. 7. Geolocation of the tangent points of all the GOMOS Sirius occultations above 65° N between September 2002 and May 2008.

12729

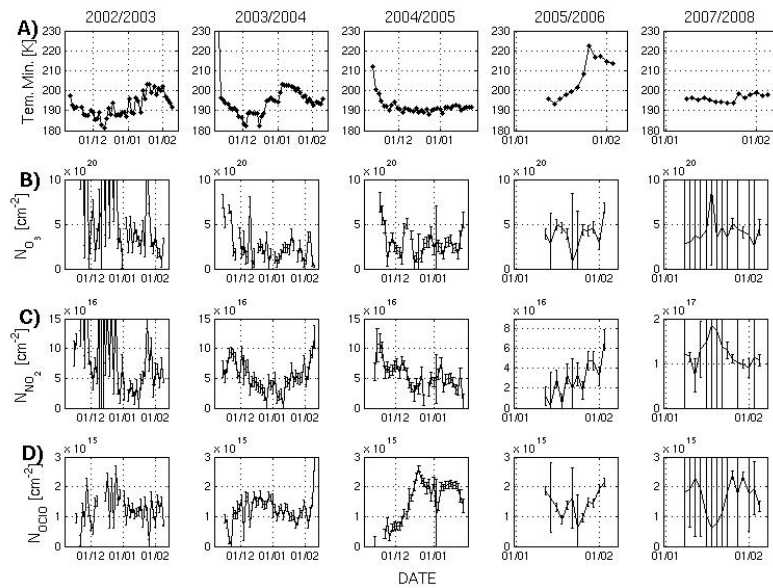


Fig. 8. Time series of the winters 2002/2003 to 2007/2008 (except 2006/2007) of the minimal temperature in the stratosphere (A) and of O₃ (B), NO₂ (C) and OCIO SCDs (D) at 19 km with the spectral inversion error bars, all retrieved from GOMOS measurements at the geolocations of Fig. 7.

12730